Supporting Information

Late-Stage Diversification Strategy for Synthesizing Ynamides Through Copper-Catalyzed Diynylation and Azide–Alkyne Cycloaddition

Ryohei Kawakami, Suguru Usui, Norihiro Tada* and Akichika Itoh*

Gifu Pharmaceutical University, 1-25-4 Daigaku-nishi, Gifu 501-1196, Japan

E-mail: ntada@gifu-pu.ac.jp, itoha@gifu-pu.ac.jp

Table of Contents

1. General information

All reactants and reagents including dry solvents were obtained from commercial suppliers and used as recieved. ^{1}H NMR, ^{13}C{^{1}H} NMR spectra were obtained on a JEOL ECA500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C{^{1}H} NMR) and JEOL ECZ400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C{^{1}H} NMR). Chemical shifts (δ) are expressed in parts per million and are internally referenced [0.00 ppm (tetramethylsilane) for ^{1}H NMR, and 77.0 ppm ($CDCl_3$) for ^{13}C{^{1}H} NMR]. The following abbreviations were used to express the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of doublets, br = broad, dt = doublet of triplets. Structural assignments were made with additional information from gNOESY experiments. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100TD and was reported as m/z. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F254). Flash column chromatography was performed with Kanto silica gel 60N (Spherical, Neutral, 63–210 μm). Visualization of the developed chromatogram was performed by UV lamp (254 nm) and iodine.

2. Optimization of the reaction conditions

Scheme S1 Synthesis of TIPS-diyne-BX

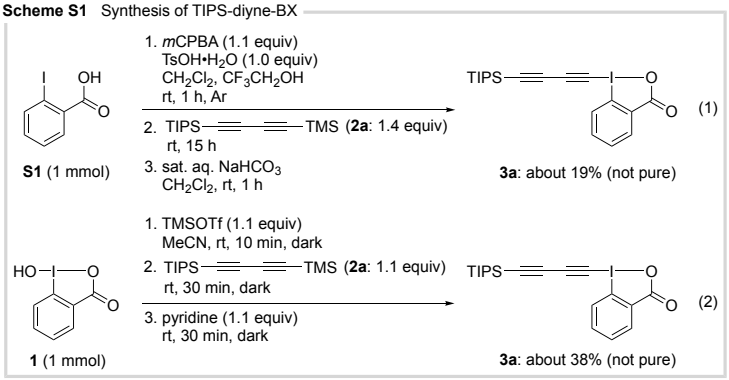
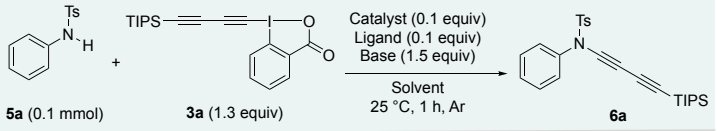
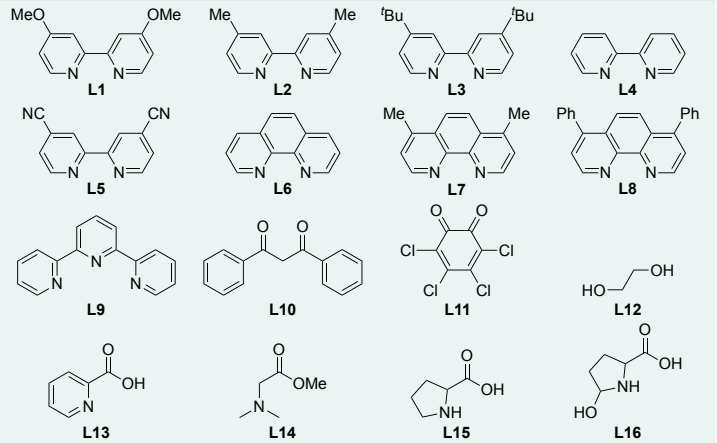


Table S1 Optimization of the *N*-diynylation of sulfonamide derived from aniline[a]



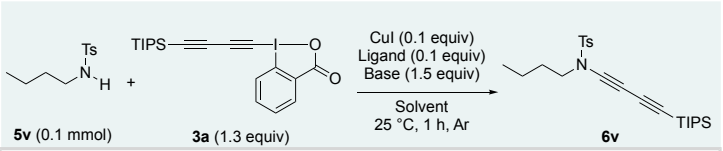
5a (0.1 mmol) **3a** (1.3 equiv) **6a**

Entry	Catalyst	Ligand	Base	Solvent	yield (%)[b]		
					6a	**5a**	**3a**
1	CuI	**L1**	K_2CO_3	EtOH	76 (70)	5	0
2	CuI	**L1**	K_2CO_3	MeOH	34	14	0
3	CuI	**L1**	K_2CO_3	IPA	62	29	0
4	CuI	**L1**	K_2CO_3	MeCN	29	71	1
5	CuI	**L1**	K_2CO_3	THF	13	77	5
6	CuI	**L1**	K_2CO_3	toluene	36	61	8
7	Cu_2O	**L1**	K_2CO_3	EtOH	36	31	0
8	CuTc	**L1**	K_2CO_3	EtOH	55	14	0
9	$(MeCN)_4Cu^+BF_4^-$	**L1**	K_2CO_3	EtOH	49	7	0
10	NiI_2	**L1**	K_2CO_3	EtOH	31	50	0
11	CoI_2	**L1**	K_2CO_3	EtOH	34	29	1
12	$FeCl_3 \cdot H_2O$	**L1**	K_2CO_3	EtOH	33	23	5
13	AuCl	**L1**	K_2CO_3	EtOH	45	33	4
14	CuI	**L2**	K_2CO_3	EtOH	66	2	0
15	CuI	**L3**	K_2CO_3	EtOH	62	7	0
16	CuI	**L4**	K_2CO_3	EtOH	60	3	0
17	CuI	**L5**	K_2CO_3	EtOH	63	32	4
18	CuI	**L6**	K_2CO_3	EtOH	60	8	0
19	CuI	**L7**	K_2CO_3	EtOH	58	8	0
20	CuI	**L8**	K_2CO_3	EtOH	55	29	0
21	CuI	**L9**	K_2CO_3	EtOH	29	27	6
22	CuI	**L10**	K_2CO_3	EtOH	61	15	0
23	CuI	**L11**	K_2CO_3	EtOH	65	23	0
24	CuI	**L12**	K_2CO_3	EtOH	22	15	0
25	CuI	**L13**	K_2CO_3	EtOH	60	14	0
26	CuI	**L14**	K_2CO_3	EtOH	69	6	0
27	CuI	**L15**	K_2CO_3	EtOH	49	26	0
28	CuI	**L16**	K_2CO_3	EtOH	39	26	4
29[c]	CuI	**L1**	K_2CO_3	EtOH	73	0	0
30[d]	CuI	**L1**	K_2CO_3	EtOH	79	0	0
31[e]	CuI	**L1**	K_2CO_3	EtOH	78	6	0
32	CuI	**L1**	Cs_2CO_3	EtOH	67	32	0
33	CuI	**L1**	Na_2CO_3	EtOH	0	100	56
34	CuI	**L1**	K_3PO_4	EtOH	53	21	7
35	CuI	**L1**	NEt_3	EtOH	14	88	0
36[f]	CuI	**L1**	K_2CO_3	EtOH	94 (87)	0	0



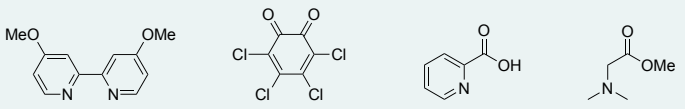
[a]Reaction conditions: **5a** (0.1 mmol), **3a** (1.3 equiv), catalyst (0.1 equiv), ligand (0.1 equiv), base (1.5 equiv), solvent (5 mL), 25 °C, 1 h, argon. [b]^{1}H NMR yields. Numbers in parentheses are isolated yields. [c]**L1** (0.2 equiv) was used. [d]**L1** (0.05 equiv) was used. [e]K_2CO_3 (2.5 equiv) was used. [f]K_2CO_3 (fine powder) was used.

Table S2 Optimization of the *N*-diynylation of sulfonamide derived from butylamine[a]



5v (0.1 mmol) **3a** (1.3 equiv) **6v**

Entry	Ligand	Base	Solvent	yield (%)[b]		
				6v	**5v**	**3a**
1	**L1**	K_2CO_3	EtOH	33 (27)	51	0
2	**L11**	K_2CO_3	EtOH	24	63	0
3	**L13**	K_2CO_3	EtOH	33	62	0
4	**L14**	K_2CO_3	EtOH	24	71	0
5[c]	**L1**	K_2CO_3	EtOH	28	51	0
6[d]	**L1**	K_2CO_3	EtOH	26	69	0
7	**L1**	Cs_2CO_3	EtOH	40	60	0
8	**L1**	K_3PO_4	EtOH	48	51	0
9	**L1**	NEt_3	EtOH	11	77	0
10	**L1**	DIPEA	EtOH	0	96	0
11	**L1**	NaH	EtOH	19	67	0
12	**L1**	KO^{t}Bu	EtOH	21	67	0
13[e]	**L1**	K_2CO_3	EtOH	31	62	0
14[f]	**L1**	K_2CO_3	EtOH	32	66	0
15	**L1**	K_2CO_3	MeCN:EtOH=1:1	40	59	0
16	**L1**	K_2CO_3	MeCN:EtOH=9:1	21	73	0
17	**L1**	K_2CO_3	MeCN:EtOH=1:9	45	57	0
18[e]	**L1**	K_2CO_3	MeCN:EtOH=1:9	44	55	0
19	**L1**	K_2CO_3	MeCN:IPA=1:1	24	71	7
20	**L1**	K_2CO_3	MeCN:IPA=9:1	13	68	11
21	**L1**	K_2CO_3	MeCN:IPA=1:9	16	80	0
22	**L1**	Cs_2CO_3	MeCN:EtOH=1:1	49	41	0
23	**L1**	Cs_2CO_3	MeCN:EtOH=1:9	52 (45)	46	0
24[f]	**L1**	Cs_2CO_3	MeCN:EtOH=1:9	18	77	0
25[g]	**L1**	Cs_2CO_3	MeCN:EtOH=1:9	40	54	0
26[h]	**L1**	Cs_2CO_3	MeCN:EtOH=1:9	35	51	0
27	**L1**	Cs_2CO_3	IPA:EtOH=1:9	47	54	0
28	**L1**	Cs_2CO_3	EtOAc:EtOH=1:9	45	54	0
29	**L1**	Cs_2CO_3	DCM:EtOH=1:9	49	52	0
30	**L1**	Cs_2CO_3	THF:EtOH=1:9	30	71	0
31[f]	**L1**	K_3PO_4	EtOH	50 (45)	39	0
32[g]	**L1**	K_3PO_4	EtOH	39	63	0
33[h]	**L1**	K_3PO_4	EtOH	26	56	0
34	**L1**	K_3PO_4	MeCN:EtOH=1:1	45	49	0
35	**L1**	K_3PO_4	MeCN:EtOH=1:9	41	51	0



L1 **L11** **L13** **L14**

[a]Reaction conditions: **5v** (0.1 mmol), **3a** (1.3 equiv), CuI (0.1 equiv), ligand (0.1 equiv), base (1.5 equiv), solvent (5 mL), 25 °C, 1 h, argon. [b]^{1}H NMR yields. Numbers in parentheses are isolated yields. [c]**L1** (0.05 equiv) was used. [d]CuI (0.2 equiv) was used. [e]K_2CO_3 (fine powder) was used. [f]Base (2.5 equiv) was used. [g]Base (1.2 equiv) was used. [h]H_2O (0.1 mL) was added.

Table S3 Study of the reaction conditions for CuAAC with diynamide

6ab (1.1 equiv) **9a** (0.05 mmol) **10a**

Entry	conditions	Yields (%)[a]
1	$Cu(OAc)_2$ (0.1 equiv), Na-ascorbate (0.2 equiv) *t*-BuOH (1 mL), H_2O (0.5 mL), 25 °C, 18 h	65, (42)[b]
2	$CuSO_4$ (0.38 equiv), Na-ascorbate (0.48 equiv) DMF (1 mL), H_2O (0.2 mL), 25 °C, 2 h	67
3	CuI (0.39 equiv) MeCN (1 mL), 25 °C, 18 h	59
4	CuI (0.39 equiv) DMF (1 mL), 25 °C, 18 h	79
5	CuI (0.5 equiv), DIPEA (1.1 equiv) DCM (3 mL), 25 °C, 18 h	87, (92)[b]

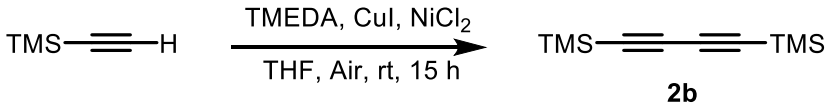
[a]^{1}H NMR yields. Numbers in parentheses are isolated yields. [b]0.1 mmol scale.

3. Experimental procedure and characterizations

The synthesis of sulfonamides (**5a-5f**, **5h**, **5j-5n**, **5r-5u**, **5w)** had described in our previous papers.[1,2] Sulfonamides (**5g,**[3] **5i,**[4] **5o,**[5] **5p,**[3] **5q,**[5] **5v**[5]), (4-bromo-1,3-butadiyn-1-yl)tris(1-methylethyl)-silane (**8**[6]) and 3-azido-*N*-[(1,1-dimethylethoxy)carbonyl]-D-alanine methyl ester (**9d**[7]) were prepared according to the reported procedures.

3.1 Synthesis of diynes

1,4-Bis(trimethylsilyl)-1,3-butadiyne (2b)



Following a slightly modified reported procedure,[8] trimethylsilyl acetylene (10 mL, 72.2 mmol) was added to a stirred suspension of TMEDA (1.5 mL, 10 mmol), CuI (476 mg, 2.5 mmol), and $NiCl_2$ (300 mg, 2.5 mmol) in THF (30 mL). The suspension was stirred for 15 h under open air at room temperature. The suspension was filtered through a pad of Celite to remove the solid and the solution was concentrated under reduced pressure to give crude solid. The residue was purified by column chromatography on silica gel (Hexane) to afford 1,4-bis(trimethylsilyl)-1,3-butadiyne (**2b**: 5.3668 g, 27.6 mmol, 76% yield).

Rf: 0.60 (Hexane)

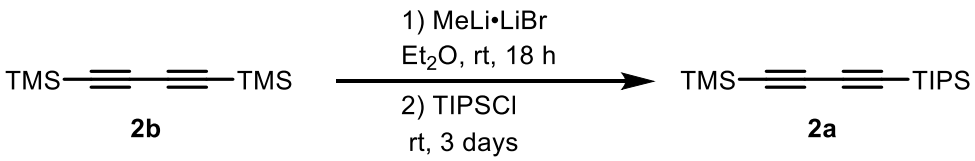
Physical state: colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.19 (s, 18H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 87.9, 85.9, -0.53

The values of the NMR spectra are in accordance with reported literature data.[9]

Trimethyl[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]silane (2a)



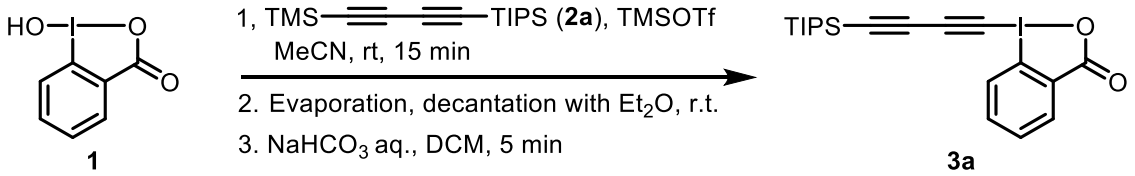
Following a slightly modified reported procedure,[6a] MeLi · LiBr (1.5 M in Et_2O, 19.25 mL) was added dropwise to a solution of 1,4-bis(trimethylsilyl)-1,3-butadiyne (**2b**: 5.00 g, 26.25 mmol) in dry Et_2O (75 mL) at room temperature under argon atmosphere. The solution was stirred for 18 h and TIPSCl (6.15 mL, 28.875 mmol) was added dropwise and the mixture was stirred for another 3 days at room

temperature before quenched by 50 mL of aqueous saturated NH_4Cl. The organic layer was separated and aqueous layer was extracted with diethyl ether (3x50 mL). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude oil. The residue was purified by column chromatography on silica gel (Hexane) to afford trimethyl[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]silane (**2a**: 5.1309 g, 18.44 mmol, 71%).

Rf: 0.69 (Hexane)
Physical state: pale yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.09-1.07 (m, 21H), 0.20 (s, 9H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 89.8, 88.5, 84.5, 83.3, 18.6, 11.3, -0.34
The values of the NMR spectra are in accordance with reported literature data.[6a]

3.2 Synthesis of diyne-BX

1-[4-[Tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-1,2-benziodoxol-3(*1H*)-one (TIPS-diyne-BX) (3a)



Trimethylsilyl trifluoromethanesulfonate (1.51 mL, 8.4 mmol, 1.4 equiv.) was added dropwise to a stirred suspension of 2-iodosylbenzoic acid (**1**, 1584.0 mg, 6.0 mmol, 1.0 equiv.) in dry acetonitrile (60 mL) under argon. Then trimethyl[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]silane (**2a**, 2.79 mL, 8.4 mmol, 1.4 equiv.) was added dropwise to the mixture. After 15 min, the reaction mixture was evaporated until a solid was obtained. The solid was washed with Et_2O at room temperature. Then the solid was stirred in sat. aqueous $NaHCO_3$ (100 mL) and CH_2Cl_2 (100 mL) for 5 minutes. The organic layer was separated and aqueous layer was extracted with CH_2Cl_2 (3x50 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford TIPS-diyne-BX (**3a**: 1.881 g, 4.16 mmol, 69%) as a colorless solid.

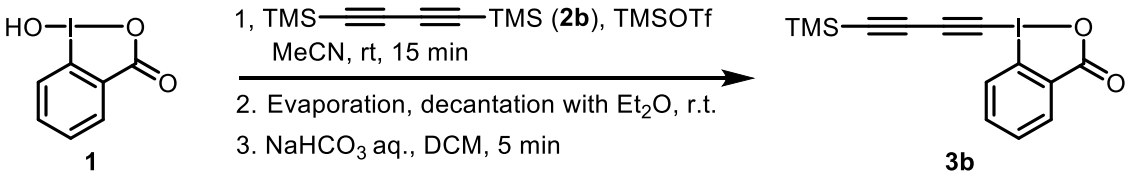
Rf: 0.63 (hexane : EtOAc = 1 : 2).
Physical state: colorless solid.
m.p.: 113.5-115.0 ℃
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (dd, J = 7.32, 1.83 Hz, 1H), 8.22 (d, J = 8.23 Hz, 1H), 7.86-7.74 (m, 2H), 1.16-1.05 (m, 21H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.6, 135.2, 132.5, 131.7, 131.0, 126.7, 116.1, 90.3, 89.8, 88.1, 41.1, 18.5, 11.2.

HRMS (ESI, positive): calcd for $C_{20}H_{25}I_1Na_1O_2Si_1$ $[M+Na]^+$ 475.05607, Found 475.05651.

FTIR (ATR): 2944, 2891, 2866, 2061, 2043, 1621, 1622, 1585, 1561, 1463, 1440, 1342, 1292, 1239, 1072, 1037, 1017, 997, 968, 882, 833, 743, 678, 662, 596, 524.

1-[4-(Trimethylsilyl)-1,3-butadiyn-1-yl]-1,2-benziodoxol-3(*1H*)-one (TMS-diyne-BX)(3b)



Trimethylsilyl trifluoromethanesulfonate (1.51 mL, 8.4 mmol, 1.4 equiv.) was added dropwise to a stirred suspension of 2-iodosylbenzoic acid (**1**, 1584.0 mg, 6.0 mmol, 1.0 equiv.) in dry acetonitrile (60 mL) under argon. Then 1,4-bis(trimethylsilyl)-1,3-butadiyne (**2b**, 1633.0 mg, 8.4 mmol, 1.4 equiv.) was added dropwise to the mixture. After 15 min, the reaction mixture was evaporated until a solid was obtained. The solid was washed with Et_2O at room temperature. Then the solid was stirred in sat. aqueous $NaHCO_3$ (100 mL) and CH_2Cl_2 (100 mL) for 5 minutes. The organic layer was separated and aqueous layer was extracted with CH_2Cl_2 (3x50 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford TMS-diyne-BX (**3b**: 1.291 g, 3.51 mmol, 58%) as colorless solid.

Rf: 0.45 (hexane : EtOAc = 1 : 2).

Physical state: colorless solid.

m.p.: 101.5-103.5 ℃

^1H NMR (500 MHz, $CDCl_3$): δ 8.39 (dd, *J* = 6.86, 2.29 Hz, 1H), 8.23 (dd, *J* = 8.23, 1.37 Hz, 1H), 7.84-7.73 (m, 2H), 0.32-0.23 (m, 9H).

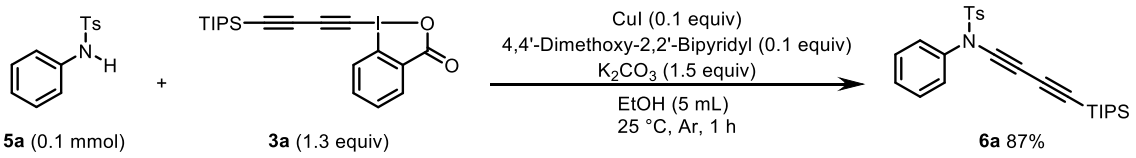
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.9, 135.1, 132.4, 131.6, 131.1, 126.7, 116.2, 91.7, 89.7, 86.4, 42.0, -0.74.

HRMS (ESI, positive): calcd for $C_{14}H_{14}I_1O_2Si_1$ $[M+H]^+$ 368.98077, Found 368.97946.

FTIR (ATR): 2962, 2066, 1623, 1564, 1440, 1349, 1250, 841, 738, 695, 637, 532, 519

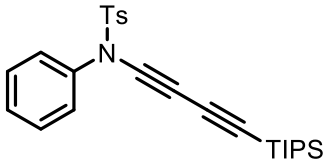
3.3 Diynylation of sulfonamide.

4-Methyl-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6a) (General procedure A)



5a (0.1 mmol) **3a** (1.3 equiv) **6a** 87%

4-Methyl-*N*-phenyl-benzenesulfonamide (**5a**: 24.7 mg, 0.1 mmol, 1.0 equiv.), 1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(*1H*)-one (**3a**: 58.8 mg, 0.13 mmol, 1.3 equiv.), CuI (2.0 mg, 0.01mmol, 0.1 equiv.), 4,4'-dimethoxy-2,2'-bipyridyl (**L1**: 2.15 mg, 0.01 mmol, 0.1 equiv.) and K_2CO_3 (fine powder: 20.85 mg, 0.15 mmol, 1.5 equiv.) were stirred in dry ethanol (5 mL) under argon at 25 ºC. After stirred for 1 h at 25 ºC, the solution was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6a**: 39.1 mg, 87%) as a yellow solid.



Rf: 0.58 (Hexane : AcOEt = 4 : 1)

Physical state: Yellow solid

m.p.:109.9-110.6 ℃

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.58 (m, 2H), 7.34-7.28 (m, 5H), 7.24-7.18 (m, 2H), 2.45 (s, 3H), 1.09-1.06 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.4, 137.8, 132.9, 129.7, 129.3, 128.8, 128.2, 126.5, 88.9, 87.6, 68.4, 58.6, 21.7, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{26}H_{34}N_1O_2S_1Si_1$ $[M + H]^+$ 452. 20740, Found 452.20595

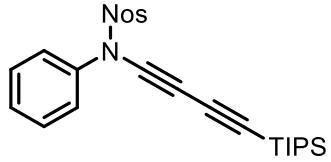
FTIR (ATR): 3068, 2944, 2892, 2866, 2727, 2220, 2107, 1918, 1797, 1732, 1595, 1490, 1462, 1380, 1328, 1311, 1241, 1212, 1189, 1176, 1120, 1090, 1075, 1028, 1018, 997, 919, 883, 836, 813, 799, 757, 704, 680, 656

1.0 mmol scale reaction

4-Methyl-*N*-phenyl-benzenesulfonamide (**5a**: 247.0 mg, 1.0 mmol, 1.0 equiv.), 1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(*1H*)-one (**3a**: 588.0 mg, 1.3 mmol, 1.3 equiv.), CuI (20.0 mg, 0.1 mmol, 0.1 equiv.), 4,4'-dimethoxy-2,2'-bipyridyl (**L1**: 21.5 mg, 0.1 mmol, 0.1 equiv.) and K_2CO_3 (fine powder: 208.5 mg, 1.5 mmol, 1.5 equiv.) were stirred in dry ethanol (50 mL) under argon at 25 ºC. After stirred for 1 h at 25 ºC, the solution was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (Hexane :

Chloroform = 1 : 1) to afford 4-methyl-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6a**: 397.9 mg, 87%) as a yellow solid.

4-Nitro-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6b)



Following the **General Procedure A**, 4-nitro-*N*-phenyl benzenesulfonamide (**5b**:27.8 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-nitro-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6b**: 36.6 mg, 76%).

Rf: 0.48 (Hexane : AcOEt = 4 : 1)

Physical state: Colorless solid

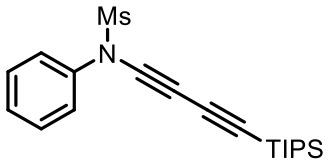
m.p.: 140.8.5-141.5 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42-8.33 (m, 2H), 7.95-7.87 (m, 2H), 7.43-7.35 (m, 3H), 7.24-7.17 (m, 2H), 1.12-1.05 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.0, 141.2, 137.3, 129.7, 129.6, 129.5, 126.5, 124.4, 88.9, 88.3, 67.1, 59.4, 18.6, 11.3

HRMS (DART, positive) calcd for $C_{25}H_{31}N_2O_4S_1Si_1$ $[M + H]^+$ 483.17683, Found 483.17547

4-Methyl-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-mathanesulfonamide (6c)



Following the **General Procedure A**, 4-methyl-*N*-phenyl mathanesulfonamide (**5c**: 17.1 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-mathanesulfonamide (**6c**: 28.4 mg, 76%).

Rf: 0.38 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

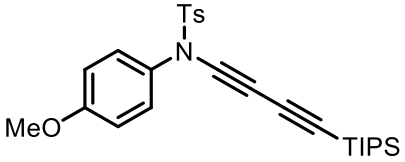
m.p.: 60.5-61.2 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-7.37 (m, 5H), 3.18-3.14 (m, 3H), 1.10-1.05 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.6, 129.7, 128.9, 125.9, 88.5, 88.2, 67.2, 59.2, 37.8, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{20}H_{30}N_1O_2S_1Si_1$ $[M + H]^+$ 376.17610, Found 376.17583

4-Methyl-*N*-(4-methoxyphenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6g)



Following the **General Procedure A**, 4-methyl-*N*-(4-methoxyphenyl) benzenesulfonamide (**5g**: 27.7 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(4-methoxyphenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6g**: 20.8 mg, 43%).

Rf: 0.50 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

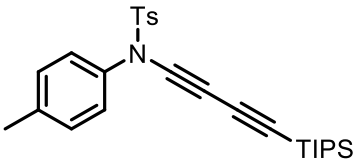
m.p.: 65.0-65.8 ℃

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.58 (m, 2H), 7.33-7.28 (m, 2H), 7.11-7.06 (m, 2H), 6.84-6.80 (m, 2H) 3.80 (s, 3H) 2.46 (s, 3H), 1.09-1.06 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.8, 145.3, 133.0, 130.3, 129.7, 128.2, 114.4, 89.0, 87.4, 68.7, 58.1, 55.5, 21.7, 18.5, 11.3

HRMS (DART, positive) calcd for $C_{27}H_{36}N_1O_3S_1Si_1$ $[M + H]^+$ 482. 21797, Found 482.21565

4-Methyl-*N*-(4-methylphenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6h)



Following the **General Procedure A**, 4-methyl-*N*-(4-methylphenyl) benzenesulfonamide (**5h**: 26.1 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(4-methylphenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6h**: 36.6 mg, 77%).

Rf: 0.35 (Hexane : AcOEt = 4 : 1)

Physical state: Yellow solid

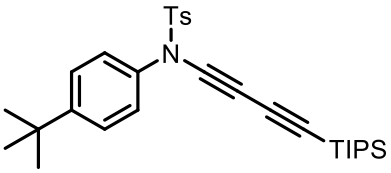
m.p.: 86.0-86.5 ℃

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.58 (m, 2H), 7.33-7.28 (m, 2H), 7.14-7.10 (m, 2H), 7.09-7.04 (m, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 1.10-1.05 (m, 21H)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 145.2, 139.0, 135.2, 133.1, 129.9, 129.7, 128.2, 126.5, 89.0, 87.4, 68.6, 58.3, 21.7, 21.1, 18.5, 11.3

HRMS (DART, positive) calcd for $C_{27}H_{36}N_1O_2S_1Si_1$ $[M + H]^+$ 466. 22305, Found 466.22360

4-Methyl-*N*-[4-(1,1-dimethylethyl)phenyl]-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6i)



Following the **General Procedure A**, 4-methyl-*N*-[4-(1,1-dimethylethyl)phenyl] benzenesulfonamide (**5i**: 30.3 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-[4-(1,1-dimethylethyl)phenyl]-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6i**: 37.4 mg, 74%).

Rf: 0.44 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

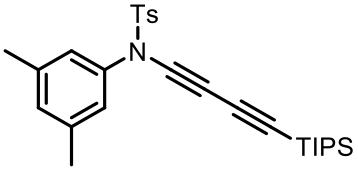
m.p.: 160.7-161.4 ℃

^{1}H NMR (500 MHz, CDCl3): δ 7.65-7.61 (m, 2H), 7.36-7.30 (m, 4H), 7.13-7.09 (m, 2H), 2.46 (s, 3H), 1.30 (s, 9H), 1.12-1.06 (m, 21H)

$^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3): δ 152.1, 145.2, 135.1, 133.2, 129.7, 128.2, 126.3, 126.2, 89.0, 87.4, 68.6, 58.4, 34.7, 31.2, 21.7, 18.5, 11.3

HRMS (DART, positive) calcd for $C_{30}H_{42}N_1O_2S_1Si_1$ $[M + H]^+$ 508. 27000, Found 508.27098

4-Methyl-*N*-(3,5-dimethylphenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6j)



Following the **General Procedure A**, 4-methyl-*N*-(3,5-dimethylphenyl) benzenesulfonamide (**5j**: 27.5 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(3,5-dimethylphenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6j**: 33.0 mg, 68%).

Rf: 0.38 (Hexane : AcOEt = 4 : 1)

Physical state: Yellow solid

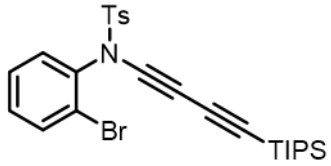
m.p.: 128.0-128.8 ℃

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.62 (m, 2H), 7.32 (d, *J* = 8.02 Hz, 2H), 6.96 (s, 1H), 6.80 (s, 2H), 2.46 (s, 3H), 2.26 (s, 6H), 1.09-1.06 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.2, 139.1, 137.5, 133.2, 130.6, 129.6, 128.2, 124.2, 89.0, 87.4, 68.6, 58.4, 21.7, 21.1, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{28}H_{38}N_1O_2S_1Si_1$ $[M + H]^+$ 480.23870, Found 480.23776

4-Methyl-*N*-(2-bromophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6k)



Following the **General Procedure A**, 4-methyl-*N*-(2-bromophenyl) benzenesulfonamide (**5k**: 32.4 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(2-bromophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6k**: 41.9 mg, 79%).

