Supporting Online Material for

Combining Photoredox and Silver Catalysis for Azidotrifluoromethoxylation of Styrenes

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[§]F. C. and Y. W. contributed equally.

Table of Contents

Materials and Methods

All reactions were conducted in oven- or flame-dried glassware under an atmosphere of nitrogen unless otherwise noted. Blue LEDs (14 W and 34 W, (as shown in Figure 1)) were used for the light irradiation. In each case, the light source was placed ~ 2 cm from the reaction vessel. CH_3CN used in reactions was Extra Dry solvent and was purchased from J&K. Other solvents were purified according to the purification handbook *Purification of Laboratory Chemicals* before using. AgF (orange powder) was purchased from Acros and stored in the glovebox. $Ru(bpy)_3(PF_6)_2$ was prepared according to a previously reported method.[1] 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one was synthesised according to literature procedures[2] and used as freshly prepared. "OCF_3" reagents was prepared according to the reported literatures.[3] 4,4',4''-tri-tert-butyl-2,2':6'2''-terpyridine was purchased from Sigma-Aldrich. Deuterated solvents were purchased from Sigma-Aldrich. TLC was performed on silica gel Huanghai $HSGF_{254}$ plates and visualized by quenching of UV fluorescence (λ_{max}= 254 nm). 200-300 mesh silica gel was purchased from Qingdao Haiyang Chemical Co., China. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. The data for NMR spectra (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) were recorded at 293 K on a Bruker AVANCE AV 400 (400MHz, 101MHz and 376MHz) and chemical shifts were recorded relative to the solvent resonance. Signal positions were recorded in ppm and the following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s singlet, d doublet, t triplet, q quartet, m multiplet, Hz Hertz. For ^{1}H NMR: $CDCl_3$ = δ 7.26 ppm, CD_3OD = δ 3.31 ppm For ^{13}C NMR: $CDCl_3$ = δ 77.16 ppm. Mass spectra were obtained on Agilent 6520 Q-TOF LC/MS and Aligent 7890/5975C-GS/MSD. HRMS were obtained on VG ZAB-HS(ESI), Thermo Fisher Q-Exactive Orbitrap(ESI) and GCT Premier(EI). Luminescence quenching studies and Stern-Volmer luminescence quenching analyses were conducted using a Agilent Technologies Cary Eclipse Fluuorescence spectrofluorometer. UV/Vis Absorption spectra were recorded on a Agilent Technologies Cary Series UV-Vis spectrofluorometer.

***Safety**: Azides are potentially explosive compounds and require appropriate safety protocols to be observed at all times.*[4]

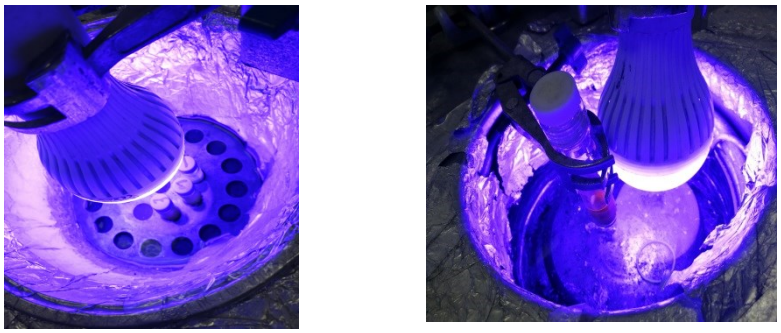
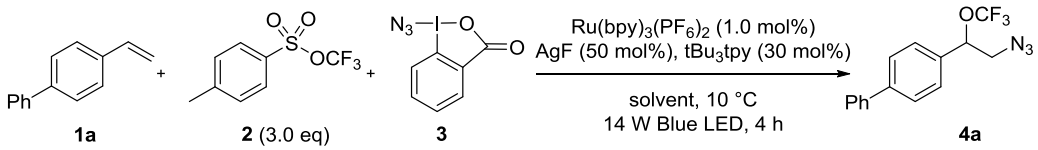


Figure 1: Blue LED with low-temperature reactor

Experimental Data

Experimental Procedures and Compound Characterization

Effect of solvents on the reaction

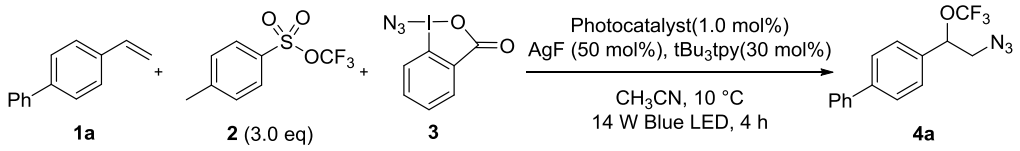


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (0.4 mg, 0.000500 mmol, 1.0 mol%), AgF (3.2 mg, 0.0250 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (6.0 mg, 0.0150 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (28.9 mg, 2.00 mmol, 2.00 equiv) and p-vinylbiphenyl (**1a**) (9.0 mg, 0.0500 mmol 1.00 equiv) in a 2.00 mL sealed vial tube were added solvent (the solvent was in advance cooled to -20 °C and then added) (0.40 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (28.0 µL, 0.150 mmol, 3.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^oC and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, benzotrifluoride (6.0 µL, 0.0490 mmol) was added to the reaction mixture. The yield of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) was determined by comparing the integration of the ^{19}F NMR resonance of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (-58.3 ppm) with that of benzotrifluoride (-62.8 ppm). Yields are reported in **Table S1**.

Table S1: Effect of solvents on the reaction

Solvent (0.4 mL)	Yield of **4a** [%] (^{19}F NMR)	Solvent (MeCN/co-solvent = 0.3 mL/0.1 mL)	Yield of **4a** [%] (^{19}F NMR)
MeCN	52	MeCN/DCM	47
DCM	5	MeCN/EA	49
EA	1	MeCN/DMC	50
DMC	14	MeCN/1,4-dioxane	48
1,4-dioxane	1	MeCN/THF	47
THF	2	MeCN/DMA	29
DMA	2	MeCN/DMSO	0
DMSO	0	MeCN/ toluene	50
toluene	1		

Effect of photocatalyst on the reaction

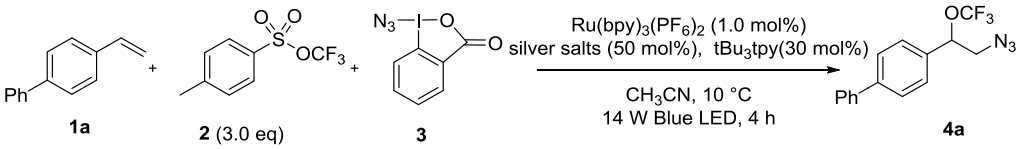


In an N_2 glovebox, to photocatalyst (0.000500 mmol, 1.0 mol%), AgF (3.2 mg, 0.0250 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (6.0 mg, 0.0150 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (28.9 mg, 2.00 mmol, 2.00 equiv) and p-vinylbiphenyl (**1a**) (9.0 mg, 0.0500 mmol 1.00 equiv) in a 2.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (0.40 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (28.0 µL, 0.150 mmol, 3.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, benzotrifluoride (6.0 µL, 0.0490 mmol) was added to the reaction mixture. The yield of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) was determined by comparing the integration of the ^{19}F NMR resonance of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (-58.3 ppm) with that of benzotrifluoride (-62.8 ppm). Yields are reported in **Table S2**.

Table S2: Effect of photocatalyst on the reaction

photocatalyst (mol%)	Yield of **4a** [%] (^{19}F NMR)	photocatalyst (mol%)	Yield of **4a** [%] (^{19}F NMR)
$[Ru(bpy)_3](PF_6)_2$ (0.5)	41	$Cu(dap)_2Cl$ (1.0)	2
$[Ru(bpy)_3](PF_6)_2$ (1.0)	52	$[Ru(bpz)_3](PF_6)_2$ (1.0)	0
$[Ru(bpy)_3](PF_6)_2$ (2.5)	52	$[Ru(phen)_3](PF_6)_2$ (1.0)	36
$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1.0)	8	$[Ir(ppy)_2(dtbbpy)](PF_6)_2$ (1.0)	2
Eosin Y (1.0)	0	*fac*-$Ir(ppy)_3$ (1.0)	2
Fluorescein (1.0)	0		

Effect of different silver salts on the reaction



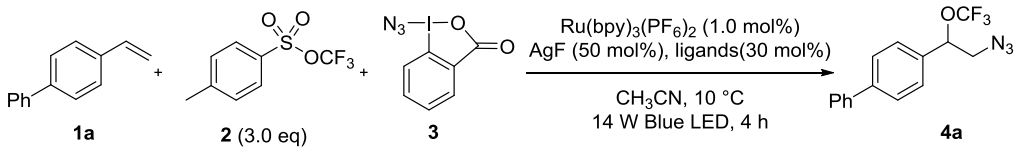
In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (0.4 mg, 0.000500 mmol, 1.0 mol%), silver salts, 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (6.0 mg, 0.0150 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (28.9 mg, 2.00 mmol, 2.00 equiv) and p-vinylbiphenyl (**1a**) (9.0 mg, 0.0500 mmol 1.00 equiv) in a 2.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (0.400 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (28.0 µL, 0.150 mmol, 3.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, benzotrifluoride

(6.0 μL, 0.0490 mmol) was added to the reaction mixture. The yield of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) was determined by comparing the integration of the ^{19}F NMR resonance of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (-58.3 ppm) with that of benzotrifluoride (-62.8 ppm). Yields are reported in **Table S3**.

Table S3: Effect of different silver salts on the reaction

silver salts	Yield of **4a** [%] (^{19}F NMR)	silver salts	Yield of **4a** [%] (^{19}F NMR)
No silver salts	1	Ag_2CO_3 (0.25 eq)	25
AgF (0.1 eq)	33	AgOTf (0.5 eq)	5
AgF (0.3 eq)	49	$AgIO_3$	13
AgF (0.5 eq)	52	$AgBF_4$ (0.5 eq)	8
AgF (1.0 eq)	26	$AgNO_3$ (0.5 eq)	25
AgF_2 (0.25 eq)	41	Ag_2SO_4 (0.5 eq)	35
Ag_2O (0.25 eq)	43	$AgSbF_6$ (0.5 eq)	1
AgO (0.5 eq)	44	AgOAc (0.5 eq)	39
AgOBz (0.5 eq)	24		

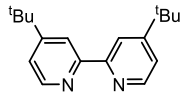
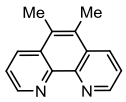
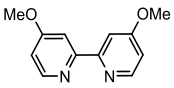
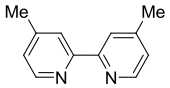
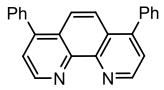
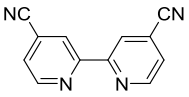
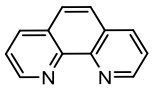
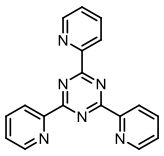
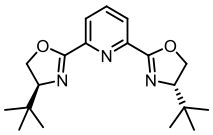
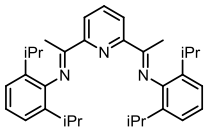
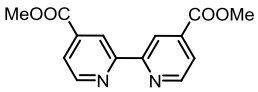
Effect of ligands on the reaction



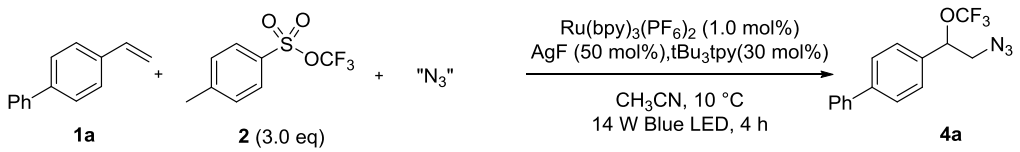
In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (0.4 mg, 0.000500 mmol, 1.0 mol%), AgF (3.2 mg, 0.0250 mmol, 50.0 mol%), ligands (0.0150 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (28.9 mg, 2.00 mmol, 2.00 equiv) and p-vinylbiphenyl (**1a**) (9.0 mg, 0.0500 mmol, 1.00 equiv) in a 2.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (0.40 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (28.0 μL, 0.150 mmol, 3.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^oC and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, benzotrifluoride (6.0 μL, 0.0490 mmol) was added to the reaction mixture. The yield of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) was determined by comparing the integration of the ^{19}F NMR resonance of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (-58.3 ppm) with that of benzotrifluoride (-62.8 ppm). Yields are reported in **Table S4**

Table S4: Effect of silver salts on the reaction

Ligand	Yield of **4a**[%] (^{19}F NMR)	Yield of **4a** [%] (^{19}F NMR)

no	20		37
4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (0.1 eq)	41		39
4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (0.3 eq)	52		42
4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (0.5 eq)	50		38
4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (1.0 eq)	43		45
2,2':6'2"-terpyridine (0.3 eq)	50		25
	36		17
	45		19
	19		

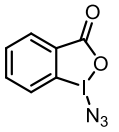
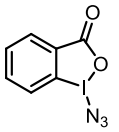
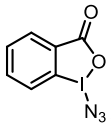
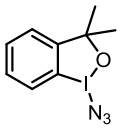
Effect of "N_3" sources on the reaction



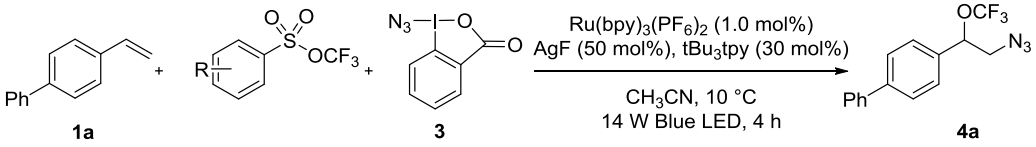
In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (0.4 mg, 0.000500 mmol, 1.0 mol%), AgF (3.2 mg, 0.0250 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (6.0 mg, 0.0150 mmol, 30.0 mol%), N_3 sources and p-vinylbiphenyl (**1a**) (9.0 mg, 0.0500 mmol 1.00 equiv) in a 2.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20° C and then added) (0.40 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (28.0 μL, 0.150 mmol, 3.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, benzotrifluoride (6.0 μL, 0.0490 mmol) was added to the reaction

mixture. The yield of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) was determined by comparing the integration of the ^{19}F NMR resonance of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (-58.3 ppm) with that of benzotrifluoride (-62.8 ppm). Yields are reported in **Table S5**

Table S5: Effect of "N_3" sources on the reaction

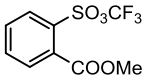
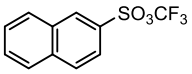
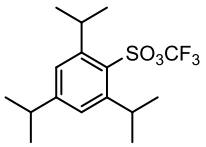
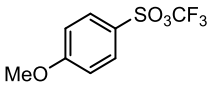
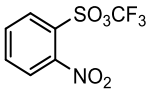
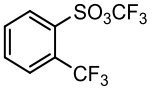
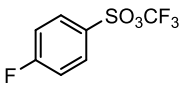
N_3 sources	Yield of **4a**[%] (^{19}F NMR)
 (1.0 eq)	39
 (1.5 eq)	43
 (2.0 eq)	52
 (2.0 eq)	3
$TMSN_3$ (2.0 eq)	0

Effect of "OCF_3" sources on the reaction

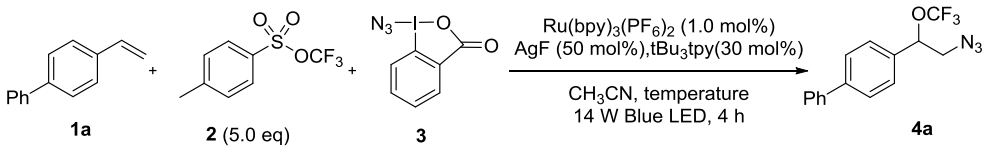


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (0.4 mg, 0.000500 mmol, 1.0 mol%), AgF(3.2 mg, 0.0250 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (6.0 mg, 0.0150 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (28.9 mg, 2.00 mmol, 2.00 equiv) and p-vinylbiphenyl (**1a**) (9.0 mg, 0.0500 mmol 1.00 equiv) in a 2.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (0.40 mL). "OCF_3" sources (0.150 mmol, 3.00 equiv) were added to the reaction and then the tube of the resulting mixture was cooled to 10 ^oC and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, benzotrifluoride (6.0 µL, 0.0490 mmol) was added to the reaction mixture. The yield of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) was determined by comparing the integration of the ^{19}F NMR resonance of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (-58.3 ppm) with that of benzotrifluoride (-62.8 ppm). Yields are reported in **Table S6**

Table S6: Effect of "OCF_3" sources on the reaction

"OCF_3" sources	Yield of **4a** [%] (^{19}F NMR)
$TsOCF_3$ (3.0 eq)	52
$TsOCF_3$ (4.0 eq)	59
$TsOCF_3$ (5.0 eq)	63
	35
	39
	24
	49
	28
	21
	23

Effect of temperatures on the reaction



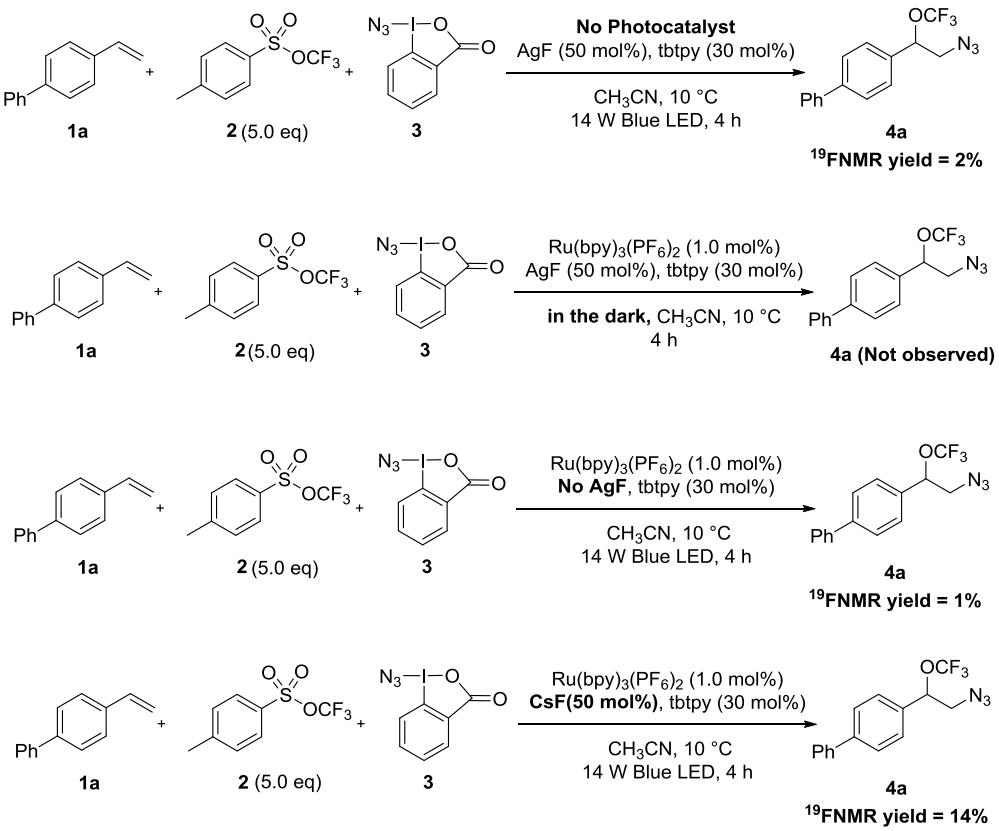
In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (0.4 mg, 0.000500 mmol, 1.0 mol%), AgF (3.2 mg, 0.0250 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (6.0 mg,

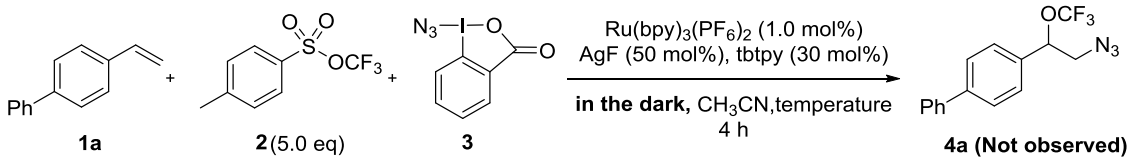
0.0150 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (28.9 mg, 2.00 mmol, 2.00 equiv) and p-vinylbiphenyl (**1a**) (9.0 mg, 0.0500 mmol 1.00 equiv)in a 2.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (0.40 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (28.0 µL, 0.150 mmol, 3.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to the corresponding temperature and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, benzotrifluoride (6.0 µL, 0.0490 mmol) was added to the reaction mixture. The yield of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) was determined by comparing the integration of the ^{19}F NMR resonance of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (-58.3 ppm) with that of benzotrifluoride (-62.8 ppm). Yields are reported in **Table S7**.

Table S7: Effect of temperatures on the reaction

Temperature	Yield of **4a** [%] (^{19}F NMR)
-20 °C	18
0 °C	58
10 °C	63
15 °C	63
25 °C	51

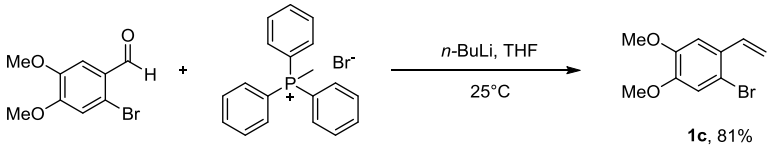
Control Reactions





Temperature	Yield of **4a** [%] (^{19}F NMR)
40 °C	0
60 °C	0
80 °C	0

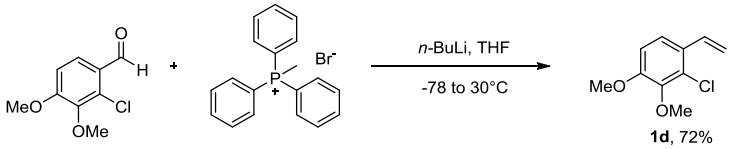
1-Bromo-4,5-dimethoxy-2-vinylbenzene (1c)



To a stirred solution of methyl(triphenyl)phosphonium bromide (1.78 g, 5.00 mmol) in dry, degassed THF (40.0 mL) at r.t. under argon atmosphere, was added n-BuLi (2.50 M in hexanes, 2.00 mL) in a slow manner. The resultant yellowish solution was stirred for an additional 15 min till the deep yellow color of the ylide was developed. 2-Bromo-4,5-dimethoxybenzaldehyde (1.22 g, 5.00 mmol) in dry THF (20.0 mL) was added to the mixture via a hypodermic syringe and the colour of the reaction mixture was soon found to fade. The resultant off-white solution was stirred at r.t. for an additional 3h, before the TLC has indicated the completion of the reaction. After NH_4Cl work-up, the organic components were extracted with DCM (3×25 mL) and the combined organic layers were washed with brine (25 mL) and water (25 mL) and finally dried on $MgSO_4$. Removal of the solvents under reduced pressure has generated the styrene **1c** as a thick oil, which was further purified by column chromatography [silica gel, hexanes/EtOAc 10:1 (v/v)] to furnish the pure product (0.980 g, 89%).

R_f = 0.2 (hexanes/DCM 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 7.01 – 6.91 (m, 2H), 5.58 (d, J = 17.4 Hz, 1H), 5.26 (d, J = 10.9 Hz, 1H), 3.87 (d, J = 10.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 148.6, 135.5, 129.5, 115.2, 114.6, 114.33, 108.7, 56.2, 56.0. The spectroscopic data (NMR) matched those reported in the literature for 1-bromo-4,5-dimethoxy-2-vinylbenzene [5].

2-Chloro-3,4-dimethoxy-1-vinylbenzene (1d)

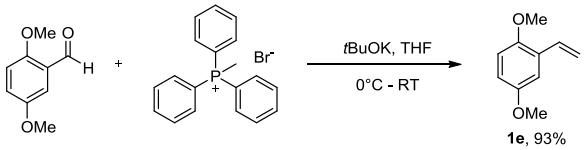


To methyltriphenylphosphonium bromide (4.28 g, 13.70 mmol, 1.20 equiv) was suspended in THF (24.0 mL) and *n*-BuLi (5.00 mL, 2.40 M solution in THF, 13.70 mmol, 1.20 equiv) was

added dropwise with stirring under N_2 at -78 °C. After the reaction was stirred 1h at 30 °C, 2-Chloro-3,4-dimethoxybenzaldehyde (2.00 g, 10.0 mmol, 1.00 equiv) in THF (8.00 mL) was added dropwise at -78 °C. Then, the reaction was stirred for 16 h at 30 °C. The reaction was quenched with H_2O (20.0 mL) and extracted 3 times with ether (20.0 mL). The combined organic layers were dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 10:1 (v/v), to afford 1.37 g 2-chloro-3,4-dimethoxy-1-vinylbenzene (**1d**) as a clear oil (72% yield).

R_f = 0.2 (hexanes/DCM 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 1H), 7.03 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 5.62 (d, *J* = 17.5 Hz, 1H), 5.34 – 5.21 (d, *J* = 11.0 Hz, 1H), 3.97 – 3.74 (d, *J* = 7.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 145.4 (s), 133.0, 129.5, 127.9, 121.4, 114.9, 110.75, 60.6, 56.2. The spectroscopic data (NMR) matched those reported in the literature for 2-chloro-3,4-dimethoxy-1-vinylbenzene.[6]

2,5-Dimethoxy-1-vinylbenzene (1e)

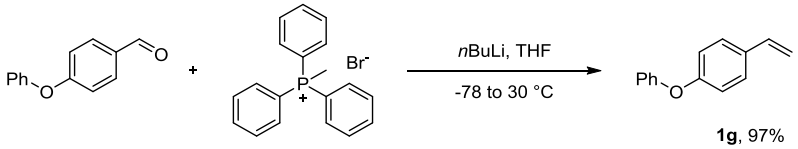


1e, 93%

To the solution of methyltriphenylphosphonium bromide (3.22 g, 9.03 mmol, 1.50 equiv.) suspended in THF (15.0 mL) was added portionwise *t*BuOK (1.01 g, 9.03 mmol, 1.5 equiv.) under N_2 at 0 °C. After the reaction was stirred 15 min at 30 °C, 2,5-dimethoxybenzaldehyde (1.00 g, 6.02 mmol, 1.00 equiv) was added dropwise at 0 °C. Then, the reaction was stirred over night at 30 °C. The reaction mixture was filtered by silica gel and washed with EtOAc. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 40:1 (v/v), to afford 920 mg 2,5-dimethoxy-1-vinylbenzene (**1e**) as a clear oil (93% yield).

R_f = 0.7 (hexanes/ EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.07-7.05 (m, 1H), 7.05 (dd, *J* = 17.7 Hz, 11.1 Hz, 1H), 6.85-6.78 (m, 2H), 5.75 (dd, *J* = 17.7 Hz, 1.4 Hz, 1H), 5.29 (dd, *J*= 11.1 Hz, 1.4 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 151.2, 131.5, 127.6, 114.9, 113.8, 112.2, 111.8, 56.2, 55.7. The spectroscopic data (NMR) matched those reported in the literature for 2,5-dimethoxy-1-vinylbenzene.[7]

1-Phenoxy-4-vinylbenzene (1g)



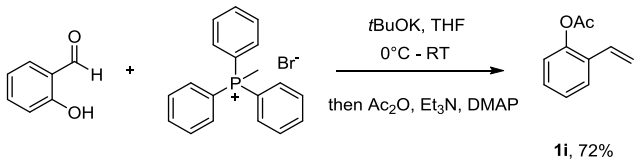
1g, 97%

To methyltriphenylphosphonium bromide (2.16 g, 6.10 mmol, 1.20 equiv) was suspended in THF (12.0 mL) and *n*-BuLi (2.50 mL, 2.5 M solution in THF, 6.10 mmol, 1.20 equiv) was added dropwise with stirring under N_2 at -78 °C. After the reaction was stirred 1h at 30 °C, 4-(phenoxy)benzaldehyde (1.00 g, 5.00 mmol, 1.00 equiv) in THF (4.0 mL) was added dropwise at -78 °C. Then, the reaction was stirred for 12 h at 30 °C. The reaction was

quenched with H_2O (10.0 mL) and extracted 3 times with ether (10.0 mL). The combined organic layers were dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes to afford 0.95 g 1-phenoxy-4-vinylbenzene (**1g**) as a clear oil (97% yield).

R_f = 0.8 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.28 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.01 (dd, *J* = 20.5, 8.2 Hz, 4H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 157.1, 136.1, 132.9, 129.9, 127.7, 123.4, 119.0, 118.9, 112.9. The spectroscopic data (NMR) matched those reported in the literature for 1-phenoxy-4-vinylbenzene.[8]

2-Vinylphenyl acetate (1i)

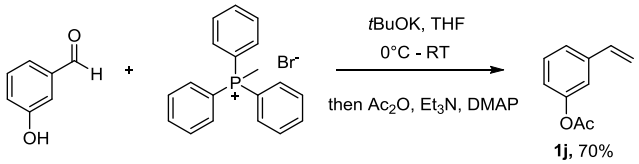


1i, 72%

To the solution of methyltriphenylphosphonium bromide (3.23 g, 9.01 mmol, 1.10 equiv.) suspended in THF (15.0 mL) was added portionwise *t*BuOK (2.02 g, 18.0 mmol, 2.20 equiv.) under N_2 at 0 °C. After the reaction was stirred 15 min at 30 °C, salicylaldehyde (1.00 g, 8.19 mmol, 1.00 equiv) was added at 0 °C. Then the reaction was stirred overnight at 30 °C. The reaction mixture was filtered by silica gel and washed with hexanes/EtOAc 1:1 (v/v). The filtrate was concentrated in vacuo and the residue was dissolved with DCM (20.0ml). Then to the mixture was added successively Et_3N (13.7 ml, 98.3 mmol, 12.0 equiv.), Ac_2O (4.60 ml, 49.1 mmol, 6.00 equiv.) and DMAP (100 mg, 0.819 mmol, 0.100 equiv.) at 0 °C. After the reaction was stirred 4 h at 30 °C, the mixture was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 8:1 (v/v), to afford 960 mg 2-vinylphenyl acetate (**1e**) as a clear oil (72% yield).

R_f = 0.5 (hexanes/ EtOAc 5:1 (v/v)). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.7, 1.7, 1H), 7.30 (td, *J* = 7.7, 1.7, 1H), 7.23 (tdd, *J* = 7.5, 1.3, 0.5, 1H), 7.06 (dd, *J* = 8.0, 1.3, 1H), 6.77 (dd, *J* = 17.6, 11.1, 1H), 5.78 (dd, *J* = 17.6, 1.1, 1H), 5.35 (dd, *J* = 11.1, 1.1, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 148.1, 130.4, 130.3, 128.8, 126.6, 126.3, 122.7, 116.5, 21.0. The spectroscopic data (NMR) matched those reported in the literature for 2-vinylphenyl acetate.[9]

3-Vinylphenyl acetate(1j)



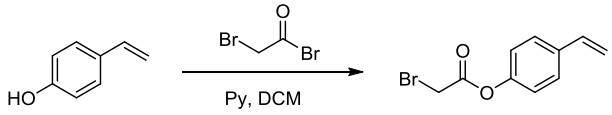
1j, 70%

To the solution of methyltriphenylphosphonium bromide (3.23 g, 9.01 mmol, 1.10 equiv.) suspended in THF (150mL) was added portionwise *t*BuOK (2.02 g, 18.0 mmol, 2.20 equiv.) under N_2 at 0 °C. After the reaction was stirred 15 min at 30 °C, salicylaldehyde (1.00 g, 8.19 mmol, 1.00 equiv) was added at 0 °C. Then the reaction was stirred overnight at 30 °C. The reaction mixture was filtered by silica gel and washed with hexanes/EtOAc 1:1 (v/v). The

filtrate was concentrated in vacuo and the residue was dissolved with DCM (20 ml). Then to the mixture was added successively Et_3N (13.7 ml, 98.3 mmol, 12.0 equiv.), Ac_2O(4.6 ml, 49.1 mmol, 6.00 equiv.) and DMAP (100 mg, 0.819mmol, 0.100equiv.) at 0 °C. After the reaction was stirred 4 h at 30 °C, the mixture was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 8:1 (v/v), to afford 935 mg 2-vinylphenyl acetate (**1e**) as a clear oil (70% yield).

R_f = 0.5 (hexanes/ EtOAc 5:1 (v/v)). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.0 Hz, 1 H), 7.24 – 7.29 (m, 1 H), 7.14 (t, *J*=1.6 Hz, 1 H), 6.99 (t, *J*=8.0 Hz, 1 H), 6.70 (dd, *J*=17.5, 10.9 Hz, 1 H), 5.75 (d, *J*=17.5 Hz, 1 H), 5.29 (d, *J*=10.9 Hz, 1 H), 2.31(s, 3 H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4,150.9,139.2, 135.9, 129.4, 123.8, 120.8, 119.0, 114.8, 21.1. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{10}H_{10}O_2Na$ $[M+Na]^+$, 185.0578. Found, 185.0578.

4-Vinylphenyl 2-bromoacetate(1k)

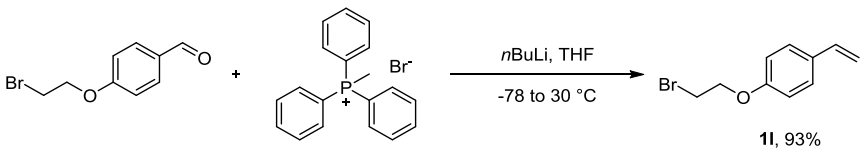


1k, 44%

To a stirred solution of 4-hydroxystyrene (0.600 g, 5.00 mmol, 1.00equiv.) in DCM(20.0 mL) was slowly added pyridine (0.60 mL, 7.50 mmol, 1.50 equiv.) and 2-bromoacetyl bromide (0.48 mL, 5.50 mmol) at 0 °C, and the mixture was stirred at 0 °C for 15 min and at room temperature for additional 20 min. Water was added to the solution, and the mixture was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 20/1) as an eluent gave 525 mg 4-vinylphenyl 2-bromoacetate (**1k**) (44% yield) as a milky solid.

R_f = 0.8 (hexanes/ EtOAc 5:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.12 – 7.06 (m, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.27 (dd, *J* = 10.9, 0.8 Hz, 1H), 4.30 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 , 149.9, 135.7, 135.7, 127.3, 127.3, 121.2, 114.5, 114.4, 25.7. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_9BrO_2$ [M], 239.9786. Found, 239.9783.

1-(2-Bromoethoxy)-4-vinylbenzene (1l)



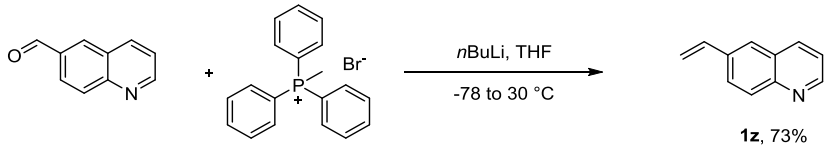
1l, 93%

To methyltriphenylphosphonium bromide (0.940 g, 2.70 mmol, 1.20 equiv) was suspended in THF (6.00 mL) and *n*-BuLi (1.20 mL, 2.40 M solution in THF, 2.70 mmol, 1.20 equiv) was added dropwise with stirring under N_2 at -78 °C. After the reaction was stirred 1h at 30 °C, 4-(2-bromoethoxy)benzaldehyde (0.500 g, 2.20 mmol, 1.00 equiv) in THF (2.00 mL) was added dropwise at -78 °C. Then, the reaction was stirred for 12 h at 30 °C. The reaction was quenched with H_2O (5.00 mL) and extracted 3 times with ether (5.00 mL). The combined organic layers were dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue

was purified by chromatography on silica gel, eluting with hexanes/DCM 30:1 (v/v) to afford 0.950 g 1-(2-bromoethoxy)-4-vinylbenzene (**1l**) as a white solid (93% yield).

R_f = 0.4 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 – 5.56 (d, *J* = 18.3 Hz,1H), 5.16 (d, *J* = 10.9 Hz, 1H), 4.29 (t, *J* = 6.3 Hz, 2H), 3.64 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 136.1, 131.2, 127.6, 114.8, 112.1, 67.9, 29.2. HRMS-EI (m/z): Calcd for $C_{10}H_{11}BrO$ [M], 225.9993. Found, 226.0001.

6-Vinylquinoline (1z)

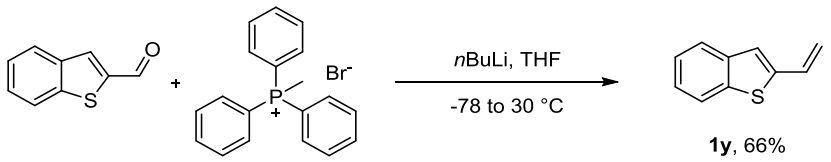


1z, 73%

To methyltriphenylphosphonium bromide (2.64 g, 7.4 mmol, 1.20 equiv) was suspended in THF (12.0 mL) and *n*-BuLi (3.10 mL, 2.4 M solution in THF, 7.4 mmol, 1.20 equiv) was added dropwise with stirring under N_2 at -78 ^{o}C. After the reaction was stirred 1h at 30 ^{o}C, quinoline-6-carbaldehyde (1.00 g, 6.20 mmol, 1.00 equiv) in THF (4.00 mL) was added dropwise at -78 ^{o}C. Then, the reaction was stirred for 12 h at 30 ^{o}C. The reaction was quenched with H_2O (10.0 mL) and extracted 3 times with ether (10.0 mL). The combined organic layers were dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 4:1 (v/v) to afford 0.720 g 6-vinylquinoline **(1z)** as a yellow oil (97% yield)

R_f = 0.4 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 3.1 Hz, 1H), 8.03 (t, *J* = 8.9 Hz, 2H), 7.82 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.63 (s, 1H), 7.30 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.83 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.36 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 148.1, 136.0, 135.92, 135.6, 129.5, 128.2, 126.8, 125.7, 121.3, 115.3. The spectroscopic data (NMR) matched those reported in the literature for 6-vinylquinoline.[10]

2-Vinylbenzo[b]thiophene (1y)

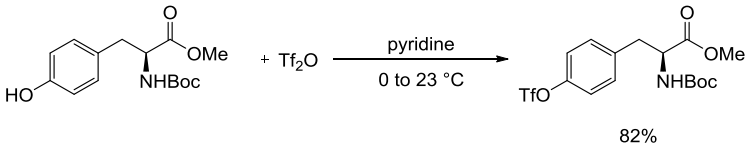


1y, 66%

To methyltriphenylphosphonium bromide (2.64 g, 7.40 mmol, 1.20 equiv) was suspended in THF (12.0 mL) and *n*-BuLi (3.10 mL, 2.40 M solution in THF, 7.40 mmol, 1.20 equiv) was added dropwise with stirring under N_2 at -78 ^{o}C. After the reaction was stirred 1h at 30 ^{o}C, benzo[b]thiophene-2-carbaldehyde(1.00 g, 6.20 mmol, 1.00 equiv) in THF (4.00 mL) was added dropwise at -78 ^{o}C. Then, the reaction was stirred for 12 h at 30 ^{o}C. The reaction was quenched with H_2O (10.0 mL) and extracted 3 times with ether (10.0 mL). The combined organic layers were dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes to afford 0.65 g 2-vinylbenzo[b]thiophene (**1y**) as a yellow solid (66% yield).

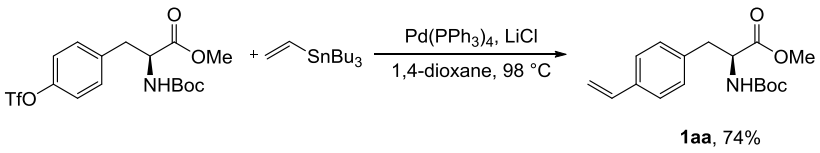
R_f = 0.9 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 6.0 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.18 (s, 1H), 6.93 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.68 (d, *J* = 17.3 Hz, 1H), 5.32 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.1, 138.9, 130.7, 124.9, 124.5, 123.6, 123.1, 122.3, 116.0. The spectroscopic data (NMR) matched those reported in the literature for 2-vinylbenzo[b]thiophene .[10]

(*S*)-methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-vinylphenyl)propanoate (1aa)



To a solution of (*S*)-methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-hydroxyphenyl)propanoate (4.50 g, 15.2 mmol, 1.00 equiv) in 30.0 mL of pyridine at 0 °C was slowly added trifluoromethanesulfonic anhydride (3.00 mL, 18.2 mmol, 1.20 equiv). The resulting mixture was stirred at 0 °C for 5 min and then allowed to warm to 23 °C and stirred at this temperature for 25 h. The resulting mixture was poured into water and extracted with ethyl ether. The ether extract was washed sequivuentially with water (50.0 ml), 10% aqueous hydrochloric acid solution (100 ml), water (50.0 ml), and a concentrated sodium chloride solution. The combined organic layers were dried over anh. $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 4:1 (v/v), to afford 5.33 g (*S*)-methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)pro-panoate as a white solid (82% yield).

R_f = 0.4 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 4H), 5.04 (d, *J* = 8.2 Hz, 1H), 4.59 (q, *J* = 6.9 Hz, 1H), 3.70 (s, 3H), 3.19 (dd, *J* = 13.8, 5.5 Hz, 1H), 3.04 (dd, *J* = 13.8, 6.9 Hz, 1H)., 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 155.2, 148.8, 137.2, 131.3, 121.5, 118.9 (q, *J* = 321.9 Hz), 80.3, 54.4, 52.5, 38.0, 28.4.

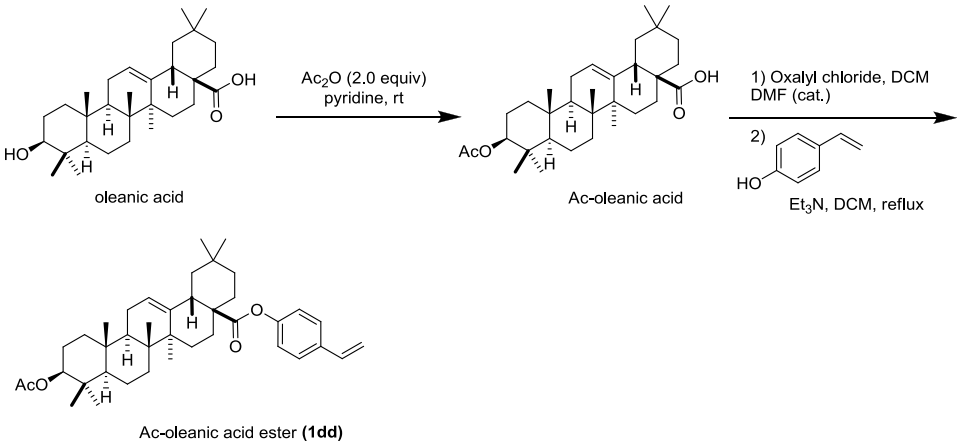


To a solution of (*S*)-methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-(((trifluoromethyl)sulfonyl)-oxy)phenyl)propanoate (5.33 g, 12.5 mmol, 1.00 equiv) in 50.0 mL of 1,4-dioxane were added *tri*-n-butylethenylstannane (3.70 mL, 12.5 mmol, 1.00 equiv), LiCl (1.49 g, 35.0 mmol, 2.80 equiv), $Pd(PPh_3)_4$ (289 mg, 0.250 mmol, 0.0200 equiv), and a few crystals of 2,6-di-*tert*-butyl-4-methyl-phenol. The resulting suspension was heated to reflux (98 °C) for 4 h, cooled to room temperature, and treated with 6.00 mL of pyridine and 12.0 mL of pyridinium fluoride (1.40 M solution in THF, 17.4 mmol). The resulting mixture was stirred at 23 °C for 16 h. The mixture was diluted with diethyl ether, filtered through a small pad of Celite, and washed with water, 10% HCl, water, and a concentrated sodium chloride solution. The combined organic layers were dried over anh. $MgSO_4$. The filtrate was concentrated *in*

vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 3:1 (v/v), to afford 2.80 g (*S*)-methyl 2-((*tert*-butoxycrbonyl)amino)-3-(4-vinylphenyl)propanoate (**1aa**) as a white solid (74% yield).

R_f = 0.5 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.68 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.72 (d, *J* = 17.5 Hz ,1H), 5.23 (d, *J* = 10.9 Hz, 1H), 4.96 (m, 1H), 4.57 (m, 1H), 3.72 (s, 3H), 3.07 (qd, *J* = 13.9, 5.9 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 155.2, 136.4, 136.4, 135.7, 129.6, 126.5, 113.8, 80.1, 54.5, 52.4, 38.1, 28.4. The spectroscopic data (NMR) matched those reported in the literature for(*S*)-methyl 2-((*tert*-butoxycrbonyl)amino)-3-(4-vinylphenyl)propanoate.[3]

Ac-oleanic acid ester (1dd)



Synthesis of Ac-oleanic acid: In a 25 mL dried Schelenk flask, to oleanic acid (2.00 mmol, 1 .00equiv) in 10 mL dry pyridine under ice-water bath was added Ac_2O (1.50 equiv). The reaction mixture was then slowly warmed to room temperature overnight. The reaction mixture was washed with water several times and extracted with ethyl acetate and then dried over $MgSO_4$. The filtrate was concentrated in vacuo to afford pure Ac-oleanic acid for further use in the next step (>99%).

Synthesis of Ac-oleanic acid ester: In a 25 mL dried Schelenk flask, to Ac-oleanic acid (698 mg, 1.40 mmol, 1.00 equiv) in 5.00 mL dry DCM was added oxalyl chloride (2.00 equiv) slowly (one drop of DMF was added). The reaction mixture was stirred at rt for 3 hours. The solvent was removed in vacuo to afford Ac-oleanic chloride. Then, to the solution of 4-vinylphenol (2.80 mmol, 2.00 equiv), Et_3N (2.80 mmol, 2.00 equiv) and DMAP (5 mol%) in 10.0 mL dry DCM, was added Ac-oleanic chloride slowly at room temperature.The resulting mixture was refluxed under N_2 for 12 hours. Washed with water and extracted with DCM (5.00 mL × 3). The combined DCM phases were dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel with eluent hexanes/EtOAc 3:1 (v/v), to afford 644 mg Ac-oleanic acid ester (**1dd**) (75%, white solid)

Rf= 0.8(hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.68 (d, *J* = 17.6 Hz, 1H), 5.35 (t, *J* = 3.2 Hz, 1H), 5.22 (d, *J* = 11.0 Hz, 1H), 4.60 – 4.41 (m, 1H), 2.98

(dd, *J* = 13.7, 3.9 Hz, 1H), 2.05 (s, 3H), 1.99 – 1.21 (m, 20H), 1.18 (s, 3H), 0.97 (s, 3H), 0.94 (s, 6H), 0.87 (s, 3H), 0.86 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 171.0, 150.7, 143.3, 136.0, 135.0, 127.0, 122.7, 121.6, 113.7, 80.9, 55.3, 47.5, 47.1, 45.8, 41.8, 41.4, 39.5, 38.1, 37.7, 36.9, 33.8, 33.1, 32.7, 32.4, 30.7, 28.0, 27.7, 25.1, 23.6, 23.5, 23.4, 23.0, 21.3, 18.2, 17.4, 16.7, 15.4. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{40}H_{56}O_4Na$ $[M+Na]^+$, 623.4076. Found, 623.4075.

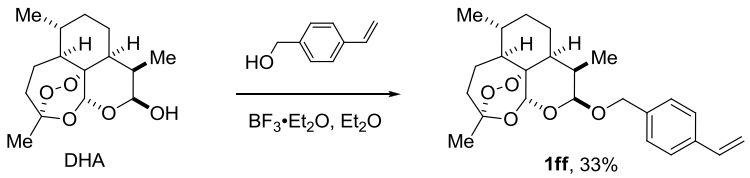
Gibberellate 4-vinylphenyl ester diacetate (1ee)

1ee, 37%

In a 50 mL dried Schelenk flask, to a solution of Gibberellic acid (880 mg, 2.54 mmol, 1.00 equiv) in 30ml DCM was successively added Et_3N (2.10 ml, 15.2 mmol, 6.00 equiv), EDCI (974 mg, 5.08 mmol, 2.00 equiv), DMAP (62.0 mg, 0.508 mmol, 0.200 equiv) and 4-hydroxystrene (458 mg, 3.81 mmol, 1.50 equiv) under ice-water bath. The reaction mixture was slowly warmed to room temperature and stirred for 24h. Then to the mixture was added Et_3N (10.5 ml, 76.2 mmol, 30.0 equiv) and Ac_2O (4.00 ml, 4.26 mmol, 16.7 equiv) . After 4 hours, the reaction was quenched by 20 ml water at iced-water bath, extracted with DCM (15 mL × 3), dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on SiO_2 with eluent hexanes/EtOAc 4:1 to 3:1 (v/v), to afford 500 mg gibberellate 4-vinylphenyl ester diacetate (**1ee**) (37%, white solid)

R_f = 0.25 (hexanes/EtOAc 4:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 7.11 – 7.02 (m, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.40 (d, *J* = 9.6 Hz, 1H), 5.90 (dd, *J* = 9.3, 3.8 Hz, 1H), 5.76 – 5.65 (m, 1H), 5.37 (d, *J* = 3.9 Hz, 1H), 5.26 (d, *J* = 11.4 Hz, 1H), 5.21 (dd, *J* = 3.3, 1.3 Hz, 1H), 5.05 (d, *J* = 2.3 Hz, 1H), 3.40 (d, *J* = 11.0 Hz, 1H), 3.02 (d, *J* = 11.2 Hz, 1H), 2.61 – 2.50 (m, 2H), 2.46 – 2.36 (m, 1H), 2.40 – 2.32 (m,1H), 2.31 – 2.24 (m, 1H), 2.10 (s, 3H), 2.07-2.02 (m, 4H), 2.02 – 1.98 (m, 1H), 1.90 – 1.78 (m, 1H), 1.80 – 1.70 (m, 1H), 1.29 – 1.25 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 170.4, 170.1, 170.0, 153.3, 149.8, 135.9, 135.8, 134.3, 129.3, 127.4, 121.6, 114.5, 108.6, 90.0, 84.0, 70.2, 53.5, 52.2, 51.4, 51.2, 50.3, 42.8, 39.6, 36.6, 22.1, 20.9, 16.9, 14.6. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{31}H_{32}O_8Na$ $[M+Na]^+$, 555.1995. Found, 555.1992.

10β-(4'- vinylphenyl)dihydroartemisinin (1ff)



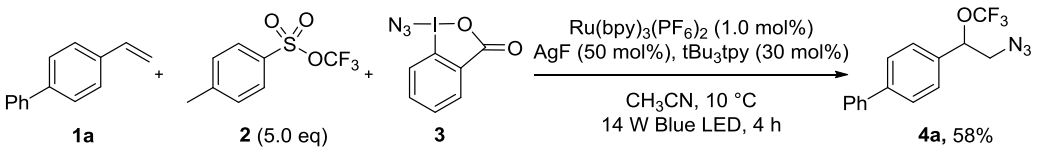
1ff, 33%

Borontrifluoride-diethyl ether (3 drops) was added to a stirred solution of DHA (426 mg, 1.50 mmol, 1.00 equiv.) and (4-vinylphenyl)methanol (370 mg, 2.76 mmol, 1.84 equiv.) in diethyl

ether (30 mL). After 6 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and dried ($MgSO_4$). Filtration and concentration of the filtrate gave a residue which on chromatography with ethyl acetate/hexane (1:10) gave the product as a colorless oil (198 mg, 33%).

R_f = 0.8 (hexanes/EtOAc 3:1 (v/v)).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.64 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.68 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.40 (s, 1H), 5.17 (dd, *J* = 10.8, 1.0 Hz, 1H), 4.88 – 4.78 (m, 2H), 4.44 (d, *J* = 12.5 Hz, 1H), 2.67 – 2.56 (m, 1H), 2.32 (ddd, *J* = 14.6, 13.4, 3.9 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.87 – 1.66 (m, 3H), 1.55 (dq, *J* = 13.4, 3.3 Hz, 1H), 1.49 – 1.34 (m, 5H), 1.32 – 1.12 (m, 3H), 0.88 (dd, *J* = 6.8, 2.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 136.8, 136.6, 127.5, 126.2, 113.8, 104.2, 101.5, 88.1, 81.2, 69.6, 52.7, 44.5, 37.5, 36.5, 34.7, 31.0, 26.3, 24.8, 24.6, 20.5, 13.2. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{24}H_{32}O_5Na$. $[M+Na]^+$, 423.2147 Found, 423.2145.

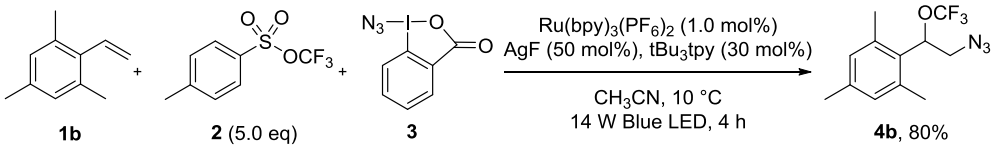
1-(2Azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (4a)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.00 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) and p-vinylbiphenyl(**1a**) (54.0 mg, 0.300 mmol, 1.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^{o}C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo.*Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 50:1 (v/v) to afford 53.4 mg1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) as a colourless liquid (58% yield).

R_f = 0.1 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 17.0, 7.7 Hz, 4H), 7.54 – 7.35 (m, 5H), 5.32 (dd, *J* = 7.8, 3.7 Hz, 1H), 3.72 (dd, *J* = 13.2, 8.1 Hz, 1H), 3.46 (dd, *J* = 13.3, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 140.3, 134.9, 129.0, 127.8, 127.7, 127.2, 126.7, 121.7 (q, *J* = 257.1 Hz), 79.4, 55.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.29 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{15}H_{12}ON_3F_3$ [M], 307.0932. Found, 307.0934.

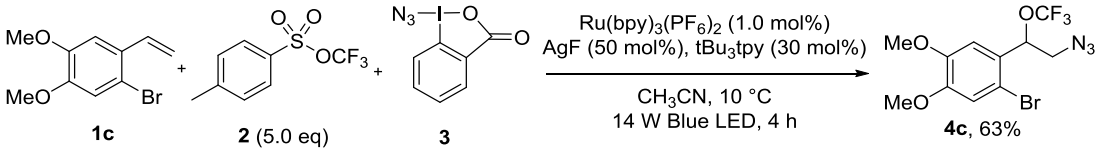
1-(2-Azido-1-(trifluoromethoxy)ethyl)-2,4,6-trimethylbenzene (4b)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 2,4,6-trimethylstyrene(**1b**) (43.9 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone (3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.0 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 100:1 (v/v) to afford 65.5 mg1-(2-azido-1-(trifluoromethoxy)ethyl)-2,4,6-trimethylbenzene (**4b**) as a colourless liquid (80% yield).

R_f = 0.3 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 5.67 (dd, *J* = 9.1, 4.5 Hz, 1H), 3.94 (dd, *J* = 13.4, 9.2 Hz, 1H), 3.33 (td, *J* = 13.6, 4.2 Hz, 1H), 2.40 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.4, 130.5, 128.7, 121.7 (q, *J* = 256.5 Hz), 77.0, 52.9, 20.9, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.05 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{14}ONF_3$ $[M-N_2]^+$, 245.1027. Found, 245.1030.

2-(2-Azido-1-(trifluoromethoxy)ethyl)-1-bromo-4,5-dimethoxybenzene (4c)

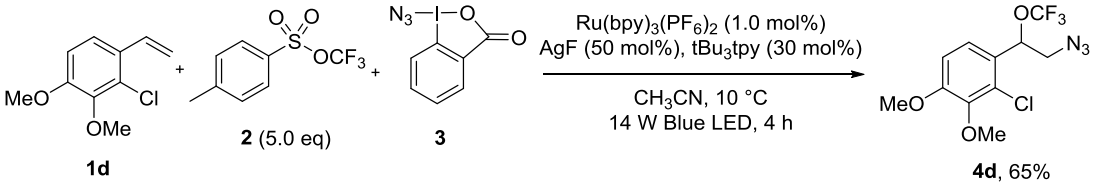


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1-bromo-4,5-dimethoxy-2-vinylbenzene (**1c**) (72.6 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EtOAc20:1-5:1 (v/v), to afford

69.7 mg 2-(2-azido-1-(trifluoromethoxy)ethyl)-1-bromo-4,5-dimethoxybenzene (**4c**) as a colourless liquid (63% yield).

R_f = 0.3 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 12.1 Hz, 2H), 5.63 (dd, *J* = 7.7, 3.4 Hz, 1H), 3.89 (d, *J* = 11.6 Hz, 6H), 3.54 (dd, *J* = 13.5, 7.7 Hz, 1H), 3.45 (dd, *J* = 13.5, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 149.1, 127.0, 121.5 (q, *J* = 257.4 Hz) 117.1, 120.2, 117.6, 115.3, 111.5, 110.0, 78.3, 56.2, 54.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.05 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{11}O_3BrF_3N_3$ [M], 368.9936. Found, 368.9939.

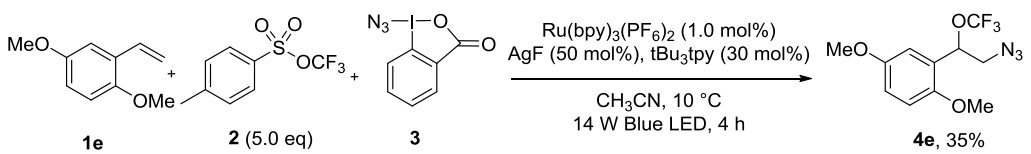
1-(2-Azido-1-(trifluoromethoxy)ethyl)-2-chloro-3,4-dimethoxybenzene (4d)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 eq) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 2-chloro-3,4-dimethoxy-1-vinylbenzene (**1d**) (59.4 mg, 0.300 mmol, 1.00 eq), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^{o}C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EtOAc20:1-5:1 (v/v), to afford 71.9 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)-2-chloro-3,4-dimethoxybenzene(**4d**) as a colourless liquid (65% yield).

R_f = 0.4 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 5.69 (dd, *J* = 7.4, 3.4 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H) , 3.61 – 3.39 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.23, 145.57, 126.44, 126.18, 121.56 (q, *J* = 257.2 Hz), 122.60, 111.09, 76.16, 60.78, 56.15, 54.46. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.90 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{11}O_3N_3F_3Cl$ [M], 325.0441. Found, 325.0453.

2-(2-Azido-1-(trifluoromethoxy)ethyl)-1,4-dimethoxybenzene (4e)

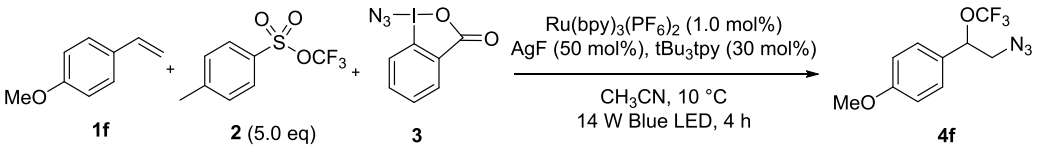


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (4.8 mg, 0.00600 mmol, 1.0 mol%), AgF (38.4 mg, 0.300 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (72.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (346.8 mg, 1.200 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added 4.8ml CH_3CN (the solvent was in advance cooled to -20 °C and then added) (4.80 mL), 1,4-dimethoxy-2-vinylbenzene

(**1e**) (98.4 mg, 0.600 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (564 µL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/DCM (1:10 to 1:5 v/v), to afford 61 mg 2-(2-azido-1-(trifluoro- methoxy)ethyl)-1,4-dimethoxybenzene (**4e**) as a colourless liquid (35% yield).

R_f = 0.25 (hexanes/ DCM (1:4 v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 2.8 Hz, 1H), 6.92 – 6.77 (m, 2H), 5.70 (dd, *J* = 7.7, 3.2 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.52 (dd, *J* = 13.4, 7.7 Hz, 1H), 3.44 (dd, *J* = 13.4, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 149.6, 125.3, 121.7(q. *J* = 257.6), 114.5, 113.0, 111.6, 74.7, 74.6, 56.0, 55.9, 54.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.16 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{12}O_3N_3F_3$ [M], 291.0831. Found, 291.0825.

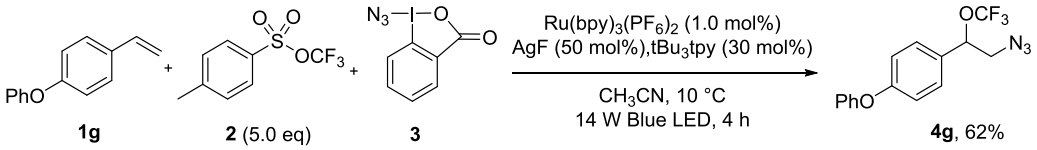
1-(2-Azido-1-(trifluoromethoxy)ethyl)-4-methoxybenzene (4f)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4''-tri-tert-butyl-2,2':6'2''-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1-methoxy-4-vinylbenzene (**1f**) (40.2 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 µL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/DCM/Et_3N 1:10:0.1 (v/v) to hexanes/EtOAc/Et_3N 1:30:0.1 (v/v) , to afford 47 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-methoxybenzene (**4f**) as a colourless liquid (60% yield).

R_f = 0.3 (hexanes/ EtOAc 1:40 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 6.97 – 6.89 (m, 2H), 5.20 (dd, *J* = 8.2, 4.1 Hz, 1H), 3.82 (s, 3H), 3.66 (dd, *J* = 13.3, 8.1 Hz, 1H), 3.38 (dd, *J* = 13.3, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 128.1, 127.8, 121.7 (q, *J* = 256.8 Hz), 79.5(m), 55.6, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.96 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_{10}O_2N_3F_3$ [M], 261.0725. Found, 261.0720.

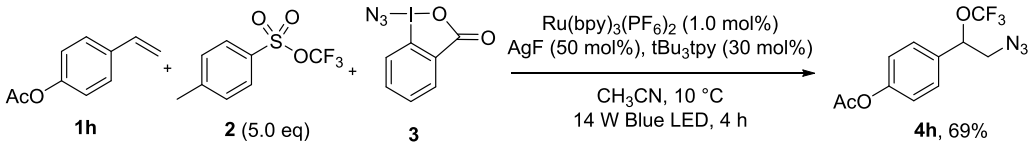
1-(2-Azido-1-(trifluoromethoxy)ethyl)-4-phenoxybenzene (4g)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1-phenoxy-4-vinylbenzene (**1g**) (58.8 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 µL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/DCM 1:10 (v/v) to afford 60.1 mg 1-(2-azido-1-(trifluoromethoxy)- ethyl)-4-phenoxybenzene (**4g**) as a colourless liquid (62% yield).

R_f = 0.5(hexanes/ EtOAc (20:1 v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 7.34 – 7.26 (m, 2H), 7.20 – 7.11 (m, 1H), 7.07 – 6.98 (m, 4H), 5.23 (dd, *J* = 8.0, 4.2 Hz, 1H), 3.67 (dd, *J* = 13.3, 8.0 Hz, 1H), 3.41 (dd, *J* = 13.3, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 156.4, 130.3, 129.9, 127.8, 124.0, 121.6(q. *J* = 258.2 Hz), 119.5, 118.6, 79.1(m), 55.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.22 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{15}H_{12}O_2N_3F_3$ [M], 323.0882. Found, 323.0881.

