Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2018

Supporting Information

Room-temperature Pd(II)-catalyzed direct C−H alkynylation of phenylacetic amides with terminal alkyne

Cui-Hong Chen,[a] Yun Chai,[a] Zheng-Xin Zhou,[a] Wei-Hao Rao,[b] Bin Liu, [a] Li Liu,[a] Ran Xu,[a] Yue-Jin Liu,*[a] and Ming-Hua Zeng*[a]

Hubei Collaborative Innovation Center for Advanced Chemical Materials, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, and College of Chemistry and Chemical Engineering, Hubei University, Wuhan, 430062, China.

Table of Contents:

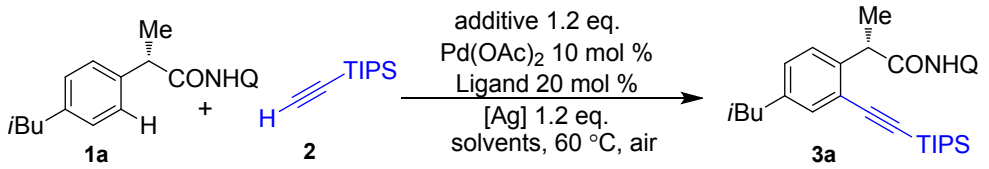
1. General Information:

All reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of air. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still. NMR spectra were measured on a Varian INOVA600 spectrometer .^{1}H NMR spectra were recorded at 500 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 125 MHz and referenced to the solvent resonance. High resolution mass spectra (HRMS) were recorded on the Thermo Scientific Exactive Plus equipped with ESI ionization source. The enantiomeric excess values were determined by chiral HPLC with an Agilent instrument and a Daicel CHIRALCEL and CHIRALPAK column and Nu-Analytical HPLC Column. The chiral HPLC methods were calibrated with the corresponding racemic mixtures. The racemic products used to determine the ee values were obtained under achiral-catalyst conditions.

Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas, and other commercial suppliers and used as received. $Pd(OAc)_2$ was purchased from Alfa Aesar and used as received.

2. Experimental Section

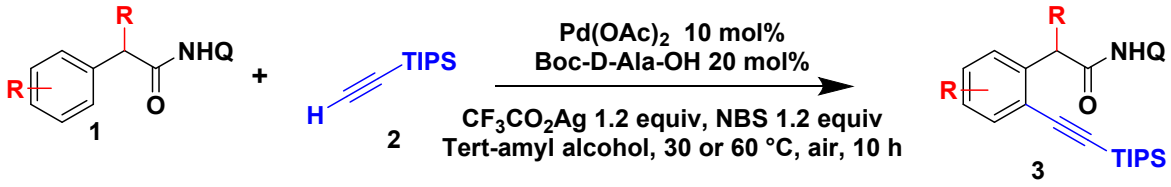
2.1 Optimization of Conditions



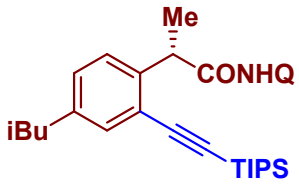
Entry	Ligand (20 mol %)	[Ag]	Additive	Solvent	Yield[a] of **3a**
1	*N*-Boc-Ala-OH	AgTFA	/	DCE	0%
2	*N*-Boc-Ala-OH	AgTFA	/	toluene	0%
3	*N*-Boc-Ala-OH	AgTFA	/	*t*-AmylOH	0%
4	*N*-Boc-Ala-OH	AgTFA	NBS	*t*-AmylOH	77%
5	*N*-Boc-Ala-OH	AgTFA	NCS	*t*-AmylOH	< 5%
6	*N*-Boc-Ala-OH	AgTFA	NIS	*t*-AmylOH	< 5%
7	*N*-Boc-Ala-OH	AgTFA	I_2	*t*-AmylOH	20%
8	*N*-Boc-Ala-OH	$AgNO_3$	NBS	*t*-AmylOH	63%
9	*N*-Boc-Ala-OH	Ag_2CO_3	NBS	*t*-AmylOH	< 5%
10	*N*-Boc-Ala-OH	Ag_2O	NBS	*t*-AmylOH	< 5%
11	PivOH	AgTFA	NBS	*t*-AmylOH	61%
12	$AdCO_2H$	AgTFA	NBS	*t*-AmylOH	62%
13	*N*-Boc-Val-OH	AgTFA	NBS	*t*-AmylOH	64%
14	*N*-Boc-Ile-OH	AgTFA	NBS	*t*-AmylOH	62%
15	*N*-Ac-Ala-OH	AgTFA	NBS	*t*-AmylOH	66%
16[b]	*N*-Boc-Ala-OH	AgTFA	NBS	*t*-AmylOH	78%[c] (99% ee)
17	CH_3CO_2H	AgTFA	NBS	*t*-AmylOH	58%
18	CF_3CO_2H	AgTFA	NBS	*t*-AmylOH	60%
19[d]	*N*-Boc-Ala-OH	AgTFA	NBS	*t*-AmylOH	35%

[a]Conditions: 1a (0.1 mmol), 2 (0.15 mmol), Pd(OAc)2 (10 mol %), ligand (20 mol %), [Ag] (0.12 mmol), additive (0.12 mmol), solvent (1 mL), at 60 °C for 24 h under air. Isolated yields. *b*mono:di = 5:1. *c*Conducted at rt. *d*Pd(OAc)2 (5 mol %) was used.

2.2 General Procedure for C-H alkynylation

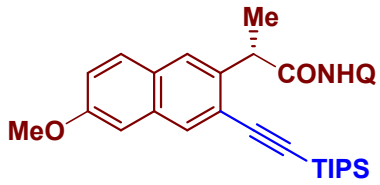


A mixture of **1** (0.2 mmol), $Pd(OAc)_2$ (10 mol%), **2** (0.24 mmol), Boc-D-Ala-OH (20 mol%), CF_3CO_2Ag (0.24 mmol) and NBS (0.24 mmol), Tertiary amyl alcohol (1 mL) in a 35 mL sealed tube was heated at room temperature or 60 ℃ for 10 h under an air atmosphere. The reaction mixture was cooled to room temperature and concentrated under a reduced pressure. The resulting residue was purified by column chromatography on silica gel to give the corresponding product **3**.



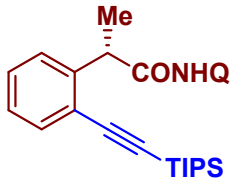
(S)-2-(4-isobutyl-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)propanamide 3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.78 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.63 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.09 – 8.07 (m, 1H), 7.52 – 7.43 (m, 3H), 7.38 – 7.34 (m, 2H), 7.12 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.59 (q, *J* = 7.2 Hz, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.92-1.82 (m, 1H), 1.65 (d, *J* = 7.2 Hz, 4H), 1.16 – 1.10 (m, 21H), 0.91 (d, *J* = 6.8 Hz, 6H);**^{13}C NMR**(101 MHz, $CDCl_3$) δ 172.7, 148.1, 140.8, 140.6, 138.7, 136.13, 134.9, 133.6, 130.3, 127.9, 127.4, 126.7, 122.9, 121.5, 121.4, 116.5, 105.5, 95.2, 45.6, 44.9, 30.2, 22.5, 18.8, 18.6, 11.5; **HRMS** (EI-TOF) calcd for $C_{33}H_{45}N_2OSi$ (M^+):513.3301, found: 513.3286.



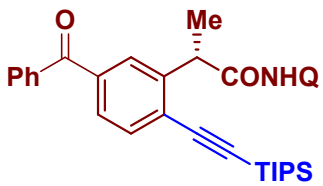
(S)-2-(6-methoxy-3-((triisopropylsilyl)ethynyl)naphthalen-2-yl)-N-(quinolin-8-yl)propanamide 3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.82 (d, *J* = 7.2 Hz, 1H), 8.60 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.07 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.01 (s, 1H), 7.92 (s, 1H), 7.69 (d, *J* = 9.2 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.35 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 4.70 (q, *J* = 7.2 Hz, 1H), 3.89 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H), 1.21 – 1.16(m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8, 158.1, 148.1, 138.6, 137.4, 136.2, 134.9, 133.2, 132.2, 129.6, 129.0, 127.9, 127.39, 125.7, 121.7 , 121.5, 121.4, 120.0, 116.4, 105.5, 105.1, 95.7, 55.4, 45.7, 19.1, 18.9, 11.5; **HRMS** (EI-TOF) calcd for $C_{34}H_{41}N_2O_2Si$ (M^+): 537.2937, found: 537.2924.



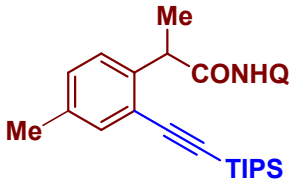
(S)-N-(quinolin-8-yl)-2-(2-((triisopropylsilyl)ethynyl)phenyl)propanamide 3c

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.85 – 8.84 (m, 1H), 8.71 (dd, J = 4.0, 1.5 Hz, 1H), 8.11 (dd, J = 8.0, 1.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.42 – 7.37 (m, 2H), 7.30 – 7.26 (m, 1H), 4.71 (q, J = 6.5 Hz, 1H), 1.72 (d, J = 7.0 Hz, 3H), 1.21-1.20 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.4, 148.1, 143.5, 138.6, 136.2, 134.8, 133.2, 129.3, 127.9, 127.4, 127.0, 126.9, 123.1, 121.6, 121.4, 116.5, 105.1, 95.8, 45.8, 18.8, 18.6, 11.5; **HRMS** (EI-TOF) calcd for $C_{29}H_{37}N_2OSi$ (M^+):457.2675, found: 457.2663.



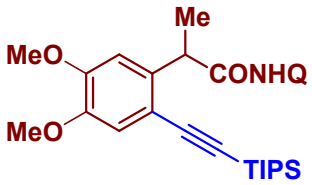
(S)-2-(5-benzoyl-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)propanamide 3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.67 (d, *J* = 6.4 Hz, 1H), 8.59 (d, *J* = 2.8 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.88 (s, 1H), 7.68 – 7.58 (m, 4H), 7.45 – 7.38 (m, 3H), 7.31 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 2H), 4.59 (d, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.09-1.05 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.9, 171.9, 147.95, 143.4, 138.3, 137.8, 137.4, 136.8, 134.6, 133.3, 132.7, 130.2, 128.9, 128.5, 128.4, 128.1, 127.6, 127.3, 121.7, 121.6, 117.1, 104.3, 99.7, 46.0, 18.8, 18.5, 11.5; **HRMS** (EI-TOF) calcd for $C_{36}H_{41}N_2O_2Si$ (M^+): 561.2937, found: 561.2922.



2-(4-methyl-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)propanamide 3e

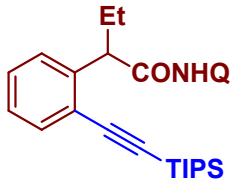
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.78 (d, *J* = 7.2 Hz, 1H), 8.67 (d, *J* = 2.8 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.35 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 1H), 4.60 (q, *J* = 6.8 Hz, 1H), 2.30 (s, 3H), 1.64 (d, *J* = 6.8 Hz, 3H), 1.14 (s, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.7, 148.1, 140.6, 138.5, 136.7, 136.2, 134.9, 133.5, 130.2, 127.9, 127.4, 126.7, 122.9, 121.5, 121.4, 116.5, 105.3, 95.2, 45.5, 20.9, 18.8, 18.6, 11.5; **HRMS** (EI-TOF) calcd for $C_{30}H_{39}FN_2OSi$ (M^+): 471.2832, found: 471.2812.



2-(4,5-dimethoxy-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)propanamide 3f

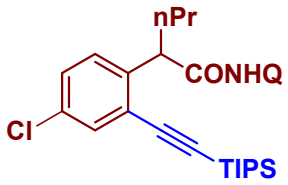
^{1}H NMR (501 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.77 (d, *J* = 6.5 Hz, 1H), 8.69 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.10 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.39 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.05 (s, 1H), 7.00 (s, 1H), 4.61 (q, *J* = 7.0 Hz, 1H), 3.88 (d, *J* = 3.5 Hz, 6H), 1.62 (d, *J* = 7.0 Hz, 3H), 1.17-1.15 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.7, 149.3, 147.2, 146.8, 137.7, 136.2, 135.2, 133.9, 127.0, 126.4, 120.6, 120.5, 115.5,

114.1, 114.0, 108.5, 106.4, 104.3, 92.8, 55.2, 55.1, 44.5, 17. 9 , 17.8, 10.6; **HRMS** (EI-TOF) calcd for $C_{31}H_{41}N_2O_3Si$ (M^+): 517.2886, found: 517.2870.



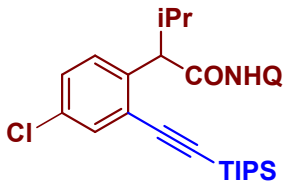
N-(quinolin-8-yl)-2-(2-((triisopropylsilyl)ethynyl)phenyl)butanamide 3g

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.79 (d, *J* = 7.5 Hz, 1H), 8.69 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 7.38 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.21 – 7.18 (m, 1H), 4.47 (t, *J* = 7.5 Hz, 1H), 2.34 – 2.25 (m, 1H), 1.99 – 1.90 (m, 1H), 1.20 – 1.18 (m, 21H), 1.00 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 148.1, 142.1, 138.6, 136.2, 134.8, 133.0, 129.2, 127.9, 127.4, 126.9, 126.9, 123.4, 121.6, 121.5, 116.5, 105.4, 95.3, 53.2, 27.3, 18.9, 12.4, 11.5; **HRMS** (EI-TOF) calcd for $C_{30}H_{39}N_2OSi$ (M^+): 471.2832, found:471.2817.



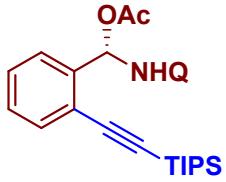
2-(4-chloro-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)pentanamide 3h

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.77 – 8.71 (m, 2H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.40 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 4.49 (t, *J* = 7.2 Hz, 1H), 2.27 – 2.18 (m, 1H), 1.91 – 1.82 (m, 1H), 1.69 (d, *J* = 6.8 Hz, 1H), 1.47 – 1.32 (m, 2H), 1.19 (s, 21H), 0.96 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.6, 148.2, 140.7, 138.6, 136.2, 134.7, 132.6, 132.5, 129.4, 128.5, 128.0, 127.4, 124.9, 121.7, 121.7, 116.6, 103.9, 97.0, 50.8, 36.3, 21.1, 18.9, 14.2, 11.5; **HRMS** (EI-TOF) calcd for $C_{31}H_{40}ClN_2OSi$ (M^+): 519.2598, found: 519.2589.



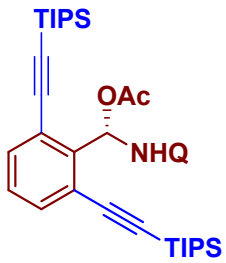
2-(4-chloro-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-N-(quinolin-8-yl)butanamide 3i

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.78 – 8.73 (m, 2H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.52 – 7.41 (m, 4H), 7.29 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.18 (d, *J* = 10.5 Hz, 1H), 2.53 – 2.47 (m, 1H), 1.28 – 1.22 (m, 21H), 1.16 (d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.6, 148.1, 140.1, 138.5, 136.2, 134.6, 132.5, 132.2, 129.4, 128.5, 128.0, 127.3, 125.3, 121.7, 121.6, 116.7, 104.3, 96.7, 58.6, 33.2, 21.9, 19.8, 19.0, 11.6; **HRMS** (EI-TOF) calcd for $C_{31}H_{40}ClN_2OSi$ (M^+): 519.2598, found: 518.2588.



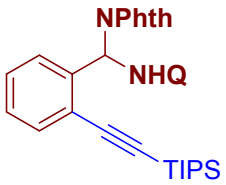
(S)-2-oxo-2-(quinolin-8-ylamino)-1-(2-((triisopropylsilyl)ethynyl)phenyl)ethyl acetate 3j

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.65 – 8.64 (m, 2H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.39-7.38 (m, 2H), 7.31 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.26-7.20 (m, 2H), 6.81 – 6.80 (m, 1H), 2.20 (s, 3H), 1.01 (s, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 166.6, 148.3, 138.6, 137.0, 136.5, 134.0, 133.6, 129.0, 129.0, 128.2, 128.1, 127.5, 123.9, 122.1, 121.7, 117.2, 103.9, 97.1, 74.3, 21.0, 18.8 , 18.8, 11.5; **HRMS** (EI-TOF) calcd for $C_{30}H_{37}N_2O_3Si$ (M^+): 501.2573, found: 501.2559.



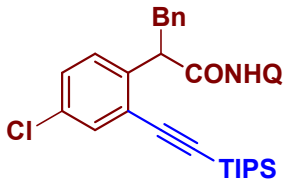
1-(2,6-bis(3,3-diisopropyl-4-methylpent-1-yn-1-yl)phenyl)-2-oxo-2-(quinolin-8-ylamino)ethyl acetate 3j,

^{1}H NMR (501 MHz, $CDCl_3$) δ 10.62 (s, 1H), 8.80 – 8.75 (m, 2H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.53 – 7.49 (m, 4H), 7.43 (dd, *J* = 8.5, 4.0 Hz, 1H), 7.33 (s, 1H), 7.27 – 7.26 (m, 1H), 2.33 (s, 3H), 0.99 – 0.95 (m, 42H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 165.8, 148.2, 138.8, 138.2, 136.3, 134.3, 134.2, 128.6, 127.9, 127.5, 121.7, 121.6, 116.8, 103.8, 97.4, 73.4, 21.1, 18.7, 18.6, 11.4; **HRMS** (EI-TOF) calcd for $C_{41}H_{57}N_2O_3Si_2$ (M^+):681.3908, found: 681.3901.



2-(1,3-dioxoisoindolin-2-yl)-N-(quinolin-8-yl)-2-(2-((triisopropylsilyl)ethynyl)phenyl)acetamide 3k

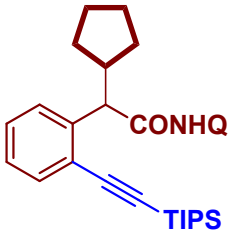
^{1}H NMR (501 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.78 (dd, *J* = 6.5, 2.0 Hz, 1H), 8.55 (dd, *J* = 4.5, 2.0 Hz, 1H), 8.12 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.94 – 7.92 (m, 2H), 7.83 – 7.72 (m, 4H), 7.54 – 7.45 (m, 4H), 7.38 (dd, *J* = 8.5, 4.5 Hz, 1H), 6.90 (s, 1H), 1.10 – 1.03 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.0, 165.1, 148.3, 138.7, 136.3, 136.1, 134.2, 134.1, 133.5, 132.2, 129.3, 128.9, 128.8, 127.8, 127.3, 124.7, 123.7, 122.0, 121.6, 116.5, 103.6, 98.4, 57.5, 18.6, 11.3; **HRMS** (EI-TOF) calcd for $C_{36}H_{38}N_3O_3Si$ (M^+): 588.2682, found: 588.2672.



2-(4-chloro-2-((triisopropylsilyl)ethynyl)phenyl)-3-phenyl-N-(quinolin-8-yl)propanamide 3i

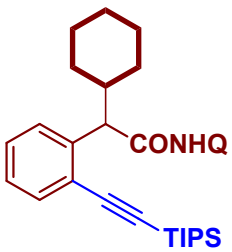
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.73 (d, *J* = 7.2 Hz, 1H), 8.65 – 8.64 (m, 1H), 8.09 – 8.07 (m, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.37 (dd, *J* =

8.0, 4.0 Hz, 1H), 7.30 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.24 – 7.09 (m, 5H), 4.81 (t, *J* = 7.6Hz, 1H), 3.61 (dd, *J* = 14.8, 84 Hz, 1H), 3.15 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.21 – 1.16 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 148.0, 139.9, 139.1, 138.4, 136.3, 134.6, 132.9 , 132.8, 129.4, 129.2, 128.9, 128.4, 128.0, 127.4, 126.4, 124.9, 121.7, 121.6, 116.9, 103.8, 97.3, 52.7, 39.7, 18.9, 11.5; **HRMS** (EI-TOF) calcd for $C_{35}H_{40}ClN_2OSi$ (M^+): 567.2598, found:567.2579.



2-cyclopentyl-N-(quinolin-8-yl)-2-(2-((triisopropylsilyl)ethynyl)phenyl)acetamide 3m

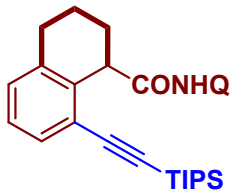
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.79 (d, *J* = 7.2 Hz, 1H), 8.72 (d, *J* = 3.2 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.39 (m, 4H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 4.38 (d, *J* = 10.8 Hz, 1H), 2.81 – 2.74 (m, 1H), 2.08 – 2.05 (m, 1H), 1.64 (d, *J* = 8.4 Hz, 4H), 1.51 – 1.40 (m, 3H), 1.23 (d, *J* = 5.4 Hz, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ172.1, 148.1, 142.0, 138.5, 136.2, 134.8, 132.8, 129.1, 127.9, 127.9, 127.2, 126.7, 123.3, 121.6, 121.5, 116.6, 105.8, 95.0, 57.0, 44.6, 32.2, 30.1, 25.5, 25.2, 19.0, 11.6; **HRMS** (EI-TOF) calcd for $C_{33}H_{43}N_2OSi$ (M^+): 511.3139, found: 511.3134.



2-cyclohexyl-N-(quinolin-8-yl)-2-(2-((triisopropylsilyl)ethynyl)phenyl)acetamide 3n

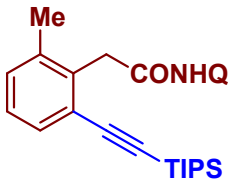
^{1}H NMR (501 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.72 (dd, *J* = 7.5, 1.5Hz, 1H), 8.65 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.02 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.32 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5

Hz, 1H), 4.24 (d, *J* = 10.5 Hz, 1H), 2.17 (q, *J* = 11.0 Hz, 1H), 1.98 (d, *J* = 13.0 Hz, 1H), 1.66 – 1.57 (m, 3H), 1.29 – 1.21 (m, 3H), 1.20 – 1.16 (m, 21H), 1.12 – 1.07 (m, 2H), 1.01 – 0.94 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.7, 148.1, 140.8, 140.6, 138.7, 136.1, 135.0, 133.6, 130.3, 128.0, 127.4, 126.7, 122.9, 121.5, 121.4, 116.5, 105.5, 95.2, 45.6, 44.9, 30.2, 22.5, 18.9, 18.62, 11.5; **HRMS** (EI-TOF) calcd for $C_{34}H_{45}N_2OSi$ (M^+): 525.3296, found: 525.3289.



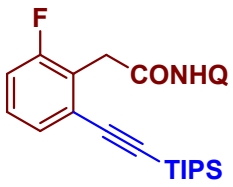
N-(quinolin-8-yl)-8-((triisopropylsilyl)ethynyl)-1,2,3,4-tetrahydronaphthalene-1-carboxamide 3o

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.68 (d, *J* = 7.5 Hz, 1H), 8.48 – 8.47 (m, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.24 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.17 – 7.11 (m, 2H), 4.27 (d, *J* = 3.5 Hz, 1H), 2.86 – 2.71 (m, 2H), 2.53 – 2.51 (m, 1H), 1.98 – 1.76 (m, 3H), 0.81 – 0.77 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.4, 148.0, 138.6, 138.5, 136.0, 135.8, 134.8, 131.2, 130.0, 127.8, 127.4, 127.0, 125.0, 121.4, 121.2, 116.2, 104.8, 96.4, 46.9, 29.6, 27.8, 19.8, 18. 6, 18.5, 11.2; **HRMS** (EI-TOF) calcd for $C_{31}H_{39}N_2OSi$ (M^+): 483.2832, found: 483.2815.



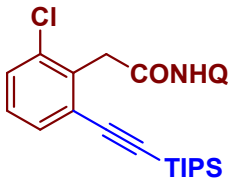
2-(2-methyl-6-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5a

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.65 (dd, *J* = 7.5, 1.0 Hz, 1H), 8.53 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.98 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.26 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.15 – 7.11 (m, 2H), 4.15 (s, 2H), 2.31 (s, 3H), 0.93-0.90 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.5, 148.1, 138.5, 138.0, 136.1, 135.3, 134.6, 130.9, 127.8, 127.4, 127.3, 124.7, 121.4, 121.4, 116.3, 105.5, 95.4, 41.1, 20.4, 18.6, 11.3; **HRMS** (EI-TOF) calcd for $C_{29}H_{37}N_2OSi$ (M^+): 457.2675, found: 457.2582.



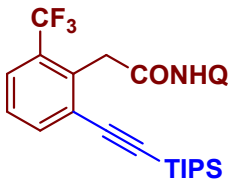
2-(2-fluoro-6-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5b

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.74 (d, *J* = 7.2 Hz, 1H), 8.68 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.37 (m, 4H), 7.29 – 7.24 (m, 1H), 7.14 – 7.09 (m, 1H), 4.19 (s, 2H), 1.02 – 0.96 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5, 161.5 (d, *J* = 245.5 Hz), 148.0, 138.4, 136.5, 134.6, 128.9, 128.8 (d, *J* = 5.7 Hz), 128.0, 127.5, 126.6 (d, *J* = 5.1 Hz), 124.4 (d, *J* = 17.0 Hz), 121.5, 116.8, 116.2, 116.0, 103.7 (d, *J* = 3.8 Hz), 97.0, 36.6 (d, *J* = 2.4 Hz), 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{28}H_{34}FN_2OSi$ (M^+): 461.2424, found: 461.2328.



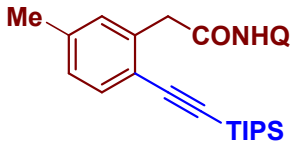
2-(2-chloro-6-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide3r-1 5c

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.75 (s, 1H), 8.63 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.59 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.02 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.29 (m, 4H), 4.31 (s, 2H), 0.88 – 0.83 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 148.1, 138.4, 136.2, 135.7, 135.0, 134.5, 131.5, 129.9, 128.4, 128.4, 127.8, 127.4, 126.5, 121.5, 126.5, 126.4, 116.4, 104.1, 97.1, 41.3, 18.6, 11.2; **HRMS** (EI-TOF) calcd for $C_{28}H_{34}ClN_2OSi$ (M^+): 477.2129, found: 477.2035.



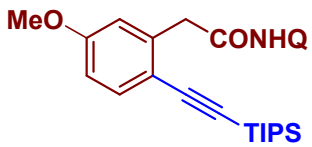
N-(quinolin-8-yl)-2-(2-(trifluoromethyl)-6-((triisopropylsilyl)ethynyl)phenyl)acetamide 5d

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.66 (d, *J* = 7.5 Hz, 1H), 8.59 – 8.58 (m, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.29 (m, 5H), 7.17 – 7.14 (m, 1H), 4.28 (s, 2H), 0.94 – 0.90 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 148.0, 138.4, 136.4, 136.3, 135.3, 134.5, 130.2 (q, *J* = 30.1 Hz), 127.8, 127.5, 127.4, 126.1 (q, *J* = 5.3 Hz), 124.1 (q, *J* = 274.3 Hz), 121.5, 121.4, 116.4, 103.4, 98.4, 40.2, 18.5, 11.2; **HRMS** (EI-TOF) calcd for $C_{29}H_{34}F_3N_2OSi$ (M^+): 511.2392, found: 511.2292.



2-(5-methyl-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5e

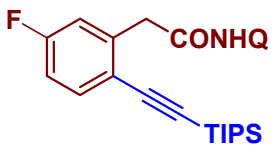
^{1}H NMR (501 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.68 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.57 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.99 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.28 (dd, *J* = 8.5, 4.0 Hz, 1H), 7.18 (s, 1H), 7.00 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.01 (s, 2H), 2.27 (s, 3H), 0.95 – 0.92 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 148.1, 139.2, 138.6, 136.7, 136.2, 134.7, 133.1, 130.9, 128.2, 127.9, 127.4, 121.5, 121.5, 121.2, 116.5, 105.1, 94.9, 43.7, 21.6, 18.7, 11.4; **HRMS** (EI-TOF) calcd for $C_{29}H_{37}N_2OSi$ (M^+): 457.2675, found: 457.2582.



2-(5-methoxy-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5f

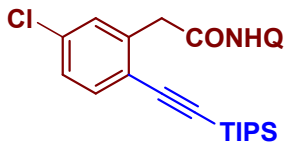
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.75 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.66 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.07 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53 – 7.42 (m, 3H), 7.36 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.11 (s, 2H), 3.81 (s, 3H), 1.02 (d, *J* = 1.9 Hz, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 159.8, 148.0, 138.4, 136.0, 134.5,134.3, 127.7, 127.2, 121.4,121.4, 116.4,116.2, 115.1, 113.4 ,

104.8, 93.8, 55.3, 43.8, 18.5, 11.2; **HRMS** (EI-TOF) calcd for $C_{29}H_{37}N_2O_2Si$ (M^+): 473.2624, found: 473.2532.



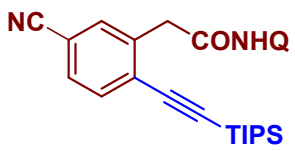
2-(5-fluoro-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5g

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.67 (dd, *J* = 7.0, 1.0 Hz, 1H), 8.61 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.04 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.49-7.46 (m, 1H), 7.44 – 7.39 (m, 2H), 7.32 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.12 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.91 (td, *J* = 8.5, 2.5 Hz, 1H), 4.04 (s, 2H), 0.96 – 0.93 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.1, 162.6 (d, *J* = 250.6 Hz), 148.2, 139.5 (d, *J* = 8.2 Hz), 138.6, 136.3, 134.9 (d, *J* = 8.6 Hz), 134.5, 128.0, 127.4, 121.7, 121.6, 120.3 (d, *J* = 3.3 Hz), 117.3 (d, *J* = 22.6 Hz), 116.7, 114.7 (d, *J* = 22.1 Hz), 104.0, 95.6 (d, *J* = 1.5 Hz), 43.6 (d, *J* = 1.4 Hz), 18.7, 11.4; **HRMS** (EI-TOF) calcd for $C_{28}H_{34}FN_2OSi$ (M^+): 461.2424, found:461.2330.



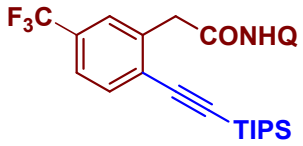
2-(5-chloro-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5h

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.74 (dd, *J* = 7.2, 2.0 Hz, 1H), 8.70 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 – 7.46 (m, 4H), 7.40 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.28 – 7.25(m, 1H), 4.09 (s, 2H), 1.05 – 0.99 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.0, 148.2, 138.5, 138.6, 136.3, 134.7, 134.5, 134.2, 130.3, 127.9, 127.7, 127.4, 122.7, 121.6 , 121.7, 116.6, 103.9, 97.1, 43.4, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{28}H_{34}ClN_2OSi$ (M^+): 477.2129, found: 477.2034.



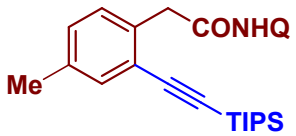
2-(5-cyano-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5i

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.73 – 8.70 (m, 2H), 8.15 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.84 (d, *J* = 1.2 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.52 – 7.50 (m, 2H), 7.44 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.18 (s, 2H), 1.05 – 1.01 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 148.3, 142.0, 138.5, 136.4, 134.3, 131.8, 131.2, 128.0, 127.5, 125.6, 121.8 , 122.0, 118.1, 116.7, 111.7, 102.5, 99.4, 43.6, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{29}H_{34}N_3OSi_2$ (M^+): 468.2471, found: 468.2378.



N-(quinolin-8-yl)-2-(5-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)phenyl)acetamide 5j

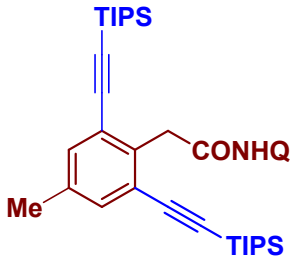
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.73 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.69 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.74 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.45 (m, 3H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.18 (s, 2H), 1.07 – 0.99 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 148.2, 138.6, 137.7, 136.3, 134.4, 133.5, 130.6 (q, *J* = 32.5 Hz), 128.0, 127.9 (q, *J* = 11.3 Hz), 127.4, 127.2 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 3.6 Hz), 123.9 (q, *J* = 270.7 Hz), 121.7, 121.6, 116.6, 103.6, 99.2, 43.4, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{29}H_{34}F_3N_2OSi$ (M^+):511.2392, found: 511.2291.



2-(4-methyl-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5k

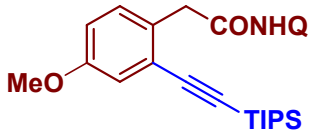
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.76 (dd, *J* = 7.2, 1.6 Hz, 1H), 8.68 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 – 7.33 (m, 5H), 7.17 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.09 (s, 2H), 2.35 (s, 3H), 1.05 – 1.00 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 148.1, 138.6, 137.1, 136.2, 134.7, 133.9, 133.6, 130.1 , 129.9,

127.9, 127.4, 123.9, 121.5 , 121.5, 116.5, 105.1, 95.3, 43.4, 21.0, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{29}H_{37}N_2OSi$ (M^+): 457.2675, found: 457.2581.



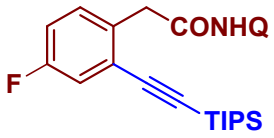
2-(4-methyl-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5k'

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.72 (dd, *J* = 7.2, 1.6 Hz, 1H), 8.65 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.38 – 7.35 (m, 3H), 4.36 (s, 2H), 2.35 (s, 3H), 1.02 – 0.95 (m, 42H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.8, 148.0, 138.6, 137.1, 136.1, 136.1, 134.9, 133.6, 127.8, 127.5, 125.0, 121.4, 121.1, 116.4, 104.7, 95.8, 42.0, 20.8, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{40}H_{57}N_2OSi_2$ (M^+): 637.4009, found: 637.3878.



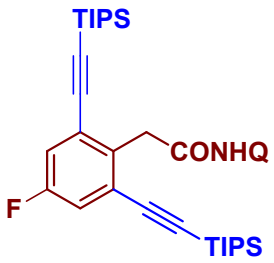
2-(4-methoxy-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5i

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.76 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.68 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.41 – 7.35 (m, 2H), 7.10 (d, *J* = 2.8 Hz, 1H), 6.93 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.06 (s, 2H), 3.84 (s, 3H), 1.03 – 1.00 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 158.6, 148.1, 138.6, 136.2, 134.7, 131.3, 129.2, 127.9, 127.4, 125.0, 121.5, 121.5, 117.7, 116.5, 115.6, 104.8, 95.68, 55.6, 43.0, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{29}H_{37}N_2O_2Si$ (M^+): 473.2624, found: 473.2529.