Rf: 0.46 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

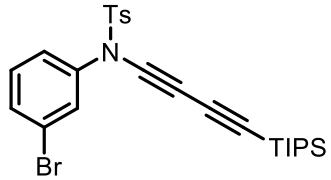
m.p.: 156.6-157.5 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.73 (m, 2H), 7.62 (dd, *J* = 7.78, 1.37 Hz, 1H), 7.37 (d, *J* = 8.23 Hz, 2H), 7.32 (dt, *J* = 7.78, 1.83 Hz, 1H), 7.28-7.23 (m, 1H), 7.21 (dd, *J* = 7.78, 1.83 Hz, 1H), 2.48 (s, 3H), 1.10-1.05 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.6, 136.3, 134.2, 134.1, 131.0, 130.4, 129.9, 128.5, 128.3, 123.6, 88.9, 88.1, 67.1, 59.4, 21.8, 18.5, 11.3

HRMS (DART, positive) calcd for $C_{26}H_{32}Br_1N_1O_2S_1Si_1$ $[M + H]^+$ 530.11792, Found 530.11792

4-Methyl-*N*-(3-bromophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6l)



Following the **General Procedure A**, 4-methyl-*N*-(3-bromophenyl) benzenesulfonamide (**5l**: 32.4 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(3-bromophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6l**: 37.1 mg, 71%).

Rf: 0.56 (Hexane : AcOEt = 4 : 1)

Physical state: Yellow solid

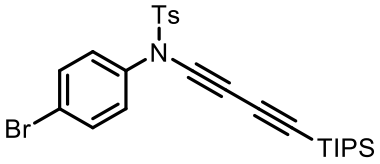
m.p.: 71.5-72.0 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65-7.58 (m, 2H), 7.49-7.43 (m, 1H), 7.38-7.36 (m, 1H), 7.33 (d, *J* = 8.02 Hz, 2H), 7.23-7.18 (m, 2H) 2.46 (s, 3H), 1.13-1.05 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.7, 139.0, 132.6, 131.8, 130.4, 129.9, 129.2, 128.2, 125.0, 122.4, 88.6, 88.3 67.6, 59.4, 21.8, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{26}H_{32}Br_1N_1O_2S_1Si_1$ $[M + H]^+$ 530.11792, Found 530.11539

4-Methyl-*N*-(4-bromophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6m)



Following the **General Procedure A**, 4-methyl-*N*-(4-bromophenyl) benzenesulfonamide (**5m**: 32.4 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(4-bromophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6m**: 42.8 mg, 81%).

Rf: 0.58 (Hexane : AcOEt = 4 : 1)

Physical state: Yellow solid

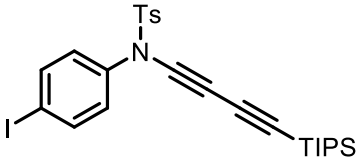
m.p.: 120.5-121.0 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62-7.58 (m, 2H), 7.47-7.44 (m, 2H), 7.34-7.30 (m, 2H), 7.12-7.09 (m, 2H), 2.46 (s, 3H), 1.11-1.05 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.6, 137.0, 132.6, 132.4, 129.8, 128.2, 127.9, 122.7, 88.6, 88.1, 67.8, 59.1, 21.7, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{26}H_{32}Br_1N_1O_2S_1Si_1$ $[M + H]^+$ 530.11792, Found 530.11554

4-Methyl-*N*-(4-iodophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6n)



Following the **General Procedure A**, 4-methyl-*N*-(4-iodophenyl) benzenesulfonamide (**5n**: 37.3 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 :

1) to afford 4-methyl-*N*-(4-iodophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6n**: 45.7 mg, 79%).

Rf: 0.63 (Hexane : AcOEt = 4 : 1)

Physical state: Yellow solid

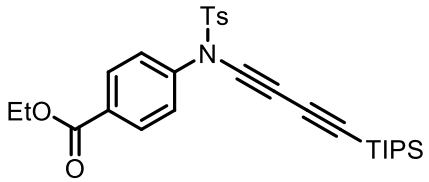
m.p.: 106.5-107.2 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67-7.63 (m, 2H), 7.61-7.58 (m, 2H), 7.34-7.30 (m, 2H), 6.99-6.95 (m, 2H), 2.46 (s, 3H), 1.11-1.05 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.6, 138.4, 137.7, 132.6, 129.8, 128.2, 128.1, 94.2, 88.6, 88.1, 67.7, 59.1, 21.8, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{26}H_{32}I_1N_1O_2S_1Si_1$ $[M + H]^+$ 578.10405, Found 578.10123

4-[[(4-Methylphenyl)sulfonyl][[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]]amino]ethylbenzoate (6o)



Following the **General Procedure A**, ethyl 4-[[(4-methylphenyl)sulfonyl]amino]benzoate (**5o**: 31.9 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-[[(4-methylphenyl)sulfonyl][[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]]amino]ethylbenzoate (**6o**: 27.9 mg, 53%).

Rf: 0.56 (Hexane : AcOEt = 4 : 1)

Physical state: Yellow solid

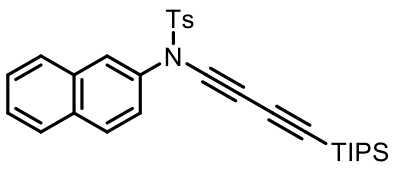
m.p.: 92.2-93.0 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-7.98 (m, 2H), 7.62-7.57 (m, 2H), 7.38-7.32 (m, 2H), 7.32-7.28 (m, 2H), 4.38 (q, J = 6.86 Hz, 2H), 2.45 (s, 3H), 1.39 (t, J = 6.86 Hz, 3H), 1.10-1.05 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.5, 145.7, 141.7, 132.7, 130.6, 129.9, 128.1, 125.5, 88.6, 88.3, 67.4, 61.3, 59.8, 21.7, 18.5, 14.3, 11.2

HRMS (DART, positive) calcd for $C_{29}H_{38}N_1O_4S_1Si_1$ $[M + H]^+$ 524.22853, Found 524.23071

4-Methyl-*N*-naphthyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6p)



Following the **General Procedure A**, 4-methyl-*N*-naphthyl benzenesulfonamide (**5p**: 29.7 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-naphthyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6p**: 30.1 mg, 60%).

Rf: 0.58 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

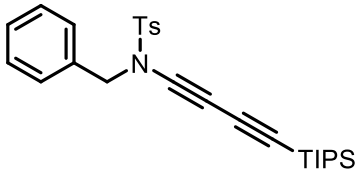
m.p.: 124.0-124.8 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85-7.80 (m, 1H), 7.80-7.76 (m, 2H), 7.71 (s, 1H), 7.63-7.58 (m, 2H), 7.54-7.49 (m, 2H), 7.32-7.25 (m, 3H), 2.44 (s, 3H), 1.12-1.05 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.4, 135.2, 133.1, 133.0, 132.8, 129.7, 129.3, 128.2, 127.7, 127.1, 126.8, 125.4, 124.0, 88.9, 87.7, 68.4, 58.9, 21.7, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{30}H_{36}N_1O_2S_1Si_1$ $[M + H]^+$ 502.22305, Found 502.22384

4-Methyl-*N*-phenylmethyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6q)



Following the **General Procedure A**, 4-methyl-*N*-phenylmethyl benzenesulfonamide (**5q**: 26.1 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-Methyl-*N*-phenylmethyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6q**: 28.8 mg, 67%).

Rf: 0.62 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

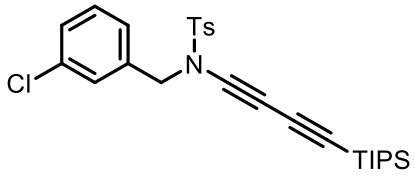
m.p.: 66.0-66.5 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.70 (m, 2H), 7.32-7.28 (m, 5H), 7.28-7.25 (m, 2H), 4.53 (s, 2H), 2.44 (s, 3H), 1.09-1.04 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.0, 134.6, 134.0, 129.8, 128.6, 128.4, 127.7, 88.9, 87.4, 68.5, 59.8, 55.6, 21.7, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{27}H_{36}N_1O_2S_1Si_1$ $[M + H]^+$ 466.22305, Found 466.22467

4-Methyl-*N*-[(3-chlorophenyl)methyl]-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6r)



Following the **General Procedure A**, 4-methyl-*N*-[(3-Chlorophenyl)methyl]-benzenesulfonamide (**5r**: 29.5 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-[(3-chlorophenyl)methyl]-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6r**: 38.8 mg, 78%).

Rf: 0.38 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

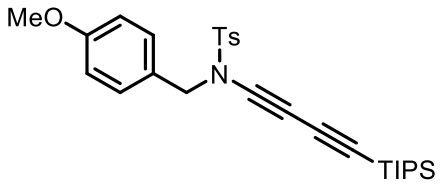
m.p.: 59.6-60.5 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.70 (m, 2H), 7.34-7.30 (m, 2H), 7.27-7.21 (m, 2H), 7.17-7.13 (m, 2H), 4.49 (s, 2H), 2.45 (s, 3H), 1.10-1.03 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.3, 135.9, 134.4, 129.92, 129.89, 128.6, 128.5, 127.6, 126.6, 88.7, 87.8, 68.2, 60.0, 55.0, 21.7, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{27}H_{35}Cl_1N_1O_2S_1Si_1$ $[M + H]^+$ 500.18408, Found 500.18299

4-Methyl-*N*-[(4-methoxyphenyl)methyl]-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6s)



Following the **General Procedure A**, 4-methyl-*N*-[(4-methoxyphenyl)methyl]-benzenesulfonamide (**5s**: 29.1 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-[(4-methoxyphenyl)methyl]-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6s**: 38.3 mg, 77%).

Rf: 0.38 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

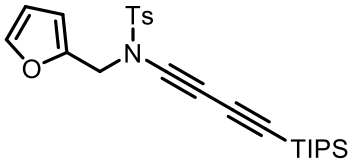
m.p.: 65.0-65.5 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.70 (m, 2H), 7.33-7.29 (m, 2H), 7.22-7.17 (m, 2H), 6.85-6.80 (m, 2H), 4.47 (s, 2H), 3.80 (s, 3H), 2.44 (s, 3H), 1.09-1.04 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.7, 144.9, 134.7, 130.2, 129.8, 127.7, 126.0, 113.9, 89.0, 68.6, 60.0, 55.3, 21.7, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{28}H_{38}N_1O_3S_1Si_1$ $[M + H]^+$ 496.23362, Found 496.23455

4-Methyl-*N*-(2-furanylmethyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6t)



Following the **General Procedure A**, 4-methyl-*N*-(2-furanylmethyl)-benzenesulfonamide (**5t**: 25.1 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(2-furanylmethyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6t**: 34.1 mg, 75%).

Rf: 0.32 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

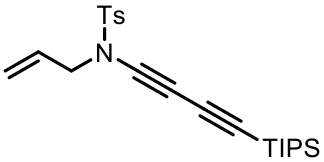
m.p.: 74.9-75.7 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-7.70 (m, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 1.7 Hz, 1H), 6.31-6.27 (m, 2H), 4.60 (s, 2H), 2.44 (s, 3H), 1.09-1.06 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 147.3, 145.0, 143.2, 134.4, 129.7, 127.7, 110.7, 110.5, 88.9, 87.5, 67.9, 59.9, 48.2, 21.7, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{25}H_{34}N_1O_3S_1Si_1$ $[M + H]^+$ 456.20232, Found 456.20269

4-Methyl-*N*-(2-propen-1-yl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6u)



Following the **General Procedure A**, 4-methyl-*N*-(2-propen-1-yl)-benzenesulfonamide (**5u**: 21.1 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(2-propen-1-yl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (**6u**: 16.9 mg, 42%).

Rf: 0.59 (Hexane : AcOEt = 4 : 1)

Physical state: Brown oil

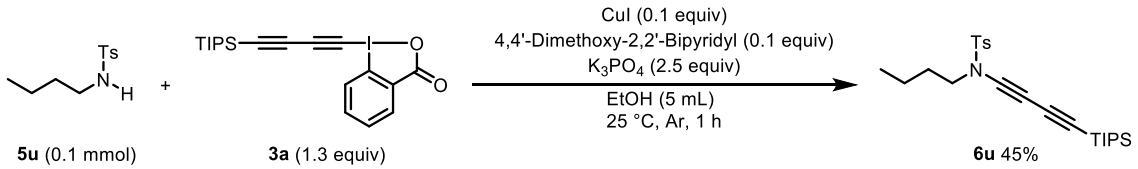
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.78 (m, 2H), 7.36 (d, *J* = 8.23 Hz, 2H), 5.76-5.64 (m, 1H), 5.29-5.20 (m, 2H), 4.00-3.96 (m, 2H), 2.46 (s, 3H), 1.09-1.00 (m, 21H)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 145.1, 134.6, 130.3, 129.9, 127.7, 120.5, 88.9, 87.2, 68.1, 59.4, 54.2, 21.7, 18.5, 11.3

HRMS (DART, positive) calcd for $C_{23}H_{34}N_1O_2S_1Si_1$ $[M + H]^+$ 416.20740, Found 416.20686

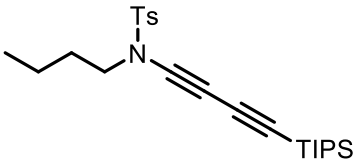
4-Methyl-*N*-(1-buthyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6v)

(General procedure B)



5u (0.1 mmol) **3a** (1.3 equiv) **6u** 45%

4-Methyl-*N*-(1-buthyl)-benzenesulfonamide (**5v**: 22.7 mg, 0.1 mmol), 1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(*1H*)-one (**3a**: 58.8 mg, 0.13 mmol, 1.3 equiv.), CuI (2.0 mg, 0.01mmol, 0.1 equiv.), 4,4'-dimethoxy-2,2'-bipyridyl (**L1**: 2.15 mg, 0.01 mmol, 0.1 equiv.) and K_3PO_4 (52.5 mg, 0.25 mmol, 2.5 equiv.) were stirred in dry ethanol (5 mL) under argon at 25 ºC . After stirred for 1 h at 25 ºC, the solution was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(1-buthyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl] benzenesulfonamide (**6v**: 19.7 mg, 45%) as brown oil.



Rf: 0.63 (Hexane : AcOEt = 4 : 1)

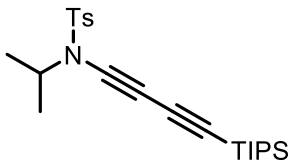
Physical state: Brown oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.78 (m, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 3.32 (t, *J* = 7.32 Hz, 2H), 2.46 (s, 3H), 1.67-1.60 (m, 2H), 1.37-1.28 (m, 2H), 1.11-1.03 (m, 21H), 0.91 (t, *J* = 7.32 Hz, 3H)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 145.1, 134.7, 130.0, 127.7, 89.2, 87.1, 68.4, 59.4, 51.4, 30.0, 21.8, 19.5, 18.7, 13.6, 11.4

HRMS (DART, positive) calcd for $C_{24}H_{38}N_1O_2S_1Si_1$ $[M + H]^+$ 432.23870, Found 432.23924

4-Methyl-*N*-(1-methylethyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl] benzenesulfonamide (6w)



Following the **General Procedure A**, 4-methyl-*N*-(1-methylethyl)-benzenesulfonamide (**5w**: 21.3 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 4-methyl-*N*-(1-methylethyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl] benzenesulfonamide (**6w**: 11.0 mg, 26%).

Rf: 0.73 (Hexane : AcOEt = 4 : 1)

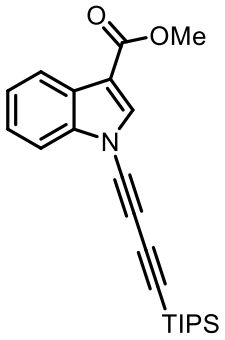
Physical state: Brown oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83-7.79 (m, 2H), 7.35 (d, *J* = 8.59 Hz, 2H), 4.14-4.06 (m, 1H), 2.46 (s, 3H), 1.13 (d, *J* = 7.45 Hz, 6H), 1.10-1.05 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 144.8, 135.7, 129.9, 127.5, 89.3, 86.7, 65.5, 61.4, 53.2, 21.7, 20.9, 18.6, 11.3

HRMS (DART, positive) calcd for $C_{23}H_{36}N_1O_2S_1Si_1$ $[M + H]^+$ 418.22305, Found 418.22481

1-[4-[Tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-1*H*-indole-3-carboxylic acid methyl ester (6x)



Following the **General Procedure A**, methyl indole-3-carboxylate (**5x**: 17.5 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : AcOEt = 20 : 1) to afford 1-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-*1H*-indole-3-carboxylic acid methyl ester (**6x**: 11.1 mg, 29%).

Rf: 0.50 (Hexane : AcOEt = 20 : 1)

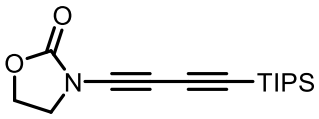
Physical state: Brown oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18-8.14 (m, 1H), 7.90 (s, 1H), 7.66-7.63 (m, 1 H), 7.43-7.39 (m, 1 H), 7.39-7.35z (m, 1 H), 3.93 (s, 3H), 1.15-1.12 (m, 21H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.0, 138.7, 134.8, 125.2, 124.9, 124.2, 122.1, 111.9, 111.8, 89.6, 87.9, 64.5, 59.7, 51.5, 18.6, 11.3

HRMS (DART, positive) calcd for $C_{23}H_{30}N_1O_2Si_1$ $[M + H]^+$ 380.20403, Found 380.20487

3-[4-[Tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-2-oxazolidinone (6y)



Following the **General Procedure A**, 2-oxazolidinone (**5y**: 8.7 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Hexane : AcOEt = 4 : 1) to afford 3-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-2-oxazolidinone (**6y**: 13.1 mg, 45%).

Rf: 0.20 (Hexane : AcOEt = 4 : 1)

Physical state: Colorless solid

m.p.: 98.3-100.0 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.50-4.45 (m, 2H), 4.00-3.95 (m, 2H), 1.09-1.06 (m, 21H)

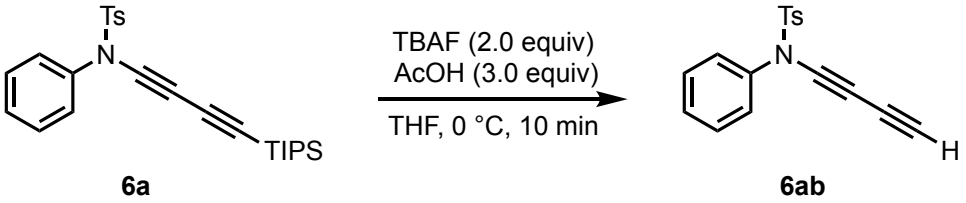
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 155.8, 88.3, 87.9, 64.5, 63.3, 59.5, 46.5, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{16}H_{26}N_1O_2Si_1$ $[M + H]^+$ 292.17273, Found 292.17389

3.4 Derivatization of diynamides.

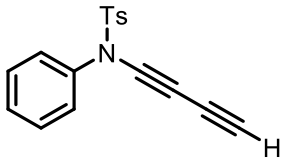
Deprotection of TIPS

4-Methyl-*N*-phenyl-*N*-[4-(1,3-butadiyn-1-yl)]-benzenesulfonamide (6ab)



6a **6ab**

Following a slightly modified reported procedure,[10] to a solution of TIPS protected ynamide (**6a:** 406.0 mg, 0.9 mmol, 1.00 eq.) in THF (11.6 mL) was added a mixture of tetra-*n*-butylammonium fluoride in THF (1.8 mL, 1.6 mmol, 2.00 equiv.) and AcOH (153.0 µL, 2.4 mmol, 3.00 equiv.) dropwise at 0 °C. The reaction mixture was stirred at 0 ℃ for 10 minutes. Then, water (10 mL) was added to the reaction mixture and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude product. The resulting crude product was purified by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) affording 4-methyl-*N*-phenyl-*N*-[4-(1,3-butadiyn-1-yl)]-benzenesulfonamide (**6ab**: 237.6 mg, 0.804 mmol, 89%) as a brown solid.



Rf: 0.30 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

m.p.: 115.5-116.0 °C

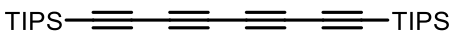
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61-7.57 (m, 2H), 7.36-7.32 (m, 3H), 7.32-7.29 (m, 2 H), 7.23-7.18 (m, 2H), 2.46 (s, 3H), 2.44 (s, 1H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.5, 137.6, 132.8, 129.8, 129.3, 128.8, 128.1, 126.4, 71.5, 68.1, 67.6, 57.5, 21.7

HRMS (DART, positive) calcd for $C_{17}H_{14}N_1O_2S_1$ $[M + H]^+$ 296.07398, Found 296.07282

FTIR (ATR): 3272, 3068, 2926, 2239, 2072, 1595, 1488, 1455, 1377, 1320, 1309, 1189, 1176, 1159, 1121, 1088, 1075, 1026, 924, 885, 838, 809, 750, 702, 692, 672, 653

1,1'-(1,3,5,7-Octatetrayne-1,8-diyl)bis[1,1,1-tris(1-methylethyl)silane] (7)



Following the **General Procedure A**, **5a** was not used. Purification by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) to afford 1,1'-(1,3,5,7-octatetrayne-1,8-diyl)bis[1,1,1-tris(1-methylethyl)silane] (**7**: 17.5 mg, 66%).

Rf: 0.86 (Hexane : AcOEt = 4 : 1)

Physical state: Brown solid

m.p.: 74.0-76.0 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16-1.04 (m, 42 H)

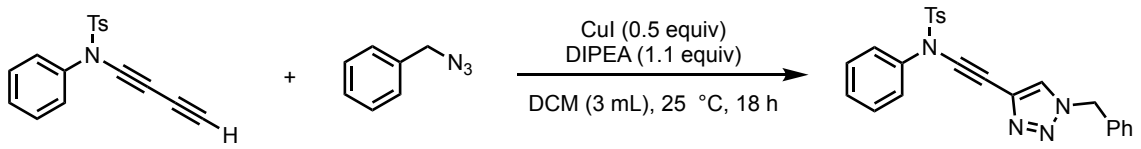
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 89.6, 85.6, 62.2, 61.3, 18.5, 11.2

HRMS (DART, positive) calcd for $C_{26}H_{42}Si_2$ $[M + H]^+$ 411.28788, Found 418.28978

3.5 Copper-catalysed azide-alkyne cycloaddition

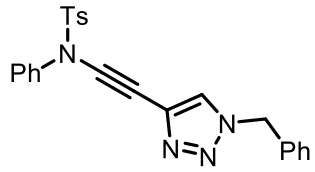
4-Methyl-*N*-phenyl-*N*-[[1-(phenylmethyl)-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10a)

(General procedure C)



6ab (1.1 equiv) **9a** (0.1 mmol) **10a** 89%

Following a slightly modified reported procedure,[11] 4-methyl-*N*-phenyl-*N*-[4-(1,3-butadiyn-1-yl)]-benzenesulfonamide (**6ab**: 0.11 mmol, 1.1 equiv., 33.0 mg), CuI (0.05 mmol, 0.5 equiv., 10.0 mg) and *N*,*N*-diisopropylethylamine (0.11 mmol, 1.1 equiv., 14.0 µL) was dissolved in dichloromethane (6.0 mL). Benzyl azide (**9a**: 0.1 mmol, 1.0 equiv., 13.0 µL) was then added and the resulting cloudy mixture was stirred for 18 h at 25 ºC. After 18 h, the reaction mixture was evaporated until a solid was obtained. Then, $NaHCO_3$ (10 mL) was added to the residue and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude product. The resulting crude product was purified by column chromatography on silica gel (Hexane : Chloroform = 1 : 1) affording 4-methyl-*N*-phenyl-*N*-[[1-(phenylmethyl)-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (**10a**: 39.3 mg, 0.092 mmol, 92%) as a colorless solid.



Rf: 0.16 (Hexane : Chloroform = 1 : 1)

Physical state: Colorless solid

m.p.: 115.0-116.0 ℃

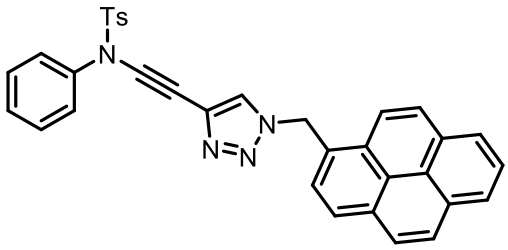
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61-7.58 (m, 2 H), 7.57 (s, 1 H), 7.40-7.35 (m, 3 H), 7.32-7.24 (m, 9 H), 5.51 (s, 2 H), 2.42 (s, 3 H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.2, 138.3, 134.0, 132.9, 130.6, 129.7, 129.2, 129.1, 129.0, 128.5, 128.2, 128.1, 126.9, 126.4, 85.7, 59.8, 54.3, 21.7

HRMS (DART, positive) calcd for $C_{24}H_{21}N_4O_2S_1$ $[M + H]^+$ 429.13797, Found 429.13818

FTIR (ATR): 3067, 2251, 1594, 1490, 1456, 1373, 1245, 1220, 1188, 1173, 1089, 1045, 1002, 923, 894, 814, 762, 729, 711, 691, 661, 574, 549, 525

4-Methyl-*N*-phenyl-*N*-[[1-(pyrenemethyl)-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10b)



Following the **General Procedure C**, 1-(azidomethyl)pyrene (**9b**: 25.8 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Chloroform) to afford 4-methyl-*N*-phenyl-*N*-[[1-(pyrenemethyl)-1H-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (**10b**: 40.1 mg, 72%).

Rf: 0.07 (Chloroform)

Physical state: Colorless solid

m.p.: 191.2-191.9 ℃

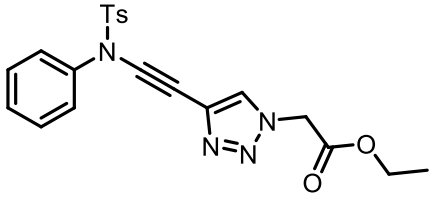
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (t, J = 7.45 Hz, 2H), 8.19 (d, *J* = 7.45 Hz, 1H), 8.16 (d, *J* = 2.29 Hz, 2H), 8.13 (d, *J* = 8.59 Hz, 1 H), 8.09-8.03 (m, 2H), 7.95 (d, *J* = 8.02 Hz, 1H), 7.52 (d, *J* = 8.02 Hz, 2H), 7.38 (s, 1H), 7.26-7.18 (m, 7H), 6.23 (s, 2H), 2.36 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.1, 138.3, 132.8, 132.3, 131.1, 130.5, 130.47, 129.6, 129.3, 129.1, 128.44, 128.4, 128.1, 127.7, 127.2, 126.9, 126.5, 126.4, 126.1, 125.9, 125.0, 124.9, 124.4, 121.7, 85.6, 59.8, 52.6, 21.6

HRMS (DART, positive) calcd for $C_{34}H_{25}N_4O_2S_1$ $[M + H]^+$ 553.16927, Found 553.17091

FTIR (ATR): 3067, 2241, 1594, 1490, 1455, 1378, 1249, 1189, 1174, 1089, 1045, 1006, 926, 888, 848, 835, 815, 753, 708, 692, 659, 577, 547, 521

4-[[(4-Phenyl)[(4-methylphenyl)sulfonyl]amino]ethynyl]-1H-1,2,3-triazole-1-acetic acid ethyl ester (10c)



Following the **General Procedure C**, ethyl azidoacetate (**9c**: 12.9 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Chloroform : EtOAc = 5 : 1) to afford 4-[[(4-phenyl)[(4-methylphenyl)sulfonyl]amino]ethynyl]-1H-1,2,3-Triazole-1-acetic acid ethyl ester (**10c**: 38.4 mg, 90%).

Rf: 0.57 (Chloroform : EtOAc = 5 : 1)

Physical state: Brown solid

m.p.: 129.3-129.9 ℃

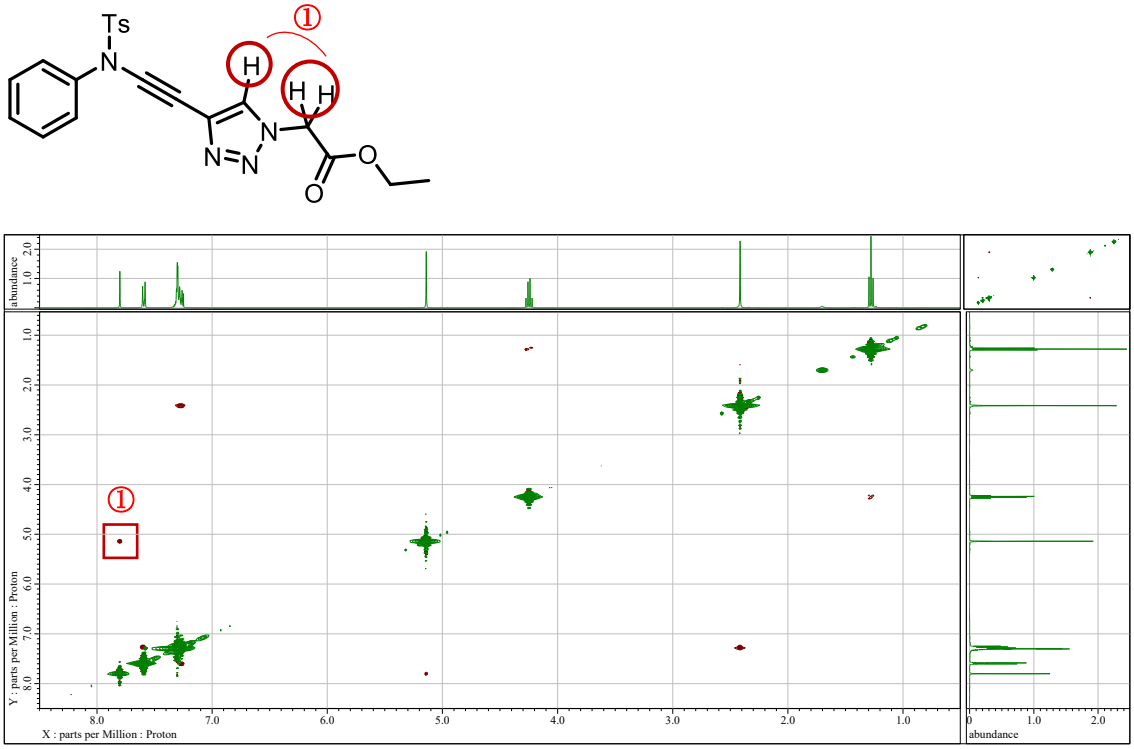
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.62 (d, *J* = 8.59 Hz, 2H), 7.35-7.28 (m, 7H), 5.16 (s, 2H), 4.29 (q, *J* = 6.87 Hz, 2H), 2.45 (s, 3H), 1.31 (t, *J* = 6.87 Hz, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.8, 145.2, 138.3, 132.8, 130.7, 129.7, 129.1, 128.5, 128.2, 128.1, 126.4, 85.8, 62.6, 59.6, 50.9, 21.7, 14.0

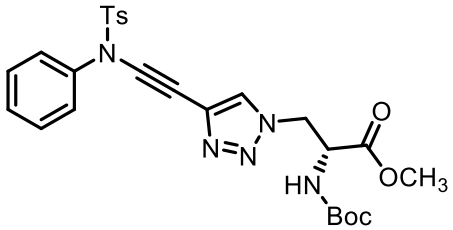
HRMS (DART, positive) calcd for $C_{21}H_{21}N_4O_4S_1$ $[M + H]^+$ 425.12780, Found 425.12697

FTIR (ATR): 1750, 1594, 1489, 1464, 1398, 1372, 1251, 1215, 1188, 1172, 1089, 1046, 1022, 1002, 924, 891, 814, 757, 719, 704, 690, 659, 575, 549, 521

Figure S1. NOESY spectra of 10c.