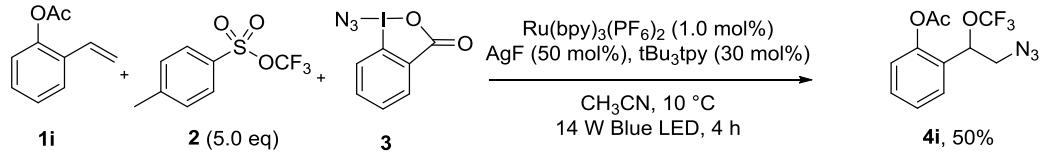
4-(2-Azido-1-(trifluoromethoxy)ethyl)phenyl acetate (4h)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 4-vinylphenyl acetate (**1h**) (48.6 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 µL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EtOAc 1:20 - 1:12 (v/v), to afford 60 mg 4-(2-azido-1-(trifluoro- methoxy)ethyl)phenyl acetate (**4h**) as a colourless liquid (69% yield).

R_f = 0.2 (hexanes/ EtOAc 1:10 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.18 – 7.11 (m, 2H), 5.25 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.64 (dd, *J* = 13.4, 8.1 Hz, 1H), 3.39 (dd, *J* = 13.4, 3.8 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 151.4, 133.5, 127.5, 122.3, 121.6(q. *J* = 258.2 Hz), 79.1(m), 55.6, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.37 (s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{11}H_{10}O_3N_3F_3Na$ $[M + Na]^+$, 312.0572, Found, 312.0570.

2-(2-Azido-1-(trifluoromethoxy)ethyl)phenyl acetate (4i)

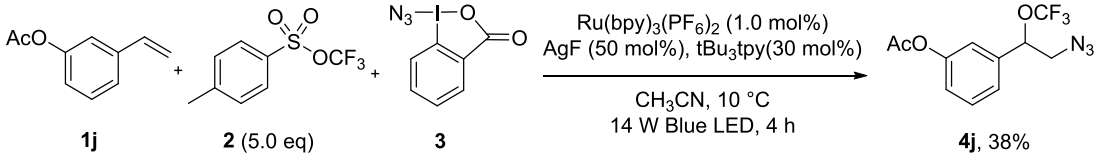


1i **2** (5.0 eq) **3** **4i**, 50%

In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 2-vinylphenyl acetate (**1i**) (48.6 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 µL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EtOAc 1:20 - 1:14 (v/v), to afford 44 mg 2-(2-azido-1-(trifluoromethoxy)ethyl)- phenyl acetate (**4i**) as a colourless liquid (50% yield).

R_f = 0.2 (hexanes/ EtOAc 1:10 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.40 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.66 (dd, *J* = 13.5, 8.4 Hz, 1H), 3.39 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 147.4, 130.3, 127.9, 127.5, 126.6, 123.0, 121.42 (q, *J* = 257.3 Hz), 74.5 (q, *J* = 2.8 Hz), 54.5, 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.79 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{10}O_3NF_3$ $[M-N_2]^+$, 261.0613. Found, 261.0610.

3-(2-Azido-1-(trifluoromethoxy)ethyl)phenyl acetate (4j)



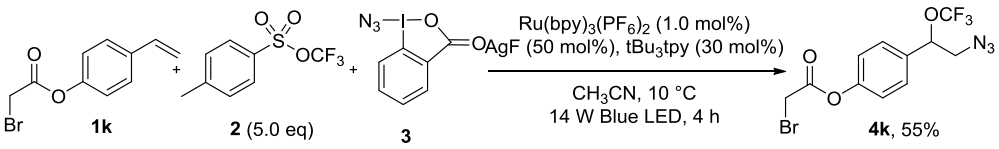
1j **2** (5.0 eq) **3** **4j**, 38%

In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 3-vinylphenyl acetate (**1j**) (48.6 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 µL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EtOAc 1:20 - 1:14 (v/v) to afford 33 mg 2-(2-azido-1-(trifluoromethoxy)- ethyl)phenyl acetate (**4j**) as a colourless liquid (38% yield).

R_f = 0.2 (hexanes/ EtOAc 1:10 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.16 – 7.10 (m, 2H), 5.24 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.65 (dd, *J* = 13.4, 8.1 Hz, 1H), 3.42 (dd, *J* = 13.5, 3.8 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 151.1, 137.6, 130.1, 123.6, 122.7, 121.6(q. *J* = 258.0

Hz),119.6, 79.1 – 78.8 (m), 55.6, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.45 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{10}O_3NF_3$ $[M-N_2]^+$, 261.0613. Found, 261.0619.

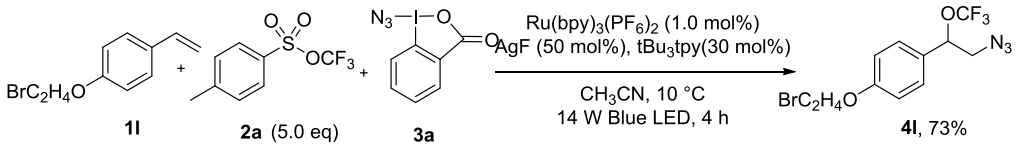
4-(2-Azido-1-(trifluoromethoxy)ethyl)phenyl 2-bromoacetate (4k)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 4-vinylphenyl 2-bromoacetate (**1k**) (72.0 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/DCM 1:10 (v/v) to hexanes/EtOAc 1:10 (v/v), to afford 61 mg 4-(2-azido-1-(trifluoromethoxy)ethyl)phenyl 2-bromoacetate (**4k**) as a colourless liquid (55% yield).

R_f = 0.25 (hexanes/ EtOAc (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.23 – 7.18 (m, 2H), 5.26 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.32 (s, 2H), 3.66 (dd, *J* = 13.4, 8.0 Hz, 1H), 3.42 (dd, *J* = 13.4, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 151.0, 134.2, 127.7, 121.6 (q, *J* = 257.3 Hz), 79.0 – 78.8 (m), 55.6, 40.9. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 121.59 (q, *J* = 257.3 Hz), 79.01 – 78.77 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.46 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_9O_3NF_3Br$ $[M-N_2]^+$, 338.9718. Found, 338.9708.

1-(2-Azido-1-(trifluoromethoxy)ethyl)-4-(2-bromoethoxy)benzene (4l)

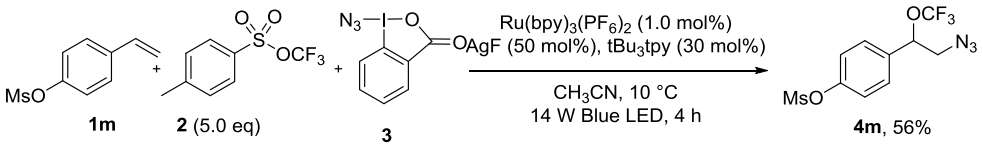


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3a**) (173.4 mg, 0.600 mmol, 2.00 equiv), 1-(2-bromoethoxy)-4-vinylbenzene (**1l**) (67.8 mg, 0.300 mmol, 1.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), Trifluoromethyl 4-methylbenzenesulfonate (**2a**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/DCM 1:15 (v/v) to hexanes/DCM 1:8 (v/v), to afford 78 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-(2-bromoethoxy)benzene (**4l**)

as a colourless liquid (73% yield).

R_f = 0.15 (hexanes/ EtOAc 1: 20 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.01 – 6.87 (m, 2H), 5.21 (dd, *J* = 8.1, 4.2 Hz, 1H), 4.30 (t, *J* = 6.2 Hz, 2H), 3.71 – 3.59 (m, 3H), 3.38 (dd, *J* = 13.3, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 128.7, 127.8, 121.5 (q, *J* = 257.0 Hz),, 115.1, 79.2 (q, *J* = 2.5 Hz), 67.9, 55.4, 28.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.14 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{11}O_2N_3F_3Br$ [M], 324.9987. Found, 324.9982.

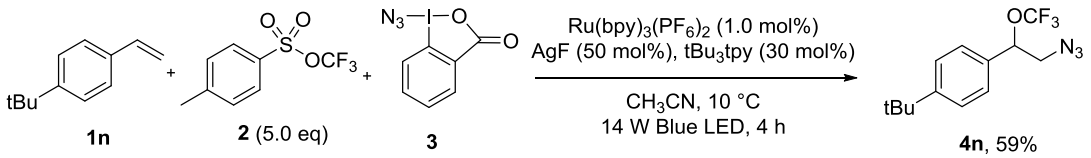
4-(2-Azido-1-(trifluoromethoxy)ethyl)phenyl methanesulfonate (4m)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 4-vinylphenyl methanesulfonate (**1m**) (59.4 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EA 1:15 (v/v) to hexanes/EA 1:6 (v/v), to afford 55 mg 4-(2-azido-1-(trifluoromethoxy)ethyl)phenyl methanesulfonate (**4m**) as a colourless liquid (56% yield).

R_f = 0.2 (hexanes/ EtOAc 1:4 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.38 – 7.30 (m, 2H), 5.27 (dd, *J* = 7.7, 4.1 Hz, 1H), 3.64 (dd, *J* = 13.4, 7.8 Hz, 1H), 3.42 (dd, *J* = 13.4, 4.0 Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 135.3, 128.1, 122.7, 121.6 (q, *J* = 258.1 Hz) , 78.6 (q, *J* = 2.2 Hz), 55.5, 37.7.^{19}F NMR (376 MHz, $CDCl_3$) δ -58.48 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_{10}O_4NF_3S$ $[M\text{-}N_2]^+$, 297.0283. Found, 297.0275.

1-(2-Azido-1-(trifluoromethoxy)ethyl)-4-(tert-butyl)benzene (4n)

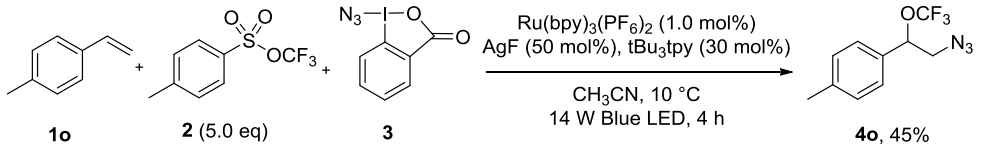


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1-(tert-butyl)-4-vinylbenzene (**1n**) (48.0 mg, 0.300 mmol, 1.00 equiv),Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.500 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was

cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.0 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 100:1 (v/v) to afford 50.8 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-(tert-butyl)benzene (**4n**) as a colourless liquid (59% yield).

R_f = 0.5 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 5.23 (dd, *J* = 8.2, 3.8 Hz, 1H), 3.66 (dd, *J* = 13.4, 8.3 Hz, 1H), 3.38 (dd, *J* = 13.4, 3.7 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 131.8, 124.84 (d, *J* = 6.4 Hz), 120.5 (q, *J* = 256.7 Hz), 77.9, 54.5, 33.6, 30.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.17 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{16}ONF_3$ $[M-N_2]^+$, 259.1184. Found, 259.1190.

1-(2-Azido-1-(trifluoromethoxy)ethyl)-4-methylbenzene (4o)

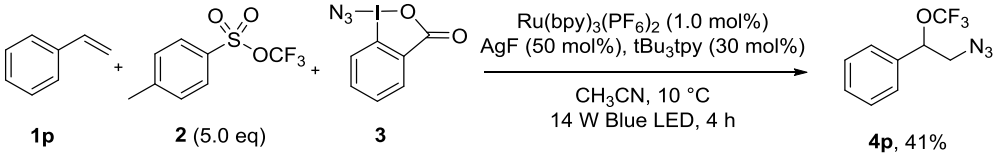


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL),1-methyl-4-vinylbenzene (**1o**) (35.4 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 100:1 (v/v) to afford 33.4 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-methylbenzene (**4o**) as a colourless liquid (45% yield).

R_f = 0.4 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (q, *J* = 8.0 Hz, 4H), 5.14 (dd, *J* = 8.1, 4.0 Hz, 1H), 3.57 (dd, *J* = 13.3, 8.2 Hz, 1H), 3.29 (dd, *J* = 13.3, 3.9 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 131.9, 128.57, 125.1, δ 120.5 (q, *J* = 256.9 Hz), 78.5, 54.4, 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.21 (s, 3F).

Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_{10}ONF_3$ $[M-N_2]^+$, 217.0714. Found, 217.0709.

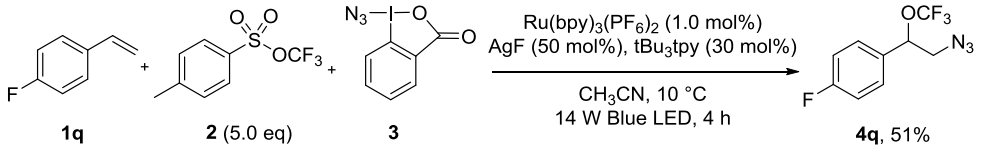
(2-Azido-1-(trifluoromethoxy)ethyl)benzene (4p)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), styrene (**1p**) (31.2 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^oC and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 100:1 (v/v) to afford 28.4 mg (2-azido-1-(trifluoromethoxy)ethyl)benzene (**4p**) as a colourless liquid (41% yield).

R_f = 0.4 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 3H), 7.36 (m, 2H), 5.25 (dd, *J* = 8.1, 4.0 Hz, 1H), 3.67 (dd, *J* = 13.4, 8.1 Hz, 1H), 3.41 (dd, *J* = 13.4, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.5, 127.0, 126.5, 123.8, 119.20 (q, *J* = 257.0 Hz). 77.15, 53.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.29 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_9H_8ONF_3$ $[M-N_2]^+$, 203.0558. Found, 203.0556.

1-(2-Azido-1-(trifluoromethoxy)ethyl)-4-fluorobenzene (4q)

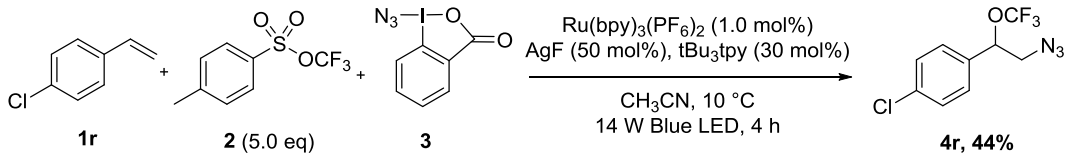


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1-fluoro-4-vinylbenzene (**1q**) (36.6 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^oC and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was

concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 100:1 (v/v) to afford 37.8 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-fluorobenzene (**4q**) as a colourless liquid (51% yield).

R_f = 0.3 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 5.23 (dd, *J* = 7.9, 4.2 Hz, 1H), 3.65 (dd, *J* = 13.3, 7.9 Hz, 1H), 3.40 (dd, *J* = 13.3, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 248.7 Hz), 130.7, 127.1, 120.4 (q, *J* = 257.3 Hz), 115.0 (d, *J* = 21.9 Hz), 77.7, 54.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.34 (s, 3F), -111.61.9(m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_9H_7F_4N_3O$ [M], 249.0525, Found, 249.0534.

1-(2-Azido-1-(trifluoromethoxy)ethyl)-4-chlorobenzene (4r)

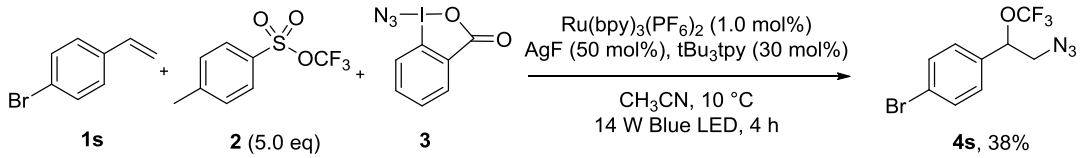


1r **2** (5.0 eq) **3** **4r, 44%**

In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4''-tri-tert-butyl-2,2':6'2''-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1-chloro-4-vinylbenzene (**1r**) (41.4 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^{o}C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10. 0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 100:1 (v/v) to afford 35.5 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-chlorobenzene (**4r**) as a colourless liquid (44% yield).

R_f = 0.4 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 5.22 (dd, *J* = 7.9, 4.1 Hz, 1H), 3.64 (dd, *J* = 13.3, 7.9 Hz, 1H), 3.40 (dd, *J* = 13.4, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 134.5, 129.3, 127.7, δ 121.6 (q, *J* = 257.5 Hz), 78.8, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.41 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_9H_7ONF_3Cl$ $[M-N_2]^+$, 237.0168. Found, 237.0170.

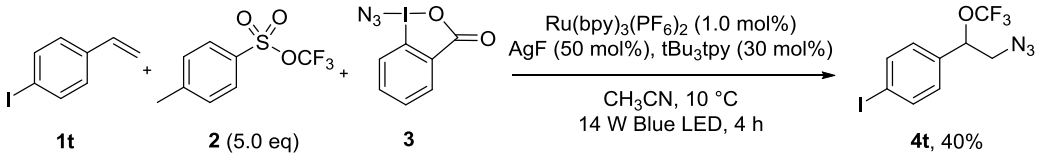
1-(2-Azido-1-(trifluoromethoxy)ethyl)-4-bromobenzene (4s)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (=tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1-bromo-4-vinylbenzene (**1s**) (54.6 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 100:1 (v/v) to afford 35.6 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-bromobenzene (**4s**) as a colourless liquid (38% yield).

R_f = 0.5 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.21 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.64 (dd, *J* = 13.3, 7.9 Hz, 1H), 3.40 (dd, *J* = 13.4, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 132.3, 127.9, 122.8, δ 121.6 (q, *J* = 257.4 Hz), 78.8, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.41. (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_9H_7ON_3F_3Br$ [M], 308.9725, Found, 308.9731.

1-(2-Azido-1-(trifluoromethoxy)ethyl)-4-iodobenzene (4t)

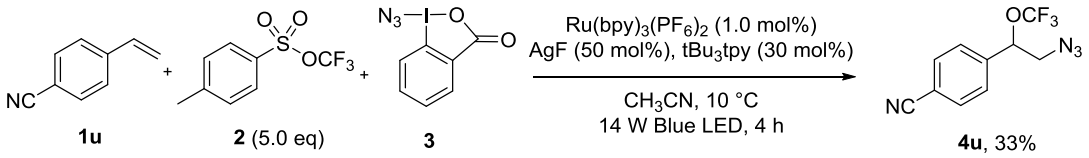


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1-iodo-4-vinylbenzene (**1t**) (69.0 mg, 0.300 mmol, 1.00 equiv), trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol,

32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/ EtOAc 30:1 (v/v) to afford 43.5 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-iodobenzene (**4t**) as a colourless liquid (40% yield).

R_f = 0.5 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 5.19 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.63 (dd, *J* = 13.3, 7.9 Hz, 1H), 3.39 (dd, *J* = 13.4, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.34, 135.81, 128.17, δ 121.68 (q, *J* = 257.4 Hz), 95.47, 79.04, 55.54. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.40 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_9H_7ON_3F_3I$ [M], 356.9586, Found, 356.9583.

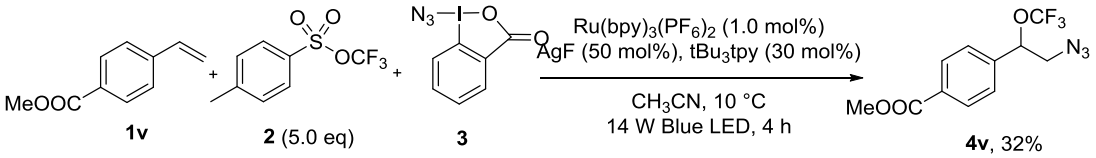
4-(2-Azido-1-(trifluoromethoxy)ethyl)benzonitrile (4u)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 4-vinylbenzonitrile (**1u**) (38.7 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^{o}C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10. 0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/ EtOAc 20:1 (v/v) to afford 43.5 mg 4-(2-azido-1-(trifluoromethoxy)ethyl)benzonitrile (**4u**) as a colourless liquid (33% yield).

R_f = 0.2 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 5.29 (dd, *J* = 7.3, 4.2 Hz, 1H), 3.65 (dd, *J* = 13.4, 7.4 Hz, 1H), 3.47 (dd, *J* = 13.4, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 132.9, 127.0, δ 121.5 (q, *J* = 257.4 Hz), 118.1, 113.5, 78.3, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.74 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_7ON_2F_3$ $[M\text{-}N_2]^+$, 228.0510, Found 228.0511.

Methyl 4-(2-azido-1-(trifluoromethoxy)ethyl)benzoate (4v)

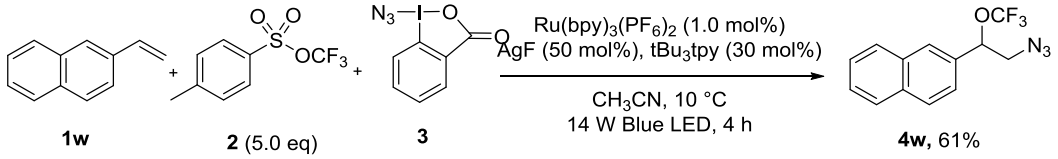


1v **2** (5.0 eq) **3** **4v**, 32%

In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), Methyl 4-vinylbenzoate (**1v**) (48.6 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EA 1:20 (v/v) to hexanes/EA 1:10 (v/v), to afford 27.7 mg methyl 4-(2-azido-1-(trifluoromethoxy)ethyl)benzoate (**4v**) as a colourless liquid (32% yield).

R_f = 0.2 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 5.30 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.93 (s, 3H), 3.66 (dd, *J* = 13.4, 7.8 Hz, 1H), 3.43 (dd, *J* = 13.4, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 140.7, 131.3, 130.3, 126.3, 121.59 (q, *J* = 257.6 Hz), 79.0 – 78.9 (m), 55.5, 52.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -58.64 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{10}O_3NF_3$ $[M-N_2]^+$,261.0613. Found, 261.0608.

2-(2-Azido-1-(trifluoromethoxy)ethyl)naphthalene (4w)



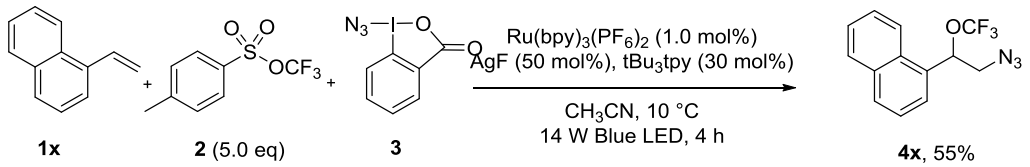
1w **2** (5.0 eq) **3** **4w,** 61%

In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 2-vinylnaphthalene (**1w**) (46.2 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo.*Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was

purified by preparative TLC, eluting with hexanes/DCM 50:1 (v/v) to afford 51.5 mg 2-(2-azido-1-(trifluoromethoxy)ethyl)naphthalene (**4w**) as a colourless liquid (61% yield).

Rf = 0.2 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (m, *J* = 14.8, 12.0, 9.7 Hz, 4H), 7.58 – 7.52 (m, 2H), 7.46 (dd, *J* = 8.5, 1.7 Hz, 1H), 5.43 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.77 (dd, *J* = 13.4, 8.2 Hz, 1H), 3.49 (dd, *J* = 13.4, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 133.3, 133.1, 129.1, 128.2, 127.9, 127.0, 126.9, 126.0, 123.2, 121.6 (q, *J* = 257.1 Hz), 79.84, 55.66. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.20 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{10}ON_3F_3$ [M], 281.0776, Found, 281.0769.

1-(2-Azido-1-(trifluoromethoxy)ethyl)naphthalene (4x)

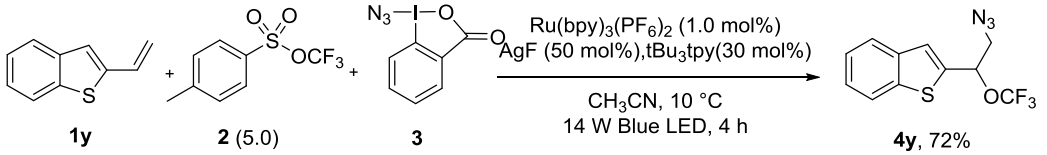


1x **2** (5.0 eq) **3** **4x**, 55%

In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4''-tri-tert-butyl-2,2':6'2''-terpyridine (= tBu3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1-vinylnaphthalene (**1x**) (46.2 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819.0 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946.0 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 50:1 (v/v) to afford 46.4 mg 1-(2-azido-1-(trifluoromethoxy)ethyl)naphthalene (**4x**) as a colourless liquid (55% yield).

Rf = 0.4 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (m, 3H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.63 – 7.47 (m, 3H), 6.04 (dd, *J* = 8.5, 3.2 Hz, 1H), 3.80 (dd, *J* = 13.6, 8.5 Hz, 1H), 3.56 (dd, *J* = 13.6, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 131.5, 129.9, 129.4, 127.2, 126.2, 125.5, 124.7, 121.9, 121.7 (d, *J* = 255.5 Hz), 77.4, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.58 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{10}ONF_3$ $[M\text{-}N_2]^+$, 253.0714, Found, 253.0721

2-(2-Azido-1-(trifluoromethoxy)ethyl)benzo[b]thiophene (4y)

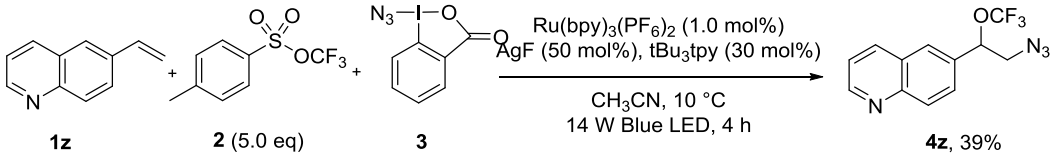


1y **2** (5.0) **3** **4y**, 72%

In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 2-vinylbenzo[*b*]thiophene (**1y**) (48.0 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 100:1 (v/v) to afford 61.9 mg 2-(2-azido-1-(trifluoromethoxy)ethyl)benzo[*b*]thiophene (**4y**) as a colourless liquid (72% yield).

R_f = 0.5 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 1H), 7.82 – 7.78 (m, 1H), 7.42 – 7.35 (m, 3H), 5.59 (dd, *J* = 7.5, 4.3 Hz, 1H), 3.82 (dd, *J* = 13.3, 7.6 Hz, 1H), 3.61 (dd, *J* = 13.3, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 138.8, 138.4, 125.4, 124.9, 124.30, 123.9, 122.6, 121.6 (q, *J* = 258.1 Hz), 75.8 (d, *J* = 2.7 Hz), 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.29 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_8ON_3F_3S$ [M], 287.0340, Found, 287.0339.

6-(2-Azido-1-(trifluoromethoxy)ethyl)quinoline (4z)

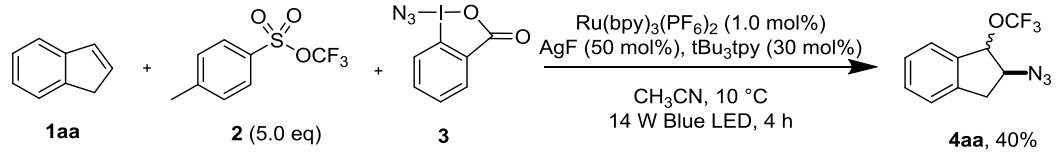


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 6-vinylquinoline (**1z**) (46.5 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1–3:1(v/v), to afford 33.0 mg 6-(2-azido-1-(trifluoromethoxy)ethyl)quinoline (**4z**) as a colourless liquid (39% yield).

R_f = 0.2 (hexanes/ EtOAc 3:1(v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 4.0 Hz, 1H), 8.18 (t, *J* = 9.0 Hz, 2H), 7.83 (s, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.46 (dd, *J* = 8.2, 4.1 Hz, 1H), 5.44 (dd, *J* = 7.6, 4.0 Hz, 1H), 3.76 (dd, *J* = 13.3, 7.8 Hz, 1H), 3.52 (dd, *J* = 13.4, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.26, 134.10, 130.62, 127.96, 126.72,

125.79, 121.56 (q, J = 257.4 Hz), 121.91 ,55.46. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.42 (s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{10}ON_4F_3$ $[M + H]^+$, 283.0807, Found, 283.0805.

2-Azido-1-(trifluoromethoxy)-2,3-dihydro-1H-indene (4aa)

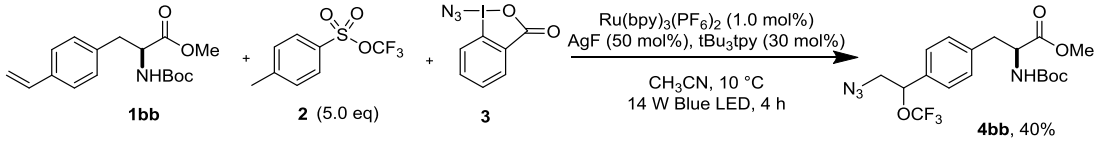


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), 1H-indene (**1aa**) (34.8 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 100:1 (v/v) to afford 29.2 mg 2-azido-1-(trifluoromethoxy)-2,3-dihydro-1H-indene (**4aa**) as a colourless liquid (40% yield, d.r.=1.7:1).

The *Trans*-diastereomer of 4aa R_f = 0.4 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 3H), 7.28 – 7.22 (m, 1H), 5.51 (d, J = 4.8 Hz, 1H), 4.36 (dd, J = 12.2, 6.1 Hz, 1H), 3.43 (dd, J = 16.1, 7.5 Hz, 1H), 2.93 (dd, J = 16.1, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 136.5, 130.3, 128.0, 125.4, 125.1, 121.7 (q, J = 256.6 Hz) 85.4, 66.9, 35.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.87 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_8ON_3F_3$ [M], 243.0619, Found, 243.0615

The *Cis*-diastereomer of 4aa R_f = 0.3 (hexanes/DCM 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, J = 7.4 Hz, 1H), 7.38 (td, J = 7.5, 1.4 Hz, 1H), 7.35 – 7.27 (m, 2H), 5.59 (d, J = 5.1 Hz, 1H), 4.19 (q, J = 6.0 Hz, 1H), 3.27 – 3.12 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 136.5, 130.4, 127.8, 125.6, 125.2, 121.8 (q, J = 257.8 Hz), 81.33 – 81.14 (m), 62.5, 35.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.02 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_8ONF_3$ $[M\text{-}N_2]^+$, 215.0558 Found, 215.0553.

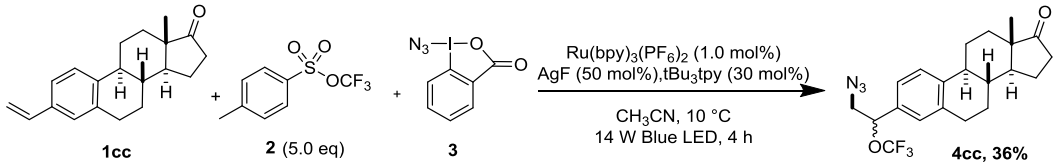
Methyl(2*S*)-3-(4-(2-azido-1-(trifluoromethoxy)ethyl)phenyl)-2-((tert-butoxycarbonyl)amino)propanoate (4bb)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv), Methyl (*S*)-2-((tert-butoxycarbonyl)amino)-3-(4-vinylphenyl)propanoate (**1bb**) (91.5 mg, 0.300 mmol, 1.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1-5:1(v/v), to afford 51.8 mg Methyl(2*S*)-3-(4-(2-azido-1-(trifluoromethoxy)ethyl)phenyl)-2-((tert-butoxycarbonyl)amino)propanoate (**4bb**) as a colourless liquid (40% yield, d.r.=8:1).

The major isomer of 4bb R_f = 0.4 (hexanes/ EtOAc 5:1(v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.23 (dd, *J* = 8.0, 3.9 Hz, 1H), 5.02 (d, *J* = 7.9 Hz, 1H), 4.60 (dd, *J* = 13.6, 6.4 Hz, 1H), 3.71 (s, 3H), 3.68 – 3.61 (m, 1H), 3.39 (dd, *J* = 13.4, 3.9 Hz, 1H), 3.19 – 3.10 (m, 1H), 3.04 (dd, *J* = 11.7, 5.6 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 155.0, 137.7, 134.7, 130.0, 126.4, 121.6 (q, *J* = 257.0 Hz), 80.1, 79.3, 55.5, 54.3, 52.3, 38.3, 28.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.29(s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_9ON_4F_3Na$ $[M + Na]^+$, 455.1813, Found, 455.1816.

3-(2- Azido -1-(trifluoromethoxy)ethyl)-1,3,5(10)-Estratrien-17-one (4cc)

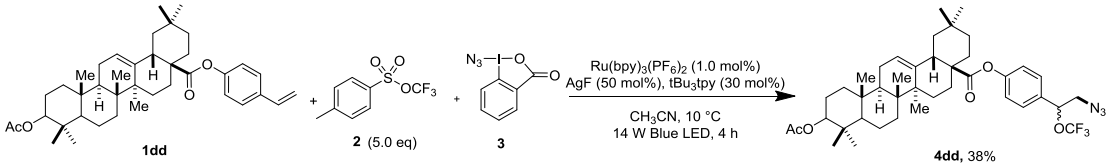


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv), 3-Vinyl-1,3,5(10)-Estratrien-17-one (**1cc**) (84.1 mg, 0.300 mmol, 1.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was

purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1-8:1 (v/v), to afford 34.9 mg 3-(2- azido -1-(trifluoromethoxy)ethyl)-1,3,5(10)-Estratrien-17-one (**4cc**) as a colourless liquid (36% yield, d.r.=10:1).

The major isomer of 4cc R_f = 0.4 (hexanes/ EtOAc 8:1(v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 5.20 (dd, *J* = 8.2, 3.9 Hz, 1H), 3.66 (dd, *J* = 13.3, 8.2 Hz, 1H), 3.38 (dd, *J* = 13.4, 3.8 Hz, 1H), 2.98 – 2.88 (m, 2H), 2.60 – 2.46 (m, 1H), 2.45 – 2.39 (m, 1H), 2.35 – 2.25 (m, 1H), 2.22 – 1.89 (m, 3H), 1.73 – 1.40 (m, 6H), 0.91 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 220.6, 141.1, 137.2, 133.3, 126.7, 125.9, 123.5, 121.5 (q, *J* = 256.9 Hz), 79.4, 55.5, 50.3, 47.9, 44.3, 37.9, 35.8, 31.5, 29.3 (d, *J* = 4.2 Hz), 26.3, 25.6, 21.5, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.22 (s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{21}H_2O_2N_3F_3Na$ $[M + Na]^+$, 430.1718, Found, 430.1716.

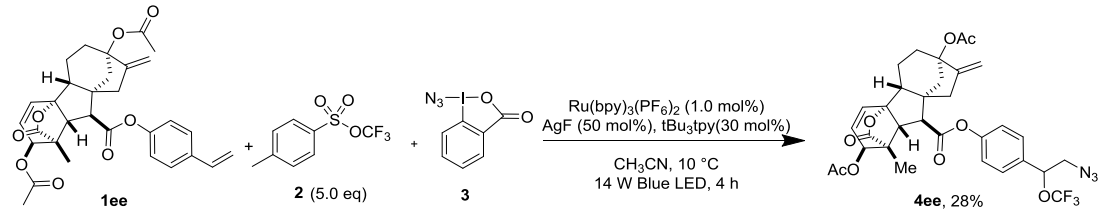
4-(2-Azido-1-(trifluoromethoxy)ethyl)phenyl(3-β)-3-acetoxy-12-en-28-oleanolic carboxylate (4dd)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.00 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv), 4-vinylphenyl-3-acetoxy-12-en-28-oleanolic carboxylate (**1dd**) (180.1 mg, 0.300 mmol, 1.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advance cooled to -20 °C and then added) (2.40 mL), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1-10:1(v/v), to afford 34.9 mg 4-(2-azido-1-(trifluoromethoxy)ethyl)phenyl(3-β)-3-acetoxy-12-en-28-oleanolic carboxylate (**4dd**) as a colourless liquid (38% yield, d.r.=4:1).

The major isomer of 4dd R_f = 0.6 (hexanes/ EtOAc 10:1(v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 5.34 (t, *J* = 3.2 Hz, 1H), 5.23 (dd, *J* = 8.2, 3.7 Hz, 1H), 4.53 – 4.46 (m, 1H), 3.63 (dd, *J* = 13.4, 8.3 Hz, 1H), 3.36 (dd, *J* = 13.4, 3.8 Hz, 1H), 2.96 (dd, *J* = 13.6, 3.9 Hz, 1H), 2.04 (s, 3H), 1.96 – 1.24 (m, 20H), 1.18 (d, *J* = 3.4 Hz, 3H), 0.95 (m, 9H), 0.89 – 0.83 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.16, 171.10, 151.89, 143.27, 133.16, 127.35, 122.97, 122.29, 121.50 (q, *J* = 257.2 Hz), 80.93, 79.15, 55.57, 55.37, 47.59, 47.28, 45.80, 41.90, 41.52, 39.60, 38.22, 37.77, 37.01, 33.92, 33.15, 32.85, 32.47, 30.81, 28.13, 27.85, 25.86, 23.67, 23.60, 23.54, 23.11, 21.41, 18.29, 17.53, 16.79, 15.50. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.21 (s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{41}H_{56}O_5N_3F_3Na$ $[M + Na]^+$, 750.4070, Found, 750.4068.

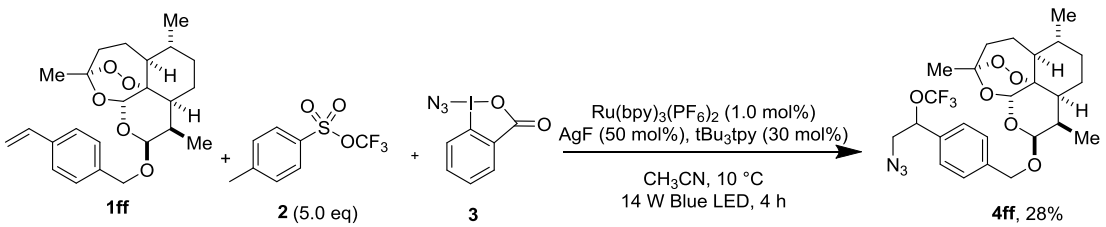
Gibberellate (4-(2-azido-1-(trifluoromethoxy)ethyl)phenyl ester diacetate (4ee)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.00 mol%), AgF (19.2mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv), gibberellate 4-vinylphenyl ester diacetate (**1ee**) (160.9 mg, 0.300 mmol, 1.00 equiv) in a 5.0 mL sealed vial tube were added CH_3CN (the solvent was in advanec cooled to -20 °C and then added) (2.40 mL), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/EA 1:15 (v/v) to hexanes/EA 1:8 (v/v) to afford 56 mg (**4ee**) as a colourless liquid (28% yield, d.r.=1.69:1). Further purification needed preparative HPLC for pure NMR Spectroscopy.

R_f = 0.25 (hexanes/ EtOAc 1:10 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.22 – 7.15 (m, 2H), 6.40 (d, *J* = 9.3 Hz, 1H), 5.91 (dd, *J* = 9.3, 3.8 Hz, 1H), 5.37 (d, *J* = 3.8 Hz, 1H), 5.26 (dd, *J* = 8.0, 3.8 Hz, 1H), 5.21 (d, *J* = 2.0 Hz, 1H), 5.05 (s, 1H), 3.65 (dd, *J* = 13.4, 8.1 Hz, 1H), 3.39 (dd, *J* = 12.5, 3.9 Hz, 2H), 3.04 (d, *J* = 11.1 Hz, 1H), 2.61 (d, *J* = 10.7 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.45 – 2.37 (m, 1H), 2.35 – 2.23 (m, 2H), 2.11 (s, 3H), 2.08 – 1.97 (m, 5H), 1.90 – 1.80 (m, 1H), 1.79 – 1.70 (m, 1H), 1.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 170.1, 169.9, 169.9, 153.1, 150.8, 134.1, 134.0, 129.3, 127.6, 122.0, 121.48 (q, *J* = 257.4 Hz), 108.5, 89.8, 83.9, 78.89 – 78.70 (m), 70.1, 55.5, 53.4, 52.2, 51.4, 51.1, 50.3, 42.8, 39.4, 36.6, 22.0, 20.7, 16.8, 14.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -58.27 s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{32}H_{34}O_9N_3F_3Na$ $[M + Na]^+$, 682.1988, Found, 682.1988.

10β-(4'- (2-azido-1-(trifluoromethoxy)ethyl)benzyl)dihydroartemisinin (4ff)

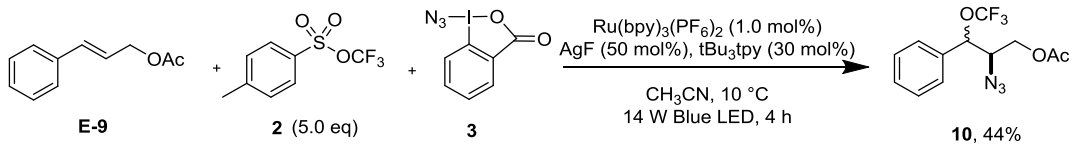


In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv), 10β-(4'- vinylphenyl)dihydroartemisinin (120.1 mg, 0.300 mmol, 1.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advanec

cooled to -20 °C and then added) (2.40 mL), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, and was purified by chromatography on silica gel, eluting with hexanes/DCM 1:5 (v/v) to hexanes/EA 1:15 (v/v) to hexanes/EA 1:10 (v/v) to afford 44 mg (**4ff**) as a colourless liquid (28% yield, d.r.=1.88:1). Further purification needed Preparative HPLC for pure NMR Spectroscopy.

R_f = 0.2 (hexanes/ EtOAc 1:8 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 4H), 5.44 (s, 1H), 5.24 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.96 – 4.86 (m, 2H), 4.54 (d, *J* = 12.8 Hz, 1H), 3.66 (dd, *J* = 13.3, 8.1 Hz, 1H), 3.40 (dd, *J* = 13.3, 4.0 Hz, 1H), 2.69 (dt, *J* = 7.8, 4.2 Hz, 1H), 2.38 (td, *J* = 14.0, 3.9 Hz, 1H), 2.04 (ddd, *J* = 14.6, 4.6, 3.1 Hz, 1H), 1.93 – 1.76 (m, 3H), 1.63 (dd, *J* = 13.2, 3.2 Hz, 1H), 1.59 – 1.41 (m, 6H), 1.36 – 1.19 (m, 2H), 0.95 (dd, *J* = 6.5, 4.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 134.9, 127.5, 126.2,121.5(q, *J* = 258.0 Hz) 104.2, 101.5, 88.0, 81.1, 79.3, 69.2, 55.5, 52.6, 44.4, 37.4, 36.4, 34.6, 30.9, 26.2, 24.7, 24.5, 20.3, 13.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.30 (s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{25}H_{32}O_6N_3F_3Na$ $[M + Na]^+$, 550.2141, Found, 550.2140.

2-Azido-3-phenyl-3-(trifluoromethoxy)propyl acetate (10)



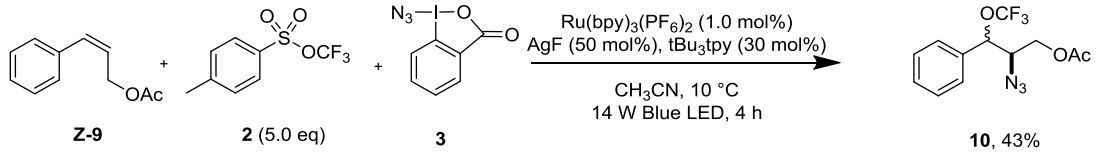
In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advanec cooled to -20 °C and then added) (2.40 mL), (E)-Methyl cinnamyl acetate (**E-9**) (52.8 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 50:1 (v/v) to afford 39.9 mg 2-azido-3-phenyl-3-(trifluoromethoxy)propyl acetate (**10**) as a colourless liquid (44% yield, d.r.=1.5:1).

The *anti*--diastereomer of 10 R_f = 0.4 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 5H), 5.17 (d, *J* = 7.1 Hz, 1H), 4.10 (dd, *J* = 11.3, 3.1 Hz, 1H), 3.93 (dd, *J* = 9.9, 6.6 Hz, 1H), 3.81 (dd, *J* = 11.5, 6.6 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 135.0, 129.7, 129.1, 126.6, 121.5 (q, *J* = 257.2 Hz), 80.2, 63.8,

62.9, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.13 (s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{12}O_3N_3F_3Na$ $[M + Na]^+$, 326.0728, Found, 326.0728.

The *syn*-diastereomer of 10 R_f = 0.4 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 5H), 5.15 (d, *J* = 6.8 Hz, 1H), 4.28 (dd, *J* = 11.7, 3.8 Hz, 1H), 4.19 (dd, *J* = 11.7, 7.0 Hz, 1H), 3.98 (td, *J* = 6.9, 3.8 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 135.0, 129.7, 129.0, 127.0, 119.4 (q, *J* = 257.6 Hz), 78.7 (dd, *J* = 4.7, 2.3 Hz), 63.5, 62.7, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.18 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{12}O_3NF_3$ $[M-N_2]^+$, 275.0769, Found, 275.0763.

2-Azido-3-phenyl-3-(trifluoromethoxy)propyl acetate (10)



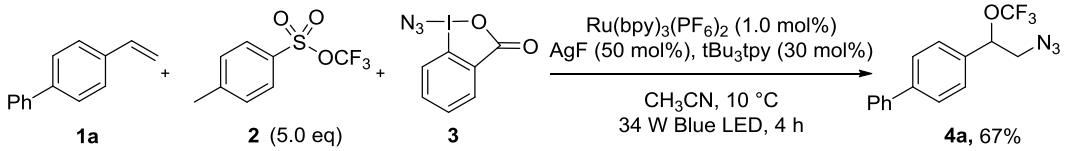
Z-9 **2** (5.0 eq) **3** **10**, 43%

In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2 mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv) in a 5.00 mL sealed vial tube were added CH_3CN (the solvent was in advanec cooled to -20 °C and then added) (2.40 mL), (Z)-Methyl cinnamyl acetate (**Z-9**) (52.8 mg, 0.300 mmol, 1.00 equiv), Trifluoromethyl 4-methylbenzenesulfonate (**2**) (282 μL, 1.50 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^{o}C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 50 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (10.0 mL), acetone(3.00 ml), $NaHCO_3$ (819 mg, 9.75 mmol, 32.5 equiv) and Na_2SO_3 (946 mg, 7.50 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (10.0 mL × 3), washed with brine (10.0 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/DCM 50:1 (v/v) to afford 39.1 mg 2-azido-3-phenyl-3-(trifluoromethoxy)propyl acetate (**10**) as a colourless liquid (43% yield, d.r.=1.5:1).

The *anti*-diastereomer of 10 R_f = 0.4 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 5H), 5.17 (d, *J* = 7.1 Hz, 1H), 4.10 (dd, *J* = 11.3, 3.1 Hz, 1H), 3.93 (dd, *J* = 9.9, 6.6 Hz, 1H), 3.81 (dd, *J* = 11.5, 6.6 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 135.0, 129.7, 129.1, 126.6, 121.5 (q, *J* = 257.2 Hz), 80.2, 63.8, 62.9, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.13 (s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{12}O_3N_3F_3Na$ $[M + Na]^+$, 326.0728, Found, 326.0728.

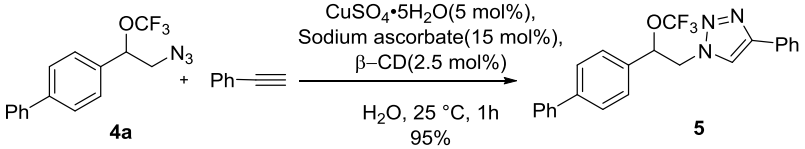
The *syn*-diastereomer of 10 R_f = 0.4 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 5H), 5.15 (d, *J* = 6.8 Hz, 1H), 4.28 (dd, *J* = 11.7, 3.8 Hz, 1H), 4.19 (dd, *J* = 11.7, 7.0 Hz, 1H), 3.98 (td, *J* = 6.9, 3.8 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 135.0, 129.7, 129.0, 127., 119.4(q, *J* = 257.6 Hz), 78.7 (dd, *J* = 4.7, 2.3 Hz), 63.5, 62.7, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.18 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{12}O_3NF_3$ $[M-N_2]^+$, 275.0769, Found, 275.0763.

Gram-scale synthesis of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (4a)



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (48.0 mg, 0.0600 mmol, 1.0 mol%), AgF (381 mg, 3.00 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (723 mg, 1.80 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (3.47g, 12.0 mmol, 2.00 equiv) and p-vinylbiphenyl(**1a**) (1.08 g, 6.00 mmol, 1.00 equiv) in a 50 mL sealed vial tube were added CH_3CN (the solvent was in advanec cooled to -20 °C and then added) (48.0 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (7.21 g, 30.0 mmol, 5.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 ^oC and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was transfered into a 500 mL round-bottom flask, and was concentrated *in vacuo*.Then, H_2O (250 mL), acetone(60.0 ml), $NaHCO_3$ (16.4 g, 650 mmol, 32.5 equiv) and Na_2SO_3 (19.0 g, 150 mmol, 25.00 equiv) were sequentially added to the reaction mixture at 25°C. Then the reaction mixture was stirring at 50°C for 4 hr, cooled to room temperature, extracted with EtOAc (30 mL × 3), washed with brine (30 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1-25:1-4:1 (v/v), to afford 1.24 g 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) as a colourless liquid (67% yield).

Synthesis of 1-(2-([1,1'-biphenyl]-4-yl)-2-(trifluoromethoxy)ethyl)-4-phenyl-1H-1,2,3-triazole (5)

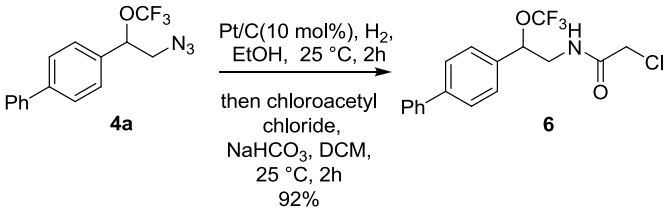


In a 10ml round bottom flask, 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (230 mg, 0.75 mmol, 1.00equiv) and phenyl acetylene (81.0 mg, 0.788 mmol, 1.05 equiv) were added to a mixture of copper(II) sulfate pentahydrate (9.4 mg, 0.0375 mmol, 0.0500 equiv), sodiumascorbate (23.0 mg, 0.113 mmol, 0.150 equiv), and β-cyclodextrin (22.0 mg, 0.0188 mmol, 0.0250 equiv) dissolved in H_2O (1.00mL) at 25 ^oC. The reaction mixture was stirred for 50 min at room temperature. The resulting mixture was poured into DCM (3.00 mL) and H_2O (3 mL), and the organic layer was separated. The aqueous layer was extracted with DCM (3*3 mL). The combined organic layer was concentrated in vacuo. The residue was purified by short column chromatography on silica gel eluted with hexane/ EtOAc 2:1 (v/v) to give 292 mg of **5** (95% yield).

R_f = 0.1 hexanes/EtOAc 8:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.78 (s, 1H), 7.68 – 7.63 (m, 2H), 7.62 – 7.57 (m, 2H), 7.51 – 7.41 (m, 6H), 7.41 – 7.33 (m, 2H), 5.63 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.85 – 4.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 142.8, 140.1, 134.0, 130.4, 129.1, 129.0, 128.5, 128.0, 127.3, 126.7, 125.9, 125.3, 121.5 (q, *J* = 258.1 Hz), 120.9, 78.8 (q, *J* = 2.6 Hz), 55.0. ^{19}F NMR (377 MHz, $CDCl_3$)

δ -58.48 (d, *J* = 2.7 Hz, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{23}H_{18}ON_3F_3Na$ $[M + Na]^+$, 432.1300, Found, 432.1295.

Synthesis of N-(2-([1,1'-biphenyl]-4-yl)-2-(trifluoromethoxy)ethyl)-2-chloroacetamide (6)



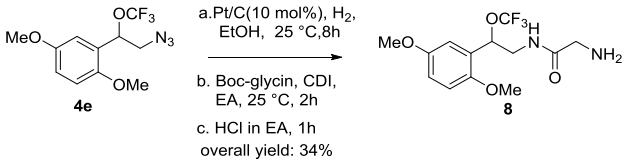
A mixture of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (60.0 mg, 0.195mmol, 1.00 equiv.), 10% Pt/C (6.0 mg, 10% wt) in EtOH (5.00 ml) was vigorously stirred under H_2 atmosphere at 25 °C for 2 h. The solvent was evaporated under vacuum after filtering over Celite. Then the residue was purified by flash chromatography over silica gel DCM/MeOH 10:1 (v/v)) to afford 54.4 mg 2-([1,1'-biphenyl]-4-yl)-2-(trifluoromethoxy)ethan-1-amine (**6a**) (99% yield).

R_f = 0.15 DCM/MeOH 10:1 (v/v)) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.45 (m, 4H), 7.41 (m, *J* = 15.0, 7.4 Hz, 5H), 5.14 (dd, *J* = 6.7, 4.9 Hz, 1H), 3.24 – 2.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.84, 140.55, 136.34, 128.98, 127.72, 127.57, 127.26, 126.77, 121.95 (q, *J* = 256.1 Hz), 82.59, 48.09. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.65 (s, 3F).Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{15}ONF_3$ $[M + H]^+$, 282.1106, Found, 282.1101.

2-([1,1'-biphenyl]-4-yl)-2-(trifluoromethoxy)ethan-1-amine was dissolved in 5ml DCM. $NaHCO_3$(33.0 mg, 0.391 mmol, 2.00 equiv.) and chloroacetyl chloride (0.0240 ml, 0.293 mmol, 1.50 equiv.) was added at 25 °C. After the reaction was stirred for 2 h, the solvent was evaporated under vacuum after filtering over Celite. Then the residue was purified by flash chromatography over silica gel (hexanes/EtOAc 3:1 (v/v)) to afford 64.0 mg N-(2-([1,1'-biphenyl]-4-yl)-2-(trifluoromethoxy)ethyl)-2-chloroacet- amide (**6**) (92% yield).

R_f = 0. 5 hexanes/EtOAc 2.5:1 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 7.49 – 7.41 (m, 4H), 7.40 – 7.34 (m, 1H), 6.96 (s, 1H), 5.33 (dd, *J* = 8.9, 3.6 Hz, 1H), 4.09 (d, *J* = 2.6 Hz, 2H), 3.87 (ddd, *J* = 14.4, 7.2, 3.6 Hz, 1H), 3.51 (ddd, *J* = 14.3, 9.0, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 142.2, 140.3, 135.1, 129.0, 127.8, 127.7, 127.2, 126.6, 121.74 (q, *J* = 256.9 Hz), 78.8, 45.2, 42.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.07 (s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{15}O_2NClF_3Na$ $[M + Na]^+$, 380.0641, Found, 380.0640.

Synthesis of 2-amino-N-(2-(2,5-dimethoxyphenyl)-2-(trifluoromethoxy)ethyl)acetamide (8)



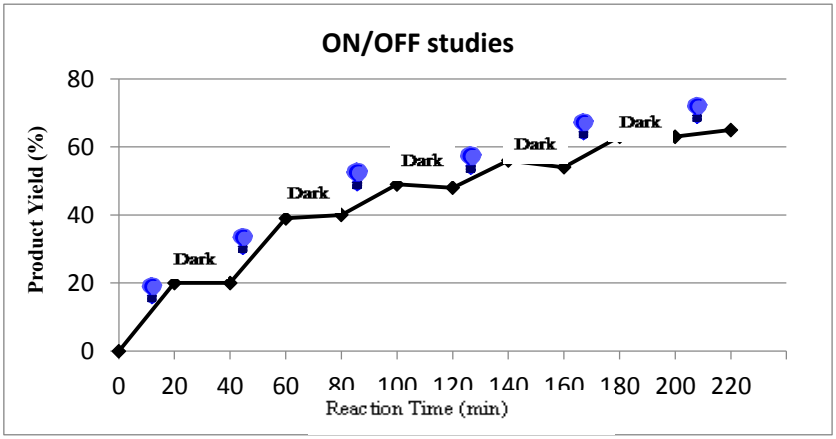
A mixture of 2-(2-azido-1-(trifluoromethoxy)ethyl)-1,4-dimethoxybenzene (**4e**) (40.0 mg, 0.136 mmol, 1.00 equiv.), 10% Pt/C (4.0 mg, 10% wt) in EtOH (2.00 ml) was vigorously stirred under H_2 atmosphere at 25 °C for 8 h. The solvent was evaporated under vacuum after

filtering over Celite. The crude product(R_f of main product = 0.1 DCM/MeOH 10:1 (v/v)) needed no further purification was dissolved in ethyl acetate (5 ml). In another flask, 1,1'-carbonyldiimidazole (97.0 mg, 0.600 mmol, 4.40 equiv.) was suspended in ethyl acetate (2.00 ml). To the beige suspension was added N-tert-butoxycarbonyl glycine (105 mg, 0.600 mmol, 4.40 equiv.). After stirring for 1 h, this solution was added to the above solution. The reaction mixture is stirred at room temperature for 1 hour. A solution of 1M HCl (3.00 ml) is added to the reaction mixture and the mixture stirred at room temperature for 15 minutes. Stirring is discontinued and the phases are separated. The organic layer was sequentially washed with water, sodium hydroxide 2.5% and water and then dried over sodium sulfate. To the clear ethyl acetate solution was bubbled HCl (gas) for 30 min, and the white suspension was stirred at room temperature for 1 h. The mixture was concentrated in vacuo. Then the residue was dissolved in ethyl acetate. The ethyl acetate solution was sequentially washed with saturated sodium carbonate and brine, then dried over sodium sulfate and concentrated in vacuo. The residue was purified by flash chromatography over silica gel (DCM/MeOH 10:1 (v/v)) to afford 15.0 mg 2-amino-N-(2-(2,5-dimethoxyphenyl)-2-(trifluoromethoxy)ethyl)acetamide (**8**).

R_f = 0. 1 DCM/MeOH 10:2 (v/v). 1H NMR (400 MHz, CD_3OD) δ 7.03 – 6.86 (m, 3H), 5.68 (t, *J* = 5.9 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.61 (d, *J* = 5.5 Hz, 2H).. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 153.8, 150.0, 126.1, 121.7 (q, *J* = 255.9 Hz), 114.2, 112.9, 111.8, 74.50 (d, *J* = 2.7 Hz), 56.2, 55.9, 44.7, 43.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.16 (s, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{18}O_4N_2F_3$ $[M + H]^+$, 323.1219, Found, 323.1216.

Mechanistic Study

ON/OFF experiment: In an N_2 glovebox, eleven vials were equipped with a stir bar and charged with to $Ru(bpy)_3(PF_6)_2$ (0.4 mg, 0.000500 mmol, 1.0 mol%), AgF (3.2 mg, 0.0250 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (6.0 mg, 0.0150 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (28.9 mg, 2.00 mmol, 2.00 equiv) and p-vinylbiphenyl(**1a**) (9.0 mg, 0.0500 mmol 1.00 equiv) in a 2.00 mL sealed vial tube were added CH_3CN (0.400 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (28.0 μL, 0.150 mmol, 3.00 equiv) was added to the reaction and then eleven vials was cooled to 10 ^oC and under irradiation of blue LEDs at λmax = 450 nm. The reactions was alternatively irradiated with blue LEDs and kept in the dark in 1 h intervals. After each interval, one vial was take out, After then, benzotrifluoride (6.0 μL, 0.0490 mmol) was added to the reaction mixture. The yield of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) was determined by comparing the integration of the ^{19}F NMR resonance of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) (-58.3 ppm) with that of benzotrifluoride (-62.8 ppm) as an internal standard.



Determination of the quantum yield:

A) Absorbance of catalyst:

The absorbance of $Ru(bpy)_3(PF_6)_2$ in CH_3CN was measured at the reaction concentration of 1.25×10^{-3} M and at a substantially more dilute concentration of 1.25×10^{-4} M. The absorbance at 450 nm for a 1.25×10^{-3} M solution is >3 (Figure S1) indicating the fraction of light absorbed is >0.999.

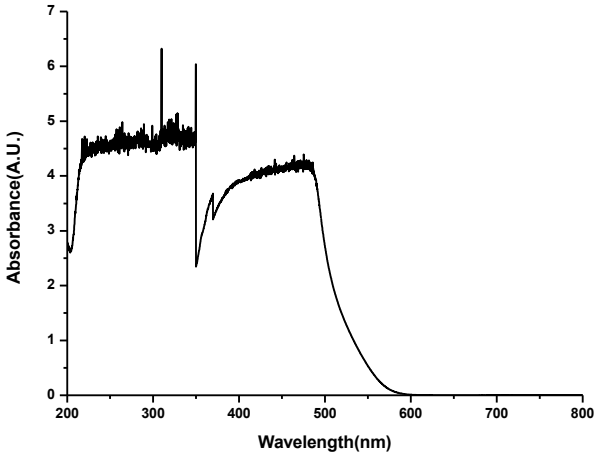


Figure S1. Absorbance of a 1.25×10^{-3} M solution of $Ru(bpy)_3(PF_6)_2$ in CH_3CN

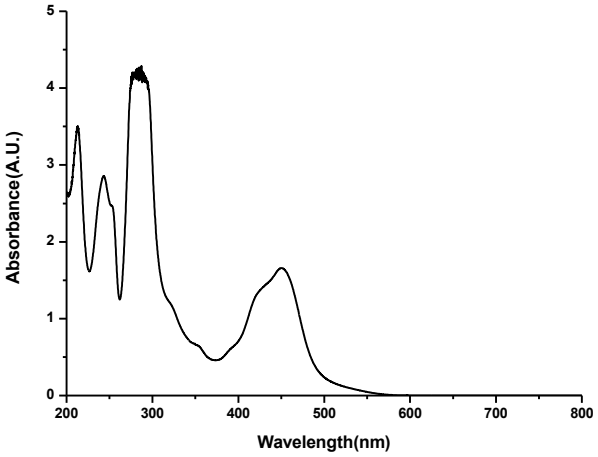


Figure S2. Absorbance of a 1.25×10^{-4} M solution of $Ru(bpy)_3(PF_6)_2$ in CH_3CN

B) Determination of the light intensity at 450 nm:

According to the procedure of Yoon,[11] the photon flux of the LED (λmax = 450 nm) was determined by standard ferrioxalate actinometry.[12,13,14] A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 450 nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the resulting solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Under light excitation the potassium ferrioxalate decomposes according to the following equations:

$$Fe(C_2O_4)_3^{3-} \xrightarrow{h\nu} Fe^{2+} + C_2O_4^{\cdot-} + 2C_2O_4^{2-}$$

$$Fe(C_2O_4)_3^{3-} + C_2O_4^{\cdot-} \xrightarrow{\triangle} Fe^{2+} + 2CO_2 + 3C_2O_4^{2-}$$

The quantity of ferrous ions formed during an irradiatin period is monitored by conversion to the colored tris-phenanthroline complex. The original ferric ions are not appreciably complexed by phenanthroline and the complex does not absorb at 510 nm. The mols of ferrous ions formed in the irradiated volume are given by eq 1.

