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

Supporting Information

Isoxazole group directed Rh(III)-catalyzed alkynylation using TIPS-EBX

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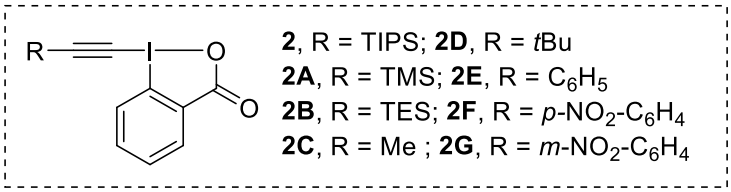
1. Experimental Section:

The glassware used for all the reactions was oven-dried. Unless otherwise indicated, all the chemicals and solvents were purchased from Sigma-Aldrich, Spectrochem, TCI, and BLDPharm, Rankem India pvt. Ltd. and used as such. Silica gel [(60-120, 230-400 mesh), Rankem, India] was used for chromatographic separation. Petroleum ether (refers to the fraction boiling between 60 °C and 80 °C). Melting points were determined in open capillaries and are uncorrected. IR spectra (v_{max} in cm^{-1}) were recorded on a Perkin-Elmer L 1600300 spectrum TWO LiTa (v_{max} in cm^{-1}) solid and neat for liquid samples ATR mode. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-300 and Bruker DPX-400 spectrometer in $CDCl_3$ and d^6-DMSO with TMS as internal standard (chemical shift in δ). HRMS mass spectra were recorded on waters quadruple time of flight mass spectrometer (XEVOG2 Q-TOF).

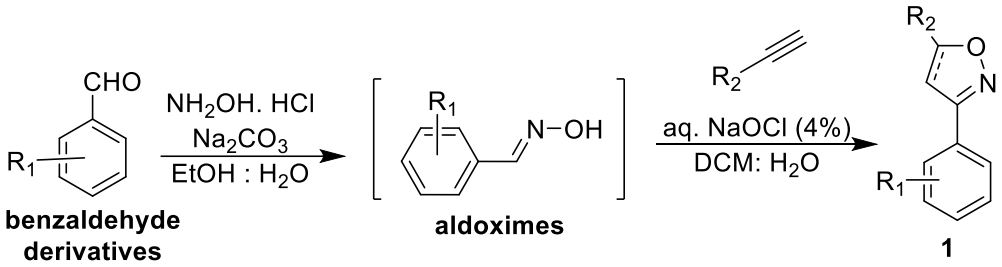
2. General Procedure:

Procedure for the Synthesis of Cyclic Hypervalent Iodine Reagents:

Cyclic hypervalent iodine reagents (**2**[S1a], **2A**[S1d], **2B**[S1c], **2C**[S1b], **2D**[S1c], **2E**[S1b], **2F**[S1c], **2G**[S1e]) were prepared in laboratory by following the reported procedure[S1a-e].



Procedure for the Synthesis of Isoxazole and isooxazoline derivatives:



Isoxazole/isooxazoline derivatives **1** were prepared by initial aldoximes formation[S2] from commercially available aldehydes (1 equiv.) using hydroxylamine hydrochloride (2 equiv.) and Na_2CO_3 (2 equiv.) in EtOH/ H_2O (v:v = 6:1). The reaction mixture was stirred 3-4 h at room temperature. On completion (monitoring by TLC), the reaction mixture was diluted with water and extracted with EtOAc (3 x 10 ml). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation under reduced pressure to give a residue, which was purified by using column chromatography to afford aldoxime derivatives in

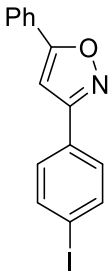
excellent yields (61-93%).

By following the reported procedure[S3], To a stirred solution of obtained aldoximes (1 equiv.) in DCM/H_2O (v:v = 6:1), alkynes/alkenes (1 equiv.) were added and the reaction mixture was stirred for 10 minutes at room temperature. Then, aq. NaOCl (4%) (2 equiv.) was added slowly and the reaction was further stirred for 3-4 h. After completion (confirmed by TLC), water was added and product was extracted with EtOAc (3 × 10 ml). The organic layer was collected, dried on anhydrous Na_2SO_4 and solvent was evaporated on rotary evaporator to get the crude product. The crude product was purified by column chromatography to get pure isoxazole/ isoxazoline products.

Known Substrates	**Unknown Substrates**
1a[S4], **1b**[S5], **1c**[S4], **1d**[S6], **1e**[S7], **1f**[S8], **1g**[S4], **1h**[S4], **1j**[S5], **1k**[S8], **1l**[S7], **1m**[S9], **1n**[S6], **1o**[S7], **1q**[S12], **1r**[S9], **1s**[S9], **1t**[S10], **1u**[S11], **1v**[S4], **1w**[S4]	**1i**, **1p**, **1x**, **1y**

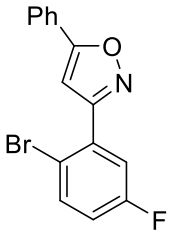
3. Experimental Data for unreported substrates 1i, 1p, 1x,y:

3-(4-iodophenyl)-5-phenylisoxazole (1i)



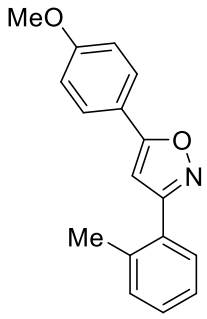
Following the general procedure, **1i** was isolated in 92% yield (647 mg, 1.864 mmol; from the 500 mg of corresponding oxime and 0.22 mL phenyl acetylene);
Yellow solid. m.p. 150-152 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.6;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 4H), 7.63 – 7.58 (m, 2H), 7.53 – 7.46 (m, 3H), 6.81 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 162.2, 138.1, 130.4, 129.0, 128.6, 128.4, 127.2, 125.8, 97.2, 96.2.

3-(2-bromo-5-fluorophenyl)-5-phenylisoxazole (1p)



Following the general procedure, **1p** was isolated in 89% yield (260 mg, 0.817 mmol; from the 200 mg of corresponding oxime and 0.1 mL phenyl acetylene);
white solid. m.p. 128-130 °C R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.6;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.67 (dd, *J* = 9, 5.1 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.10-7.04 (m, 1H), 6.98 (s, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 163.4, 135.1, 134.9, 130.4, 129.1, 127.2, 125.9, 118.6, 118.4, 118.2, 118.1, 100.5.

5-(4-methoxyphenyl)-3-(o-tolyl)isoxazole (1x)

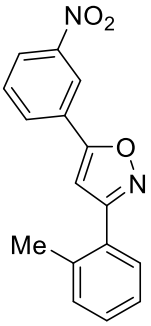


Following the general procedure, **1x** was isolated in 87% yield (255 mg, 0.961 mmol; from the 150 mg of corresponding oxime and 147 mg *p*-methoxyphenyl acetylene); yellow liquid. R_f (9.0:1.0 Hexane /Ethyl acetate) = 0.6;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.55 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.03 – 6.98 (m, 2H), 6.57 (s, 1H), 3.88 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 163.5, 161.0, 136.8, 131.0, 129.3, 129.37, 128.9, 127.4, 125.9, 120.3, 114.3, 98.8, 55.3, 21.1.

5-(3-nitrophenyl)-3-(o-tolyl)isoxazole (1y)

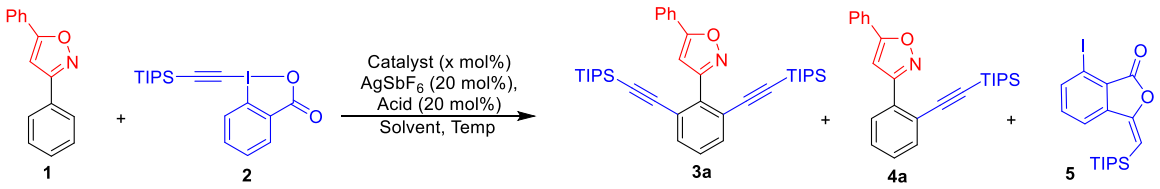


Following the general procedure, **1y** was isolated in 87% yield (180 mg, 0.642 mmol; from the 100 mg of corresponding oxime and 109 mg *m*-nitrophenyl acetylene); off-white solid. m.p. 58-60 °C; R_f (9.0:1.0 Hexane /Ethyl acetate) = 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (t, *J* = 2.0 Hz, 1H), 8.33-8.30 (m, 1H), 8.20-8.17 (m, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.41-7.29 (m, 3H), 6.87 (s, 1H), 2.54 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 163.9, 148.6, 136.9, 131.3, 131.1, 130.2, 129.8, 129.4, 128.9, 128.1, 126.1, 124.5, 120.7, 101.8, 21.1.

4. (A) Optimization of Reaction Conditions (Table S1):



entry	Catalyst (% loading)	TIPS-EBX (equiv.)	acid (20 mol%)	solvent	*t* (°C)	time (h)	yield (%)		
							Di (**3a**)	Mono (**4a**)	Pdt-**5**
1.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	PivOH	DCE	rt	48	5	13	ND
2.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	PivOH	DCM	rt-90	22	8	29	ND
3.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	PivOH	toluene	rt-90	22	2	14	ND
4.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	PivOH	THF	rt-90	22	9	29	ND

5.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	PivOH	Et_2O	rt-90	22	2	23	ND
6.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	PivOH	EtOH	rt-90	22	7	32	ND
7.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	PivOH	TFE	rt-90	22	34	25	ND
8.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	PivOH	HFIP	rt-90	22	37	29	ND
9.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	-	HFIP	rt-90	56	29	8	ND
10.	$[RhCp^*Cl_2]_2$ (4 mol%)	1.1	NaOAc	HFIP	90	6	ND	5	67
11.	$[RhCp^*Cl_2]_2$ (4 mol%)	2.0	PivOH	HFIP	90	22	67	17	ND
12.	**$[RhCp^*Cl_2]_2$ (4 mol%)**	**3.0**	**PivOH**	**HFIP**	**90**	**6**	**82**	**7**	**ND**
13.	**-**	3.0	PivOH	HFIP	90	12 h	ND	ND	ND
14.	[Ru(*p*-cymene)Cl_2]$_2$ (4 mol%)	1.1	PivOH	HFIP	rt-90	24	ND	ND	ND
15.	Pd $(OAc)_2$ (4 mol%)	1.1	PivOH	HFIP	rt-90	24	ND	ND	ND
16.	CuI (4 mol%)	1.1	PivOH	HFIP	rt-90	24	ND	ND	ND
17.	$SnCl_2$ (4 mol%)	1.1	PivOH	HFIP	rt-90	24	ND	ND	ND
18.	$FeSO_4$ (4 mol%)	1.1	PivOH	HFIP	rt-90	24	ND	ND	ND
19.	$Mn(OAc)_2$ (4 mol%)	1.1	PivOH	HFIP	rt-90	24	ND	ND	ND
20.	$[RhCp^*Cl_2]_2$ (4 mol%)[a]	1.1	AcOH	DCE	rt-90	22	6	22	ND
21.	$[RhCp^*Cl_2]_2$ (4 mol%)[b]	1.1	AcOH	HFIP	rt-90	22	33	14	ND
22.	$[RhCp^*Cl_2]_2$ (4 mol%)[c]	1.1	PivOH $Zn(OTf)_2$	DCE	rt-90	22	ND	ND	ND
23.	$[RhCp^*Cl_2]_2$ (4 mol%)	4.0	PivOH	HFIP	90	6	68	ND	5
24.	$[RhCp^*Cl_2]_2$ (2.5 mol%)	3.0	PivOH	HFIP	90	6	21	ND	10
25.	$[RhCp^*Cl_2]_2$ (10 mol%)	3.0	PivOH	HFIP	90	6	65	ND	18
26.	$[RhCp^*Cl_2]_2$ (4 mol%)	3.0	PivOH	HFIP	rt-90	12	68	25	ND

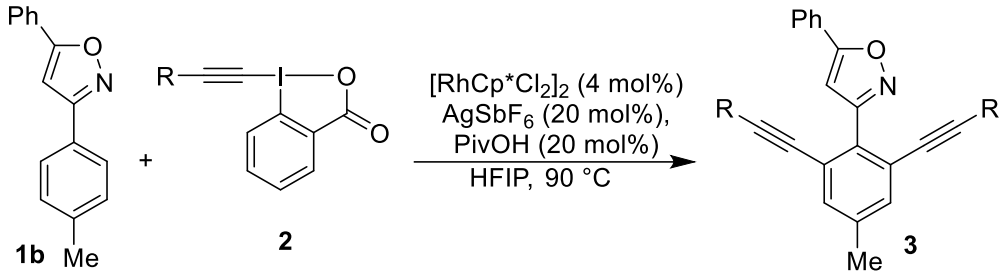
Reaction conditions: Optimized reaction Condition **1a** (1 equiv.)), **2a** (3 equiv.), $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (20 mol%), PivOH (20 mol%), HFIP (1.5 mL) at 90 ^oC for 6 h.

[a,b]AcOH shows better result than PivOH in DCE but poor result in HFIP. So PivOH was chosen to be optimum acid.

[c]No reaction was observed using $Zn(OTf)_2$ instead of $AgSbF_6$.

ND = Not Detected.

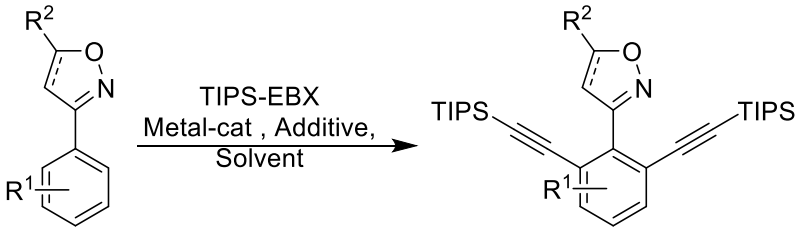
(B) Influence of different substituents on the alkyne part of cyclic hypervalent iodine reagent (Table S2):



entry	Hypervalent iodine reagents	Yield
1.	R = TIPS (**2**)	97% (**3b**)
2.	R = TMS (**2A**)[a, b, c]	ND (**3A**)
3.	R = TES (**2B**)[c,d]	ND (**3B**)
4.	R = Me (**2C**)[c]	ND (**3C**)
5.	R = *t*Bu (**2D**)[c]	ND (**3D**)
6.	R = Ph (**2E**)[c]	ND (**3E**)
7.	R = *p*-NO_2-C_6H_4 (**2F**)[c]	ND (**3F**)
8.	R = *m*-NO_2-C_6H_4 (**2G**)[c]	ND (**3G**)

ND = Not Detected; [a]DCE solvent used instead of HFIP; [b]Reaction carried out without $AgSbF_6$. [c]Hypervalent iodine reagents are found to be decomposed within 1 h even at room temperature under the optimized condition. [d]Reaction was carried out without 1b, the reagent 2B degrade within 30 min in the standard condition.

5. General Procedure for the synthesis of alkynylated derivatives (GP-A):

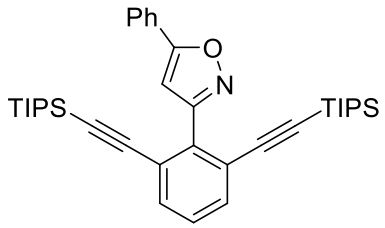


1a: (R = H; R^2 =Ph) **3a: 82%**

To a clean oven-dried 15 mL sealed tube equipped with a magnetic stir bar were sequentially added Aryl isoxazole derivatives **1a** (0.1 mmol, 1.0 equiv, 50 mg), $[RhCp^*Cl_2]_2$ (4 mol %, 2.5 mg), PivOH (20 mol %), $AgSbF_6$ (20 mol%). Then HFIP (1.5 mL) was added, followed by the addition of TIPS-EBX (3.0 equiv.) into the reaction mixture. The tube was tightly closed and placed in an oil bath at 90 ^oC and was stirred for 6 h according to the conversion estimated by TLC. After completion (monitoring by TLC), the reaction mixture was cooled to room temperature and quenched with saturated solution of $NaHCO_3$ and was diluted with EtOAc (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and filtered. Concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by column chromatography using silica gel (100-200 mess) using ethyl acetate/hexanes (9.8: 0.2) as eluent to afford the product **3a** in 82% yields. The di-alkynylated product was observed in 82% along with 7.0% mono- alkynylated product, and 24% (12 mg) of starting material was recovered.

6. Characterization of Products:

3-(2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3a)



Following GP-A, **3a** was isolated in 82% yield (108 mg, 0.185 mmol) from **1a** (50 mg, 0.226 mmol) and **2** (291 mg, 0.679 mmol); yellow solid; m.p. 50-52 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.7;

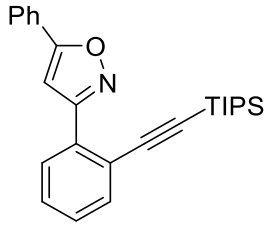
IR (ATR): 2941, 2891, 2864, 2150, 1456, 1232, 1072 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.76 (m, 2H), 7.55 (d, *J* = 8 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.34 (t, *J* = 8 Hz, 1H), 6.66 (s, 1H), 0.95 (s, 42H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 161.4, 135.0, 132.4, 129.7, 128.7, 127.7, 125.6, 124.3, 103.9, 101.6, 95.8, 18.3, 11.1.

HRMS (ESI-TOF): m/z calculated for $C_{37}H_{51}NOSi_2$ $[M+H]^+$ 582.3587 found 582.3583.

5-phenyl-3-(2-((triisopropylsilyl)ethynyl)phenyl)isoxazole (4a): Following GP-A, **4a** was isolated in 7% yield (6 mg, 0.015 mmol); from **1a** (50 mg, 0.226 mmol) and **2** (291 mg, 0.679 mmol); yellow liquid; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.7;



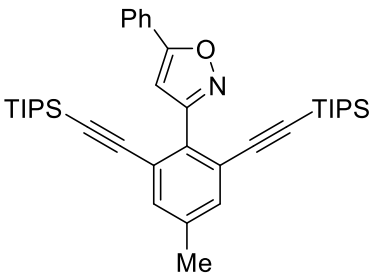
IR(ATR): 2942, 2891, 2864, 2153, 1563, 1459, 1397, 1219, 1017 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.82 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.66 – 7.64 (m, 1H), 7.50 – 7.40 (m, 5H), 7.30 (s, 1H), 1.08 (d, *J* = 3.6 Hz, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 162.6, 134.4, 130.9, 130.0, 129.3, 128.8, 128.7, 128.7, 127.6, 125.7, 122.2, 105.4, 100.6, 96.5, 18.6, 11.2.

HRMS (ESI-TOF): m/z calculated for $C_{26}H_{31}NOSi$ $[M+H]^+$ 402.2253 found 402.2231.

3-(4-methyl-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3b)



Following GP-A, **3b** was isolated in 97% yield (123 mg, 0.206 mmol) from **1b** (50 mg, 0.213 mmol) and **2** (273 mg, 0.638 mmol); yellow solid; m.p. 53-55 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

In gram scale, 2.33 gm of **3b** obtained from 1 gm starting material.

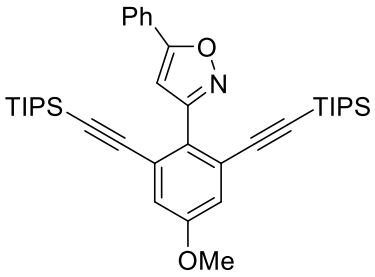
IR(ATR): 2942, 2864, 2156, 1593, 1462,1382, 1259,1027 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.49 – 7.42 (m, 3H), 7.37 (d, *J* = 0.9 Hz, 2H), 6.64 (s, 1H), 2.36 (s, 3H), 0.95 (s, 42H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 161.4, 138.9, 133.1, 132.3, 129.7, 128.7, 127.8, 125.6, 124.2, 104.3, 101.7, 95.2, 20.8, 18.4, 11.1.

HRMS (ESI-TOF): m/z calculated for $C_{38}H_{53}NOSi_2$ $[M+H]^+$ 596.3744 found 596.3746.

3-(4-methoxy-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3c)



Following GP-A, **3c** was isolated in 95% yield (116 mg, 0.189 mmol); from **1c** (50 mg, 0.199 mmol) and **2** (256 mg, 0.598 mmol); yellow solid; m.p. 65-67 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

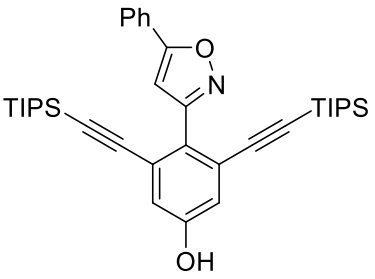
IR(ATR): 2941, 2891, 2864, 2149, 1588, 1461, 1381, 1326, 1155, 1005 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.49 – 7.42 (m, 3H), 7.07 (s, 2H), 6.63 (s, 1H), 3.86 (s, 3H), 0.95 (s, 42H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 161.3, 159.4, 129.7, 128.7, 127.8, 127.7, 125.6, 125.3, 118.2, 104.0, 101.9, 95.5, 55.6, 18.4, 11.1.

HRMS (ESI-TOF): m/z calculated for $C_{38}H_{53}NO_2Si_2$ $[M+H]^+$ 612.3693 found 612.3686.

4-(5-phenylisoxazol-3-yl)-3,5-bis((triisopropylsilyl)ethynyl)phenol (3d)



Following GP-A, **3d** was isolated in 47% yield (59 mg, 0.099 mmol); from **1d** (50 mg, 0.211 mmol) and **2** (271 mg, 0.633 mmol); yellow liquid; R_f (9.0:1.0 Hexane /Ethyl acetate) = 0.7;

IR(ATR): 3194, 2943, 2865, 2146, 1743, 1593, 1463, 1388, 1159, 1005 cm^{-1}.

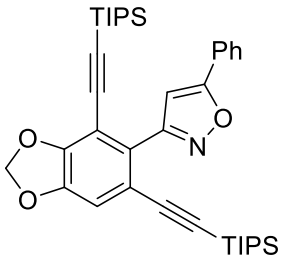
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.50 – 7.42 (m, 3H), 7.02 (s, 2H), 6.64 (s, 1H), 0.95 (s, 42H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 161.3, 155.8, 129.8, 128.80, 127.73, 127.46, 125.64, 125.44, 119.88, 103.79, 101.9, 95.6, 18.3, 11.1.

HRMS (ESI-TOF): m/z calculated for $C_{38}H_{53}NOSi_2$ $[M+H]^+$ 598.3537 found 598.3528.

3-(4,6-bis((triisopropylsilyl)ethynyl)benzo[d][1,3]dioxol-5-yl)-5-phenylisoxazole (3e)

Following GP-A, **3e** was isolated in 91% yield (103 mg, 0.165 mmol); from **1e** (50 mg, 0.181 mmol) and **2** (232 mg, 0.542 mmol); yellow solid; m.p. 72-74 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;



IR (ATR): 2942, 2891, 2864, 2156, 1574, 1460, 1420, 1230, 1071, 1028 cm^{-1}.

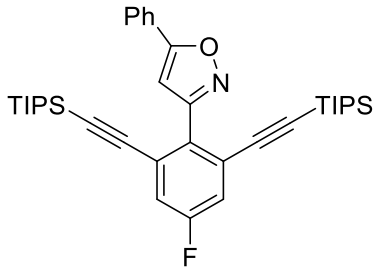
^1H NMR (300 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2H), 7.49– 7.42 (m, 3H), 6.96 (s, 1H), 6.63 (s, 1H), 6.11 (s, 2H), 0.95 (d, *J* = 3.9 Hz, 42H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 161.0, 149.7, 147.9, 129.7, 129.3, 128.7, 127.7, 125.6, 117.8, 111.9, 106.1, 104.1, 102.3, 101.8, 100.3, 97.5, 93.8, 18.4, 18.3, 11.1, 11.0.

HRMS (ESI-TOF): m/z calculated for $C_{38}H_{51}NO_3Si_2$ $[M+H]^+$ 626.3486 found 626.3472.

3-(4-fluoro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3f)

Following GP-A, **3f** was isolated in 71% yield (89 mg, 0.148 mmol); from **1f** (50 mg, 0.209 mmol) and **2** (269 mg, 0.628 mmol); orange solid; m.p. 55-57 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;



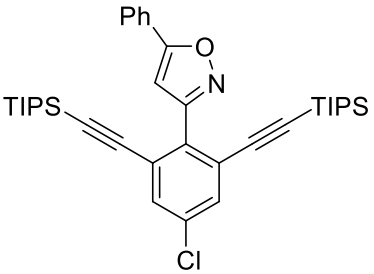
IR(ATR): 2942, 2891, 2864, 2164, 1589, 1578, 1461, 1381, 1135, 1005 cm^{-1} .

^1H NMR (300 MHz, $CDCl_3$) δ 7.81-7.77 (m, 2H), 7.53 – 7.46 (m, 3H), 7.29 (s, 2H), 6.66 (s, 1H), 0.97 (d, *J* = 1.8 Hz, 42H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 160.8, 129.9, 128.8, 127.5, 126.2, 126.1, 125.6, 119.6, 119.3, 102.8, 102.8, 101.6, 97.3, 18.3, 11.0.

HRMS (ESI-TOF): m/z calculated for $C_{37}H_{50}FNOSi_2$ $[M+H]^+$ 600.3493 found 600.3488.

3-(4-chloro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3g)



Following GP-A, **3g** was isolated in 74% yield (89 mg, 0.145 mmol); from **1g** (50 mg, 0.196 mmol) and **2** (252 mg, 0.588 mmol); yellow solid; m.p. 50-52 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

IR(ATR): 2943, 2864, 2159, 1574, 1463, 1378, 1004 cm^{-1}.

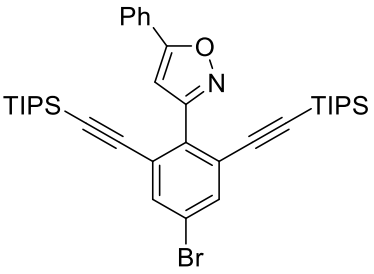
^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.75 (m, 2H), 7.52 (s, 2H), 7.47 – 7.44 (m, 3H), 6.64 (s, 1H), 0.95 (d, *J* = 2.4 Hz, 42H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 160.7, 134.7, 133.4, 132.1, 129.9, 128.8, 127.5, 125.8, 125.6, 102.6, 101.4, 97.6, 18.3, 11.0.

HRMS (ESI-TOF): m/z calculated for $C_{37}H_{50}ClNOSi_2$ $[M+H]^+$ 616.3198 found 616.3191.

3-(4-bromo-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3h)

For compound **3h** *we observe decomposition of product or fastest formation of self-cyclized product of TIPS-EBX with increase of temperature. In case of these substrate, we performed the reactions at room temperature which were more time consuming (almost 36 hours)*



3h was isolated in 68% yield (75 mg, 0.113 mmol); from **1h** (50 mg, 0.167 mmol) and **2** (215 mg, 0.502 mmol); yellow solid; m.p. 55-57 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

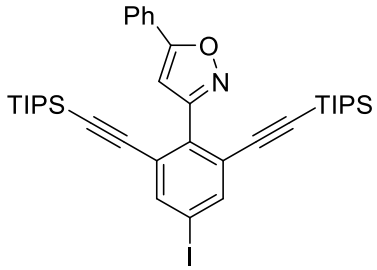
IR(ATR): 2943, 2890, 2864, 2157, 1573, 1557, 1462, 1379, 995 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.67 (s, 2H), 7.49 – 7.43 (m, 3H), 6.64 (s, 1H), 0.95 (d, *J* = 1.8 Hz, 42H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 160.7, 134.9, 133.9, 129.9, 128.8, 127.5, 125.9, 125.6, 122.4, 102.5, 101.4, 97.7, 18.3, 11.0.

HRMS (ESI-TOF): m/z calculated for $C_{37}H_{50}BrNOSi_2$ $[M+H]^+$ 660.2693 found 660.2695.

3-(4-iodo-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3i)



Following GP-A, **3i** was isolated in 81% yield (83 mg, 0.117 mmol); from **1i** (50 mg, 0.145 mmol) and **2** (186 mg, 0.434 mmol); yellow solid; m.p. 55-57 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

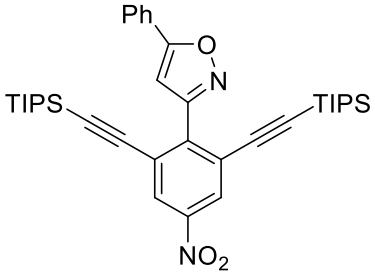
IR(ATR): 2943, 2864, 2153, 1574, 1552, 1461, 1379, 1219, 998 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.77-7.74 (m, 2H), 7.50 – 7.41 (m, 3H), 6.63 (s, 1H), 0.95 (s, 42H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 160.8, 140.7, 134.5, 129.9, 128.8, 127.5, 125.8, 125.6, 102.3, 101.3, 97.7, 93.7, 18.3, 11.1.

HRMS (ESI-TOF): m/z calculated for $C_{37}H_{50}INOSi_2$ $[M+ H]^+$ 708.2554 found 708.2525.

3-(4-nitro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3j)



Following GP-A, **3j** was isolated in 71% yield (50 mg, 0.080 mmol

); from **1j** (30 mg, 0.113 mmol) and **2** (145 mg, 0.338 mmol); yellow solid; m.p. 78-80 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

IR(ATR): 2943, 2924, 2866, 2162, 1530, 1462, 1348, 1003 cm^{-1}.

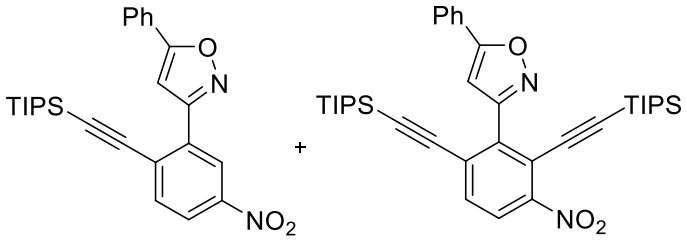
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 2H), 7.79 – 7.76 (m, 2H), 7.52-7.47 (m, 3H), 6.68 (s, 1H), 0.96 (d, *J* = 2.7 Hz, 42H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 160.2, 147.8, 140.6, 130.2, 128.9, 127.2, 126.4, 126.1, 125.6, 101.7, 101.0, 99.7, 18.3, 11.0.

HRMS (ESI-TOF): m/z calculated for $C_{37}H_{50}N_2O_3Si_2$ $[M+ Na]^+$ 649.3258 found 649.3257.

3-(5-nitro-2-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4k)

3-(3-nitro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3k)



Following GP-A, a mixture of **4k** and **3k** was isolated in 62 mg (**4k**:**3k** = 3:1; NMR ratio); from **1k** (50 mg, 0.221 mmol) and **2** (284 mg, 0.664 mmol); off-white solid; m.p. 80-82 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8; NMR yield: **4k** is 43% (43 mg, 0.096 mmol) and **3k** is 13% (19 mg (0.03 mmol). IR(ATR): 3108, 2963, 2925, 2864, 2158, 1731, 1522, 1459, 1348, 1068 cm^{-1}.

For 4k: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 2.4 Hz, 1H,), 8.25 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.84 – 7.77 (m, 3H), 7.54 – 7.46 (m, 3H), 7.27 (s, 1H), 1.31 – 1.01 (m, 21H).

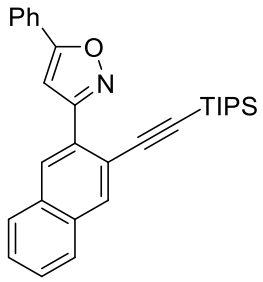
For 3k: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.54 – 7.46 (m, 1H), 7.35 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.27-7.22 (m, 3H) 6.65 (s, 1H), 1.31 – 1.01 (m, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 160.9, 147.1, 142.8, 135.2, 134.3, 132.4, 130.4, 129.0, 128.4, 127.1, 125.9, 125.7, 124.1, 123.7, 116.9, 103.5, 100.1, 18.5, 18.4, 11.2, 10.4.

HRMS (ESI-TOF): m/z calculated for $C_{26}H_{30}N_2O_3Si$ (**4k**) $[M+ H]^+$ 447.2104 found 447.2061

m/z calculated for $C_{37}H_{50}N_2O_3Si_2$ (**3k**) $[M+ H]^+$ 627.3438 found 627.3375.

5-phenyl-3-(3-((triisopropylsilyl)ethynyl)naphthalen-2-yl)isoxazole (4l)



Following GP-A, **4l** was isolated in 88% yield (77 mg, 0.171 mmol); from **1l** (50 mg, 0.194 mmol) and **2** (249 mg, 0.581 mmol); yellow solid; m.p. 52-54 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

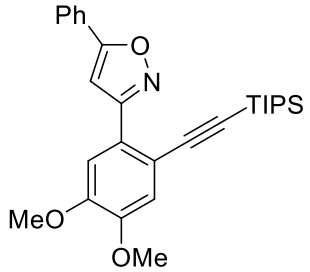
IR(ATR): 3055, 2941, 2890, 2841, 2146, 1572, 1507, 1448, 1169, 1064 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.17 (s, 1H), 7.91 – 7.82 (m, 4H), 7.58 – 7.42 (m, 5H), 7.28 (s, 1H), 1.10 (d, *J* = 3.0 Hz, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 162.8, 134.5, 133.5, 133.1, 132.5, 130.0, 128.8, 128.6, 128.4, 127.5, 127.5, 127.4, 127.3, 125.7, 119.4, 113.8, 105.6, 101.0, 95.9, 18.6, 11.3.

HRMS (ESI-TOF): m/z calculated for $C_{30}H_{33}NOSi$ $[M+ H]^+$ 452.2410 found 452.2421.

3-(4,5-dimethoxy-2-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4m)



Following GP-A, **4m** was isolated in 71% yield (58 mg, 0.126 mmol); from **1m** (50 mg, 0.178 mmol) and **2** (229 mg, 0.534 mmol); yellow liquid; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

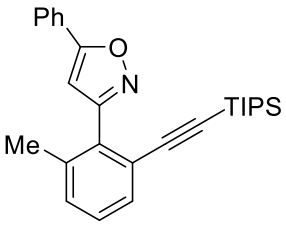
IR(ATR): 2926, 2864, 2145, 1601, 1521, 1493, 1362, 1261, 1218, 1001 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.51 – 7.45 (m, 3H), 7.42 (s, 1H), 7.38 (s, 1H), 7.04 (s, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 1.10 (d, *J* = 3.0 Hz, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 162.4, 149.6, 129.9, 128.8, 127.67, 125.71, 124.37, 122.32, 116.23, 114.74, 110.94, 105.72, 100.5, 94.9, 56.1, 56.0, 18.6, 11.3.

HRMS (ESI-TOF): m/z calculated for $C_{28}H_{35}NO_3Si$ $[M+H]^+$ 462.2464 found 462.2463.

3-(2-methyl-6-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4n)



Following GP-A, **4n** was isolated in 91% yield (81 mg, 0.194 mmol); from **1n** (50 mg, 0.213 mmol) and **2** (273 mg, 0.638 mmol); yellow liquid; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

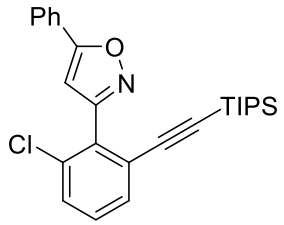
IR(ATR): 2942, 2891, 2864, 2149, 1592, 1573, 1383, 1257, 1017 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, J = 8.1, 2.1 Hz, 2H), 7.51 – 7.44 (m, 4H), 7.32-7.21 (m, 2H), 6.66 (s, 1H), 2.31 (s, 3H), 0.94 (s, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 162.1, 137.7, 131.8, 130.4, 130.3, 129.9, 128.8, 128.8, 127.61, 125.7, 124.0, 105.0, 101.6, 95.1, 20.4, 18.4, 11.1.

HRMS (ESI-TOF): m/z calculated for $C_{27}H_{33}NOSi$ $[M+H]^+$ 416.2410 found 416.2409.

3-(2-chloro-6-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4o)



Following GP-A, **4o** was isolated in 68% yield (35 mg, 0.080 mmol); from **1o** (30 mg, 0.118 mmol) and **2** (151 mg, 0.353 mmol); yellow liquid; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

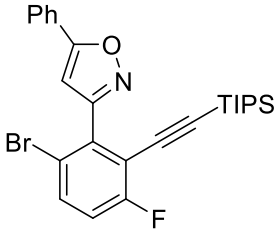
IR(ATR): 2942, 2864, 2165, 1592, 1574, 1448, 1382, 1219, 1073 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.53 – 7.45 (m, 5H), 7.34 (t, *J* = 8.0 Hz, 1H), 6.66 (s, 1H), 0.95 (d, *J* = 2.4 Hz, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 160.4, 134.2, 131.5, 131.2, 130.1, 130.0, 129.6, 128.9, 127.4, 126.1, 125.7, 103.5, 101.3, 96.9, 18.4, 11.0.