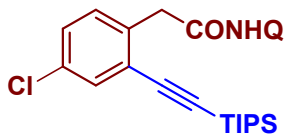
2-(4-fluoro-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5m

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.75 (dd, *J* = 6.8, 1.6 Hz, 1H), 8.69 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.12 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.53 – 7.39 (m, 4H), 7.29 – 7.26 (m, 1H), 7.10-7.05 (m, 1H), 4.09 (s, 2H), 1.05 – 0.98 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 161.5 (d, *J* = 247.5 Hz), 148.1, 138.4, 136.2, 134.4, 132.7 (d, *J* = 3.3 Hz), 131.8 (d, *J* = 8.5 Hz), 127.8, 127.3, 125.7 (d, *J* = 9.5 Hz), 121.5 (d, *J* = 2.7 Hz), 119.6, 119.5, 116.4, 116.2 (d, *J* = 21.3 Hz), 103.6 (d, *J* = 2.9 Hz), 97.1, 42.8, 18.6, 11.2; **HRMS** (EI-TOF) calcd for $C_{28}H_{34F}N_2OSi$ (M^+): 461.2424, found: 461.2326.



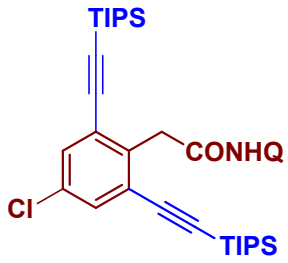
2-(4-fluoro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5m'

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.72 – 8.67 (m, 2H), 8.11 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.39 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.27 – 7.25 (m, 2H), 4.36 (s, 2H), 1.02-0.95 (m, 42H; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 162.2 (d, *J* = 247.9 Hz), 148.1, 138.6, 136.2, 135.3, 134.7, 127.8, 127.5, 126.8 (d, *J* = 10.2 Hz), 121.5, 121.2, 119.8 (d, *J* = 22.7 Hz), 116.5, 103.5, 97.8, 41.6, 18.6, 11.3; **HRMS** (EI-TOF) calcd for $C_{39}H_{54}FN_2OSi_2$ (M^+):641.3759, found: 641.3629



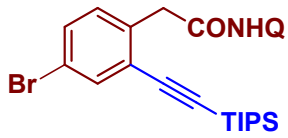
2-(4-chloro-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5n

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.74 – 8.70 (m, 2H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.32 (m, 7H), 4.09 (s, 2H), 1.05-1.01 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 148.2, 138.5, 136.3, 135.4, 134.5 133.1, 132.7, 131.5, 129.1, 127.9, 127.4, 125.7, 121.7, 121.6, 116.5, 103.5, 97.5, 43.1, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{28}H_{34}ClN_2OSi$ (M^+): 477.2129, found: 477.2032



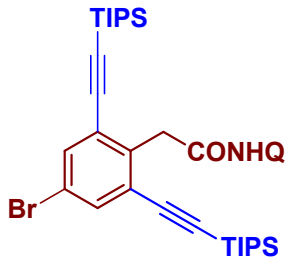
2-(4-chloro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5n,

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.71 – 8.68 (m, 2H), 8.11 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.40 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.36 (s, 2H), 1.02 – 0.95 (m, 42H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 148.1, 138.6, 137.6, 136.2, 134.7, 132.8, 132.5, 127.8, 127.5, 126.6, 121.5, 121.3, 116.5, 103.2, 98.0, 41.8, 18.6, 11.3; **HRMS** (EI-TOF) calcd for $C_{39}H_{54}ClN_2OSi_2$ (M^+): 657.3463, found: 657.3330



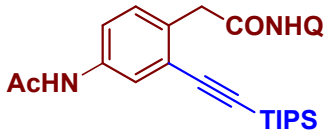
2-(4-bromo-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5o

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.67 – 8.62 (m, 2H), 8.05 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.34 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 4.00 (s, 2H), 0.95-0.93 (m , 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 148.2, 138.4, 136.3, 135.9, 135.5, 134.4, 132.0, 131.7, 127.9, 127.41, 126.0, 121.7, 121.6, 120.9, 116.5, 103.3, 97.7, 43.1, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{28}H_{34}BrN_2OSi$ (M^+): 521.1624, found: 521.1522.



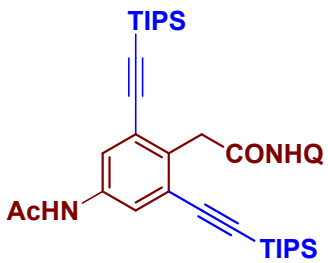
2-(4-bromo-2,5-bis((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5o,

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.75 – 8.74 (m, 2H), 8.16 (d, *J* = 8.0Hz, 1H), 7.71 (s, 2H), 7.55 – 7.49 (m, 2H), 7.45 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.40 (s, 2H), 1.04 – 1.02(m, 42H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 146.8, 137.1, 135.8, 135.7, 134.3, 133.6, 127.0, 126.7, 125.9, 120.4, 120.3, 119.5, 116.0, 102.1, 97.1, 40.9, 17.7, 10.3; **HRMS** (EI-TOF) calcd for $C_{39}H_{54}N_2OSi_2$ (M^+): 701.2958, found: 701.2822.



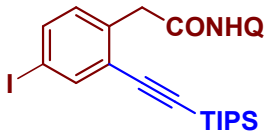
2-(4-acetamido-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5p

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.76 – 8.68 (m, 2H), 8.12 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.52 – 7.39 (m, 4H), 7.34-7.31 (m, 1H), 4.09 (s, 2H), 2.15 (s, 3H), 0.99 – 0.98 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 168.8, 148.3, 138.5, 137.4, 136.3, 134.5, 132.3, 130.7, 127.9 127.4, 124.5, 124.2, 121.7, 121.6, 120.7, 116.5, 104.6, 95.9, 43.1, 24.6, 18.7, 11.3; HRMS (EI-TOF) calcd for $C_{30}H_{38}N_3O_2Si$ (M+): 500.2733, found:500.2632.



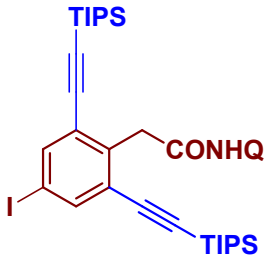
2-(4-acetamido-2,5-bis((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5p'

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.65 – 8.60 (m, 2H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.64 (s, 3H), 7.41 – 7.35 (m, 2H), 7.30 (dd, *J* = 8.5, 4.5 Hz, 1H), 4.30 (s, 2H), 2.09 (s, 3H), 0.92-0.87 (m, 42H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 168.0, 148.1, 138.5, 137.2, 136.1, 134.6, 127.8, 127.4, 125.6, 124.3, 121.5, 121.3, 116.4, 104.1, 96.5, 41.8, 24.6, 18.6, 11.2; HRMS (EI-TOF) calcd for $C_{41}H_{58}N_3O_2Si_2$ (M+): 680.4068, found:680.3928.



2-(4-iodo-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5q

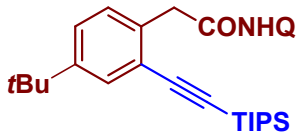
^{1}H NMR (501 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.66 – 8.62 (m, 2H), 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.33 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 3.98 (s, 2H), 0.97 – 0.92 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 148.2, 141.3, 138.4, 137.9, 136.5, 136.3, 134.4, 131.8, 127.9, 127.4, 126.2, 121.7, 121.6, 116.5, 103.1, 97.7, 92.2, 43.2, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{28}H_{34}IN_2OSi$ (M^+): 569.1485, found: 569.1375



2-(4-iodo-2,5-bis((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5q'

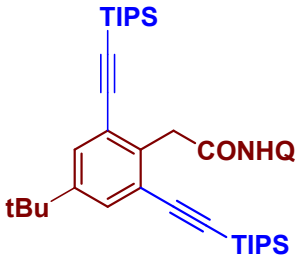
^{1}H NMR (501 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.63 – 8.62 (m, 2H), 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.78 (s, 2H), 7.43 – 7.37 (m, 2H), 7.33 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.27 (s,

2H), 0.92 – 0.90 (m, 42H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 148.0, 141.0, 138.7, 138.4, 136.2, 134.6, 127.8, 127.4, 126.9, 121.5, 121.3, 116.4, 102.8, 98.0, 91.5, 41.9, 18.6, 11.2; **HRMS** (EI-TOF) calcd for $C_{39}H_{54}FN_2OSi_2$ (M^+): 749.2819, found: 749.2668



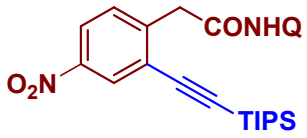
2-(4-(tert-butyl)-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5r

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.76 (d, *J* = 7.6 Hz, 1H), 8.62 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.08 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.58 (s, 1H), 7.51 – 7.35 (m, 5H), 4.10 (s, 2H), 1.35 (s, 9H), 1.04 – 1.03 (d, *J* = 3.2 Hz, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 150.4, 148.0, 138.6, 136.2, 134.7, 134.0, 129.9, 130.0, 127.9, 127.4, 126.4, 123.7, 121.4, 121.5, 116.4, 105.5, 95.0, 43.3, 34.6, 31.3, 18.7, 11.4; **HRMS** (EI-TOF) calcd for $C_{32}H_{43}N_2OSi$ (M^+): 499.3145, found: 499.3040.



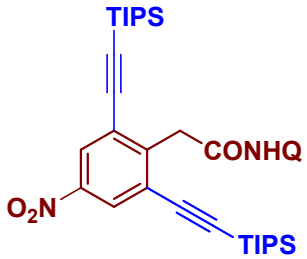
2-(4-(tert-butyl)-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5r'

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.72 (d, *J* = 7.6 Hz, 1H), 8.60 (dd, *J* = 4.4, 1.6Hz, 1H), 8.08 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.56 – 7.55 (m, 2H), 7.49 – 7.41 (m, 2H), 7.35 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.37 (s, 2H), 1.37 (s, 9H),1.02 – 0.99 (m, 42H); **^{13}C NMR**(101 MHz, $CDCl_3$) δ 167.8, 150.3, 147.8, 138.7, 136.3, 136.1, 134.9, 130.1, 127.8, 127.5, 124.8, 121.4, 121.0, 116.4, 105.1, 95.5, 41.9, 34.6, 31.3, 18.7, 11.4; **HRMS** (EI-TOF) calcd for $C_{43}H_{63}N_2OSi_2$ (M^+):679.4479, found: 649.4338.



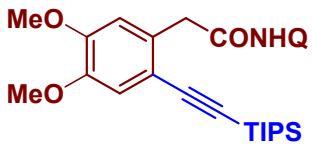
2-2-(4-nitro-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5s

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.73 – 8.70 (m, 2H), 8.39 (d, *J* = 2.4 Hz, 1H), 8.20 – -8.14 (m, 2H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.51 (m, 2H), 7.44 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.22 (s, 2H), 1.06 – 1.02 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 148.3, 147.2, 143.9, 138.5, 136.4, 134.3, 131.3, 128.0, 127.8, 127.5, 125.7, 123.4 , 122.0 , 121.8, 116.7, 102.5, 99.5, 43.4, 18.7, 11.3; **HRMS** (EI-TOF) calcd for $C_{28}H_{34}N_3O_3Si$ (M^+): 488.2369, found: 488.2274.



2-(4-nitro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5s'

^{1}H NMR (501 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.72 – 8.66 (m, 2H), 8.32 (s, 2H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.50 – 7.42 (m, 3H), 4.50 (s, 2H), 1.02 – 0.99 (m, 42H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 148.0, 146.7, 145.6, 138.3, 136.2, 134.3, 127.7, 127.4, 126.6, 126.7, 121.4, 121.5, 116.5, 102.2, 99.7, 42.1, 18.5, 11.1; **HRMS** (EI-TOF) calcd for $C_{39}H_{54}N_3O_3Si_2$ (M^+): 668.3704, found: 668.3571.

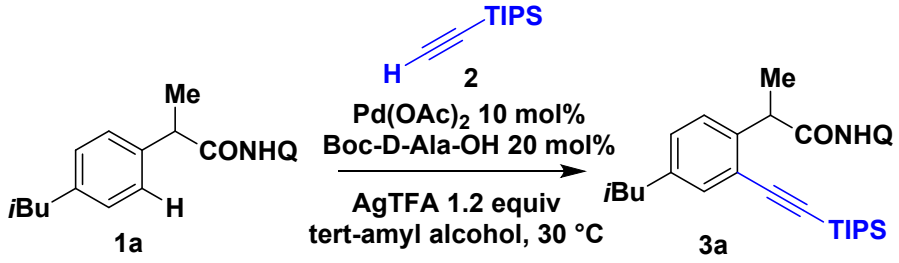


2-(4,5-dimethoxy-2-((triisopropylsilyl)ethynyl)phenyl)-N-(quinolin-8-yl)acetamide 5t

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.74 (dd, *J* = 7.2, 1.6 Hz, 1H), 8.68 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.6Hz, 1H), 7.52 – 7.45 (m, 2H), 7.39 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.04 (s, 1H), 6.96 (s, 1H), 4.08 (s, 2H), 3.92 (d, *J* = 3.2 Hz, 6H), 1.05 – 1.00 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 149.8, 148.2, 148.0, 138.6, 136.2, 134.6, 130.4, 127.9, 127.4, 121.6, 116.5, 116.1, 115.1, 112.8, 105.0, 94.0, 56.2, 56.1, 43.5, 18.7, 11.4; **HRMS** (EI-TOF) calcd for $C_{30}H_{39}N_2O_3Si$ (M^+): 503.2730, found:503.2622.

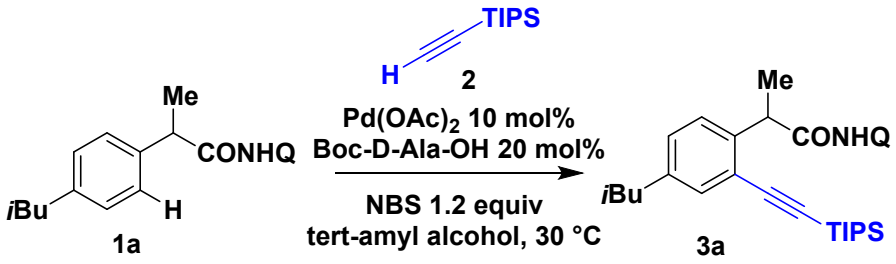
2.3 Mechanistic Investigation

a) control experiments without NBS



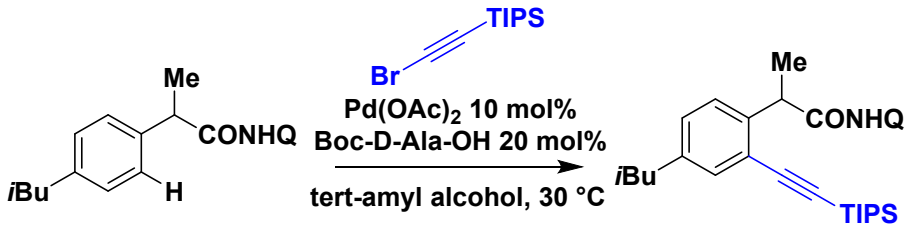
A mixture of **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **2** alkynyl (1.2 mmol), Boc-D-Ala-OH (20 mol%), and AgTHF (1.2 mmol), tert-amyl alcohol (1 mL) in a 35 mL sealed tube was conducted at 30 °C for 10 h under air atmosphere. no product **3a** was detected.

b) control experiments without AgTFA



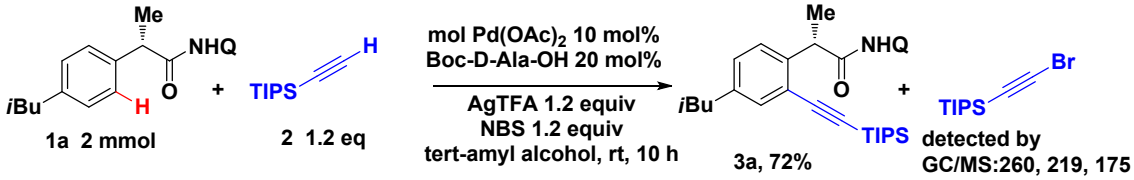
A mixture of **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **2** alkynyl (1.2 mmol), Boc-D-Ala-OH (20 mol%), and NBS (1.2 mmol), tert-amyl alcohol (1 mL) in a 35 mL sealed tube was conducted at 30 °C for 10 h under air atmosphere. no product **3a** was detected.

c) control experiments use bromoalkyne instead of AgTFA, NBS and 2

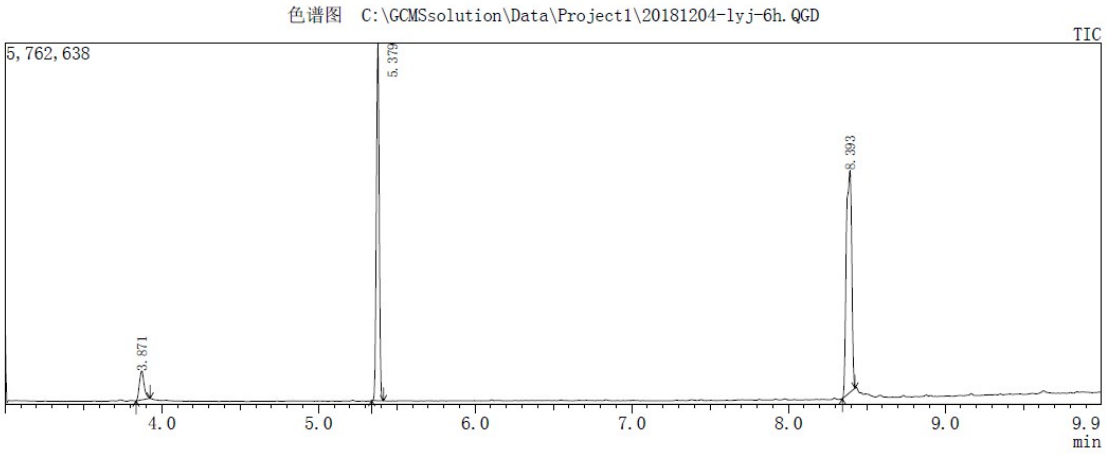


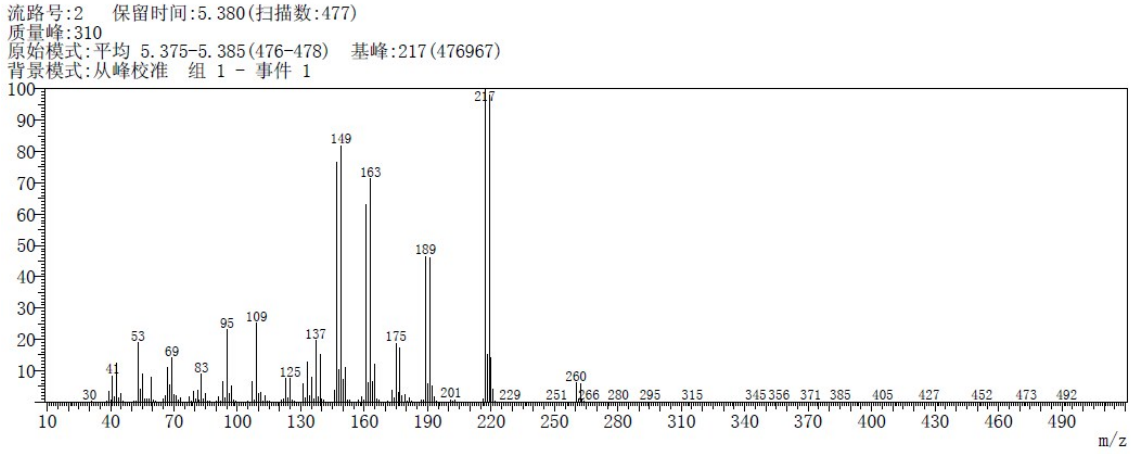
A mixture of **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), bromoalkyne (1.2 mmol), Boc-D-Ala-OH (20 mol%), tert-amyl alcohol (1 mL) in a 35 mL sealed tube was conducted at 30 °C for 10 h under air atmosphere. the alkynylation product **3a** could be obtained in 40% yield.

d) detection of bromoalkyne

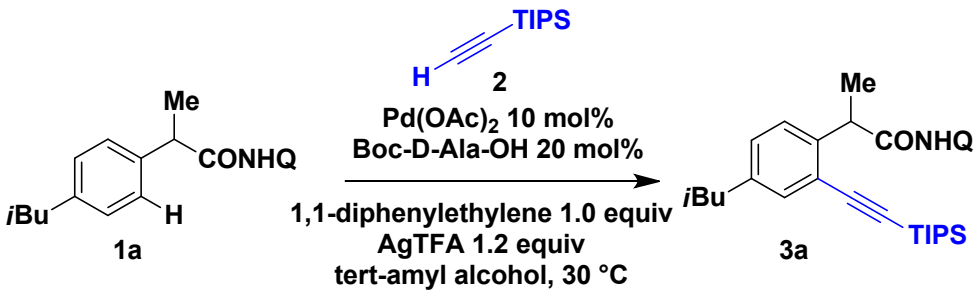


A mixture of **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **2** alkynyl (0.12 mmol), N-Boc-phe-OH (20 mol%), AgOAc (2.4 mmol) and NBS (0.12 mmol), t-AmylOH (1 mL) in a 35 mL sealed tube was conducted at rt for 24 h under air atmosphere. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. After filtration, the mixture was analyzed by GC/MS.



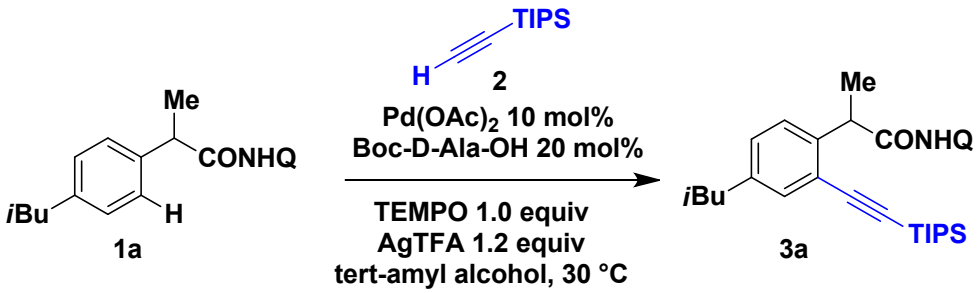


e) experiments with radical scavengers 1,1-diphenylethylene



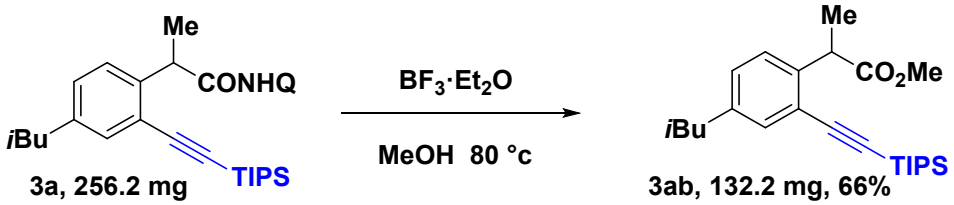
A mixture of **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **2** alkyne (1.2 mmol), Boc-D-Ala-OH (20 mol%), NBS (1.2 mmol), AgTHF (1.2 mmol) and 1,1-diphenylethylene (1.0 mmol), tert-amyl alcohol (1 mL) in a 35 mL sealed tube was conducted at 30 °C for 10 h under air atmosphere. **3a** were obtained in 48 % yield.

f) experiments with radical scavengers TEMPO

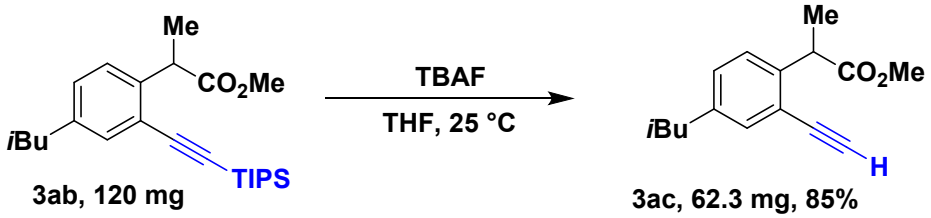


A mixture of **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **2** alkyne (1.2 mmol), Boc-D-Ala-OH (20 mol%), NBS (1.2 mmol), AgTHF (1.2 mmol)and TEMPO (1.0 mmol), tert-amyl alcohol (1 mL) in a 35 mL sealed tube was conducted at 30 °C for 10 h under air atmosphere. **3a** were obtained in 56 % yield.

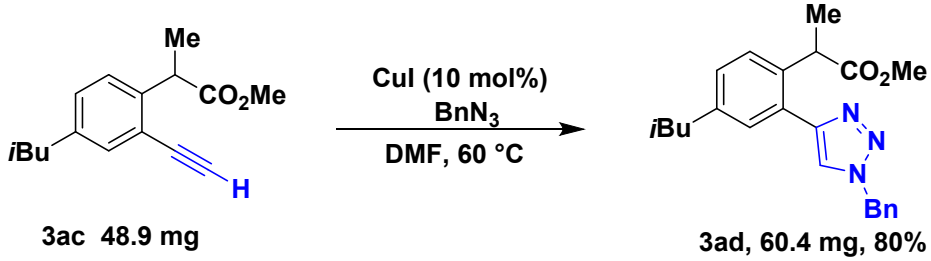
2.4 Diversication of ortho-Alkynylated phenylacetic amides



A mixture of **3a** (0.5 mmol, 256 mg), BF3.Et2O (10.0 eq, 5.0 mmol, 0.6mmL), MeOH (2 mL) in a 35 mL sealed tube was stirred at 80 ℃ for 24 h. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography on silica gel to give the corresponding product **3ab** (66%, 132.2 mg).

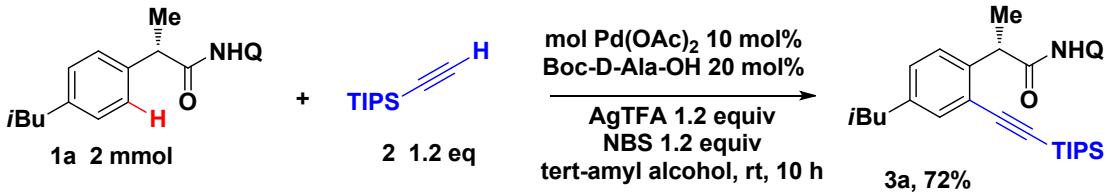


A mixture of **3ab** (0.3 mmol, 120 mg), TBAF (4.0 eq, 1.2 mmol, 313.8 mg), THF (1 mL) in a 35 mL sealed tube was stirred at 25 ℃ for 1.5 h. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography on silica gel to give the corresponding product **3ac** (85%, 62.3 mg).**^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.22 (d, *J* = 1.5 Hz, 1H), 7.14 – 7.13 (m, 1H), 7.04 – 7.03 (m, J = 8.0, 1.7 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 1H), 3.59 (s, 3H), 3.17 (s, 1H), 2.35 (d, *J* = 7.0 Hz, 2H), 1.82 – 1.73 (m, 1H), 1.41 (d, *J* = 7.0 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.1, 140.6, 140.5, 133.7, 130.4, 126.6, 121.3, 82.1, 81.1, 52.1, 44.8, 42.9, 30.1, 22.5, 18.5.



A 30 mL reaction tube equipped with a magnetic stir bar was charged with **3ac** (0.2 mmol) followed by CuI (10 mol%), BnN_3 (0.4 mmol) and DMF (1 mL). The reaction tube was sealed with a Teflon cap and the reaction mixture was stirred at 60 ℃ for 14 h, after which it was diluted with water (5 mL) and extracted by ethyl acetate (5 mL×3). The organic phase was combined and washed with aqueous HCl (1.0 N, 5 mL) and brine (5 mL). The reaction mixture was dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give the corresponding product **3ad** (80%, 60.4 mg).**^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.46 – 7.33 (m, 7H), 7.19 – 7.17 (m, 1H), 5.68 – 5.61 (m, 2H), 4.29 (q, *J* = 7.0 Hz, 1H), 3.62 (s, 3H), 2.49 (d, *J* = 7.0 Hz, 2H), 1.93 – 1.87 (m, 2H), 1.50 (d, *J* = 7.5 Hz, 3H), 0.94 (d, *J* = 6.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.6, 147.5, 140.6, 136.2, 134.8, 130.7, 129.7, 129.4, 129.2, 128.8, 128.2, 127.2, 122.4, 54.3, 52.0, 45.0, 41.1, 30.2, 22.5, 22.5, 19.1; **HRMS** (EI-TOF) calcd for $C_{24}H_{34}N_4OSi$ (M^+): 378.2182, found: 378.2163.

2.5. Gram-Scale Reaction



A mixture of **1a** (2 mmol), $Pd(OAc)_2$ (10 mol%), **2** alkynyl (2.4 mmol), N-Boc-phe-OH (20 mol%), AgOAc (2.4 mmol) and NBS (2.4mmol), DCE (5 mL) in a 35 mL sealed tube was conducted at rt for 16 h under air atmosphere. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel to give the corresponding product **3a** (72%).

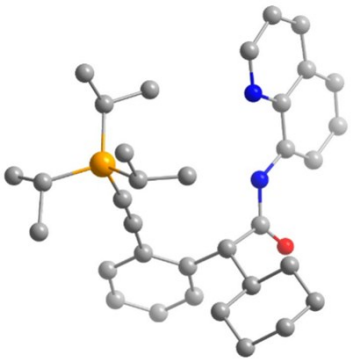
2.6 Crystal structure data

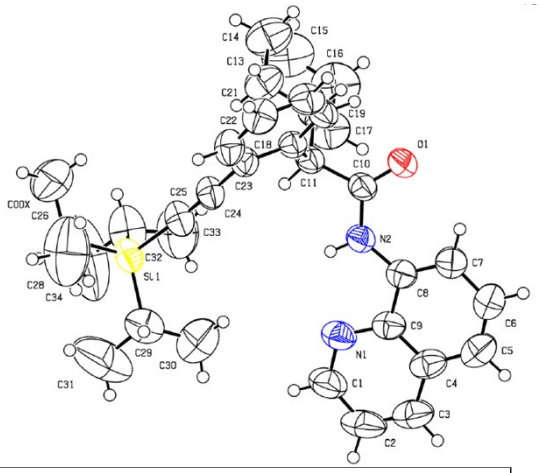
Single-crystal X-ray Diffraction

The diffraction data of crystals were collected on a Rigaku XtaLAB Synergy CCD diffractometer with graphite monochromated Cu-Ka radiation (λ = 1.54056 A˚) at 293 K. Absorption corrections were applied by SADABS[4]. All the structures were solved by direct methods and refined by full-matrix least-squares method on F^2 using SHELXTL-2014.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the ligand were generated geometrically.