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \qquad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity of phenanthroline complex at

510 nm (11,100 L mol^{-1} cm^{-1}). The difference in absorbance at 510 nm between the irradiated and non-irradiated solutions was measured to be 1.213 (average of three experiments). The conversion was calculated using eq 2.

$$\text{mol } Fe^{2+} = \frac{0.00235\text{L} \cdot 1.213}{1.000\text{cm} \cdot 11{,}100\ \text{L mol}^{-1}\text{cm}^{-1}} = 2.513 \times 10^{-7}\text{mol} \qquad (2)$$

The photon flux can be calculated using eq 3.

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi Fe \cdot t \cdot f_{Fe}} \qquad (3)$$

Where mol Fe^{2+} is the mols of Fe^{2+} formed during irradiation (2.513×10^{-7} mol), ΦFe is the quantum yield for the ferrioxalate actinometer (0.92 for a 0.15 M solution at λ = 468 nm),[15] t is the time (90.0 s), and f_{Fe} is the fraction of light absorbed of the ferrioxalate solution at λ = 450 nm.

The fraction of light absorbed (f_{Fe}) by this solution was calculated using eq 4, where A is the measured absorbance at 450 nm.

$$f_{Fe} = 1 - 10^{-A} \qquad (4)$$

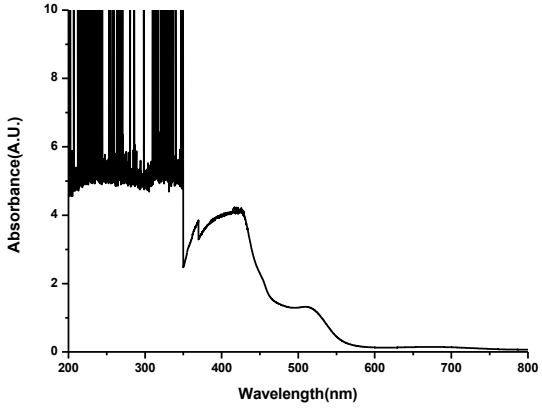


Figure S3. Absorbance of the ferrioxalate actinometer solution.

The absorbance of the above ferrioxalate solution at 450 nm was measured to be 2.279 (average of three experiments). The light absorbed (f_{Fe}) was calculated using eq 4.

$$f_{Fe} = 1 - 10^{-2.279} = 0.99474$$

The photon flux was calculated using eq 3.

$$\text{photon flux} = \frac{2.523 \times 10^{-7}}{0.92 \times 90.0\text{s} \times 0.99474} = 3.05 \times 10^{-9}\text{einstein s}^{-1}$$

C) Determination of quantum yield:

A clear vial was charged with $Ru(bpy)_3(PF_6)_2$ (0.8 mg, 0.00100 mmol, 1.0 mol%), AgF (6.4mg, 0.0500 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (12.0mg, 0.0300 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (58.0 mg, 4.000 mmol, 2.00 equiv) and p-vinylbiphenyl(**1a**) (18.0 mg, 0.100 mmol 1.00 equiv), in vial tube were added CH_3CN (0.800 mL). Trifluoromethyl 4-methylbenzenesulfonate (**2**) (94.0 μL, 0.500 mmol, 5.00 equiv) was added to the reaction, resulting mixture was purged with Ar and the cuvette was then capped with a PTFE stopper. The reaction mixture was irradiated (λ= 450 nm, slit width= 10.0 nm) for 1800 s (30 min). After irradiation, The yield of 1-(2-azido-1-(trifluoromethoxy)ethyl)-4-phenylbenzene (**4a**) was determined by the ^{19}F NMR resonance based on a benzotrifluoride standard to be 3% .

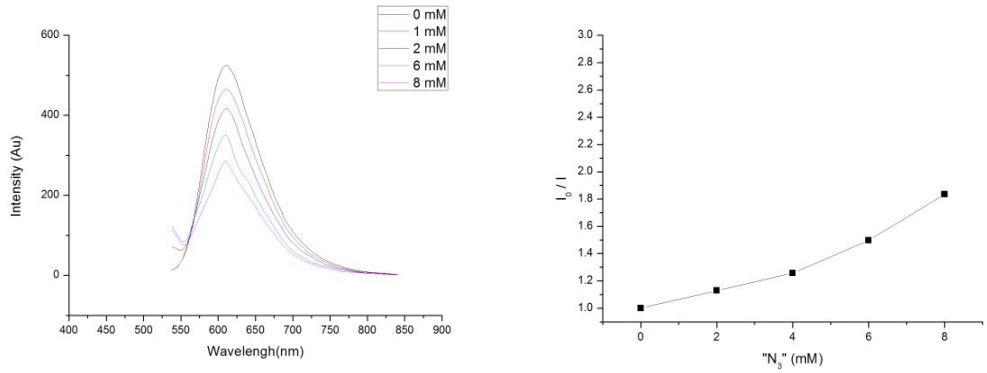
The quantum yield was calculated using eq 5.

$$\Phi = \frac{\text{mols of starting material} \cdot \text{yield}}{\text{fluxl} \cdot \text{t} \cdot \text{f}} = \frac{0.1mmol \cdot 3\%}{3.05\times10^{-9}\times1800s\times1} = 0.55$$

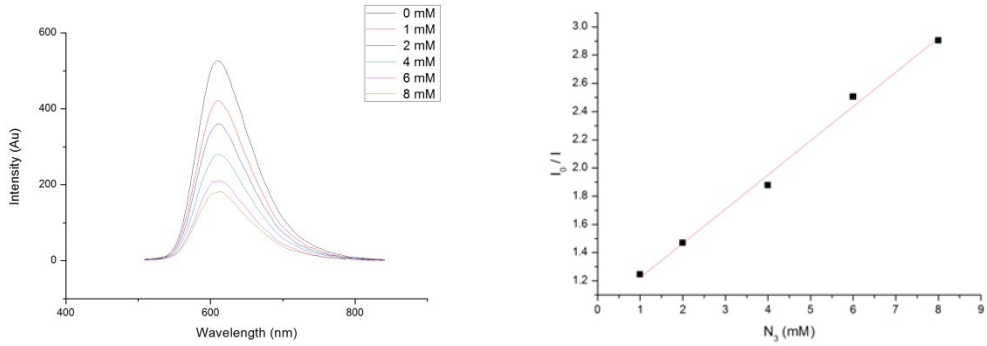
luminescence quenching studies：

To probe the detail electron transfer between the catalyst and substrates, a series of luminescence quenching experiments were conducted.

1. $Ru(bpy)_3(PF_6)_2$ + 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one



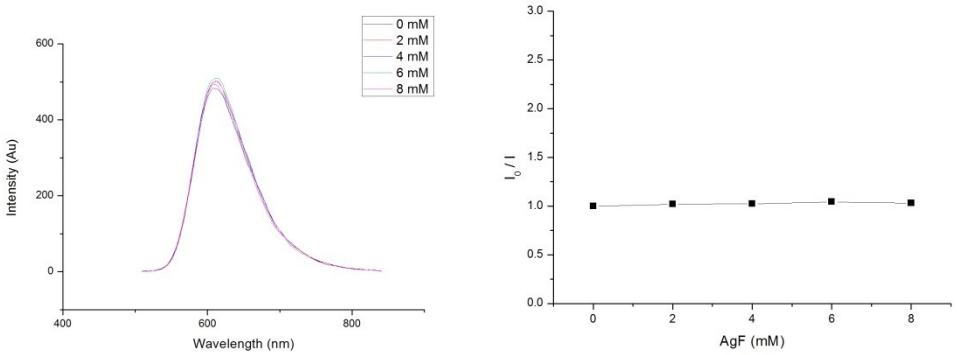
Condition: To the solution of $Ru(bpy)_3(PF_6)_2$ (0.2 mM) in CH_3CN was added 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one(= N_3) of different concentrations including 0, 1, 2, 6 and 8 mM at 15℃ temperature under N_2 atmosphere. (excitation wavelength: 450 nm)



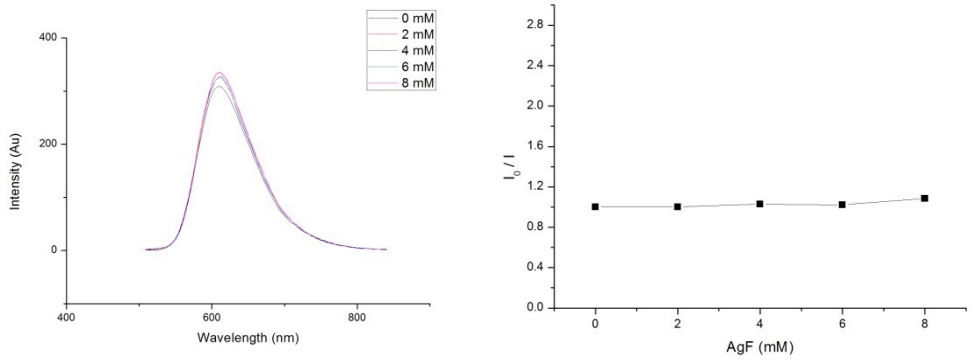
Condition: To the solution of $Ru(bpy)_3(PF_6)_2$ (0.2 mM) AgF (5.0mM), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (3.0mM), trifluoromethyl 4-methylbenzenesulfonate

(20.0mM) in CH_3CN was added 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one(=N_3) of different concentrations including 0, 1, 2, 4, 6 and 8 mM at 15℃ temperature under N_2 atmosphere. (excitation wavelength: 450 nm).

2. $Ru(bpy)_3(PF_6)_2$ + AgF

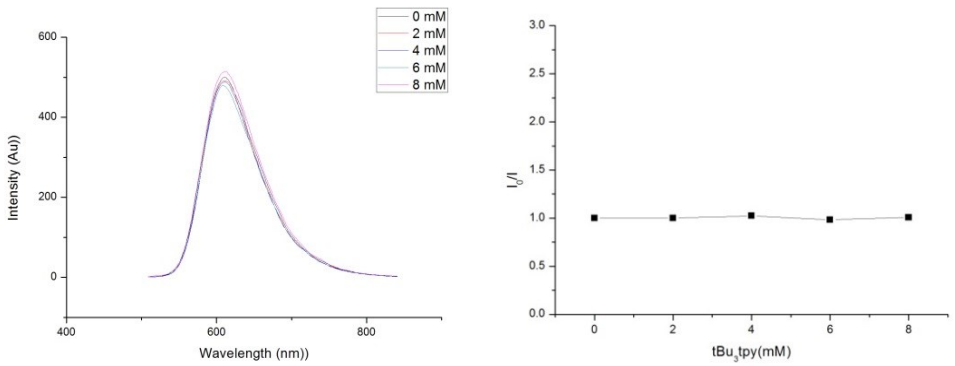


Condition: To the solution of $Ru(bpy)_3(PF_6)_2$ (0.2 mM) inCH_3CN was added AgF of different concentrations including 0, 2, 4, 6 and 8 mM at 15℃ temperature under N_2 atmosphere. (excitation wavelength: 450 nm).

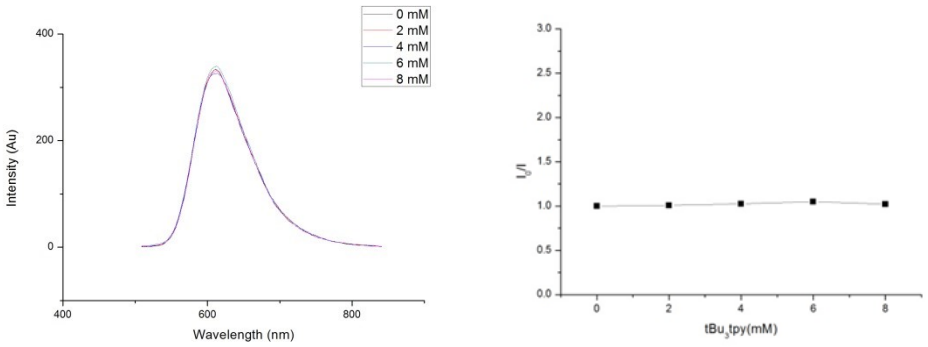


Condition: To the solution of $Ru(bpy)_3(PF_6)_2$ (0.2 mM) 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (2.0 mM), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (3.0 mM), trifluoromethyl 4-methylbenzenesulfonate (20.0 mM) in CH_3CN was added AgF of different concentrations including 0, 2, 4, 6 and 8 mM at 15℃ temperature under N_2 atmosphere. (excitation wavelength: 450 nm).

3. $Ru(bpy)_3(PF_6)_2$ + tBu_3tpy

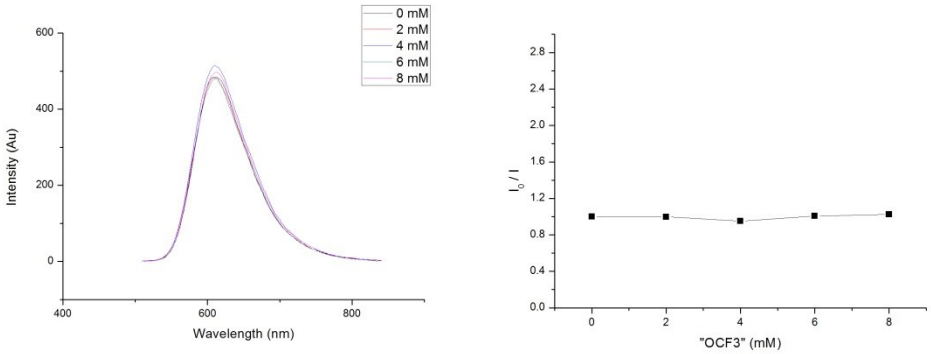


Condition: To the solution of $Ru(bpy)_3(PF_6)_2$ (0.2 mM) inCH_3CN was added tBu_3tpy of different concentrations including 0, 2, 4, 6 and 8 mM at 15℃ temperature under N_2 atmosphere. (excitation wavelength: 450 nm).

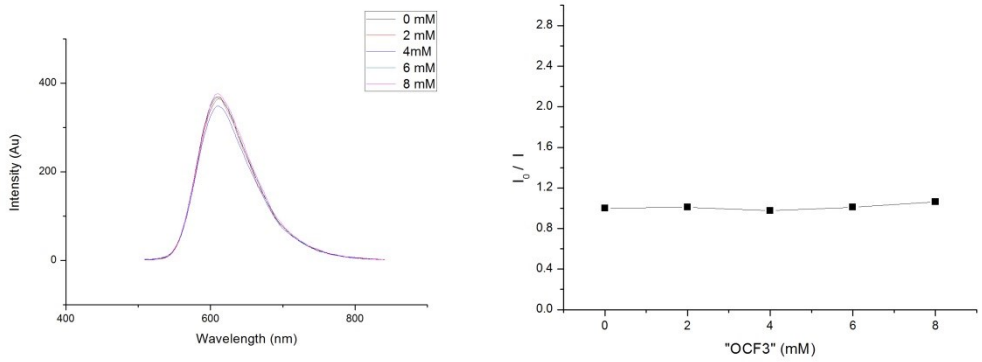


Condition: To the solution of $Ru(bpy)_3(PF_6)_2$ (0.2 mM)，AgF (5.0 mM)，1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (2.0 mM), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (3.0 mM), trifluoromethyl 4-methylbenzenesulfonate (20.0 mM) in CH_3CN was added AgF of different concentrations including 0, 2, 4, 6 and 8 mM at 15℃ temperature under N_2 atmosphere. (excitation wavelength: 450 nm).

4. $Ru(bpy)_3(PF_6)_2$ + "OCF_3"



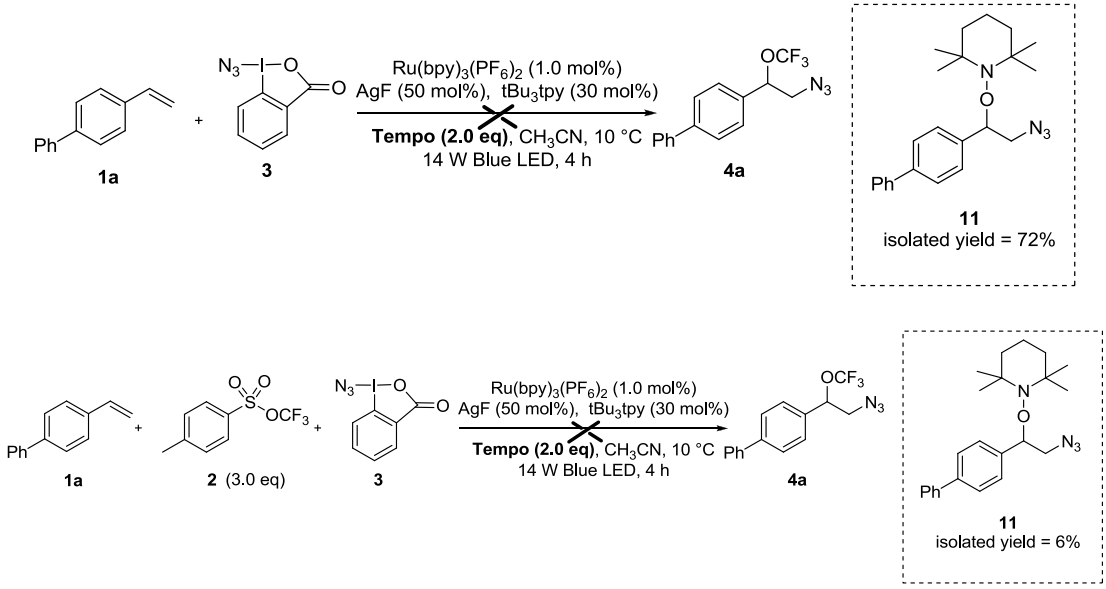
Condition: To the solution of $Ru(bpy)_3(PF_6)_2$ (0.2 mM) in CH_3CN was added trifluoromethyl 4-methylbenzenesulfonate of different concentrations including 0, 2, 4, 6 and 8 mM at 15℃ temperature under N_2 atmosphere. (excita



Condition: To the solution of $Ru(bpy)_3(PF_6)_2$ (0.2 mM), AgF (5.0 mM)，1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (2.0 mM), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (3.0 mM) in CH_3CN was added trifluoromethyl

4-methylbenzenesulfonate of different concentrations including 0, 2, 4, 6 and 8 mM at 15℃ temperature under N_2 atmosphere. (excitation wavelength: 450 nm).

TEMPO radical trapping experiments:



In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv), tempo(46.9 mg, 0.600 mmol, 2.00 eq) and p-Vinylbiphenyl(**1a**) (54.0 mg, 0.300 mmol, 1.00 equiv) in a 5.00 mL sealed vial tube were added solvent (2.40 mL). trifluoromethyl 4-methylbenzenesulfonate (**2**) (169 µL, 0.900 mmol, 3.00 equiv) was added to the reaction and then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, the residue was purified by preparative TLC, eluting with hexanes/DCM 50:1 (v/v) to afford 6.8 mg 1-(1-([1,1'-biphenyl]-4-yl)-2-azidoethoxy)-2,2,6,6-tetramethylpiperidine (**11**) as a colourless liquid (6% yield).

In an N_2 glovebox, to $Ru(bpy)_3(PF_6)_2$ (2.4 mg, 0.00300 mmol, 1.0 mol%), AgF (19.2mg, 0.150 mmol, 50.0 mol%), 4,4',4"-tri-tert-butyl-2,2':6'2"-terpyridine (= tBu_3tpy) (36.0 mg, 0.0900 mmol, 30.0 mol%), 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**3**) (173.4 mg, 0.600 mmol, 2.00 equiv), tempo(46.9 mg, 0.600 mmol, 2.00 eq) and p-Vinylbiphenyl(**1a**) (54.0 mg, 0.300 mmol, 1.00 equiv) in a 5.00 mL sealed vial tube were added solvent (2.40 mL). then the tube of the resulting mixture was cooled to 10 °C and stirred under irradiation of blue LEDs at λmax = 450 nm for the indicated time. After then, the reaction mixture was concentrated *in vacuo*, the residue was purified by preparative TLC, eluting with hexanes/DCM 50:1 (v/v) to afford 81.6 mg 1-(1-([1,1'-biphenyl]-4-yl)-2-azidoethoxy)-2,2,6,6-tetramethylpiperidine (**11**) as a colourless liquid (72% yield).

R_f = 0.4 (hexanes/ EtOAc 20:1(v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 8.5 Hz, 4H), 7.42 (dd, *J* = 12.0, 7.8 Hz, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 4.92 – 4.83 (m, 1H), 3.78 (dd, *J* = 12.3, 4.5 Hz, 1H), 3.69 (dd, *J* = 12.2, 6.9 Hz, 1H), 1.53 – 1.27 (m, 9H), 1.20 (s, 3H), 1.06 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 140.6, 139.7, 128.7, 127.9, 127.2, 127.1, 126.9, 84.6, 60.1, 55.3, 34.4, 34.1, 20.3, 20.3, 17.1. The spectroscopic data (NMR) matched those reported in the literature for1-(1-([1,1'-biphenyl]-4-yl)-2-azidoethoxy)-2,2,6,6-tetramethylpiperidine.[16]

References

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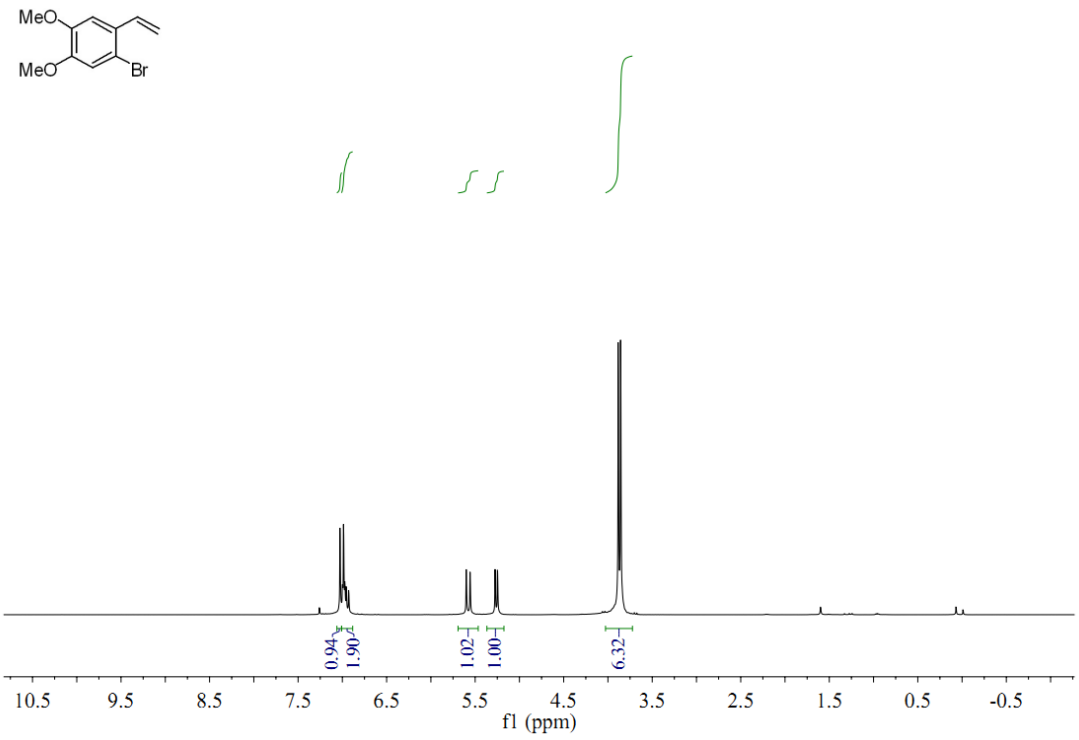
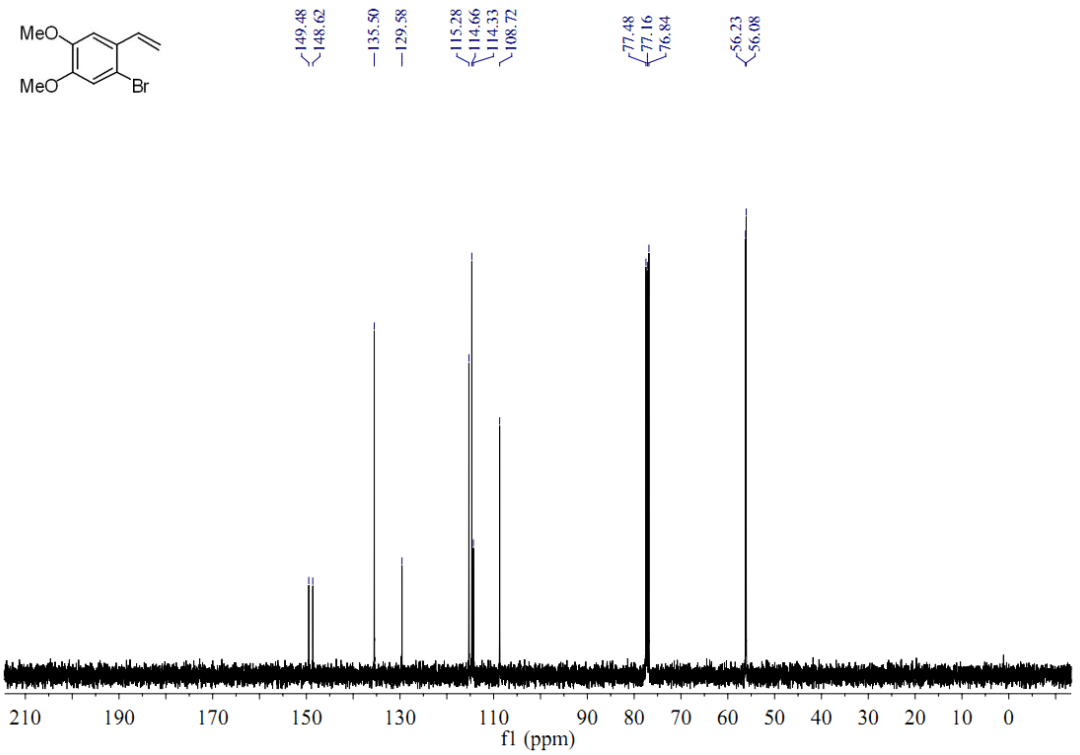
Spectroscopic Data



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1c**



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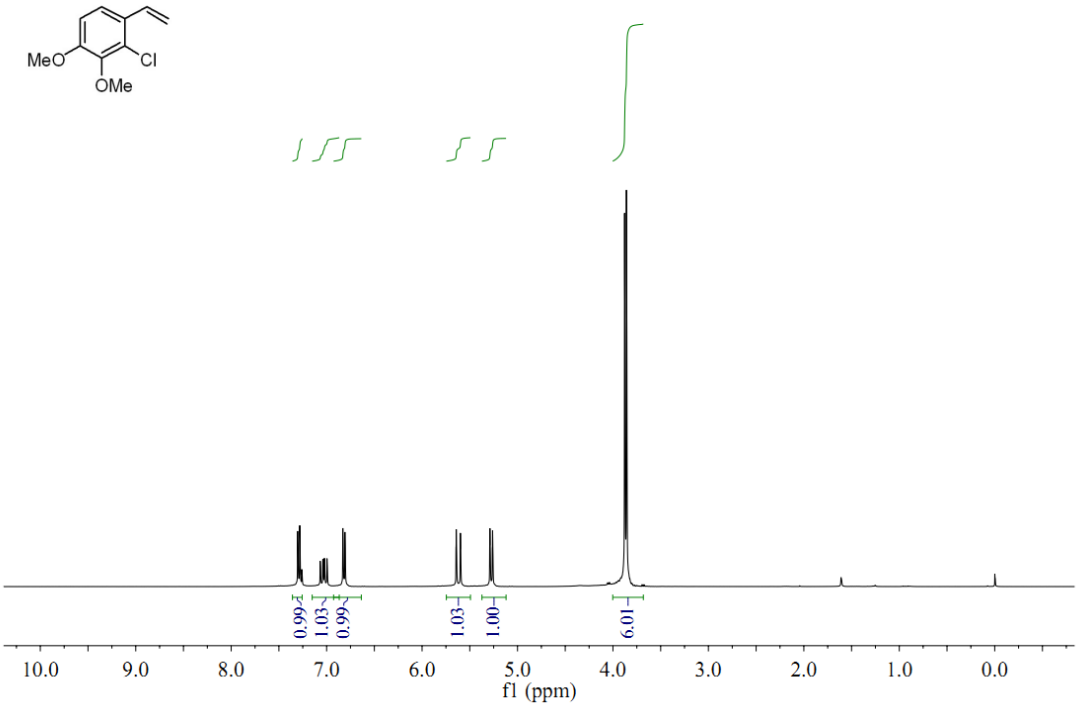

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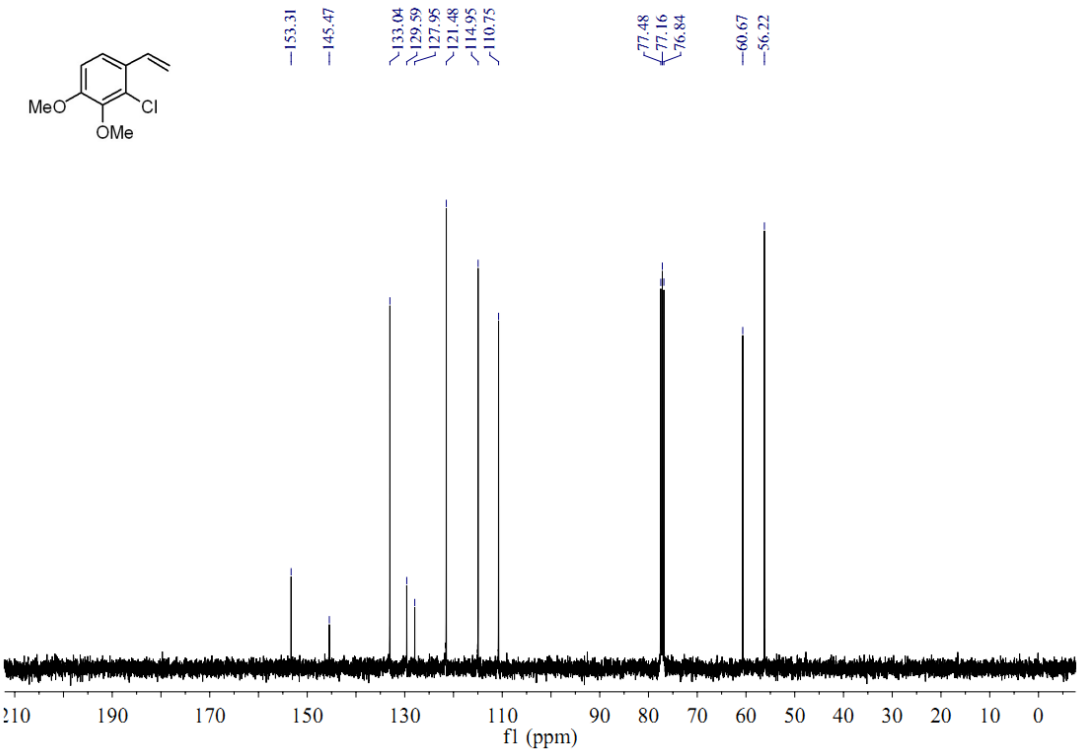

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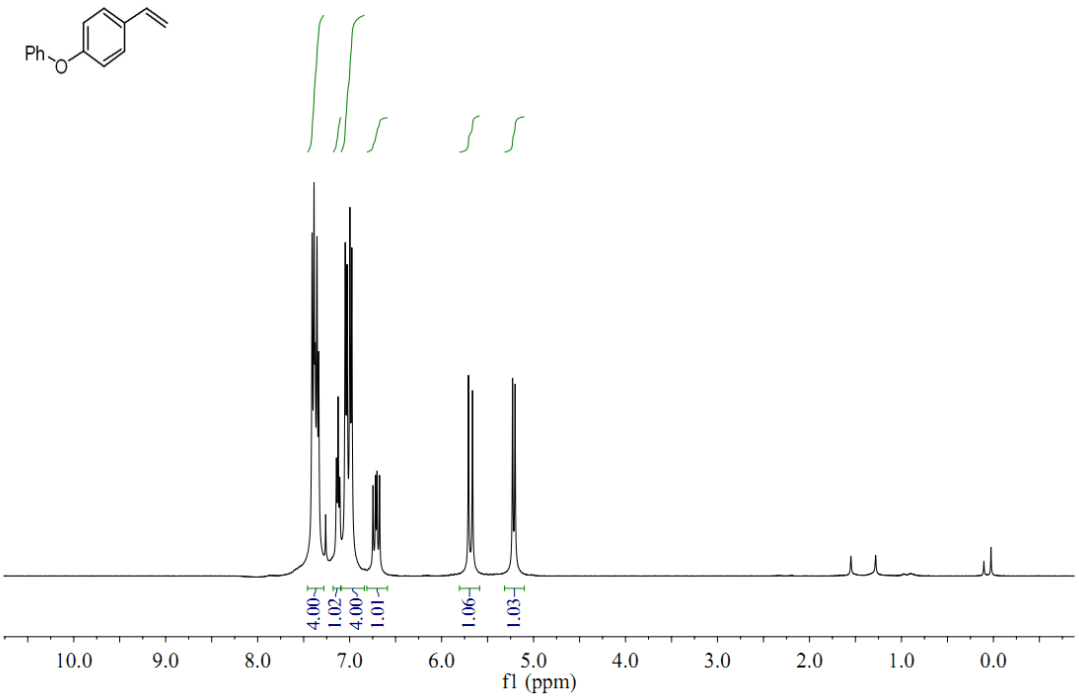

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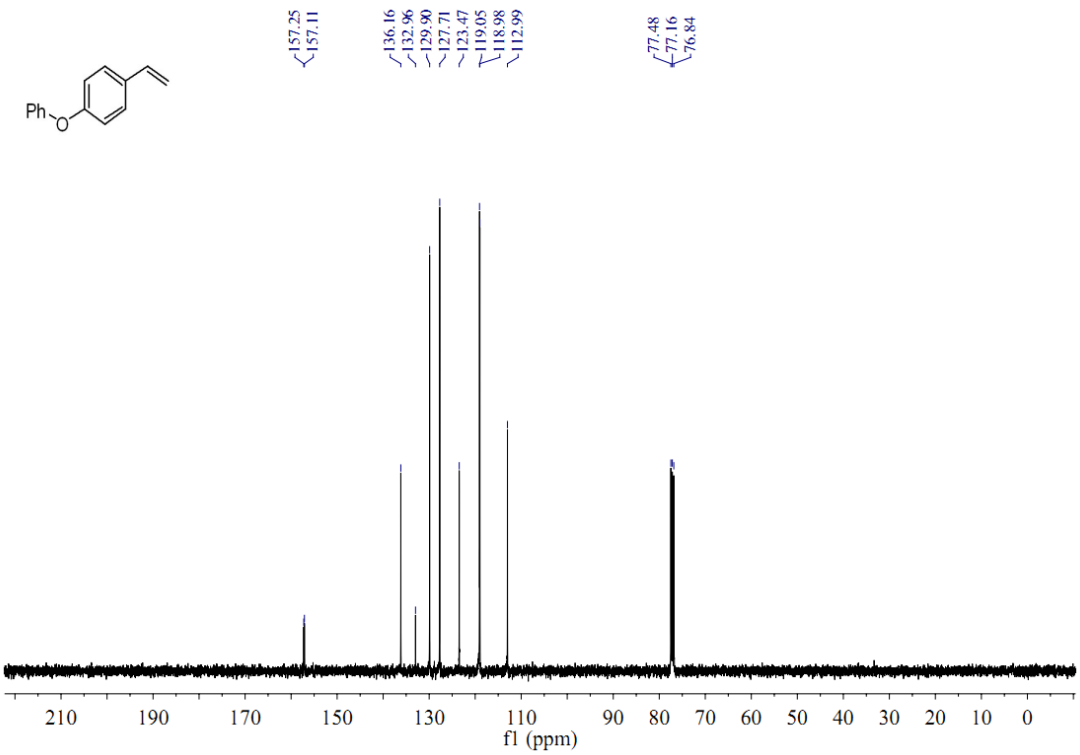

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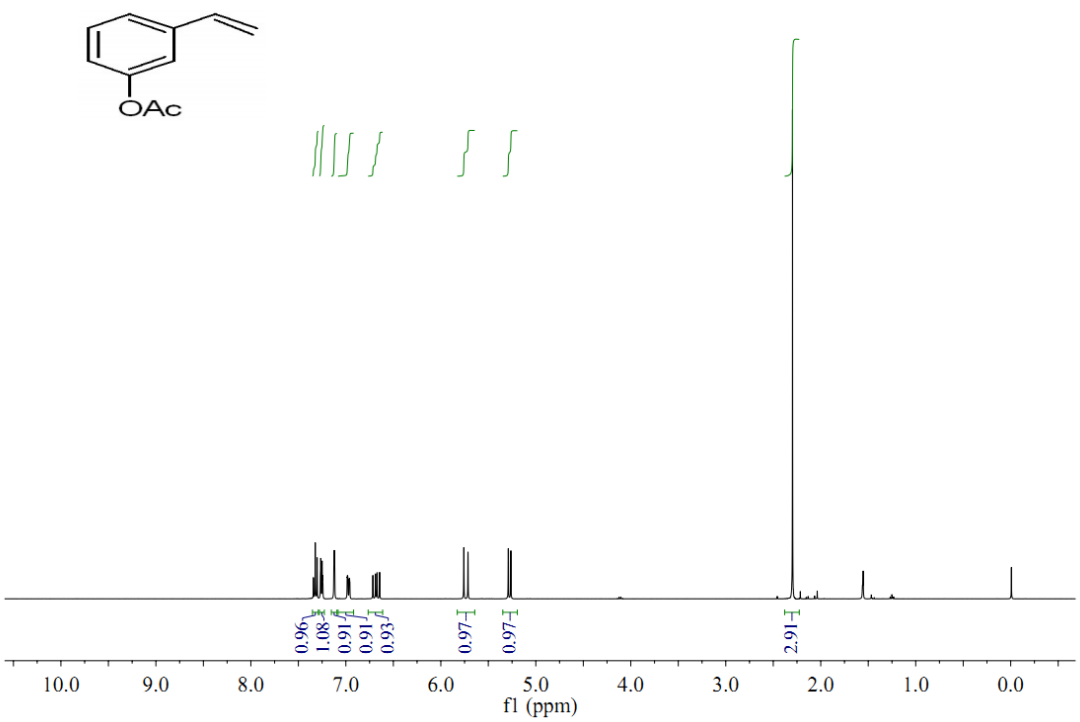

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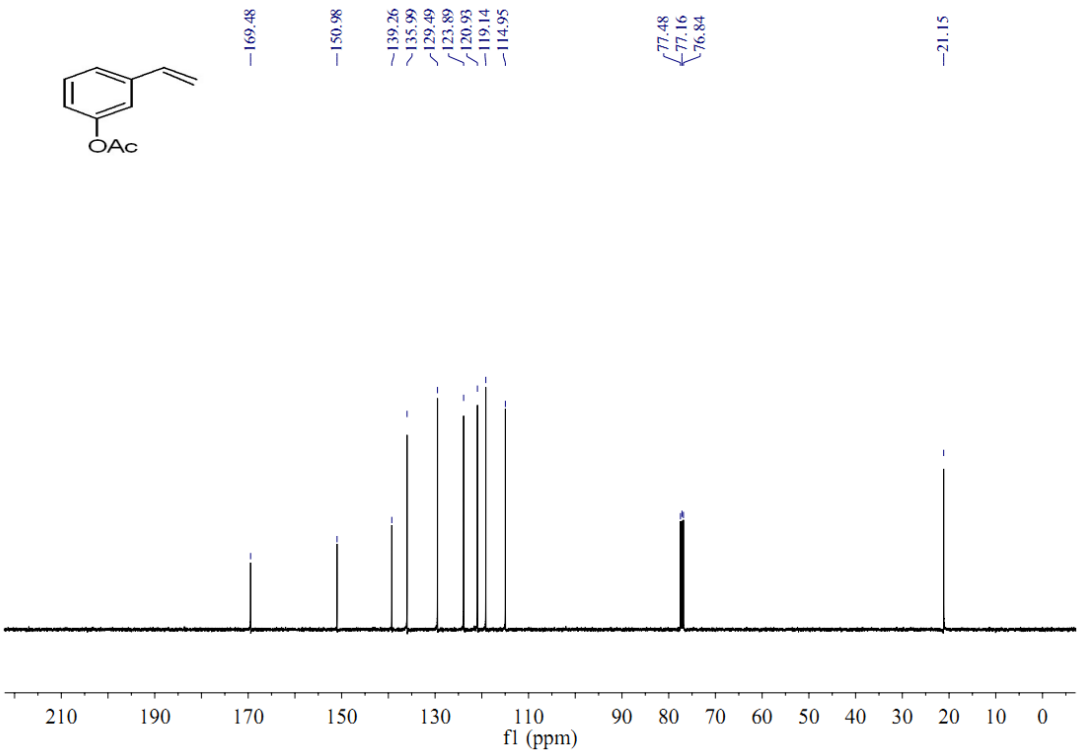

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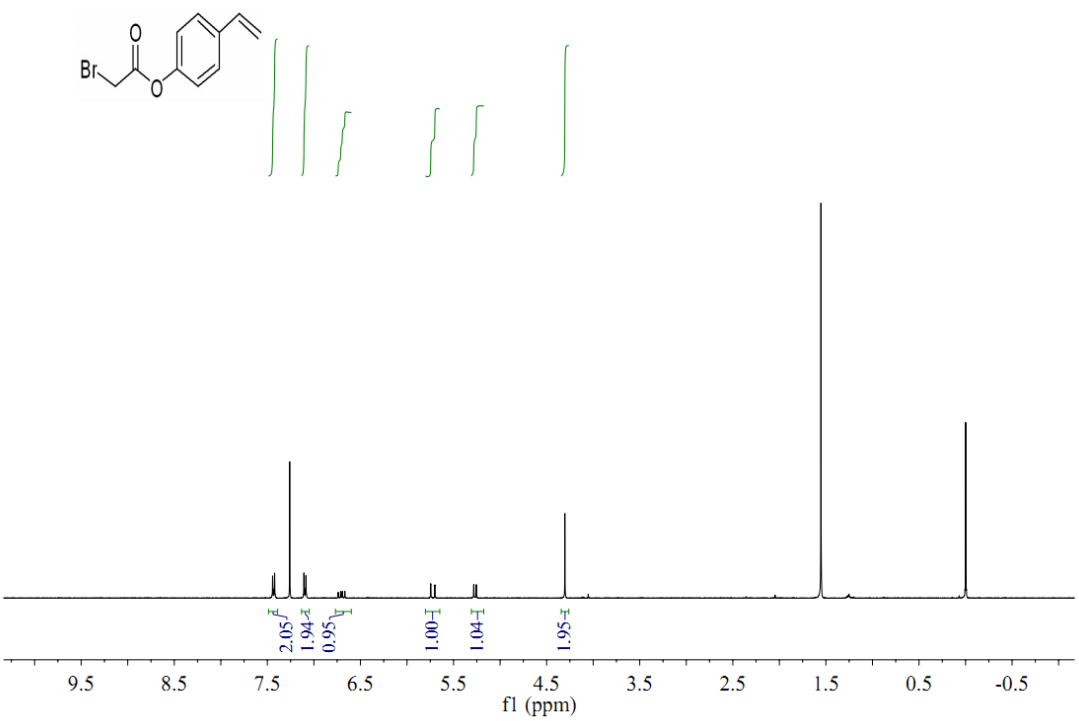

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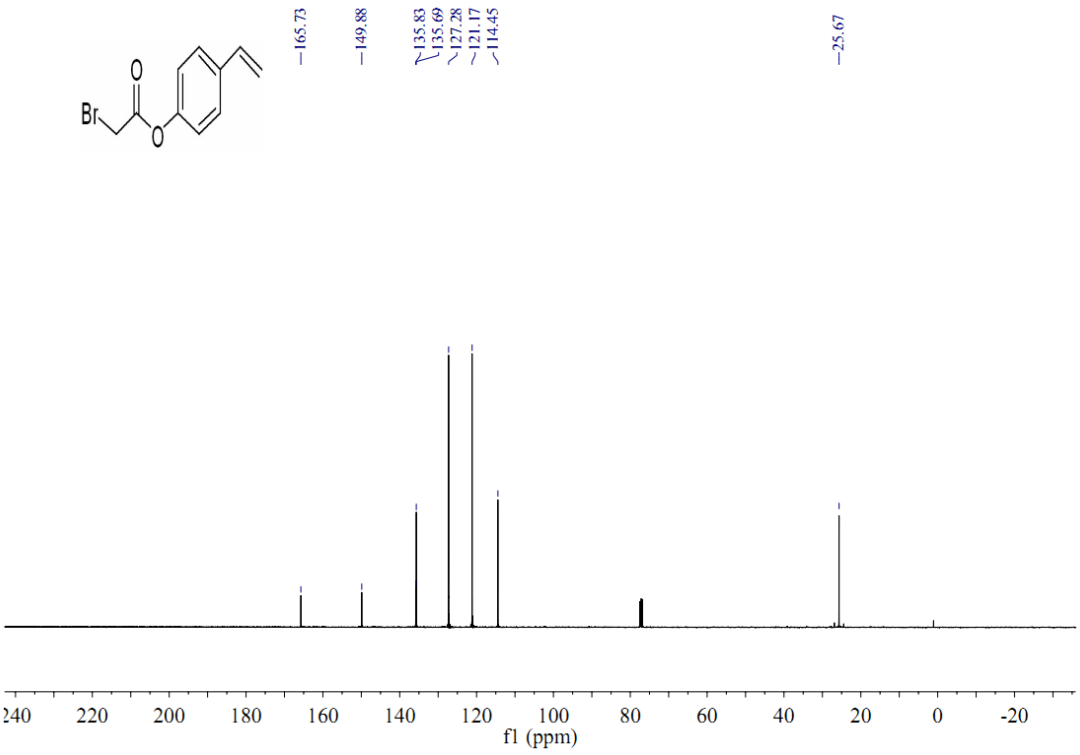

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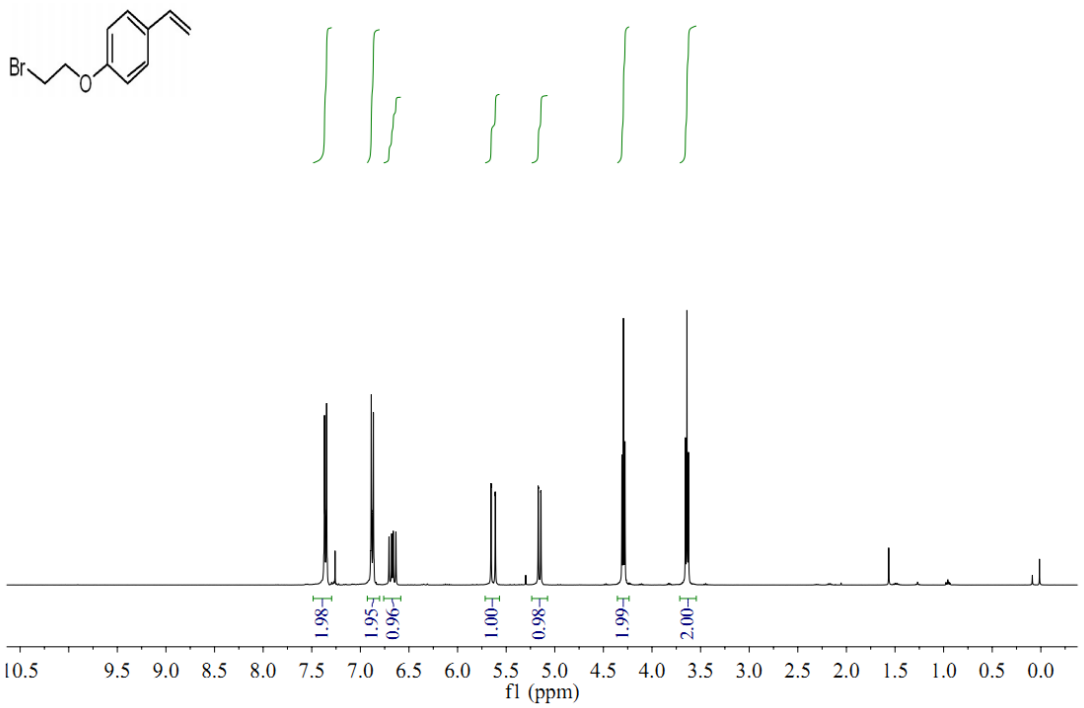

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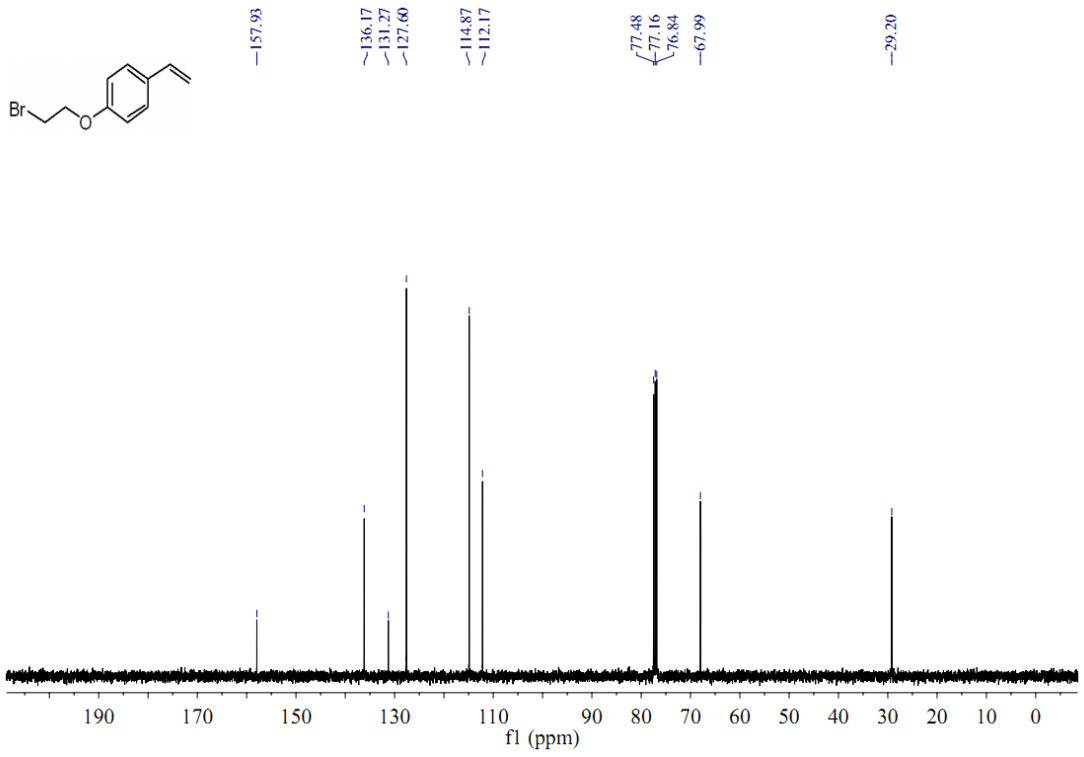

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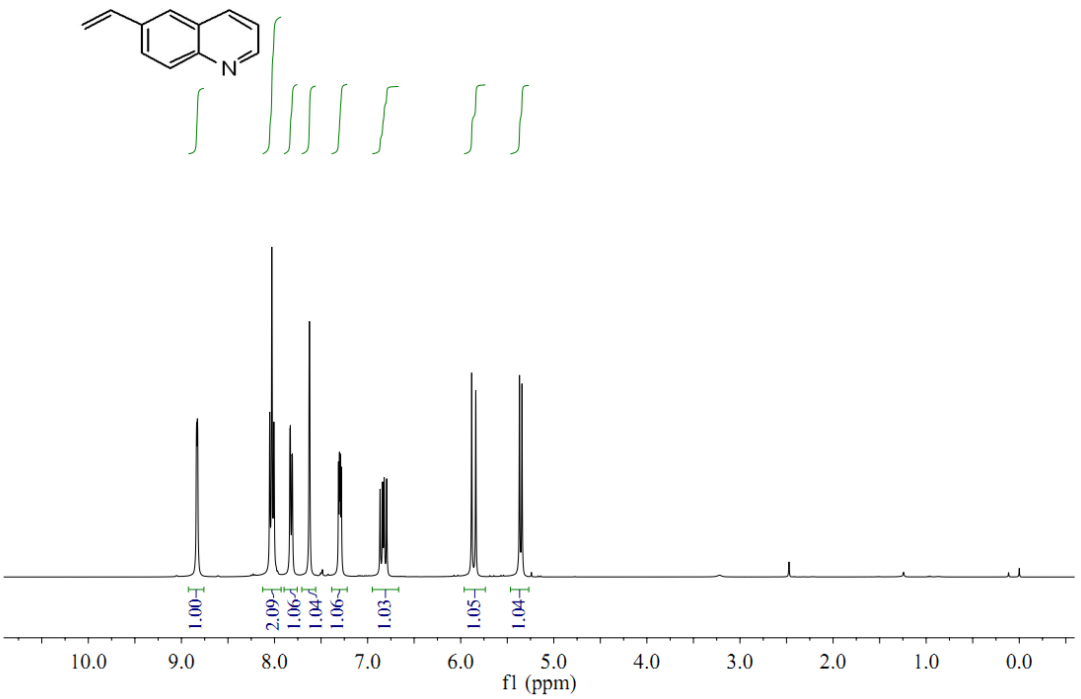

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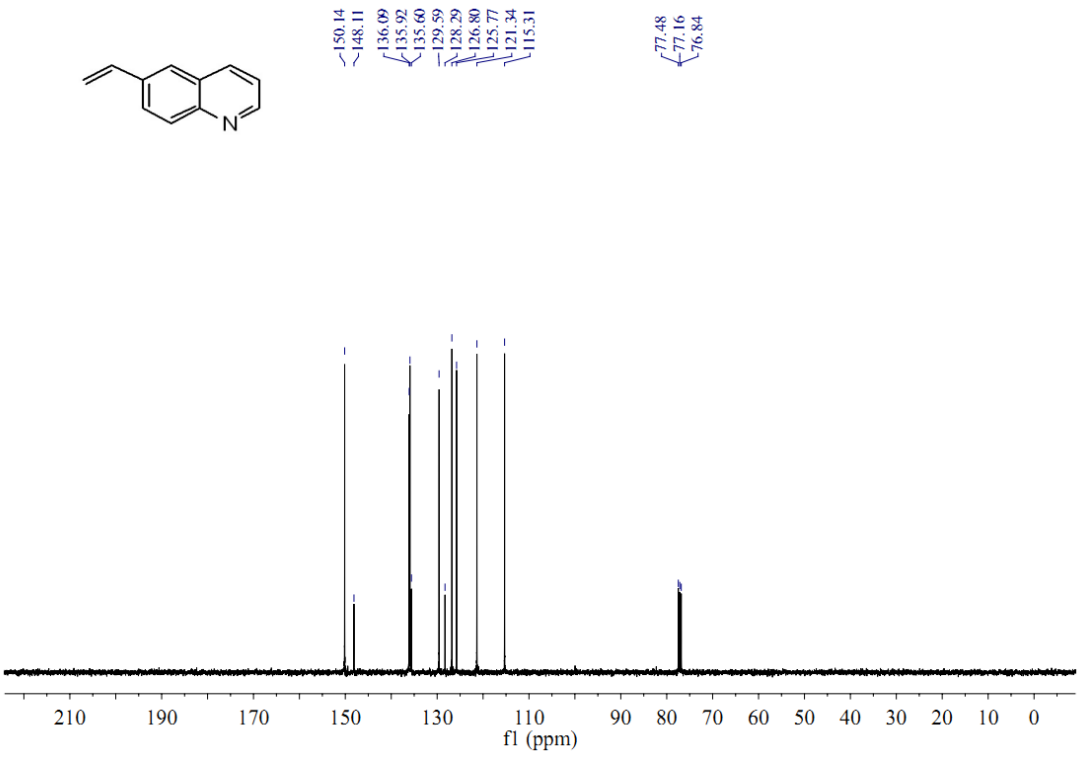

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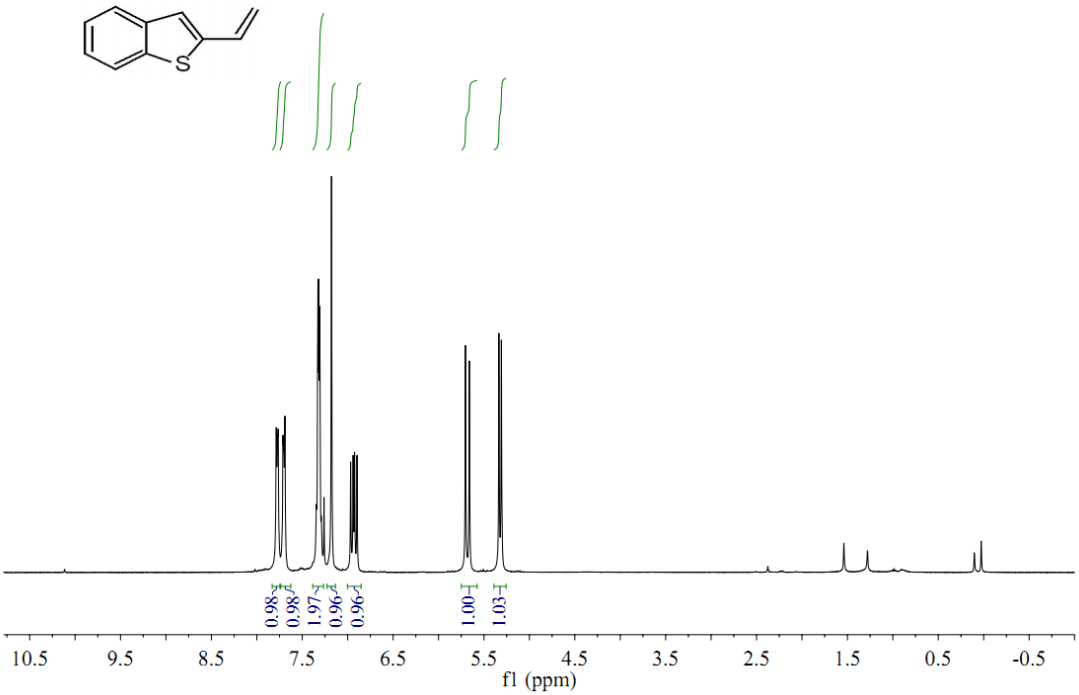

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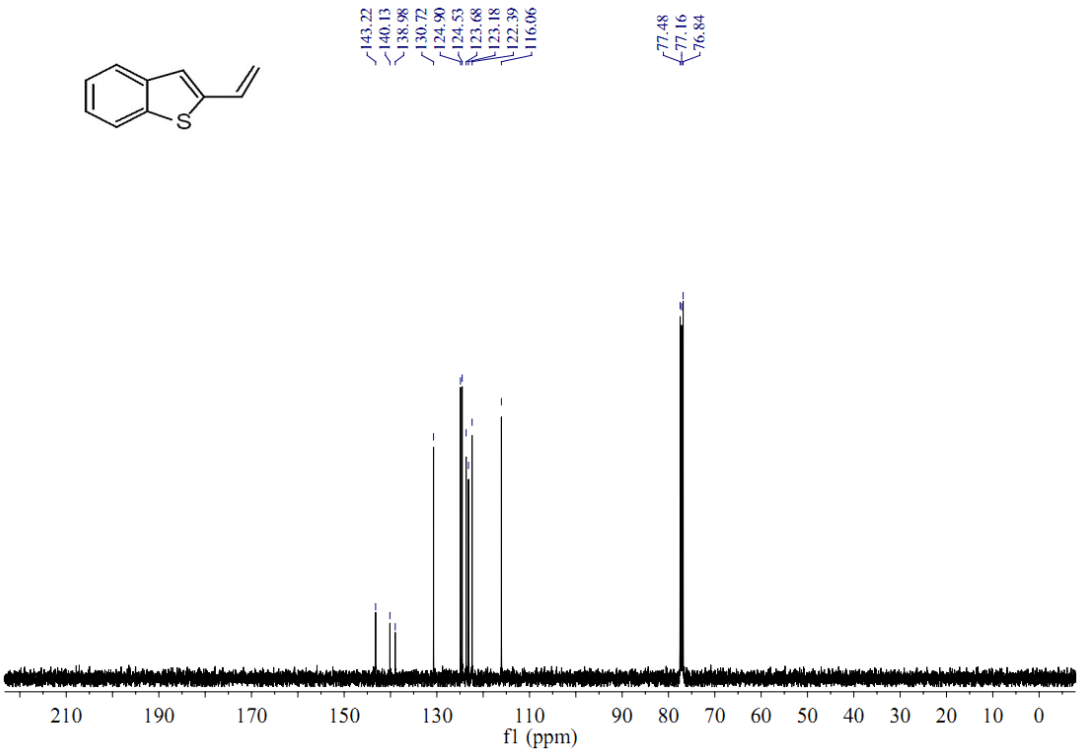

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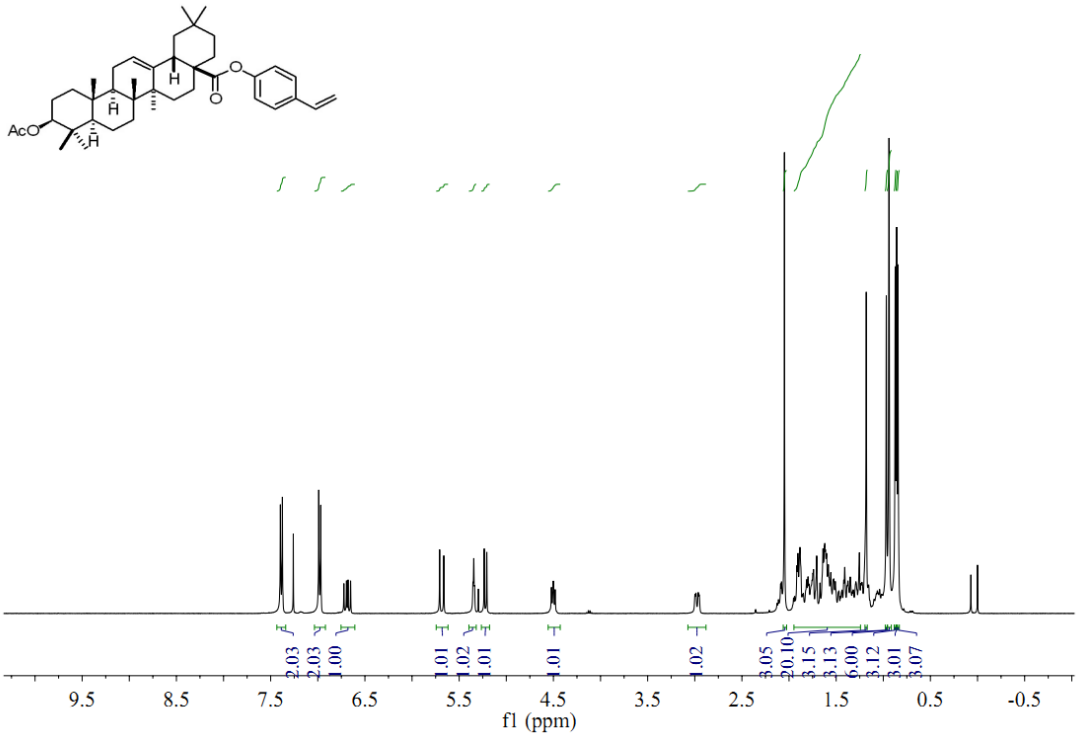

