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Supporting Information (55 pages)

Synthesis of 4-Amino-5-allenylisoxazoles via Gold(I)-Catalysed Propargyl Aza-Claisen Rearrangement

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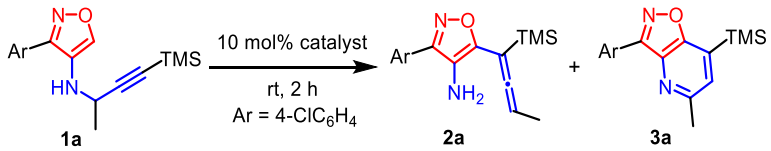
1. General techniques

NMR spectra were recorded on a Bruker biospin AVANCE II (400 MHz for ^{1}H, 100 MHz for ^{13}C) or a Bruker biospin AVANCE III (500 MHz for ^{1}H, 125 MHz for ^{13}C, 160 MHz for ^{11}B) instrument in the indicated solvent. Chemical shifts are reported in units parts per million (ppm) relative to the signal (0.00 ppm) for internal tetramethylsilane for solutions in $CDCl_3$ (7.26 ppm for 1H, 77.16 ppm for ^{13}C). Multiplicities are reported using the following abbreviations: s; singlet, d; doublet, dd; doublet of doublets, t; triplet, q; quartet, m; multiplet, br; broad, *J*; coupling constants in Hertz. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer. Only the strongest and/or structurally important peaks are reported as IR data given in cm^{-1}. Mass spectra were measured using a JMS-700 Mstation and Bruker micrOTOF II. HRMS (EI, 70 eV) was calibrated as perfluorokerosene and HRMS (ESI-TOF) was calibrated as sodium formate. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light (254 nm), and were visualized using an aqueous alkaline $KMnO_4$ solution. Gel permeation chromatography (GPC) for purification was performed on Japan Analytical Industry Model LC- 9225 NEXT (recycling preparative HPLC) and a Japan Analytical Industry Model UV-600 NEXT ultra violet detector with a polystyrene gel column (JAIGEL-1H, 20 mm × 600 mm), using chloroform as solvent (3.5 mL/min). Column chromatography was performed on Silica Gel 60 N, purchased from Fuji Silysia Chemical Ltd. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (1.0 mm) prepared in our laboratory. 3-(4-chlorophenyl)isoxazole-4-amine,[1] isoxazol-4-amine,[2] trimethylsilyl ynone[3] and trimethylsilyl propargyl bromide[4] were synthesized according to the literatures.

2. Table S1

Table S1. Optimization of reaction conditions for the aza-Claisen rearrangement[a]



entry	catalyst	solvent	yield[b]	
			allene **2a**	pyridine **3a**
1	JohnPhosAuCl/$AgSbF_6$	DCE	54	24
2	Et_3PAuCl/$AgSbF_6$	DCE	63	37
3	Cy_3PAuCl/$AgSbF_6$	DCE	41	21
4	*t*-Bu_3PAuCl/$AgSbF_6$	DCE	0	0
5	Ph_3PAuCl/$AgSbF_6$	DCE	32	68
6	CyJhonPhosAuCl/$AgSbF_6$	DCE	68	29

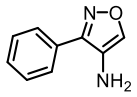
7	SPhosAuCl/$AgSbF_6$	DCE	31	41
8	RuPhosAuCl/$AgSbF_6$	DCE	77	21
9	XPhosAuCl/$AgSbF_6$	DCE	10	6
10	*t*-BuXPhosAuCl/$AgSbF_6$	DCE	0	0
11	BrettPhosAuCl/$AgSbF_6$	DCE	0	0
12	*t*-BuBrettPhosAuCl/$AgSbF_6$	DCE	0	0
13	Me-DalPhosAuCl/$AgSbF_6$	DCE	18	28
14	BINAPAuCl/$AgSbF_6$	DCE	38	12
15	IPrAuCl/$AgSbF_6$	DCE	37	22
16	L[c]AuCl/$AgSbF_6$	DCE	4	80
17	$AuCl_3$/ $AgSbF_6$[d]	DCE	0	29
18	RuPhosAuCl/$AgNTf_2$	DCE	75	18
19	RuPhosAuCl/AgOTf	DCE	91	9
20	RuPhosAuCl/AgOTf	toluene	75	25
21	RuPhosAuCl/AgOTf	1,4-dioxane	86	14
22	RuPhosAuCl/AgOTf	MeCN	93	7
23	RuPhosAuCl	MeCN	0	0
24	AgOTf	MeCN	3	0

[a]Reaction conditions: **1a** (0.1 mmol), [Au] catalyst (10 mol%), [Ag] catalyst (10 mol%), solvent (1 mL) at r.t. [b]NMR yield using dibromomethane as an internal standard. [c]L = Tris(2,4-di-*tert*-butylphenyl)phosphite. [d]The amount of $AgSbF_6$ was 30 mol%. TMS = tirimethylsilyl, DCE = 1,2-dichloroethane, JohnPhos = (2-biphenyl)di-*tert*-butylphosphine, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-yli-dene, CyJohnPhos = 2-(dicyclohexylphosphino)biphenyl, XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl, *t*-BuXPhos = 2-di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl, BrettPhos = 2-(dicyclohexylphosphino)3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl, *t*-BuBrettPhos = 2-(di-*tert*-butylphosphino)-2′,4′,6′- triisopropyl-3,6-dimethoxy-1,1′-biphenyl, RuPhos = 2-dicyclohex-ylphosphino-2’,6’-diisopropoxybiphenyl, Tf = trifluoromethanesulfonyl.

3. Synthesis of 3-substituted-4-aminoisoxazoles

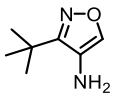
Representative procedure for the synthesis of 3-phenylisoxazol-4-amine

To a mixture of *N*-hydroxybenzimidoyl chloride[5] (2.38 g, 12.5 mmol) and ethyl (*E*)-3-(pyrrolidin- 1-yl)acrylate[6] (21.2 g, 12.5 mmol) in MeCN (2 mL/mmol of 3-(pyrrolidin-1-yl)acrylate), NEt_3 (2.07 mL, 15 mmol) was added dropwise at 0 °C under an argon atmosphere. After being stirred at room temperature for 3 h, the residue was poured into diethyl ether and water. The aqueous layer was extracted with diethyl ether. The combined extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was dissolved in acetic acid (4 mL/mmol of 3-(pyrrolidin-1-yl)acrylate), 6 M HCl (10 mL/mmol of 3-(pyrrolidin-1-yl)acrylate was added under an argon atmosphere. After being refluxed for 6 h, the residue was poured into ethyl acetate and water. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was dissolved in *tert*-butyl alcohol (3 mL/mmol of 3-(pyrrolidin-1-yl)acrylate), diphenyl phosphoryl azide (2.69 mL, 12.5 mmol) and NEt_3 (1.73 mL, 12.5 mmol) were added. After being stirred at 85 °C for 12 h, the residue was passed through a pad of silica gel and concentrated *in vacuo*. Then, 4 M HCl in dioxane (10 mL/mmol of 3-(pyrrolidin-1-yl)acrylate) was added to the residue. After being stirred at room temperature for 3 h, saturated aq. $NaHCO_3$ was added. The mixture was poured into ethyl acetate, the aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford 3-phenylisoxazol-4-amine (755 mg, 3.88 mmol, 31% in 4 steps) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) 8.03 (s, 1H), 7.73 (d, J = 7.9 Hz, 2H), 7.46-7.41 (m, 3H), 3.13 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 155.7, 144.1, 129.6, 129.0, 128.4, 127.6, 125.6; FT-IR (neat): 3400, 3333, 3222, 3124, 3124, 3065, 1633, 1454, 1396, 895, 698 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_9H_8N_2O]^+$, 160.0637: found 160.0638.



3-(*tert*-Butyl)isoxazol-4-amine

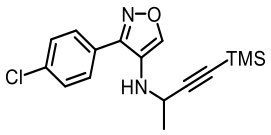
Following the representative procedure using *N*-hydroxypivalimidoyl chloride (4.07 g, 30.0 mmol), 3-(*tert*-butyl)isoxazol-4-amine was obtained (1.64 g, 11.7 mmol, 39% in 4 steps) as a pink solid. Mp 60-61 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 2.80 (brs, 2H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 145.3 , 125.2, 32.6, 28.3; FT-IR (neat): 3397, 3299, 3136, 2967, 2933, 2870, 1637, 1485, 1262cm^{-1}; HRMS (ESI): calcd. for $[C_7H_{12}N_2O$ +Na$]^+$, 163.0841: found 163.0843.



4. *N*-Propargylation of 4-aminoisoxazoles

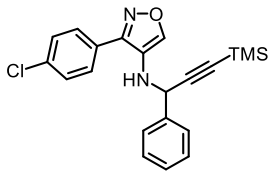
Representative procedure A for the synthesis of 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1a)

A mixture of 4-(trimethylsilyl)but-3-yn-2-one (976 mg, 7.50 mmol), 3-(4-chlorophenyl)isoxazol-4-amine (974 mg, 5.00 mmol) and $MgSO_4$ (1.20 g, 10.0 mmol) in dry dichloromethane (15 mL) was stirred at room temperature for 2 h. The mixture was filtered and concentrated *in vacuo*. The imine residue was dissolved in MeOH (20 mL). To the solution was added $NaBH_3CN$ (3.18 g, 15.0 mmol). After the addition, the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of water. The resultant mixture was extracted with dichloromethane and the combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*, and the redisue was purified by silica gel column chromatography with hexane : ethyl acetate (19 : 1) to give 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (1.83 g, 5.75 mmol, 58%) as a white solid. Mp 69-71 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 3.87-3.85 (m, 1H), 2.96 (brs, 1H), 1.49 (d, J = 6.5 Hz, 3H), 0.137 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 144.2, 135.9, 129.4, 129.2, 127.6, 127.3, 106.3, 88.4, 45.2, 22.3, 0.02; FT-IR (neat): 3337, 3129, 2949, 2888, 2153, 1363, 1245, 1088, 835 cm^{-1}; HRMS (ESI): calcd. for $[C_{16}H_{19}ClN_2OSi]^+$, 318.0955: found 318.0955.



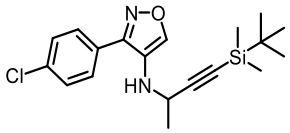
Representative procedure B for the synthesis of 3-(4-chlorophenyl)-*N*-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1j)

A mixture of (3-bromo-3-phenylprop-1-yn-1-yl)trimethylsilane (1.34 g, 5 mmol), 3-(4-chlorophenyl)isoxazol-4-amine (973 mg, 5.00 mmol) and *N*,*N*-diisopropylethylamine (1.70 mL, 10.0 mmol) in acetonitrile (15 mL) was stirred at 60 ºC for 6 h. The reaction was quenched by addition of 1.0 M HCl. The resultant mixture was extracted with ethyl acetate and the combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*, and the residue was purified by silica gel column chromatography with hexane : ethyl acetate (19 : 1) to give 3-(4-chlorophenyl)-*N*-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine **1j** (623 mg, 1.64 mmol, 33%) as a yellow solid. Mp 92-95 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.76 (d, J = 8.5 Hz, 2H), 7.45-7.36 (m, 4H), 7.37-7.34 (m, 1H), 5.02 (s, 1H), 3.43 (brs, 1H), 0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 144.7, 138.2, 135.8, 129.3, 129.1, 128.8, 128.5, 127.5, 127.2, 103.4, 91.7, 53.7, -0.06; FT-IR (neat): 2958, 2899, 2169, 1412, 1250, 842 cm^{-1}; HRMS (ESI): calcd. for $[C_{21}H_{21}ClN_2OSi + Na]^+$, 403.1003: found 403.0997.



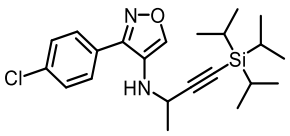
***N*-(4-(*tert*-Butyldimethylsilyl)but-3-yn-2-yl)-3-(4-chlorophenyl)isoxazol-4-amine (1b)**

Following the representative procedure A using 4-(*tert*-butyldimethylsilyl)but-3-yn-2-one (85.7 mg, 0.480 mmol), compound **1b** was obtained (39.7 mg, 0.110 mmol, 27%) after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1) as a white solid. Mp 99-100 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 3.87 (q, *J* = 6.8 Hz, 1H), 3.00 (brs, 1H), 1.50 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H), 0.064 (d, *J* = 2.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 144.2, 135.9, 129.4, 129.1, 127.6, 127.3, 106.9, 86.5, 45.2, 26.1, 22.4, 16.6, -4.56, -4.57; FT-IR (neat): 2928, 1725, 1602, 1413, 1093, 901, 836, 775, 669 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{19}H_{25}ClN_2OSi]^+$, 360.1425: found 360.1422.



3-(4-Chlorophenyl)-*N*-(4-(triisopropylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1c)

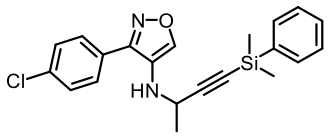
Following the representative procedure A using 4-(triisopropylsilyl)but-3-yn-2-one (128 mg, 0.480 mmol), compound **1c** was obtained (119 mg, 0.294 mmol, 74%) after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 3.90 (q, *J* = 6.8 Hz, 1H), 2.96 (brs, 1H), 1.52 (d, *J* = 6.9 Hz, 3H), 1.02 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 144.2, 135.9, 129.4, 129.1, 127.6, 127.3, 108.3, 84.3, 45.2, 22.6, 18.6, 11.2; FT-IR (neat): 3434, 2943, 2891, 2865, 2161, 1621, 1463, 1094, 882, 835, 678 cm^{-1}; HRMS (ESI): calcd. for $[C_{22}H_{31}ClN_2OSi + Na]^+$, 425.1786: found 425.1774.



3-(4-Chlorophenyl)-*N*-(4-(dimethyl(phenyl)silyl)but-3-yn-2-yl)isoxazol-4-amine (1d)

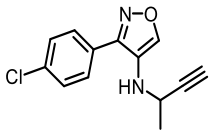
Following the representative procedure A using 4-(dimethyl(phenyl)silyl)but-3-yn-2-one (304 mg, 1.5 mmol), compound **1d** was obtained (308 mg, 0.807 mmol, 81%) after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.55 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.38 (m, 3H), 3.91 (q, *J*

= 6.5 Hz, 1H), 2.99 (brs, 1H), 1.53 (d, *J* = 7.0 Hz, 3H), 0.386 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 144.4, 136.8, 136.0, 133.7, 129.7, 129.4, 129.2, 128.1, 127.5, 127.3, 108.1, 86.5, 45.4, 22.3, -0.81, -0.82; FT-IR (neat): 3341, 3289, 3068, 2961, 2163, 1618, 1414, 1116, 1093, 732, 701, 661 cm^{-1}; HRMS (ESI): calcd. for $[C_{21}H_{21}ClN_2OSi + Na]^+$, 403.1003: found 403.0996.



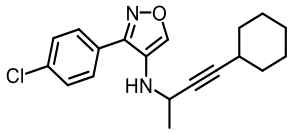
_N_-(But-3-yn-2-yl)-3-(4-chlorophenyl)isoxazol-4-amine (1e)

A mixture of 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (95.7 mg, 0.300 mmol) and cesium fluoride (91.1 mg, 0.600 mmol) in ethanol (3 mL) was stirred at room temperature for 2 h. After being stirred, the residue was poured into ethyl acetate and water. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified silica gel colum chromatography with hexane : ethyl acetate (19 : 1) to give *N*-(But-3-yn-2-yl)-3-(4-chlorophenyl)isoxazol-4-amine **1e** (72.1 mg, 0.292 mmol, 97%) as a white solid. Mp 89-90 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 3.86 (qd, *J* = 6.8 Hz, *J* = 1.9 Hz, 1H) 3.01 (br, 1H), 2.30 (d, *J* = 2.1 Hz, 3H), 1.52 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 144.2, 135.9, 129.4, 129.2, 127.6, 127.3, 106.3, 88.4, 45.2, 22.3, 0.02; FT-IR (neat): 3144, 2850, 2800, 2025, 1569, 1371, 1067, 992, 886, 825 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{13}H_{11}ClN_2O+Na]^+$, 246.0560: found 246.0556.



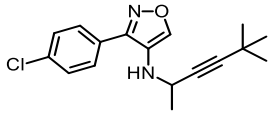
3-(4-Chlorophenyl)-_N_-(4-cyclohexylbut-3-yn-2-yl)isoxazol-4-amine (1f)

Following the representative procedure A using 4-cyclohexylbut-3-yn-2-one (225 mg, 1.50 mmol), compound **1f** was obtained (118 mg, 0.358 mmol, 36%) as a yellow oil after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 3.87 (qd, *J* = 6.7 Hz, *J* = 1.7 Hz, 1H), 2.93 (br, 1H), 2.33 (t, *J* = 8.4, H), 1.75-1.72 (m, 2H), 1.65-1.63 (m, 2H), 1.48 (d, *J* = 6.8, 3H), 1.39-1.25 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 144.0, 135.9, 129.4, 129.2, 127.8, 127.4, 88.4, 80.4, 44.7, 32.8, 29.0, 25.9, 25.0, 22.9; FT-IR (neat): 2930, 2853, 1619, 1448, 1412, 1093, 938, 835cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{19}H_{21}ClN_2OSi]^+$, 328.1342: found 328.1344.



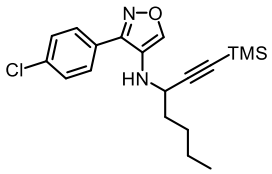
3-(4-Chlorophenyl)-*N*-(5, 5-dimethylhex-3-yn-2-yl)isoxazol-4-amine (1g)

Following the representative procedure A using 5,5-dimethylhex-3-yn-2-one (298 mg, 2.40 mmol), compound **1g** was obtained (471 mg, 1.56 mmol, 78%) as a brown oil after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 3.85 (q, *J* = 6.7 Hz, 1H), 2.91 (brs, 1H), 1.46 (d, *J* = 7.0 Hz, 1H), 1.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 144.0, 135.9, 129.4, 129.2, 127.8, 127.4, 92.7, 44.7, 31.2, 27.4, 22.8 ; FT-IR (neat): 2968, 2867, 1618, 1413, 1093, 835cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{17}H_{19}ClN_2O]^+$, 302.1186: found 302.1182.



3-(4-Chlorophenyl)-*N*-(1-(trimethylsilyl)hept-1-yn-3-yl)isoxazol-4-amine (1h)

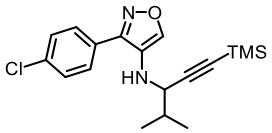
Following the representative procedure A using 1-(trimethylsilyl)hept-1-yn-3-one (274 mg, 1.50 mmol), compound **1h** was obtained (53.7 mg, 0.148 mmol, 15%) as a yellow oil after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 3.72 (t, *J* = 8.4 Hz, 1H), 1.77-1.73 (m, 2H), 1.51-1.45 (m, 2H), 1.40-1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.138 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 144.2, 135.9, 129.4, 127.7, 127.4, 105.6, 89.2, 50.1, 35.5, 28.3, 22.4, 14.1, 0.045 ; FT-IR (neat): 2961, 2931, 2898, 2872, 2165, 1413, 1249, 841 cm^{-1}; HRMS (ESI): calcd. for $[C_{19}H_{25}ClN_2OSi + Na]^+$, 383.1317: found 383.1310.



3-(4-Chlorophenyl)-*N*-(4-methyl-1-(trimethylsilyl)pent-1-yn-3-yl)isoxazol-4-amine (1i)

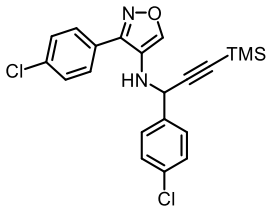
Following the representative procedure A using 4-methyl-1-(trimethylsilyl)pent-1-yn-3-one (253 mg, 1.50 mmol), compound **1i** was obtained (47.4 mg, 0.136 mmol, 14%) as a yellow oil after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 3.54 (d, *J* = 5.8 Hz, 1H), 2.02-1.95 (m, 1H), 1.07 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.140 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

154.7, 144.1, 135.9, 129.4, 129.2, 128.0, 127.4, 104.2, 56.3, 32.8, 19.5, 18.3, 0.0722; FT-IR (neat): 2957, 2933, 2871, 2861, 2166, 1413, 1250, 1093, 760 cm^{-1}; HRMS (ESI): calcd. for $[C_{18}H_{23}ClN_2OSi +Na]^+$, 369.1160: found 369.1153.



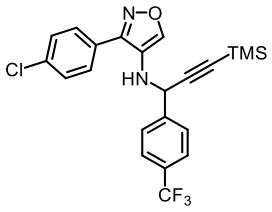
3-(4-Chlorophenyl)-*N*-(1-(4-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1k)

Following the representative procedure B using (3-bromo-3-(4-chlorophenyl)prop-1-yn-1-yl)trimethylsilane (290 mg, 0.960 mmol), compound **1k** was obtained (109 mg, 0.520 mmol, 65%) as a yellow solid after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). Mp 108-109 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 4.96 (s, 1H), 3.37 (brs, 1H), 0.187 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 1448.3, 136.7, 136.0, 134.4, 129.4, 129.1, 129.0, 128.9, 127.1, 126.8, 102.8, 92.3, 53.1, -0.07; FT-IR (neat): 3337, 3127, 3065, 2953, 2943, 2167, 1486, 1245, 1088, 841 cm^{-1}; HRMS (ESI): calcd. for $[C_{21}H_{20}Cl_2N_2OSi +Na]^+$, 437.0614: found 437.0606.



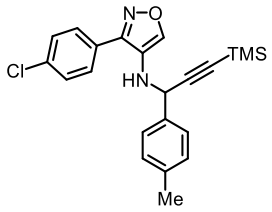
3-(4-Chlorophenyl)-*N*-(1-(4-(trifluoromethyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1l)

Following the representative procedure B using (3-bromo-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)trimethylsilane (156 mg, 0.800 mmol), compound **1l** was obtained (248 mg, 0.550 mmol, 69%) as a yellow oil after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 5.04 (s, 1H), 3.42 (brs, 1H), 0.193 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 145.0, 142.0, 136.1, 130.8 (q, $J_{C\text{-}F}$ = 32.5 Hz), 129.5, 129.2, 128.0, 127.0, 126.7, 125.9 (q, $J_{C\text{-}F}$ = 3.5 Hz), 124.1 (q, $J_{C\text{-}F}$ = 270.5 Hz), 102.4, 92.8, 53.4, -0.093; FT-IR (neat): 3340, 3276, 2961, 2900, 2171, 1619, 1414, 1326, 1128, 1068, 844 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{22}H_{20}ClF_3N_2OSi]^+$, 448.0986: found 448.0990.



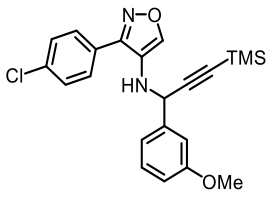
3-(4-Chlorophenyl)-*N*-(1-(*p*-tolyl)-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1m)

Following the representative procedure B using (3-bromo-3-(p-tolyl)prop-1-yn-1-yl)trimethylsilane (270 mg, 0.96 mmol), compound **1m** was obtained (106 mg, 0.268 mmol, 33%) as a yellow oil after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.96 (s, 1H), 3.35 (brs, 1H), 2.38 (s, 3H), 0.196 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 144.6, 138.4, 135.9, 135.3, 129.6, 129.4, 127.4, 127.2, 127.1, 103.6, 91.5, 53.5, 21.3, -0.025; FT-IR (neat): 3343, 2958, 2921, 2898, 2170, 1619, 1513, 1413, 1251, 1093, 743 cm^{-1}; HRMS (ESI): calcd. for $[C_{22}H_{23}ClN_2OSi + Na]^+$, 417.1160: found 417.1151.



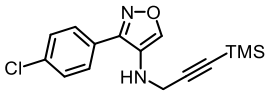
3-(4-Chlorophenyl)-*N*-(1-(3-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1n)

Following the representative procedure B using (3-bromo-3-(3-methoxyphenyl)prop-1-yn-1-yl)trimethylsilane (356 mg, 0.960 mmol), compound **1n** was obtained (97.0 mg, 0.236 mmol, 30%) as a brown oil after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.33-7.27 (m, 1H), 7.25 (d, *J* = 7.2 Hz, 2H), 6.88 (m, 1H) 4.97 (s, 1H), 3.82 (s, 3H), 3.39 (brs, 1H), 0.191 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 154.7, 144.7, 139.7, 135.9, 129.9, 129.4, 129.2, 127.2, 127.1, 119.8, 113.9, 113.3, 103.3, 91.7, 55.3, 53.7, -0.044; FT-IR (neat): 3331, 2958, 2898, 2834, 2170, 1602, 1488, 1413, 1251, 1093, 842, 760 cm^{-1}; HRMS (ESI): calcd. for $[C_{22}H_{23}ClN_2O_2Si + Na]^+$, 433.1109: found 433.1097.



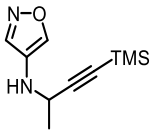
3-(4-Chlorophenyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1o)

Following the representative procedure A using 3-(trimethylsilyl)propiolaldehyde (284 mg, 2.25 mmol), compound **1o** was obtained (161 mg, 0.520 mmol, 35%) as a white solid after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). Mp 84-85 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 2H), 3.20 (brs, 1H), 0.150 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 143.1, 135.9, 129.3, 129.0, 128.5, 127.1, 101.7, 89.7, 37.8, -0.121; FT-IR (neat): 3356, 3133, 2959, 2897, 2171, 1621, 1415, 1250, 1093, 843 cm^{-1}; HRMS (ESI): calcd. for $[C_{15}H_{17}ClN_2OSi + Na]^+$, 327.0690: found 327.0683.



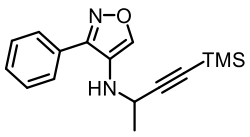
***N*-(4-(Trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1p)**

Following the representative procedure A using 4-(trimethylsilyl)but-3-yn-2-one (421 mg, 3.00 mmol) and isoxazol-4-amine (168 mg, 2.00 mmol), compound **1p** was obtained (68.5 mg, 0.329 mmol, 33%) as a brown oil after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.09 (s, 1H), 3.87 (q, *J* = 6.8 Hz, 2H), 3.02 (brs, 1H), 1.45 (d, *J* = 7.0 Hz, 3H), 0.116 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 143.1, 129.0, 106.6, 88.3, 45.3, 22.2, 0.0; FT-IR (neat): 3322, 2960, 1629, 1251, 878, 842, 759 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{10}H_{16}N_2OSi]^+$, 208.1032: found 208.1033.



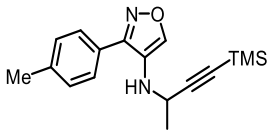
3-Phenyl-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1q)

Following the representative procedure A using 4-(trimethylsilyl)but-3-yn-2-one (316 mg, 2.25 mmol) and 3-phenylisoxazol-4-amine (240 mg, 1.50 mmol), compound **1q** was obtained (309 mg, 1.08 mmol, 72%) as a brown oil after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.77 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.48-7.42 (m, 3H), 3.88 (q, *J* = 6.5 Hz, 1H), 3.09 (brs, 1H), 1.48 (d, *J* = 6.5 Hz, 3H), 0.143 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 144.0, 135.9, 131.8, 129.4, 129.2, 128.5, 128.4, 127.7, 127.3, 122.6, 89.6, 83.7, 45.1, 22.5; FT-IR (neat): 3435, 2090, 1638, 1516, 1413, 1092, 834, 756 cm^{-1}; HRMS (ESI): calcd. for $[C_{16}H_{20}N_2OSi + Na]^+$, 307.1237: found 307.1233.



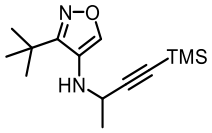
3-(*p*-Tolyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1r)

Following the representative procedure A using 3-(*p*-tolyl)isoxazol-4-amine (190 mg, 1.09 mmol), compound **1r** was obtained (79.3 mg, 0.266 mmol, 24%) as a yellow after purification by silica gel chromatography with hexane and ethyl acetate (19 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 3.87 (d, *J* = 6.0 Hz, 1H), 3.03 (s, 1H), 2.41 (s, 3H), 1.49 (d, *J* = 4.0 Hz, 3H), 0.140 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 143.3, 139.8, 129.8, 127.74, 127.68, 125.9, 106.5, 88.1, 45.2, 22.3, 21.5, -0.013; FT-IR (neat): 3321, 3121, 3065, 2953, 2827, 2151, 1612, 1245, 835 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{17}H_{22}N_2O_2Si]^+$, 314.1451: found 314.1445.



3-(*tert*-Butyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1s)

Following the representative procedure A using 4-(trimethylsilyl)but-3-yn-2-one (421 mg, 3.00 mmol) and 3-(*tert*-butyl)isoxazol-4-amine (280 mg, 2.00 mmol), compound **1s** was obtained (171 mg, 0.647 mmol, 32%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 3.75 (quin., *J* = 7.6 Hz, 1H), 2.72 (d, *J* = 8.4 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.34 (s, 9H), 0.097 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 144.4, 127.5, 107.1, 87.7, 45.3, 32.5, 28.3, 22.4, -0.053; FT-IR (neat): 3331, 3121, 2953, 2157, 1606, 1492, 1245, 878, 841 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{14}H_{24}N_2OSi]^+$, 264.1658: found 264.1656.