4-Methyl-*N*-phenyl-*N*-[[*N*-(*tert*-butoxycarbonyl)-D-alanine methyl ester]-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10d)



Following the **General Procedure C**, 3-azido-*N*-[(1,1-dimethylethoxy)carbonyl]-D-alanine methyl ester (**9d**: 24.4 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Chloroform : EtOAc = 10 : 1) to afford 4-methyl-*N*-phenyl-*N*-[[*N*-(*tert*-butoxycarbonyl)-D-alanine

methyl ester]-1H-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (**10d**: 24.2 mg, 45%).

Rf: 0.38 (Chloroform : EtOAc = 10 : 1)

Physical state: Brown oil

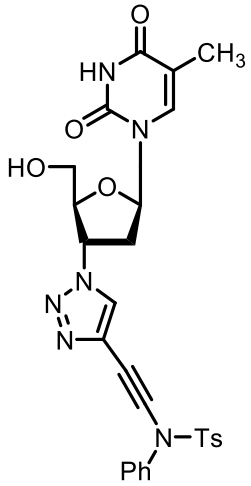
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.63-7.60 (m, 2H), 7.35-7.28 (m, 7H), 5.32 (d, *J* = 6.87 Hz, 1H), 4.89-4.75 (m, 2H), 4.73-4.67 (m, 1H), 3.80 (s, 3H), 2.44 (s, 3H), 1.45 (s, 9H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 169.2, 155.1, 145.3, 138.4, 132.9, 130.4, 129.7, 129.2, 128.5, 128.2, 128.0, 126.5, 85.9, 81.0, 59.6, 53.7, 53.2, 51.1, 28.2, 21.7

HRMS (DART, positive) calcd for $C_{26}H_{29}N_5O_6S_1$ $[M + H]^+$ 540.19073, Found 540.19113

FTIR (ATR): 3383, 3146, 2980, 2932, 2251, 1745, 1710, 1595, 1492, 1455, 1438, 1368, 1287, 1249, 1221, 1188, 1170, 1090, 1047, 1028, 1000, 925, 893, 855, 814, 756, 704, 691, 659

4-Methyl-*N*-phenyl-*N*-[[1-(thymidine)-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10e)



Following the **General Procedure C**, Azidothymidine (**9e**: 25.8 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Chloroform : EtOAc = 1 : 5) to afford 4-methyl-*N*-phenyl-*N*-[[1-(thymidine)-1H-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (**10e**: 37.8 mg, 67%).

Rf: 0.35 (Chloroform : EtOAc = 1 : 5)

Physical state: Colorless solid

m.p.: 111.5-112.5 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.15 (s, 1H), 7.86 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.43 (s, 1H), 7.35-7.26 (m, 7H), 6.21 (t, *J* = 6.87 Hz, 1H), 5.50-5.44 (m, 1H), 4.44-4.40 (m, 1H), 4.02 (d, *J* = 12.60 Hz, 1H), 3.84-3.75 (m, 1H), 3.53-3.46 (m, 1H), 3.03-2.91 (m, 2H), 2.43 (s, 3H), 1.91 (s, 3H)

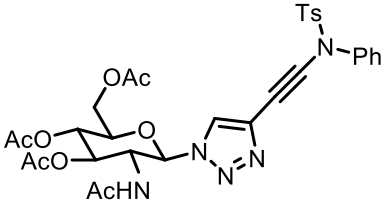
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.1, 150.6, 145.4, 138.1, 137.8, 132.7, 130.4, 129.7, 129.2, 128.6, 128.1, 127.2, 126.3, 111.2, 88.0, 86.0, 85.0, 61.3, 59.6, 59.5, 37.5, 29.7, 21.7, 12.4

HRMS (DART, positive) calcd for $C_{27}H_{27}N_6O_6S_1$ $[M + H]^+$ 563.16679, Found 563.17073

FTIR (ATR): 3020, 2251, 1679, 1594, 1472, 1455, 1370, 1273, 1254, 1220, 1188, 1172, 1090, 1042,

955, 924, 890, 813, 753, 713, 691, 660, 576, 549, 521

4-Methyl-*N*-phenyl-*N*-[[[1-{3-(acetylamino)-2,6-anhydro-1,3-dideoxy-4,5,7-triacetate}-D-glycero-D-ido-heptitol]-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10f)



Following the **General Procedure C**, 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-beta-D-glucopyranosyl azide (**9f**: 37.2 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Chloroform : EtOAc = 1 : 1) to afford 4-methyl-*N*-phenyl-*N*-[[[1-{3-(acetylamino)-2,6-anhydro-1,3-dideoxy-4,5,7-triacetate}-D-glycero-D-ido-heptitol]-*1H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (**10f**: 60.1 mg, 93%).

Rf: 0.31 (Chloroform : EtOAc = 1 : 1)

Physical state: Brown solid

m.p.: 96.3-97.0 ℃

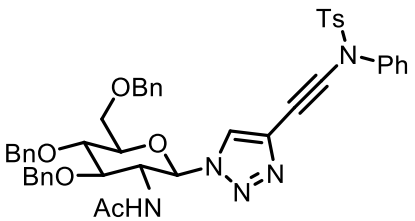
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.64-7.59 (m, 2H), 7.36-7.28 (m, 7H), 6.42 (d, *J* = 8.7 Hz, 1H), 6.16 (d, *J* = 10.1 Hz, 1H), 5.59 (t, *J* = 10.1 Hz, 1H), 5.25 (t, J = 9.6 Hz, 1H), 4.49 (q, *J* = 9.61 Hz, 1H), 4.30 (dd, *J* = 12.35, 4.57 Hz, 1H), 4.14 (dd, *J* = 12.35, 1.83 Hz, 1H), 4.10-4.04 (m, 1H), 2.44 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.81 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 170.9, 170.6, 169.3, 145.3, 138.2, 132.9, 130.7, 129.7, 129.2, 128.6, 128.2, 126.5, 126.1, 86.3, 85.6, 74.9, 71.9, 67.9, 61.6, 59.4, 53.8, 22.9, 21.7, 20.7, 20.6, 20.58

HRMS (DART, positive) calcd for $C_{31}H_{34}N_5O_{10}S_1$ $[M + H]^+$ 668.20209, Found 668.20209

FTIR (ATR): 3281, 2252, 1747, 1667, 1594, 1544, 1490, 1454, 1371, 1295, 1226, 1188, 1174, 1090, 1038, 924, 897, 815, 756, 715, 692, 661, 598, 577, 550

4-Methyl-*N*-phenyl-*N*-[[[1-{3-(acetylamino)-2,6-anhydro-1,3-dideoxy-4,5,7-tris-*O*-(phenylmethyl)}-D-glycero-D-ido-heptitol]-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10g)



Following the **General Procedure C**, 2-acetamido-3,4,6-tri-O-benzyl-2-deoxy-β-D-glucopyranosyl

azide (**9g**: 51.6 mg, 0.1 mmol) was used. Purification by column chromatography on silica gel (Chloroform : MeOH = 10 : 1) to afford 4-methyl-*N*-phenyl-*N*-[[[1-{3-(acetylamino)-2,6-anhydro-1,3-dideoxy-4,5,7-tris-O-(phenylmethyl)}-D-glycero-D-ido-heptitol]-*1H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (**10g**: 57.1 mg, 70%).

Rf: 0.71 (Chloroform : MeOH = 10 : 1)

Physical state: Brown solid

m.p.: 144.2-144.8 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.62-7.57 (m, 2H), 7.35-7.23 (m, 20H), 7.21-7.17 (m, 2H), 6.35-6.29 (m, 1H), 6.04 (d, *J* = 9.7 Hz, 1H), 4.86 (d, *J* = 11.5 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.59 (d, *J* = 10.9 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.26-4.19 (m, 1H), 4.17-4.12 (m, 1H), 3.85-3.67 (m, 4H), 2.40 (s, 3H), 1.66 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.0, 145.4, 138.4, 138.2, 137.9, 133.0, 130.4, 129.9, 129.3, 128.68, 128.65, 128.58, 128.56, 128.5, 128.29, 128.25, 128.2, 128.09, 128.06, 128.03, 127.99, 127.93, 127.91, 127.85, 127.81, 126.6, 126.4, 86.1, 85.9, 81.2, 78.14, 78.11, 75.4, 75.2, 73.6, 68.5, 59.6, 55.7, 23.2, 21.8

HRMS (DART, positive) calcd for $C_{46}H_{46}N_5O_7S_1$ $[M + H]^+$ 812.31125, Found 812.31125

FTIR (ATR): 1658, 1547, 1495, 1454, 1371, 1307, 1264, 1216, 1188, 1174, 1156, 1089, 1028, 1003, 924, 890, 814, 751, 715, 693, 660, 639, 619, 576, 550

4. References

1. M. Yudasaka, D. Shimbo, T. Maruyama, N. Tada and A. Itoh, *Org. Lett.,* 2019, **21**, 1098–1102.

2. D. Shimbo, A. Shibata, M. Yudasaka, T. Maruyama, N. Tada, B. Uno and A. Itoh, *Org. Lett.,* 2019, **21**, 9769–9773.

3. T. W. Liwosz and S. R. Chemler, *Chem. Eur. J.*, 2013, **19**, 12771–12777.

4. F. Buckingham, S. Calderwood, B. Checa, T. Keller, M. Tredwell, T. L. Collier, I. M. Newington, R. Bhalla, M. Glaser and V. Gouverneur, *J. Fluorine. Chem.,* 2015, **180**, 33–39.

5. G. Sun, Y. Wang and Q. Kang, *Synthesis,* 2015, **47**, 2931–2936.

6. (a) B. Pigulski, N. Gulia and S. Szafert, *Chem. Eur. J.*, 2015, **21**, 17769–17778. (b) A. S. Dillon and B. L. Flynn, *Org. Lett.*, 2020, **22**, 8, 2987–2990.

7. D. Shetty, J. M. Jeong, C. H. Ju, Y. J. Kim, J. Lee, Y. Lee, D. S. Lee, J. Chung and M. C. Lee, *Bioorg. Med. Chem.*, 2010, **18**, 7338–7347.

8. W. Yin, C. He, M. Chen, H. Zhang and A. Lei, *Org. Lett.*, 2009, **11**, 709–712.

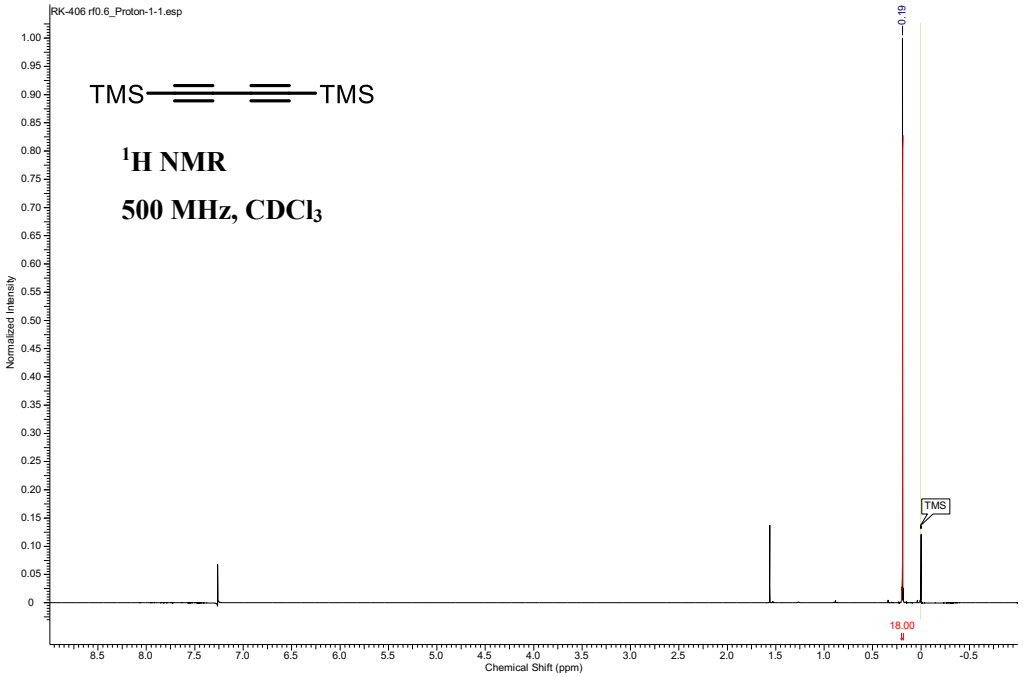
9. T. N. Hoheisel and H. Frauenrath, *Org. Lett.*, 2008, **10**, 3, 4525–528.

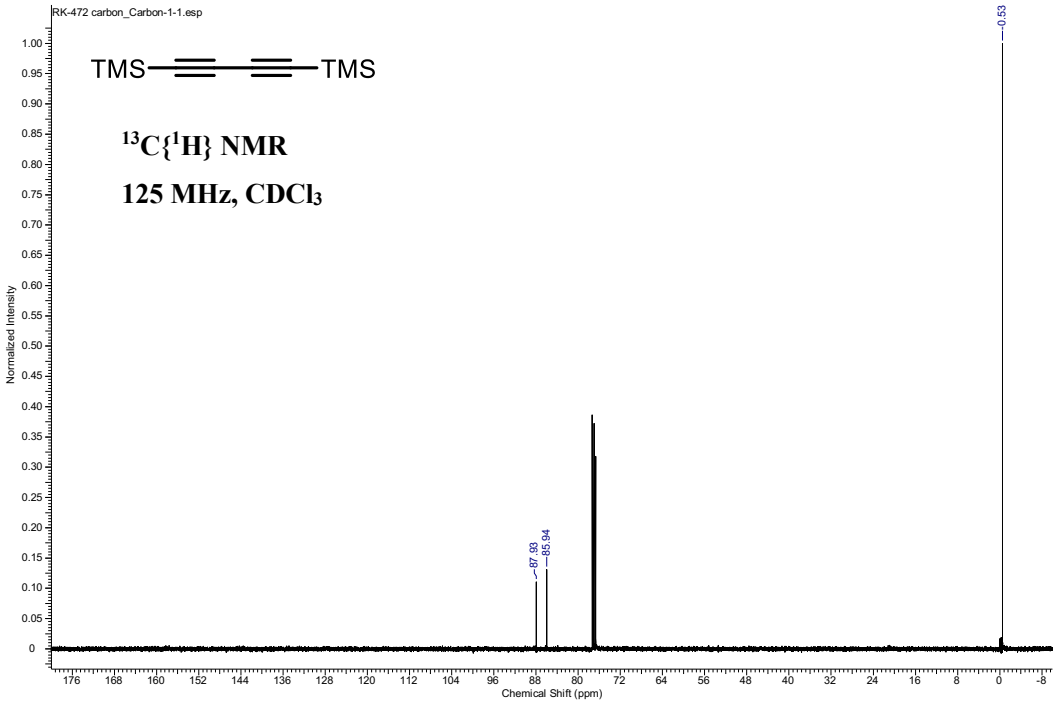
10. R. Frei and J. Waser, *J. Am. Chem. Soc.*, 2013, **135**, 9620–9623.

11. B. C. Doak, M. J. Scanlon and J. S. Simpson, *Org. lett.*, 2011, **13**, 537–539.

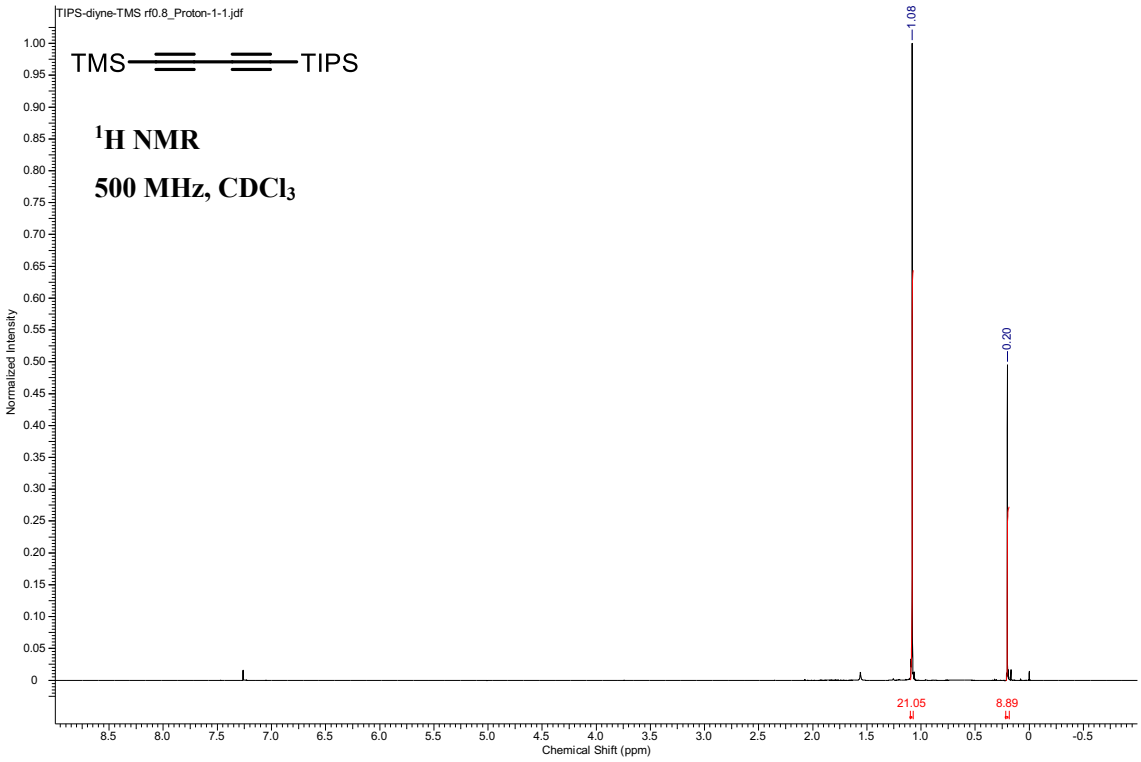
5. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra

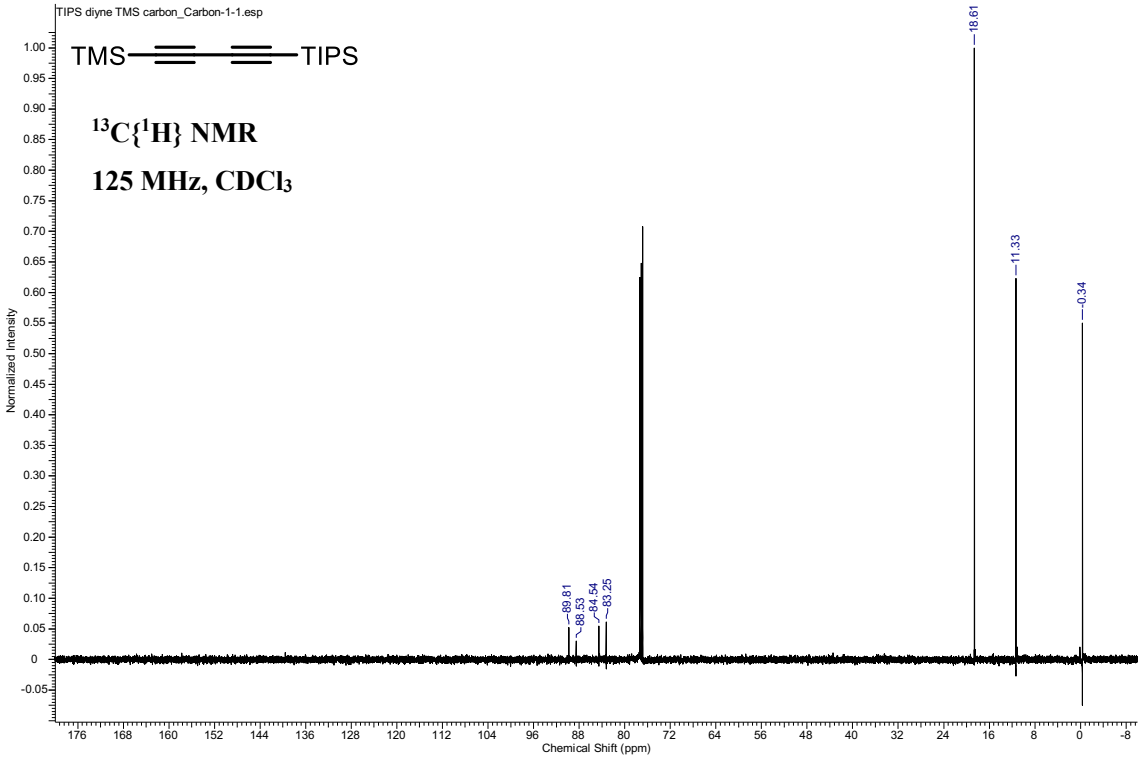
1,4-Bis(trimethylsilyl)-1,3-butadiyne (2b)



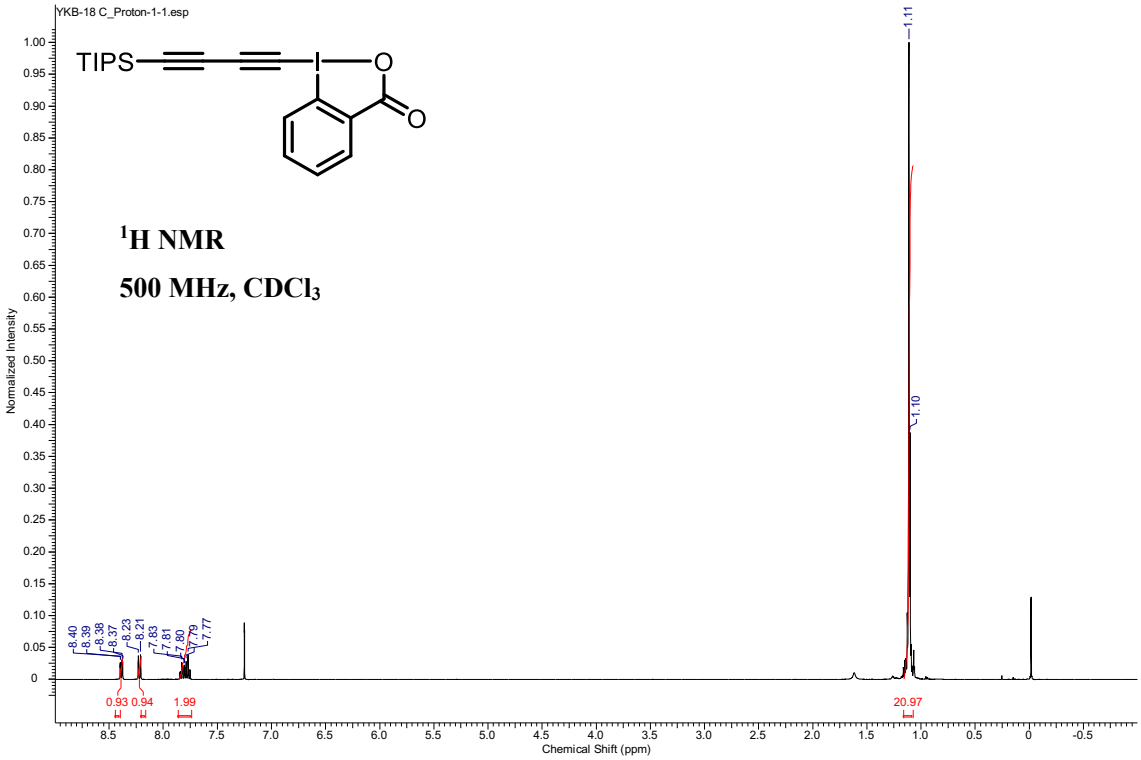


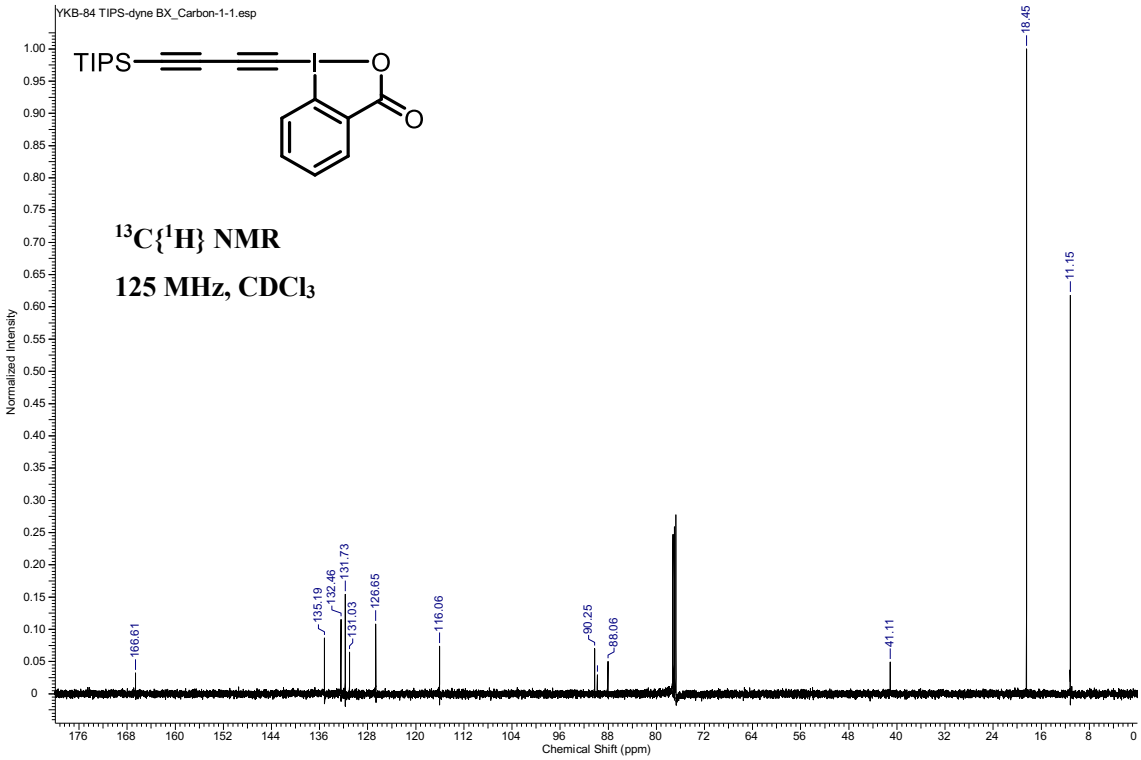
Trimethyl[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]silane (2a)



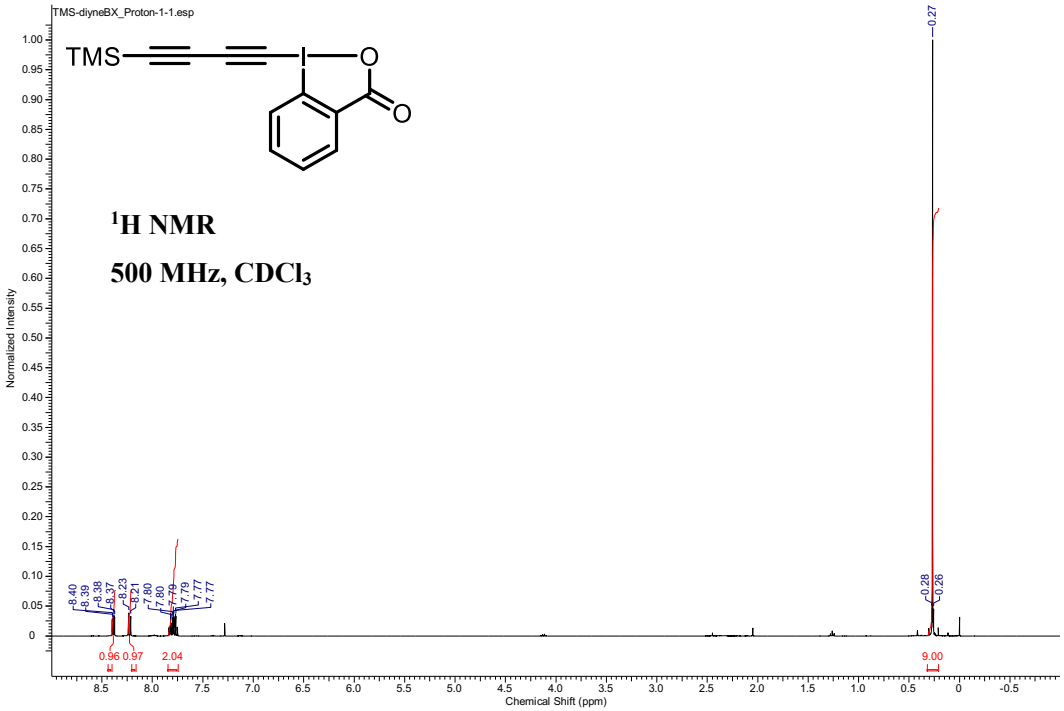


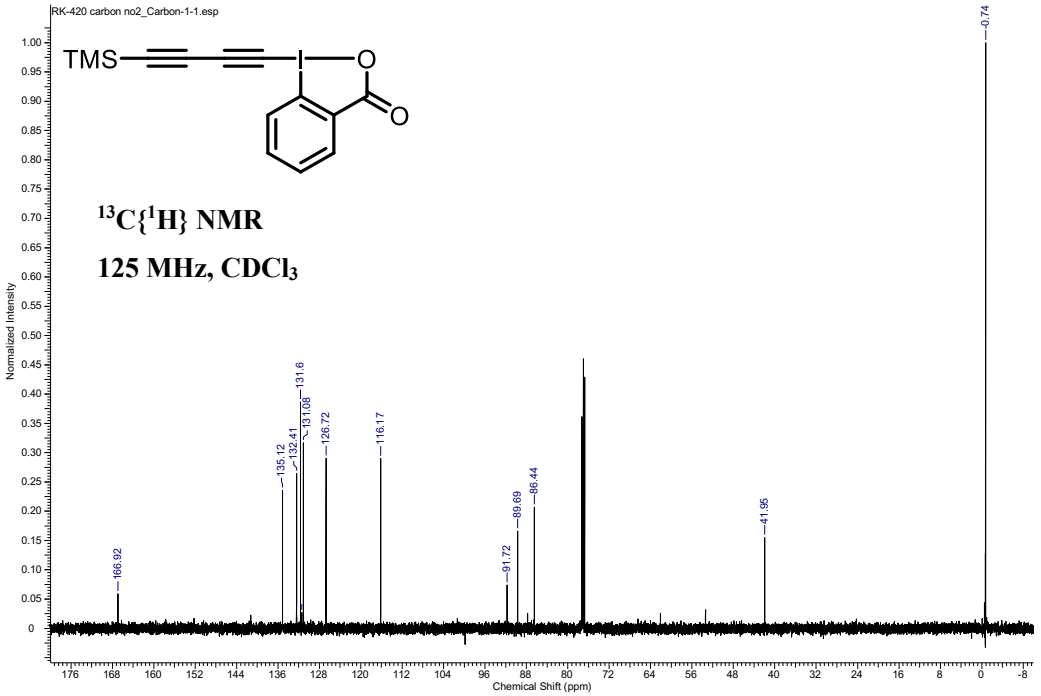
1-[4-[Tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-1,2-benziodoxol-3(*1H*)-one (TIPS-diyne-BX) (3a)