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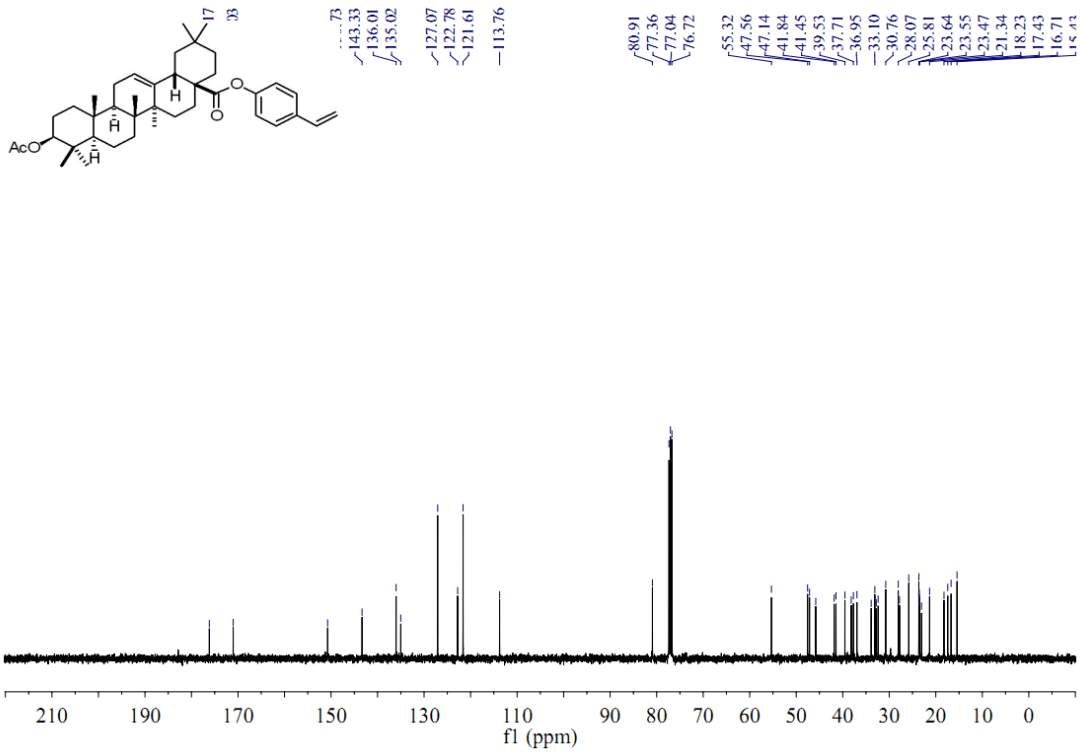

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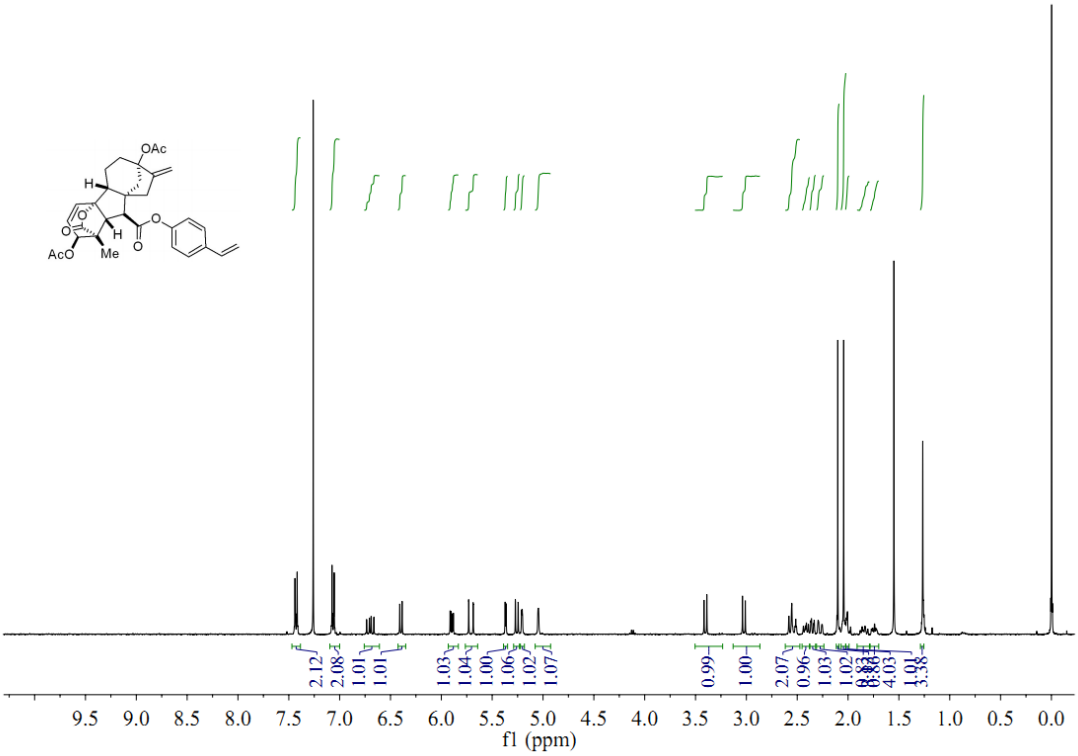

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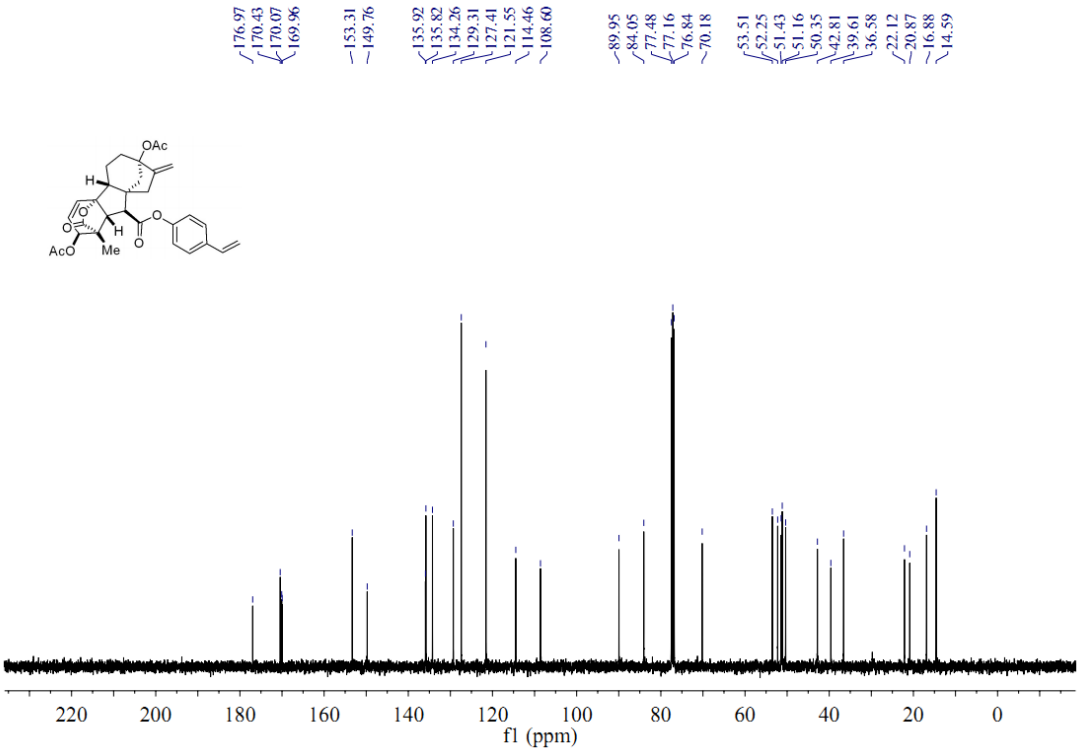

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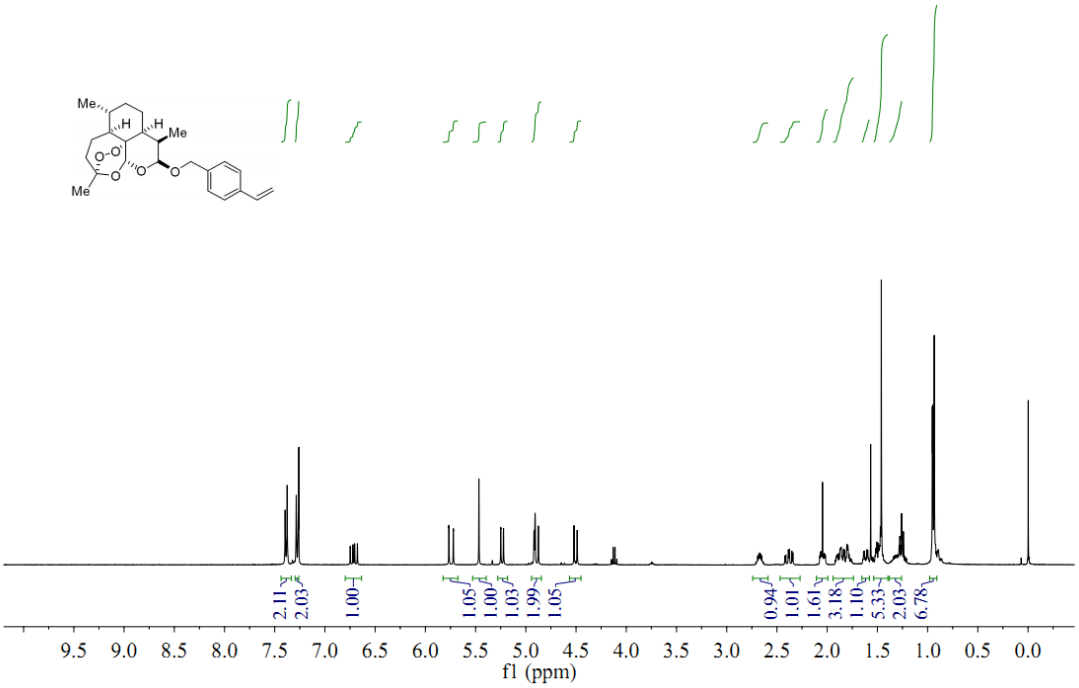

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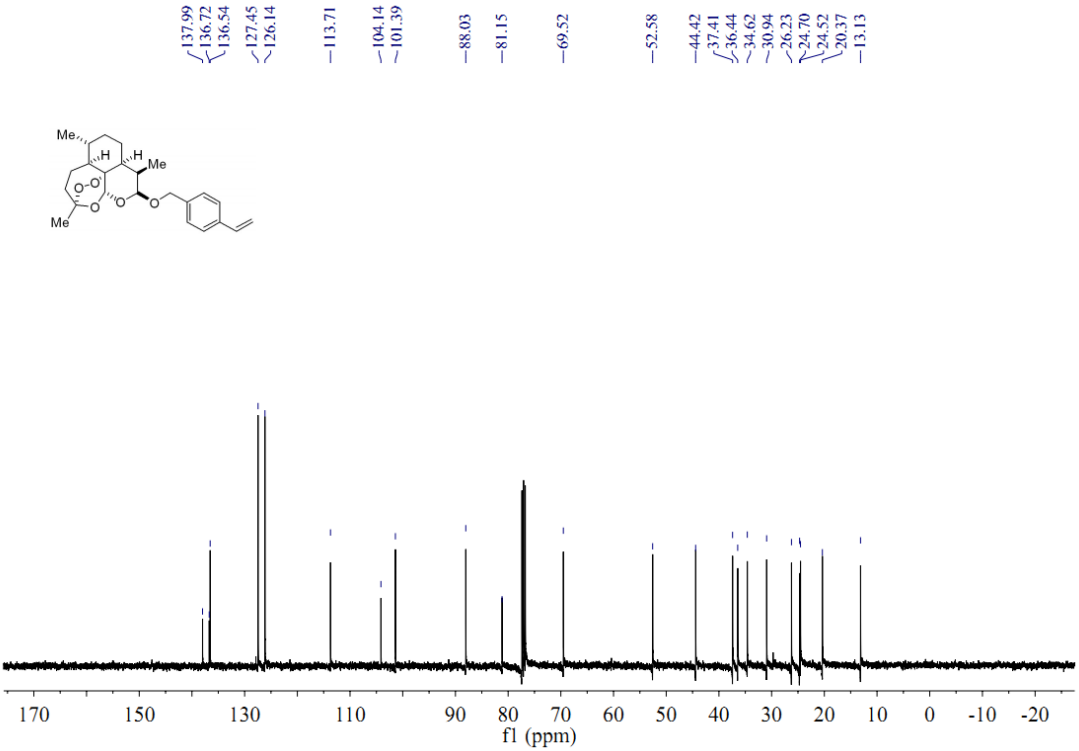

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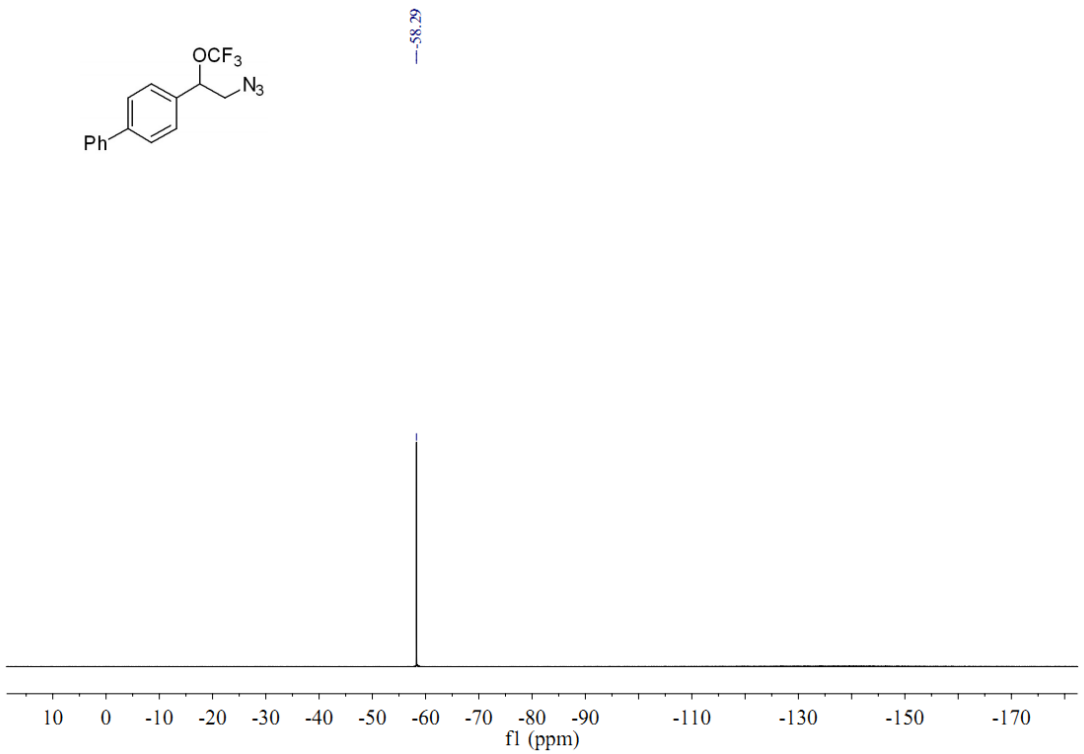
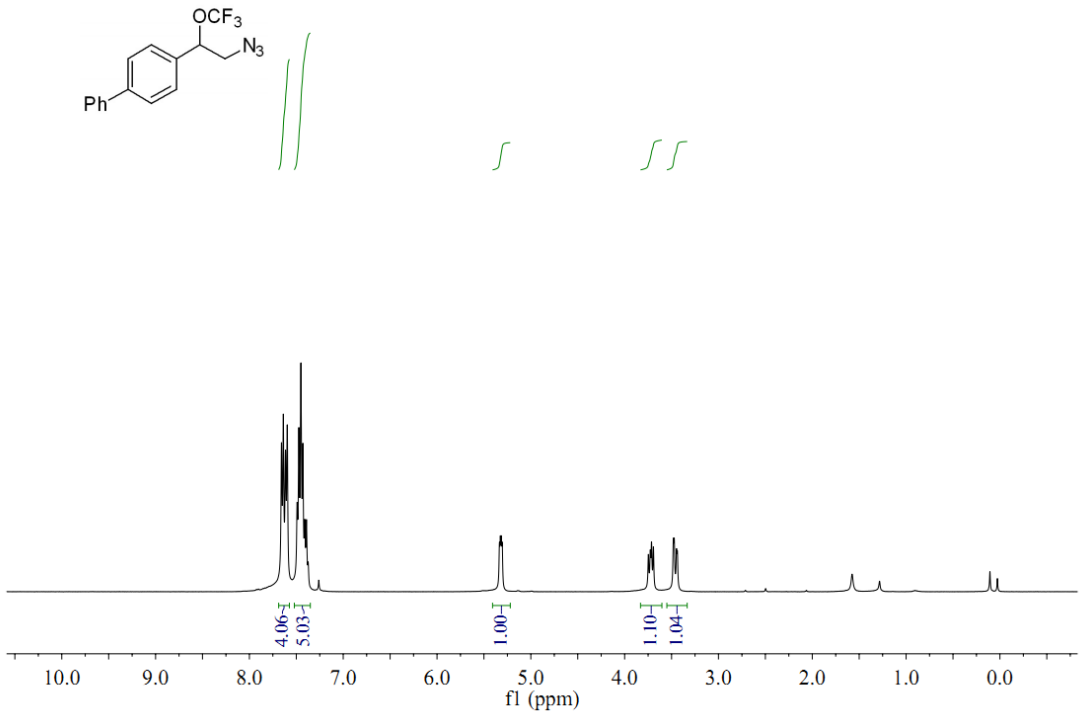


^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4a**



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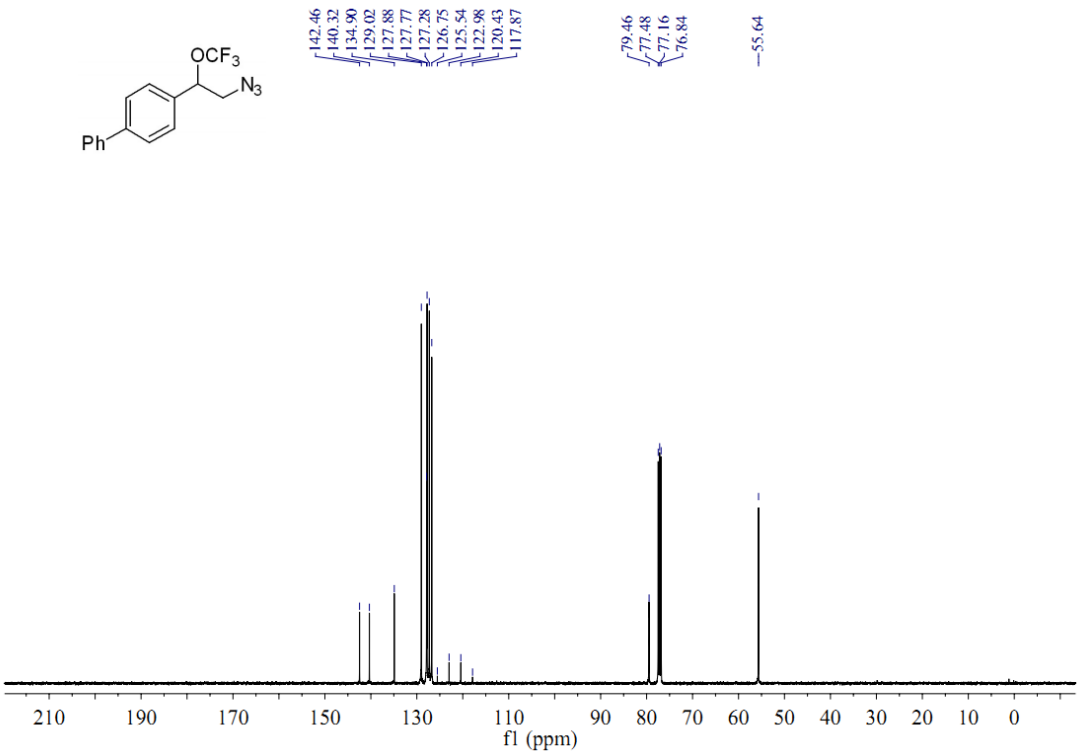

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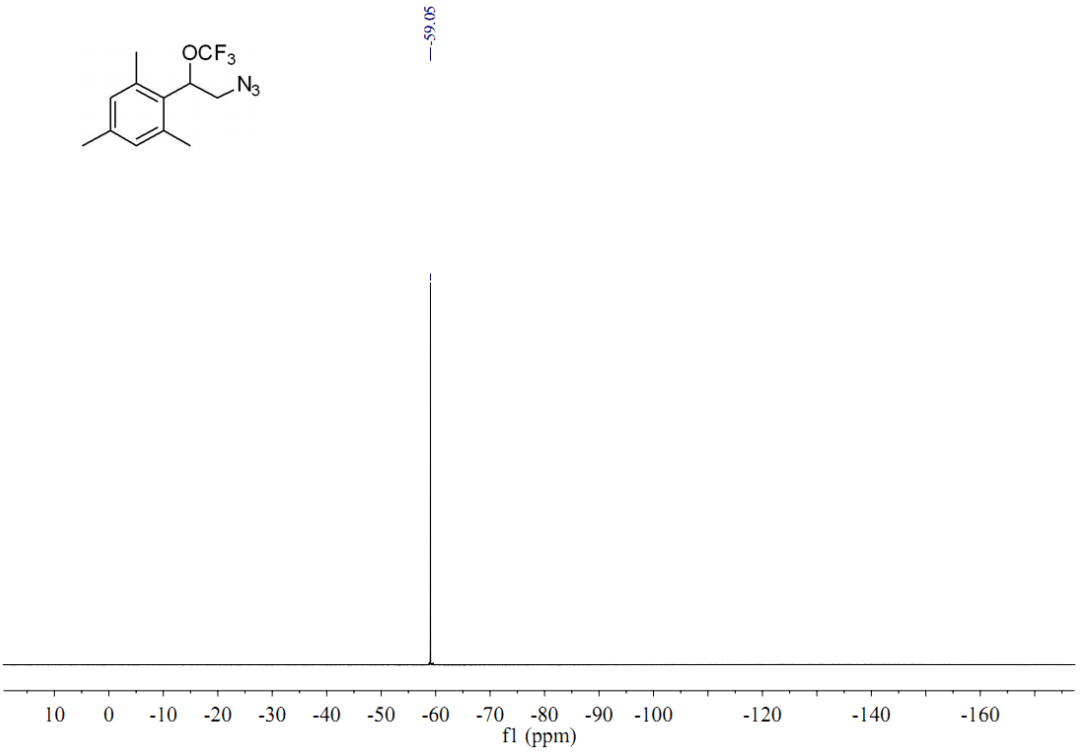

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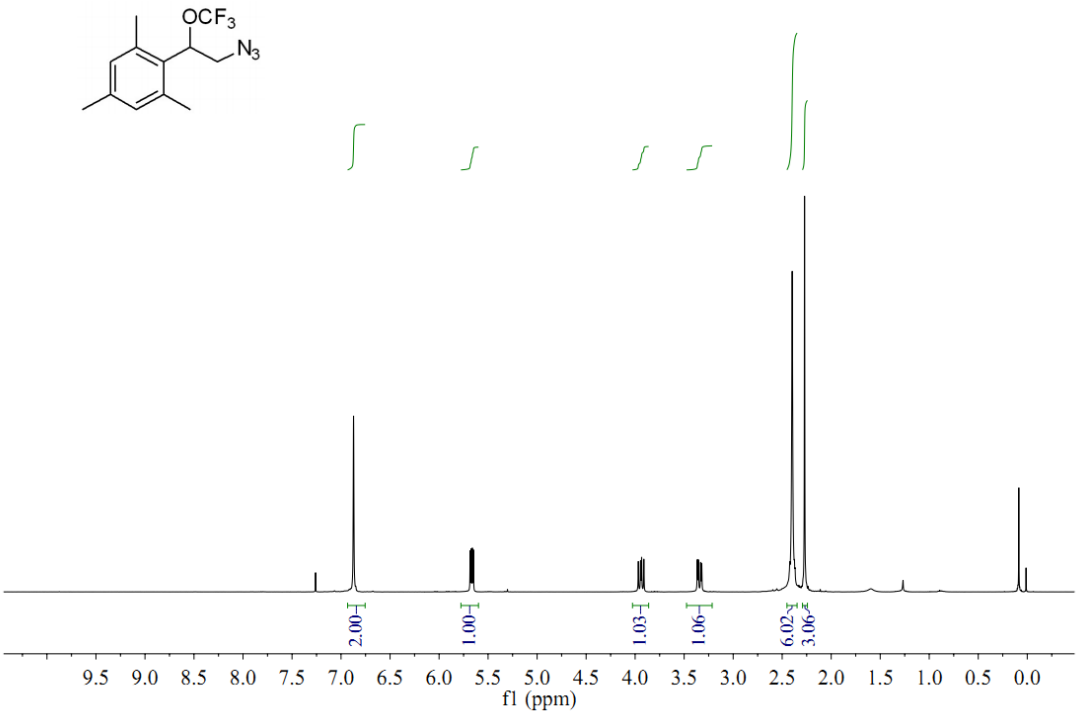

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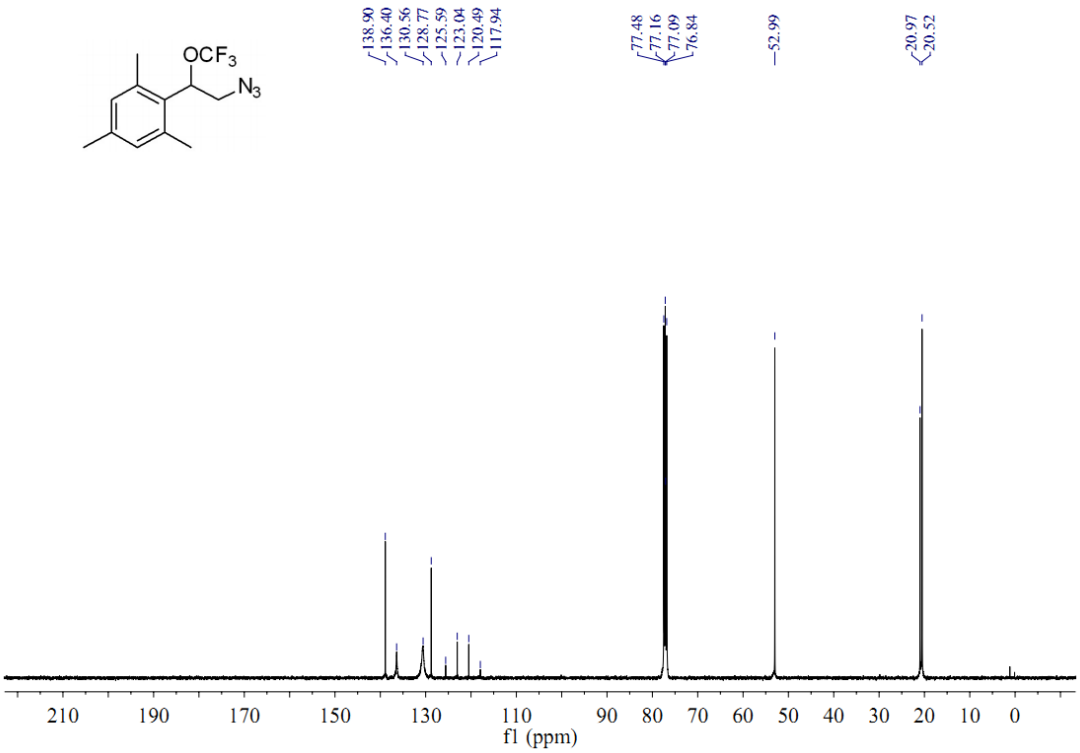

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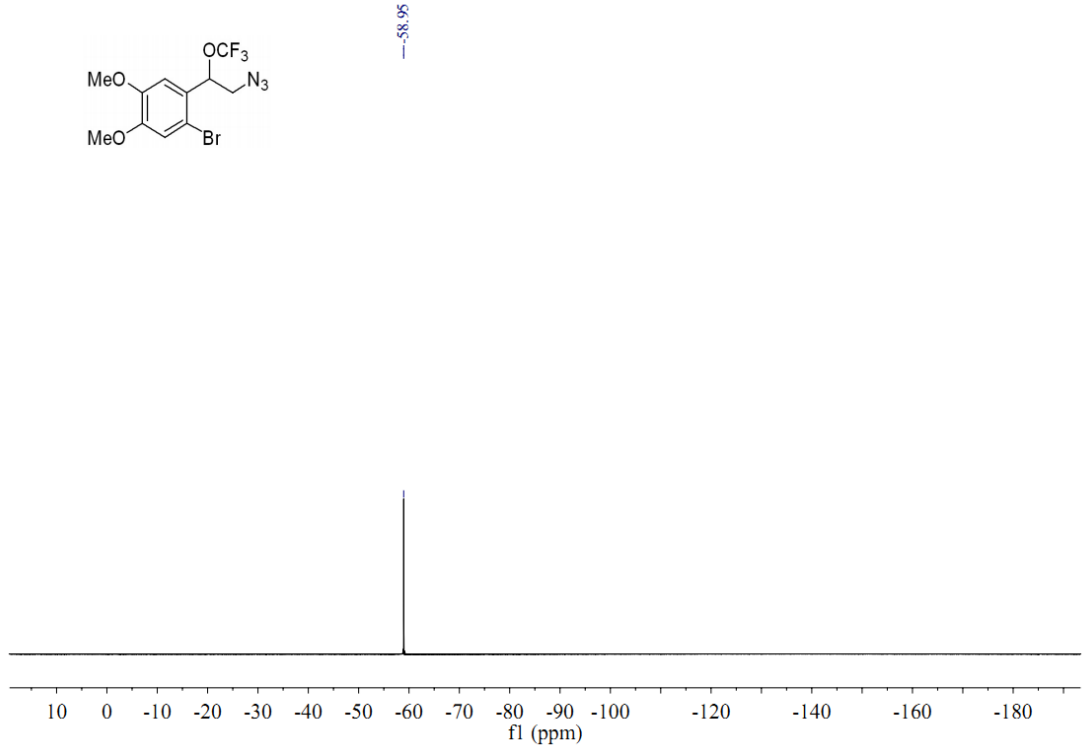

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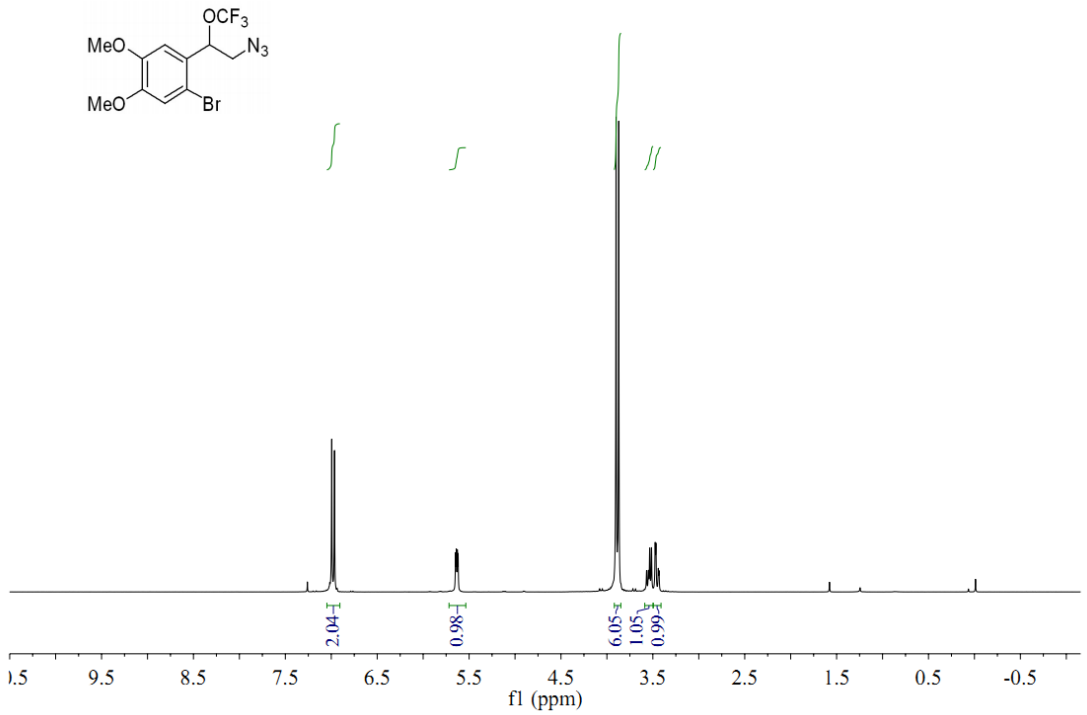

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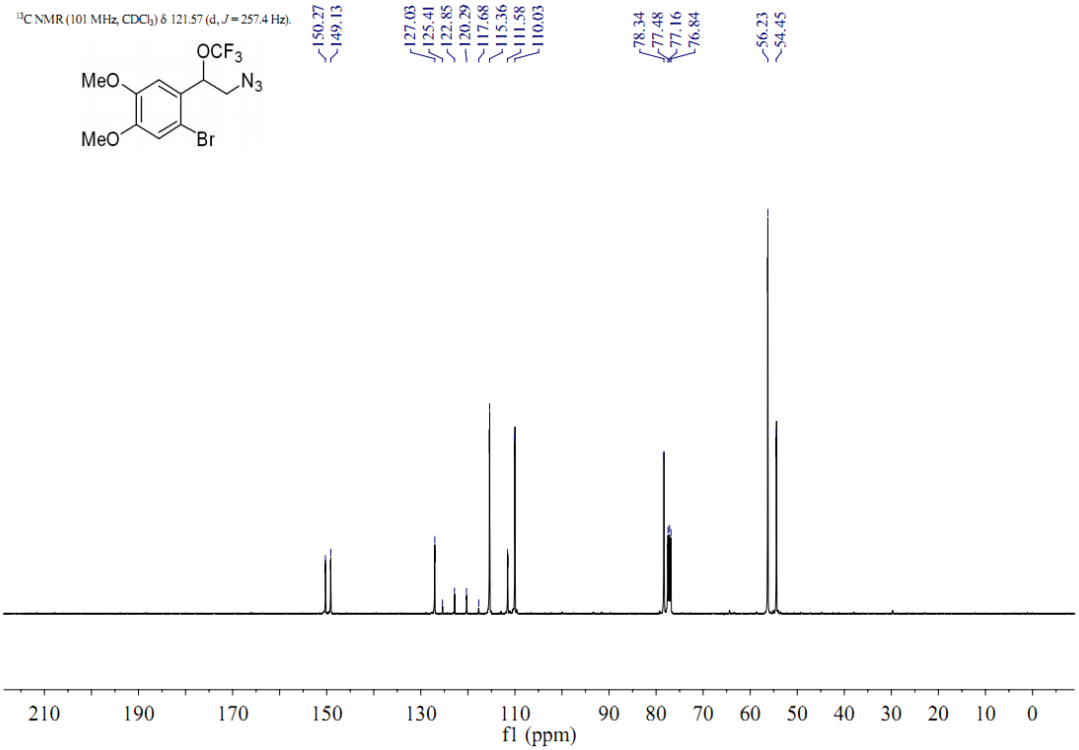

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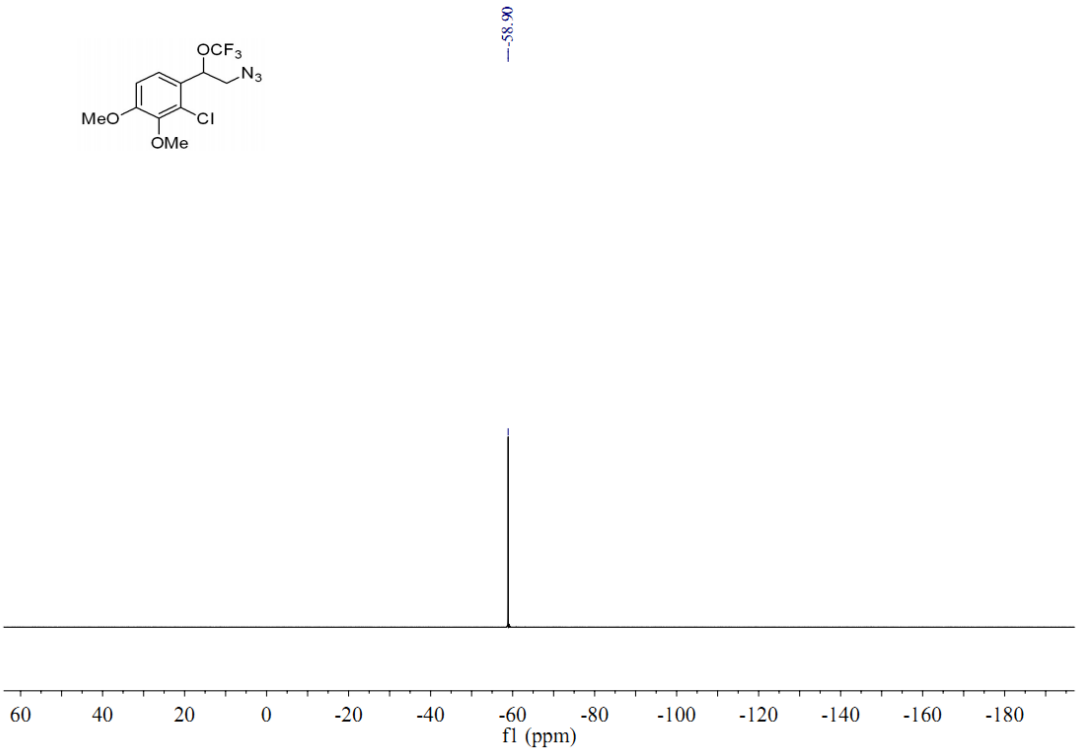

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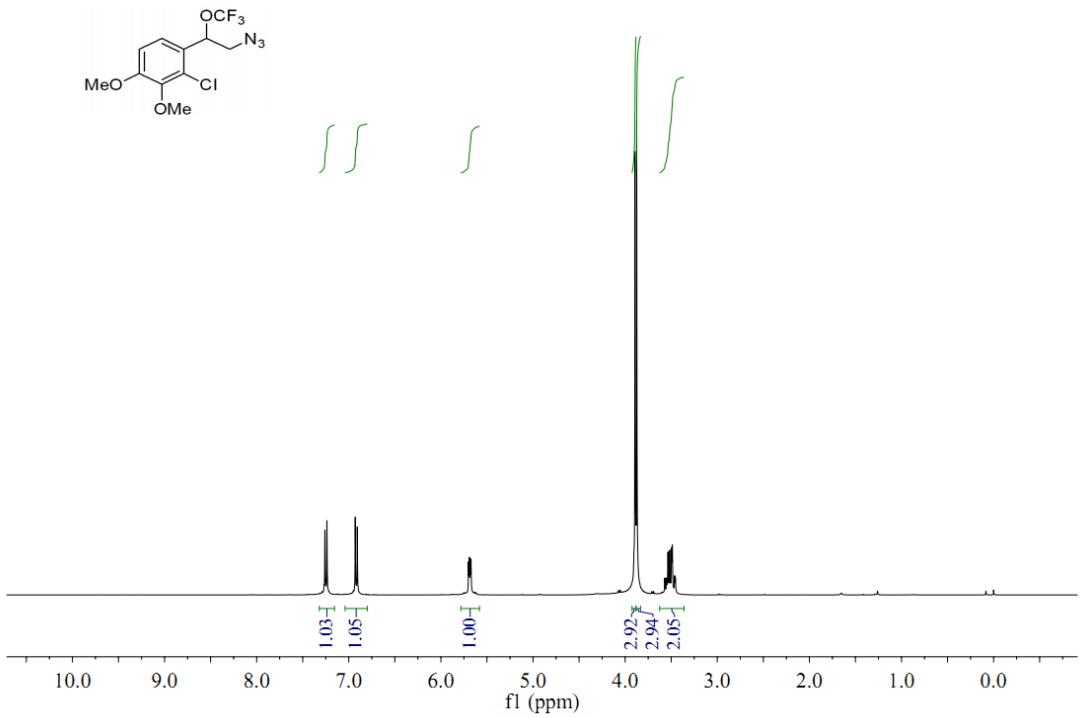

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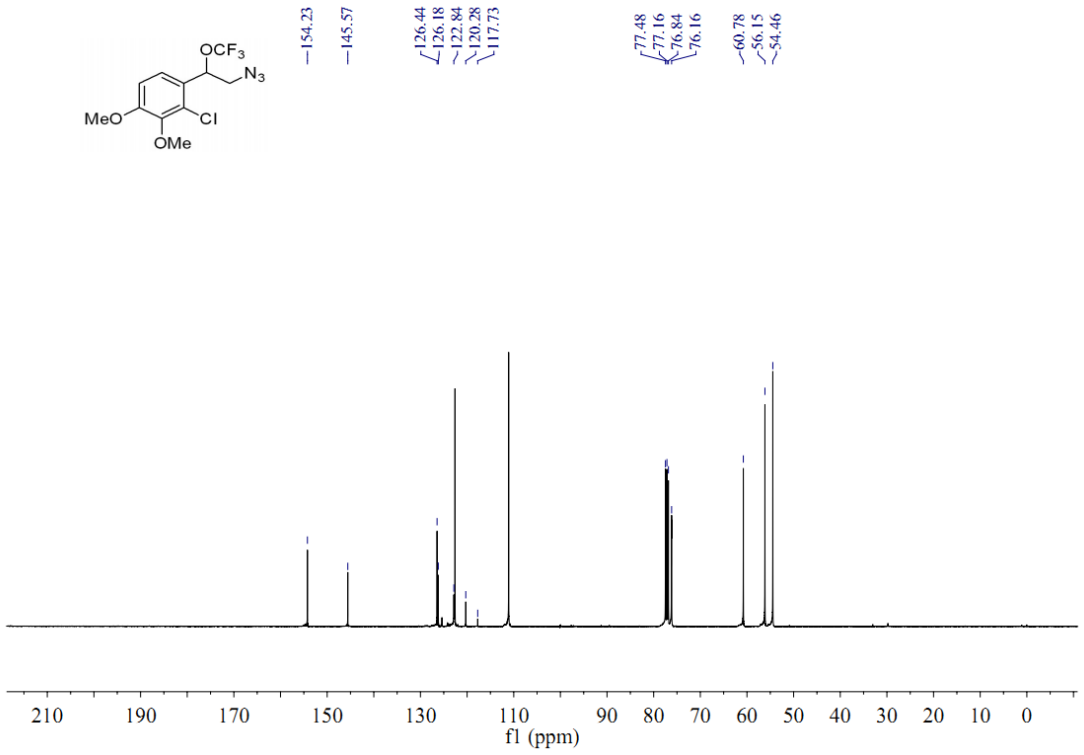

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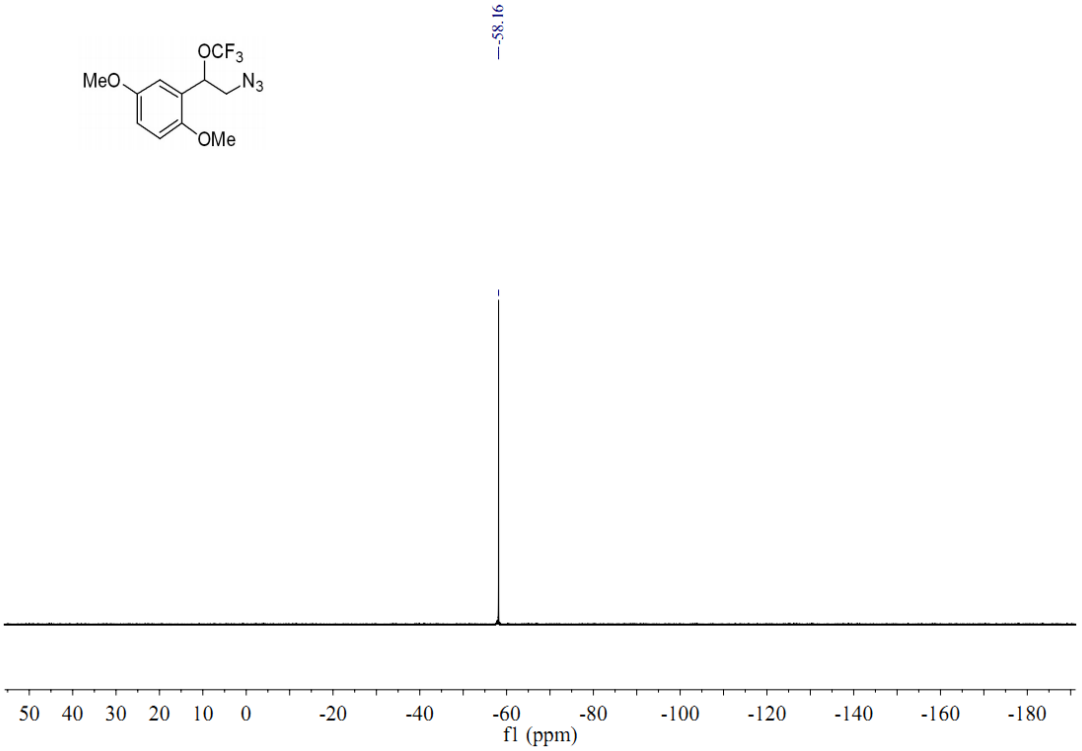

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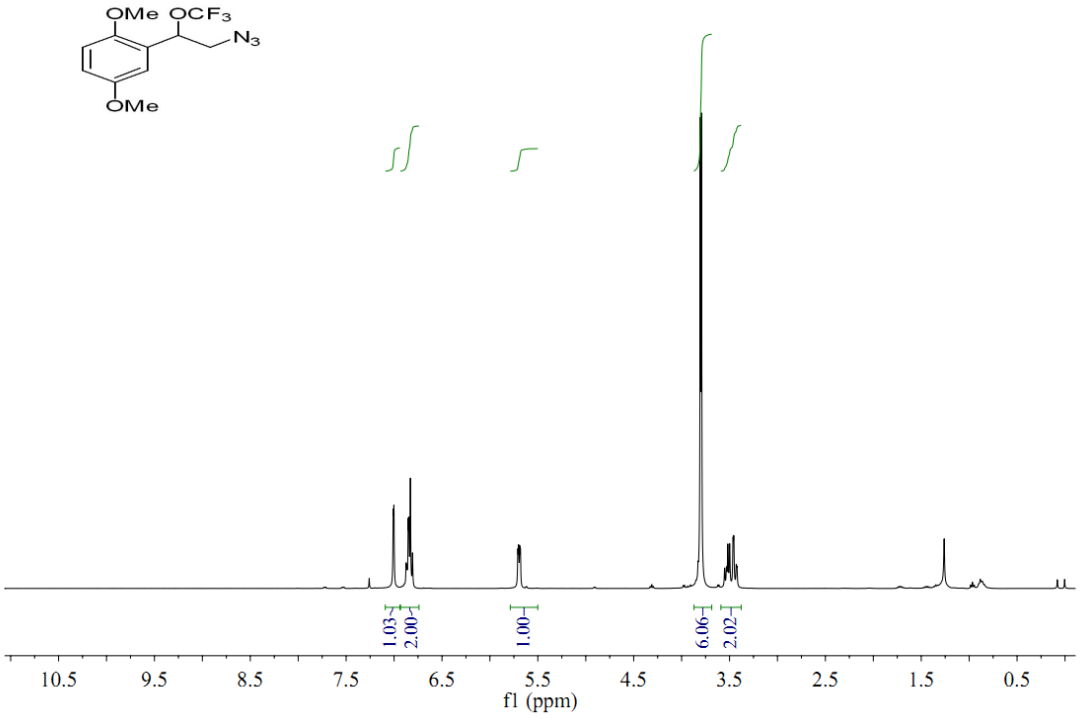

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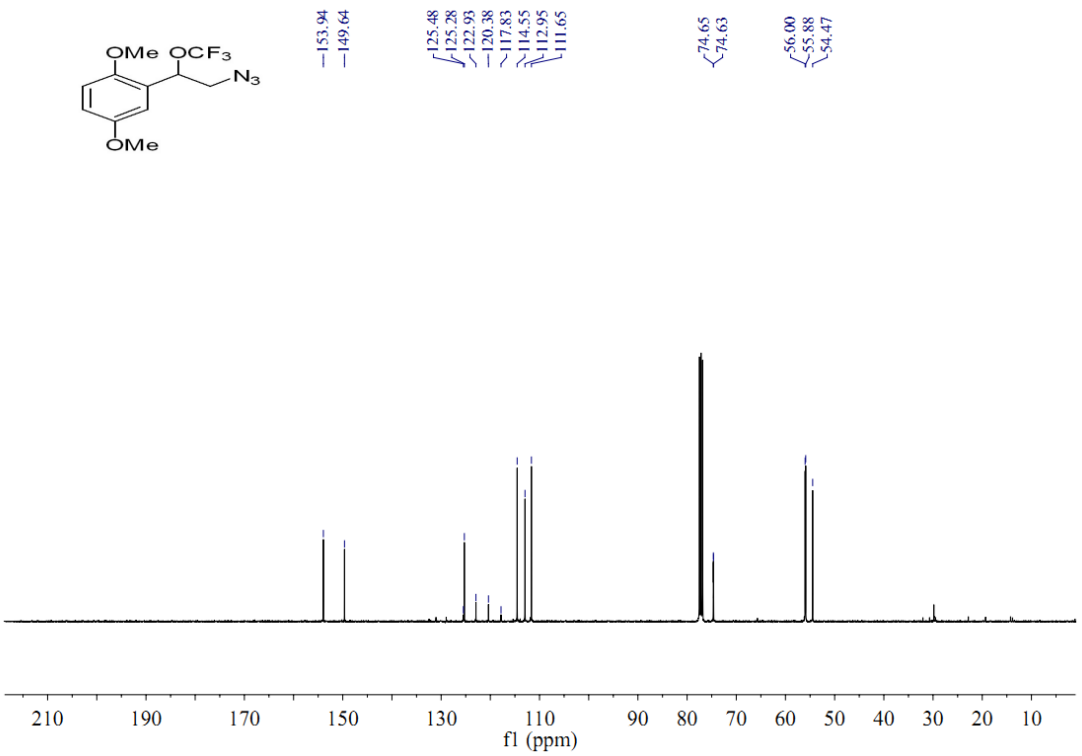

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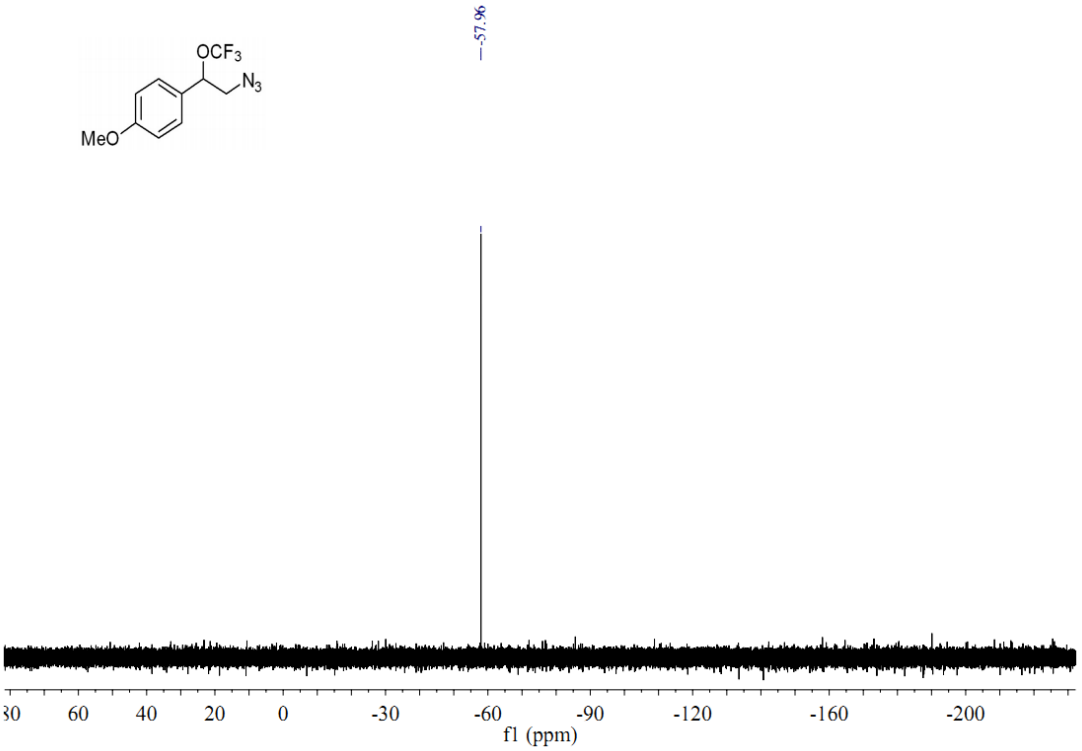

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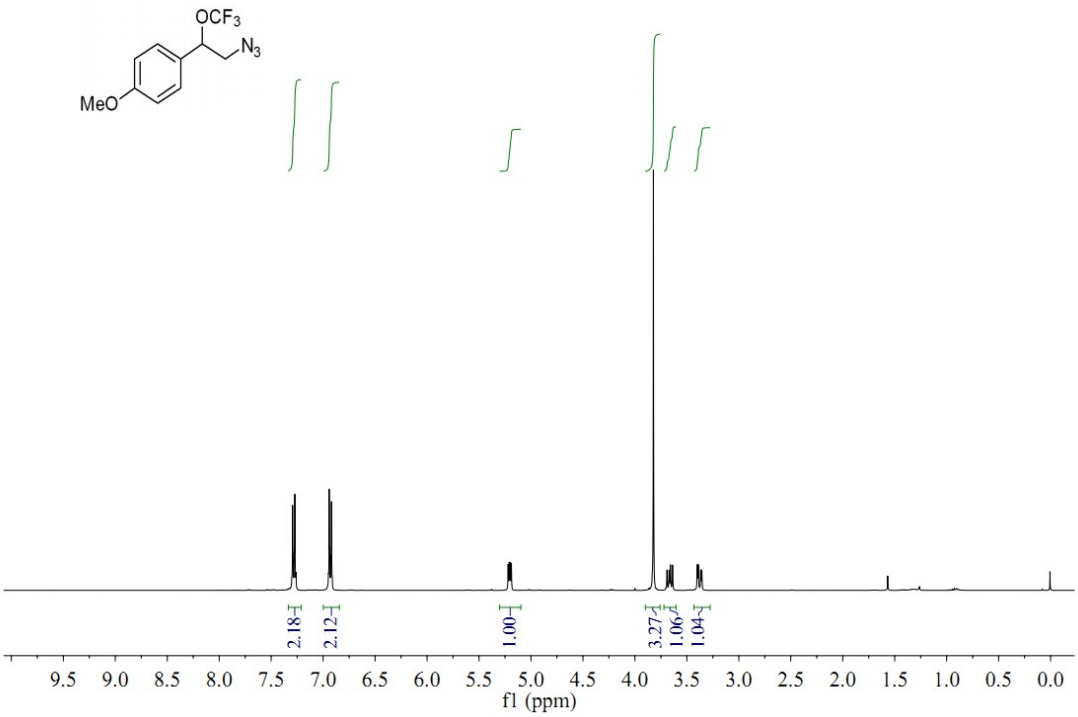

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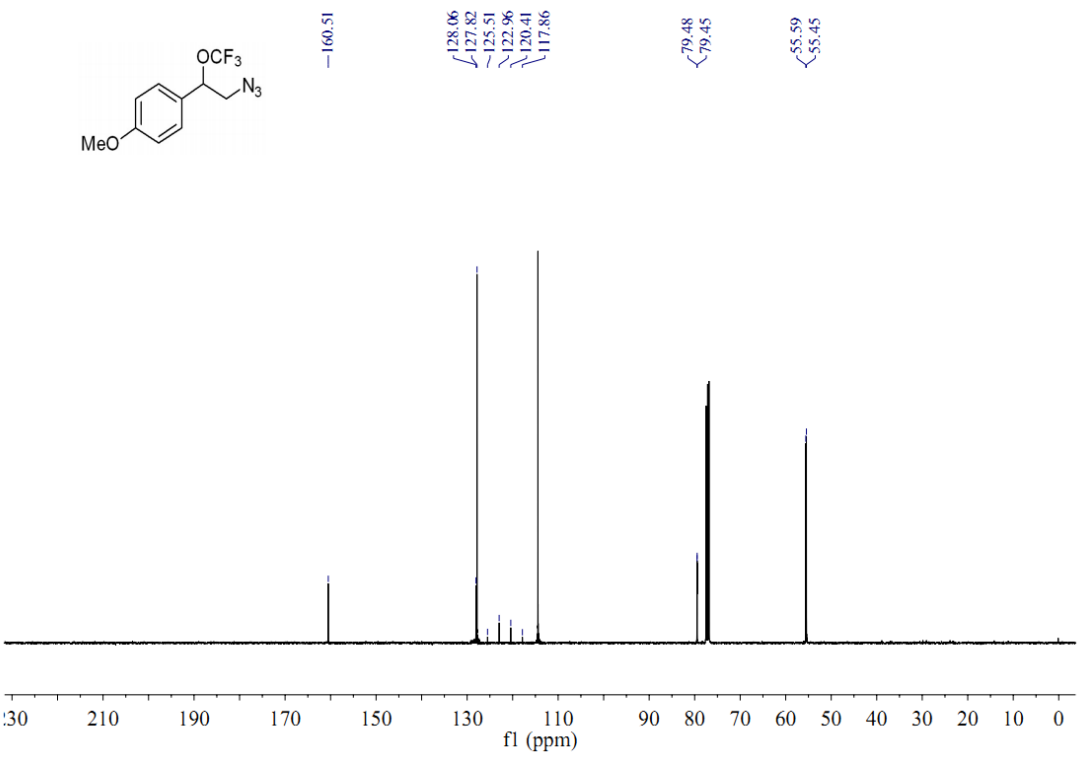

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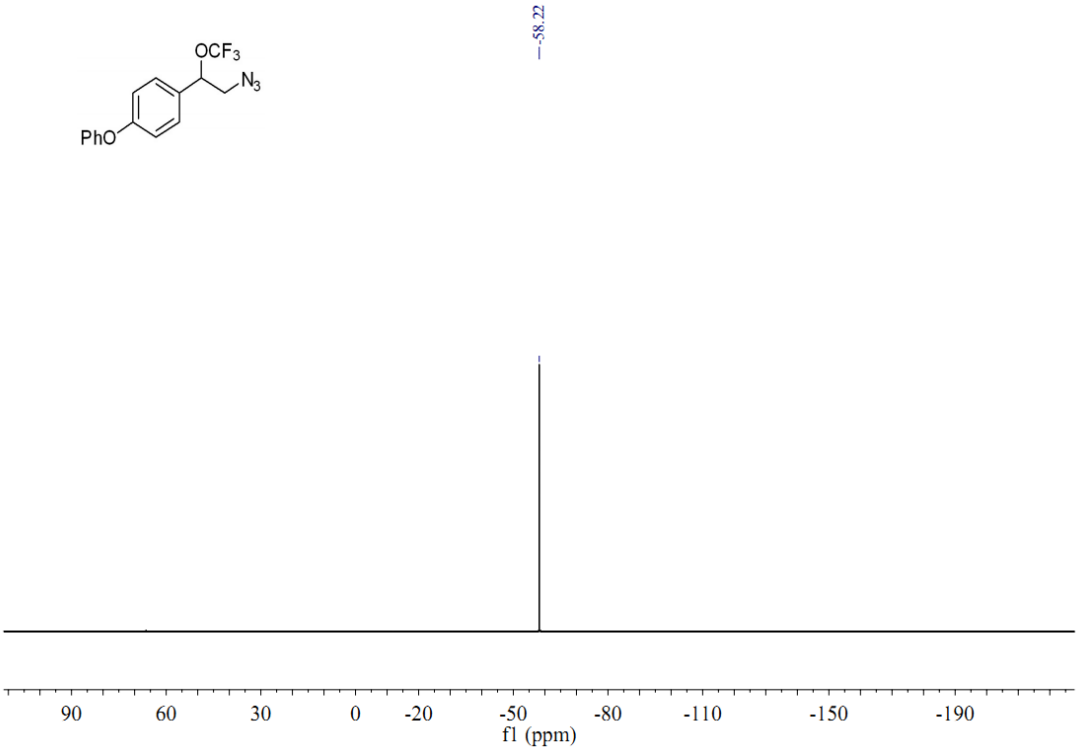

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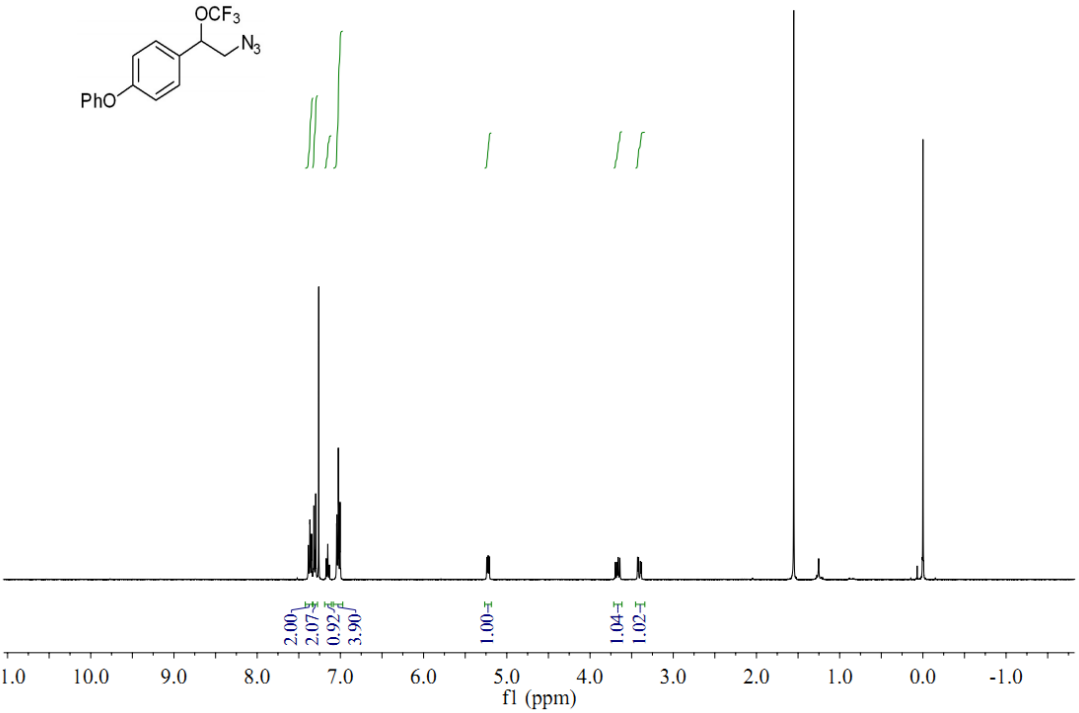

