Rh(III)-catalyzed Olefinic C-H Alkynylation of Enamides at Room Temerature.

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Supporting Information

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General information

$[Cp^*Rh(MeCN)_3][SbF_6]_2$, $[Cp^*RhCl_2]_2$, CuCl, PivOH and solvents were purchased from commercial suppliers and used as received unless otherwise noted. All reactions were carried out using 8mL sample vial or standard Schlenk technic. Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using basic solution of potassium permanganate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. HRMS spectra were recorded on a Waters Q–Tof Permier Spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00, singlet), methanol-d_4 (δ 3.31, quintet), DMSO-d_6 (δ 2.50, quintet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); td (triplet of doublet); m (multiplets); ddt (doublet of doublet of triplet) and etc. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.00, triplet), methanol-d_4(δ 49.00, heptet), DMSO-d_6(δ 40.00, heptet)

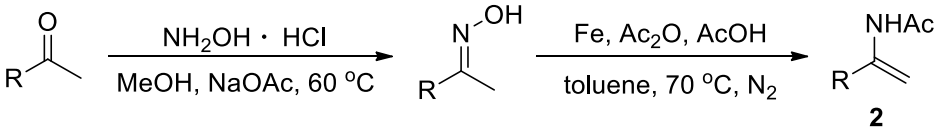
Experimental section

Substrate synthesis

Alkynyliodonium reagent **1** was synthesized following the reported method.[1]

2a-2k, 2n-2r were synthesized using reported methods.[2]

General reaction procedure A

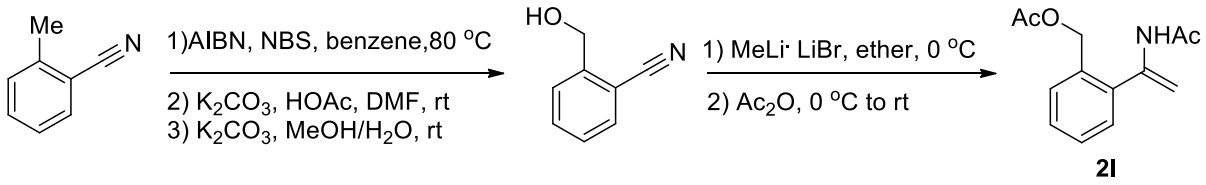


Synthetic procedure: a) A mixture of ketone (1 equiv.), NaOAc (1.2 equiv.) and hydroxylamine hydrochloride (1.2 equiv.) in methanol (0.5M) was stirred for 2 h at 60 ^{o}C. Add water after cooling down to room temperature, then the mixture was extracted with ethyl acetate twice. The organic layer was collected, dried over $MgSO_4$ and *vacuo* to afford the ketoxime pure enough for next step.
b) To an oven-dried 50 mL two-neck RBF assembled with condenser was added the before-metioned ketoxime. The flask was vacuumed and back filled with N_2 for three times. Anhydrous toluene (0.5 M) was added followed by acetic anhydride (3 equiv.), acetic acid (3 equiv.) and iron powder (2 equiv.). The reaction flask was put into a 70 ^{o}C preheated oil bath and allowed to stir under nitrogen atomsphere. After reaction completed and cooling to room temperature, ethyl acetate was added and the mixture was filtered through a short pad of celite. The solution thus obtained was evapoured to product crude enamide, which was directly purified by column chromatography.

[1] J.P. Brand, J. Waser, *Angew. Chem., Int. Ed.*, 2010, **49**, 7304.

[2] (a) M. Berg, R. M. Haak, A. J. Minnaard, A. H. M. Vries, J. G. Vries, B. L. Feringa, *Adv. Synth. Catal*., 2002, **344**, 1003; (b) M. J. Burk, G. Casy, N. B. Johnsonn, *J. Org. Chem.*, 1998, **63**, 6084; (c) H. Zhou, W. J. Chung, Y. H. Xu, T. P. Loh, *Chem. Commun*., 2009, **23**, 3472.

Reaction scheme for 2l synthesis



Synthetic procedure: a) The mixture of o-tolunitrile (20 mmol), NBS (21 mmol), and AIBN (1 mmol) in benzene (20 ml) was stirred at 80 ℃ for 1 h. After cooling to room temperature, the reaction was quenched with water and the mixture was extracted with ether followed by drying over $MgSO_4$. The organic solvent was evaporated to give the residue which is used directly in next step without purification.

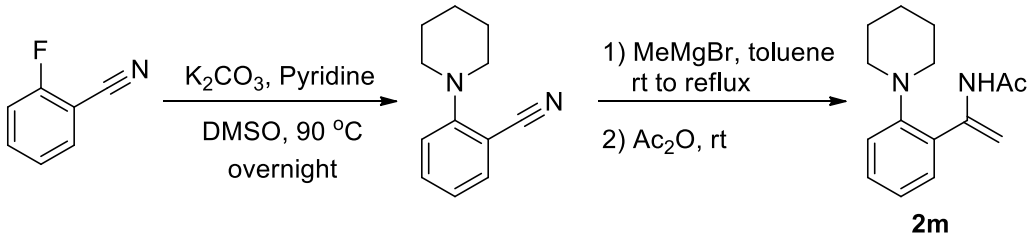
b) To a suspension of AcOH (80 mmol) and K_2CO_3 (80 mmol) in DMF (90 mL) was added the crude 2-(bromomethyl)benzonitrile in DMF (10 mL) at room temperature, and the mixture was stirred at the same temperature for 1 hour. After quenching with water the mixture was extracted with ether followed by drying over $MgSO_4$. The organic solvent was evaporated to give the residue which is used directly in next step without purification.

c) To a suspension of K_2CO_3 (100 mmol) in 30 mL MeOH/H_2O (2:1) was added the above obtained 2-cyanobenzyl acetate. The mixture was stirred at room temperature and the progress of reaction was monitored through TLC. Once the reaction finished, water was added and thus resulting solution was extracted with ethyl acetate. After drying over $MgSO_4$, the organic solvent was evaporated and the residue was subjected to silica gel column chromatography to afford the desired product 2-(hydroxymethyl)benzonitrile in 75% yield.

d) To an oven-dried 50 mL two-neck RBF assembled with condenser was added 2-(hydroxymethyl)benzonitrile (5 mmol) and dry ether (10 mL). MeLi·LiBr (7.5 mmol, 1M in ether) was slowly added into the solution under N_2 at 0 °C. After stirring for 2 hours at the same temperature, Ac_2O (15 mmol) was added and the resulting mixture was stirred at room temperature overnight. Saturated

$NaHCO_3$ solution was added followed by extraction with ethyl acetate (2×50 mL), and drying over $MgSO_4$. The organic solvent was evaporated and the residue was subjected to column chromatography on silica gel to deliver the product **2l** in 23% yield.

Reaction scheme for 2m synthesis

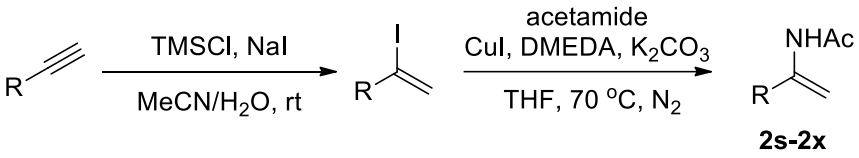


2m

Synthetic procedure: a) An 50 mL RBF was charged with 2-fluorobenzonitrile (10 mmol), K_2CO_3 (20 mmol), pyridine (12 mmol), and DMSO (5 mL) sequentially. The reaction flask was subjected to a 90 ^oC preheated oil bath and stirred overnight, at which time the resulting mixture was cooled down to room temperature, diluted with ethyl acetate, and washed thoroughly with water. Removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product 2-(piperidin-1-yl) benzonitrile in 90% yield.

b) To an oven-dried 50 mL two-neck RBF assembled with condenser was added 2-(piperidin-1-yl)benzonitrile and dry toluene (15 mL). MeMgBr (12 mmol, 3M in ether) was added to the solution under N_2 at room temperature. After stirring 10 minutes, the mixture was subjected to a 110 ^oC preheated oil bath and stirred overnight. After cooling to room temperature, Ac_2O (15 mmol) was added into the solution dropwise and the resulting mixture was stirred at room temperature for 2 hours, at which time saturated $NaHCO_3$ solution was added followed by extraction with ethyl acetate (2×50 mL), and drying over $MgSO_4$. The organic solvent was evaporated and the residue was subjected to column chromatography on silica gel to deliver the product **2m** in 56% yield.

Reaction scheme for 2s, 2v, 2w synthesis

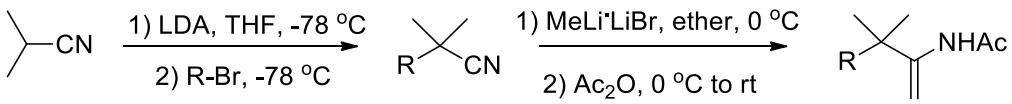


2s-2x

Synthetic procedure: a) At room temperature TMSCl (10 mmol) was added to a solution of NaI (10 mmol) in MeCN (10 mL) followed by H_2O (5 mmol). After stirring for 10 minutes, alkyne (6 mmol) was added and the resulting solution was stirred for 1 hour at room temperature. The reaction was quenched with H_2O (20 mL) and extracted with ethyl acetate followed by drying over $MgSO_4$. The organic solvent was evaporated to give the crude (3- iodobut-3-enyl)benzene, which is used directly in next step without further purification.

b) To an oven-dried 50 mL two-neck RBF assembled with condenser was added CuI (1.5 mmol), K_2CO_3 (9 mmol), acetamide (12 mmol). The flask was vacuumed and backfilled with N_2 for three times. Anhydrous THF (5 mL) was added followed by DMEDA (3 mmol) and crude (3-iodobut-3-enyl)benzene. The reaction flask was put into a 70 ^oC preheated oil bath and allowed to stir overnight. After cooling to room temperature, water was added and the mixture was extracted with ethyl acetate (2×50 mL) followed by drying over $MgSO_4$. The organic solvent was evaporated and the residue was subjected to column chromatography on silica gel to deliver the product.

Reaction scheme for 2t, 2u synthesis



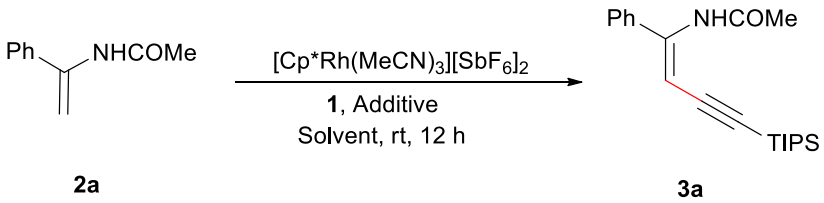
Synthetic procedure: a) To an oven-dried 50 mL RBF, isobutyronitrile (22 mmol) was dissolved in THF (10 mL). The flask was subjected to a -78 ^oC cold bath and a 1M THF solution of LDA (24 mmol) was added dropwisely. The reaction was allowed to stir under -78 ^oC for 1 hour, and then R-Br (22 mmol)

was slowly dropped in the flask. Then the resulting mixture was naturally warmed up to room temperature. When the reaction finished, the mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. Removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product.

b) To an oven-dried 50 mL RBF was added 3^o-alkyl nitrile (10 mmol) and dry diethyl ether (15 mL). MeLi·LiBr (20 mmol, 3M in ether) was added to the solution under N_2 at 0 ^oC. After stirring 2 hours, Ac_2O (30 mmol) was added into the solution dropwise and the resulting mixture was stirred at room temperature for 2 hours, at which time saturated $NaHCO_3$ solution was added followed by extraction with ethyl acetate (2×50 mL), and drying over $MgSO_4$. The organic solvent was evaporated and the residue was subjected to column chromatography on silica gel to deliver the desired product.

Optimaization of reaction condtion

Table 1 Optimization of reaction condition.[a]



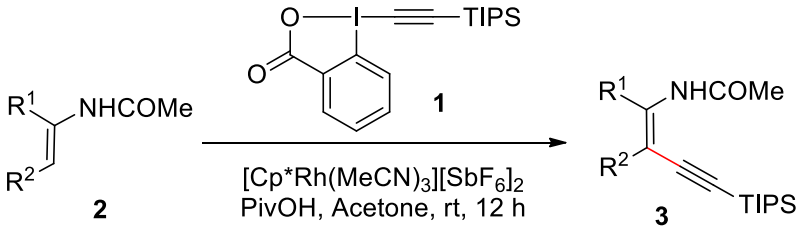
2a **3a**

Entry	Additive	Solvent	Yield[b] (%)
1	-	THF	50
2	-	DCE	52
3	-	DME	35
4	-	MeCN	<10
5	-	Acetone	83
6	-	Dioxane	<10
7	-	PhCl	59
8	-	MeOH	33
9	-	*t*-BuOH	81
10	NaOAc	Acetone	27
11	PivOH	Acetone	91
12	$AgSbF_6$	Acetone	59[c]
13	-	Acetone	NR[d]
14	-	Acetone	NR[e]
15	PivOH	Acetone	NR[f]
16	PivOH	Acetone	80[g]

[a] Unless otherwise noted, the reactions were carried out using **2a** (0.1 mmol), hypervalent aklynyliodonium reagent **1** (0.11 mmol), additive (0.01 mmol), catalyst (0.002 mmol) in solvent (0.5 mL) and stirred at room temperature for 12 h. [b] Isolated yields. [c] $[Cp^*RhCl_2]_2$ (0.002 mmol) was used as the catalyst. [d] CuCl (0.01 mmol) was used as the catalyst. [e] $Pd(OAc)_2$ (0.005 mmol) was used at the catalyst. [f] No catalyst was added. [g] **2a** was used in 1g scale.

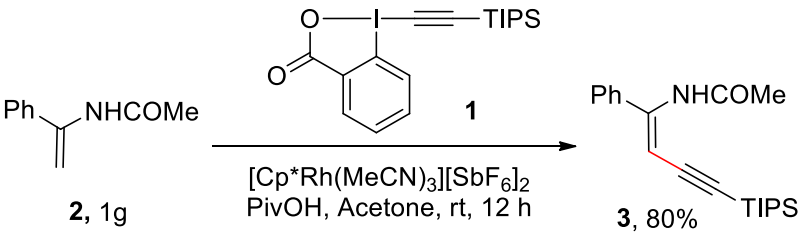
Rh(III) catalyzed olefinic C-H alkynylation of enamides

General reaction procedure B



Synthetic procedure: The enamide **2** (0.1 mmol, 1 equiv.), alkynyliodonium reagent **1** (0.11 mmol, 1.1 equiv.), $[Cp^*Rh(MeCN)_3][SbF_6]$ (0.002 mmol, 2 mol %), PivOH (0.01 mmol, 10 mol %) and Acetone (0.5 mL) were placed in a 8 mL glass vial under air. After stirring at room temperature for 12 hours, saturated $NaHCO_3$ solution (5 mL) was added and the resulting mixture was extracted with dichloromethane (2x10mL). Removal of the solvent in vacuo and purified by column chromatography afforded the desired product **3**.

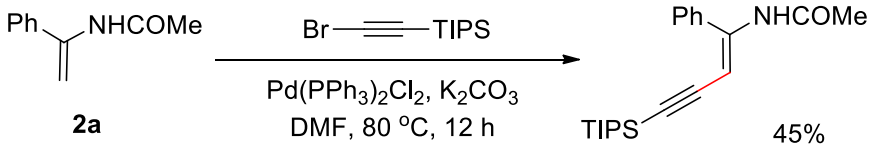
Large scale reaction



Synthetic procedure E: The *N*-(1-phenylvinyl)acetamide **2a** (1.0 g, 1 equiv.), alkynyliodonium reagent **1** (2.9 g, 1.1 equiv.), $[Cp^*Rh(MeCN)_3][SbF_6]$ (105.4 mg, 2 mol %), PivOH (63 mg, 10 mol %) and Acetone (30 mL) were placed in a 100 mL RBF under air. After stirring at room temperature for 12 hours, saturated $NaHCO_3$ solution (50 mL) was added and the resulting mixture was extracted with dichloromethane (2x50mL). Removal of the solvent in vacuo and purified by column chromatography afforded the desired product **3a** 1.70 g (80% yield).

Heck-type alkynylation reaction of enamide

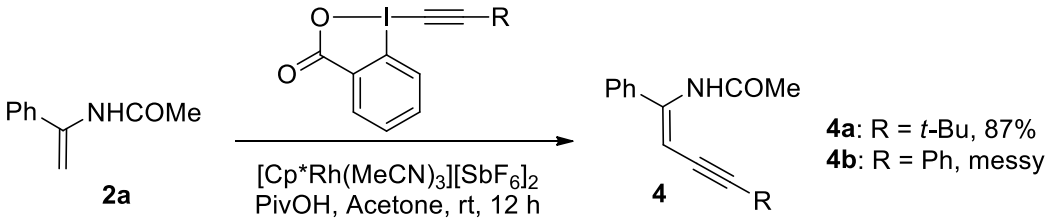
General reaction procedure C



Synthetic procedure: The enamide **2a** (0.1 mmol, 1 equiv.), $Pd(PPh_3)_2Cl_2$ (0.005 mmol, 5 mol %) and K_2CO_3 (0.25 mmol, 2.5 equiv.) was stirred in DMF at room temperature under N_2 atomosphere for 5 min. Then, bromoethynyl triisopropylsilane (0.11 mmol, 1.1 equiv.) was slowly added into the system. The reaction was then allowed to stir for 12 hours at 80 °C. After quenched with water, the mixture was extracted using ethylacetate. Then the organic layer was evaporated and the residue was directed subject to column chromatography on silica gel to afford the desired product 15.4 mg (45% yield).

Alkynylation reaction scheme using other alkynyliodonium reagent

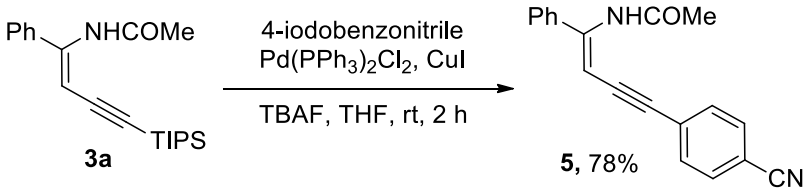
General reaction procedure B



Synthetic procedure: The enamide **2a** (0.1 mmol, 1 equiv.), alkynyliodonium reagent (0.11 mmol, 1.1 equiv.), $[Cp^*Rh(MeCN)_3][SbF_6]$ (0.002 mmol, 2 mol %), PivOH (0.01 mmol, 10 mol %) and Acetone (0.5 mL) were placed in a 8 mL glass vial under air. After stirring at room temperature for 12 hours, saturated $NaHCO_3$ solution (5 mL) was added and the resulting mixture was extracted with dichloromethane (2x10mL). Removal of the solvent in vacuo and purified by column chromatography afforded the desired product **4**.

Sonogashira reaction between 3a and 4-iodobenzonitrile.

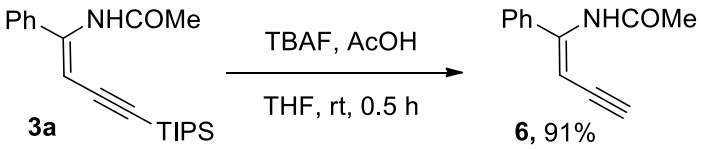
General reaction procedure D



Synthetic procedure: The **3a** (0.1 mmol, 1 equiv.), 4-iodobenzonitrile (0.11 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (0.002 mmol, 2 mol %) and CuI (0.001 mmol, 1 mol %) was stirred in THF under N_2 atomosphere. After cooling down to 0 ^oC, TBAF (0.12 mmol, 1.2 equiv.) was slowly added. The reaction was allowed to stir for 2 hours under room temperature. After quenched with water, the mixture was extracted using dichloromethane. Then the organic layer was evaporated and the residue was directed subject to column chromatography on silica gel to afford the product **5** 22.3 mg (78% yield).

Desilylation reaction of 3a

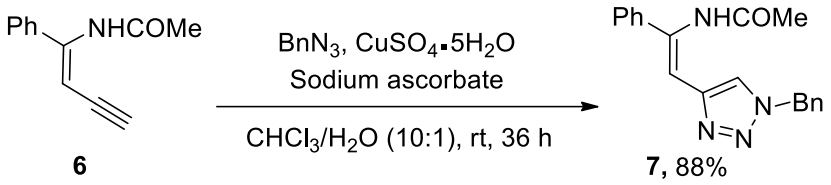
General reaction procedure E



Synthetic procedure: The **3a** (0.2 mmol, 1 equiv.) was dissolved into 1 mL THF in a 10 mL RBF. Then, the mixture of TBAF (0.4 mmol, 4 equiv.), acetic acid (0.6 mmol, 6 equiv.) and 1 mL THF was added dropwisely. The reaction was allowed to stir for 0.5 hour at room temperature and quenched with saturated $NaHCO_3$ solution. After extracting with dichloromethane (2x10mL), the organic layer was evaporated and the residue was subjected to column chromatography on silica gel to deliver the product **6** 33.7 mg (91% yield).

Cycloaddition reaction between 6 and benzyl azide

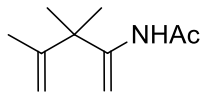
General reaction procedure F



Synthetic procedure: The **6** (0.1 mmol, 1 equiv.) and BnN_3 (0.12 mmol, 1.2 equiv.) were dissolved into 1 mL $CHCl_3$ in a 5 mL RBF. Then the aqueous solution of $CuSO_4 \cdot 5H_2O$ (0.01 mmol, 0.1 equiv.) and sodium ascorbate (0.02 mmol, 0.2 equiv.) was added dropwisely. The reaction was allowed to stir for 36 hours under room temperature and quenched with saturated NH_3Cl solution. After extracting with dichloromethane (2x10mL), the organic layer was evaporated and the residue was subjected to column chromatography on silica gel to deliver the product **7** 28.0 mg (88% yield).

Characterization of unknow substrates and alkynylation products

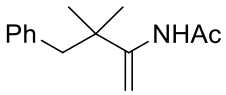
***N*-(3,3,4-trimethylpenta-1,4-dien-2-yl)acetamide:**



4t

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (s, 6H), 1.73 (s, 3H), 2.08 (s, 3H), 2.13 (s, 2H), 4.70 (s, 1H), 4.79 (s, 1H), 4.87 (s, 1H), 5.71 (s, 1H), 6.60 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.3, 24.7, 27.0, 38.4, 48.7, 100.1, 114.5, 142.8, 146.4, 168.4 ppm.

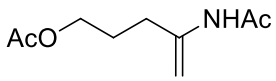
***N*-(3,3-dimethyl-4-phenylbut-1-en-2-yl)acetamide:**



4u

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (s, 6H), 1.94 (s, 3H), 2.67 (s, 2H), 4.71 (s, 1H), 5.71 (s, 1H), 6.32 (brs, 1H), 7.11-7.12 (m, 2H), 7.20-7.29 (m, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.6, 26.2, 29.5, 39.3, 47.6, 100.7, 126.4, 127.9, 130.2, 137.8, 145.9, 168.4 ppm.

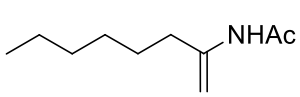
4-acetamidopent-4-en-1-yl acetate:



4v

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74-1.78 (m, 2H), 2.00 (m, 6H), 2.17 (t, *J* = 8.0 Hz, 2H), 4.03 (t, *J* = 8.0 Hz, 2H), 4.44 (s, 1H), 5.40 (s, 1H), 7.13 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.9, 24.4, 26.7, 63.4, 99.2, 140.5, 169.0, 171.2 ppm.

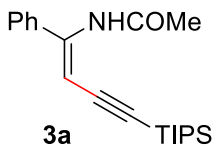
***N*-(oct-1-en-2-yl)acetamide:**



4w

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87-0.90 (m, 3H), 1.29-1.33 (m, 6H), 1.45-1.49 (m, 2H), 2.06 (s, 3H), 2.12 (t, *J* = 8.0 Hz, 2H), 4.50 (s, 1H), 5.51 (s, 1H), 6.96 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 14.0, 22.5, 24.5, 27.4, 28.6, 31.5, 35.7, 98.4, 141.3, 168.9 ppm.

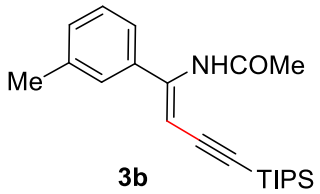
(*Z*)-*N*-(1-phenyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



3a

Following the general reaction procedure B, **3a** was obtained as a white solid (31.0 mg, 0.091 mmol, Yield: 91%); m.p. = 78-80 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.14 (m, 21H), 2.12 (s, 3H), 6.03 (s, 1H), 7.34-7.49 (m, 5H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 23.0, 99.4, 104.7, 126.8, 129.6, 130.2, 137.5, 146.8, 171.65 ppm; **HRMS (ESI, m/z):** calcd for $C_{21}H_{32}NOSi$ $[M+H]^+$ 342.2253, found: 342.2246.

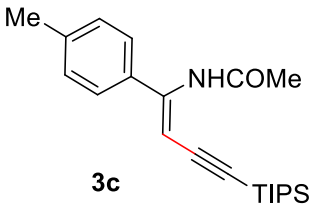
(*Z*)-*N*-(1-(*m*-tolyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



3b

Following the general reaction procedure B, **3b** was obtained as a white solid (32.7 mg, 0.092 mmol, Yield: 92%); m.p. = 67-69 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.13 (m, 21H), 2.12 (s, 3H), 2.35 (s, 3H), 6.01(s, 1H), 7.16-7.30 (m, 4H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 21.5, 23.0, 99.3, 104.6, 104.8, 124.1, 127.4, 129.5, 131.0, 137.4, 139.4, 146.9, 171.6 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{34}NOSi$ $[M+H]^+$ 356.2410, found: 356.2413.

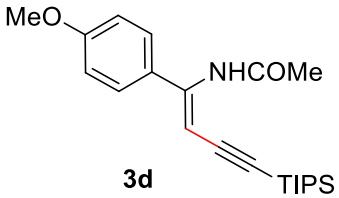
(*Z*)-*N*-(1-(*p*-tolyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



3c

Following the general reaction procedure B, **3c** was obtained as a white solid (31.8 mg, 0.089 mmol, Yield: 89%); m.p. = 140-142 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.13 (m, 21H), 2.11 (s, 3H), 2.34 (s, 3H), 5.99 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 21.3, 23.0, 99.0, 103.9, 104.9, 126.8, 130.3, 134.6, 140.6, 146.7, 171.6 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{34}NOSi$ $[M+H]^+$ 356.2410, found: 356.2414.

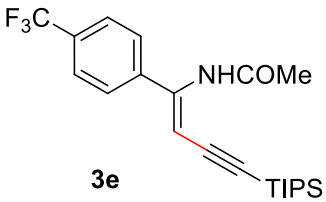
(*Z*)-*N*-(1-(4-methoxyphenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl) acetamide:



3d

Following the general reaction procedure B, **3d** was obtained as a white solid (30.1 mg, 0.081 mmol, Yield: 81%); m.p. = 121-123 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.13 (m, 21H), 2.11 (s, 3H), 3.80 (s, 3H), 5.93 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.6, 19.1, 23.1, 55.8, 98.5, 102.8, 105.1, 115.0, 128.3, 129.8, 146.4, 162.2, 171.6 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{34}NO_2Si$ $[M+H]^+$ 372.2359, found: 372.2365.

(*Z*)-*N*-(1-(4-(trifluoromethyl)phenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl) acetamide:

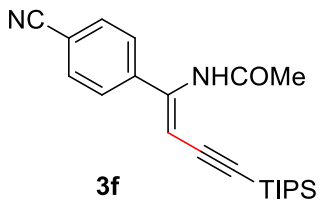


3e

Following the general reaction procedure B, **3e** was obtained as a white solid (37.6 mg, 0.092 mmol, Yield: 92%); m.p. = 112-114 ℃; **^{1}H NMR (400 MHz,**

CD_3OD): δ 1.14 (m, 21H), 2.13 (s, 3H), 6.14 (s, 1H), 7.65(m, 4H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 23.0, 101.1, 104.2, 106.8, 125.6 (q, *J* = 270.0 Hz), 126.4, 127.4, 131.7 (q, *J* = 30.0 Hz), 141.3, 145.6, 171.8 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{31}F_3NOSi$ $[M+H]^+$ 410.2127, found: 410.2146.

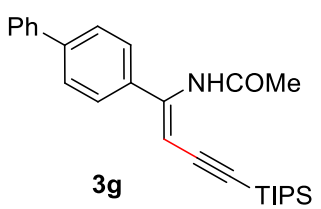
(*Z*)-*N*-(1-(4-cyanophenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



3f

Following the general reaction procedure B, **3f** was obtained as a white solid (35.4 mg, 0.097 mmol, Yield: 97%); m.p. = 139-141 ℃; **^1H NMR (400 MHz, CD_3OD):** δ 1.14 (m, 21H), 2.13 (s, 3H), 6.17 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 23.0, 101.9, 104.0, 107.6, 113.2, 119.5, 127.6, 133.4, 142.1, 145.4, 171.8 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{31}N_2OSi$ $[M+H]^+$ 367.2206, found: 367.2214.

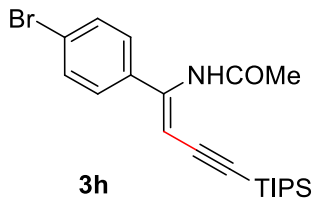
(*Z*)-*N*-(1-([1,1'-biphenyl]-4-yl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl) acetamide:



3g

Following the general reaction procedure B, **3g** was obtained as a white solid (38.2 mg, 0.092 mmol, Yield: 92%); m.p. = 166-168 ℃; **^1H NMR (400 MHz, CD_3OD):** δ 1.13 (m, 21H), 2.14 (s, 3H), 6.08 (s, 1H), 7.31-7.35 (m, 1H), 7.41-7.44 (m, 2H), 7.54-7.62 (m, 6H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.2, 23.1, 99.7, 104.7, 104.8, 127.3, 127.9, 128.1, 128.7, 129.9, 136.3, 141.5, 143.2, 146.4, 171.8 ppm; **HRMS (ESI, m/z):** calcd for $C_{27}H_{36}NOSi$ $[M+H]^+$ 418.2566, found: 418.2555.

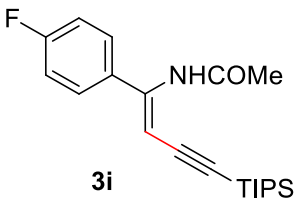
(*Z*)-*N*-(1-(4-bromophenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



3h

Following the general reaction procedure B, **3h** was obtained as a white solid (40.0 mg, 0.095 mmol, Yield: 95%); m.p. = 122-124 ℃; **^1H NMR (400 MHz, CD_3OD):** δ 1.13 (m, 21H), 2.11 (s, 3H), 6.05 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 23.0, 100.2, 104.5, 105.3, 124.1, 128.6, 132.7, 136.7, 145.9, 171.7 ppm; **HRMS (ESI, m/z):** calcd for $C_{21}H_{31}BrNOSi$ $[M+H]^+$ 420.1358, found: 420.1364.