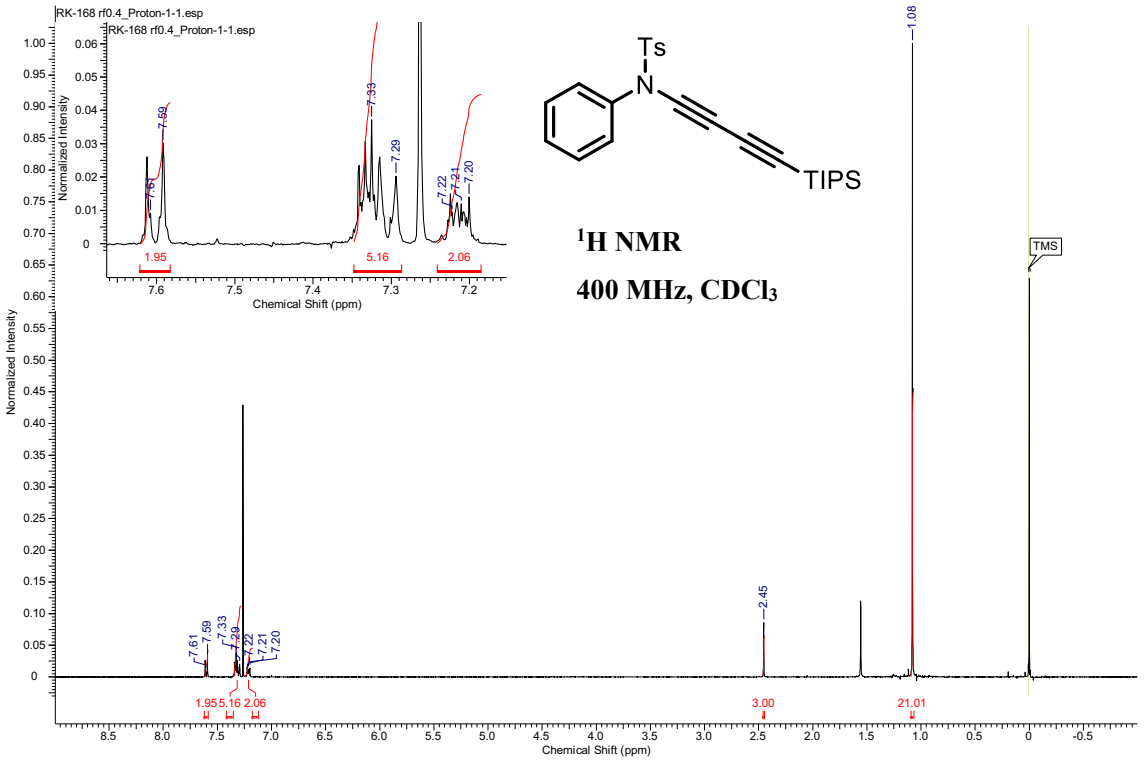


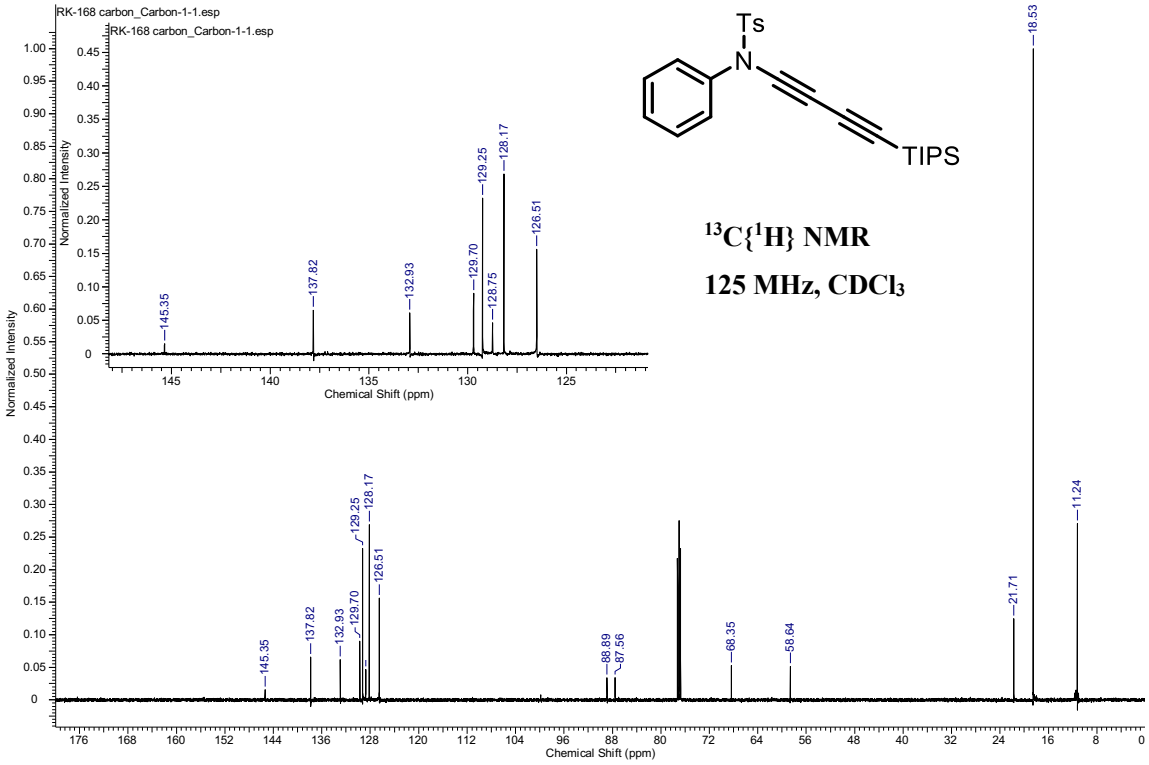
1-[4-(Trimethylsilyl)-1,3-butadiyn-1-yl]-1,2-benziodoxol-3(*1H*)-one (TMS-diyne-BX) (3b)



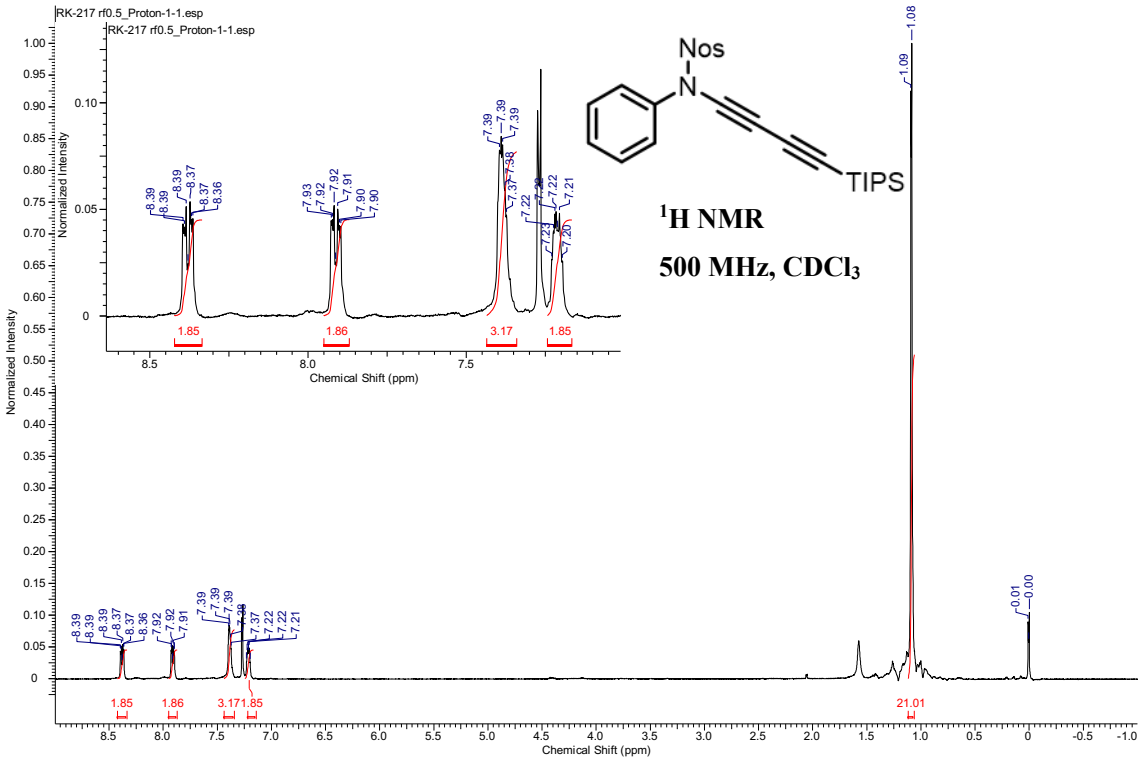


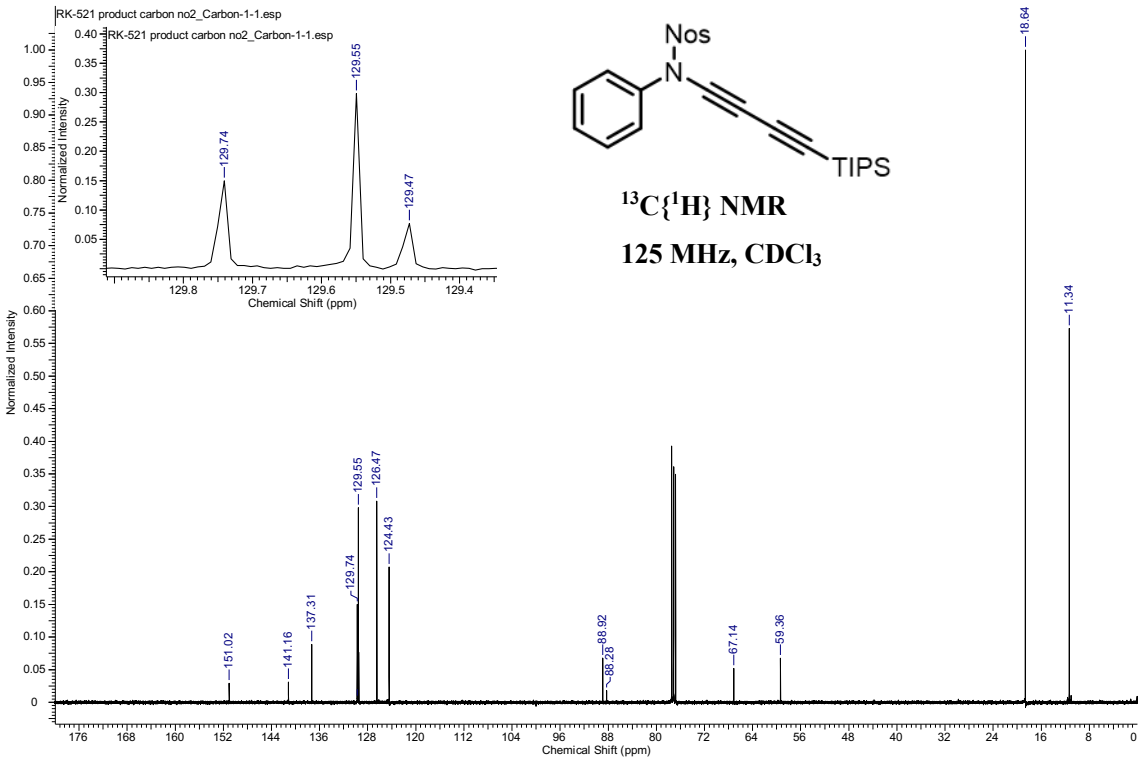
4-Methyl-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6a)



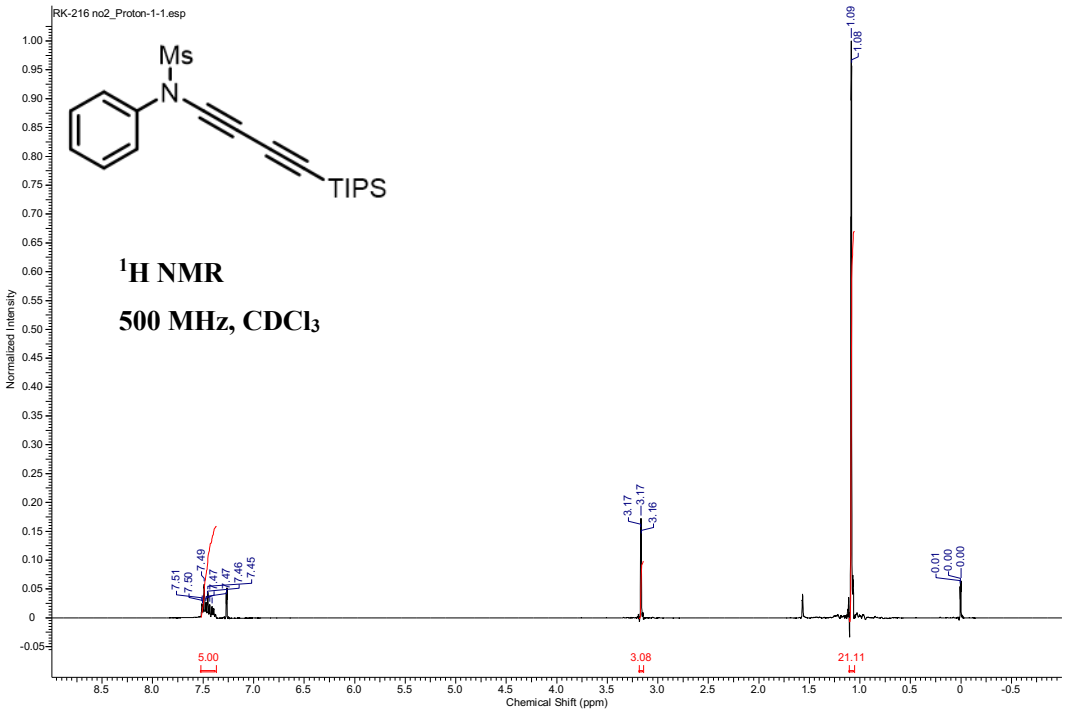


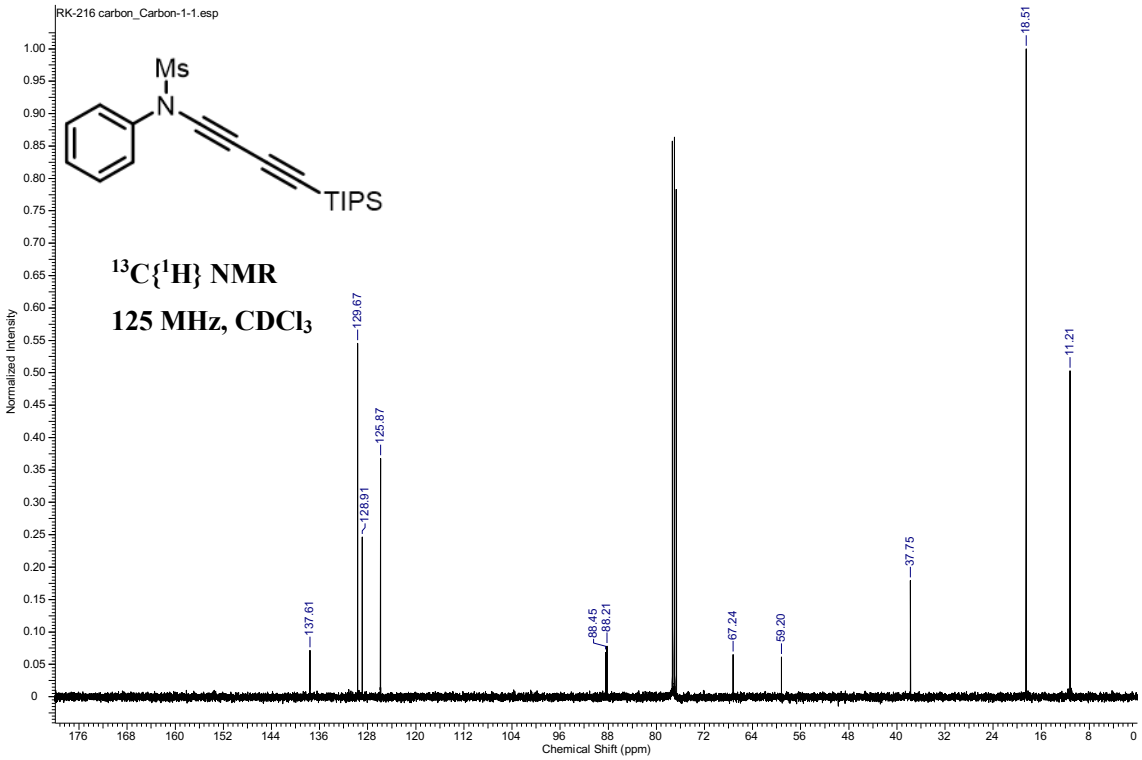
4-Nitro-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6b)



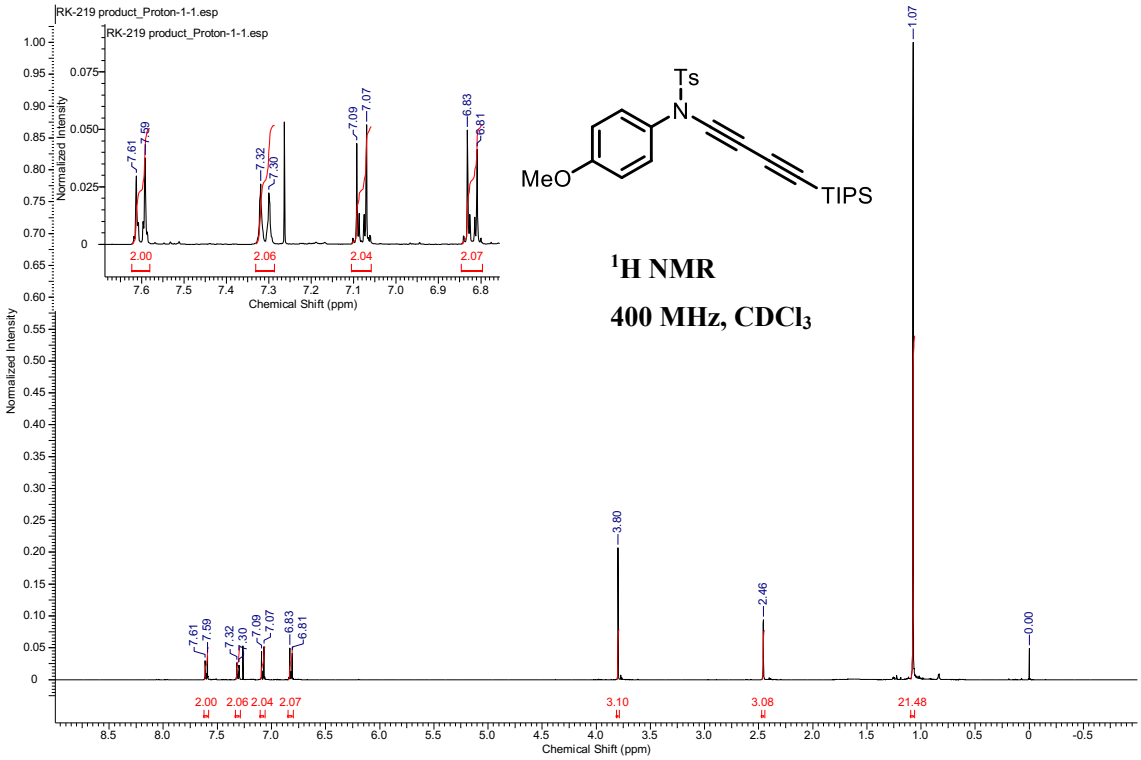


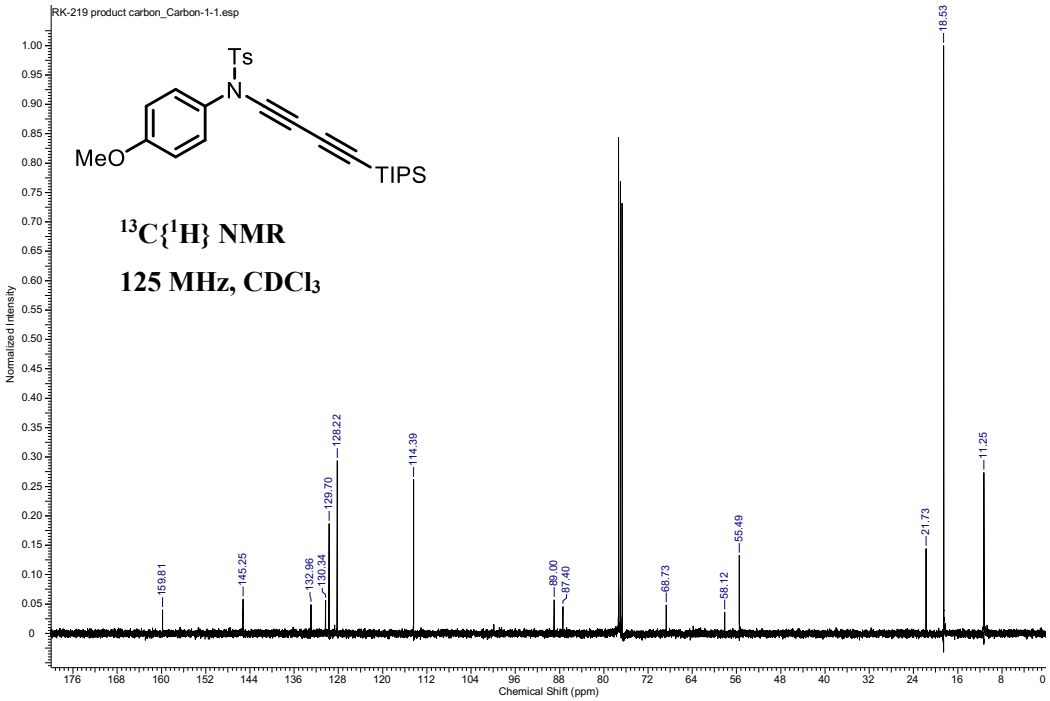
4-Methyl-*N*-phenyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-mathanesulfonamide (6c)



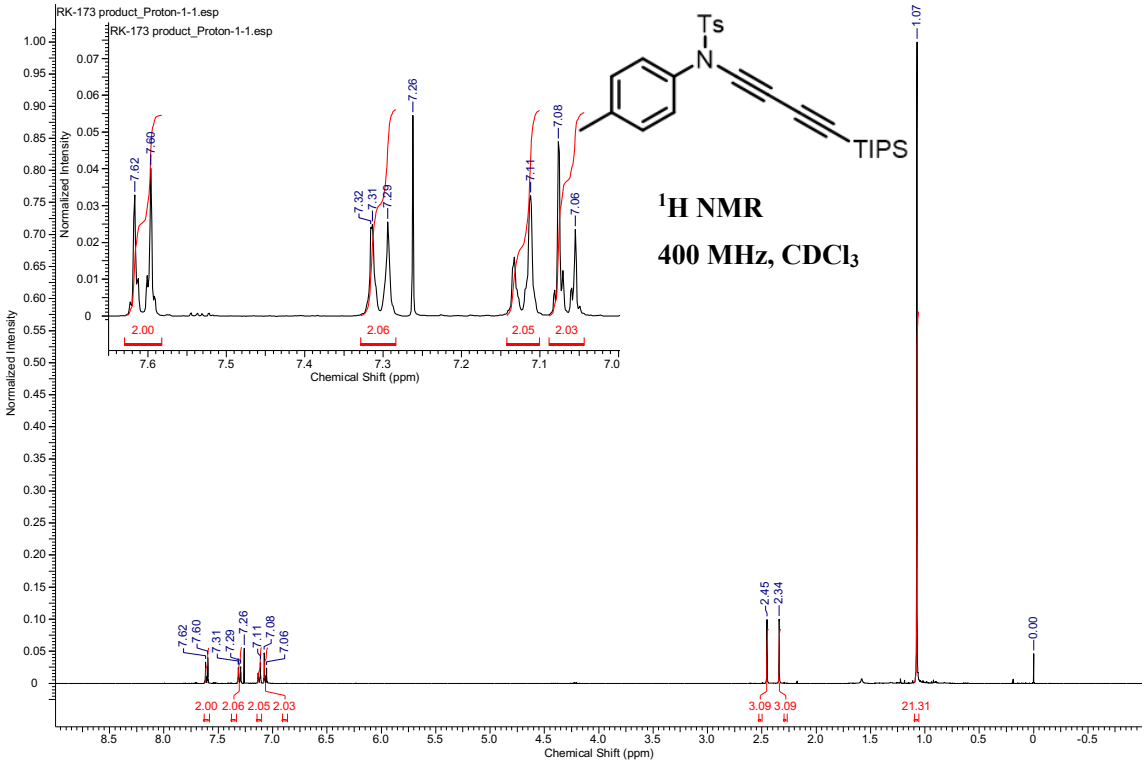


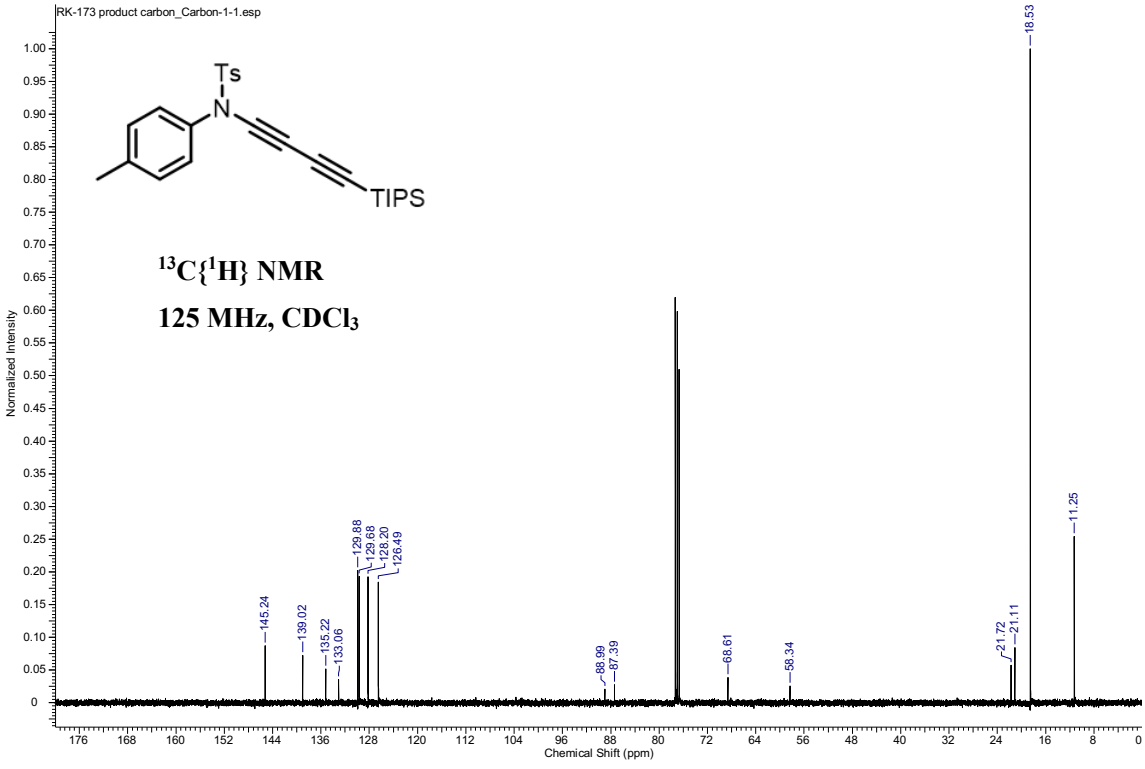
4-Methyl-*N*-(4-methoxyphenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6g)



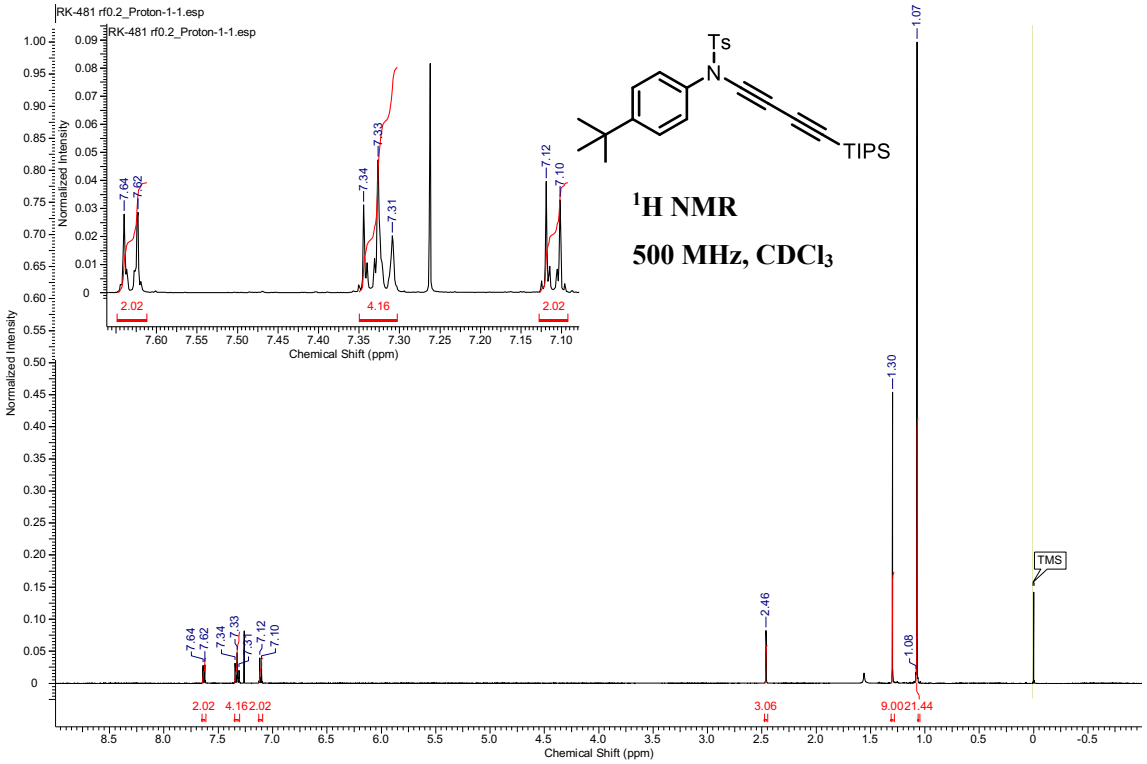


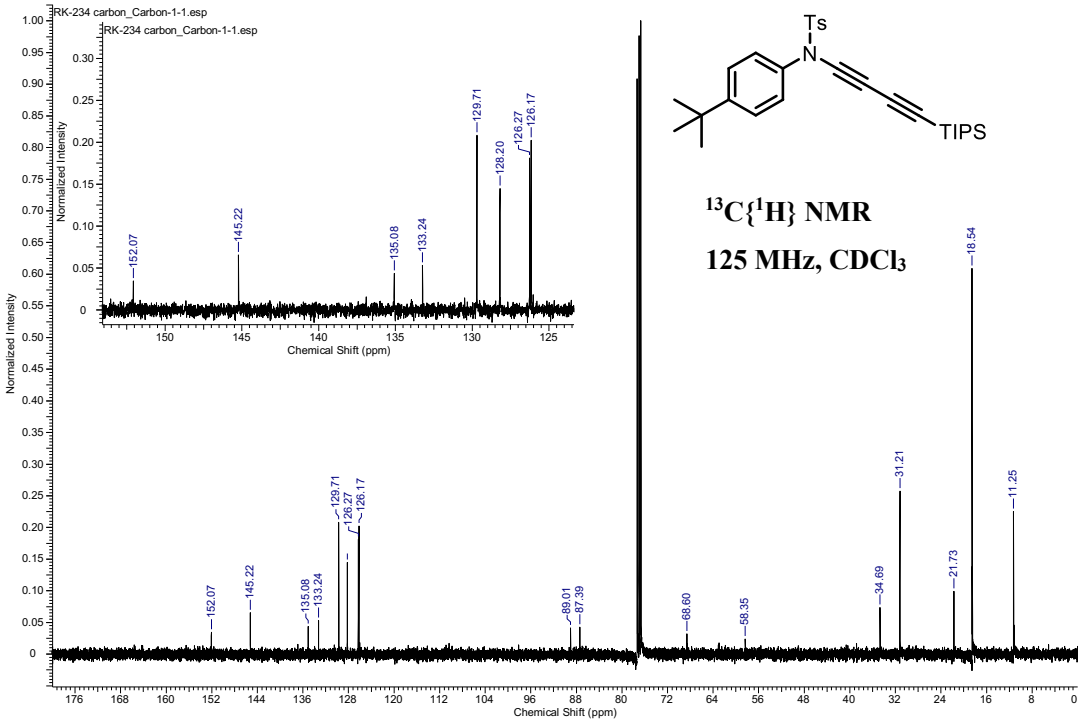
4-Methyl-*N*-(4-methylphenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6h)