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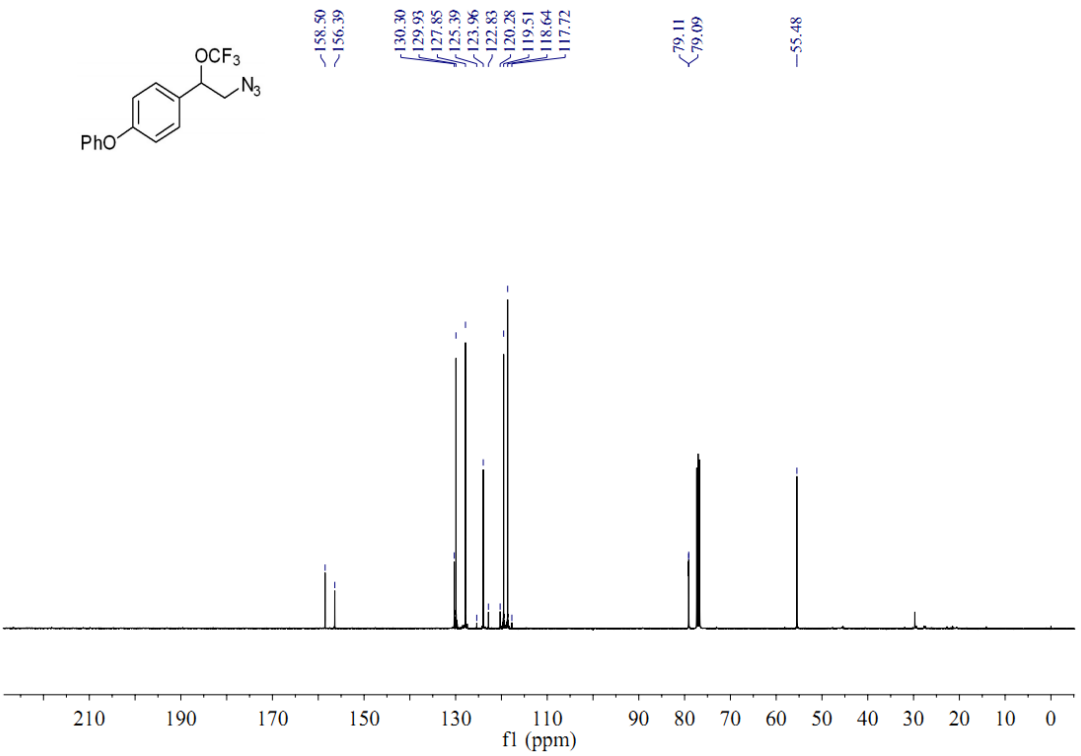

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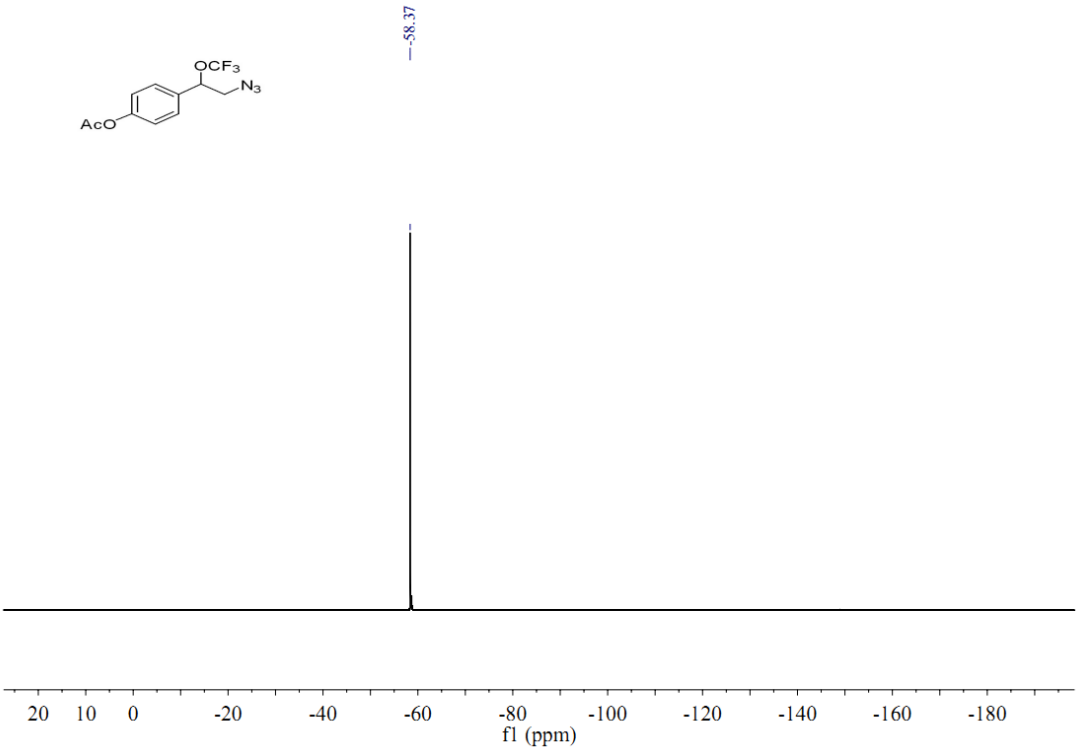

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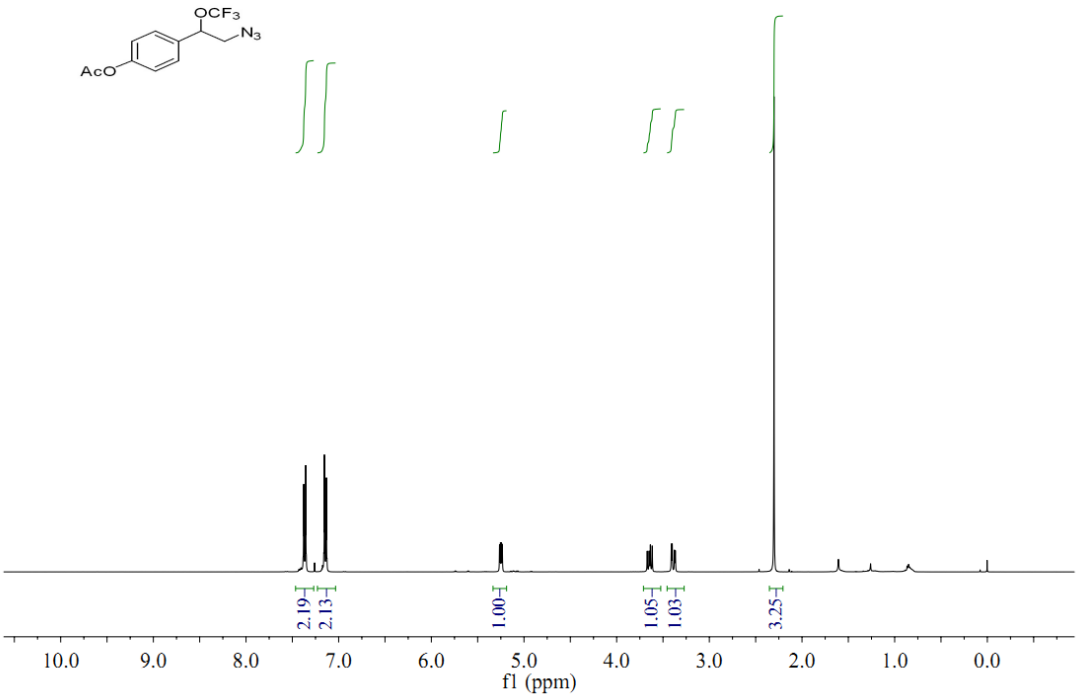

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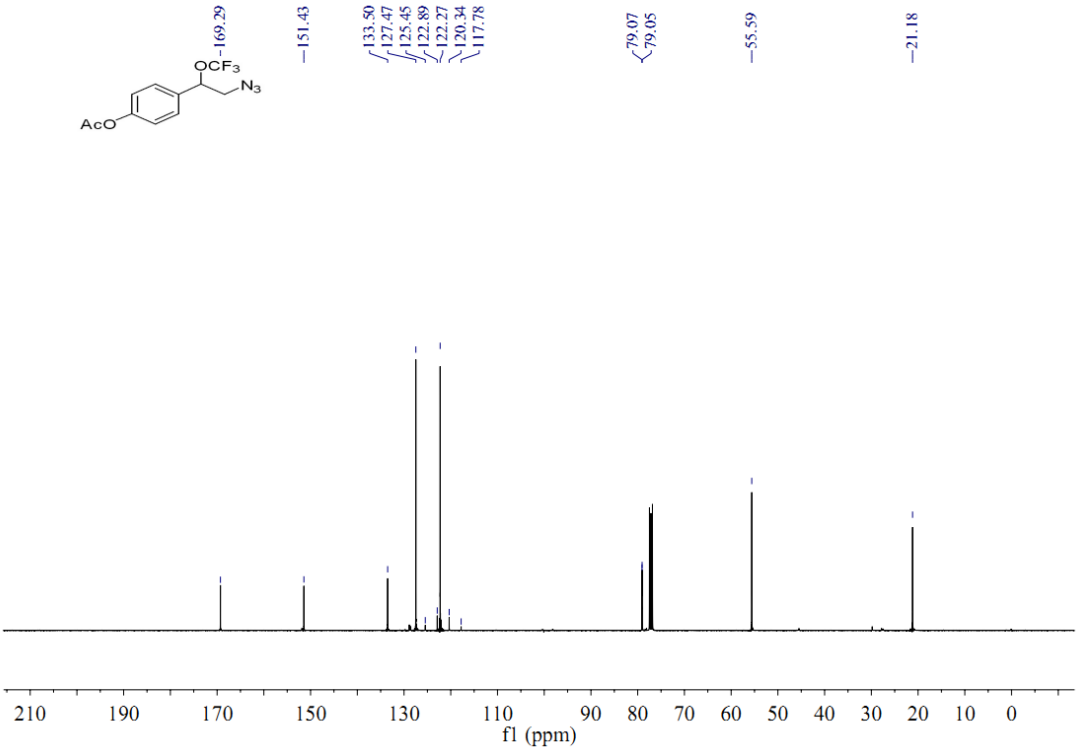

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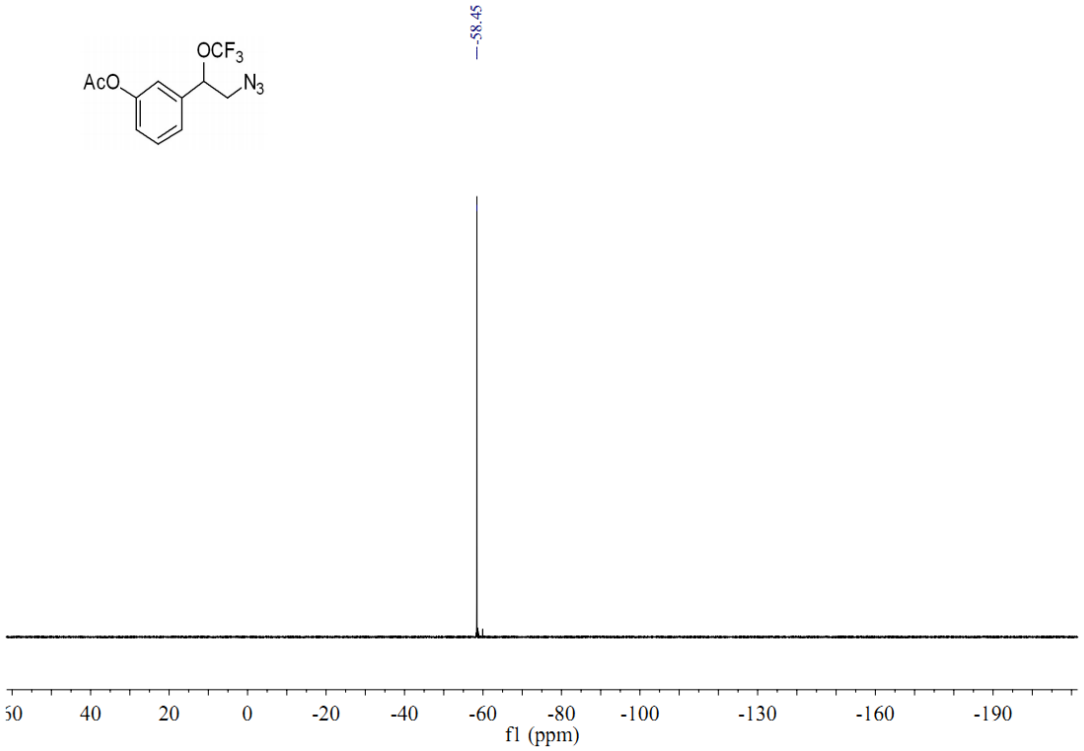
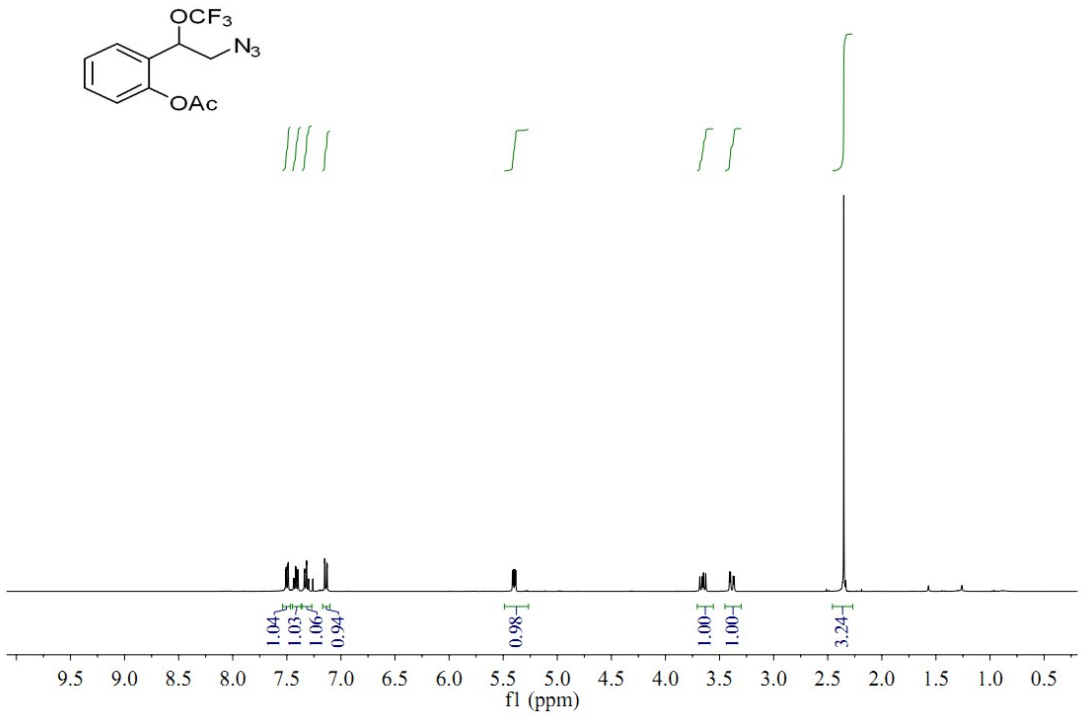
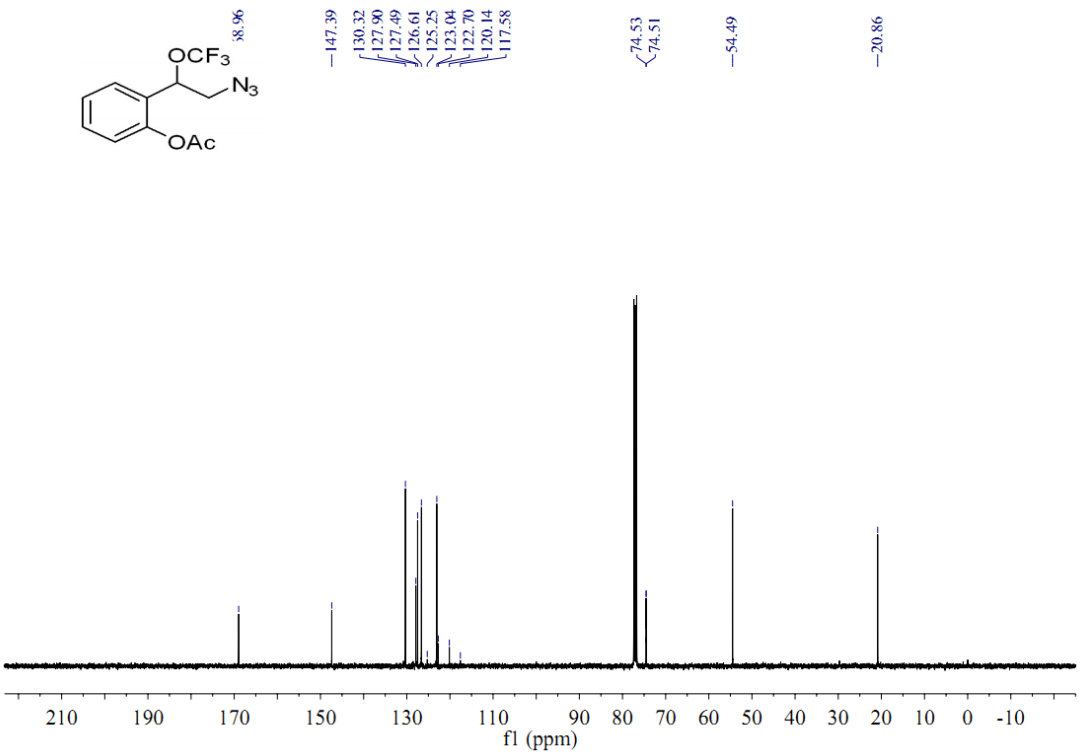


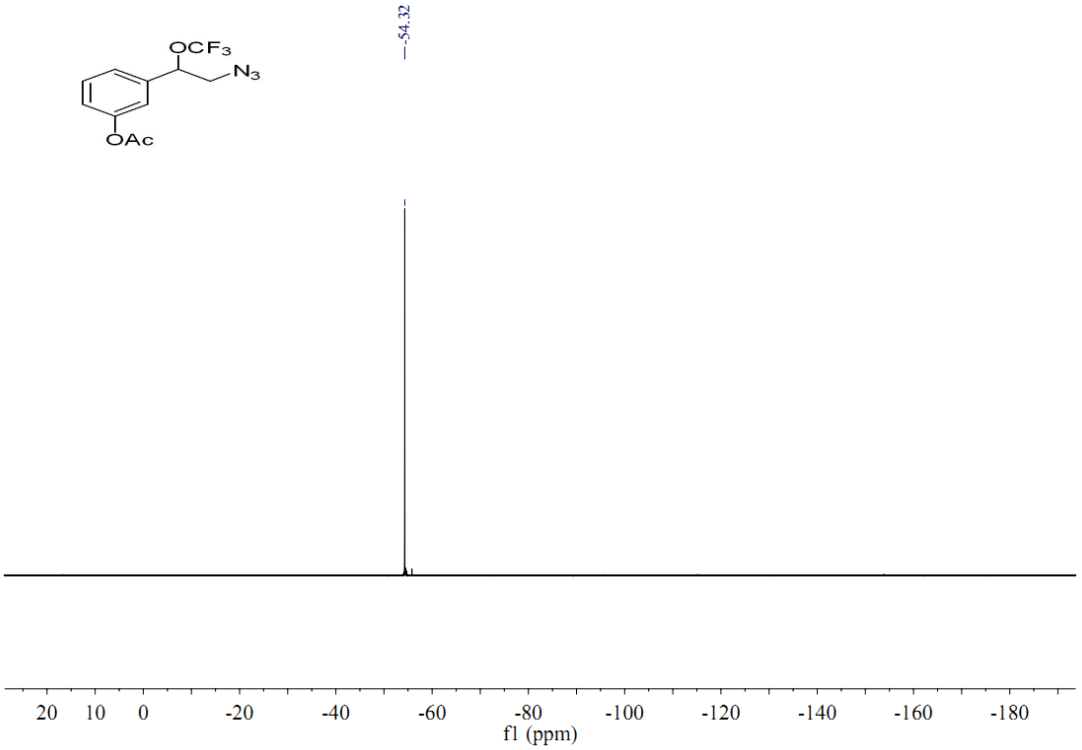
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4i**



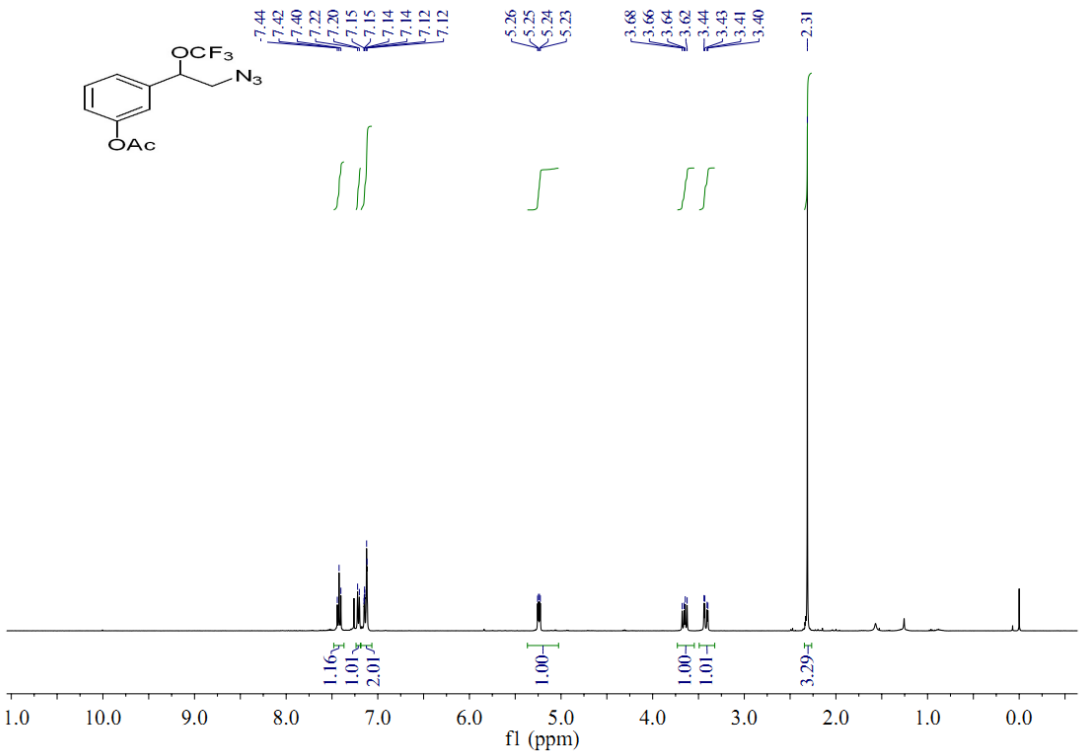
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4i**



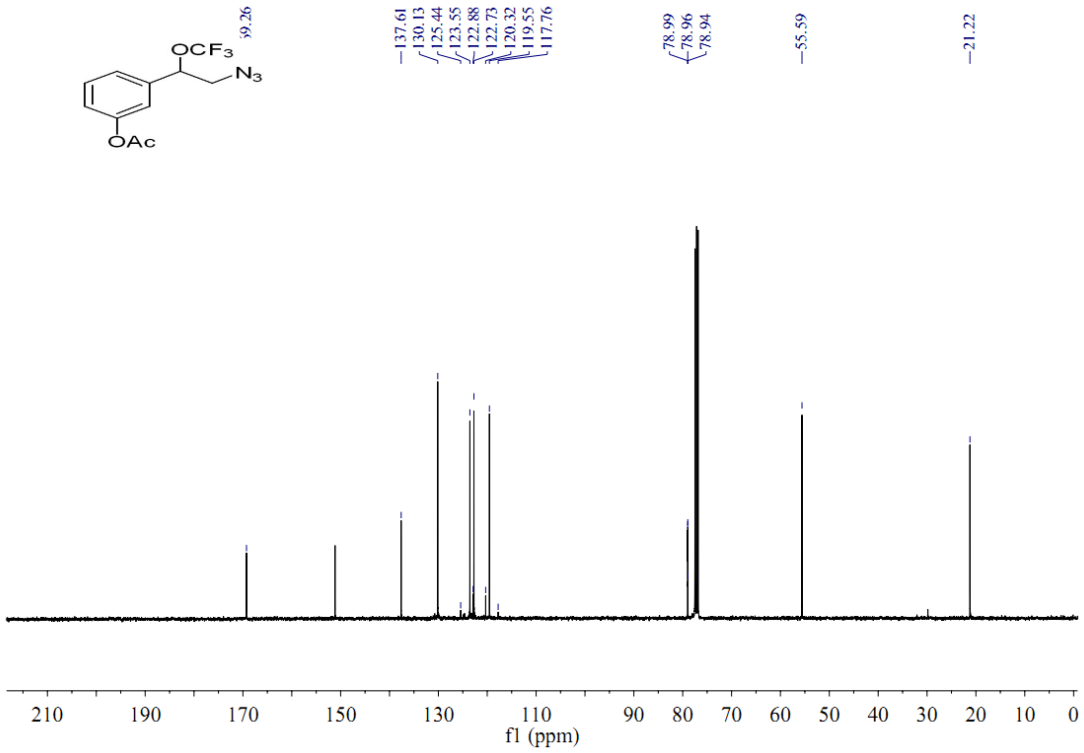
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4i**



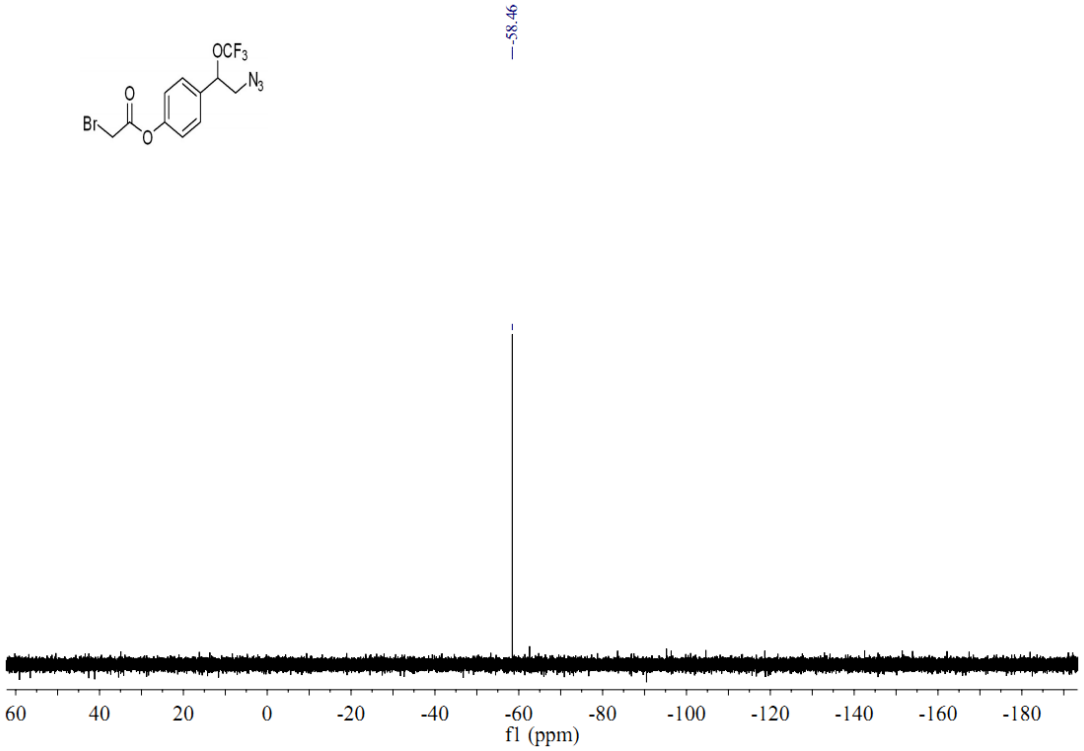
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4j**



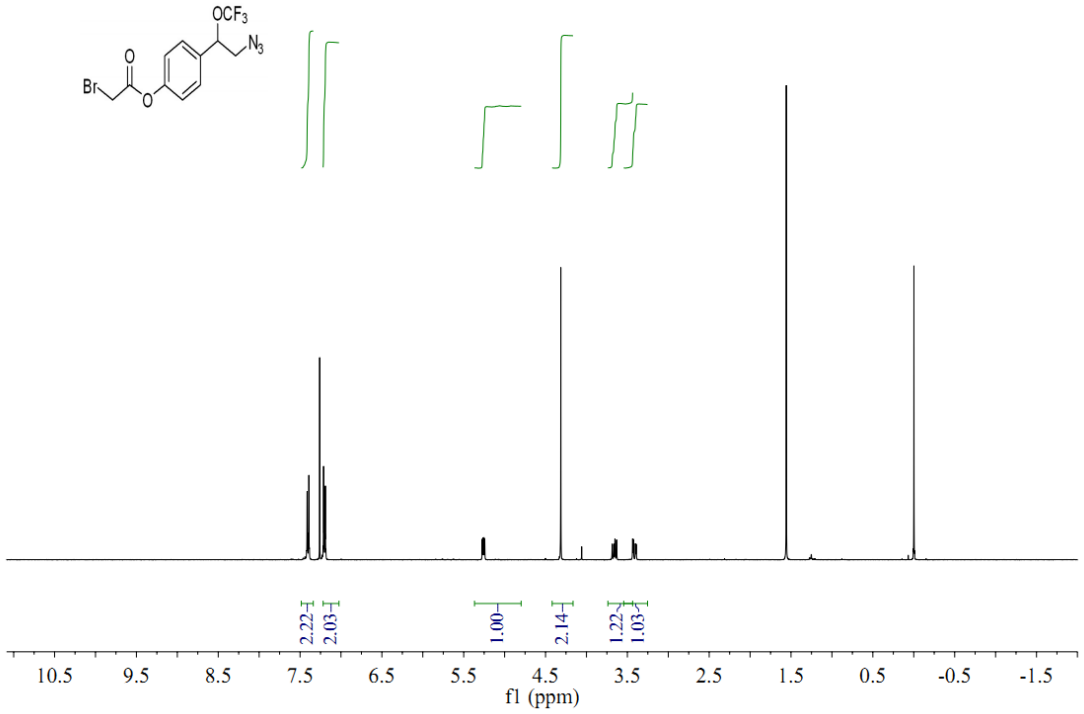
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4j**



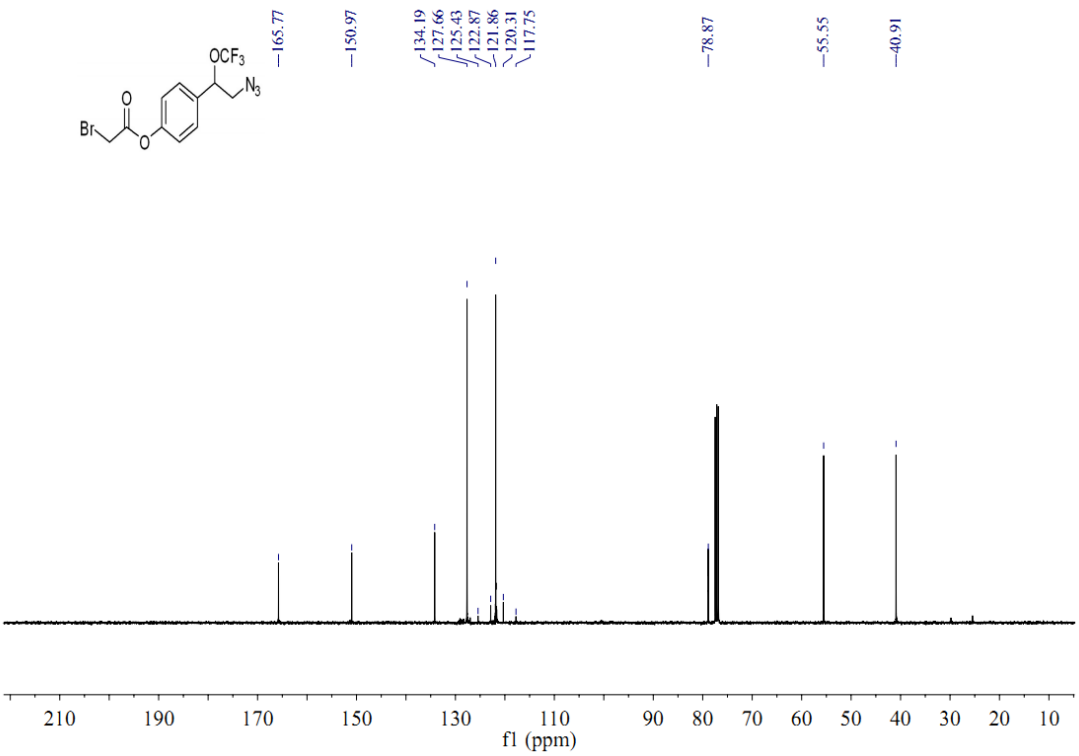
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4j**



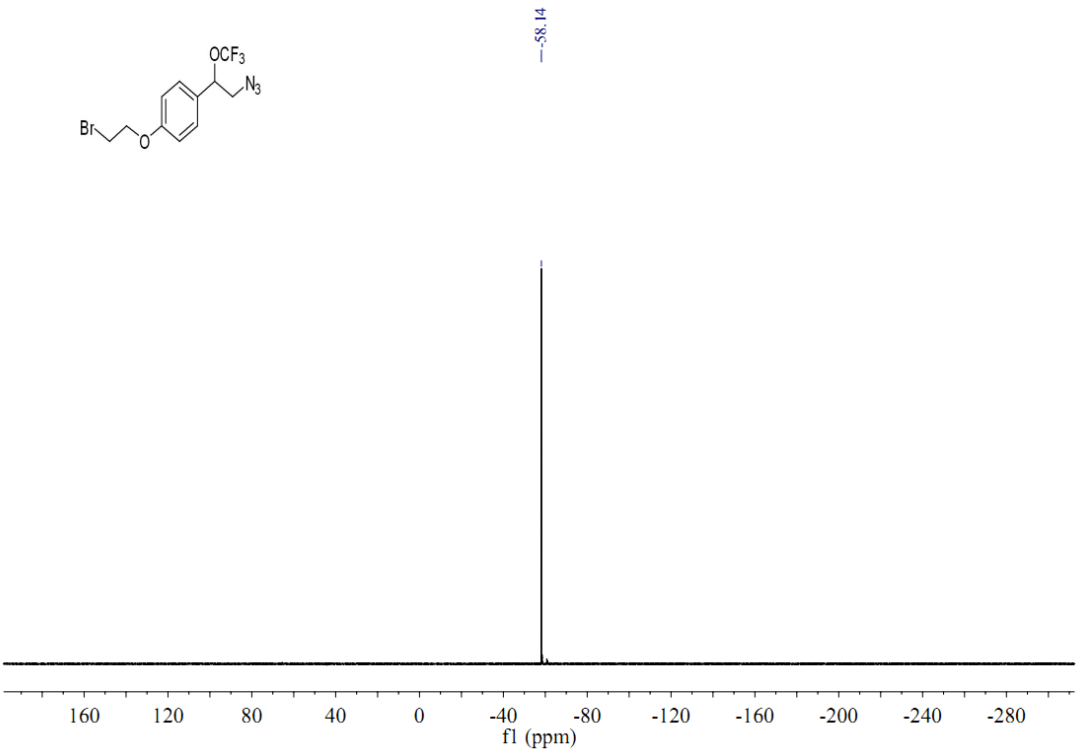
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4k**



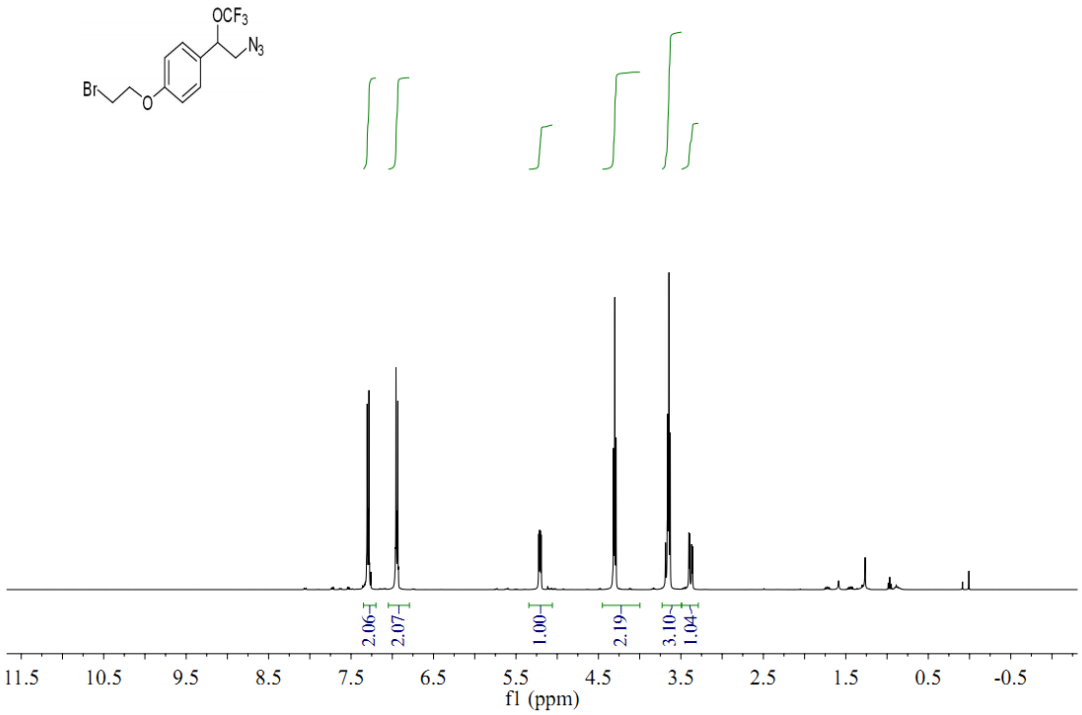
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4k**



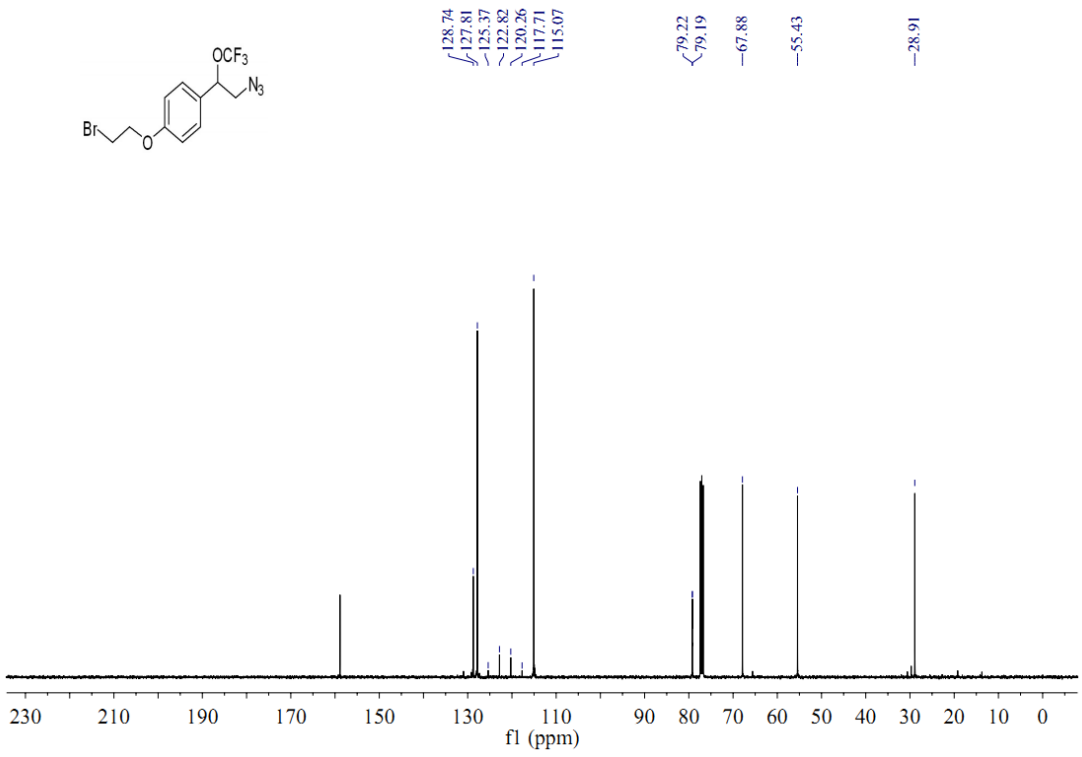
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4k**



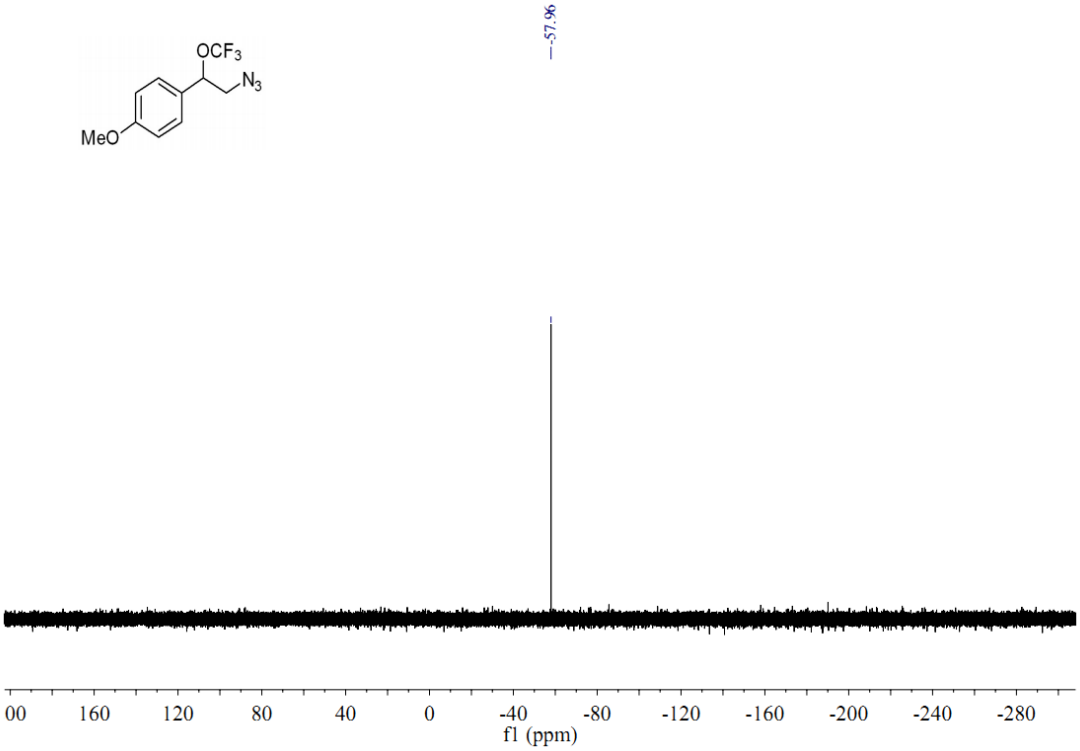
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4l**



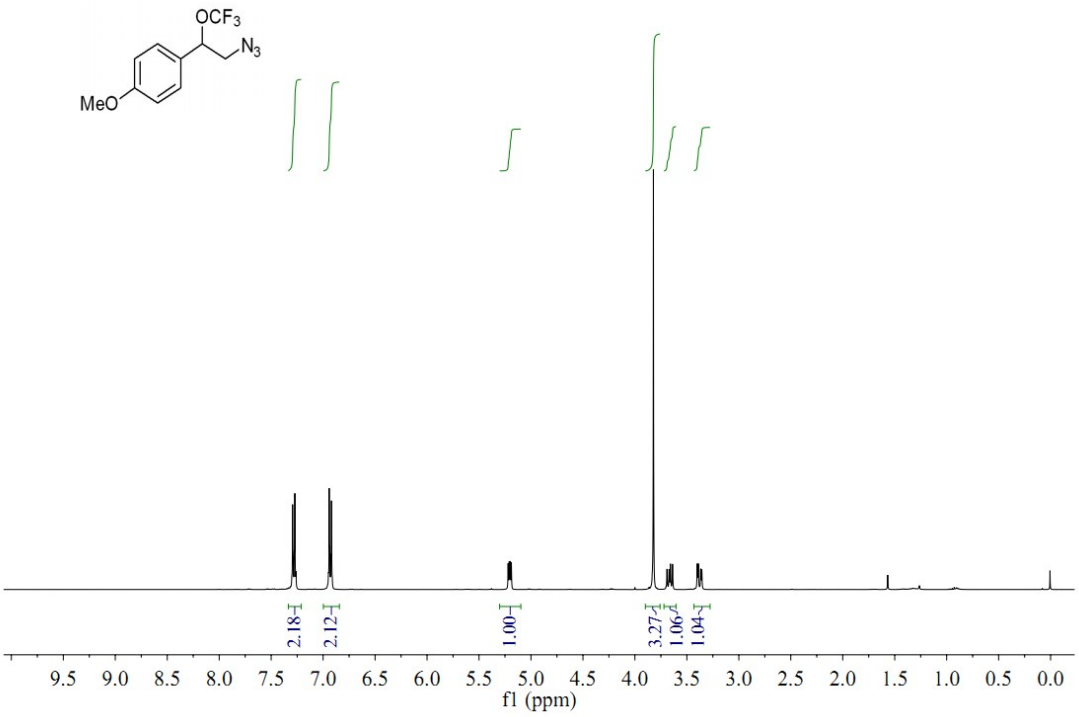
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4l**



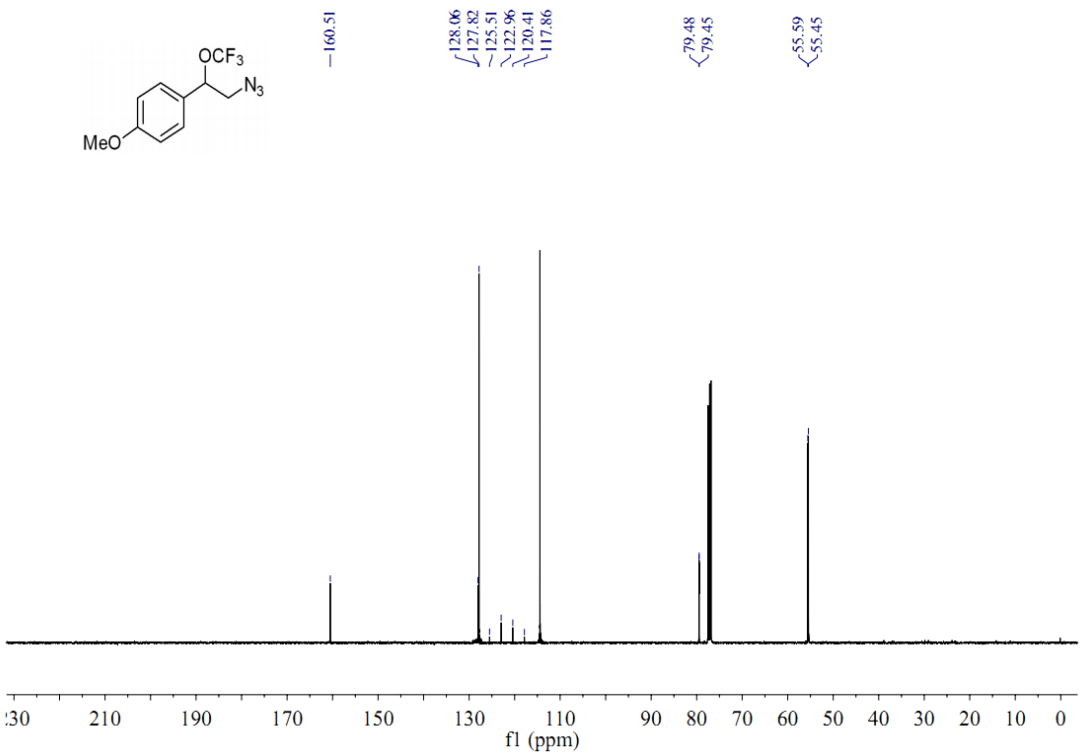
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4l**



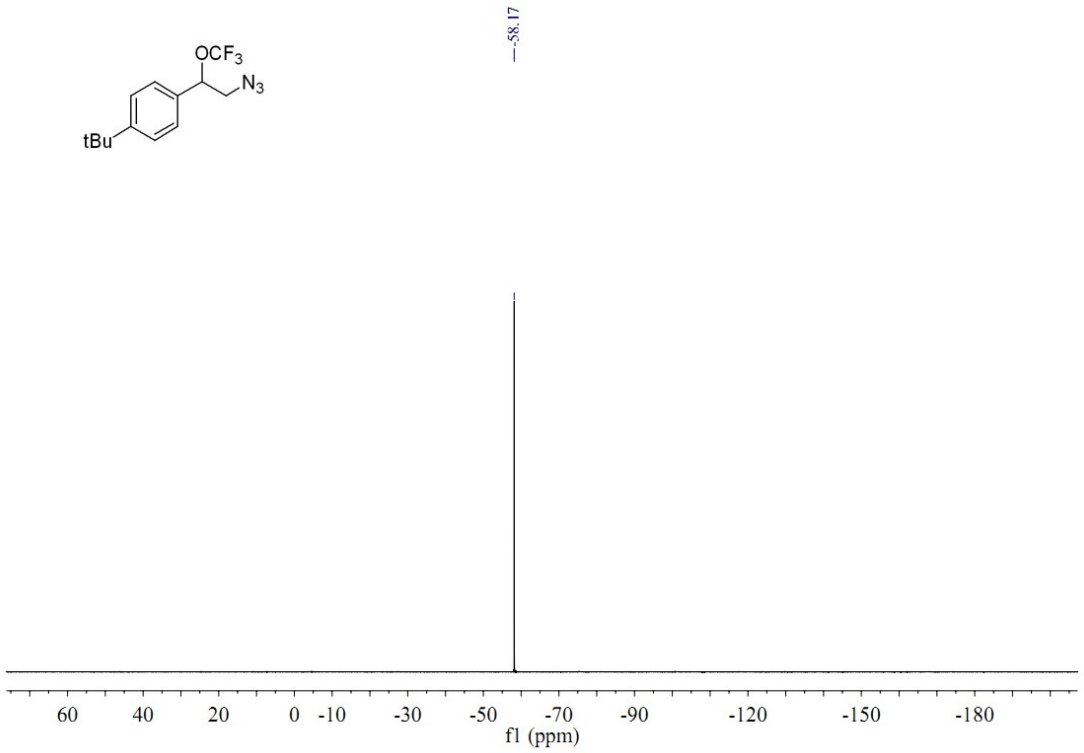
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4m**



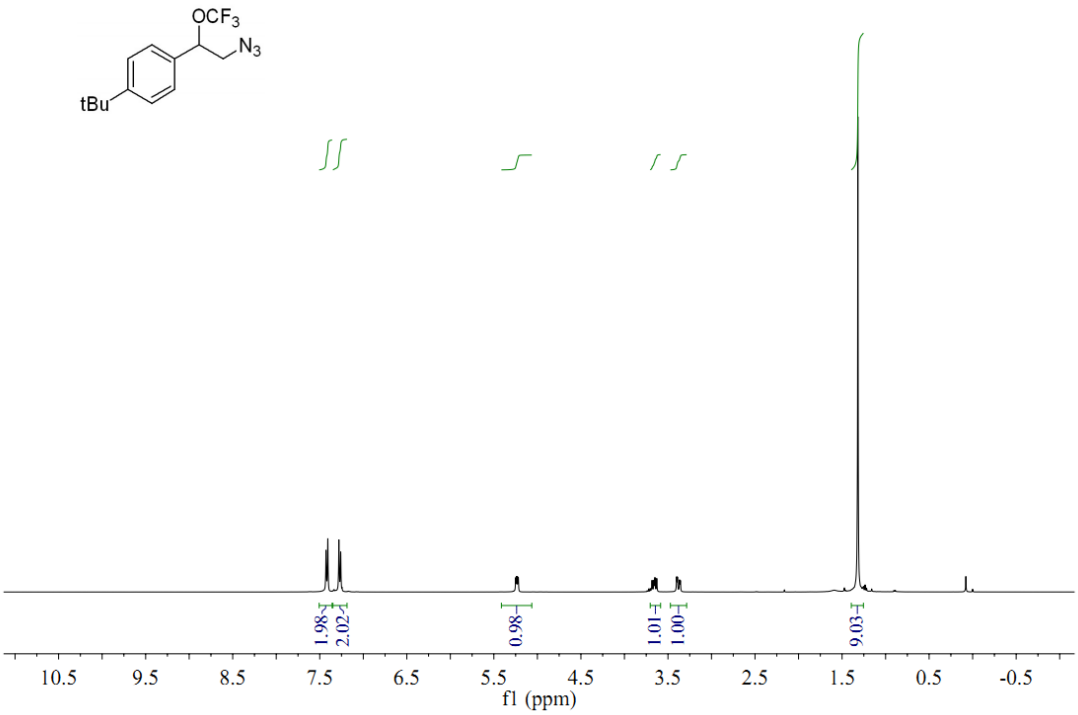
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4m**



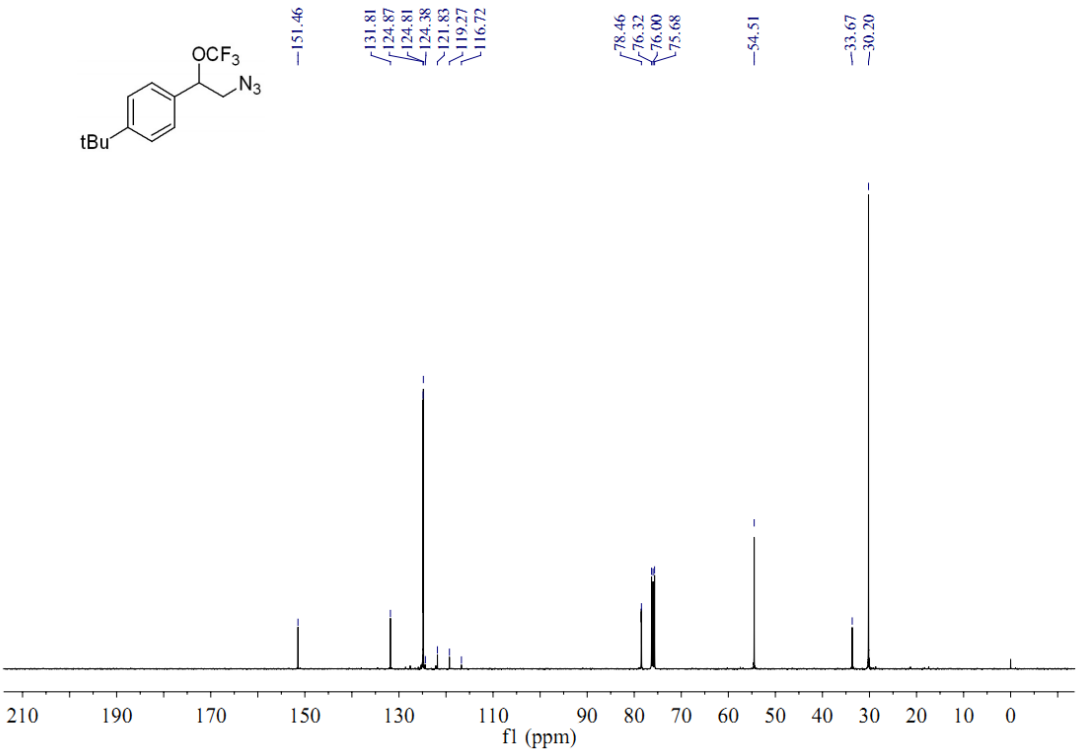
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4m**



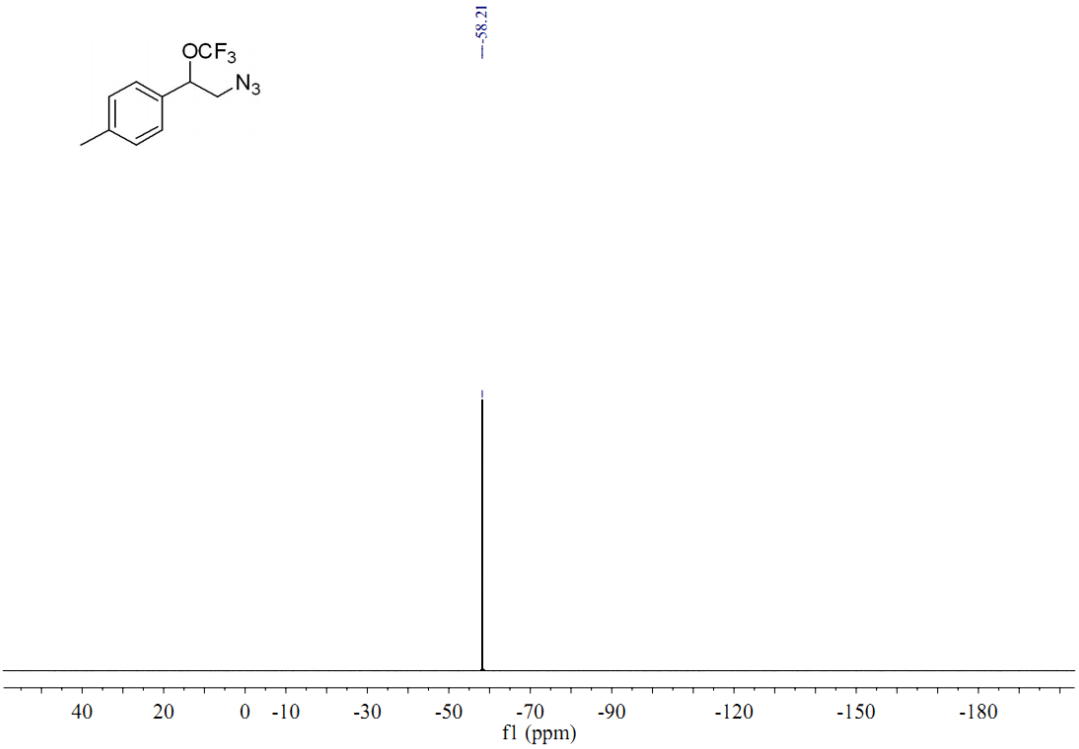
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4n**



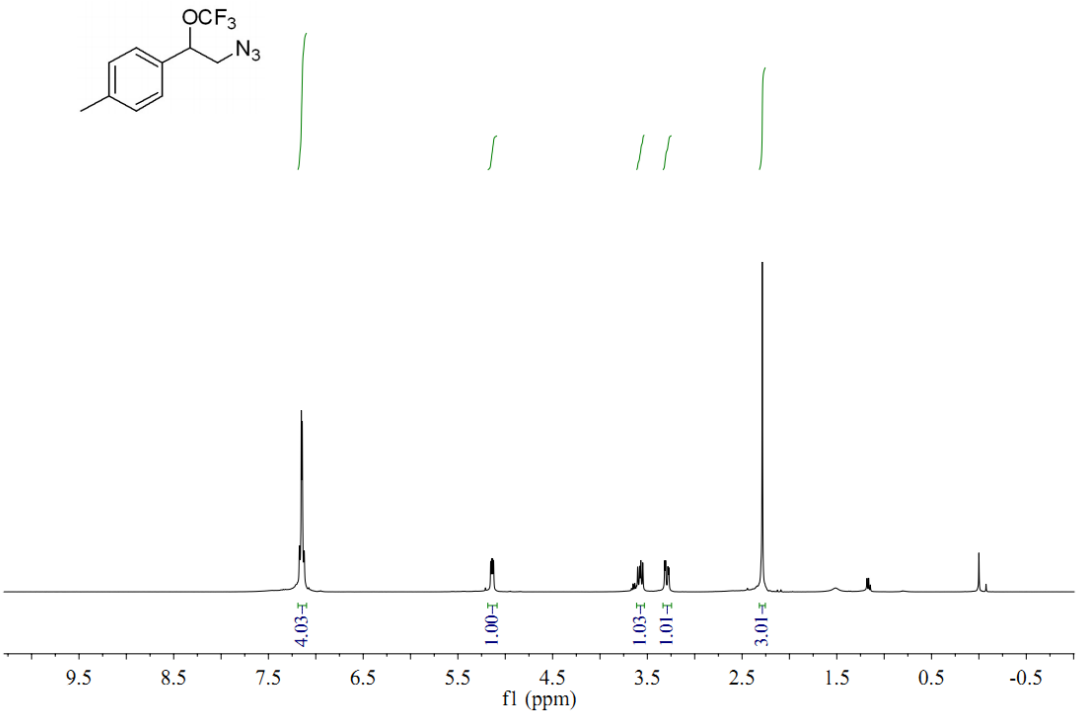
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4n**



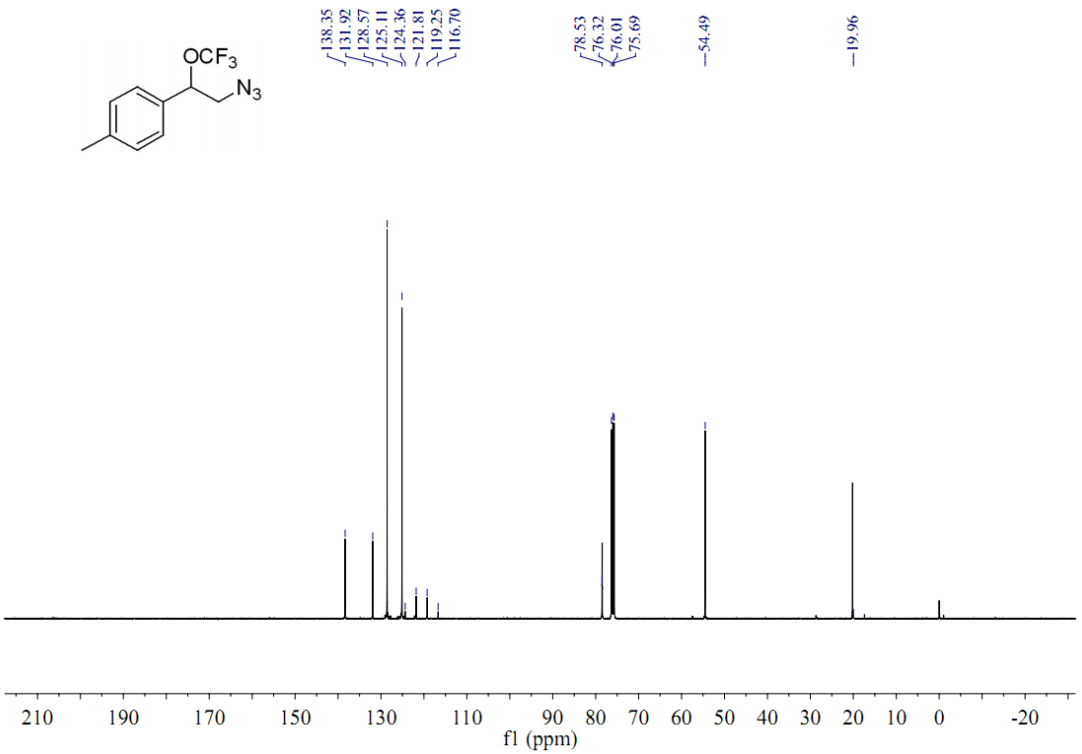
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4n**