X-ray data for 3n

3n

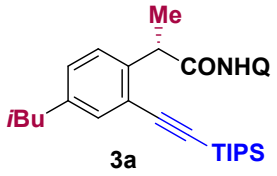




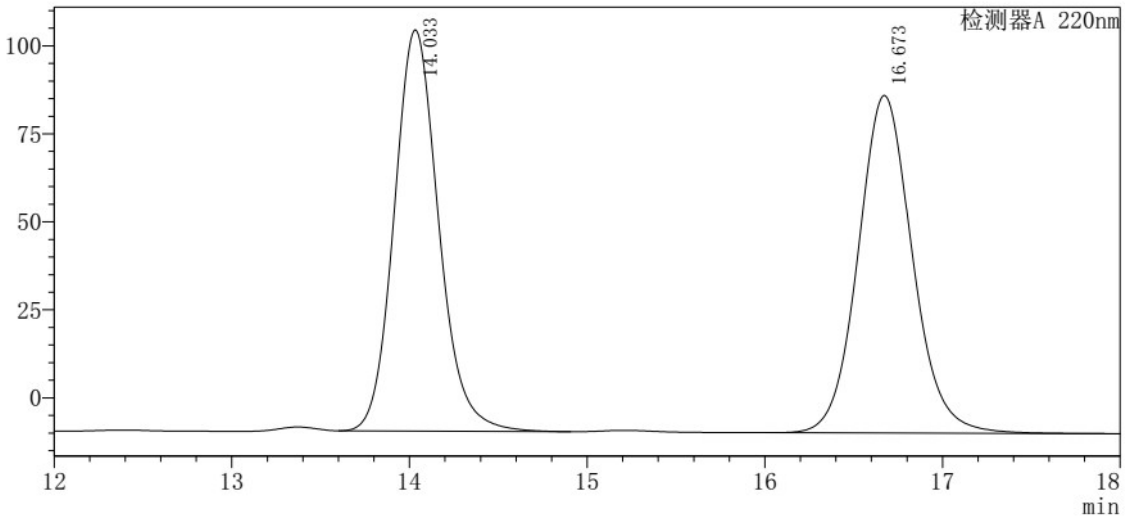
Identification code	1-64-5
Empirical formula	$C_{34}H_{44}N_2OSi$
Formula weight	524.8
Temperature/K	293
Crystal system	triclinic
Space group	P-1
a/Å	8.8134(2)
b/Å	10.3559(3)
c/Å	18.0350(4)
α/°	100.993(2)
β/°	95.022(2)
γ/°	92.933(2)
Volume/Å^3	1605.78(7)
Z	2
ρ_{calc}g/cm^3	1.085
μ/mm^{-1}	0.835
F(000)	568
Crystal size/mm^3	0.3 × 0.3 × 0.1
2Θ range for data collection/°	5.016 to 153.632
Index ranges	$-11 \le h \le 9$, $-13 \le k \le 13$, $-21 \le l \le 22$
Reflections collected	17410
Independent reflections	6387 [R_{int} = 0.0392, R_{sigma} = 0.0437]
Data/restraints/parameters	6387/3/349
Goodness-of-fit on F^2	1.199
Final R indexes [I>=2σ (I)]	R_1 = 0.0837, wR_2 = 0.2634
Final R indexes [all data]	R_1 = 0.0943, wR_2 = 0.2881
Largest diff. peak/hole / e Å^{-3}	1.15/-0.40

2.7. Chirality retention experiment

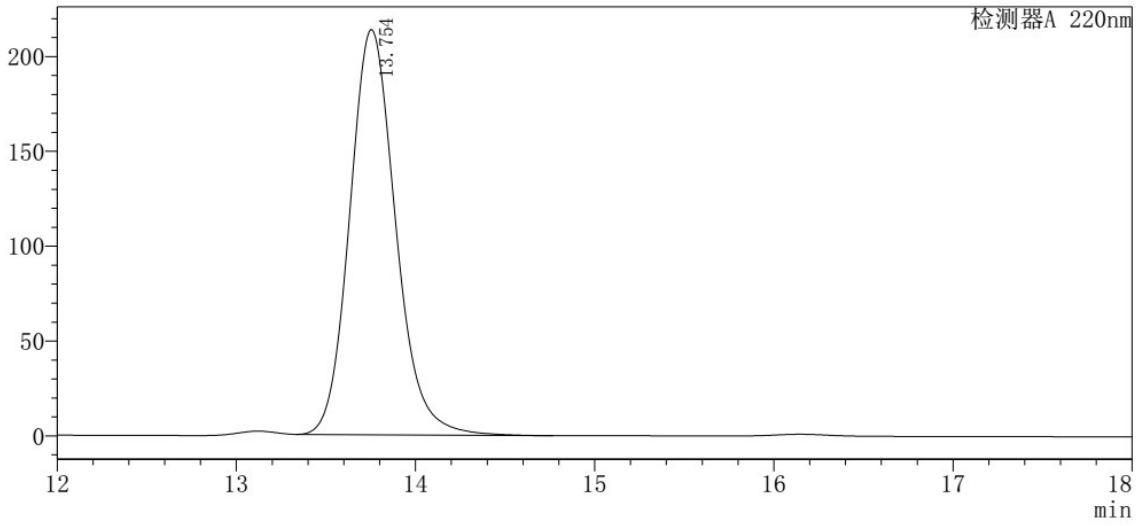
Enantiomeric excess of final product was determined by HPLC with chiralcel AD-H column. eluent: Hex/iPrOH= 99/1, rate= 0.6 mL/min, λ = 220 nm



3a



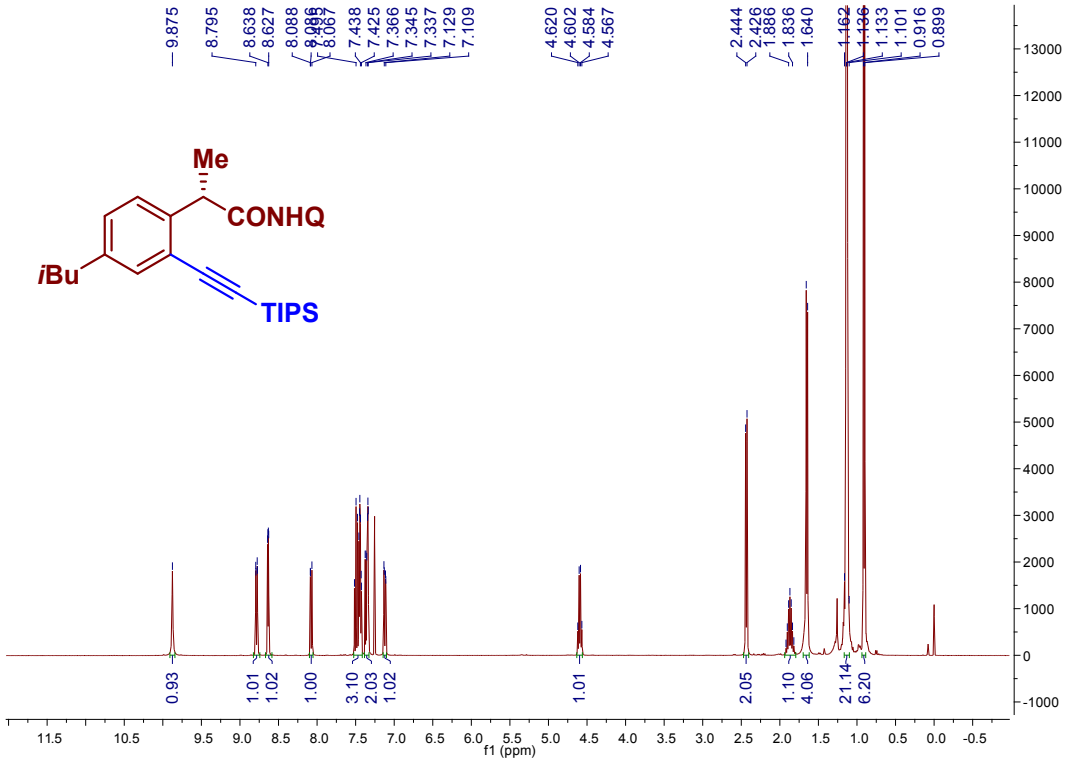
#	time	Area	Height	Area %
1	14.033	1988415	114040	49.434
2	16.673	2033923	95909	50.566

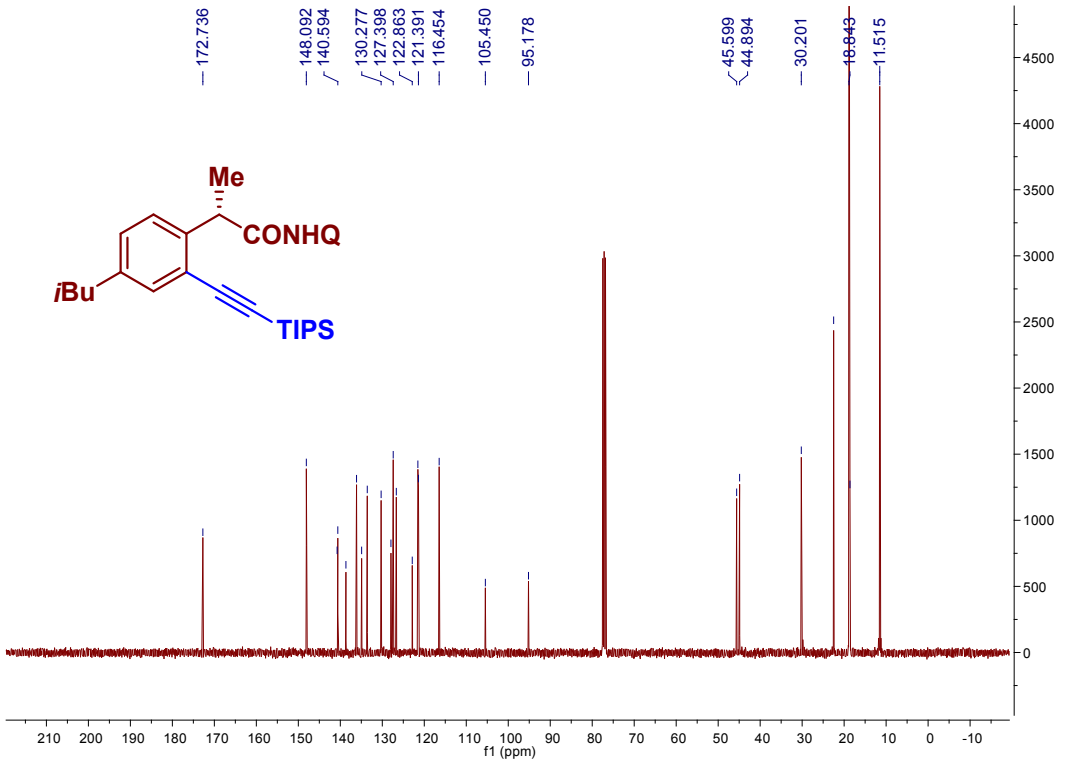


#	time	Area	Height	Area %
1	13.754	3809813	213618	100
2	16.952	0	0	0

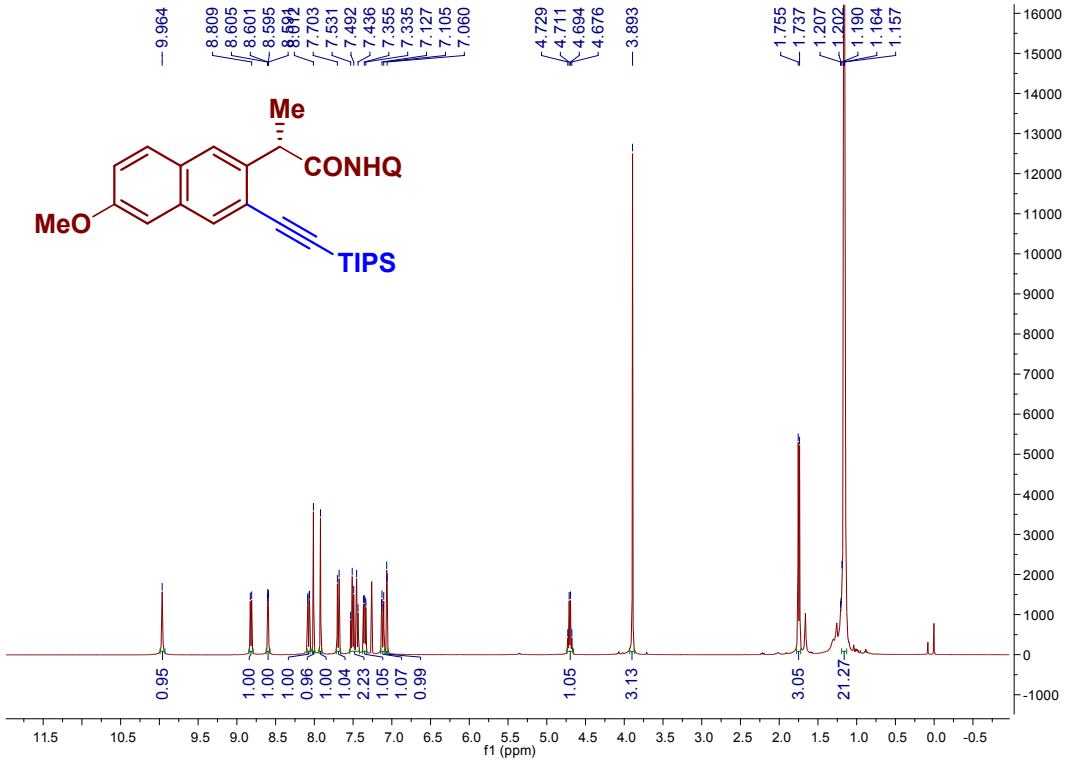
4. NMR Spectra

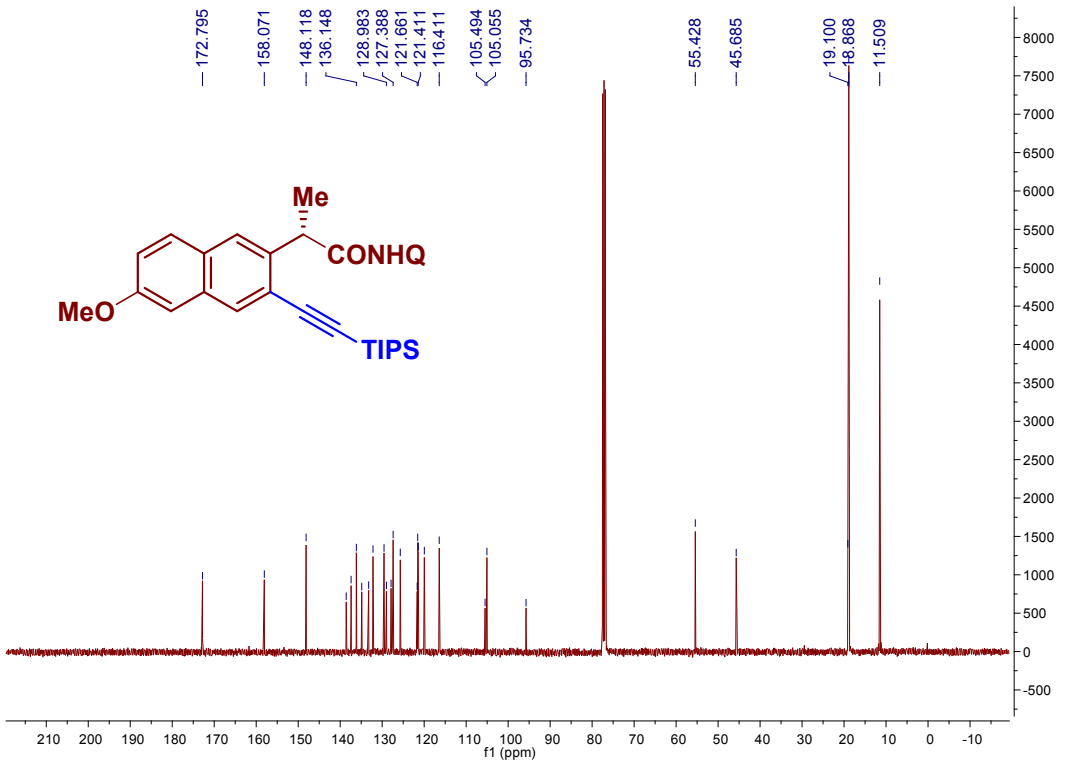
3a



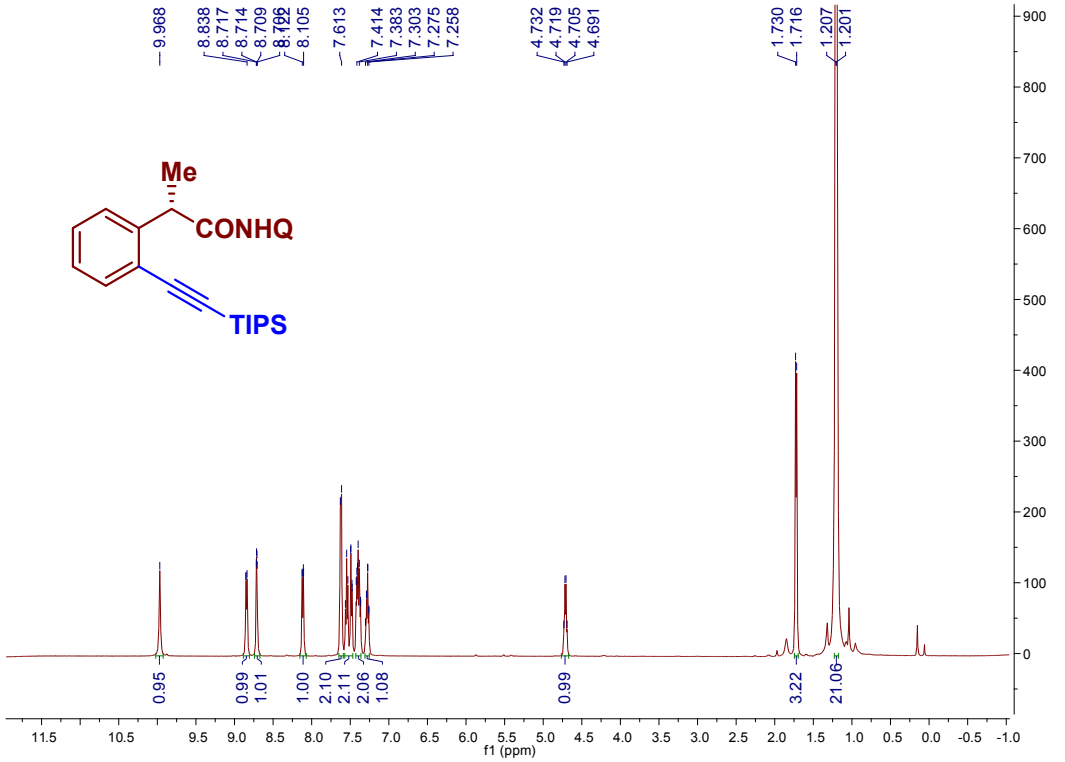


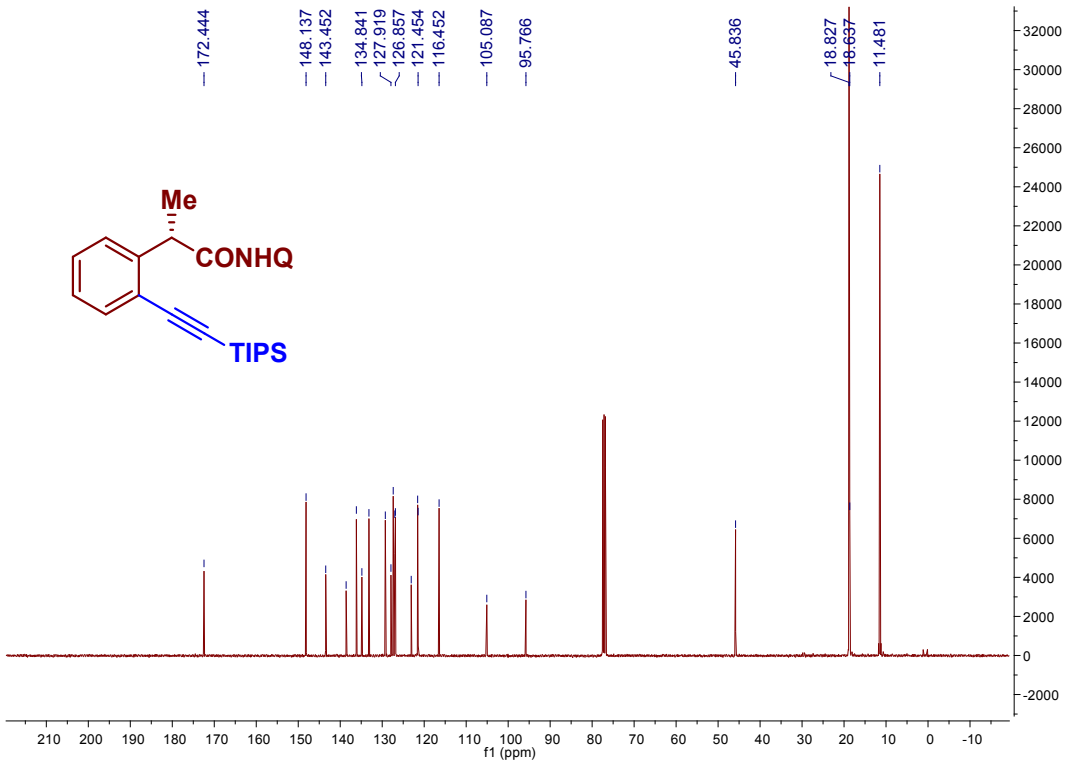
3b


9.964
8.809
8.605
8.601
8.595
7.703
7.531
7.492
7.436
7.355
7.335
7.127
7.105
7.060
4.729
4.711
4.694
4.676
3.893
1.755
1.737
1.207
1.202
1.190
1.164
1.157
Me
CONHQ
MeO
TIPS
0.95
1.00
1.00
1.00
0.96
1.00
1.04
2.23
1.05
1.07
0.99
1.05
3.13
3.05
21.27
f1 (ppm)

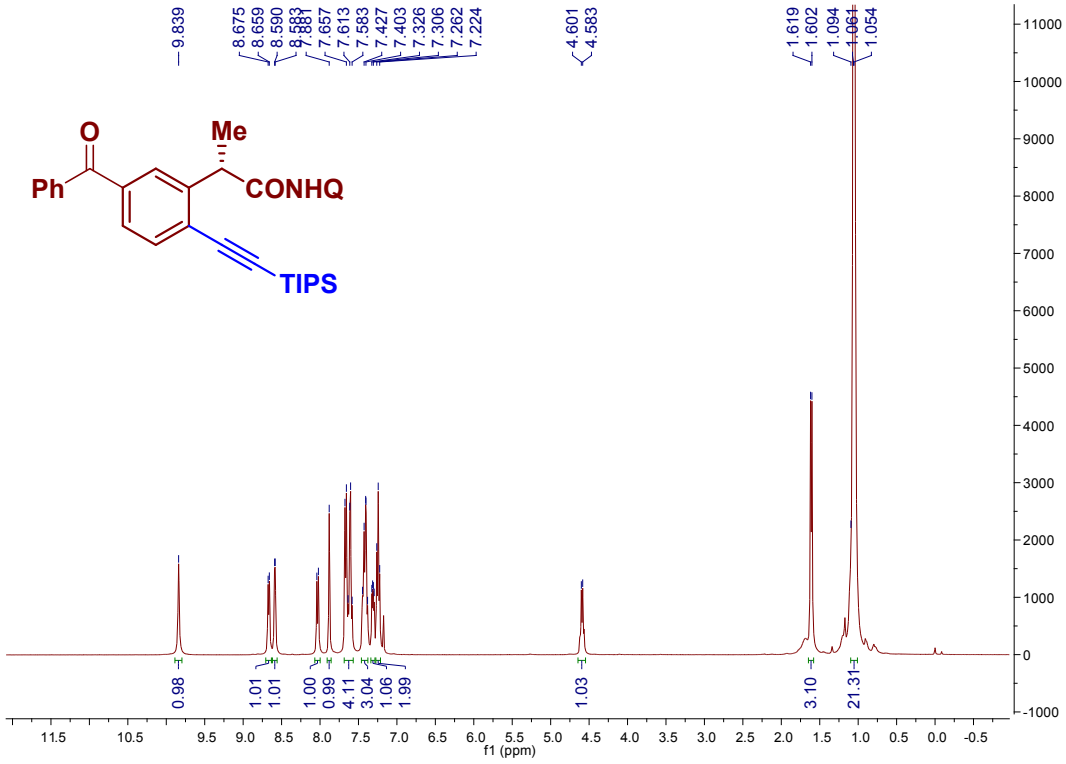

172.795
158.071
148.118
136.148
128.983
127.388
121.661
121.411
116.411
105.494
105.055
95.734
55.428
45.685
19.100
18.868
11.509
Me
CONHQ
MeO
TIPS
f1 (ppm)

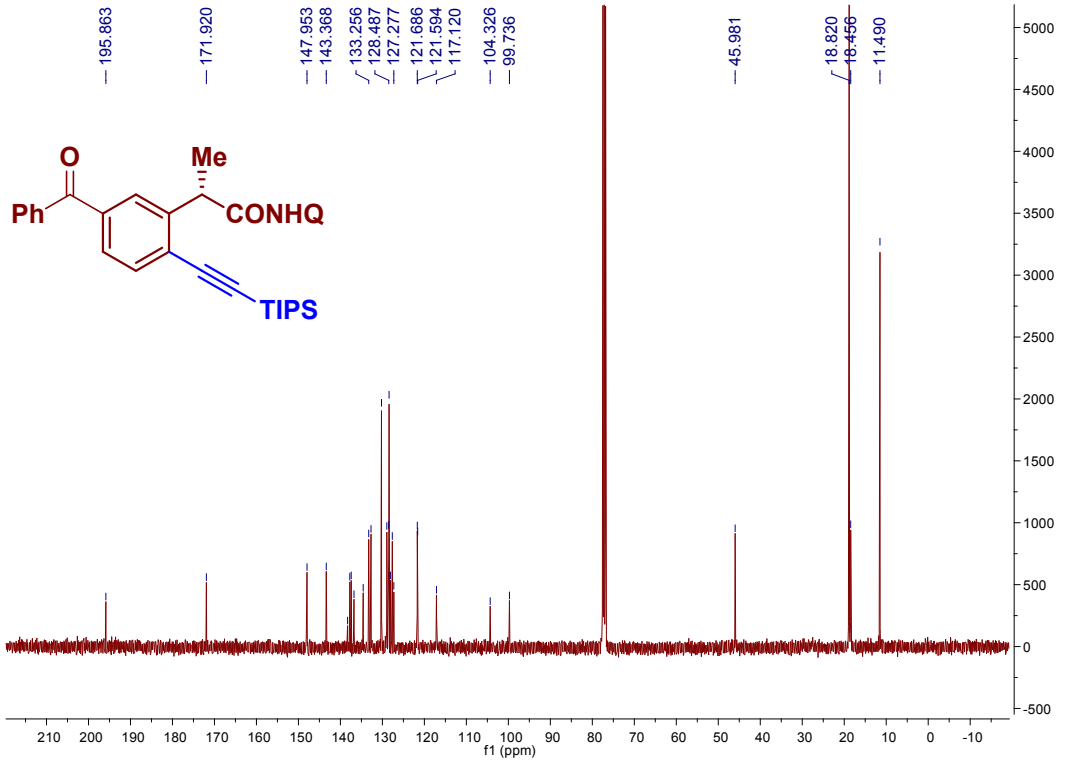
3c


9.968
8.838
8.717
8.714
8.709
8.105
7.613
7.414
7.383
7.303
7.275
7.258
4.732
4.719
4.705
4.691
1.730
1.716
1.207
1.201
Me
CONHQ
TIPS
0.95
0.99
1.01
1.00
2.10
2.11
2.06
1.08
0.99
3.22
21.06
f1 (ppm)

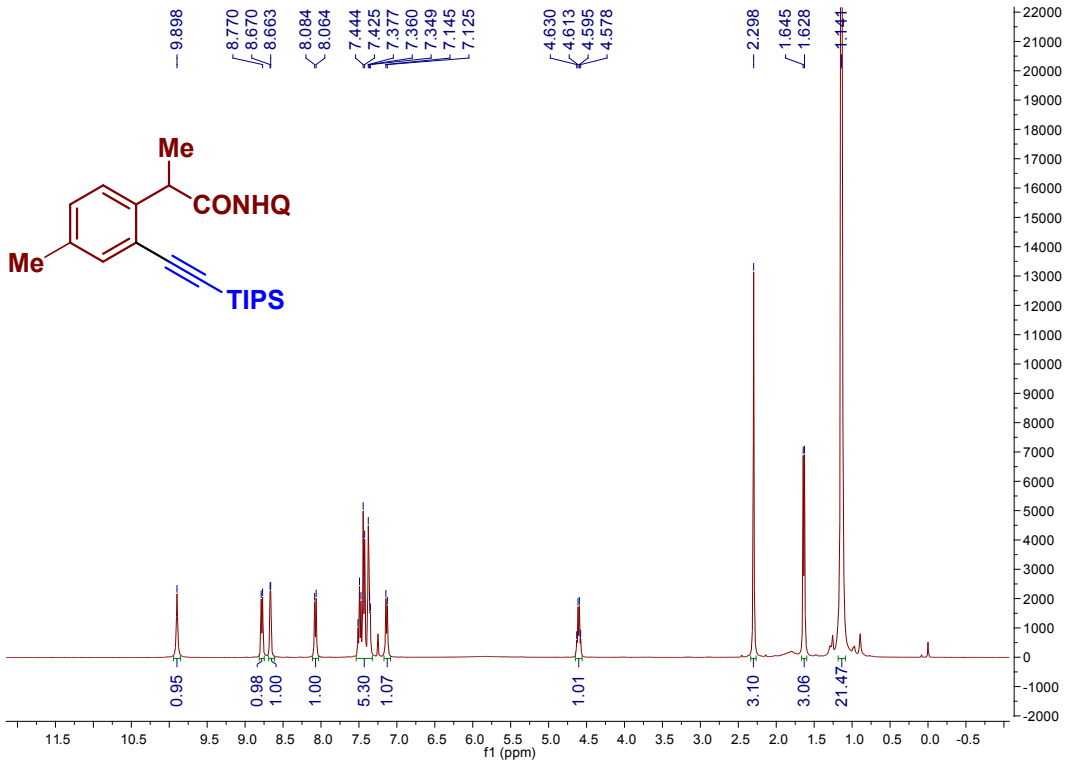

172.444
148.137
143.452
134.841
127.919
126.857
121.454
116.452
105.087
95.766
45.836
18.827
18.637
11.481
Me
CONHQ
TIPS
f1 (ppm)

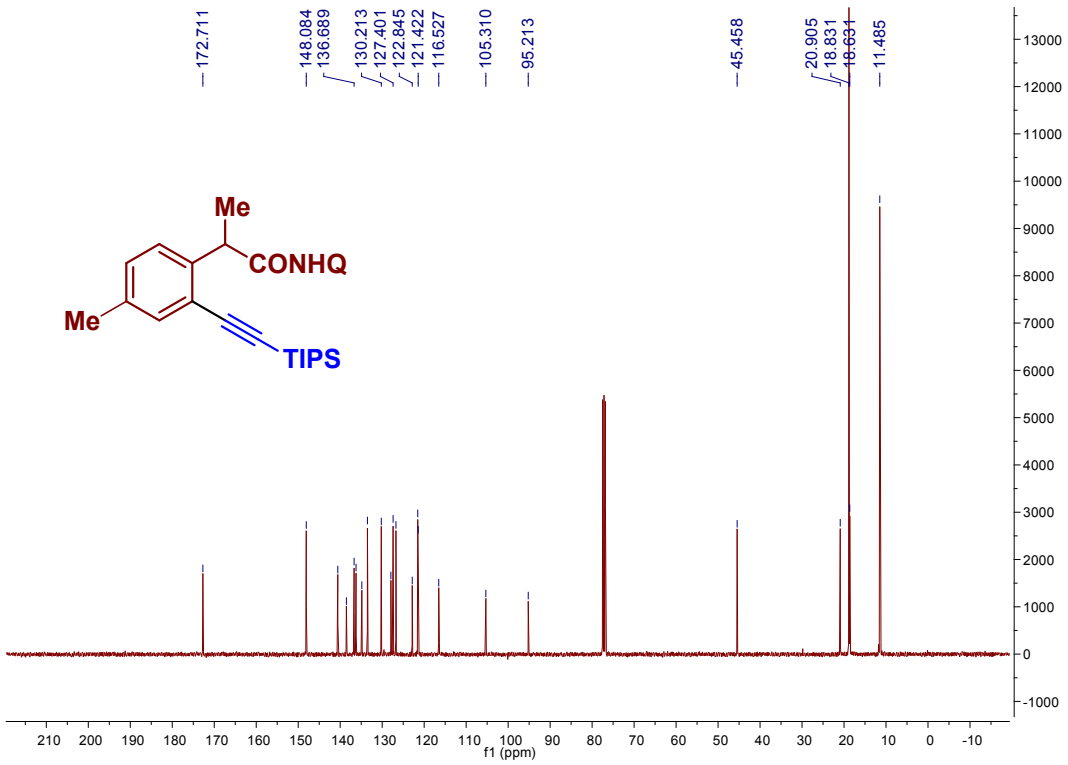
3d


9.839
8.675
8.659
8.590
8.583
8.581
7.657
7.613
7.583
7.427
7.403
7.326
7.306
7.262
7.224
4.601
4.583
1.619
1.602
1.094
1.061
1.054
O
Me
Ph
CONHQ
TIPS
0.98
1.01
1.01
1.00
0.99
4.11
3.04
1.06
1.99
1.03
3.10
21.31
f1 (ppm)

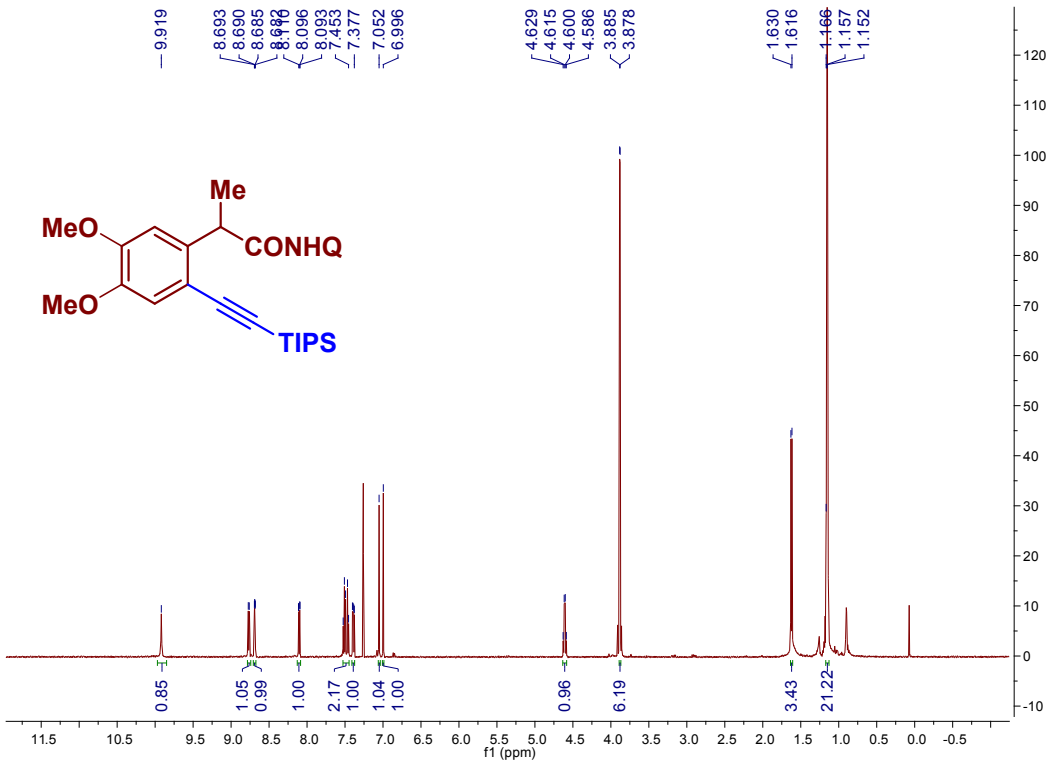

195.863
171.920
147.953
143.368
133.256
128.487
127.277
121.686
121.594
117.120
104.326
99.736
45.981
18.820
18.456
11.490
O
Me
Ph
CONHQ
TIPS
f1 (ppm)