5. References

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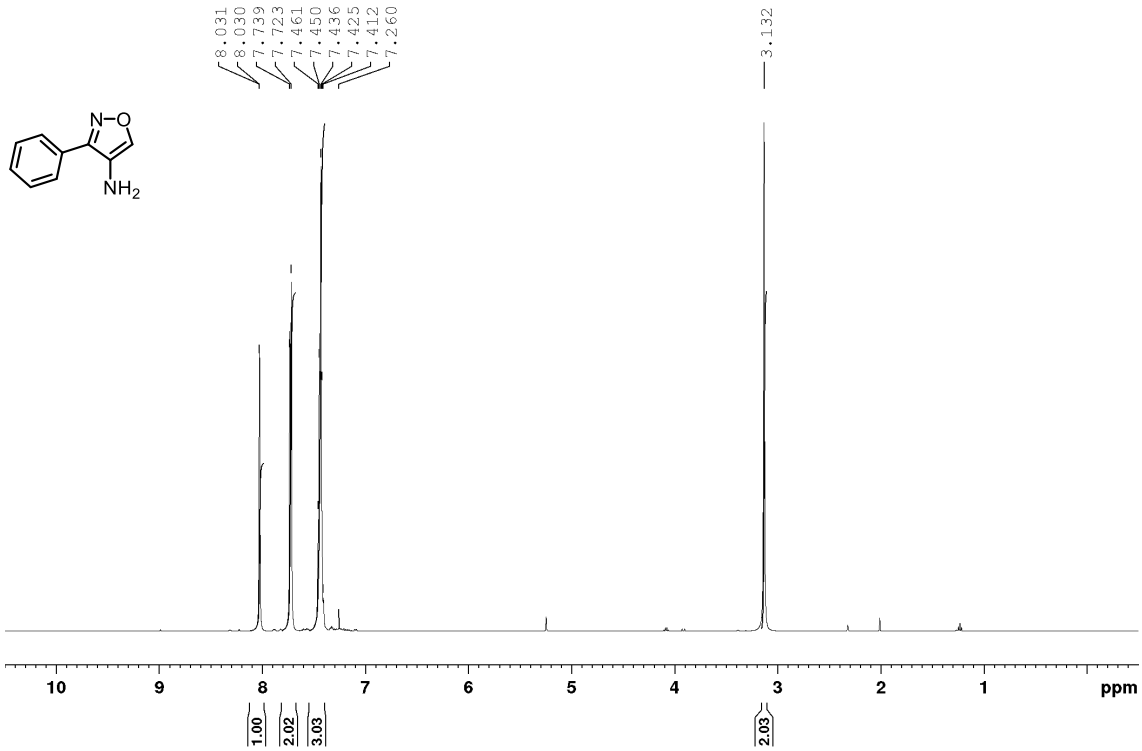
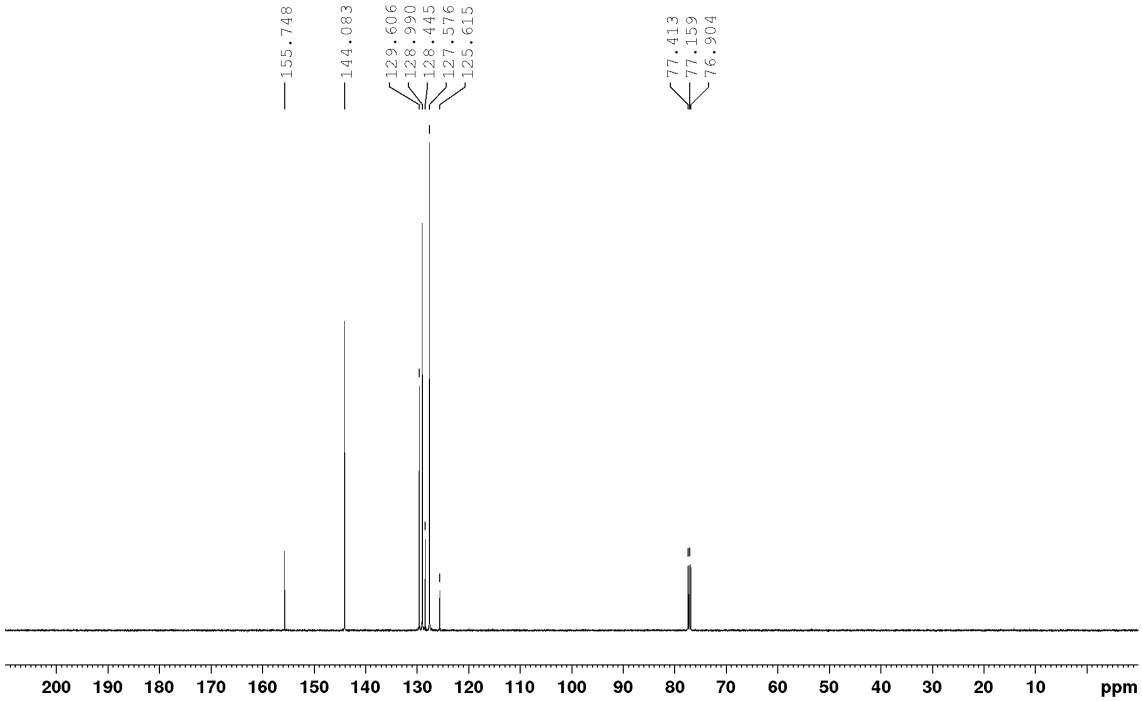
6. NMR spectra

3-Phenylisoxazol-4-amine

^{1}H NMR (500 MHz, $CDCl_3$)

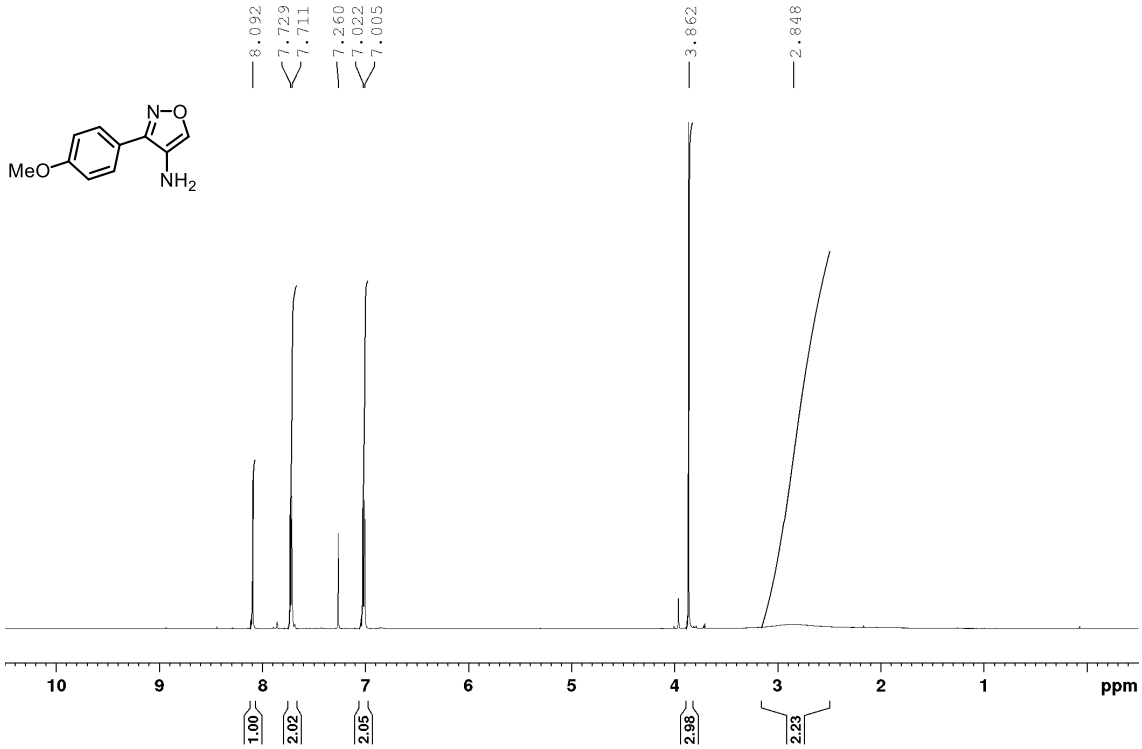


^{13}C NMR (125 MHz, $CDCl_3$)

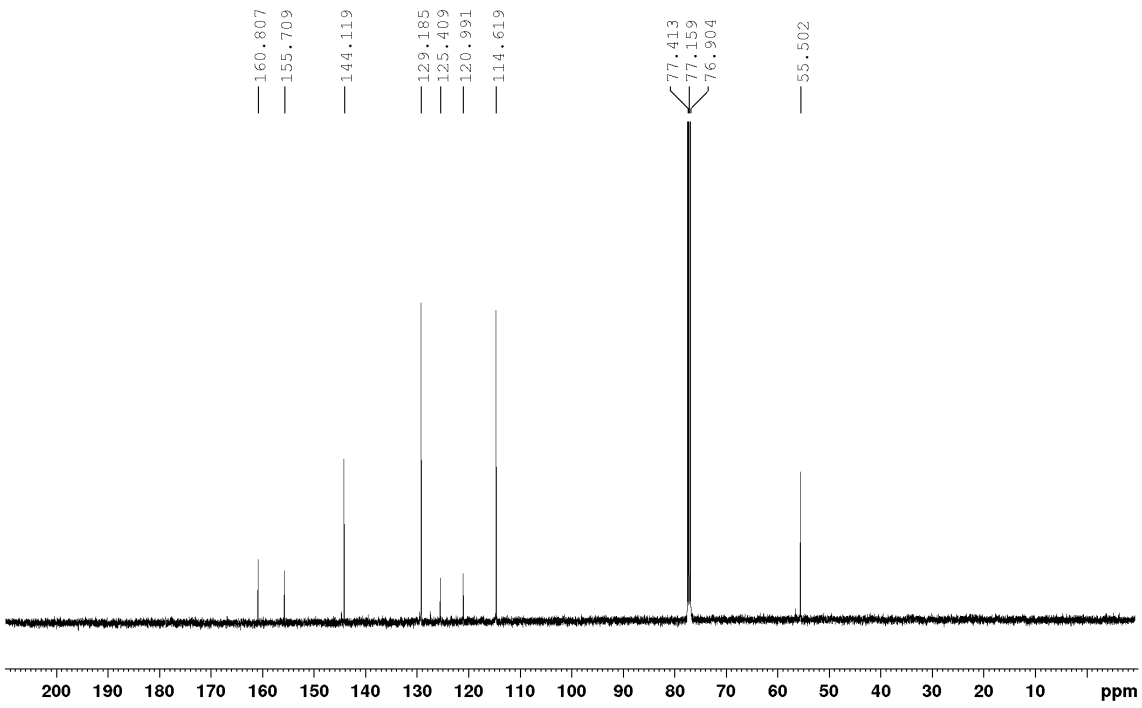


3-(4-Methoxyphenyl)isoxazol-4-amine

^{1}H NMR (500 MHz, $CDCl_3$)

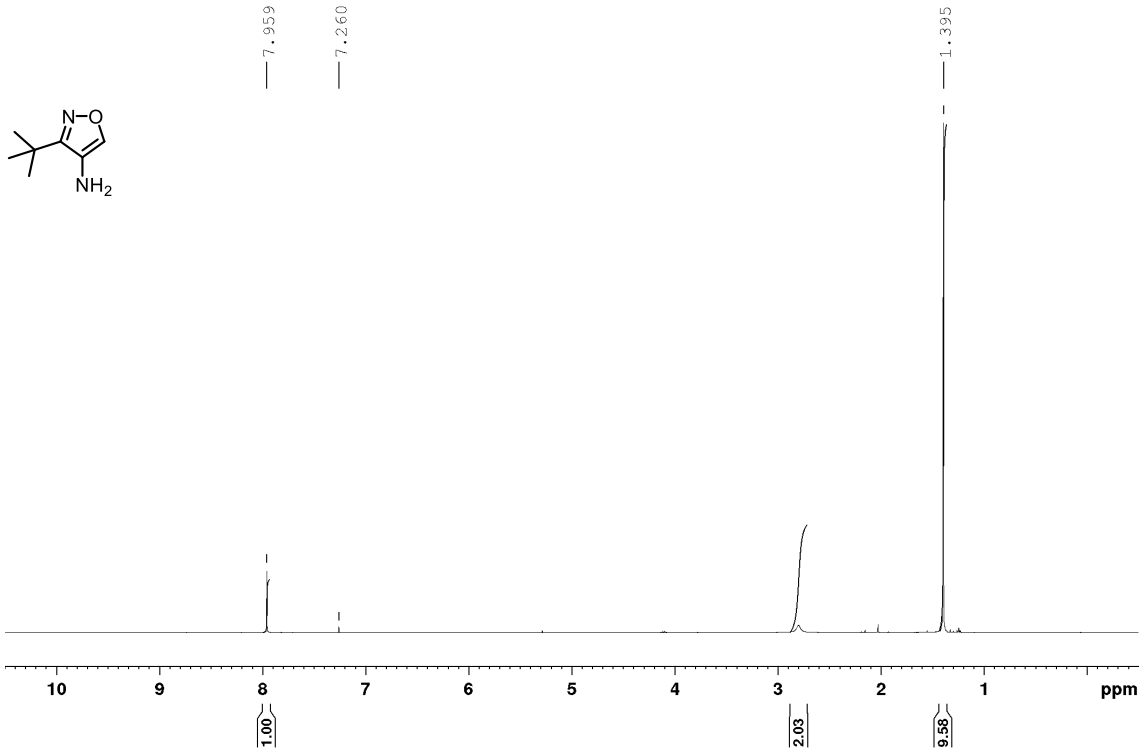


^{13}C NMR (125 MHz, $CDCl_3$)

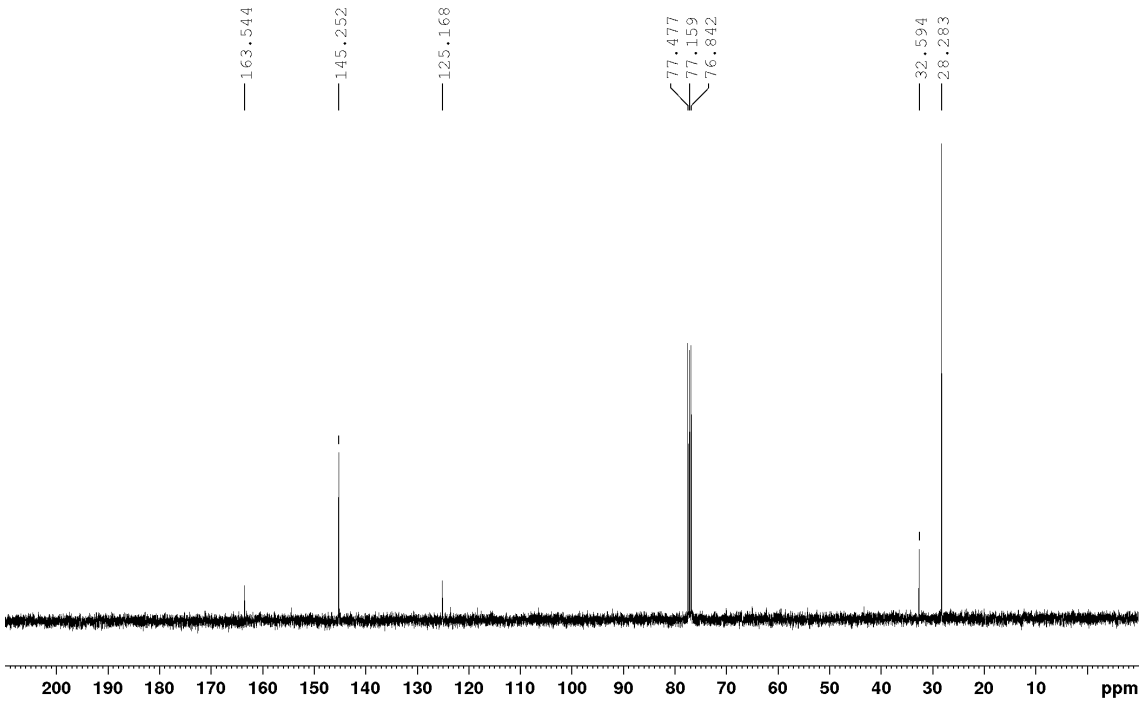


3-(*tert*-Butyl)isoxazol-4-amine

^{1}H NMR (500 MHz, $CDCl_3$)

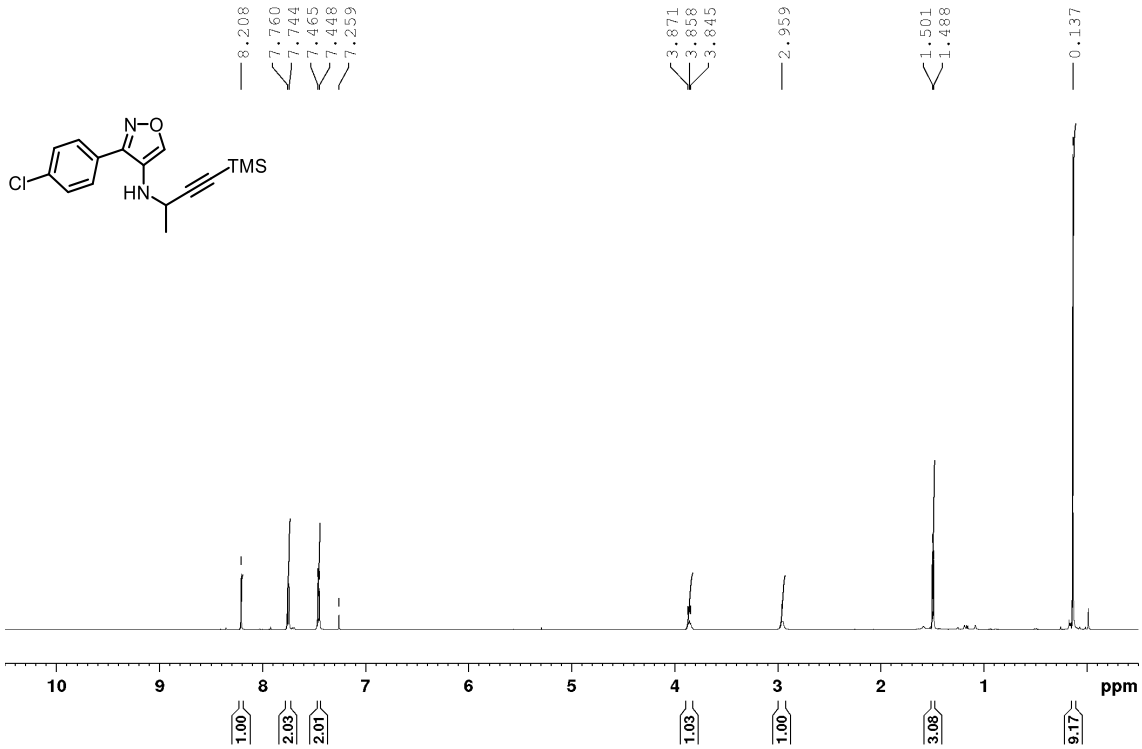


^{13}C NMR (125 MHz, $CDCl_3$)

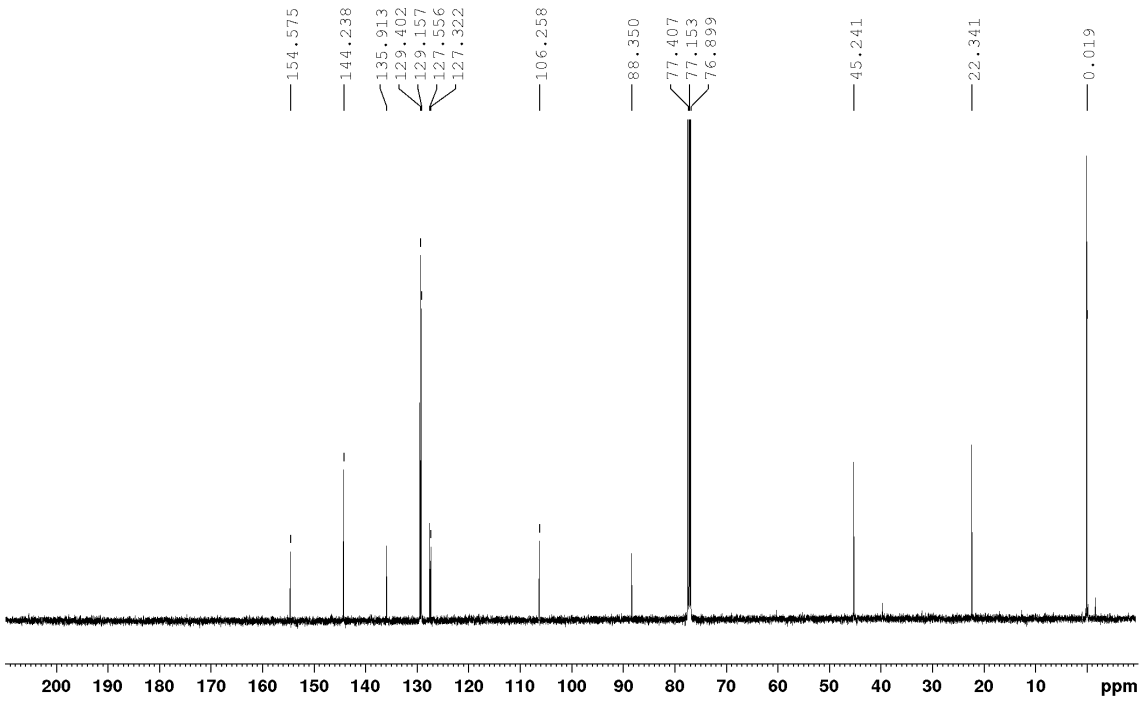


3-(4-Chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1a)

^{1}H NMR (500 MHz, $CDCl_3$)

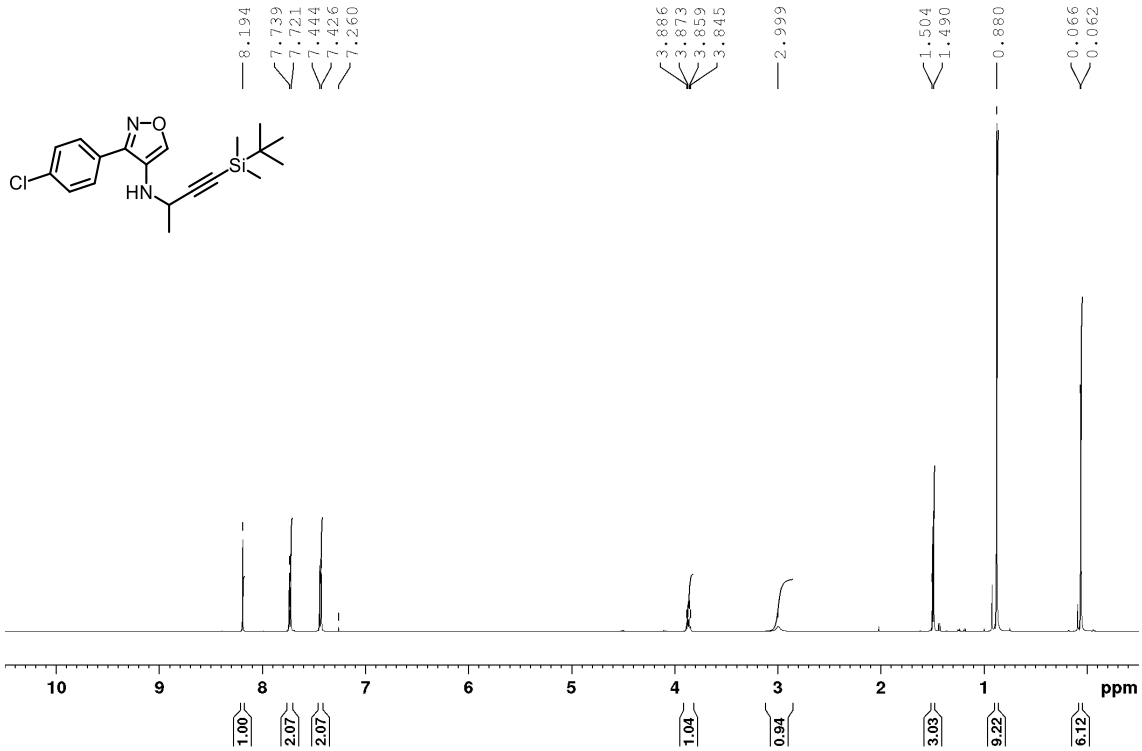


^{13}C NMR (125 MHz, $CDCl_3$)

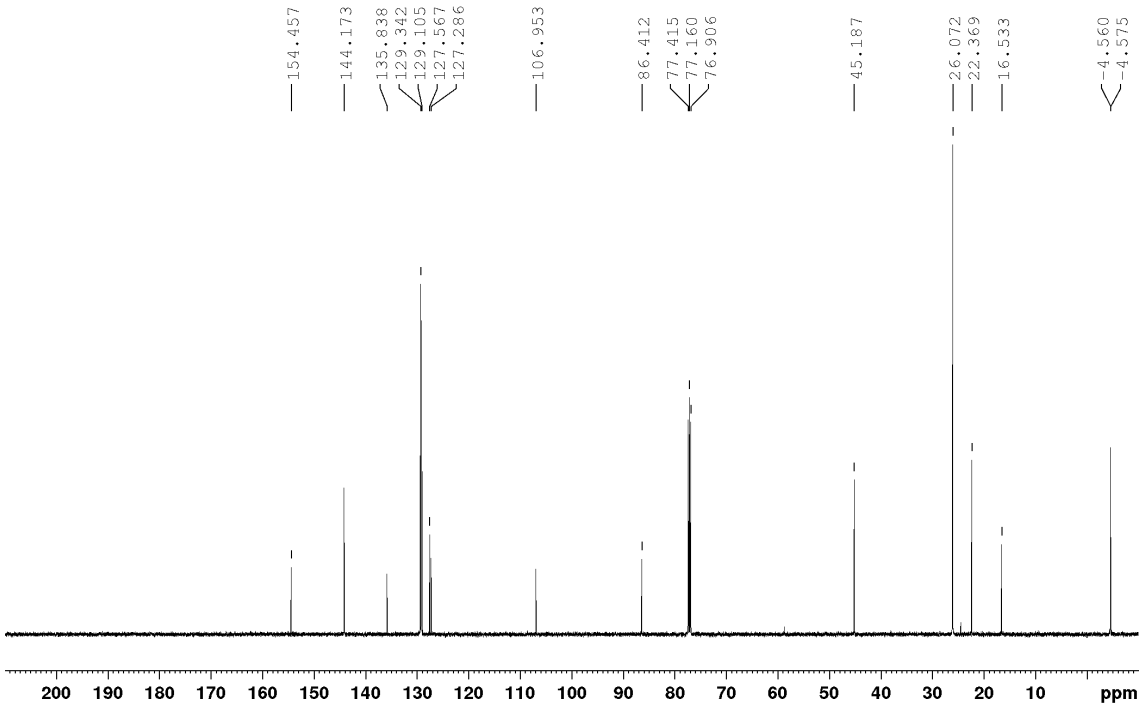


***N*-(4-(*tert*-Butyldimethylsilyl)but-3-yn-2-yl)-3-(4-chlorophenyl)isoxazol-4-amine (1b)**

^{1}H NMR (500 MHz, $CDCl_3$)

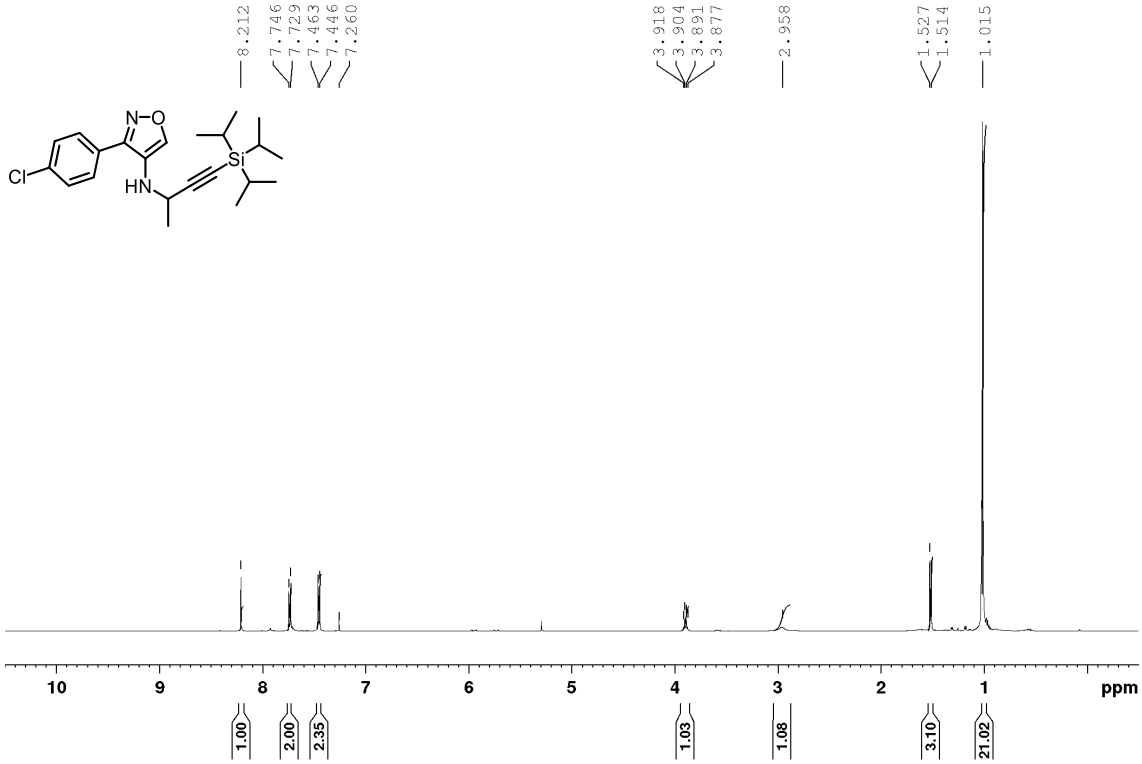


^{13}C NMR (125 MHz, $CDCl_3$)

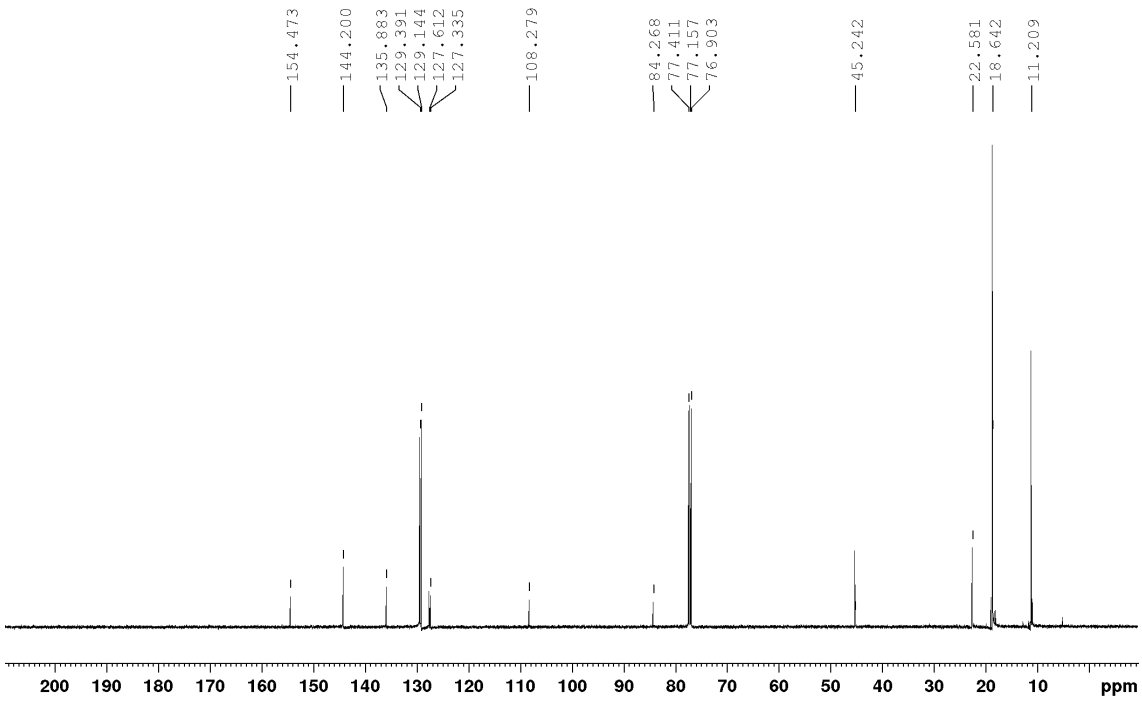


3-(4-Chlorophenyl)-*N*-(4-(triisopropylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1c)

^{1}H NMR (500 MHz, $CDCl_3$)

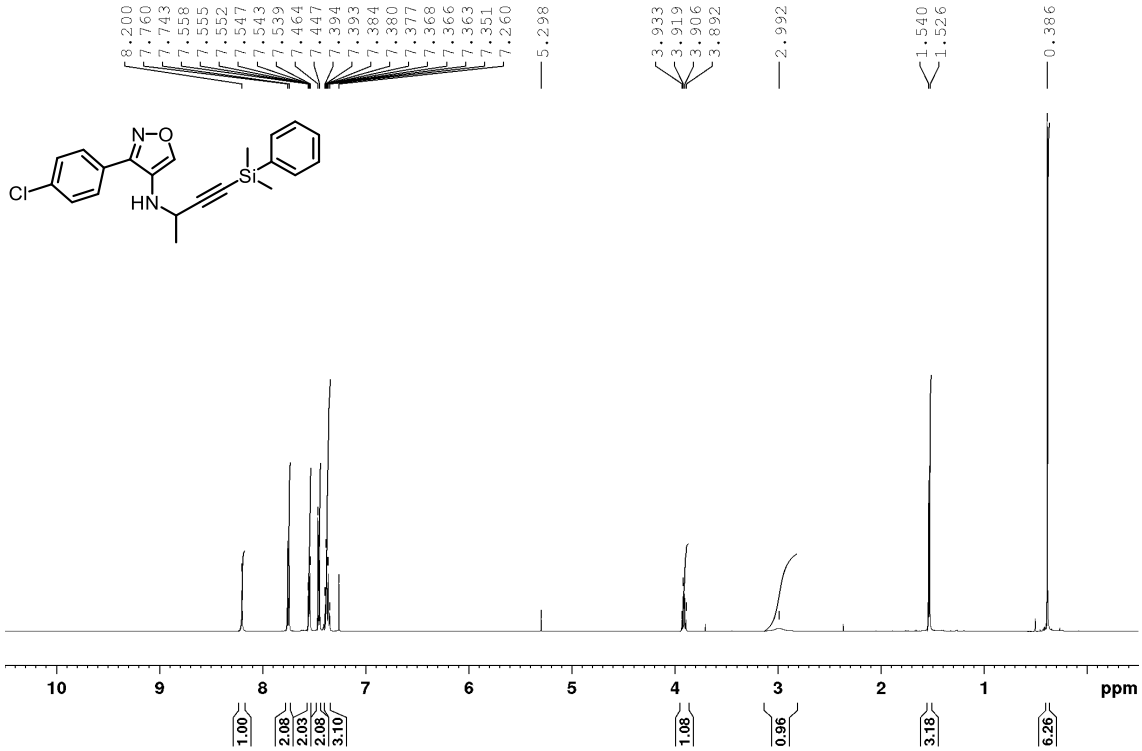


^{13}C NMR (125 MHz, $CDCl_3$)