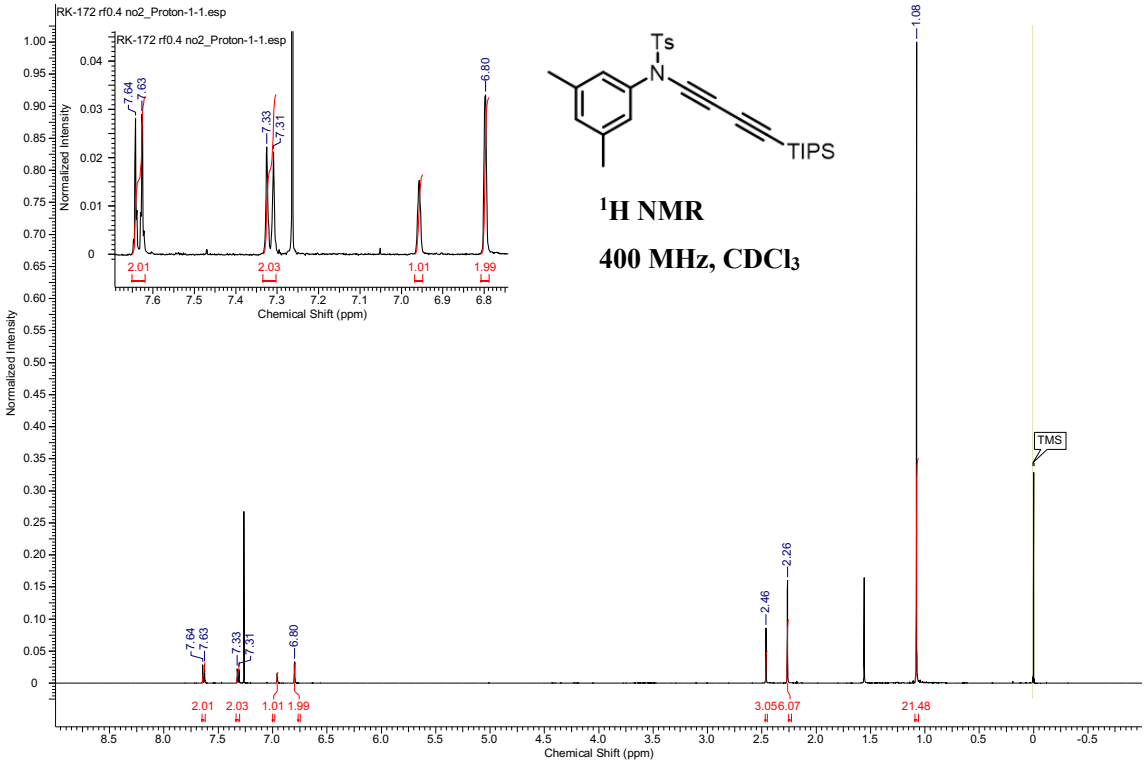


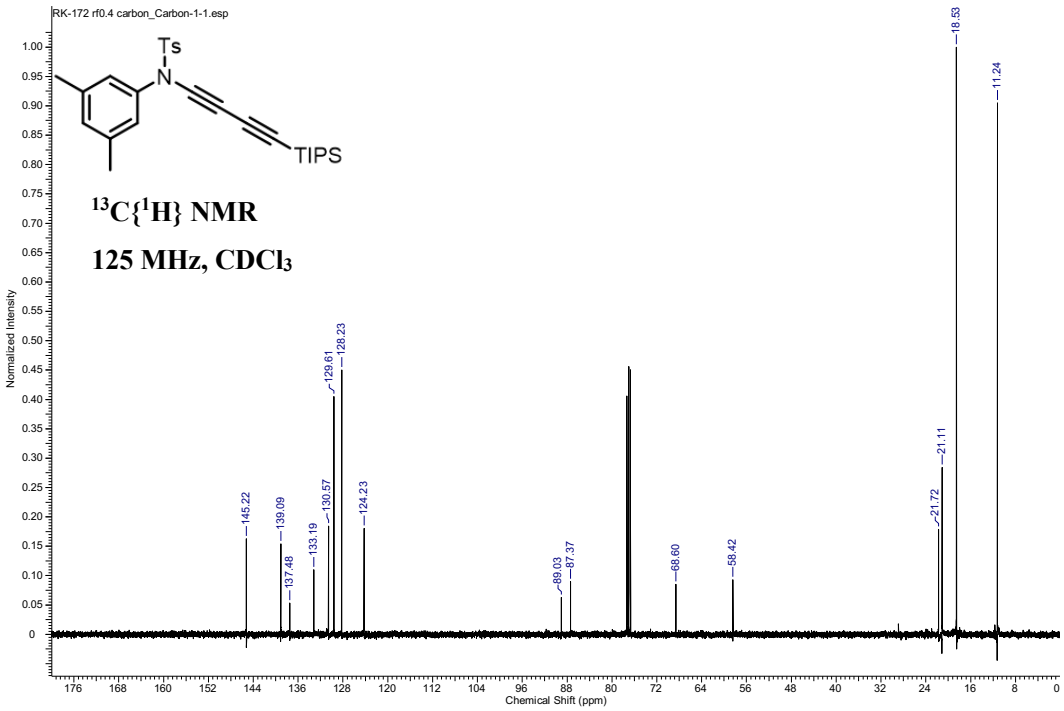
4-Methyl-*N*-[4-(1,1-dimethylethyl)phenyl]-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6i)



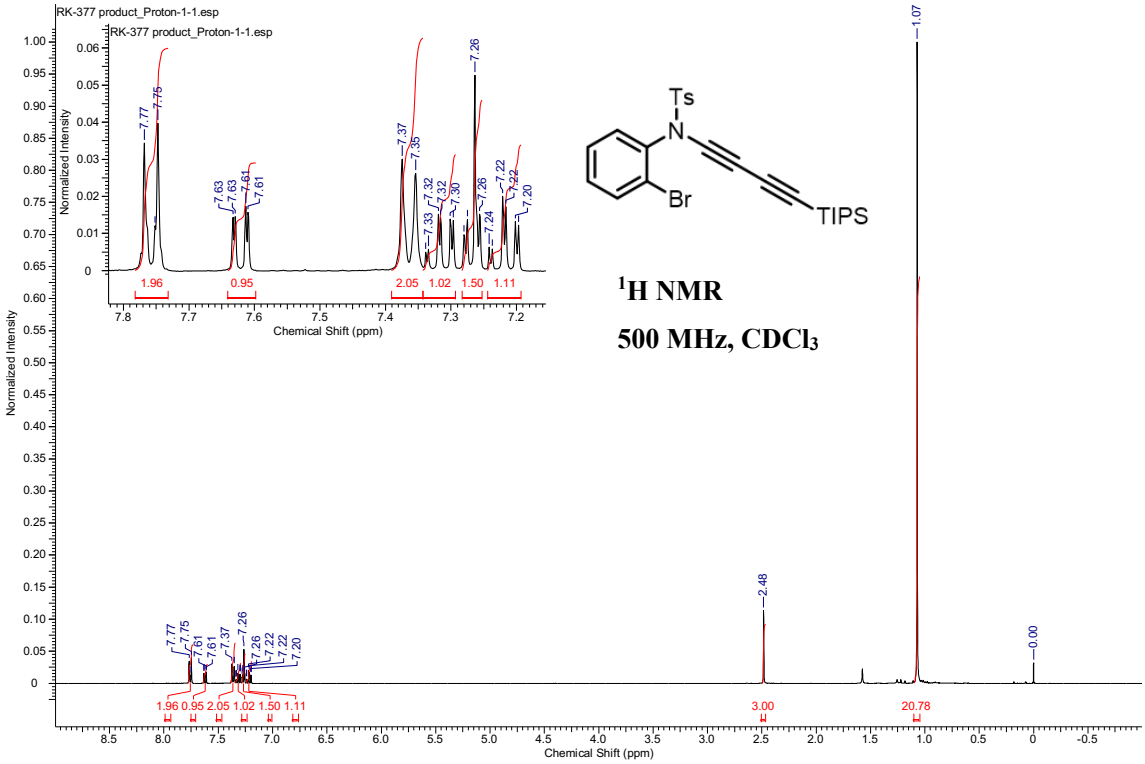


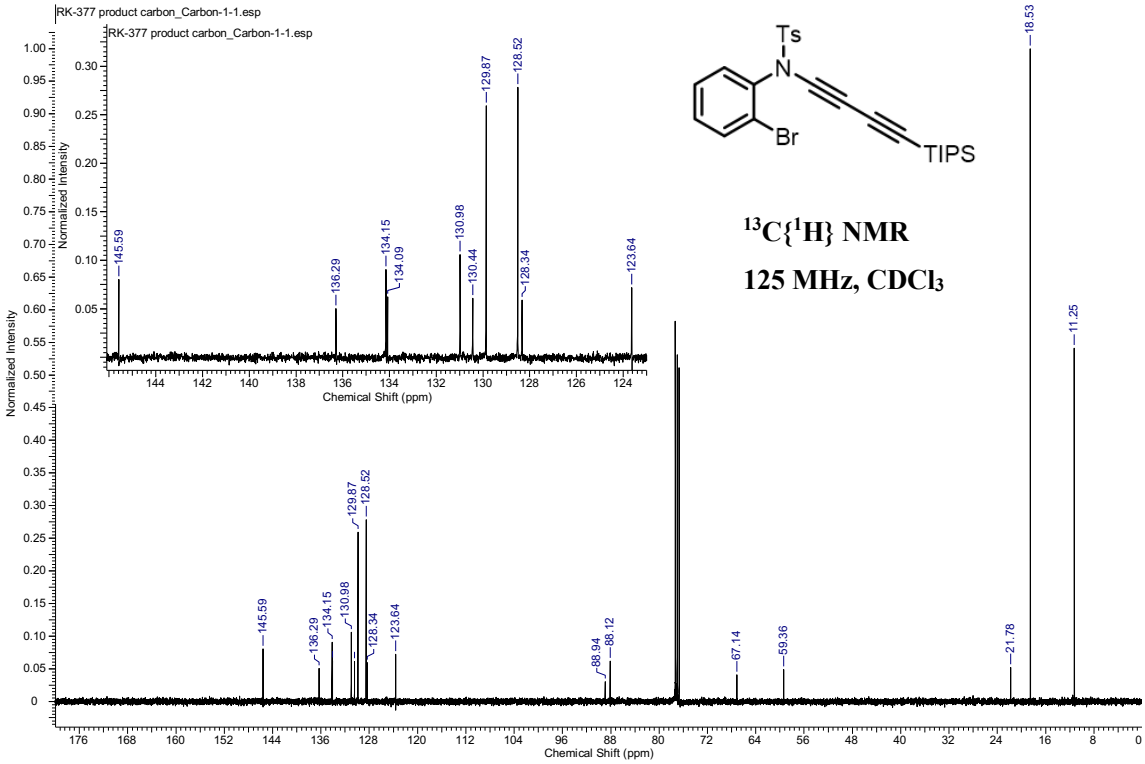
4-Methyl-*N*-(3,5-dimethylphenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6j)



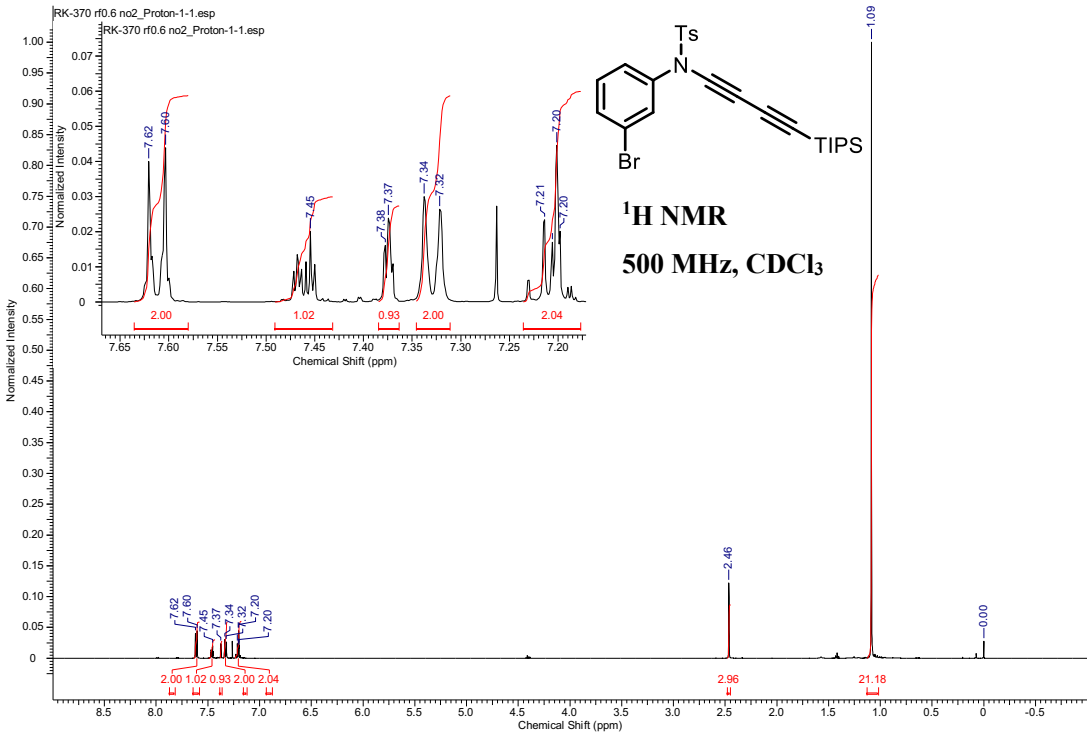


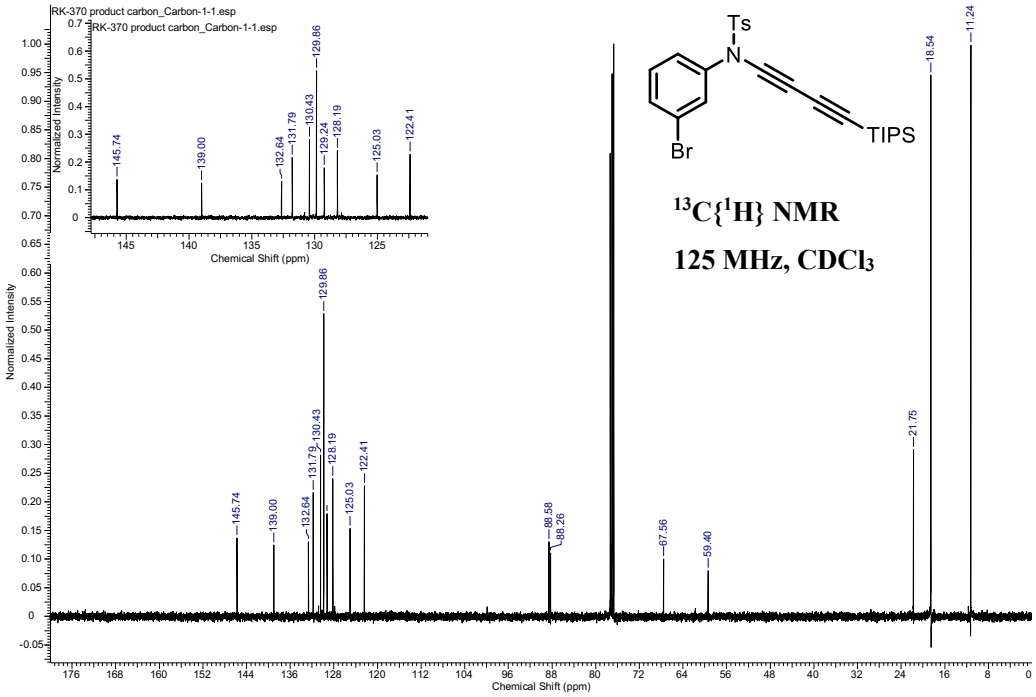
4-Methyl-*N*-(2-bromophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6k)



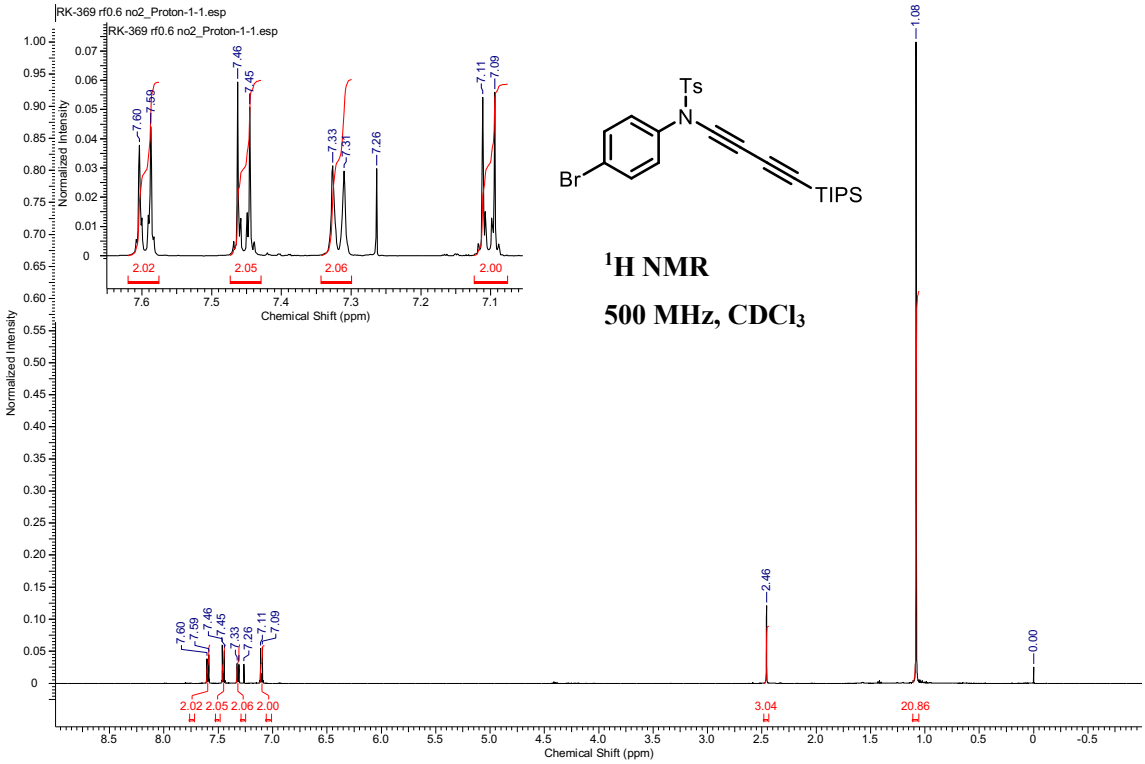


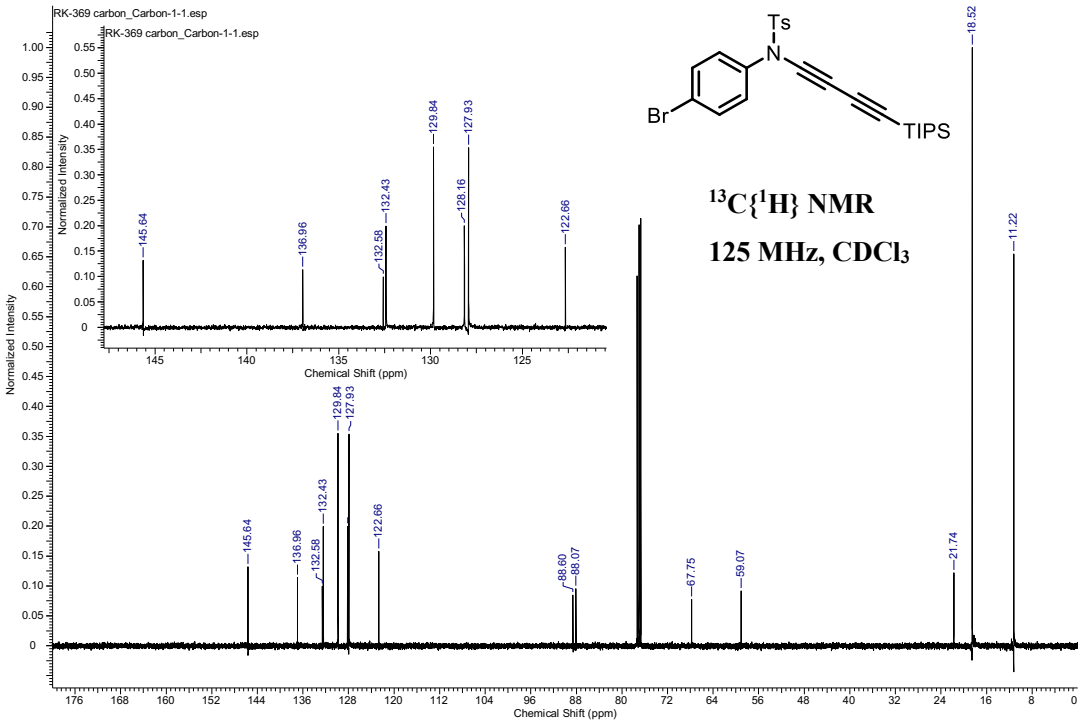
4-Methyl-*N*-(3-bromophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6l)



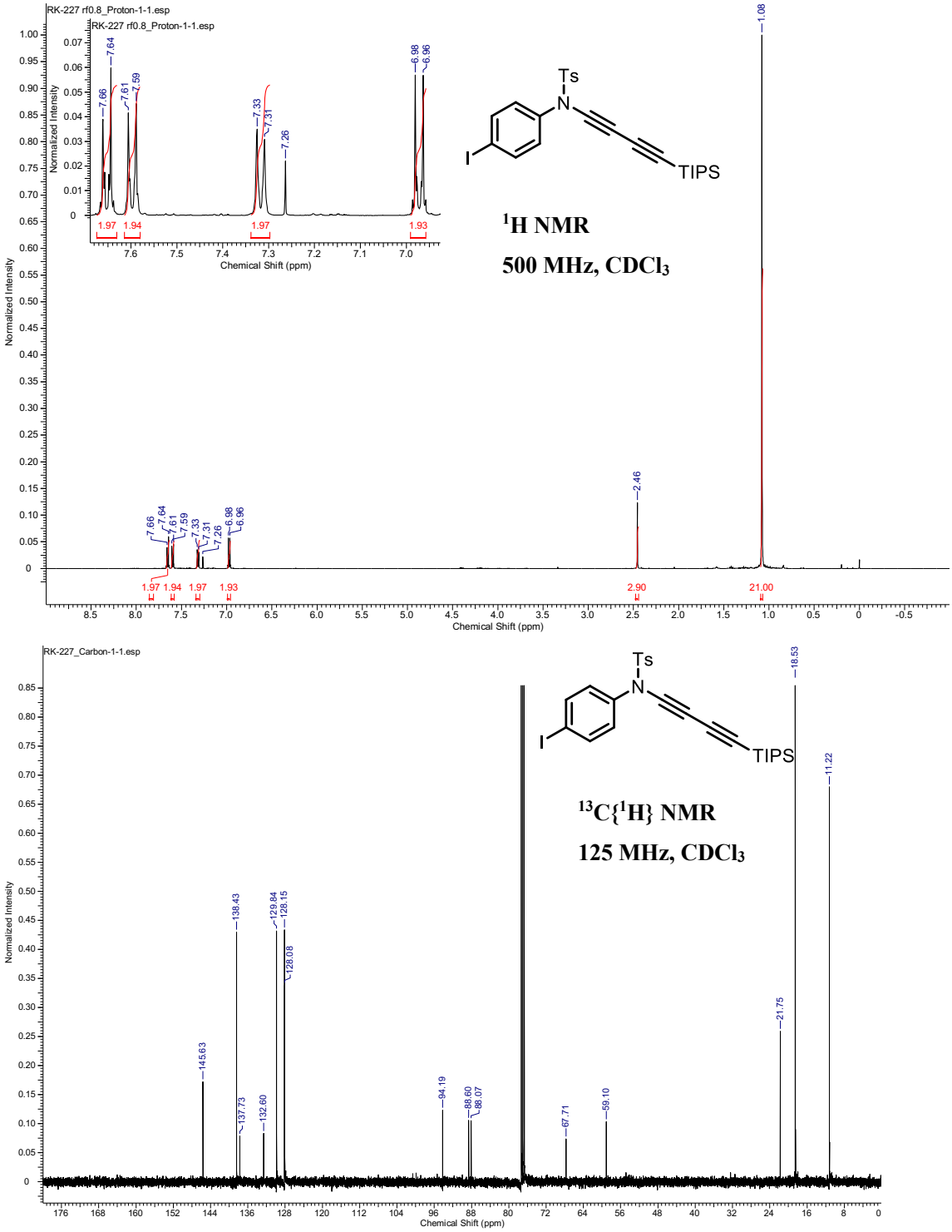


4-Methyl-*N*-(4-bromophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6m)

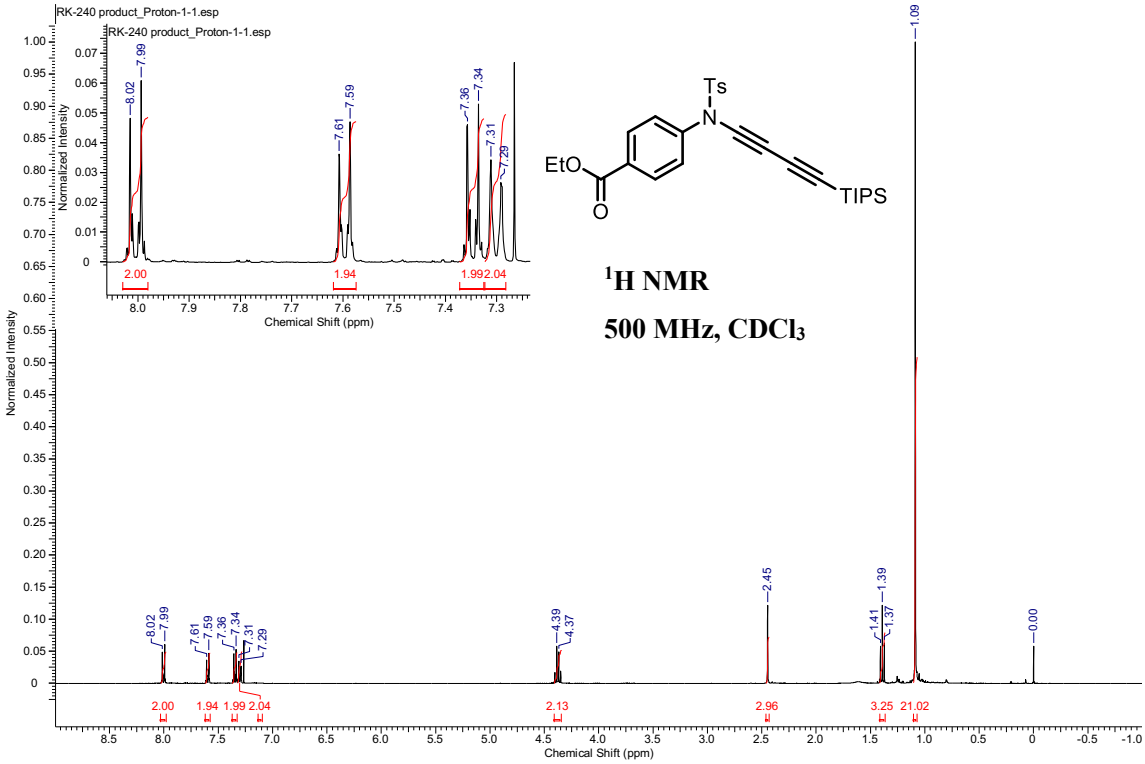


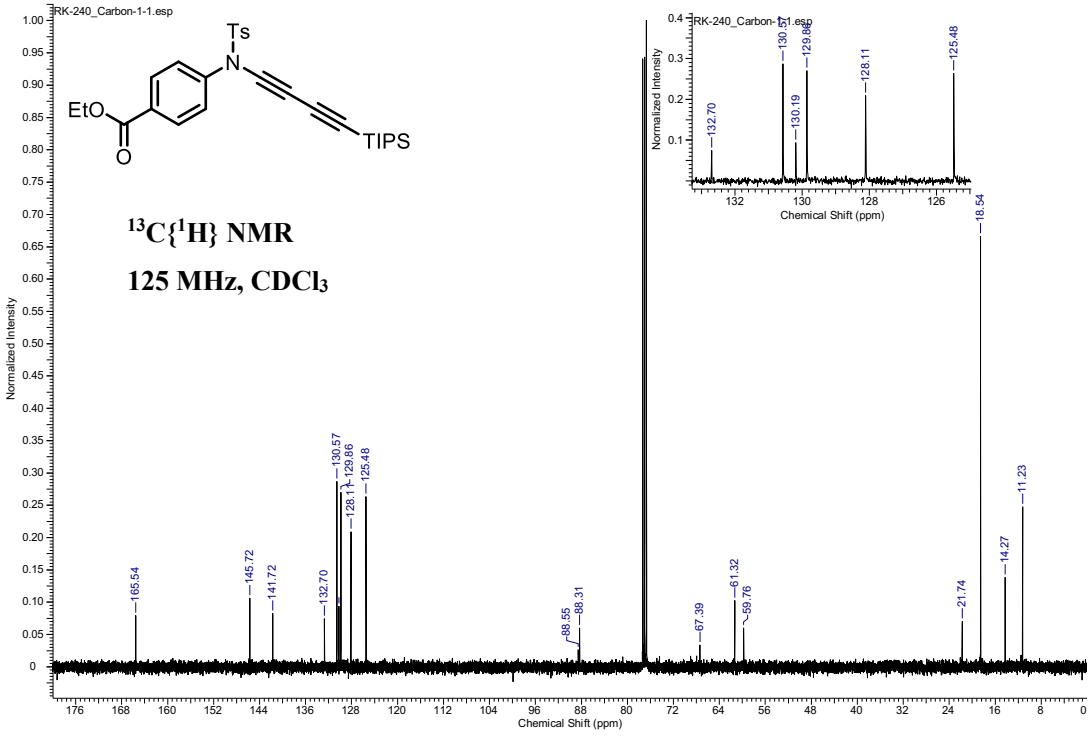


4-Methyl-*N*-(4-iodophenyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6n)