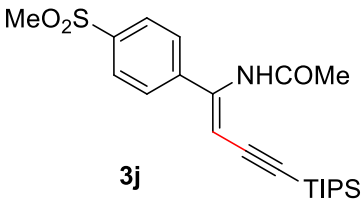
(*Z*)-*N*-(1-(4-fluorophenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



3i

Following the general reaction procedure B, **3i** was obtained as a white solid (32.1 mg, 0.089 mmol, Yield: 89%); m.p. = 81-83 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.13 (m, 21H), 2.11 (s, 3H), 5.98 (s, 1H), 7.07-7.11 (m, 2H), 7.49-7.53 (m, 2H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 23.0, 99.5, 104.6, 116.4 (d, *J* = 22.0 Hz), 129.0 (d, *J* = 8.0 Hz), 133.8 (d, *J* = 3.0 Hz), 145.9, 164.8 (d, *J* = 247.0 Hz), 171.7 ppm; **HRMS (ESI, m/z):** calcd for $C_{21}H_{31}FNOSi$ $[M+H]^+$ 360.2159, found:360.2159.

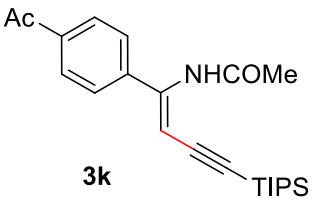
(*Z*)-*N*-(1-(4-(methylsulfonyl)phenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl) acetamide:



3j

Following the general reaction procedure B, **3j** was obtained as a white solid (41.5 mg, 0.099 mmol, Yield: 99%); m.p. = 160-162 ℃; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.13 (m, 21H), 2.14 (s, 3H), 3.06 (s, 3H), 5.44 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 11.1, 18.6, 23.7, 44.5, 100.2, 101.6, 102.5, 126.8, 127.4, 140.3, 141.0, 145.8, 168.2 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{34}NO_3SSi$ $[M+H]^+$ 420.2029, found: 420.2021.

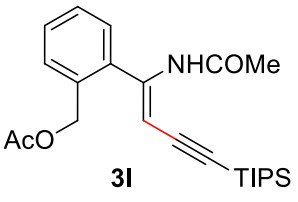
(*Z*)-*N*-(1-(4-acetylphenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



3k

Following the general reaction procedure B, **3k** was obtained as a white solid (36.7 mg, 0.096 mmol, Yield: 96%); m.p. = 150-152 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.14 (m, 21H), 2.13 (s, 3H), 2.59 (s, 3H), 6.17 (s, 1H), 7.59-7.62 (m, 2H), 7.96-7.98 (m, 2H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 23.0, 26.7, 101.3, 104.4, 106.9, 127.0, 129.7, 138.4, 142.1, 145.9, 171.7, 199.7 ppm; **HRMS (ESI, m/z):** calcd for $C_{23}H_{34}NO_2Si$ $[M+H]^+$ 384.2359, found: 384.2356.

(*Z*)-2-(1-acetamido-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)benzyl acetate:

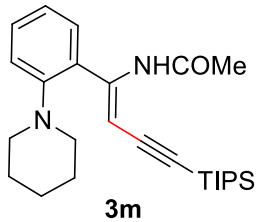


3l

Following the general reaction procedure B, **3l** was obtained as colorless oil (37.6 mg, 0.091 mmol, Yield: 91%); **^{1}H NMR (400 MHz, CD_3OD):** δ 1.15 (m, 21H), 2.02 (s, 3H), 2.07 (s, 3H), 5.15 (s, 2H), 5.41 (s, 1H), 7.33-

7.42 (m, 4H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 20.9, 23.3, 99.7, 103.7, 104.2, 129.3, 129.9, 130.3,130.7, 135.1, 138.5, 146.6, 170.5, 172.4 ppm; **HRMS (ESI, m/z):** calcd for $C_{24}H_{36}NO_3Si$ $[M+H]^+$ 414.2464, found: 414.2468.

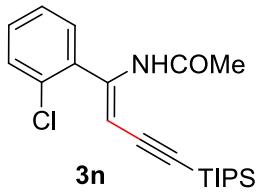
(*Z*)-*N*-(1-(2-(piperidin-1-yl)phenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl) acetamide:



3m

Following the general reaction procedure B, **3m** was obtained as a white solid (40.7 mg, 0.096 mmol, Yield: 96%); m.p. = 79-81 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.14 (m, 21H), 1.56-1.59 (m, 2H), 1.67-1.72 (m, 4H), 2.04 (s, 3H), 2.91-2.94 (m, 4H), 5.87 (s, 1H), 6.96-7.06 (m, 2H), 7.22-7.27 (m, 2H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.2, 23.6, 25.3, 27.7, 99.8, 102.2, 104.9, 120.1, 123.5, 130.7, 131.3, 133.9, 147.1, 153.1, 170.0 ppm; **HRMS (ESI, m/z):** calcd for $C_{26}H_{41}N_2OSi$ $[M+H]^+$ 425.2988, found: 425.2985.

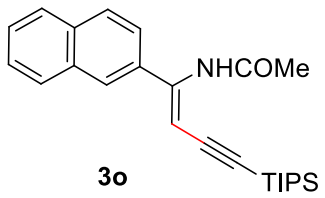
(*Z*)-*N*-(1-(2-chlorophenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



3n

Following the general reaction procedure B, **3n** was obtained as a white solid (35.1 mg, 0.094 mmol, Yield: 94%); m.p. = 89-91 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.15 (m, 21H), 2.04 (s, 3H), 5.45 (s, 1H), 7.29-7.40 (m, 4H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 23.0, 100.2, 103.5, 104.3,128.0, 130.9, 131.0, 132.0, 133.3, 137.1, 146.0, 170.6 ppm; **HRMS (ESI, m/z):** calcd for $C_{21}H_{31}ClNOSi$ $[M+H]^+$ 376.1863, found: 376.1876.

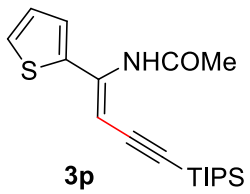
(*Z*)-*N*-(1-(naphthalen-2-yl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl) acetamide:



3o

Following the general reaction procedure B, **3o** was obtained as a white solid (34.9 mg, 0.087 mmol, Yield: 87%); m.p. = 134-136 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.15 (m, 21H), 2.18 (s, 3H), 6.19 (s, 1H), 7.46-7.49 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.80-7.87 (m, 3H), 7.93 (s, 1H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.2, 23.1, 100.0, 104.9, 105.4, 124.3, 126.3, 127.6, 127.8, 128.6, 129.3, 129.6, 134.6, 135.2, 146.7, 171.8 ppm; **HRMS (ESI, m/z):** calcd for $C_{25}H_{34}NOSi$ $[M+H]^+$ 392.2410, found: 392.2414.

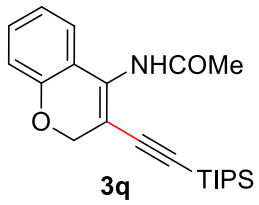
(*Z*)-*N*-(1-(thiophen-2-yl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



3p

Following the general reaction procedure B, **3p** was obtained as a white solid (22.5 mg, 0.065 mmol, Yield: 65%); m.p. = 108-110 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.12 (m, 21H), 2.10 (s, 3H), 6.05 (s, 1H), 7.02-7.04 (m, 1H), 7.23-7.24 (m, 1H), 7.39-7.40 (m, 1H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 11.2, 17.7, 21.5, 98.7, 102.8, 103.0, 125.3, 126.4, 127.6, 139.5, 140.8, 170.2 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{30}NOSSi$ $[M+H]^+$ 348.1817, found: 348.1820.

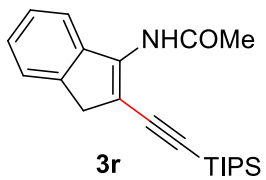
***N*-(3-((triisopropylsilyl)ethynyl)-2*H*-chromen-4-yl)acetamide:**



3q

Following the general reaction procedure B, **3q** was obtained as a white solid (25.3 mg, 0.069 mmol, Yield: 69%); m.p. = 180-182 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.13 (m, 21H), 2.14 (s, 3H), 4.79 (s, 2H), 6.82-6.96 (m, 2H), 7.16-7.20 (m, 2H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.4, 19.1, 22.9, 68.6, 101.6, 102.8, 112.4, 117.1, 122.2, 122.8, 124.6, 131.5, 136.2, 156.2, 172.1 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{32}NO_2Si$ $[M+H]^+$ 370.2202, found:370.2207.

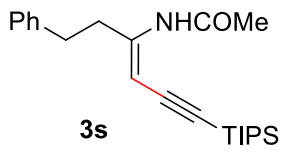
***N*-(2-((triisopropylsilyl)ethynyl)-1*H*-inden-3-yl)acetamide:**



3r

Following the general reaction procedure B, **3r** was obtained as a white solid (21.6 mg, 0.061 mmol, Yield: 61%); m.p. = 151-153 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.14 (m, 21H), 2.17 (s, 3H), 3.56 (s, 2H), 7.27-7.42 (m, 4H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 22.8, 41.0, 101.4, 103.2, 119.8, 120.8, 124.9, 127.7, 141.9, 142.7, 144.2, 171.7, 178.1 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{32}NOSi$ $[M+H]^+$ 354.2253, found: 354.2254.

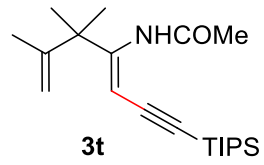
(*Z*)-*N*-(1-phenyl-6-(triisopropylsilyl)hex-3-en-5-yn-3-yl)acetamide:



3s

Following the general reaction procedure B, **3s** was obtained as colorless oil (30.6 mg, 0.083 mmol, Yield: 83%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.11 (m, 21H), 2.10 (s, 3H), 2.79-2.99 (m, 4H), 4.69 (s, 1H), 7.18-7.29 (m, 5H), 7.77 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 11.2, 18.7, 24.7, 34.9, 35.2, 90.3, 98.3, 102.0, 126.0, 128.3, 128.5, 141.2, 150.9, 167.5 ppm; **HRMS (ESI, m/z):** calcd for $C_{23}H_{36}NOSi$ $[M+H]^+$ 370.2566, found: 370.2559.

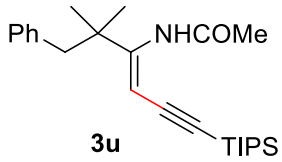
(*Z*)-*N*-(5,5,6-trimethyl-1-(triisopropylsilyl)hepta-3,6-dien-1-yn-4-yl) acetamide:



3t

Following the general reaction procedure B, **3t** was obtained as colorless oil (32.5 mg, 0.090 mmol, Yield: 90%); **^{1}H NMR (400 MHz, CD_3OD):** δ 1.09 (m, 27H), 1.75 (s, 3H), 2.06 (s, 3H), 2.18 (s, 2H), 4.69 (s, 1H), 4.87 (s, 1H), 5.63 (s, 1H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 23.0, 25.0, 26.5, 41.3, 96.2, 104.8, 106.6, 115.4, 143.9, 154.8, 171.2 ppm; **HRMS (ESI, m/z):** calcd for $C_{21}H_{38}NOSi$ $[M+H]^+$ 348.2723, found: 348.2724.

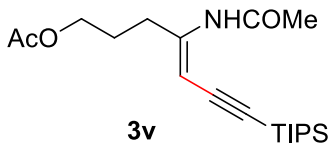
(*Z*)-*N*-(2,2-dimethyl-1-phenyl-6-(triisopropylsilyl)hex-3-en-5-yn-3-yl) acetamide:



3u

Following the general reaction procedure B, **3u** was obtained as colorless oil (38.4 mg, 0.097 mmol, Yield: 97%); **^{1}H NMR (400 MHz, CD_3OD):** δ 1.02 (s, 6H), 1.11 (m, 21H), 2.09 (s, 3H), 2.62 (1s, 2H), 5.48 (s, 1H), 7.13-7.26 (m, 5H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 23.1, 25.7, 42.1, 46.7, 96.2, 104.7, 107.3, 127.3, 128.7, 131.8, 139.2, 154.4, 171.4 ppm; **HRMS (ESI, m/z):** calcd for $C_{25}H_{40}NOSi$ $[M+H]^+$ 398.2879, found: 398.2881.

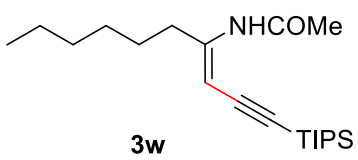
(*Z*)-4-acetamido-7-(triisopropylsilyl)hept-4-en-6-yn-1-yl acetate:



3v

Following the general reaction procedure B, **3v** was obtained as colorless oil (30.0 mg, 0.082 mmol, Yield: 82%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.10 (m, 21H), 1.85 (t, 2H), 2.06 (d, *J* = 8.0 Hz, 6H), 2.77 (t, *J* = 8.0 Hz, 2H), 4.09 (t, *J* = 8.0 Hz, 2H), 4.71 (s, 1H), 7.74 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 11.2, 18.7, 21.0, 24.7, 27.1, 29.6, 63.7, 90.4, 98.5, 101.8, 150.3, 167.3, 171.1 ppm; **HRMS (ESI, m/z):** calcd for $C_{20}H_{36}NO_2Si$ $[M+H]^+$ 366.2464, found: 366.2464.

(*Z*)-*N*-(1-(triisopropylsilyl)dec-3-en-1-yn-4-yl)acetamide:

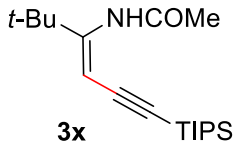


3w

Following the general reaction procedure B, **3w** was obtained as colorless oil (30.1 mg, 0.086 mmol, Yield: 86%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 0.86-0.89 (m, 3H), 1.08 (m, 21H), 1.26-1.34 (m, 6H), 1.46-1.48 (m, 2H), 2.06 (s, 3H), 2.66-2.69 (m, 2H), 4.69 (s, 1H), 7.72 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 11.2, 14.0, 18.7, 22.6, 24.7, 28.1, 28.9, 31.6, 32.9, 89.5,

97.8, 102.3, 152.1, 167.4 ppm; **HRMS (ESI, m/z):** calcd for $C_{21}H_{40}NOSi$ $[M+H]^+$ 350.2879, found: 350.2876.

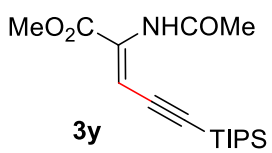
(*Z*)-*N*-(2,2-dimethyl-6-(triisopropylsilyl)hex-3-en-5-yn-3-yl)acetamide:



3x

Following the general reaction procedure B, **3x** was obtained as a white solid (26.7 mg, 0.083 mmol, Yield: 83%); m.p. = 122-124 ℃ **^{1}H NMR (400 MHz, CD_3OD):** δ 1.10 (m, 30H), 2.04 (s, 3H), 5.67 (s, 1H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 12.5, 19.1, 22.9, 28.3, 38.2, 95.8, 104.6, 106.0, 156.0, 171.4 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{36}NOSi$ $[M+H]^+$ 322.2566, found: 322.2565.

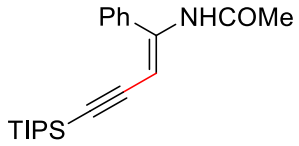
(*Z*)-methyl 2-acetamido-5-(triisopropylsilyl)pent-2-en-4-ynoate:



3y

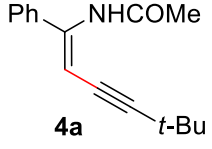
Following the general reaction procedure B, **3y** was obtained as colorless oil (20.1 mg, 0.062 mmol, Yield: 62%); **^{1}H NMR (400 MHz, DMSO-d_6):** δ 1.06 (m, 30H), 1.93 (s, 3H), 3.69 (s, 3H), 6.32 (s, 1H), 9.57 (s, 1H) ppm; **^{13}C NMR (100 MHz, DMSO-d_6):** δ 11.1, 18.9, 22.7, 52.9, 101.9, 104.6, 111.6, 137.8, 164.6, 168.6 ppm; **HRMS (ESI, m/z):** calcd for $C_{17}H_{30}NO_3Si$ $[M+H]^+$ 324.1995, found: 324.1986.

(*E*)-*N*-(1-phenyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)acetamide:



Following the general reaction procedure C, the desired product was obtained as a white solid (15.4 mg, 0.045 mmol, Yield: 45%); m.p. = 94-96 ℃; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 0.97 (m, 21H), 1.98 (s, 3H), 6.70 (s, 1H), 7.30-7.36 (m, 4H), 7.57-7.58 (m, 2H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 11.2, 18.5, 24.4, 95.2, 96.5, 104.2, 128.2, 128.4, 129.0, 136.0, 145.1, 169.2 ppm; **HRMS (ESI, m/z):** calcd for $C_{21}H_{32}NOSi$ $[M+H]^+$ 342.2253, found: 342.2249.

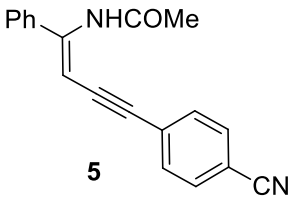
(*Z*)-*N*-(5,5-dimethyl-1-phenylhex-1-en-3-yn-1-yl)acetamide:



4a

Following the general reaction procedure B, **4a** was obtained as a white solid (21.0 mg, 0.087 mmol, Yield: 87%); m.p. = 126-128 ℃; **^{1}H NMR (400 MHz, CD_3OD):** δ 1.29 (m, 9H), 2.13 (s, 3H), 5.88 (s, 1H), 7.32-7.45 (m, 5H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 22.8, 29.4, 31.4, 76.9, 105.0, 107.7, 126.6, 129.5, 129.7, 137.8, 144.6, 171.8 ppm; **HRMS (ESI, m/z):** calcd for $C_{16}H_{20}NO$ $[M+H]^+$ 242.1545, found: 242.1547.

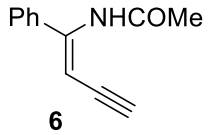
(*Z*)-*N*-(4-(4-cyanophenyl)-1-phenylbut-1-en-3-yn-1-yl)acetamide:



5

Following the general reaction procedure D, **5** was obtained as a white solid (22.9 mg, 0.080 mmol, Yield: 80%); m.p. = 192-194 ℃ **^{1}H NMR (400 MHz, DMSO-d_6):** δ 2.07-2.09 (m, 3H), 6.09 (s, 1H), 7.38-7.40 (m, 3H), 7.50-7.52 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 9.78 (s, 1H) ppm; **^{13}C NMR (100 MHz, DMSO-d_6):** δ 22.9, 91.8, 94.8, 99.6, 110.4, 118.5, 126.0, 127.9, 128.4, 129.2, 131.8, 132.5, 136.2, 147.4, 168.3 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{15}N_2O$ $[M+H]^+$ 287.1184, found: 287.1196.

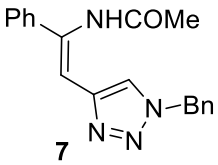
(*Z*)-*N*-(1-phenylbut-1-en-3-yn-1-yl)acetamide:



6

Following the general reaction procedure E, **6** was obtained as a white solid (17.0 mg, 0.092 mmol, Yield: 92%); m.p. = 162-164 ℃ **^{1}H NMR (400 MHz, CD_3OD):** δ 2.13 (s, 3H), 3.74 (s, 1H), 5.81 (s, 1H), 7.34-7.35 (m, 3H), 7.44-7.45 (m, 2H) ppm; **^{13}C NMR (100 MHz, CD_3OD):** δ 22.9, 80.8, 86.4, 102.6, 126.9, 129.5, 130.2, 137.5, 147.8, 172.0 ppm; **HRMS (ESI, m/z):** calcd for $C_{12}H_{12}NO$ $[M+H]^+$ 186.0919, found: 186.0910.

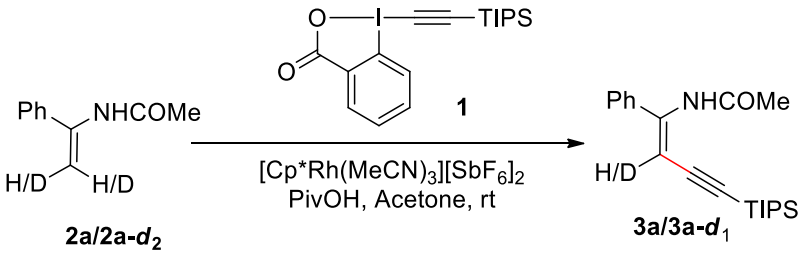
(*Z*)-*N*-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-1-phenylvinyl)acetamide:



7

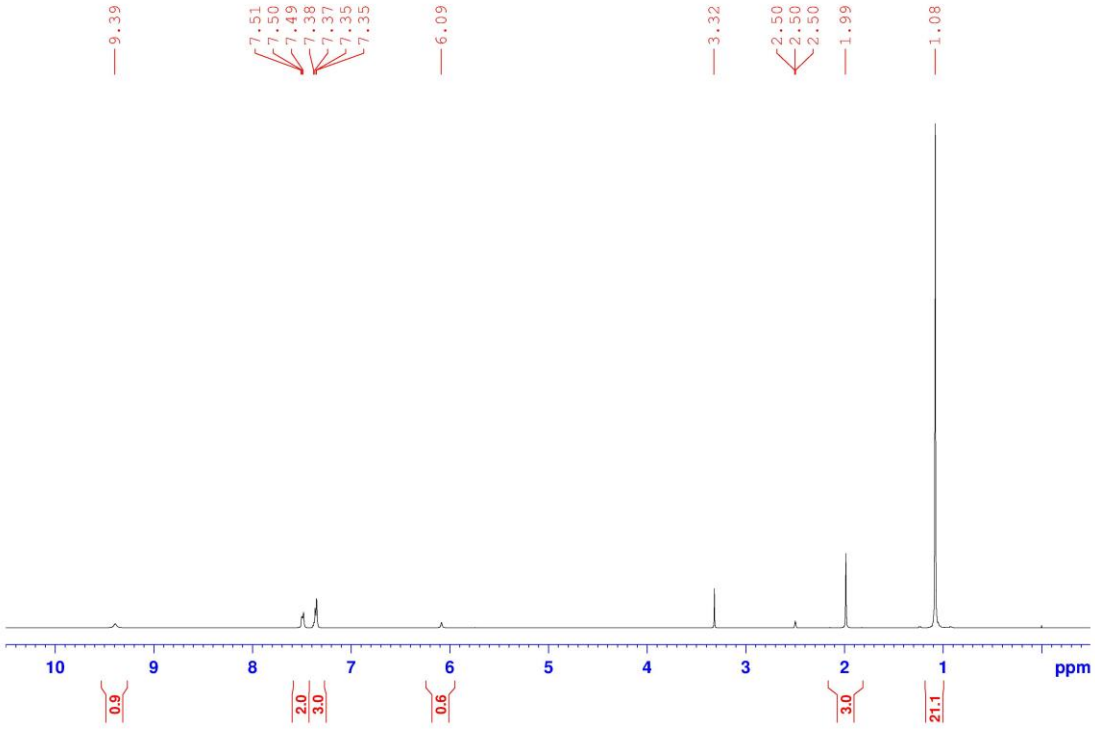
Following the general reaction procedure F, **7** was obtained as colorless oil (28.9 mg, 0.091 mmol, Yield: 91%); **^{1}H NMR (400 MHz, DMSO-d_6):** δ 2.10 (s, 3H), 5.67 (s, 2H), 6.79 (s, 1H), 7.29-7.42 (m, 8H), 7.50-7.52 (m, 2H), 8.16 (s, 1H), 9.59 (s, 1H) ppm; **^{13}C NMR (100 MHz, DMSO-d_6):** δ 23.7, 53.2, 112.3, 123.9, 126.0, 128.4, 128.8, 129.2, 135.7, 136.5, 138.2, 143.7, 168.9 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{19}N_4O$ $[M+H]^+$ 319.1559, found: 319.1571.

KIE study

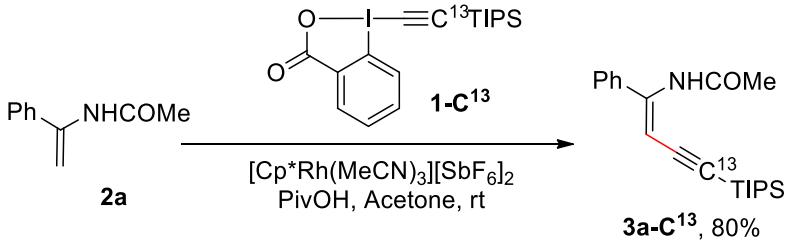


Synthetic procedure: The *N*-(1-phenylvinyl)acetamide **2a** (0.1 mmol, 1 equiv.), **2a-*d*$_2$** (0.1 mmol, 1 equiv.), hypervalent alkynyliodonium reagent **1** (0.1 mmol, 1 equiv.), [Cp*Rh(MeCN)$_3$][SbF$_6$] (0.004 mmol, 2 mol %), PivOH (0.02 mmol, 10 mol %) and Acetone (1 mL) were placed in a 8 mL glass vial under air. After stirring at room temperature for 12 hours, saturated $NaHCO_3$ solution (10 mL) was added and the resulting mixture was extracted with dichloromethane (2x20mL). Removal of the solvent in vacuo and purified by column chromatography afforded the the mixture of **3a** and **3a-*d*$_1$**.

(^{1}H NMR in DMSO-d_6)

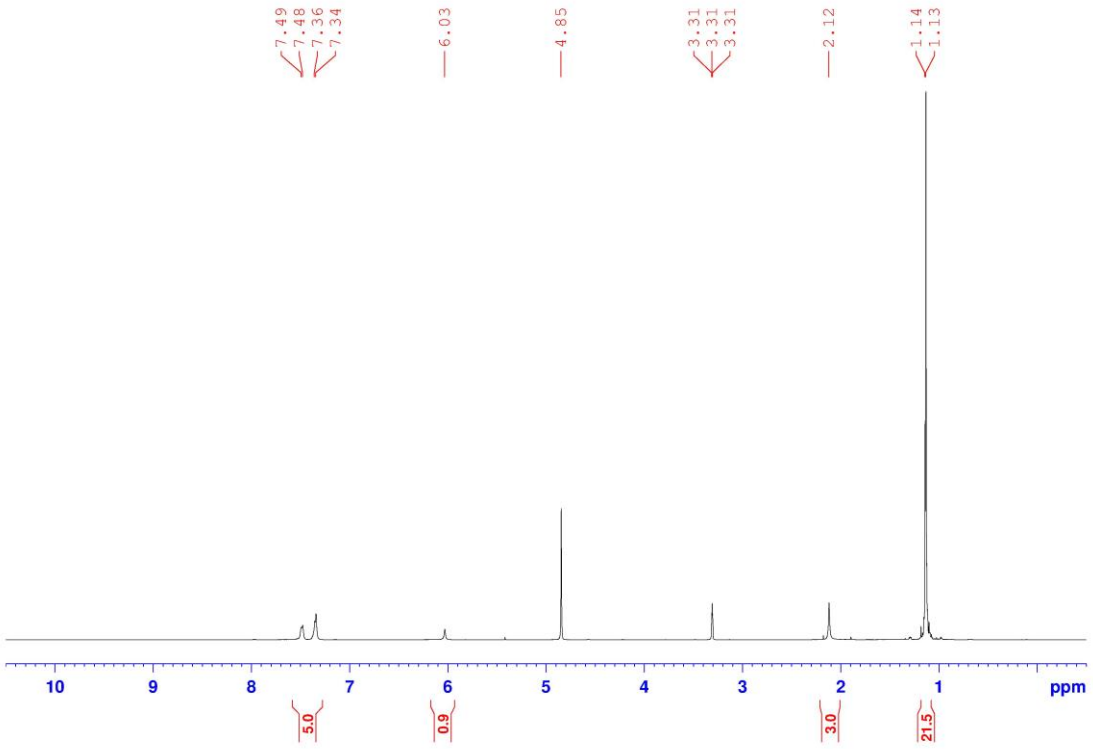


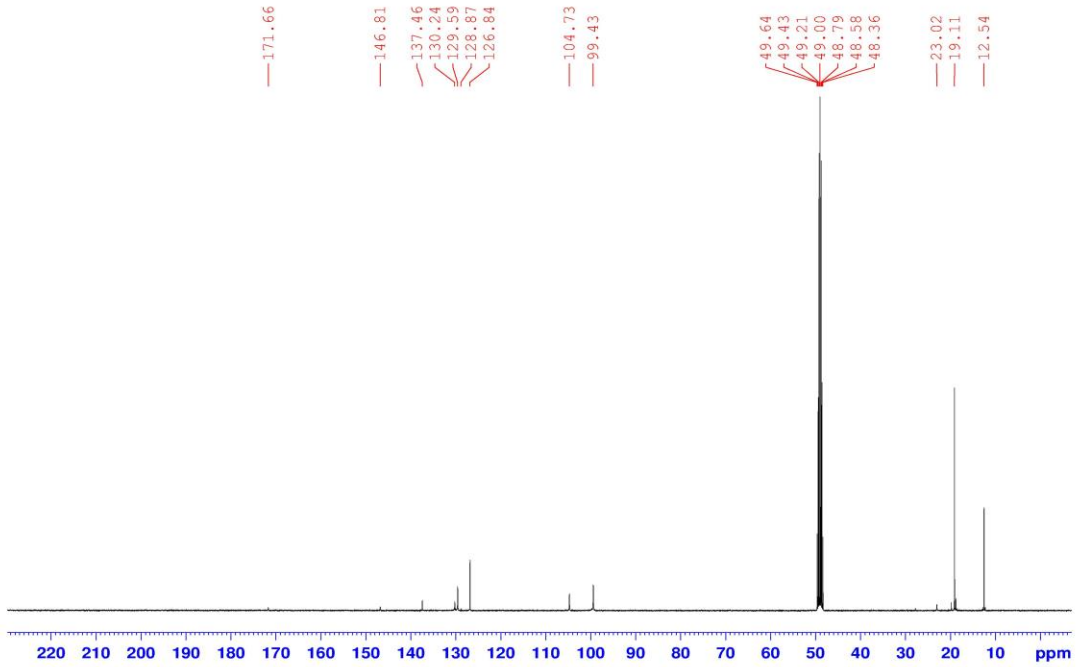
Isotope experiment



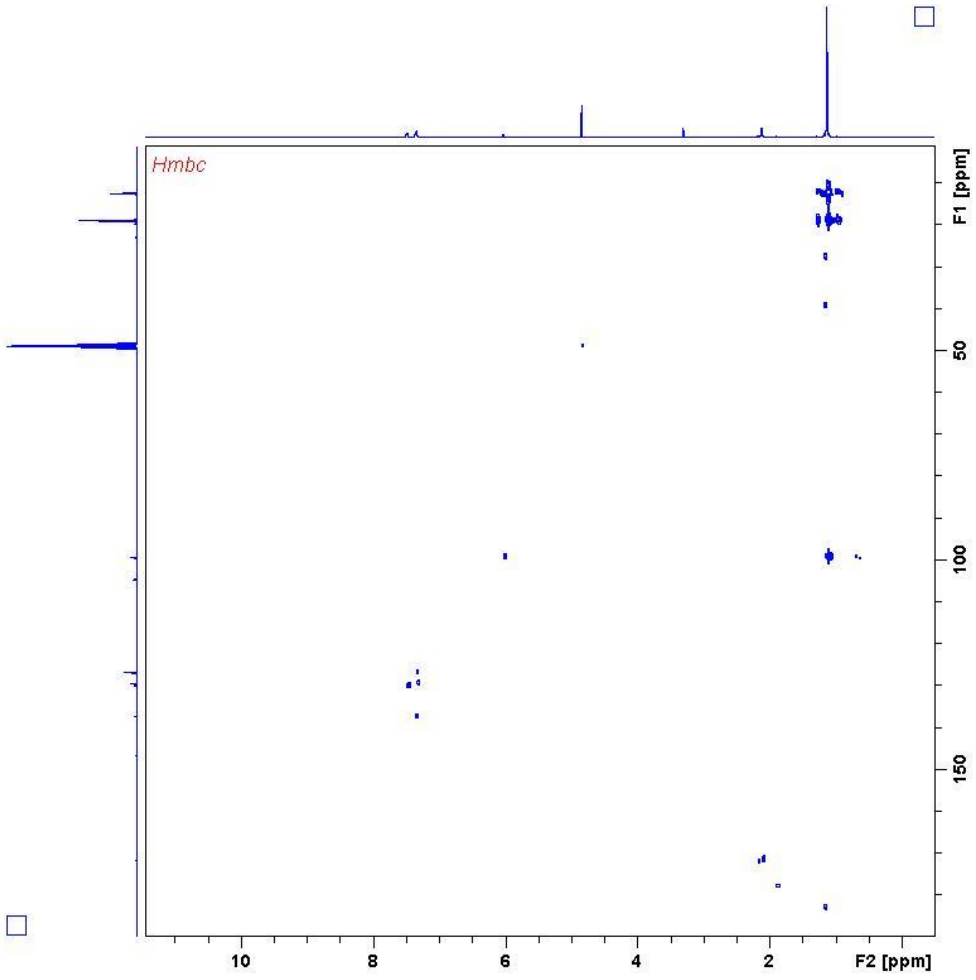
Synthetic procedure: The *N*-(1-phenylvinyl)acetamide **2a** (0.2 mmol, 1 equiv.), ^{13}C labeled hypervalent alkynyliodonium reagent **1-C^{13}** (0.22 mmol, 1.1 equiv.), [Cp*Rh(MeCN)$_3$][SbF$_6$] (0.004 mmol, 2 mol %), PivOH (0.02 mmol, 10 mol %) and Acetone (1 mL) were placed in a 8 mL glass vial under air. After stirring at room temperature for 12 hours, saturated $NaHCO_3$ solution (10 mL) was added and the resulting mixture was extracted with dichloromethane (2x20mL). Removal of the solvent in vacuo and purified by column chromatography afforded the desired product **3a-C^{13}** 54.8 mg (80% yield).