HRMS (ESI-TOF): m/z calculated for $C_{26}H_{30}ClNOSi$ $[M+H]^+$ 436.1863 found 436.1851.

3-(6-bromo-3-fluoro-2-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4p)



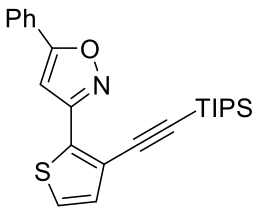
Following GP-A, **4p** was isolated in 92% yield (43 mg, 0.086 mmol); from **1p** (30 mg, 0.094 mmol) and **2** (121 mg, 0.283 mmol); yellow solid; m.p. 75-77 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;
IR(ATR): 2942, 2865, 2167, 1591, 1453, 1415, 1374, 1253, 1064 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.60 (dd, *J* = 9.0, 5.1 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.08 (t, *J* = 8.4 Hz, 1H), 6.64 (s, 1H), 0.95 (s, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 164.1, 161.2, 161.1, 160.7, 135.0, 133.4, 133.3, 130.2, 128.9, 127.2, 125.7, 117.8, 117.7, 117.6, 117.5, 115.2, 115.0, 103.5, 103.5, 100.9, 96.3, 18.3, 10.9.

HRMS (ESI-TOF): m/z calculated for $C_{26}H_{29}BrFNOSi$ $[M+H]^+$ 498.1264 found 498.1258.

5-phenyl-3-(3-((triisopropylsilyl)ethynyl)thiophen-2-yl)isoxazole (4s)



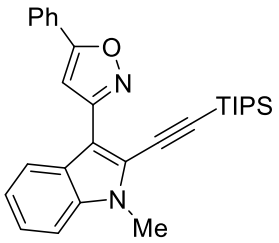
Following GP-A, **4s** was isolated in 53% yield (29 mg, 0.070 mmol); from **1s** (30 mg, 0.132 mmol) and **2** (170 mg, 0.396 mmol); yellow gummy; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;
IR(ATR): 2924, 2854, 2148, 1574, 1492, 1424, 1192, 1220, 1192, 981 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 2H), 7.53 (s, 1H), 7.51 – 7.45 (m, 3H), 7.31 (d, *J* = 5.2 Hz, 1H), 7.17 (d, *J* = 5.2 Hz, 1H), 1.17 (d, *J* = 4.0 Hz, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 157.8, 132.6, 131.9, 130.3, 128.9, 127.4, 126.2, 125.8, 122.3, 101.2, 98.0, 96.7, 18.7, 11.4.

HRMS (ESI-TOF): m/z calculated for $C_{24}H_{29}NOSSi$ $[M+H]^+$ 408.1817 found 408.1784.

3-(1-methyl-2-((triisopropylsilyl)ethynyl)-1H-indol-3-yl)-5-phenylisoxazole (4t)



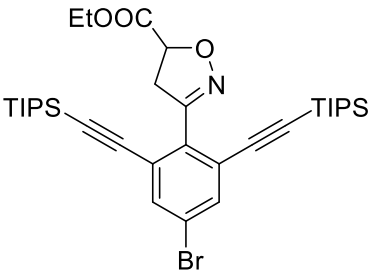
Following GP-A, **4t** was isolated in 56% yield (28 mg, 0.061 mmol); from **1t** (30 mg, 0.109 mmol) and **2** (141 mg, 0.328 mmol); yellow solid; m.p. 80-82 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;
IR(ATR): 2942, 2864, 2145, 1683, 1577, 1461, 1340, 1283, 1151, 1034 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.49 – 7.42 (m, 5H), 7.38 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.24 – 7.21 (m, 1H), 6.94 (s, 1H), 3.86 (s, 3H), 0.91 (d, *J* = 3.9 Hz, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 158.5, 137.5, 130.7, 129.7, 128.7, 128.1, 127.7, 125.8, 125.5, 121.9, 115.0, 110.4, 106.1, 104.8, 103.3, 95.5, 18.4, 11.2.

HRMS (ESI-TOF): m/z calculated for $C_{29}H_{34}N_2OSi$ $[M+H]^+$ 455.2519 found 455.2497.

Ethyl 3-(4-bromo-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-4,5-dihydroisoxazole-5-carboxylate (3u)



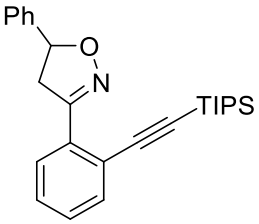
Following GP-A, **3u** was isolated in 44% yield (29 mg, 0.044 mmol); from **1u** (30 mg, 0.101 mmol) and **2** (129 mg, 0.302 mmol); yellow liquid; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8; IR(ATR): 2924, 2865, 2154, 1740, 1557, 1463, 1219, 997 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 2H), 5.08 (t, *J* = 11.1 Hz, 1H), 4.32 – 4.21 (m, 2H), 3.67 (d, *J* = 11.1 Hz, 2H), 1.34 (t, *J* = 2.7 Hz, 3H), 1.10 (d, *J* = 2.1 Hz, 42H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 154.4, 135.6, 132.4, 125.2, 122.5, 102.2, 98.2, 78.8, 61.8, 40.8, 18.5, 18.2, 11.1.

HRMS (ESI-TOF): m/z calculated for $C_{34}H_{52}BrNO_3Si_2$ $[M+ 2+H]^+$ 660.2727 found 660.2722.

5-phenyl-3-(2-((triisopropylsilyl)ethynyl)phenyl)-4,5-dihydroisoxazole (4v)



Following GP-A, **4v** was isolated in 53% yield (29 mg, 0.072 mmol); from **1v** (30 mg, 0.135 mmol) and **2** (173 mg, 0.404 mmol); yellow gummy; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

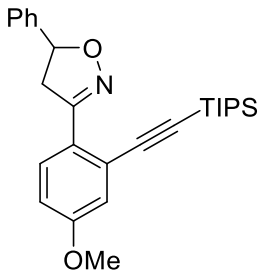
IR(ATR): 2922, 2852, 2151, 1462, 1219, 995 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 1H), 7.57 – 7.52 (m, 1H), 7.41 – 7.29 (m, 7H), 5.73 (dd, *J* = 10.8, 9.0 Hz, 1H), 4.15-4.06 (m, 1H), 3.74 (dd, *J* = 17.4, 9.3 Hz, 1H), 1.07 (s, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 140.7, 134.9, 131.3, 129.3, 128.6, 128.6, 128.4, 128.0, 125.7, 121.9, 105.6, 97.5, 83.4, 45.1, 18.6, 11.3.

HRMS (ESI-TOF): m/z calculated for $C_{26}H_{33}NOSi$ $[M+ H]^+$ 404.2410 found 404.2404.

3-(4-methoxy-2-((triisopropylsilyl)ethynyl)phenyl)-5-phenyl-4,5-dihydroisoxazole (4w)



Following GP-A, **4w** was isolated in 55% yield (28 mg, 0.065 mmol); from **1w** (30 mg, 0.119 mmol) and **2** (152 mg, 0.356 mmol); yellow gummy; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

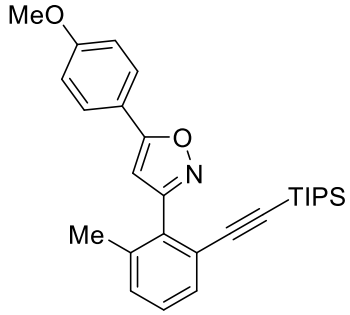
IR(ATR): 2925, 2864, 2150, 1601, 1463, 1345, 1286, 1220, 1165, 1049 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.0 Hz, 1H), 7.40 – 7.30 (m, 5H), 7.01 (d, *J* = 2.7 Hz, 1H), 6.91 (dd, *J* = 9.0, 3.0 Hz, 1H), 5.70 (dd, *J* = 10.8, 9.0 Hz, 1H), 4.08 (dd, *J* = 17.1, 10.5 Hz, 1H), 3.83 (s, 3H), 3.71 (dd, *J* = 17.1, 9.0 Hz, 1H), 1.06 (d, J = 2.4 Hz, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 156.6, 140.9, 130.0, 128.6, 128.0, 125.7, 124.0, 123.1, 119.2, 115.3, 105.5, 97.3, 83.1, 55.4, 45.3, 18.6, 11.3.

HRMS (ESI-TOF): m/z calculated for $C_{27}H_{35}NO_2Si$ $[M+H]^+$ 434.2515 found 434.2511.

5-(4-methoxyphenyl)-3-(2-methyl-6-((triisopropylsilyl)ethynyl)phenyl)isoxazole (4x)



Following GP-A, **4x** was isolated in 94% yield (47 mg, 0.106 mmol); from **1x** (30 mg, 0.113 mmol) and **2** (145 mg, 0.339 mmol); yellow gummy; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

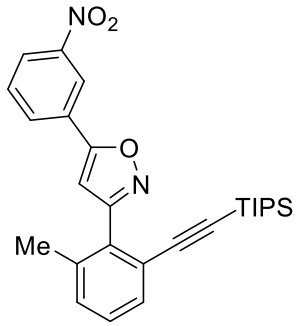
IR(ATR): 2941, 2864, 2149, 1615, 1514, 1460, 1383, 1304, 1253, 1175, 996 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 7.48 – 7.45 (m, 1H), 7.33-7.28 (m, 2H), 7.03 – 6.99 (m, 2H), 6.55 (s, 1H), 3.90 (s, 3H), 2.32 (s, 3H), 0.97 (s, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 162.1, 160.9, 137.7, 132.0, 130.4, 130.2, 128.7, 127.2, 124.0, 120.5, 114.2, 105.1, 100.2, 95.0, 55.3, 20.4, 18.4, 11.1.

HRMS (ESI-TOF): m/z calculated for $C_{28}H_{35}NO_2Si$ $[M+H]^+$ 446.2515 found 446.2479.

3-(2-methyl-6-((triisopropylsilyl)ethynyl)phenyl)-5-(3-nitrophenyl)isoxazole (4y)



Following GP-A, **4y** was isolated in 81% yield (40 mg, 0.087 mmol); from **1y** (30 mg, 0.107 mmol) and **2** (138 mg, 0.321 mmol); yellow gummy; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.8;

IR(ATR): 2942, 2891, 2864, 2149, 1532, 1461, 1833, 1348, 1220, 1065 cm^{-1}.

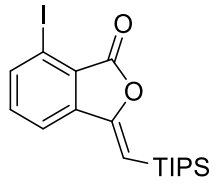
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (t, *J* = 1.8 Hz, 1H), 8.33-8.29 (m, 1H), 8.17-8.13 (m, 1H), 7.70 (t, *J* = 8.1 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.34 – 7.27 (m, 2H), 6.85 (s, 1H), 2.32 (s, 3H), 0.94 (d, *J* = 1.2 Hz, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 162.4, 148.6, 137.7, 131.1, 130.9, 130.6, 130.4, 130.2, 129.1, 129.0, 124.4, 123.9, 120.6, 104.9, 103.5, 95.4, 20.4, 18.4, 11.1.

HRMS (ESI-TOF): m/z calculated for $C_{27}H_{32}N_2O_3Si$ $[M+H]^+$ 461.2260 found 461.2255.

(Z)-7-iodo-3-((triisopropylsilyl)methylene)isobenzofuran-1(3H)-one (5)

Following the procedure enlisted in table1, entry 10, **5** was isolated in 67% yield (71 mg, 0.166 mmol); **2** (107 mg, 0.249 mmol); white solid; m.p. 80-82 °C; R_f (9.5:0.5 Hexane /Ethyl acetate) = 0.7;



IR(ATR): 2939, 2865, 1785, 1636, 1573, 1458, 1238, 1070 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 5.63 (s, 1H), 1.40-1.31 (m, 3H), 1.10 (d, *J* = 7.2 Hz, 18H).

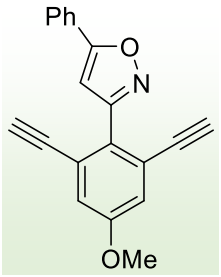
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 154.3, 141.3, 141.0, 134.8, 126.1, 120.5, 101.4, 91.2, 18.7, 11.5.

HRMS (ESI-TOF): m/z calculated for $C_{18}H_{25}IO_2Si$ $[M+H]^+$ 429.0747 found 429.0717.

7. Product Modification:

Procedure for the Synthesis of 3-(2,6-diethynyl-4-methoxyphenyl)-5-phenylisoxazole (6) (via deprotection of TIPS Group). By following reported procedure**,** [13, 14]

3c was dissolved in anhydrous THF (1 equivalent, 0.196 mmol), followed by the addition of 2 equivalents of tetrabutylammonium fluoride (TBAF) dropwise to the reaction mixture in an ice bath, the reaction was left to stir at room temperature for 30 minutes. On completion (monitoring by TLC), the reaction mixture was diluted with saturated NH_4Cl (aq.) and the organic phase was separated using Et_2O, dried over anhydrous Na_2SO_4, and filtered. Under lower pressure, the solvent was eliminated. The residue afforded a yellow solid **6** after purified by column chromatography on silica gel.



6 was isolated in 94% yield (55 mg, 0.184 mmol); yellow solid; m.p. 98 °C; R_f (9.0:1.0 Hexane /Ethyl acetate) = 0.5;

IR(ATR): 3278, 3227, 2929, 1611, 1587, 1563, 1488, 1444, 1381, 1316, 1149, 1045 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.52 – 7.44 (m, 3H), 7.16 (s, 2H), 6.77 (s, 1H), 3.86 (s, 3H), 3.11 (s, 2H).

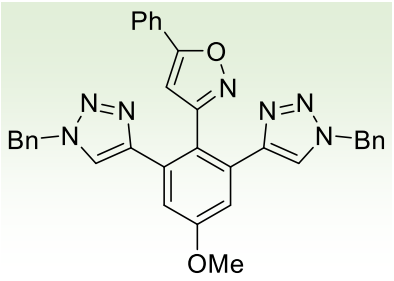
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 160.7, 159.4, 130.0, 128.9, 127.6, 127.1, 125.8, 123.9, 119.5, 101.5, 81.5, 81.1, 55.6.

HRMS (ESI-TOF): m/z calculated for $C_{20}H_{13}NO_2$ $[M+H]^+$ 300.1025 found 300.1024

Procedure for the Synthesis of 3-(2,6-bis(1-benzyl-1H-1,2,3-triazol-4-yl)-4-methoxyphenyl)-5-phenylisoxazole (7). By following reported procedure**,** [15]

The prepared terminal alkyne **6** (1 equivalent, 0.167 mmol) was dissolved in DMF (1 ml) in a clean oven-dried sealed tube and allowed to stirred at 60 °C after adding 10 mol% CuI and 2 equivalents BnN_3. On completion after 3 h (monitored by TLC), it was diluted with cold water (10 ml) and extracted with DCM. The combined organic part was dried over anhydrous Na_2SO_4, and filtered. Under lower pressure, the solvent was eliminated. The residue afforded

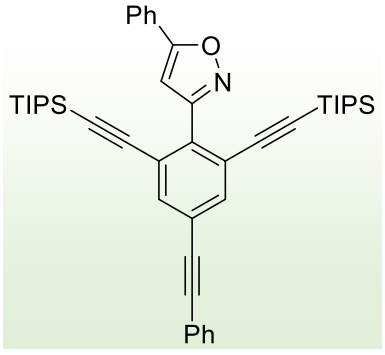
a brown solid **7** after purified by column chromatography on silica gel.



7 was isolated in 47% yield (44 mg, 0.078 mmol); brown solid; m.p. 145 °C; R_f (9.5:0.5 MeOH /DCM) = 0.4;
IR(ATR): 3378, 2924, 2852, 1605, 1486, 1455, 1385, 1352, 1247, 1165, 1049 cm^{-1}.
^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.59 – 7.55 (m, 2H), 7.53 – 7.49 (m, 3H), 7.04-6.70 (m, 12H), 6.05 (s, 1H), 5.37 (s, 4H), 3.96 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 162.9, 160.7, 145.5, 134.1, 132.6, 130.5, 128.9, 128.8, 128.5, 127.7, 126.7, 125.8, 122.5, 117.1, 114.1, 101.1, 55.7, 54.0.
HRMS (ESI-TOF): m/z calculated for $C_{34}H_{27}N_7O_2$ $[M+H]^+$ 566.2304 found 566.2311.

Procedure for the Synthesis of 5-phenyl-3-(4-(phenylethynyl)-2,6-bis((triisopropylsilyl)ethynyl)phenyl)isoxazole (8). (*via* Sonogashira Coupling) By following reported procedure**, [16]**

1 equivalent (0.042 mmol) **3i** was dissolved in anhydrous THF, followed by the sequential addition of 1.2 equivalents (0.051 mmol) phenyl acetylene, 0.1 ml Et_3N, 2 mol% of each $Pd(PPh_3)_2Cl_2$ and CuI. After stirring the reaction at room temperature for 2 h, the reaction mixture was diluted with water and the organic phase was separated using DCM (10 ml x 3), dried over anhydrous Na_2SO_4, and filtered. Under lower pressure, the solvent was eliminated. The residue afforded a yellow solid **8** after purified by column chromatography on silica gel.

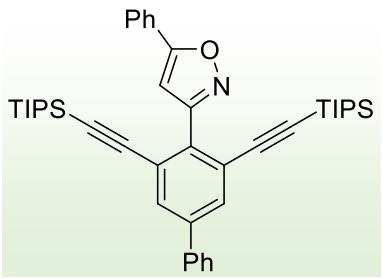


8 was isolated in 80% yield (23 mg, 0.034 mmol); yellow solid; m.p. 60 °C; R_f (9.9:0.1 Hexane /Ethyl acetate) = 0.8;
IR(ATR): 2142, 2863, 2156, 2116, 1584, 1490, 1462, 1383, 1221, 1006 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.70 (s, 2H), 7.57 – 7.53 (m, 2H), 7.50 – 7.44 (m, 3H), 7.38 – 7.36 (m, 3H), 6.68 (s, 1H), 0.97 (s, 42H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 161.0, 135.0, 134.3, 131.7, 129.8, 128.8, 128.7, 128.4, 127.6, 125.6, 124.7, 124.5, 122.5, 103.2, 101.5, 96.6, 91.3, 87.3, 18.3, 11.1.
HRMS (ESI-TOF): m/z calculated for $C_{45}H_{55}NOSi_2$ $[M+H]^+$ 682.3900 found 682.3896

Procedure for the Synthesis of 3-(3,5-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-yl)-

5-phenylisoxazole (9). (via Suzuki Coupling) By following reported procedure**,** [17]

In a clean, over-dried sealed tube, **3i** (1 equivalent, 0.042 mmol), phenyl boronic caid (1.2 equivalents, 0.051 mmol), 2.5 equivalents K_2CO_3, 1 mol% $Pd(PPh_3)_4$ was dissolved in a mixture of 1.5 ml THF:H_2O (2:1). After completion (monitored by TLC), it was diluted with water and the organic phase was separated using DCM (10 ml x 3), dried over anhydrous Na_2SO_4, and filtered. Under lower pressure, the solvent was eliminated. The residue afforded a viscous off-white liquid **9** after purified by flash column chromatography on silica gel.

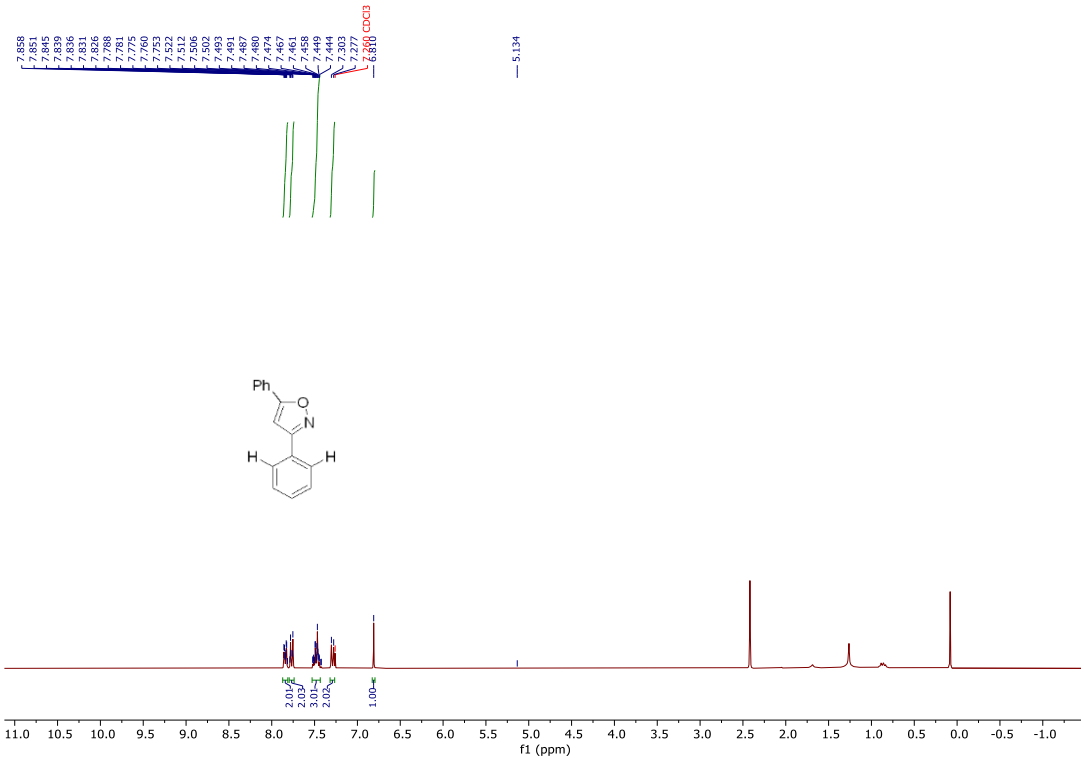


9 was isolated in 97% yield (27 mg, 0.041 mmol); viscous off-white liquid; R_f (9.9:0.1 Hexane /Ethyl acetate) = 0.7;
IR(ATR): 2942, 2892, 2865, 2154, 1591, 1462, 1383, 1195, 1072, 1004 cm^{-1}.
^1H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.75 (s, 2H), 7.65 – 7.62 (m, 2H), 7.51 – 7.40 (m, 6H), 6.69 (s, 1H), 0.97 (d, *J* = 1.5 Hz, 42H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 161.3, 142.1, 139.1, 133.6, 131.1, 129.8, 128.9, 128.8, 128.1, 127.7, 127.1, 125.6, 124.8, 104.0, 101.6, 95.9, 18.4, 11.1.
HRMS (ESI-TOF): m/z calculated for $C_{43}H_{55}NOSi_2$ $[M+H]^+$ 658.3900 found 658.3892.

8. Mechanistic Study:

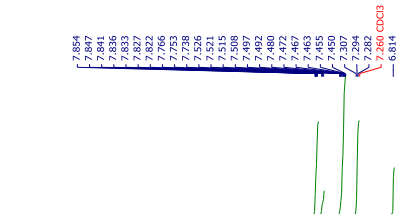
A. **Procedure for H/D-Exchange experiment without TIPS-EBX in D_2O**:

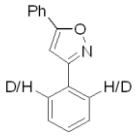
To a clean oven-dried 15 mL sealed tube equipped with a magnetic stir bar were sequentially added isoxazole derivatives (0.2 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (4 mol %, 5.25 mg), $AgSbF_6$ (20 mol %), then DCE (1.5 mL) was added, followed by the addition of D_2O (10 equiv.) into the reaction mixture. The reaction carried out under nitrogen atmosphere, and the reaction tube was flushed with nitrogen. The tube was tightly closed and the reaction was monitored from room temperature to 90 °C for 24 h according to the conversion estimated by TLC. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite and washed with DCM (20 mL x 3). The filtrate was concentrated and the residue was taken up for NMR analysis. The amount of deuterium incorporation was determined by ^1H NMR analysis.



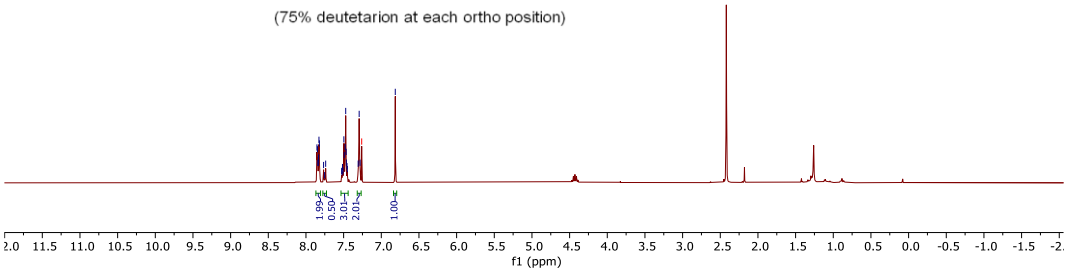
B. **Procedure for H/D-Exchange experiment with TIPS-EBX in D_2O**:

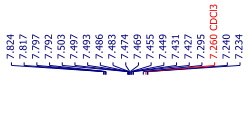
To a clean oven-dried 15 mL sealed tube equipped with a magnetic stir bar were sequentially added isoxazole derivatives (0.1 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (4 mol %, 2.63 mg), $AgSbF_6$ (20 mol %), then DCE (1.5 mL) was added, followed by the addition of D_2O (10 equiv.) into the reaction mixture. TIPS-EBX (3.0 equiv.) was then added into the reaction mixture. The reaction carried out under nitrogen atmosphere, and the reaction tube was flushed with nitrogen. The tube was tightly closed and the reaction was monitored from room temperature to 90 °C for 24 h according to the conversion estimated by TLC. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite and washed with DCM (20 mL x 3). The filtrate was concentrated and the residue was taken up for NMR analysis. The amount of deuterium incorporation was determined by ^1H NMR analysis.

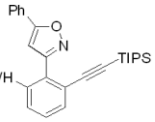




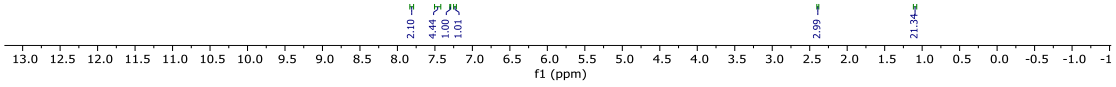
(75% deutetarion at each ortho position)

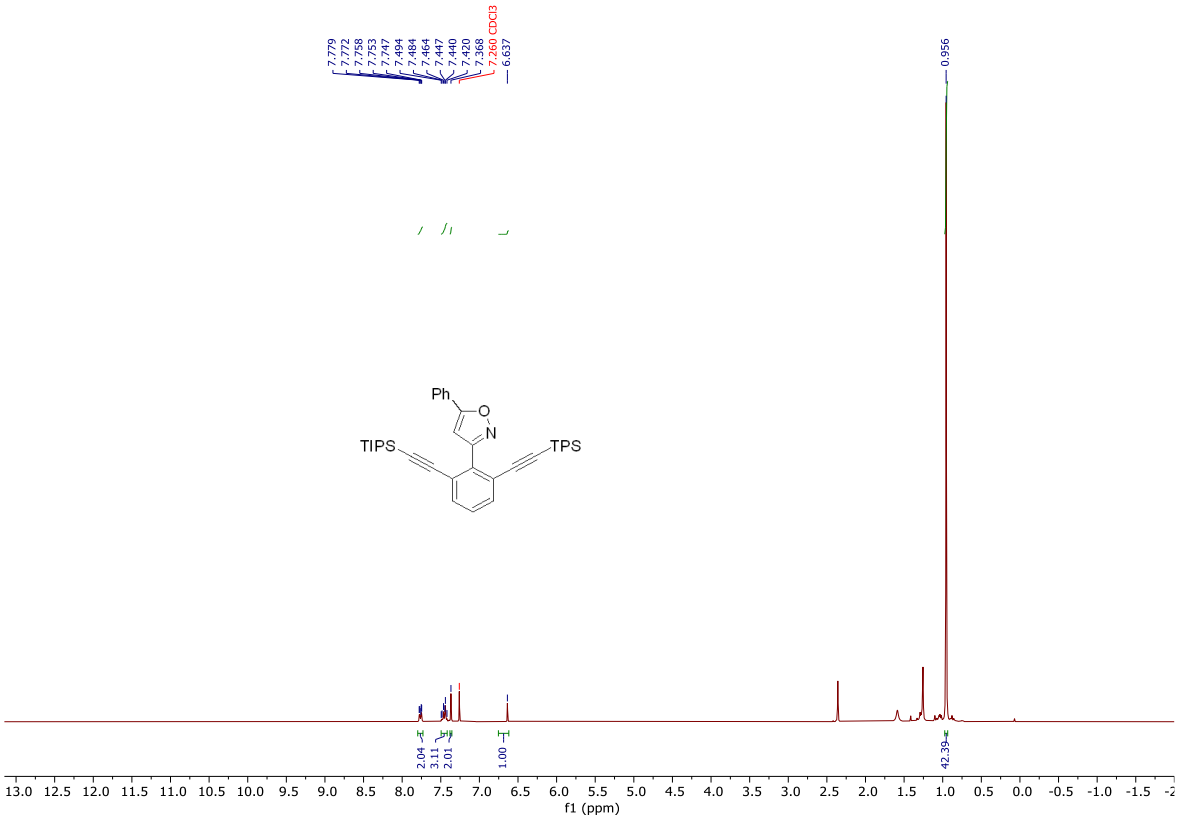




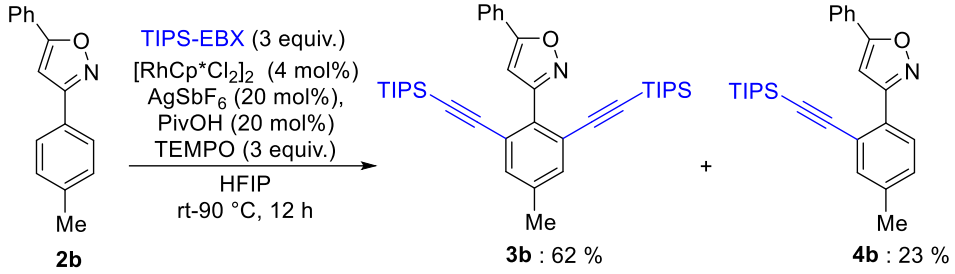


(52% deutetarion at ortho position)





C. **Procedure for radical inhibition experiment with TEMPO**:



To a clean oven-dried 15 mL sealed tube equipped with a magnetic stir bar were sequentially added isoxazole derivatives (0.02 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (4 mol %, 0.53 mg), $AgSbF_6$ (20 mol %), PivOH (20 mol%), then HFIP (1.5 mL) was added, followed by the addition of TIPS-EBX (3.0 equiv.) into the reaction mixture. TEMPO (3.0 equiv.) was then added into the reaction mixture. The reaction carried out under nitrogen atmosphere, and the reaction tube was flushed with nitrogen. The tube was tightly closed and the reaction was monitored from room temperature to 90 °C for 12 h according to the conversion estimated by TLC. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite and washed with DCM (20 mL x 3). The filtrate was concentrated and the residue was taken up for NMR analysis. The desired products 3b and 4b were obtained in 62% and 23% yields respectively.