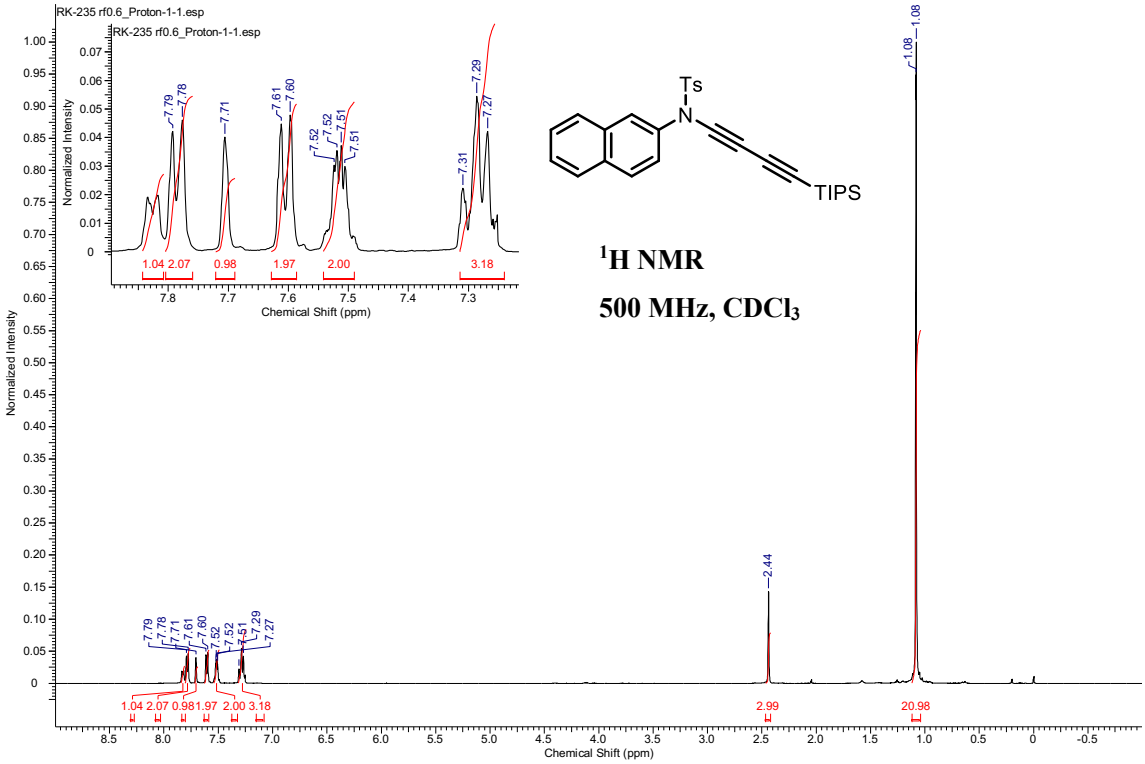


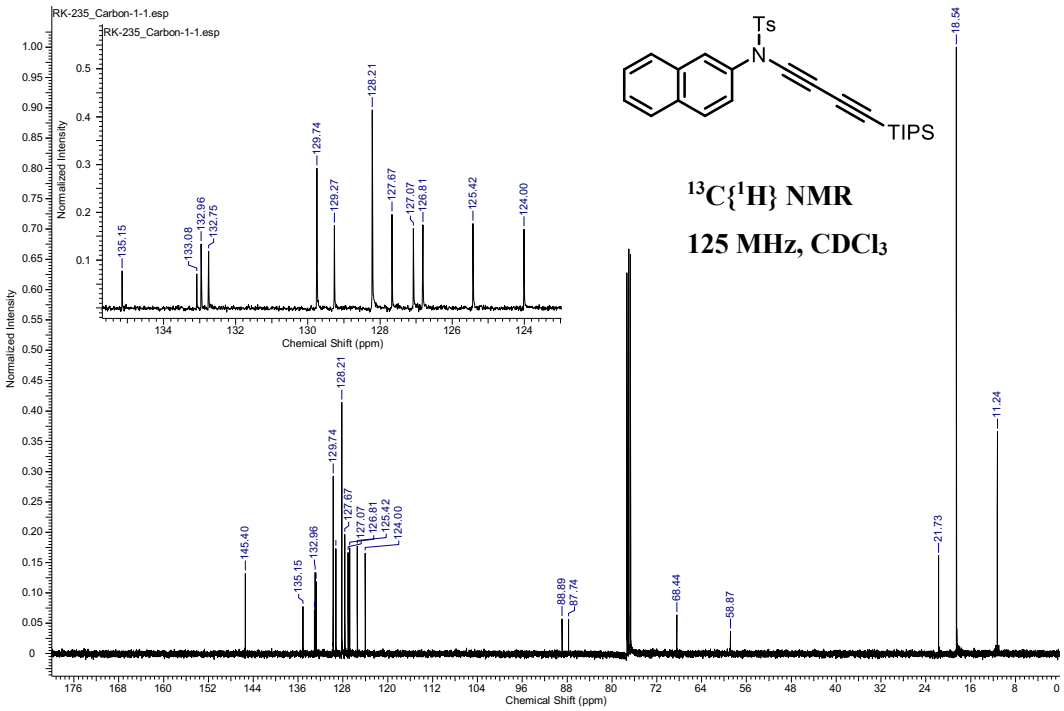
4-[[(4-Methylphenyl)sulfonyl][[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]]amino]ethylbenzoate (6o)



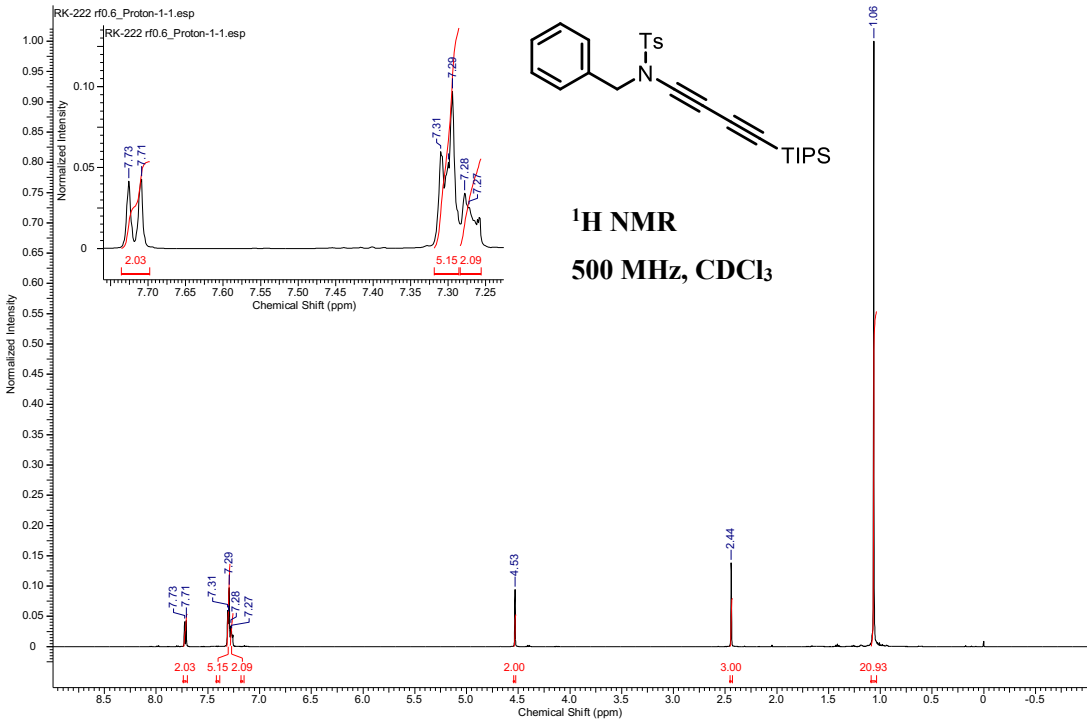


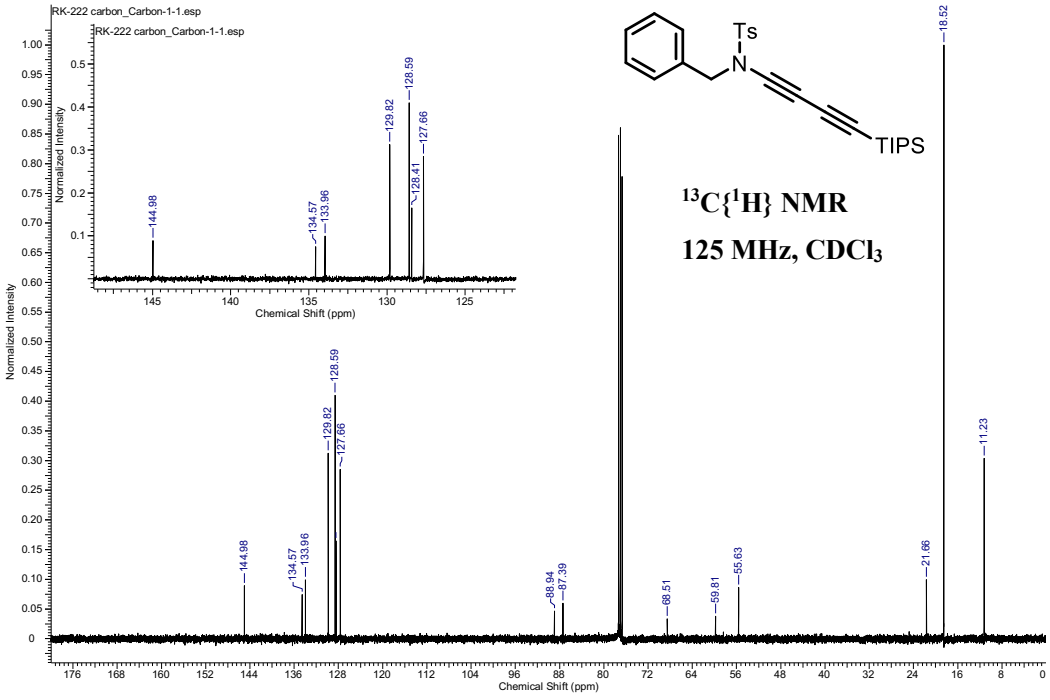
4-Methyl-*N*-naphthyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6p)



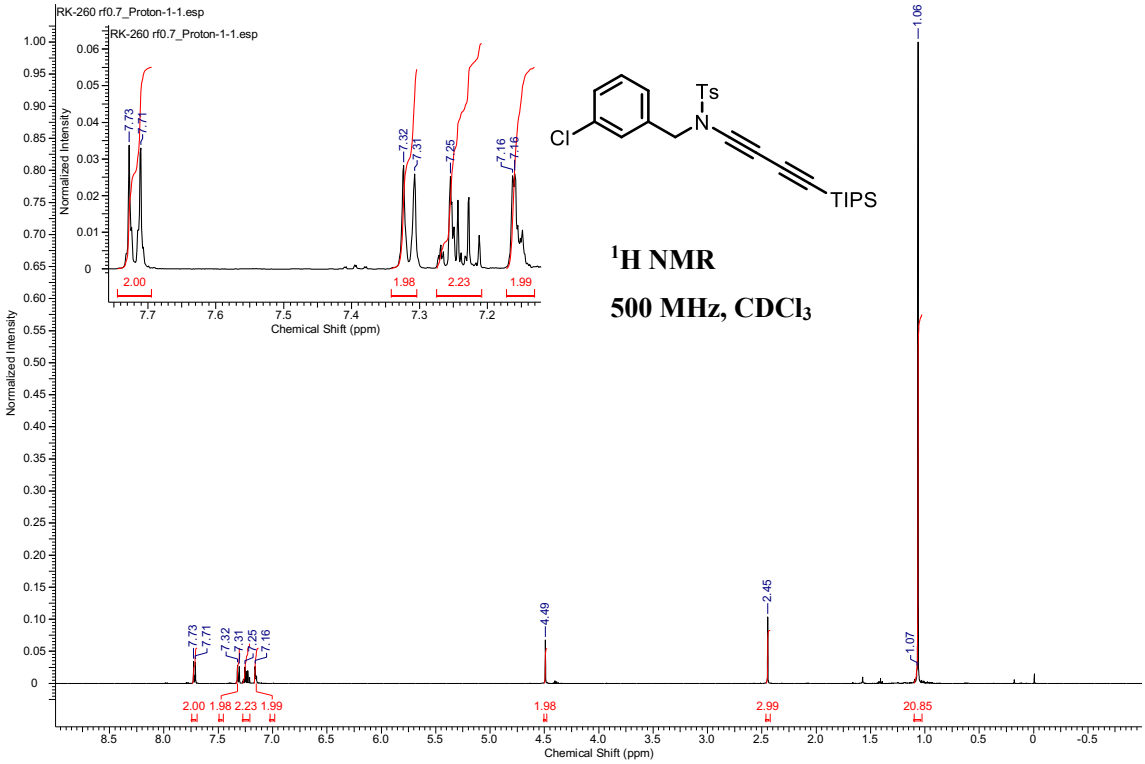


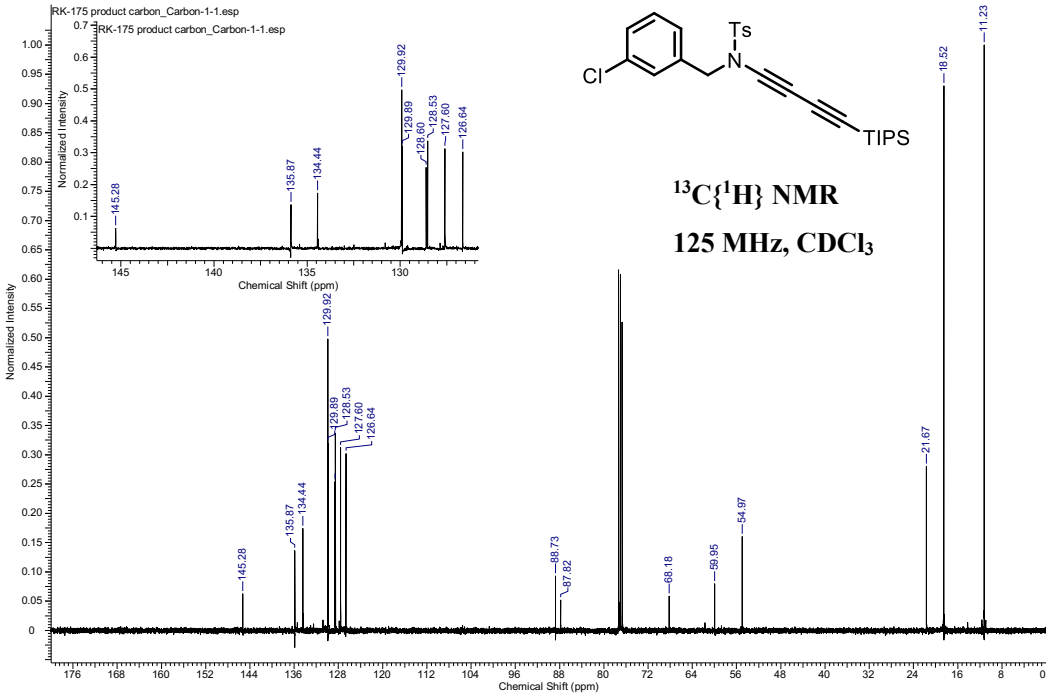
4-Methyl-*N*-phenylmethyl-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6q)



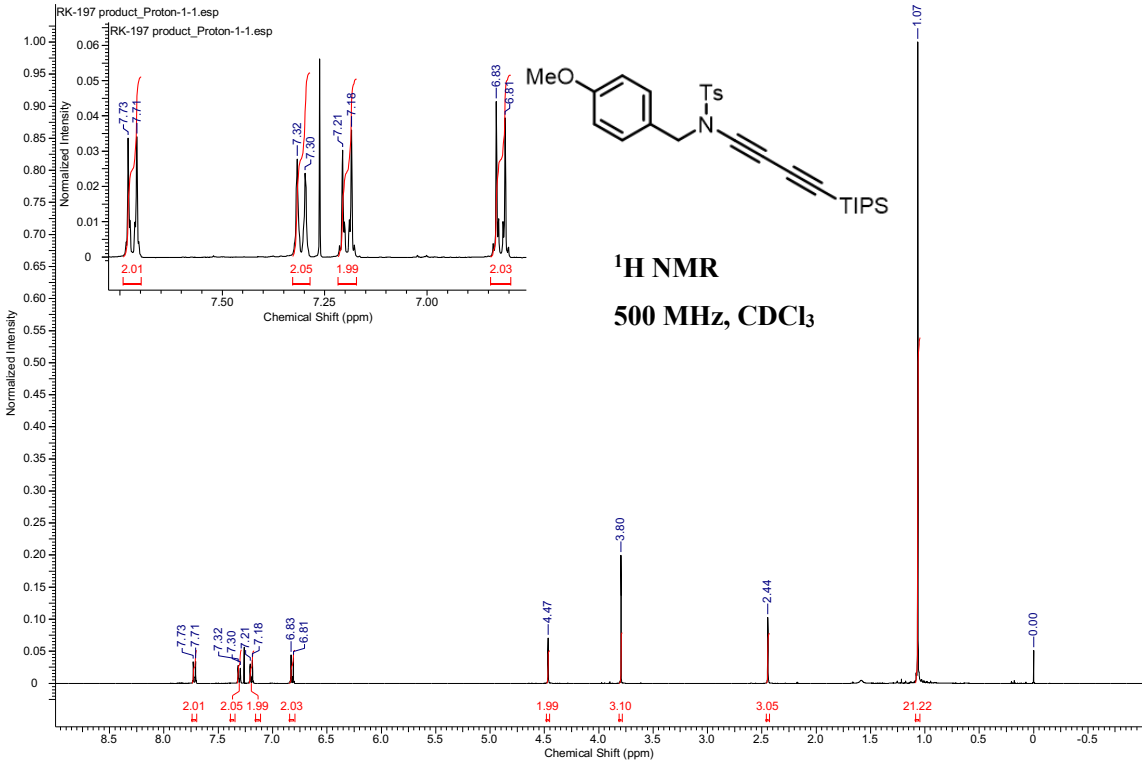


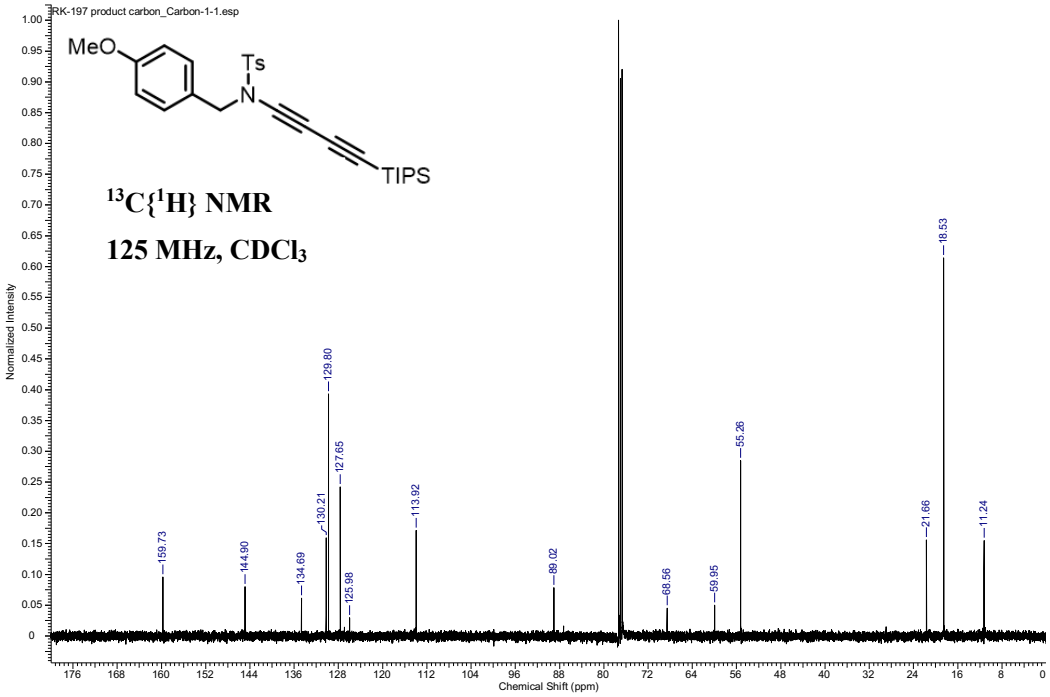
4-Methyl-*N*-[(3-chlorophenyl)methyl]-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6r)



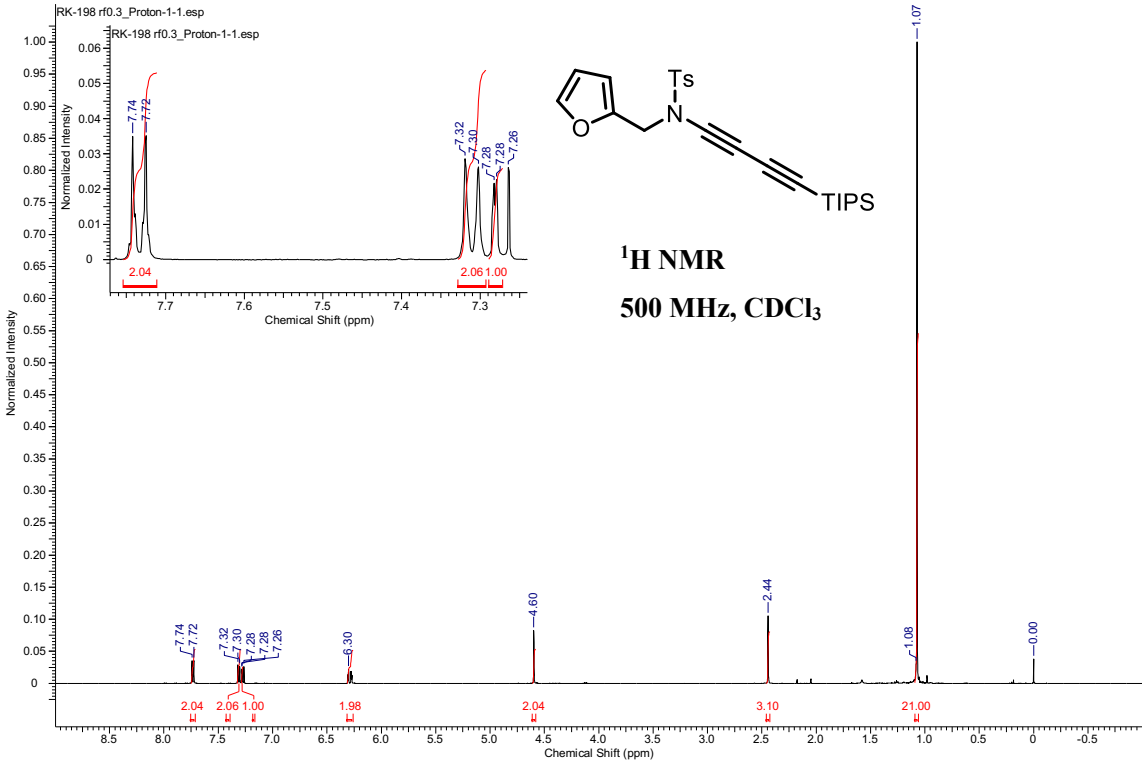


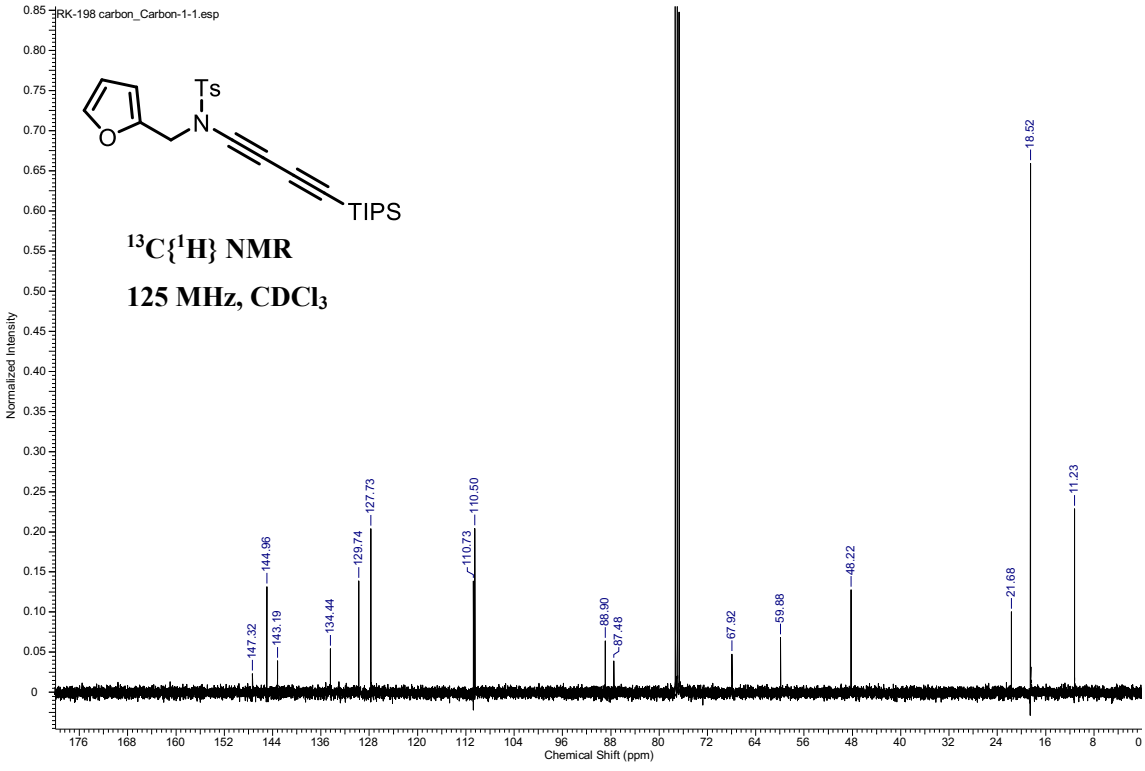
4-Methyl-*N*-[(4-methoxyphenyl)methyl]-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6s)



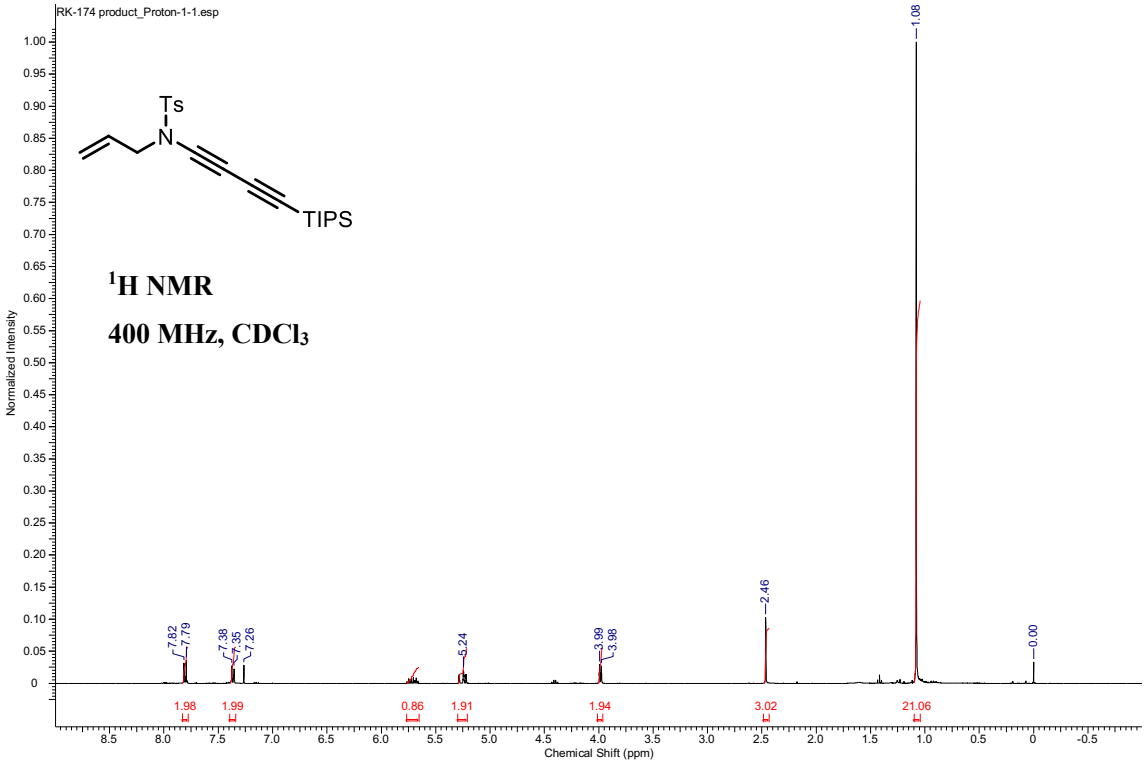


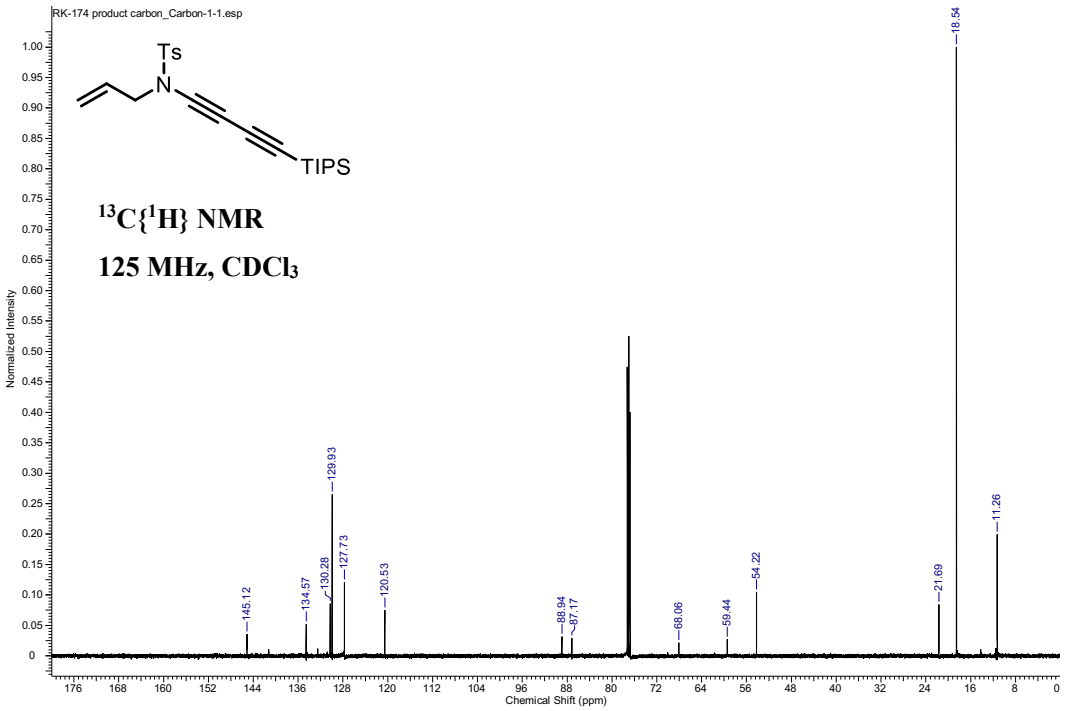
4-Methyl-*N*-(2-furanylmethyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6t)