(^{1}H NMR, 13C NMR and Hmbc in CD_3OD)



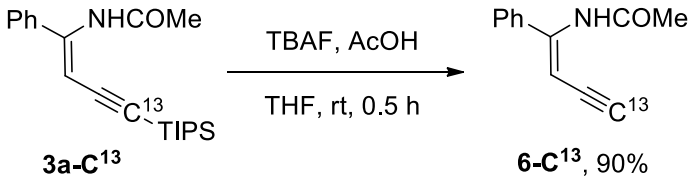

171.66
146.81
137.46
130.24
129.59
128.87
126.84
104.73
99.43
49.64
49.43
49.21
49.00
48.79
48.58
48.36
23.02
19.11
12.54
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Hmbc


Hmbc
F1 [ppm]
50
100
150
10
8
6
4
2
F2 [ppm]

Desilylation reaction of 3a-C^{13}

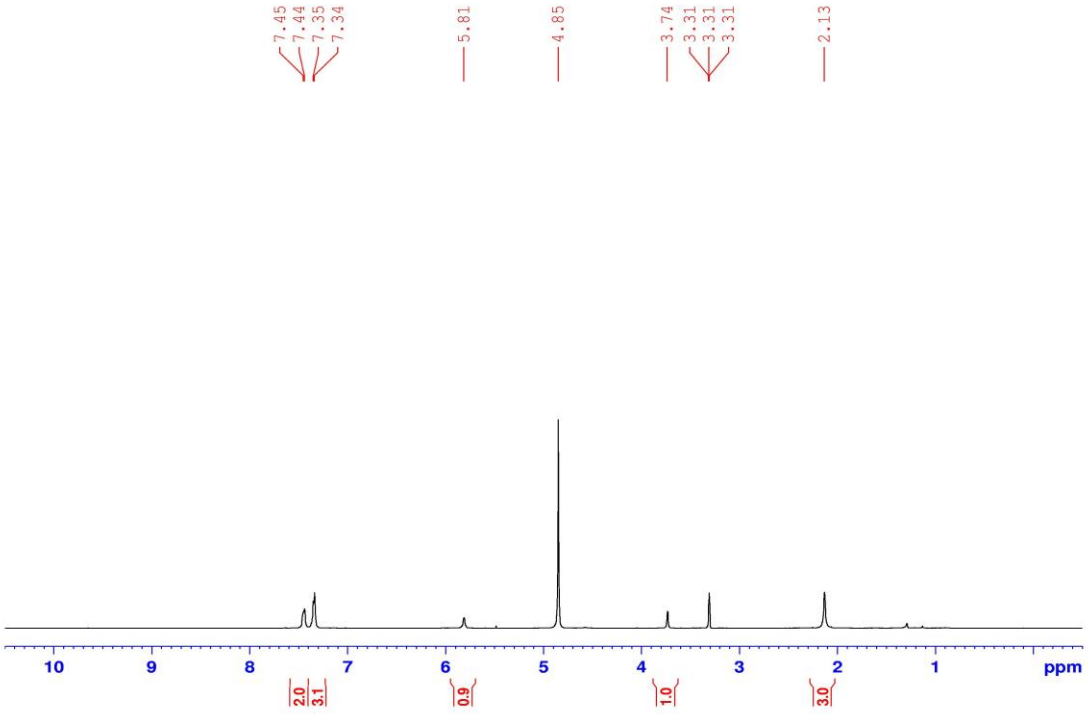
General reaction procedure D

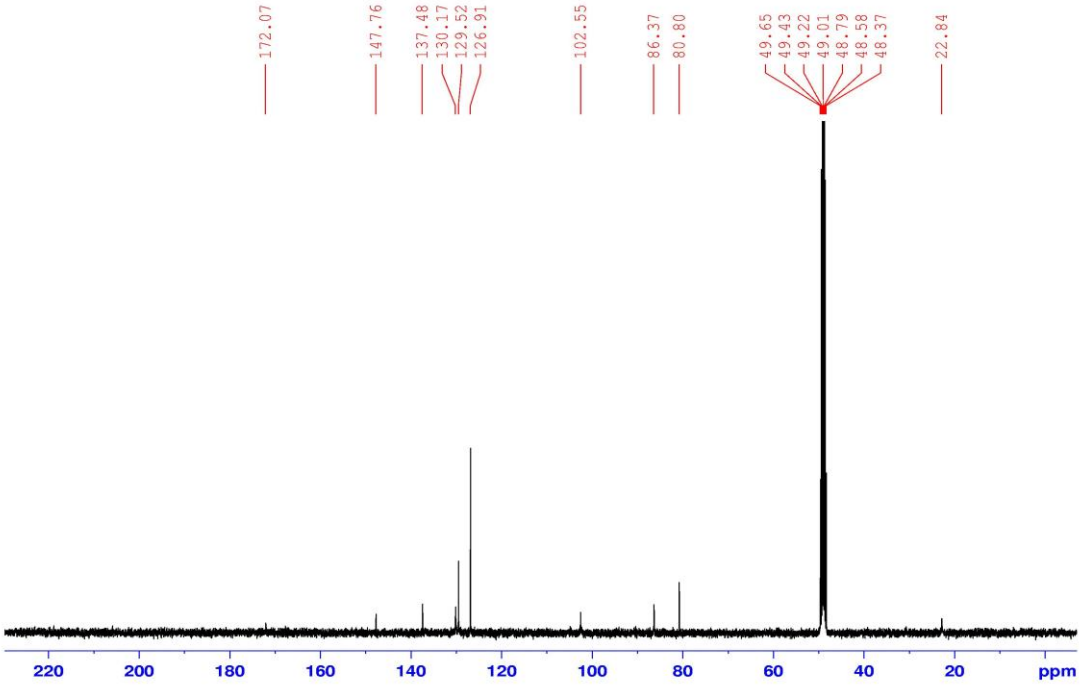


3a-C^{13} **6-C^{13}**, 90%

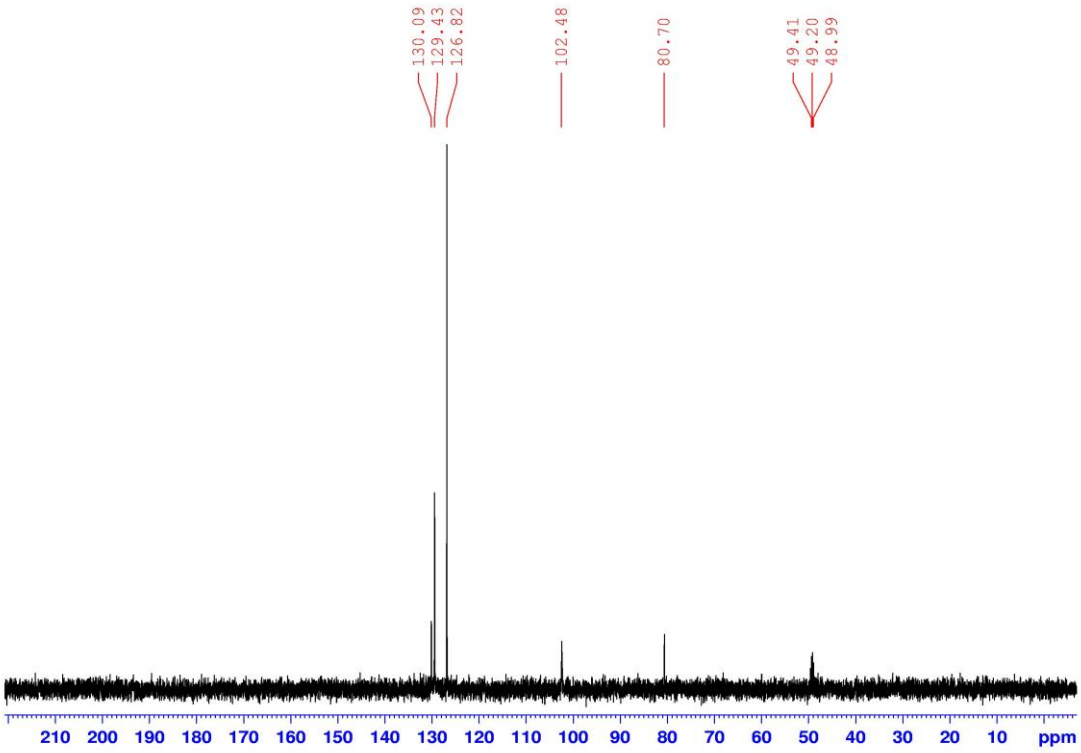
Synthetic procedure: The ^{13}C labeled **3a-C^{13}** (0.1 mmol, 1 equiv.) was dissolved into 0.5 mL THF in a 10 mL RBF. Then added the mixture of TBAF (0.2 mmol, 2 equiv.), AcOH(0.3 mmol, 3 equiv.) and 0.5 mL THF dropwisely. The reaction was allowed to stir for 0.5 hour under room temperature and quenched with saturated $NaHCO_3$ solution (10 mL). After the extraction with dichloromethane (2x10mL), the organic layer was evaporated and the residue was subjected to column chromatography on silica gel to deliver the product **6-C^{13}** 16.7 mg (90% yield).

(^{1}H NMR, 13C NMR, Dept 90, Dept 135 and Hmqc in CD_3OD)

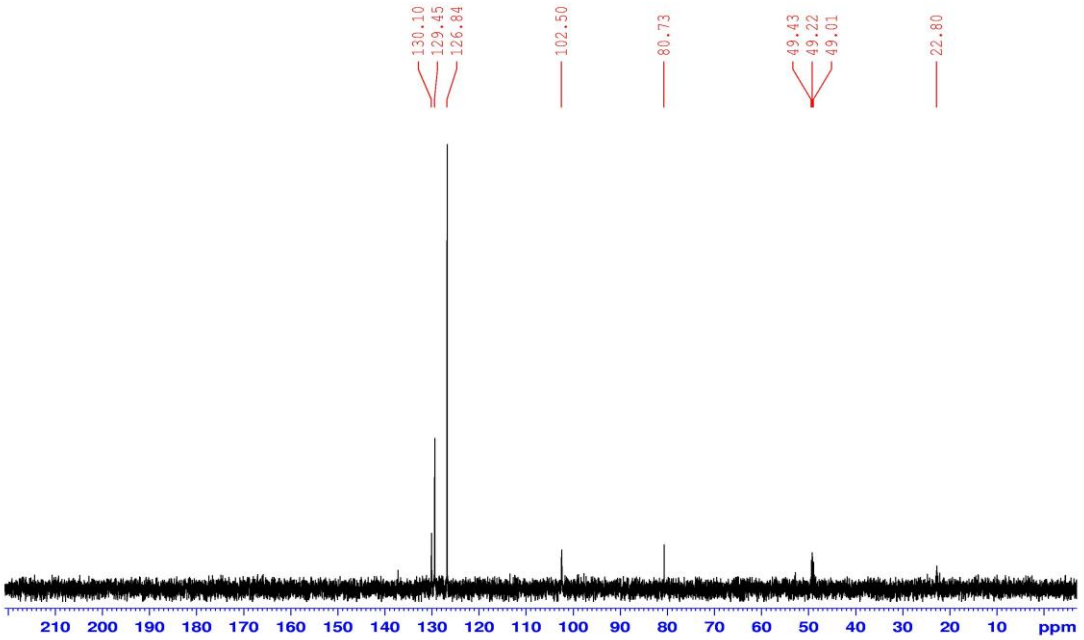



172.07
147.76
137.48
130.17
129.52
126.91
102.55
86.37
80.80
49.65
49.43
49.22
49.01
48.79
48.58
48.37
22.84
220
200
180
160
140
120
100
80
60
40
20
ppm

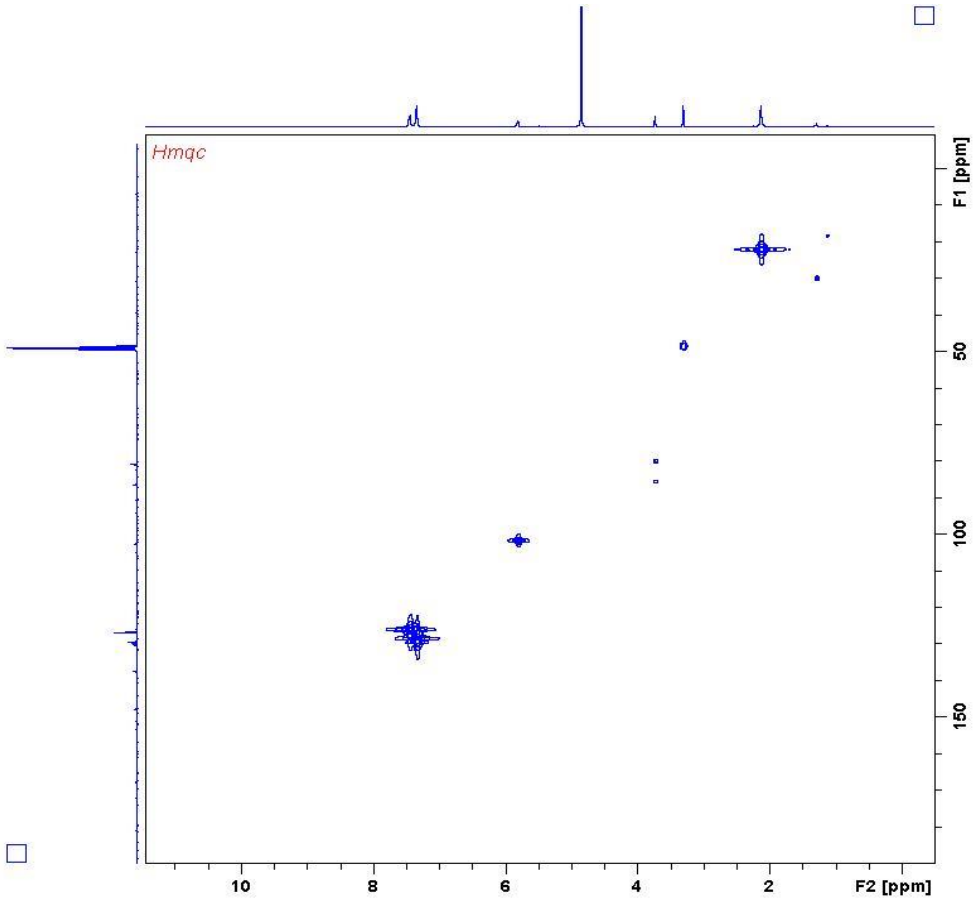
Dept 90


130.09
129.43
126.82
102.48
80.70
49.41
49.20
48.99
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

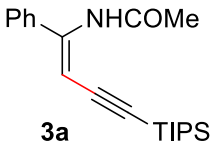
Dept 135



Hmqc

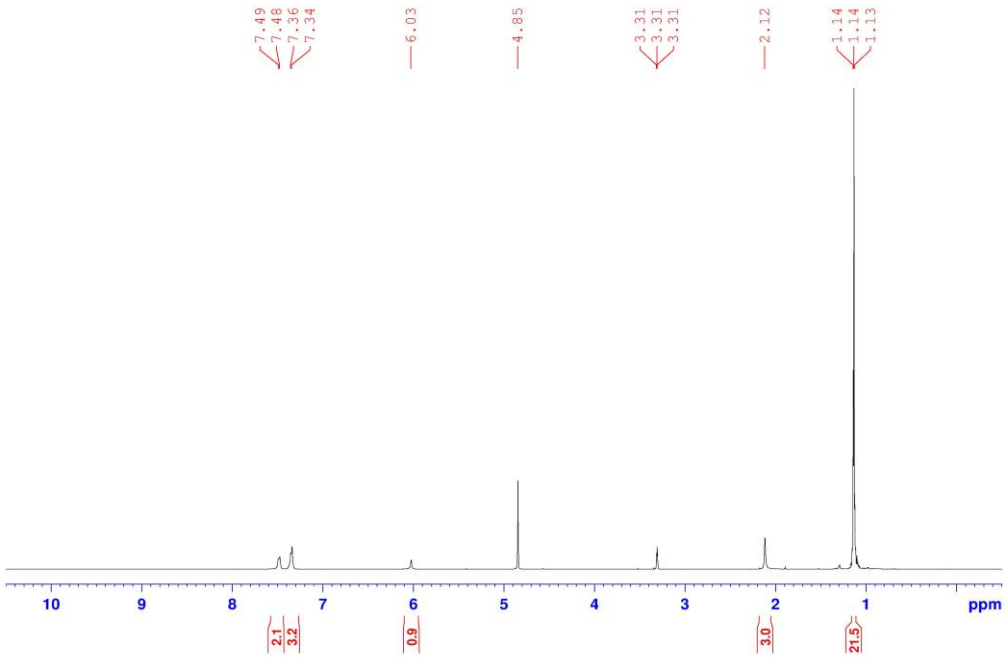


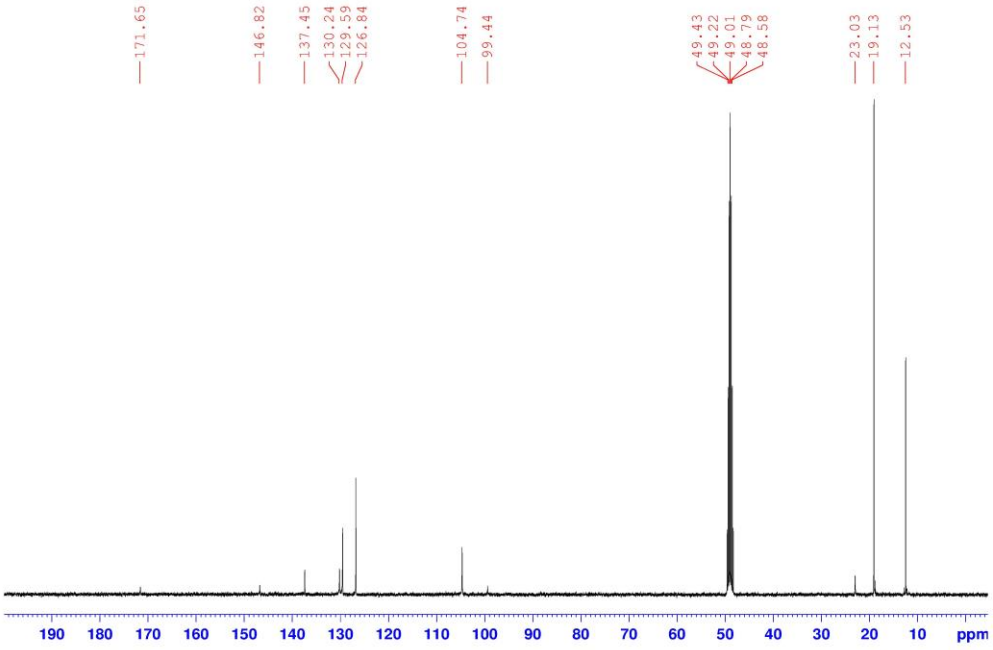
^{1}H and ^{13}C NMR spectra of products