9. References:

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10. Crystallographic data of compound 3b (CCDC 2340037):

Bond precision: C-C = 0.0179 A Wavelength=0.71073

Cell: a=17.157(4) b=13.818(3) c=17.350(3)
alpha=90 beta=111.124(5) gamma=90
Temperature: 299 K

	Calculated	Reported
Volume	3836.9(14)	3836.8(13)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C38 H53 N O Si2	C38 H53 N O Si2
Sum formula	C38 H53 N O Si2	C38 H53 N O Si2
Mr	595.99	595.99
Dx,g cm-3	1.032	1.032
Z	4	4
Mu (mm-1)	0.119	0.119
F000	1296.0	1296.0

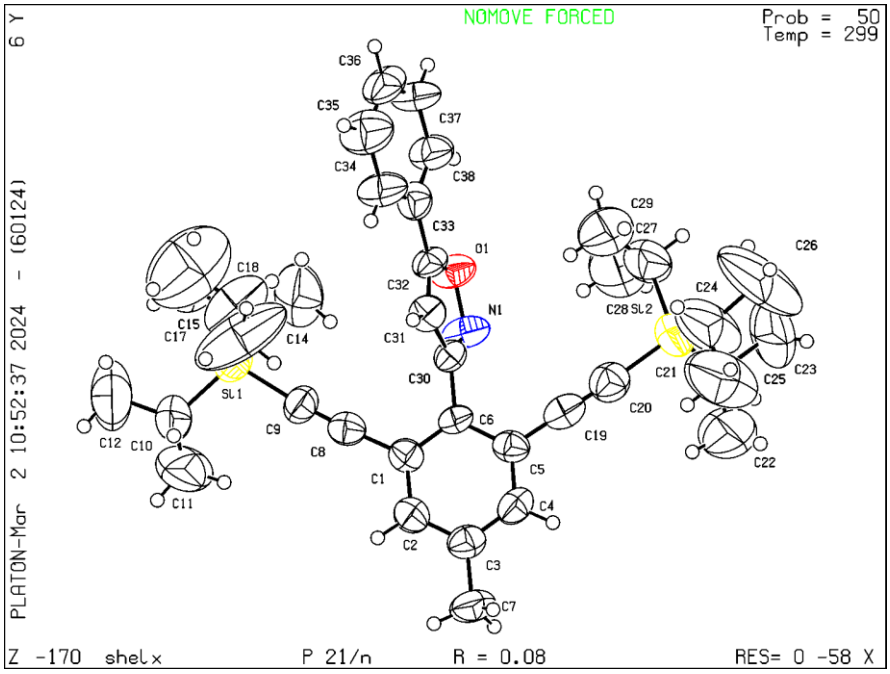
F000′	1297.05	
h,k,lmax	15,12,15	15,12,14
Nref	3096	2713
Tmin,Tmax	0.983,0.991	0.983,0.991
Tmin′	0.981	

Correction method= # Reported T Limits: Tmin=0.983 Tmax=0.991 AbsCorr = MULTI-SCAN

Data completeness= 0.876 Theta(max)= 19.035

R(reflections)= 0.0817(1806) wR2 (reflections) = 0.2086(2713)

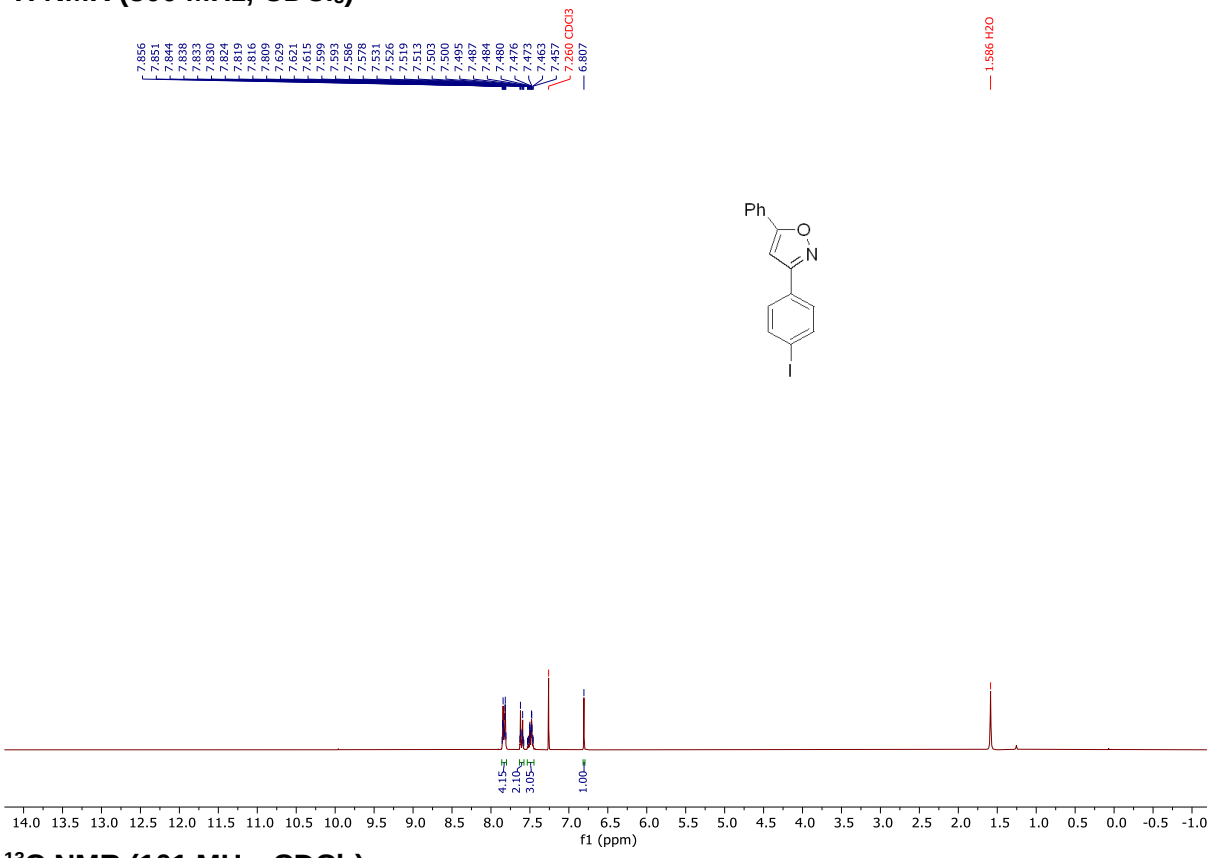
S = 1.060 Npar= 379



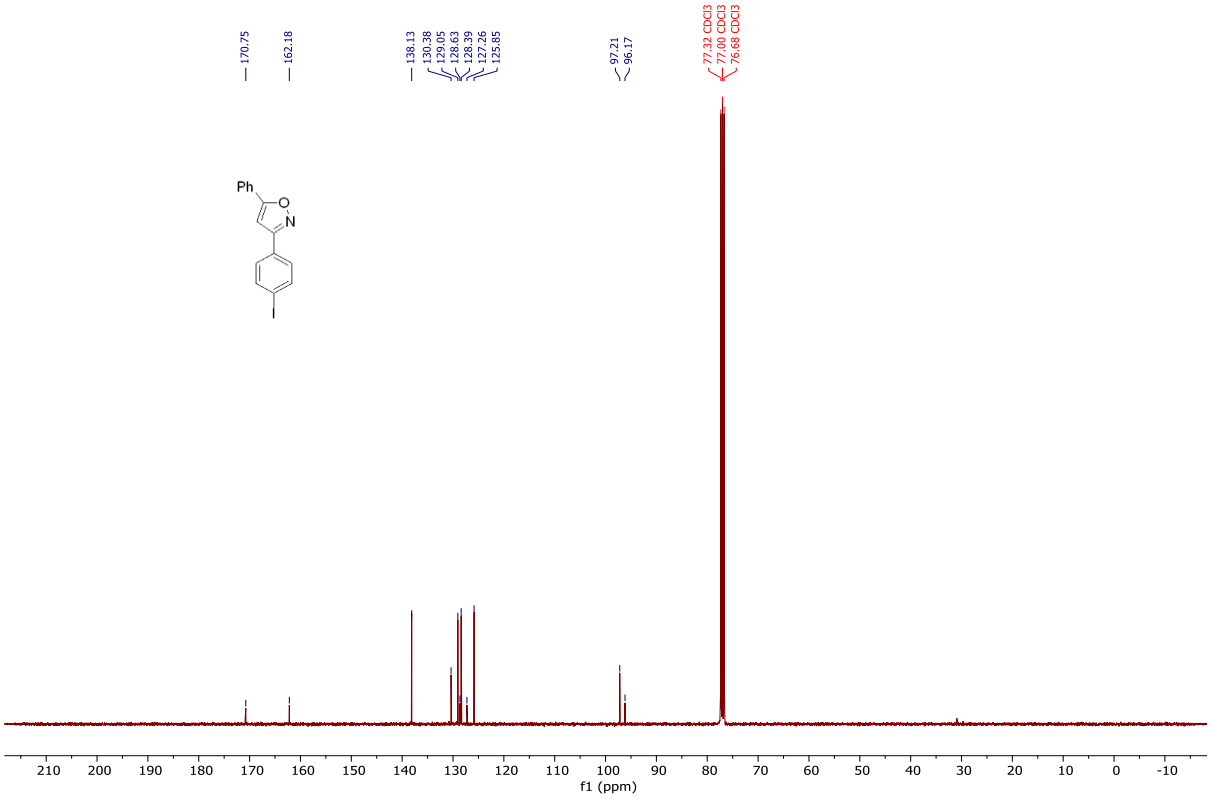
11. Copies of NMR-Spectra:

3-(4-iodophenyl)-5-phenylisoxazole (1i)

^{1}H NMR (300 MHz, $CDCl_3$)

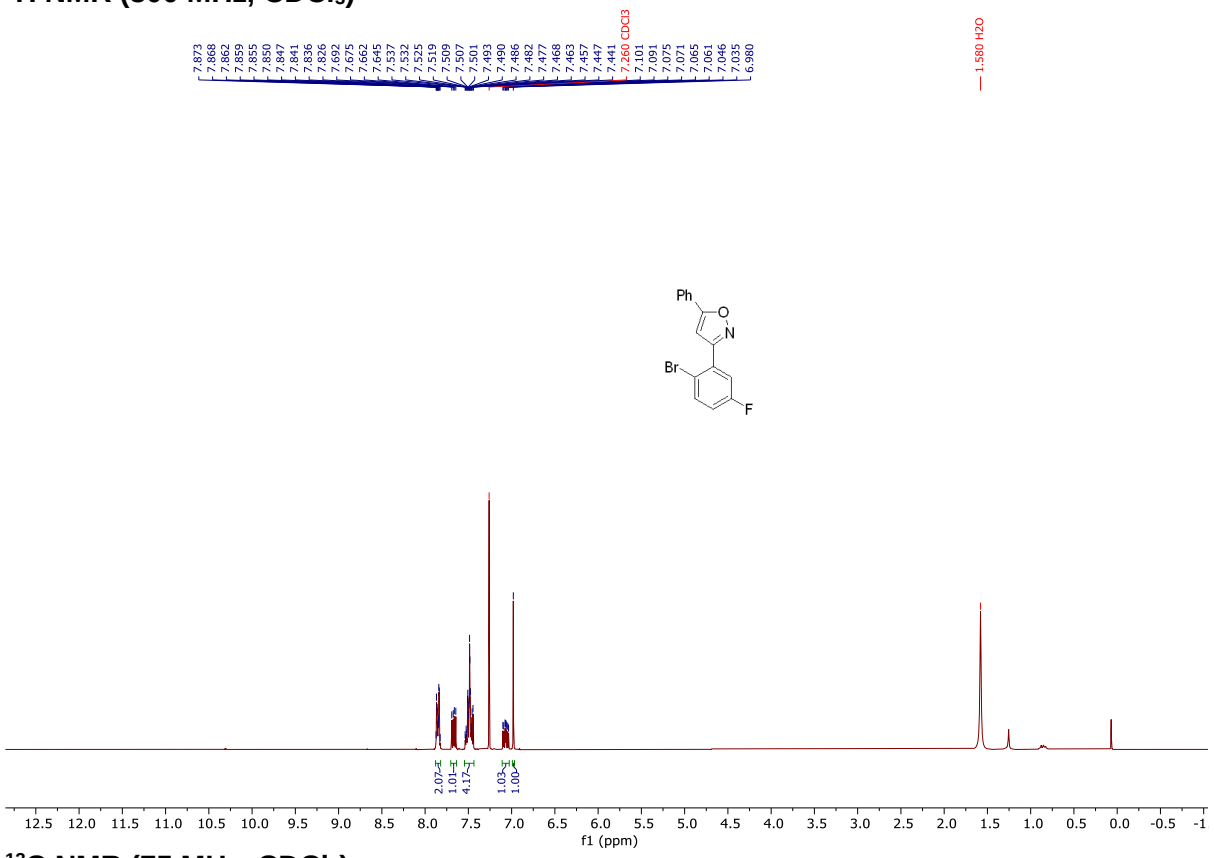


^{13}C NMR (101 MHz, $CDCl_3$)

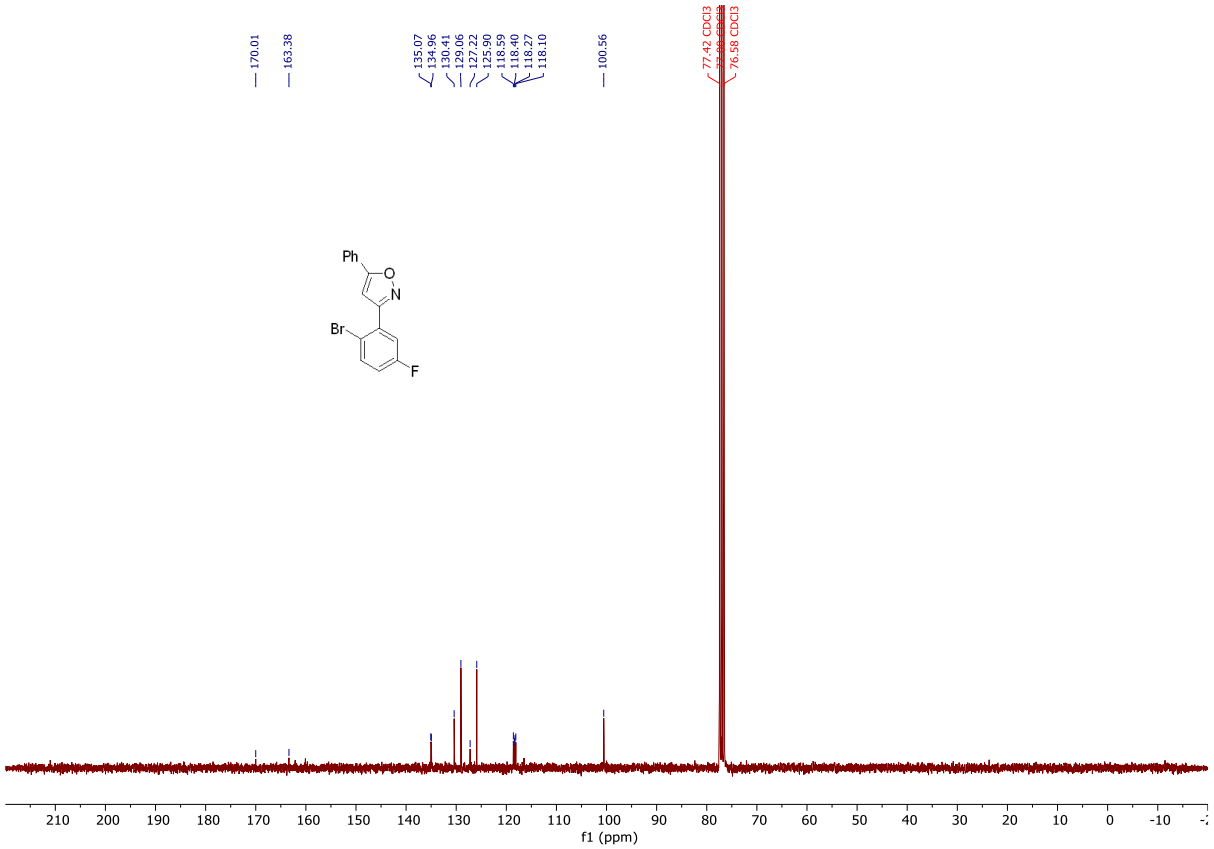


3-(2-bromo-5-fluorophenyl)-5-phenylisoxazole (1p)

^{1}H NMR (300 MHz, $CDCl_3$)

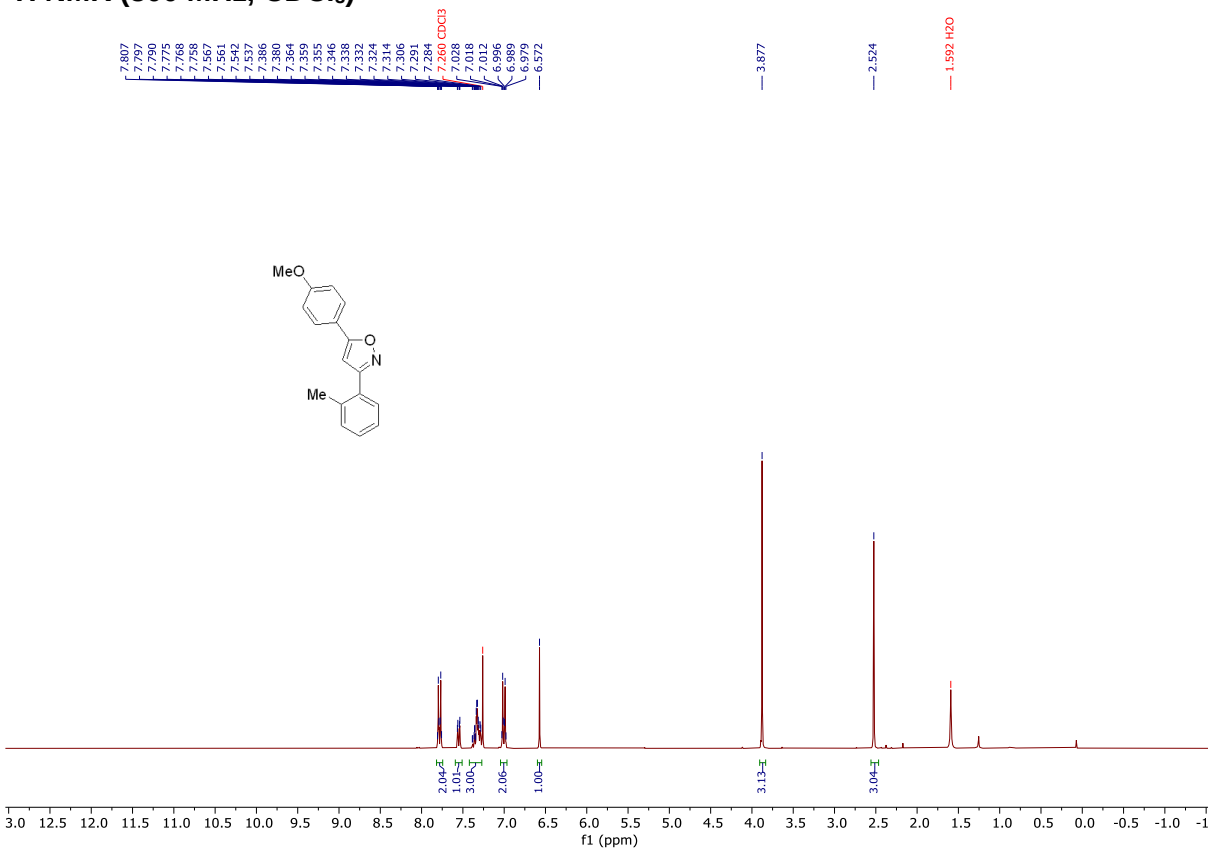


^{13}C NMR (75 MHz, $CDCl_3$)

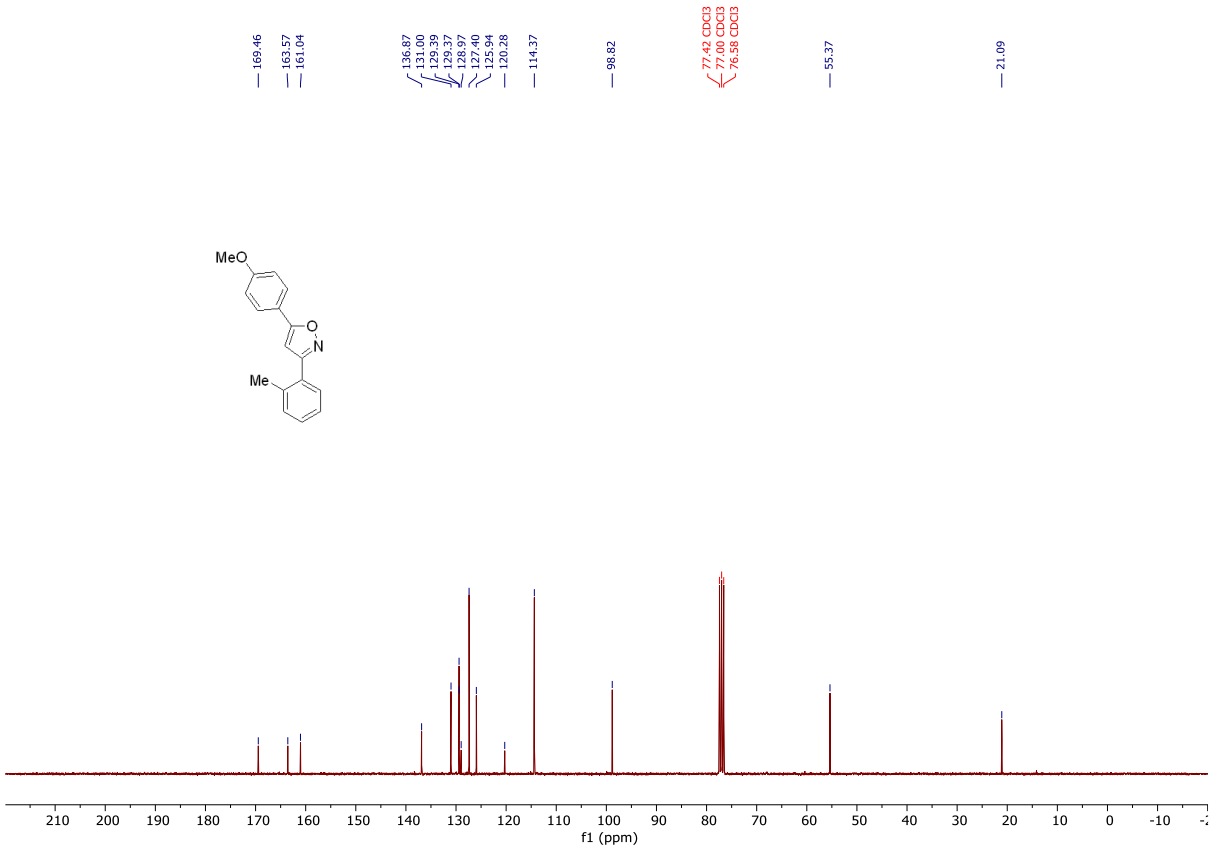


5-(4-methoxyphenyl)-3-(o-tolyl)isoxazole (1x)

^{1}H NMR (300 MHz, $CDCl_3$)

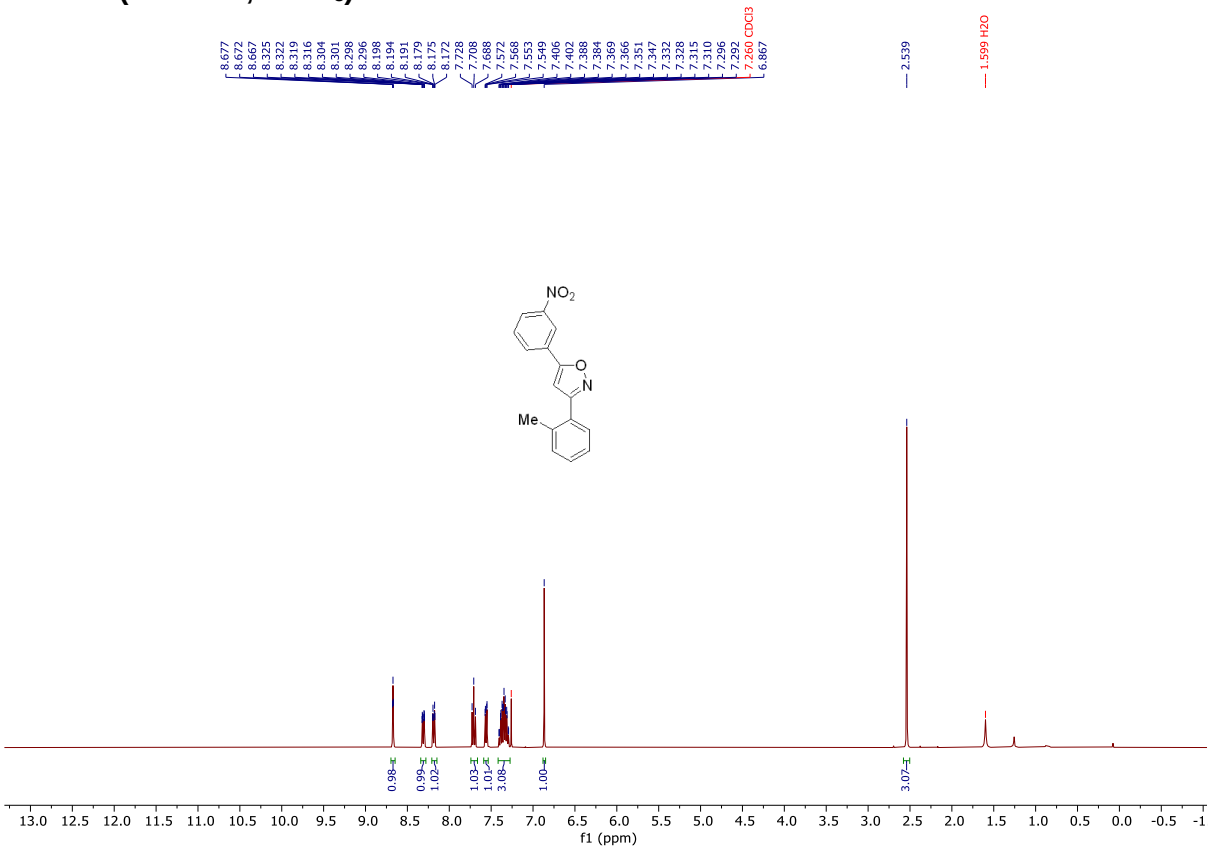


^{13}C NMR (75 MHz, $CDCl_3$)

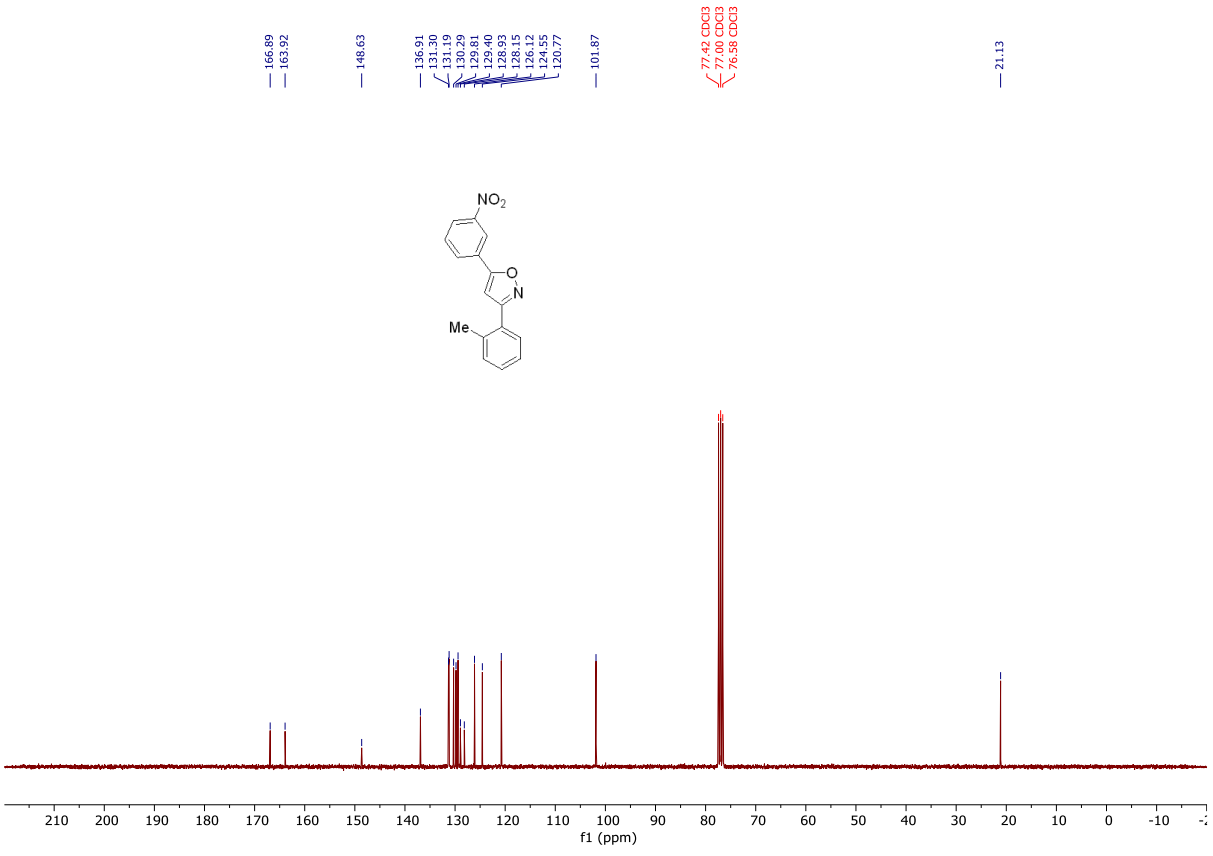


5-(3-nitrophenyl)-3-(o-tolyl)isoxazole (1y)

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

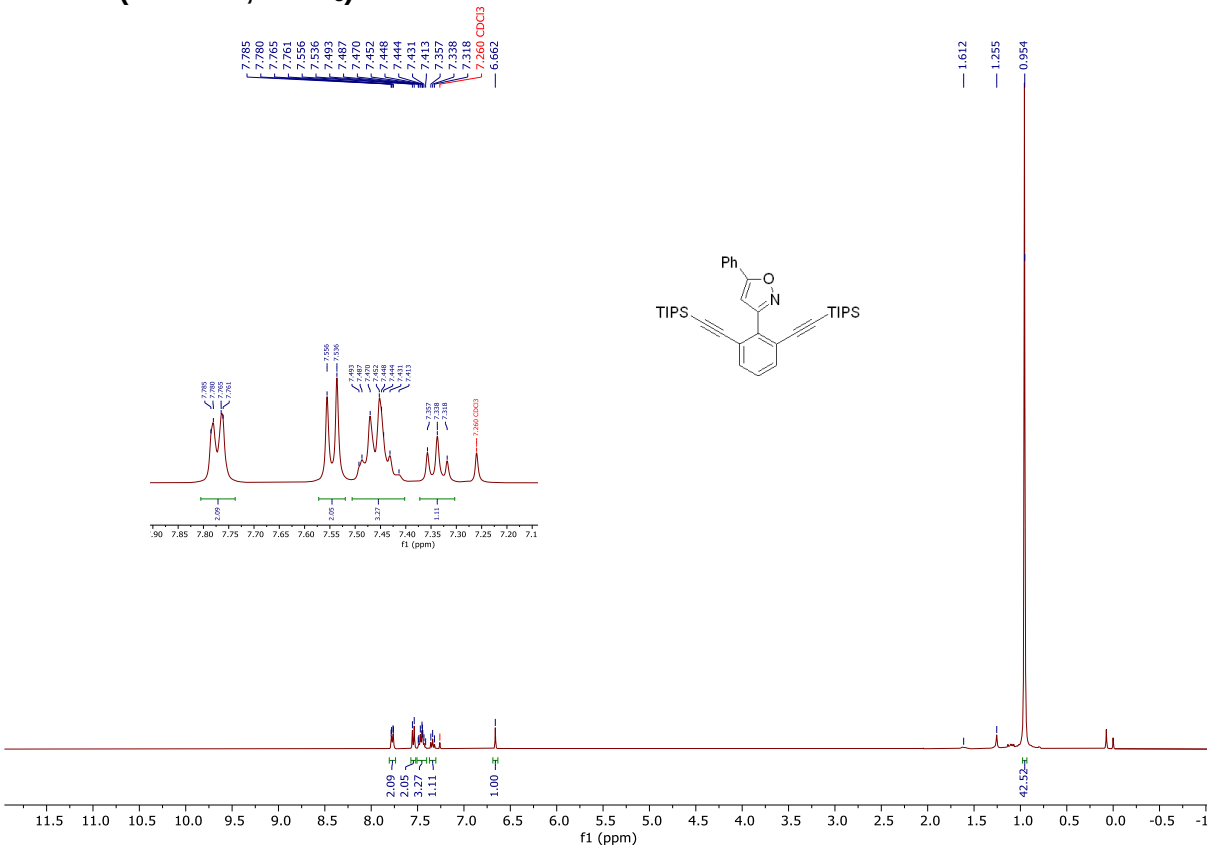


^{13}C NMR (75 MHz, $CDCl_3$)

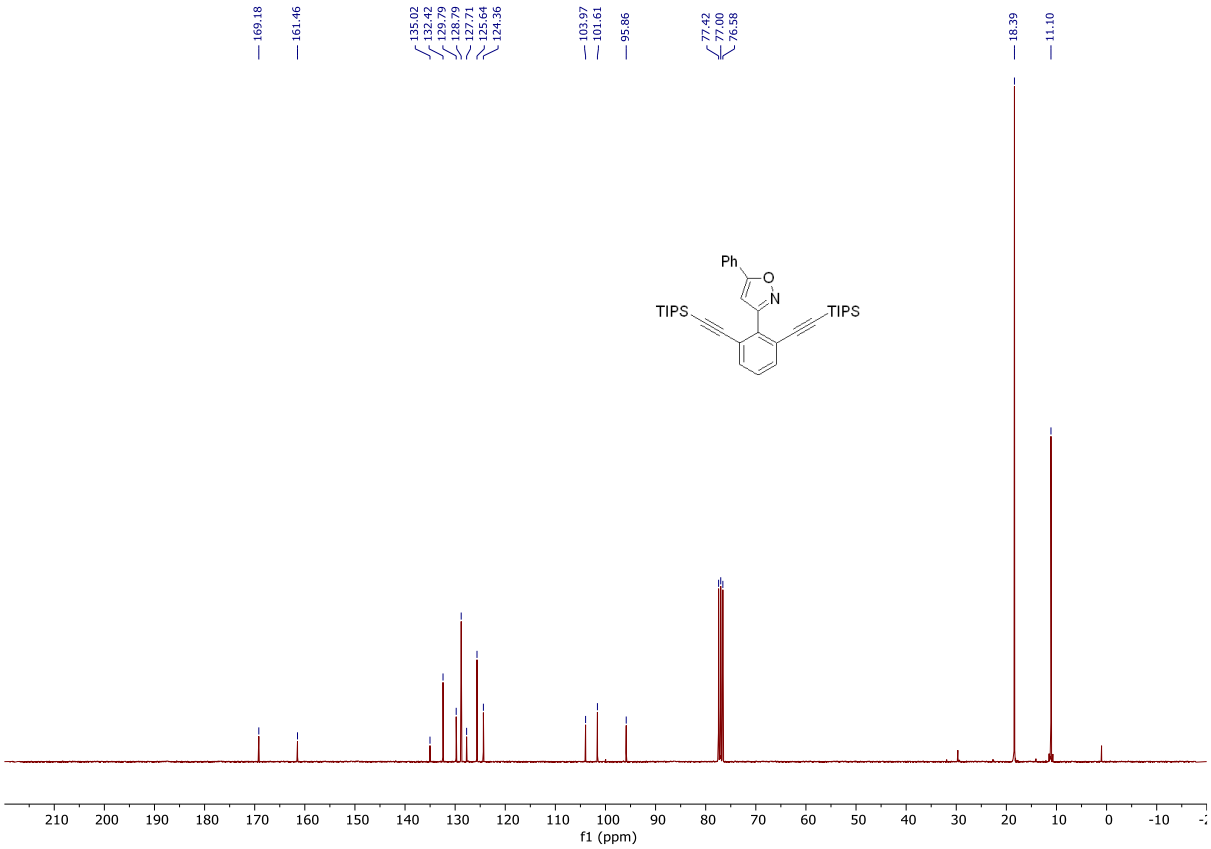


3-(2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3a)

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

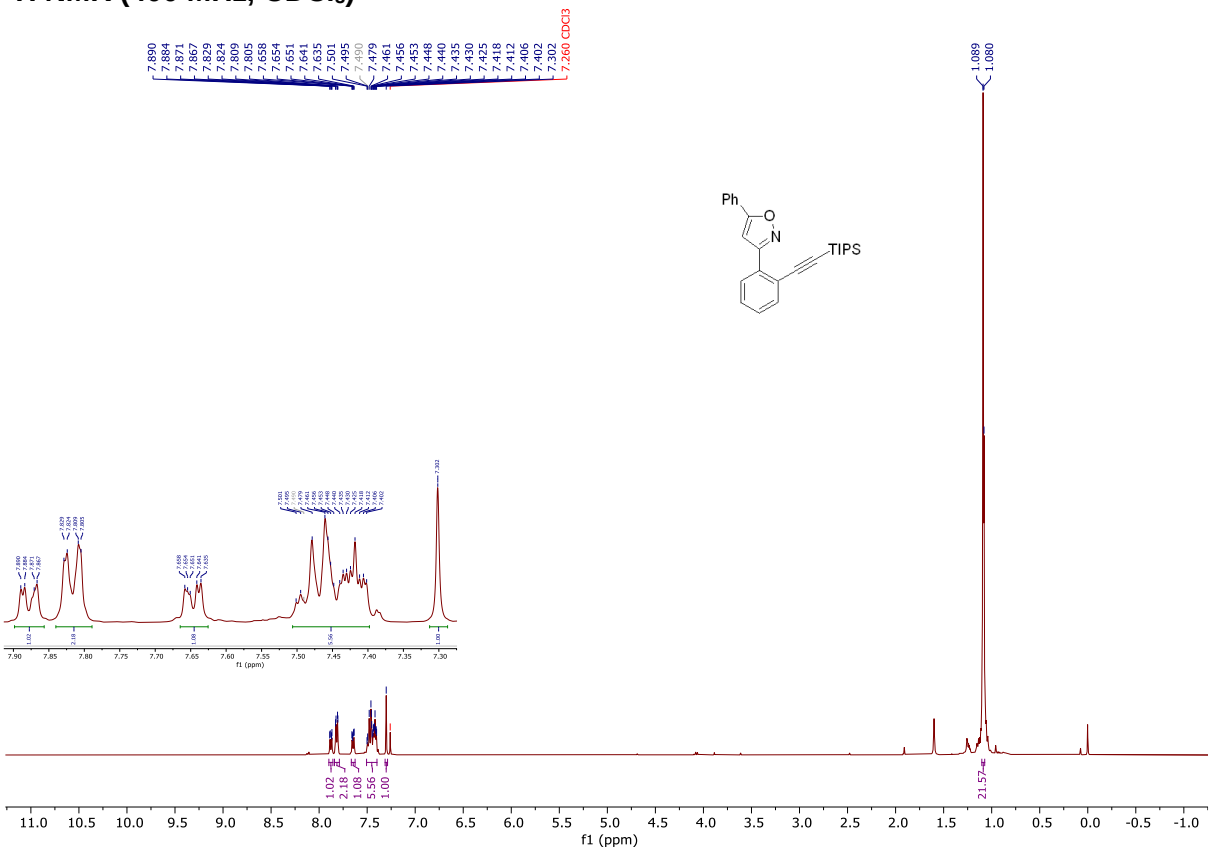


^{13}C NMR (75 MHz, $CDCl_3$)