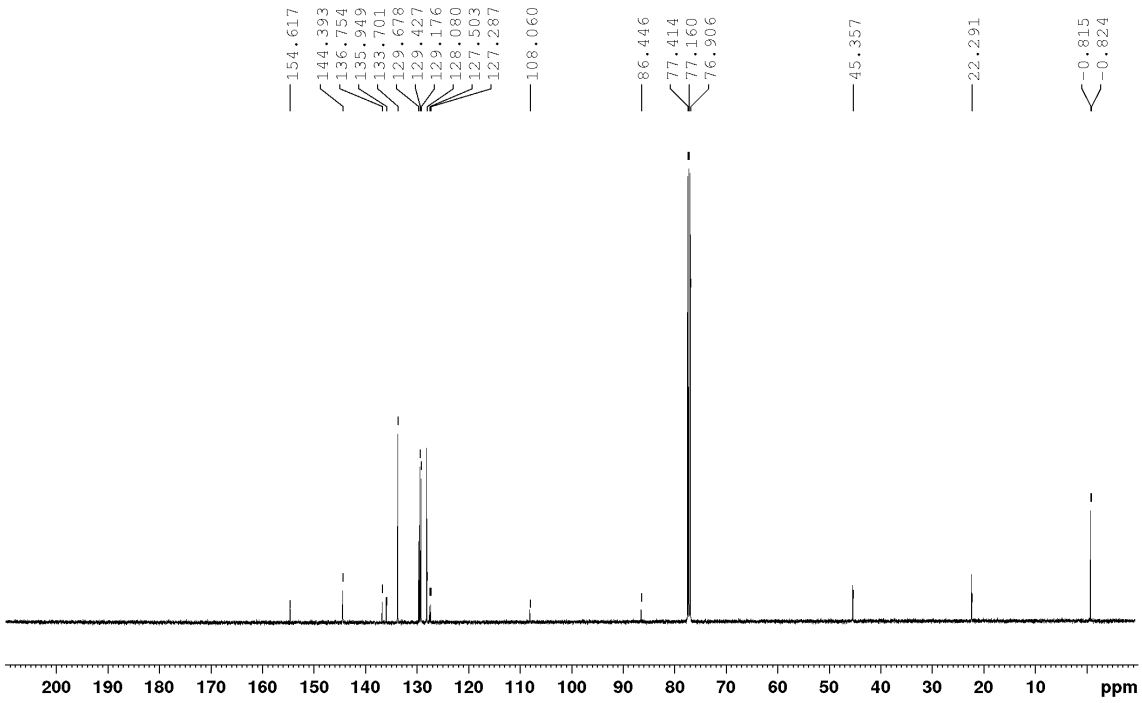


3-(4-Chlorophenyl)-*N*-(4-(dimethyl(phenyl)silyl)but-3-yn-2-yl)isoxazol-4-amine (1d)

^{1}H NMR (500 MHz, $CDCl_3$)

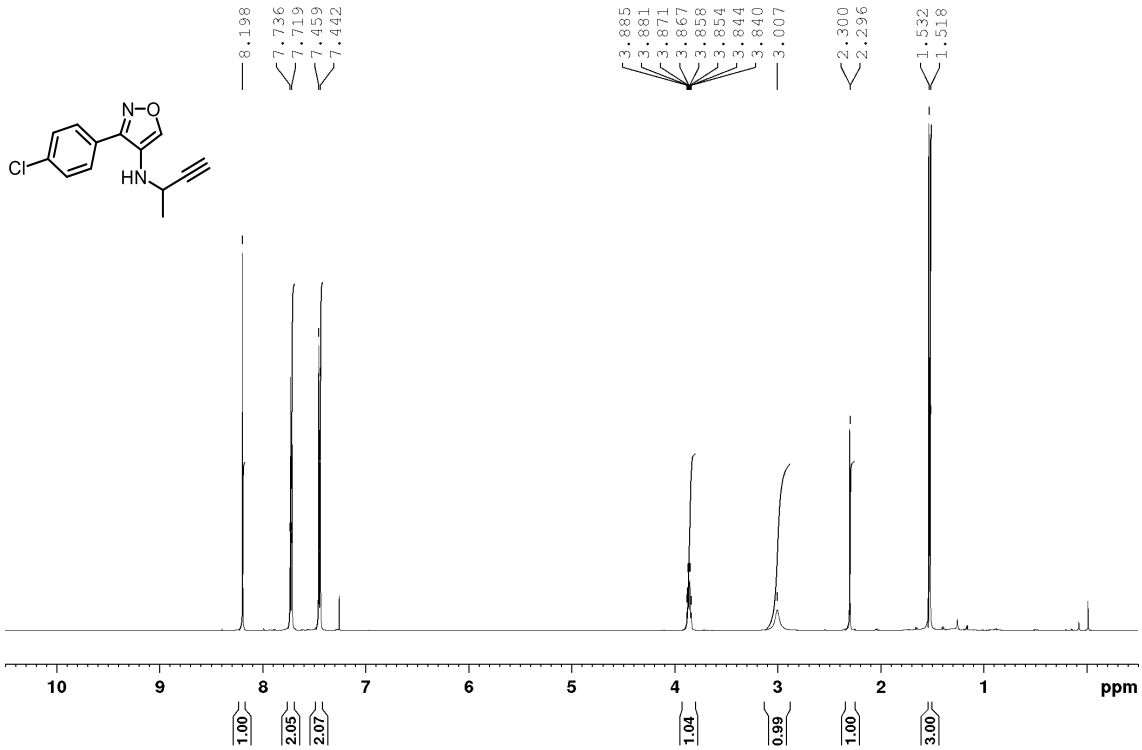


^{13}C NMR (125 MHz, $CDCl_3$)

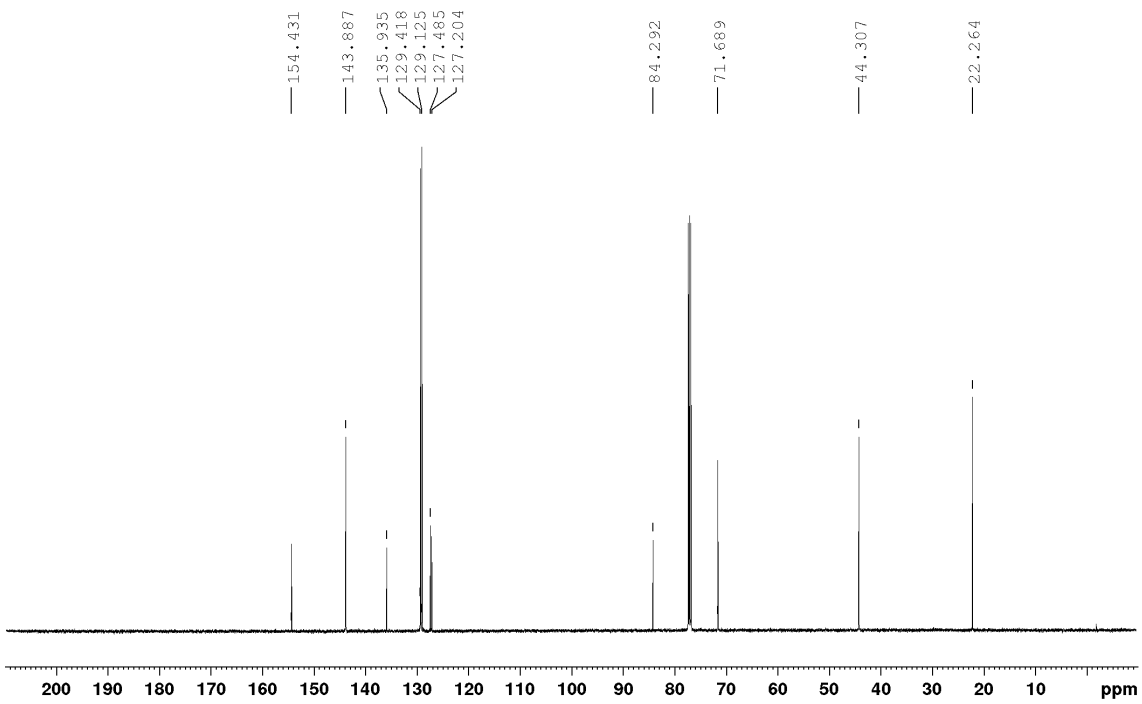


***N*-(But-3-yn-2-yl)-3-(4-chlorophenyl)isoxazol-4-amine (1e)**

^{1}H NMR (500 MHz, $CDCl_3$)

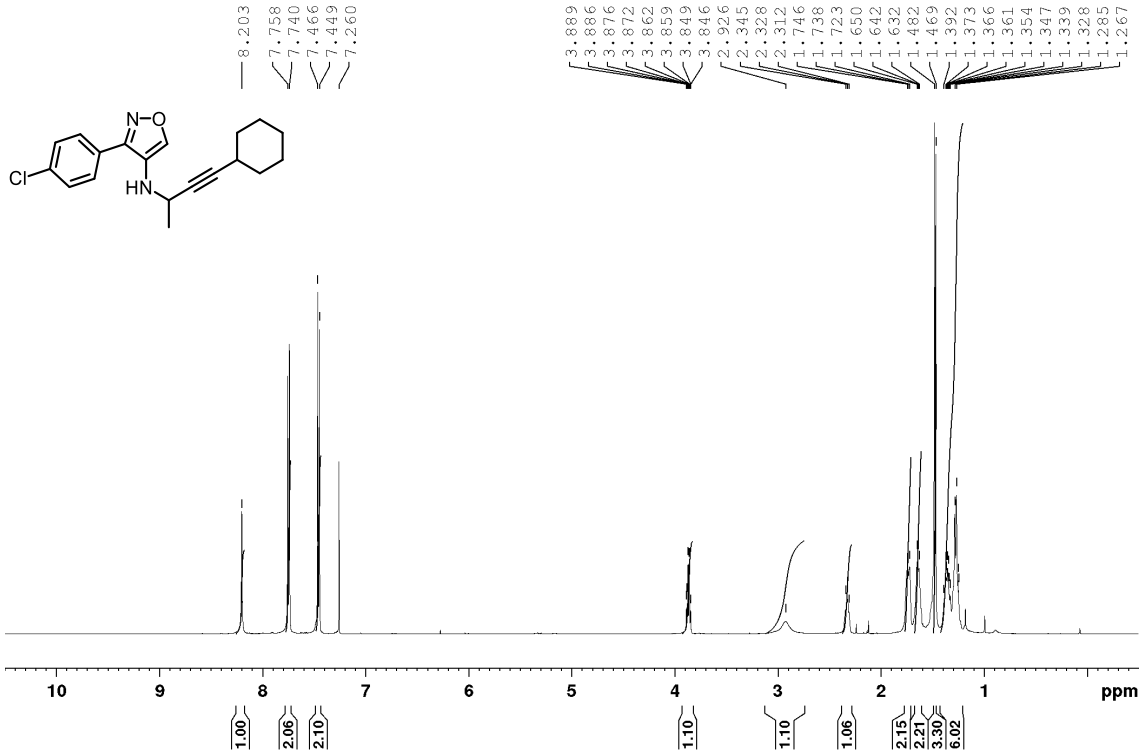


^{13}C NMR (125 MHz, $CDCl_3$)

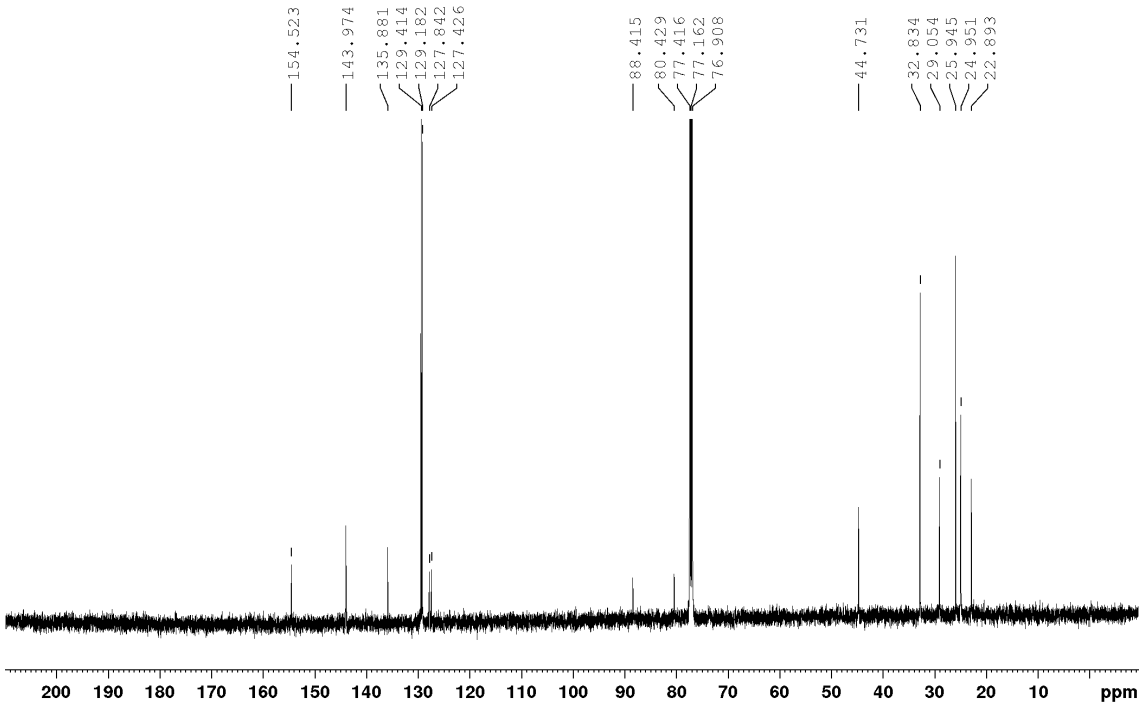


3-(4-Chlorophenyl)-*N*-(4-cyclohexylbut-3-yn-2-yl)isoxazol-4-amine (1f)

^{1}H NMR (500 MHz, $CDCl_3$)

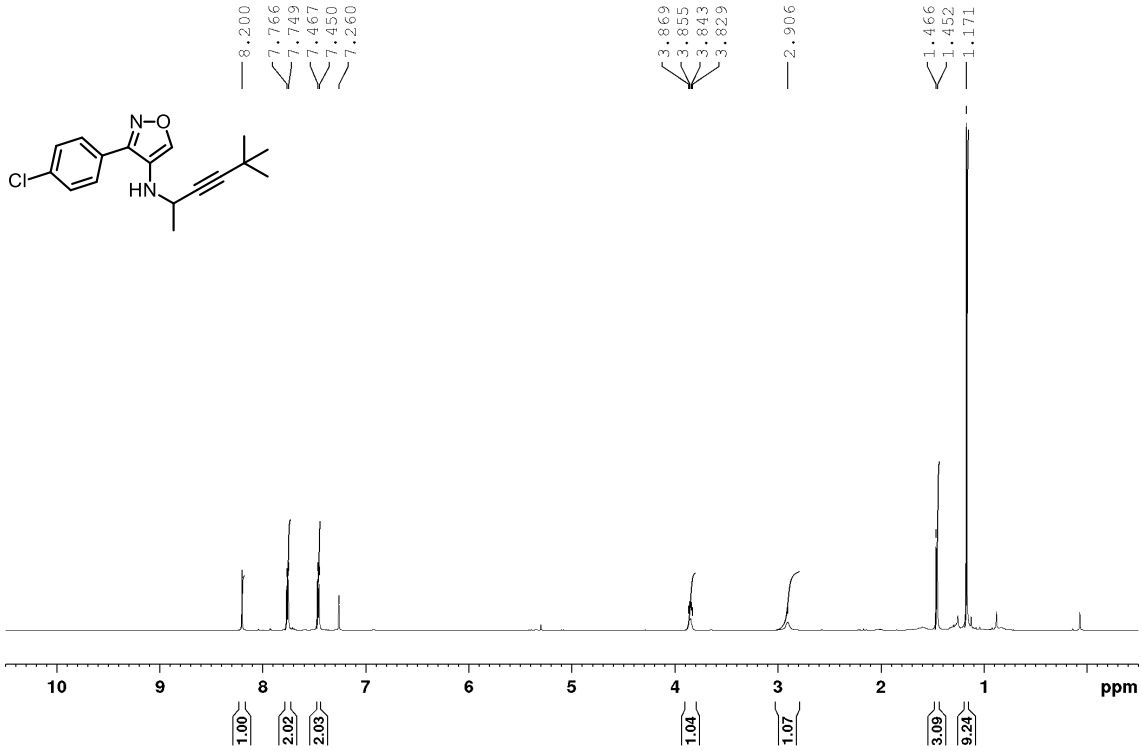


^{13}C NMR (125 MHz, $CDCl_3$)

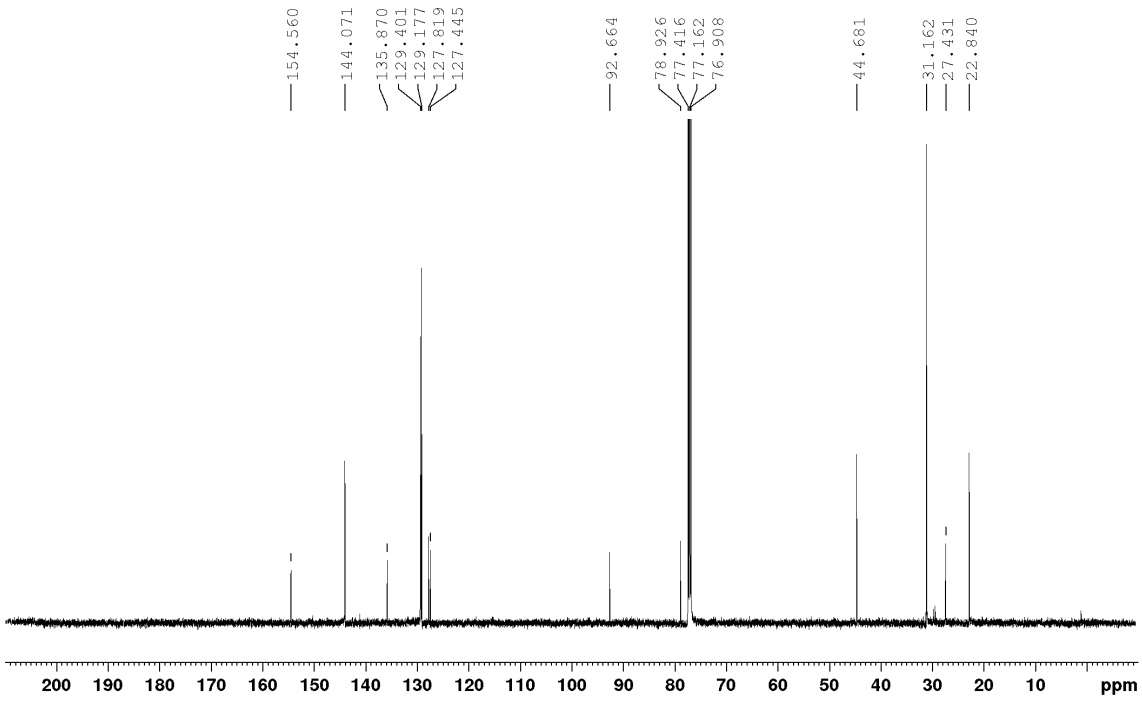


3-(4-chlorophenyl)-*N*-(5, 5-dimethylhex-3-yn-2-yl)isoxazol-4-amine (1g)

^{1}H NMR (500 MHz, $CDCl_3$)

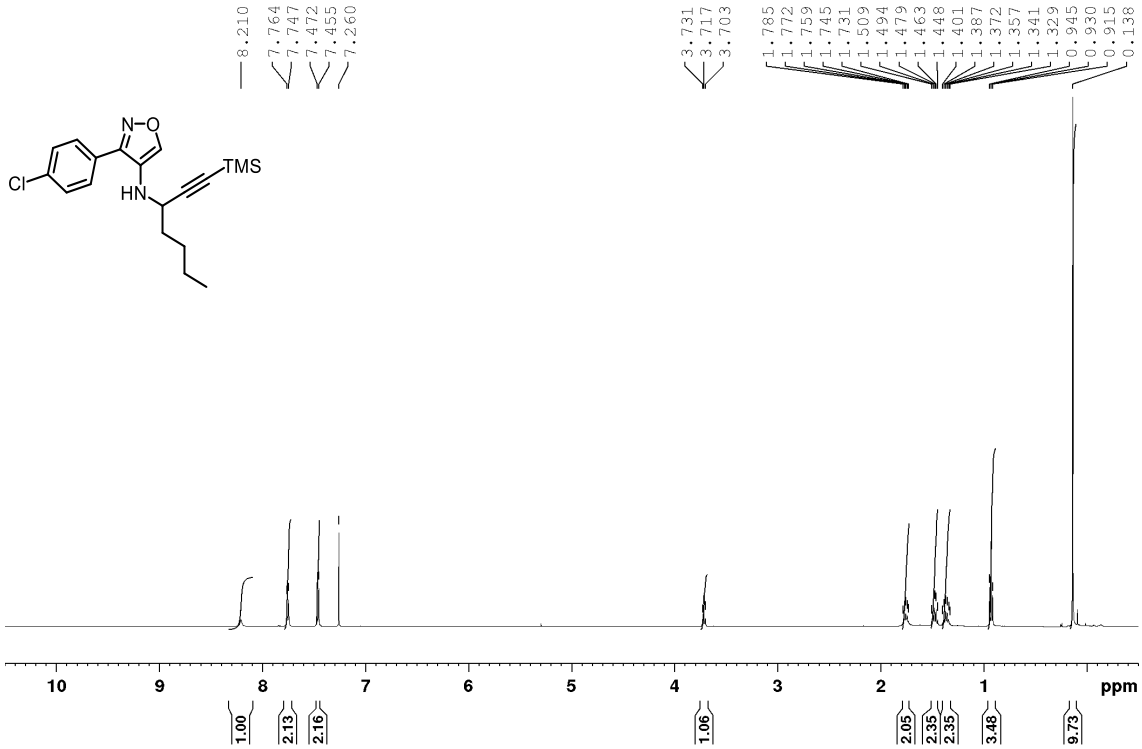


^{13}C NMR (125 MHz, $CDCl_3$)

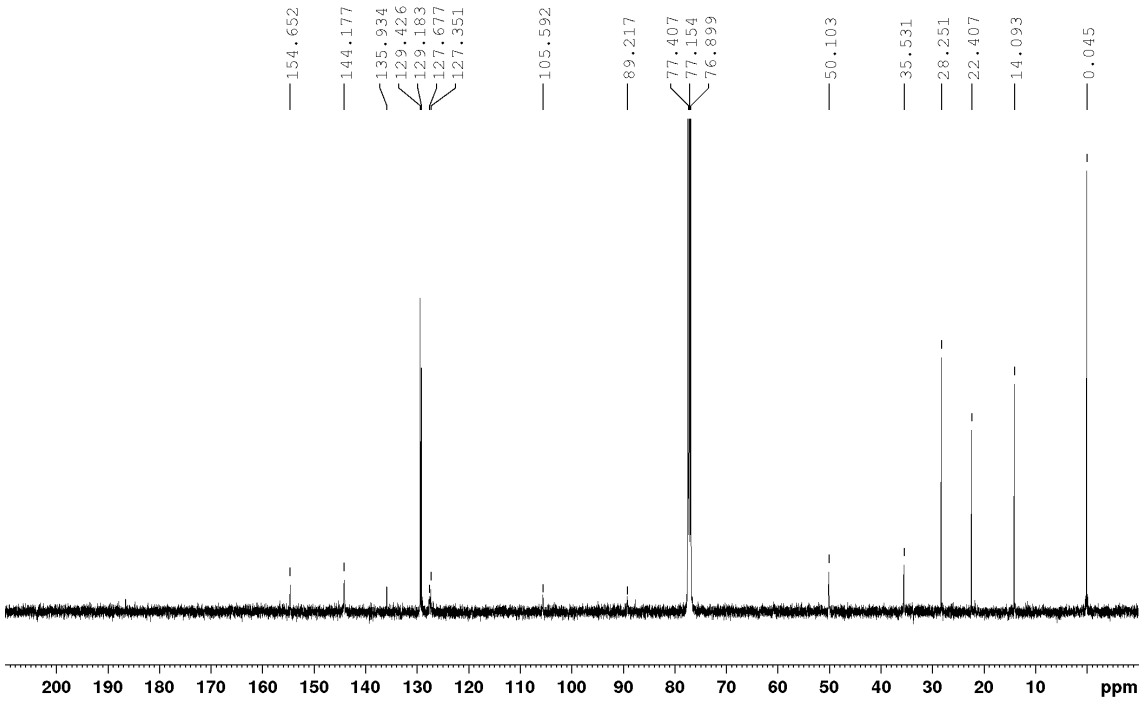


3-(4-Chlorophenyl)-*N*-(1-(trimethylsilyl)hept-1-yn-3-yl)isoxazol-4-amine (1h)

^{1}H NMR (500 MHz, $CDCl_3$)

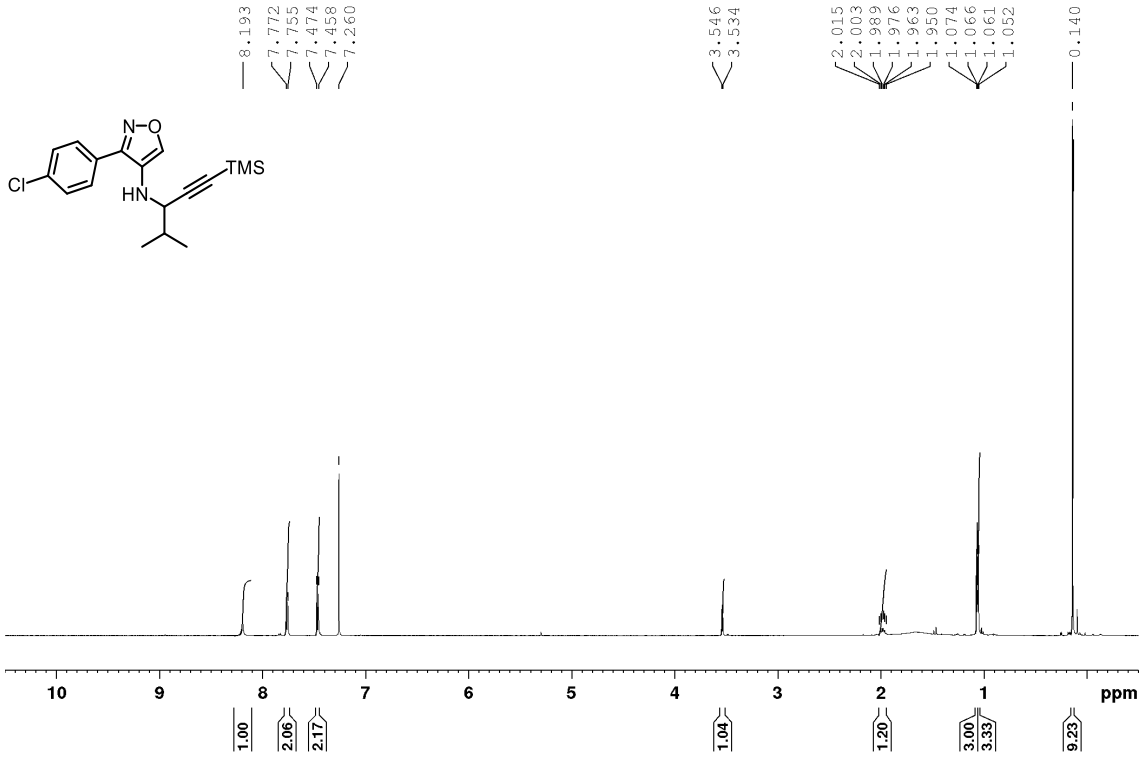


^{13}C NMR (125 MHz, $CDCl_3$)

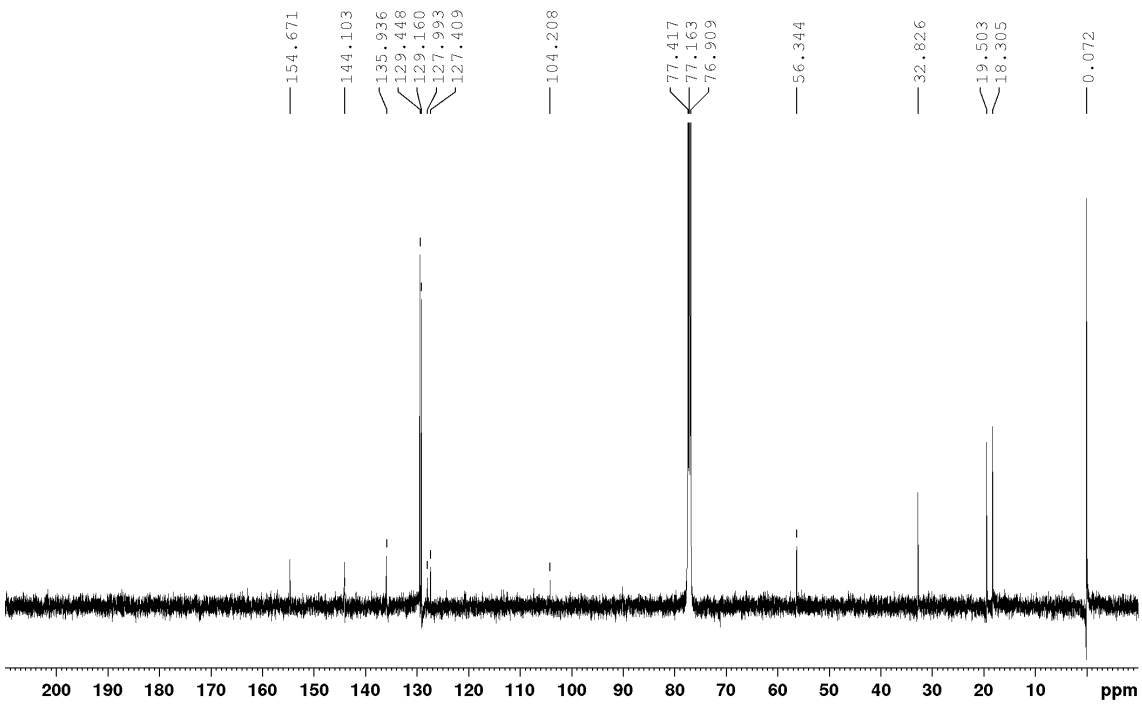


3-(4-Chlorophenyl)-*N*-(4-methyl-1-(trimethylsilyl)pent-1-yn-3-yl)isoxazol-4-amine (1i)

^{1}H NMR (500 MHz, $CDCl_3$)

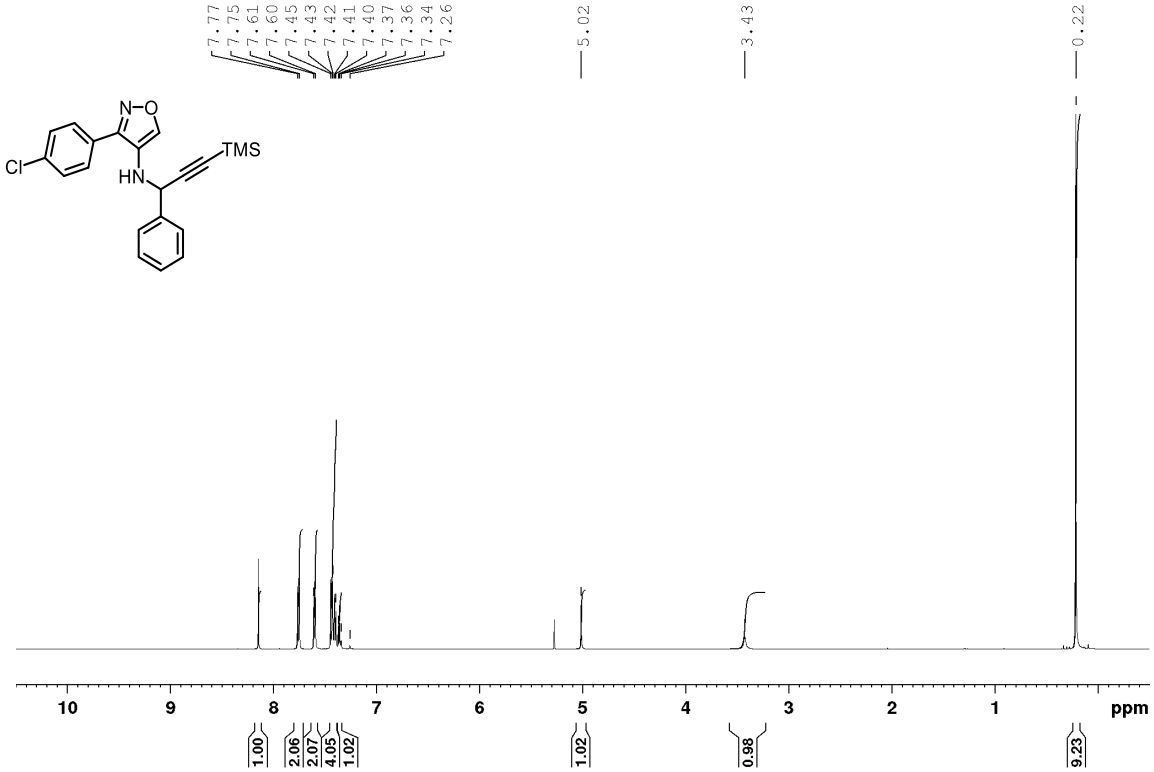


^{13}C NMR (125 MHz, $CDCl_3$)