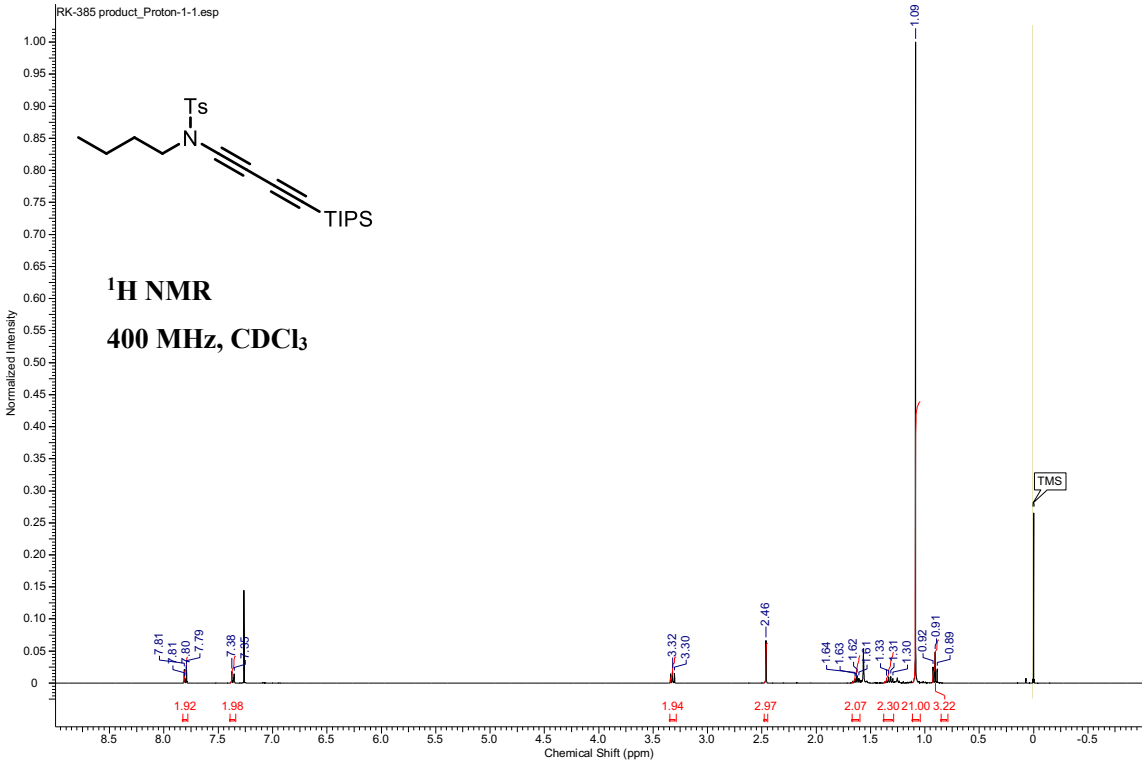


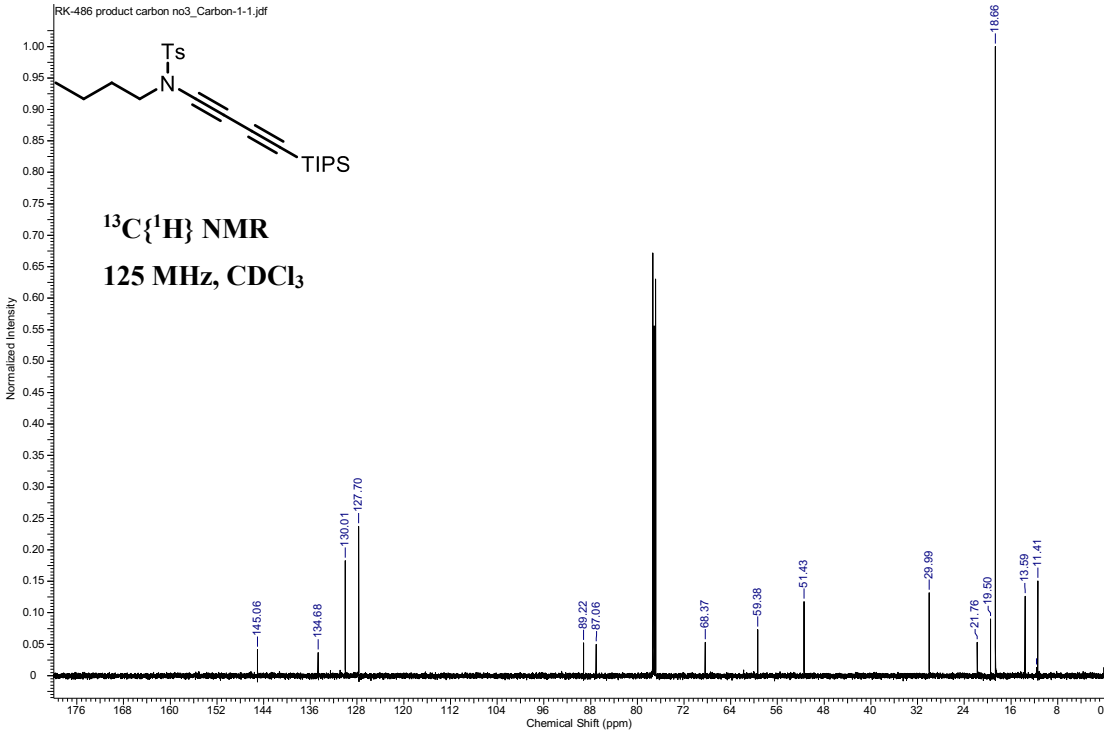
4-Methyl-*N*-(2-propen-1-yl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6u)



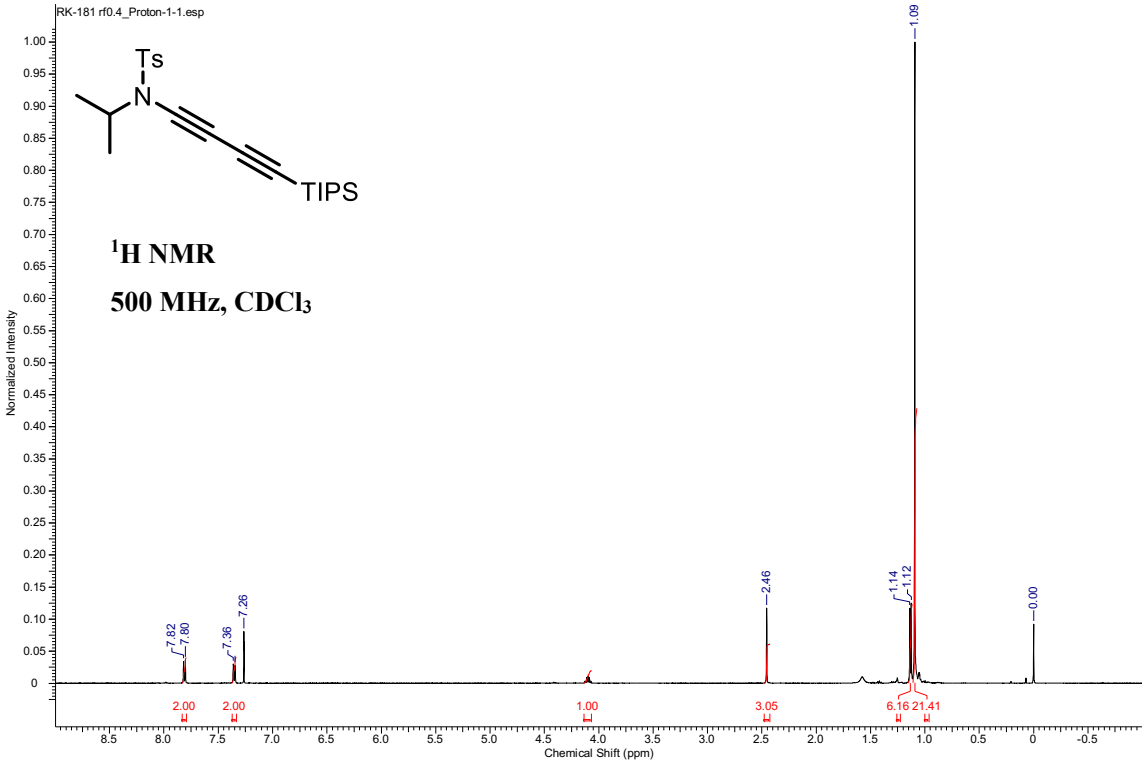


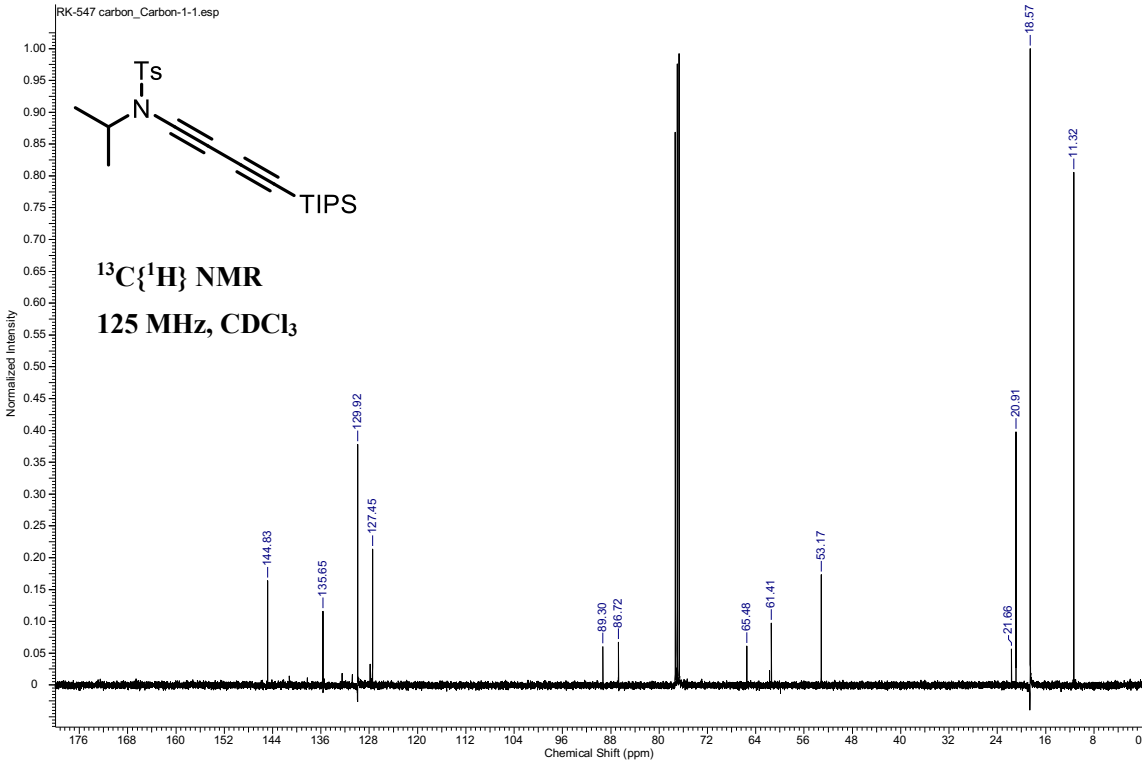
4-Methyl-*N*-(1-buthyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-benzenesulfonamide (6v)



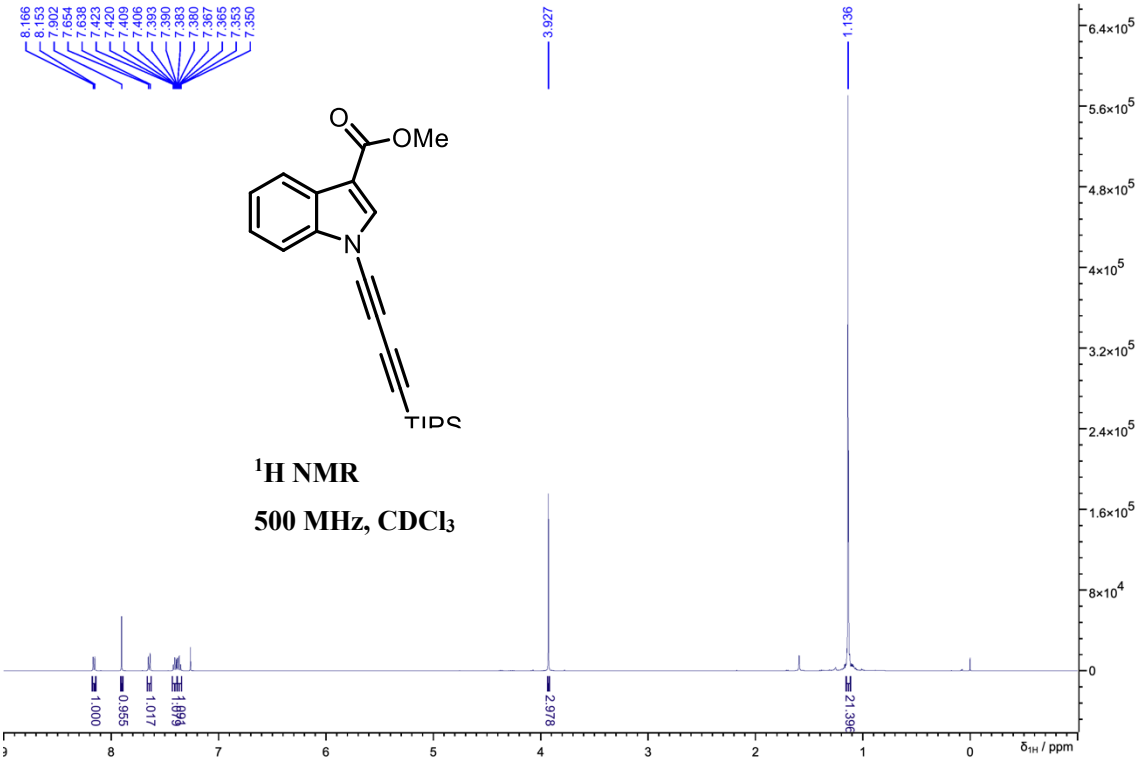


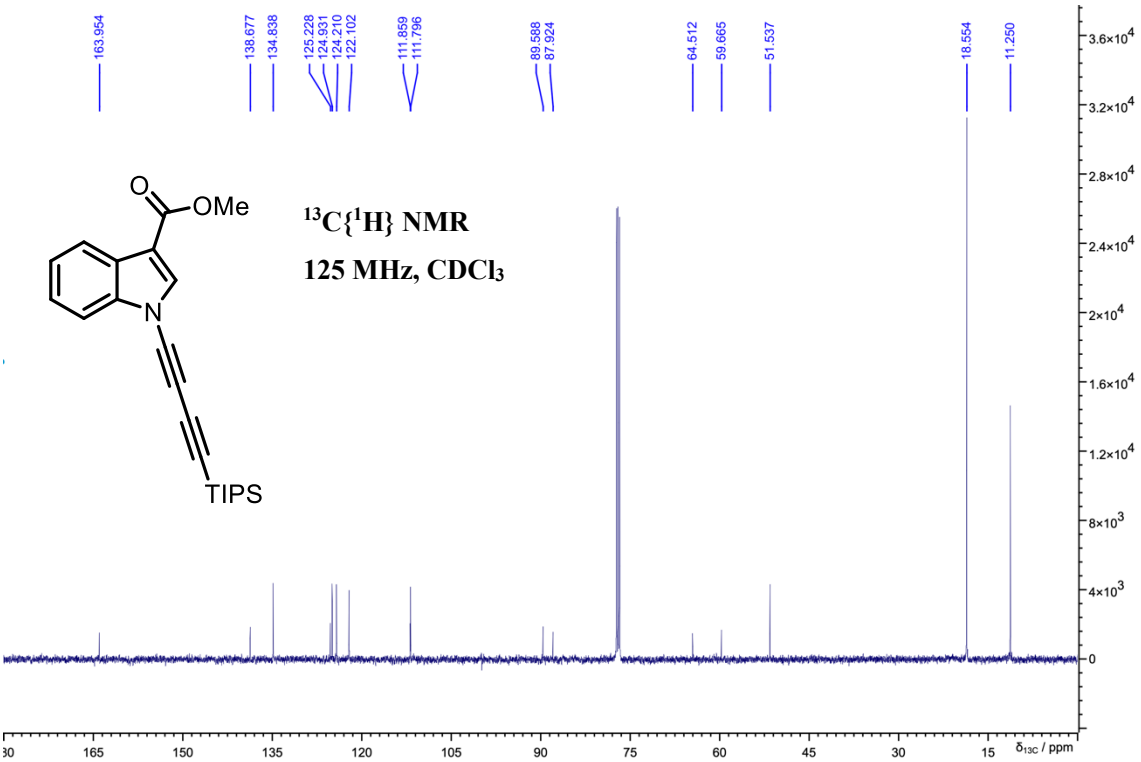
4-Methyl-*N*-(1-methylethyl)-*N*-[4-[tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl] benzenesulfonamide (6w)



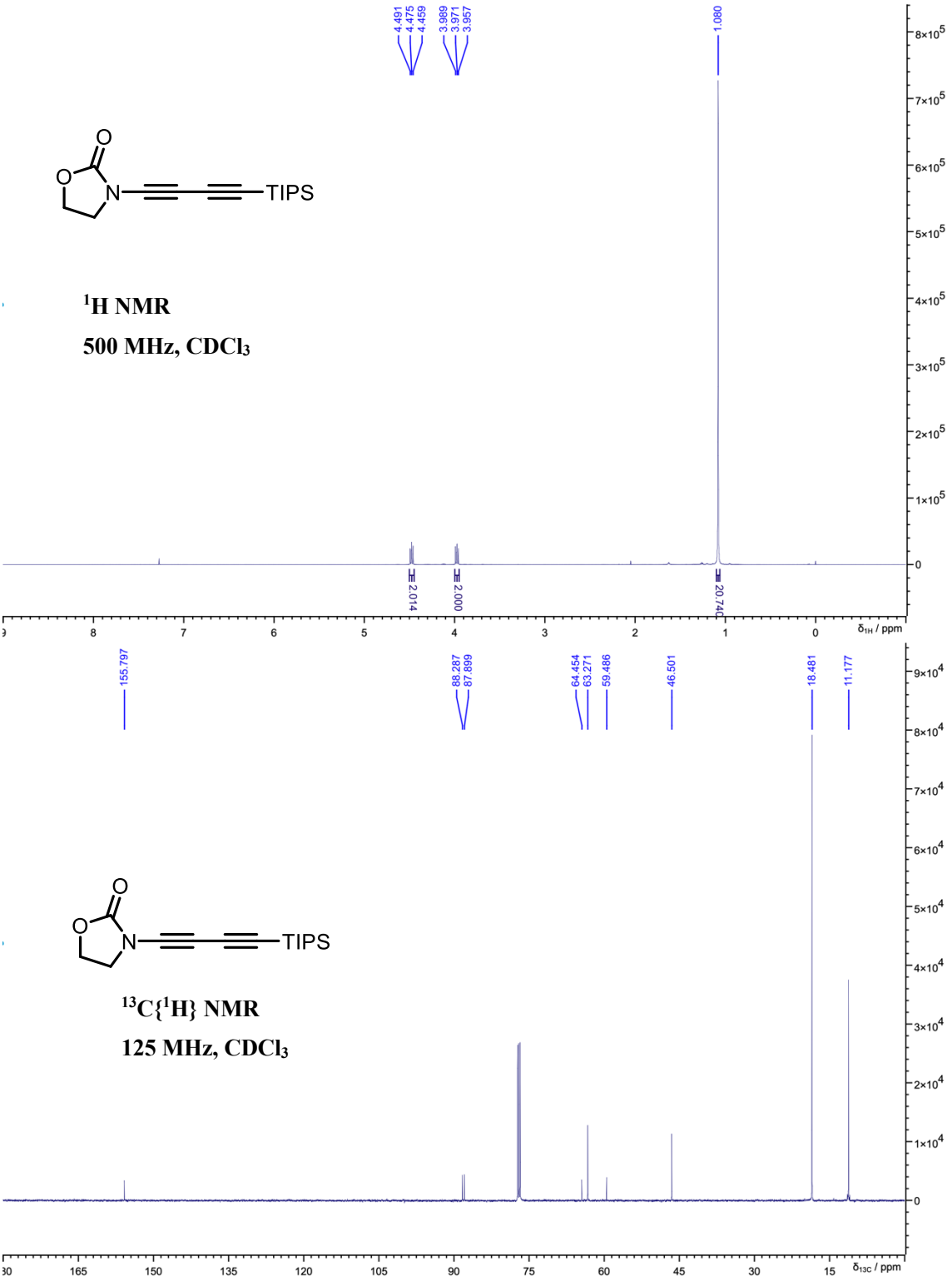


1-[4-[Tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-1*H*-indole-3-carboxylic acid methyl ester (6x)





3-[4-[Tris(1-methylethyl)silyl]-1,3-butadiyn-1-yl]-2-oxazolidinone (6y)



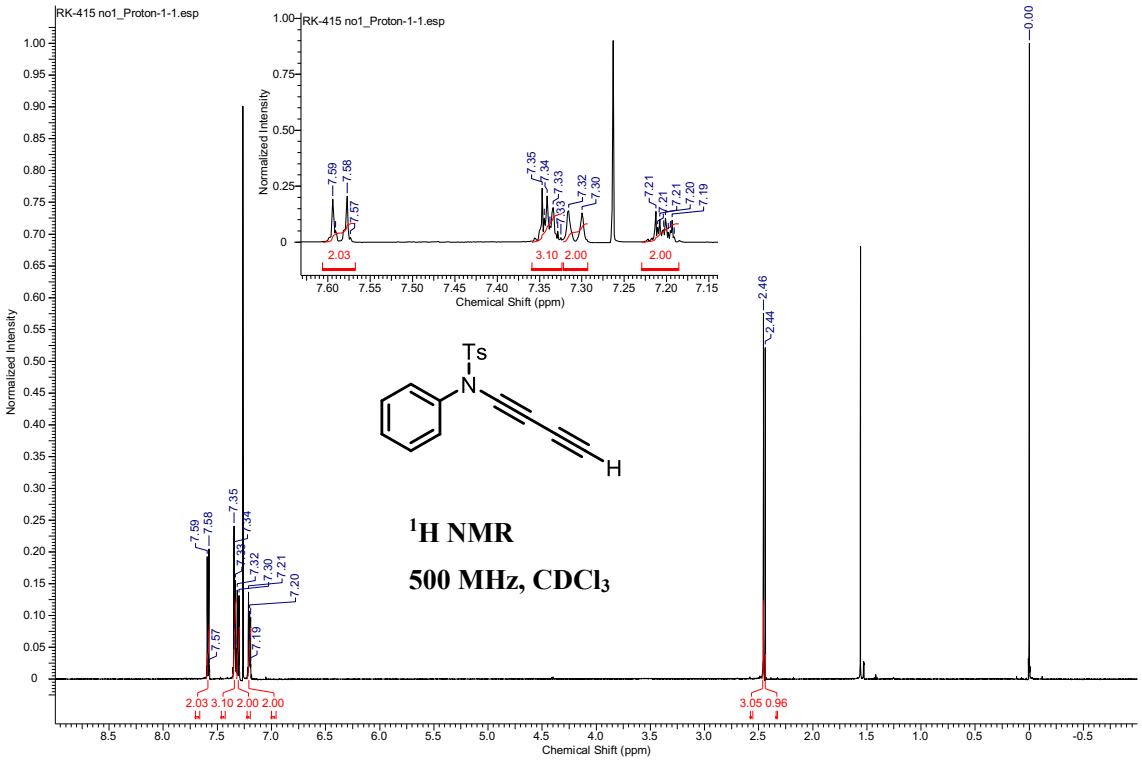
^{1}H NMR

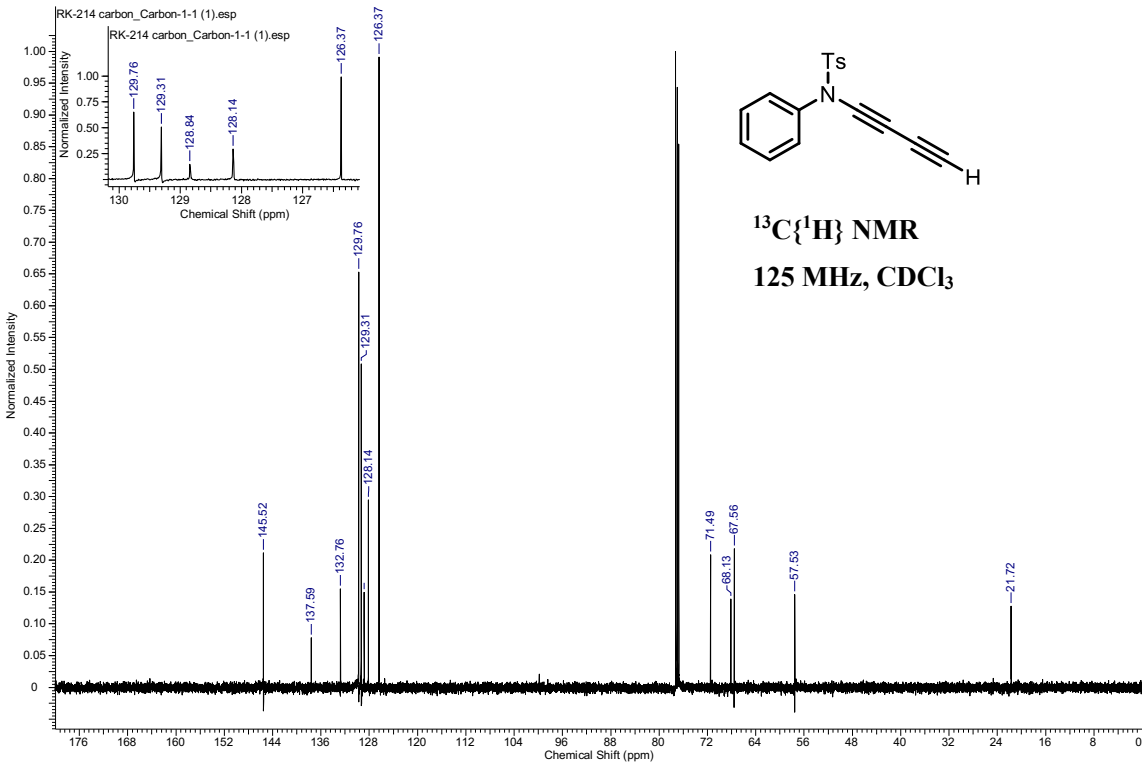
500 MHz, $CDCl_3$

$^{13}C\{^{1}H\}$ NMR

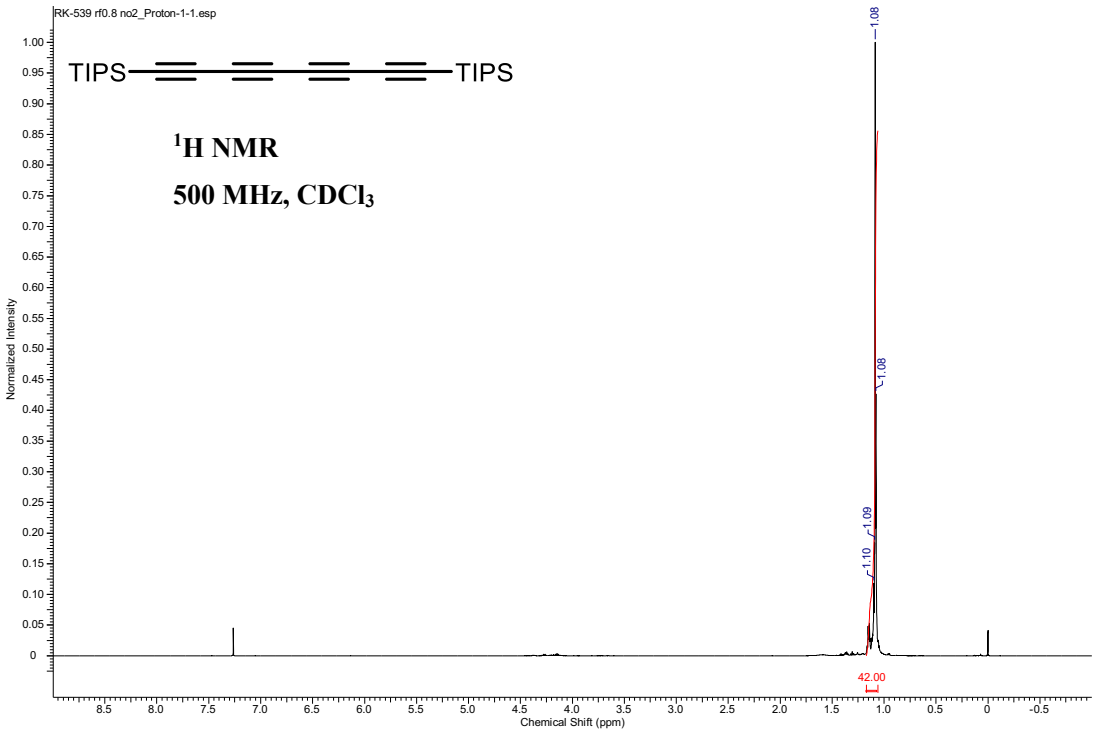
125 MHz, $CDCl_3$

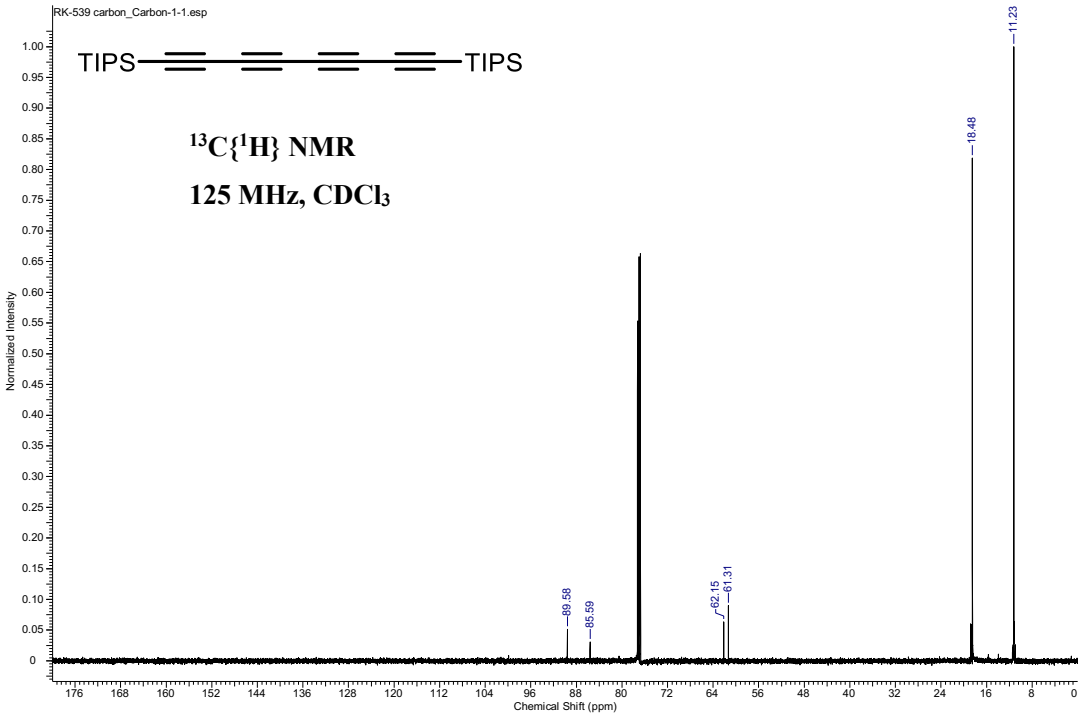
4-Methyl-*N*-phenyl-*N*-[4-(1,3-butadiyn-1-yl)]-benzenesulfonamide (6ab)