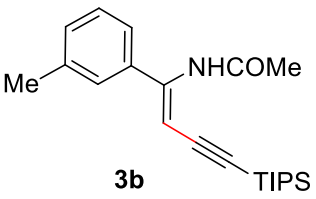


3a

^{1}H NMR & ^{13}C NMR in CD_3OD

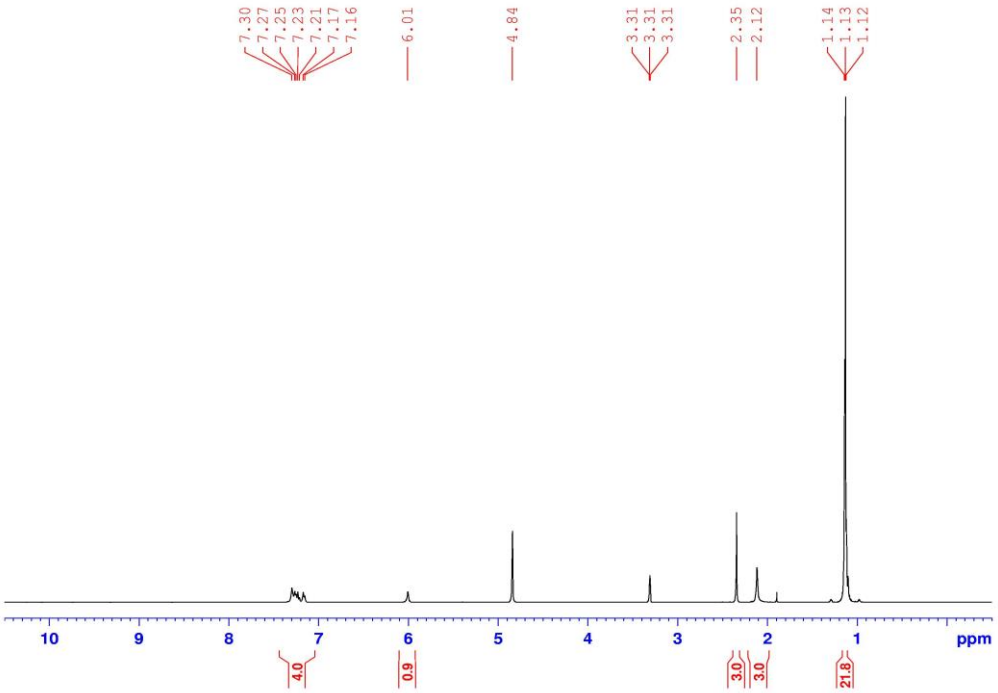


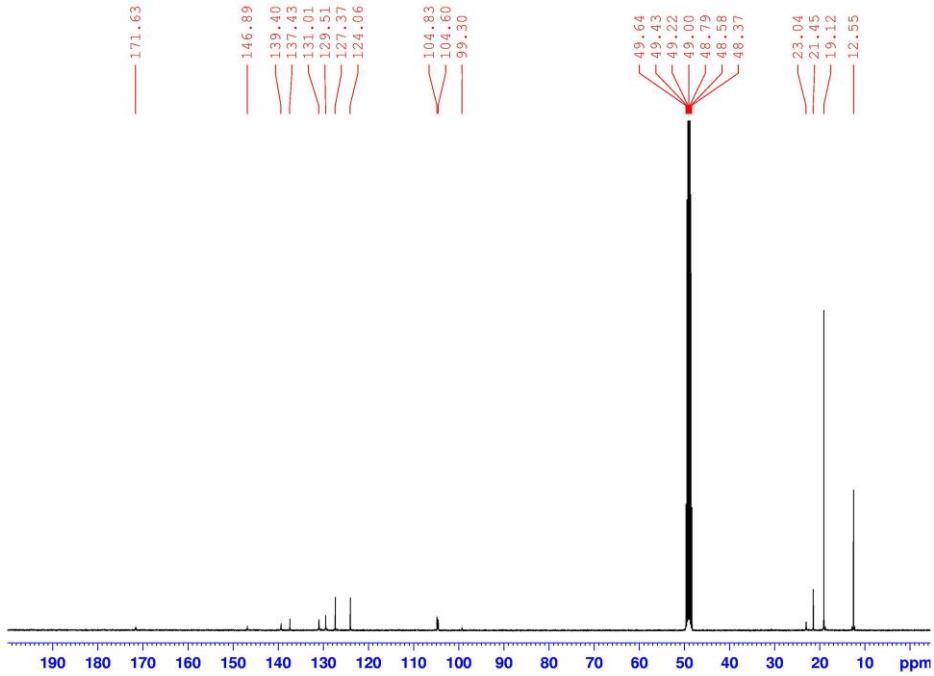


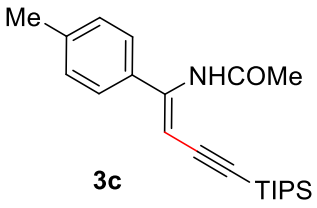


3b

^{1}H NMR & ^{13}C NMR in CD_3OD

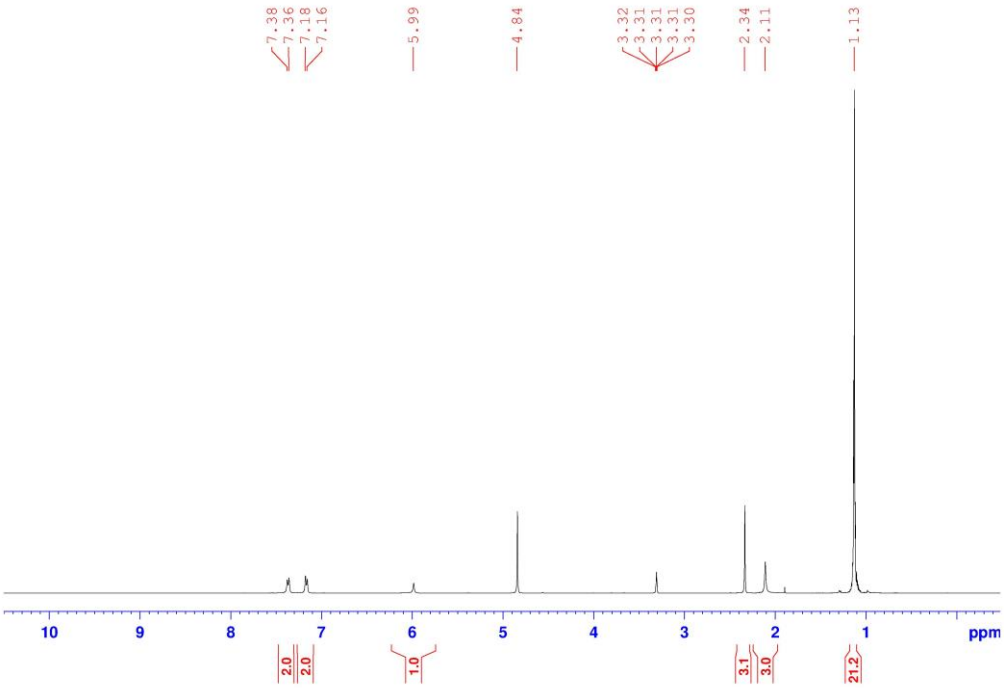


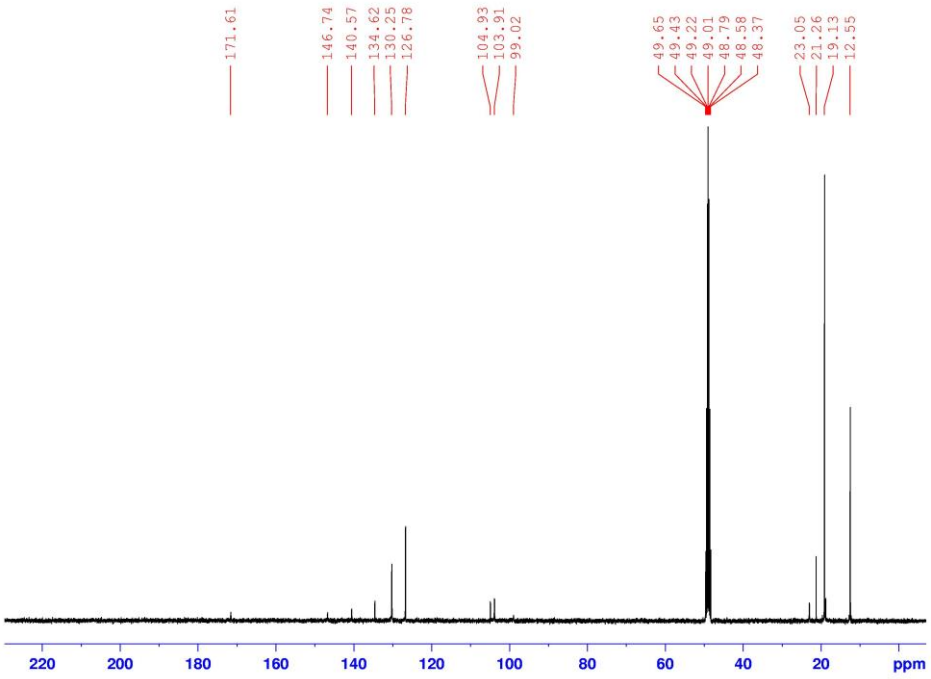


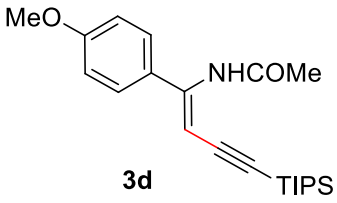


3c

^{1}H NMR & ^{13}C NMR in CD_3OD

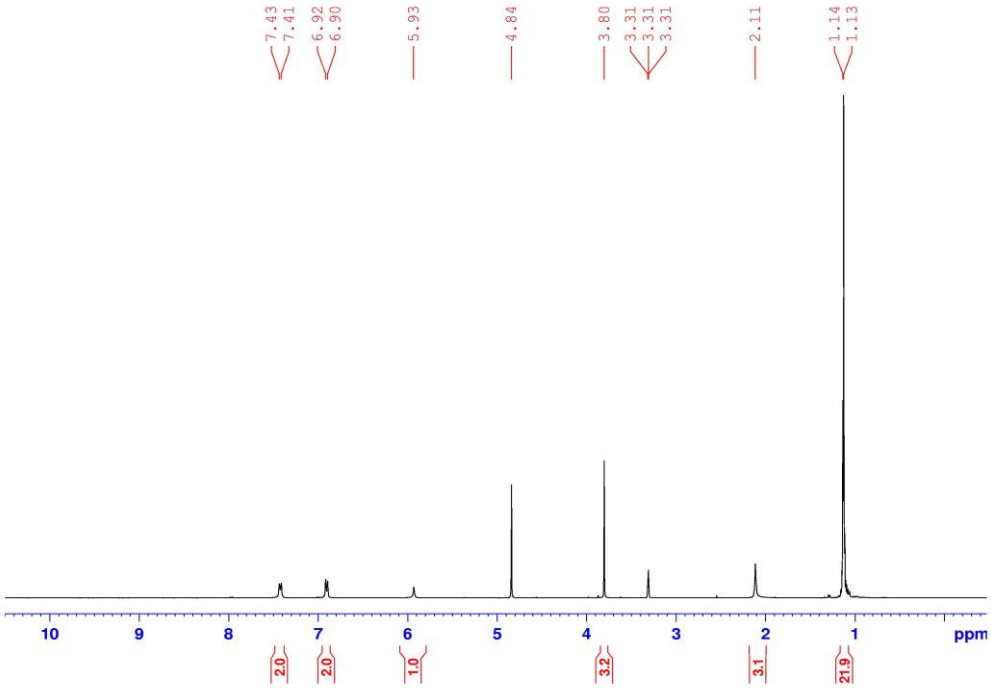


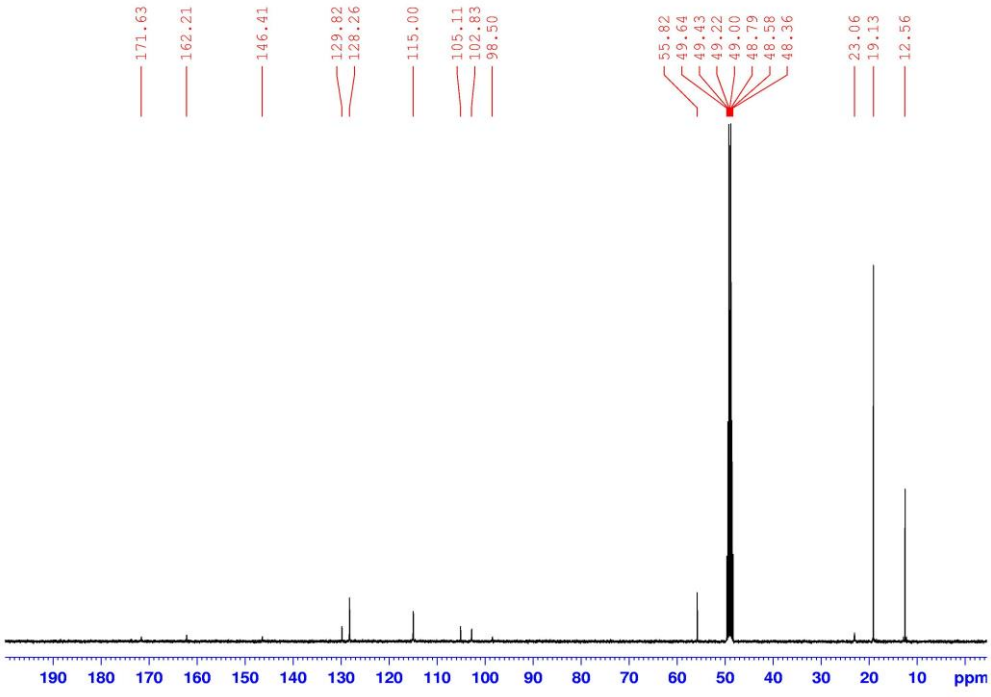


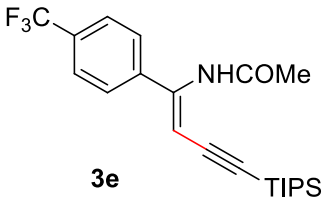


3d

^{1}H NMR & ^{13}C NMR in CD_3OD

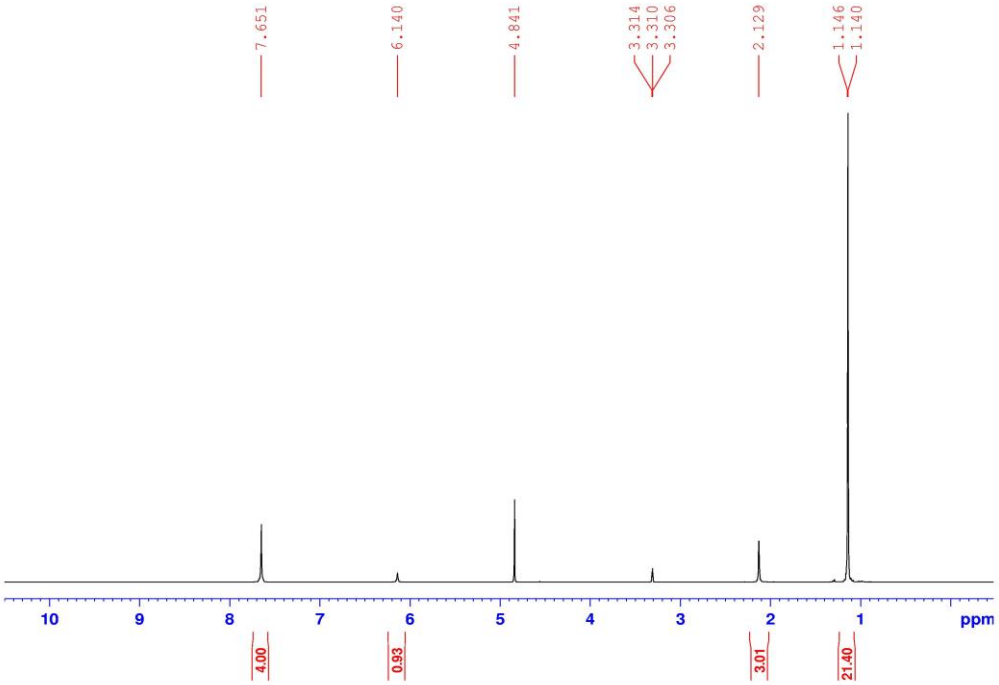


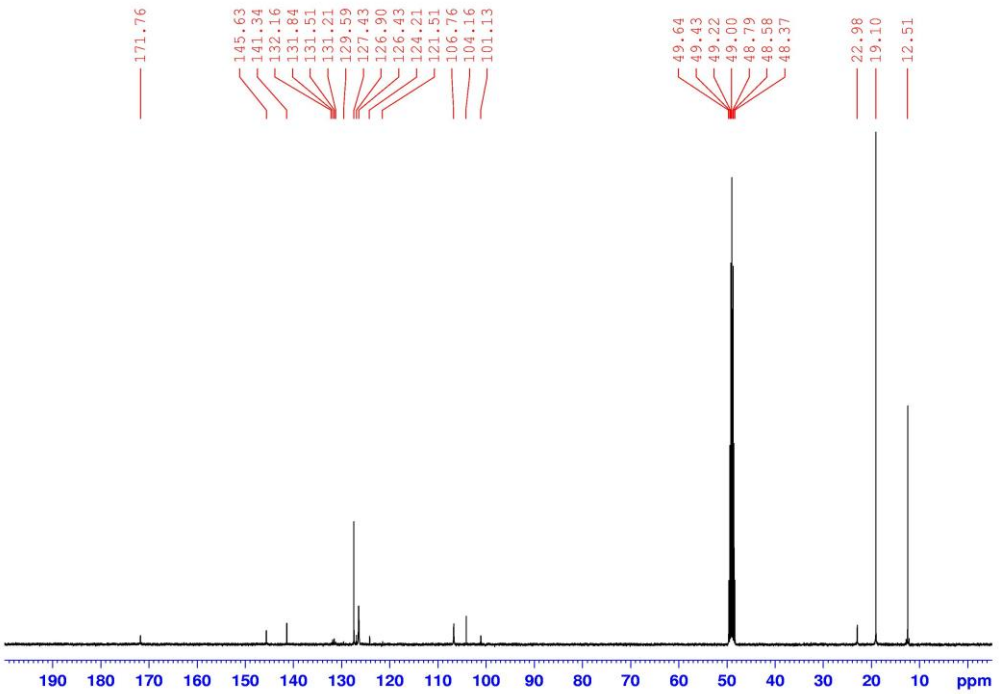


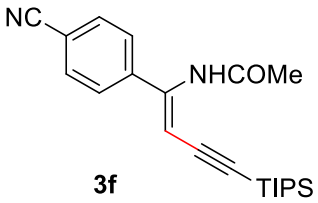


3e

^{1}H NMR & ^{13}C NMR in CD_3OD

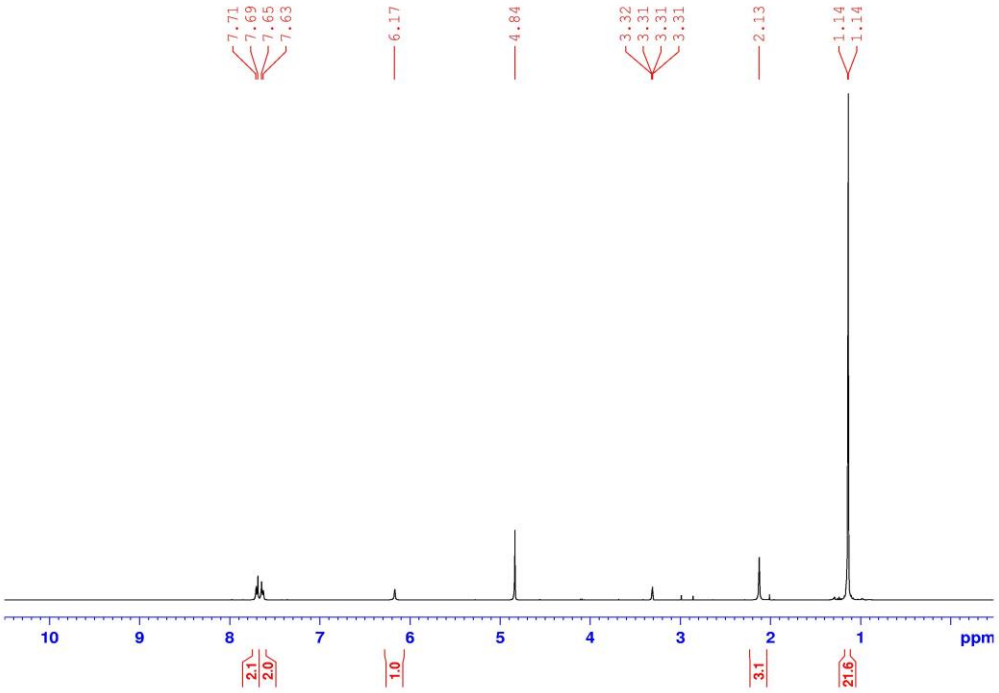


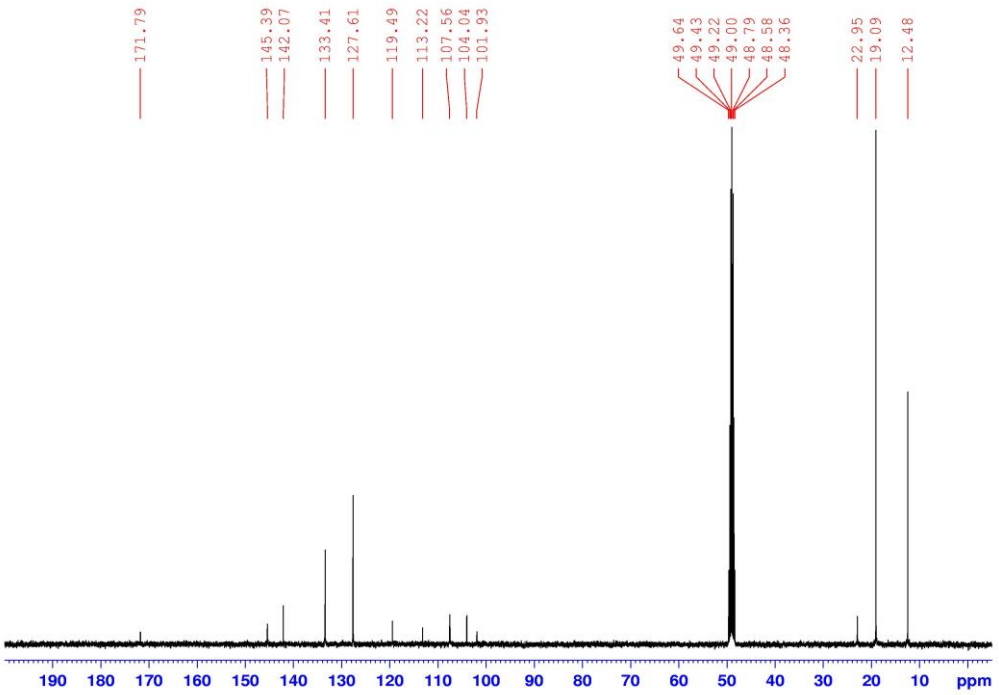


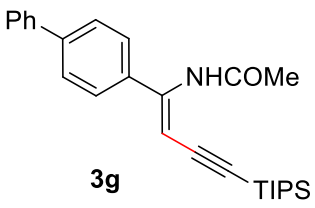


3f

^{1}H NMR & ^{13}C NMR in CD_3OD

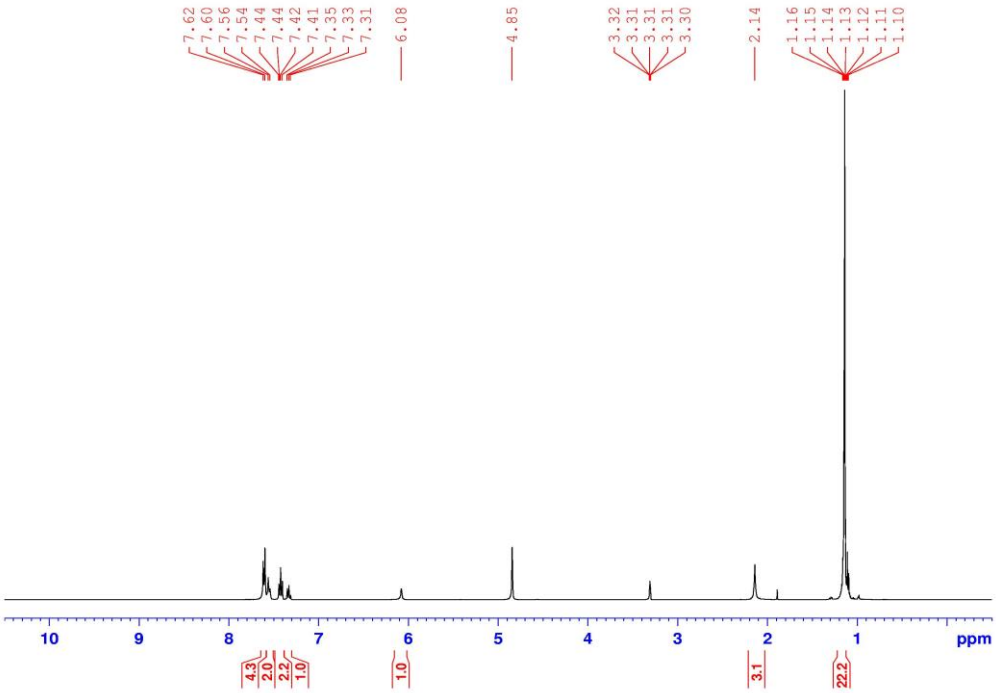


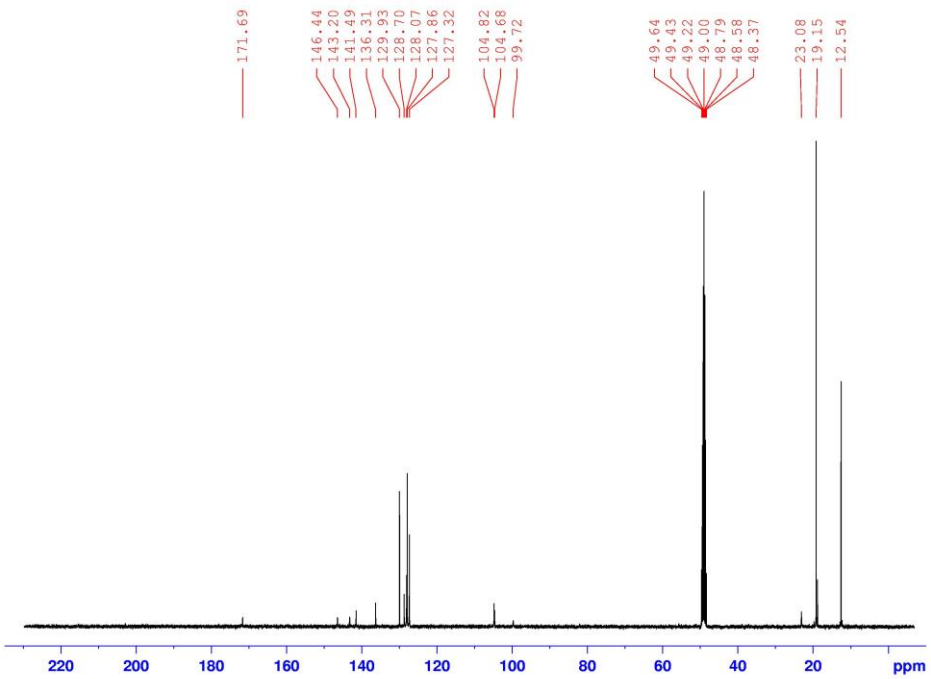


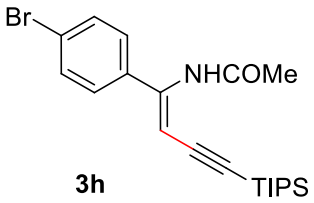


3g

^{1}H NMR & ^{13}C NMR in CD_3OD

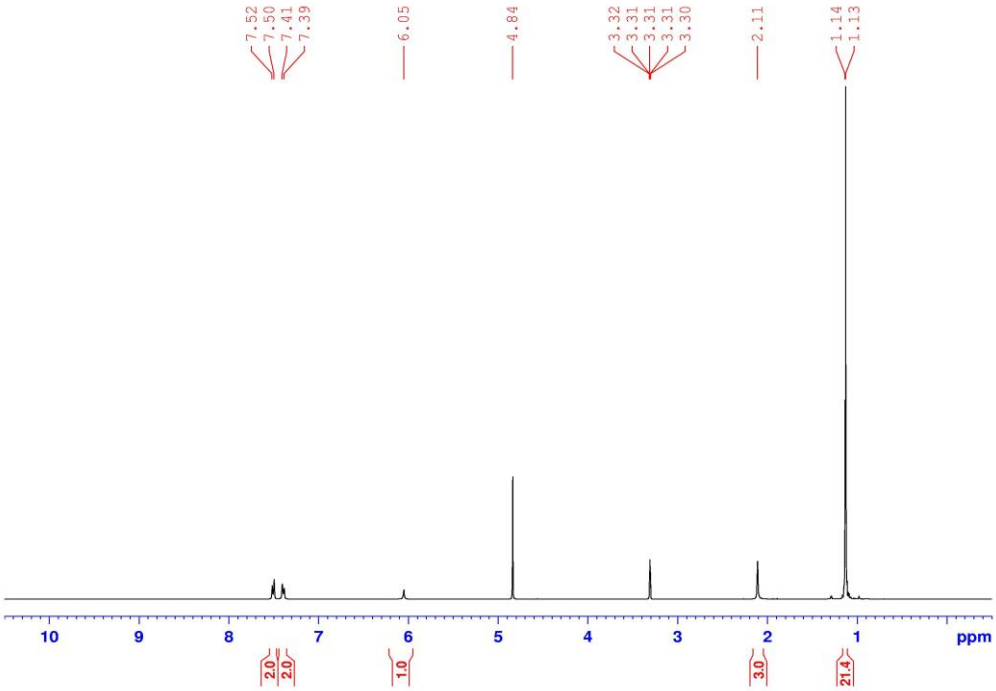


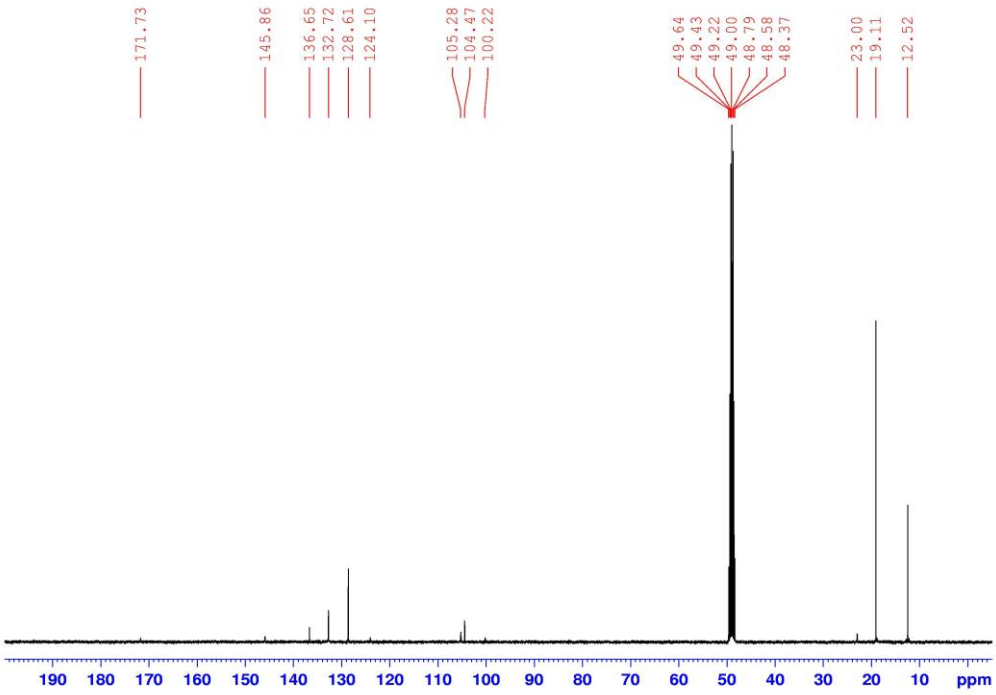


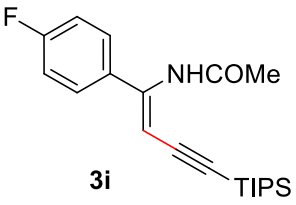


3h

^{1}H NMR & ^{13}C NMR in CD_3OD