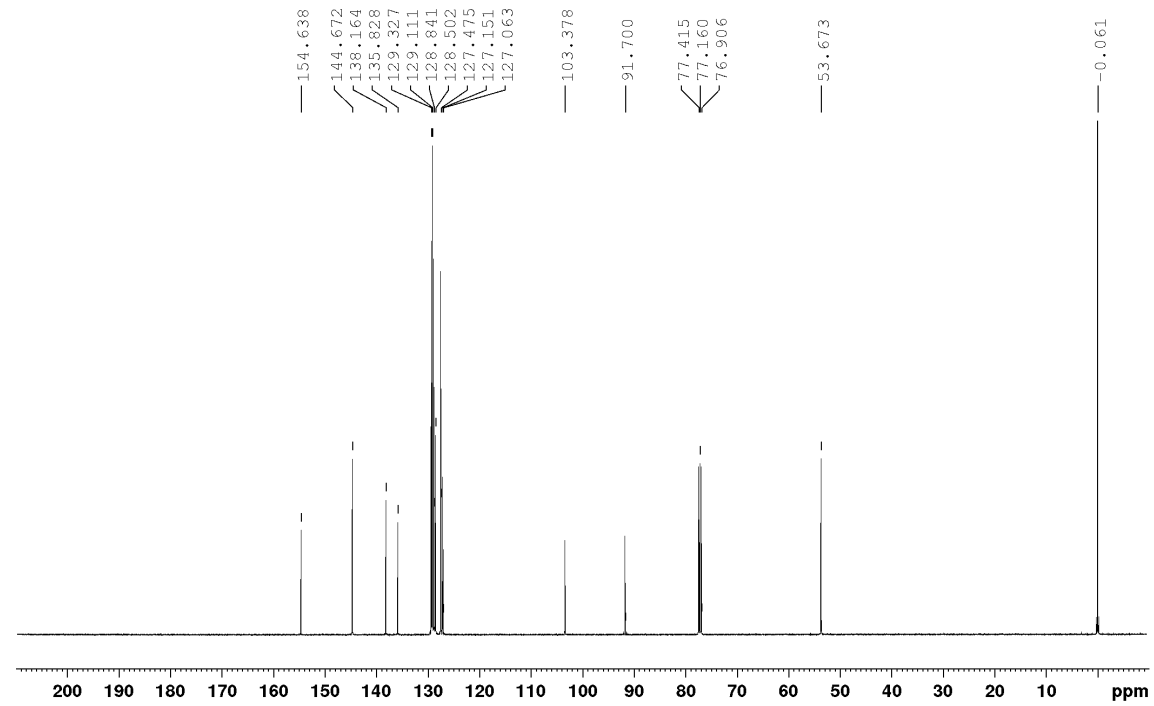


3-(4-Chlorophenyl)-*N*-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1j)

^{1}H NMR (500 MHz, $CDCl_3$)

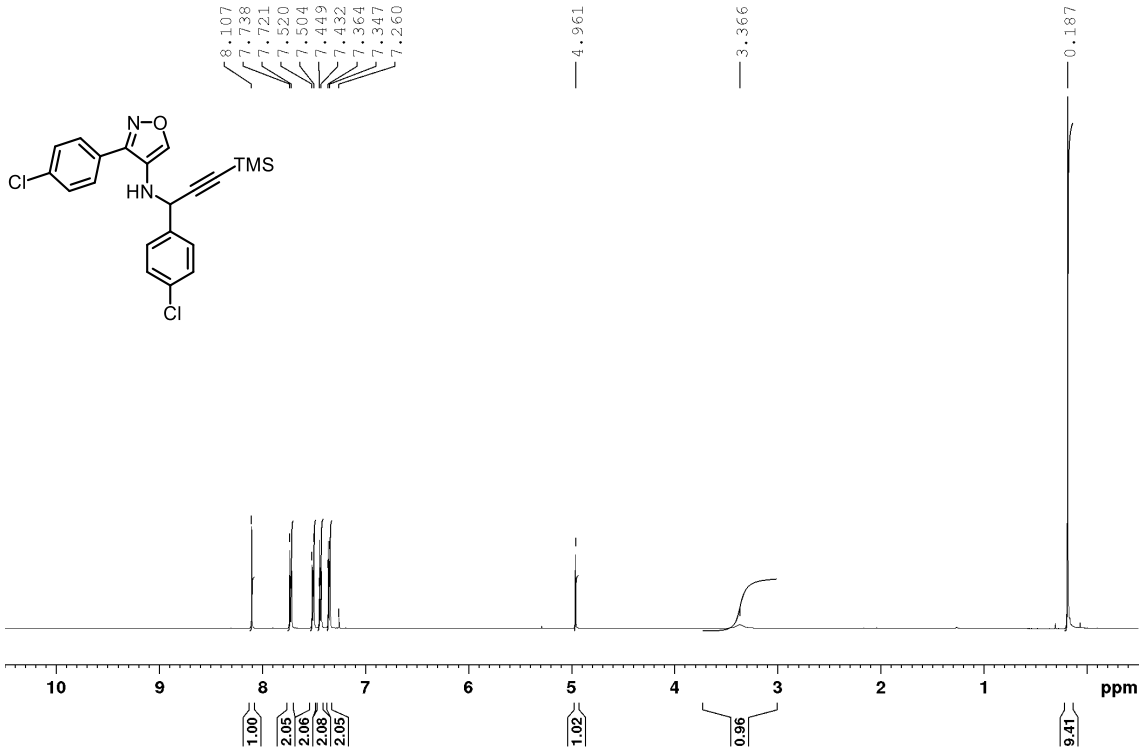


^{13}C NMR (125 MHz, $CDCl_3$)

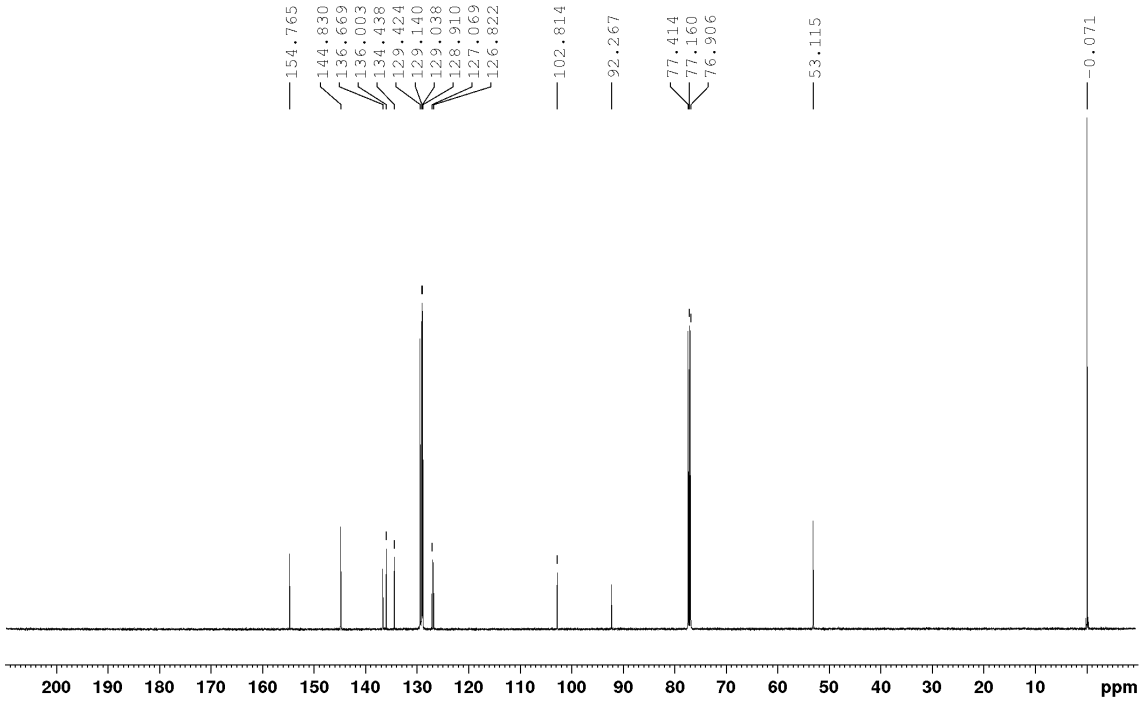


3-(4-Chlorophenyl)-*N*-(1-(4-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1k)

^{1}H NMR (500 MHz, $CDCl_3$)

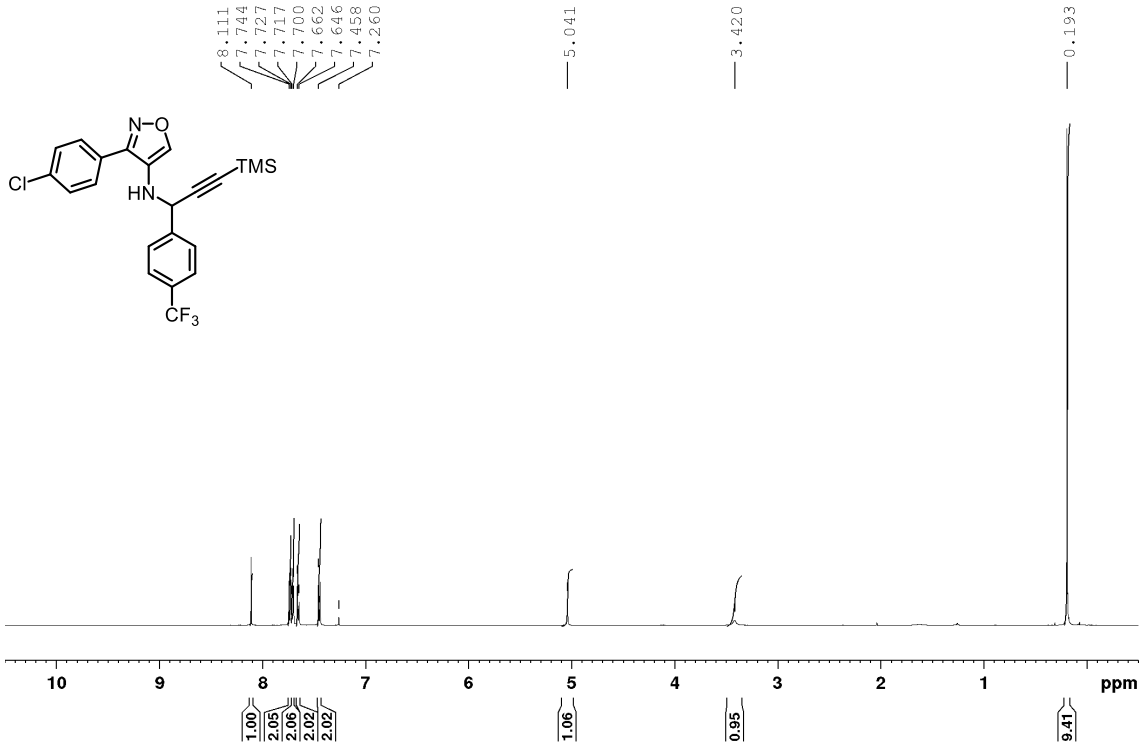


^{13}C NMR (125 MHz, $CDCl_3$)

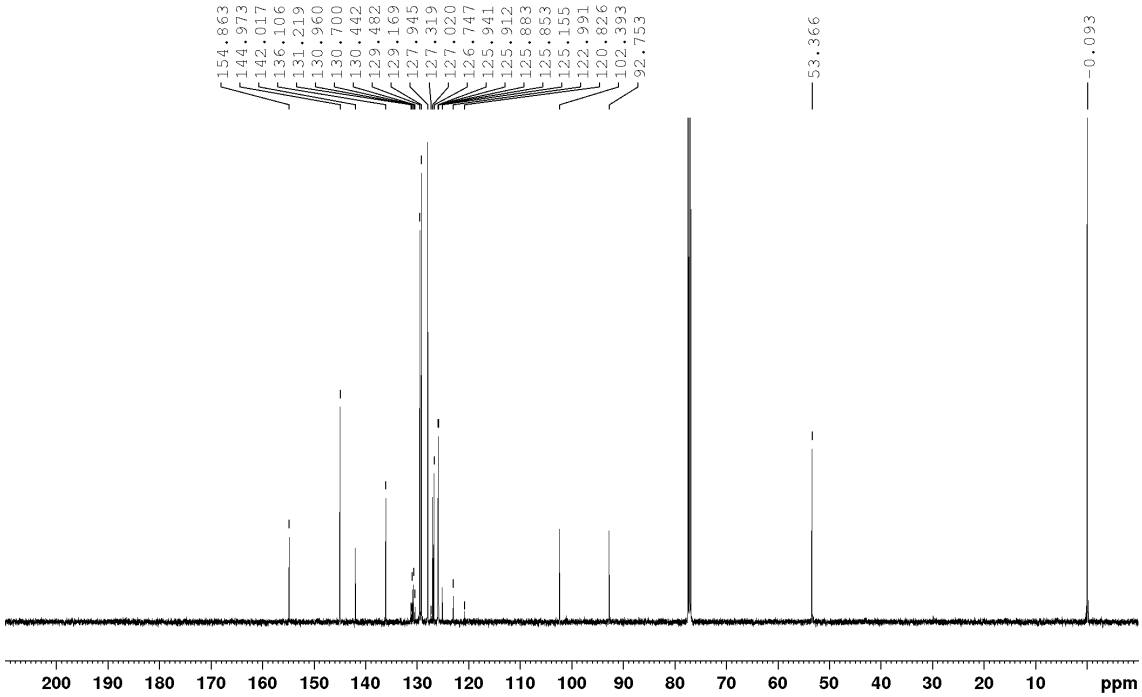


3-(4-Chlorophenyl)-*N*-(1-(4-(trifluoromethyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1l)

^{1}H NMR (500 MHz, $CDCl_3$)

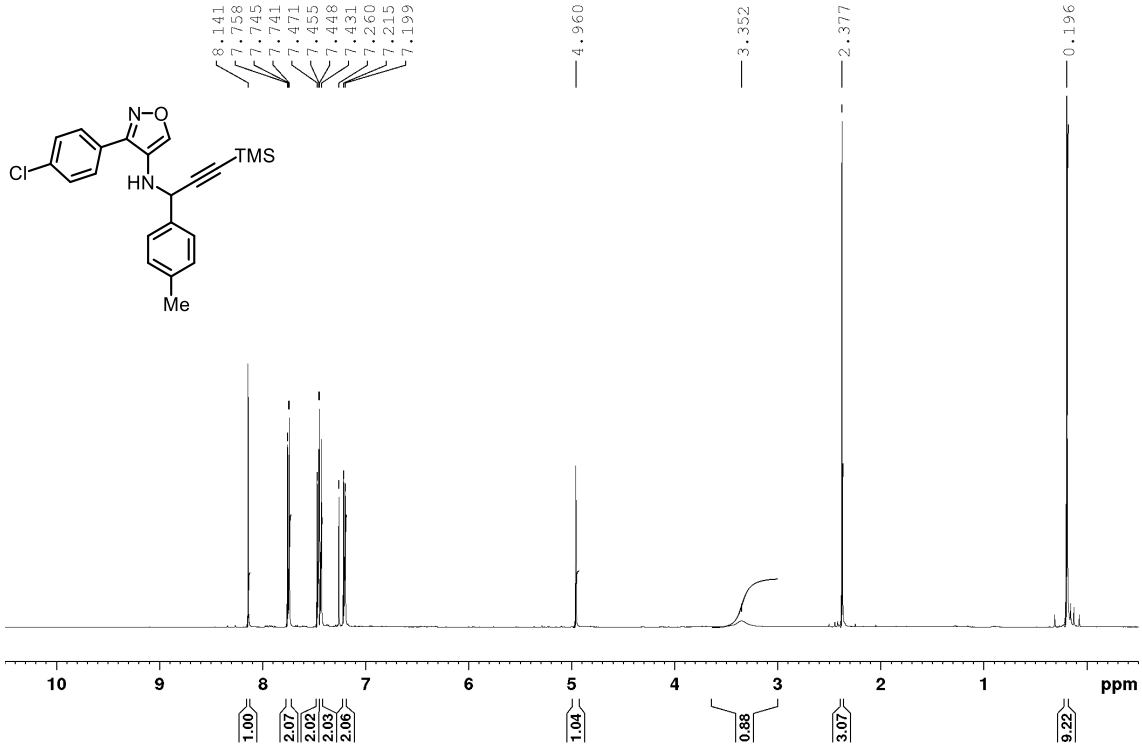


^{13}C NMR (125 MHz, $CDCl_3$)

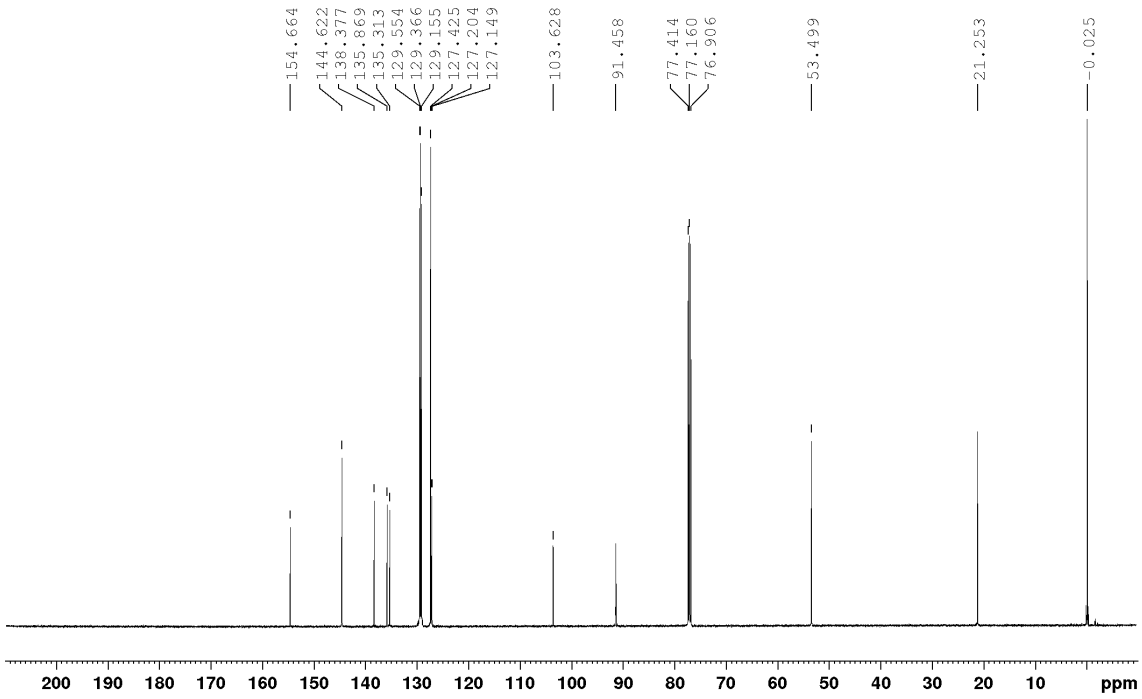


3-(4-Chlorophenyl)-*N*-(1-(p-tolyl)-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1m)

^{1}H NMR (500 MHz, $CDCl_3$)

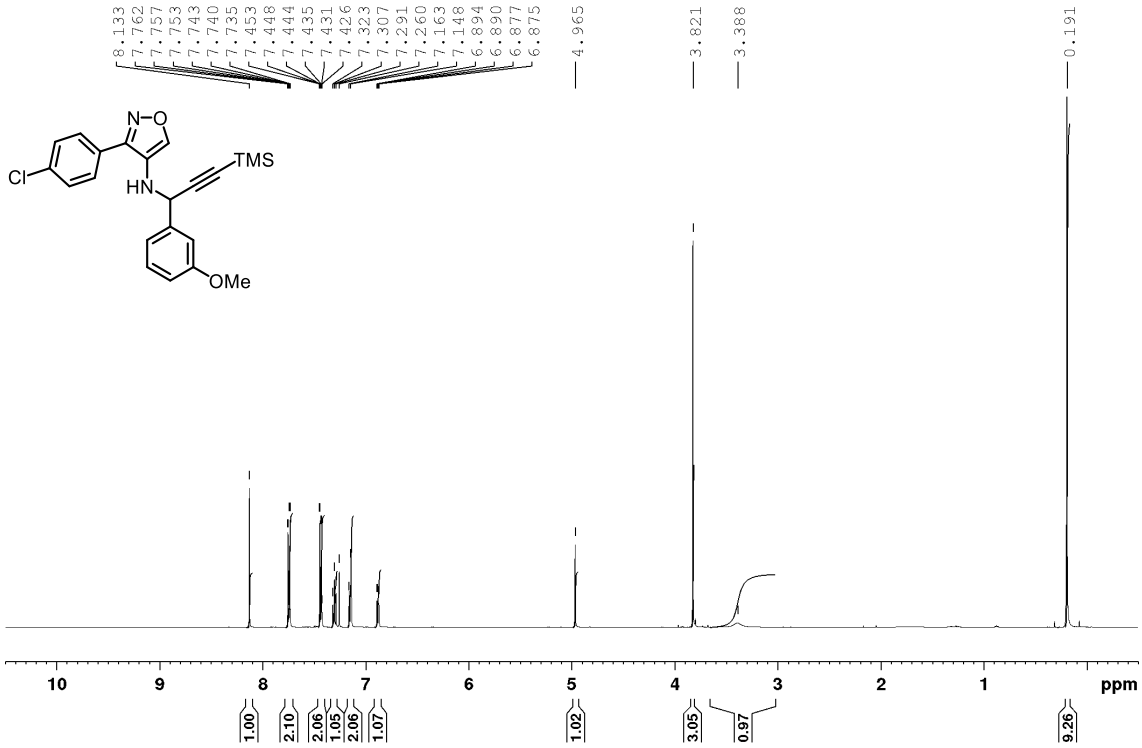


^{13}C NMR (125 MHz, $CDCl_3$)

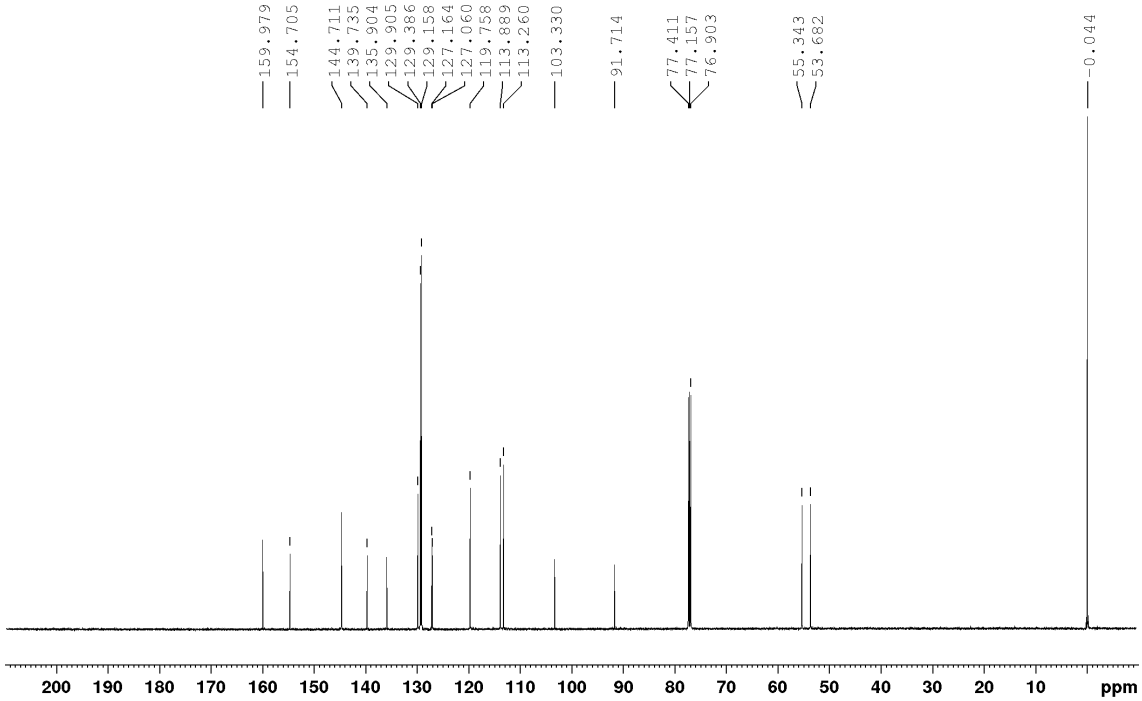


3-(4-Chlorophenyl)-*N*-(1-(3-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1n)

^{1}H NMR (500 MHz, $CDCl_3$)

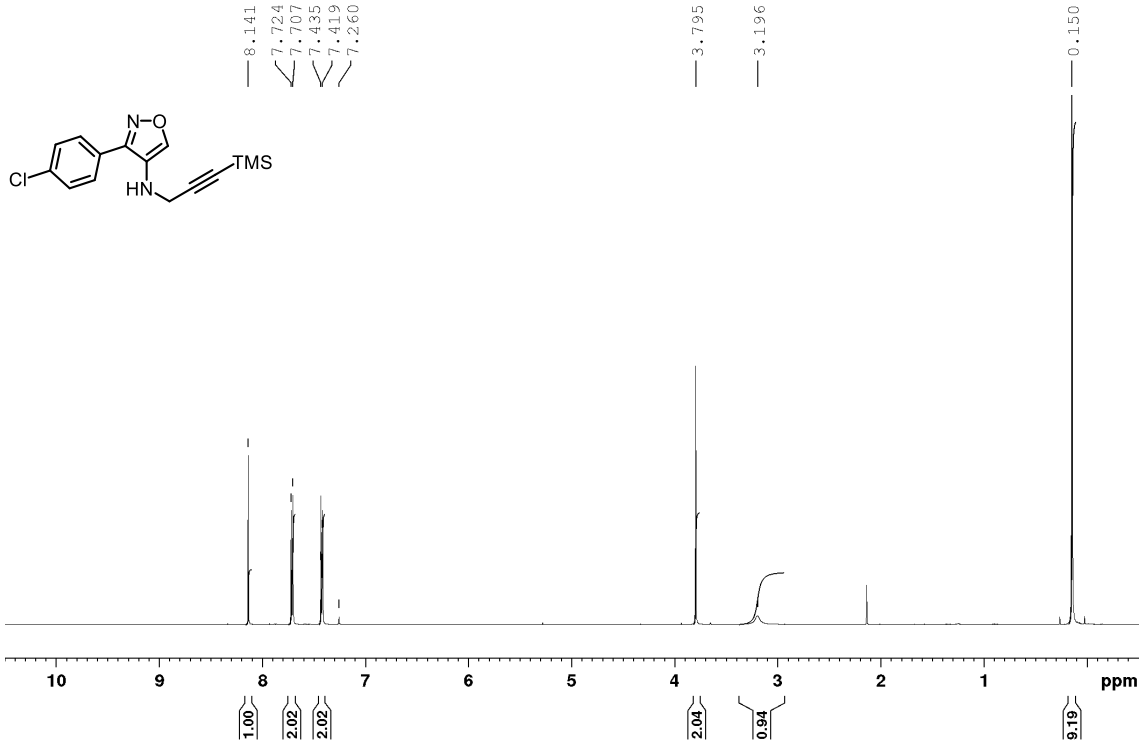


^{13}C NMR (125 MHz, $CDCl_3$)

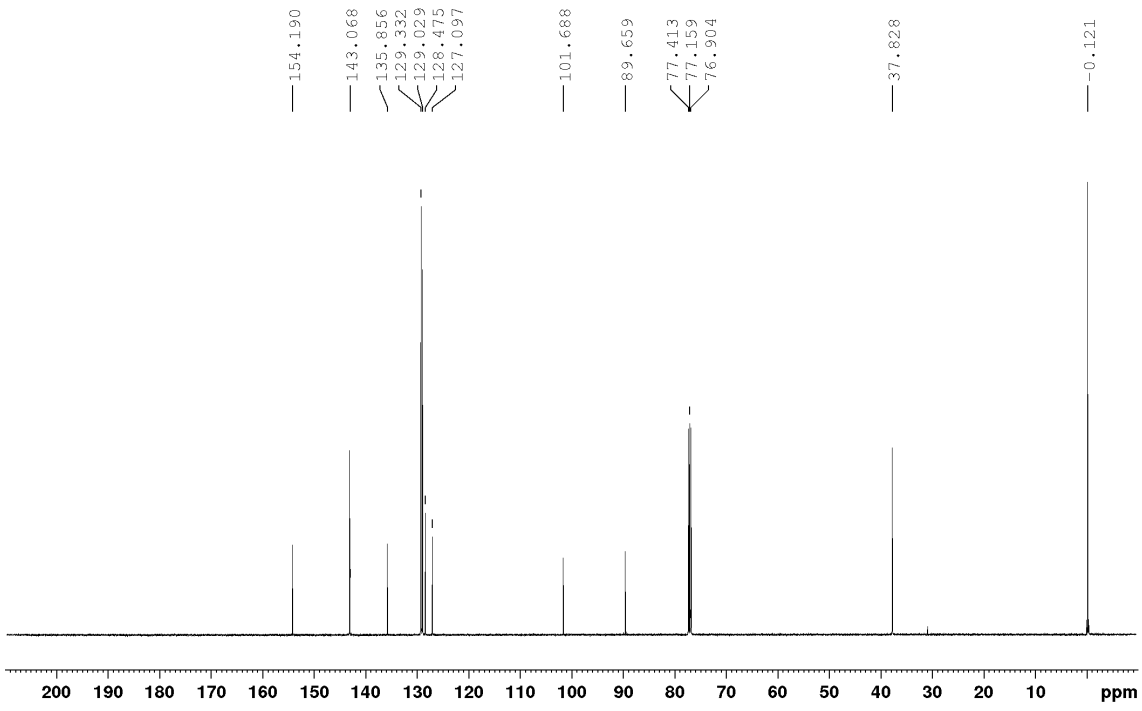


3-(4-Chlorophenyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1o)

^{1}H NMR (500 MHz, $CDCl_3$)

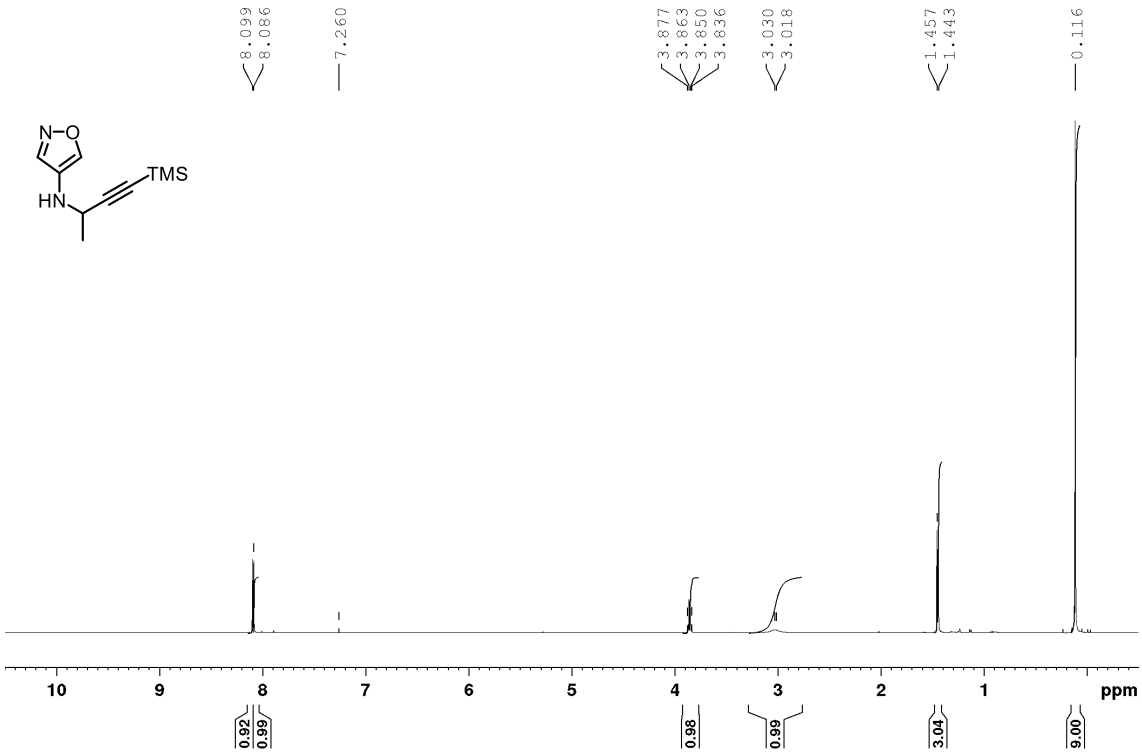


^{13}C NMR (125 MHz, $CDCl_3$)