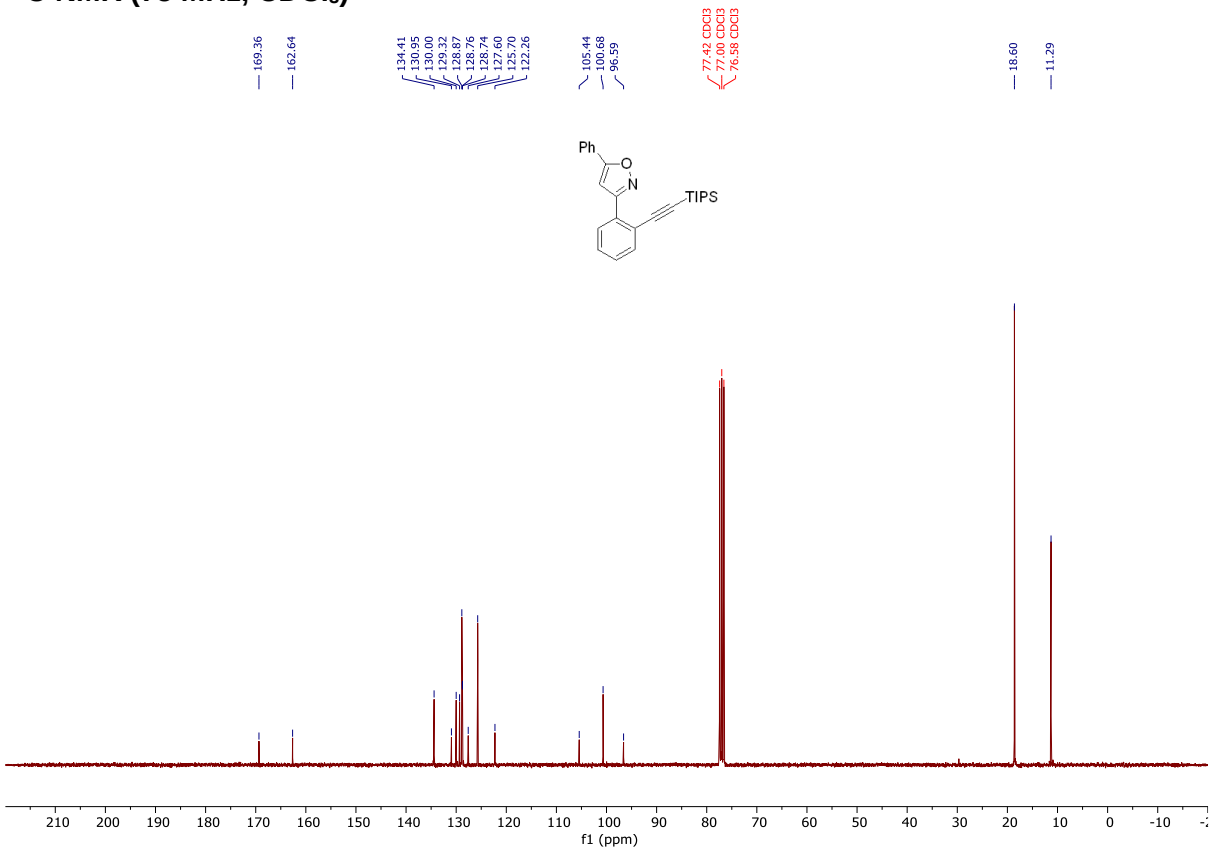


5-phenyl-3-(2-((triisopropylsilyl)ethynyl)phenyl)isoxazole (4a)

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

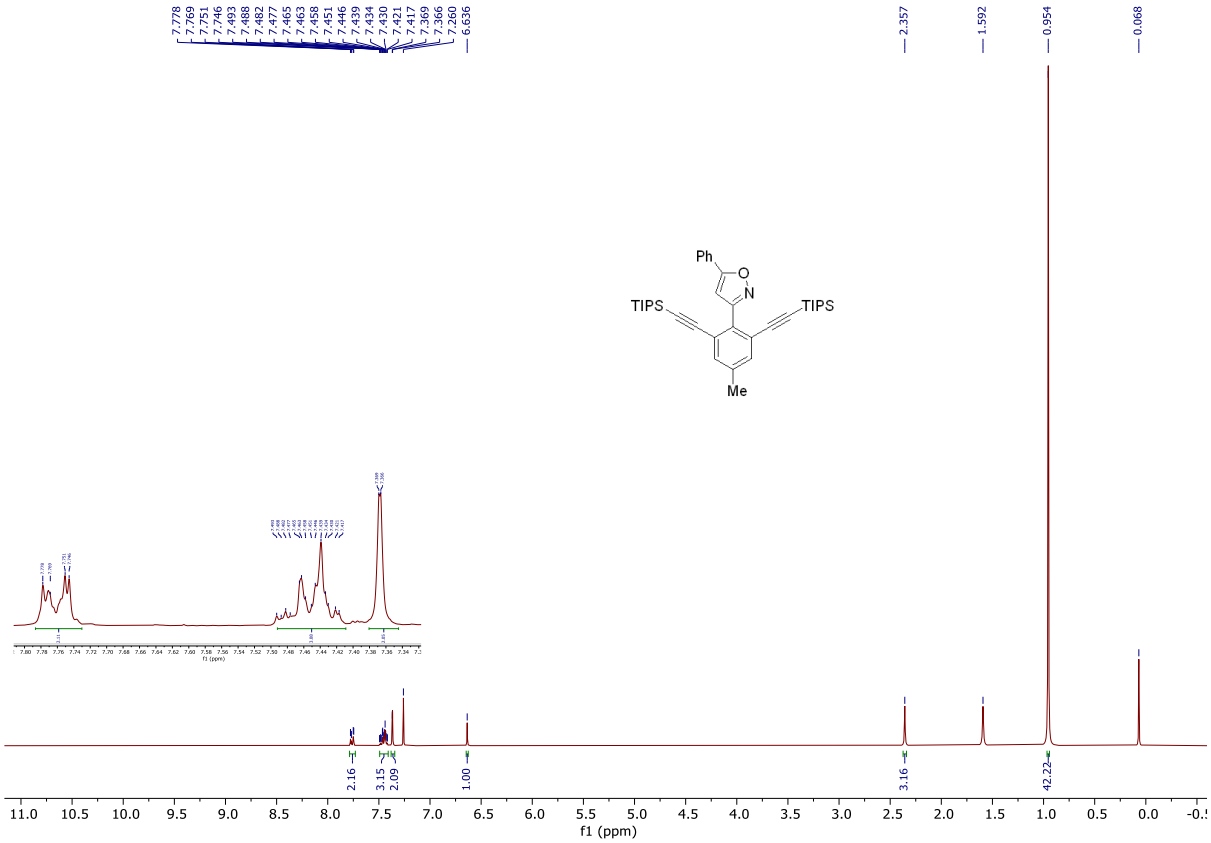


^{13}C NMR (75 MHz, $CDCl_3$)

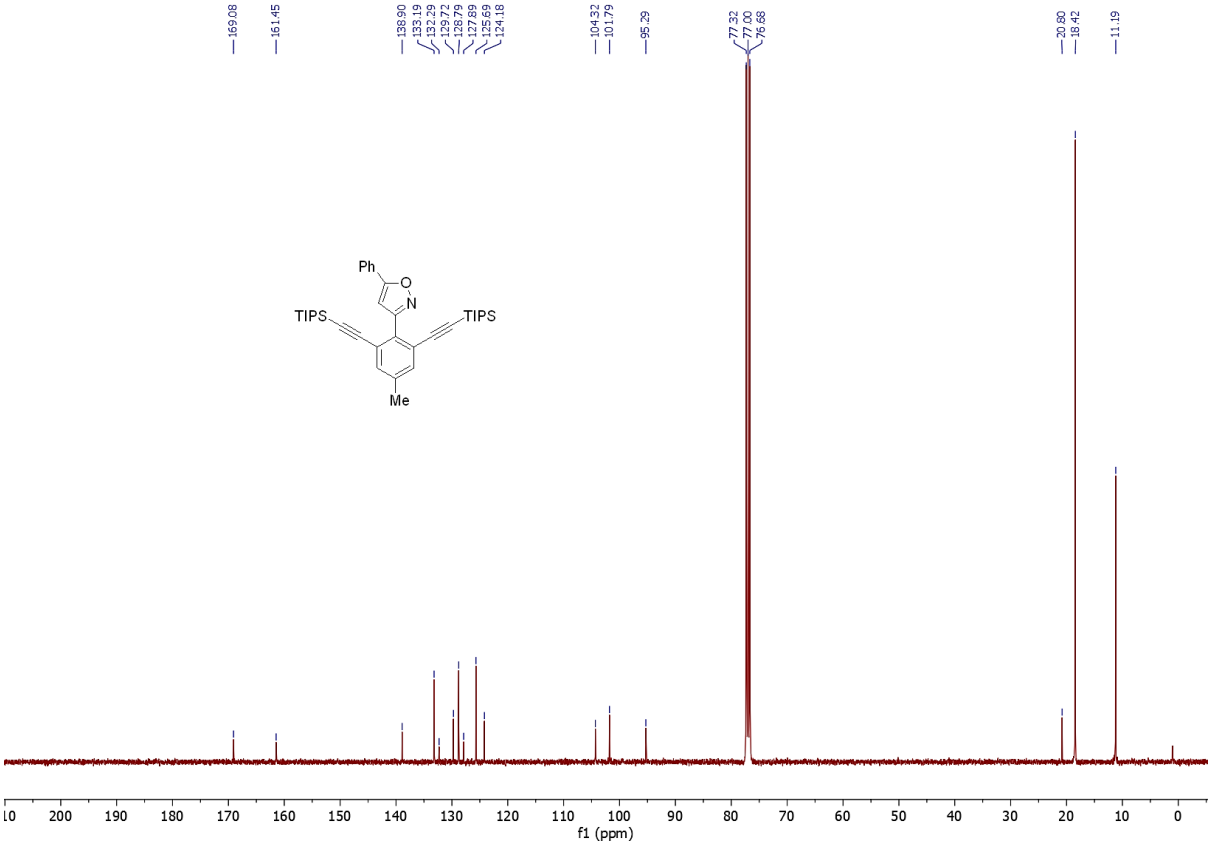


3-(4-methyl-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3b)

^{1}H NMR (300 MHz, $CDCl_3$)

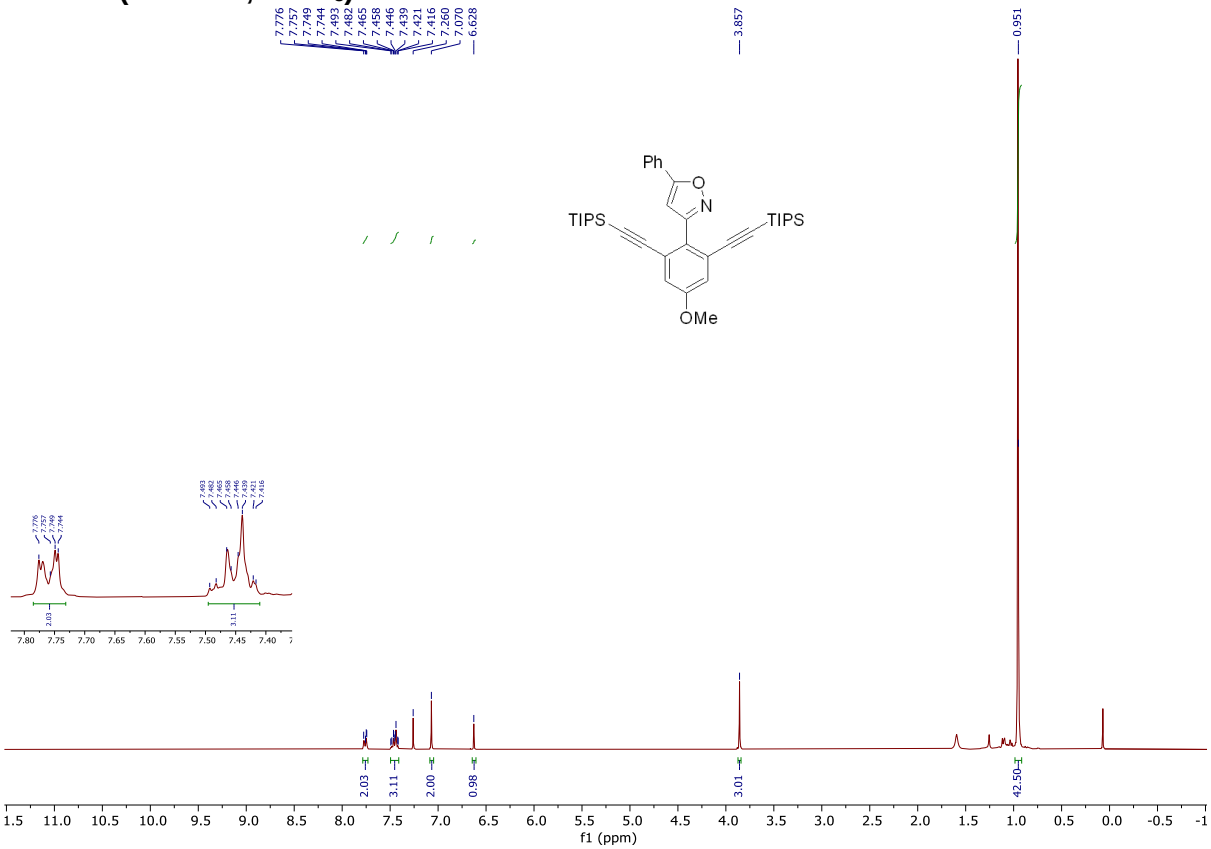


^{13}C NMR (101 MHz, $CDCl_3$)

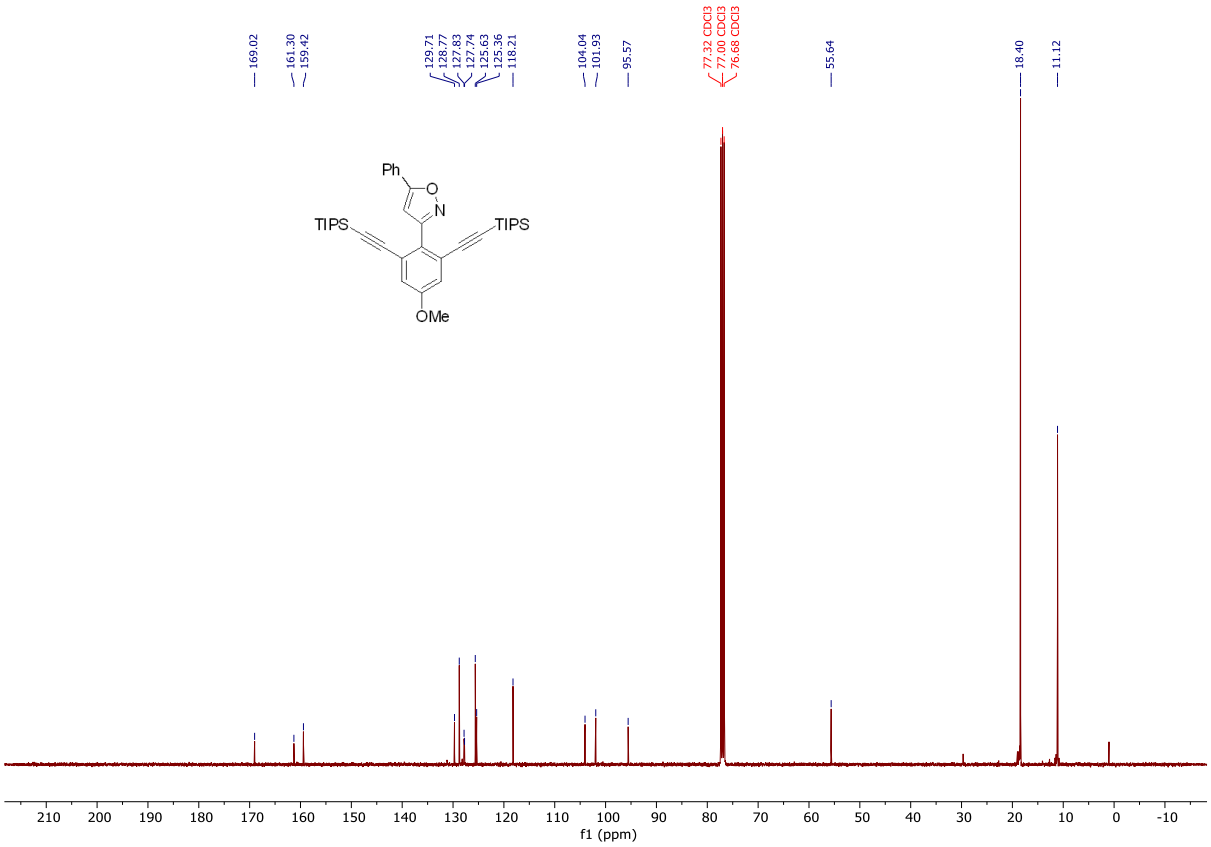


3-(4-methoxy-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3c)

^{1}H NMR (300 MHz, $CDCl_3$)

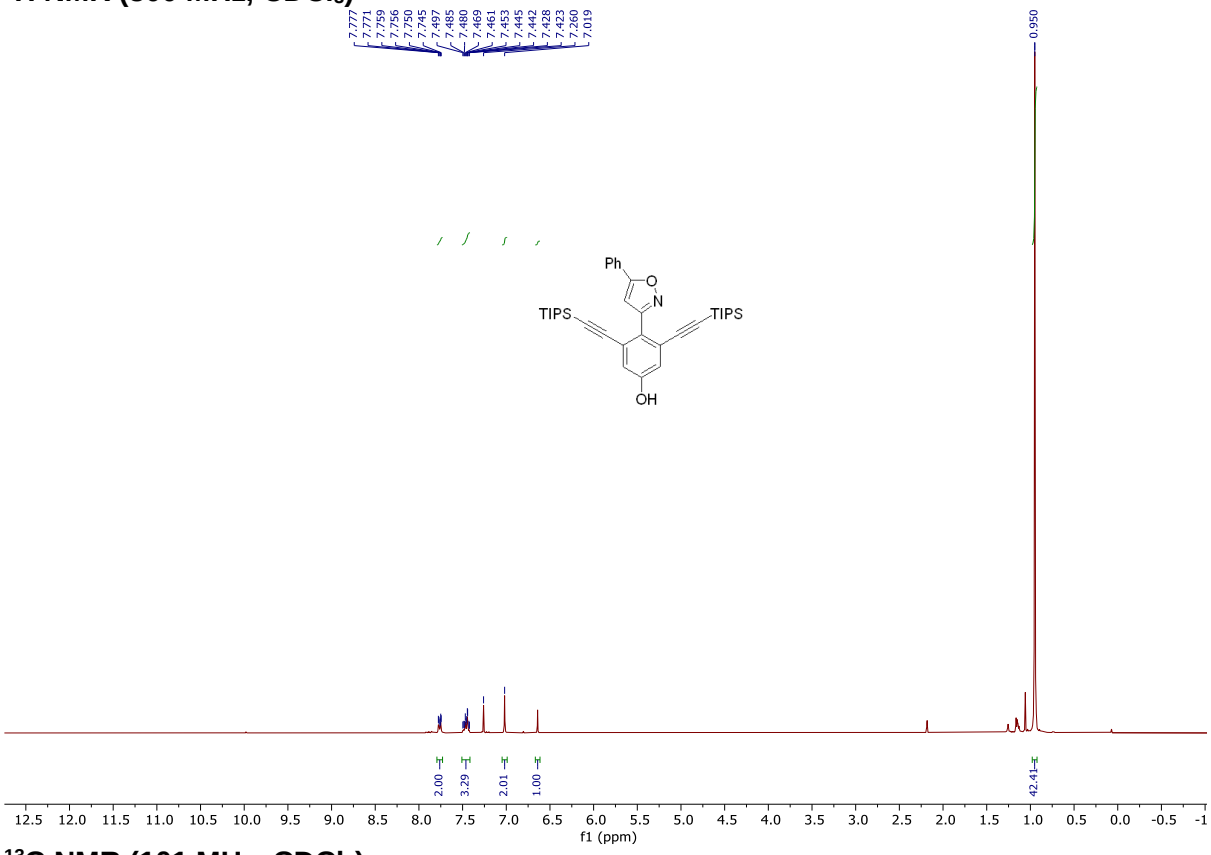


^{13}C NMR (101 MHz, $CDCl_3$)

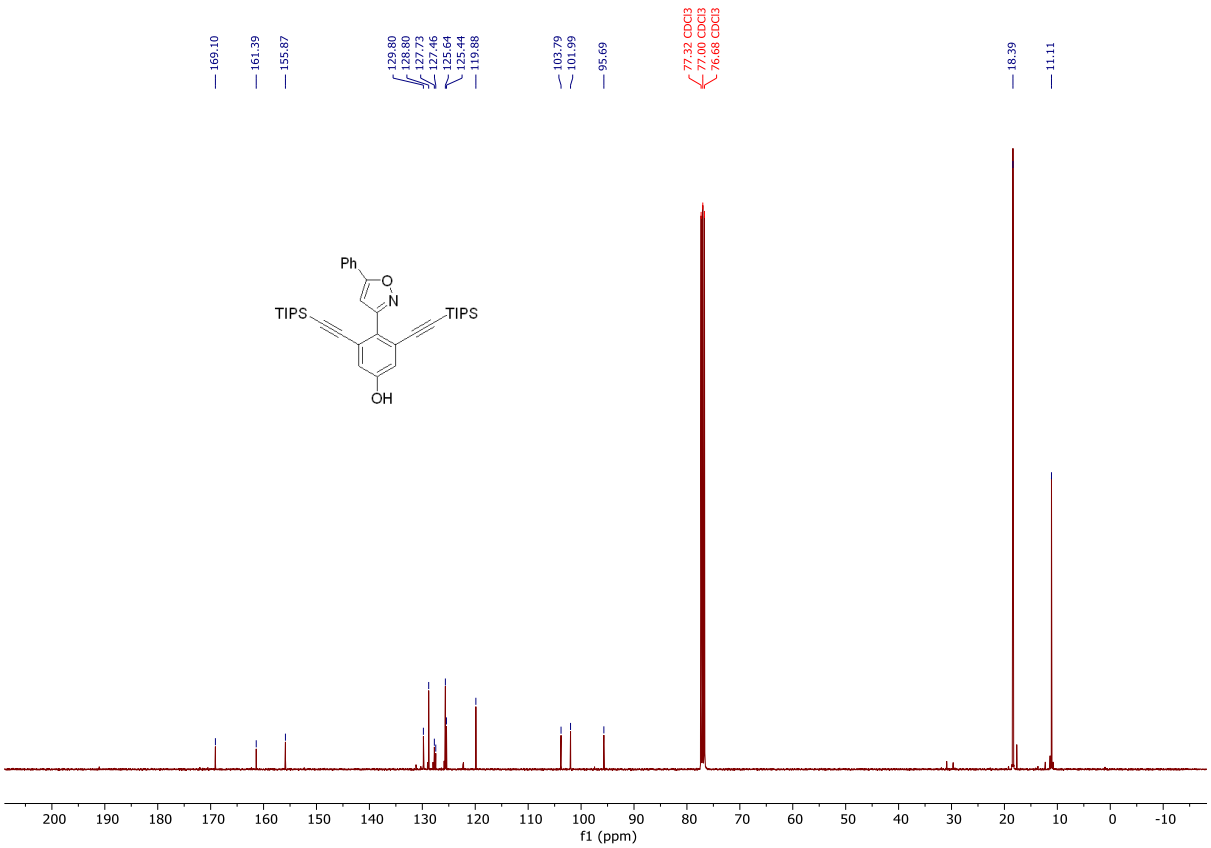


4-(5-phenylisoxazol-3-yl)-3,5-bis((triisopropylsilyl)ethynyl)phenol (3d)

^{1}H NMR (300 MHz, $CDCl_3$)

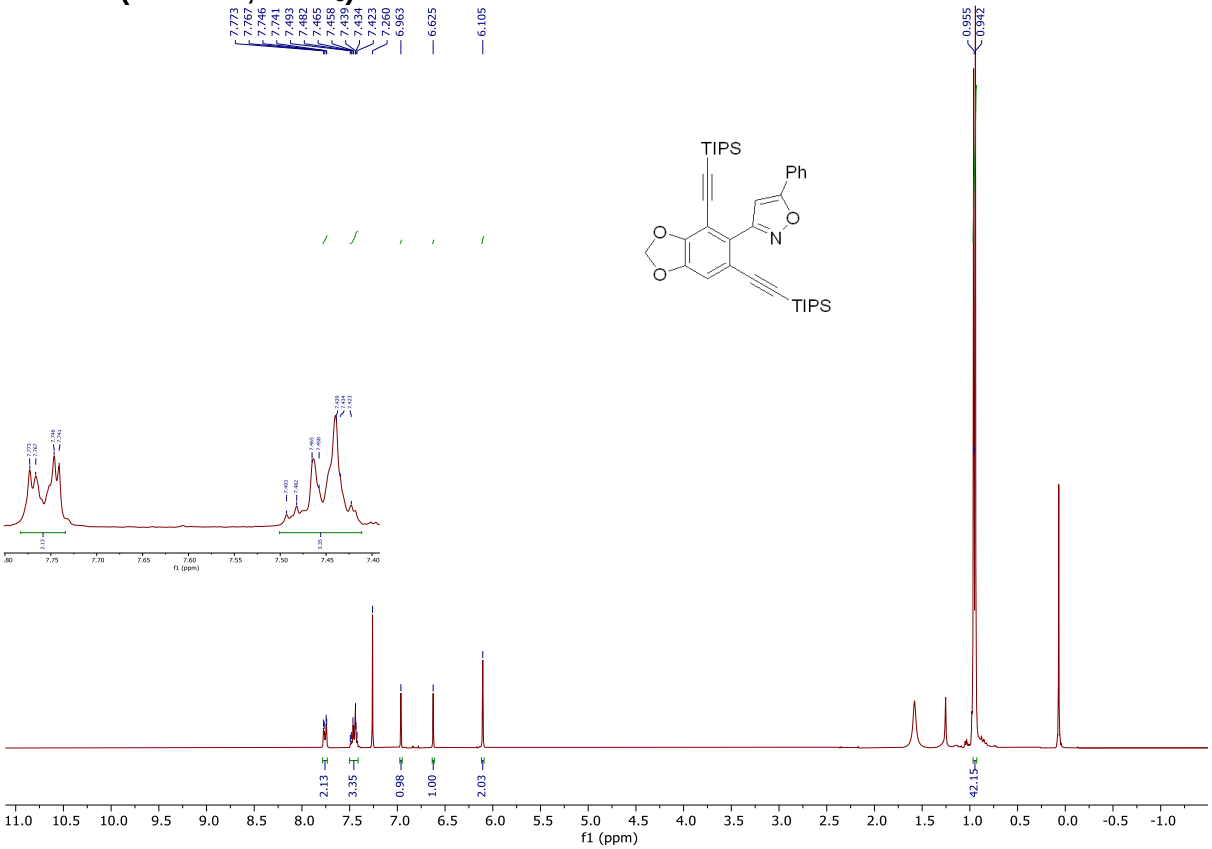


^{13}C NMR (101 MHz, $CDCl_3$)

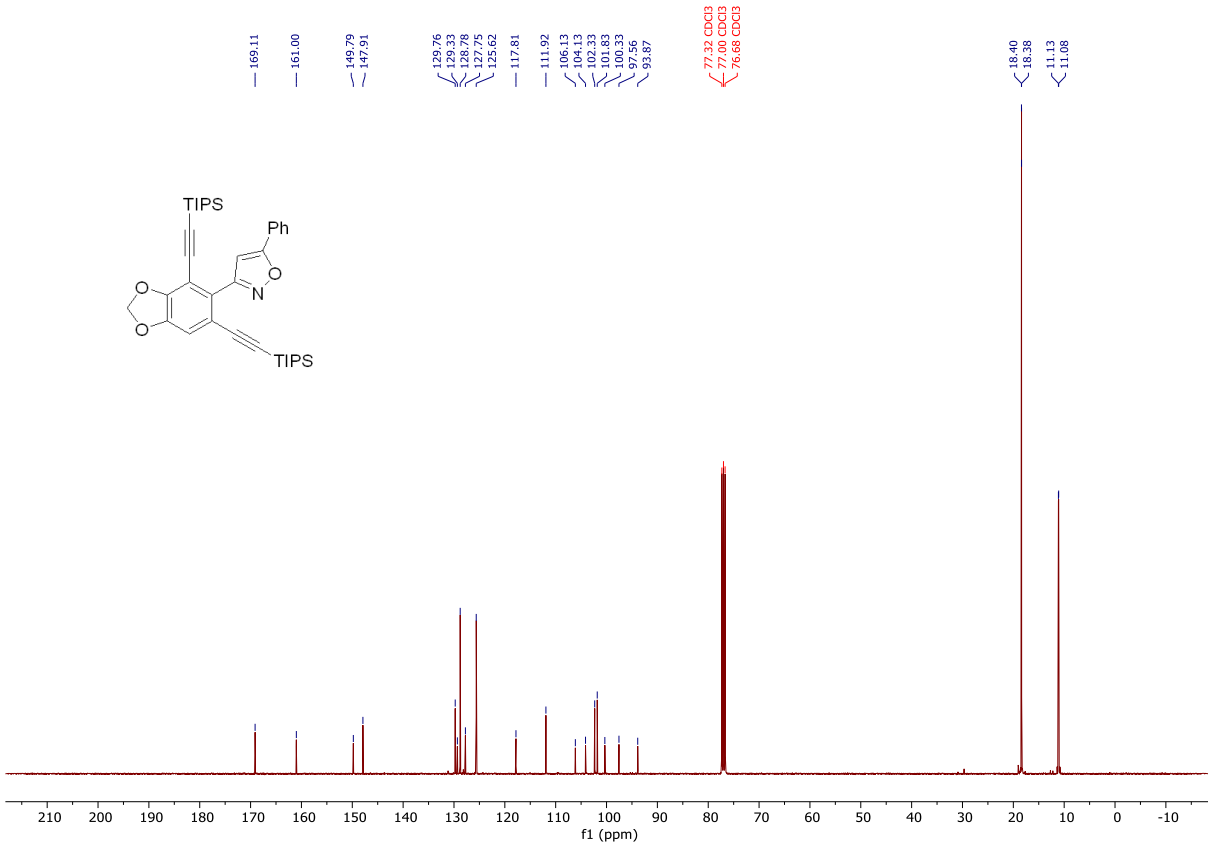


3-(4,6-bis((triisopropylsilyl)ethynyl)benzo[d][1,3]dioxol-5-yl)-5-phenylisoxazole (3e)

^{1}H NMR (300 MHz, $CDCl_3$)

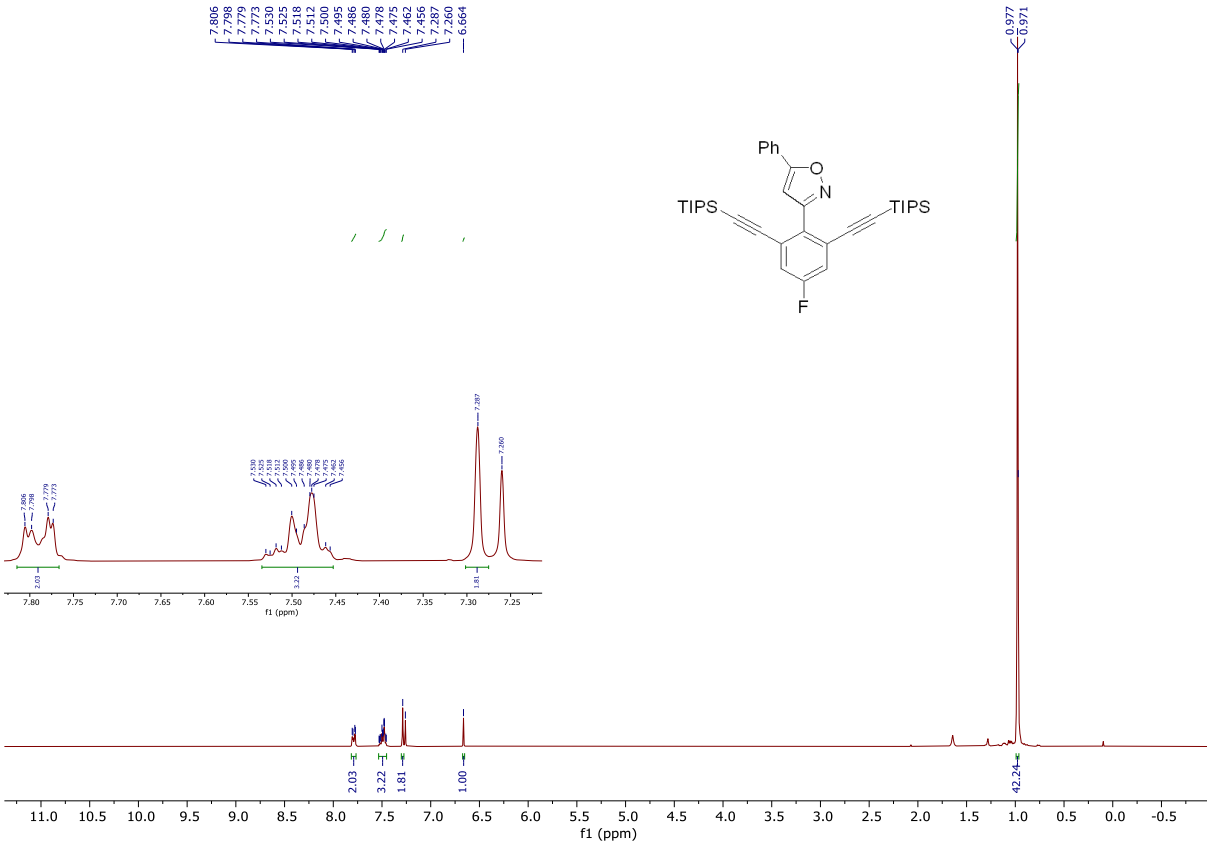


^{13}C NMR (101 MHz, $CDCl_3$)

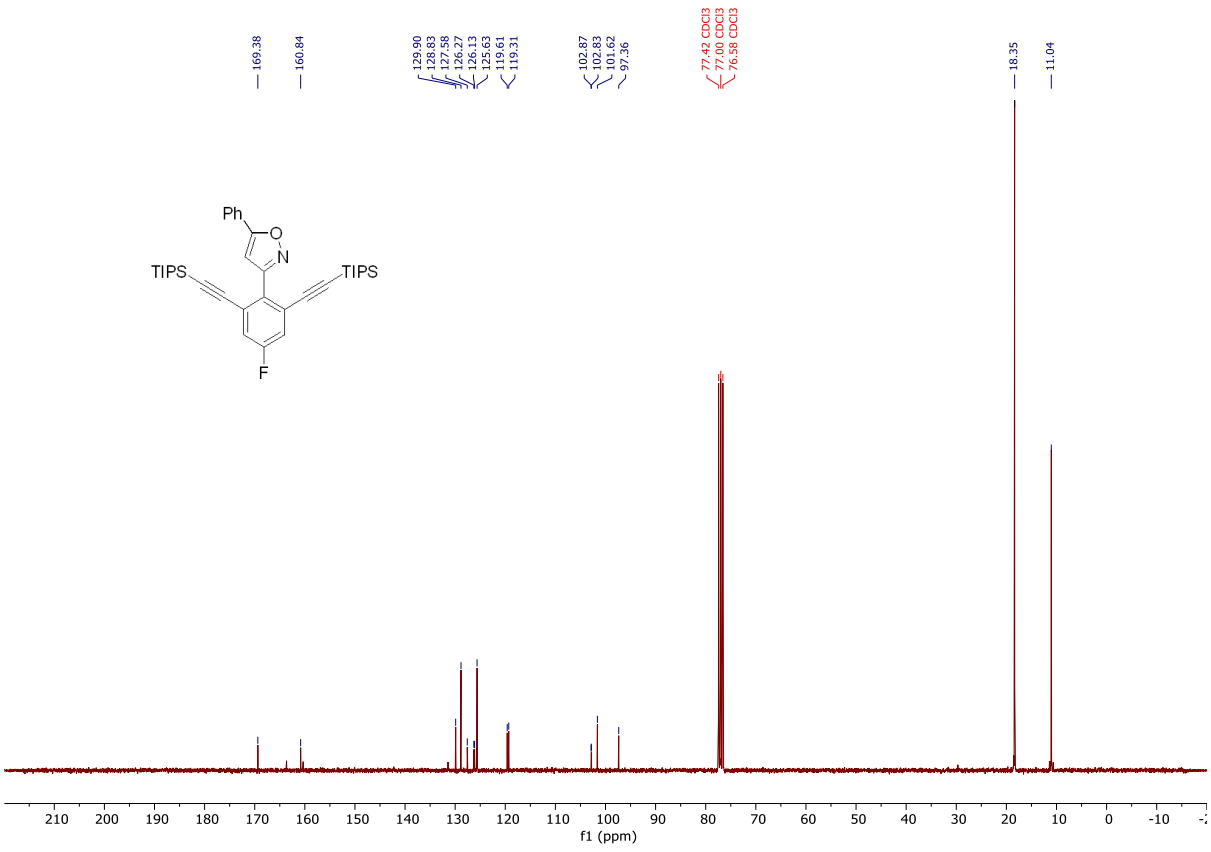


3-(4-fluoro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3f)

^{1}H NMR (300 MHz, $CDCl_3$)