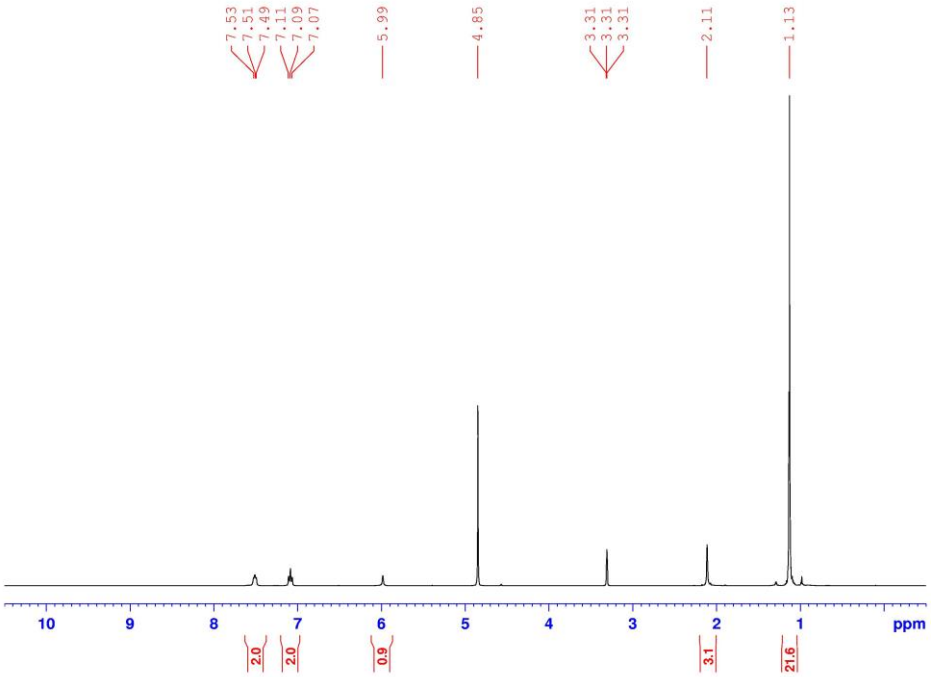


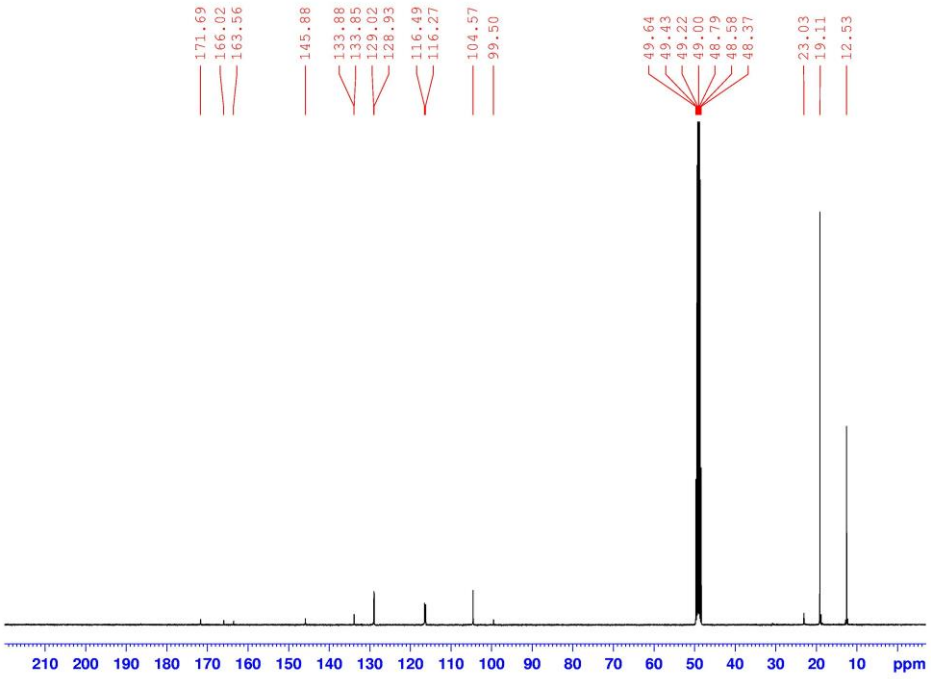


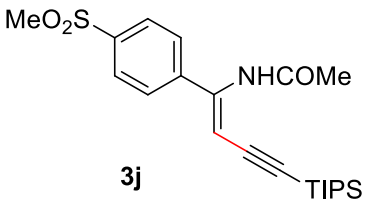


3i

^{1}H NMR & ^{13}C NMR in CD_3OD

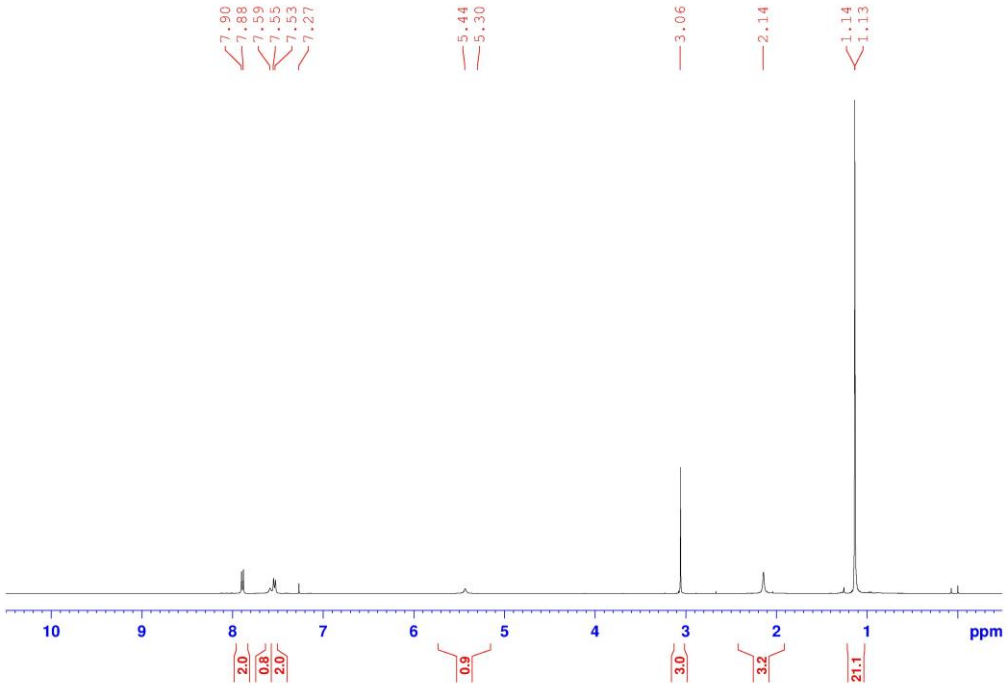


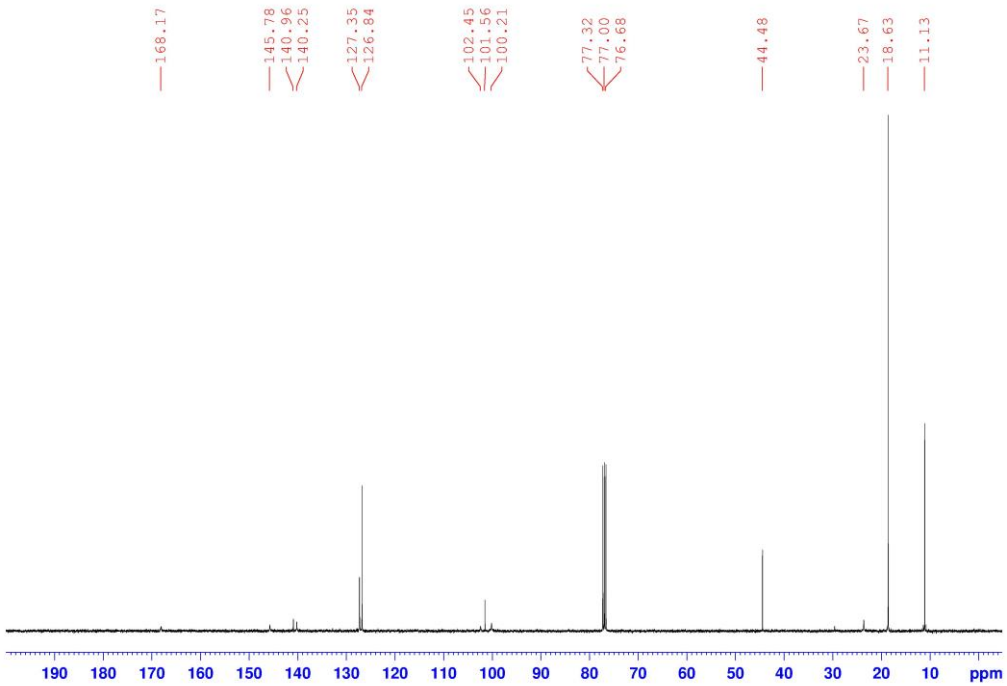


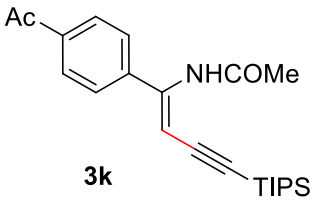


3j

^{1}H NMR & ^{13}C NMR in $CDCl_3$

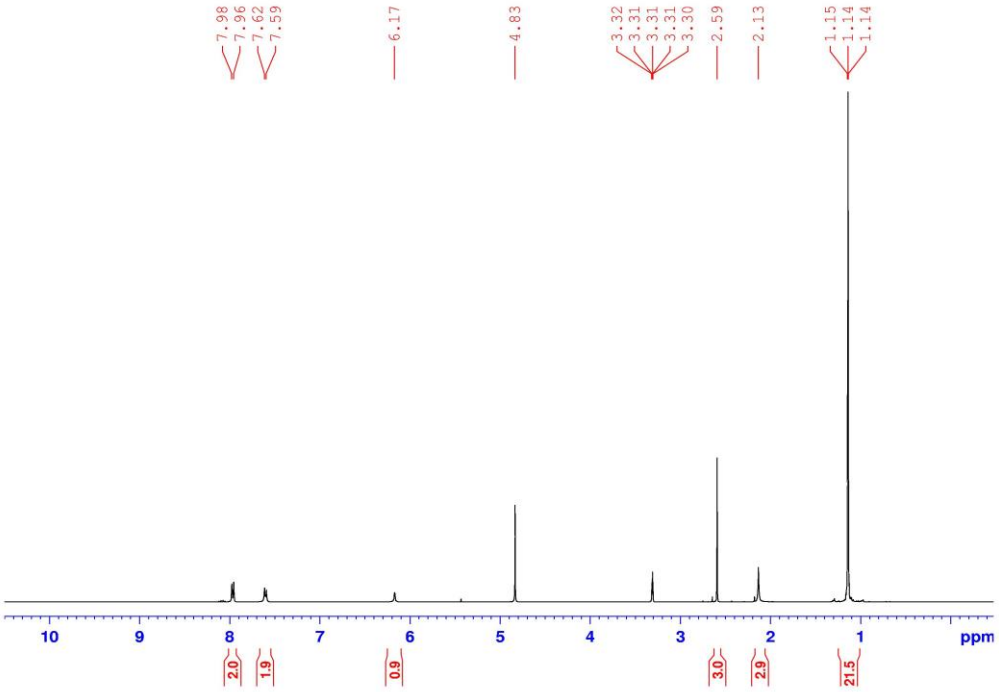


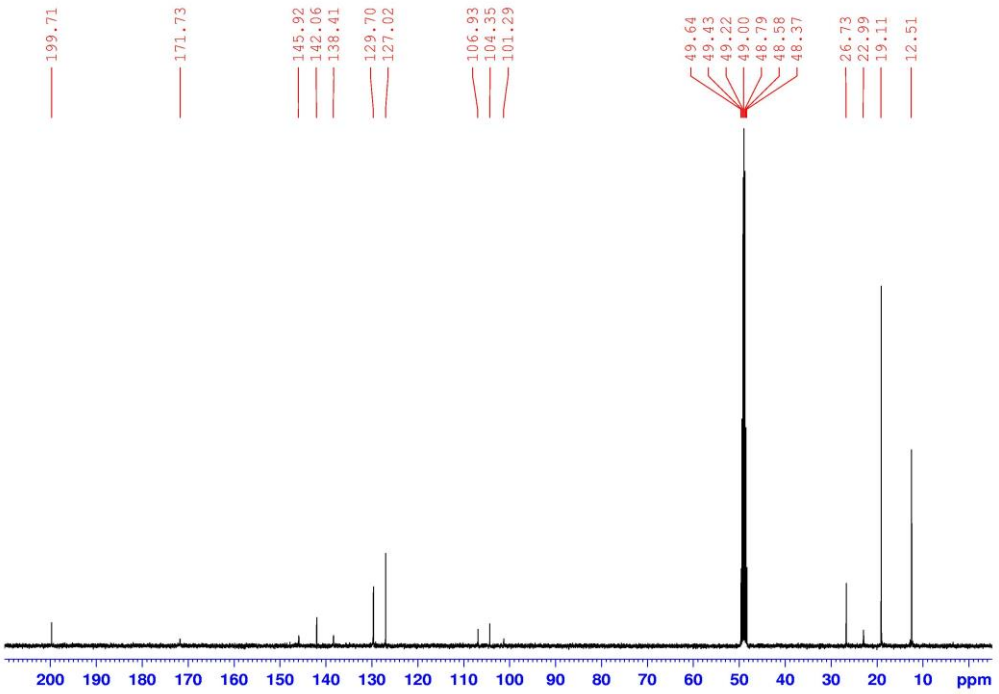


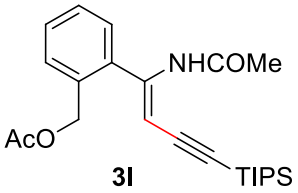


3k

^{1}H NMR & ^{13}C NMR in CD_3OD

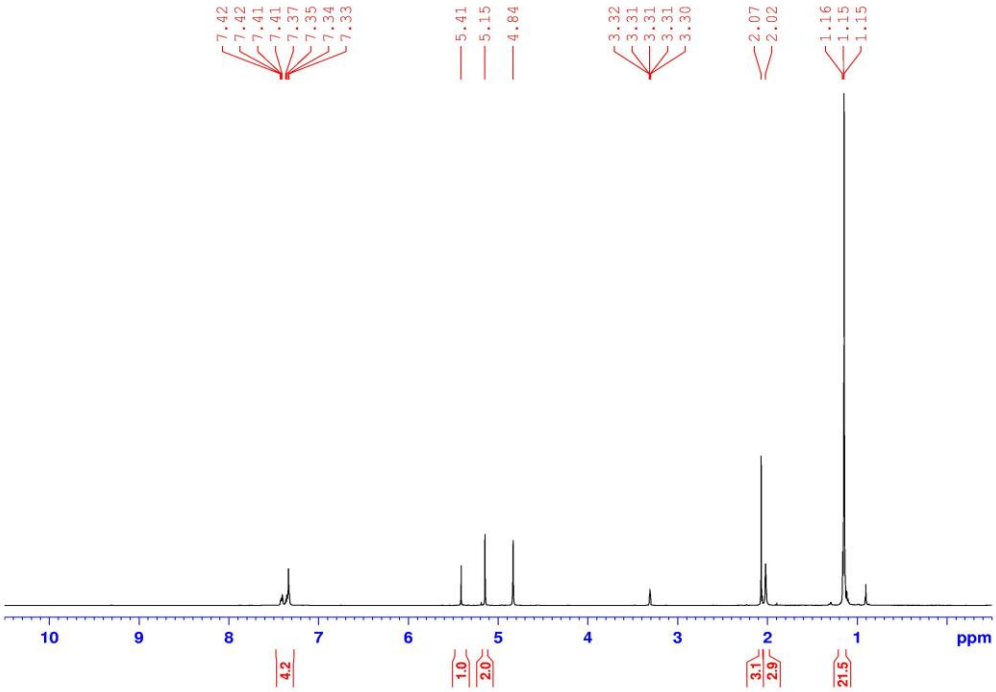


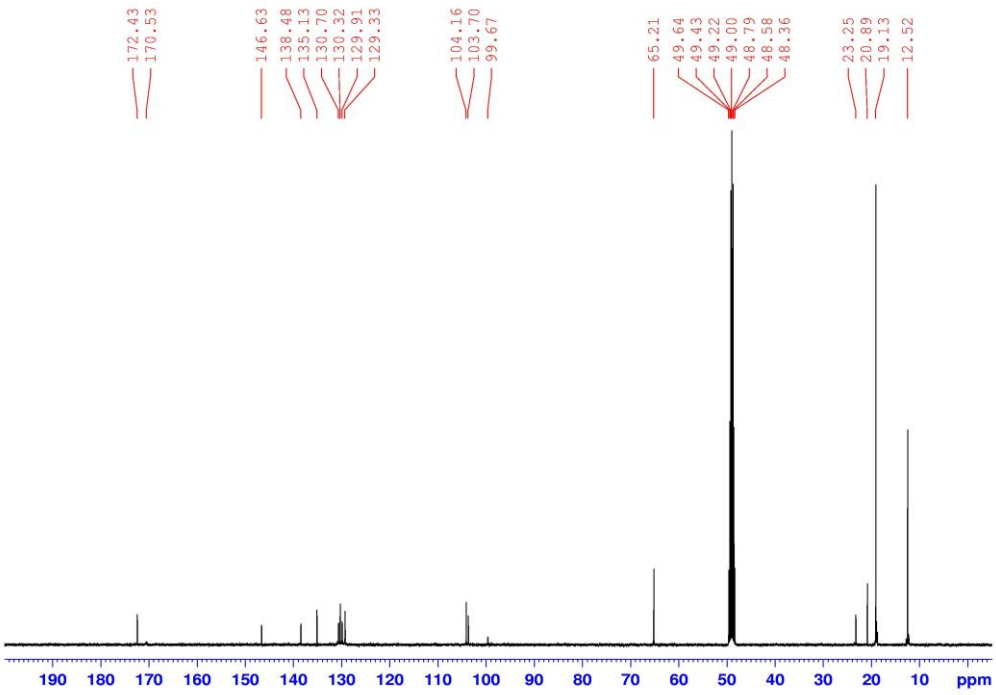


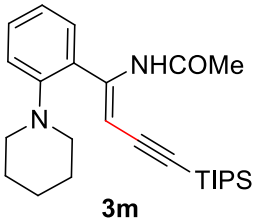


3l

^{1}H NMR & ^{13}C NMR in CD_3OD

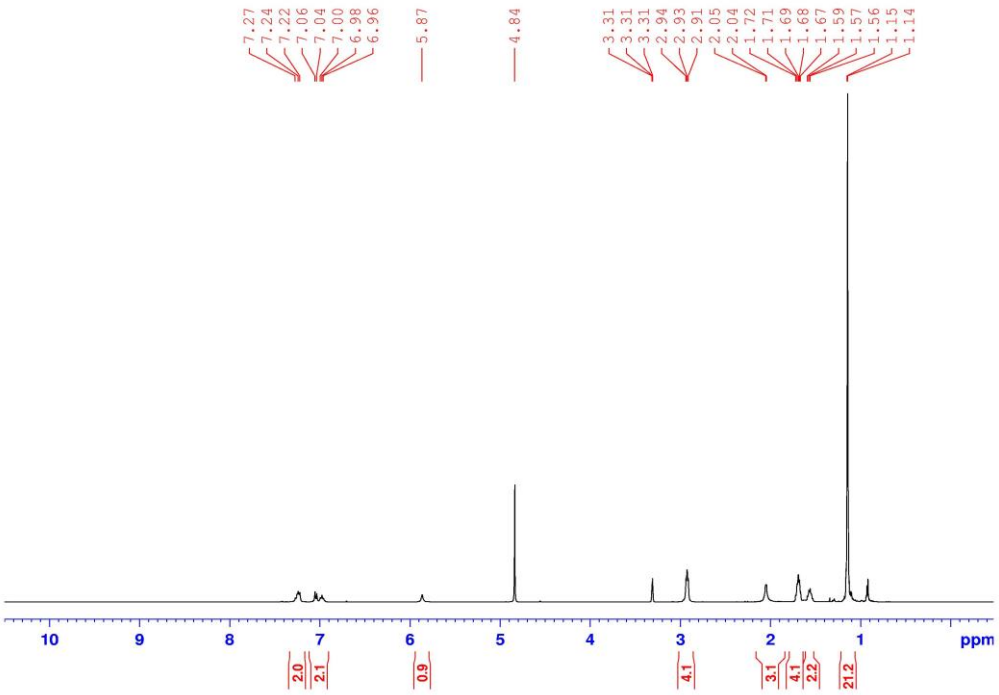


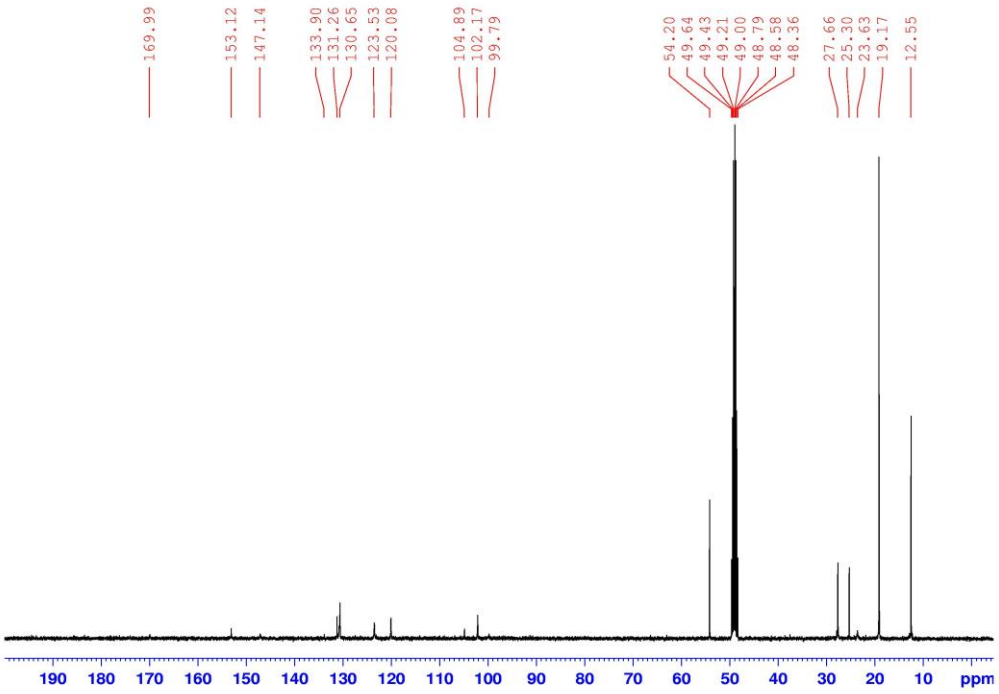


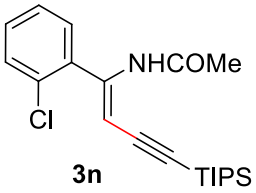


3m

^{1}H NMR & ^{13}C NMR in CD_3OD

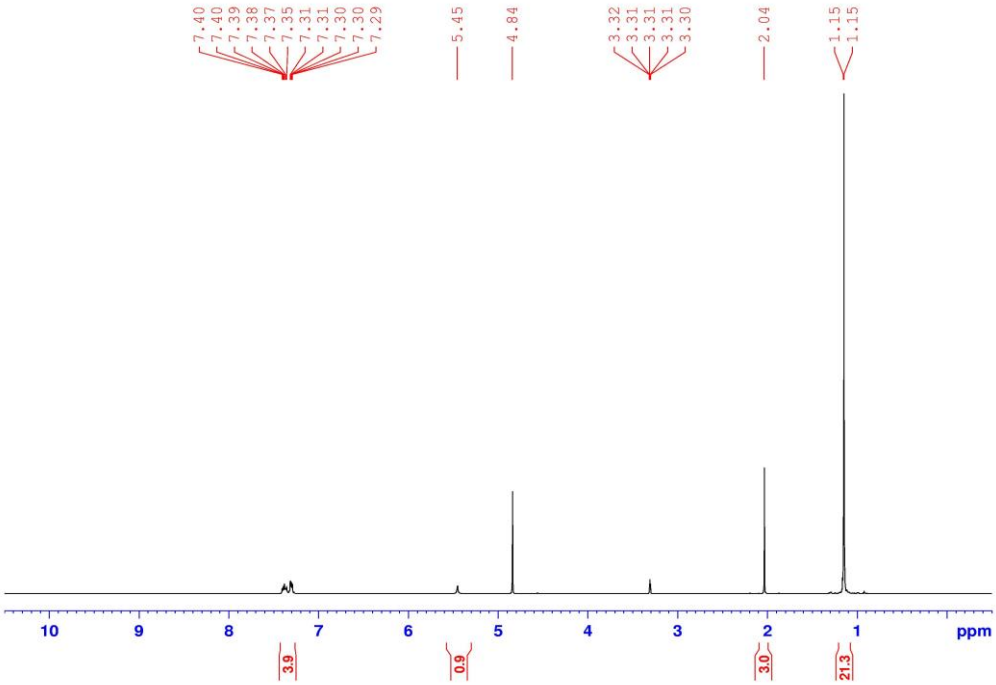


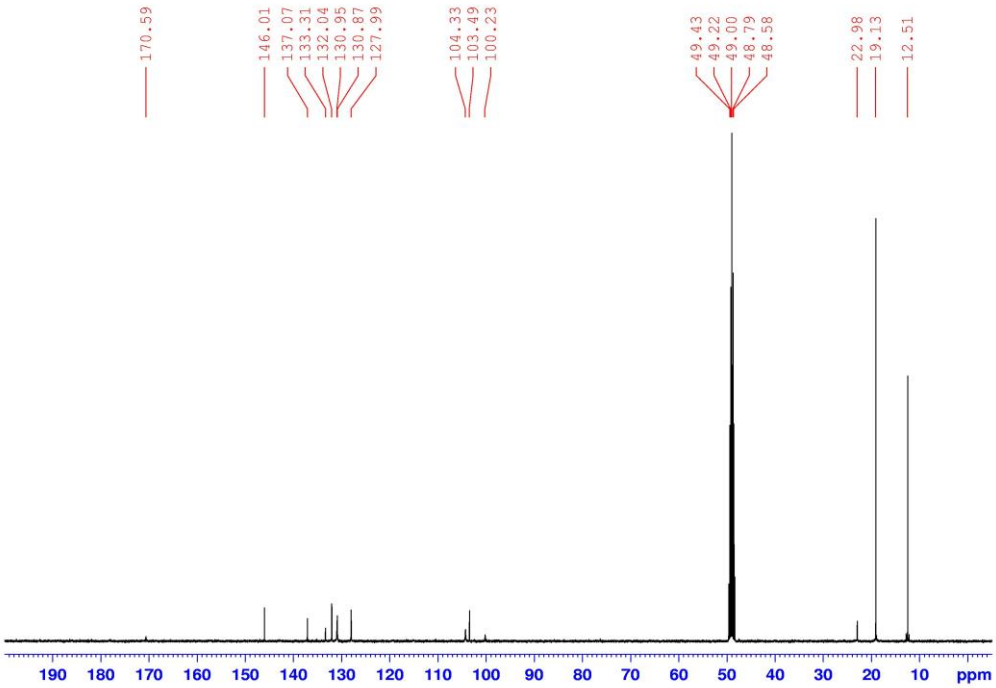


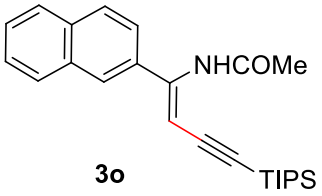


3n

^{1}H NMR & ^{13}C NMR in CD_3OD

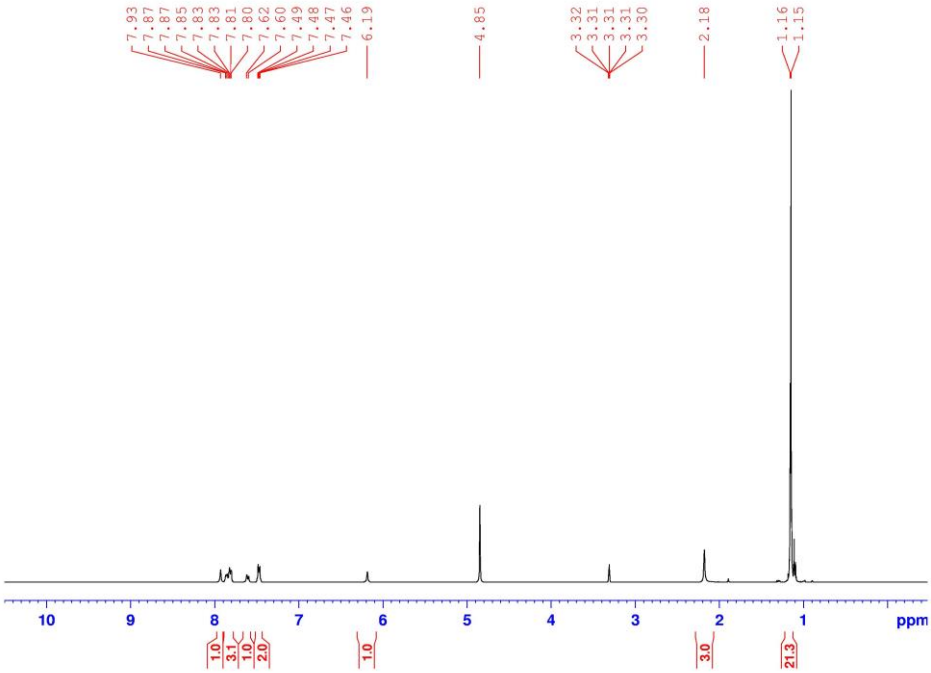


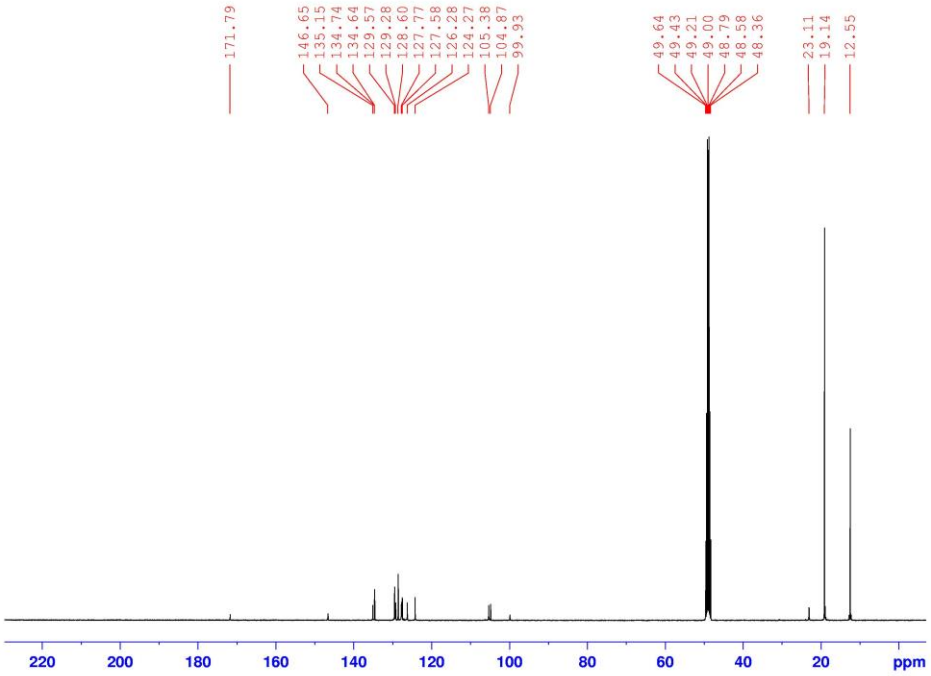


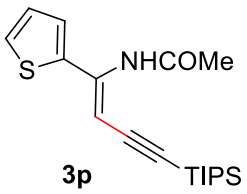


3o

^{1}H NMR & ^{13}C NMR in CD_3OD

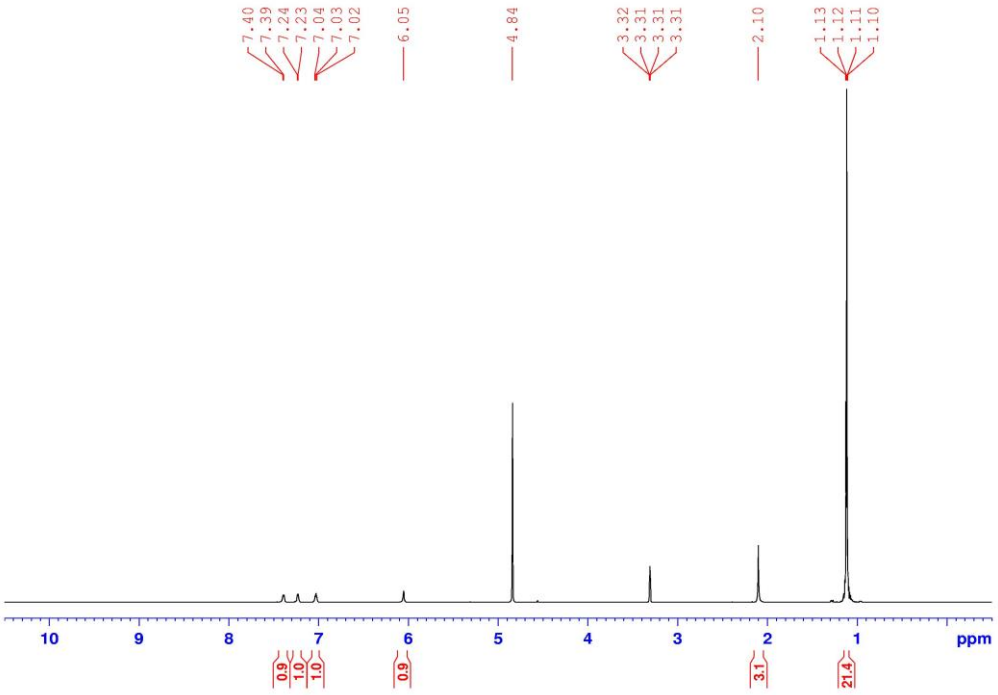


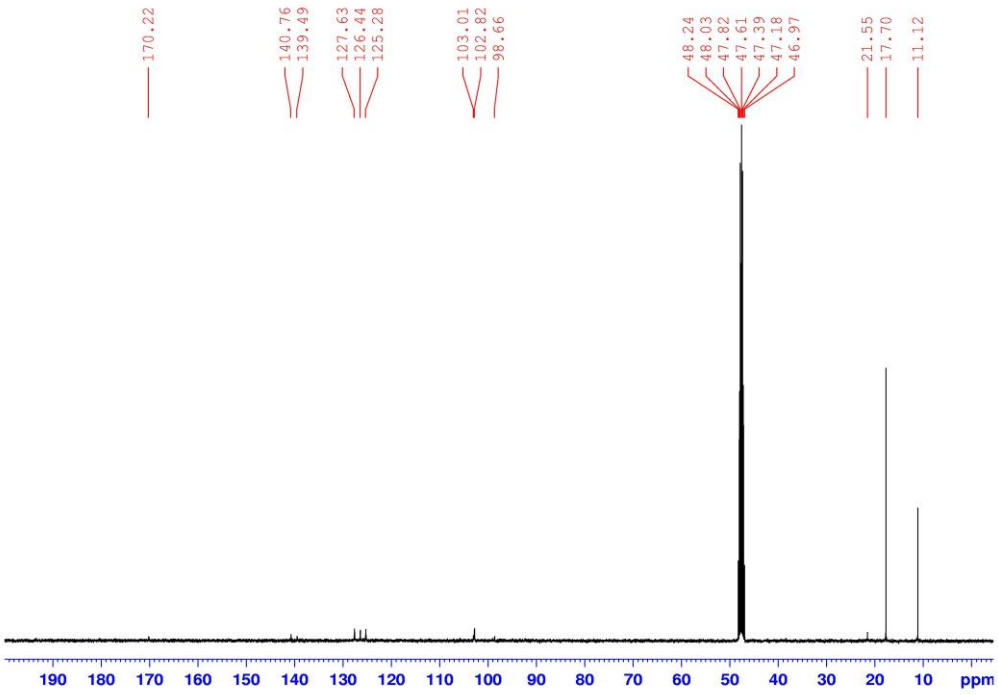


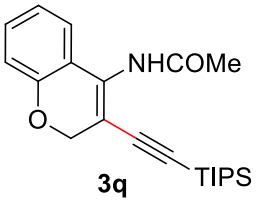