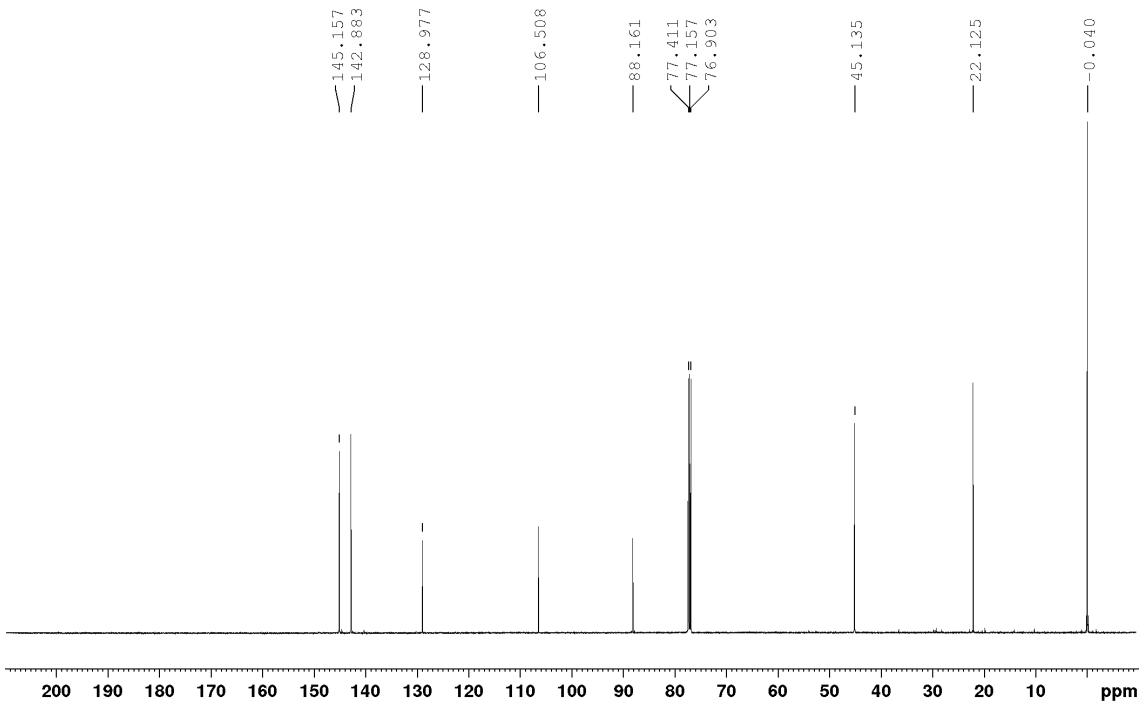


***N*-(4-(Trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1p)**

^{1}H NMR (500 MHz, $CDCl_3$)

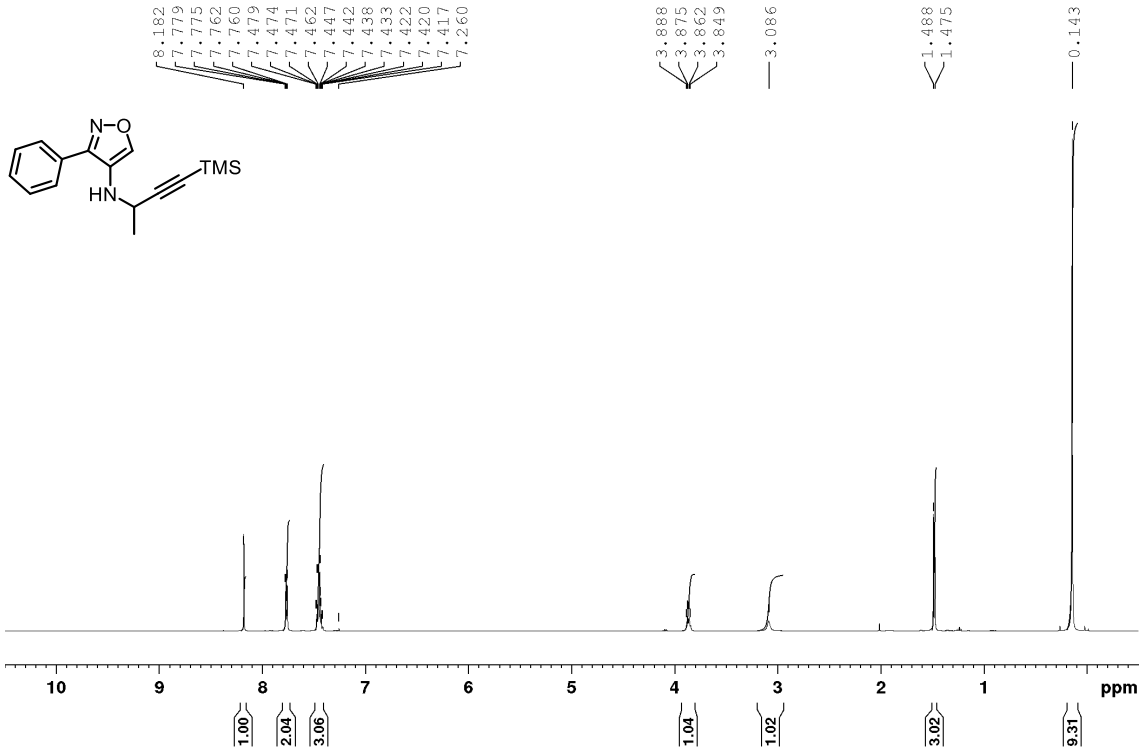


^{13}C NMR (125 MHz, $CDCl_3$)

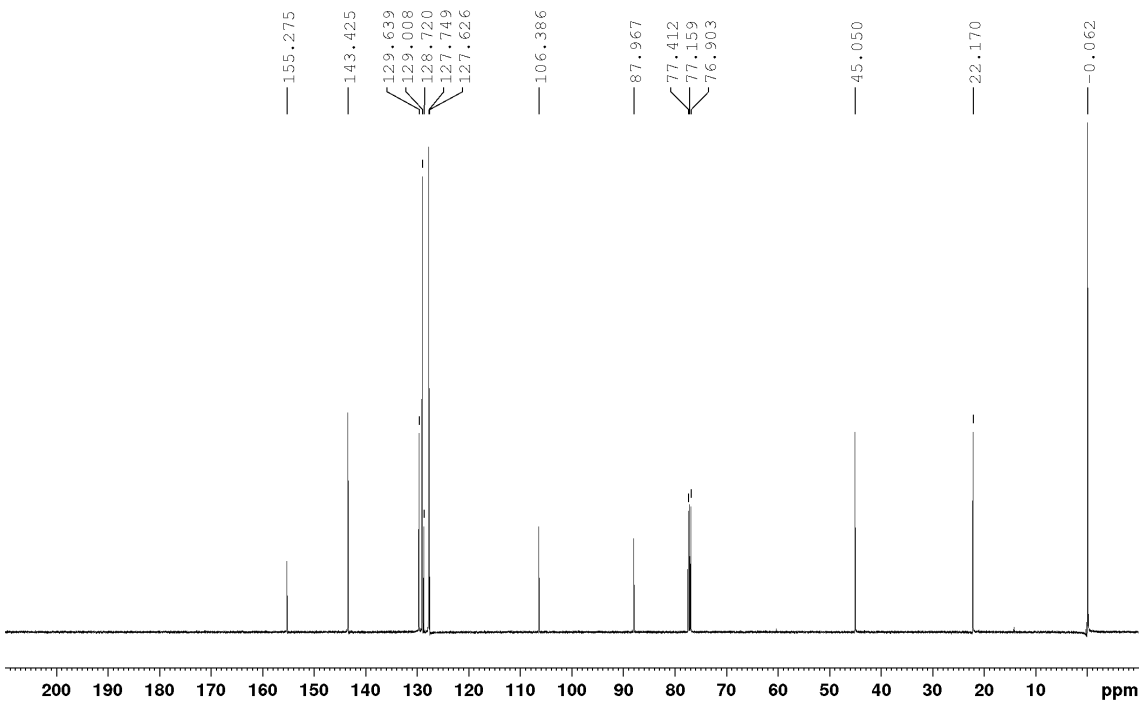


3-Phenyl-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1q)

^{1}H NMR (500 MHz, $CDCl_3$)

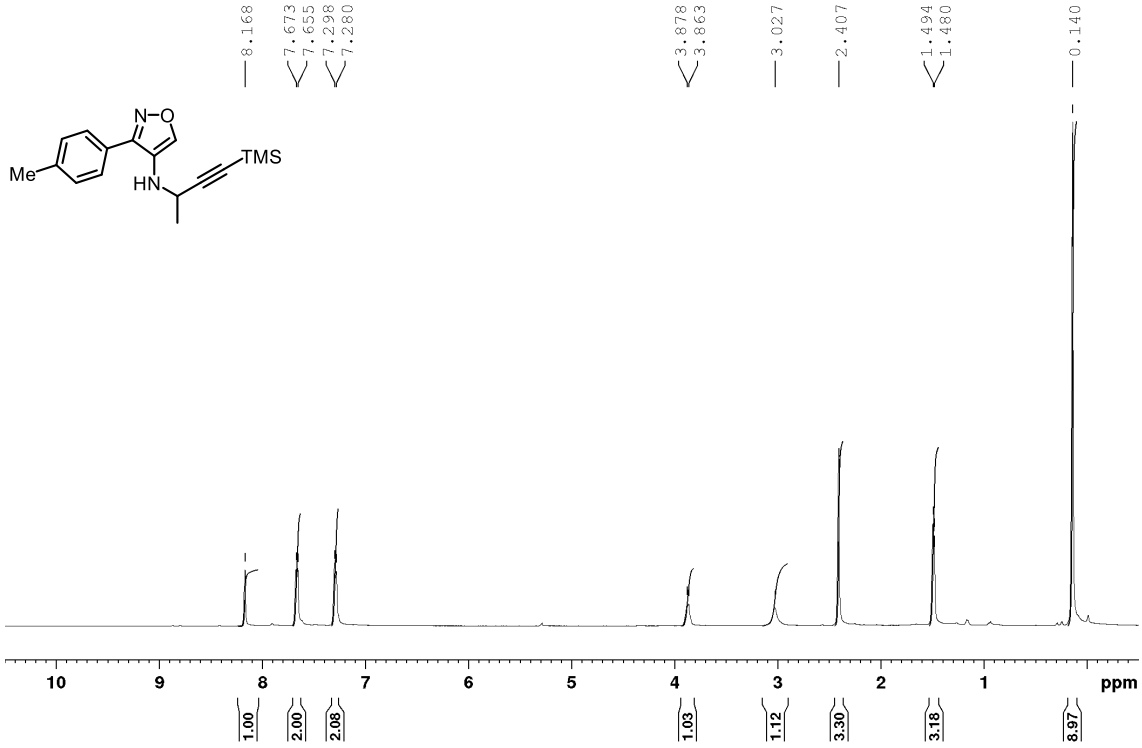


^{13}C NMR (125 MHz, $CDCl_3$)

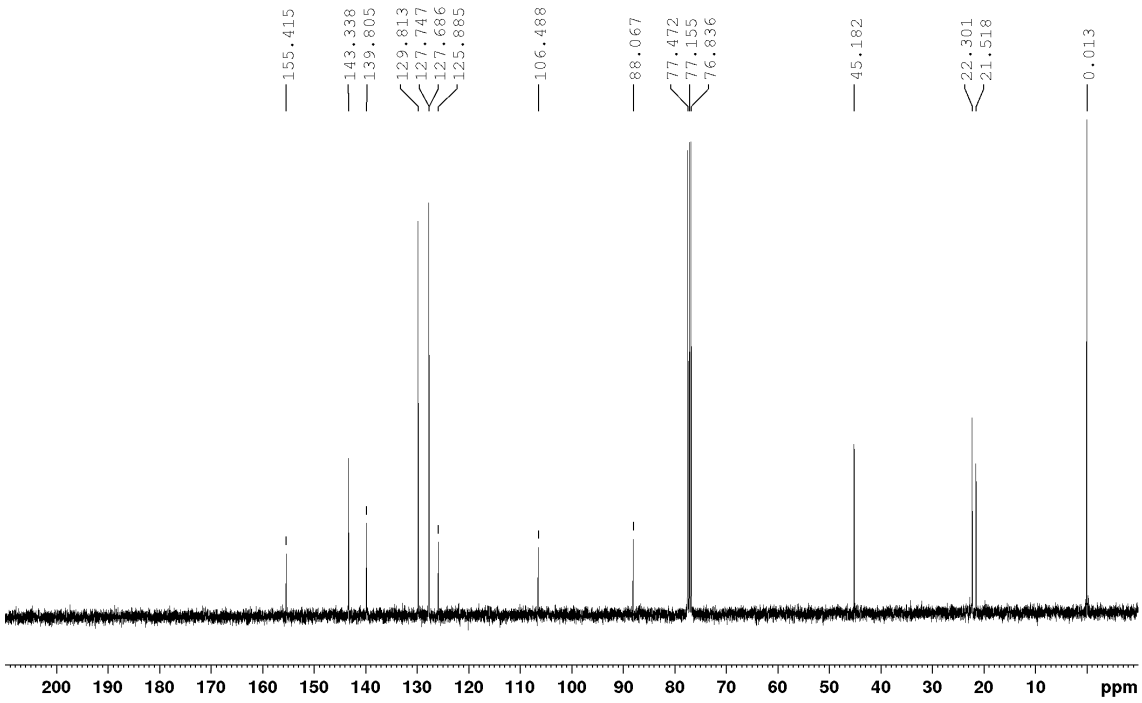


3-(*p*-Tolyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1r)

^{1}H NMR (500 MHz, $CDCl_3$)

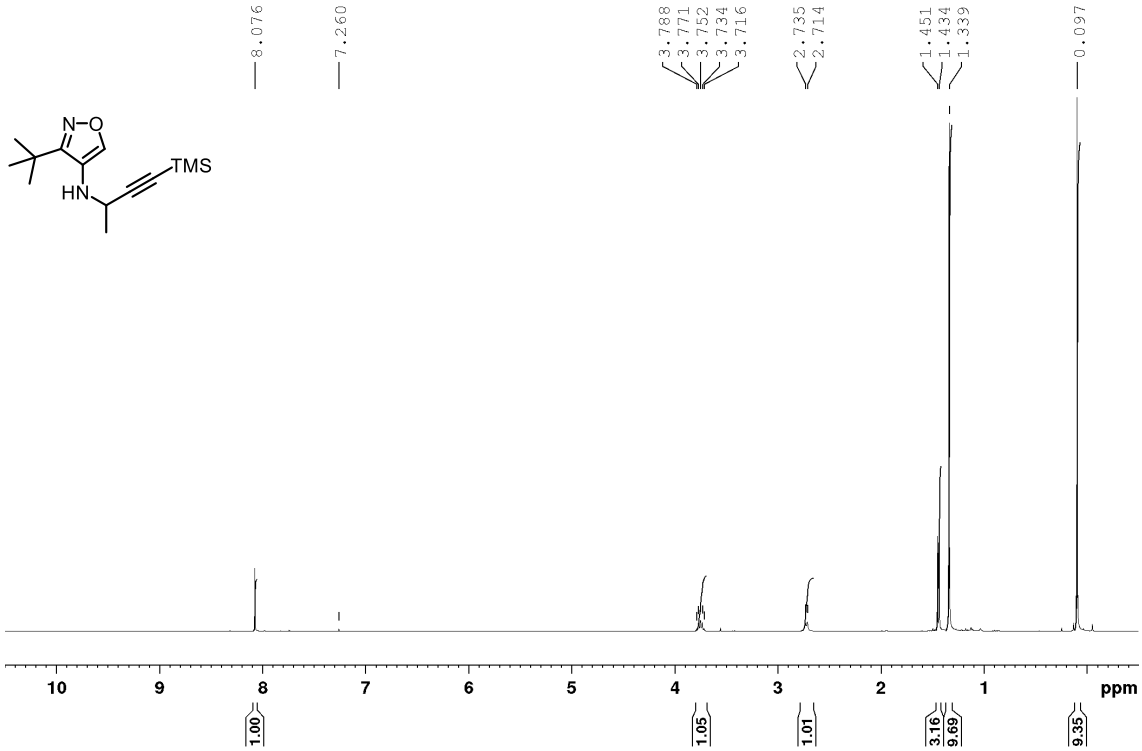


^{13}C NMR (125 MHz, $CDCl_3$)

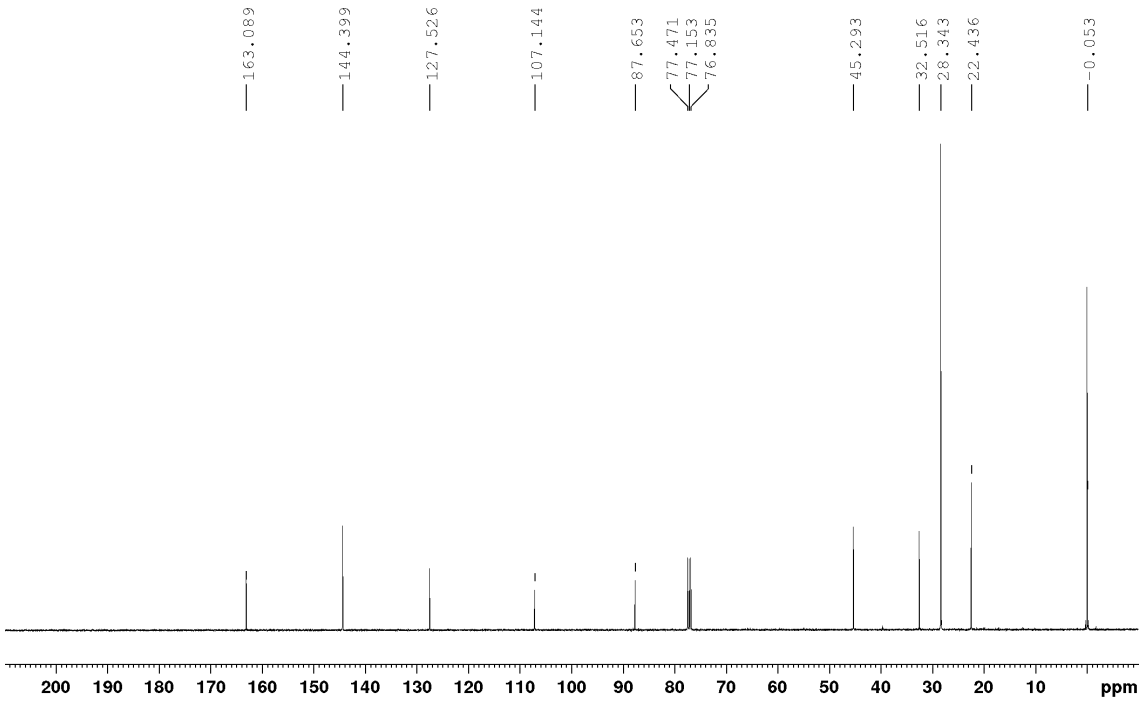


3-(*tert*-Butyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1s)

^{1}H NMR (500 MHz, $CDCl_3$)

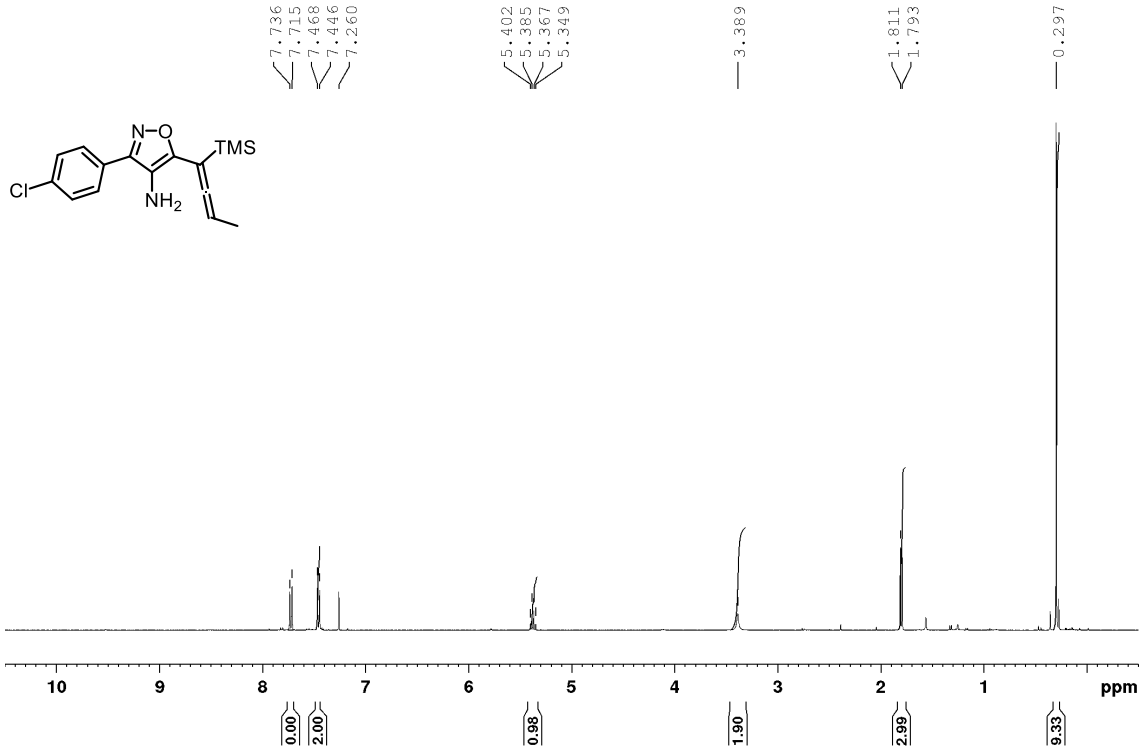


^{13}C NMR (125 MHz, $CDCl_3$)

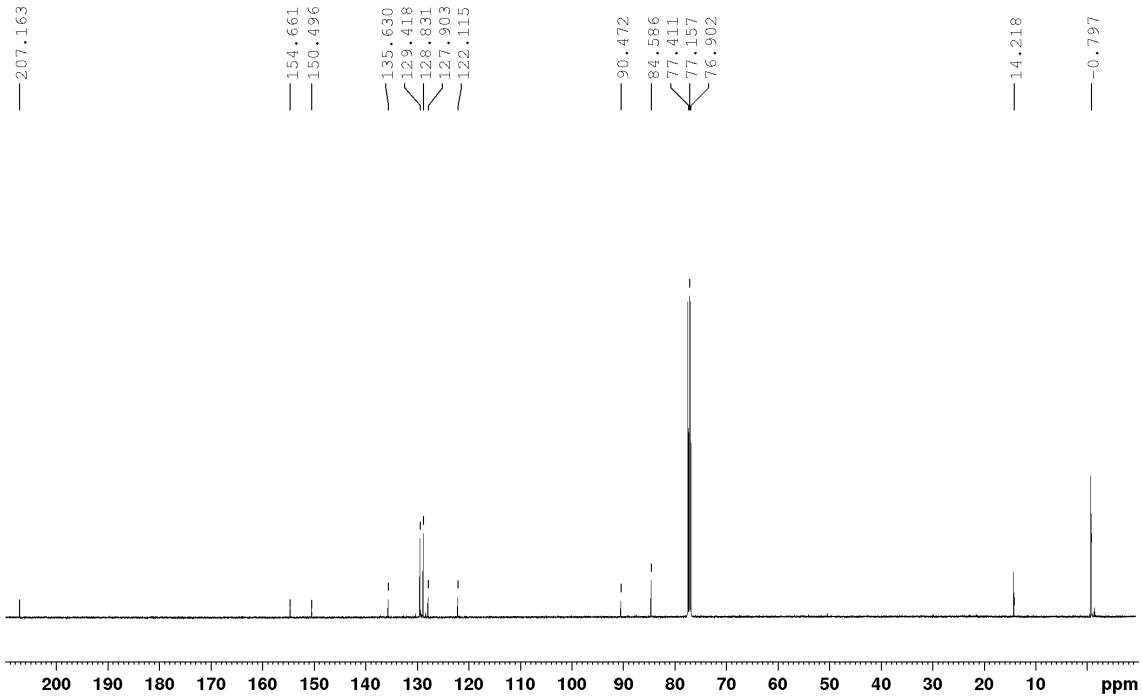


***N*-(3-(4-Chlorophenyl)-5-(1-(trimethylsilyl)buta-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (2a)**

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

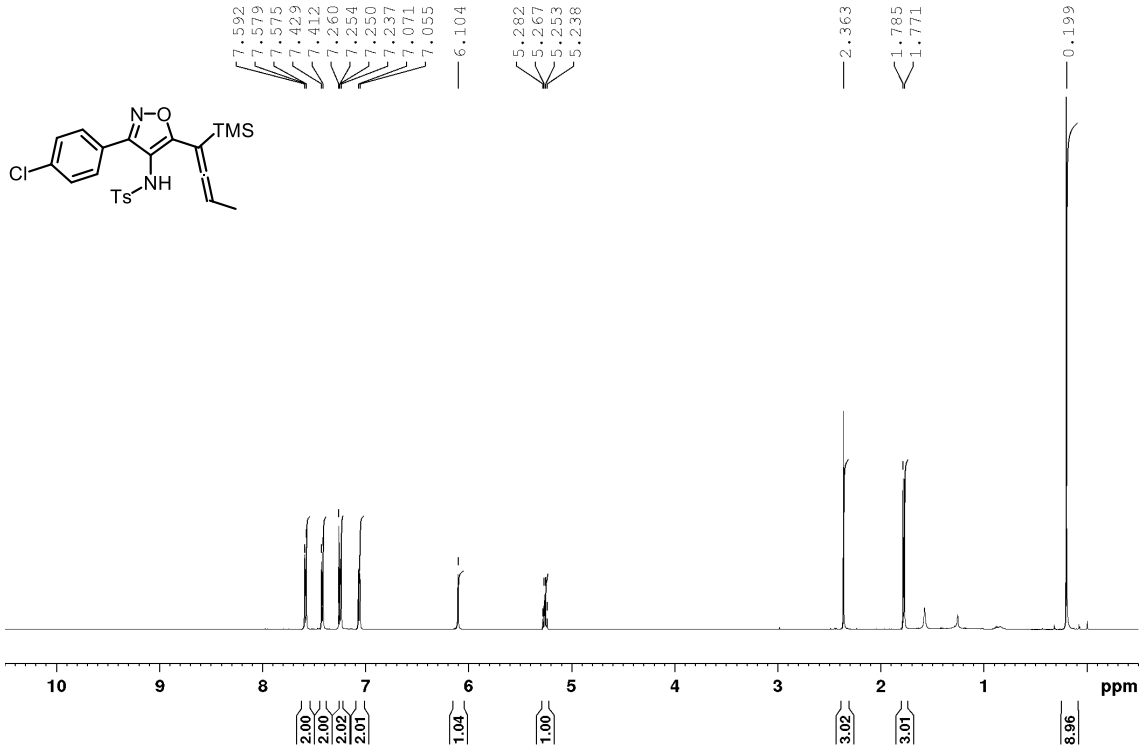


^{13}C NMR (100 MHz, $CDCl_3$)

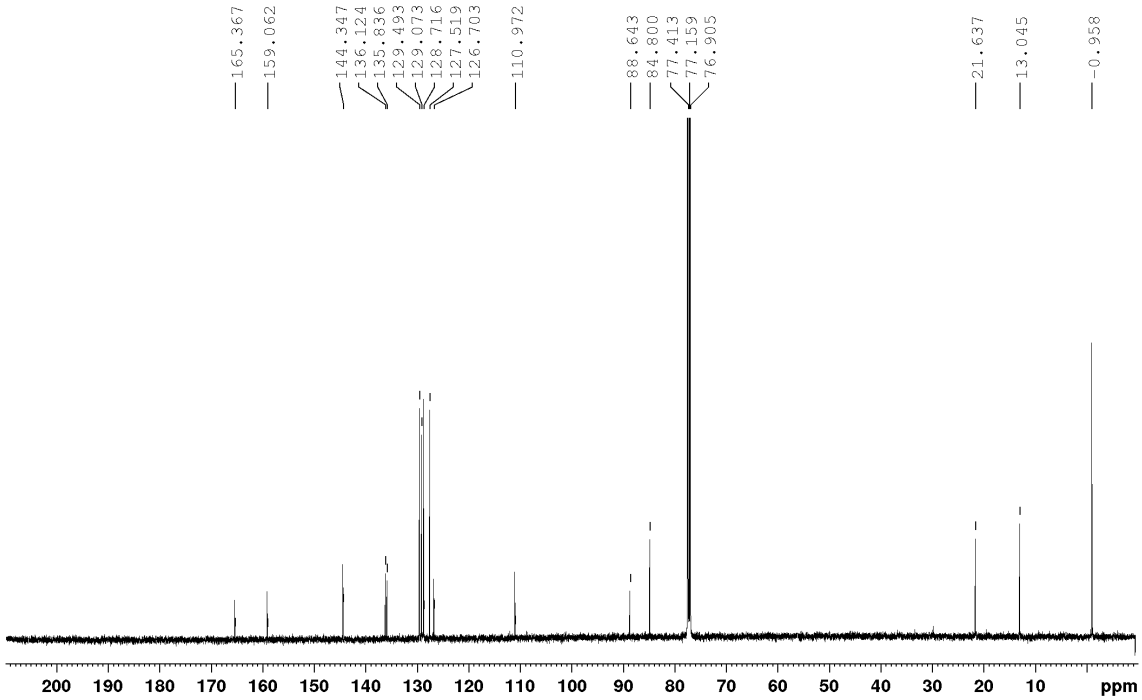


***N*-(3-(4-Chlorophenyl)-5-(1-(trimethylsilyl)buta-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4a)**

^{1}H NMR (500 MHz, $CDCl_3$)

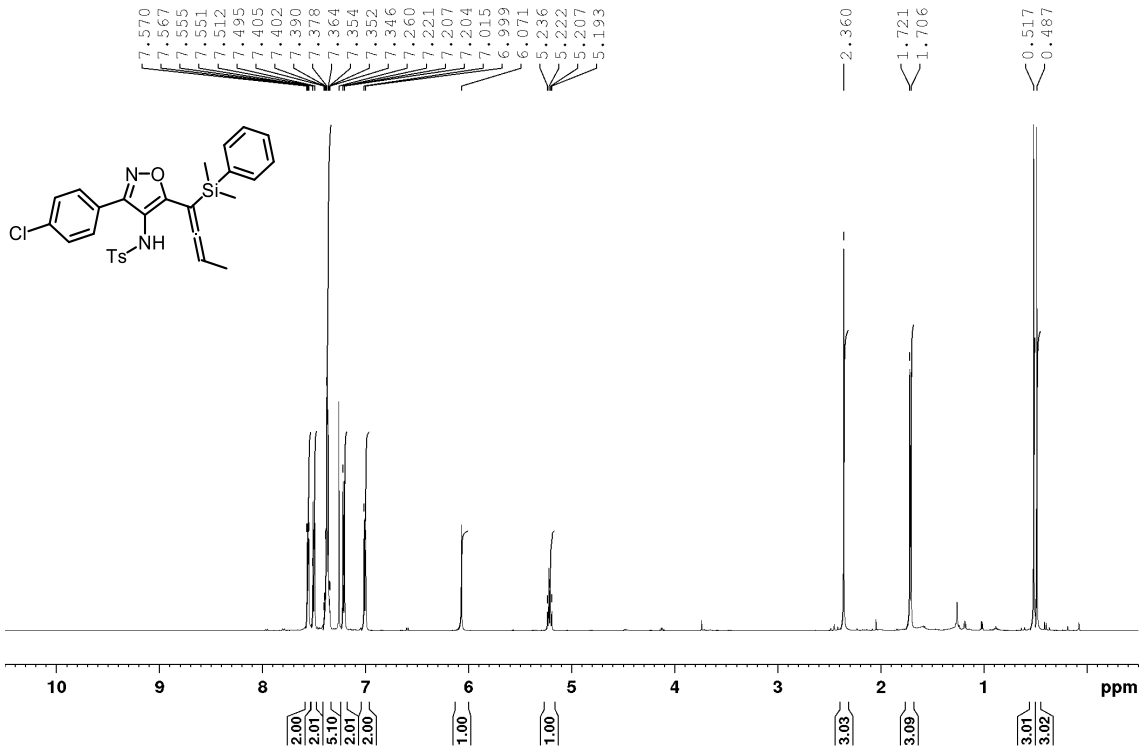


^{13}C NMR (125 MHz, $CDCl_3$)