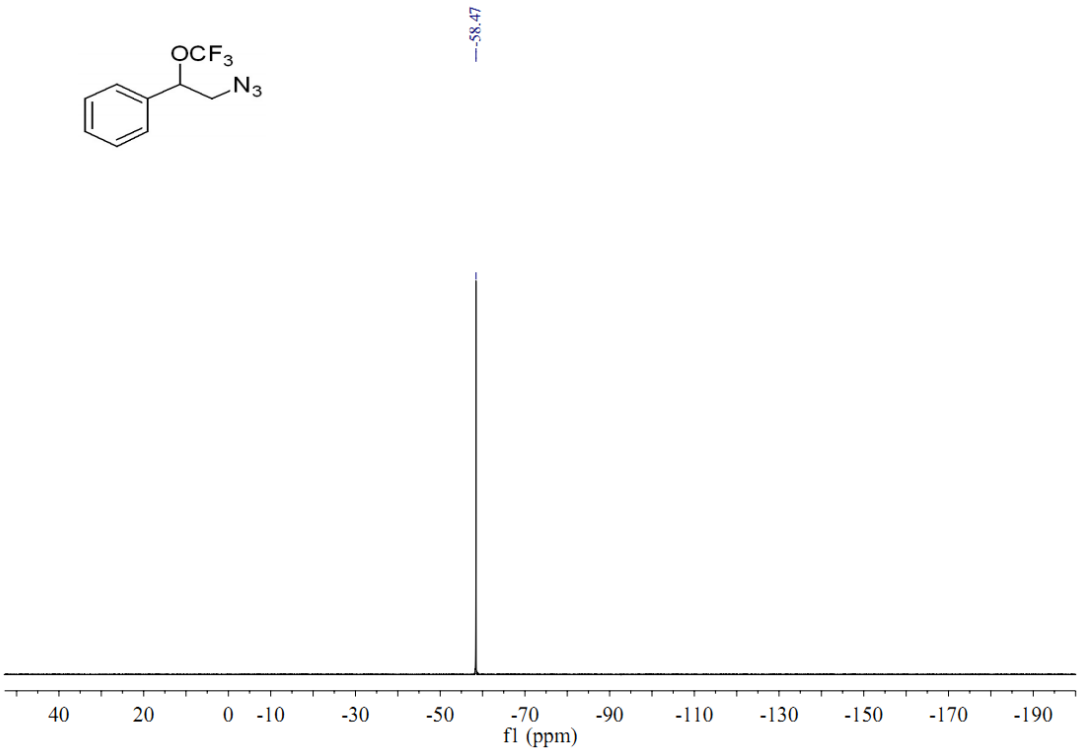
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4o**



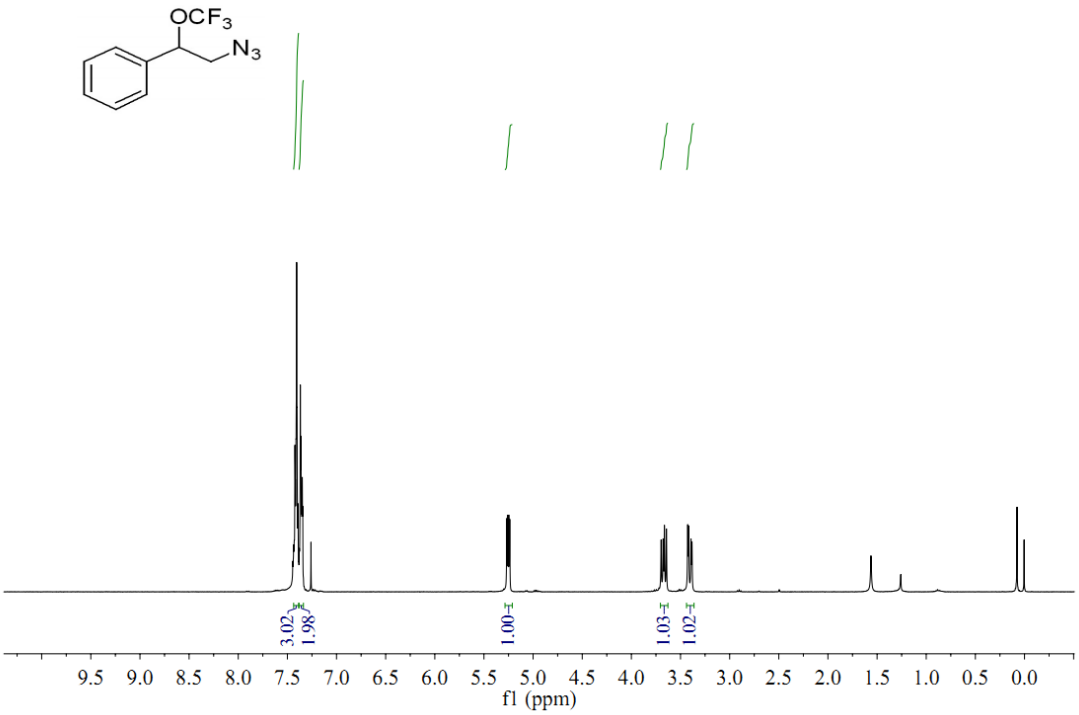
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4o**



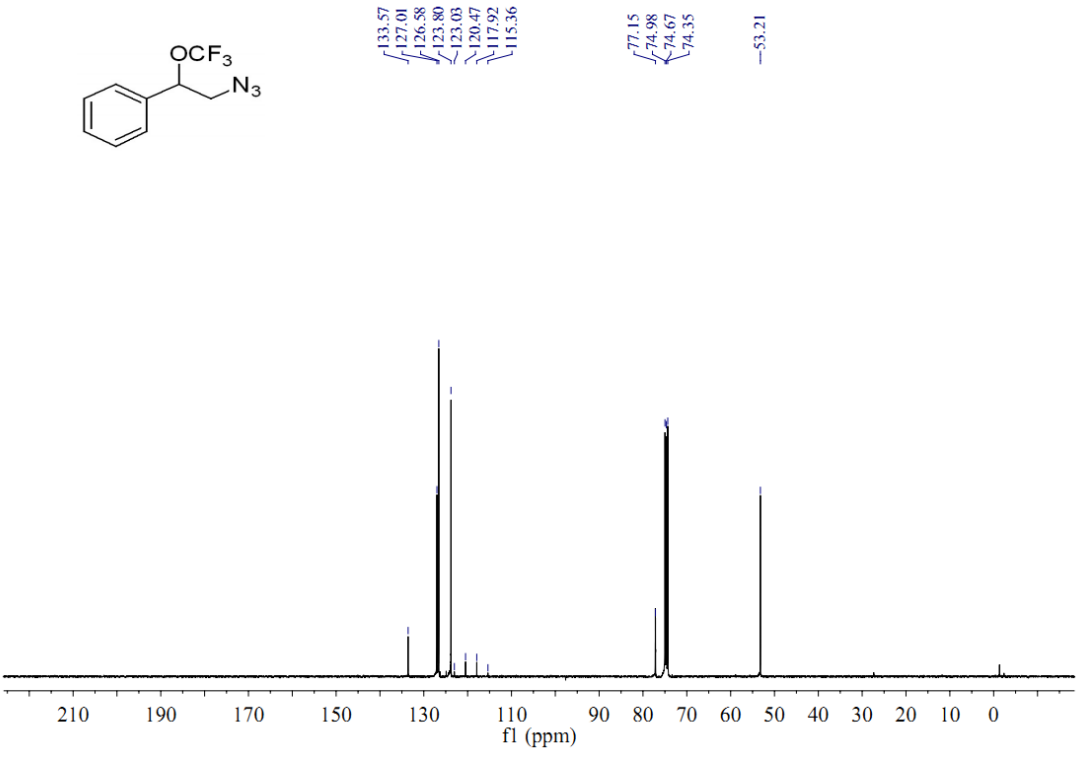
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4o**



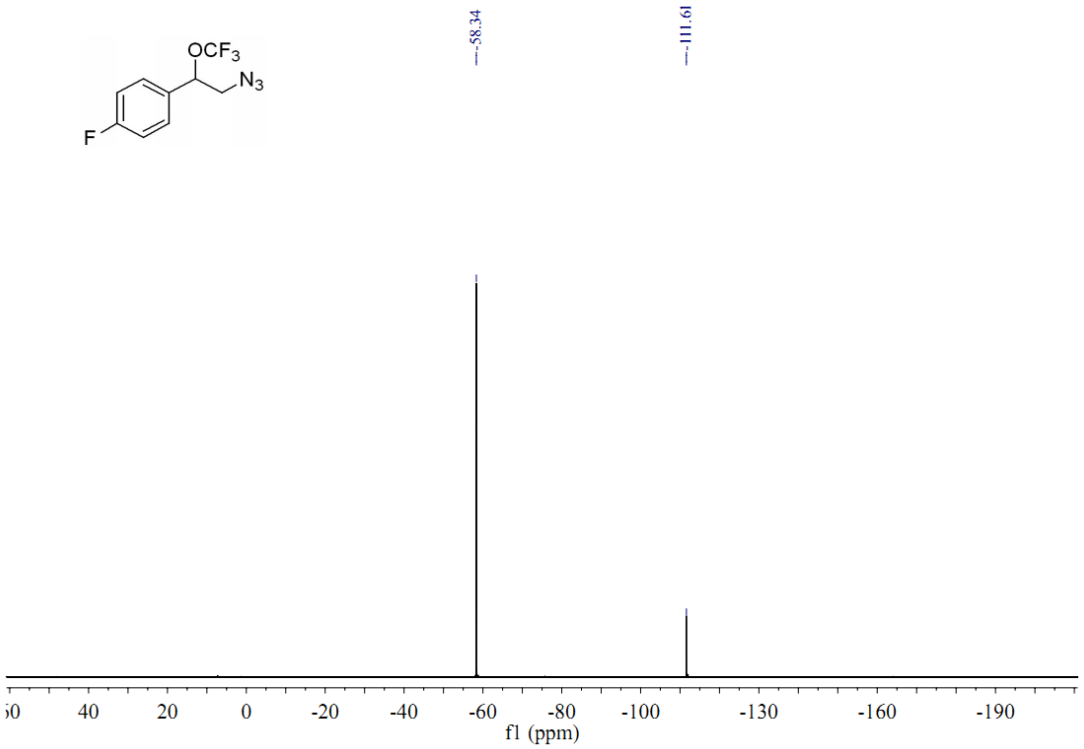
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4p**



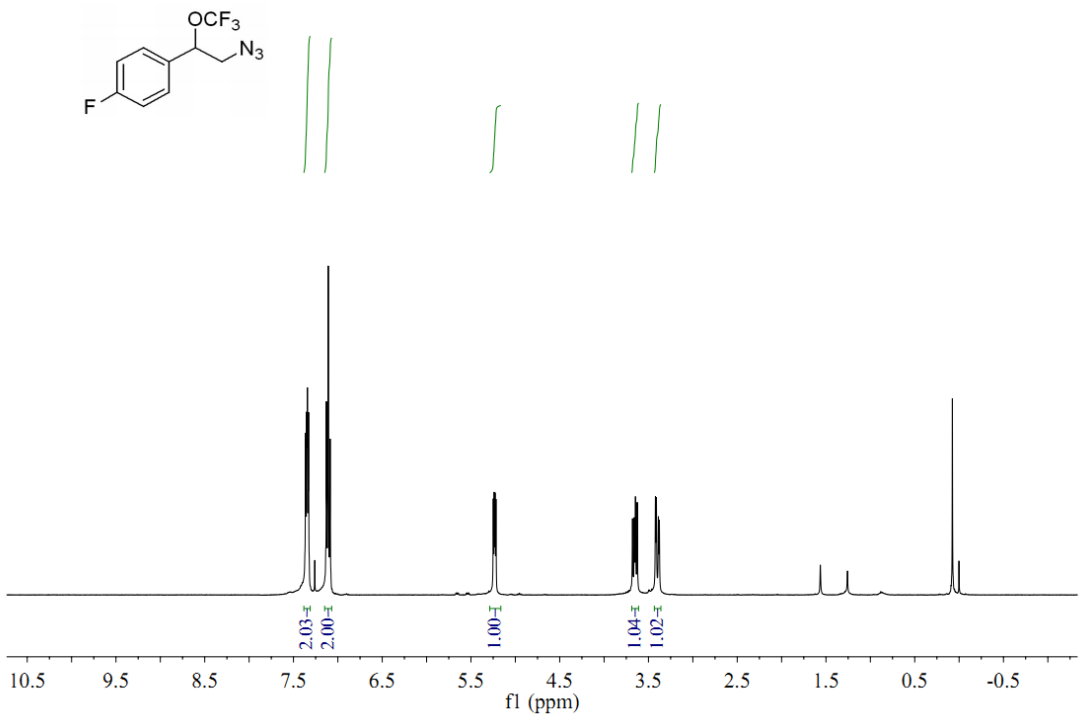
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4p**



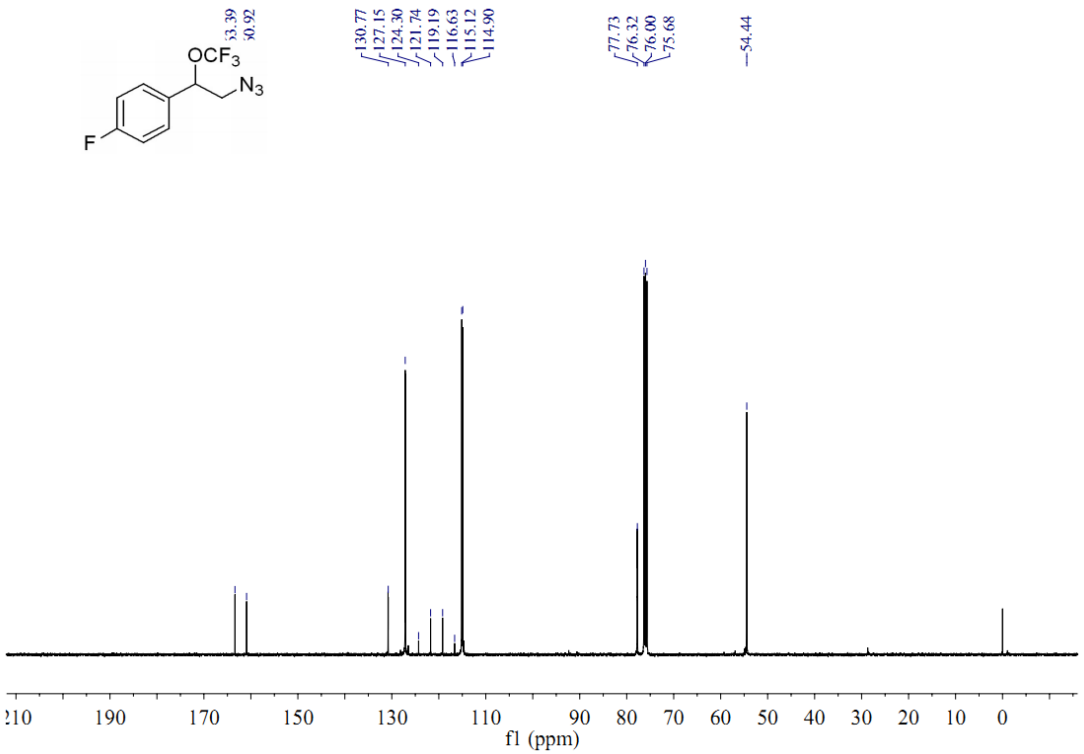
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4p**



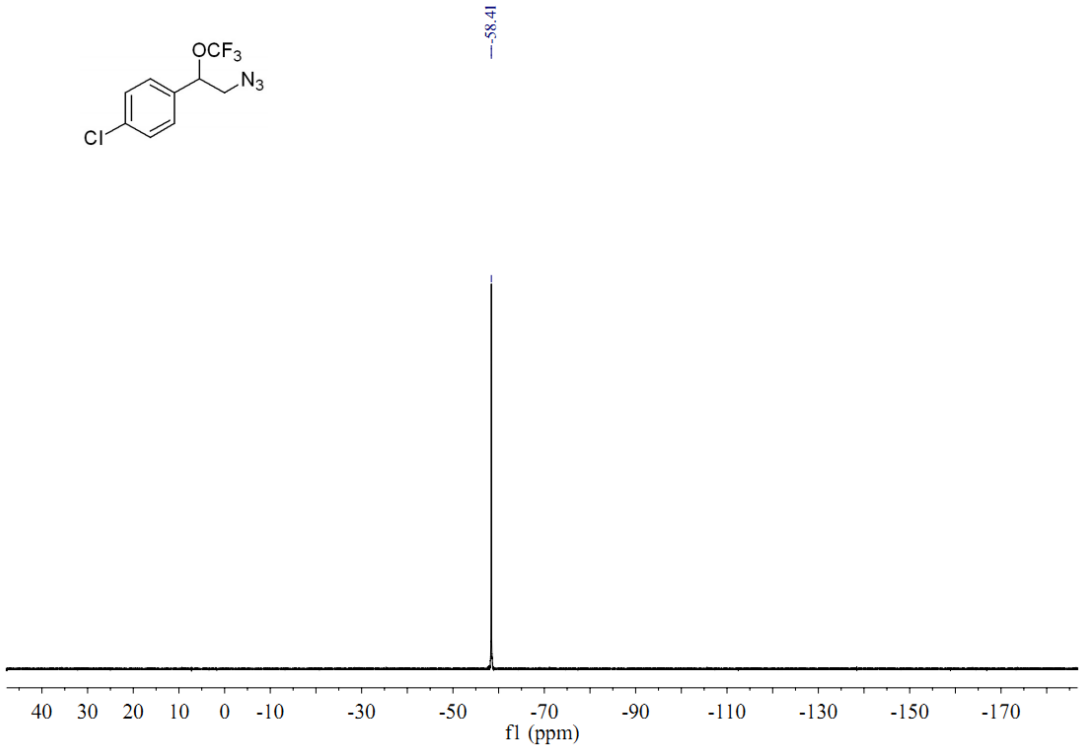
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4q**



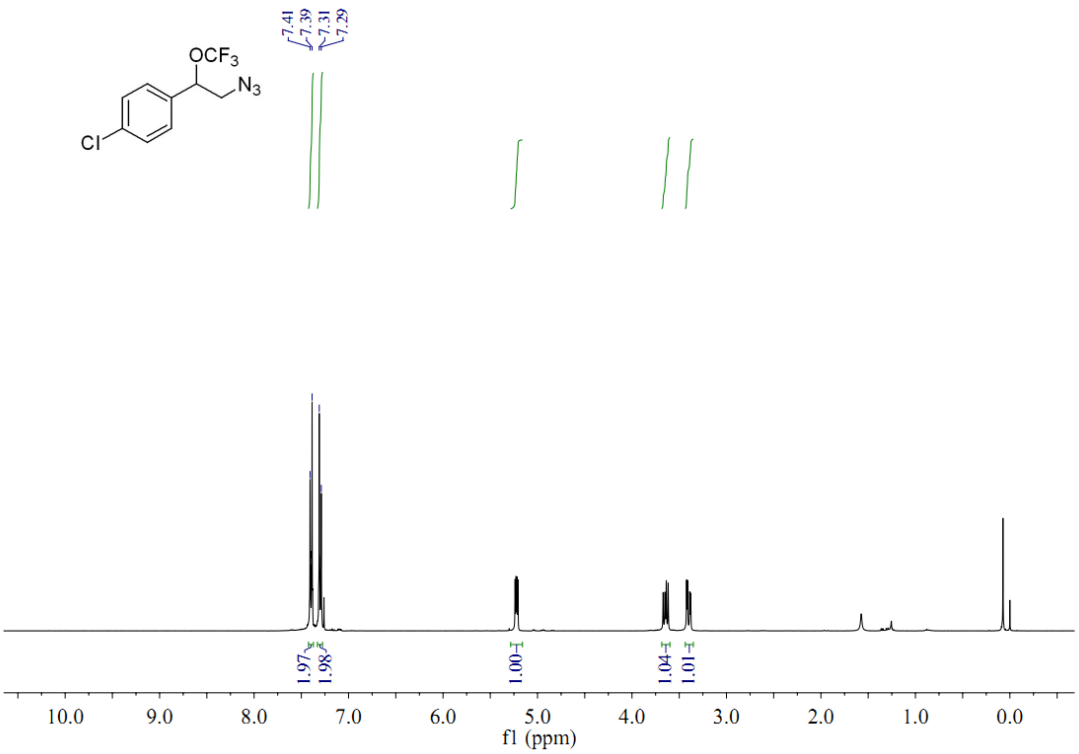
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4q**



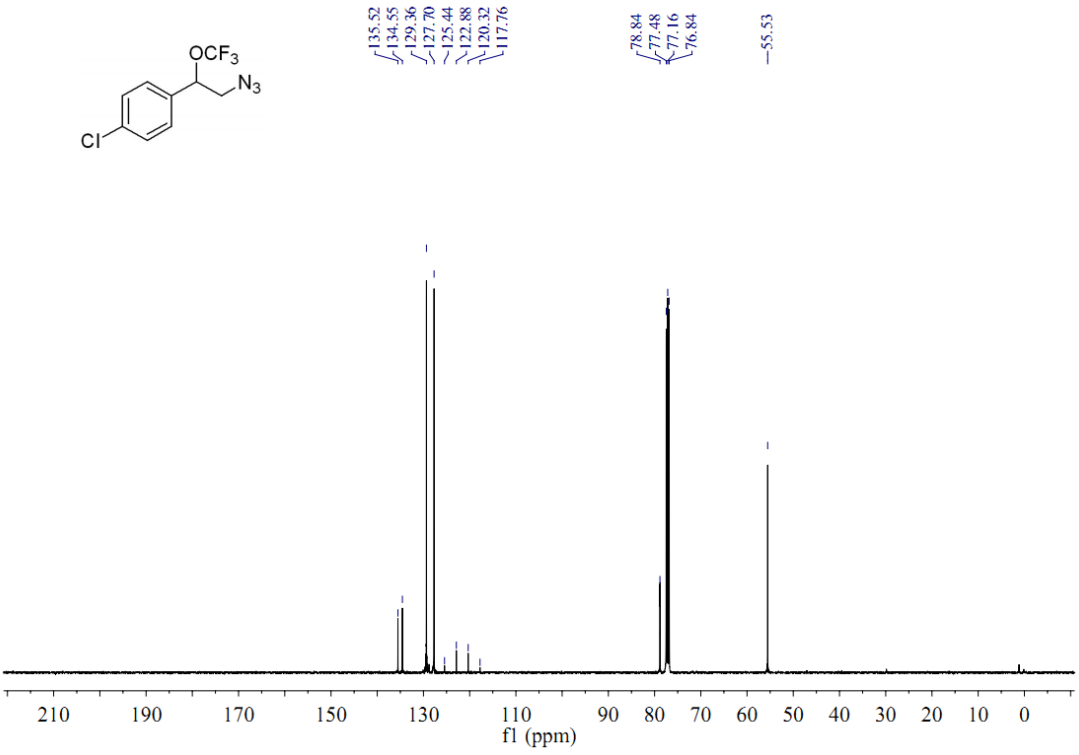
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4q**



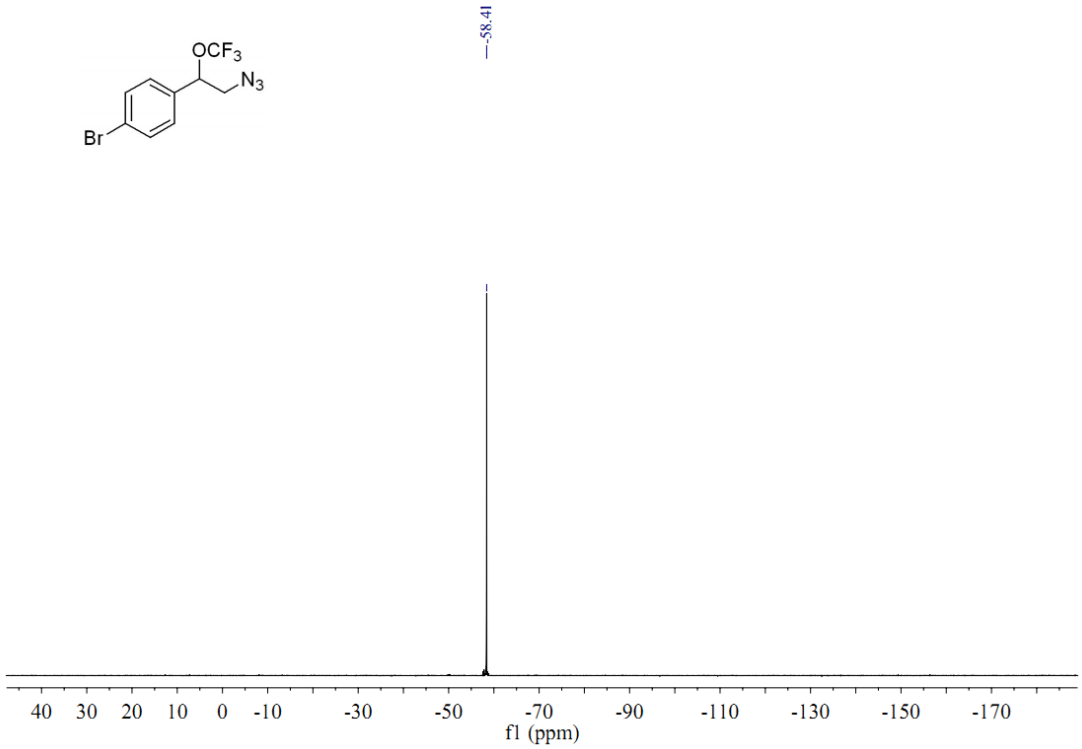
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4r**



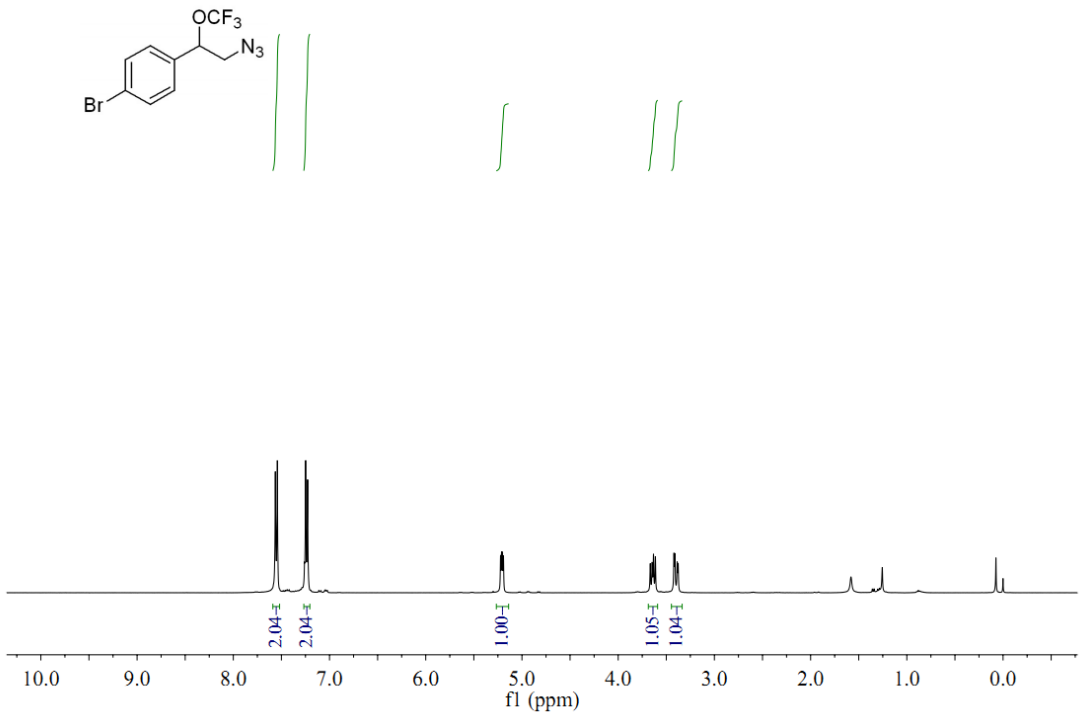
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4r**



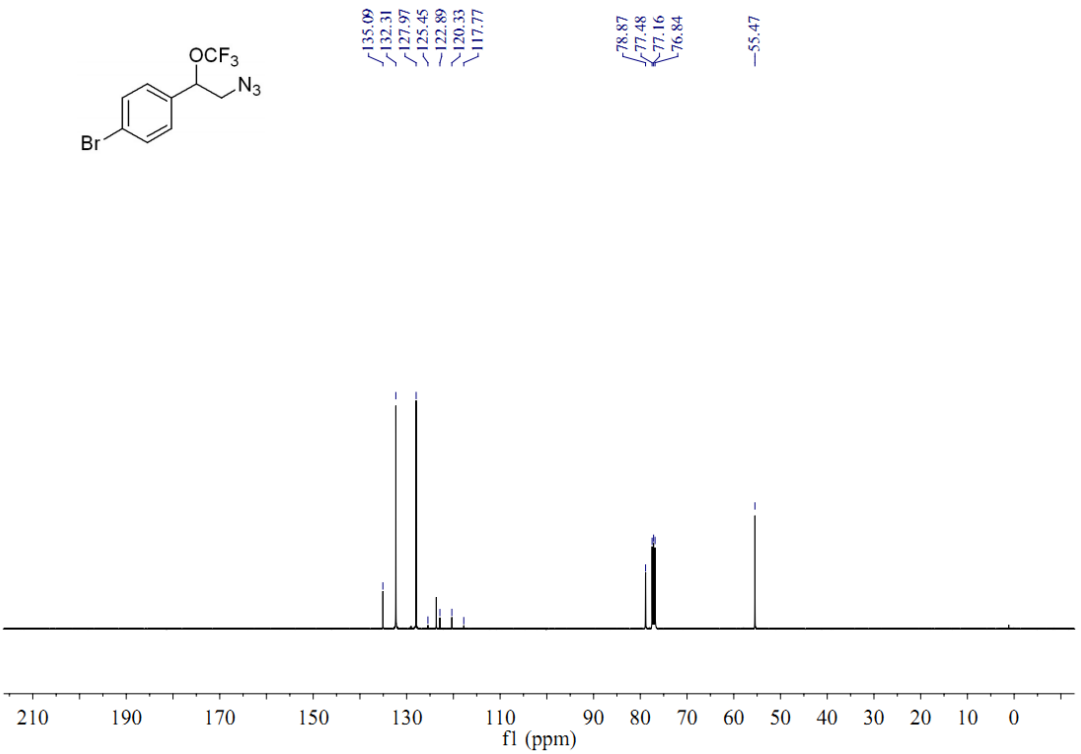
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4r**



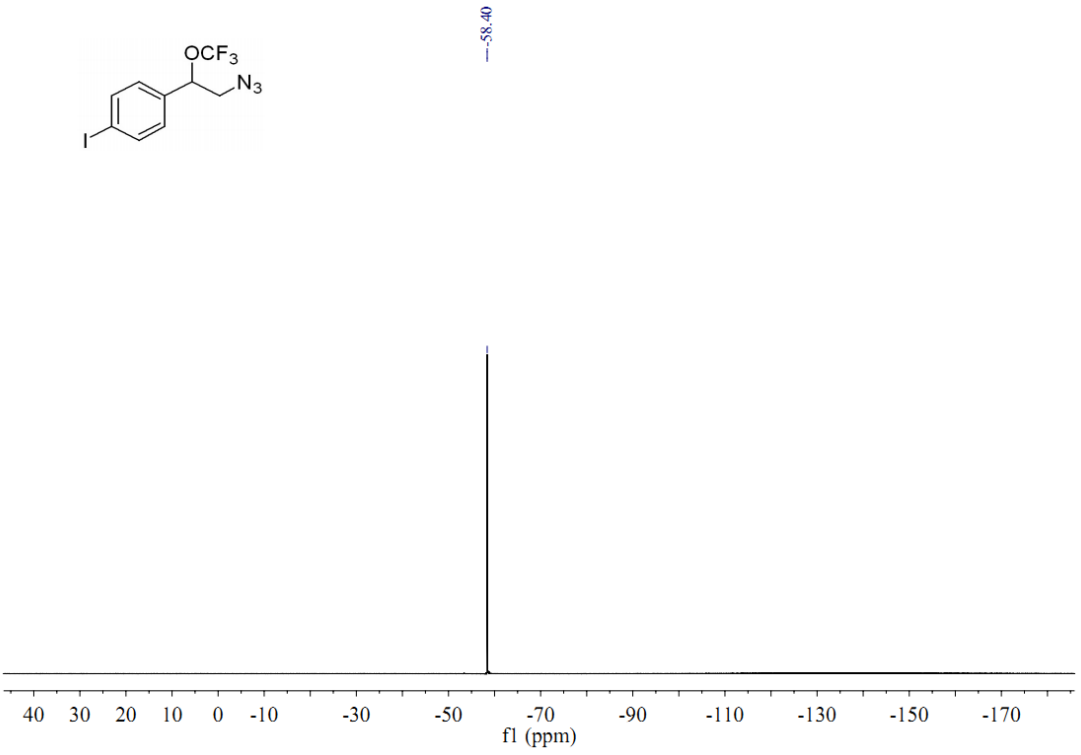
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4s**



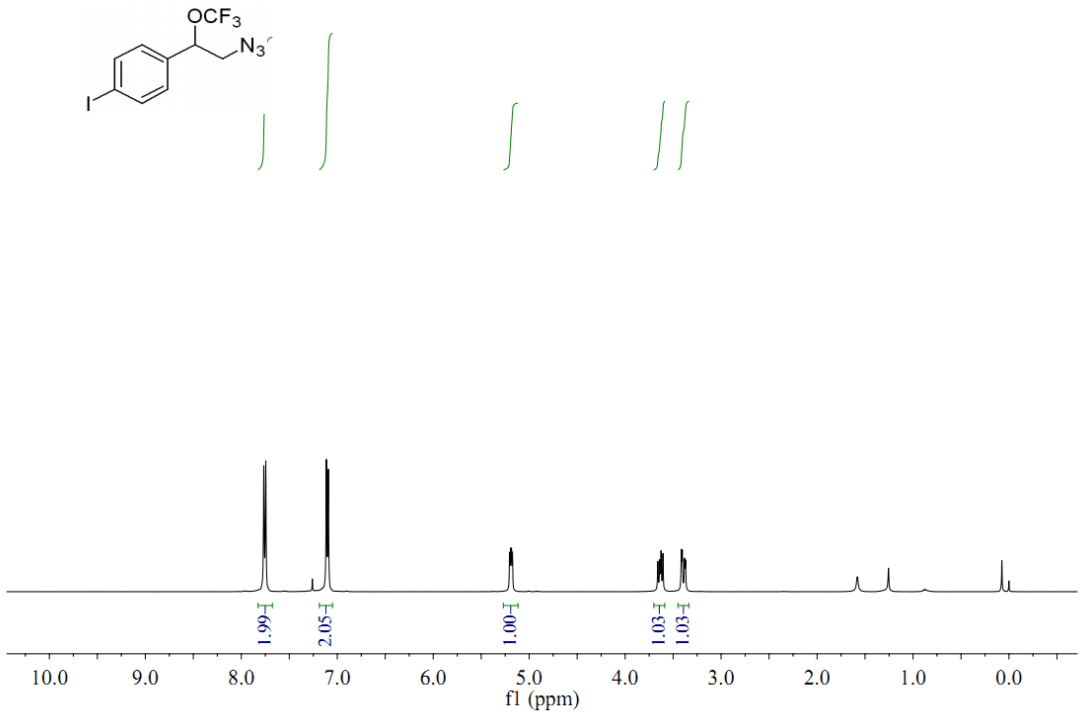
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4s**



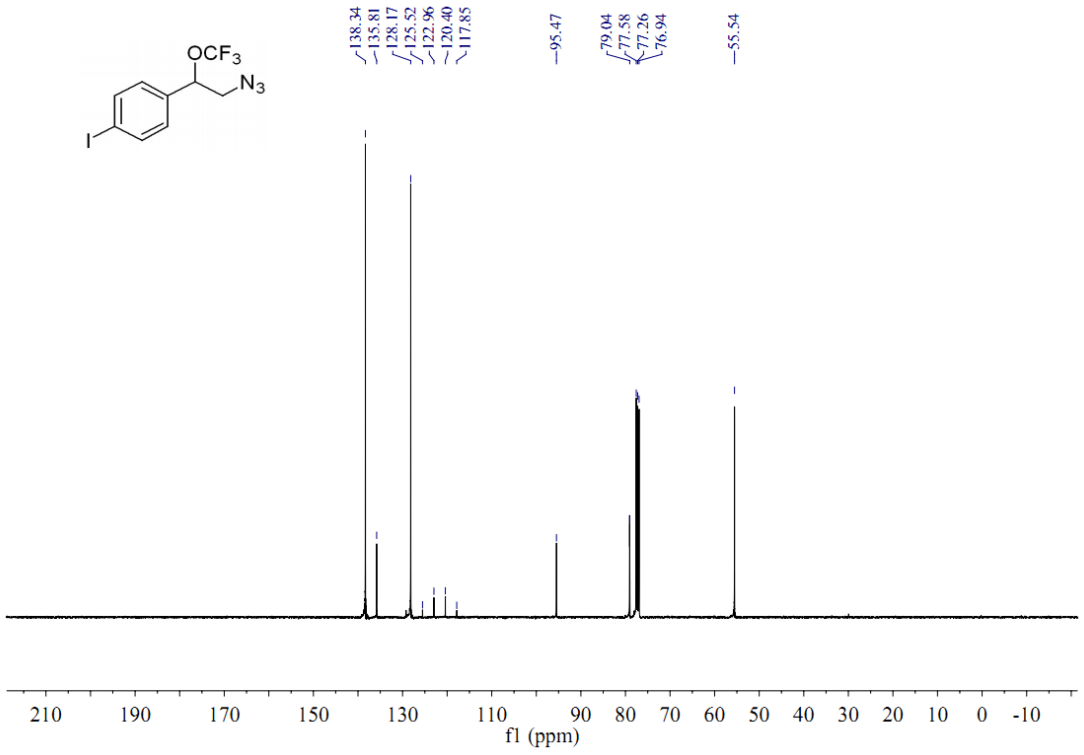
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4s**



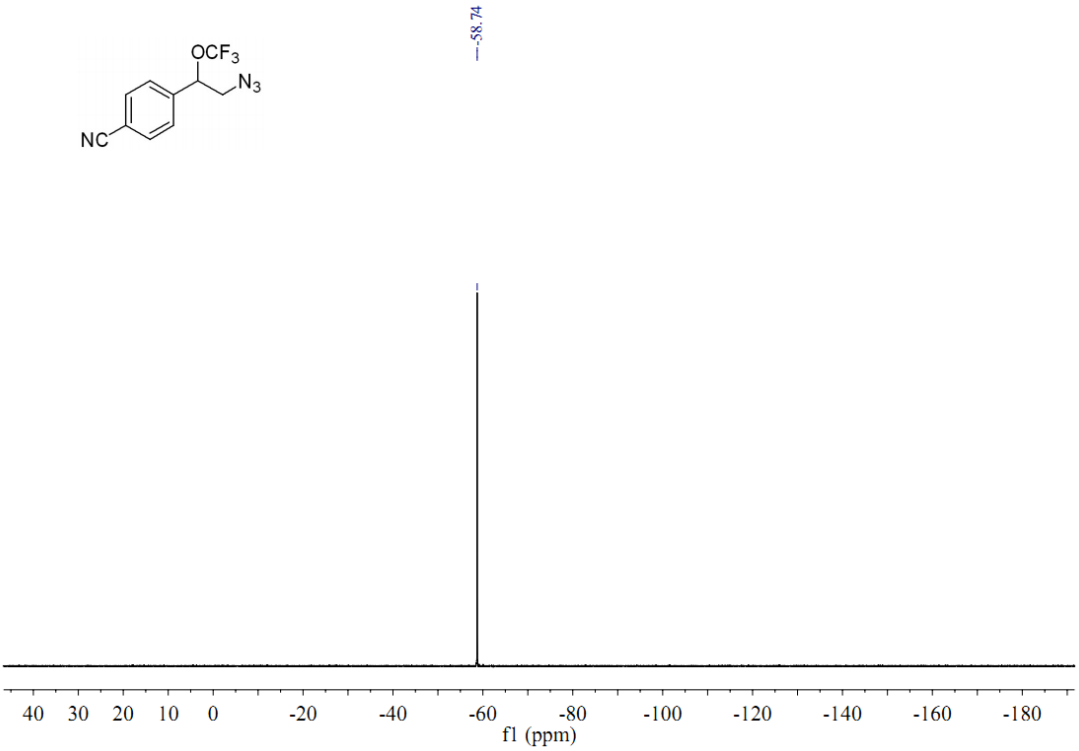
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4t**



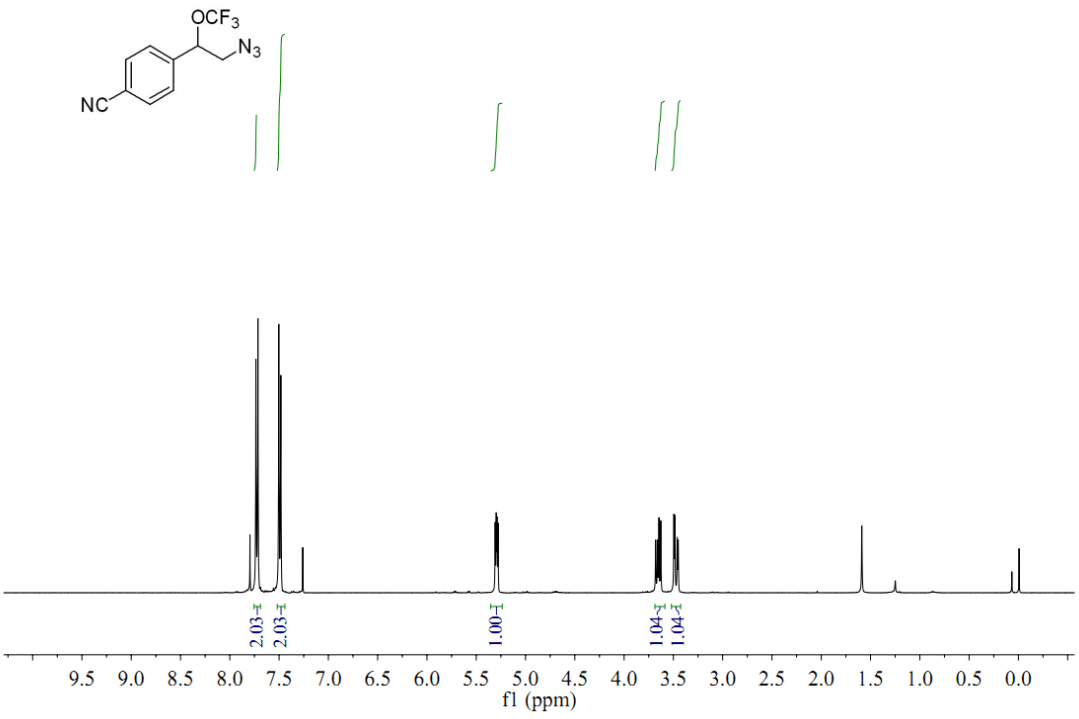
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) o**f 4t**



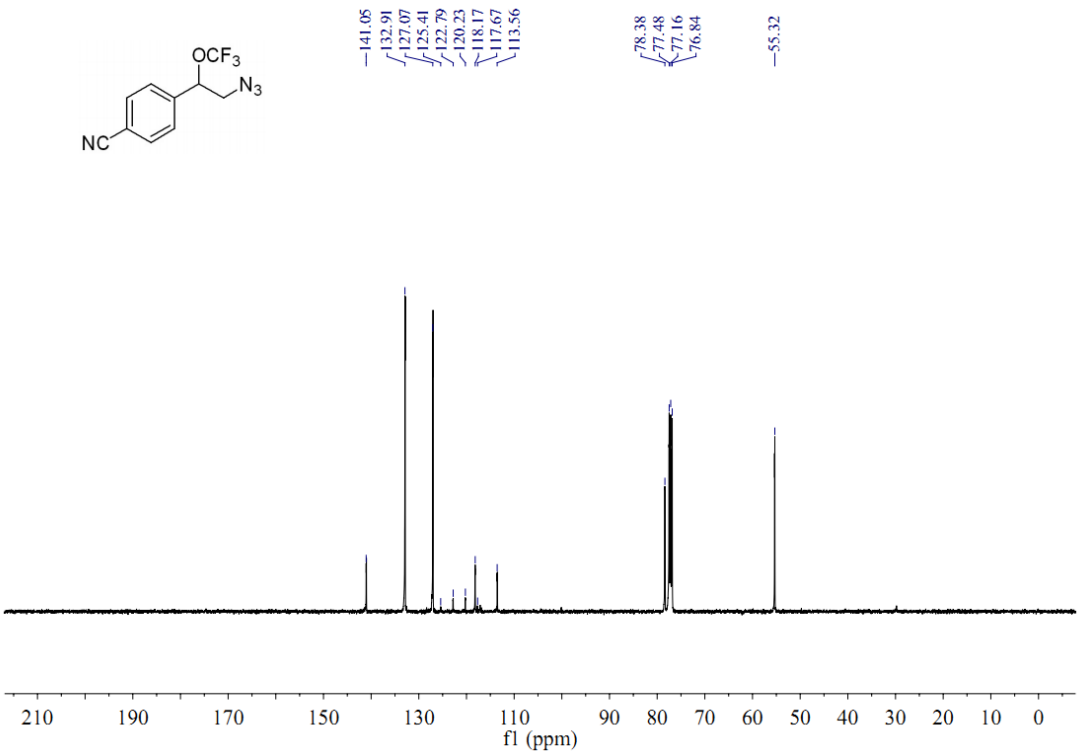
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4t**



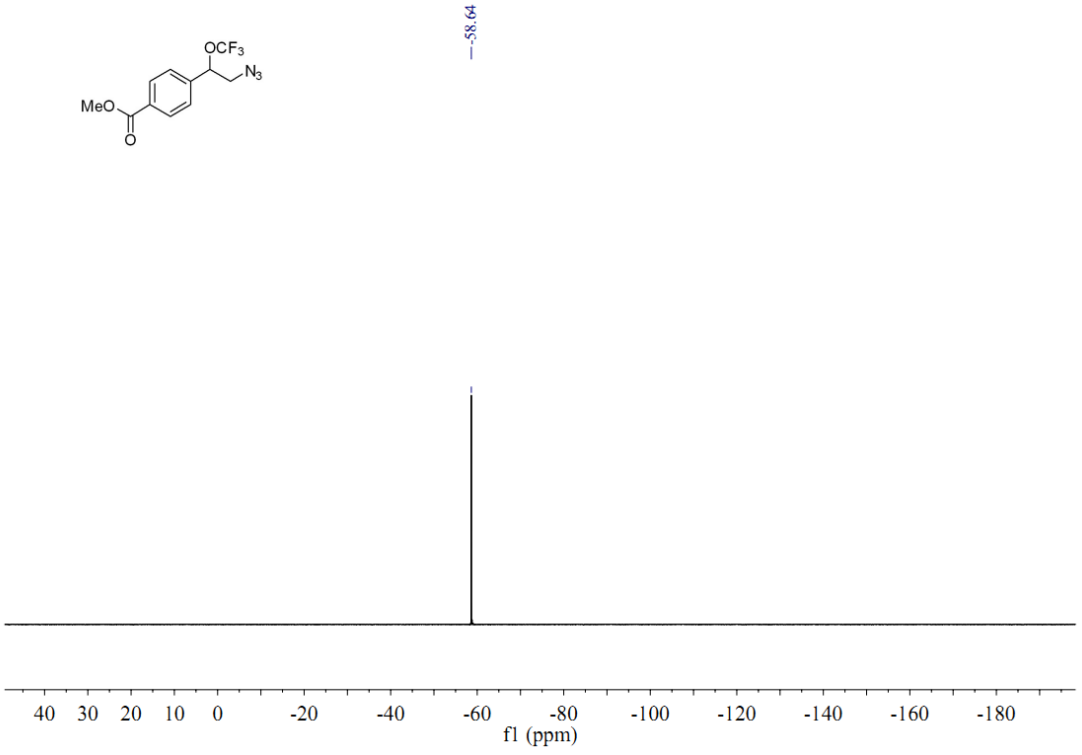
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4u**



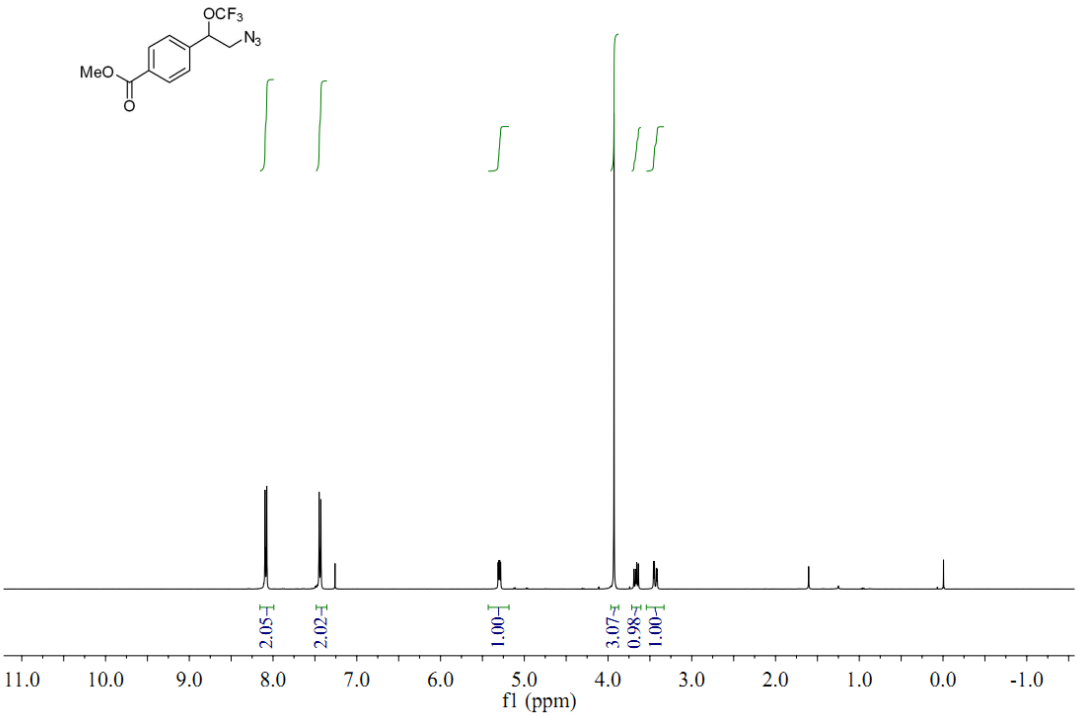
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4u**



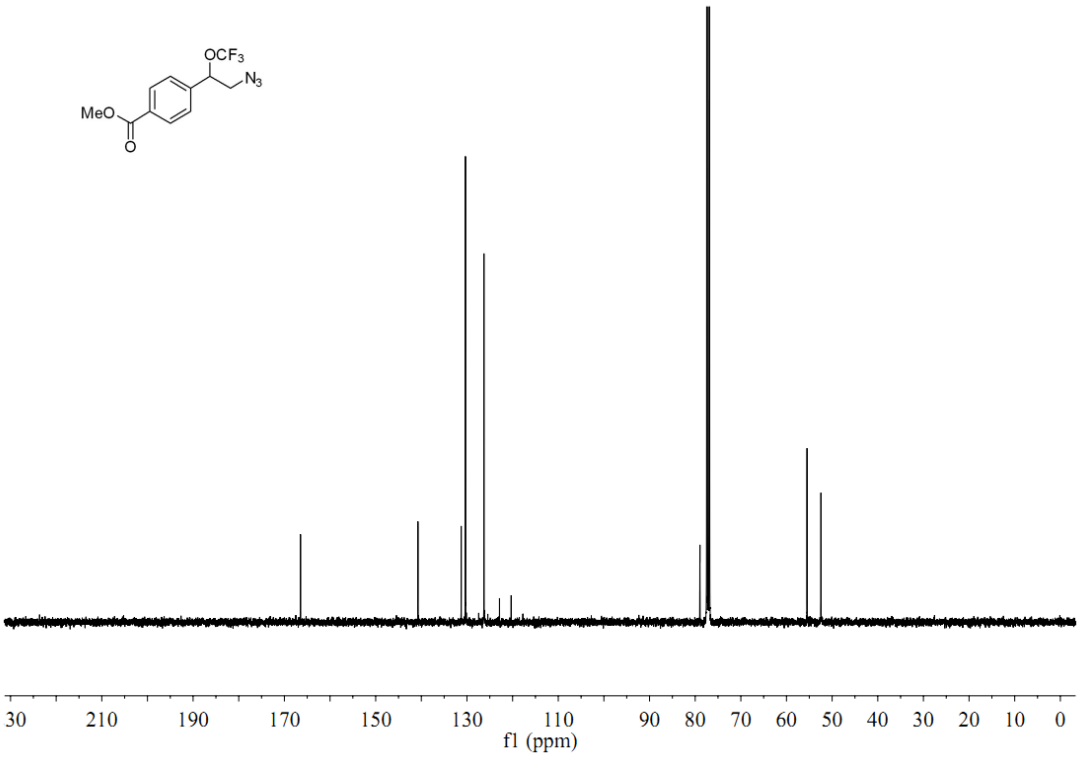
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4u**



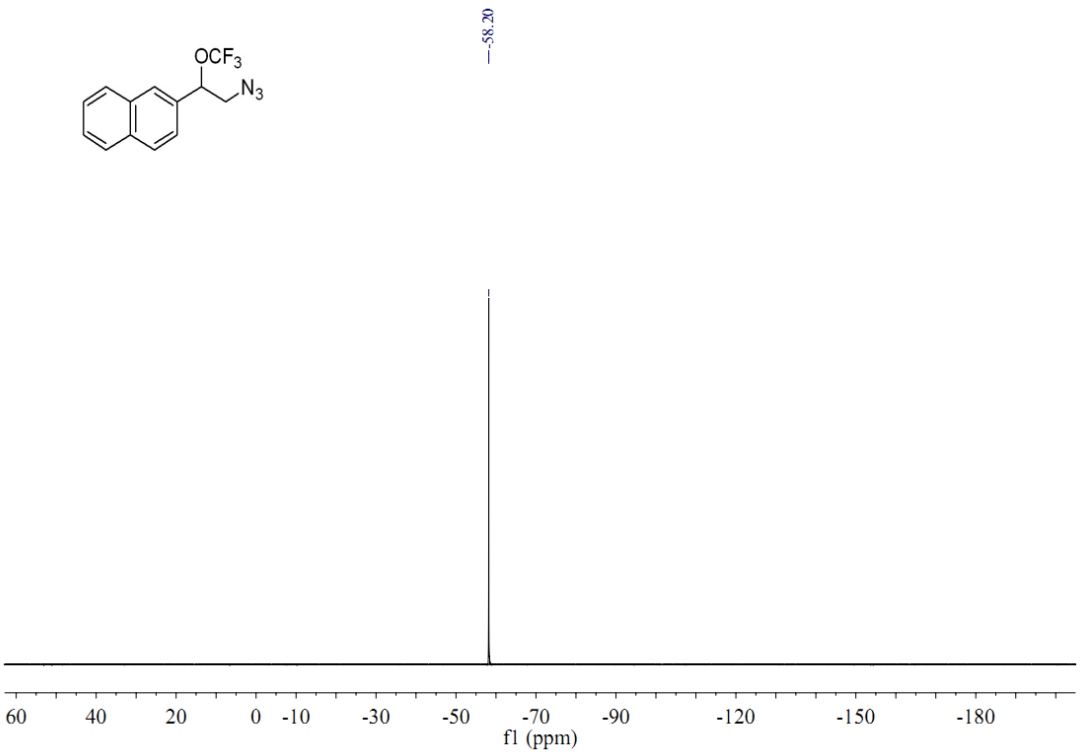
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4v**



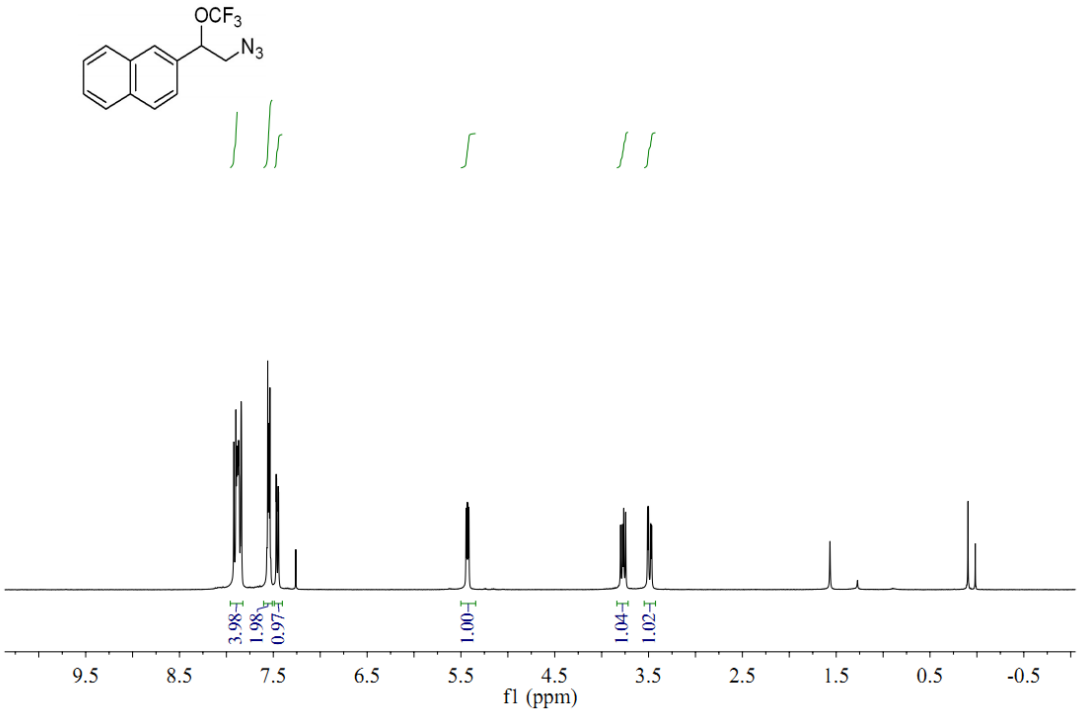
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4v**



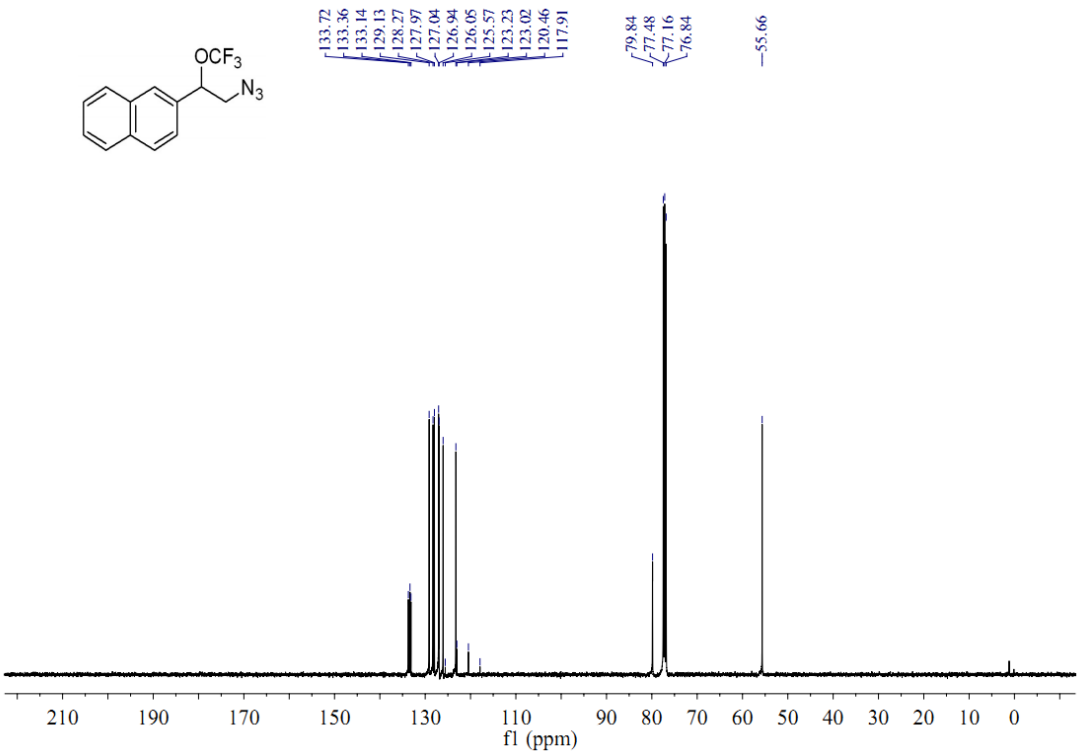
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4v**



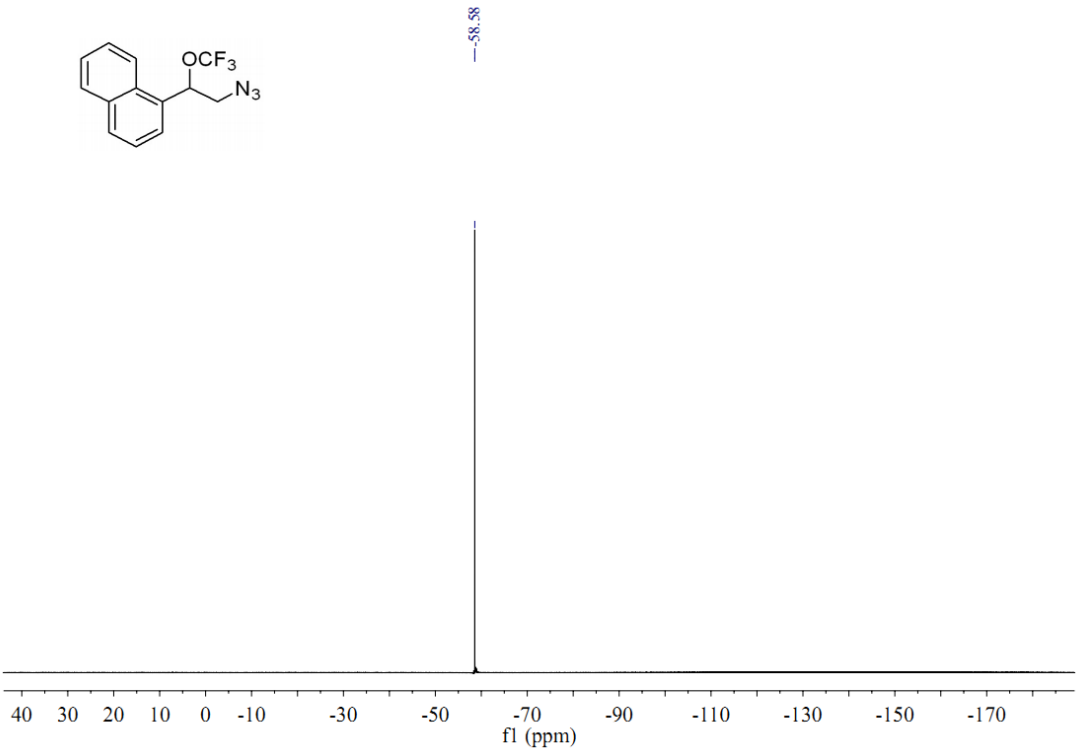
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4w**