3p

^{1}H NMR & ^{13}C NMR in CD_3OD

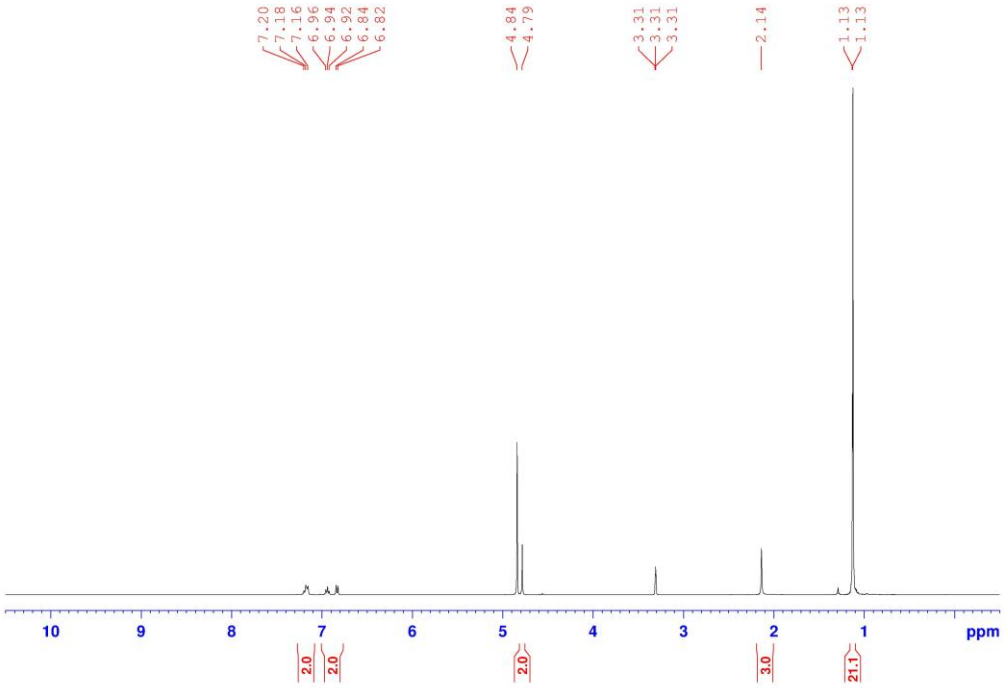


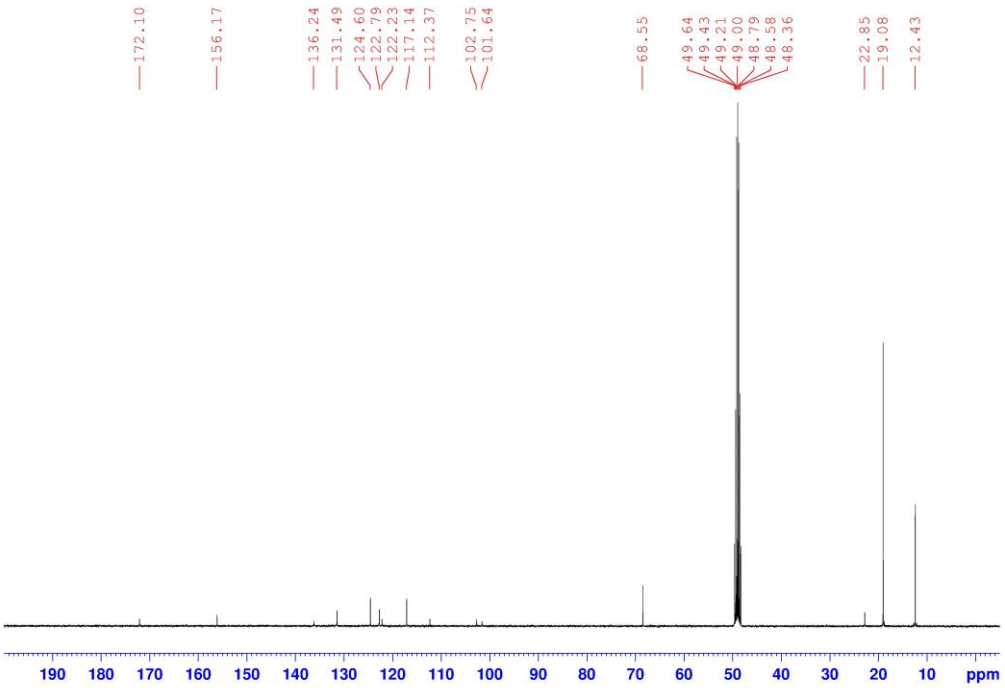


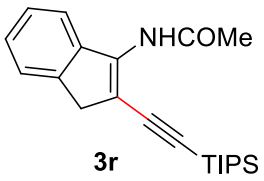


3q

^{1}H NMR & ^{13}C NMR in CD_3OD

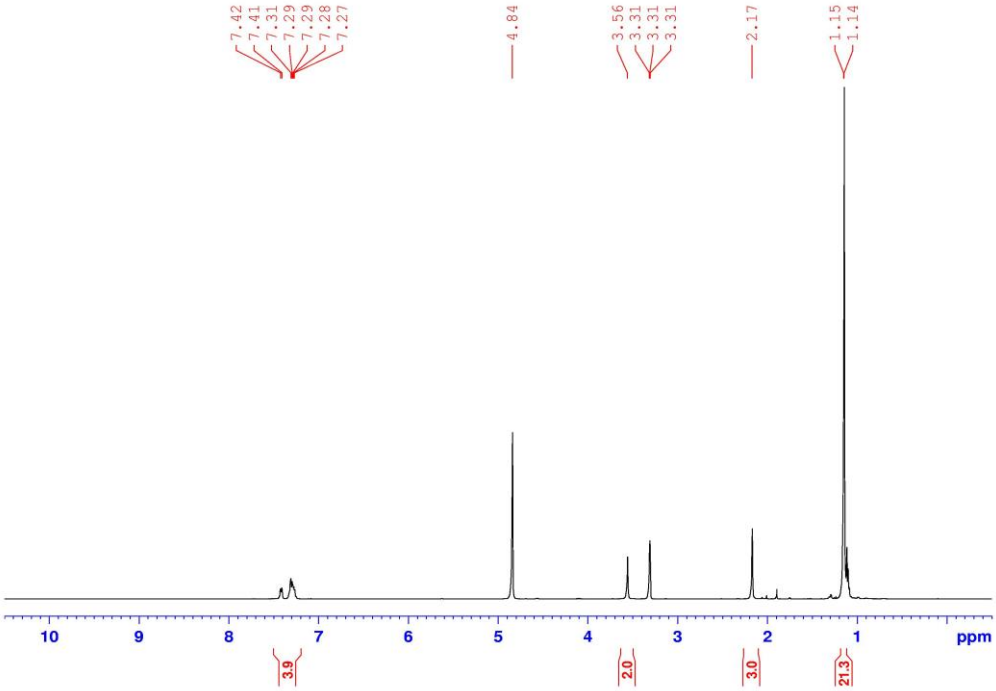


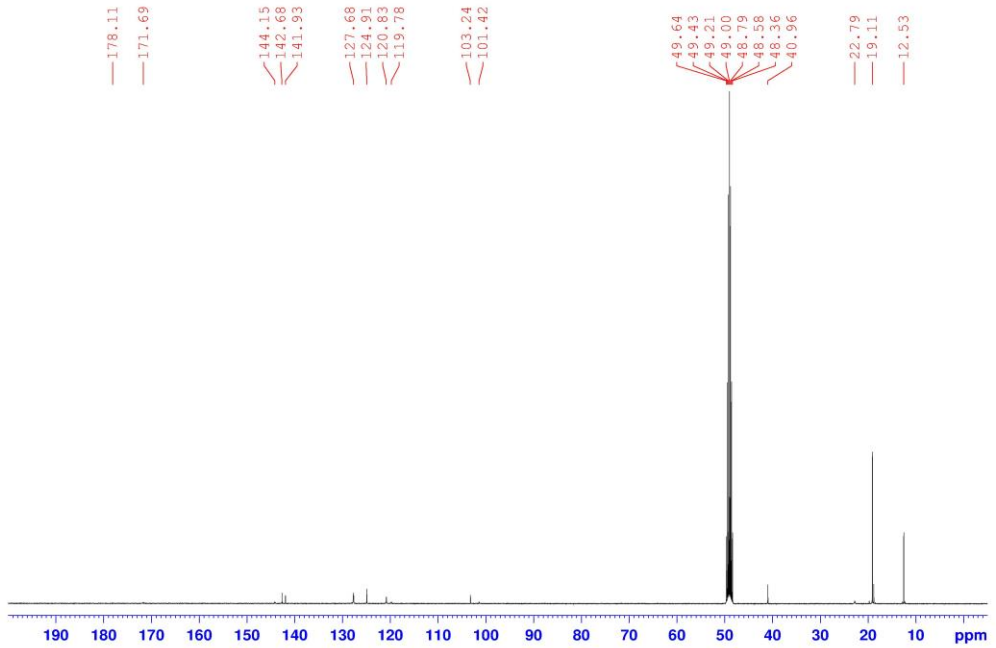


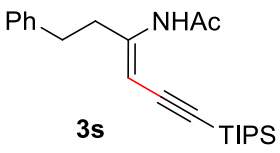


3r

^{1}H NMR & ^{13}C NMR in CD_3OD

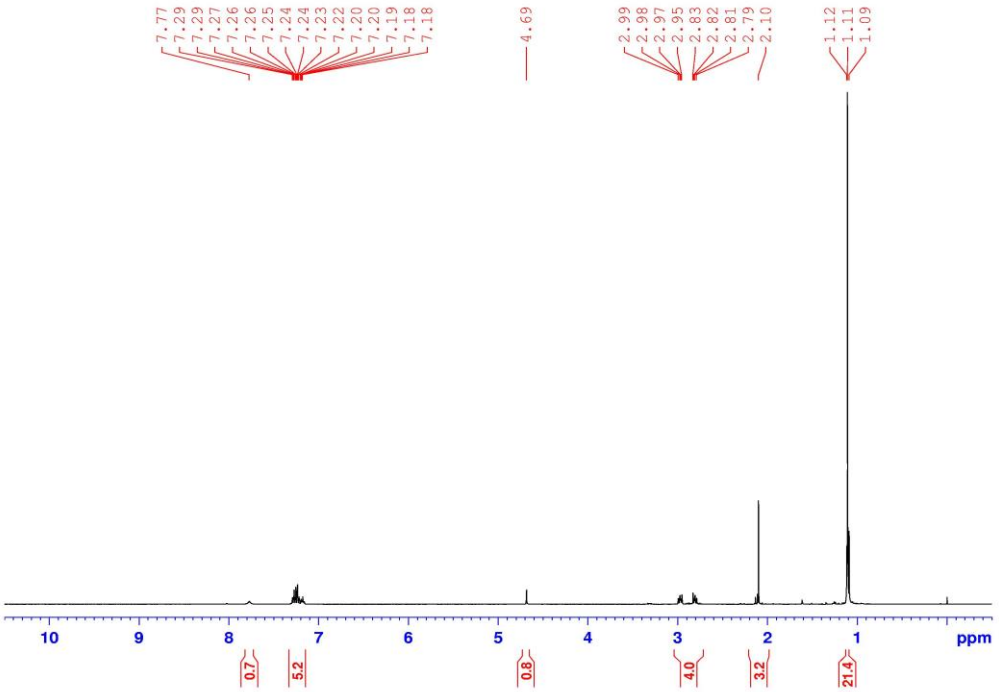


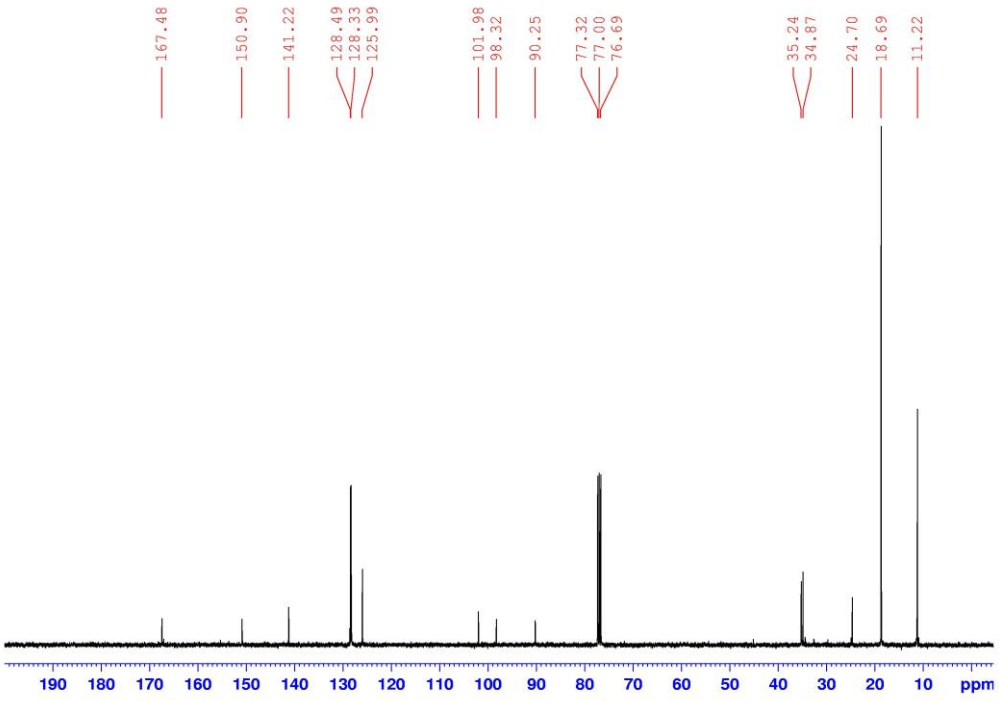


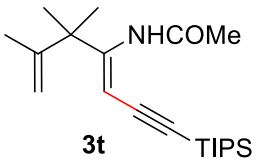


3s

^{1}H NMR & ^{13}C NMR in $CDCl_3$

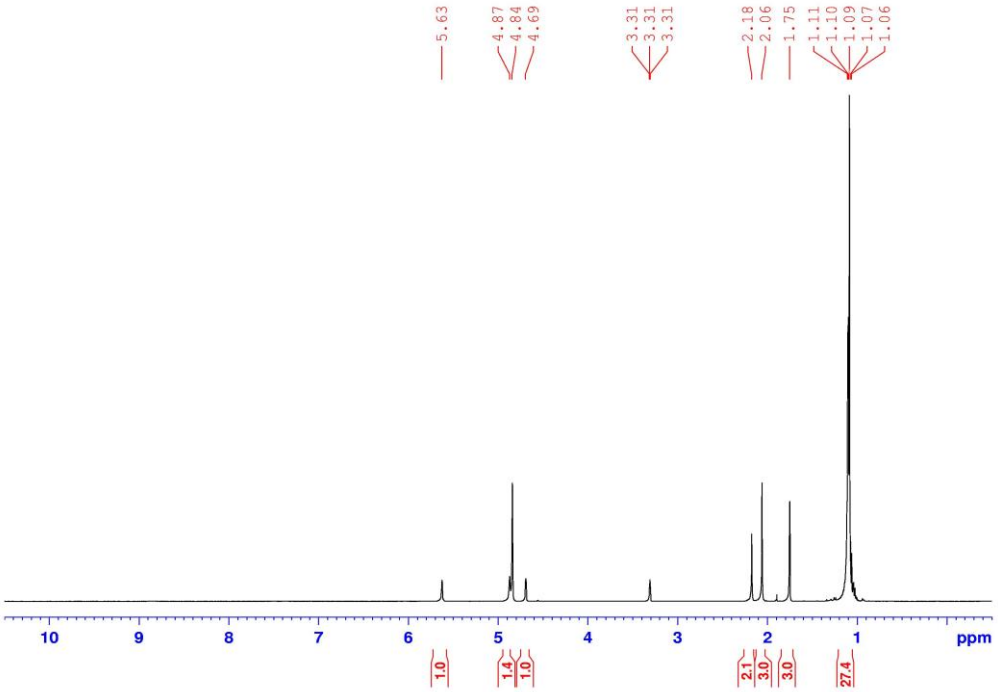


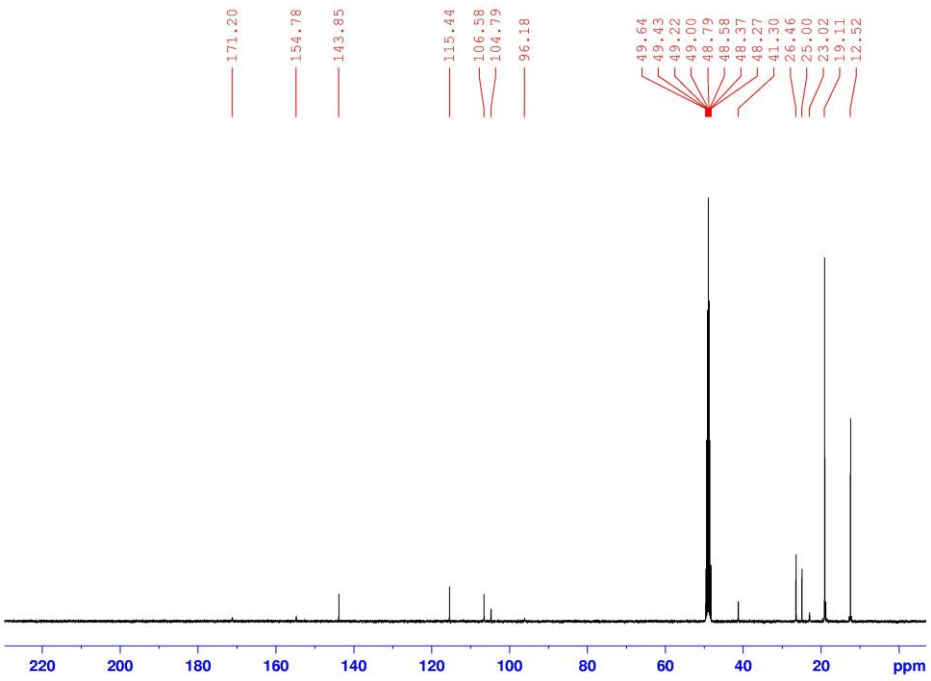


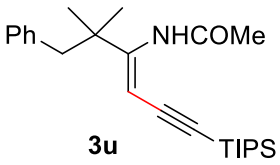


3t

^{1}H NMR & ^{13}C NMR in CD_3OD

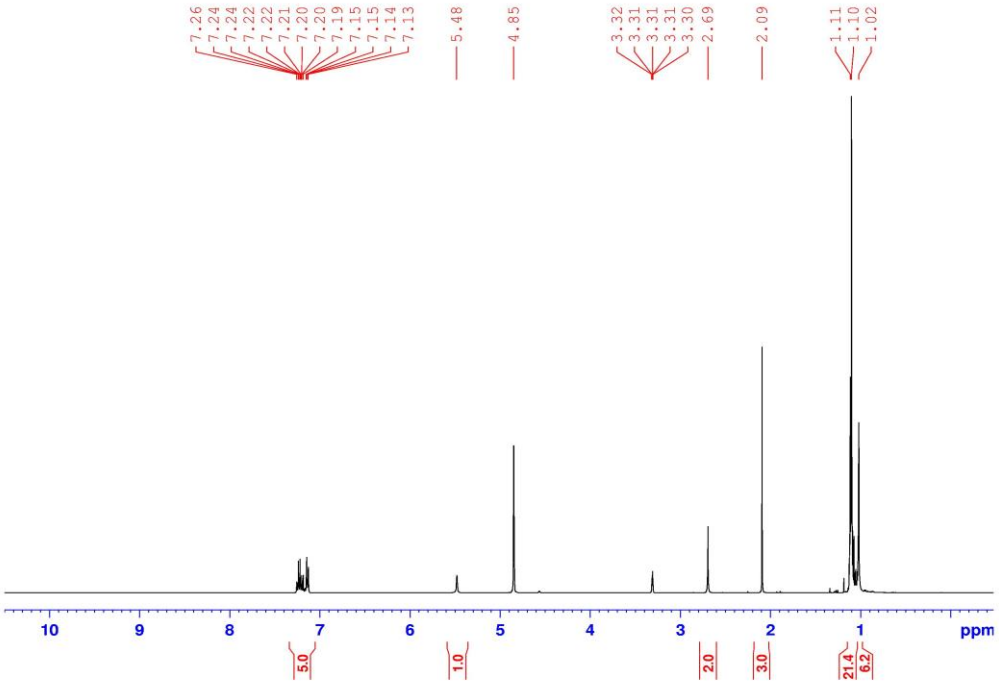


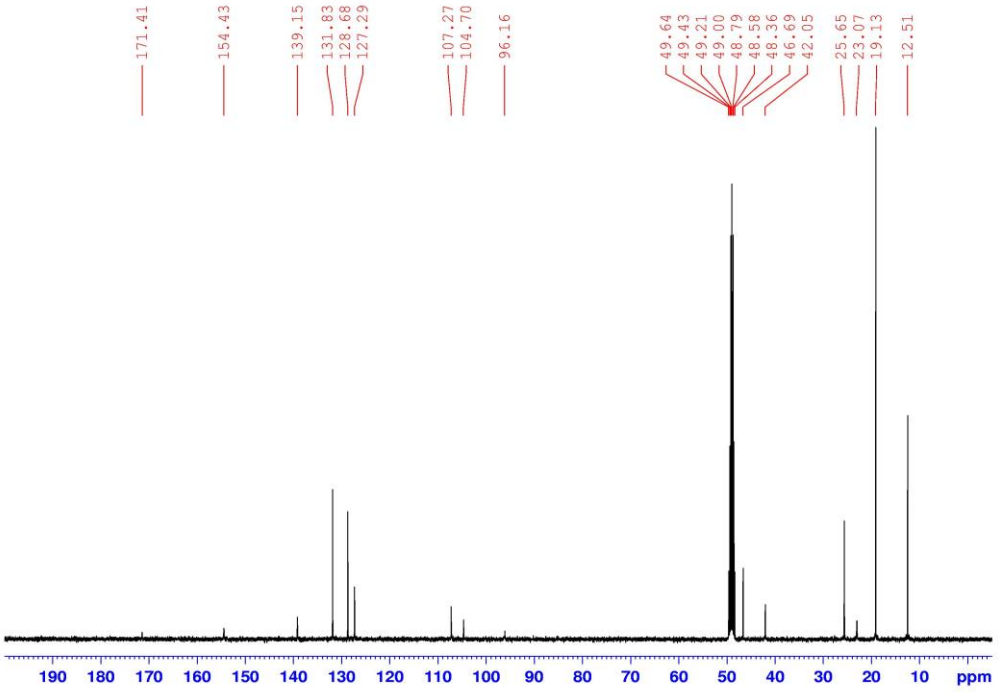


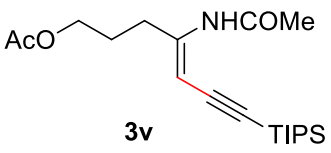


3u

^{1}H NMR & ^{13}C NMR in CD_3OD

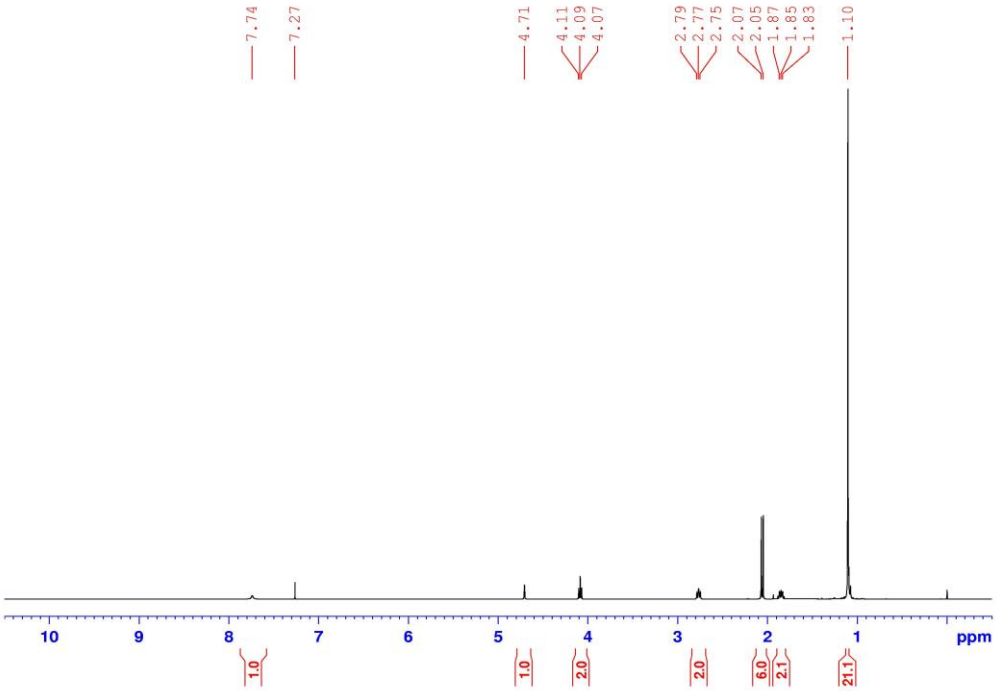


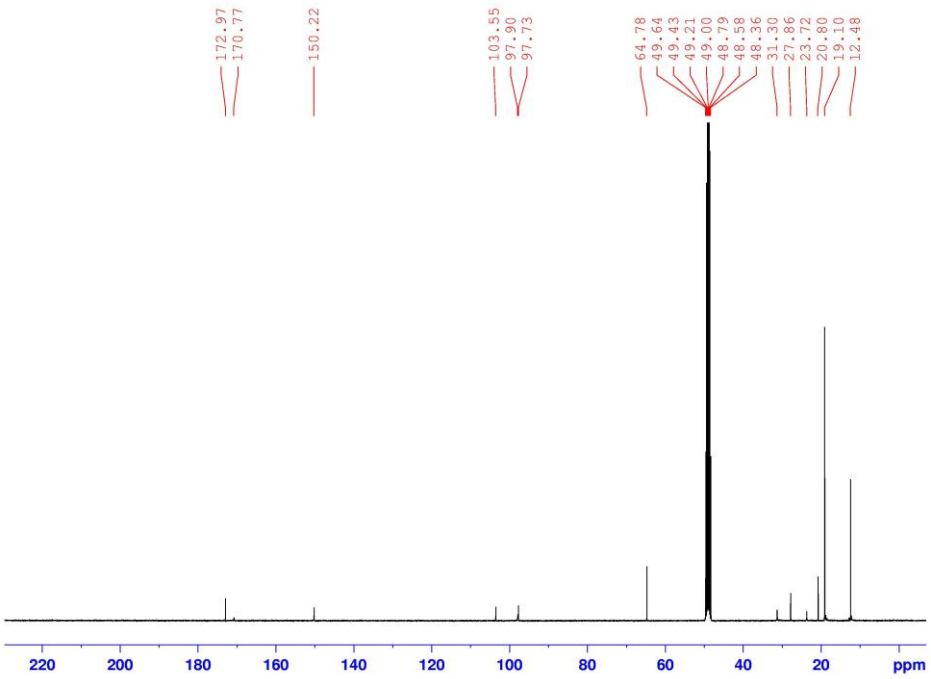


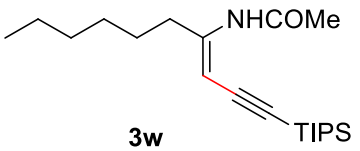


3v

^{1}H NMR & ^{13}C NMR in CD_3OD

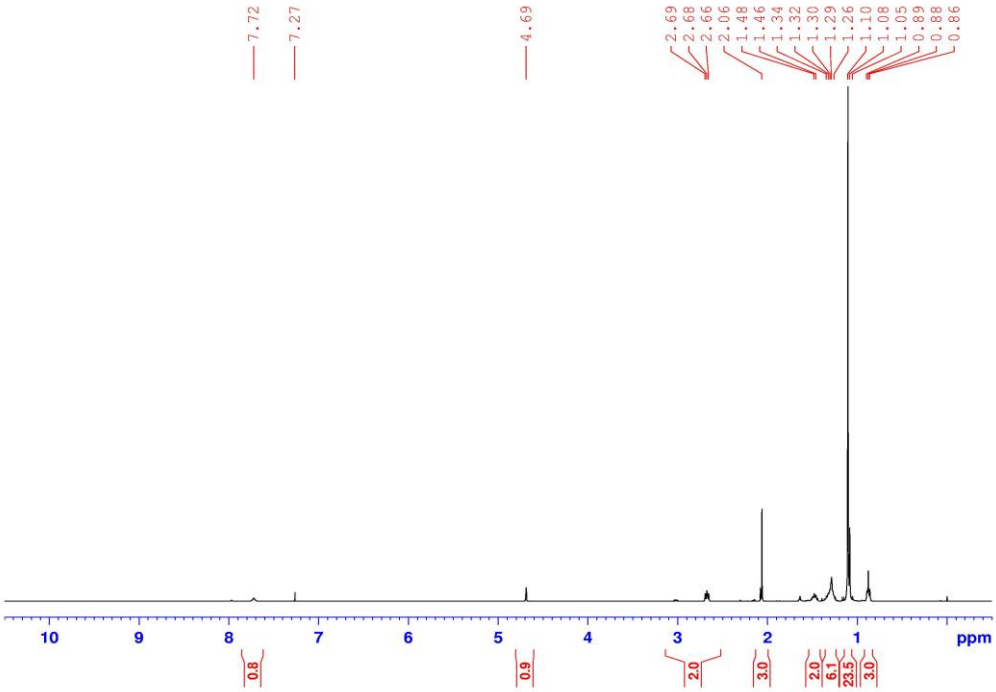


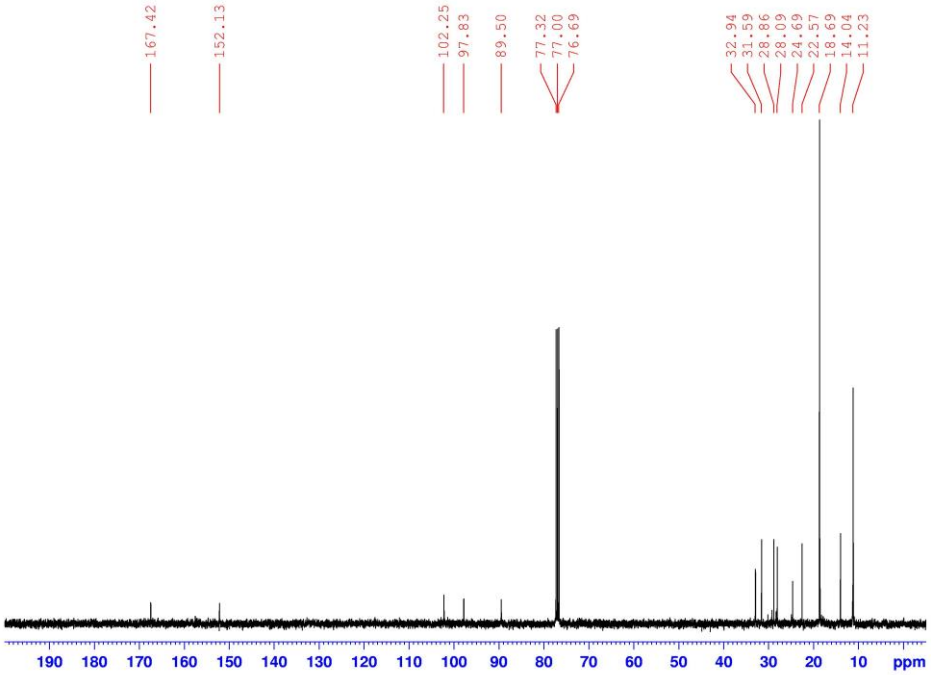


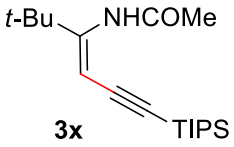


3w

^{1}H NMR & ^{13}C NMR in $CDCl_3$

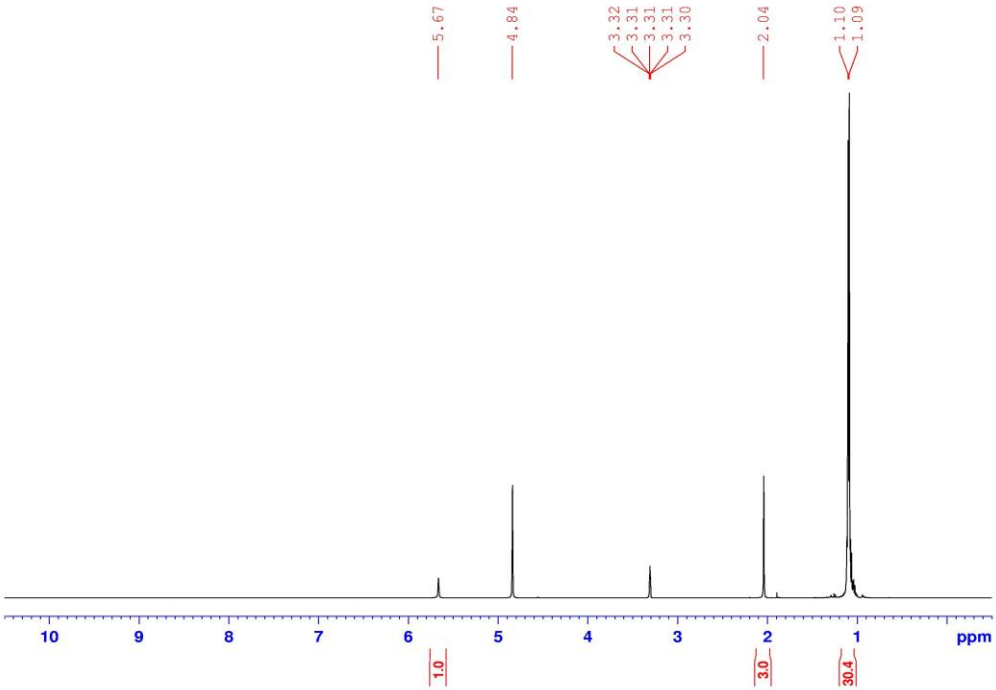