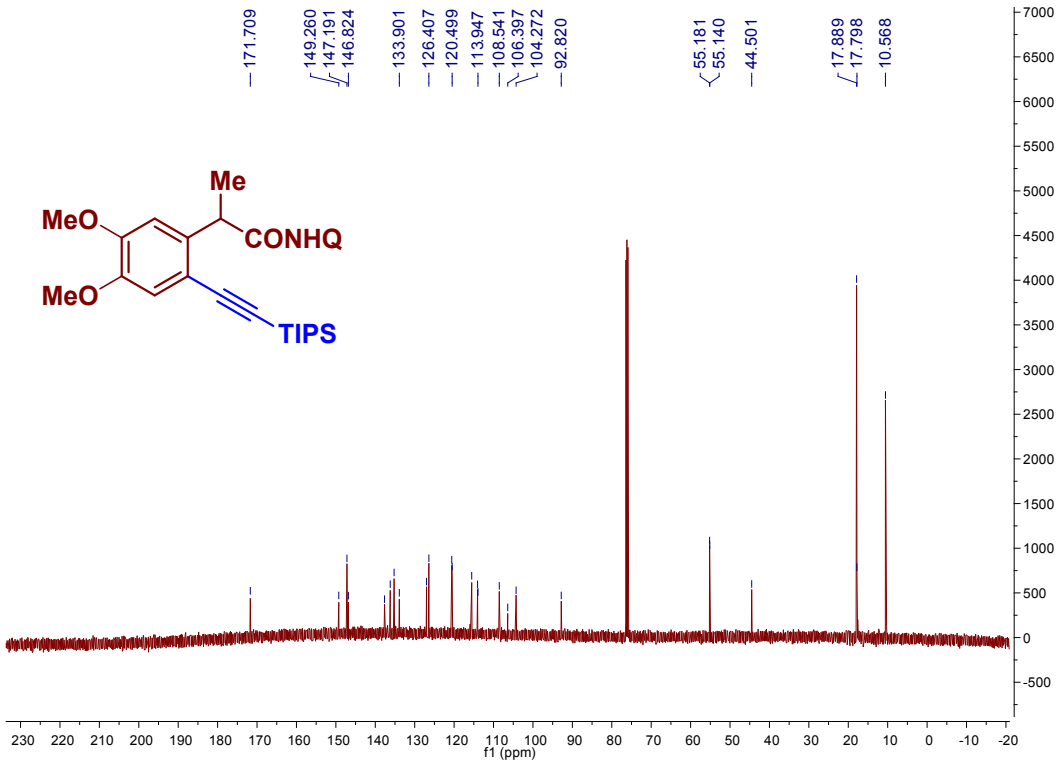
3e


9.898
8.770
8.670
8.663
8.084
8.064
7.444
7.425
7.377
7.360
7.349
7.145
7.125
4.630
4.613
4.595
4.578
2.298
1.645
1.628
1.441
Me
CONHQ
Me
TIPS
0.95
0.98
1.00
1.00
5.30
1.07
1.01
3.10
3.06
21.47
f1 (ppm)

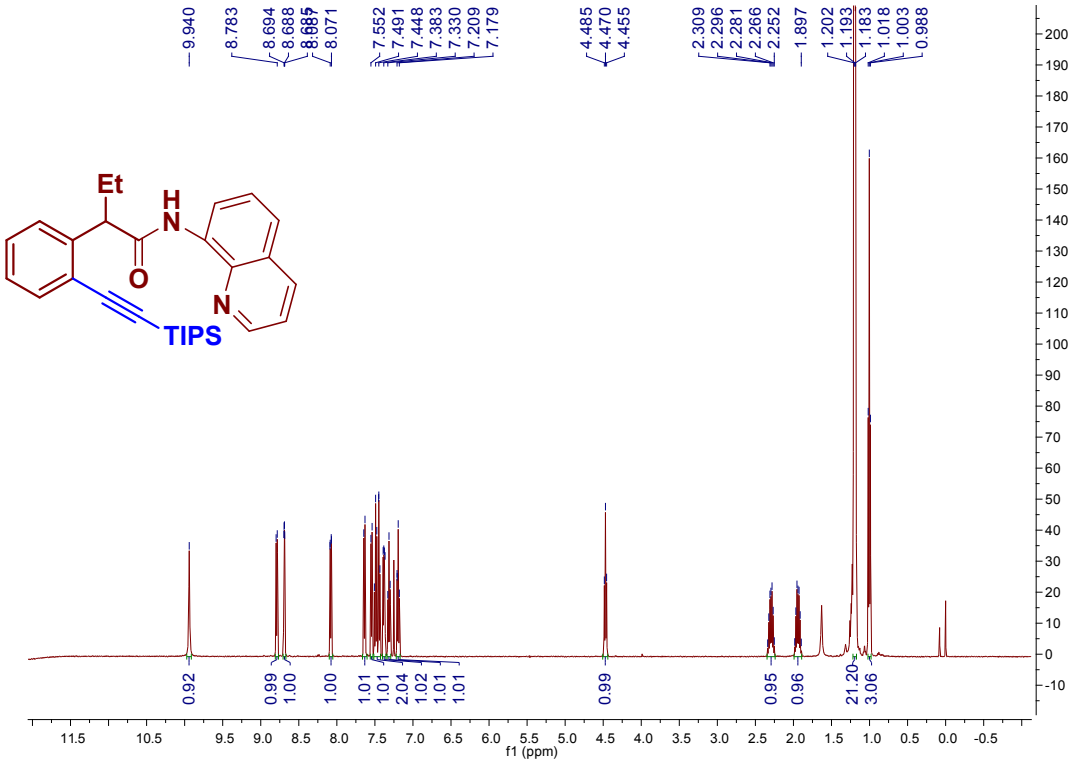

172.711
148.084
136.689
130.213
127.401
122.845
121.422
116.527
105.310
95.213
45.458
20.905
18.831
18.631
11.485
Me
CONHQ
Me
TIPS
f1 (ppm)

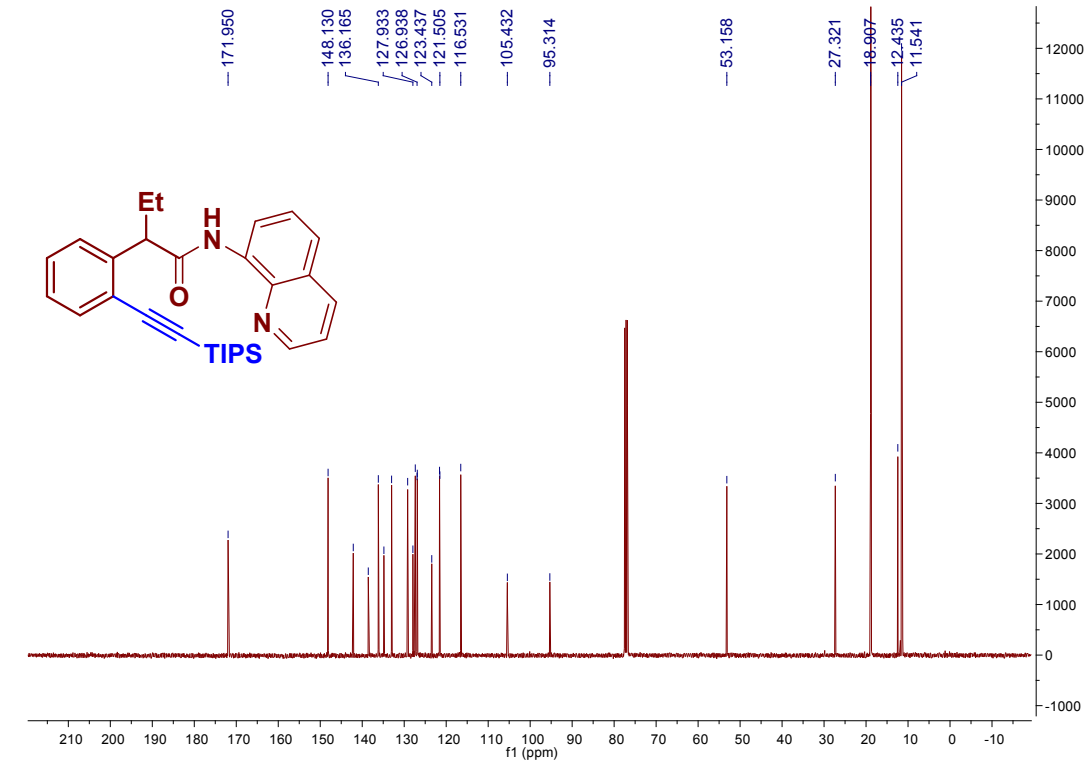
3f


9.919
8.693
8.690
8.685
8.096
8.093
7.453
7.377
7.052
6.996
4.629
4.615
4.600
4.586
3.885
3.878
1.630
1.616
1.166
1.157
1.152
Me
MeO
CONHQ
MeO
TIPS
0.85
1.05
0.99
1.00
2.17
1.00
1.04
1.00
0.96
6.19
3.43
21.22
f1 (ppm)

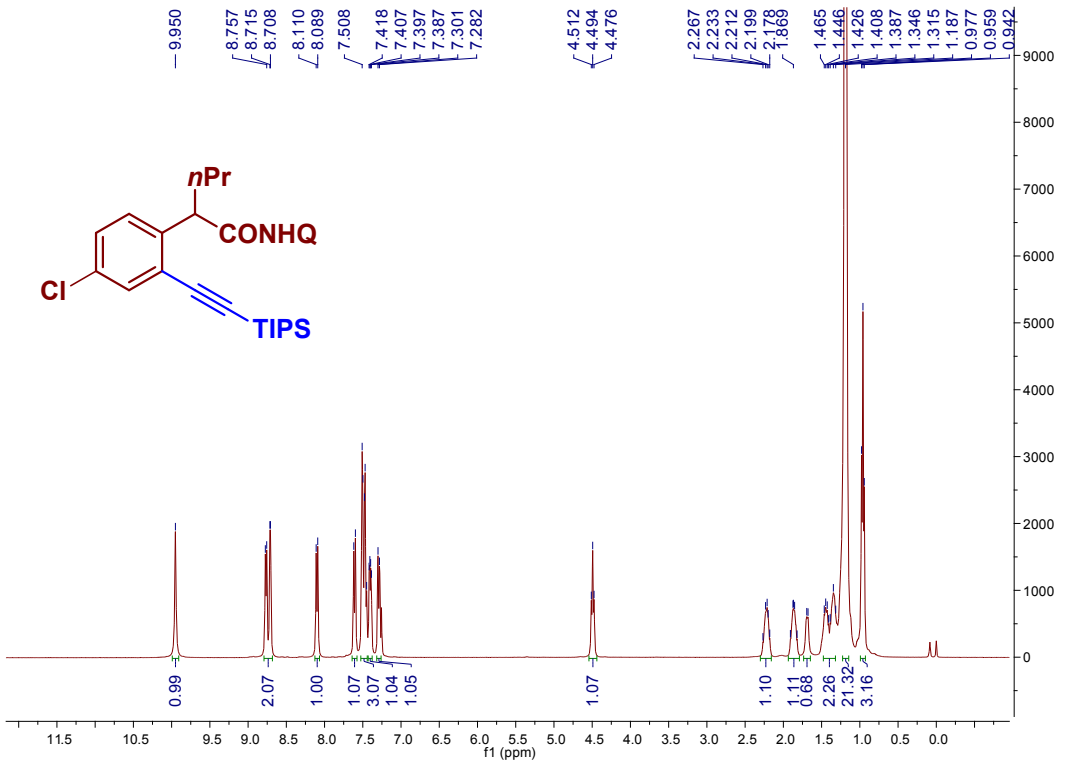

171.709
149.260
147.191
146.824
133.901
126.407
120.499
113.947
108.541
106.397
104.272
92.820
55.181
55.140
44.501
17.889
17.798
10.568
Me
MeO
CONHQ
MeO
TIPS
f1 (ppm)

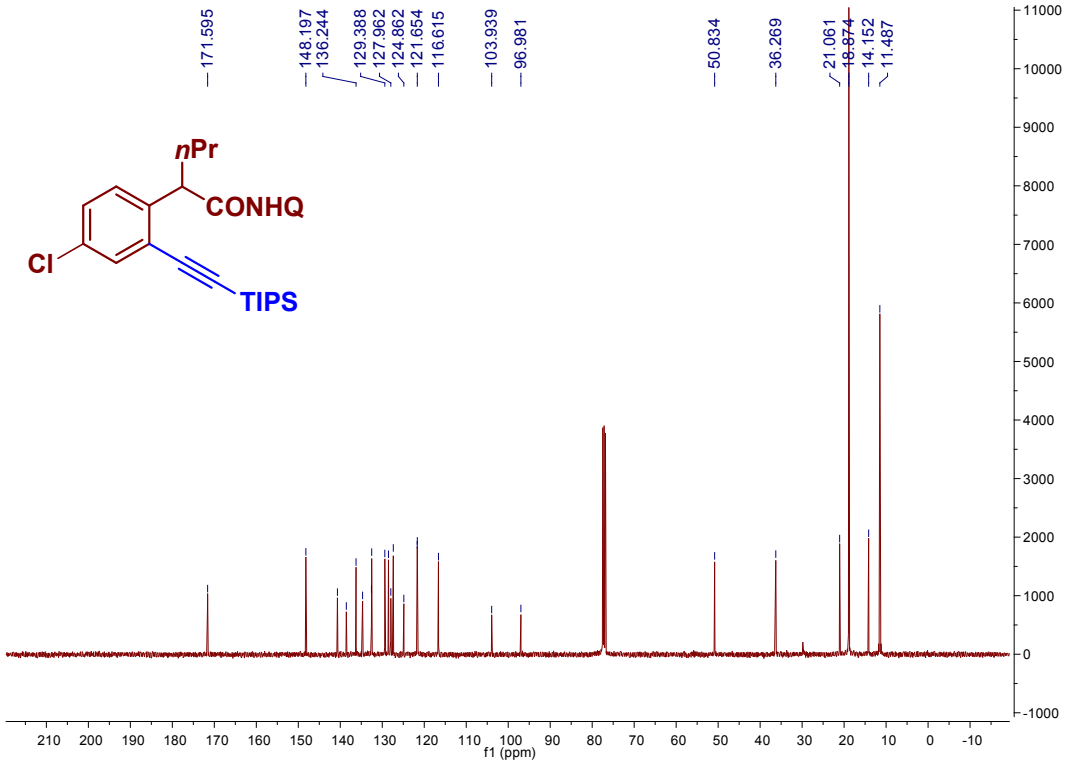
3g


9.940
8.783
8.694
8.688
8.071
7.552
7.491
7.448
7.383
7.330
7.209
7.179
4.485
4.470
4.455
2.309
2.296
2.281
2.266
2.252
1.897
1.202
1.193
1.183
1.018
1.003
0.988
Et
H
N
O
N
TIPS
0.92
0.99
1.00
1.00
1.01
1.01
2.04
1.02
1.01
1.01
0.99
0.95
0.96
21.20
3.06
f1 (ppm)

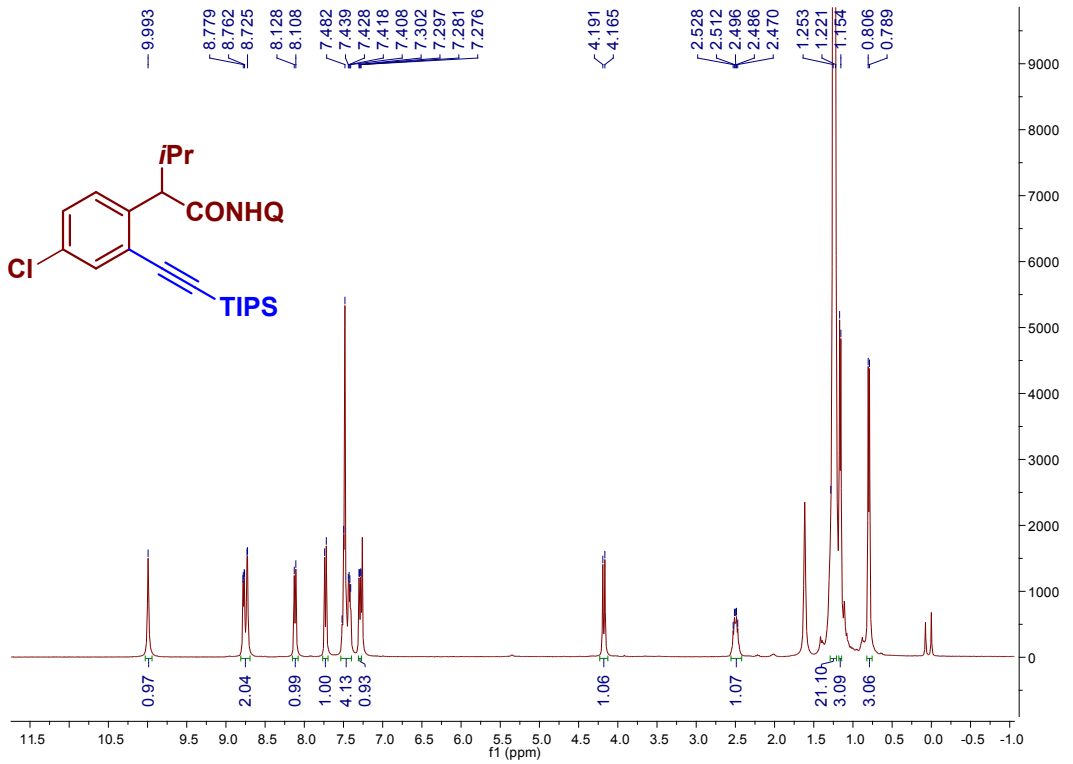

171.950
148.130
136.165
127.933
126.938
123.437
121.505
116.531
105.432
95.314
53.158
27.321
18.907
12.435
11.541
Et
H
N
O
N
TIPS
f1 (ppm)

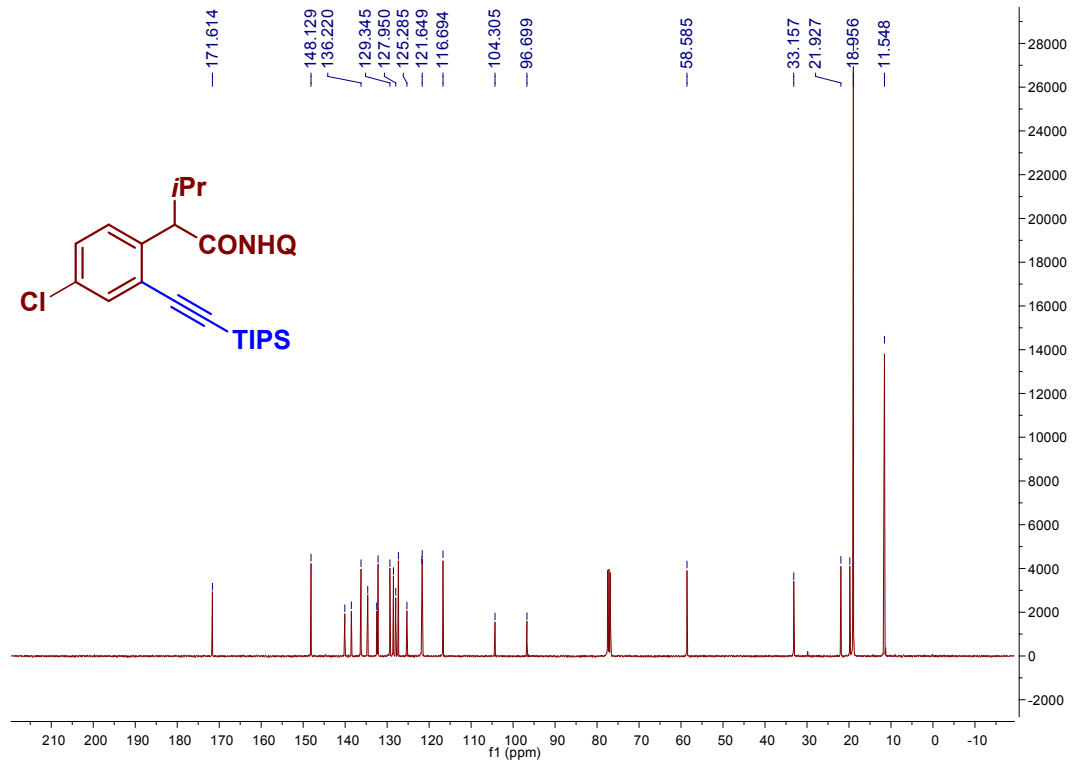
3h


9.950
8.757
8.715
8.708
8.110
8.089
7.508
7.418
7.407
7.397
7.387
7.301
7.282
4.512
4.494
4.476
2.267
2.233
2.212
2.199
2.178
1.869
1.465
1.446
1.426
1.408
1.387
1.346
1.315
1.187
0.977
0.959
0.942
nPr
CONHQ
Cl
TIPS
0.99
2.07
1.00
1.07
3.07
1.04
1.05
1.07
1.10
1.11
0.88
2.26
21.32
3.16
f1 (ppm)

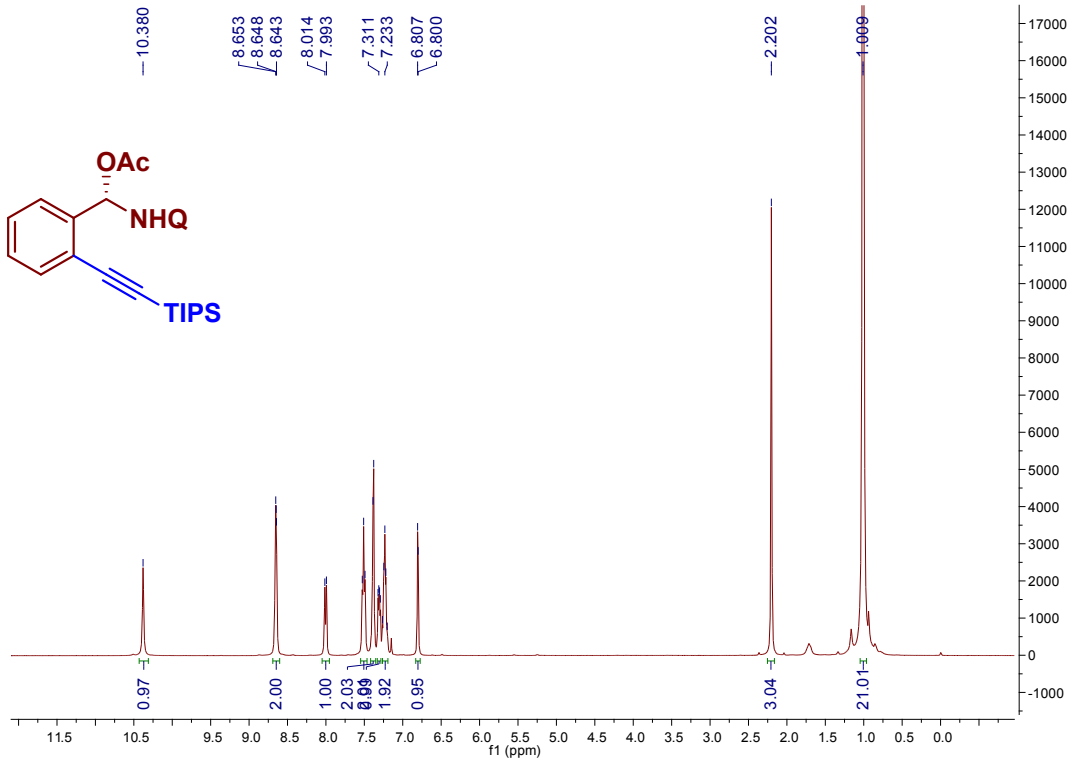

171.595
148.197
136.244
129.388
127.962
124.862
121.654
116.615
103.939
96.981
50.834
36.269
21.061
18.874
14.152
11.487
nPr
CONHQ
Cl
TIPS
f1 (ppm)

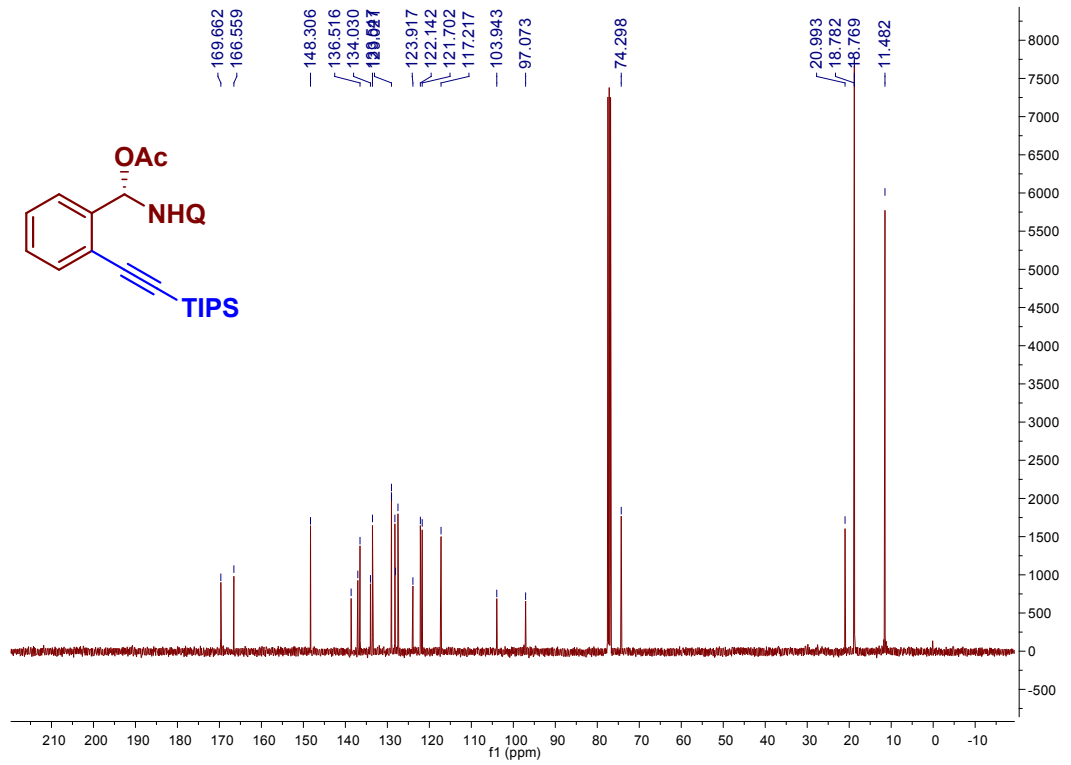
3i


9.993
8.779
8.762
8.725
8.128
8.108
7.482
7.439
7.428
7.418
7.408
7.302
7.297
7.281
7.276
4.191
4.165
2.528
2.512
2.496
2.486
2.470
1.253
1.221
1.154
0.806
0.789
iPr
CONHQ
Cl
TIPS
0.97
2.04
0.99
1.00
4.13
0.93
1.06
1.07
21.10
3.09
3.06
f1 (ppm)

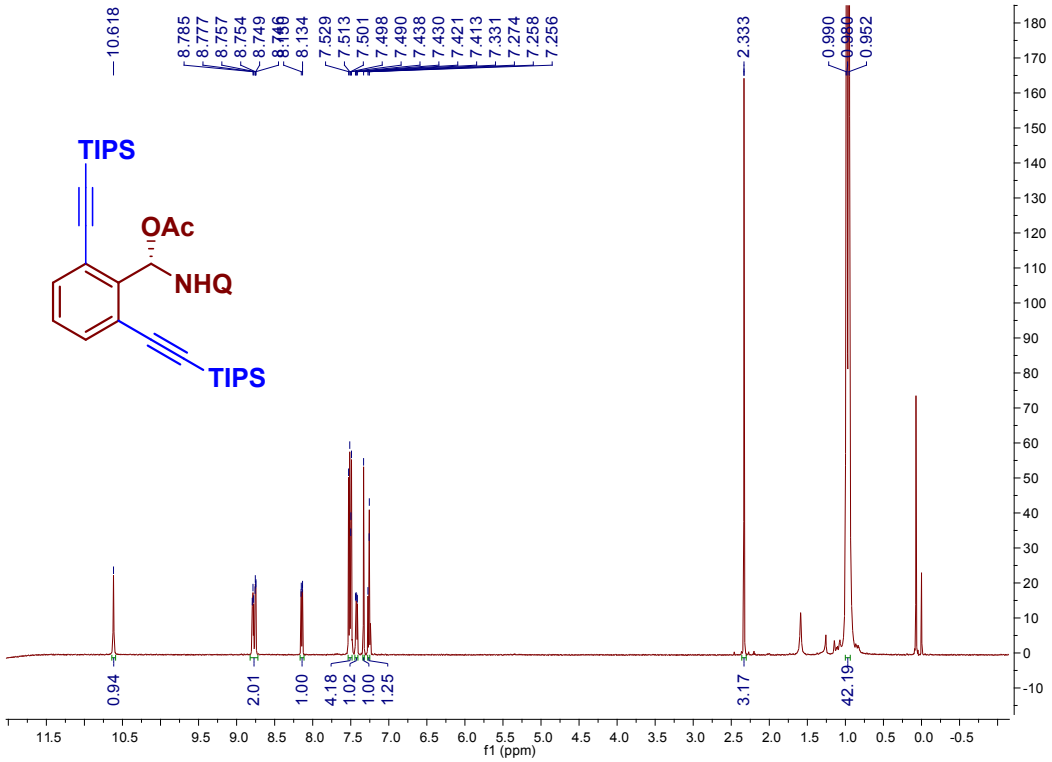

171.614
148.129
136.220
129.345
127.950
125.285
121.649
116.694
104.305
96.699
58.585
33.157
21.927
18.956
11.548
iPr
CONHQ
Cl
TIPS
f1 (ppm)

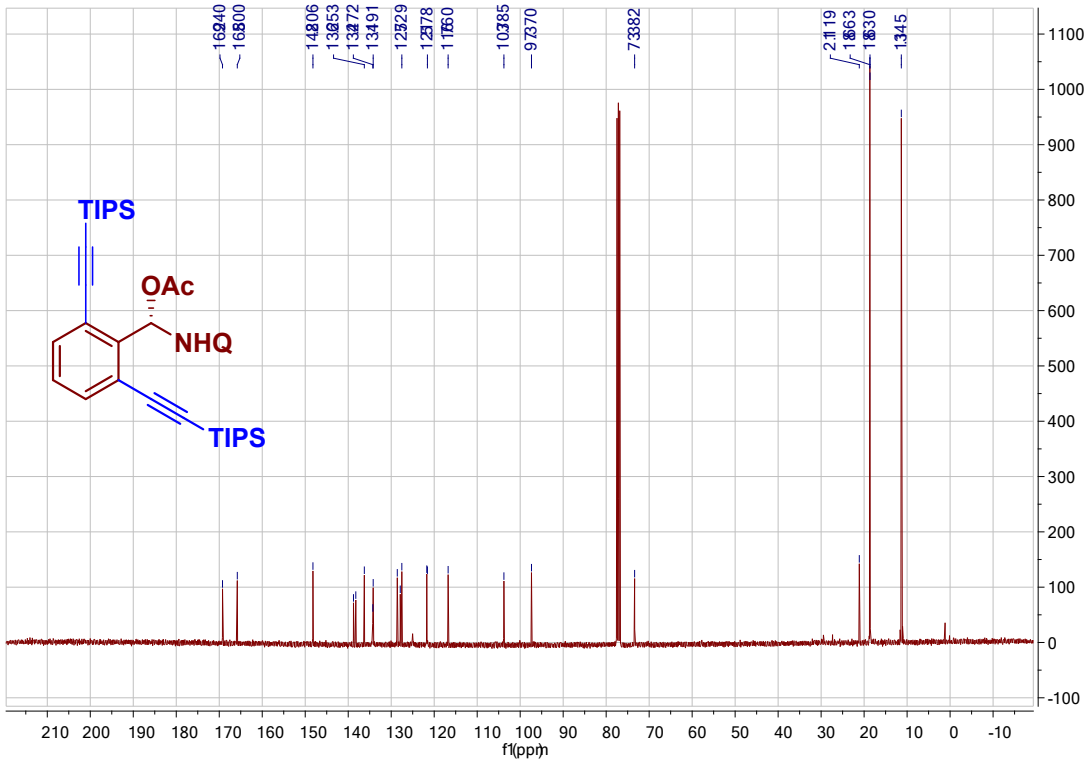
3j


10.380
8.653
8.648
8.643
8.014
7.993
7.311
7.233
6.807
6.800
2.202
1.000
OAc
NHQ
TIPS
0.97
2.00
1.00
2.03
1.92
0.95
3.04
21.01
f1 (ppm)

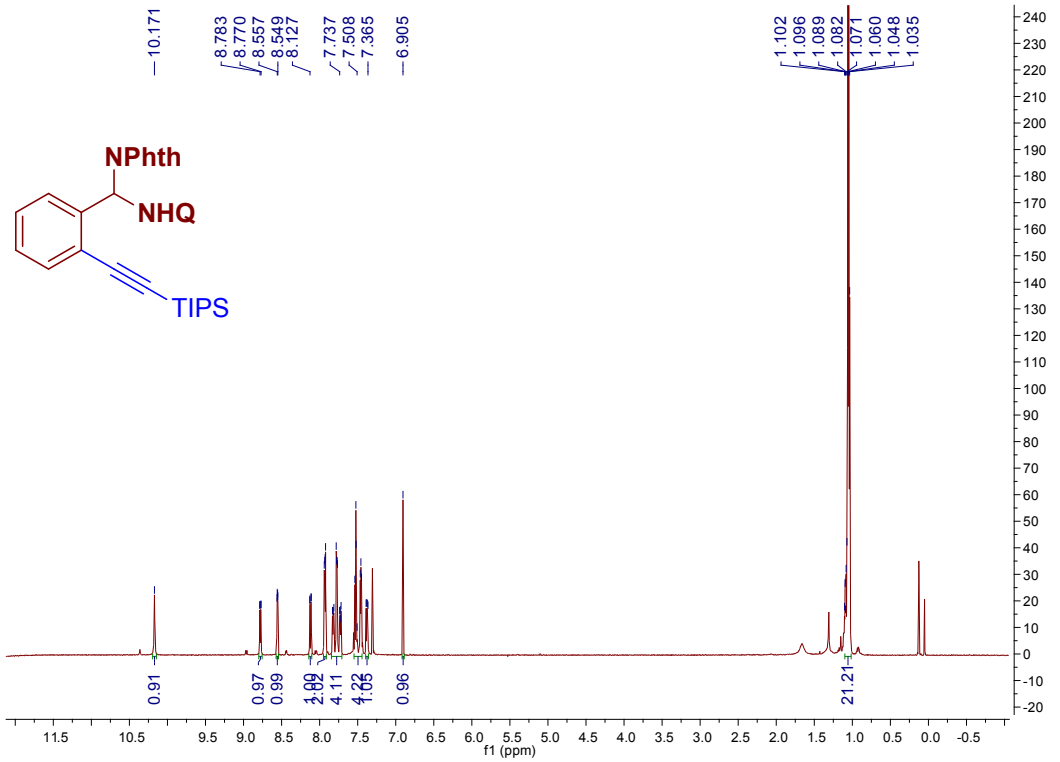

169.662
166.559
148.306
136.516
134.030
123.917
122.142
121.702
117.217
103.943
97.073
74.298
20.993
18.782
18.769
11.482
OAc
NHQ
TIPS
f1 (ppm)