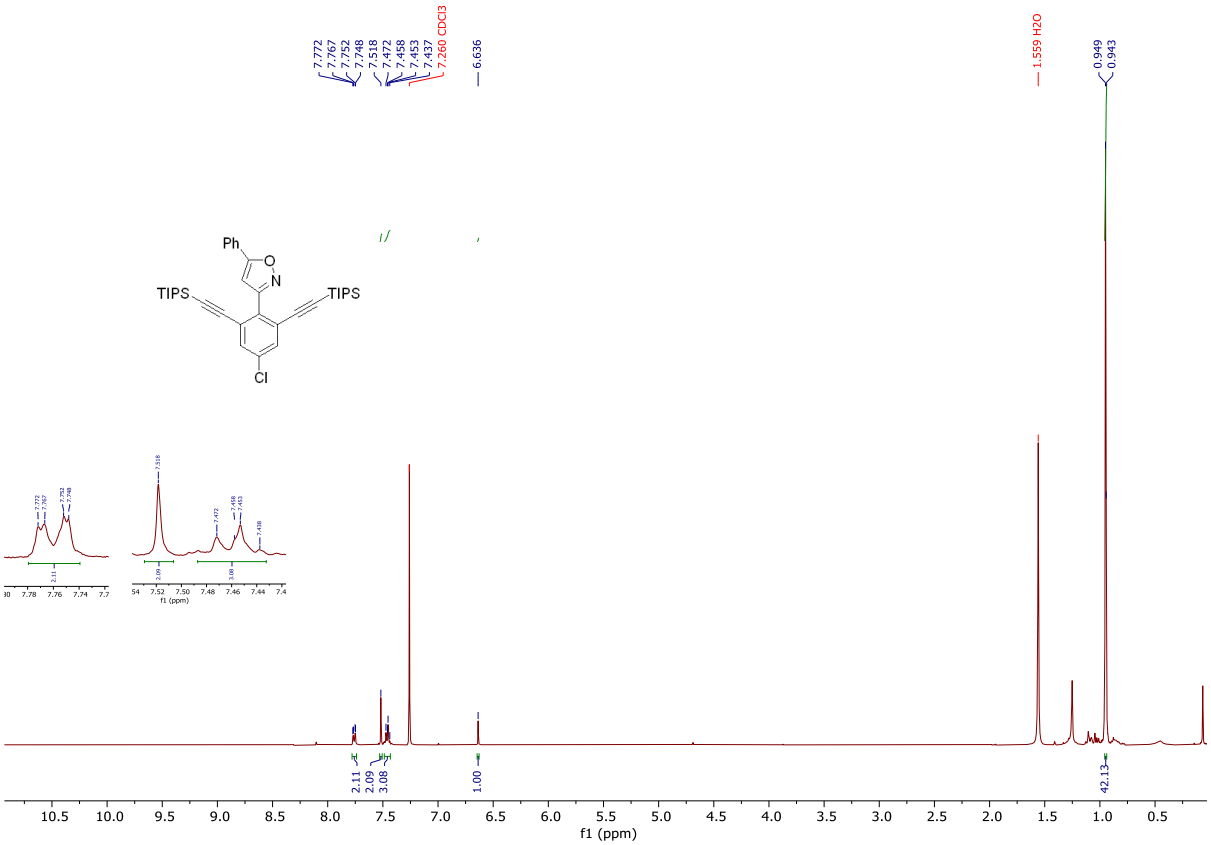


^{13}C NMR (75 MHz, $CDCl_3$)

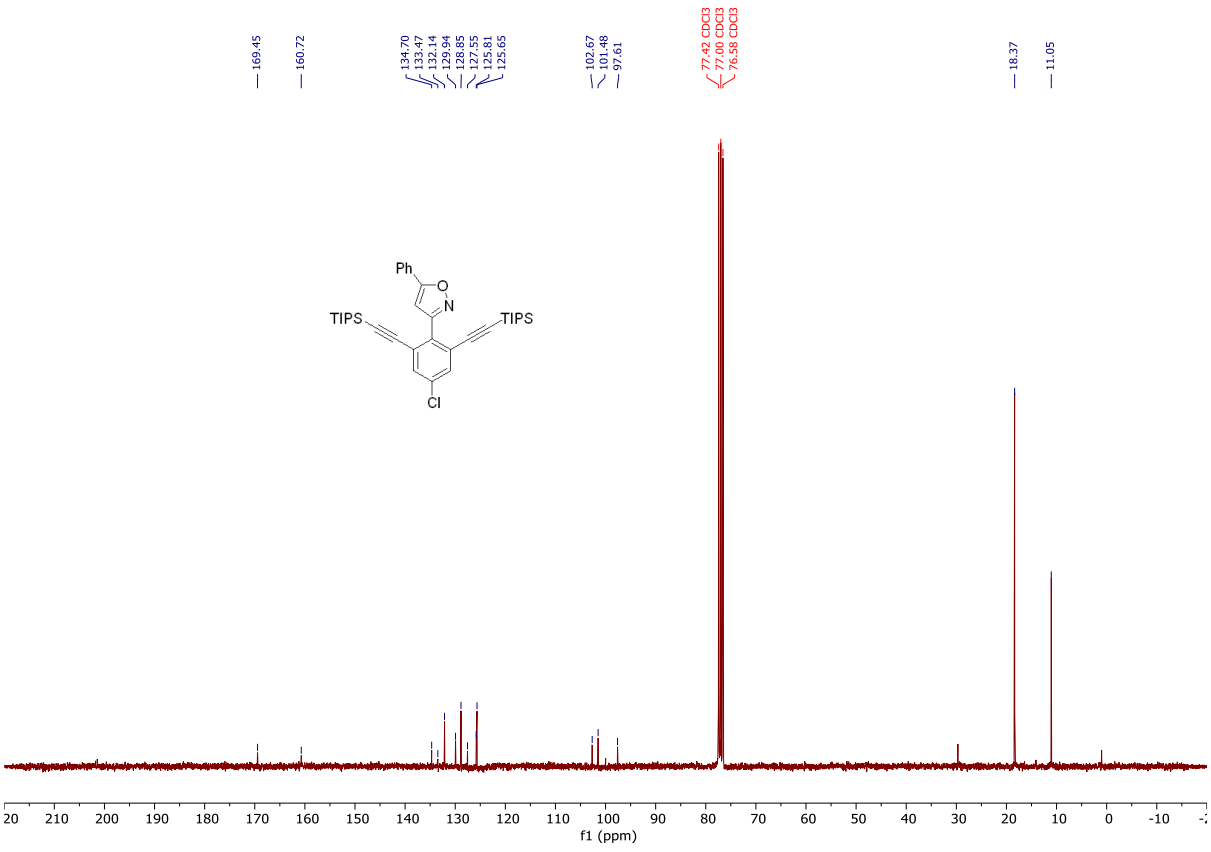


3-(4-chloro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3g)

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

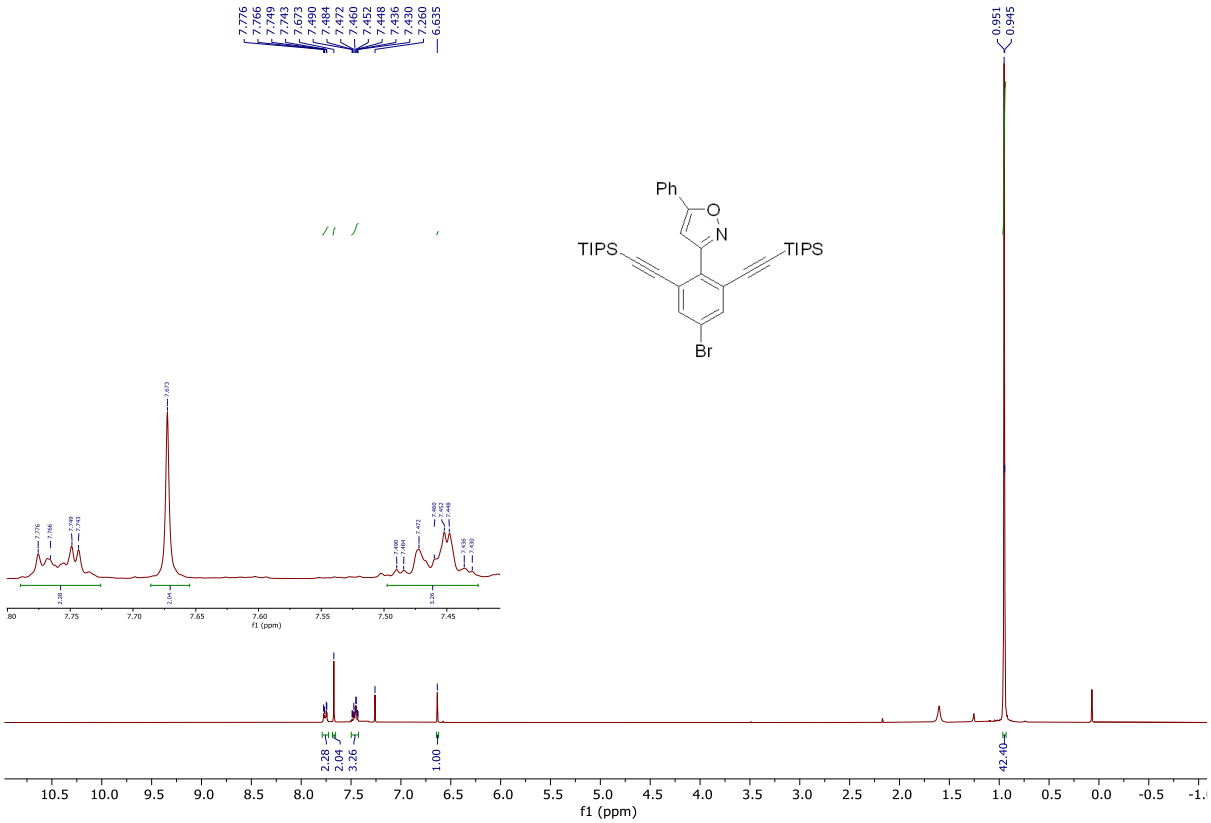


^{13}C NMR (75 MHz, $CDCl_3$)

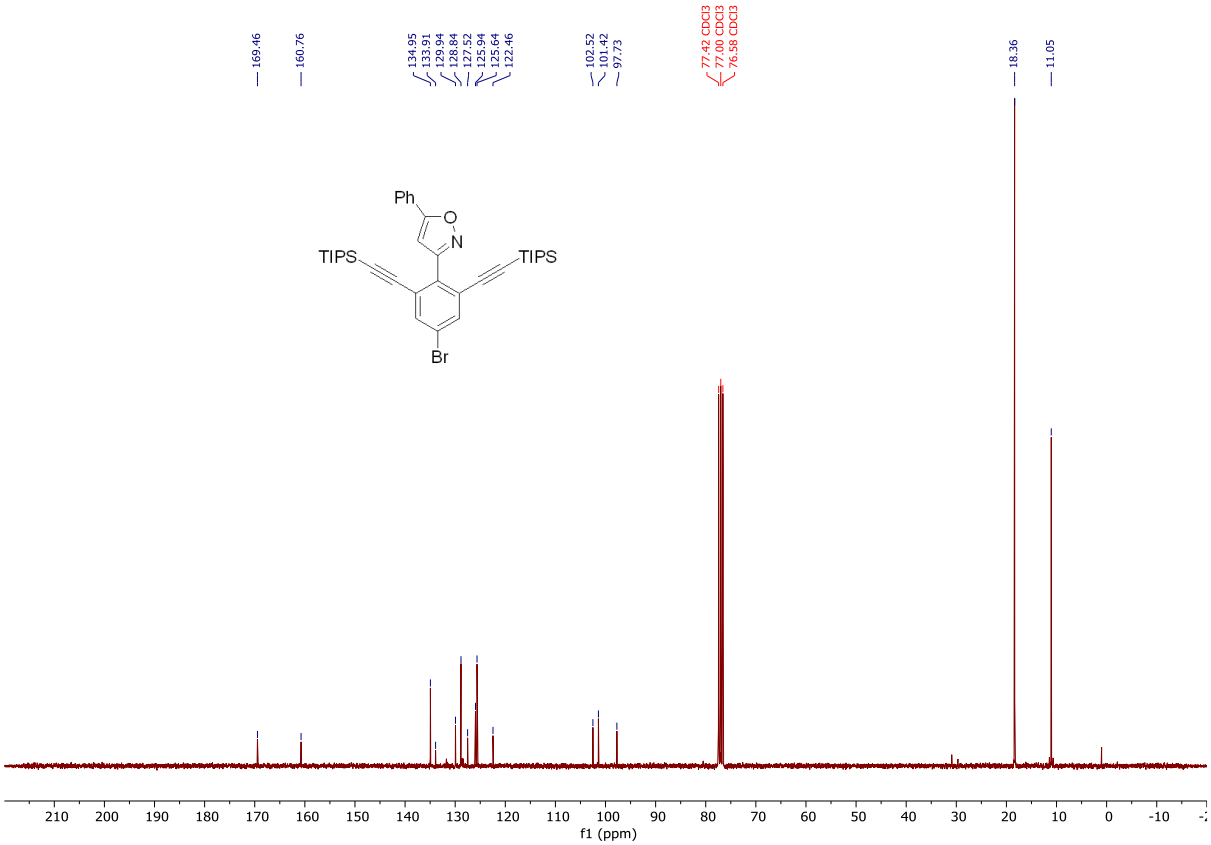


3-(4-bromo-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3h)

^{1}H NMR (300 MHz, $CDCl_3$)

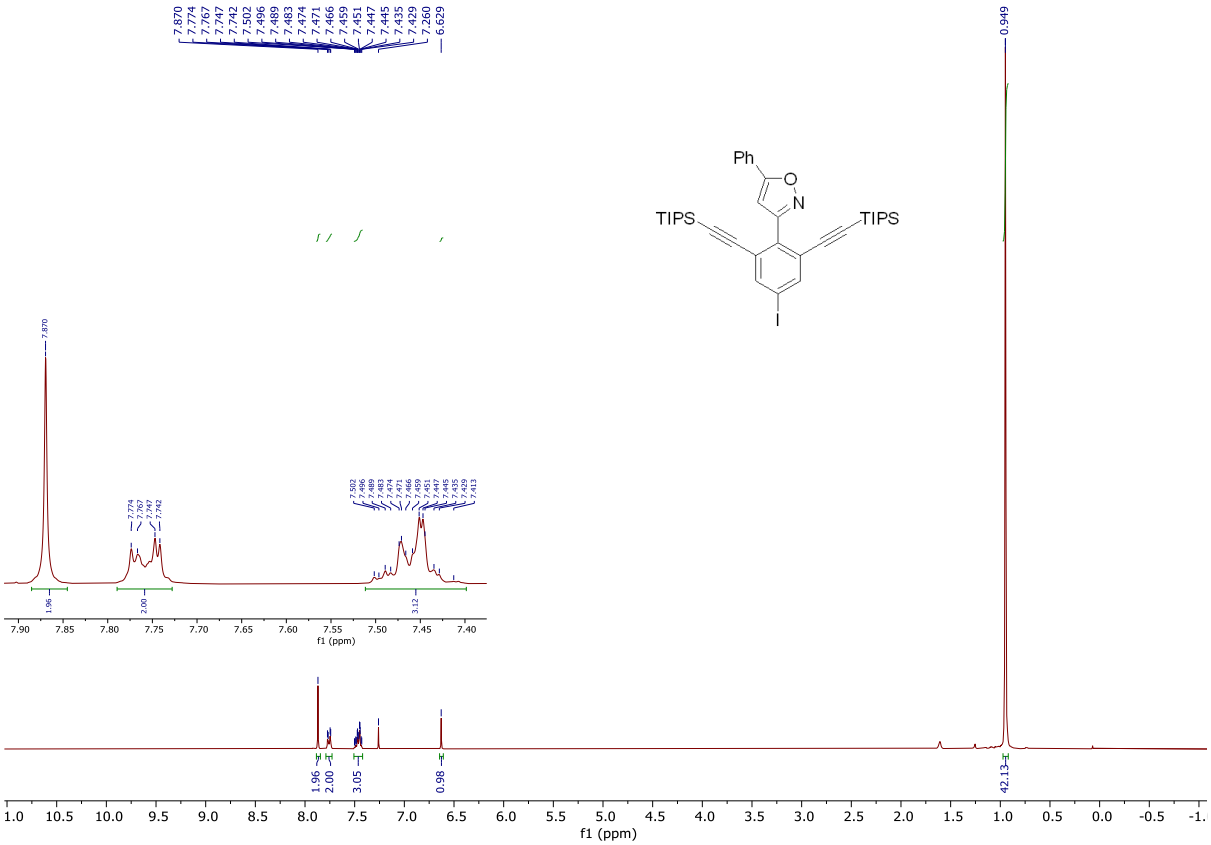


^{13}C NMR (75 MHz, $CDCl_3$)



3-(4-iodo-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3i)

^{1}H NMR (300 MHz, $CDCl_3$)



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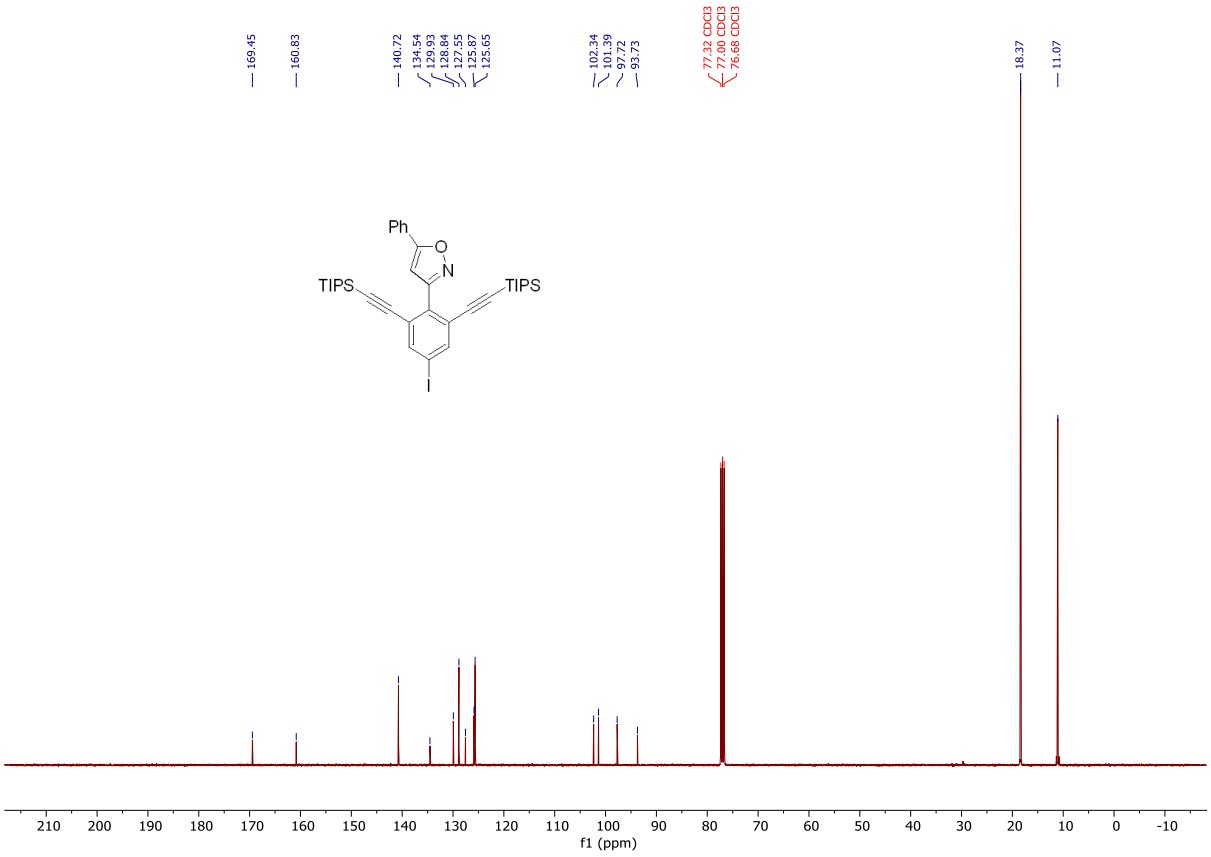
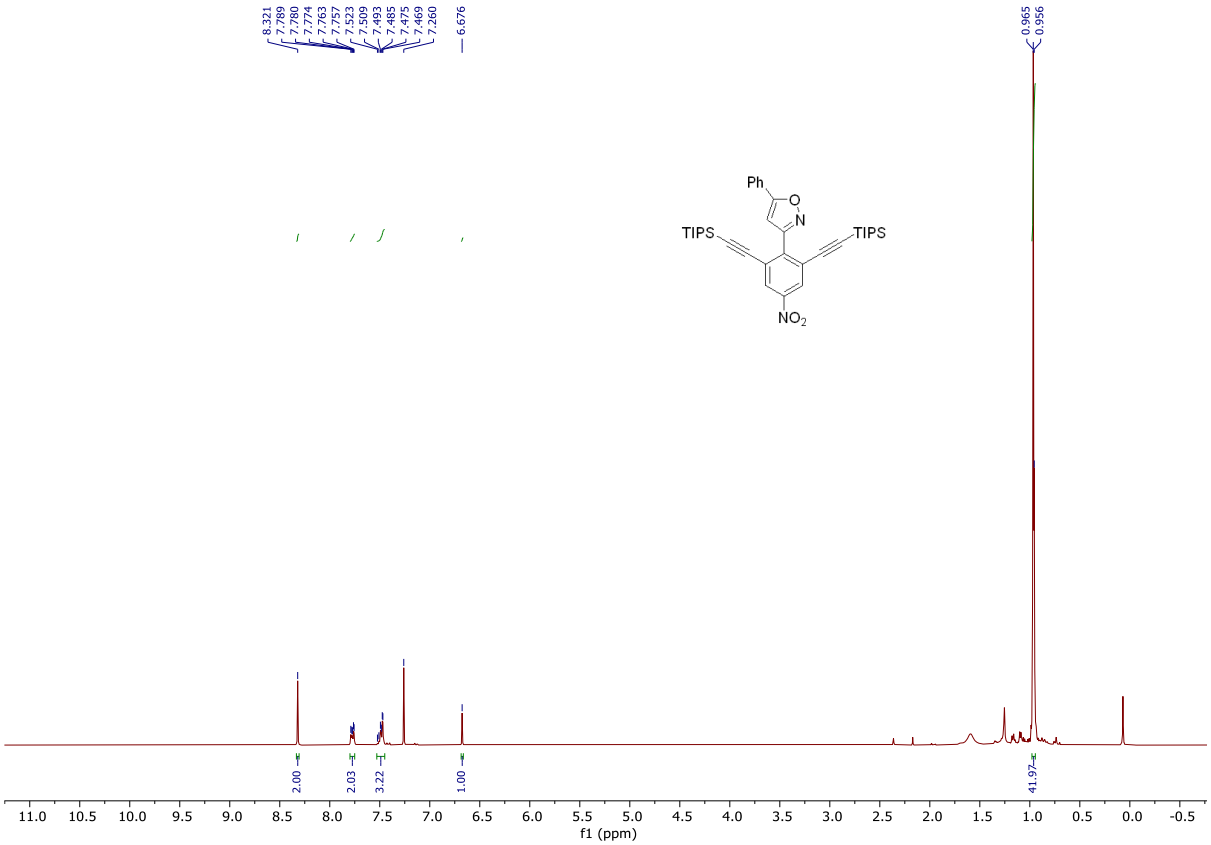
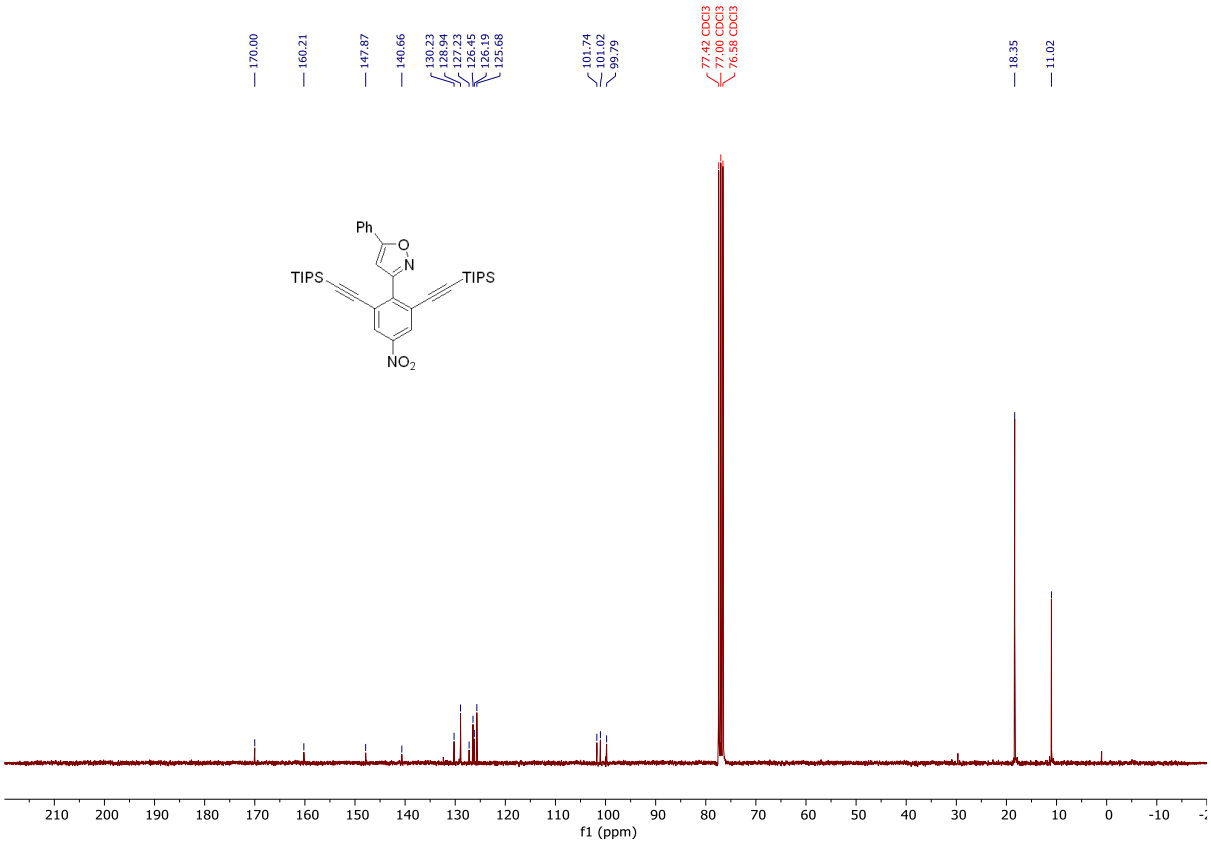


3-(4-nitro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3j)

^{1}H NMR (300 MHz, $CDCl_3$)

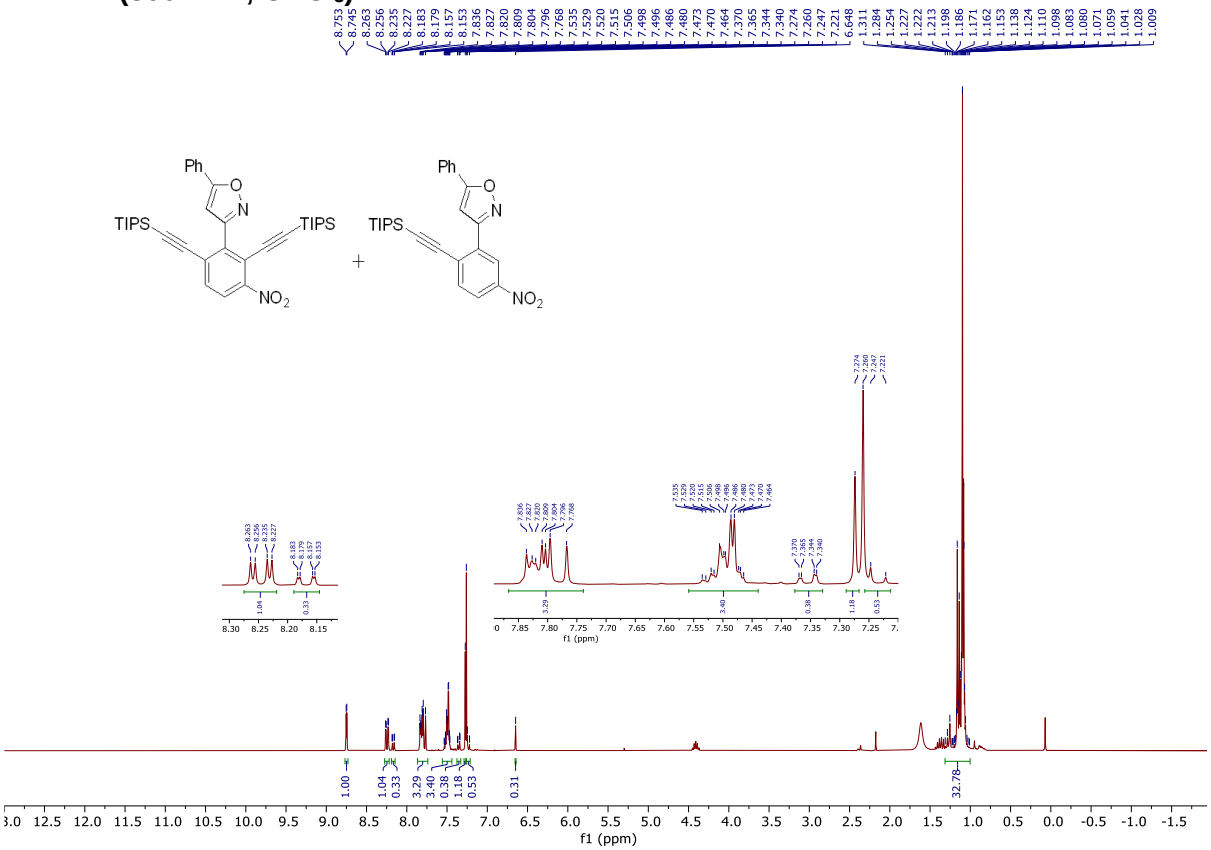


^{13}C NMR (75 MHz, $CDCl_3$)

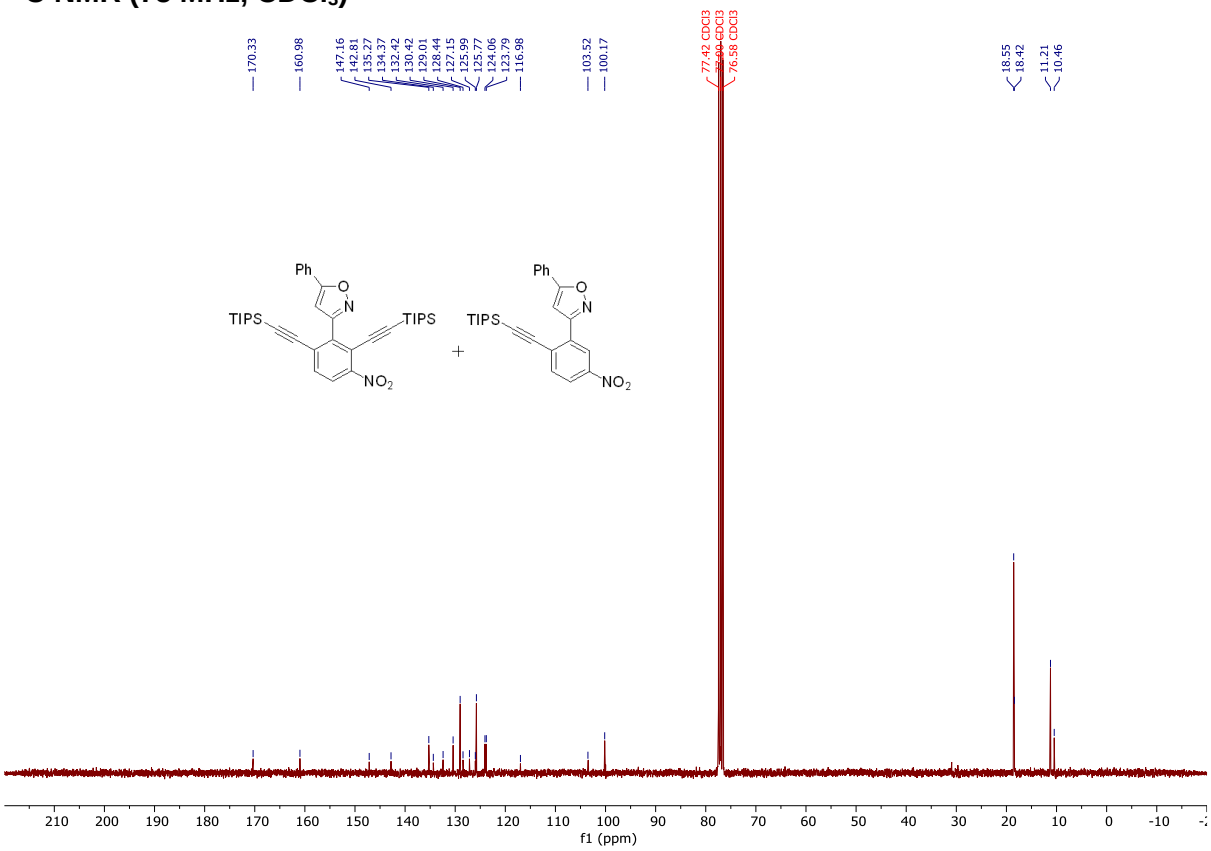


3-(5-nitro-2-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4k)
3-(3-nitro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (3k)

^{1}H NMR (300 MHz, $CDCl_3$)

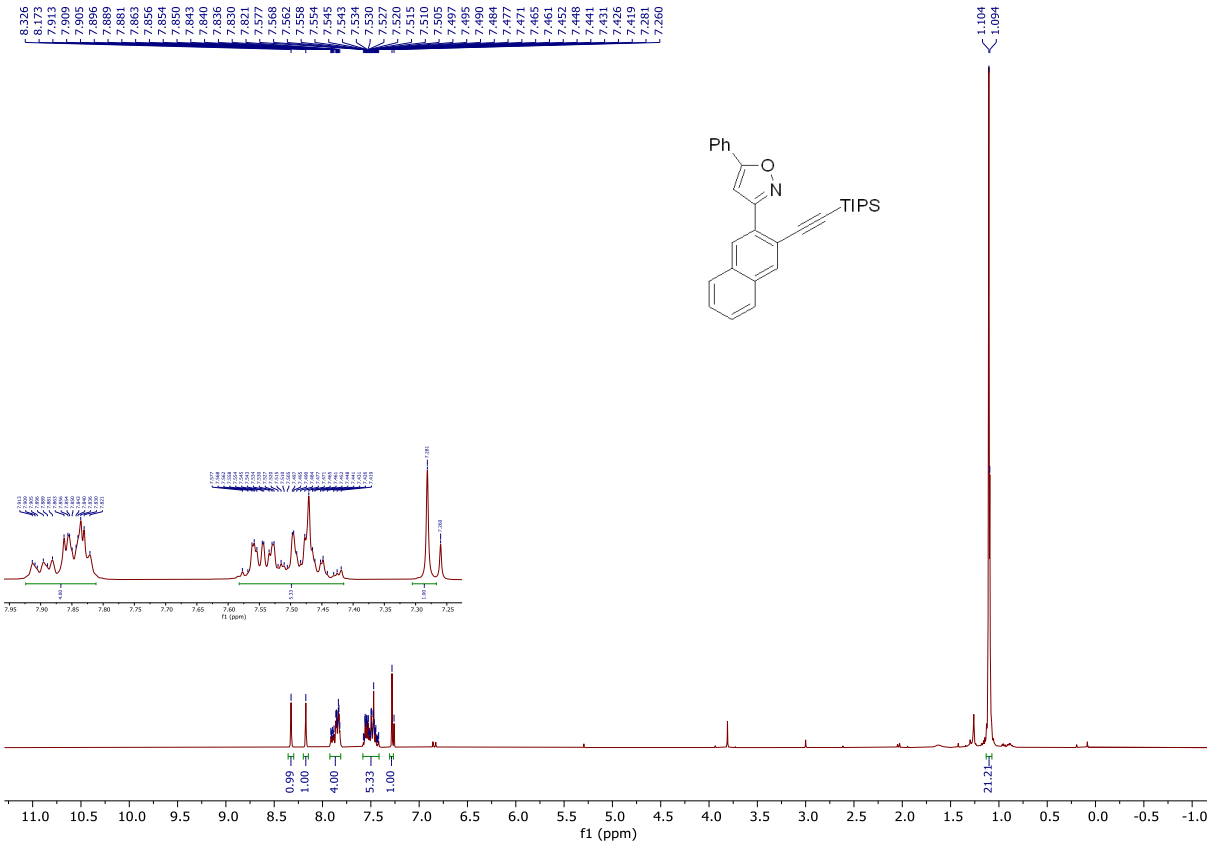


^{13}C NMR (75 MHz, $CDCl_3$)