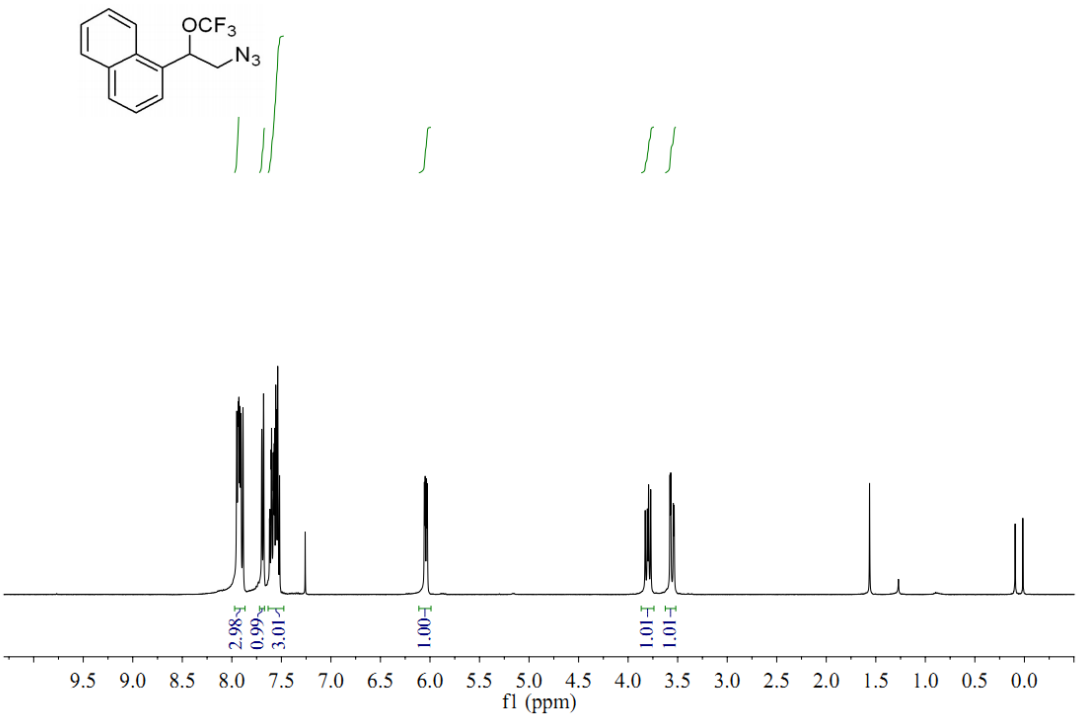
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) o**f 4w**



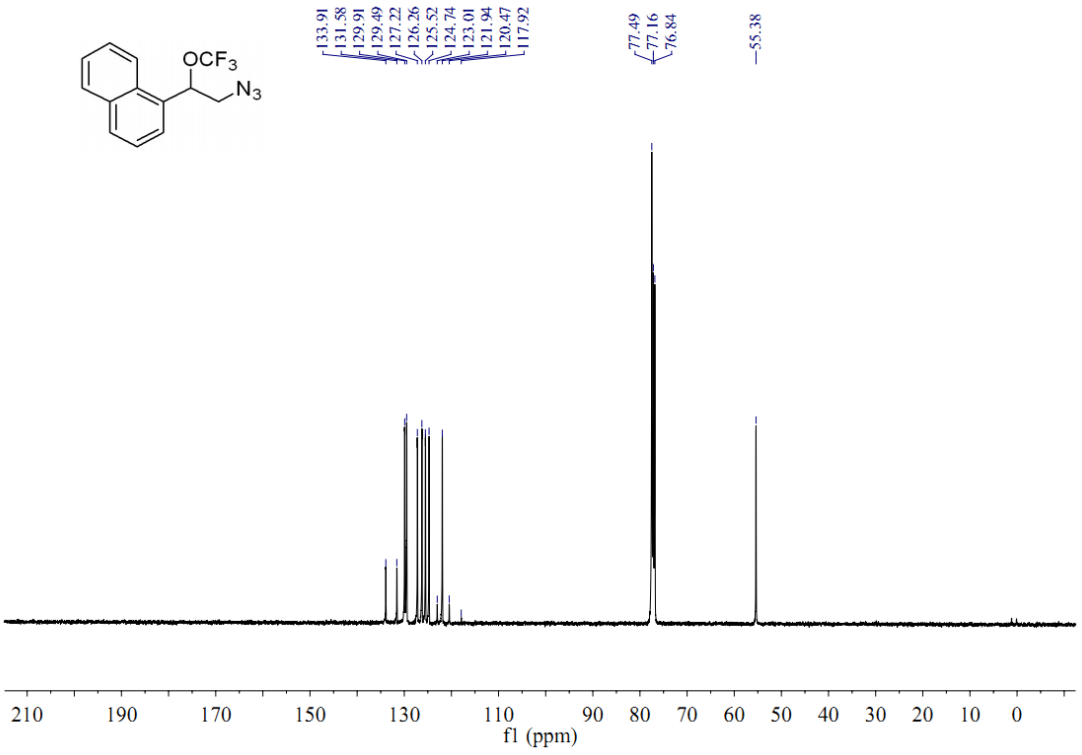
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4w**



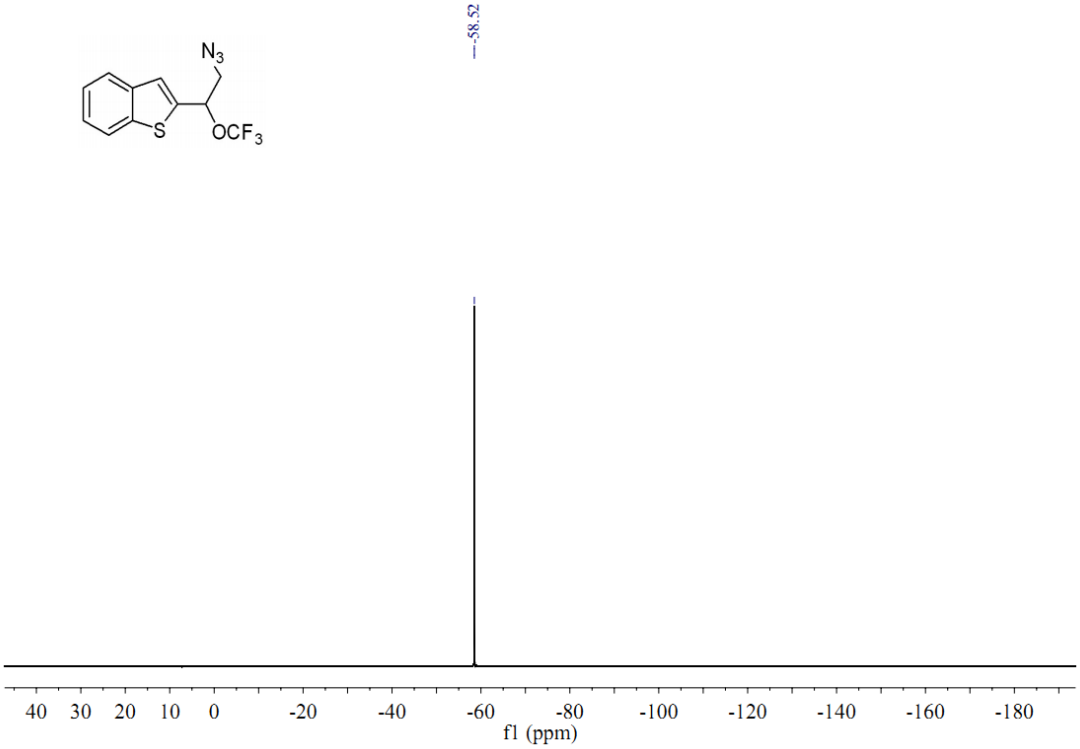
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4x**



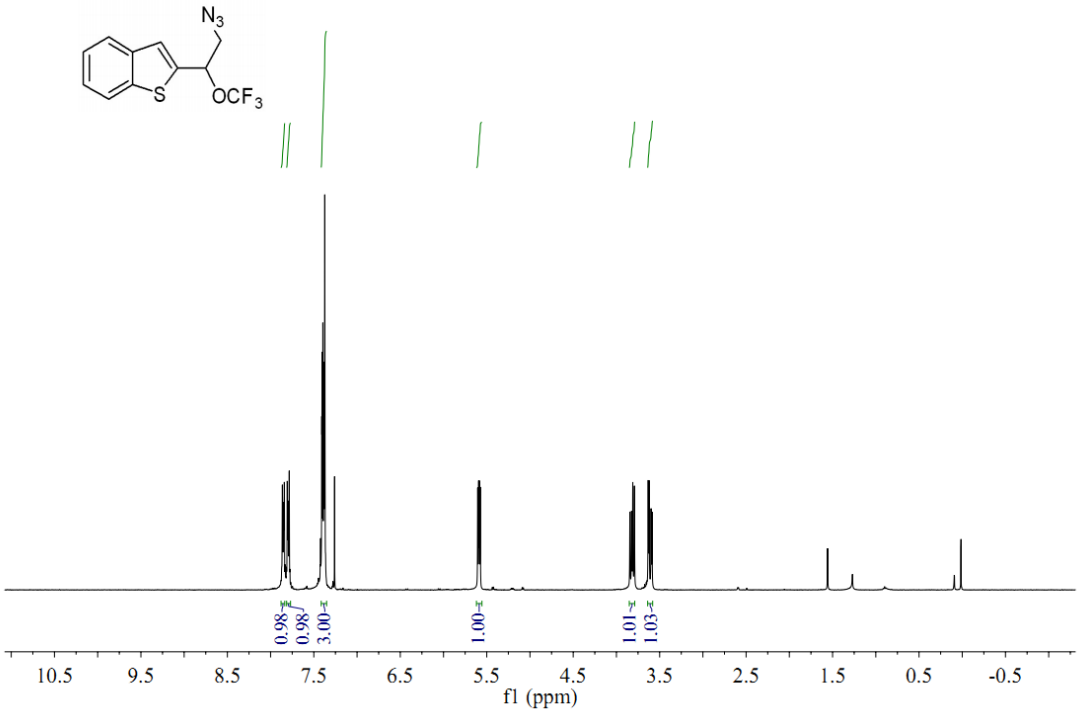
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4x**



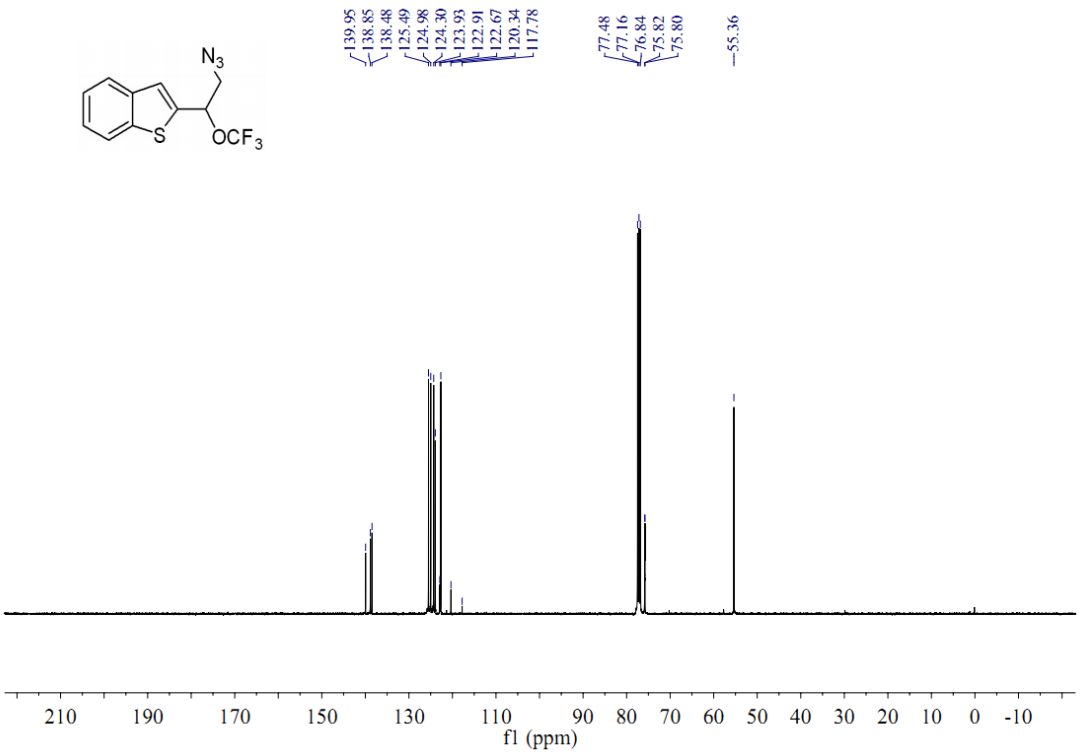
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4x**



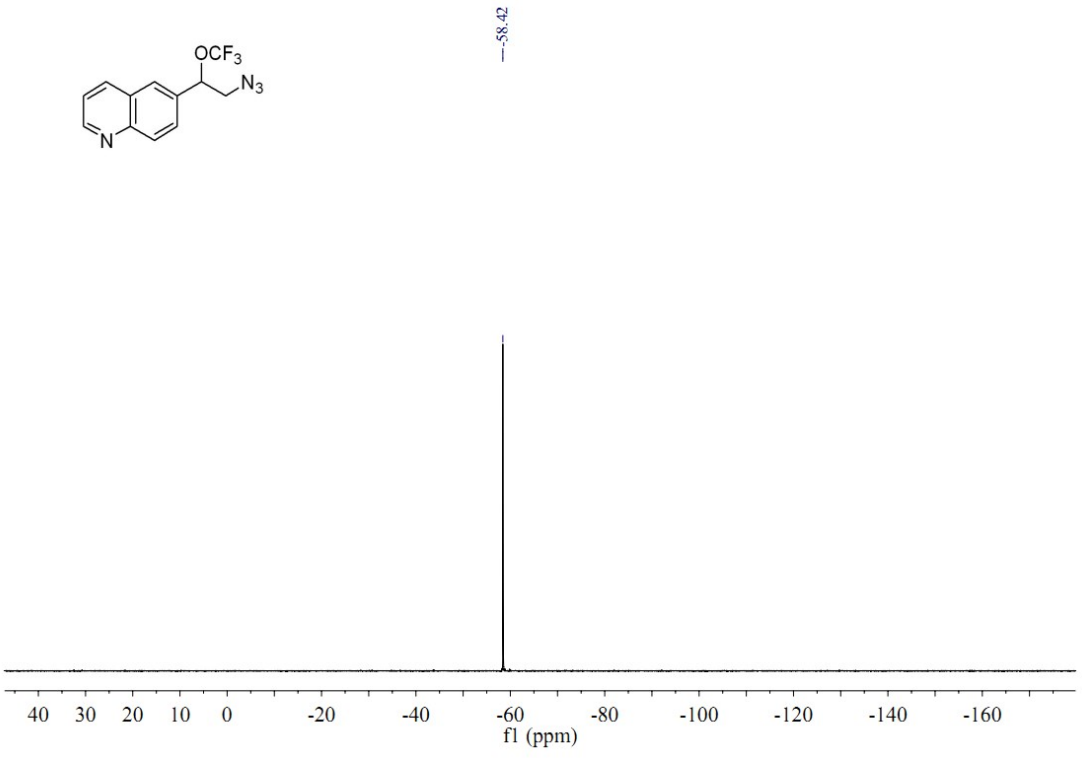
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4y**



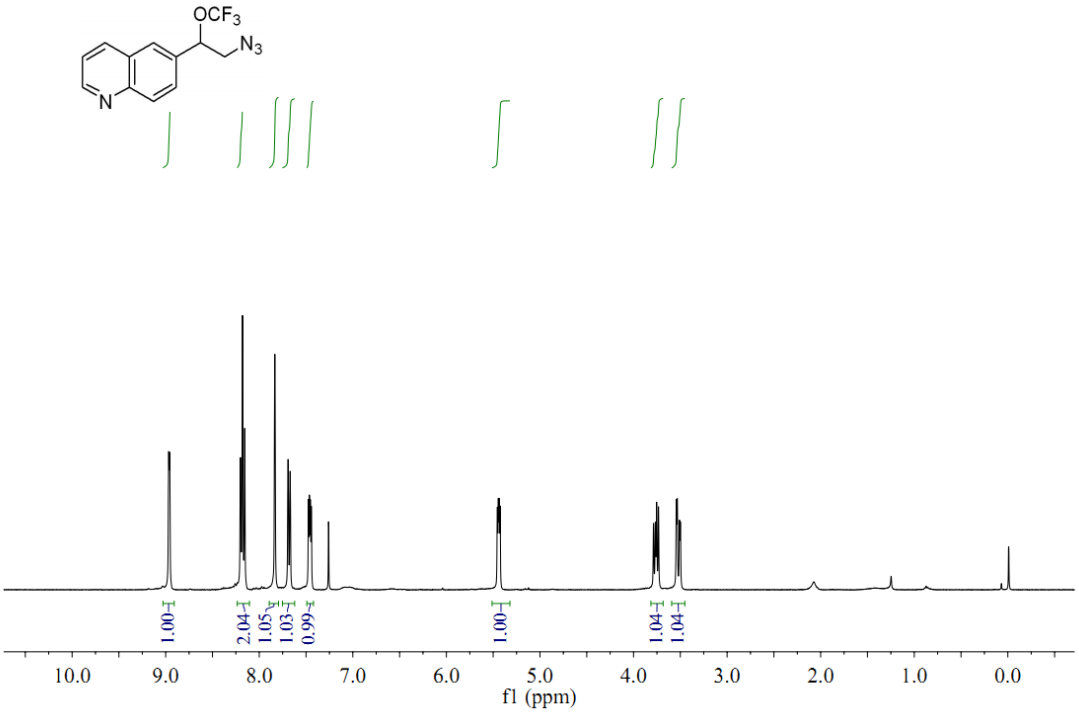
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4y**



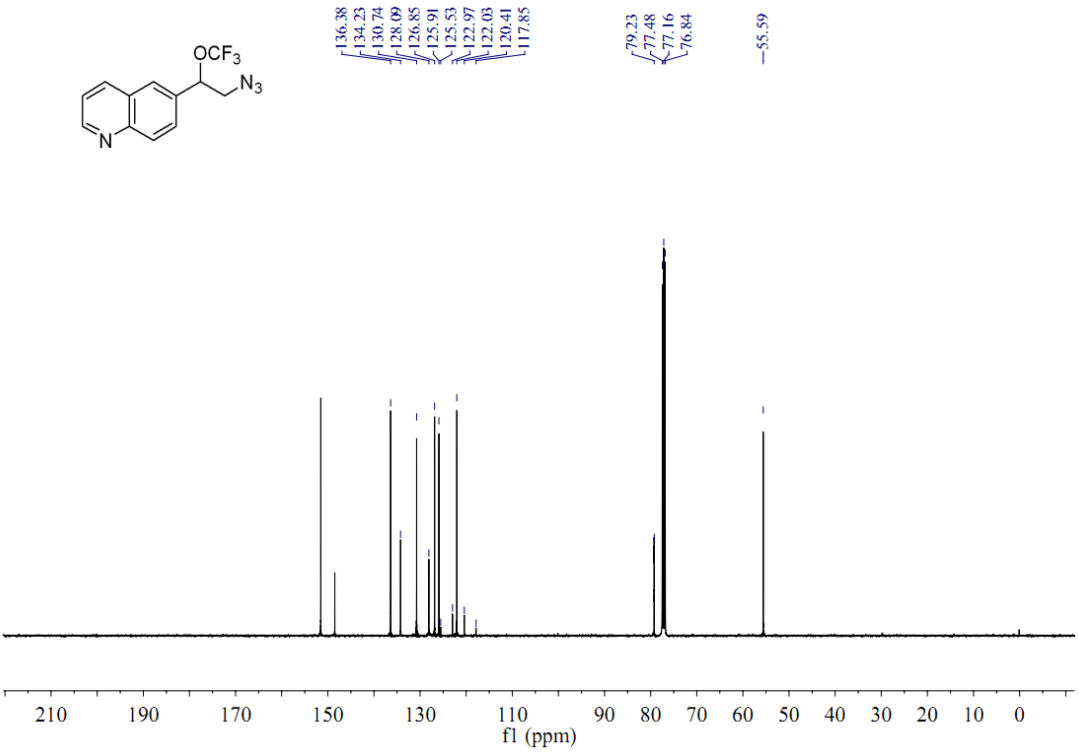
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4y**



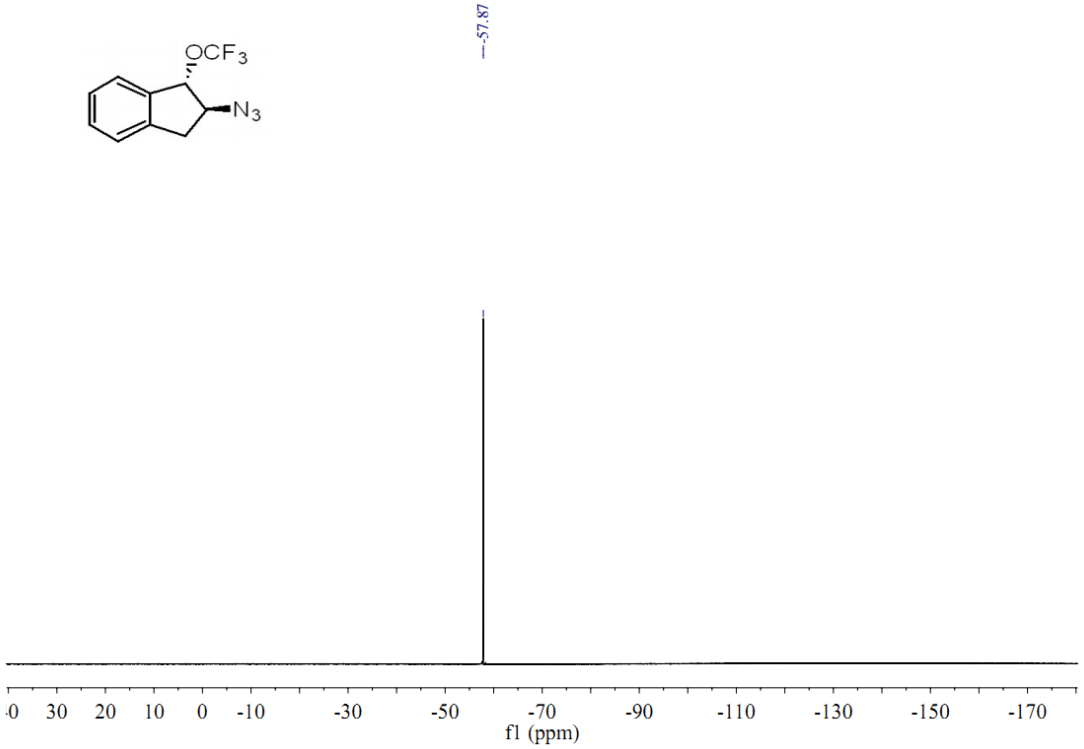
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4z**



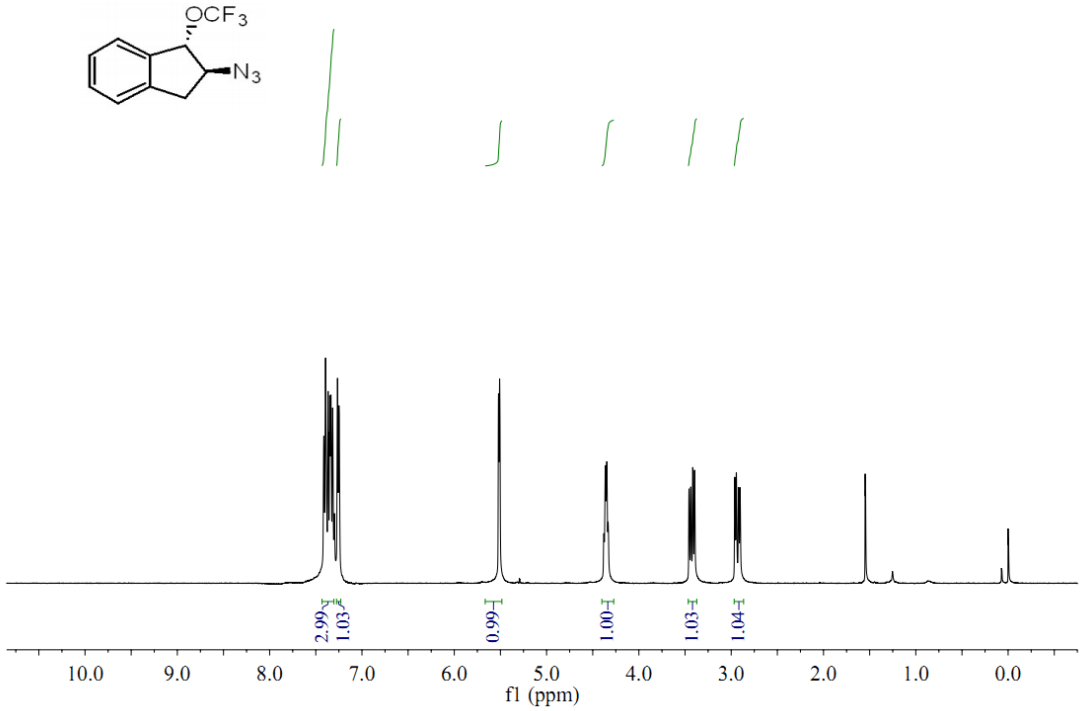
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4z**



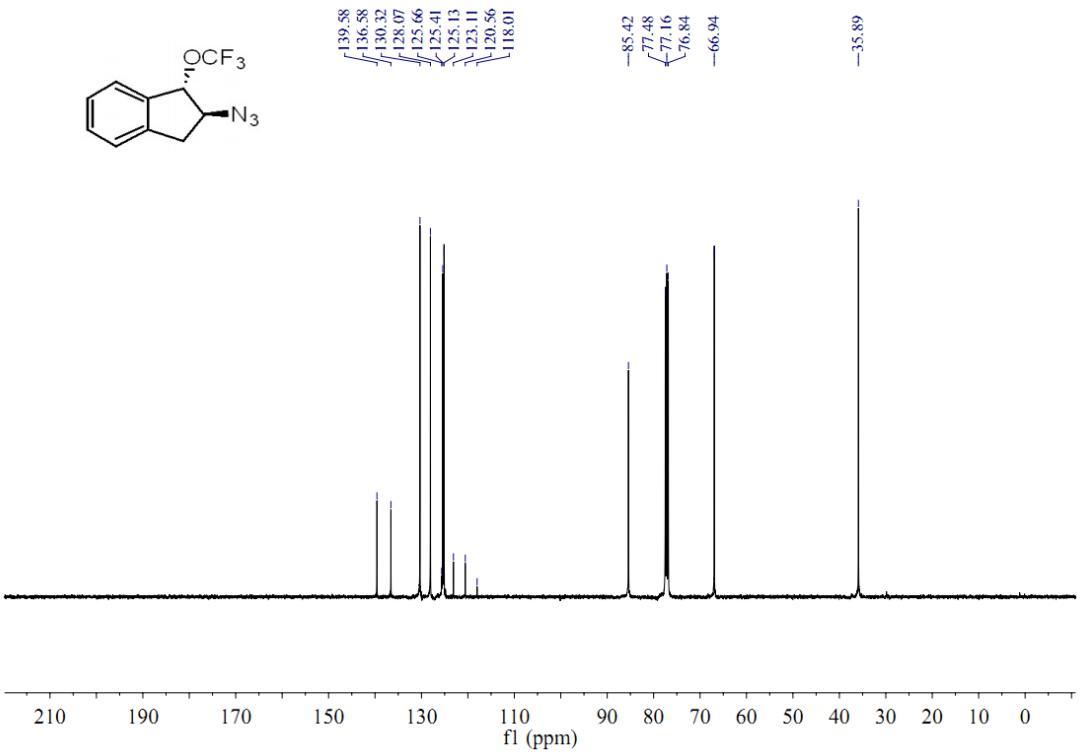
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4z**



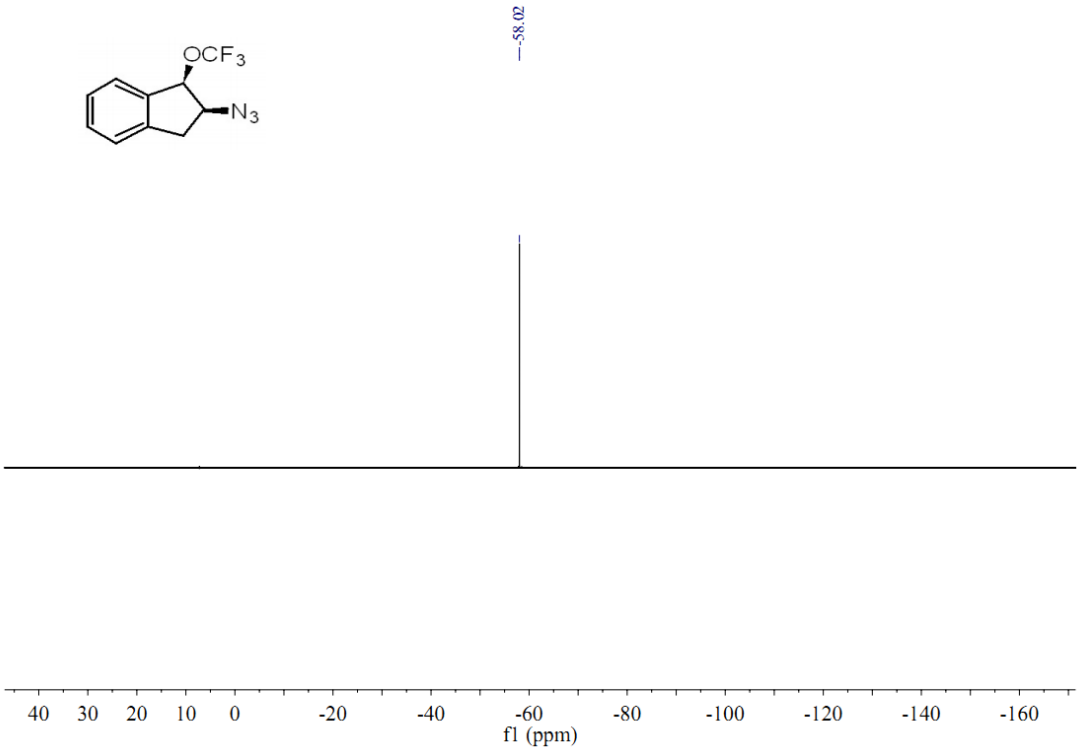
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of ***trans*-4aa**



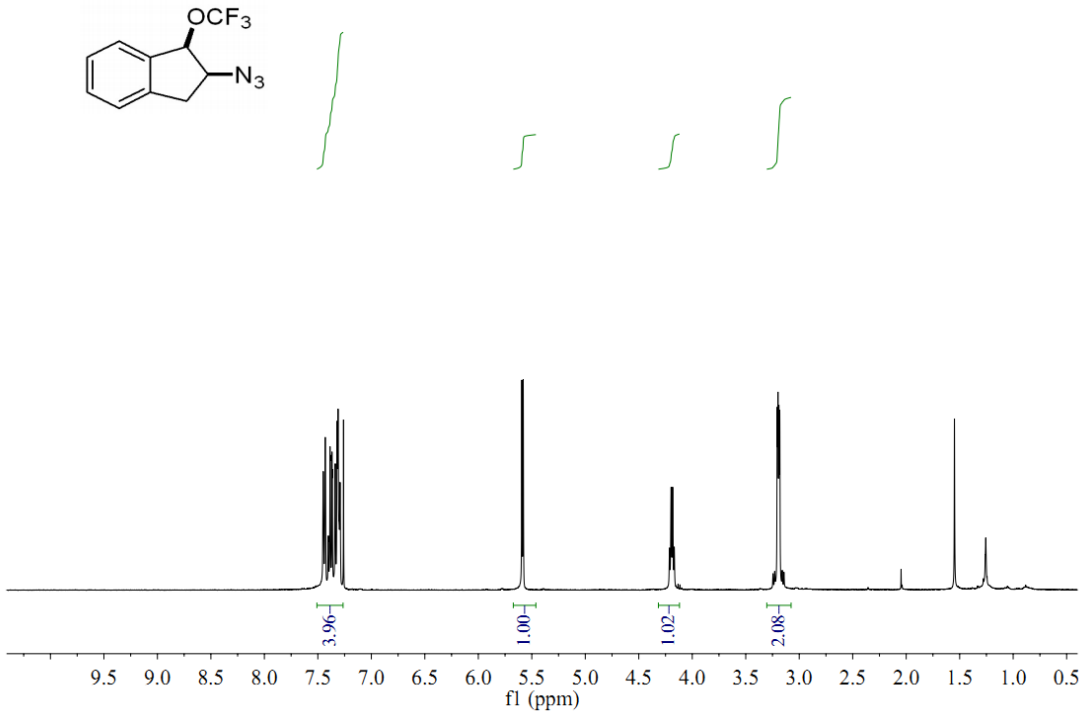
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of ***trans*-4aa**



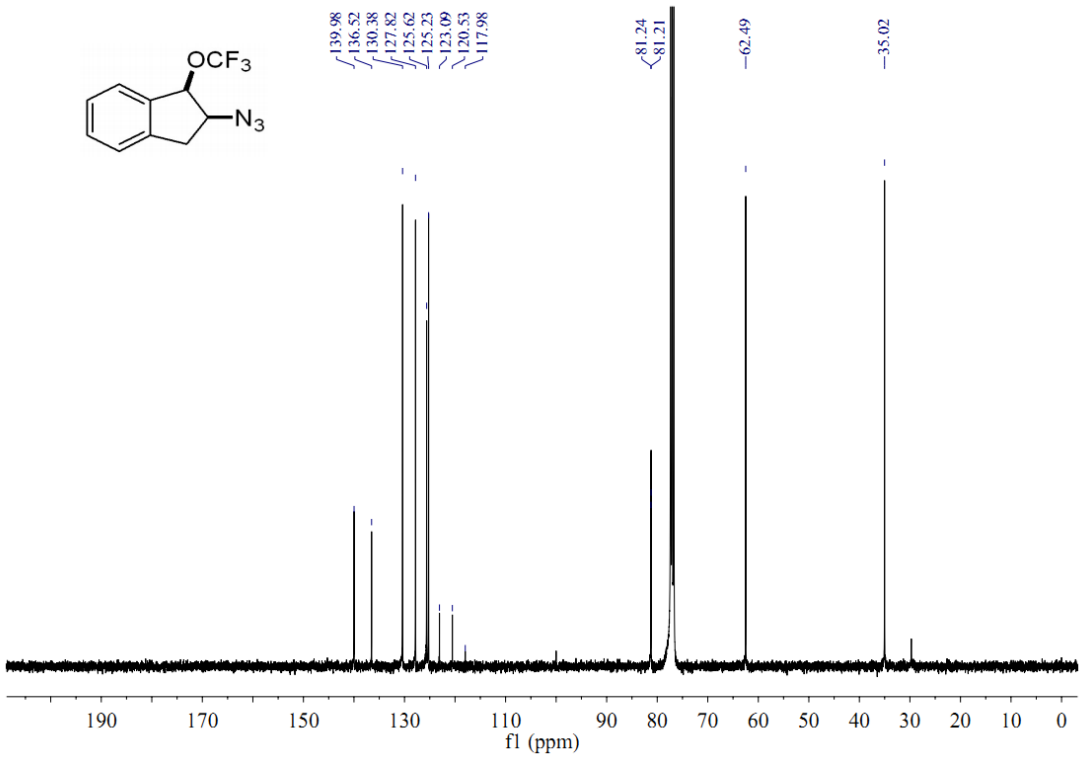
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of ***trans*-4aa**



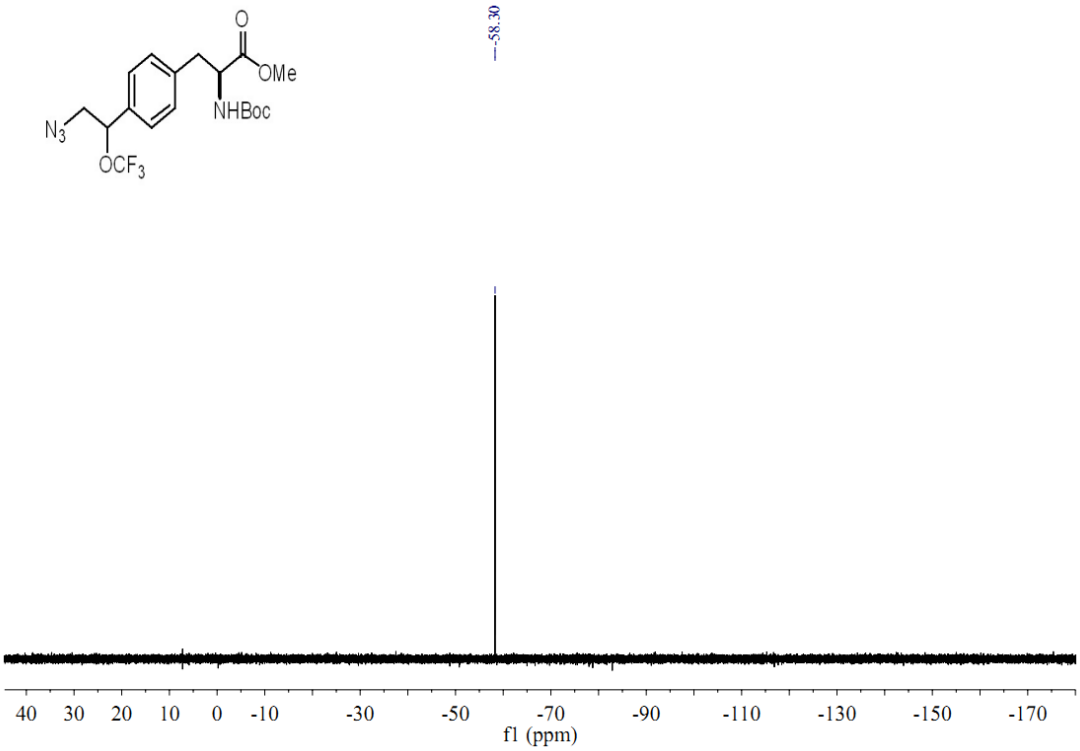
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of ***cis*-4aa**



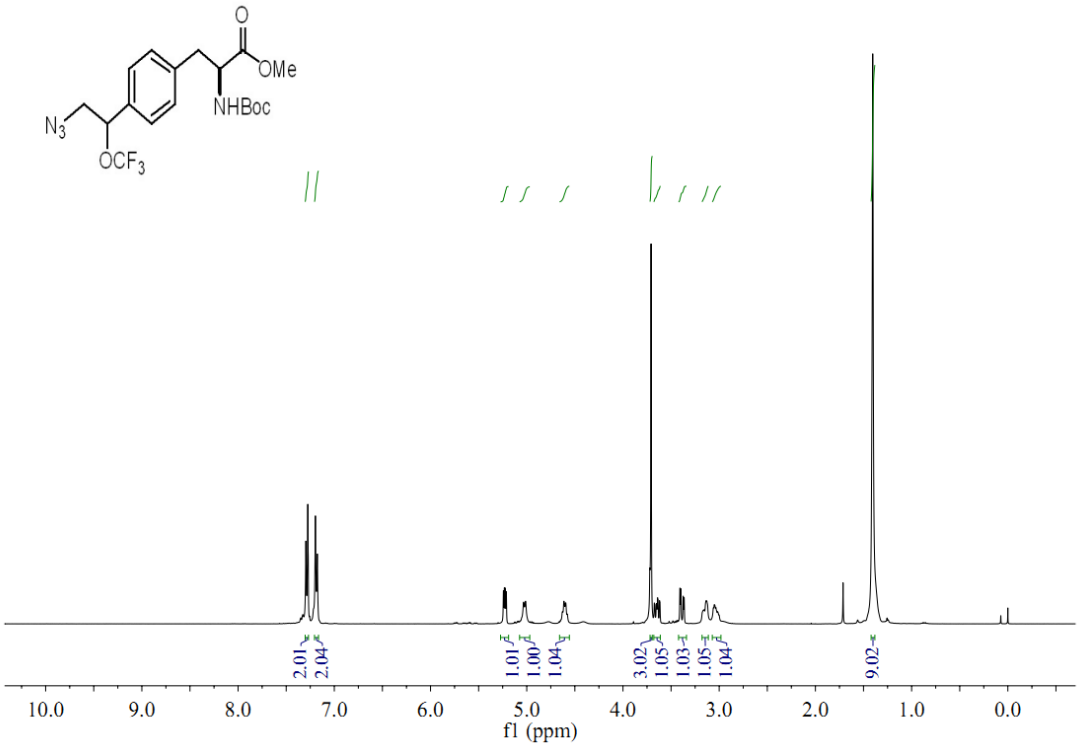
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of ***cis*-4aa**



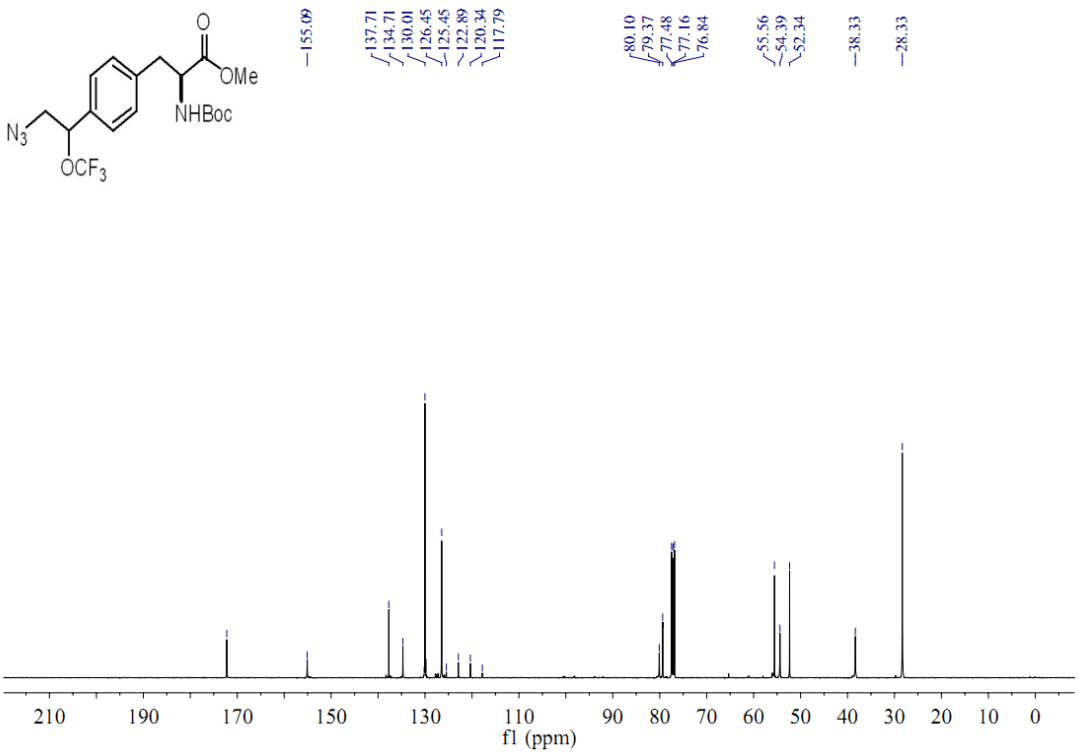
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of ***cis*-4aa**



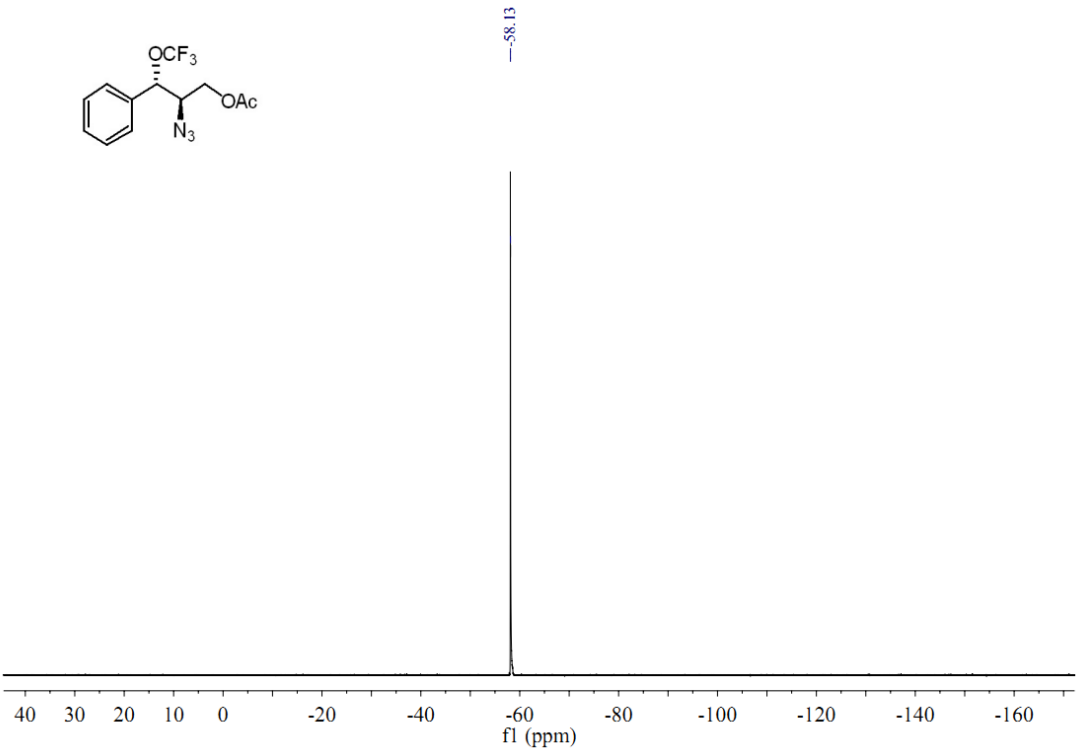
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4bb**



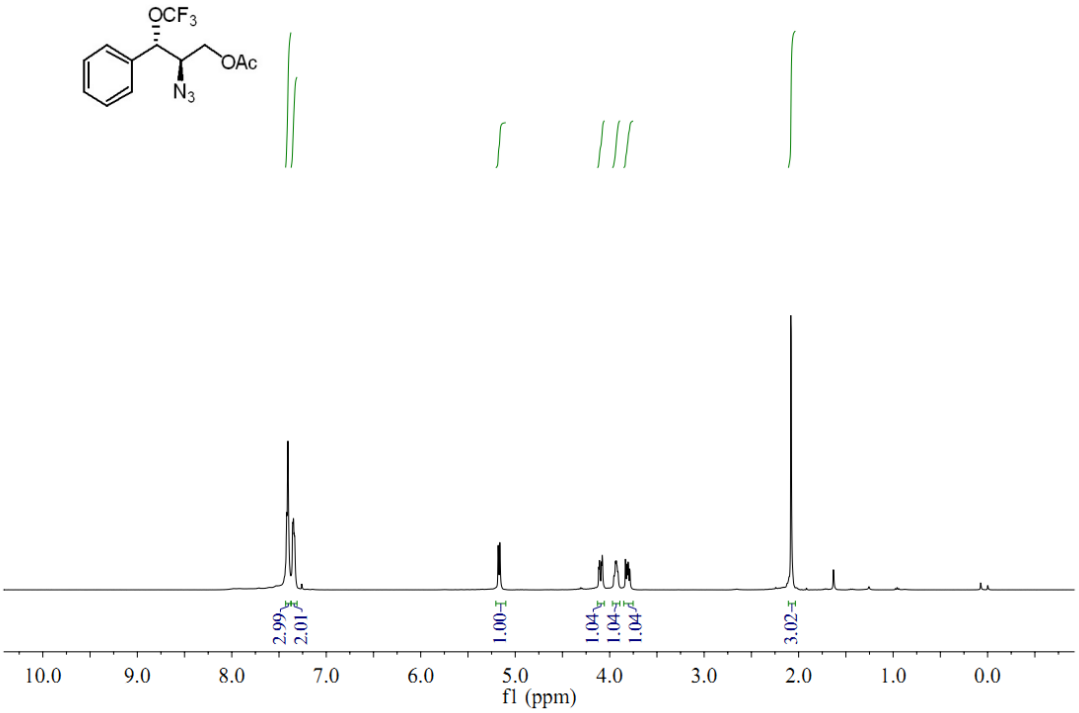
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4bb**



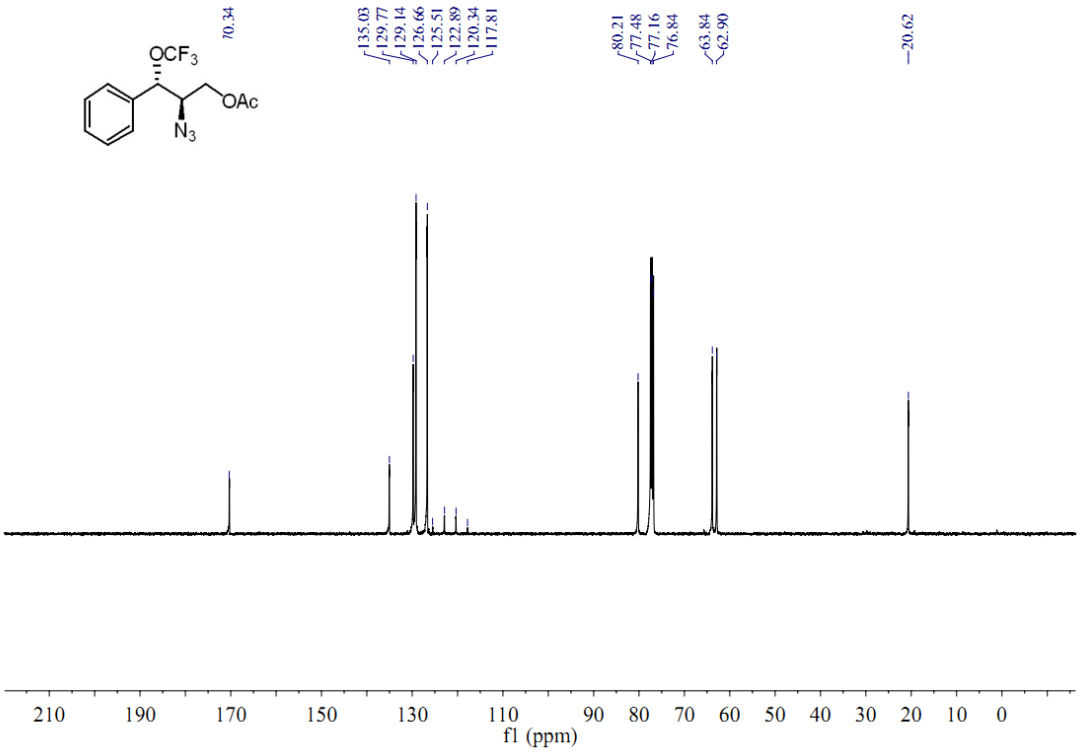
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4bb**



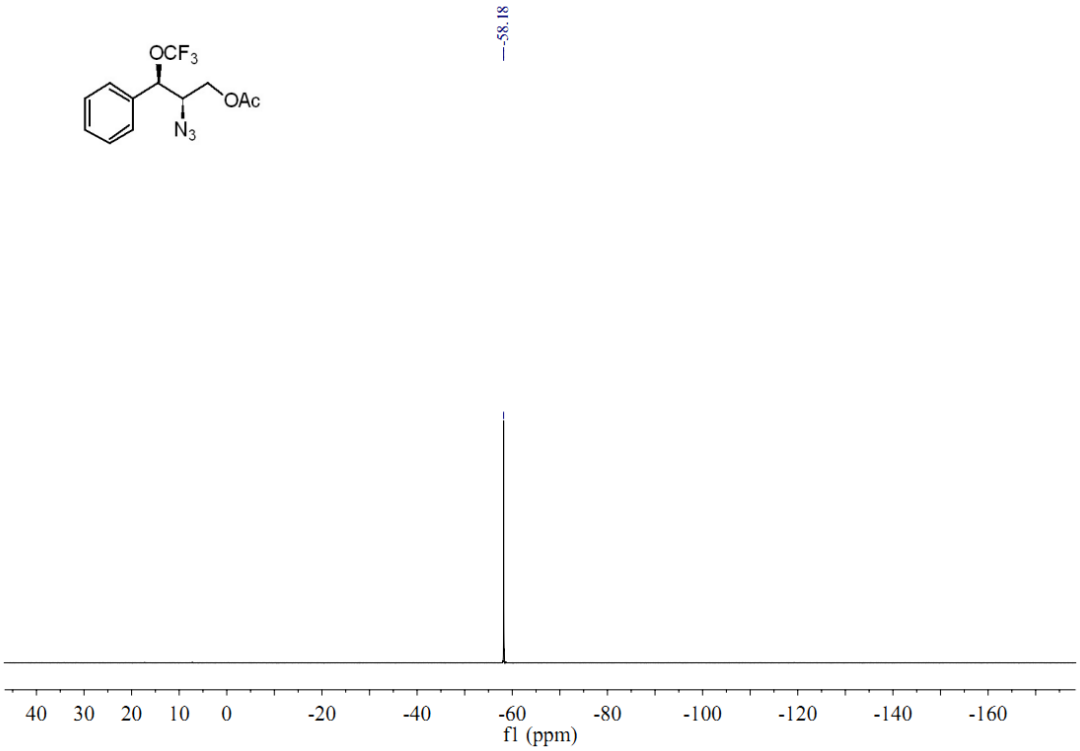
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of ***trans*-10**



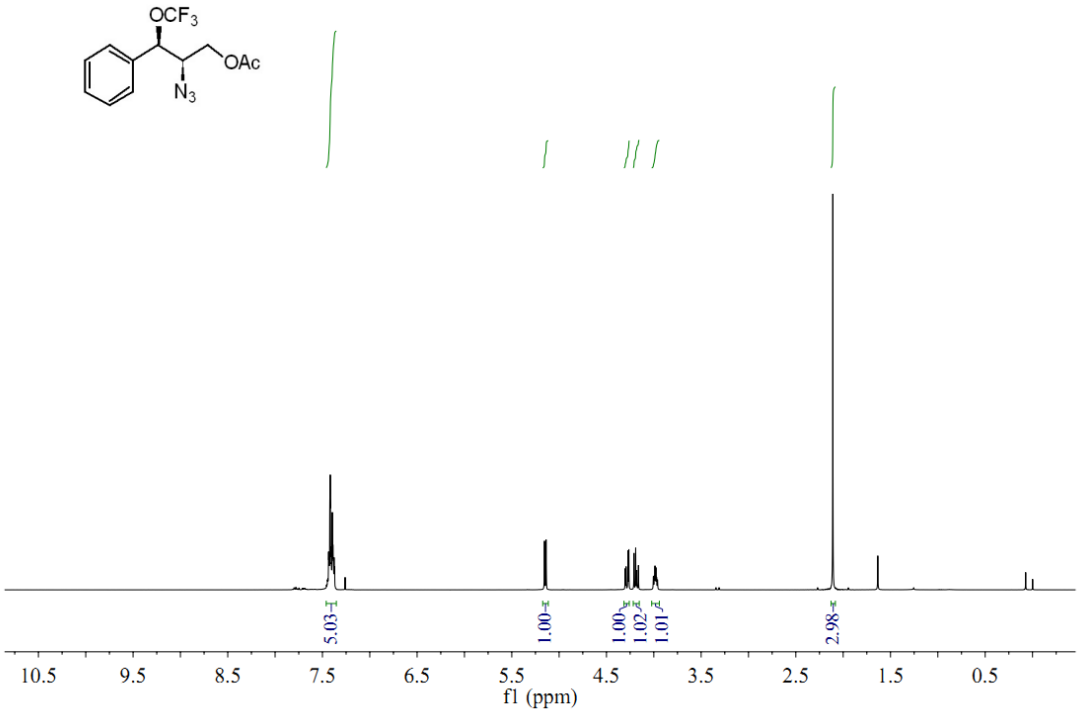
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of ***trans*-10**



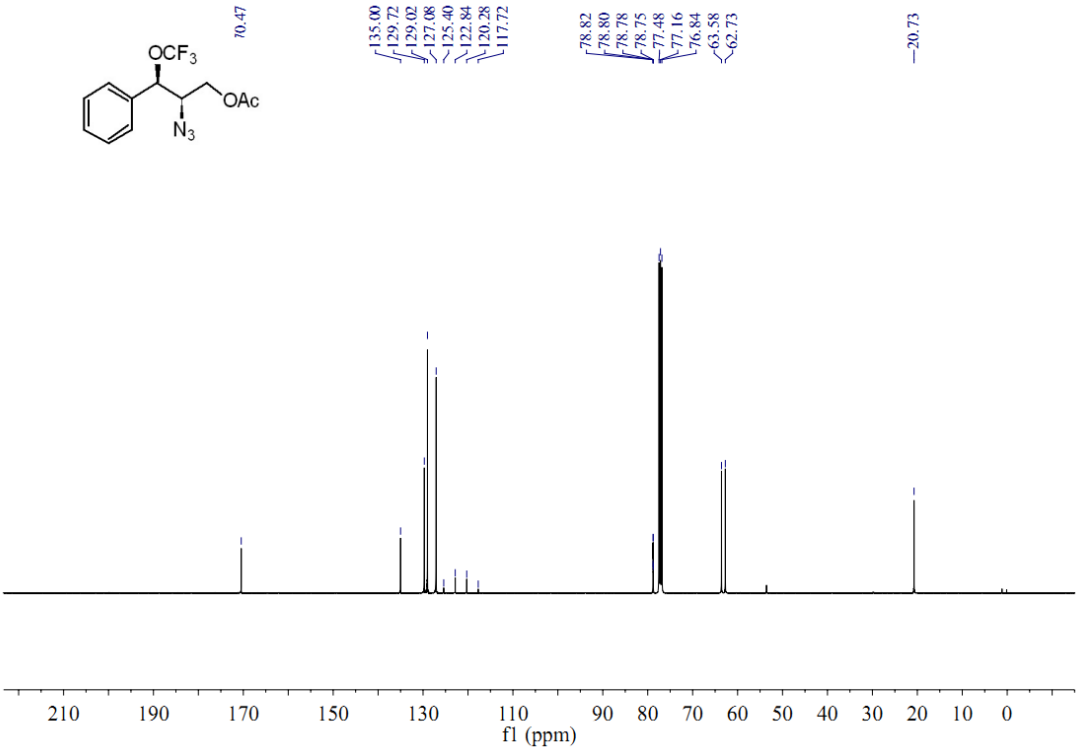
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of ***trans*-10**



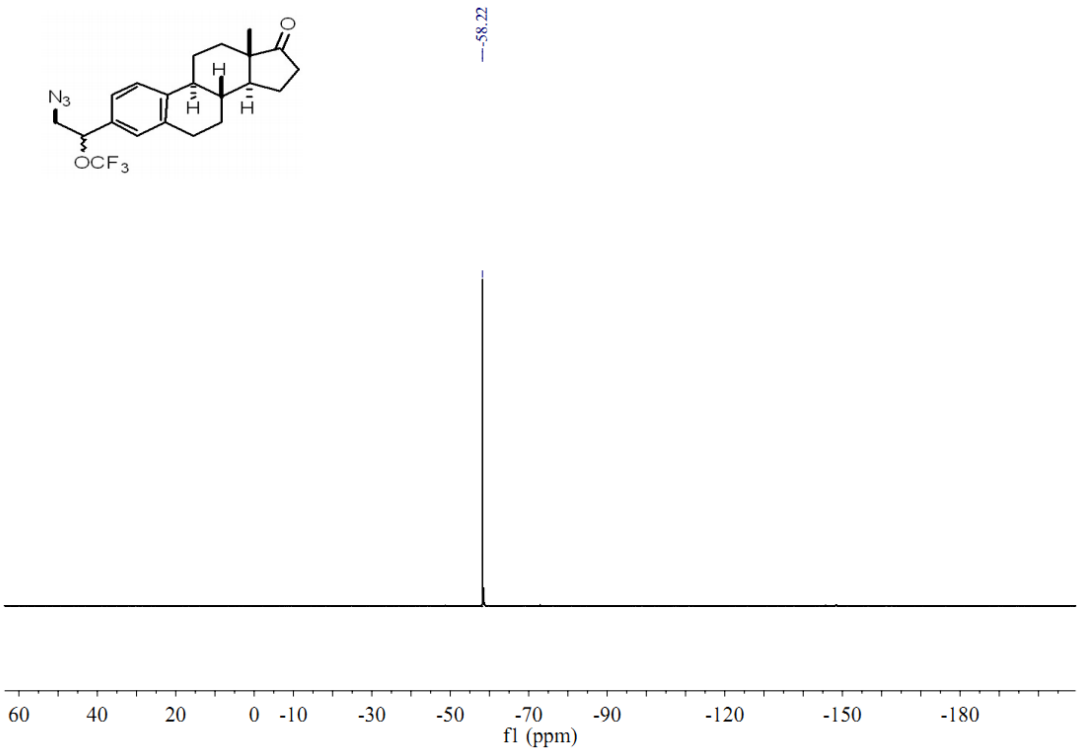
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of ***cis*-10**