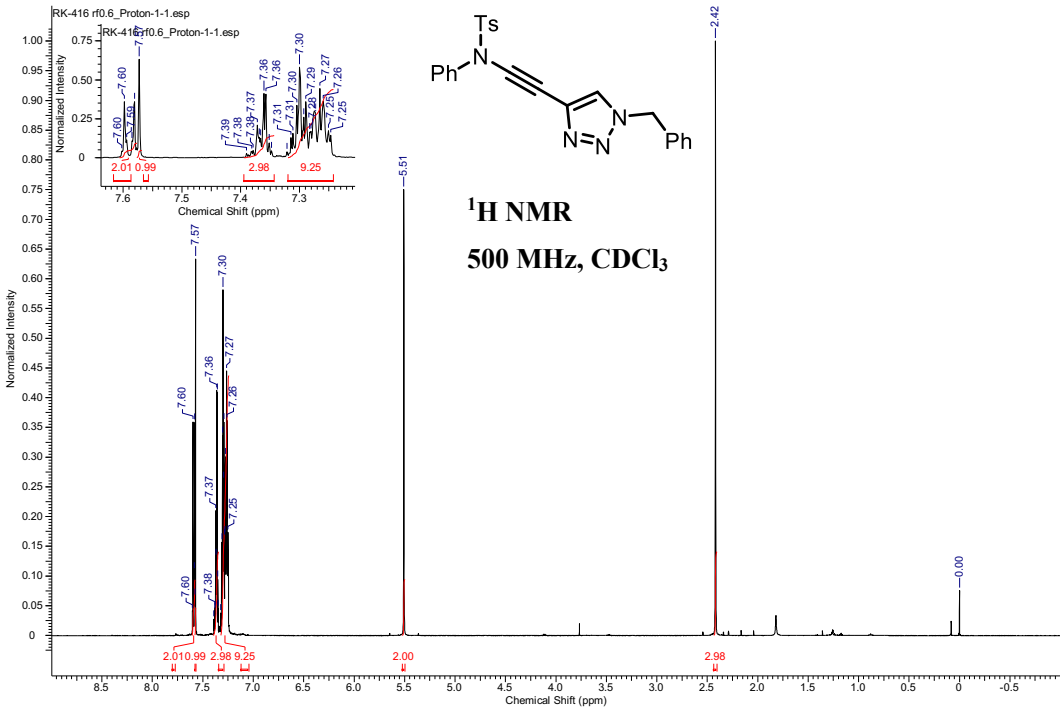


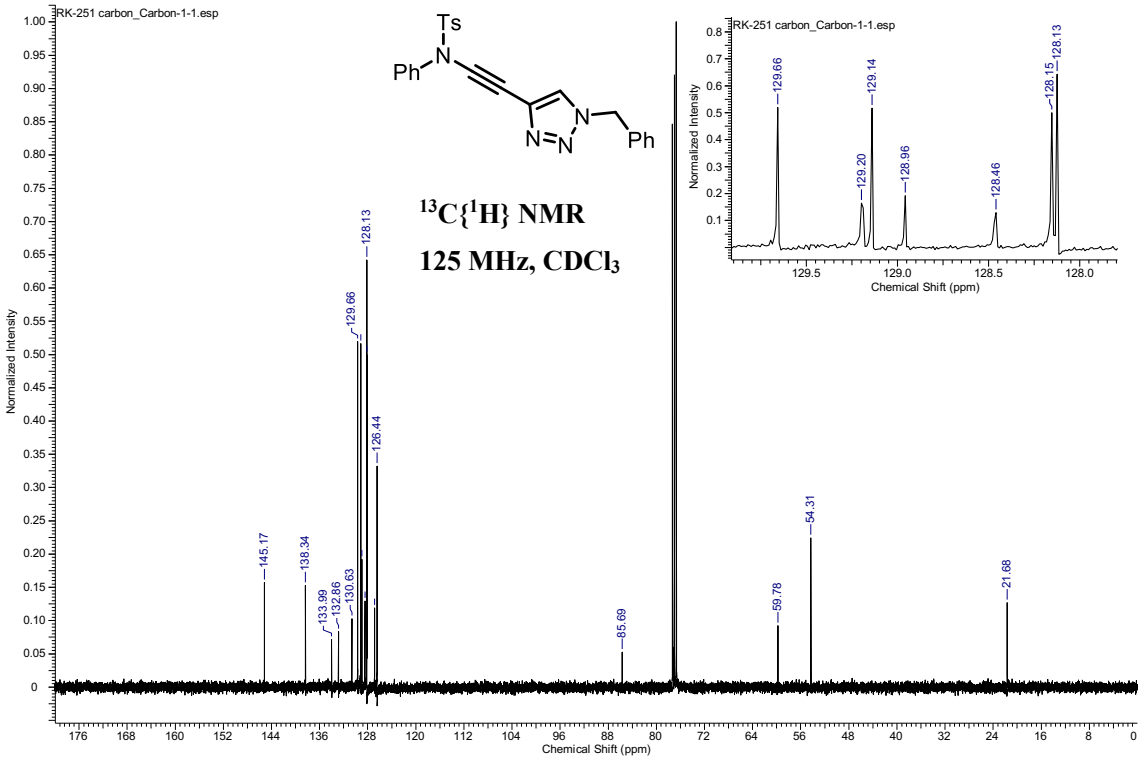
1,1′-(1,3,5,7-Octatetrayne-1,8-diyl)bis[1,1,1-tris(1-methylethyl)silane] (7)



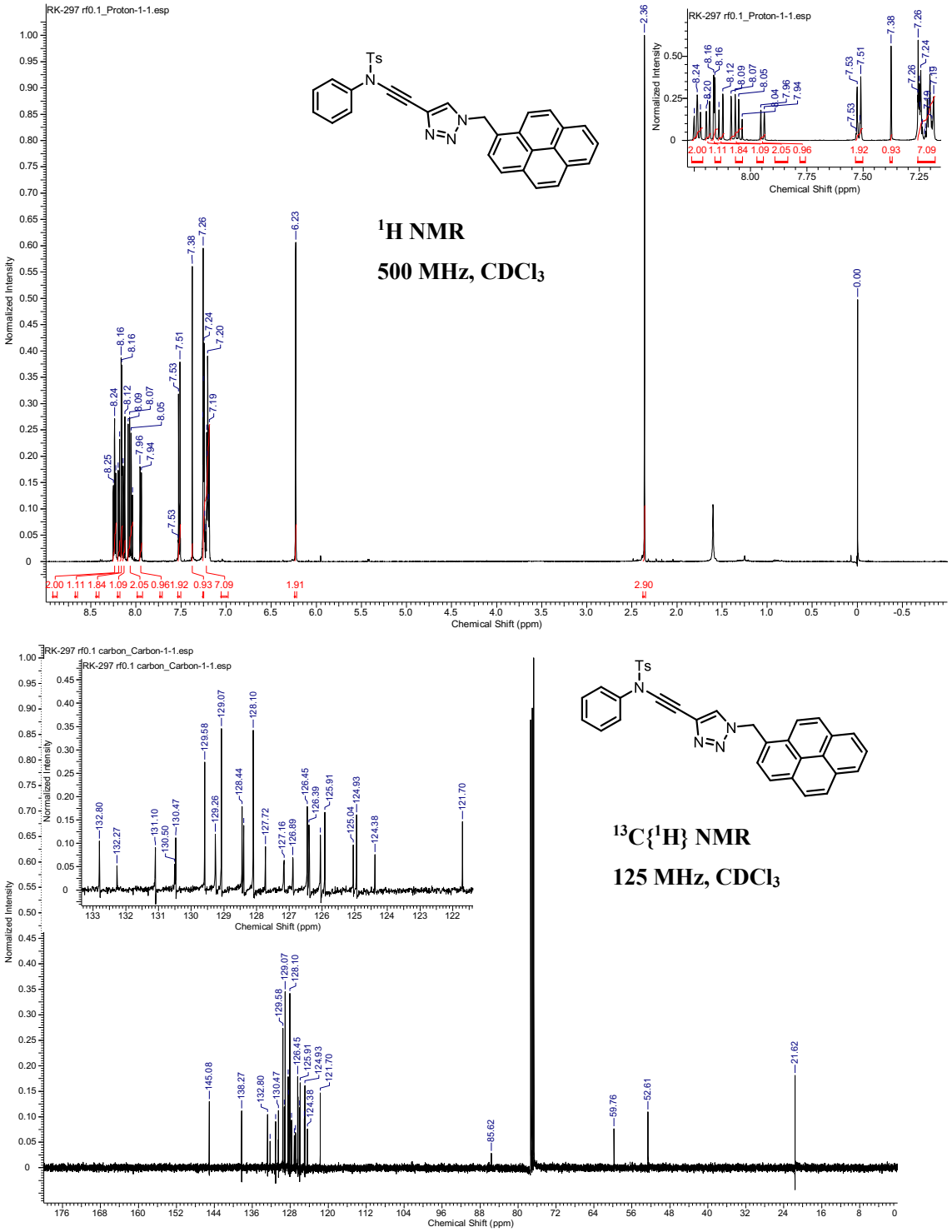


4-Methyl-*N*-phenyl-*N*-[[1-(phenylmethyl)-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10a)

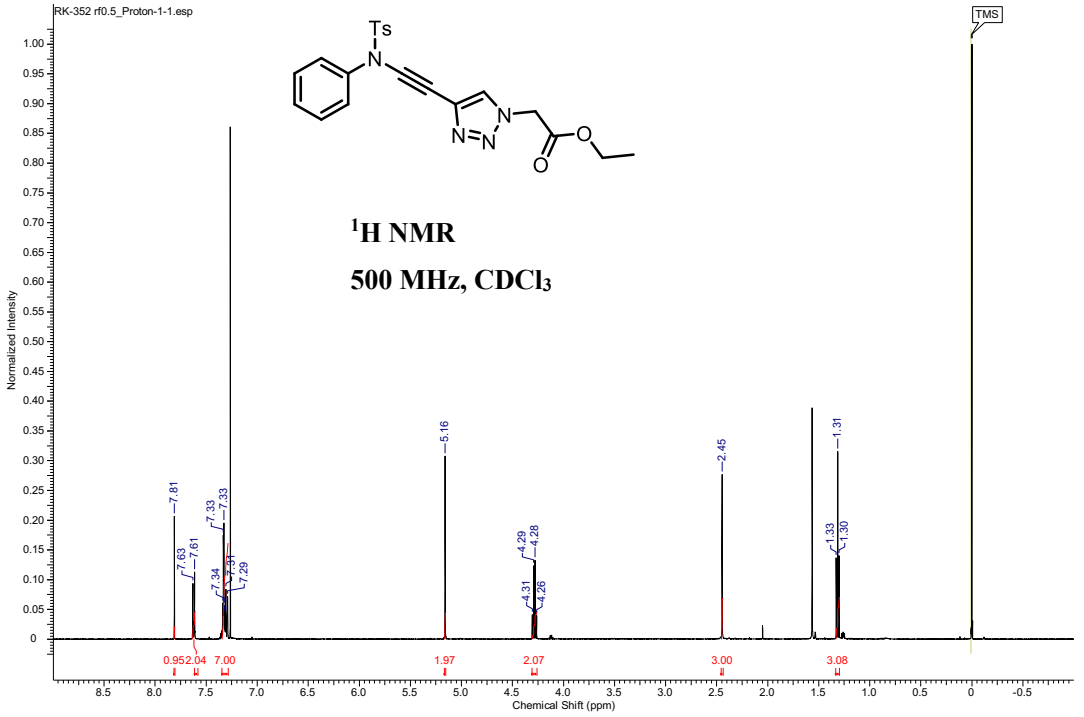


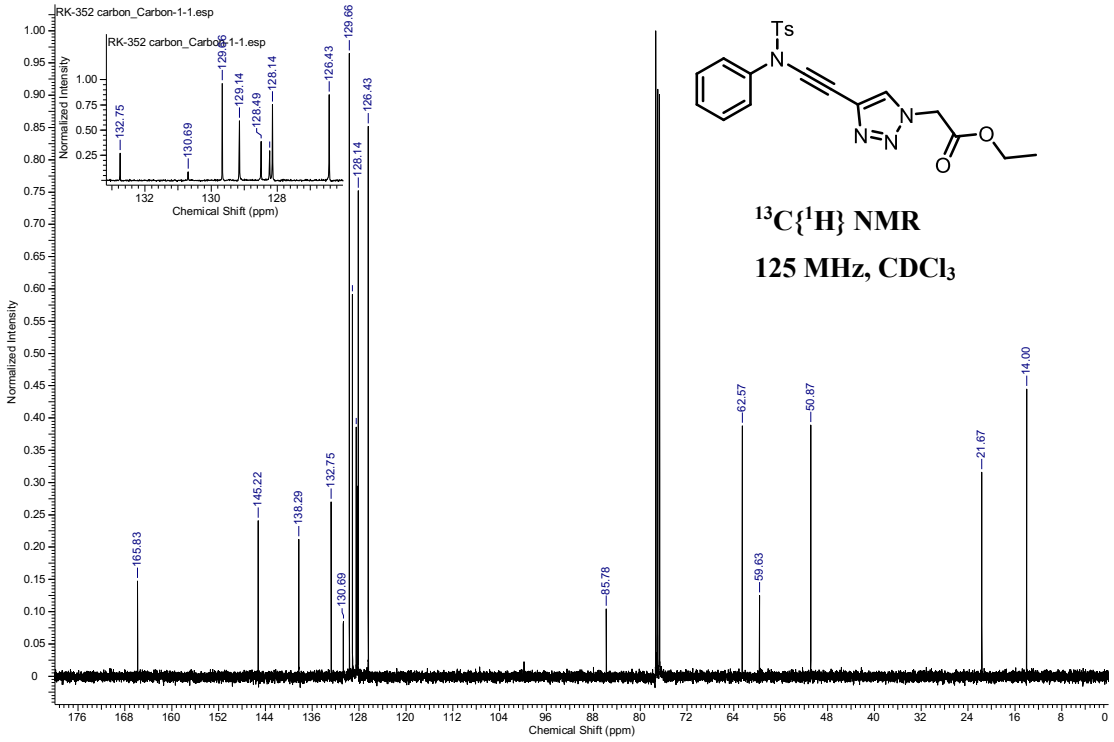


4-Methyl-*N*-phenyl-*N*-[[1-(pyrenemethyl)-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10b)

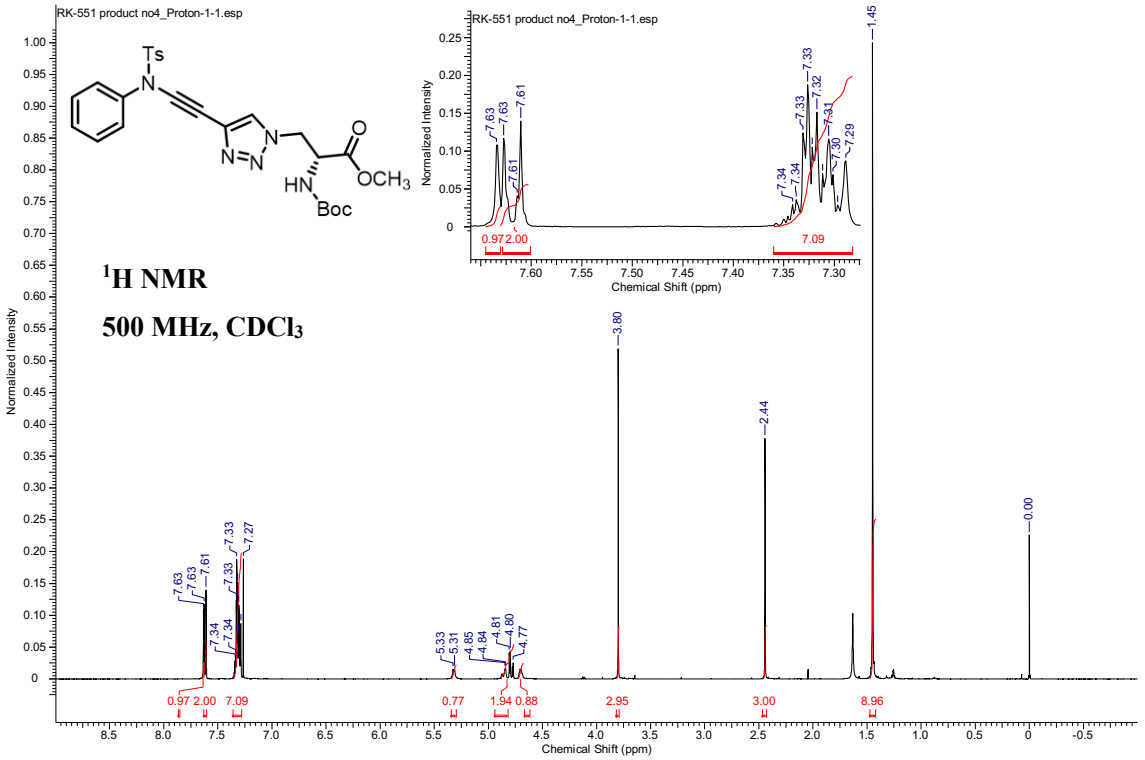


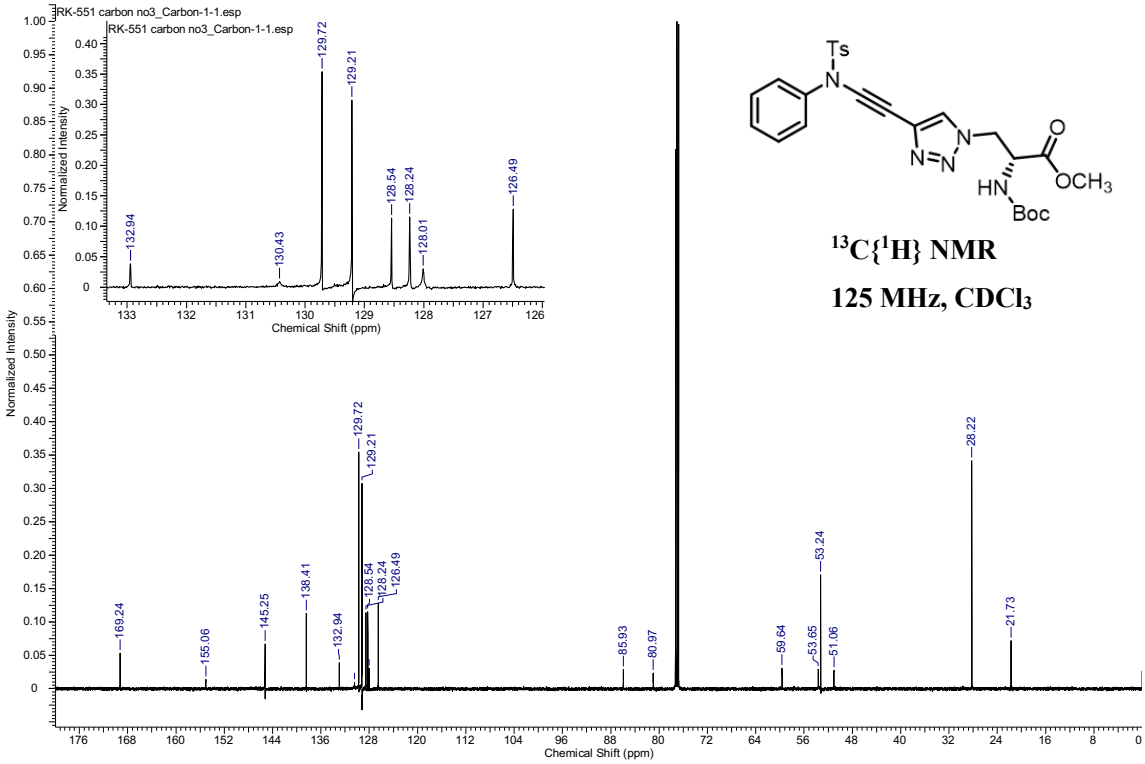
4-[[(4-phenyl)[(4-methylphenyl)sulfonyl]amino]ethynyl]-1H-1,2,3-Triazole-1-acetic acid ethyl ester (10c)



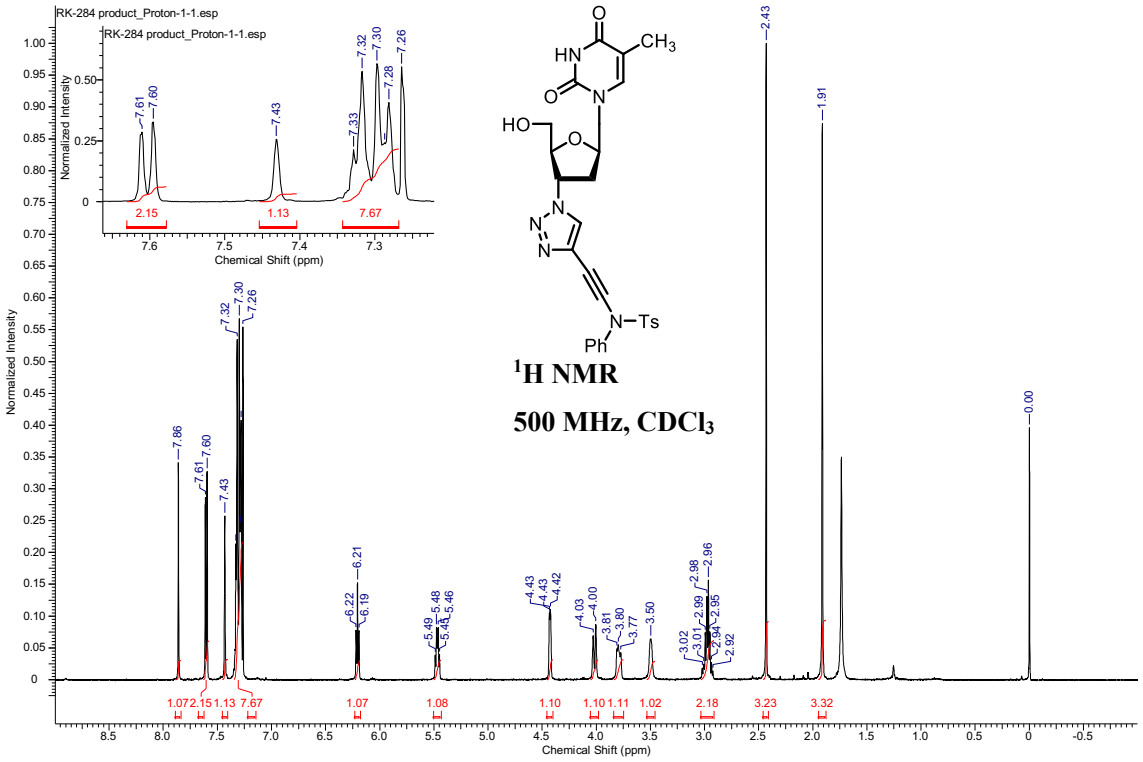


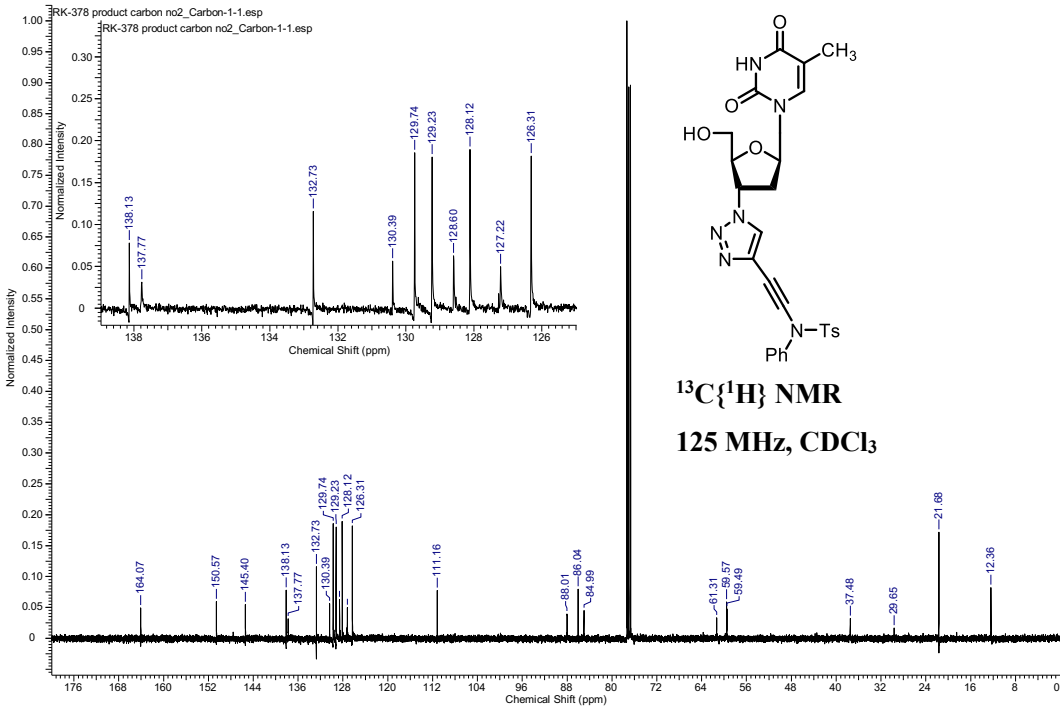
4-Methyl-*N*-phenyl-*N*-[[*N*-(*tert*-butoxycarbonyl)-D-alanine methyl ester]-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10d)



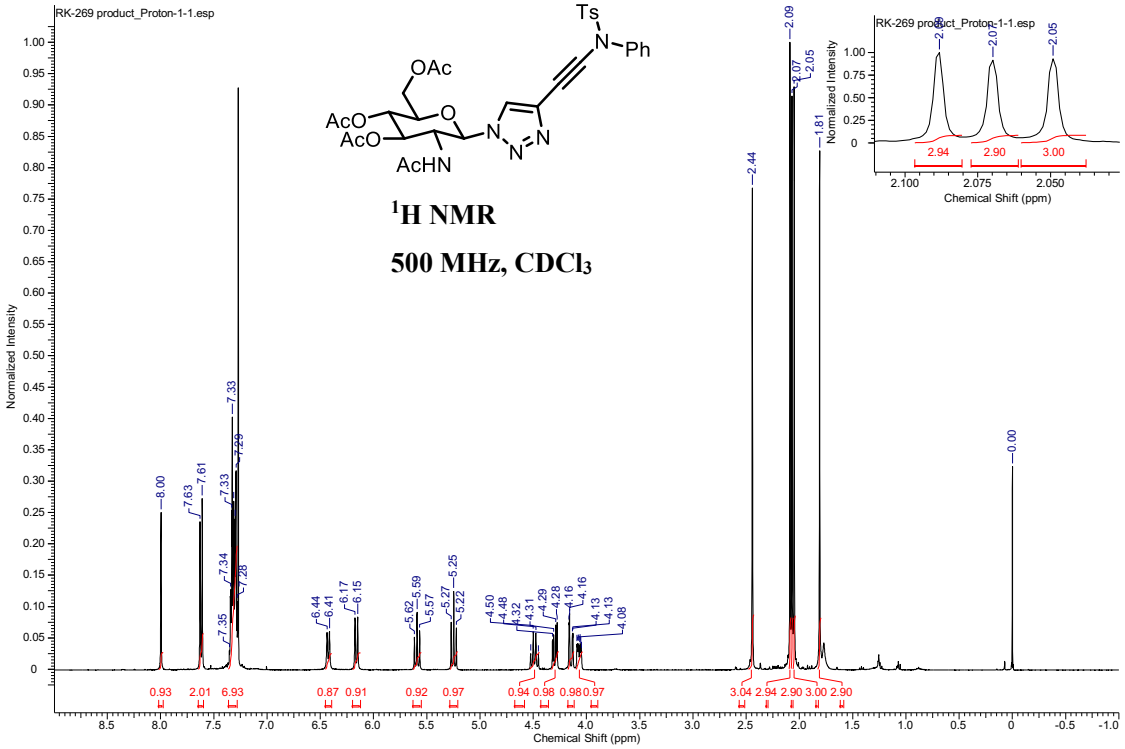


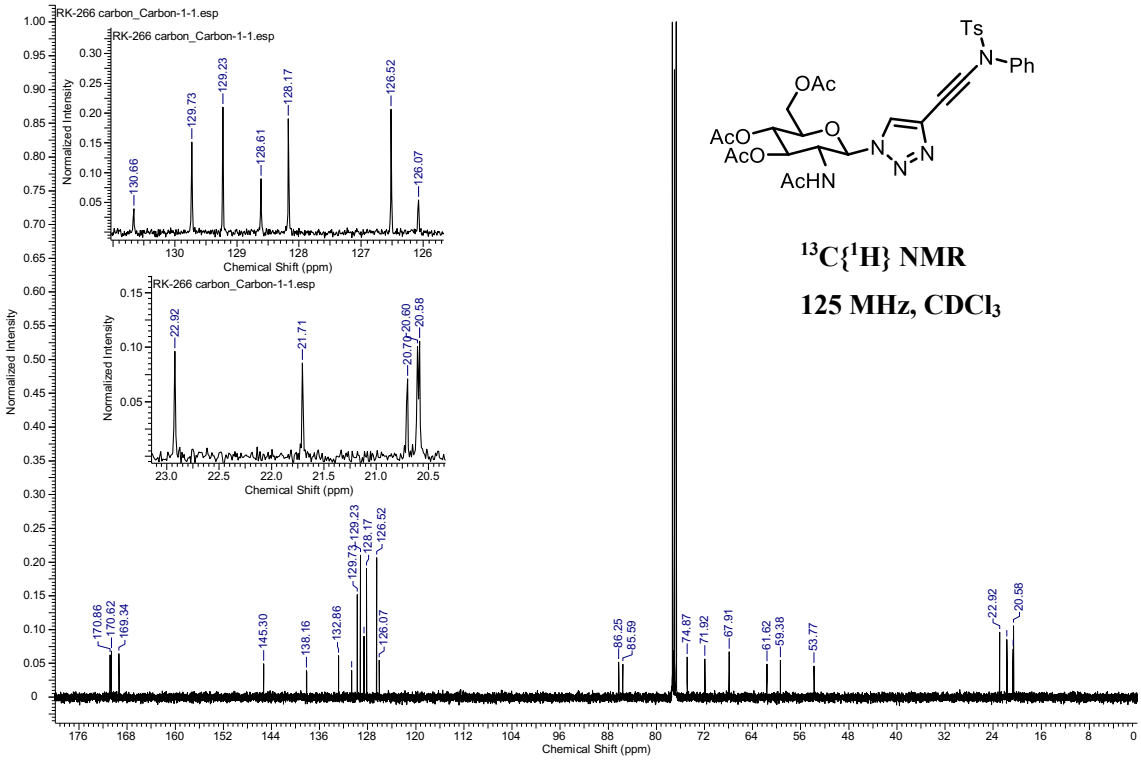
4-Methyl-*N*-phenyl-*N*-[[1-(thymidine)-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10e)





4-Methyl-*N*-phenyl-*N*-[[[1-{3-(acetylamino)-2,6-anhydro-1,3-dideoxy-4,5,7-triacetate}-D-glycero-D-ido-heptitol]-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10f)





4-Methyl-*N*-phenyl-*N*-[[[1-{3-(acetylamino)-2,6-anhydro-1,3-dideoxy-4,5,7-tris-*O*-(phenylmethyl)}-D-glycero-D-ido-heptitol]-1*H*-1,2,3-triazol-4-yl]ethynyl]-benzenesulfonamide (10g)