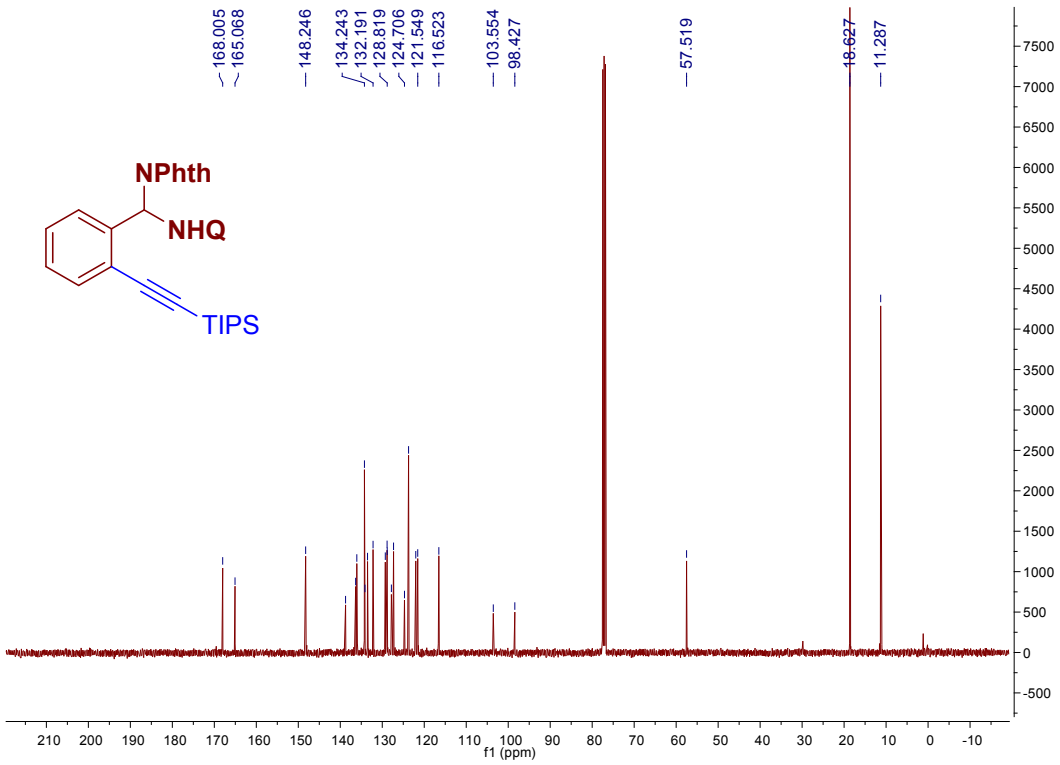
3j,



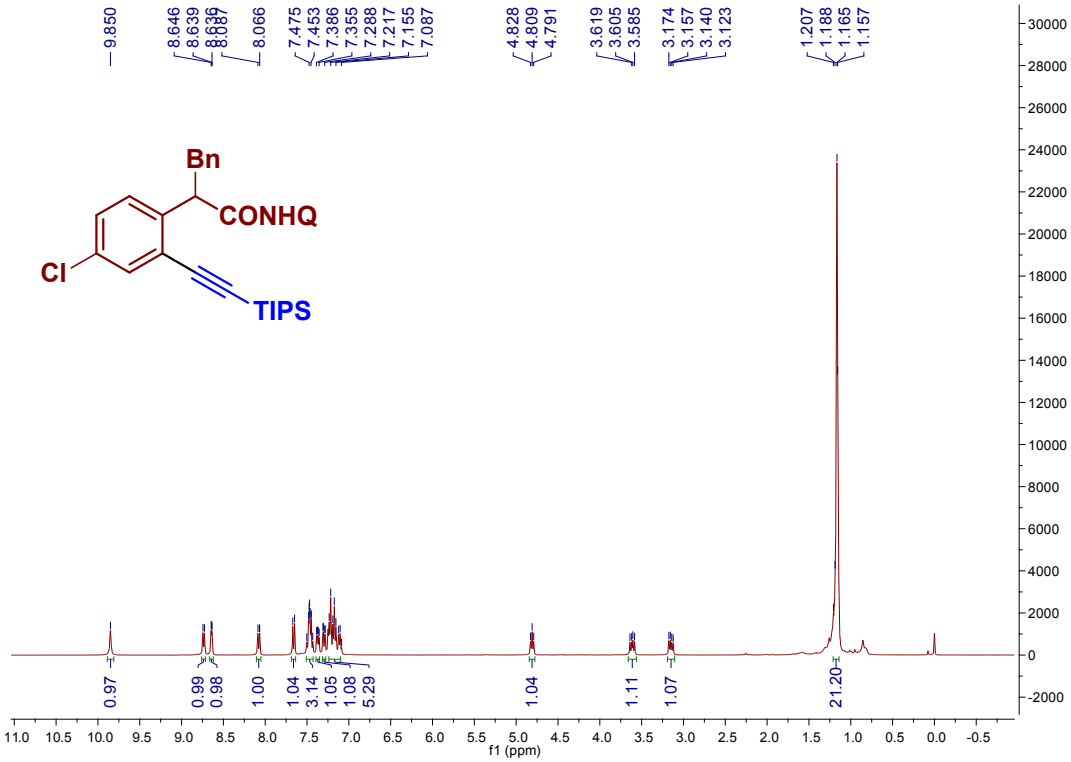


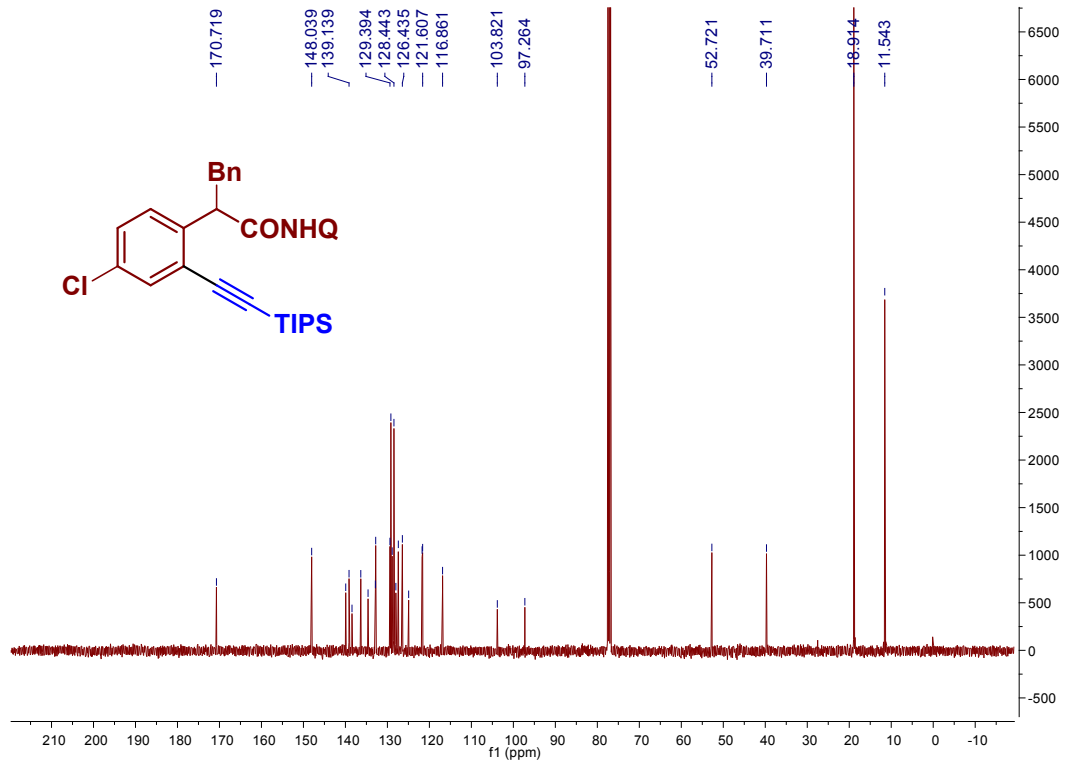
3k


10.171
8.783
8.770
8.557
8.549
8.127
7.737
7.508
7.365
6.905
1.102
1.096
1.089
1.082
1.071
1.060
1.048
1.035
NPhth
NHQ
TIPS
0.91
0.97
0.99
4.11
0.96
21.21
f1 (ppm)

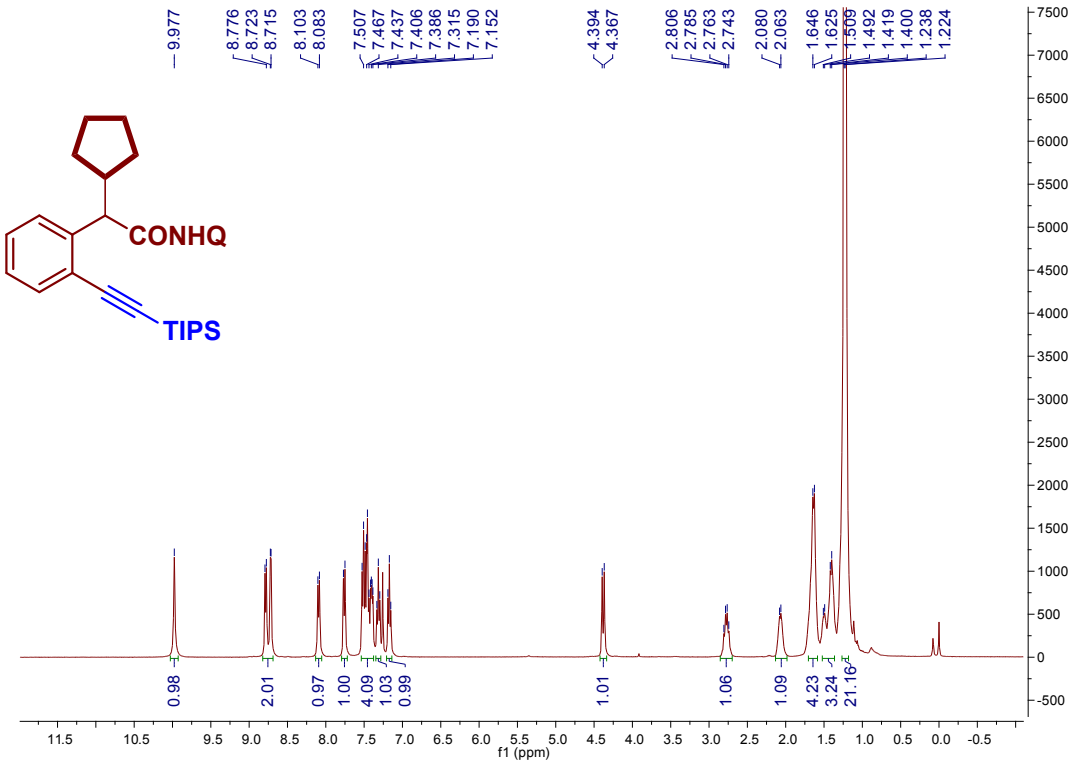

168.005
165.068
148.246
134.243
132.191
128.819
124.706
121.549
116.523
103.554
98.427
57.519
18.627
11.287
NPhth
NHQ
TIPS
f1 (ppm)

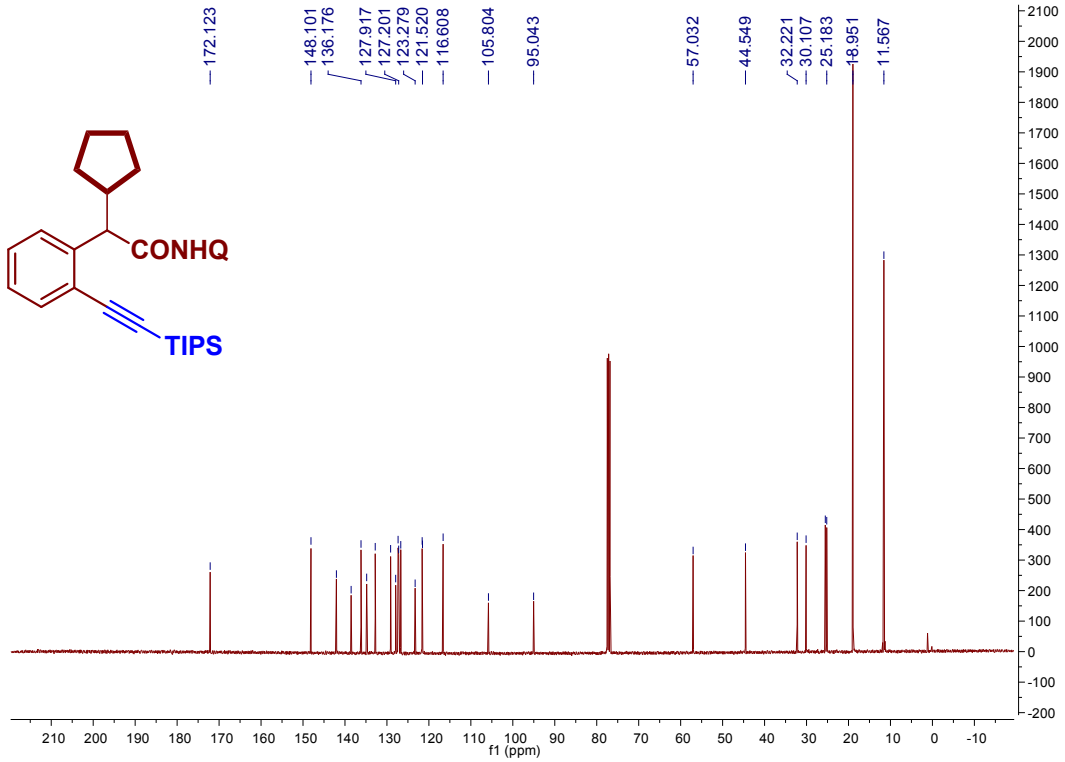
3l


9.850
8.646
8.639
8.087
8.066
7.475
7.453
7.386
7.355
7.288
7.217
7.155
7.087
4.828
4.809
4.791
3.619
3.605
3.585
3.174
3.157
3.140
3.123
1.207
1.188
1.165
1.157
Bn
CONHQ
Cl
TIPS
0.97
0.99
0.98
1.00
1.04
3.14
1.05
1.08
5.29
1.04
1.11
1.07
21.20
f1 (ppm)

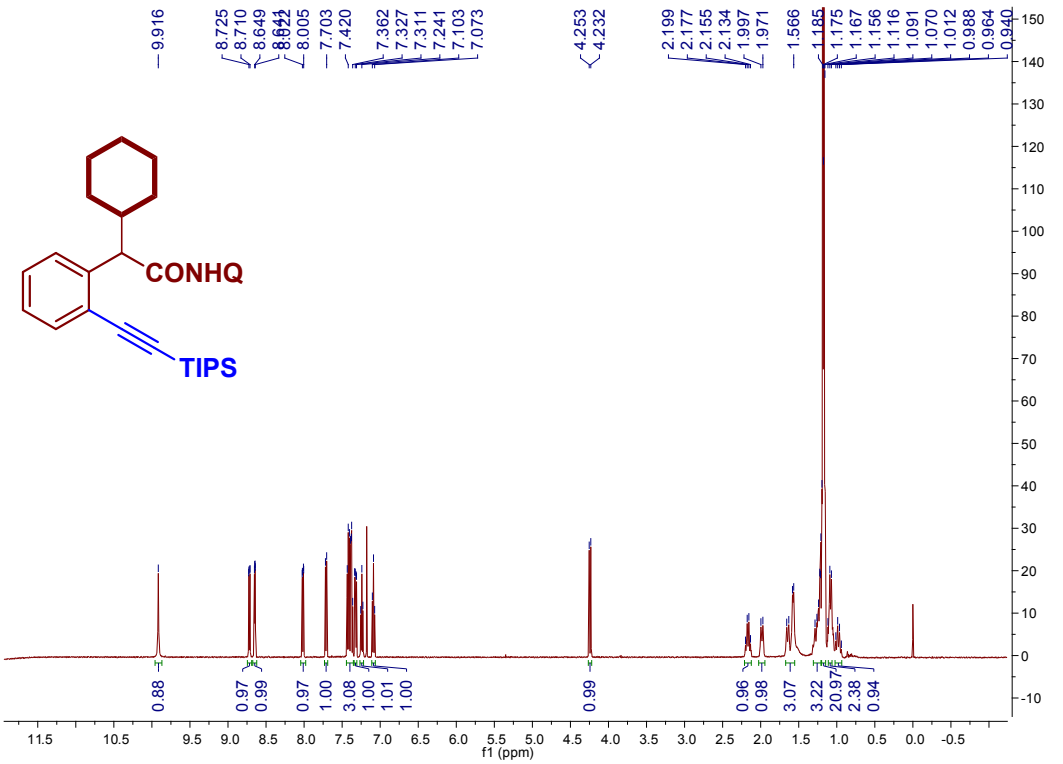

170.719
148.039
139.139
129.394
128.443
126.435
121.607
116.861
103.821
97.264
52.721
39.711
18.914
11.543
Bn
CONHQ
Cl
TIPS
f1 (ppm)

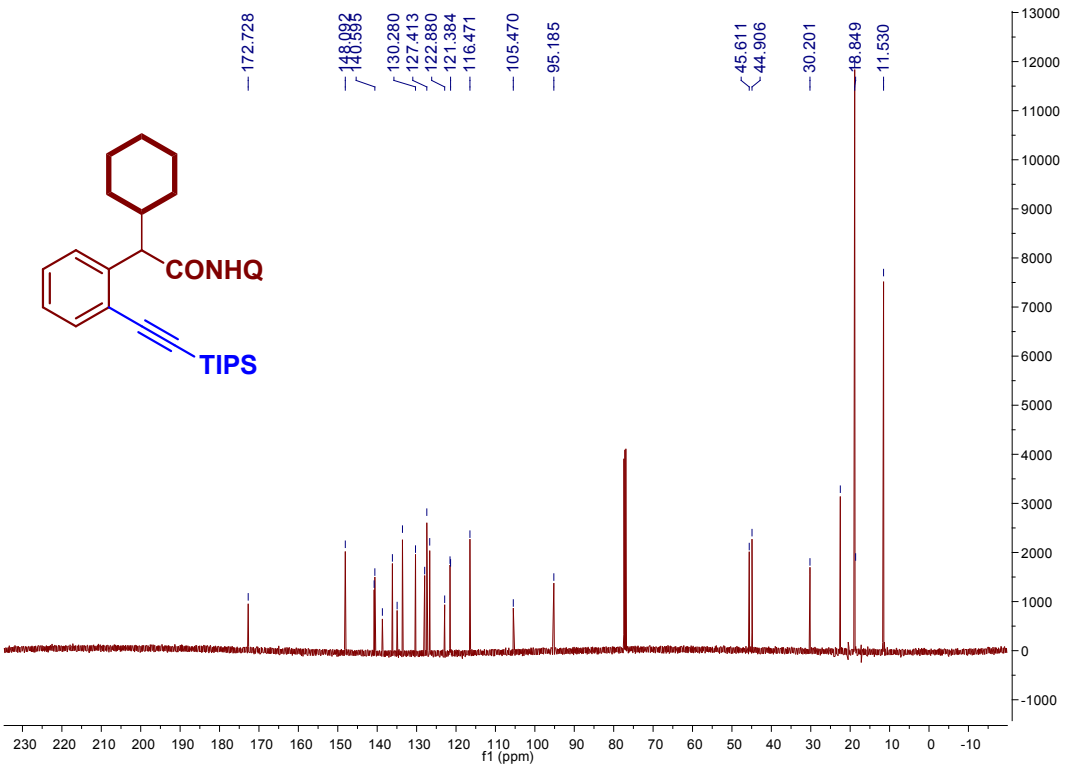
3m


9.977
8.776
8.723
8.715
8.103
8.083
7.507
7.467
7.437
7.406
7.386
7.315
7.190
7.152
4.394
4.367
2.806
2.785
2.763
2.743
2.080
2.063
1.646
1.625
1.509
1.492
1.419
1.400
1.238
1.224
CONHQ
TIPS
0.98
2.01
0.97
1.00
4.09
1.03
0.99
1.01
1.06
1.09
4.23
3.24
21.16
f1 (ppm)

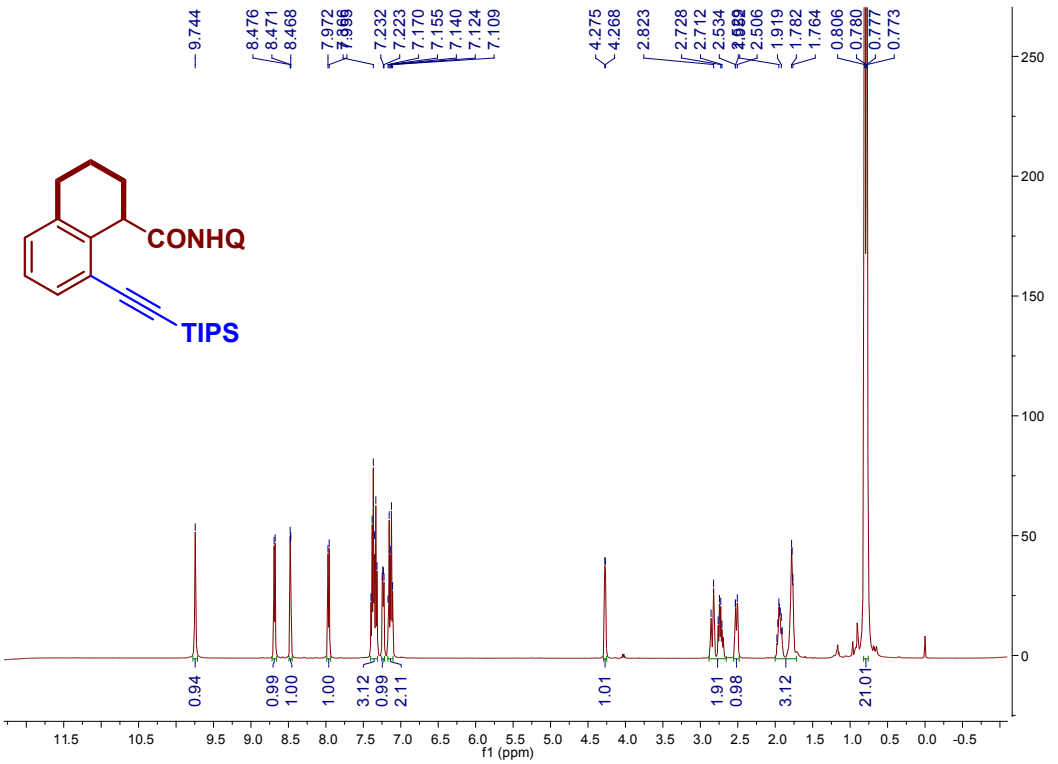

172.123
148.101
136.176
127.917
127.201
123.279
121.520
116.608
105.804
95.043
57.032
44.549
32.221
30.107
25.183
18.951
11.567
CONHQ
TIPS
f1 (ppm)

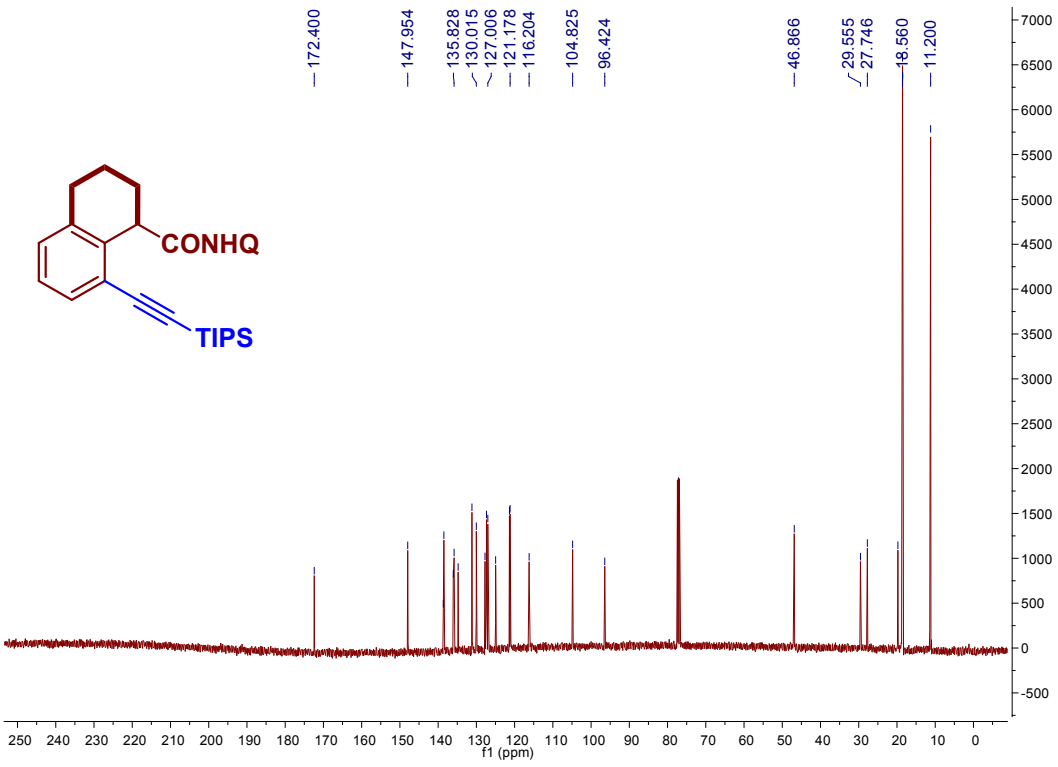
3n


9.916
8.725
8.710
8.649
8.641
8.622
8.005
7.703
7.420
7.362
7.327
7.311
7.241
7.103
7.073
4.253
4.232
2.199
2.177
2.155
2.134
1.997
1.971
1.566
1.185
1.175
1.167
1.156
1.116
1.091
1.070
1.012
0.988
0.964
0.940
CONHQ
TIPS
0.88
0.97
0.99
0.97
1.00
3.08
1.00
1.01
1.00
0.99
0.96
0.98
3.07
3.22
20.97
2.38
0.94
f1 (ppm)

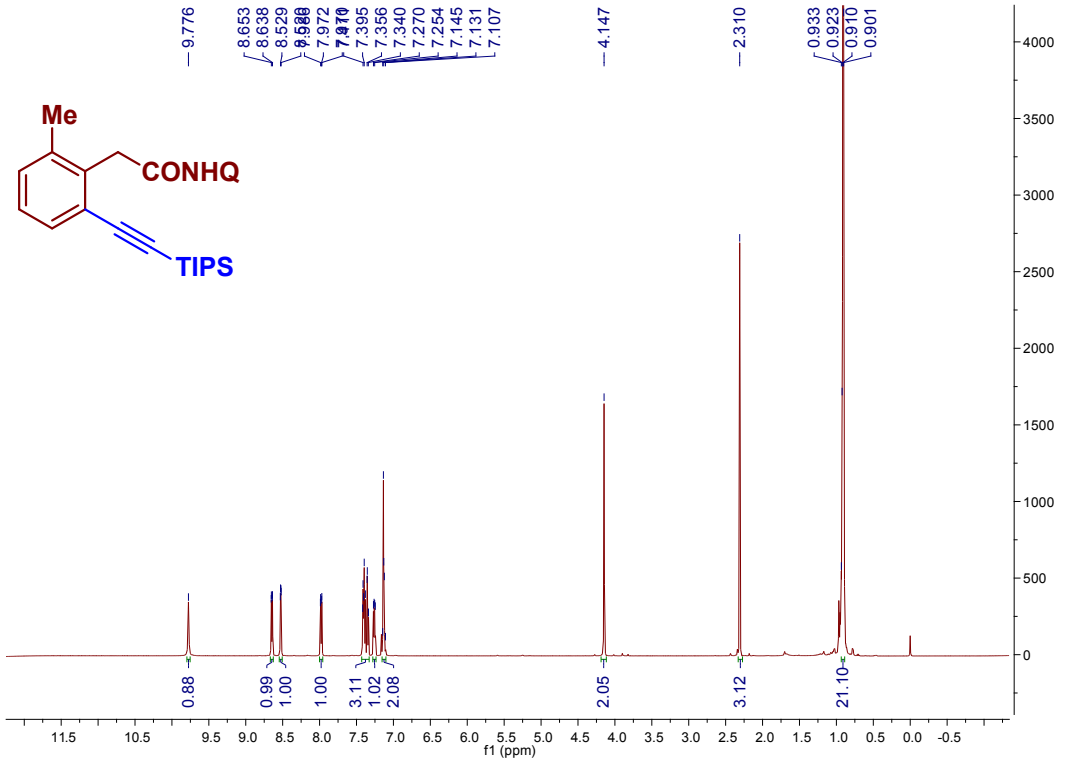

172.728
148.092
140.995
130.280
127.413
122.880
121.384
116.471
105.470
95.185
45.611
44.906
30.201
18.849
11.530
CONHQ
TIPS
f1 (ppm)

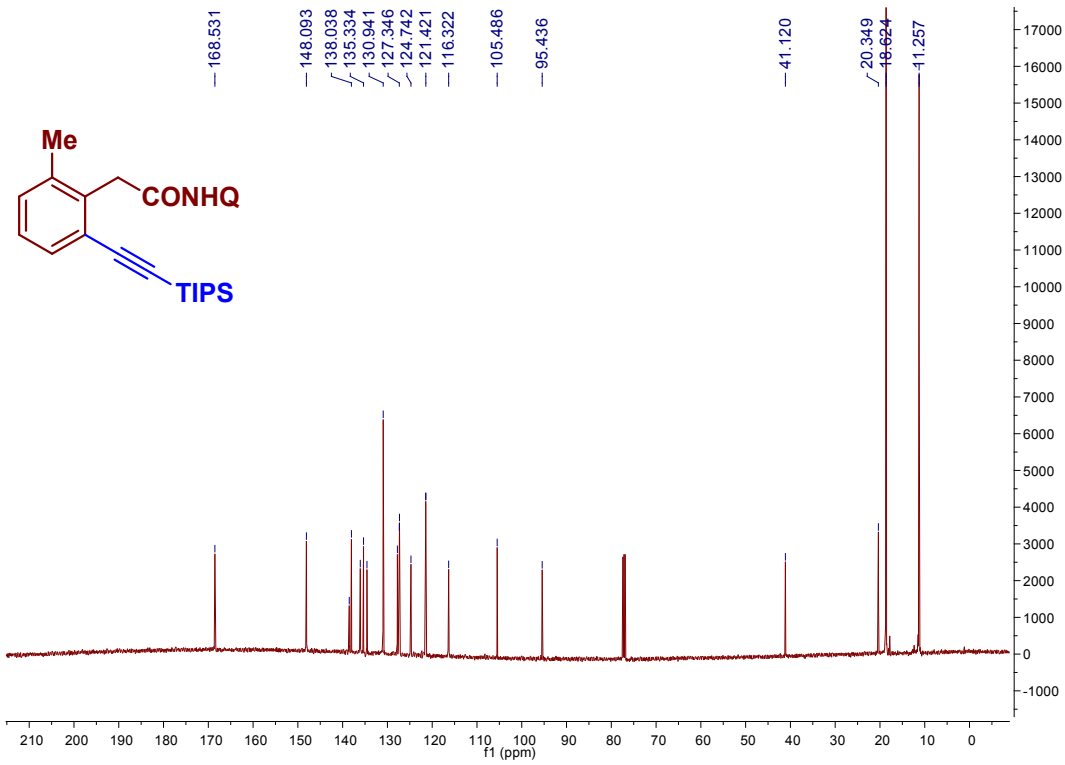
3o


9.744
8.476
8.471
8.468
7.972
7.232
7.223
7.170
7.155
7.140
7.124
7.109
4.275
4.268
2.823
2.728
2.712
2.534
2.506
1.919
1.782
1.764
0.806
0.780
0.777
0.773
CONHQ
TIPS
0.94
0.99
1.00
1.00
3.12
0.99
2.11
1.01
1.91
0.98
3.12
21.01
f1 (ppm)

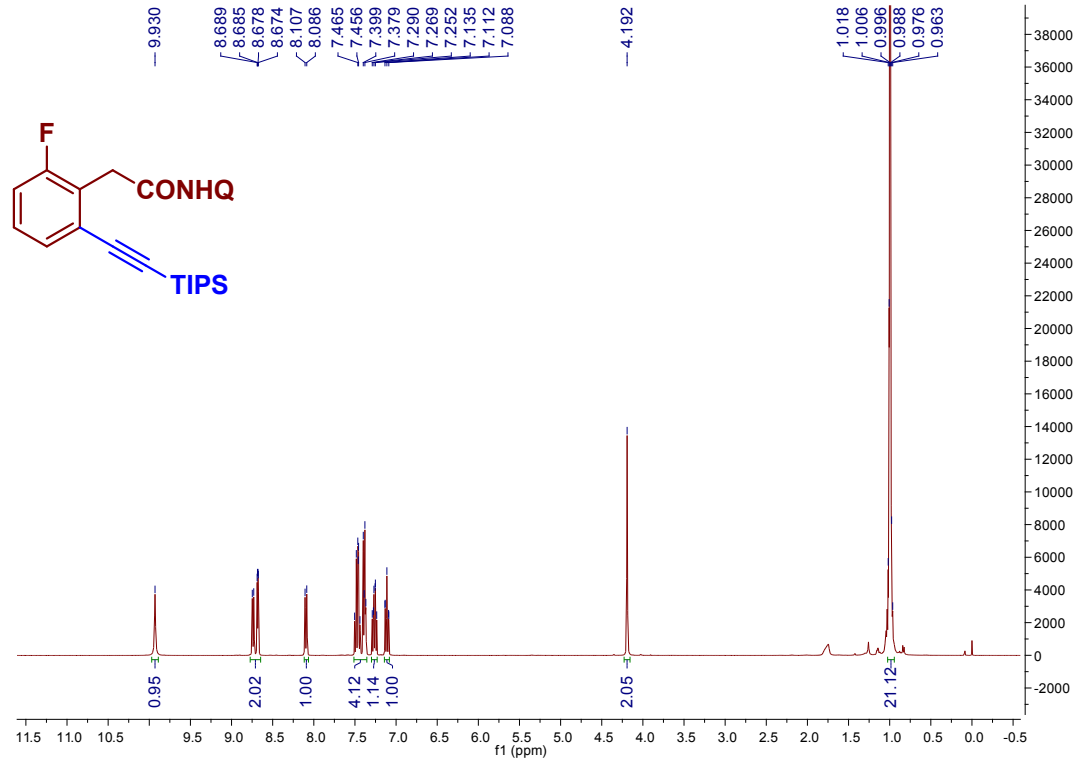

172.400
147.954
135.828
130.015
127.006
121.178
116.204
104.825
96.424
46.866
29.555
27.746
18.560
11.200
CONHQ
TIPS
f1 (ppm)