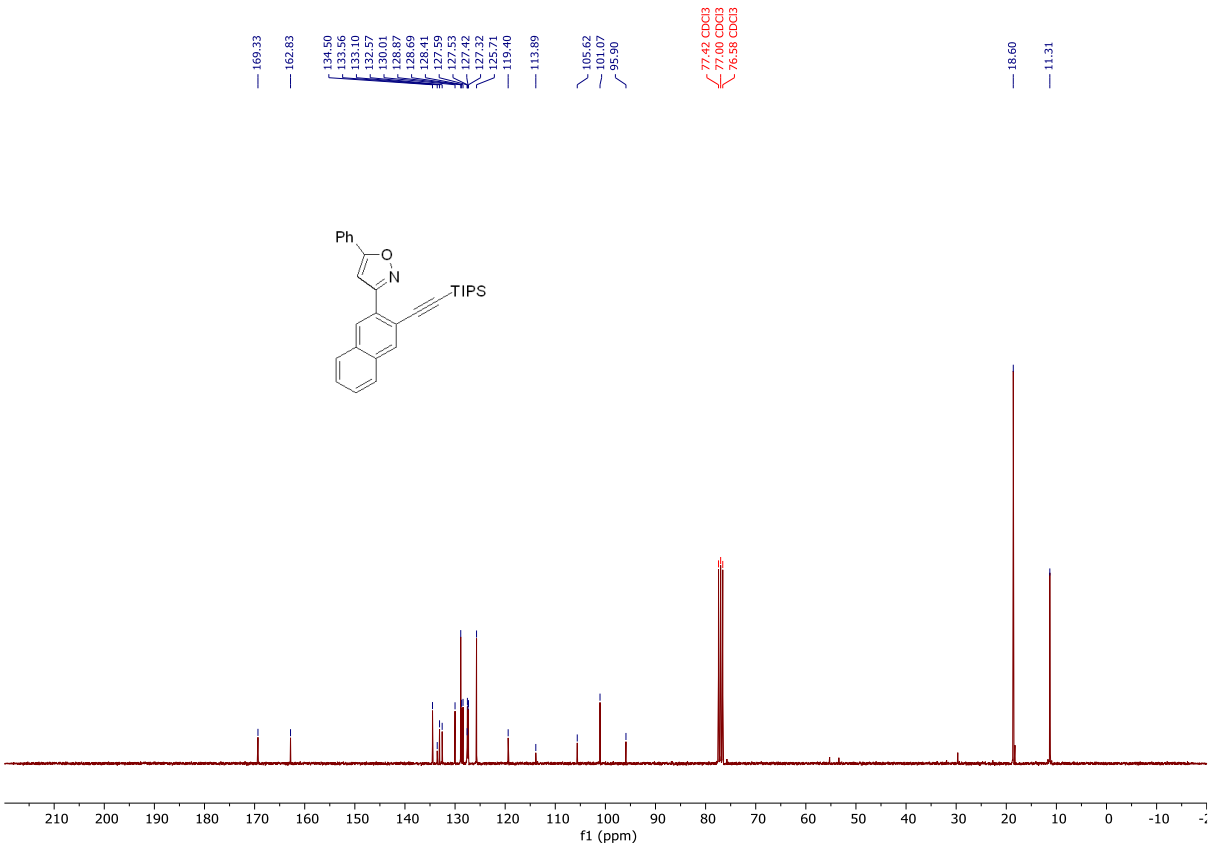


5-phenyl-3-(3-((triisopropylsilyl)ethynyl)naphthalen-2-yl)isoxazole (4l)

^{1}H NMR (300 MHz, $CDCl_3$)

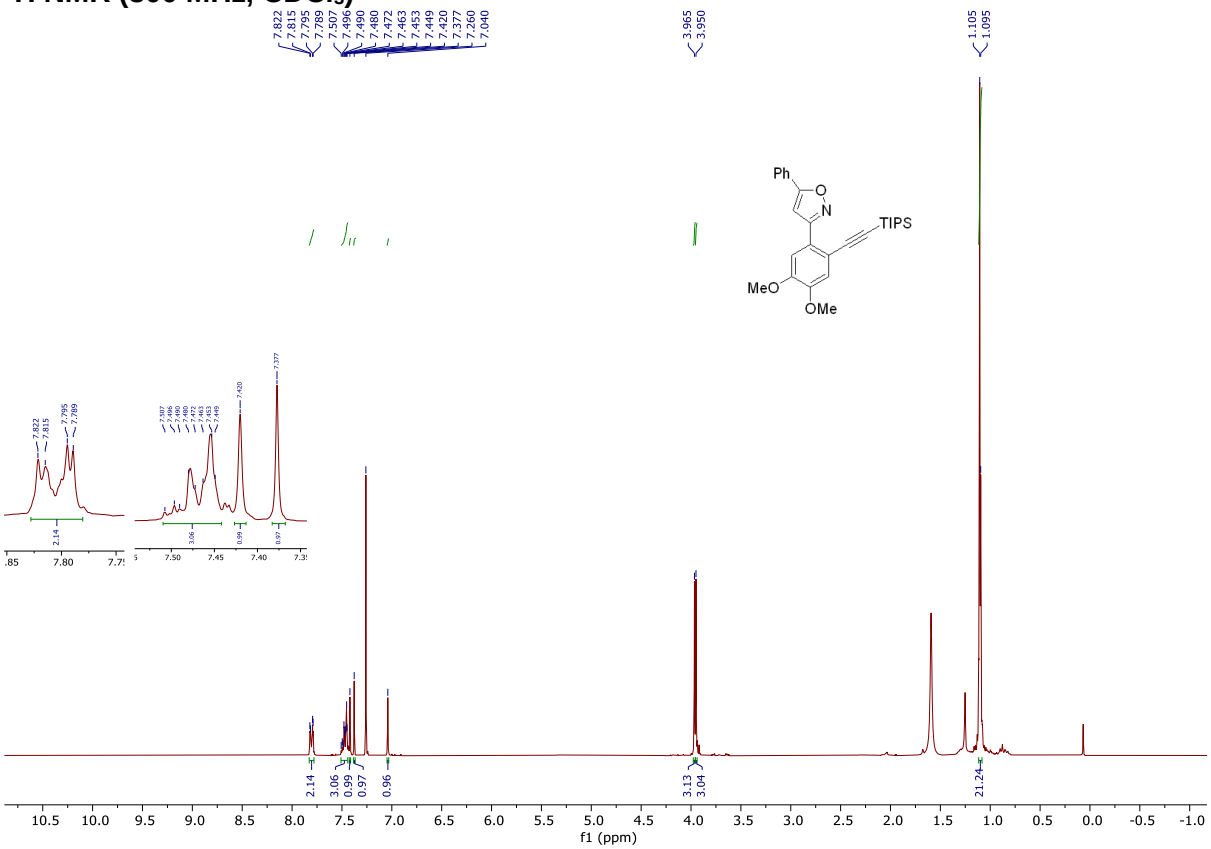


^{13}C NMR (75 MHz, $CDCl_3$)

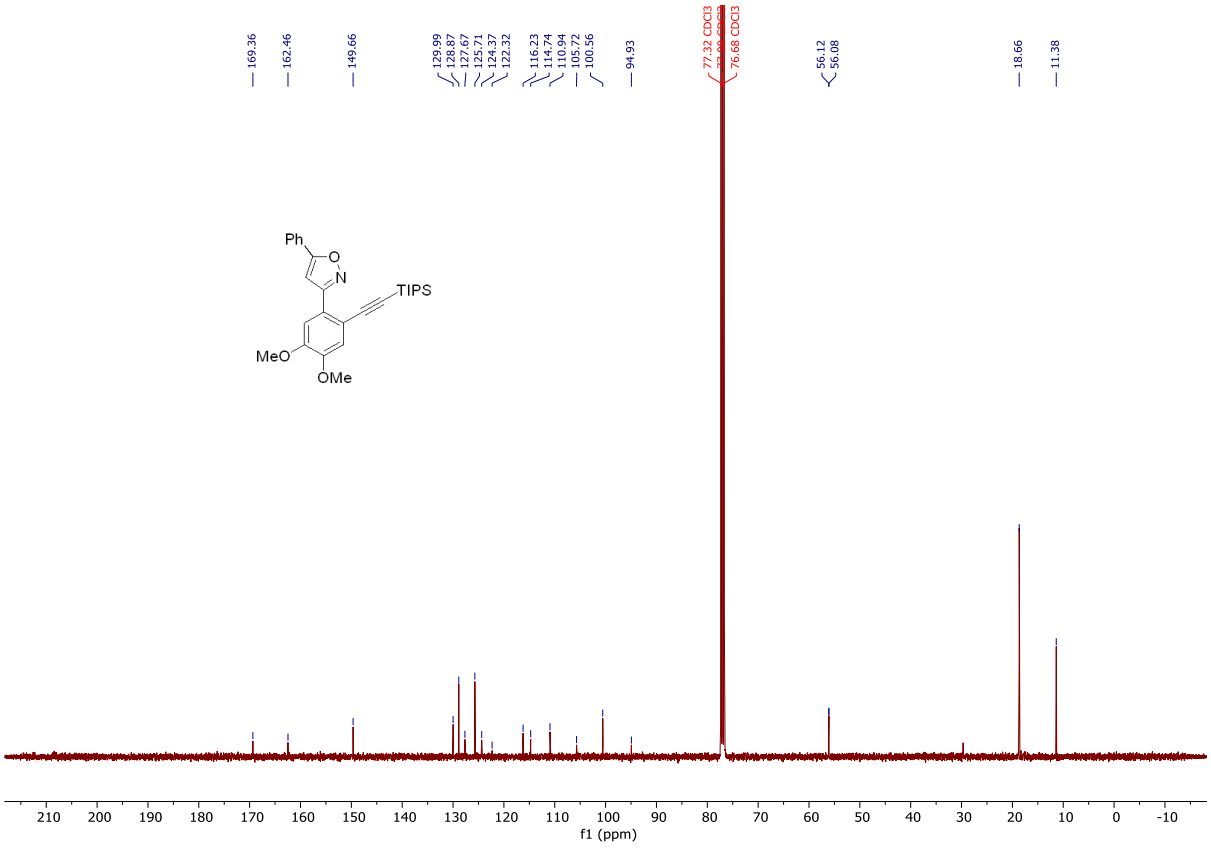


3-(4,5-dimethoxy-2-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4m)

^{1}H NMR (300 MHz, $CDCl_3$)

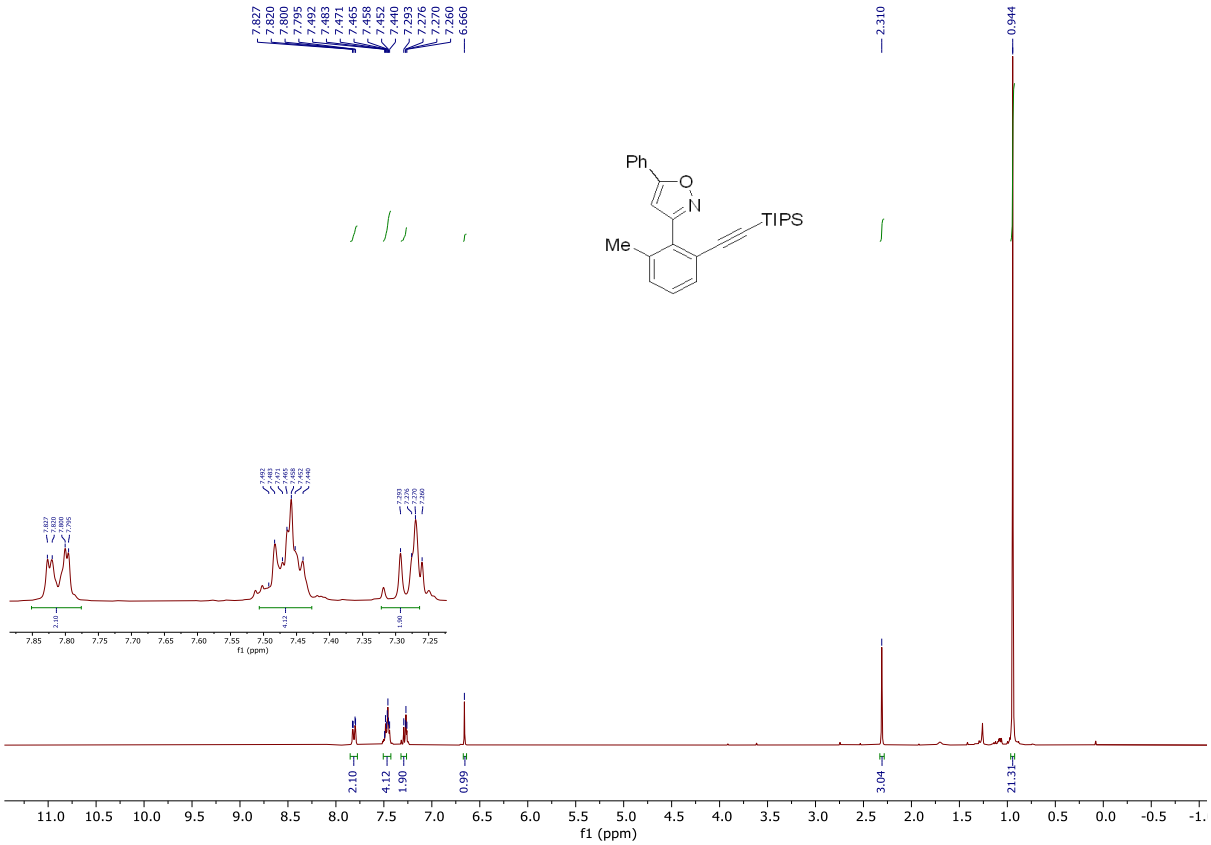


^{13}C NMR (101 MHz, $CDCl_3$)

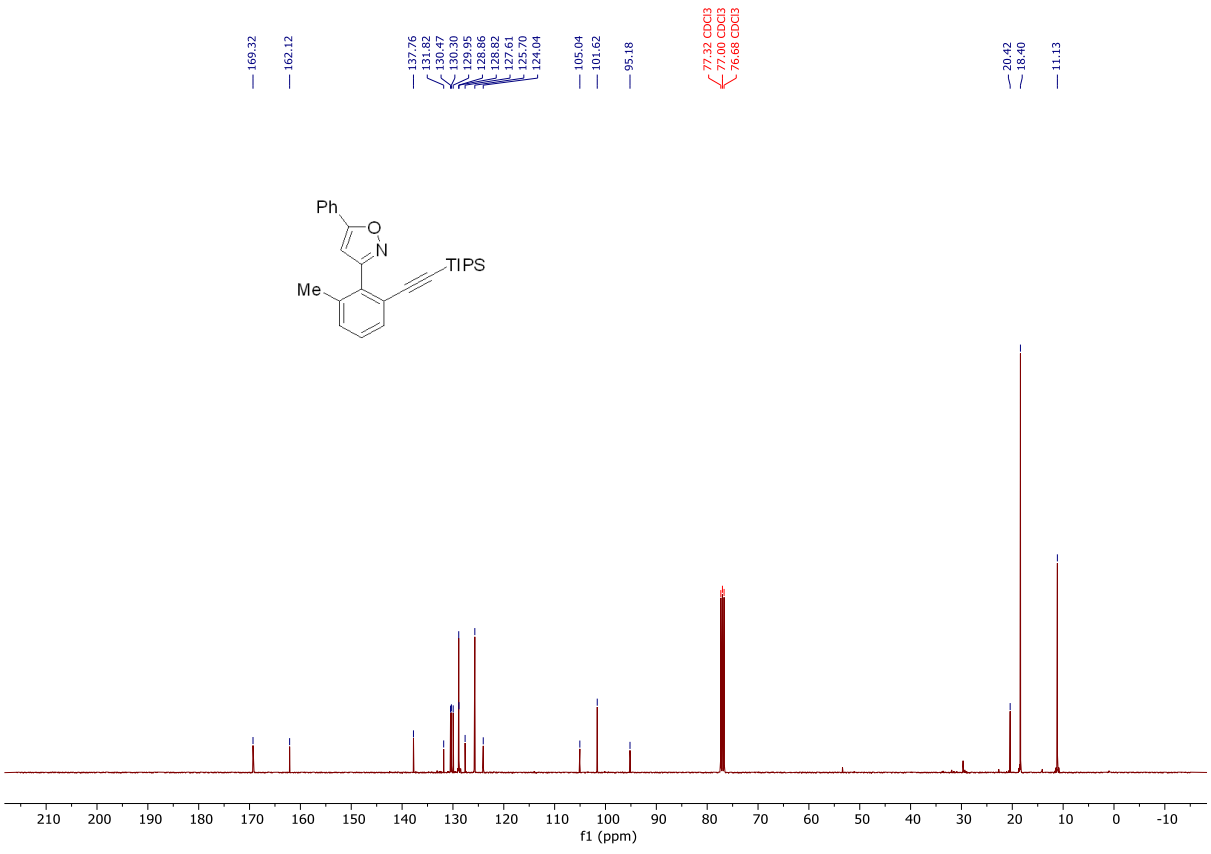


3-(2-methyl-6-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4n)

^{1}H NMR (300 MHz, $CDCl_3$)

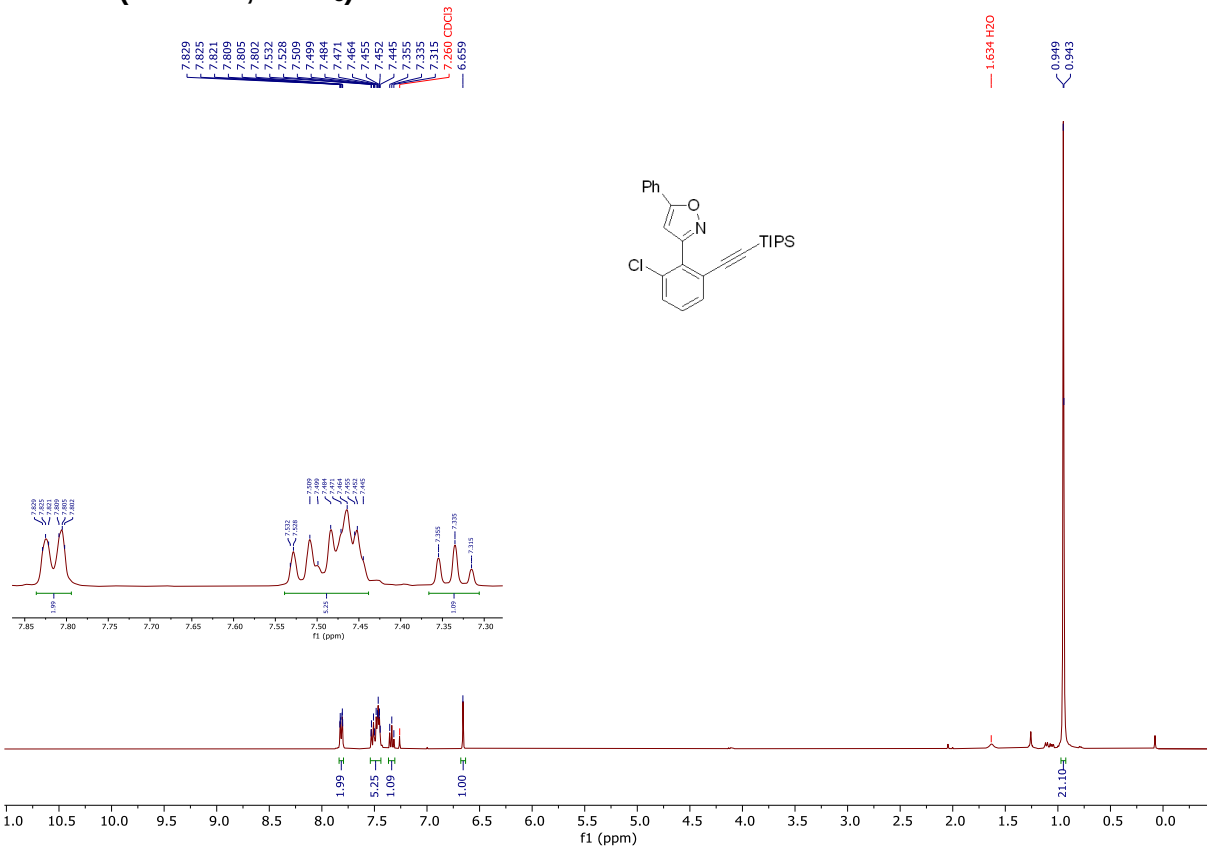


^{13}C NMR (101 MHz, $CDCl_3$)

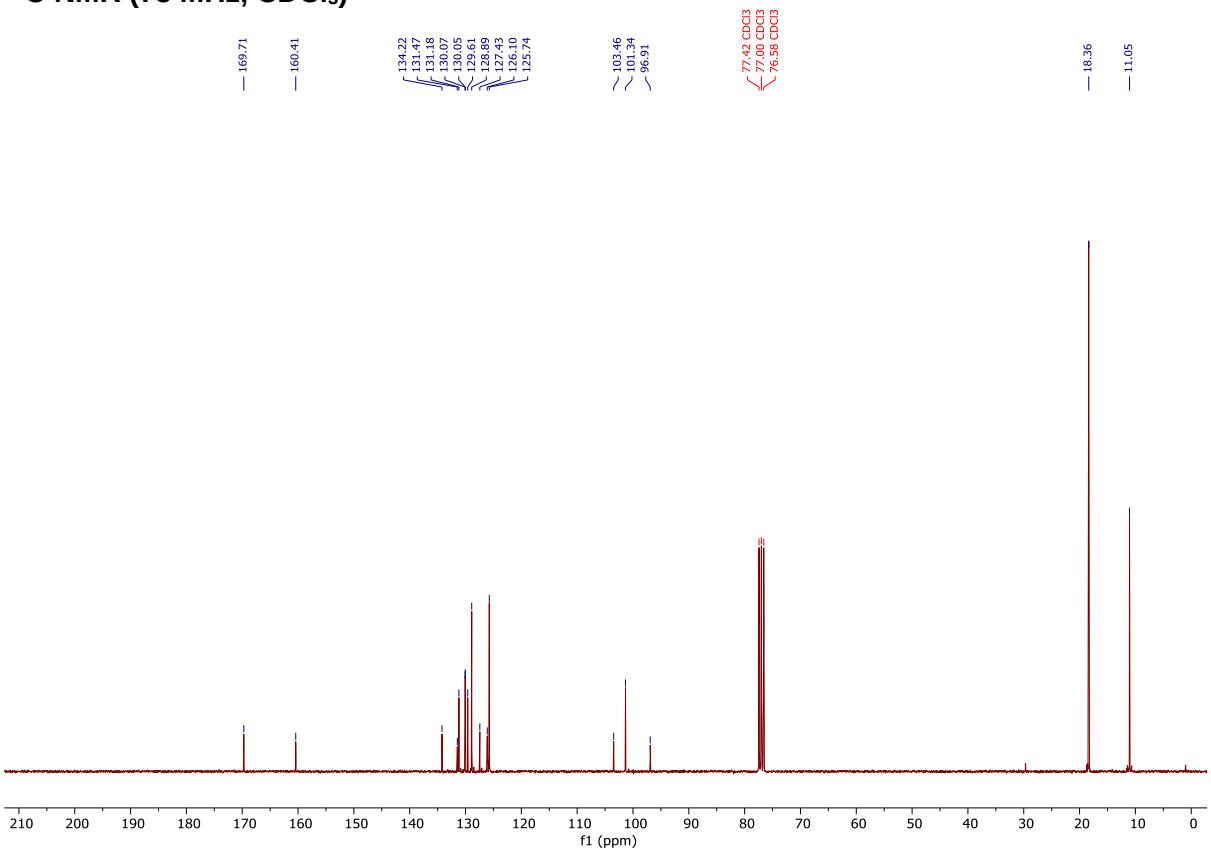


3-(2-chloro-6-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4o)

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

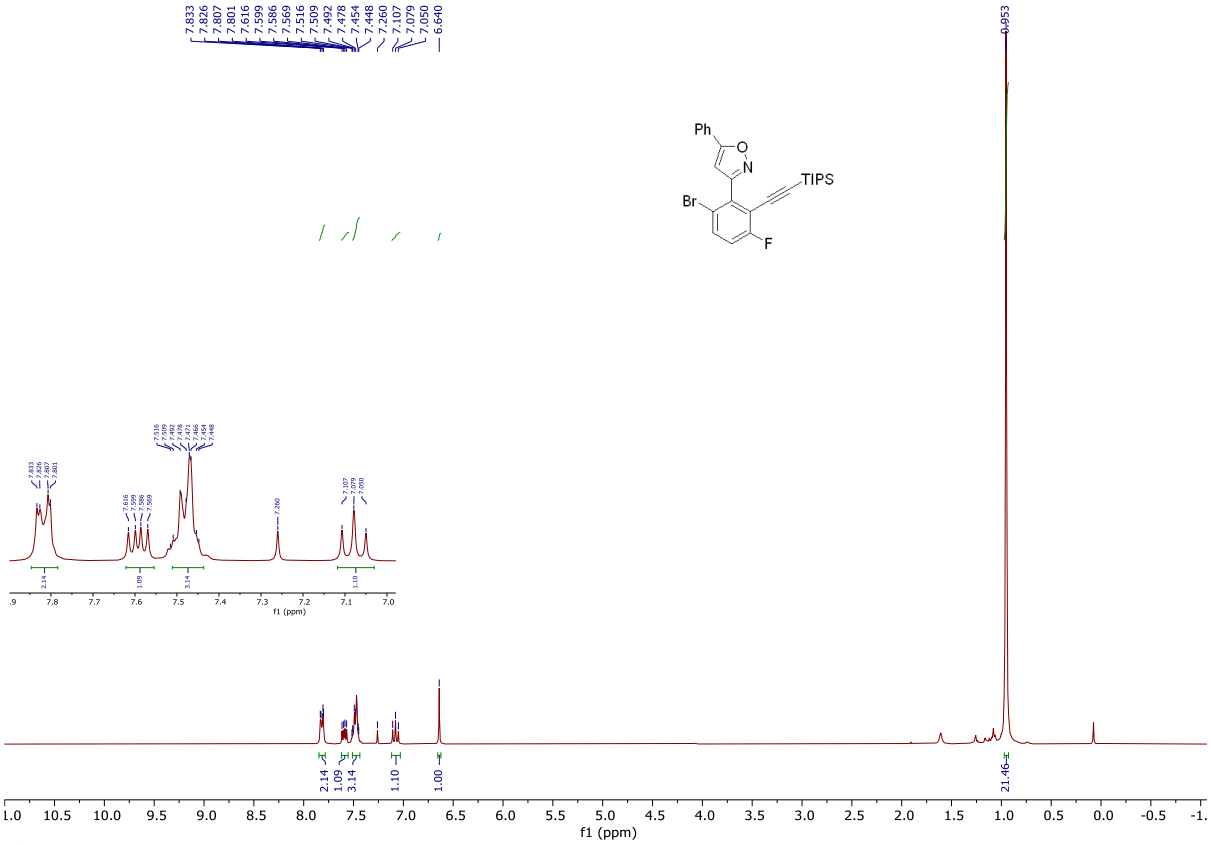


^{13}C NMR (75 MHz, $CDCl_3$)

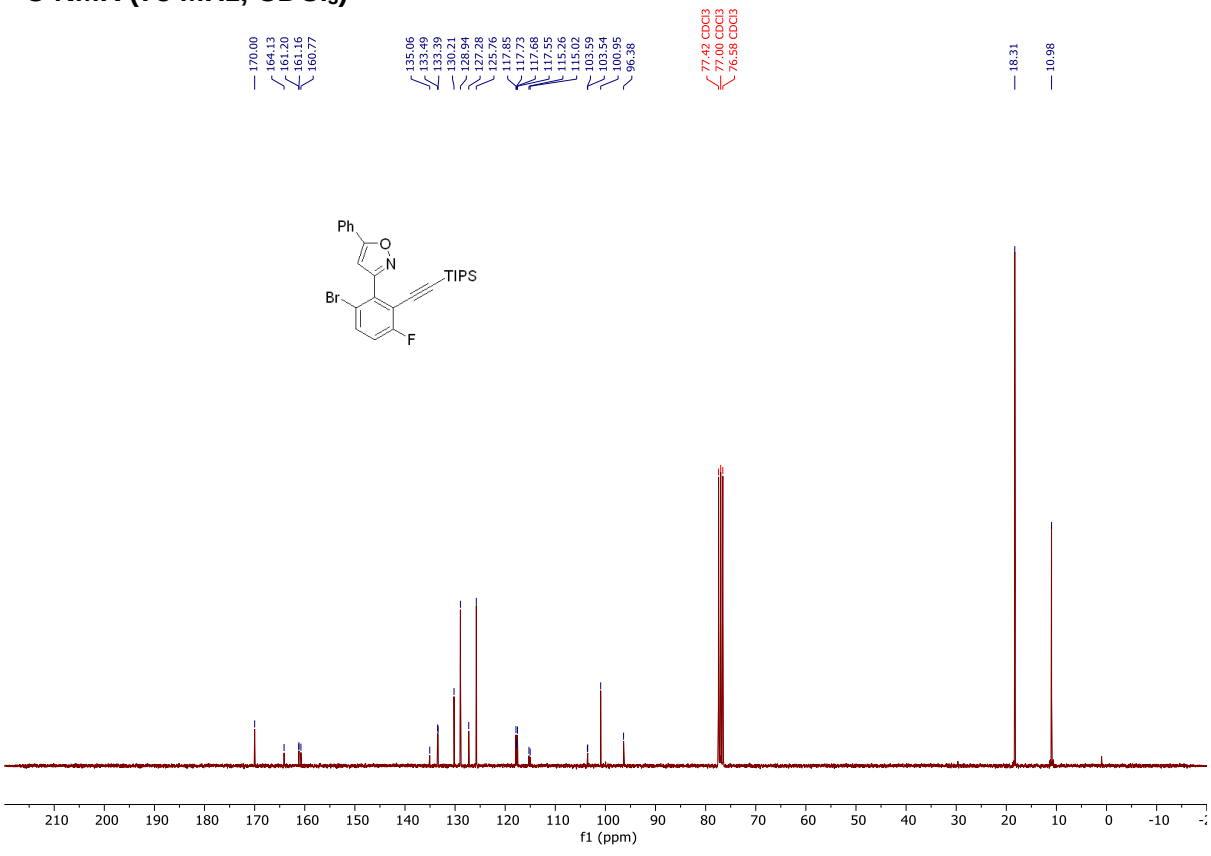


3-(6-bromo-3-fluoro-2-((triisopropylsilyl)ethynyl)phenyl)-5-phenylisoxazole (4p)

^{1}H NMR (300 MHz, $CDCl_3$)

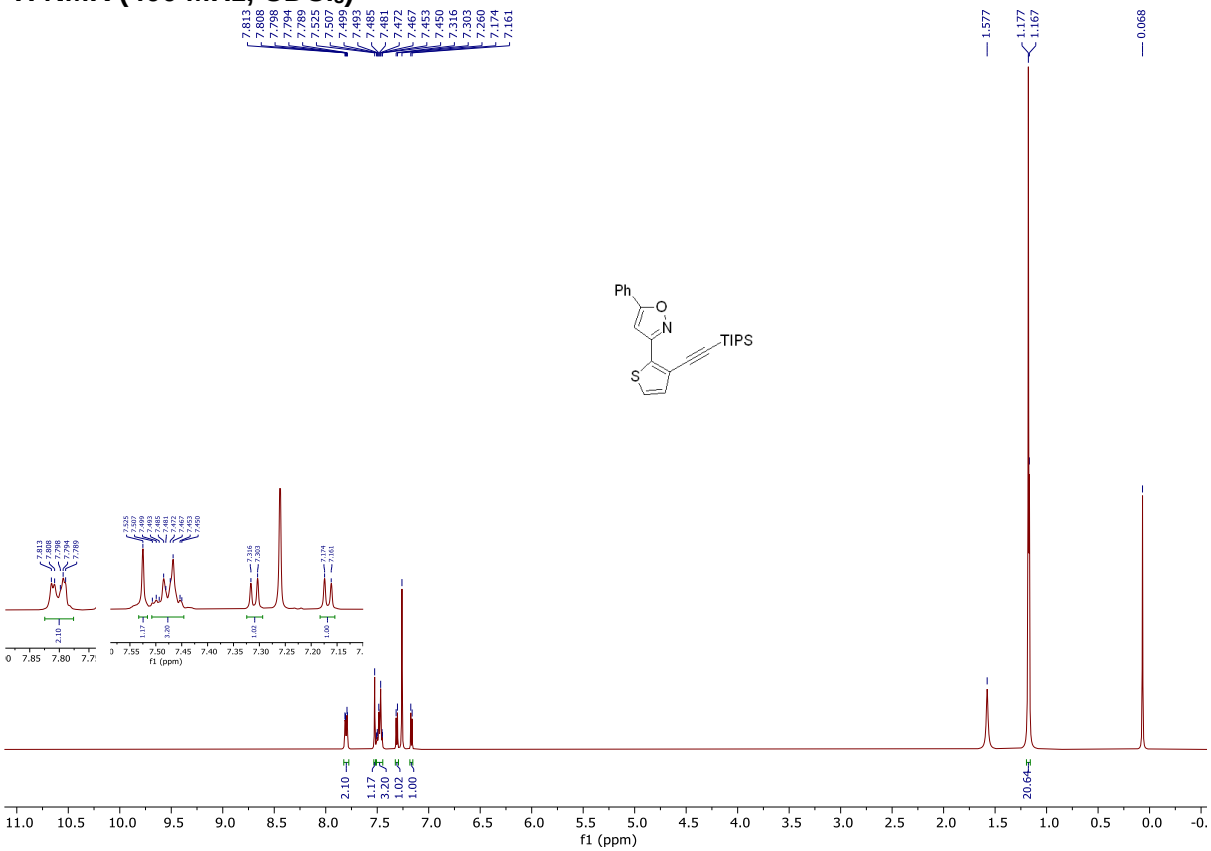


^{13}C NMR (75 MHz, $CDCl_3$)

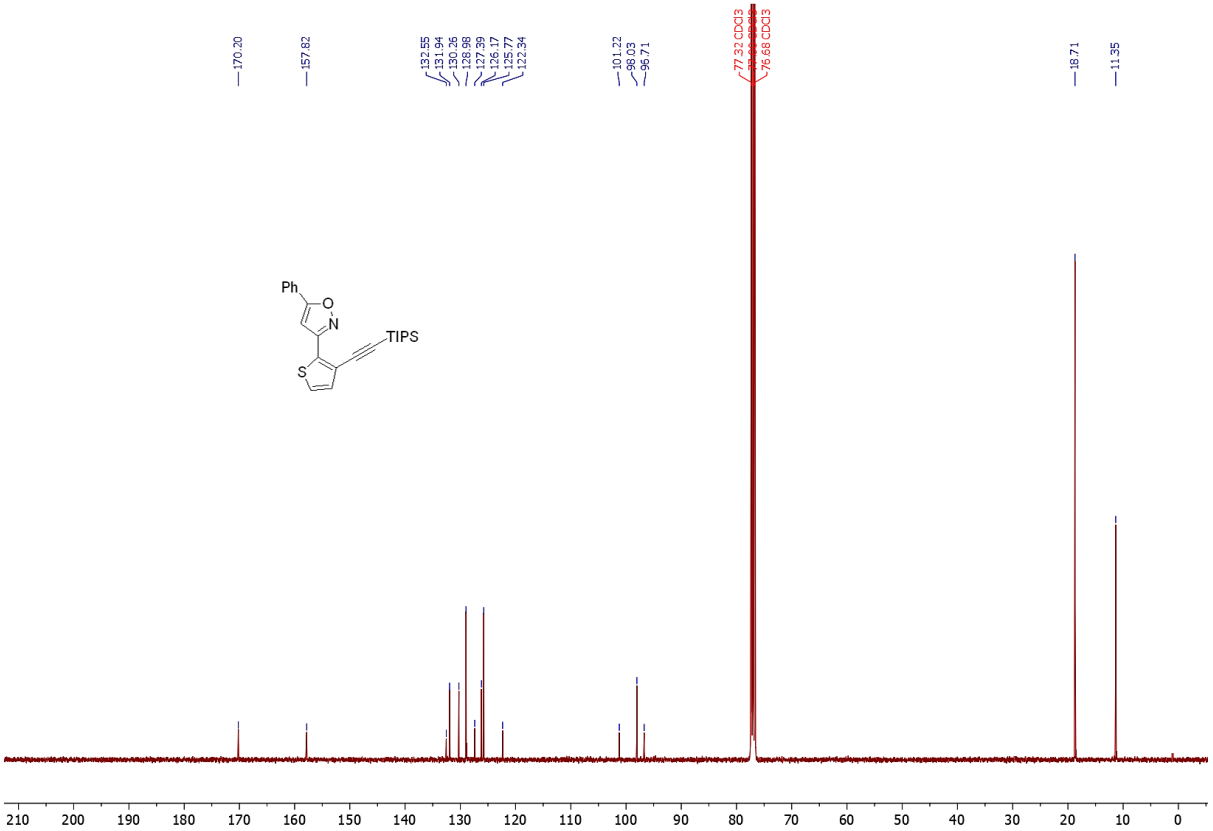


5-phenyl-3-(3-((triisopropylsilyl)ethynyl)thiophen-2-yl)isoxazole (4s)