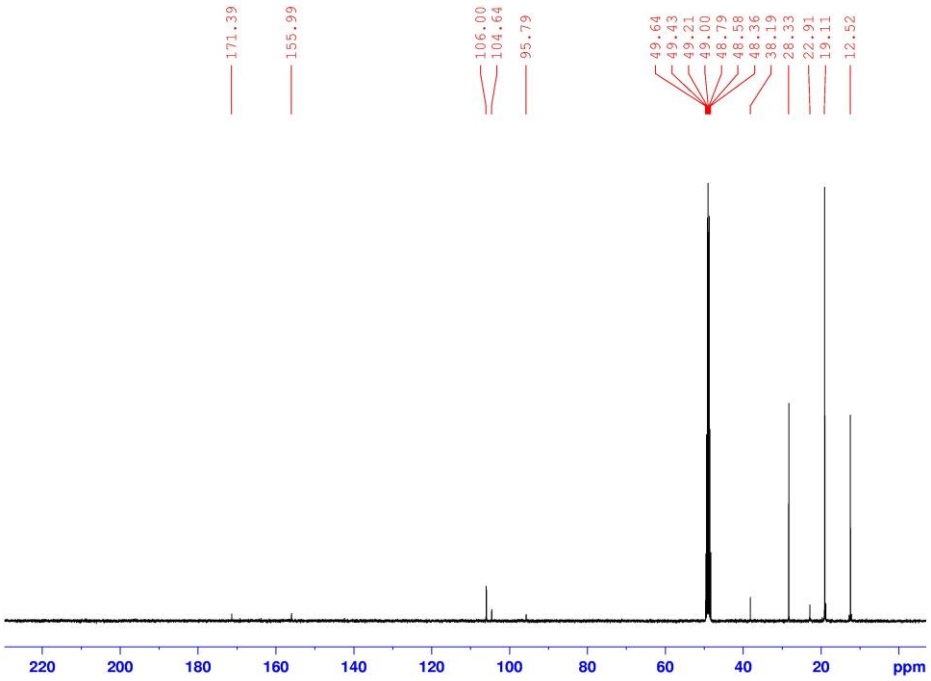


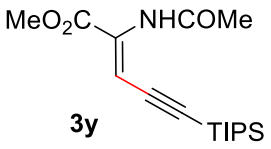


3x

^{1}H NMR & ^{13}C NMR in CD_3OD

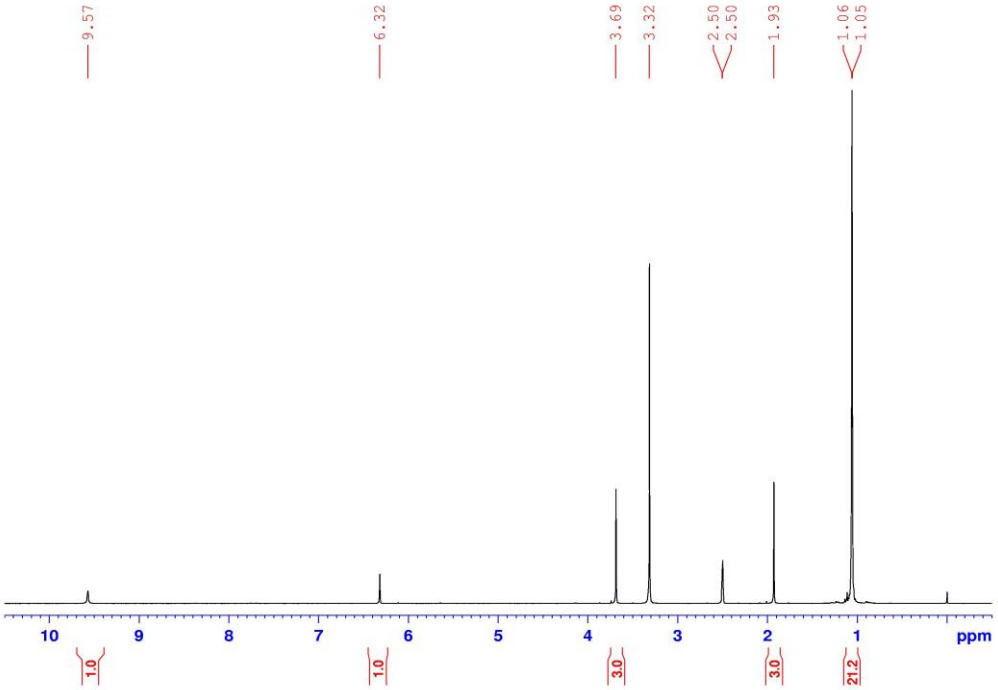


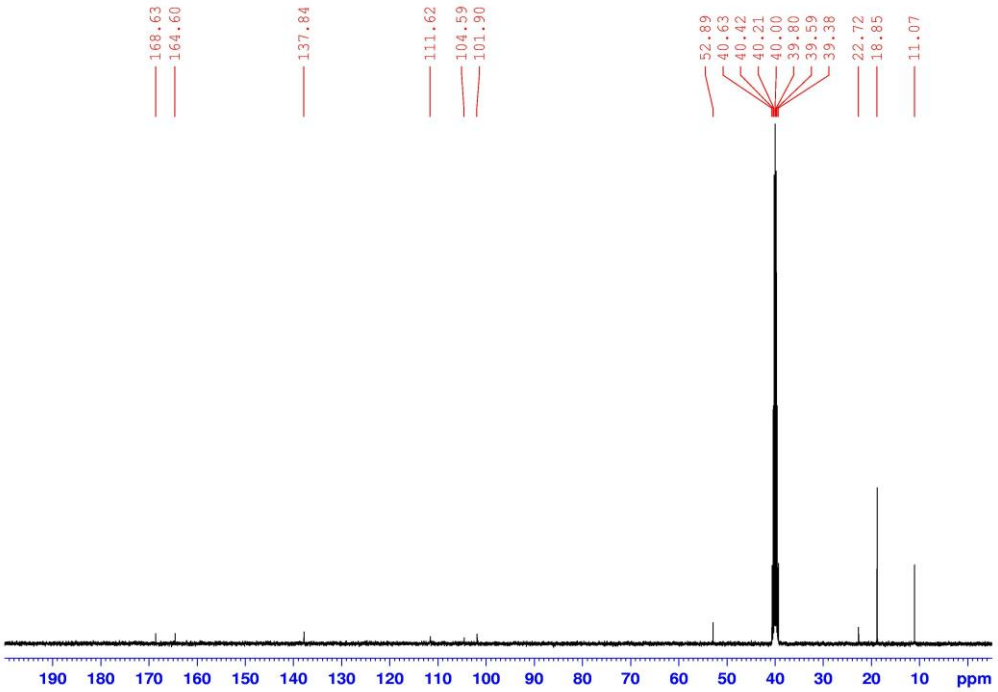


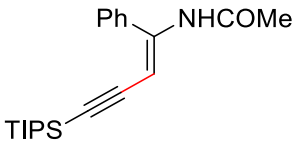


3y

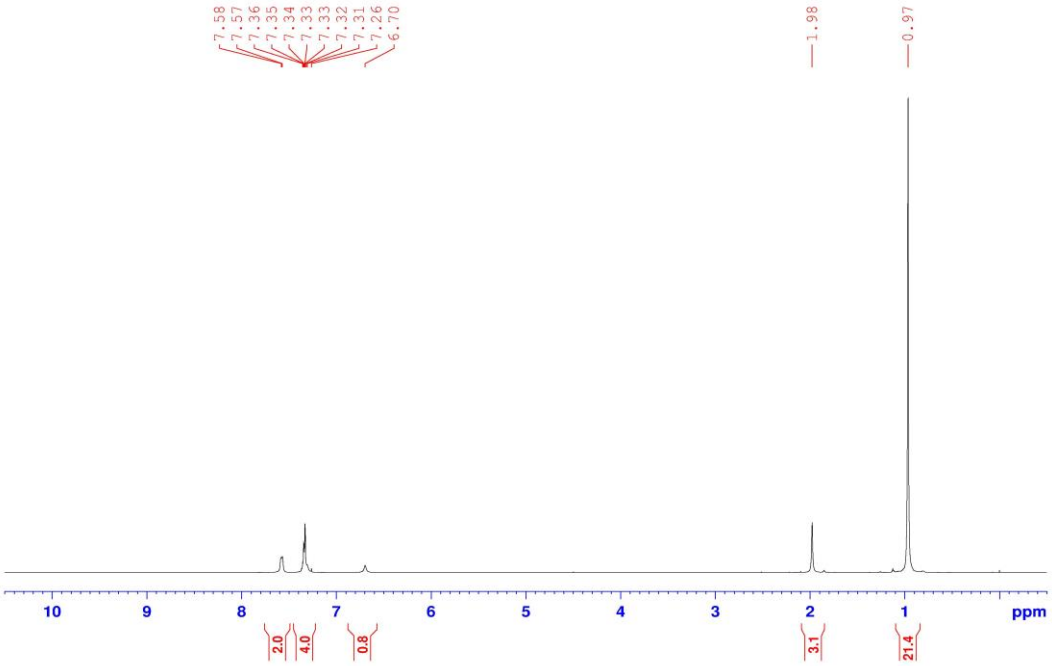
^{1}H NMR & ^{13}C NMR in DMSO-d_6

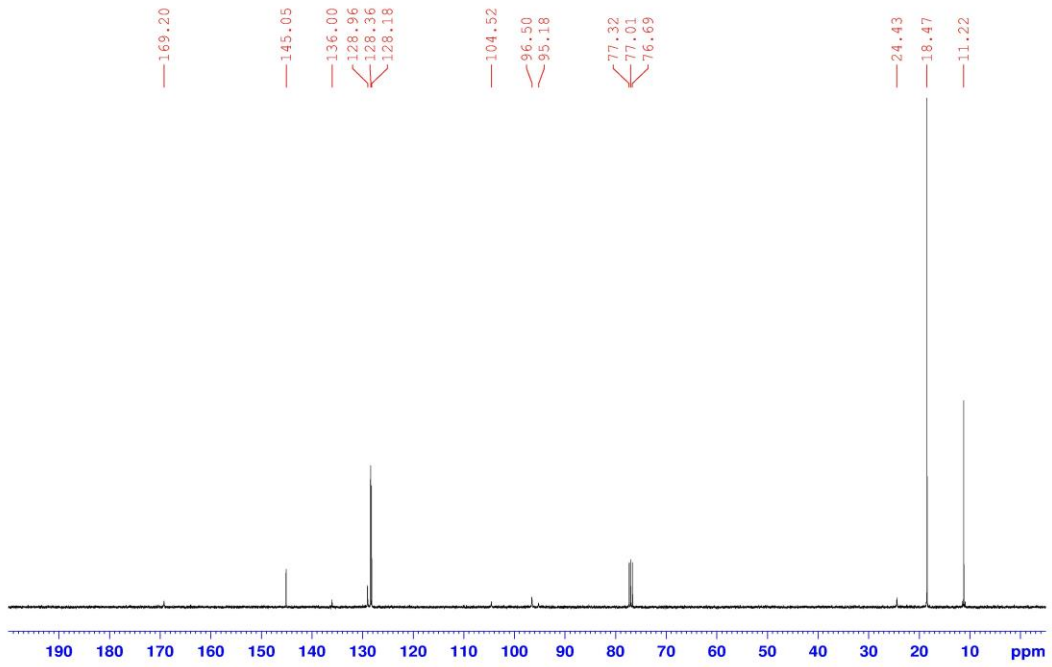


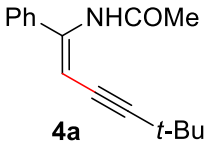




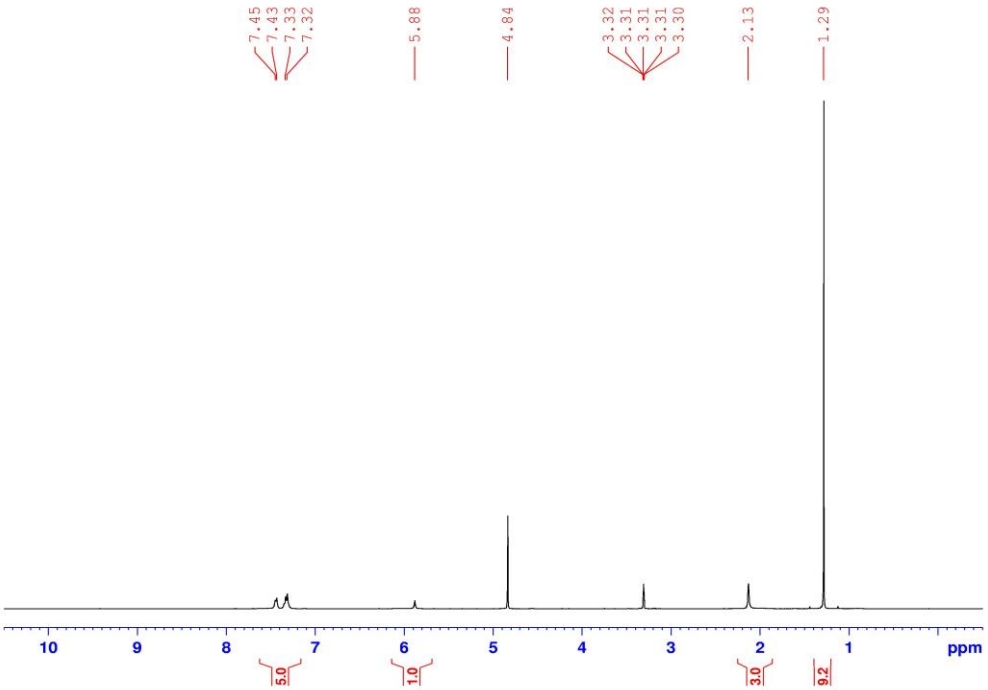
^{1}H NMR & ^{13}C NMR in $CDCl_3$

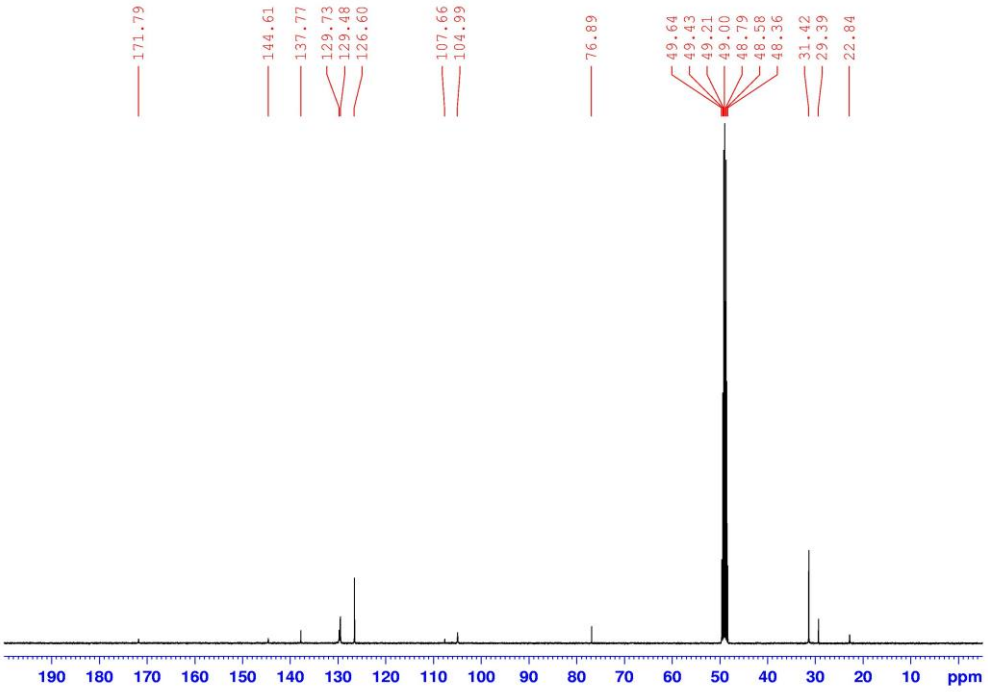


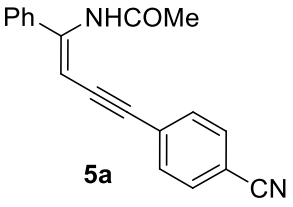




^{1}H NMR & ^{13}C NMR in CD_3OD

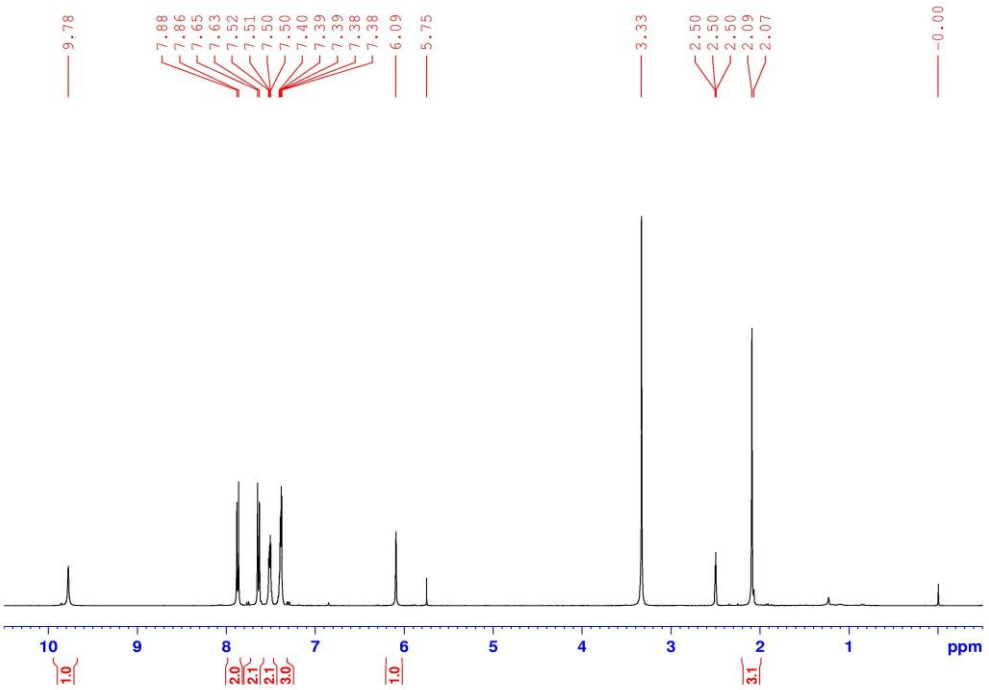


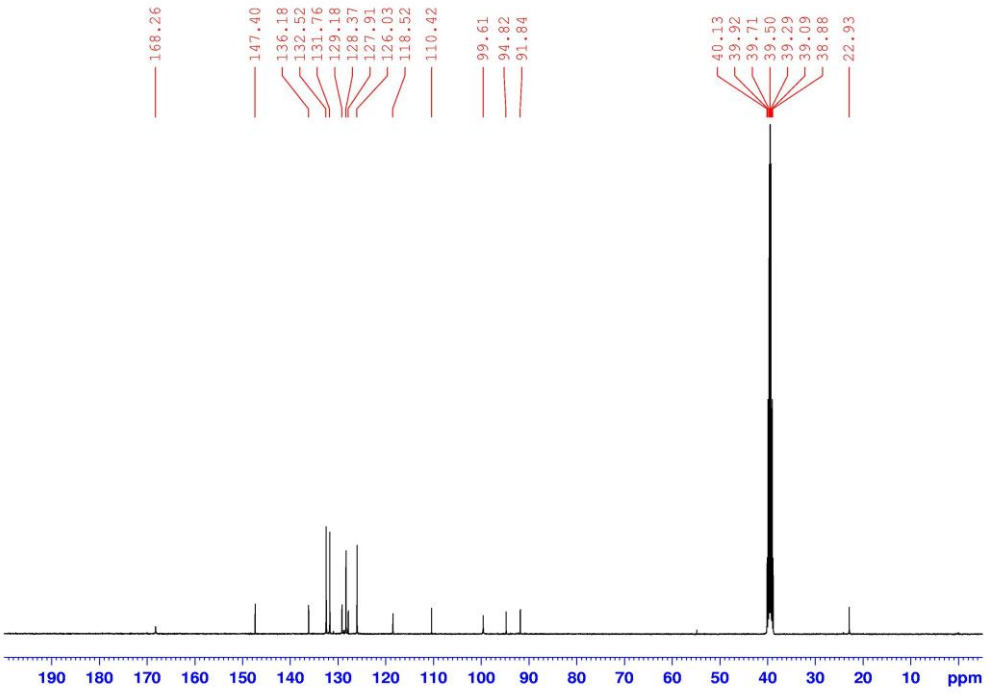


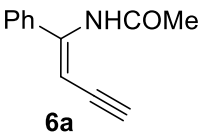


5a

^{1}H NMR & ^{13}C NMR in DMSO-d_6

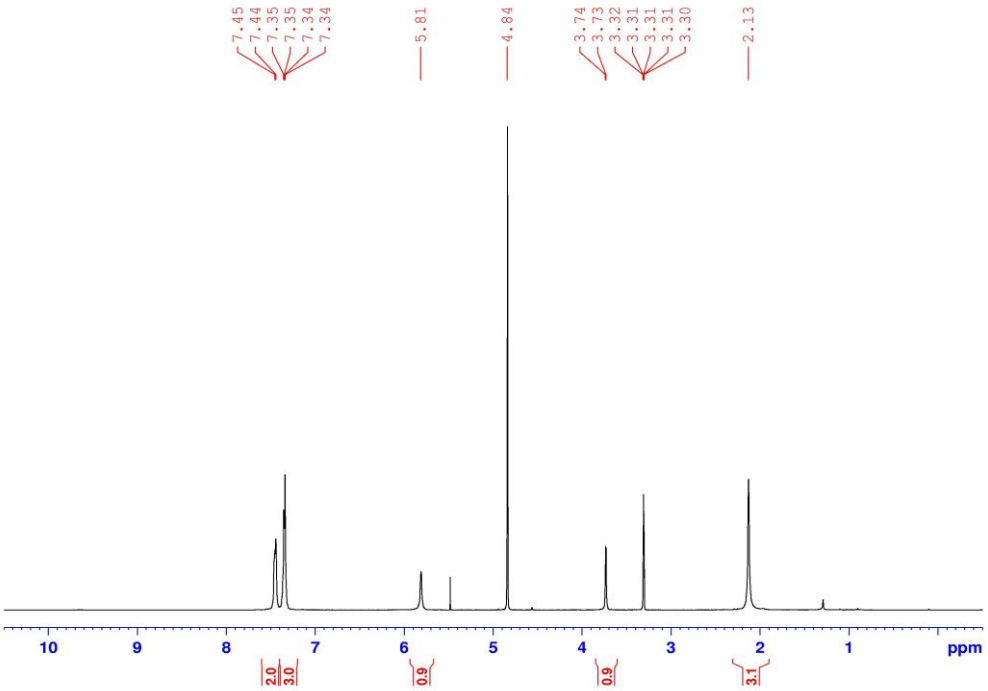


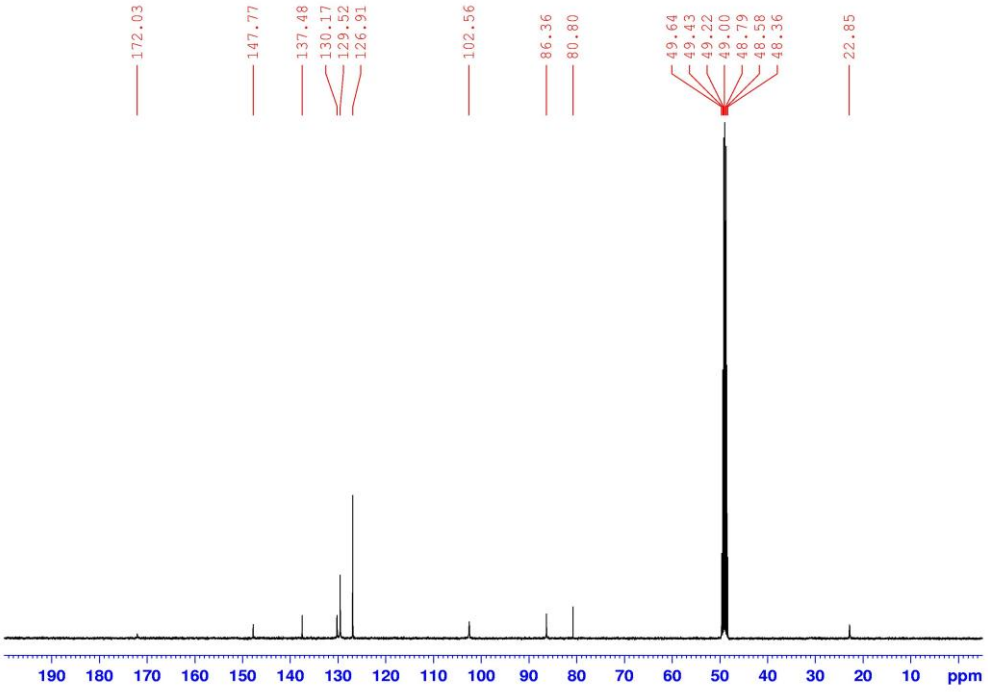


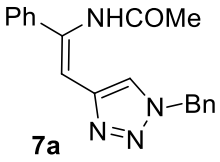


6a

^{1}H NMR & ^{13}C NMR in CD_3OD

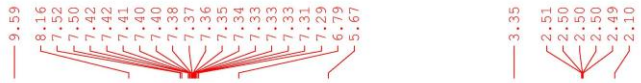


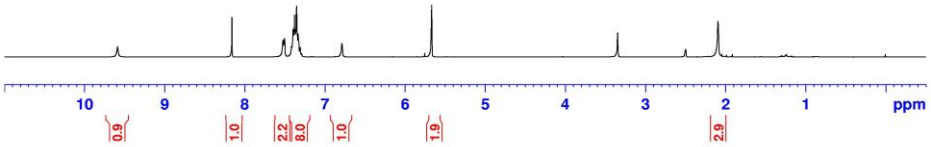


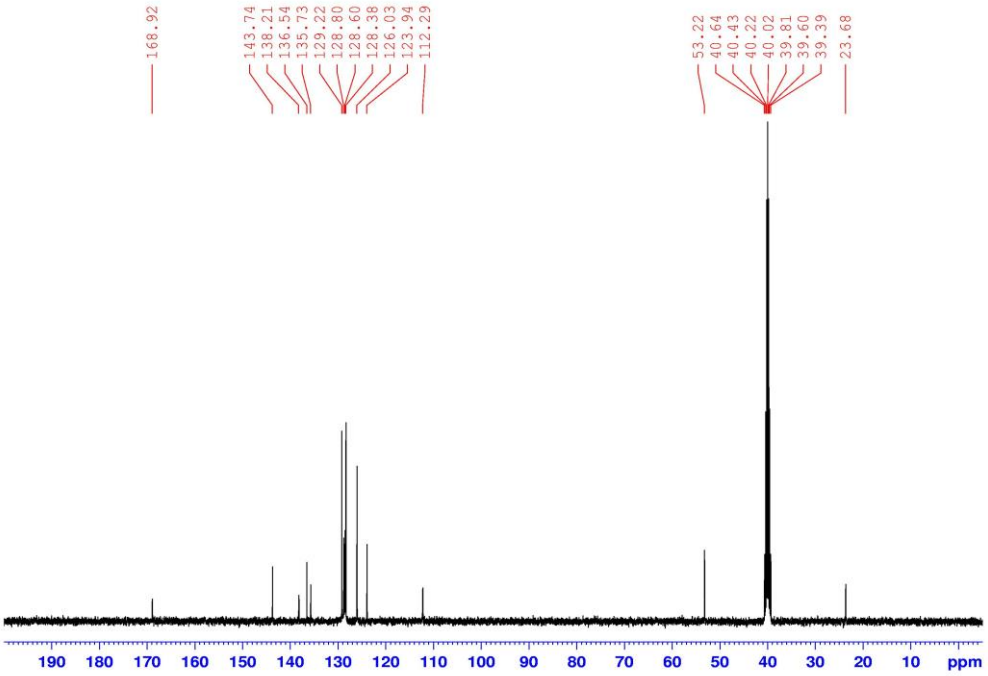


7a

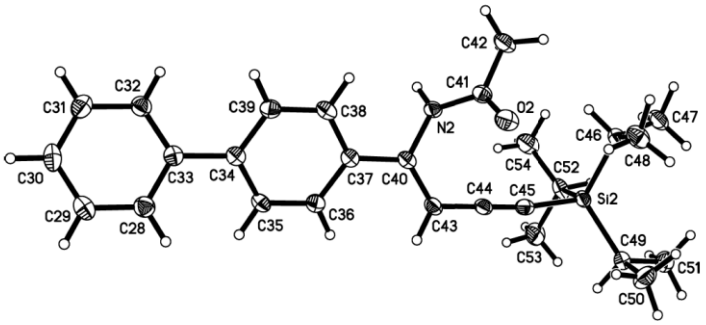
^{1}H NMR & ^{13}C NMR in DMSO-d_6







X-ray data



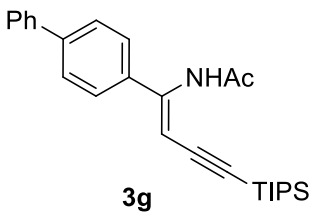


Table 1. Sample and crystal data for 3g.