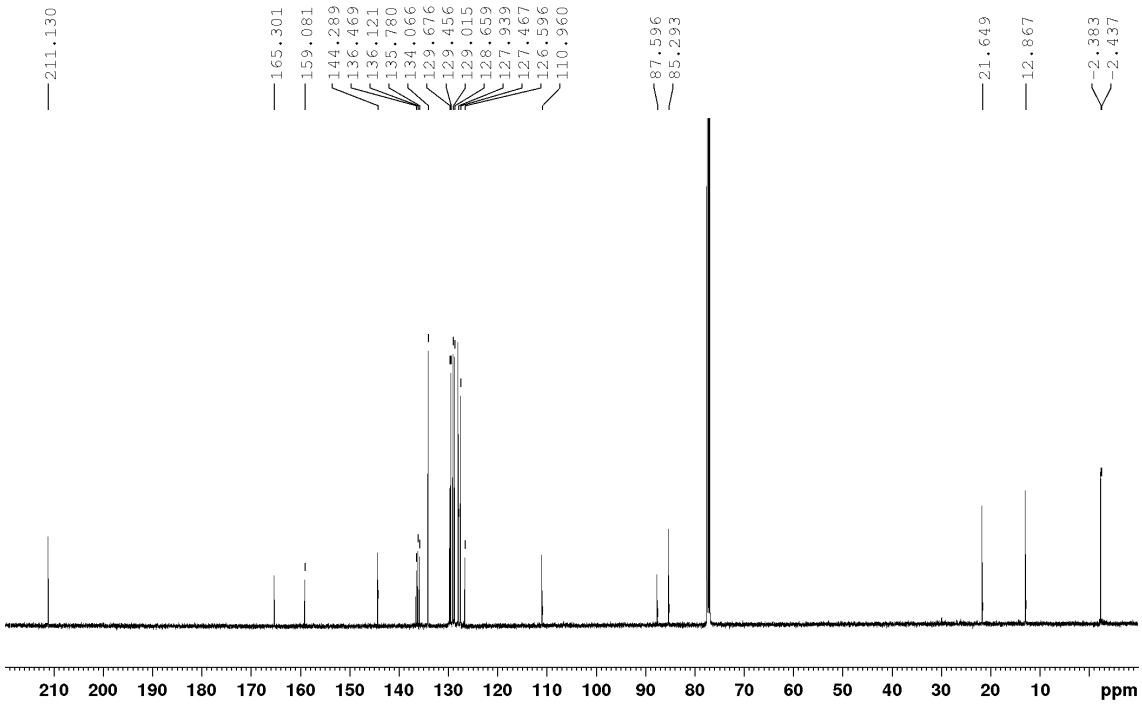


***N*-(3-(4-Chlorophenyl)-5-(1-(dimethyl(phenyl)silyl)buta-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4d)**

^{1}H NMR (500 MHz, $CDCl_3$)

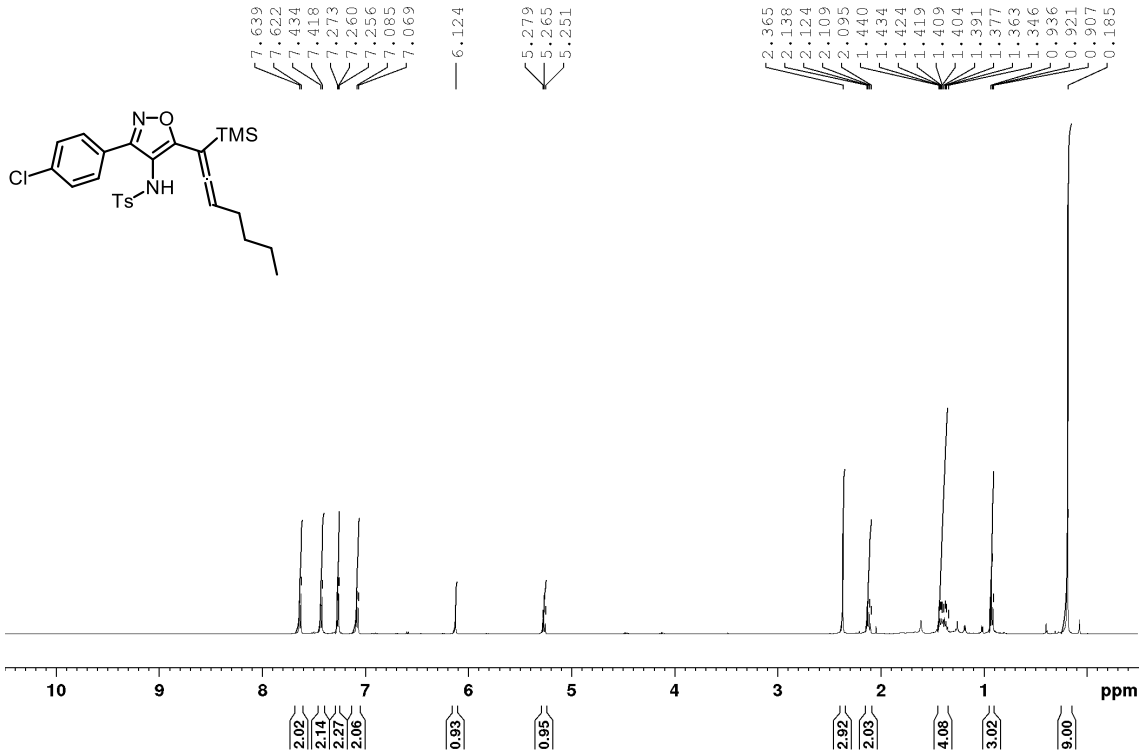


^{13}C NMR (125 MHz, $CDCl_3$)

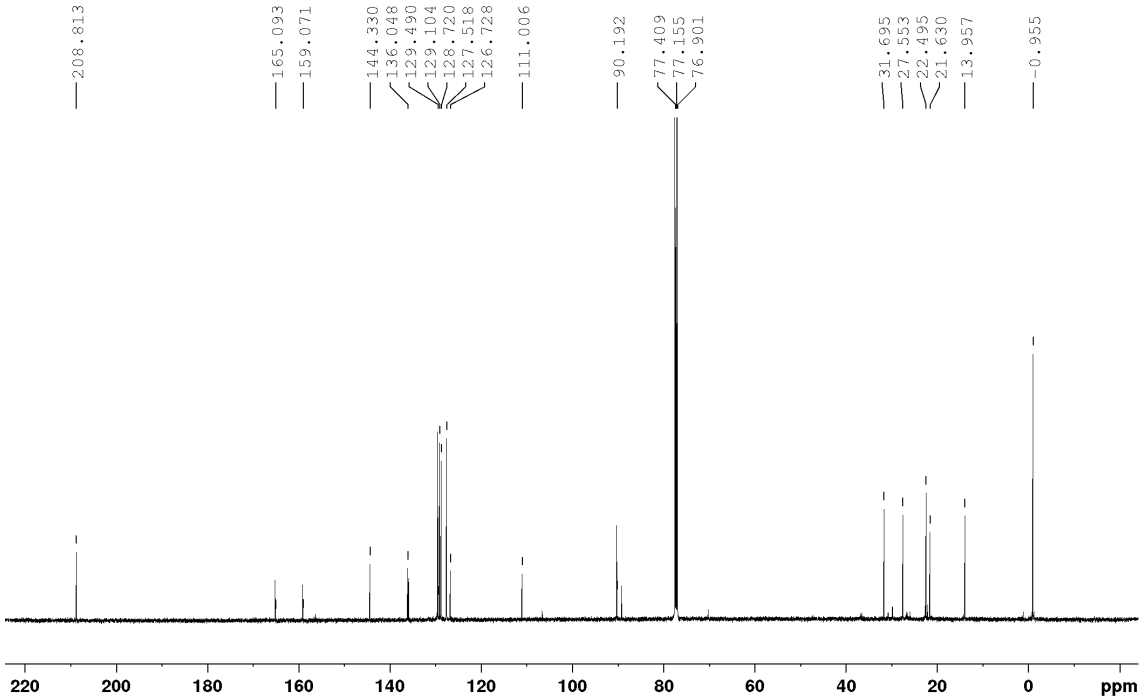


***N*-(3-(4-Chlorophenyl)-5-(1-(trimethylsilyl)hepta-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4h)**

^{1}H NMR (500 MHz, $CDCl_3$)

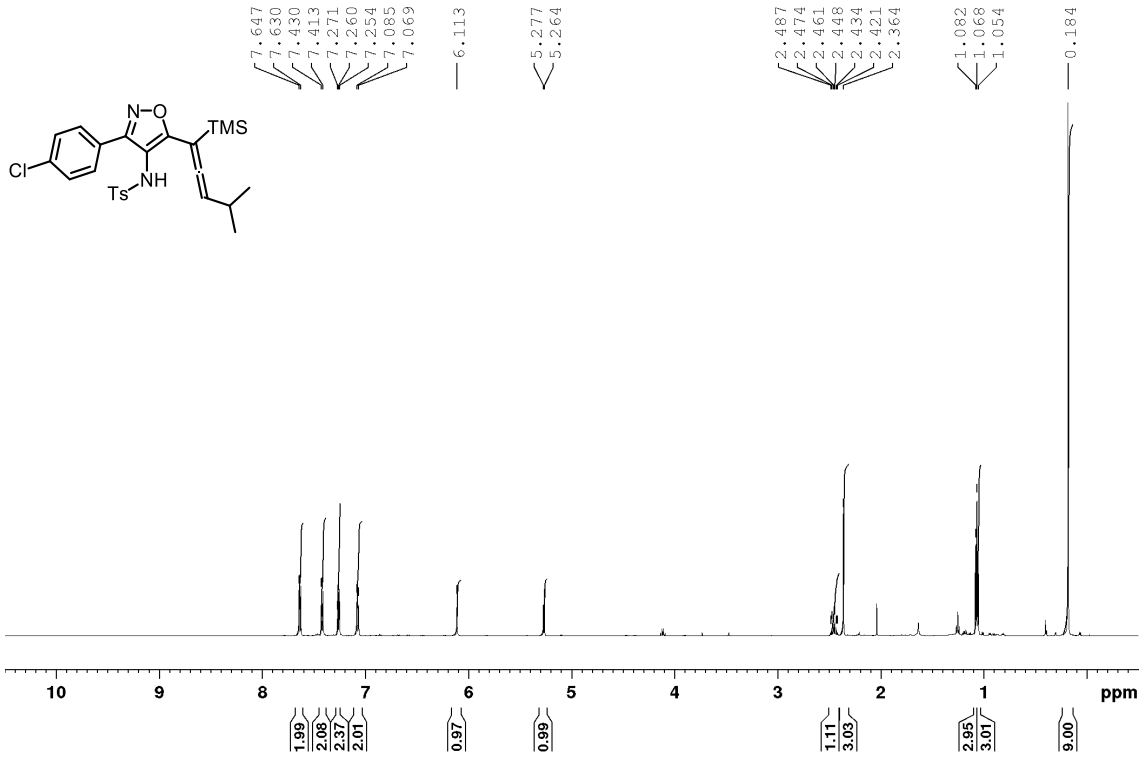


^{13}C NMR (125 MHz, $CDCl_3$)

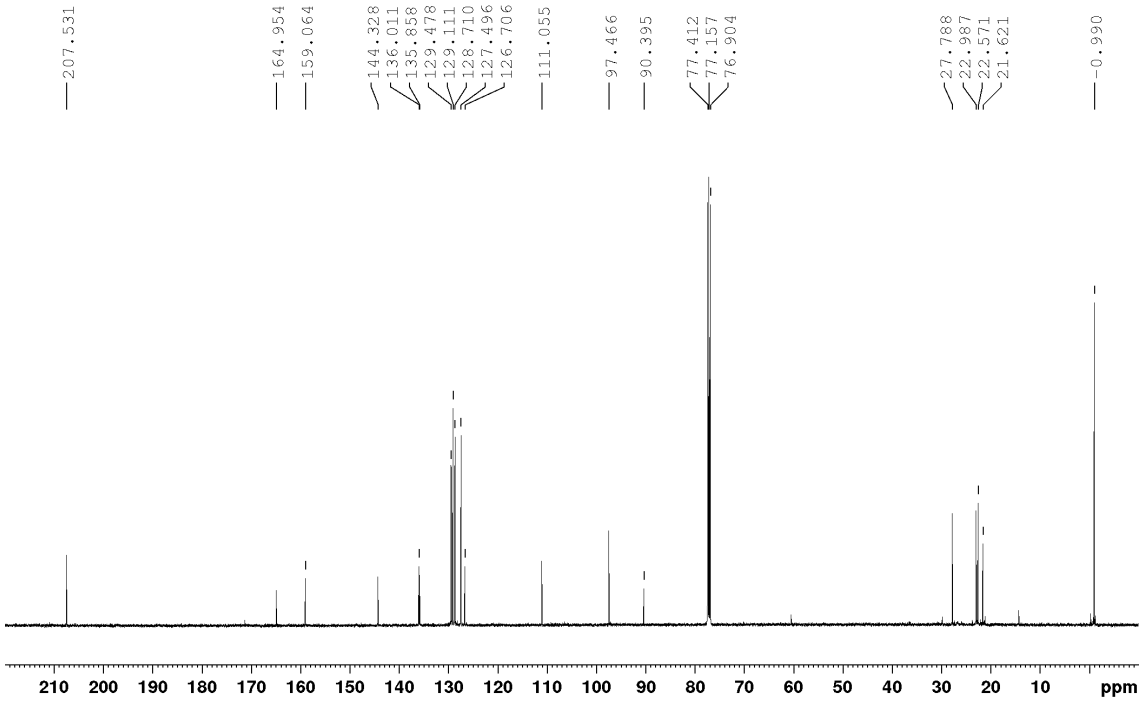


***N*-(3-(4-Chlorophenyl)-5-(4-methyl-1-(trimethylsilyl)penta-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4i)**

^{1}H NMR (500 MHz, $CDCl_3$)

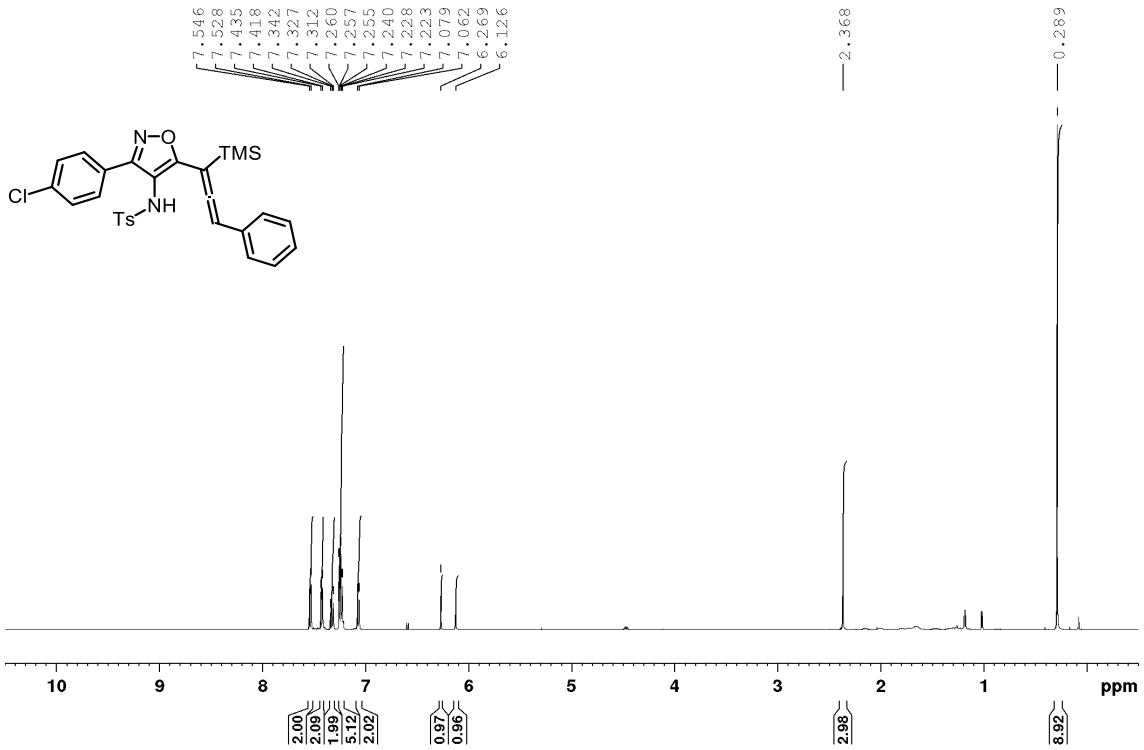


^{13}C NMR (125 MHz, $CDCl_3$)

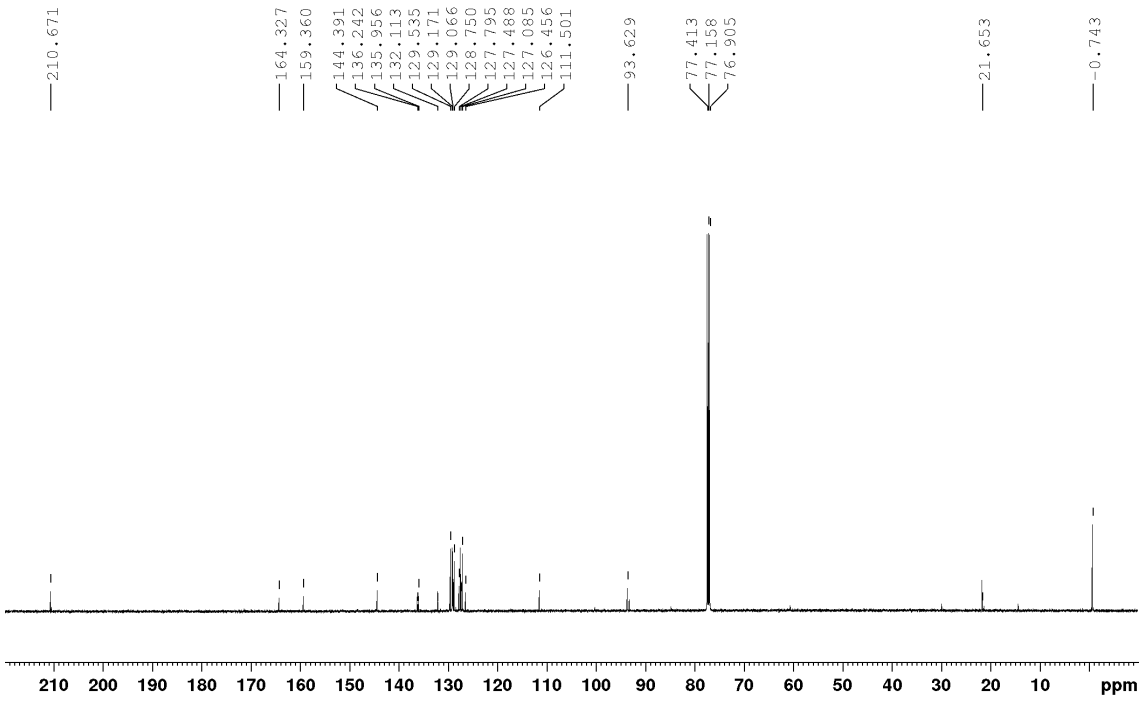


***N*-(3-(4-Chlorophenyl)-5-(3-phenyl-1-(trimethylsilyl)propa-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4j)**

^{1}H NMR (500 MHz, $CDCl_3$)

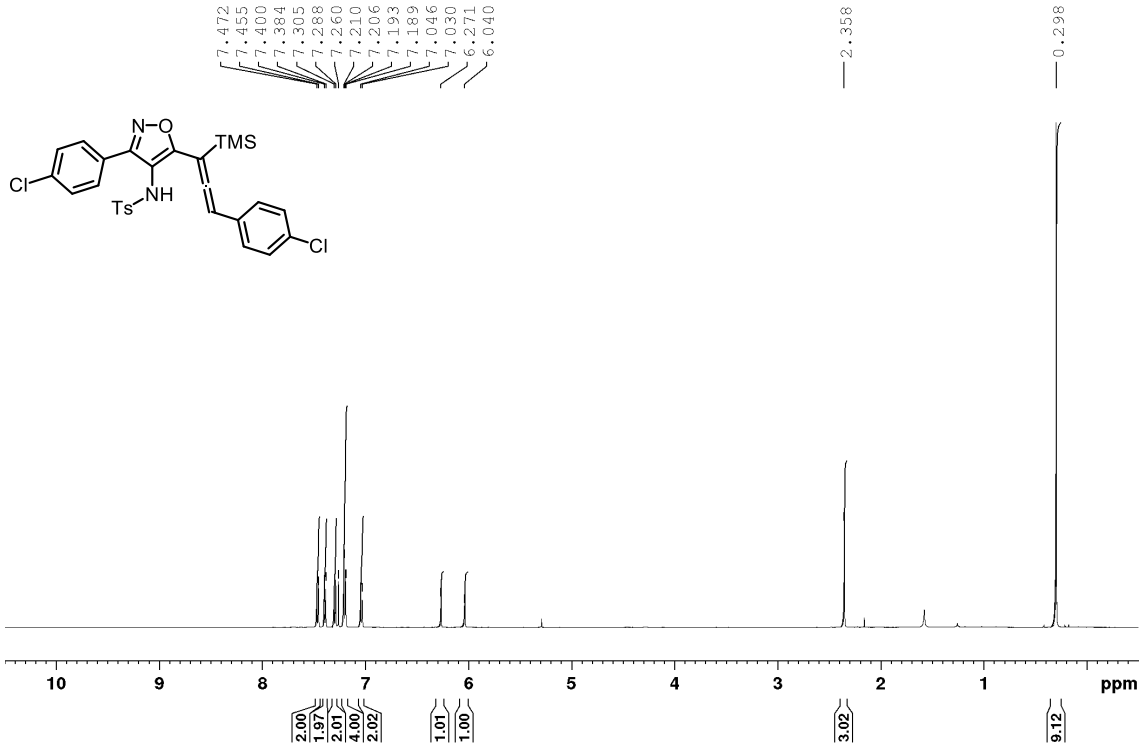


^{13}C NMR (125 MHz, $CDCl_3$)

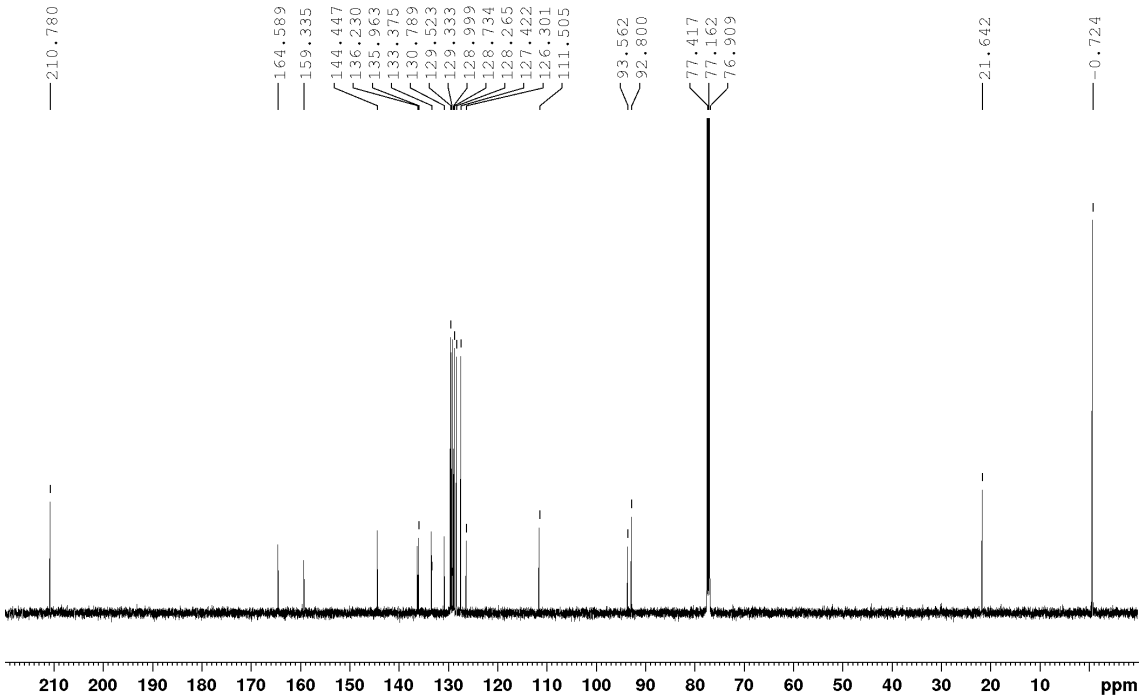


***N*-(3-(4-Chlorophenyl)-5-(3-(4-chlorophenyl)-1-(trimethylsilyl)propa-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4k)**

^{1}H NMR (500 MHz, $CDCl_3$)

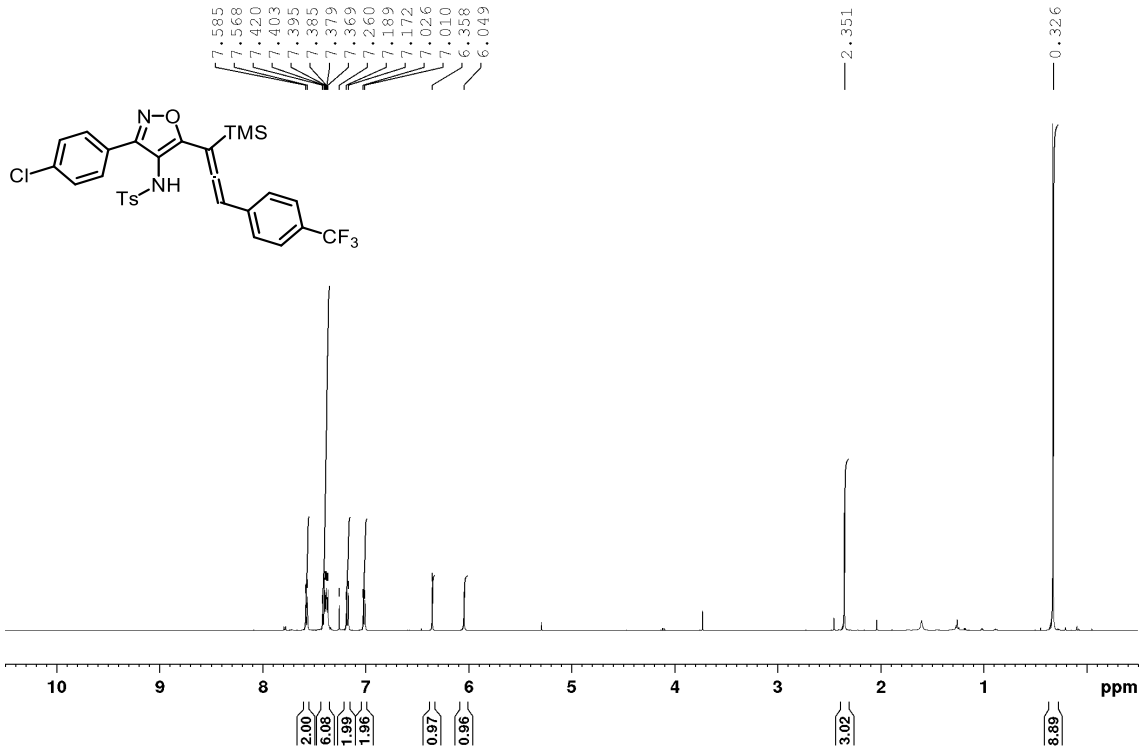


^{13}C NMR (125 MHz, $CDCl_3$)

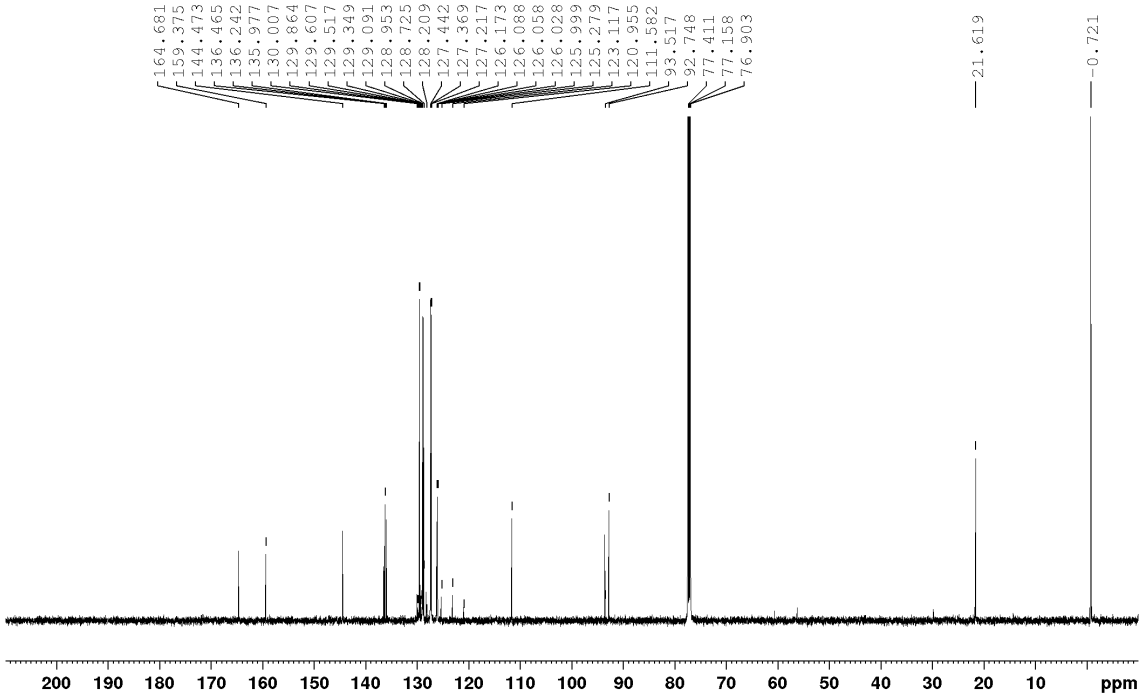


***N*-(3-(4-Chlorophenyl)-5-(3-(4-(trifluoromethyl)phenyl)-1-(trimethylsilyl)propa-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4l)**

^{1}H NMR (500 MHz, $CDCl_3$)

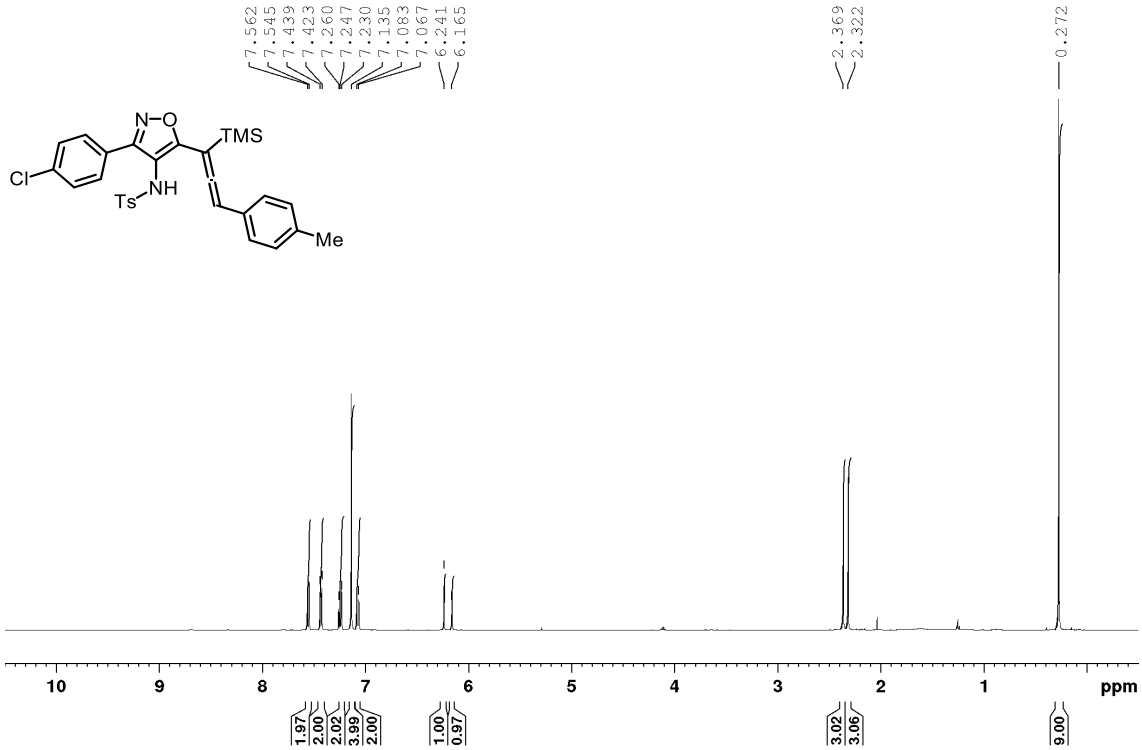


^{13}C NMR (125 MHz, $CDCl_3$)