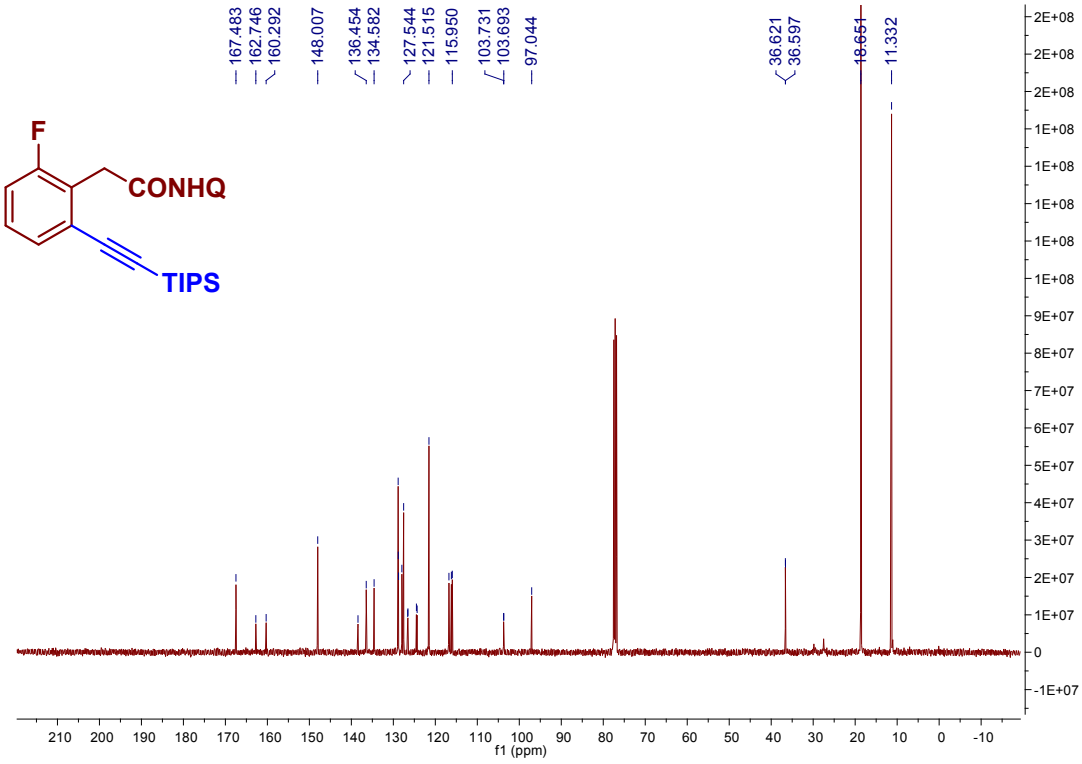
5a


9.776
8.653
8.638
8.529
7.972
7.395
7.356
7.340
7.270
7.254
7.145
7.131
7.107
4.147
2.310
0.933
0.923
0.910
0.901
Me
CONHQ
TIPS
0.88
0.99
1.00
1.00
3.11
1.02
2.08
2.05
3.12
21.10
f1 (ppm)

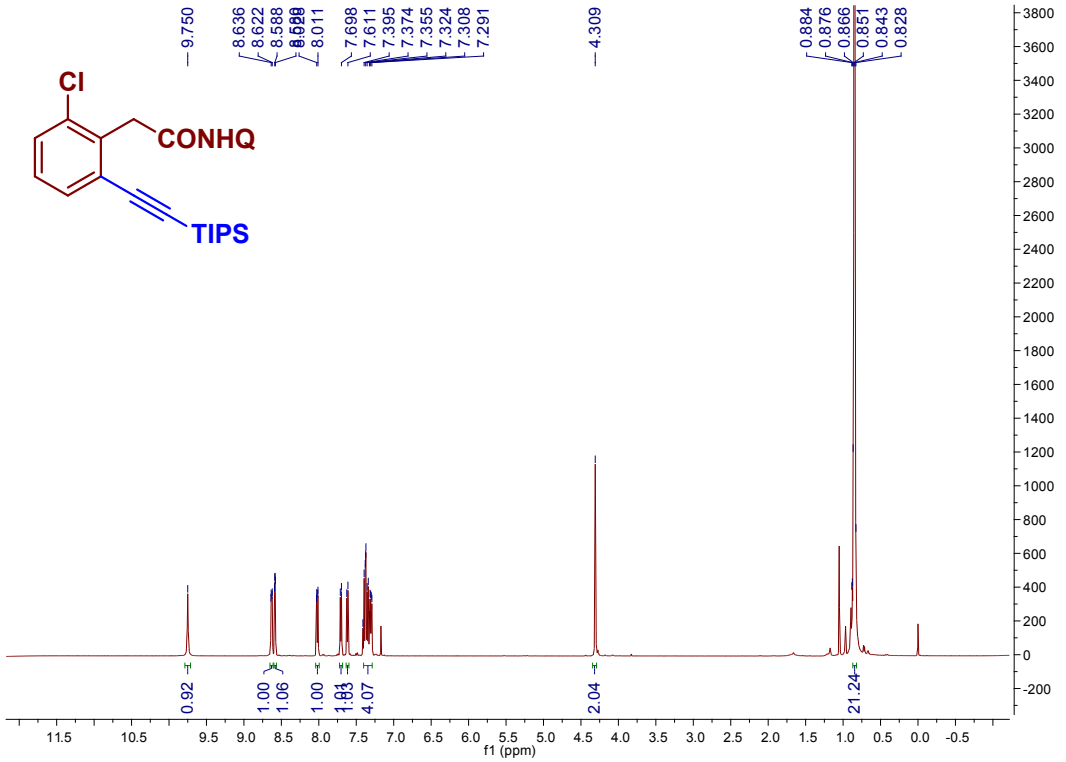

168.531
148.093
138.038
135.334
130.941
127.346
124.742
121.421
116.322
105.486
95.436
41.120
20.349
18.624
11.257
Me
CONHQ
TIPS
f1 (ppm)

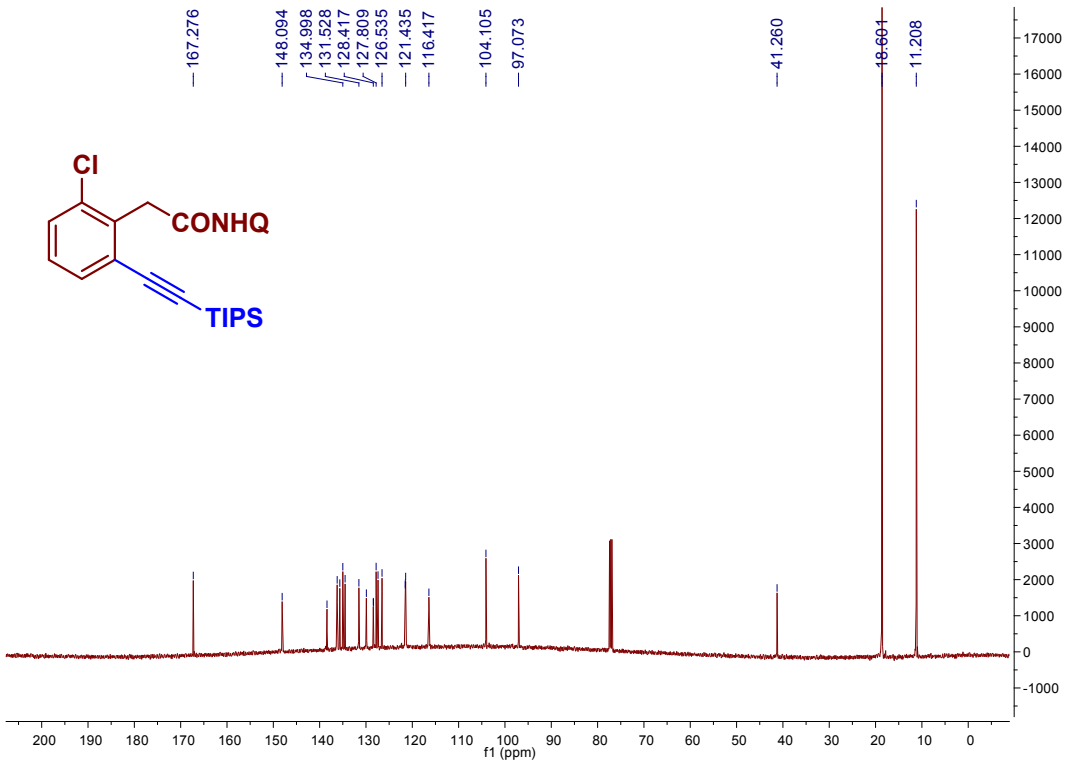
5b


F
CONHQ
TIPS
9.930
8.689
8.685
8.678
8.674
8.107
8.086
7.465
7.456
7.399
7.379
7.290
7.269
7.252
7.135
7.112
7.088
4.192
1.018
1.006
0.996
0.988
0.976
0.963
0.95
2.02
1.00
4.12
1.14
1.00
2.05
21.12
f1 (ppm)

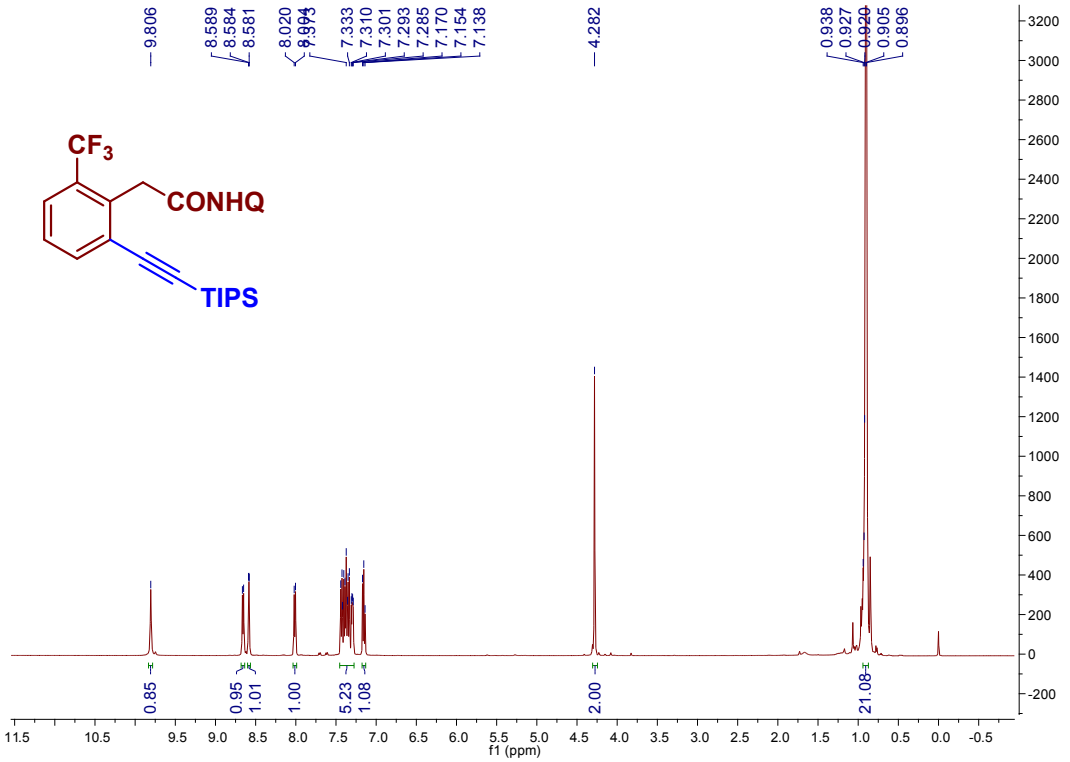

F
CONHQ
TIPS
167.483
162.746
160.292
148.007
136.454
134.582
127.544
121.515
115.950
103.731
103.693
97.044
36.621
36.597
18.851
11.332
f1 (ppm)

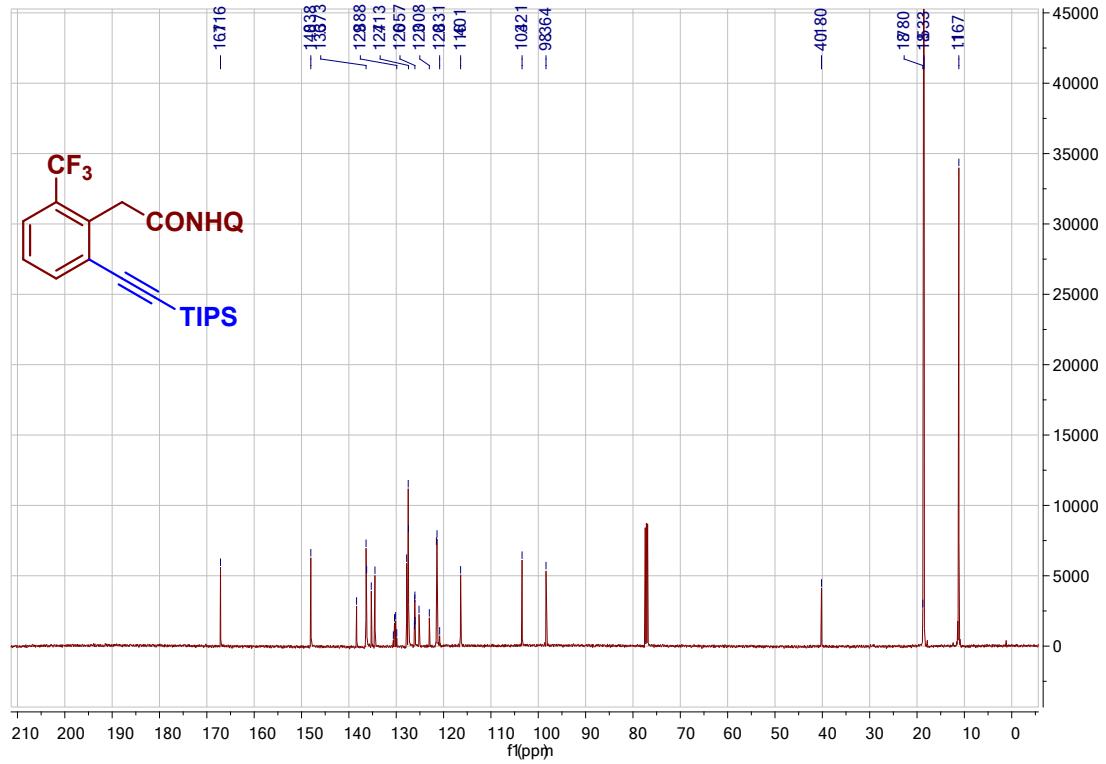
5c


9.750
8.636
8.622
8.588
8.011
7.698
7.611
7.395
7.374
7.355
7.324
7.308
7.291
4.309
0.884
0.876
0.866
0.851
0.843
0.828
Cl
CONHQ
TIPS
0.92
1.00
1.06
1.00
4.07
2.04
21.24
f1 (ppm)

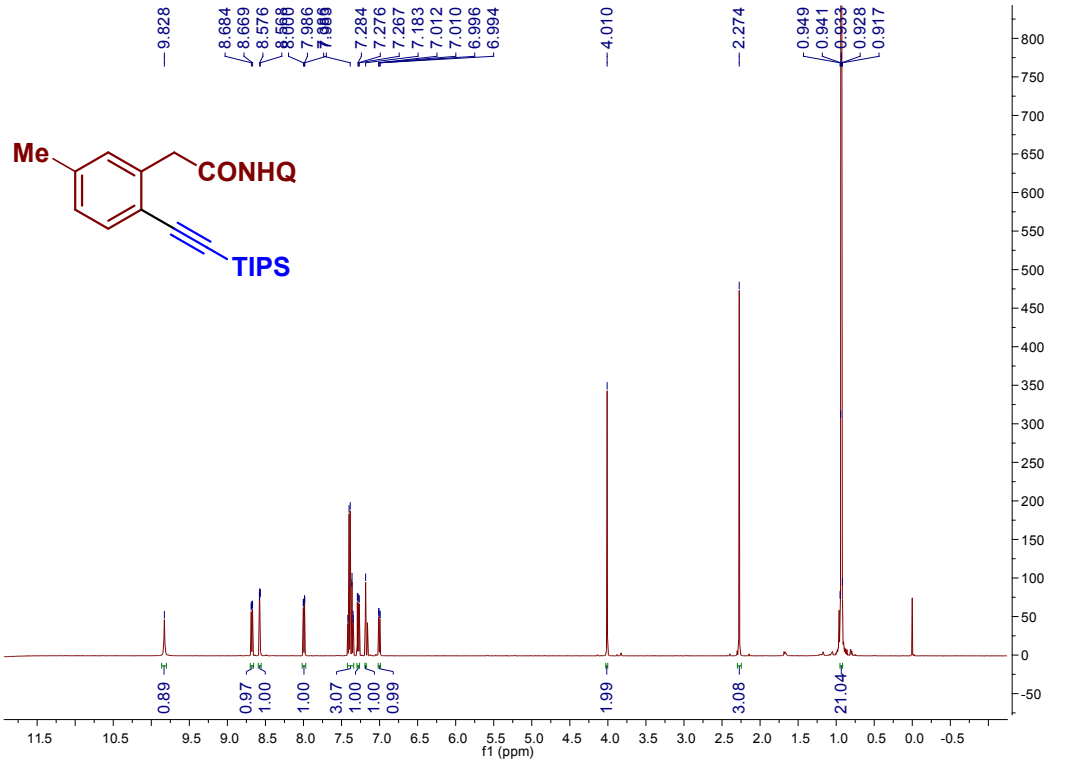

167.276
148.094
134.998
131.528
128.417
127.809
126.535
121.435
116.417
104.105
97.073
41.260
18.601
11.208
Cl
CONHQ
TIPS
f1 (ppm)

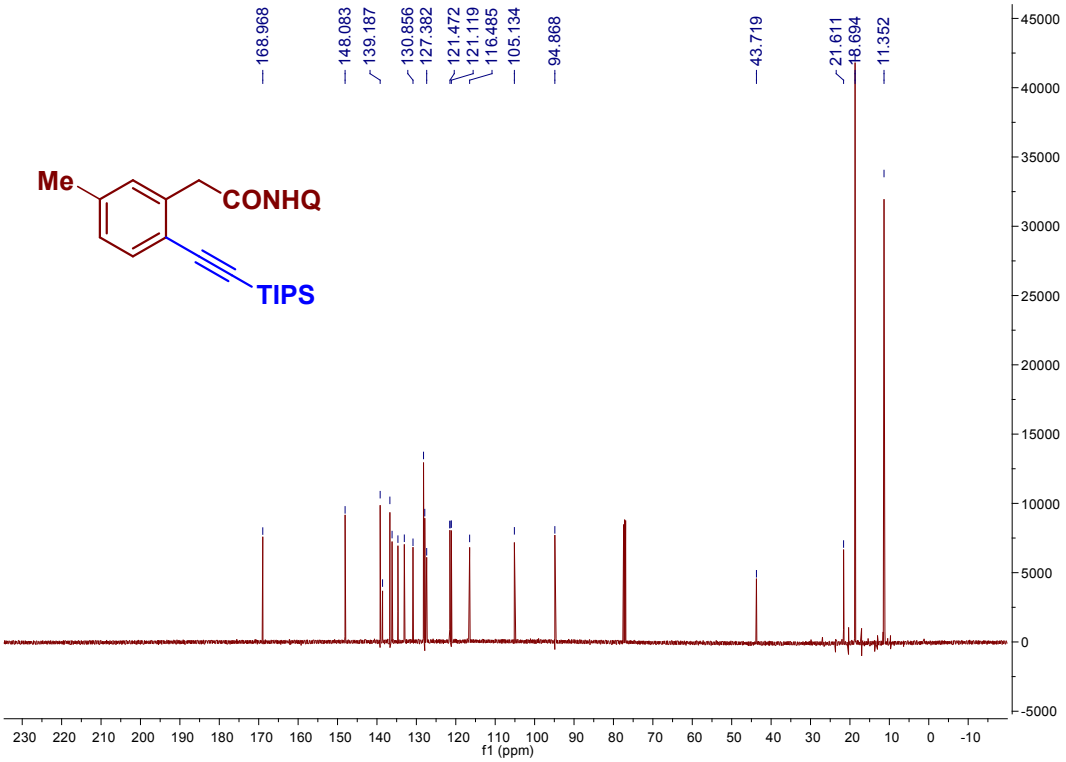
5d


9.806
8.589
8.584
8.581
8.020
7.333
7.310
7.301
7.293
7.285
7.170
7.154
7.138
4.282
0.938
0.927
0.905
0.896
CF3
CONHQ
TIPS
0.85
0.95
1.01
1.00
5.23
1.08
2.00
21.08
f1 (ppm)

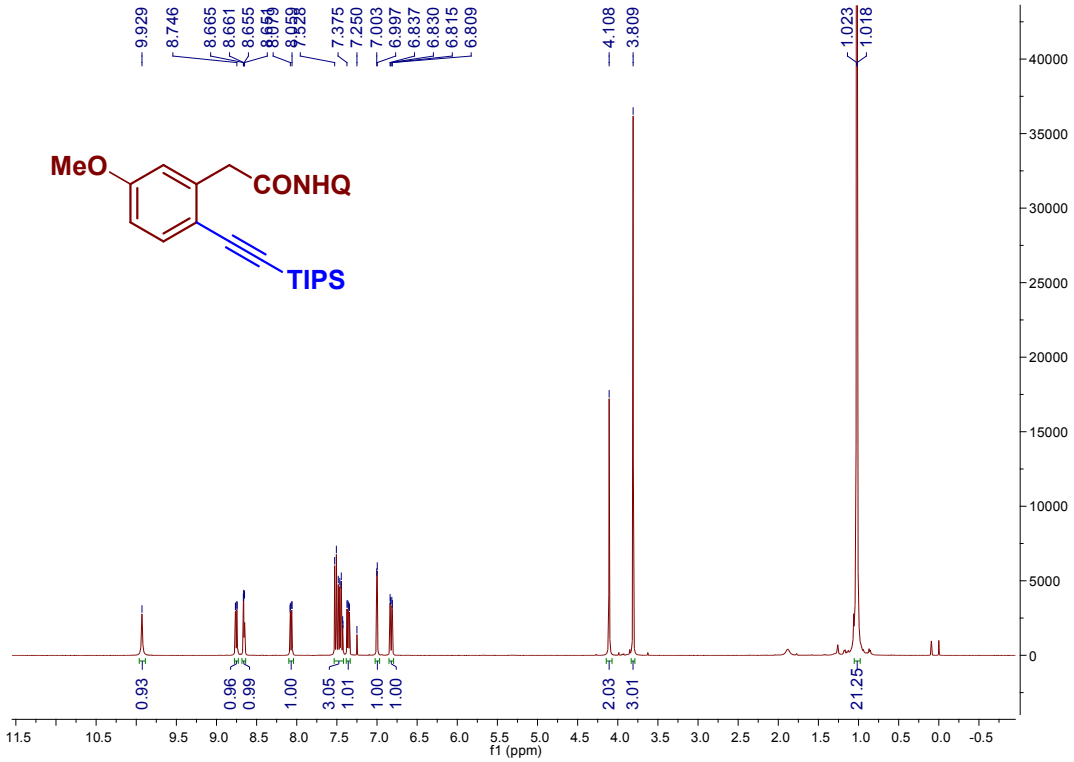

CF3
CONHQ
TIPS
f1 (ppm)

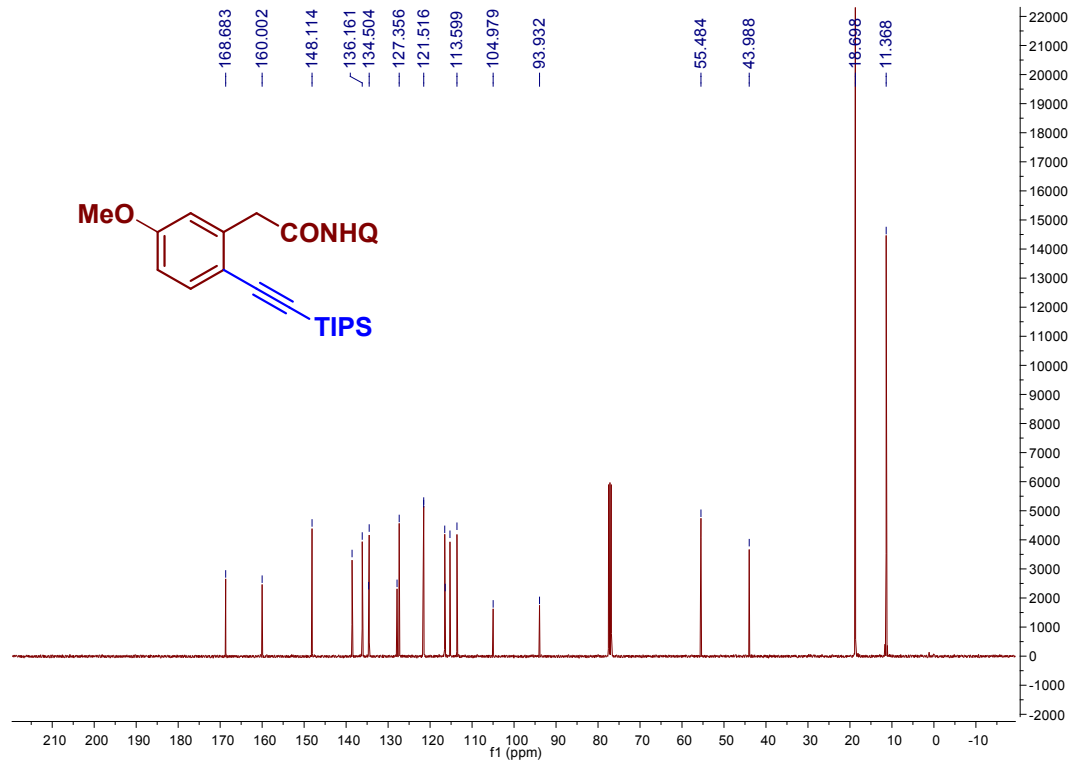
5e


9.828
8.684
8.669
8.576
7.986
7.284
7.276
7.267
7.183
7.012
7.010
6.996
6.994
4.010
2.274
0.949
0.941
0.933
0.928
0.917
Me
CONHQ
TIPS
0.89
0.97
1.00
1.00
3.07
1.00
1.00
0.99
1.99
3.08
21.04
f1 (ppm)

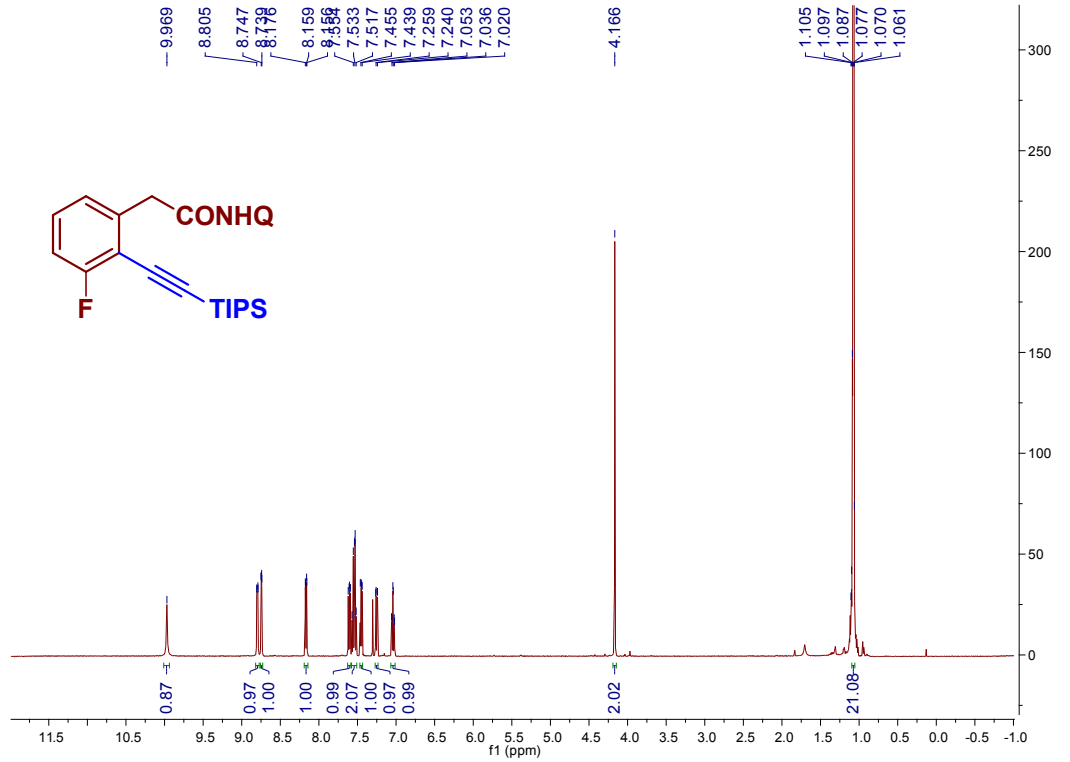

168.968
148.083
139.187
130.856
127.382
121.472
121.119
116.485
105.134
94.868
43.719
21.611
18.694
11.352
Me
CONHQ
TIPS
f1 (ppm)

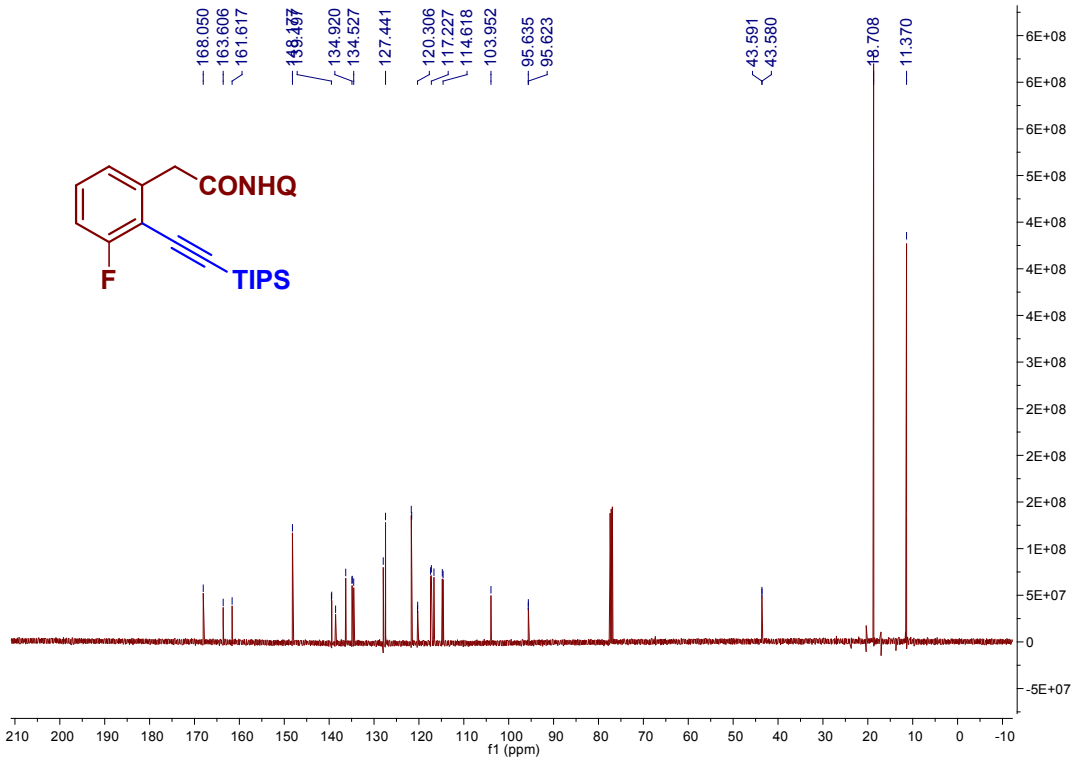
5f


9.929
8.746
8.665
8.661
8.655
7.375
7.250
7.003
6.997
6.837
6.830
6.815
6.809
4.108
3.809
1.023
1.018
MeO
CONHQ
TIPS
0.93
0.96
0.99
1.00
3.05
1.01
1.00
1.00
2.03
3.01
21.25
f1 (ppm)

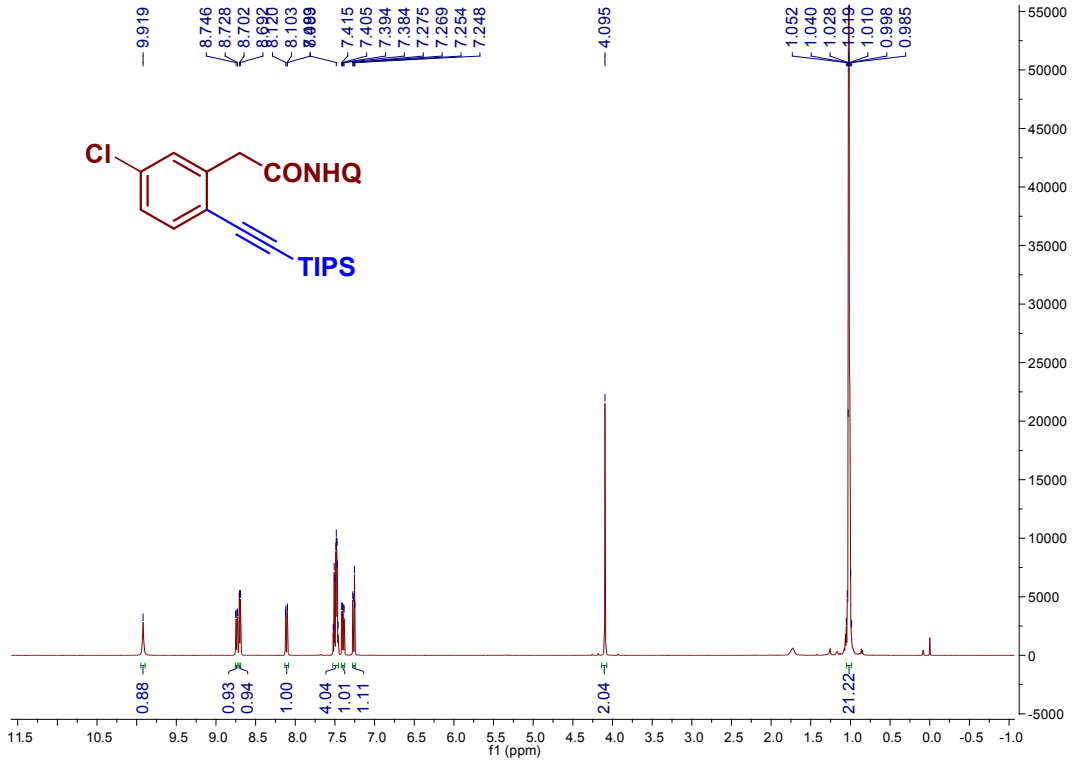

168.683
160.002
148.114
136.161
134.504
127.356
121.516
113.599
104.979
93.932
55.484
43.988
18.698
11.368
MeO
CONHQ
TIPS
f1 (ppm)