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

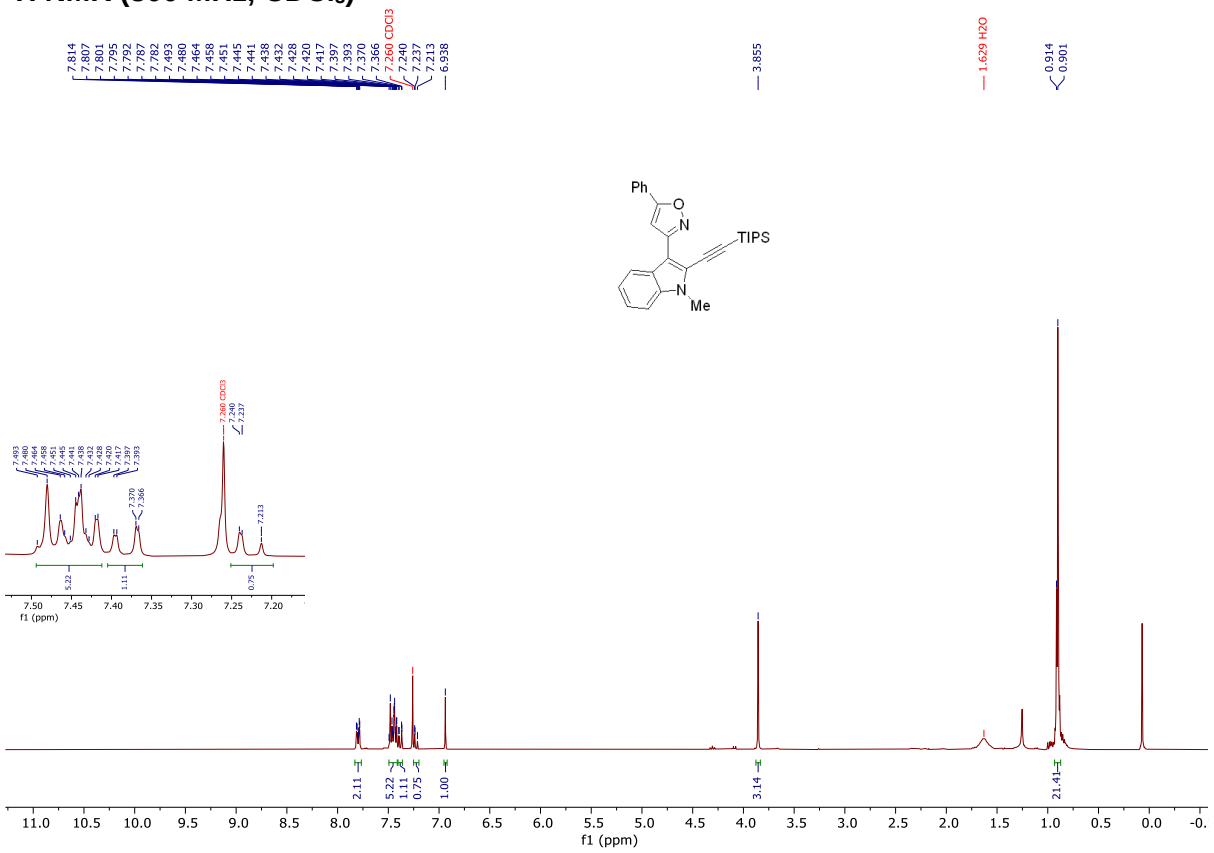


^{13}C NMR (101 MHz, $CDCl_3$)

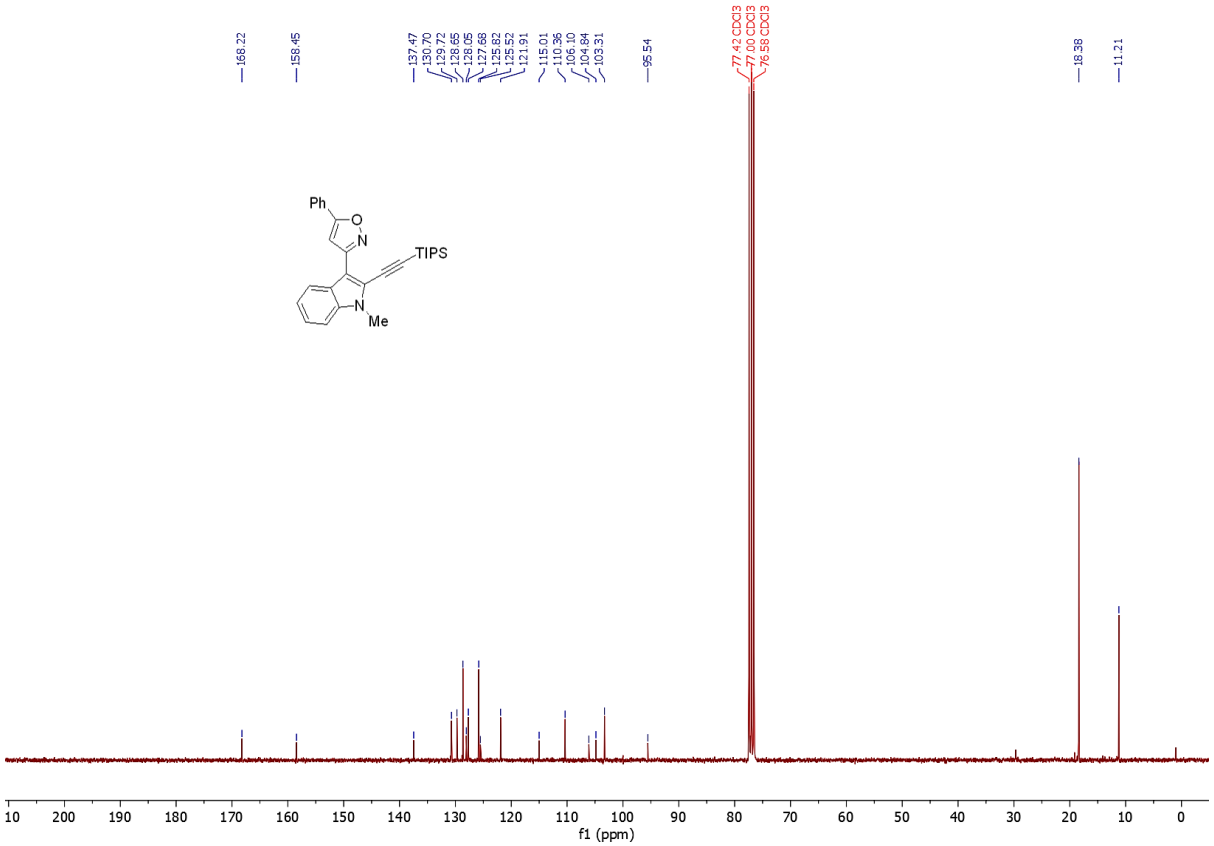


3-(1-methyl-2-((triisopropylsilyl)ethynyl)-1H-indol-3-yl)-5-phenylisoxazole (4t)

^{1}H NMR (300 MHz, $CDCl_3$)

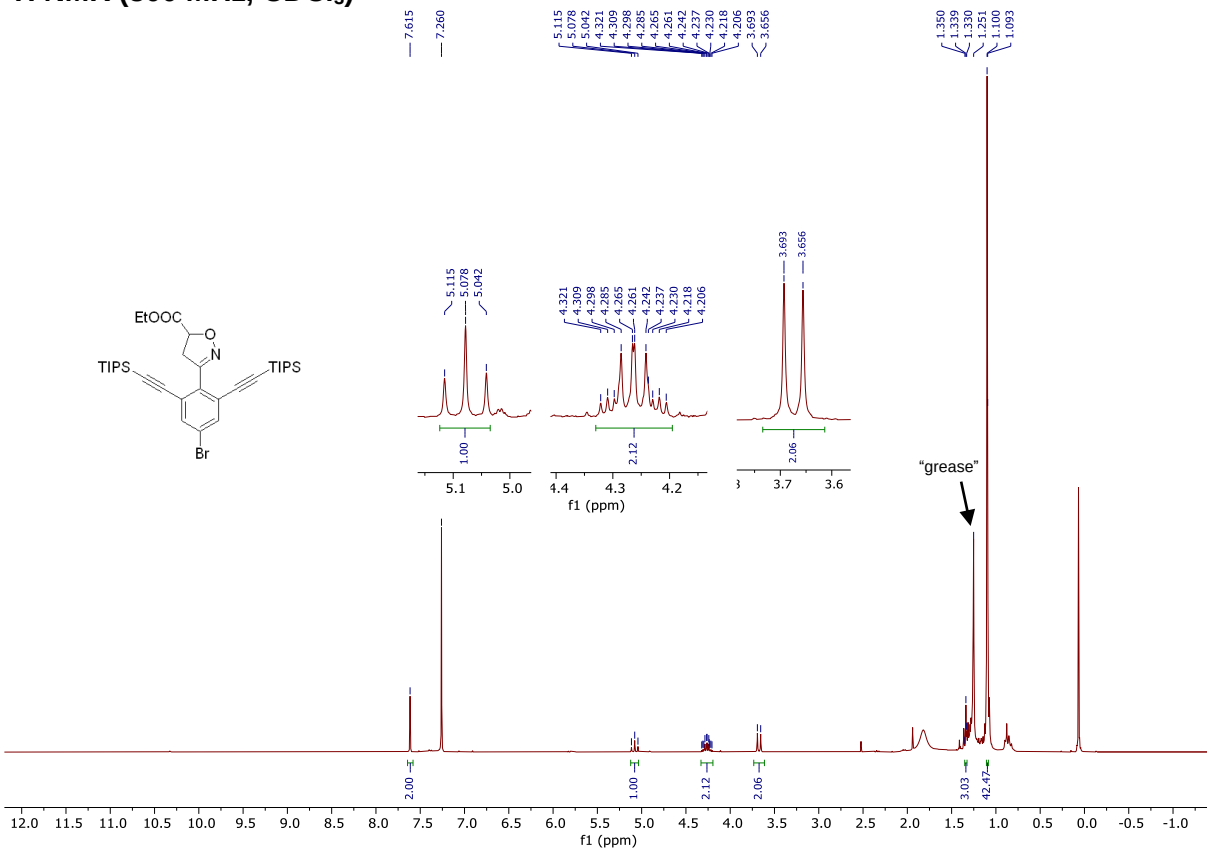


^{13}C NMR (75 MHz, $CDCl_3$)

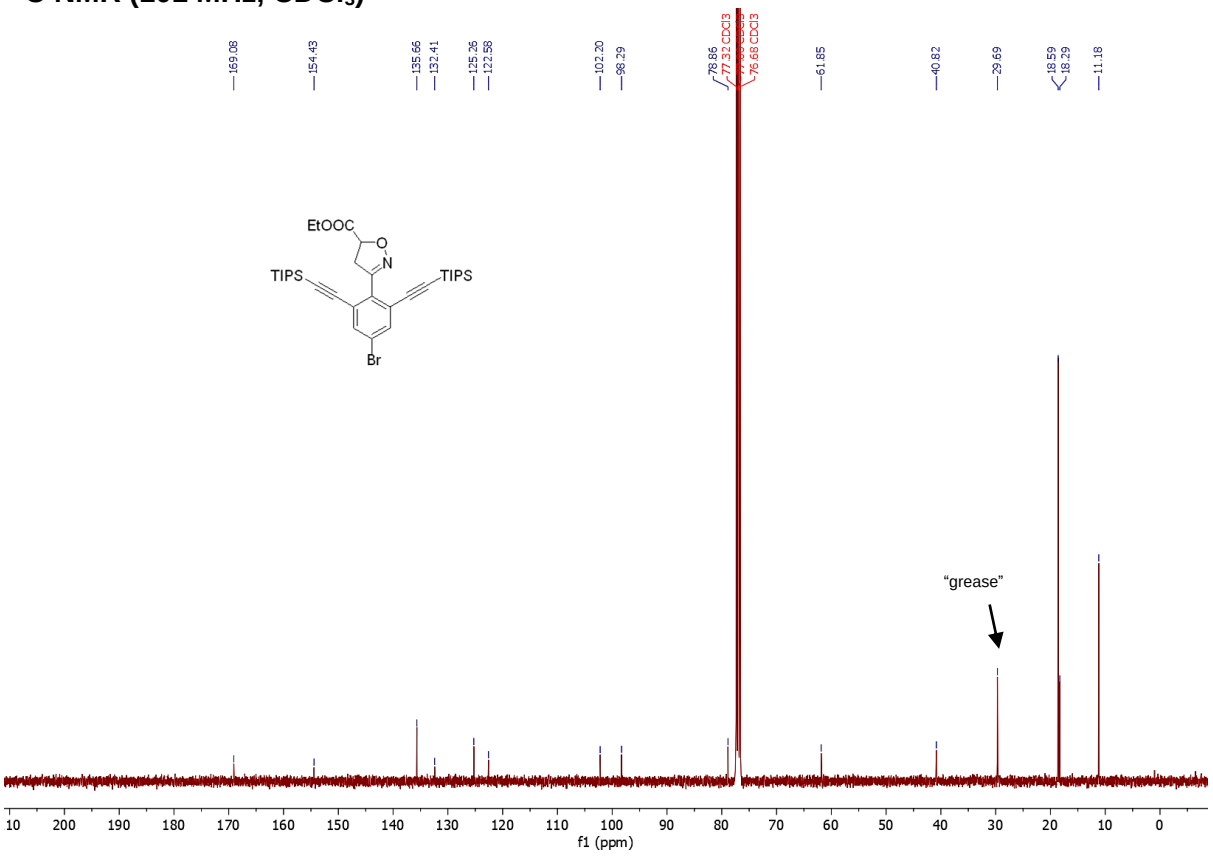


ethyl 3-(4-bromo-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-4,5-dihydroisoxazole-5-carboxylate (3u)

^{1}H NMR (300 MHz, $CDCl_3$)

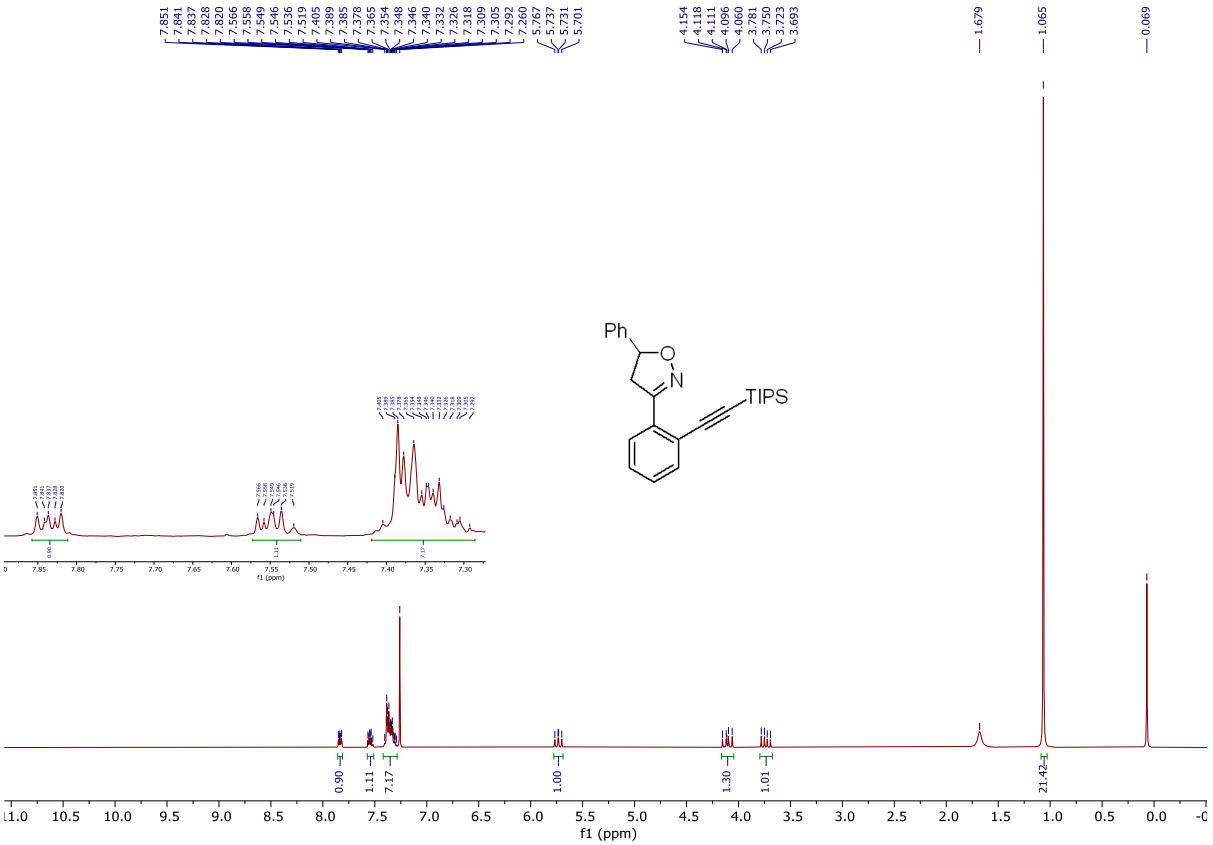


^{13}C NMR (101 MHz, $CDCl_3$)

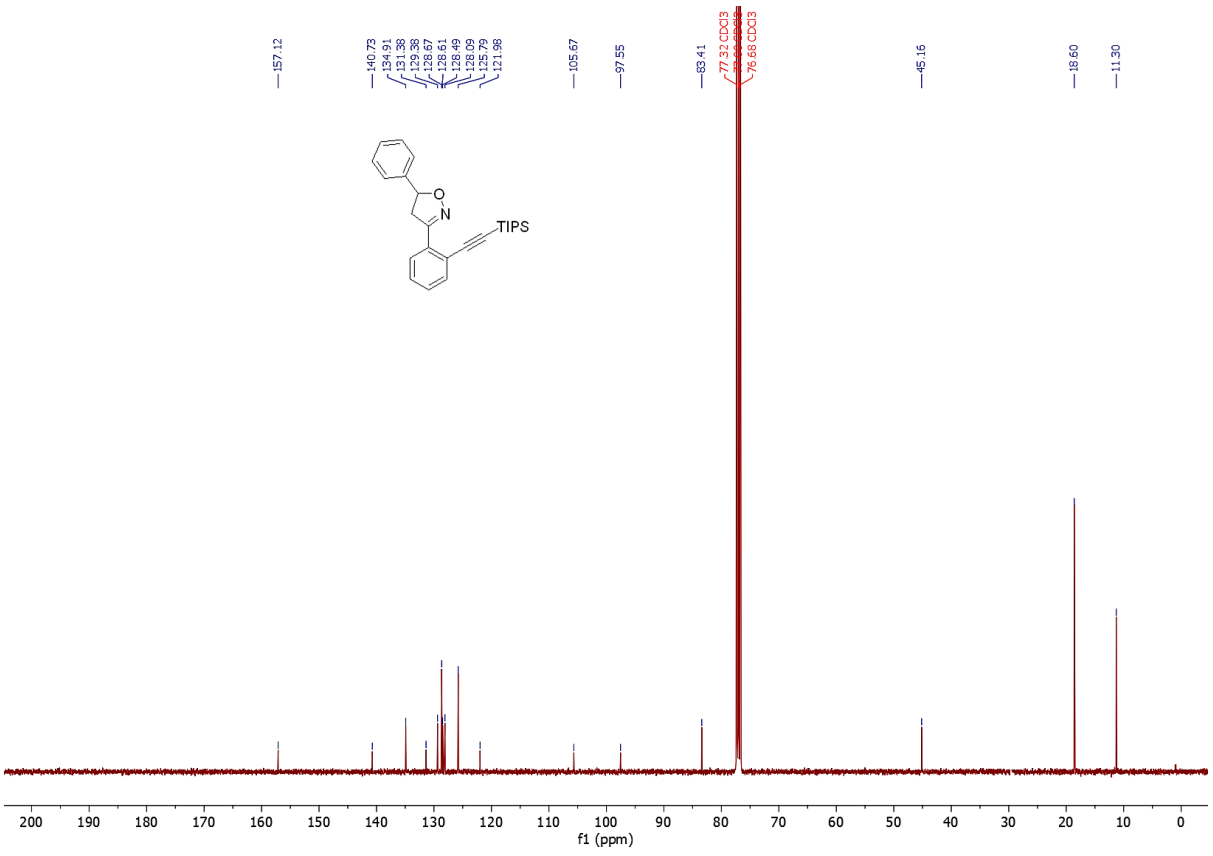


5-phenyl-3-(2-((triisopropylsilyl)ethynyl)phenyl)-4,5-dihydroisoxazole (4v)

^{1}H NMR (300 MHz, $CDCl_3$)

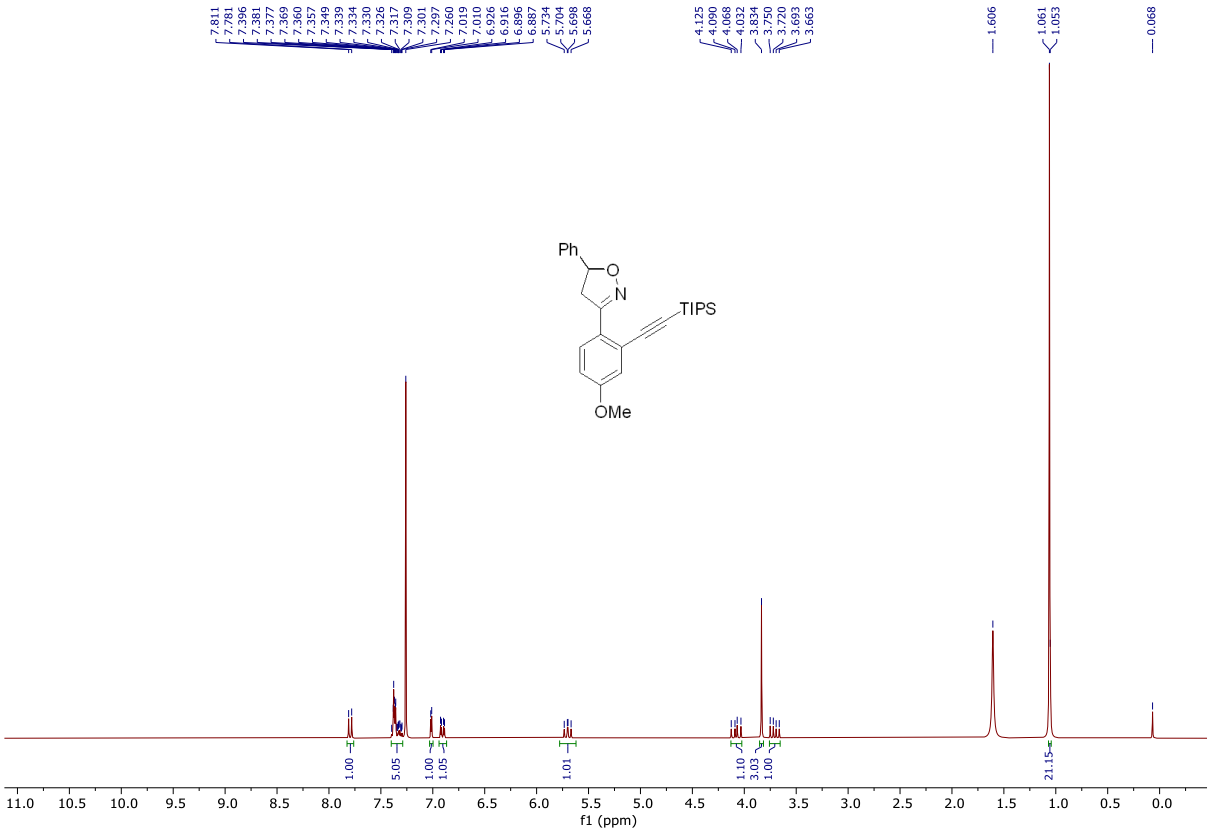


^{13}C NMR (101 MHz, $CDCl_3$)

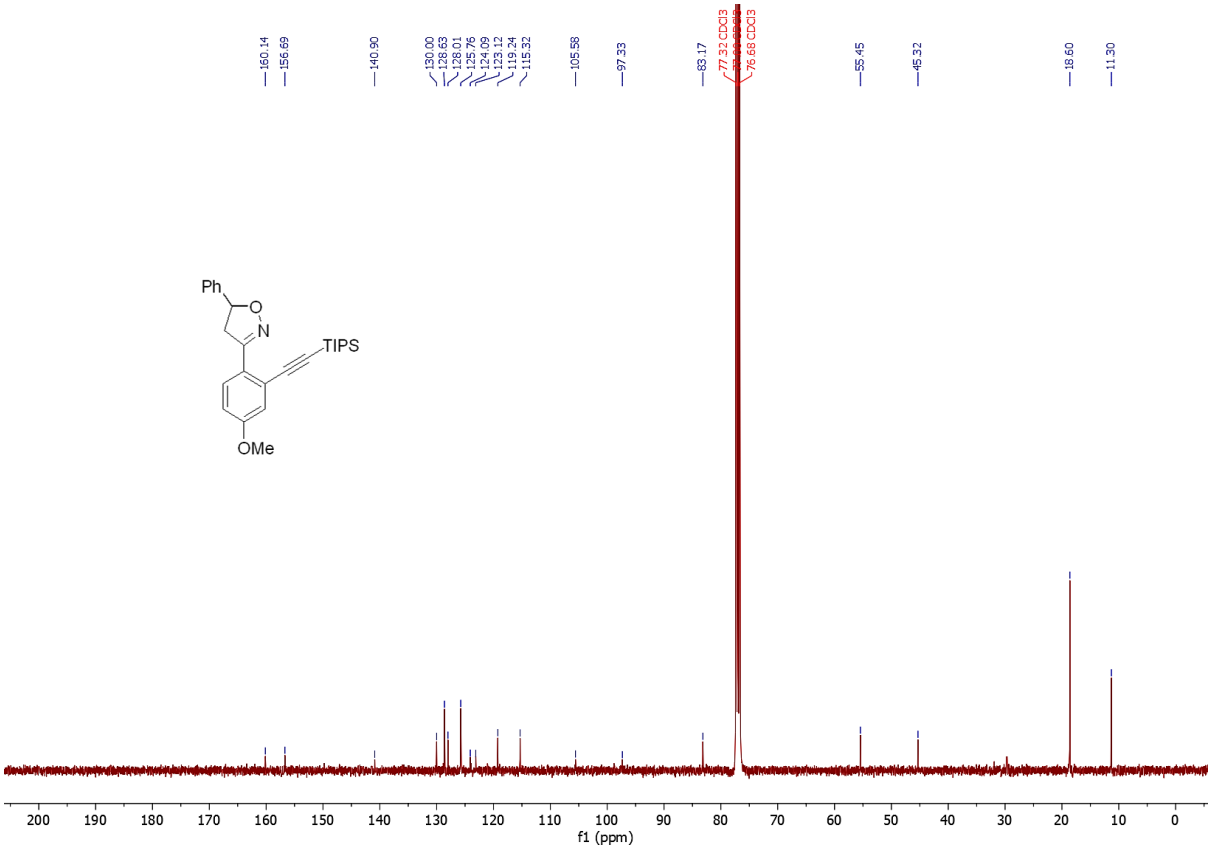


3-(4-methoxy-2-((triisopropylsilyl)ethynyl)phenyl)-5-phenyl-4,5-dihydroisoxazole (4w)

^{1}H NMR (300 MHz, $CDCl_3$)

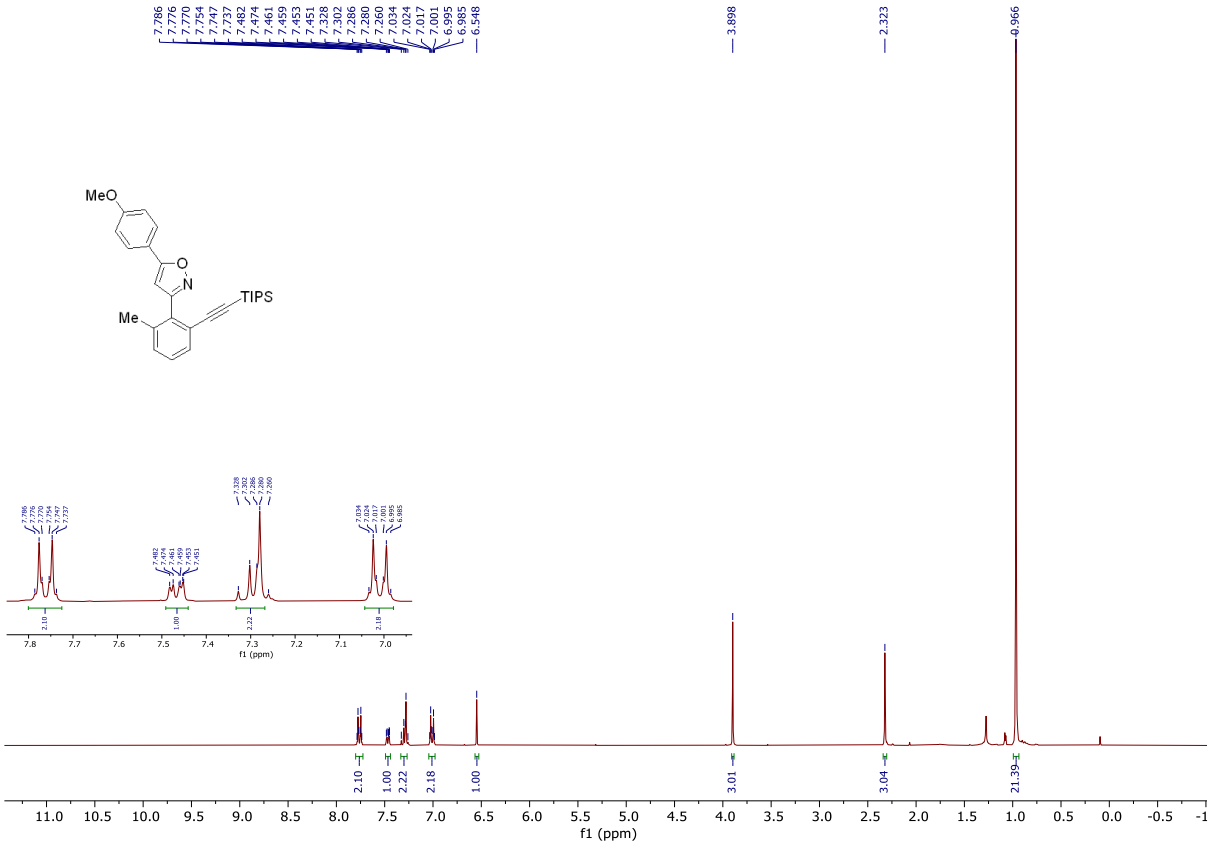


^{13}C NMR (101 MHz, $CDCl_3$)

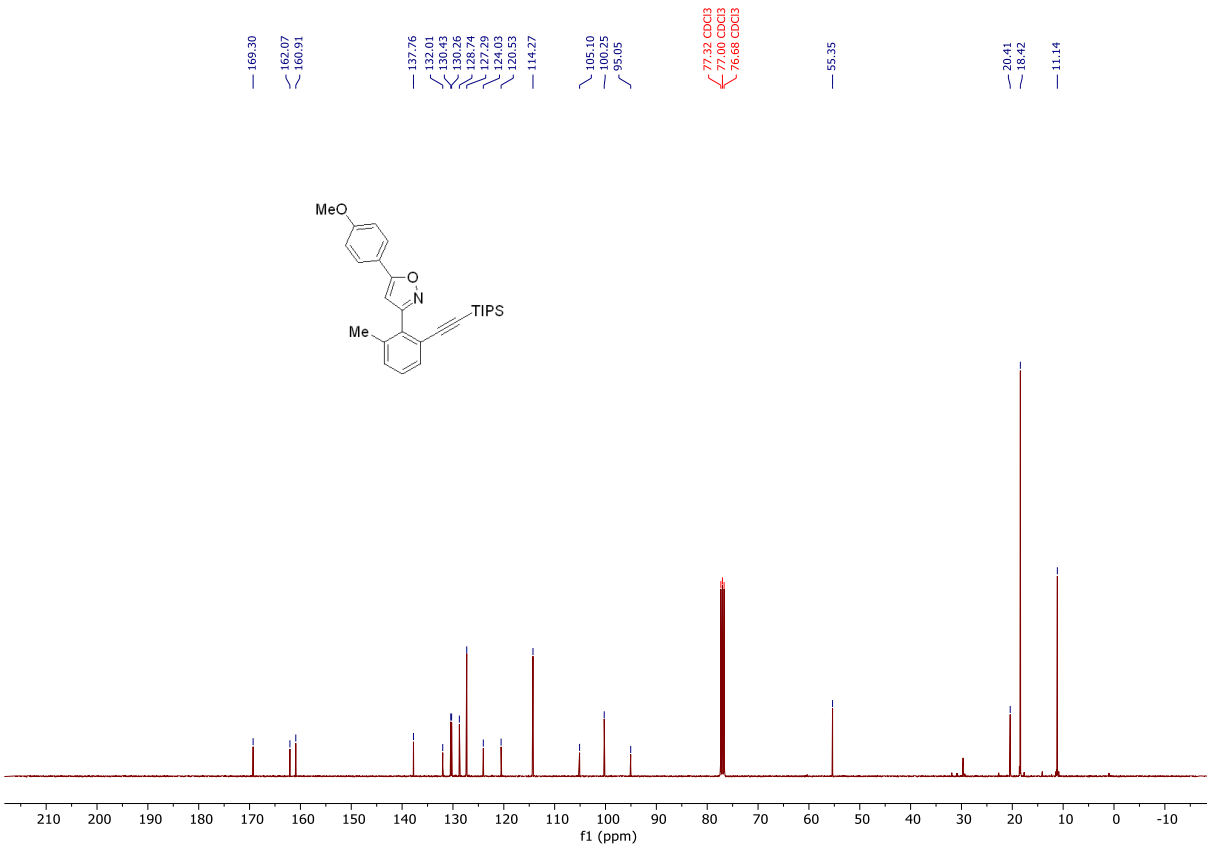


5-(4-methoxyphenyl)-3-(2-methyl-6-((triisopropylsilyl)ethynyl)phenyl)isoxazole (4x)

^{1}H NMR (300 MHz, $CDCl_3$)