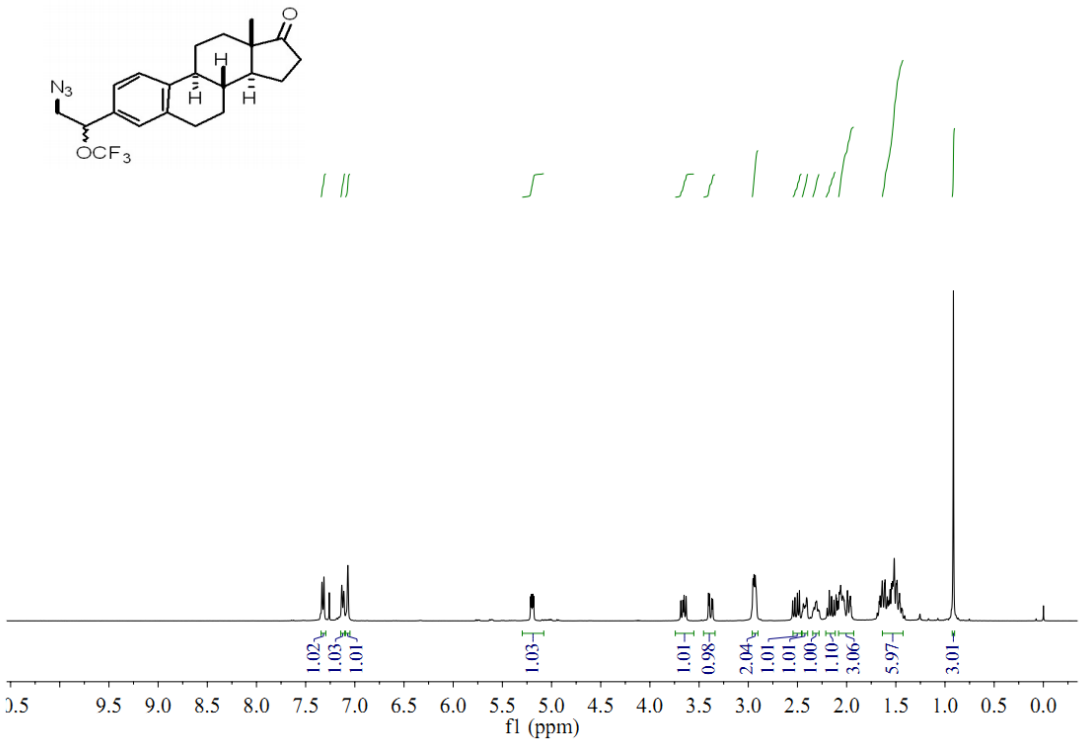
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of ***cis*-10**



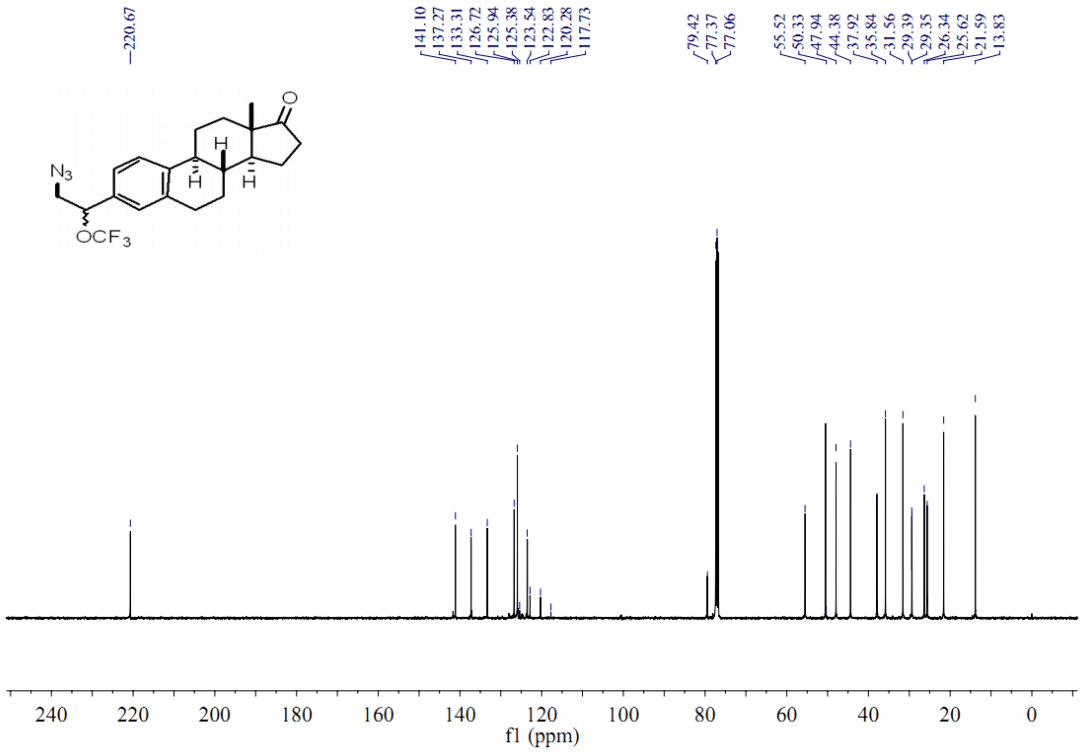
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of ***cis*-10**



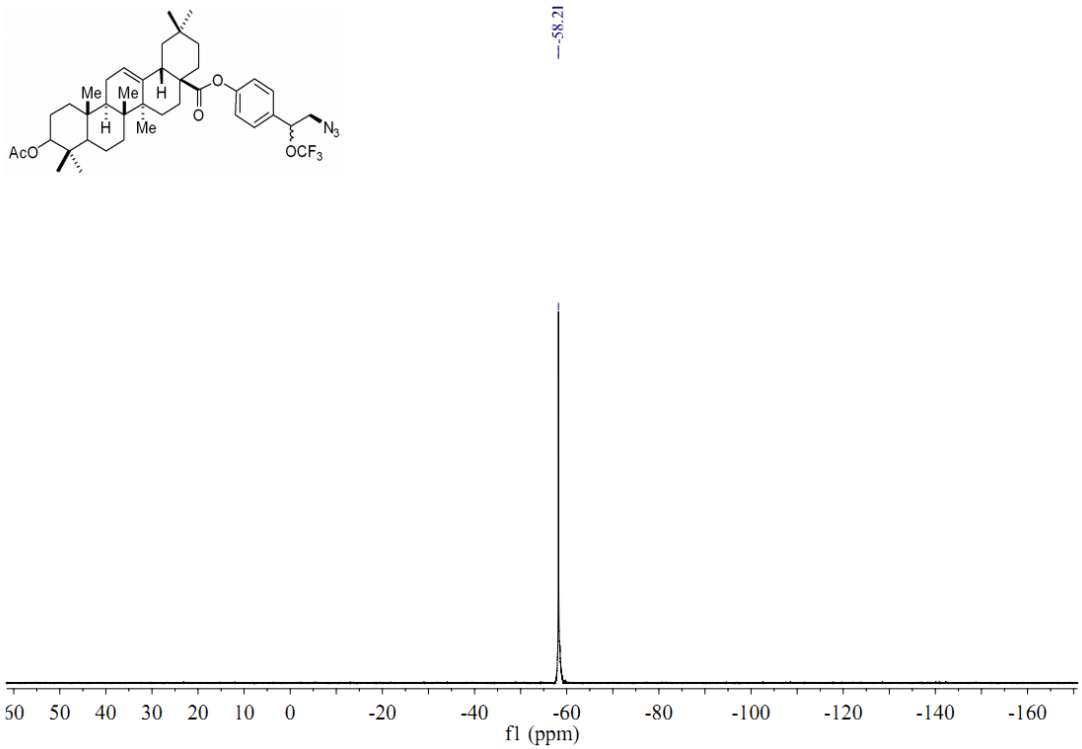
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4cc**



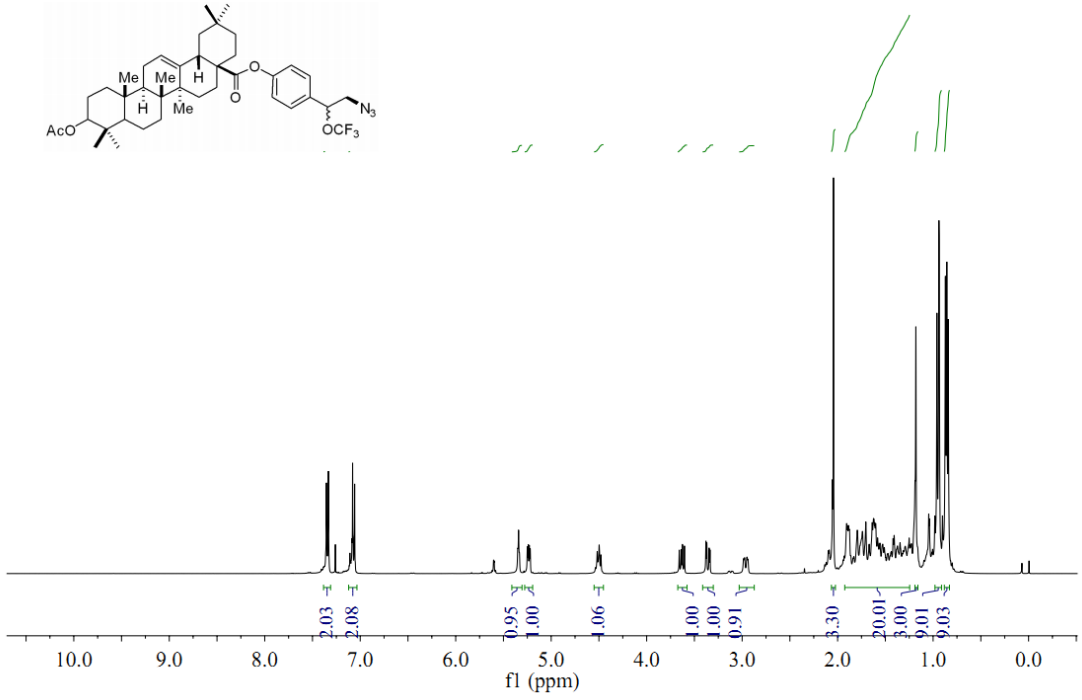
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4cc**



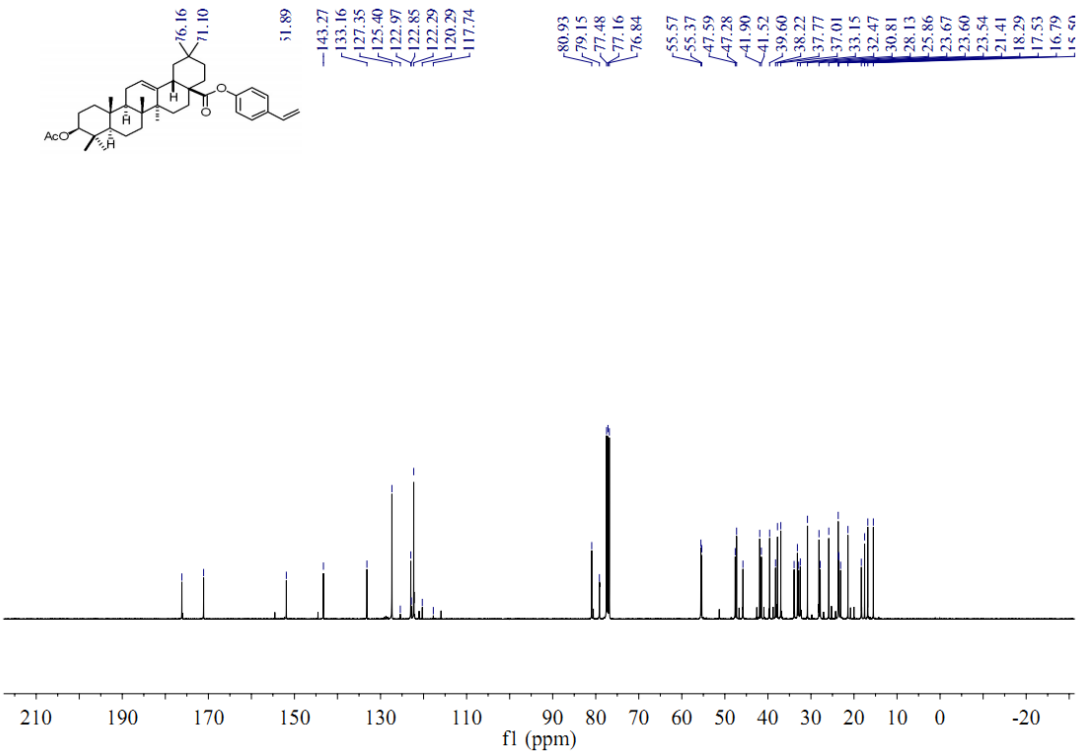
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4cc**



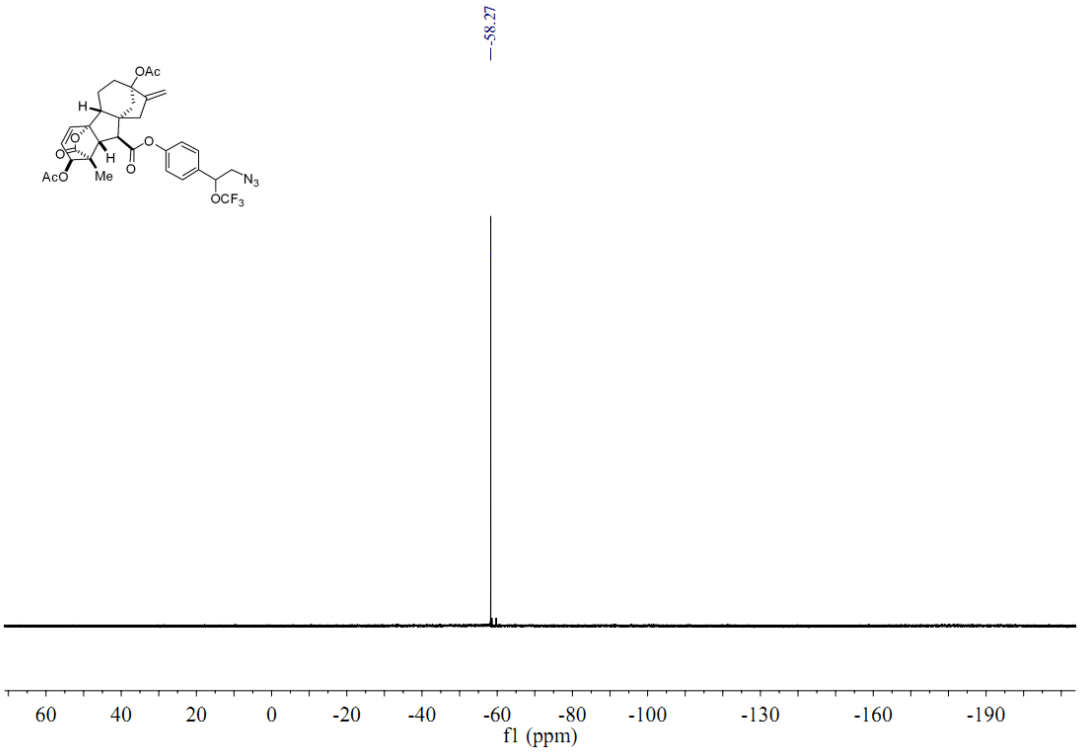
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4dd**



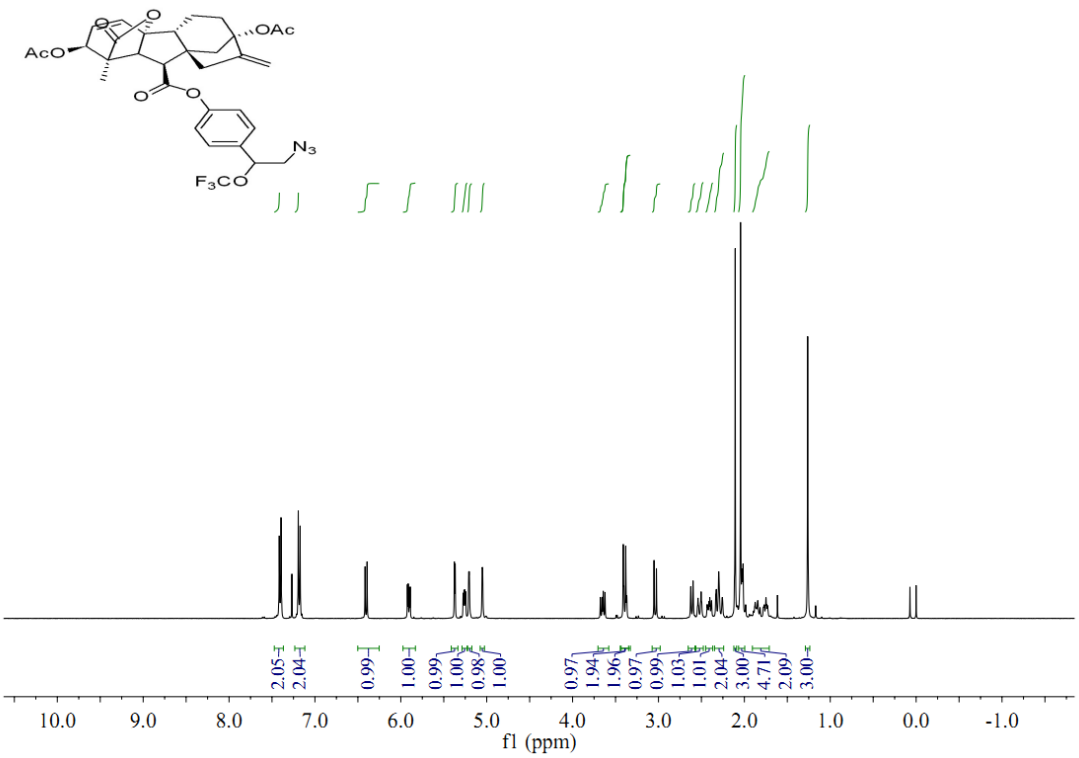
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4dd**



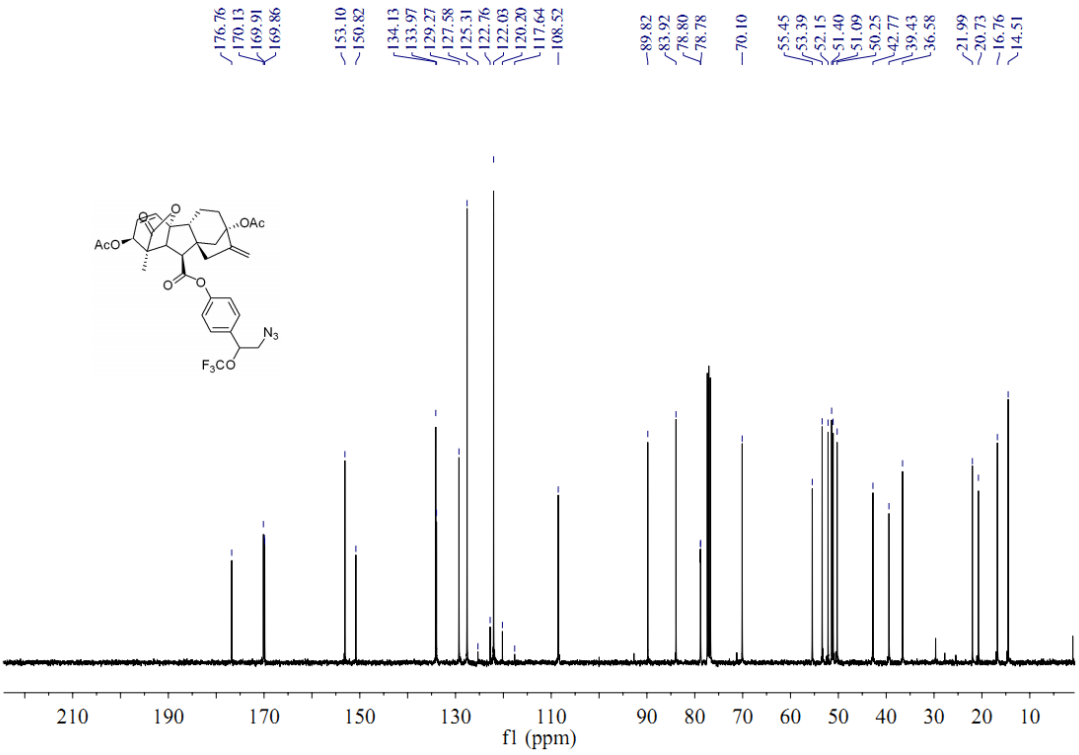
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4dd**



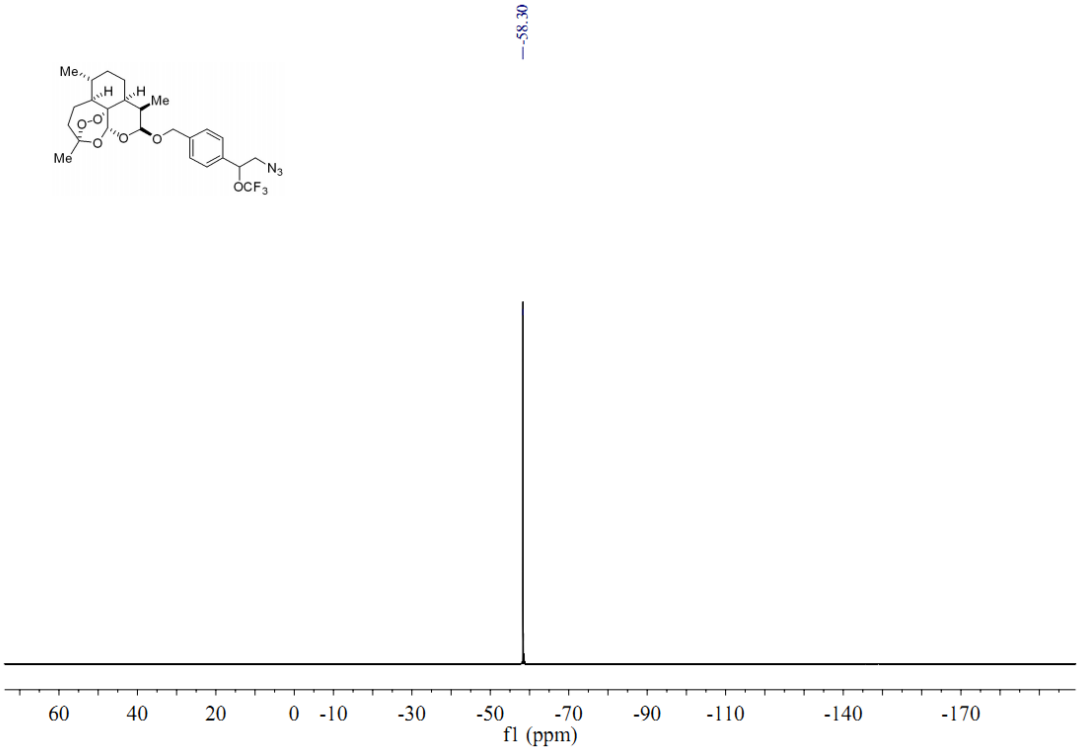
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4ee**



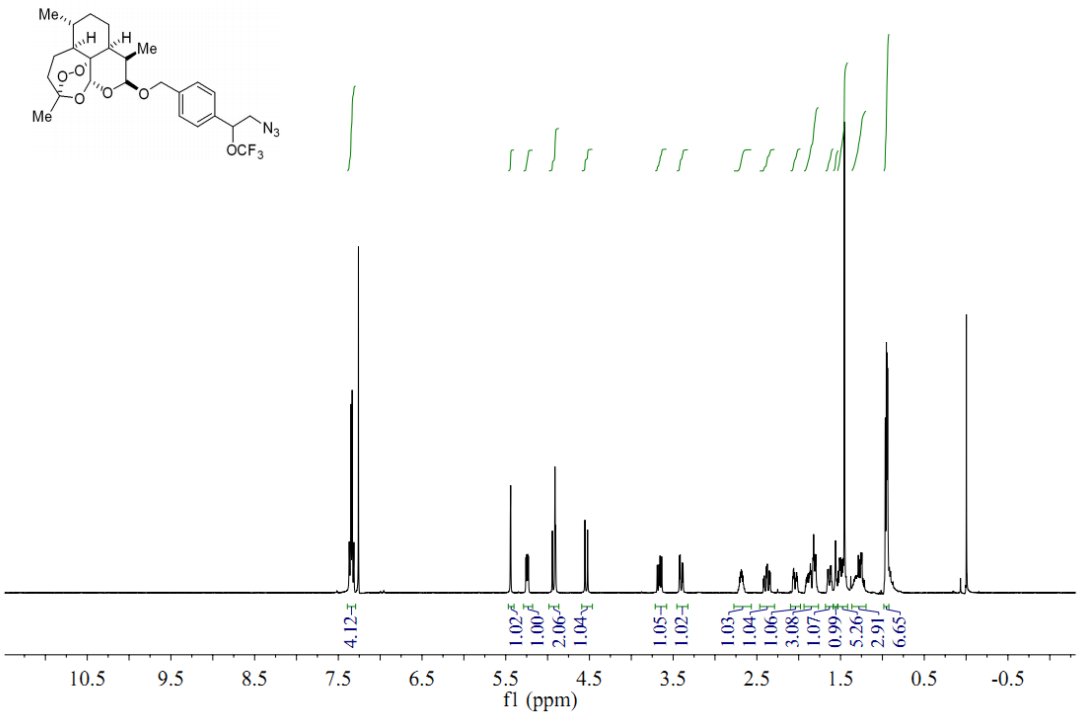
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4ee**



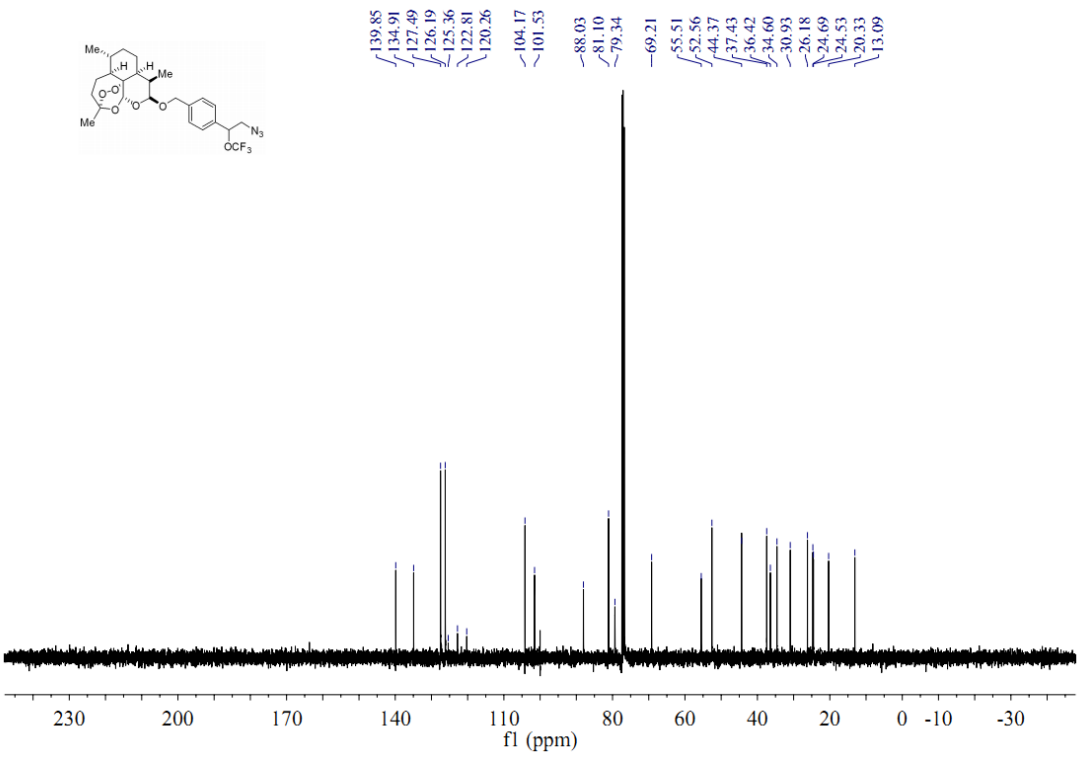
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4ee**



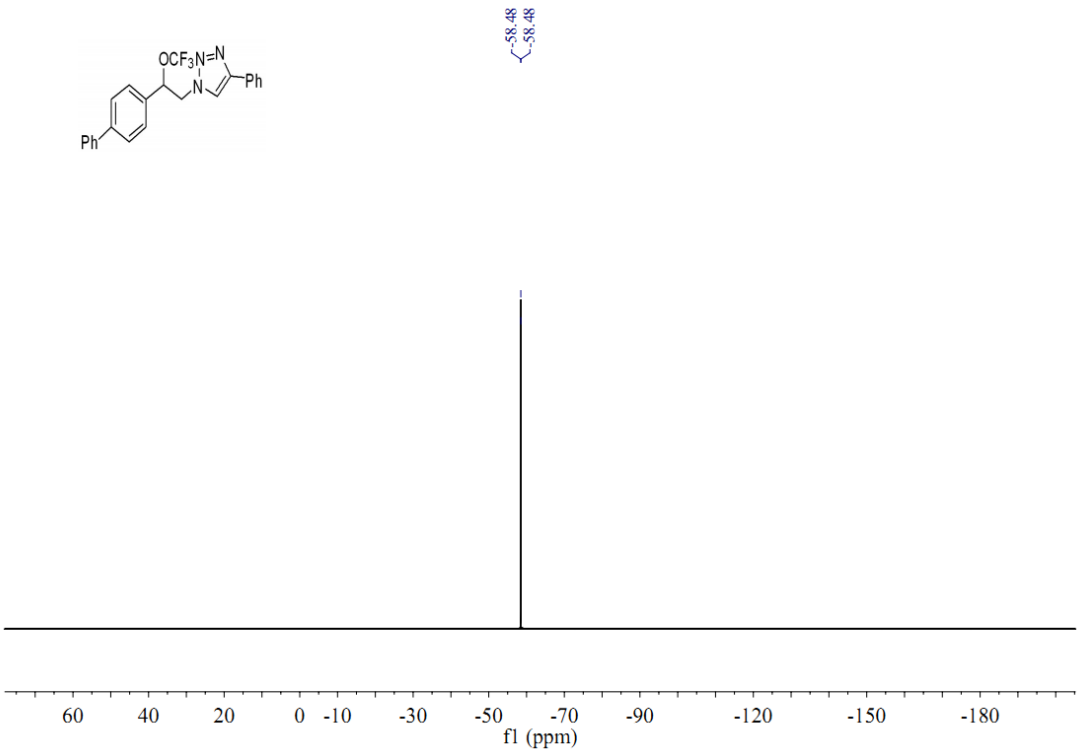
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4ff**



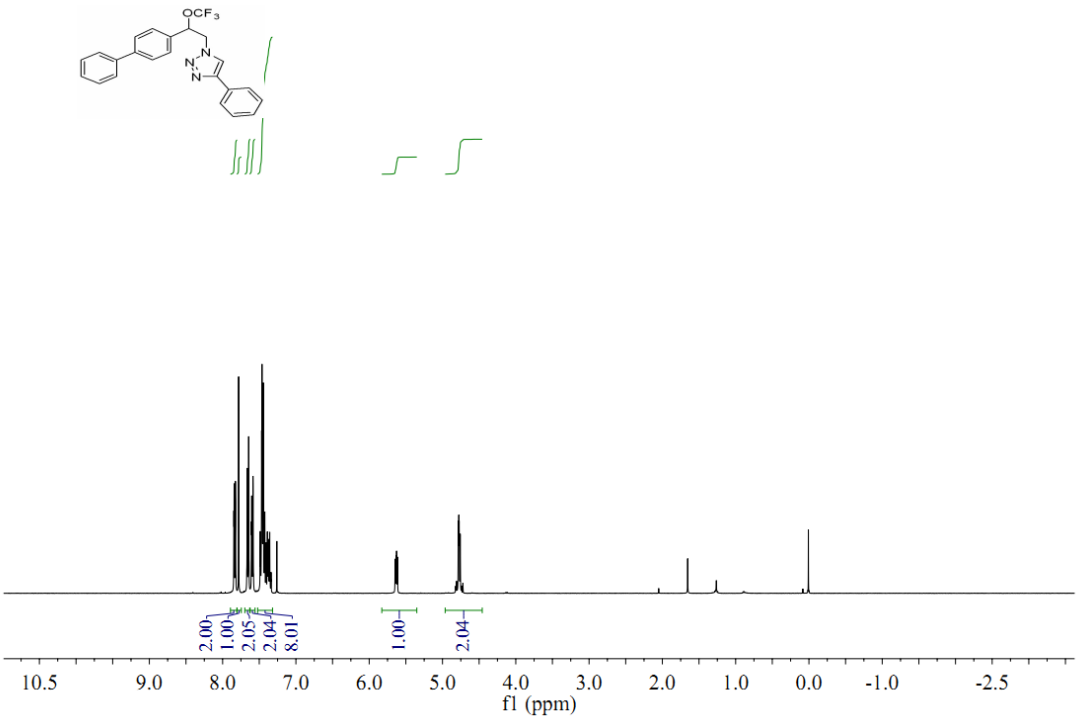
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4ff**



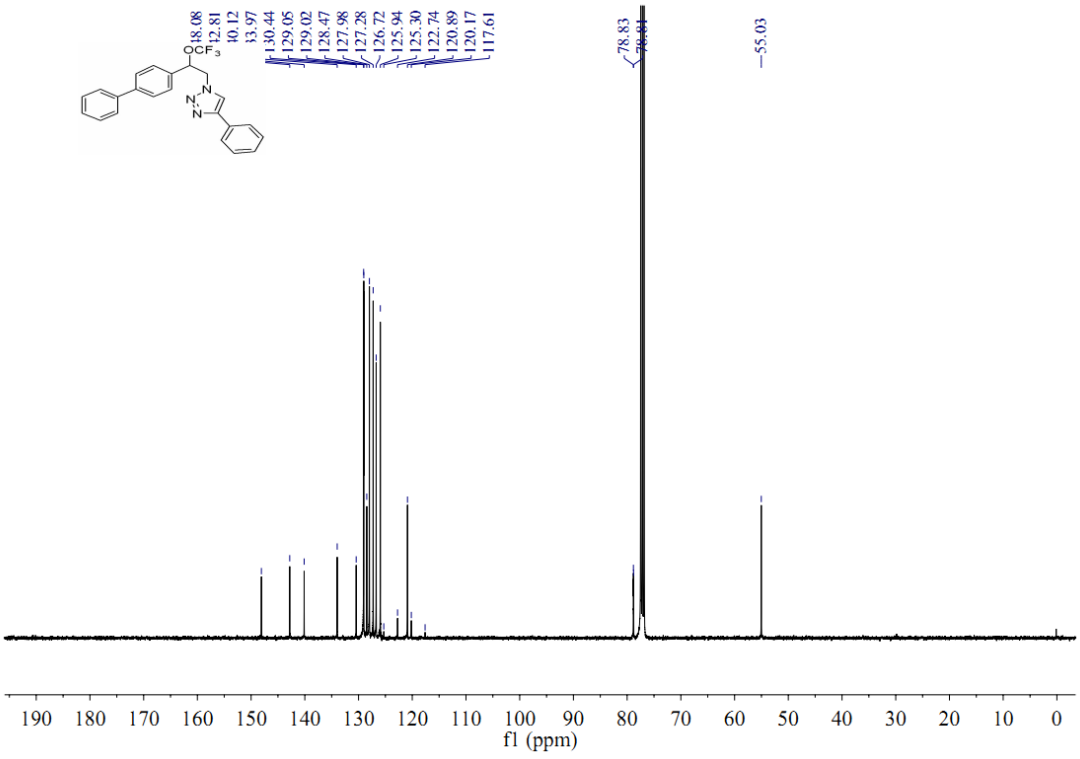
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **4ff**



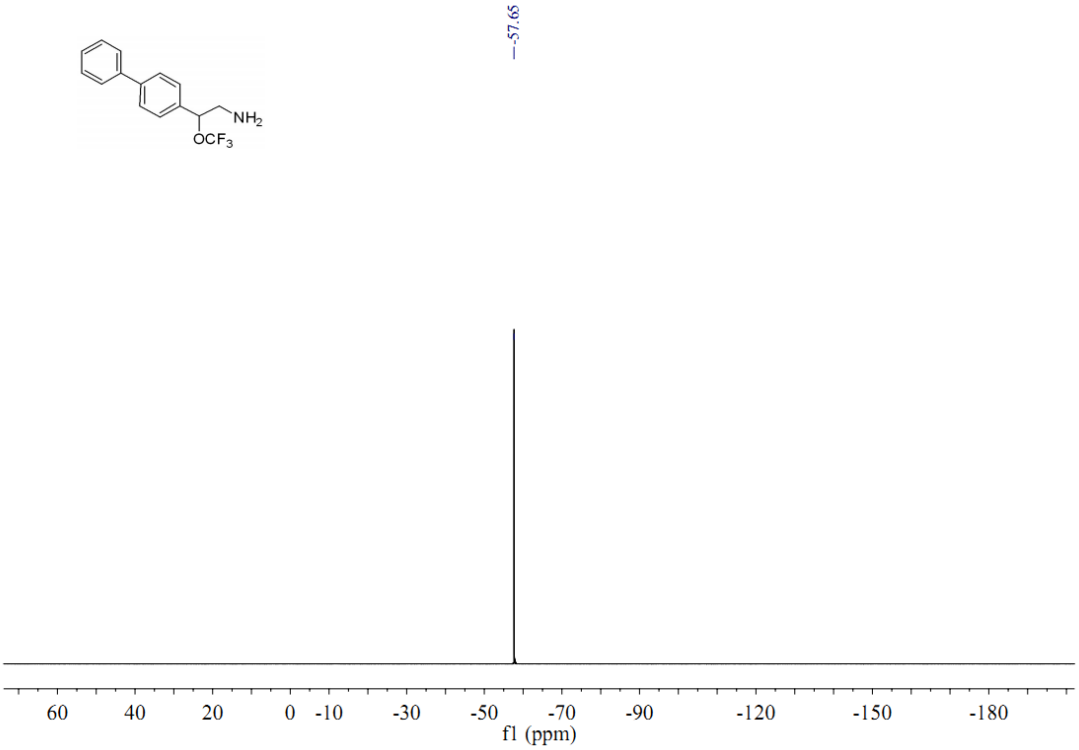
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **5**



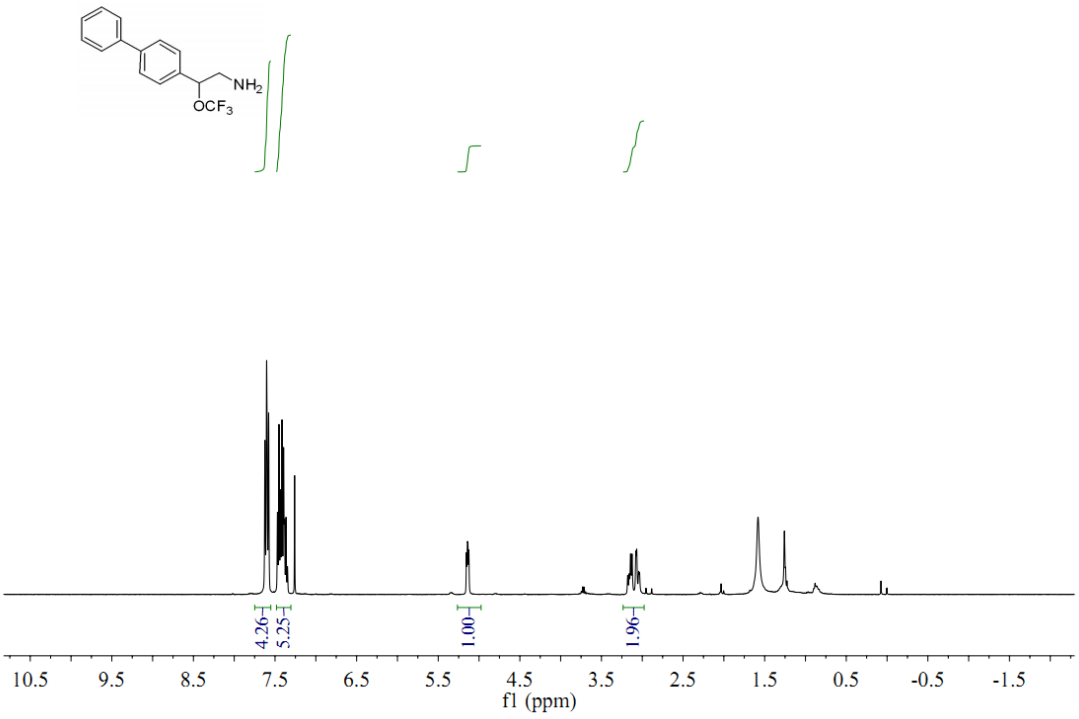
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **5**



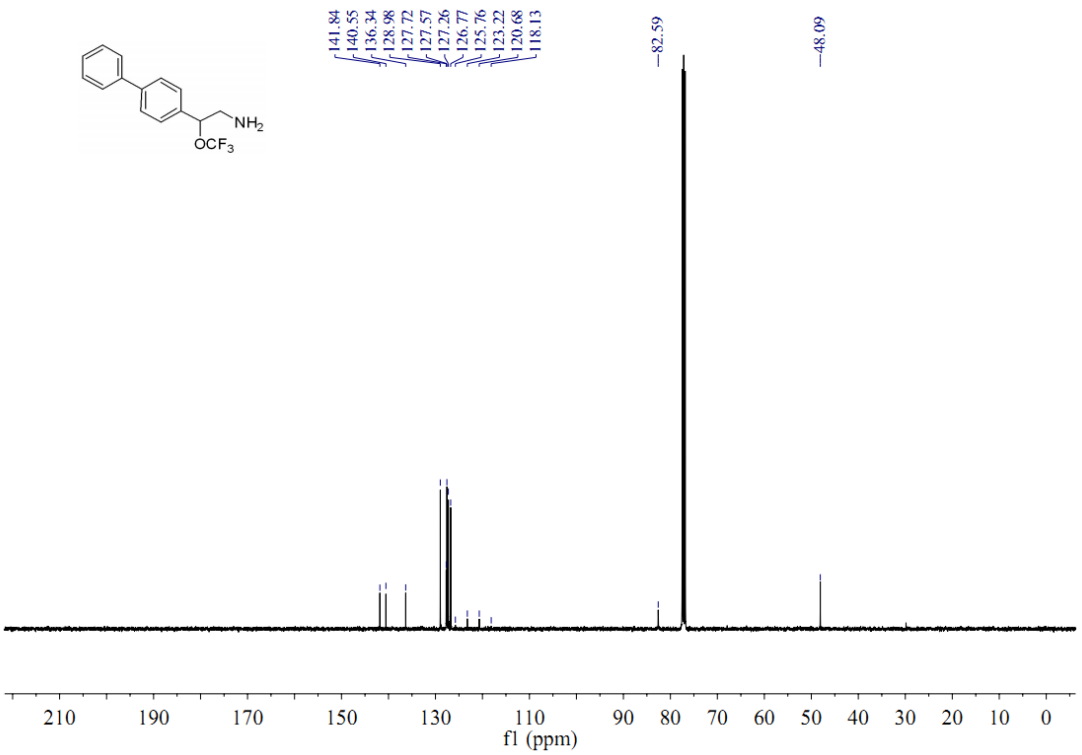
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **5**



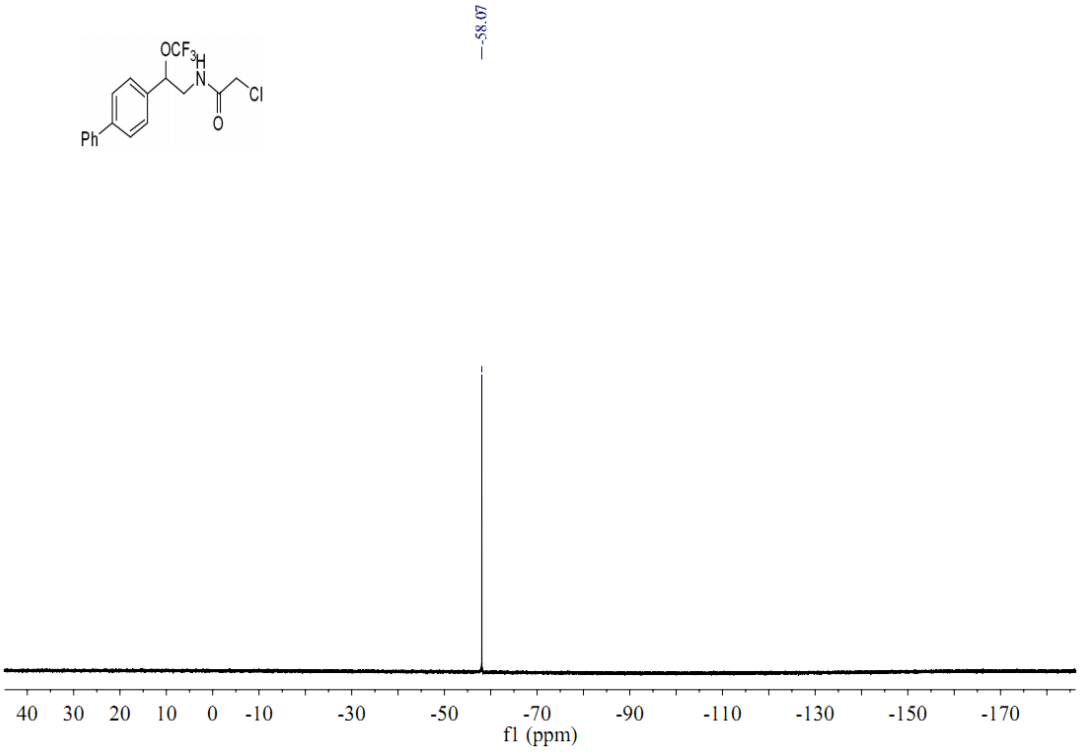
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **6a**



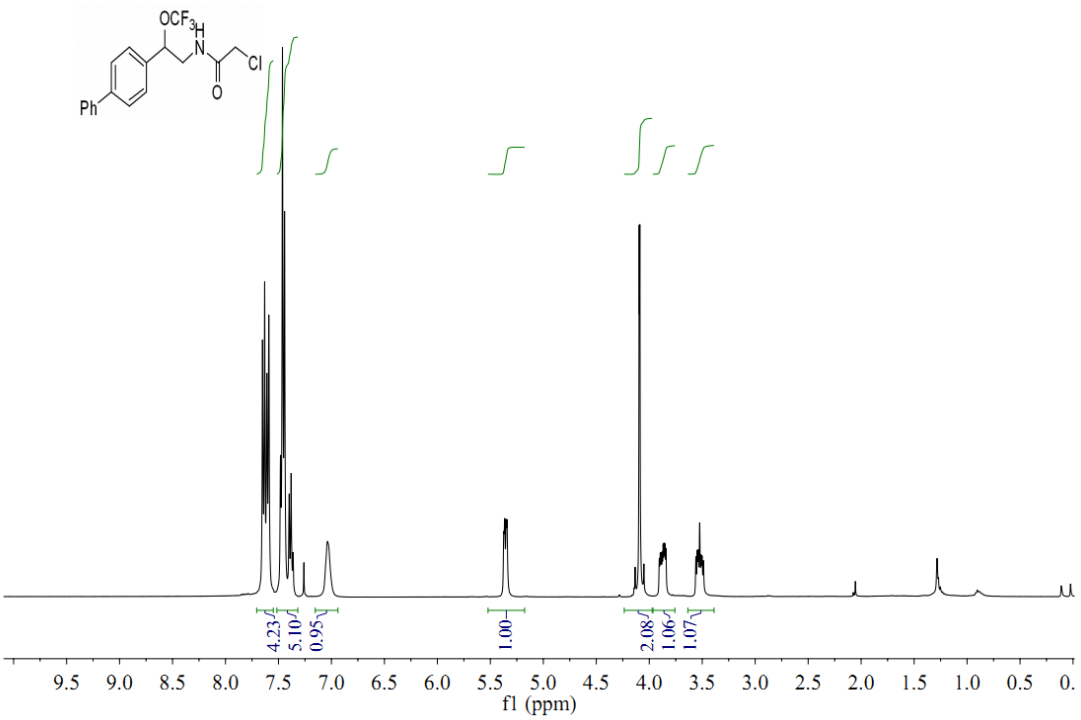
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **6a**



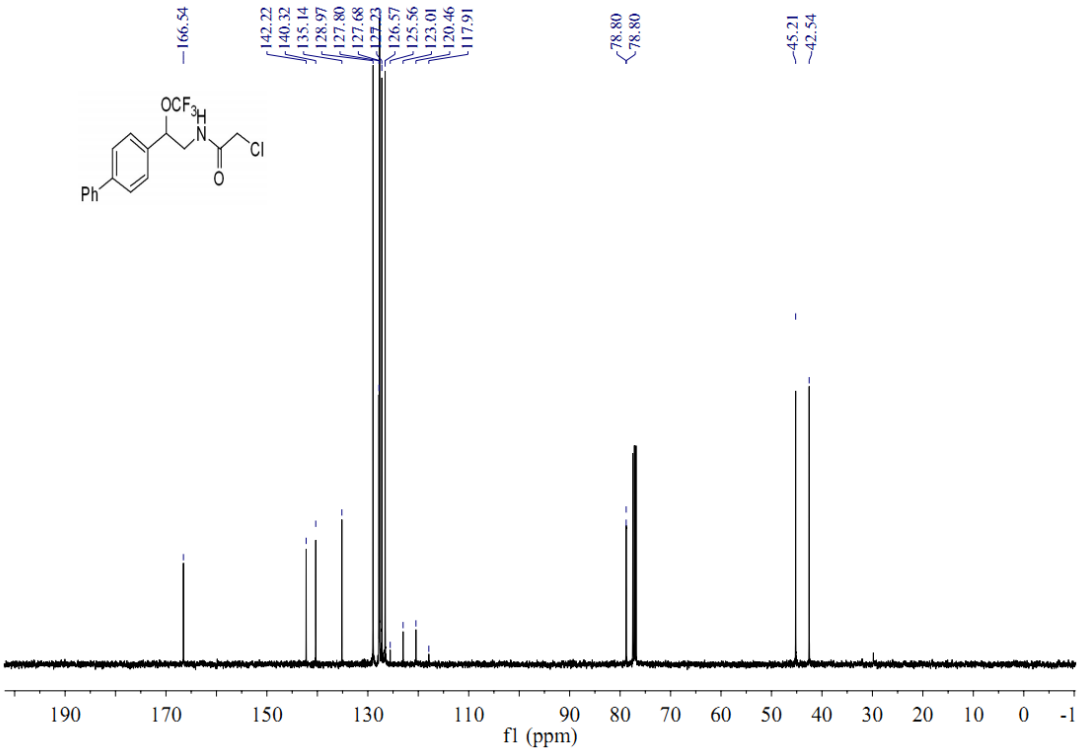
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **6a**



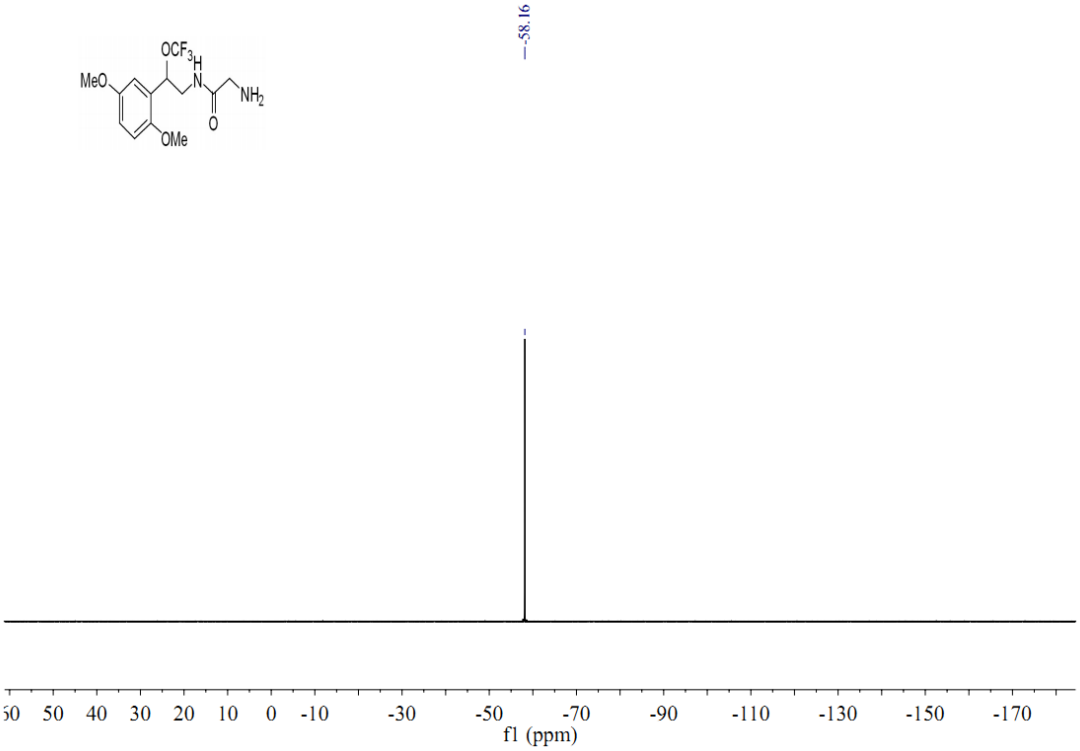
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **6**



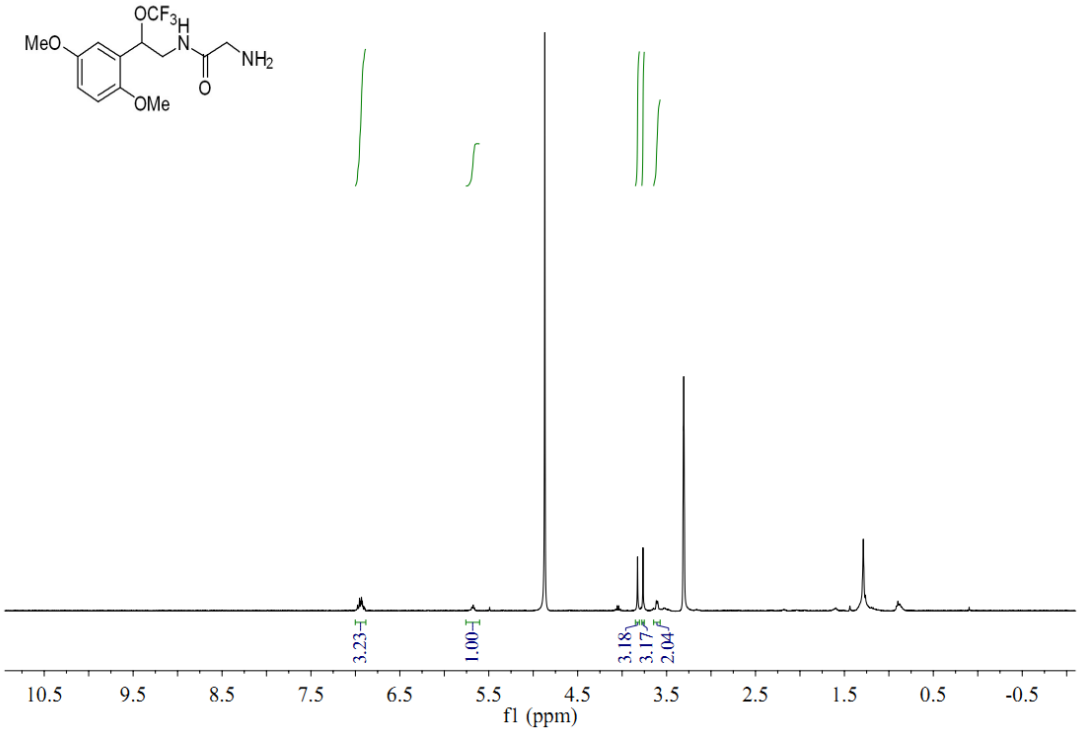
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **6**



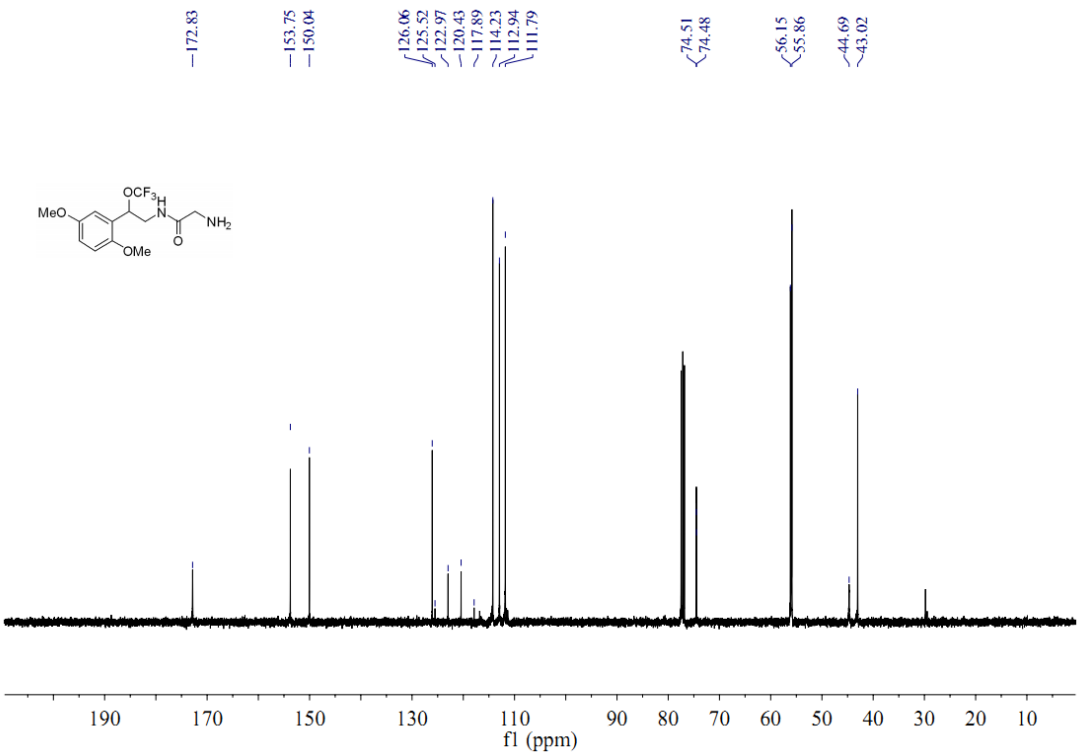
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **6**



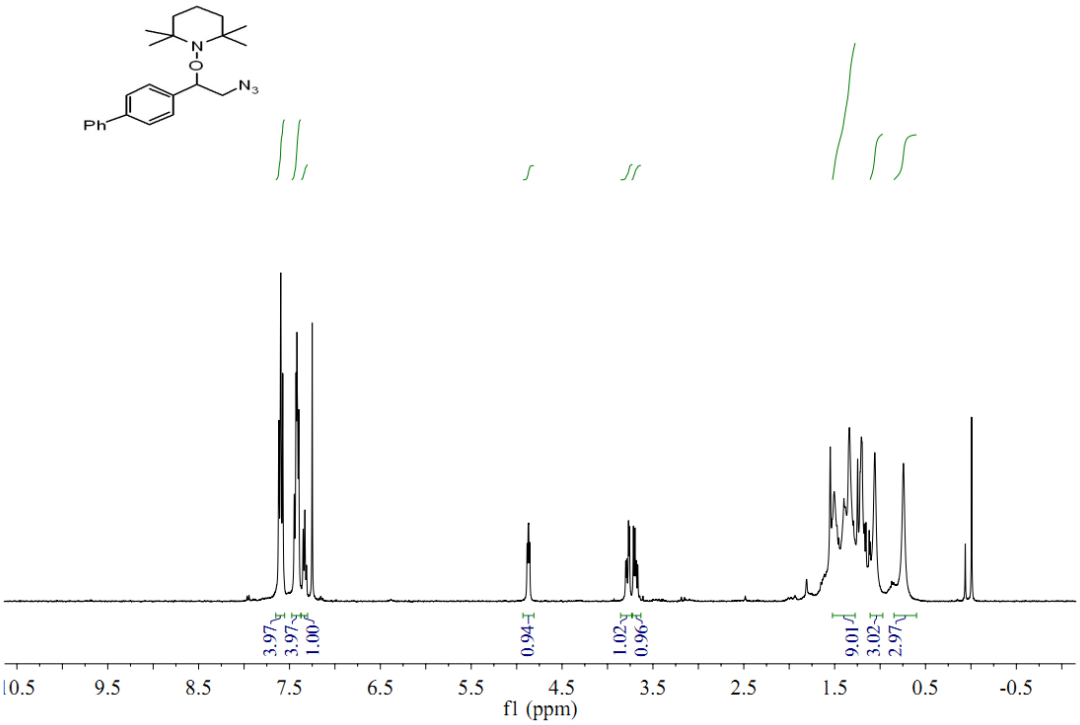
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **8**



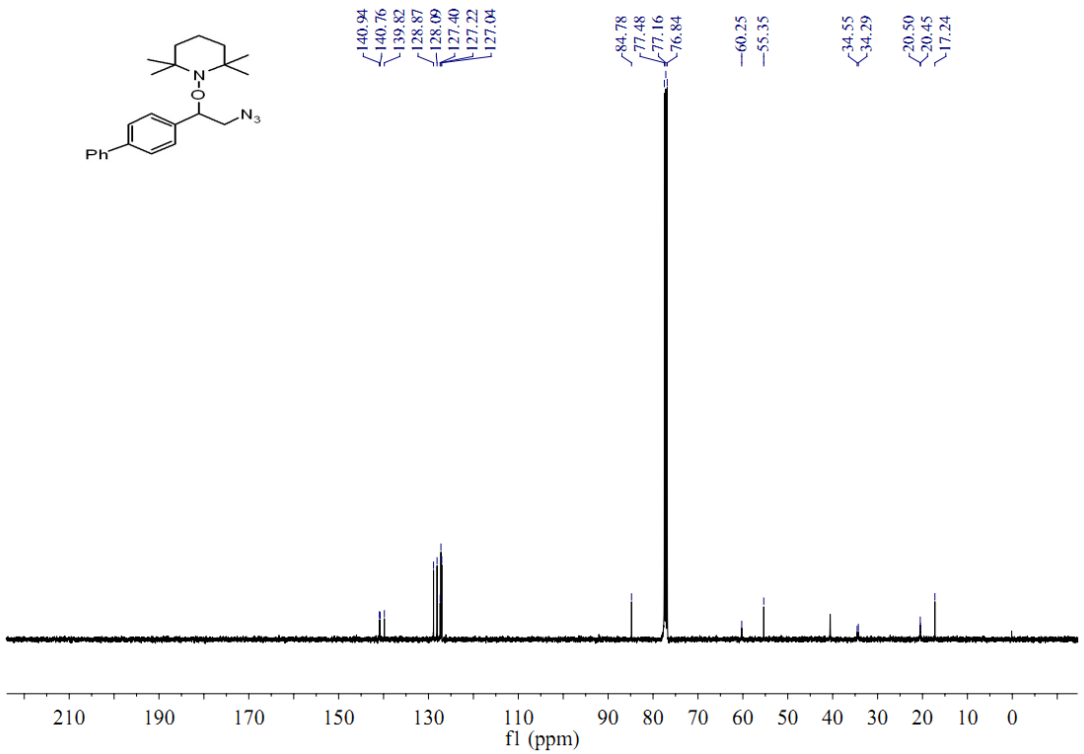
^{1}H NMR spectrum (400 MHz, CD_3OD, 23 ºC) of **8**



^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of **8**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 11



^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 °C) of 11