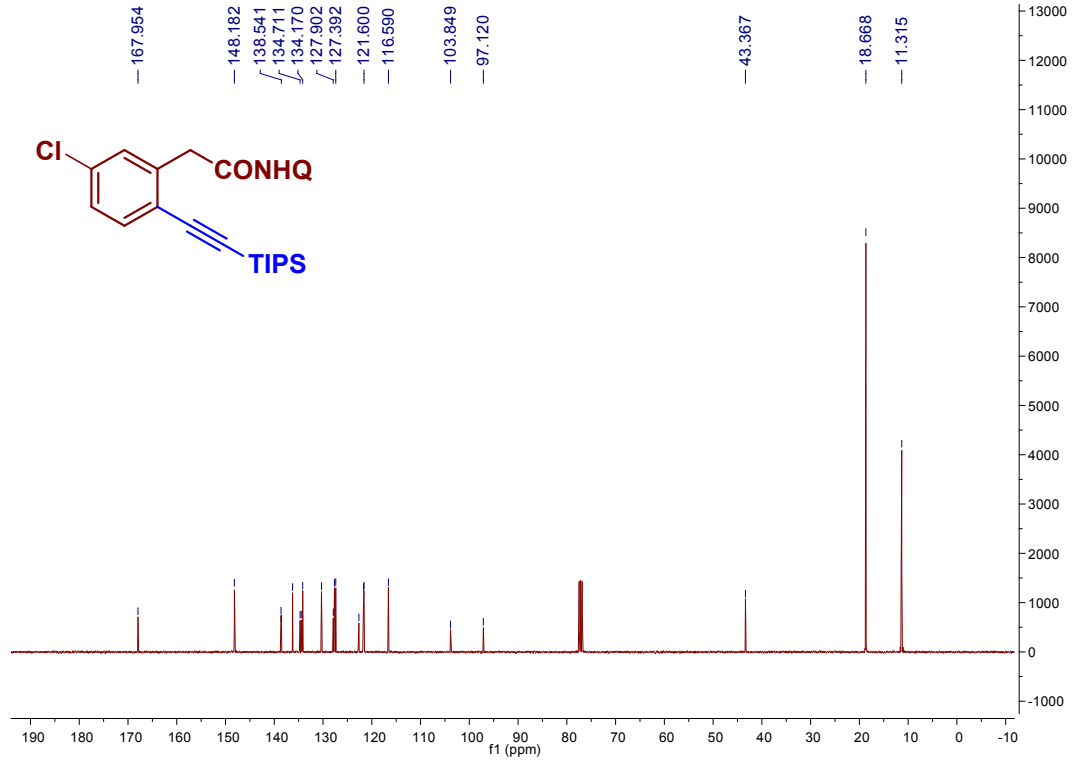
5g


9.969
8.805
8.747
8.739
8.176
8.159
7.554
7.533
7.517
7.455
7.439
7.259
7.240
7.053
7.036
7.020
4.166
1.105
1.097
1.087
1.077
1.070
1.061
CONHQ
F
TIPS
0.87
0.97
1.00
1.00
0.99
2.07
1.00
0.97
0.99
2.02
21.08
f1 (ppm)

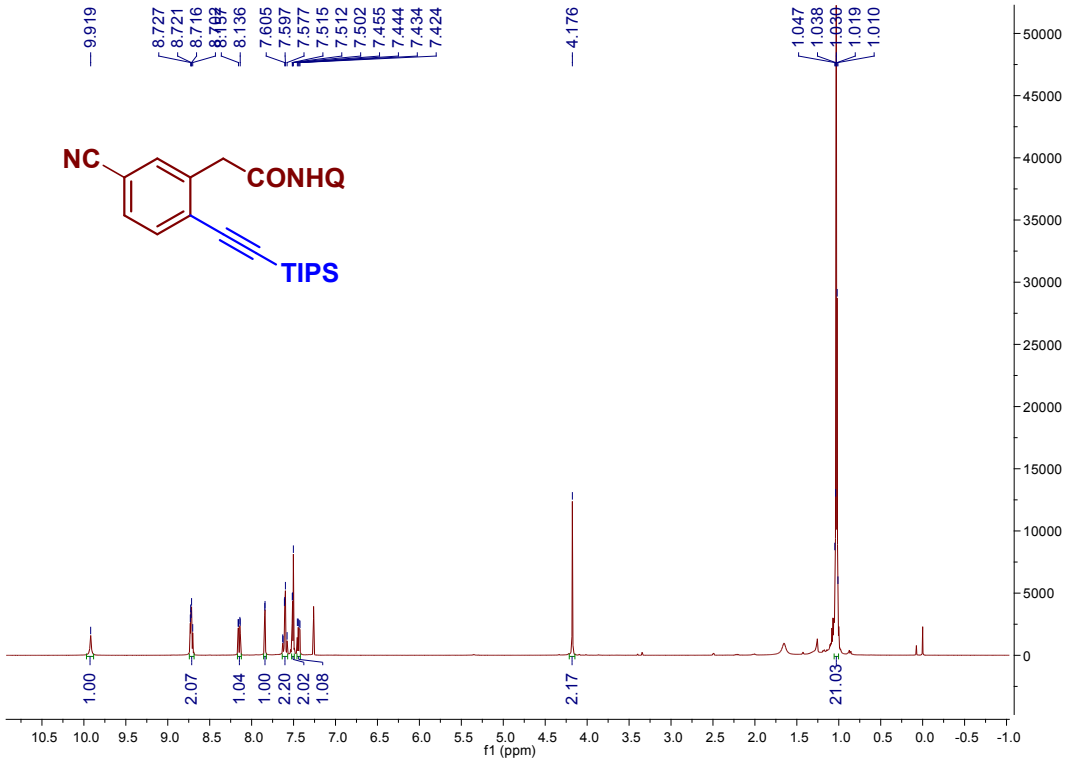

168.050
163.606
161.617
134.920
134.527
127.441
120.306
117.227
114.618
103.952
95.635
95.623
43.591
43.580
18.708
11.370
CONHQ
F
TIPS
f1 (ppm)

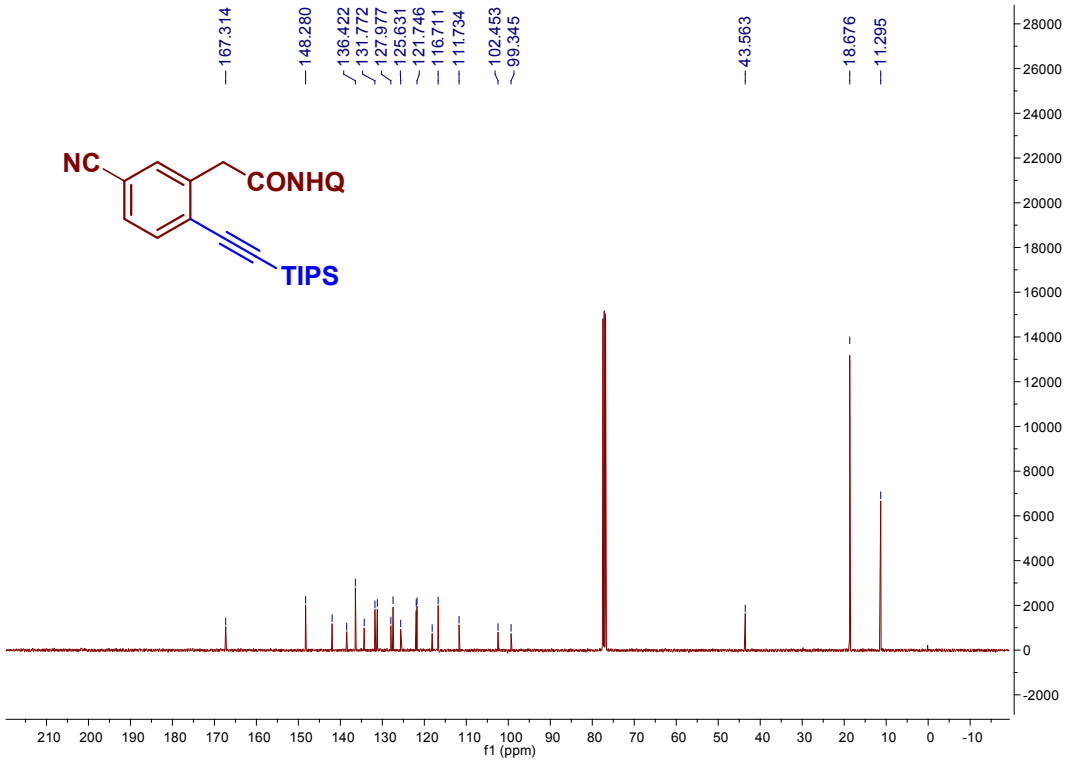
5h


9.919
8.746
8.728
8.702
8.692
8.120
8.103
7.415
7.405
7.394
7.384
7.275
7.269
7.254
7.248
4.095
1.052
1.040
1.028
1.019
1.010
0.998
0.985
Cl
CONHQ
TIPS
0.88
0.93
0.94
1.00
4.04
1.01
1.11
2.04
21.22
f1 (ppm)

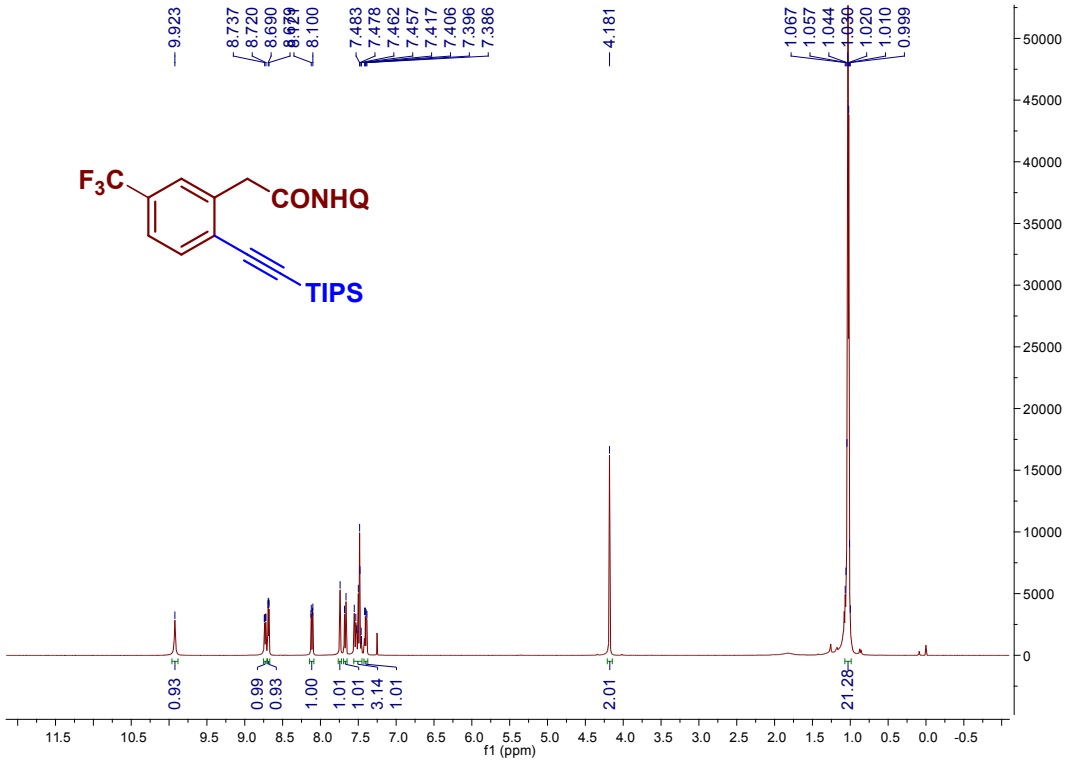

167.954
148.182
138.541
134.711
134.170
127.902
127.392
121.600
116.590
103.849
97.120
43.367
18.668
11.315
Cl
CONHQ
TIPS
f1 (ppm)

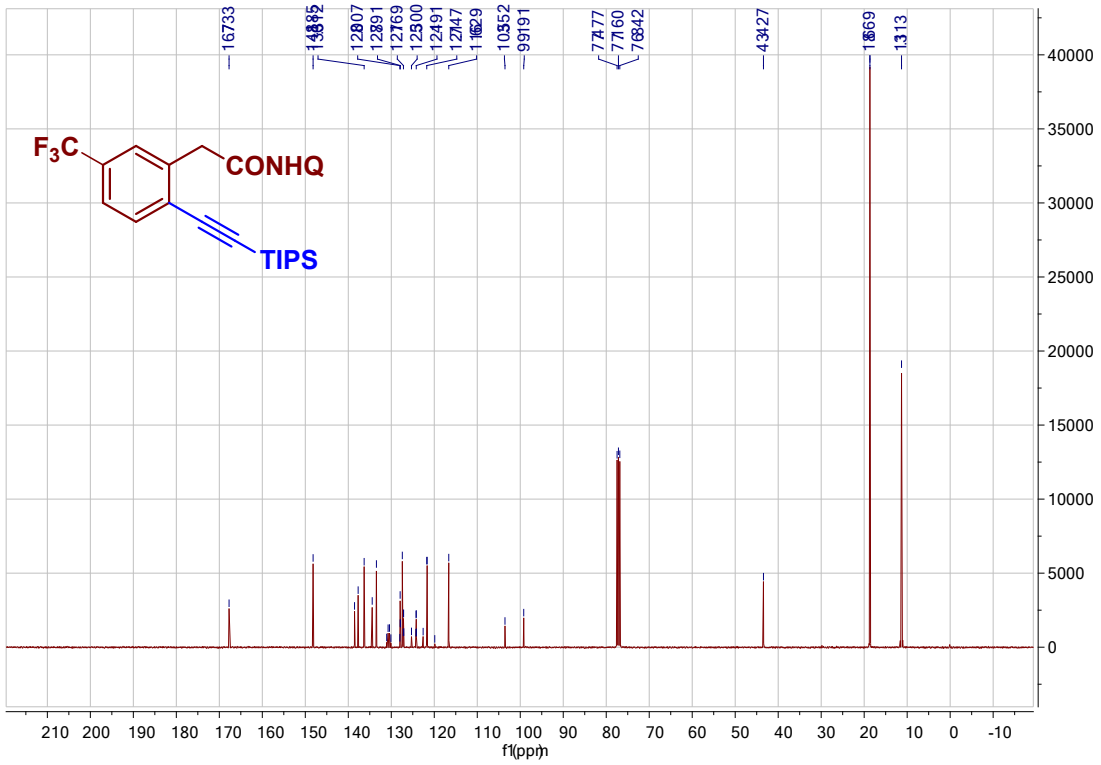
5i


9.919
8.727
8.721
8.716
8.136
7.605
7.597
7.577
7.515
7.512
7.502
7.455
7.444
7.434
7.424
4.176
1.047
1.038
1.019
1.010
NC
CONHQ
TIPS
1.00
2.07
1.04
1.00
2.20
2.02
1.08
2.17
21.03
f1 (ppm)

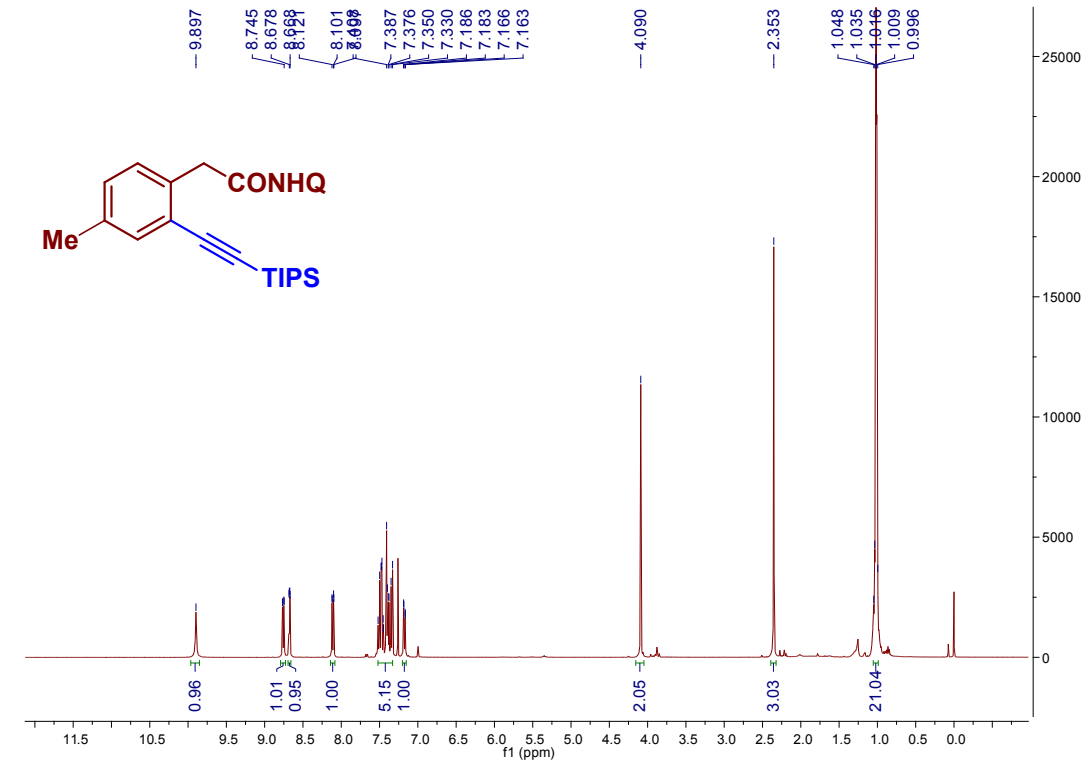

167.314
148.280
136.422
131.772
127.977
125.631
121.746
116.711
111.734
102.453
99.345
43.563
18.676
11.295
NC
CONHQ
TIPS
f1 (ppm)

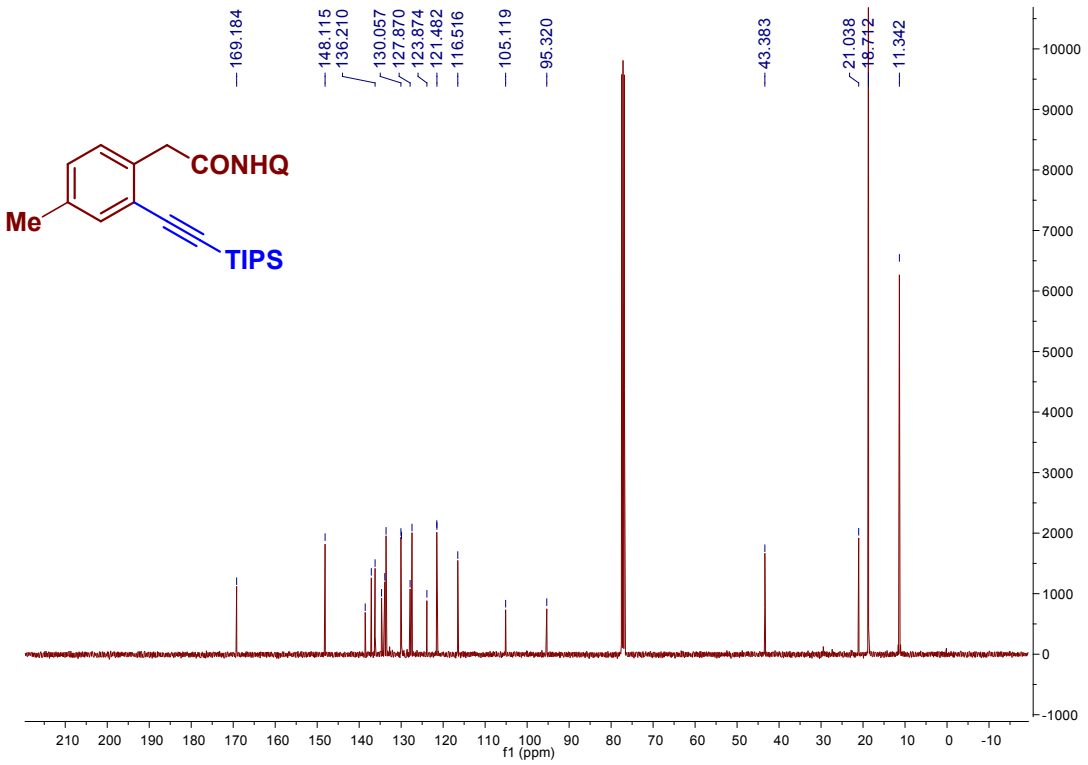
5j


9.923
8.737
8.720
8.690
8.100
7.483
7.478
7.462
7.457
7.417
7.406
7.396
7.386
4.181
1.067
1.057
1.044
1.020
1.010
0.999
F3C
CONHQ
TIPS
0.93
0.99
0.93
1.00
1.01
1.01
3.14
1.01
2.01
21.28
f1 (ppm)

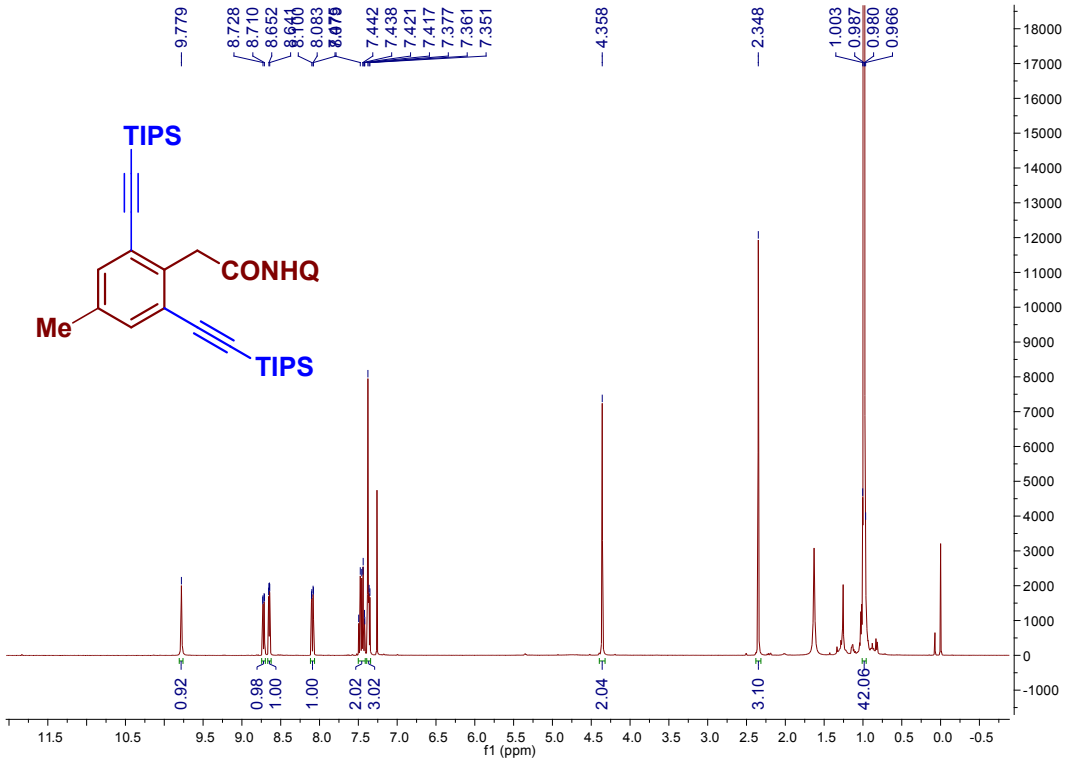

F3C
CONHQ
TIPS
f1(ppm)

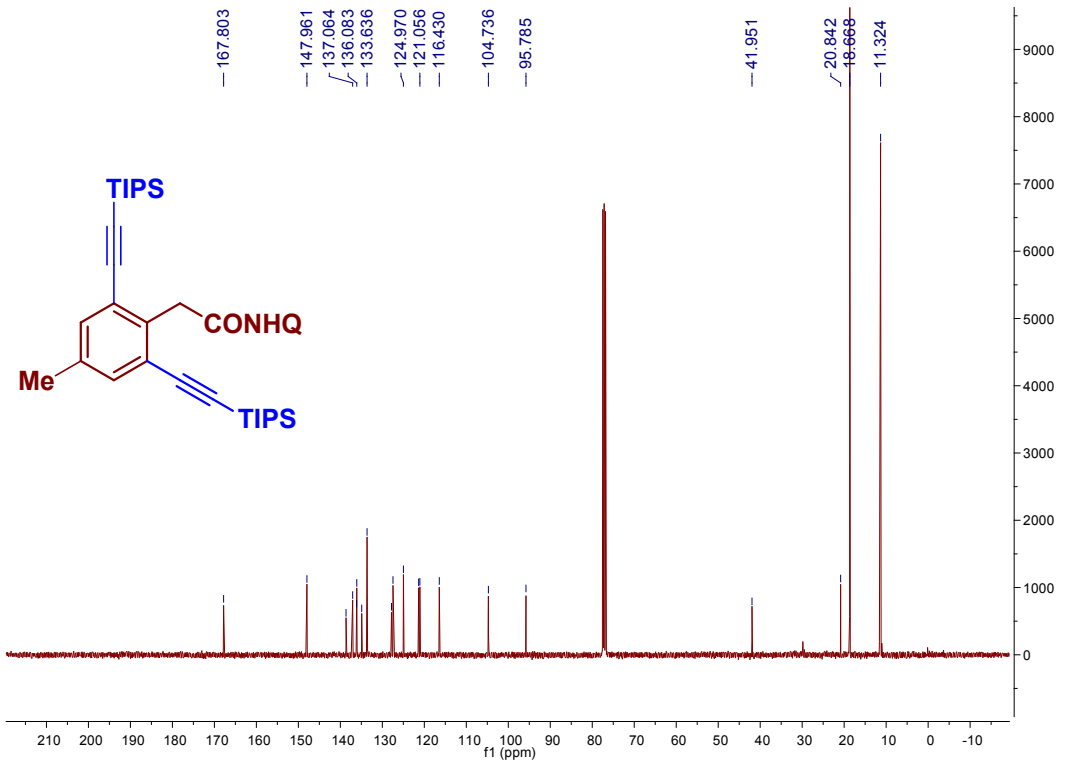
5k


9.897
8.745
8.678
8.668
8.121
8.101
7.387
7.376
7.350
7.330
7.186
7.183
7.166
7.163
4.090
2.353
1.048
1.035
1.016
1.009
0.996
CONHQ
Me
TIPS
0.96
1.01
0.95
1.00
5.15
1.00
2.05
3.03
21.04
f1 (ppm)

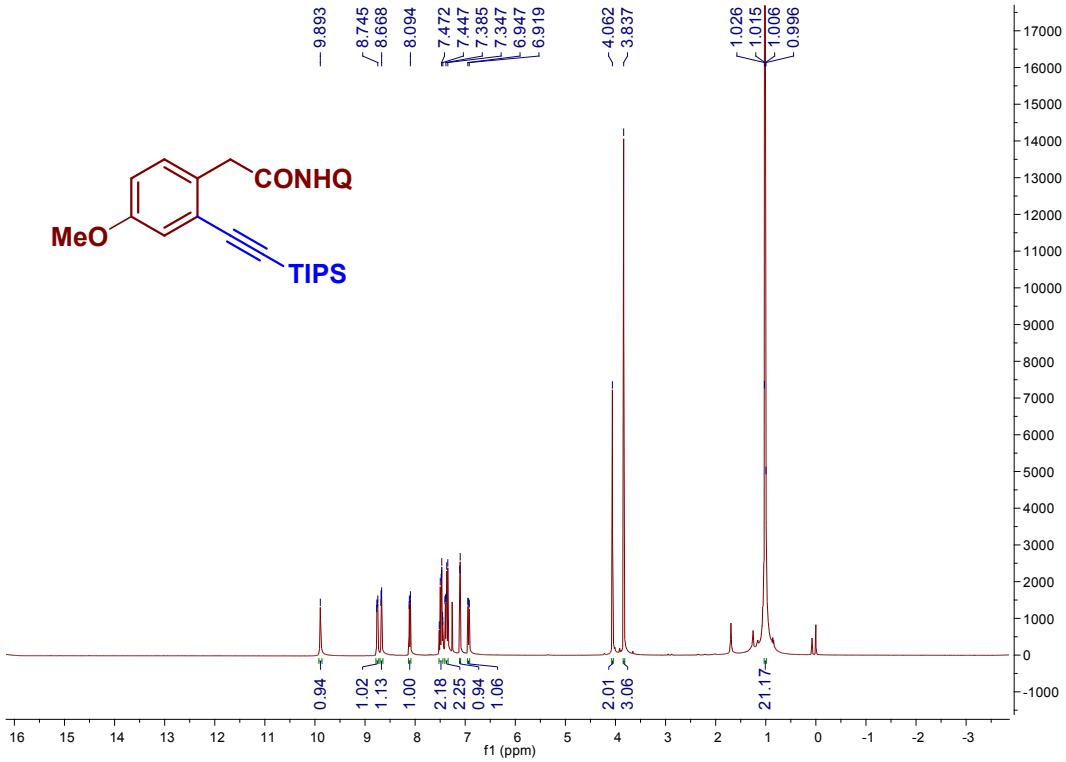

169.184
148.115
136.210
130.057
127.870
123.874
121.482
116.516
105.119
95.320
43.383
21.038
18.712
11.342
CONHQ
Me
TIPS
f1 (ppm)

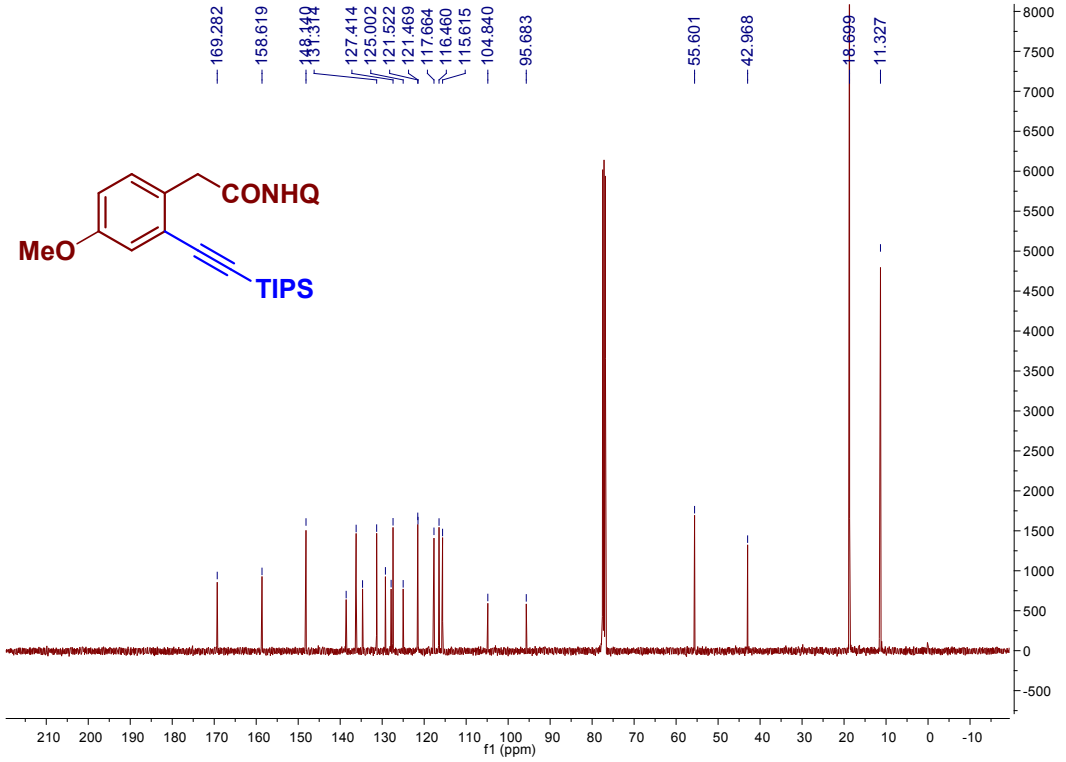
5k'


9.779
8.728
8.710
8.652
8.641
8.083
7.442
7.438
7.421
7.417
7.377
7.361
7.351
4.358
2.348
1.003
0.987
0.980
0.966
TIPS
CONHQ
Me
TIPS
0.92
0.98
1.00
1.00
2.02
3.02
2.04
3.10
42.06
f1 (ppm)