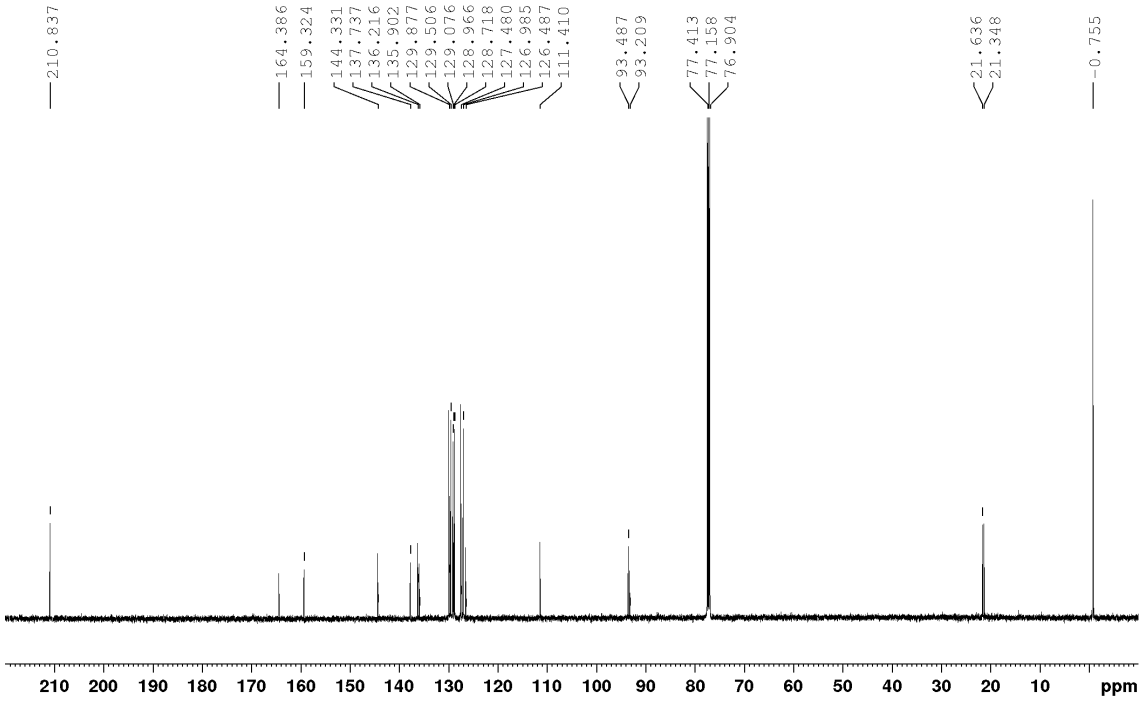


***N*-(3-(4-Chlorophenyl)-5-(3-(p-tolyl)-1-(trimethylsilyl)propa-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4m)**

^{1}H NMR (500 MHz, $CDCl_3$)

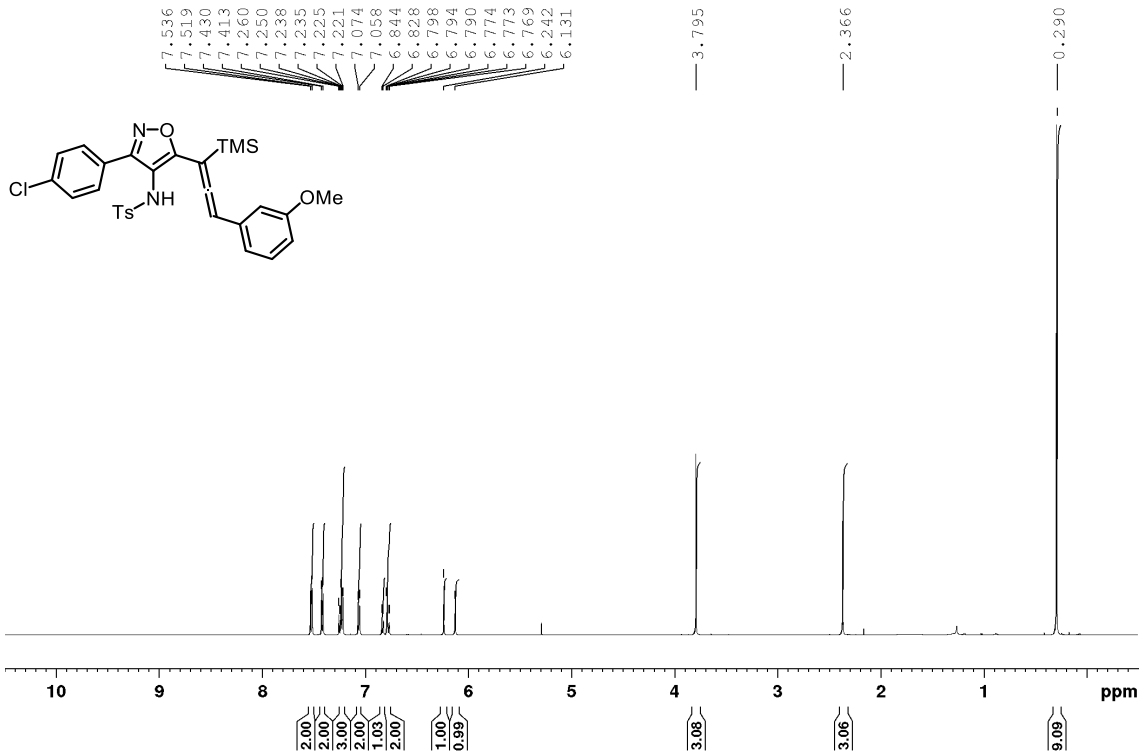


^{13}C NMR (125 MHz, $CDCl_3$)

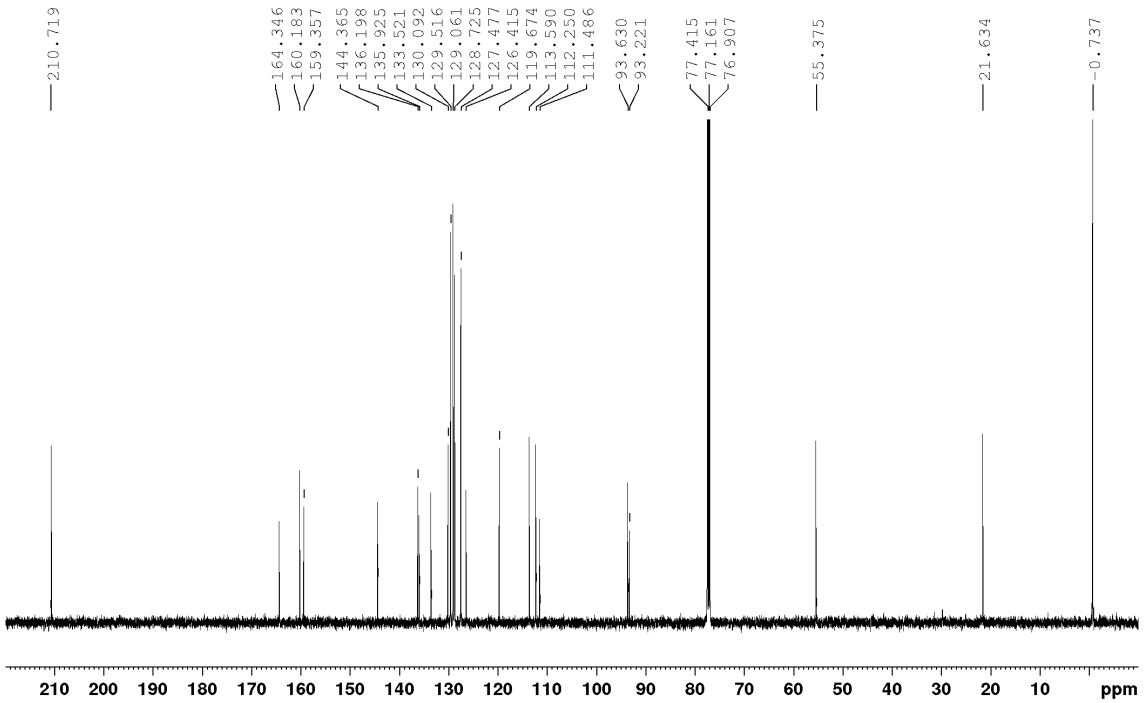


5-(3-(3-Methoxyphenyl)-1-(trimethylsilyl)propa-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4n)

^{1}H NMR (500 MHz, $CDCl_3$)

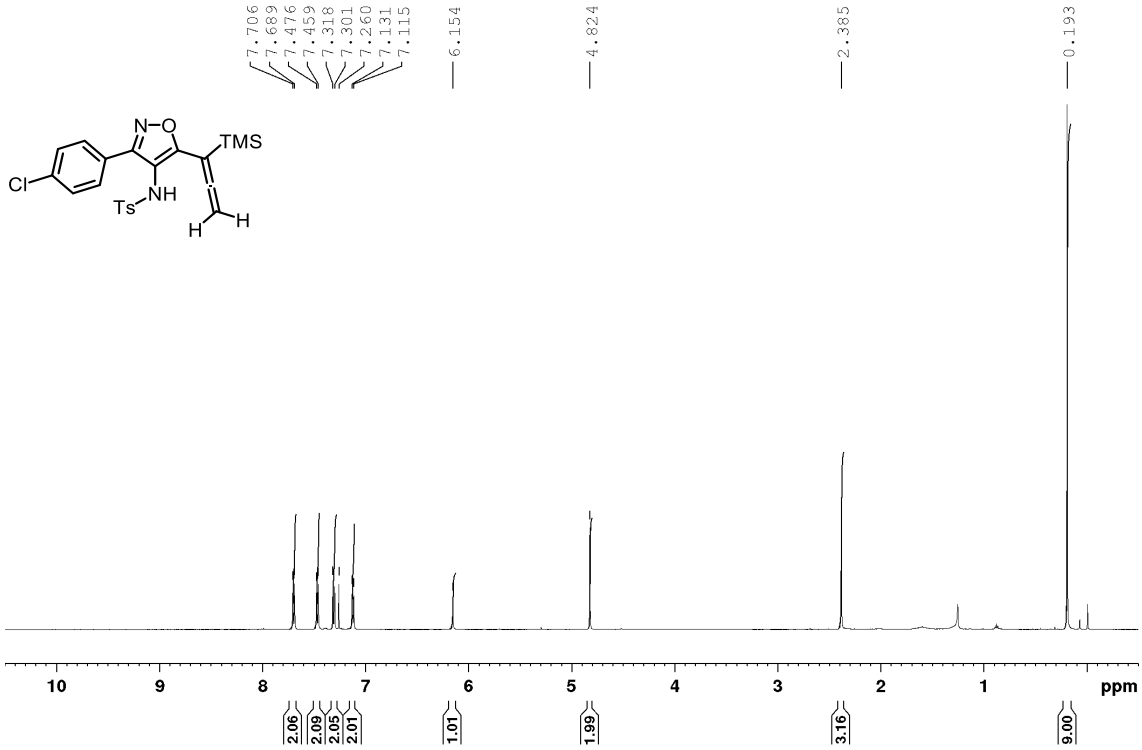


^{13}C NMR (125 MHz, $CDCl_3$)

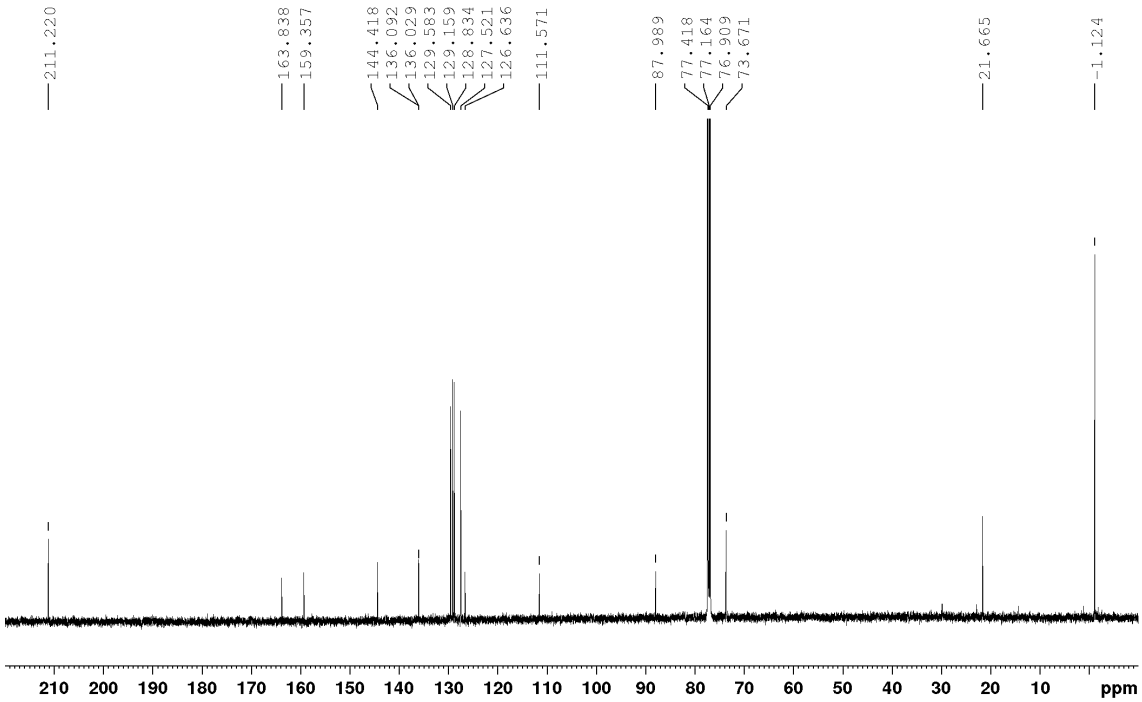


***N*-(3-(4-Chlorophenyl)-5-(1-(trimethylsilyl)propa-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4o)**

^{1}H NMR (500 MHz, $CDCl_3$)

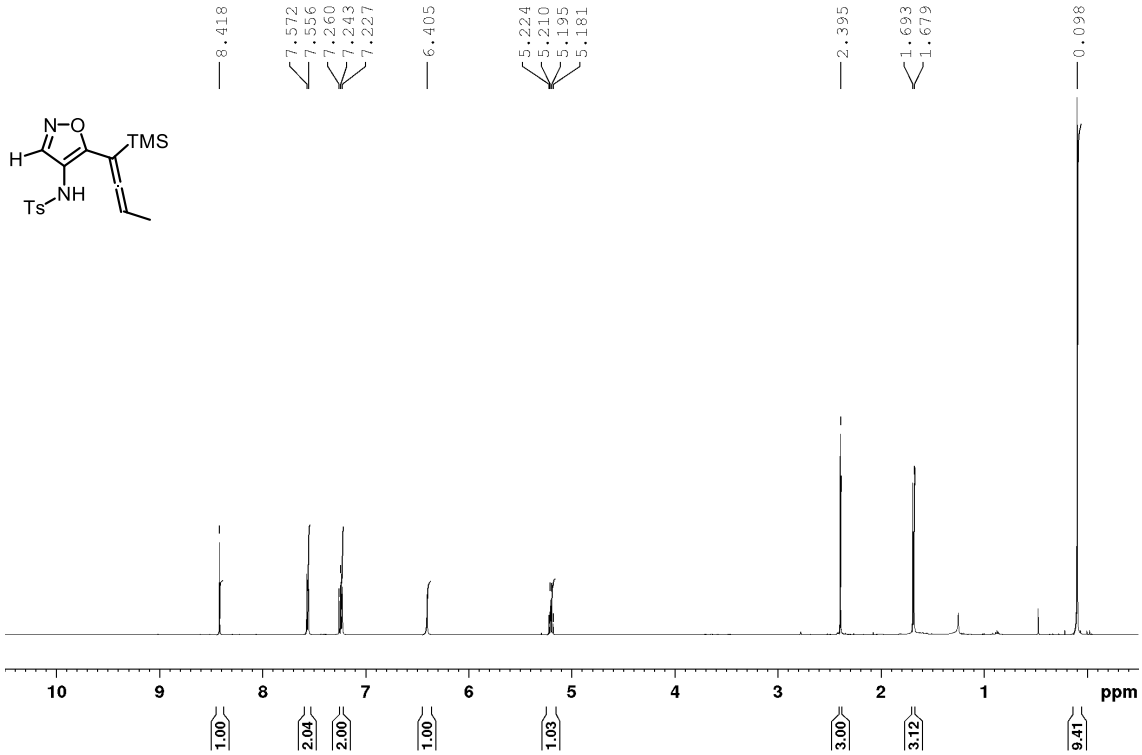


^{13}C NMR (125 MHz, $CDCl_3$)

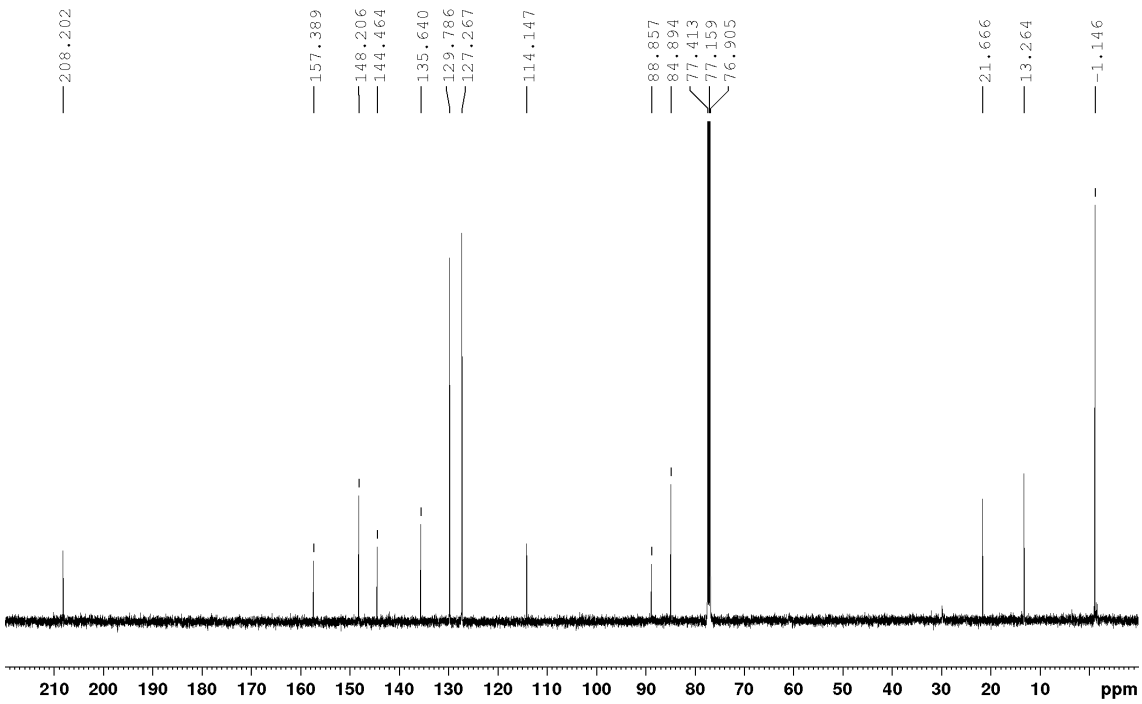


4-Methyl-*N*-(5-(1-(trimethylsilyl)buta-1,2-dien-1-yl)isoxazol-4-yl)benzenesulfonamide (4p)

^{1}H NMR (500 MHz, $CDCl_3$)

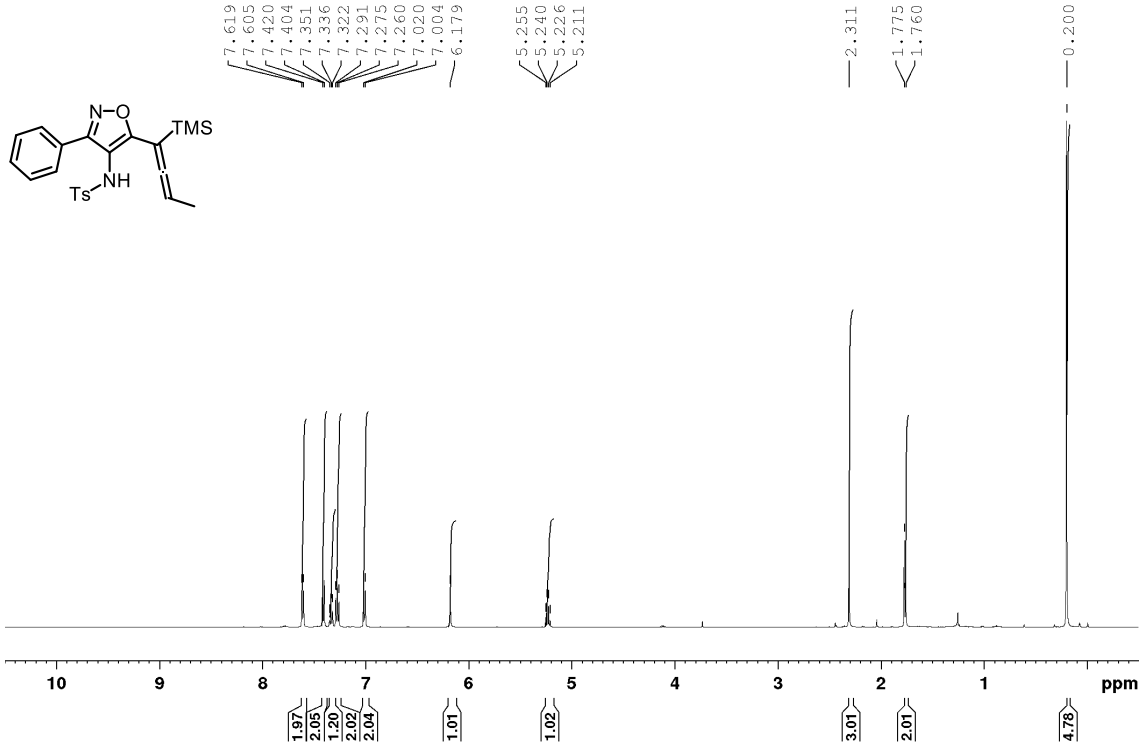


^{13}C NMR (125 MHz, $CDCl_3$)

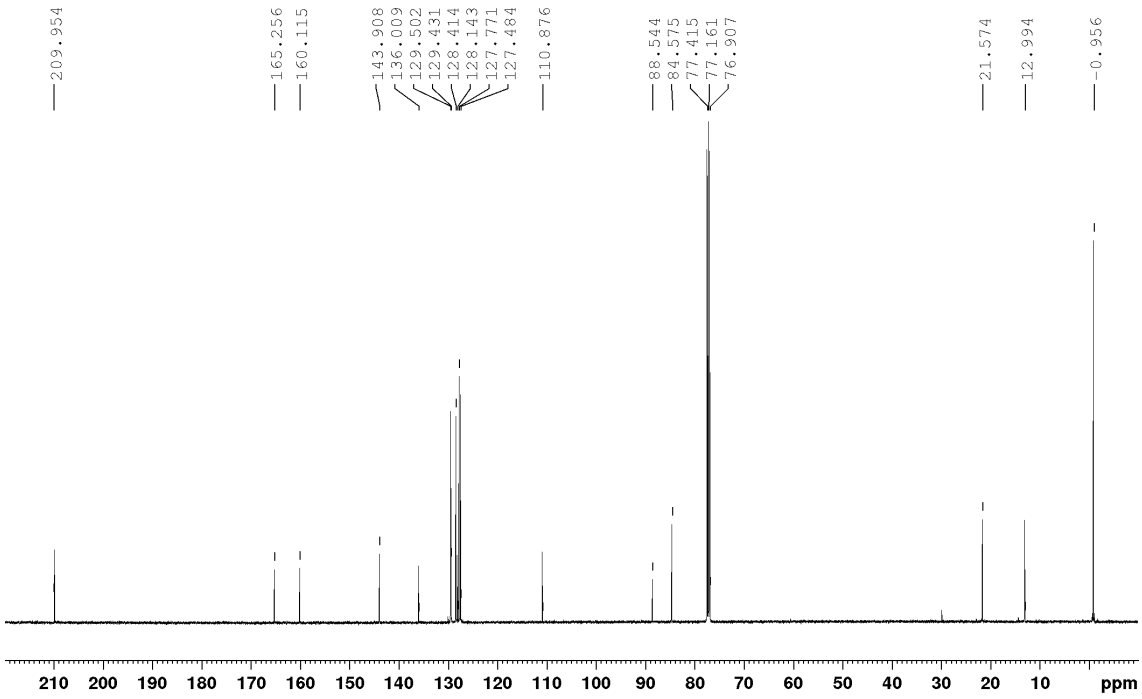


4-Methyl-*N*-(3-phenyl-5-(1-(trimethylsilyl)buta-1,2-dien-1-yl)isoxazol-4-yl)benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$) (4q)

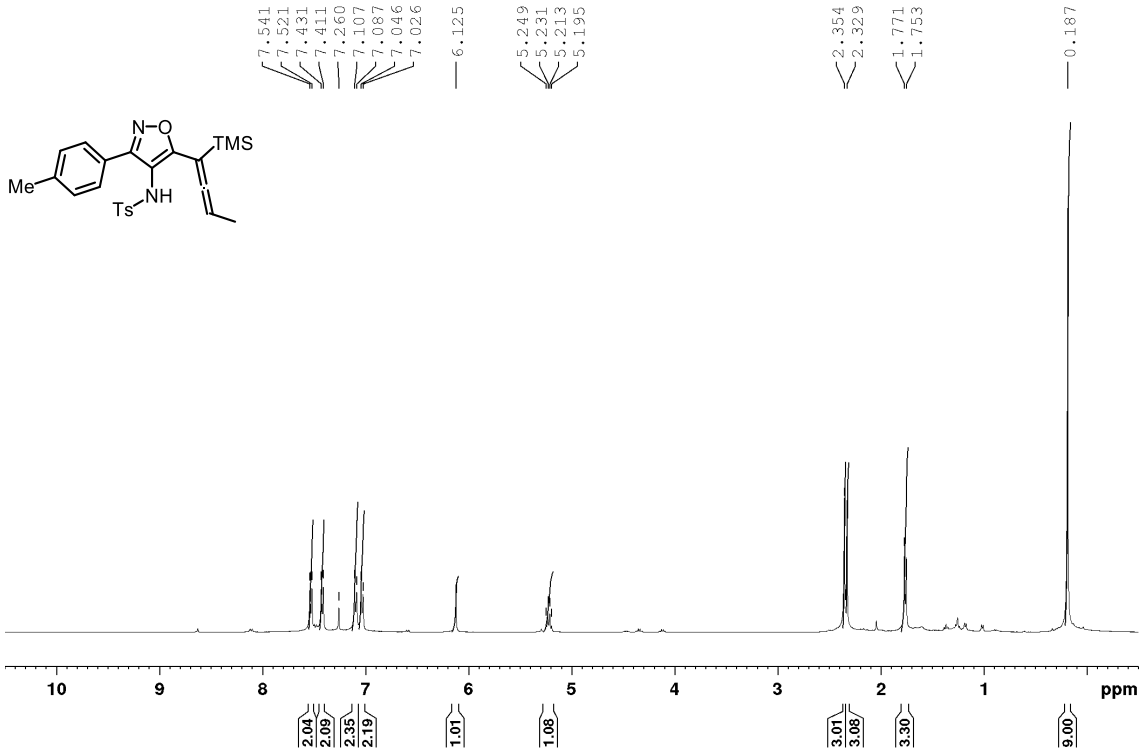


^{13}C NMR (125 MHz, $CDCl_3$)

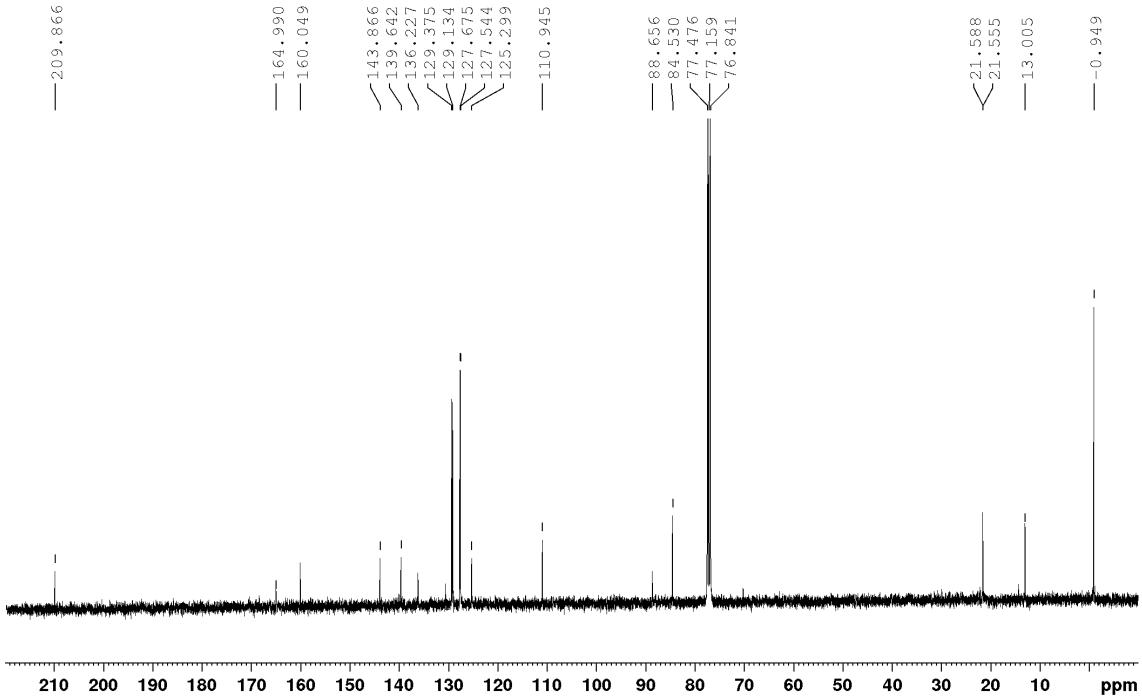


***N*-(3-(4-Methoxyphenyl)-5-(1-(trimethylsilyl)buta-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4r)**

^{1}H NMR (500 MHz, $CDCl_3$)

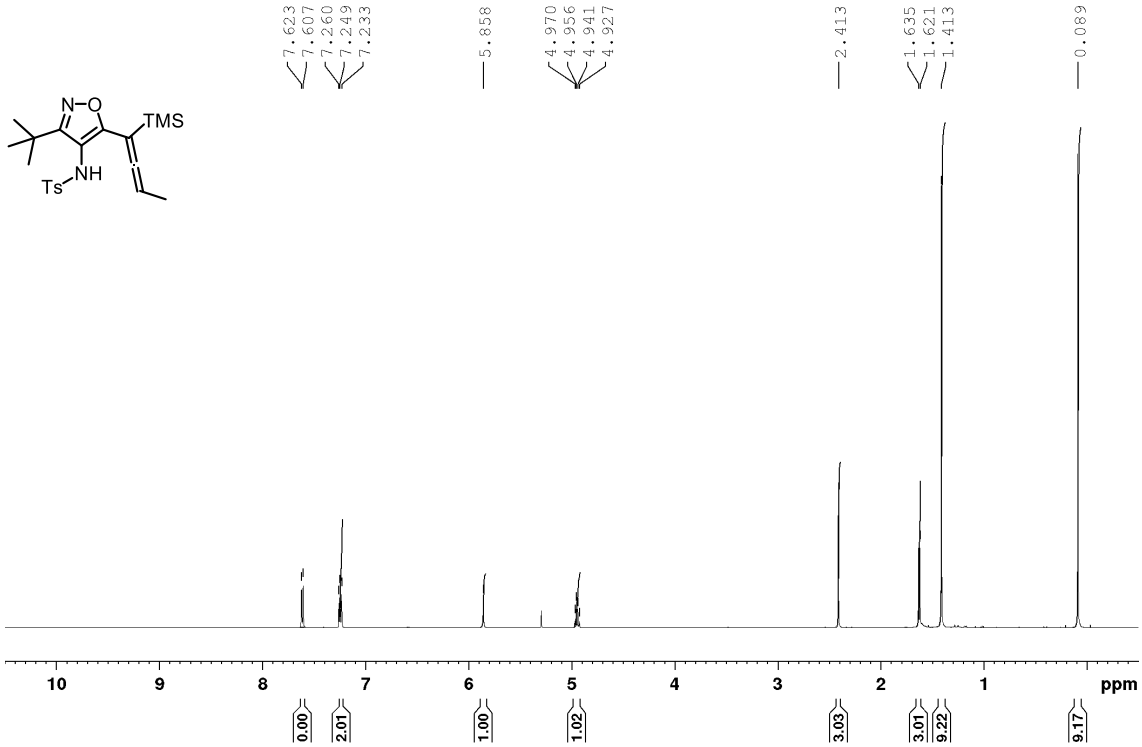


^{13}C NMR (125 MHz, $CDCl_3$)