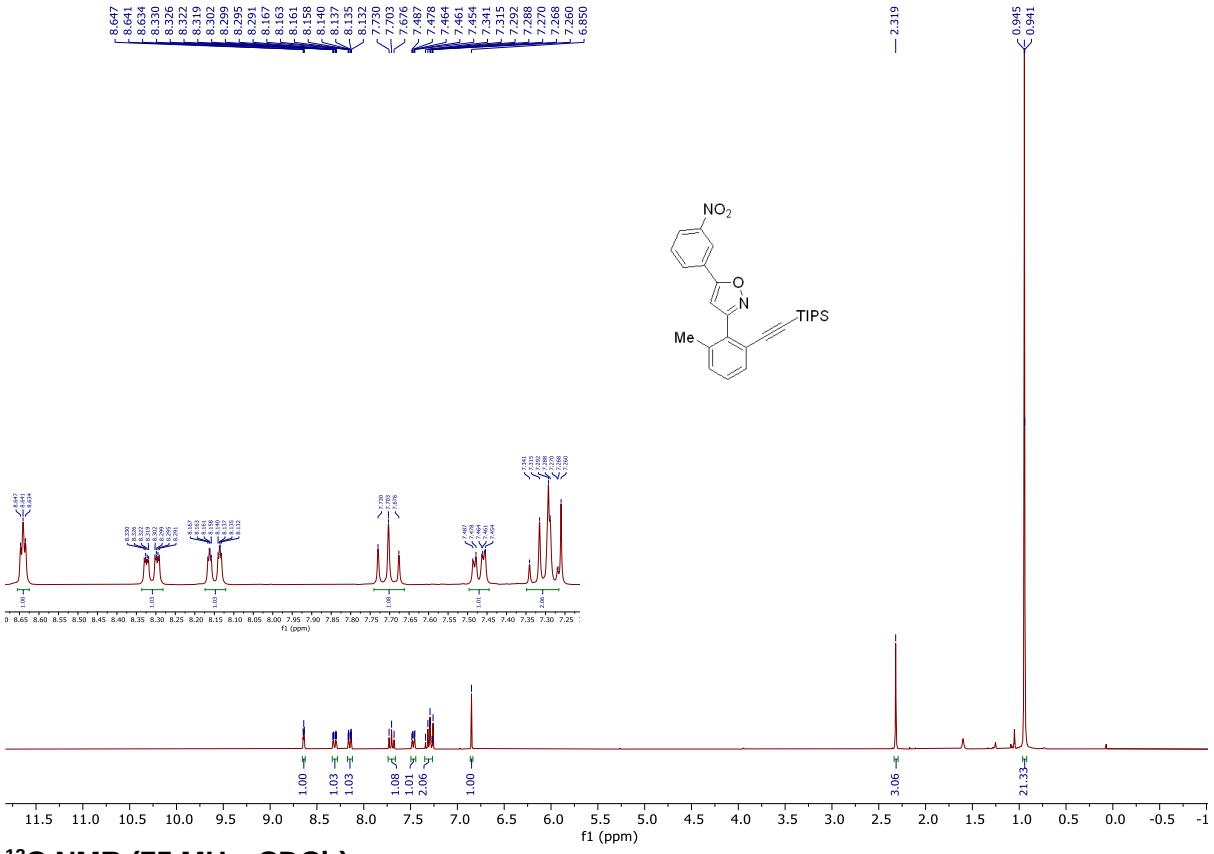


^{13}C NMR (101 MHz, $CDCl_3$)

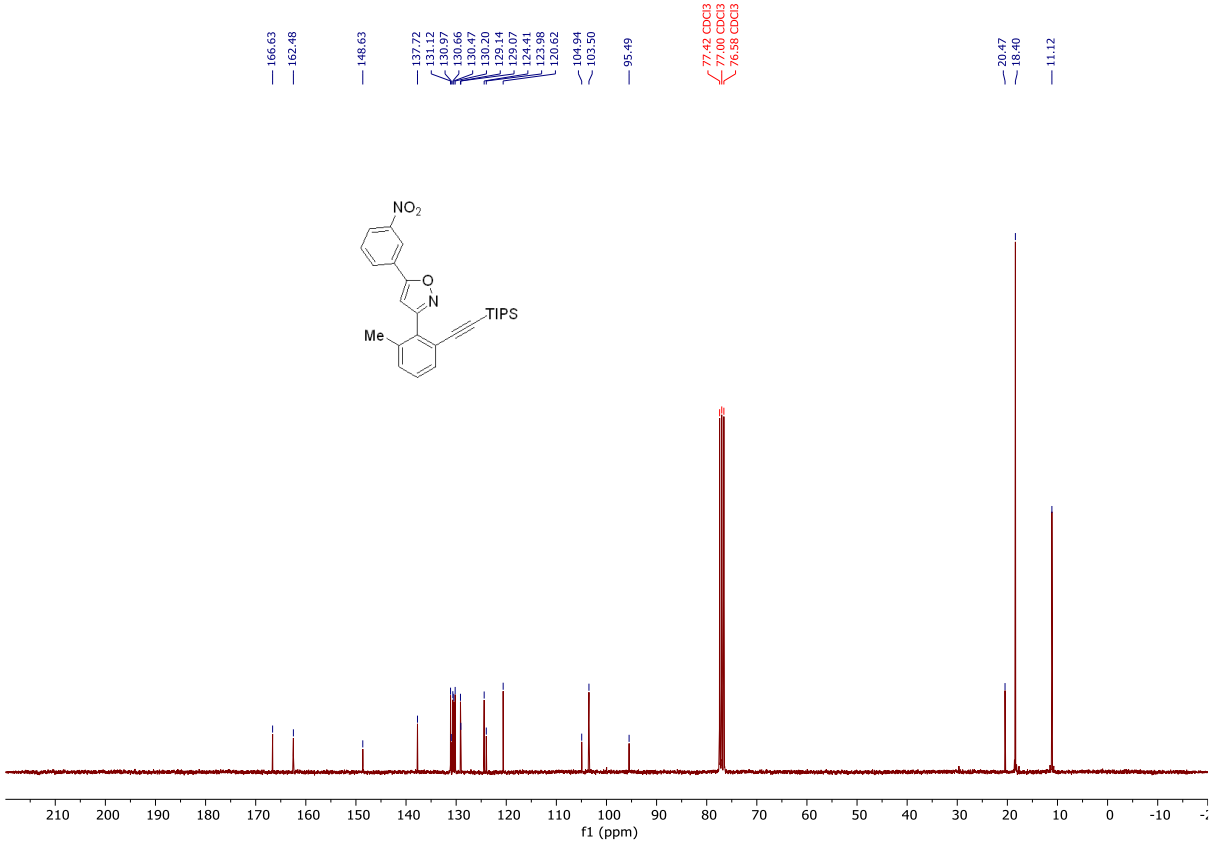


3-(2-methyl-6-((triisopropylsilyl)ethynyl)phenyl)-5-(3-nitrophenyl)isoxazole (4y)

^{1}H NMR (300 MHz, $CDCl_3$)

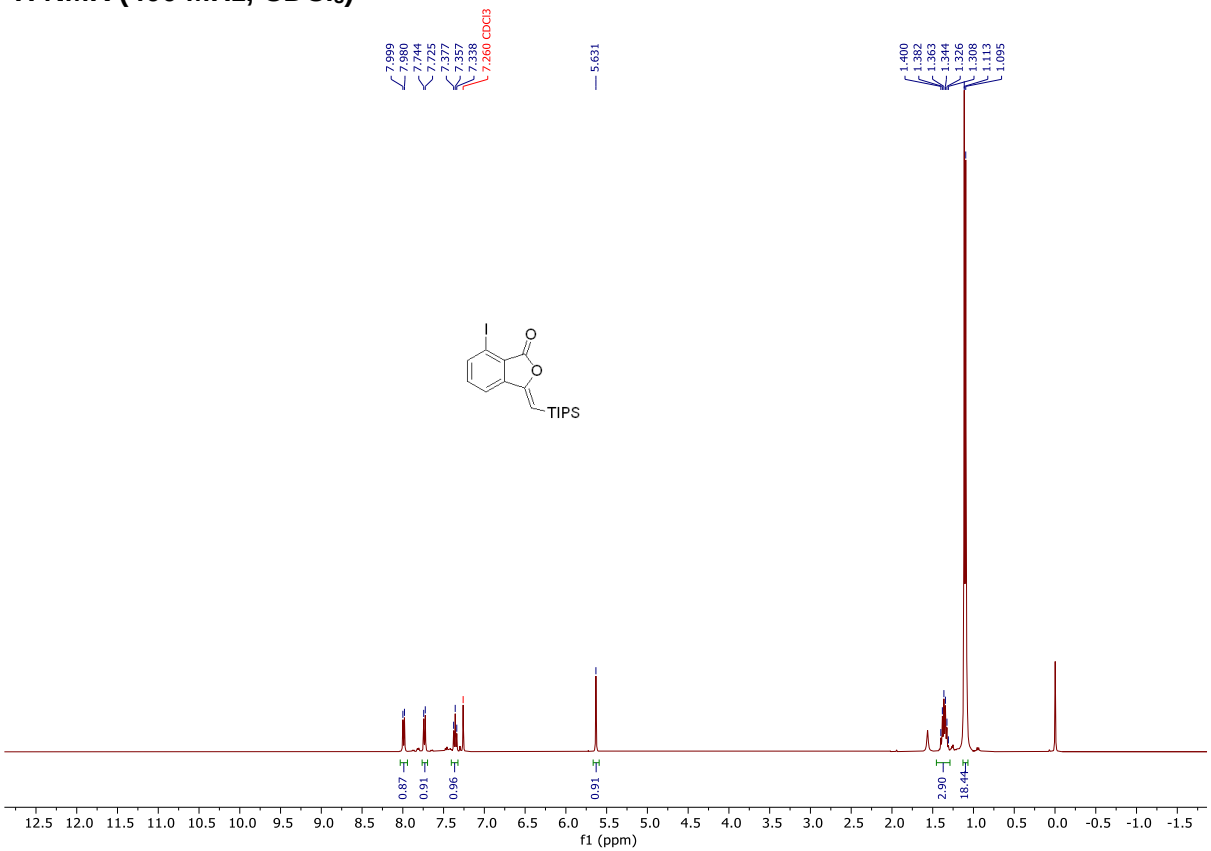


^{13}C NMR (75 MHz, $CDCl_3$)

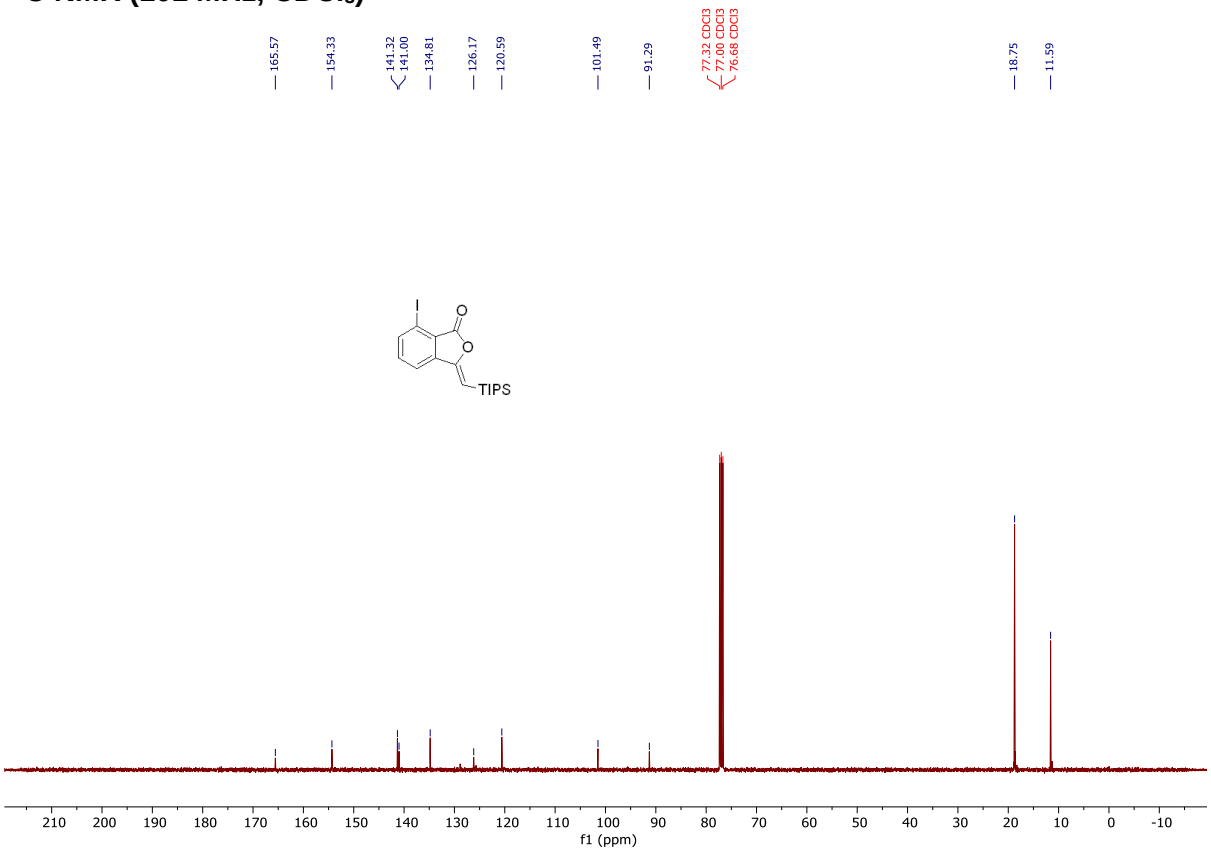


(Z)-7-iodo-3-((triisopropylsilyl)methylene)isobenzofuran-1(3H)-one (5)

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

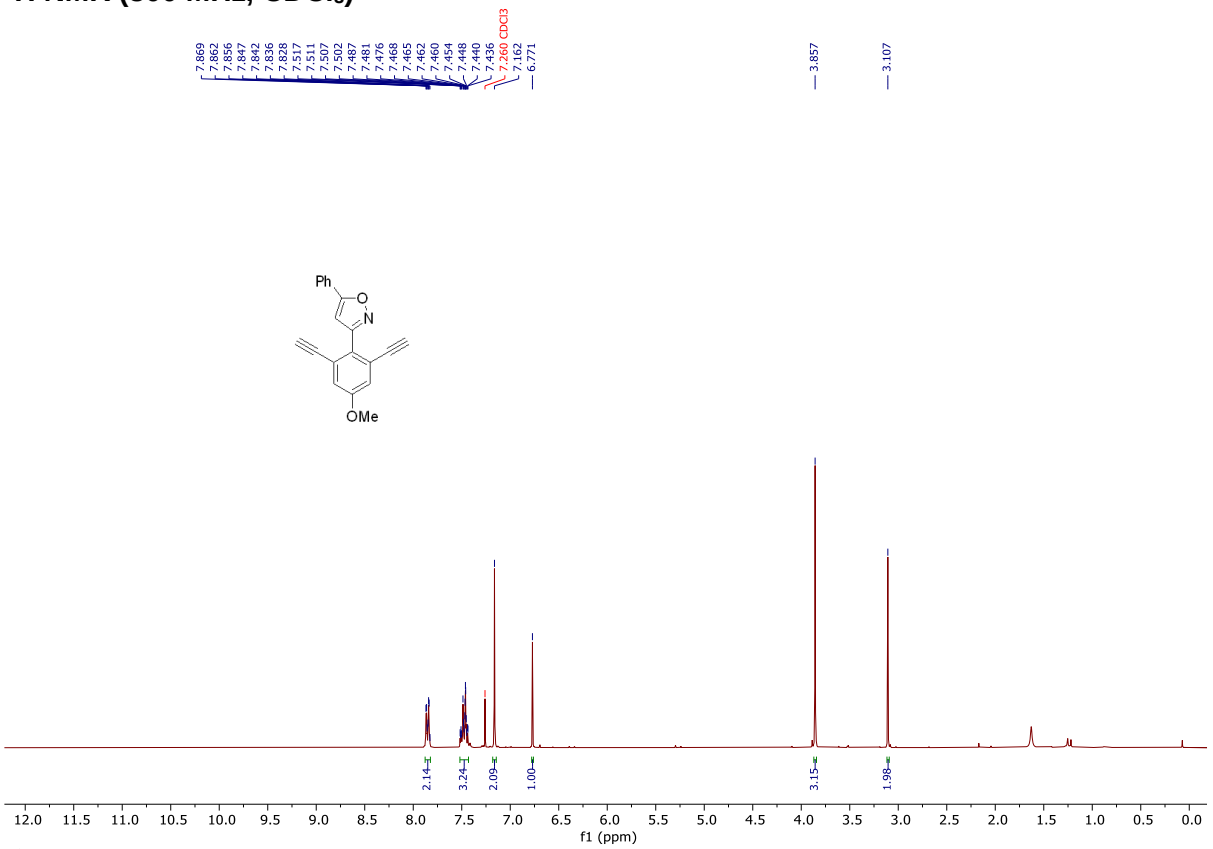


^{13}C NMR (101 MHz, $CDCl_3$)

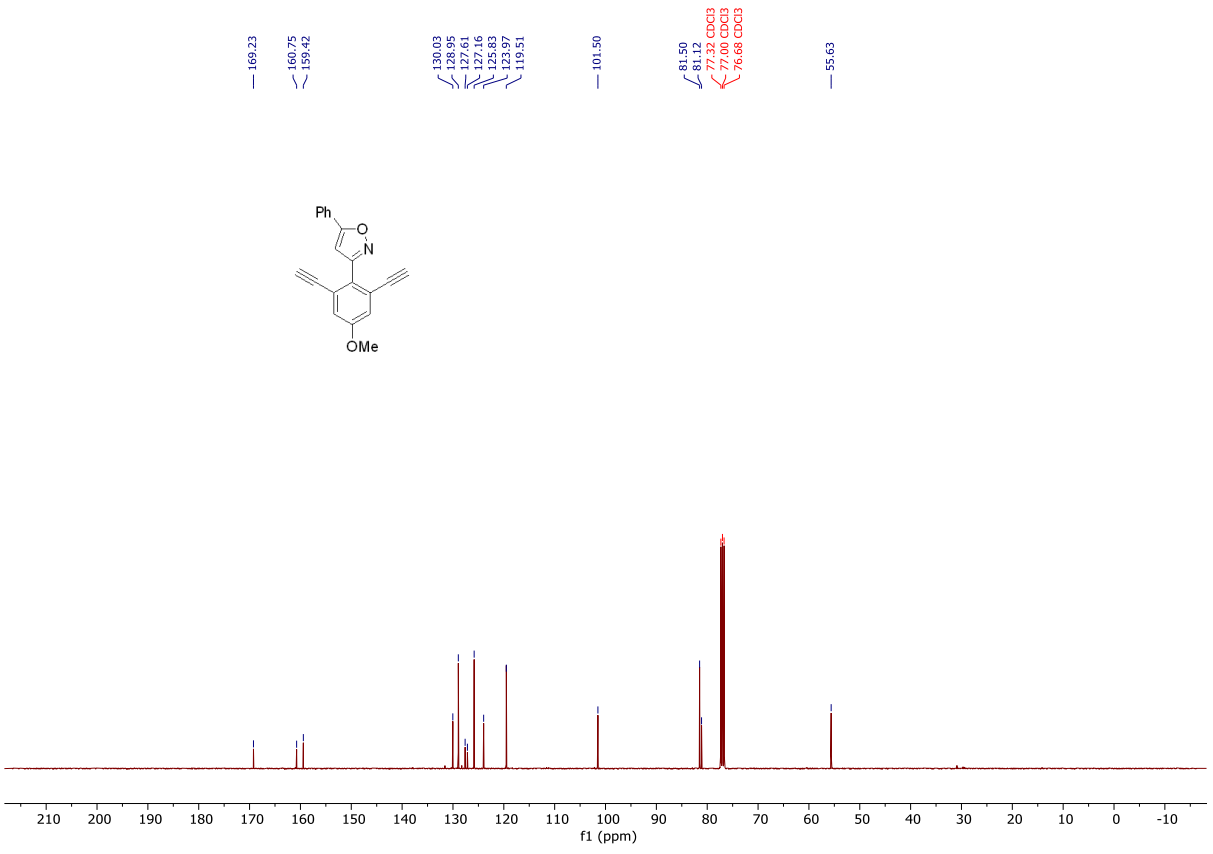


3-(2,6-diethynyl-4-methoxyphenyl)-5-phenylisoxazole (6)

^{1}H NMR (300 MHz, $CDCl_3$)

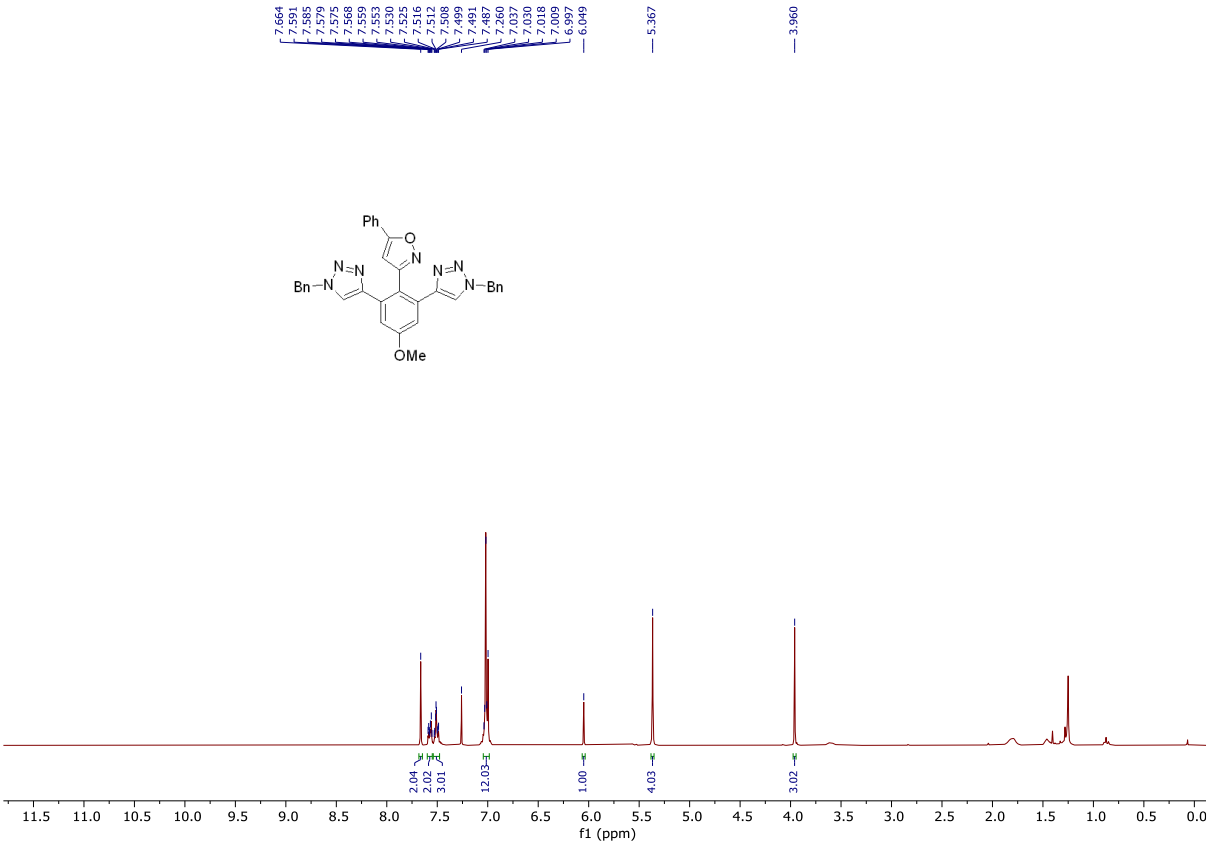


^{13}C NMR (101 MHz, $CDCl_3$)

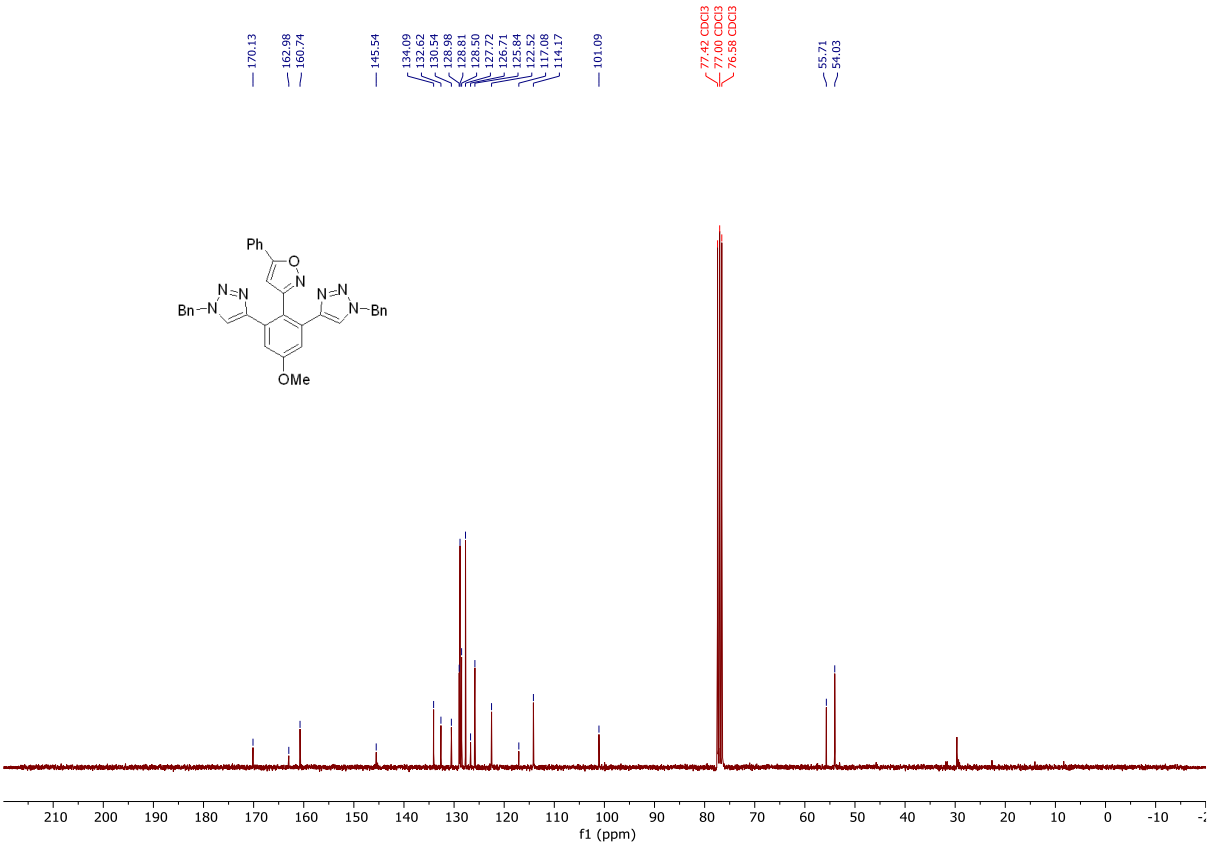


3-(2,6-bis(1-benzyl-1H-1,2,3-triazol-4-yl)-4-methoxyphenyl)-5-phenylisoxazole (7)

^{1}H NMR (300 MHz, $CDCl_3$)

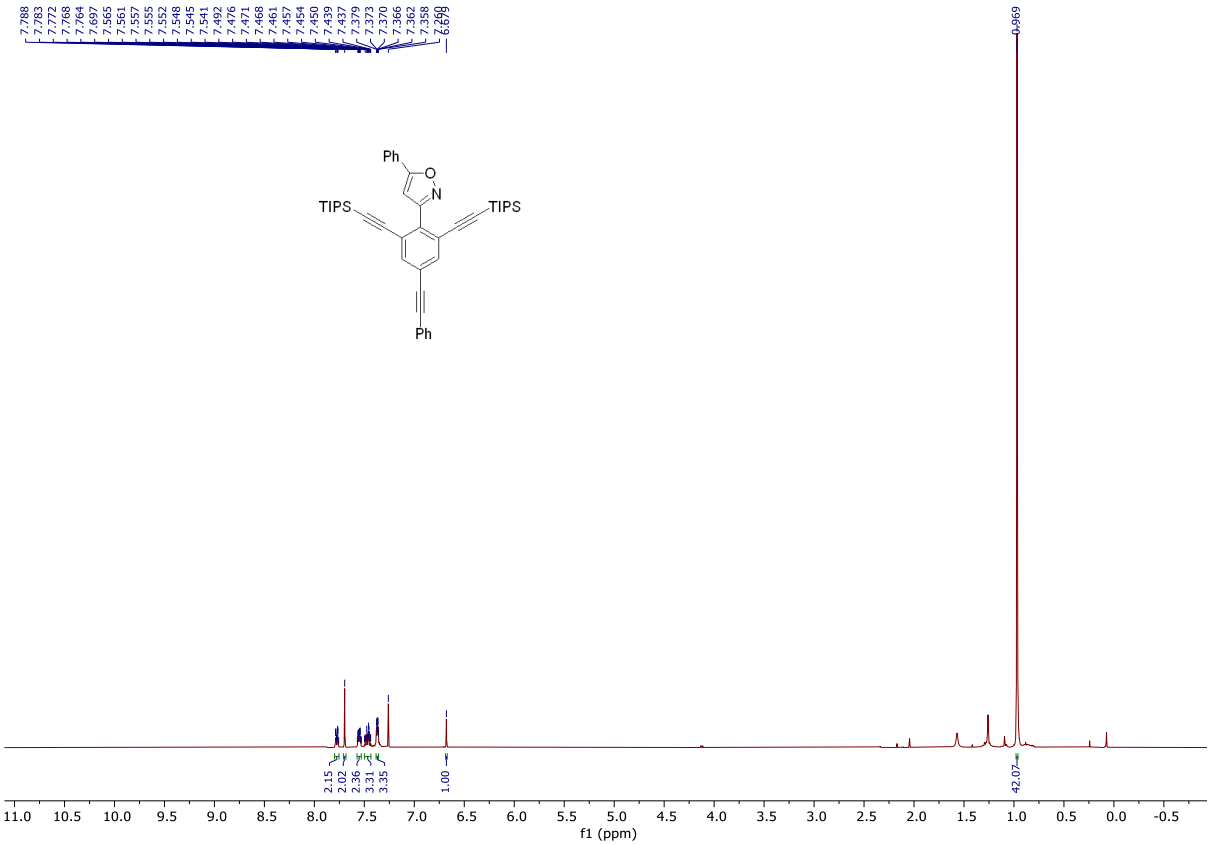


^{13}C NMR (75 MHz, $CDCl_3$)

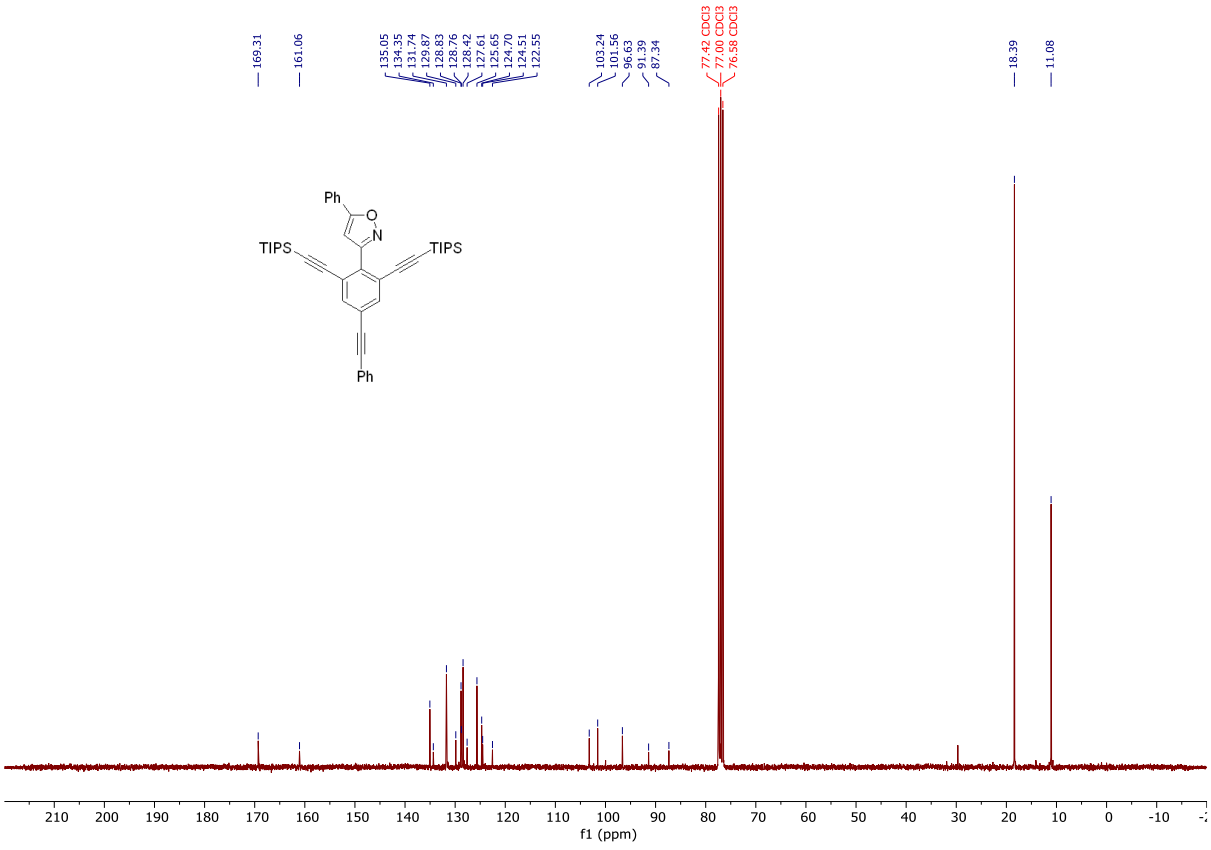


5-phenyl-3-(4-(phenylethynyl)-2,6-bis((triisopropylsilyl)ethynyl)phenyl)isoxazole (8)

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

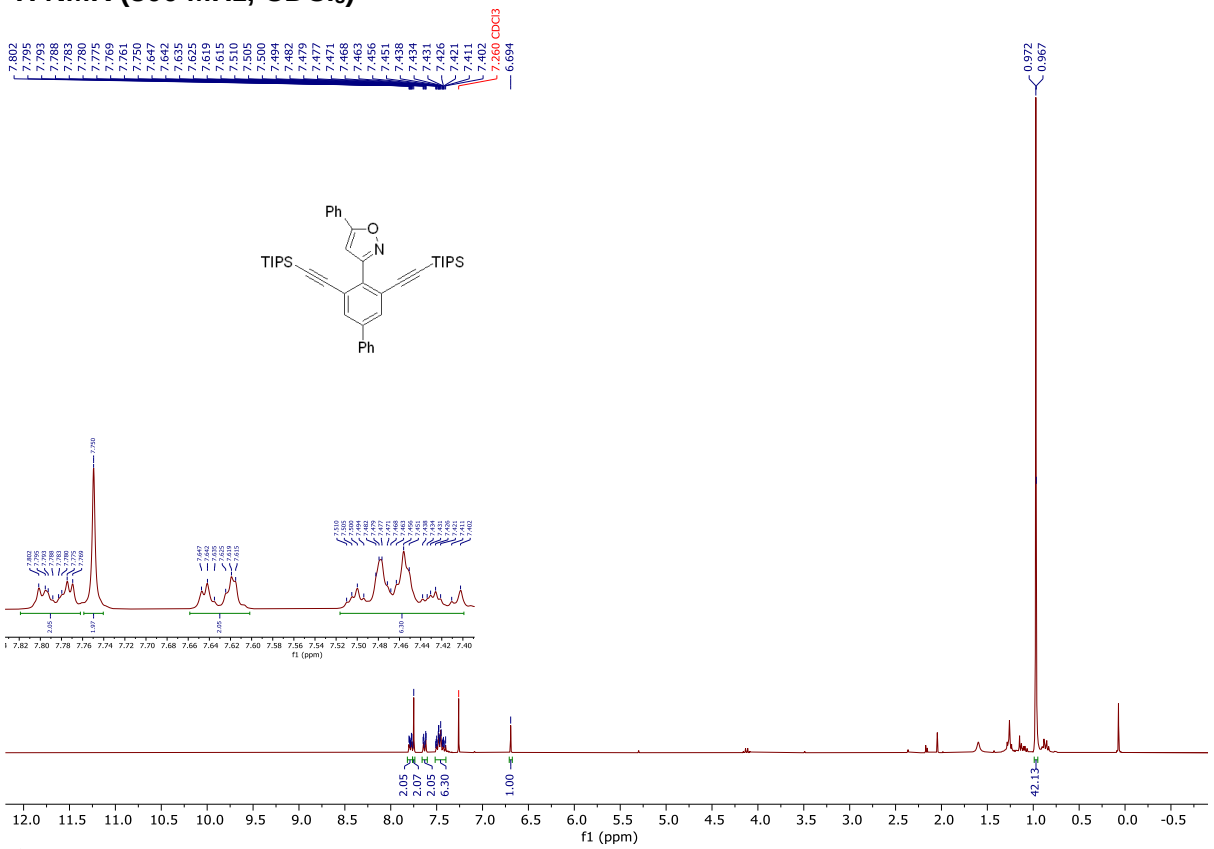


^{13}C NMR (75 MHz, $CDCl_3$)



3-(3,5-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-yl)-5-phenylisoxazole (9)

^{1}H NMR (300 MHz, $CDCl_3$)



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