Identification code	**3g**	
Chemical formula	$C_{27}H_{35}NOSi$	
Formula weight	417.65	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.390 x 0.400 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.5690(11) Å	α = 90°
	b = 9.0333(9) Å	β = 95.9944(13)°
	c = 46.939(5) Å	γ = 90°
Volume	4878.6(8) $Å^3$	
Z	8	
Density (calculated)	1.137 g/cm^3	
Absorption coefficient	0.114 mm^{-1}	
F(000)	1808	

Table 2. Data collection and structure refinement for 3g.

Theta range for data collection	3.07 to 25.38 °
Index ranges	-13<=h<=13, -10<=k<=10, -56<=l<=54

Reflections collected	31196	
Independent reflections	8673 [R(int) = 0.0389]	
Coverage of independent reflections	97.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9860 and 0.9560	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8673 / 0 / 555	
Goodness-of-fit on F^2	1.021	
Δ/σ_{max}	0.001	
Final R indices	7084 data; I>2σ(I)	R1 = 0.0458, wR2 = 0.1005
	all data	R1 = 0.0587, wR2 = 0.1069
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0406P)^2+3.0763P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.439 and -0.318 eÅ^{-3}	
R.M.S. deviation from mean	0.045 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 3g.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.82360(15)	0.4763(2)	0.30068(4)	0.0240(4)
C2	0.77806(16)	0.4778(2)	0.32686(4)	0.0255(5)
C3	0.71858(16)	0.6009(2)	0.33513(4)	0.0254(5)
C4	0.70517(15)	0.7227(2)	0.31723(4)	0.0246(5)
C5	0.75059(15)	0.7210(2)	0.29107(4)	0.0226(4)
C6	0.81079(14)	0.5975(2)	0.28219(4)	0.0201(4)
C7	0.85909(15)	0.5969(2)	0.25413(4)	0.0201(4)
C8	0.95205(15)	0.5041(2)	0.24910(4)	0.0241(4)
C9	0.99664(15)	0.5032(2)	0.22307(4)	0.0242(5)
C10	0.95265(15)	0.5965(2)	0.20083(4)	0.0198(4)

	x/a	y/b	z/c	U(eq)
C11	0.85881(15)	0.6875(2)	0.20565(4)	0.0204(4)
C12	0.81318(15)	0.6870(2)	0.23156(4)	0.0212(4)
C13	0.00367(15)	0.6023(2)	0.17351(4)	0.0196(4)
C14	0.83057(15)	0.5795(2)	0.13961(4)	0.0208(4)
C15	0.76273(17)	0.6495(2)	0.11423(4)	0.0301(5)
C16	0.11631(15)	0.5739(2)	0.17086(4)	0.0219(4)
C17	0.16707(15)	0.5755(2)	0.14452(4)	0.0220(4)
C18	0.21353(15)	0.5754(2)	0.12269(5)	0.0234(4)
C19	0.16905(16)	0.6008(2)	0.05802(4)	0.0265(5)
C20	0.04500(16)	0.5625(3)	0.06438(5)	0.0358(5)
C21	0.19843(19)	0.5217(3)	0.03074(5)	0.0362(5)
C22	0.40165(15)	0.7086(2)	0.09124(4)	0.0222(4)
C23	0.47186(17)	0.7027(2)	0.06534(5)	0.0308(5)
C24	0.35508(17)	0.8651(2)	0.09513(5)	0.0313(5)
C25	0.34624(15)	0.3746(2)	0.08701(4)	0.0213(4)
C26	0.44924(16)	0.3467(2)	0.10977(5)	0.0284(5)
C27	0.25294(17)	0.2552(2)	0.08878(5)	0.0291(5)
C28	0.53115(16)	0.4615(2)	0.22544(4)	0.0252(5)
C29	0.57615(17)	0.4656(2)	0.19935(4)	0.0292(5)
C30	0.53257(17)	0.5630(2)	0.17839(4)	0.0293(5)
C31	0.44262(17)	0.6571(2)	0.18353(4)	0.0288(5)
C32	0.39819(16)	0.6545(2)	0.20977(4)	0.0240(4)
C33	0.44153(15)	0.5574(2)	0.23127(4)	0.0202(4)
C34	0.39754(15)	0.5574(2)	0.25990(4)	0.0194(4)
C35	0.47169(15)	0.5227(2)	0.28432(4)	0.0236(4)
C36	0.43467(15)	0.5254(2)	0.31100(4)	0.0238(4)
C37	0.32021(15)	0.5625(2)	0.31521(4)	0.0182(4)
C38	0.24570(15)	0.5985(2)	0.29091(4)	0.0227(4)
C39	0.28319(15)	0.5961(2)	0.26396(4)	0.0224(4)
C40	0.28313(14)	0.5660(2)	0.34423(4)	0.0186(4)
C41	0.08740(15)	0.5933(2)	0.35917(4)	0.0207(4)
C42	0.99832(16)	0.7075(2)	0.36496(5)	0.0284(5)
C43	0.34115(15)	0.4987(2)	0.36698(4)	0.0212(4)
C44	0.31372(15)	0.5177(2)	0.39547(4)	0.0203(4)
C45	0.29014(15)	0.5353(2)	0.41978(4)	0.0213(4)
C46	0.08091(15)	0.6107(2)	0.44883(4)	0.0226(4)
C47	0.03122(16)	0.6807(2)	0.47463(5)	0.0304(5)
C48	0.01156(17)	0.4733(2)	0.43835(5)	0.0320(5)
C49	0.29744(16)	0.4343(2)	0.48109(4)	0.0244(4)
C50	0.2492(2)	0.2800(2)	0.47412(5)	0.0356(5)

	x/a	y/b	z/c	U(eq)
C51	0.28440(17)	0.4739(3)	0.51232(4)	0.0310(5)
C52	0.31414(15)	0.7631(2)	0.46613(4)	0.0250(5)
C53	0.44711(17)	0.7502(3)	0.47127(5)	0.0358(5)
C54	0.28005(18)	0.8851(2)	0.44436(5)	0.0364(6)
N1	0.93062(12)	0.65003(17)	0.14899(3)	0.0202(4)
N2	0.18217(12)	0.64955(17)	0.34801(3)	0.0194(3)
O1	0.79951(11)	0.46517(15)	0.15060(3)	0.0280(3)
O2	0.07463(11)	0.46165(15)	0.36377(3)	0.0286(3)
Si1	0.28300(4)	0.56494(6)	0.08926(2)	0.01865(13)
Si2	0.24334(4)	0.58210(6)	0.45484(2)	0.01907(13)

Table 4. Bond lengths (Å) for 3g.

C1-C2	1.387(3)	C1-C6	1.396(3)
C1-H1	0.95	C2-C3	1.385(3)
C2-H2	0.95	C3-C4	1.383(3)
C3-H3	0.95	C4-C5	1.385(3)
C4-H4	0.95	C5-C6	1.402(3)
C5-H5	0.95	C6-C7	1.483(3)
C7-C12	1.396(3)	C7-C8	1.403(3)
C8-C9	1.375(3)	C8-H8	0.95
C9-C10	1.396(3)	C9-H9	0.95
C10-C11	1.399(2)	C10-C13	1.467(3)
C11-C12	1.375(3)	C11-H11	0.95
C12-H12	0.95	C13-C16	1.347(2)
C13-N1	1.422(2)	C14-O1	1.225(2)
C14-N1	1.354(2)	C14-C15	1.497(3)
C15-H15A	0.98	C15-H15B	0.98
C15-H15C	0.98	C16-C17	1.423(3)
C16-H16	0.95	C17-C18	1.206(3)
C18-Si1	1.839(2)	C19-C21	1.535(3)
C19-C20	1.536(3)	C19-Si1	1.895(2)
C19-H19	1.0	C20-H20A	0.98
C20-H20B	0.98	C20-H20C	0.98
C21-H21A	0.98	C21-H21B	0.98
C21-H21C	0.98	C22-C24	1.531(3)
C22-C23	1.532(3)	C22-Si1	1.8843(19)
C22-H22	1.0	C23-H23A	0.98
C23-H23B	0.98	C23-H23C	0.98
C24-H24A	0.98	C24-H24B	0.98

C24-H24C	0.98	C25-C27	1.535(3)
C25-C26	1.536(3)	C25-Si1	1.8758(19)
C25-H25	1.0	C26-H26A	0.98
C26-H26B	0.98	C26-H26C	0.98
C27-H27A	0.98	C27-H27B	0.98
C27-H27C	0.98	C28-C29	1.380(3)
C28-C33	1.400(3)	C28-H28	0.95
C29-C30	1.376(3)	C29-H29	0.95
C30-C31	1.384(3)	C30-H30	0.95
C31-C32	1.383(3)	C31-H31	0.95
C32-C33	1.390(3)	C32-H32	0.95
C33-C34	1.486(3)	C34-C35	1.394(3)
C34-C39	1.401(2)	C35-C36	1.365(3)
C35-H35	0.95	C36-C37	1.400(2)
C36-H36	0.95	C37-C38	1.394(3)
C37-C40	1.470(3)	C38-C39	1.380(3)
C38-H38	0.95	C39-H39	0.95
C40-C43	1.346(3)	C40-N2	1.417(2)
C41-O2	1.221(2)	C41-N2	1.362(2)
C41-C42	1.503(3)	C42-H42A	0.98
C42-H42B	0.98	C42-H42C	0.98
C43-C44	1.417(3)	C43-H43	0.95
C44-C45	1.211(3)	C45-Si2	1.834(2)
C46-C47	1.530(3)	C46-C48	1.531(3)
C46-Si2	1.8887(18)	C46-H46	1.0
C47-H47A	0.98	C47-H47B	0.98
C47-H47C	0.98	C48-H48A	0.98
C48-H48B	0.98	C48-H48C	0.98
C49-C50	1.525(3)	C49-C51	1.532(3)
C49-Si2	1.879(2)	C49-H49	1.0
C50-H50A	0.98	C50-H50B	0.98
C50-H50C	0.98	C51-H51A	0.98
C51-H51B	0.98	C51-H51C	0.98
C52-C54	1.526(3)	C52-C53	1.536(3)
C52-Si2	1.880(2)	C52-H52	1.0
C53-H53A	0.98	C53-H53B	0.98
C53-H53C	0.98	C54-H54A	0.98
C54-H54B	0.98	C54-H54C	0.98
N1-H1A	0.88	N2-H2A	0.88

Table 5. Bond angles (°) for 3g.

C2-C1-C6	121.19(19)	C2-C1-H1	119.4
C6-C1-H1	119.4	C3-C2-C1	120.13(19)
C3-C2-H2	119.9	C1-C2-H2	119.9
C4-C3-C2	119.77(19)	C4-C3-H3	120.1
C2-C3-H3	120.1	C3-C4-C5	120.04(19)
C3-C4-H4	120.0	C5-C4-H4	120.0
C4-C5-C6	121.24(19)	C4-C5-H5	119.4
C6-C5-H5	119.4	C1-C6-C5	117.63(18)
C1-C6-C7	121.60(17)	C5-C6-C7	120.77(17)
C12-C7-C8	117.26(17)	C12-C7-C6	121.55(16)
C8-C7-C6	121.19(17)	C9-C8-C7	121.23(18)
C9-C8-H8	119.4	C7-C8-H8	119.4
C8-C9-C10	121.28(17)	C8-C9-H9	119.4
C10-C9-H9	119.4	C9-C10-C11	117.54(17)
C9-C10-C13	121.76(16)	C11-C10-C13	120.69(17)
C12-C11-C10	121.14(18)	C12-C11-H11	119.4
C10-C11-H11	119.4	C11-C12-C7	121.50(17)
C11-C12-H12	119.3	C7-C12-H12	119.3
C16-C13-N1	118.83(17)	C16-C13-C10	123.73(17)
N1-C13-C10	117.31(15)	O1-C14-N1	122.57(18)
O1-C14-C15	122.62(17)	N1-C14-C15	114.78(17)
C14-C15-H15A	109.5	C14-C15-H15B	109.5
H15A-C15-H15B	109.5	C14-C15-H15C	109.5
H15A-C15-H15C	109.5	H15B-C15-H15C	109.5
C13-C16-C17	124.71(18)	C13-C16-H16	117.6
C17-C16-H16	117.6	C18-C17-C16	177.8(2)
C17-C18-Si1	177.07(18)	C21-C19-C20	110.49(17)
C21-C19-Si1	111.66(13)	C20-C19-Si1	113.58(15)
C21-C19-H19	106.9	C20-C19-H19	106.9
Si1-C19-H19	106.9	C19-C20-H20A	109.5
C19-C20-H20B	109.5	H20A-C20-H20B	109.5
C19-C20-H20C	109.5	H20A-C20-H20C	109.5
H20B-C20-H20C	109.5	C19-C21-H21A	109.5
C19-C21-H21B	109.5	H21A-C21-H21B	109.5
C19-C21-H21C	109.5	H21A-C21-H21C	109.5
H21B-C21-H21C	109.5	C24-C22-C23	110.45(17)
C24-C22-Si1	112.24(12)	C23-C22-Si1	112.37(14)
C24-C22-H22	107.2	C23-C22-H22	107.2
Si1-C22-H22	107.2	C22-C23-H23A	109.5
C22-C23-H23B	109.5	H23A-C23-H23B	109.5

C22-C23-H23C	109.5	H23A-C23-H23C	109.5
H23B-C23-H23C	109.5	C22-C24-H24A	109.5
C22-C24-H24B	109.5	H24A-C24-H24B	109.5
C22-C24-H24C	109.5	H24A-C24-H24C	109.5
H24B-C24-H24C	109.5	C27-C25-C26	110.26(16)
C27-C25-Si1	111.15(13)	C26-C25-Si1	112.95(14)
C27-C25-H25	107.4	C26-C25-H25	107.4
Si1-C25-H25	107.4	C25-C26-H26A	109.5
C25-C26-H26B	109.5	H26A-C26-H26B	109.5
C25-C26-H26C	109.5	H26A-C26-H26C	109.5
H26B-C26-H26C	109.5	C25-C27-H27A	109.5
C25-C27-H27B	109.5	H27A-C27-H27B	109.5
C25-C27-H27C	109.5	H27A-C27-H27C	109.5
H27B-C27-H27C	109.5	C29-C28-C33	120.83(19)
C29-C28-H28	119.6	C33-C28-H28	119.6
C30-C29-C28	120.50(19)	C30-C29-H29	119.7
C28-C29-H29	119.7	C29-C30-C31	119.61(19)
C29-C30-H30	120.2	C31-C30-H30	120.2
C32-C31-C30	120.05(19)	C32-C31-H31	120.0
C30-C31-H31	120.0	C31-C32-C33	121.16(18)
C31-C32-H32	119.4	C33-C32-H32	119.4
C32-C33-C28	117.83(18)	C32-C33-C34	121.65(17)
C28-C33-C34	120.50(17)	C35-C34-C39	116.94(17)
C35-C34-C33	120.28(16)	C39-C34-C33	122.75(16)
C36-C35-C34	121.68(17)	C36-C35-H35	119.2
C34-C35-H35	119.2	C35-C36-C37	121.72(17)
C35-C36-H36	119.1	C37-C36-H36	119.1
C38-C37-C36	116.96(17)	C38-C37-C40	122.52(16)
C36-C37-C40	120.51(16)	C39-C38-C37	121.32(17)
C39-C38-H38	119.3	C37-C38-H38	119.3
C38-C39-C34	121.37(17)	C38-C39-H39	119.3
C34-C39-H39	119.3	C43-C40-N2	119.38(17)
C43-C40-C37	123.77(16)	N2-C40-C37	116.82(15)
O2-C41-N2	123.27(17)	O2-C41-C42	122.61(17)
N2-C41-C42	114.11(17)	C41-C42-H42A	109.5
C41-C42-H42B	109.5	H42A-C42-H42B	109.5
C41-C42-H42C	109.5	H42A-C42-H42C	109.5
H42B-C42-H42C	109.5	C40-C43-C44	123.49(17)
C40-C43-H43	118.3	C44-C43-H43	118.3
C45-C44-C43	179.4(2)	C44-C45-Si2	172.75(17)
C47-C46-C48	111.20(16)	C47-C46-Si2	112.86(13)

C48-C46-Si2	114.63(13)	C47-C46-H46	105.8
C48-C46-H46	105.8	Si2-C46-H46	105.8
C46-C47-H47A	109.5	C46-C47-H47B	109.5
H47A-C47-H47B	109.5	C46-C47-H47C	109.5
H47A-C47-H47C	109.5	H47B-C47-H47C	109.5
C46-C48-H48A	109.5	C46-C48-H48B	109.5
H48A-C48-H48B	109.5	C46-C48-H48C	109.5
H48A-C48-H48C	109.5	H48B-C48-H48C	109.5
C50-C49-C51	110.40(17)	C50-C49-Si2	114.81(14)
C51-C49-Si2	113.73(14)	C50-C49-H49	105.7
C51-C49-H49	105.7	Si2-C49-H49	105.7
C49-C50-H50A	109.5	C49-C50-H50B	109.5
H50A-C50-H50B	109.5	C49-C50-H50C	109.5
H50A-C50-H50C	109.5	H50B-C50-H50C	109.5
C49-C51-H51A	109.5	C49-C51-H51B	109.5
H51A-C51-H51B	109.5	C49-C51-H51C	109.5
H51A-C51-H51C	109.5	H51B-C51-H51C	109.5
C54-C52-C53	110.15(17)	C54-C52-Si2	111.39(14)
C53-C52-Si2	112.19(14)	C54-C52-H52	107.6
C53-C52-H52	107.6	Si2-C52-H52	107.6
C52-C53-H53A	109.5	C52-C53-H53B	109.5
H53A-C53-H53B	109.5	C52-C53-H53C	109.5
H53A-C53-H53C	109.5	H53B-C53-H53C	109.5
C52-C54-H54A	109.5	C52-C54-H54B	109.5
H54A-C54-H54B	109.5	C52-C54-H54C	109.5
H54A-C54-H54C	109.5	H54B-C54-H54C	109.5
C14-N1-C13	122.43(16)	C14-N1-H1A	118.8
C13-N1-H1A	118.8	C41-N2-C40	123.82(16)
C41-N2-H2A	118.1	C40-N2-H2A	118.1
C18-Si1-C25	107.62(9)	C18-Si1-C22	107.68(9)
C25-Si1-C22	110.35(8)	C18-Si1-C19	108.72(9)
C25-Si1-C19	110.93(9)	C22-Si1-C19	111.40(9)
C45-Si2-C49	108.38(9)	C45-Si2-C52	107.00(9)
C49-Si2-C52	109.12(9)	C45-Si2-C46	106.25(9)
C49-Si2-C46	116.95(9)	C52-Si2-C46	108.68(9)

Table 6. Anisotropic atomic displacement parameters (Å^2) for 3g.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0202(9)	0.0237(11)	0.0285(12)	-0.0021(9)	0.0045(8)	0.0001(8)
C2	0.0239(10)	0.0269(11)	0.0258(12)	0.0035(9)	0.0035(8)	-0.0042(8)
C3	0.0214(9)	0.0350(12)	0.0202(11)	-0.0050(9)	0.0046(8)	-0.0056(8)
C4	0.0193(9)	0.0273(11)	0.0278(12)	-0.0053(9)	0.0051(8)	-0.0006(8)
C5	0.0195(9)	0.0223(11)	0.0264(11)	0.0005(9)	0.0041(8)	-0.0011(8)
C6	0.0143(8)	0.0221(11)	0.0238(11)	-0.0008(8)	0.0018(8)	-0.0024(7)
C7	0.0160(8)	0.0202(10)	0.0245(11)	-0.0023(8)	0.0039(8)	-0.0023(7)
C8	0.0199(9)	0.0271(11)	0.0256(12)	0.0049(9)	0.0037(8)	0.0043(8)
C9	0.0172(9)	0.0272(11)	0.0291(12)	0.0022(9)	0.0066(8)	0.0076(8)
C10	0.0170(8)	0.0187(10)	0.0241(11)	-0.0015(8)	0.0039(8)	-0.0019(7)
C11	0.0194(9)	0.0170(10)	0.0252(11)	0.0021(8)	0.0038(8)	0.0012(7)
C12	0.0179(9)	0.0197(10)	0.0265(12)	-0.0029(8)	0.0050(8)	0.0037(7)
C13	0.0204(9)	0.0138(10)	0.0251(11)	-0.0025(8)	0.0050(8)	-0.0013(7)
C14	0.0199(9)	0.0170(10)	0.0266(11)	-0.0056(8)	0.0071(8)	0.0009(7)
C15	0.0289(10)	0.0260(12)	0.0338(13)	-0.0013(10)	-0.0039(9)	-0.0007(9)
C16	0.0200(9)	0.0226(11)	0.0237(11)	-0.0018(9)	0.0052(8)	0.0004(8)
C17	0.0179(9)	0.0184(10)	0.0301(12)	-0.0015(9)	0.0044(9)	-0.0014(7)
C18	0.0191(9)	0.0193(11)	0.0323(13)	-0.0012(9)	0.0053(9)	0.0000(7)
C19	0.0240(10)	0.0189(11)	0.0358(13)	0.0041(9)	-0.0011(9)	0.0006(8)
C20	0.0212(10)	0.0331(13)	0.0517(15)	-0.0015(11)	-0.0033(10)	0.0019(9)
C21	0.0394(12)	0.0398(14)	0.0281(13)	0.0080(10)	-0.0025(10)	-0.0056(10)
C22	0.0178(9)	0.0191(10)	0.0298(12)	0.0017(9)	0.0029(8)	-0.0006(7)
C23	0.0237(10)	0.0273(12)	0.0434(14)	0.0046(10)	0.0123(9)	-0.0032(8)
C24	0.0273(10)	0.0209(11)	0.0456(14)	-0.0037(10)	0.0041(10)	-0.0028(8)
C25	0.0226(9)	0.0188(10)	0.0236(11)	0.0008(8)	0.0078(8)	0.0032(8)
C26	0.0241(10)	0.0241(11)	0.0374(13)	0.0041(9)	0.0049(9)	0.0049(8)
C27	0.0306(10)	0.0172(11)	0.0393(13)	0.0028(9)	0.0026(9)	-0.0006(8)
C28	0.0256(10)	0.0237(11)	0.0266(12)	-0.0002(9)	0.0034(9)	0.0011(8)
C29	0.0266(10)	0.0314(12)	0.0307(13)	-0.0054(10)	0.0078(9)	0.0009(9)
C30	0.0281(10)	0.0401(13)	0.0208(11)	-0.0051(10)	0.0077(9)	-0.0089(9)
C31	0.0296(10)	0.0327(12)	0.0237(12)	0.0032(9)	0.0004(9)	-0.0036(9)
C32	0.0212(9)	0.0256(11)	0.0252(12)	-0.0002(9)	0.0025(8)	0.0004(8)
C33	0.0179(9)	0.0204(11)	0.0219(11)	-0.0020(8)	0.0007(8)	-0.0042(7)
C34	0.0201(9)	0.0141(10)	0.0240(11)	-0.0018(8)	0.0031(8)	-0.0019(7)
C35	0.0155(9)	0.0283(11)	0.0276(12)	0.0013(9)	0.0053(8)	0.0021(8)
C36	0.0187(9)	0.0296(11)	0.0229(11)	0.0023(9)	0.0015(8)	0.0019(8)
C37	0.0185(8)	0.0137(10)	0.0226(11)	-0.0024(8)	0.0031(8)	-0.0021(7)
C38	0.0161(9)	0.0239(11)	0.0283(12)	-0.0025(9)	0.0028(8)	0.0007(8)
C39	0.0191(9)	0.0239(11)	0.0236(11)	-0.0005(9)	-0.0008(8)	0.0004(8)
C40	0.0161(8)	0.0145(10)	0.0254(11)	-0.0025(8)	0.0040(8)	-0.0008(7)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C41	0.0171(9)	0.0225(11)	0.0220(11)	-0.0022(8)	-0.0004(8)	-0.0006(7)
C42	0.0180(9)	0.0278(12)	0.0401(13)	0.0004(10)	0.0064(9)	0.0023(8)
C43	0.0189(9)	0.0214(11)	0.0242(11)	-0.0017(8)	0.0062(8)	0.0034(7)
C44	0.0151(8)	0.0198(10)	0.0262(12)	0.0020(8)	0.0028(8)	0.0015(7)
C45	0.0177(9)	0.0178(10)	0.0280(12)	0.0022(9)	0.0009(8)	0.0010(7)
C46	0.0183(9)	0.0222(11)	0.0278(11)	0.0031(9)	0.0053(8)	0.0003(7)
C47	0.0207(9)	0.0321(12)	0.0398(13)	0.0002(10)	0.0097(9)	0.0021(8)
C48	0.0222(10)	0.0308(12)	0.0432(14)	-0.0044(10)	0.0041(9)	-0.0053(9)
C49	0.0214(9)	0.0283(12)	0.0242(11)	0.0036(9)	0.0064(8)	0.0021(8)
C50	0.0494(13)	0.0251(12)	0.0328(13)	0.0070(10)	0.0058(10)	0.0041(10)
C51	0.0289(10)	0.0386(13)	0.0256(12)	0.0039(10)	0.0041(9)	-0.0003(9)
C52	0.0207(9)	0.0264(11)	0.0292(12)	-0.0061(9)	0.0095(8)	-0.0047(8)
C53	0.0238(10)	0.0427(14)	0.0404(14)	0.0036(11)	0.0013(9)	-0.0113(9)
C54	0.0279(11)	0.0204(12)	0.0623(17)	0.0018(11)	0.0109(10)	-0.0010(9)
N1	0.0184(7)	0.0199(9)	0.0234(9)	0.0034(7)	0.0067(6)	-0.0022(6)
N2	0.0201(8)	0.0135(8)	0.0252(9)	0.0015(7)	0.0052(7)	0.0035(6)
O1	0.0271(7)	0.0172(8)	0.0399(9)	0.0009(6)	0.0044(6)	-0.0037(6)
O2	0.0225(7)	0.0197(8)	0.0436(9)	0.0009(7)	0.0035(6)	-0.0028(5)
Si1	0.0163(2)	0.0162(3)	0.0243(3)	0.0008(2)	0.0059(2)	0.00119(19)
Si2	0.0161(2)	0.0199(3)	0.0218(3)	0.0005(2)	0.0049(2)	-0.0005(2)

Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for 3g.

	x/a	y/b	z/c	U(eq)
H1	-0.1358	0.3912	0.2952	0.029
H2	-0.2123	0.3941	0.3391	0.031
H3	-0.3129	0.6017	0.3530	0.03
H4	-0.3352	0.8076	0.3229	0.03
H5	-0.2592	0.8052	0.2789	0.027
H8	-0.0152	0.4407	0.2640	0.029
H9	0.0586	0.4377	0.2202	0.029
H11	-0.1740	0.7508	0.1908	0.025
H12	-0.2511	0.7493	0.2341	0.025
H15A	-0.2236	0.5950	0.0968	0.045
H15B	-0.2123	0.7525	0.1125	0.045
H15C	-0.3203	0.6469	0.1167	0.045
H16	0.1654	0.5512	0.1878	0.026
H19	0.1704	0.7095	0.0540	0.032
H20A	-0.0097	0.5861	0.0476	0.054

	x/a	y/b	z/c	U(eq)
H20B	0.0252	0.6203	0.0809	0.054
H20C	0.0403	0.4567	0.0687	0.054
H21A	0.1981	0.4144	0.0338	0.054
H21B	0.2756	0.5529	0.0262	0.054
H21C	0.1404	0.5474	0.0148	0.054
H22	0.4565	0.6858	0.1086	0.027
H23A	0.4210	0.7261	0.0479	0.046
H23B	0.5043	0.6032	0.0637	0.046
H23C	0.5352	0.7750	0.0678	0.046
H24A	0.4200	0.9353	0.0972	0.047
H24B	0.3140	0.8684	0.1123	0.047
H24C	0.3015	0.8919	0.0784	0.047
H25	0.3758	0.3654	0.0678	0.026
H26A	0.4235	0.3576	0.1289	0.043
H26B	0.5109	0.4186	0.1074	0.043
H26C	0.4790	0.2463	0.1076	0.043
H27A	0.2874	0.1572	0.0866	0.044
H27B	0.1899	0.2707	0.0734	0.044
H27C	0.2219	0.2613	0.1074	0.044
H28	0.5614	0.3927	0.2396	0.03
H29	0.6377	0.4007	0.1958	0.035
H30	0.5640	0.5657	0.1605	0.035
H31	0.4114	0.7235	0.1690	0.035
H32	0.3370	0.7202	0.2132	0.029
H35	0.5500	0.4965	0.2824	0.028
H36	0.4880	0.5015	0.3271	0.029
H38	0.1675	0.6251	0.2930	0.027
H39	0.2303	0.6213	0.2478	0.027
H42A	-0.0448	0.7382	0.3468	0.043
H42B	0.0373	0.7937	0.3743	0.043
H42C	-0.0557	0.6652	0.3775	0.043
H43	0.4038	0.4350	0.3638	0.025
H46	0.0680	0.6849	0.4330	0.027
H47A	-0.0522	0.6984	0.4700	0.046
H47B	0.0707	0.7749	0.4794	0.046
H47C	0.0433	0.6136	0.4911	0.046
H48A	0.0138	0.4004	0.4539	0.048
H48B	0.0457	0.4301	0.4220	0.048
H48C	-0.0692	0.5013	0.4325	0.048
H49	0.3830	0.4272	0.4798	0.029

	x/a	y/b	z/c	U(eq)
H50A	0.2953	0.2066	0.4858	0.053
H50B	0.2533	0.2589	0.4538	0.053
H50C	0.1681	0.2752	0.4784	0.053
H51A	0.2017	0.4826	0.5149	0.046
H51B	0.3233	0.5684	0.5171	0.046
H51C	0.3198	0.3962	0.5249	0.046
H52	0.2853	0.7928	0.4847	0.03
H53A	0.4775	0.7164	0.4537	0.054
H53B	0.4681	0.6789	0.4867	0.054
H53C	0.4804	0.8471	0.4767	0.054
H54A	0.3173	0.9782	0.4510	0.055
H54B	0.1954	0.8976	0.4423	0.055
H54C	0.3056	0.8579	0.4258	0.055
H1A	-0.0488	0.7283	0.1396	0.024
H2A	0.1806	0.7432	0.3428	0.023