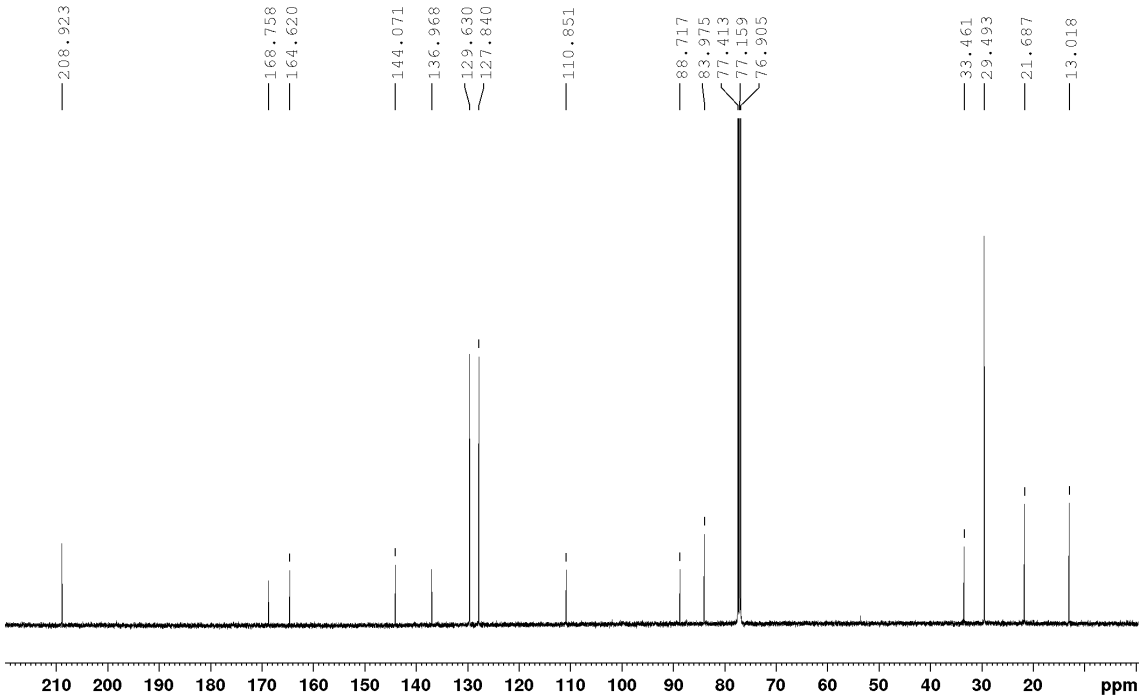


***N*-(3-(*tert*-Butyl)-5-(1-(trimethylsilyl)buta-1,2-dien-1-yl)isoxazol-4-yl)-4-methylbenzenesulfonamide (4s)**

^{1}H NMR (500 MHz, $CDCl_3$)

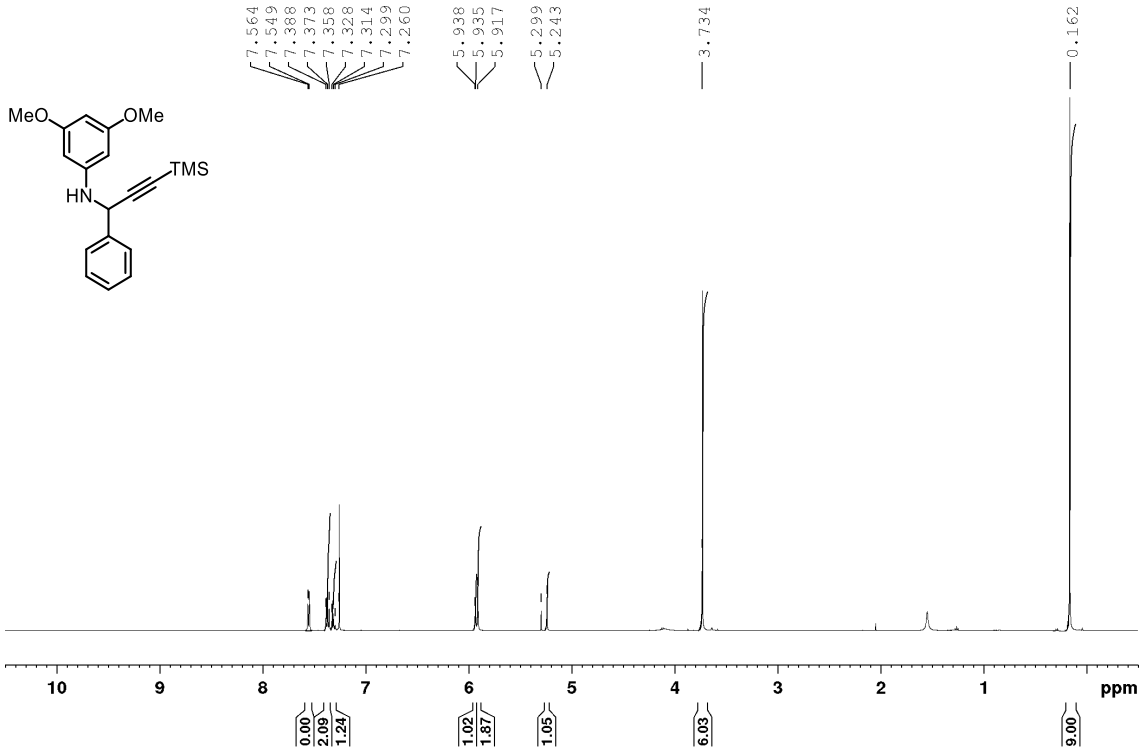


^{13}C NMR (125 MHz, $CDCl_3$)

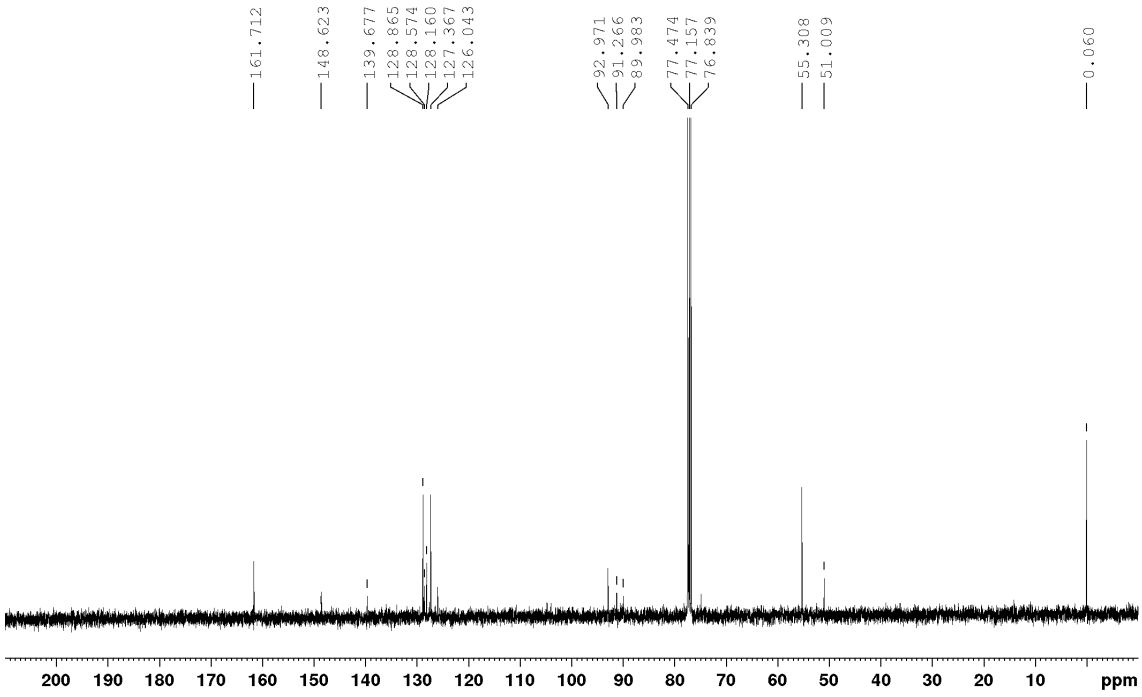


3, 5-Dimethoxy-*N*-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)aniline (5)

^{1}H NMR (500 MHz, $CDCl_3$)

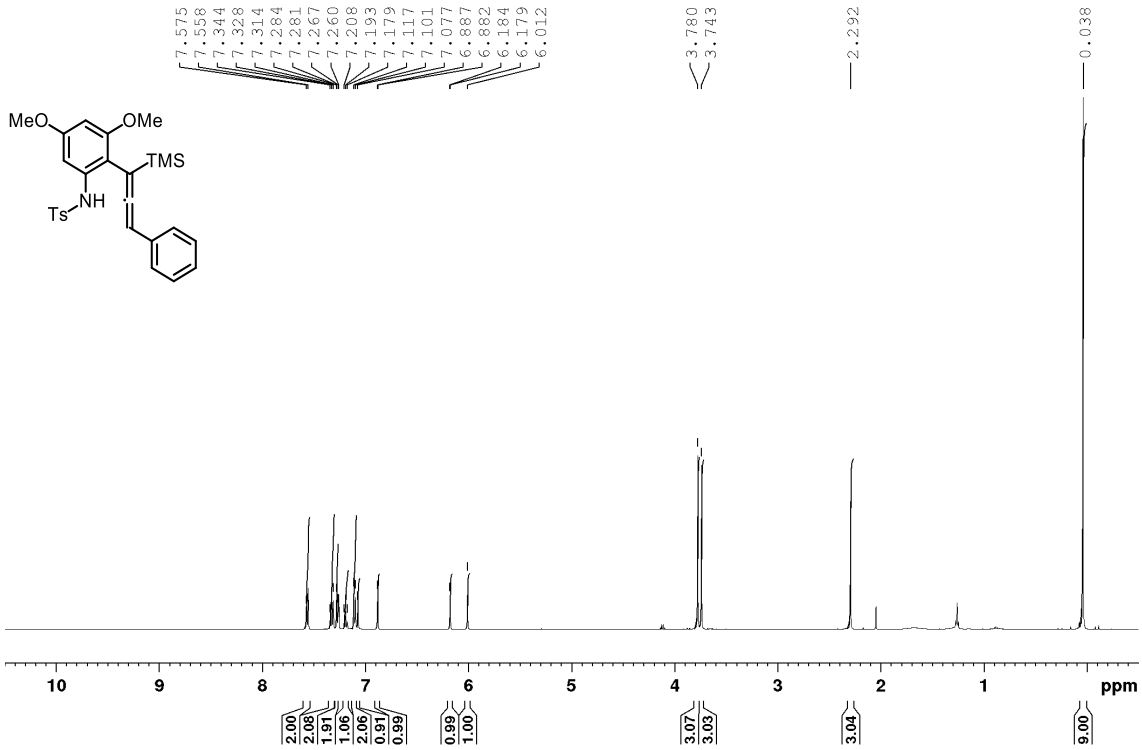


^{13}C NMR (100 MHz, $CDCl_3$)

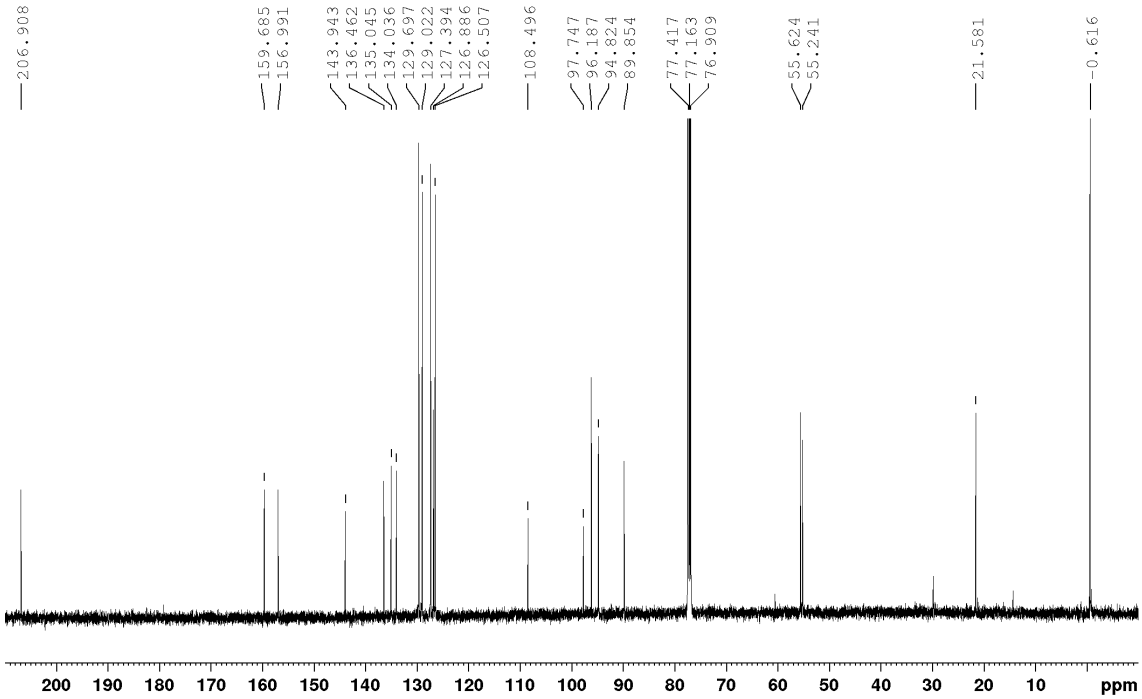


***N*-(3, 5-Dimethoxy-2-(3-phenyl-1-(trimethylsilyl)propa-1,2-dien-1-yl)phenyl)-4-methylbenzenesulfonamide (6)**

^{1}H NMR (500 MHz, $CDCl_3$)

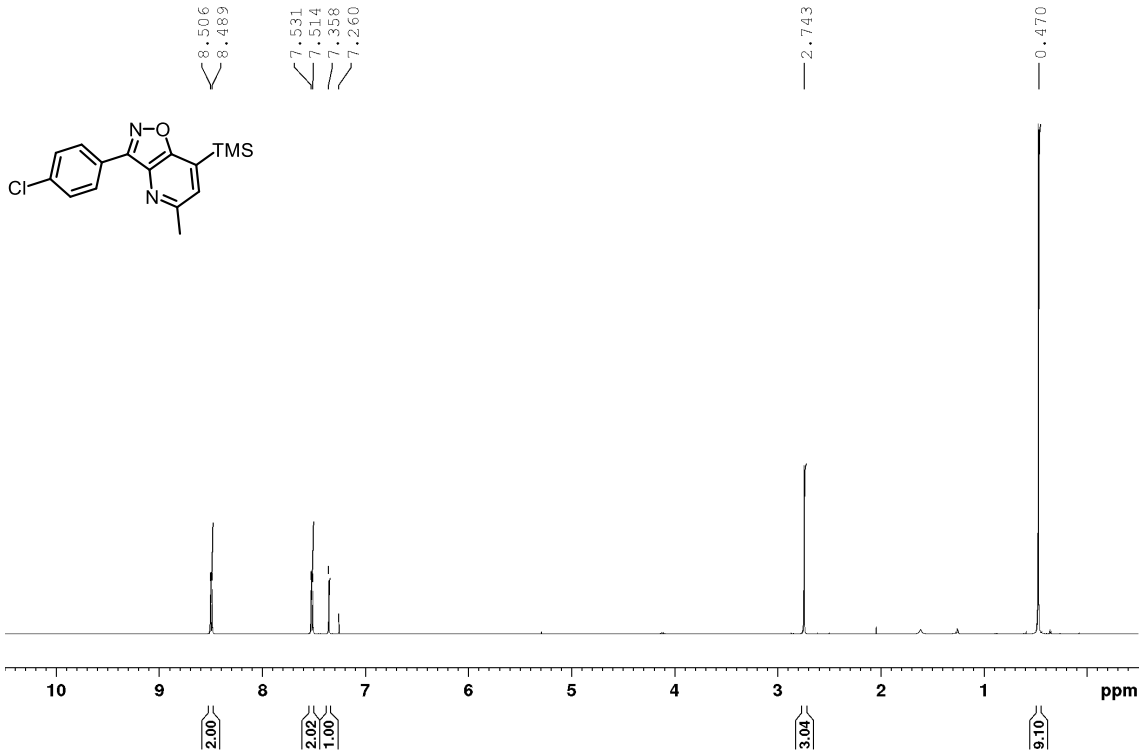


^{13}C NMR (125 MHz, $CDCl_3$)

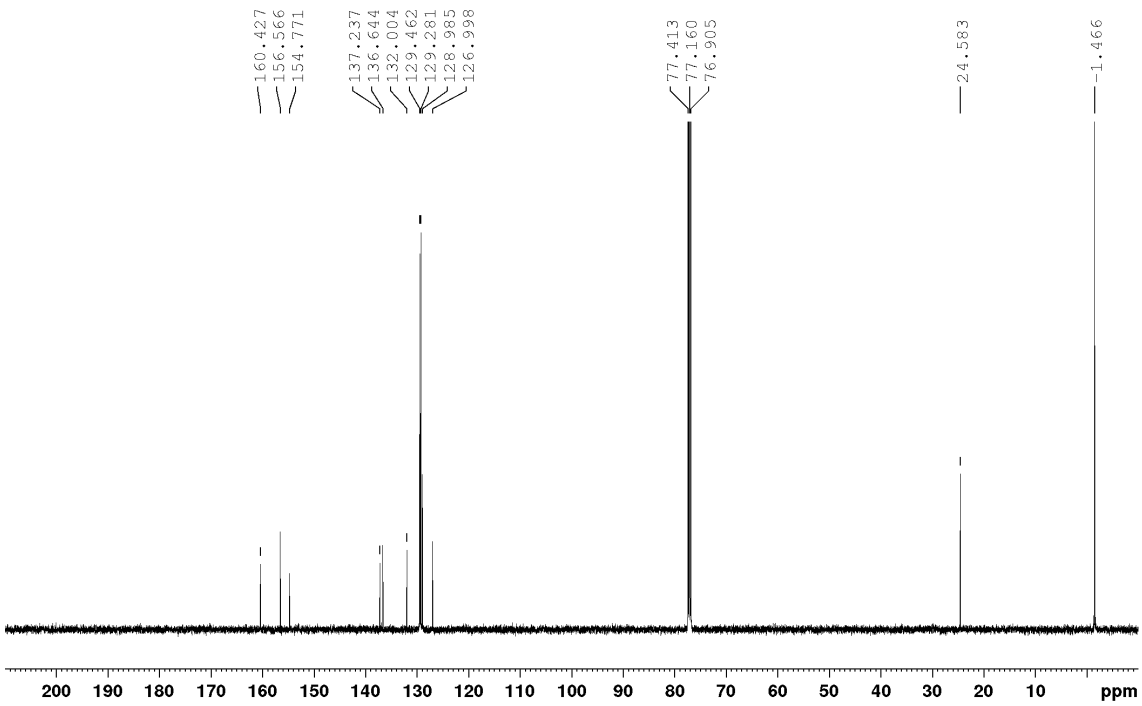


3-(4-Chlorophenyl)-5-methyl-7-(trimethylsilyl)isoxazolo[4,5-*b*]pyridine (3a)

^{1}H NMR (500 MHz, $CDCl_3$)

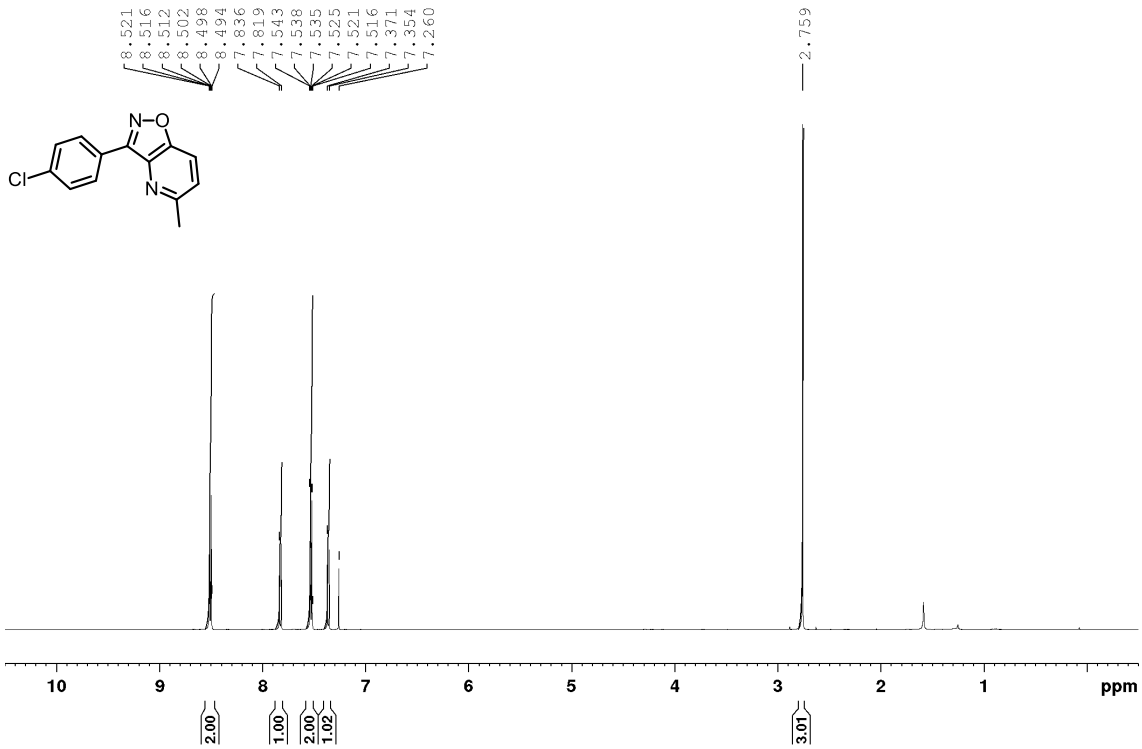


^{13}C NMR (125 MHz, $CDCl_3$)

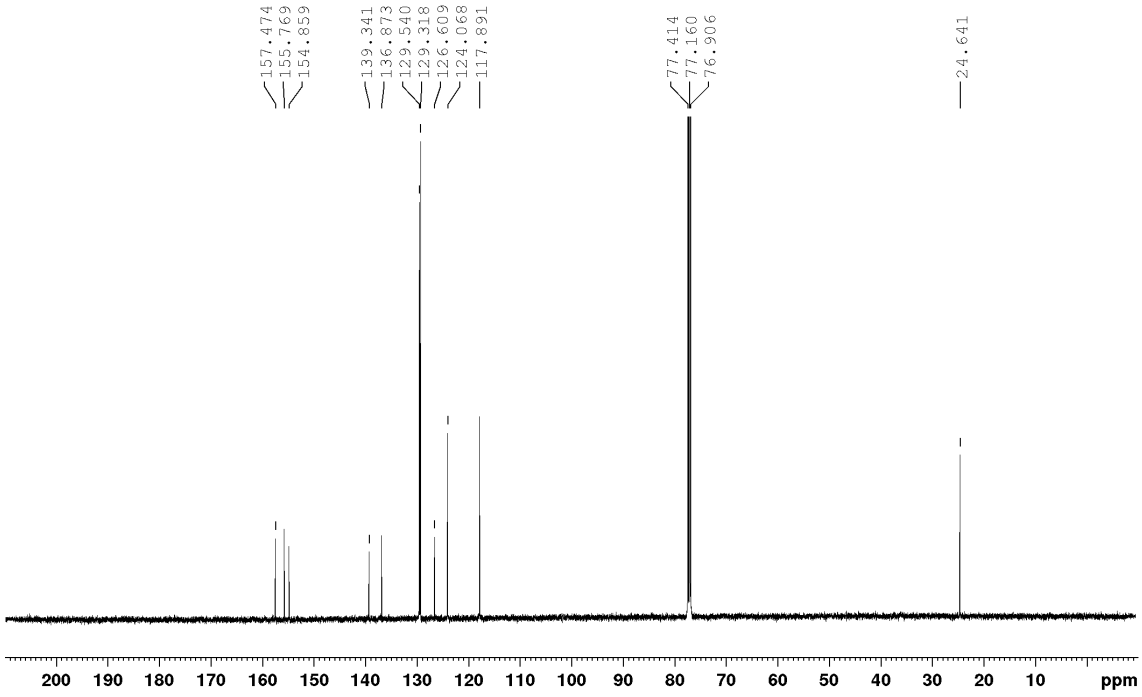


3-(4-Chlorophenyl)-5-methylisoxazolo[4,5-*b*]pyridine (3e)

^{1}H NMR (500 MHz, $CDCl_3$)

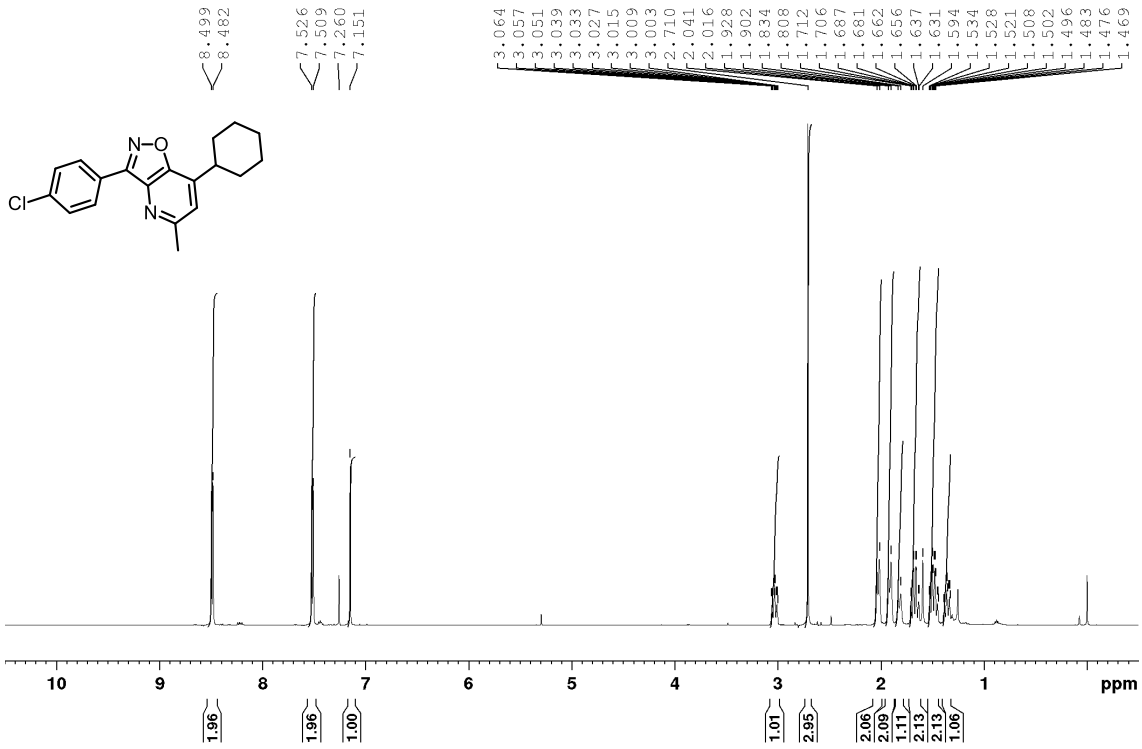


^{13}C NMR (125 MHz, $CDCl_3$)

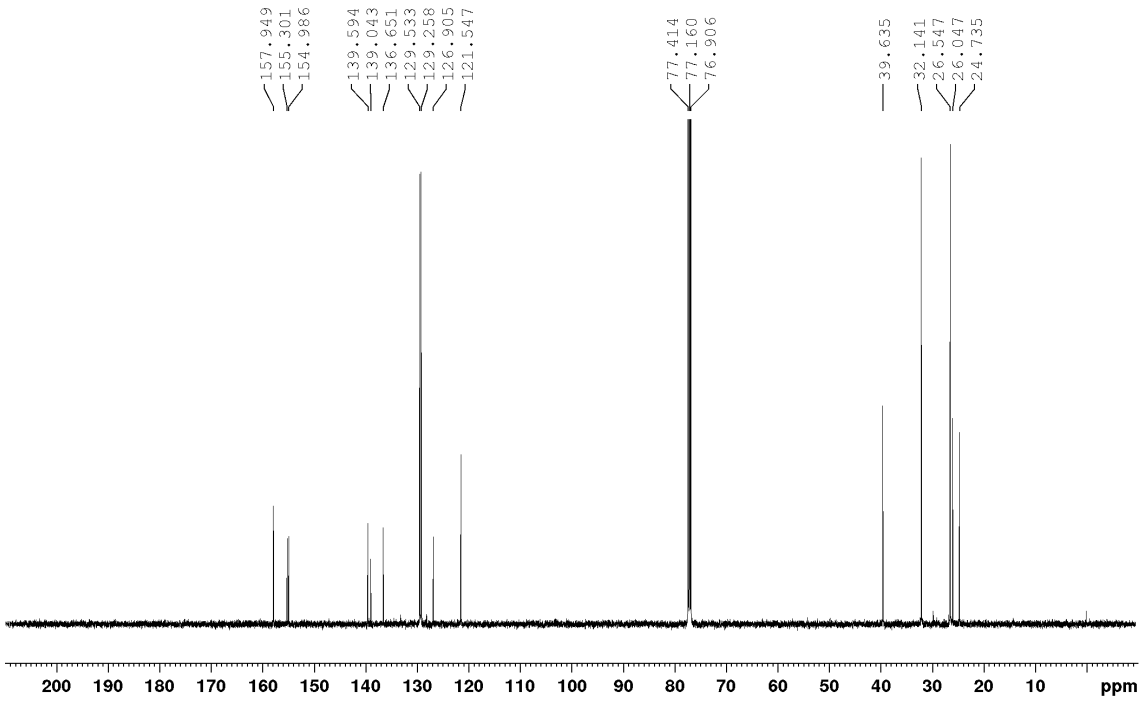


3-(4-Chlorophenyl)-7-cyclohexyl-5-methylisoxazolo[4,5-*b*]pyridine (3f)

^{1}H NMR (500 MHz, $CDCl_3$)

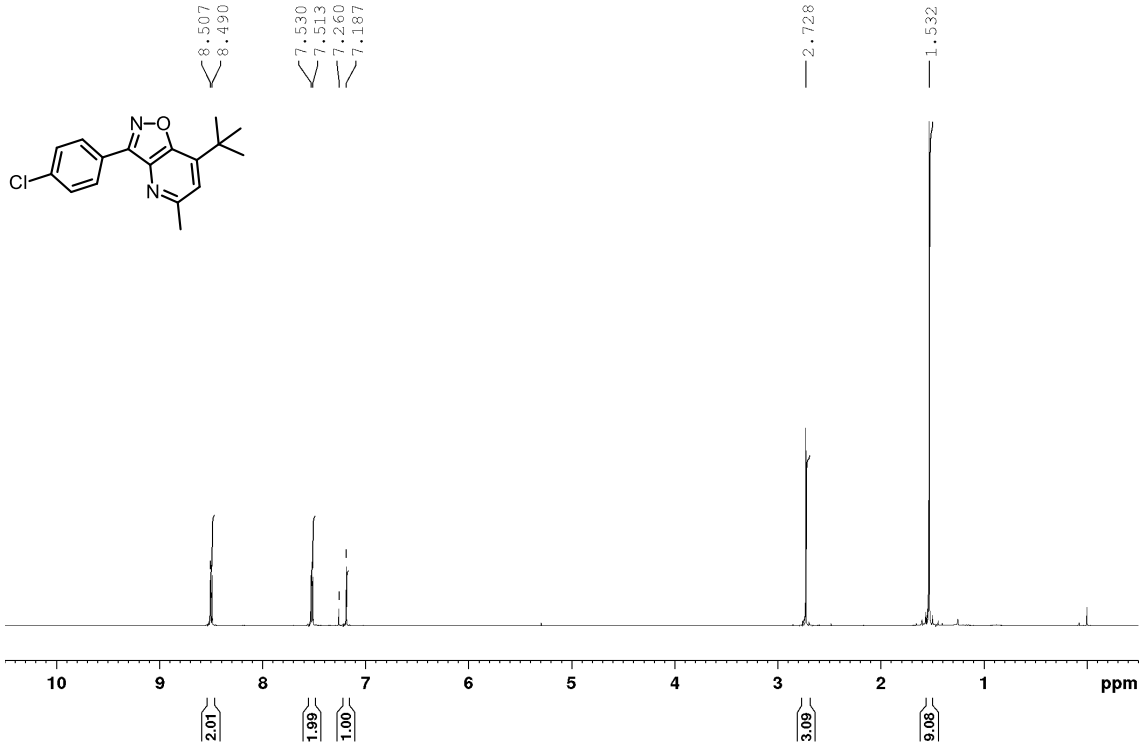


^{13}C NMR (125 MHz, $CDCl_3$)



7-(*tert*-Butyl)-3-(4-chlorophenyl)-5-methylisoxazolo[4,5-*b*]pyridine (3g)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)