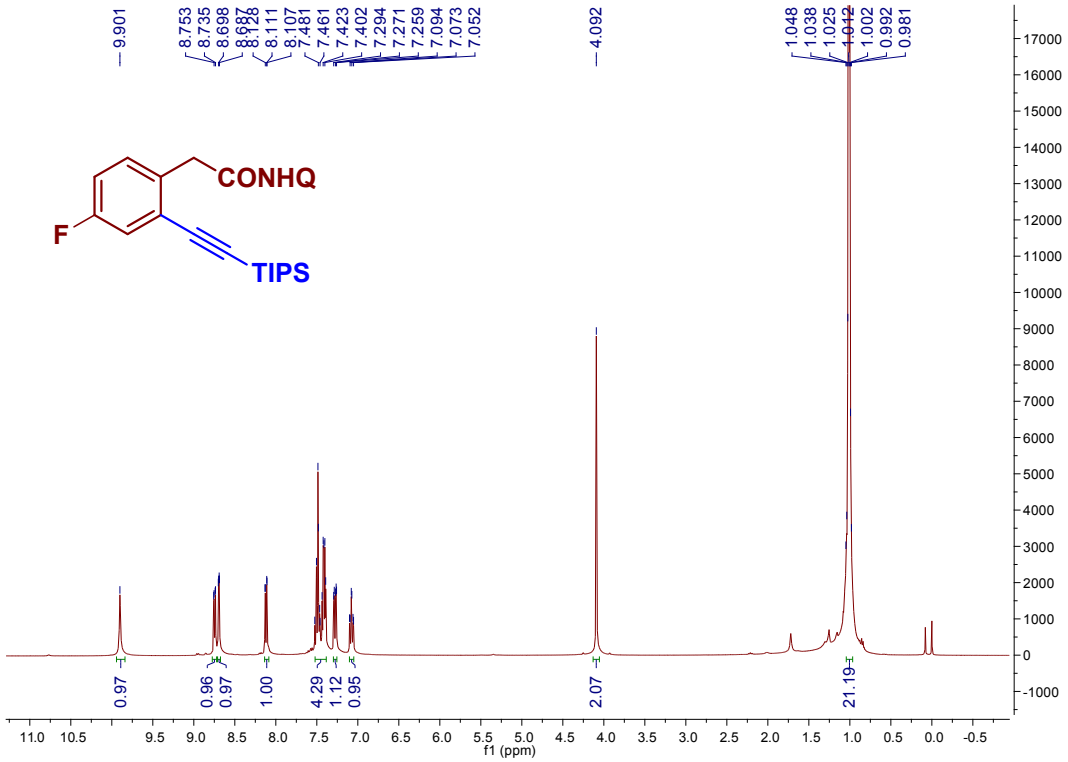

167.803
147.961
137.064
136.083
133.636
124.970
121.056
116.430
104.736
95.785
41.951
20.842
18.668
11.324
TIPS
CONHQ
Me
TIPS
f1 (ppm)

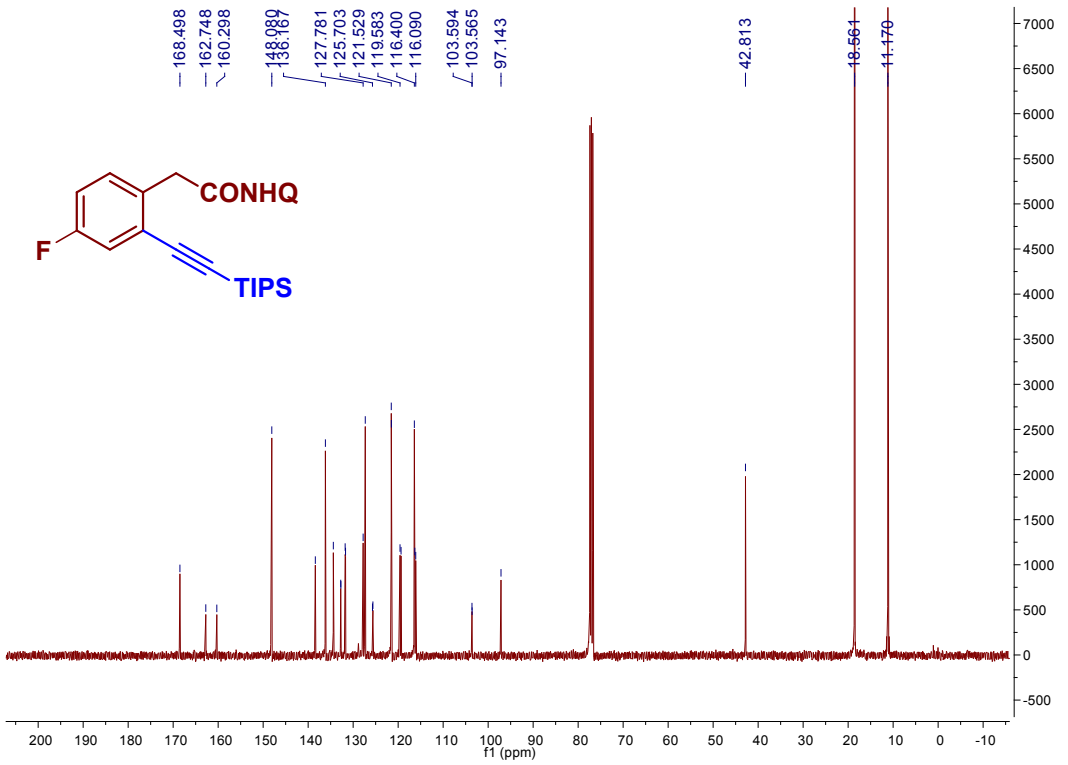
5i


9.893
8.745
8.668
8.094
7.472
7.447
7.385
7.347
6.947
6.919
4.062
3.837
1.026
1.015
1.006
0.996
CONHQ
MeO
TIPS
0.94
1.02
1.13
1.00
2.18
2.25
0.94
1.06
2.01
3.06
21.17
f1 (ppm)

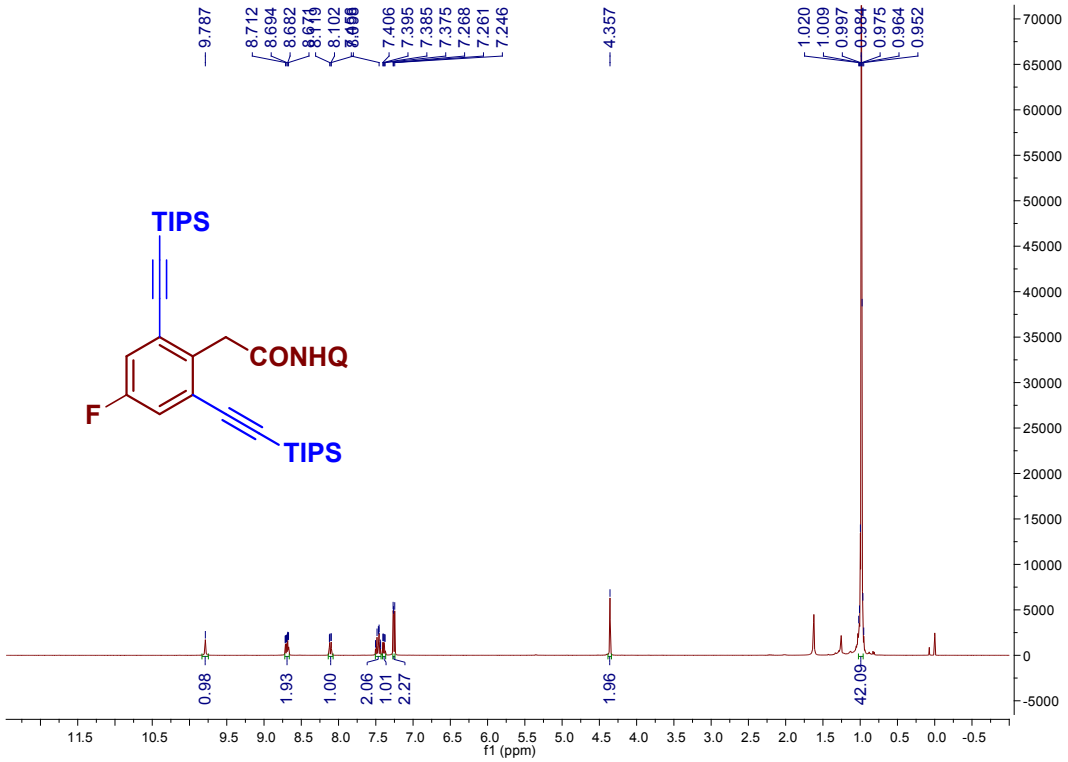

169.282
158.619
148.140
131.314
127.414
125.002
121.522
121.469
117.664
116.460
115.615
104.840
95.683
55.601
42.968
18.699
11.327
CONHQ
MeO
TIPS
f1 (ppm)

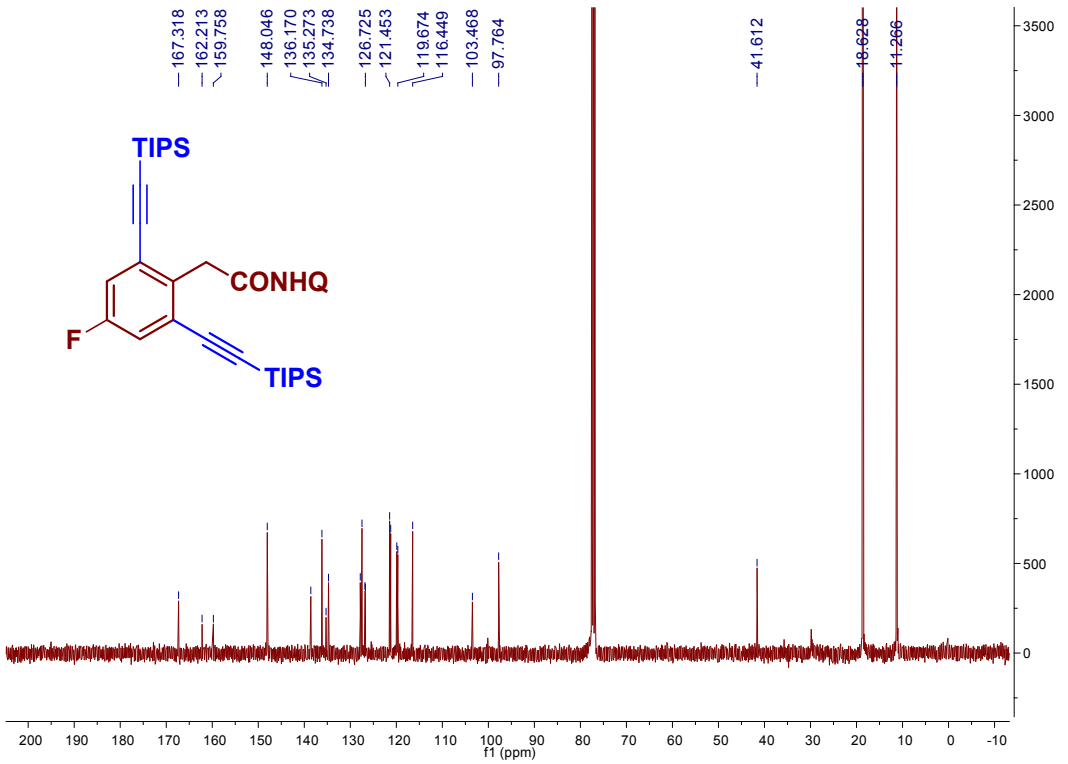
5m


9.901
8.753
8.735
8.698
8.687
8.128
8.111
8.107
7.481
7.461
7.423
7.402
7.294
7.271
7.259
7.094
7.073
7.052
4.092
1.048
1.038
1.025
1.012
1.002
0.992
0.981
CONHQ
F
TIPS
0.97
0.96
0.97
1.00
4.29
1.12
0.95
2.07
21.19
f1 (ppm)

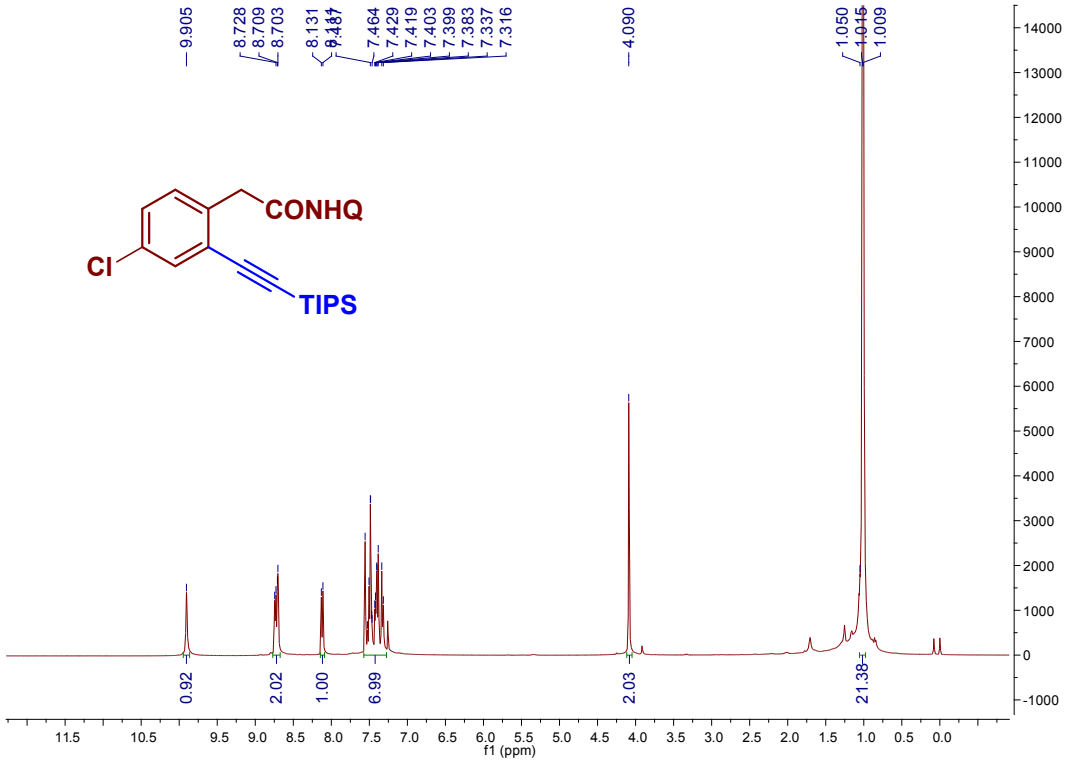

168.498
162.748
160.298
148.080
138.167
127.781
125.703
121.529
119.583
116.400
116.090
103.594
103.565
97.143
42.813
18.561
11.170
CONHQ
F
TIPS
f1 (ppm)

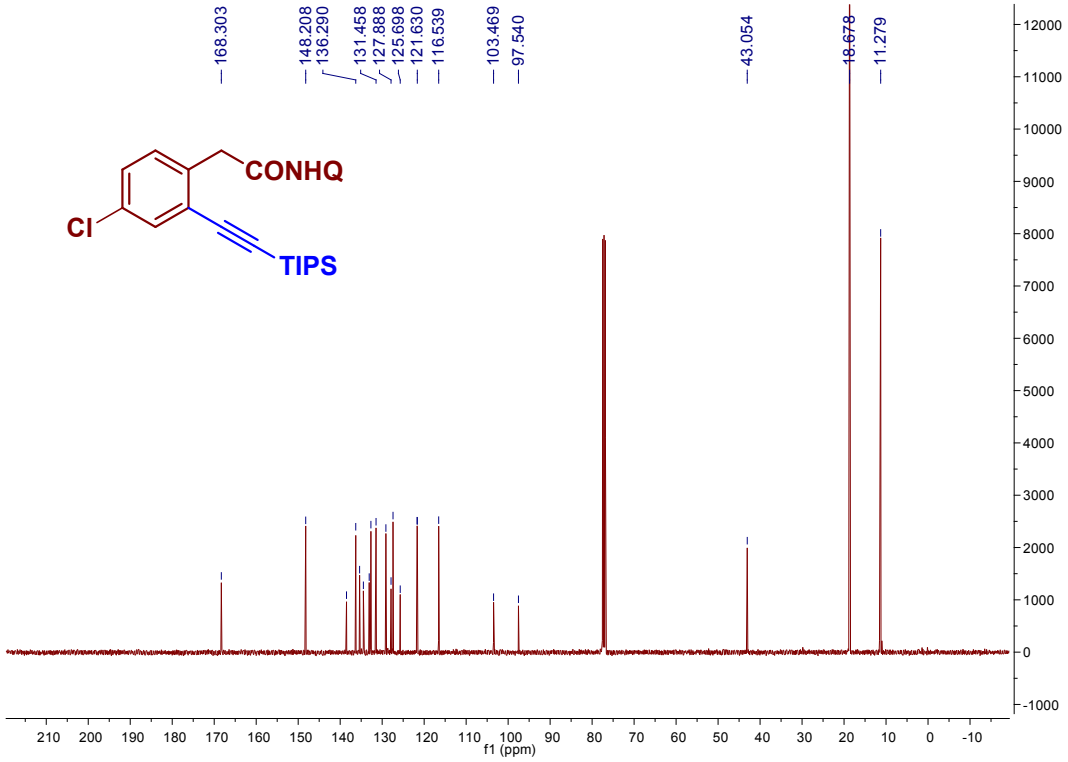
5m


9.787
8.712
8.694
8.682
8.102
7.406
7.395
7.385
7.375
7.268
7.261
7.246
4.357
1.020
1.009
0.997
0.984
0.975
0.964
0.952
TIPS
CONHQ
F
TIPS
0.98
1.93
1.00
2.06
1.01
2.27
1.96
42.09
f1 (ppm)

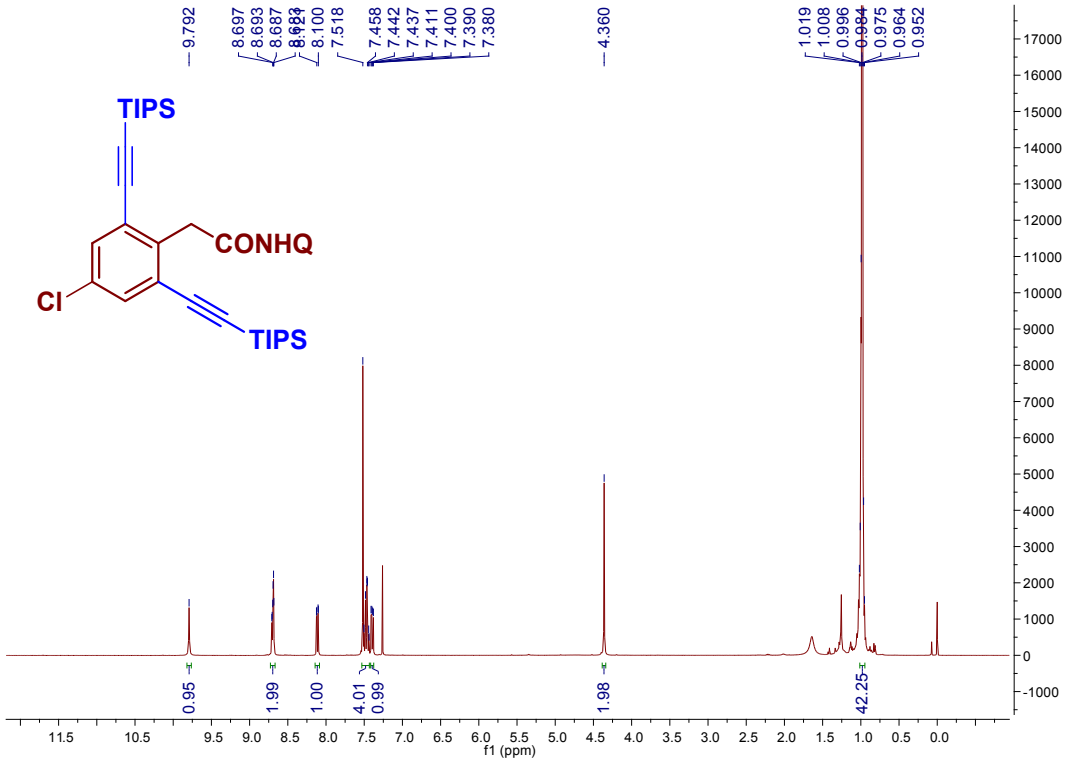

167.318
162.213
159.758
148.046
136.170
135.273
134.738
126.725
121.453
119.674
116.449
103.468
97.764
41.612
18.628
11.266
TIPS
CONHQ
F
TIPS
f1 (ppm)

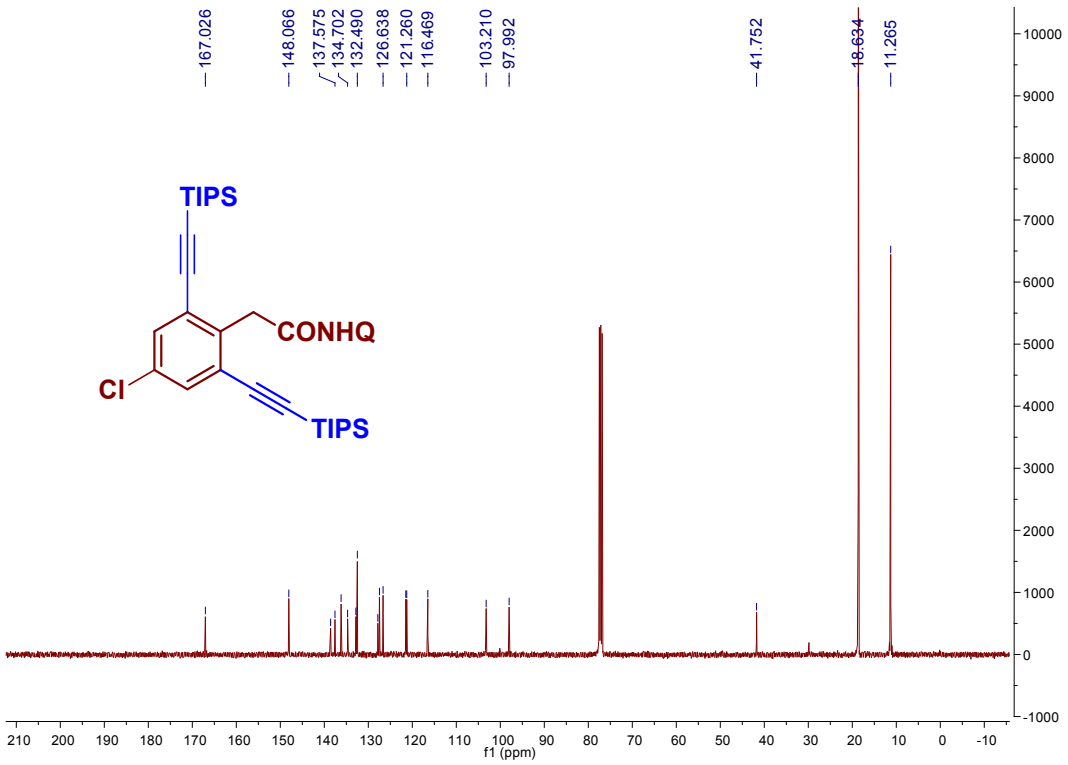
5n


9.905
8.728
8.709
8.703
8.131
7.464
7.429
7.419
7.403
7.399
7.383
7.337
7.316
4.090
1.050
1.015
1.009
CONHQ
Cl
TIPS
0.92
2.02
1.00
6.99
2.03
21.38
f1 (ppm)

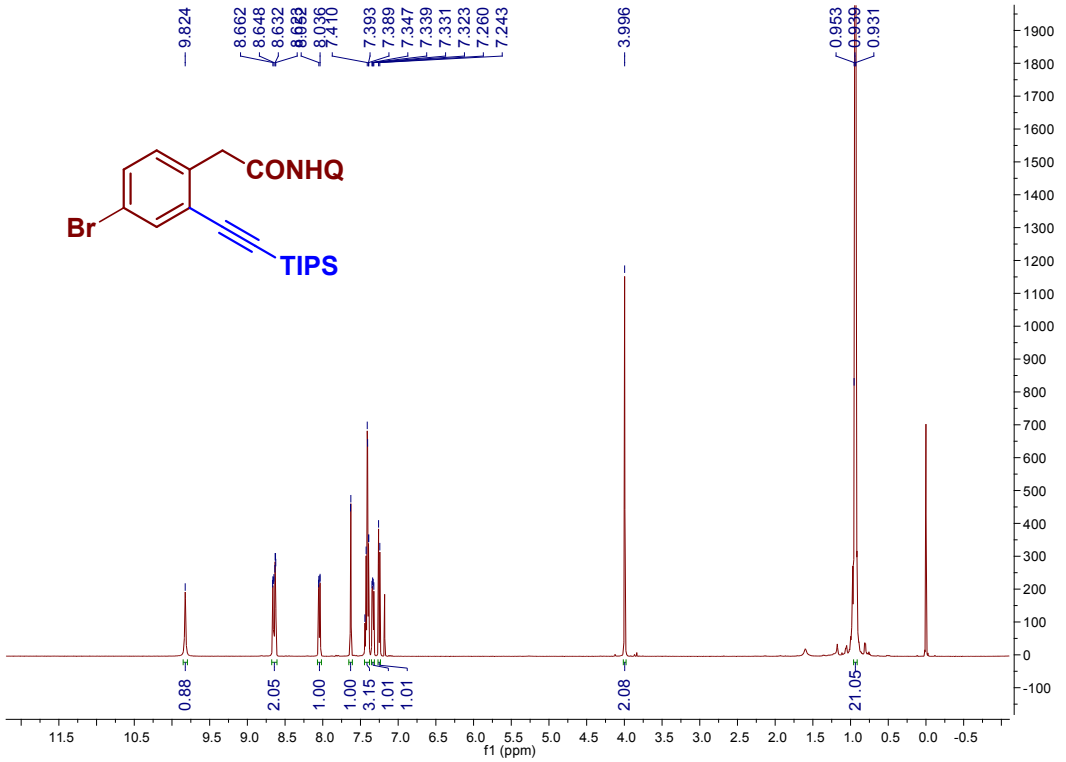

168.303
148.208
136.290
131.458
127.888
125.698
121.630
116.539
103.469
97.540
43.054
18.678
11.279
CONHQ
Cl
TIPS
f1 (ppm)

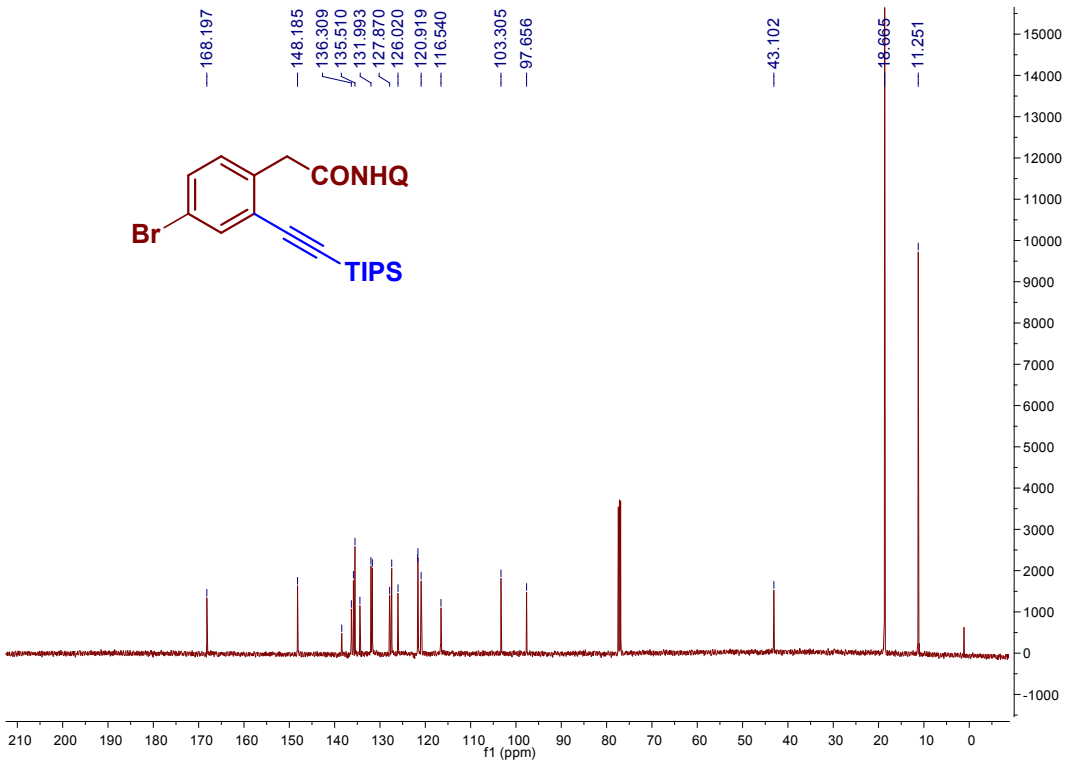
5n'


9.792
8.697
8.693
8.687
8.100
7.518
7.458
7.442
7.437
7.411
7.400
7.390
7.380
4.360
1.019
1.008
0.996
0.984
0.975
0.964
0.952
TIPS
CONHQ
Cl
TIPS
0.95
1.99
1.00
4.01
0.99
1.98
42.25
f1 (ppm)

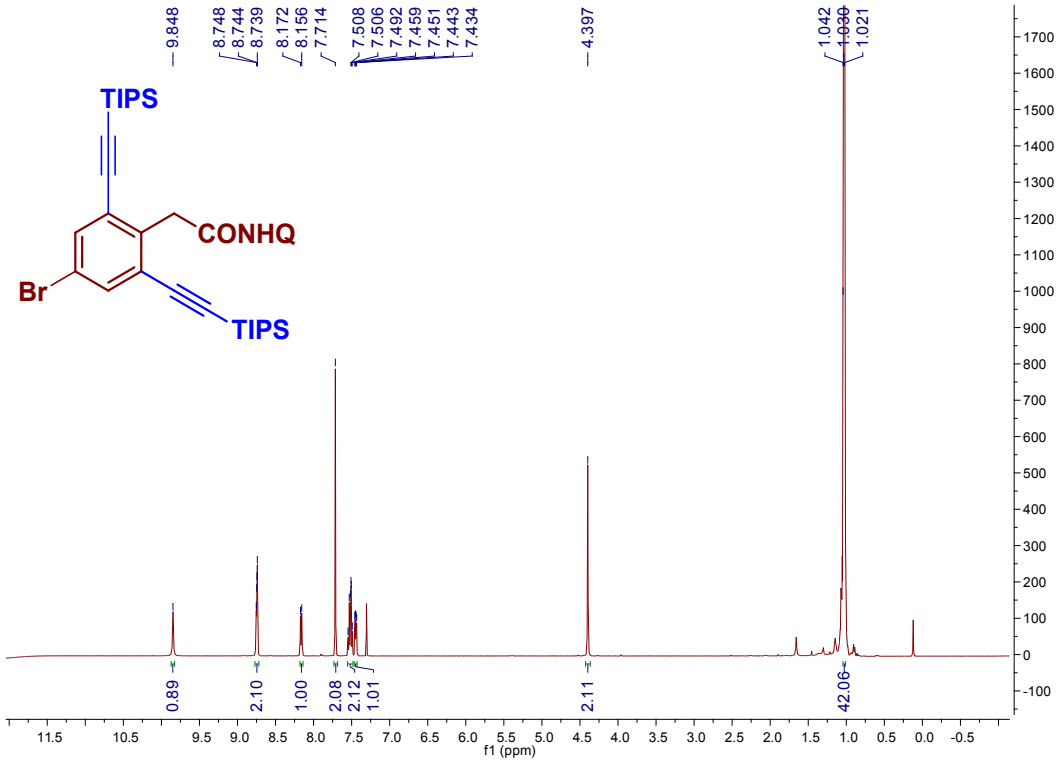

167.026
148.066
137.575
134.702
132.490
126.638
121.260
116.469
103.210
97.992
41.752
18.634
11.265
TIPS
CONHQ
Cl
TIPS
f1 (ppm)

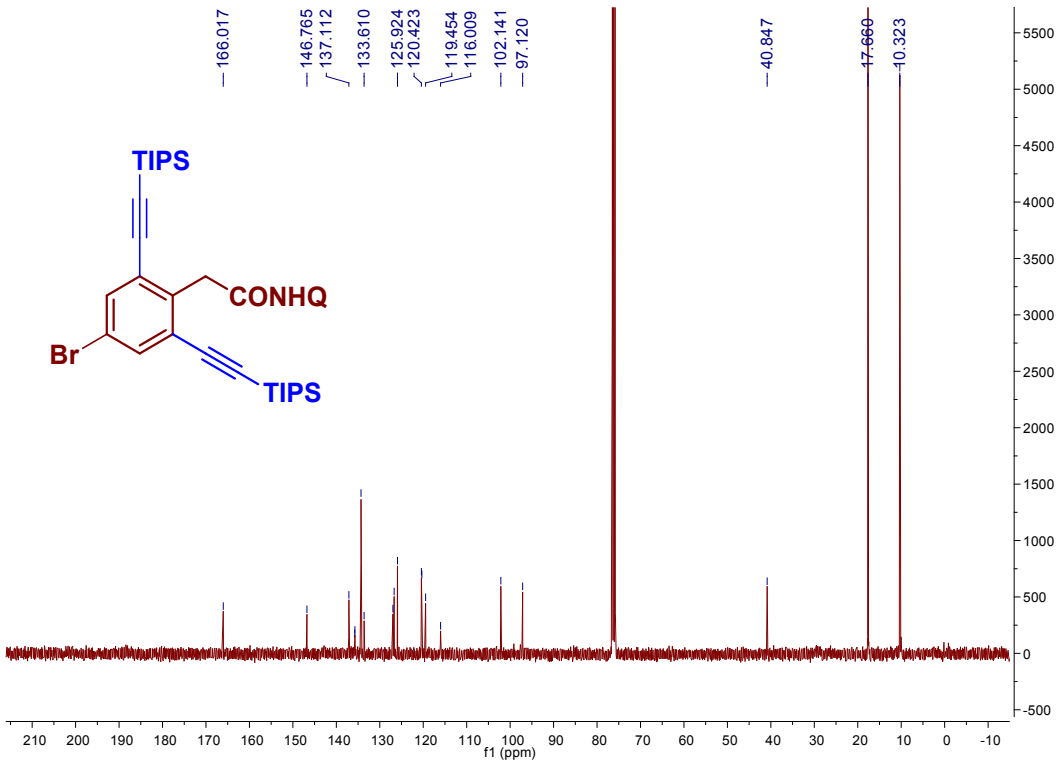
5o


9.824
8.662
8.648
8.632
7.410
7.393
7.389
7.347
7.339
7.331
7.323
7.260
7.243
3.996
0.953
0.939
0.931
CONHQ
Br
TIPS
0.88
2.05
1.00
1.00
3.15
1.01
1.01
2.08
21.05
f1 (ppm)

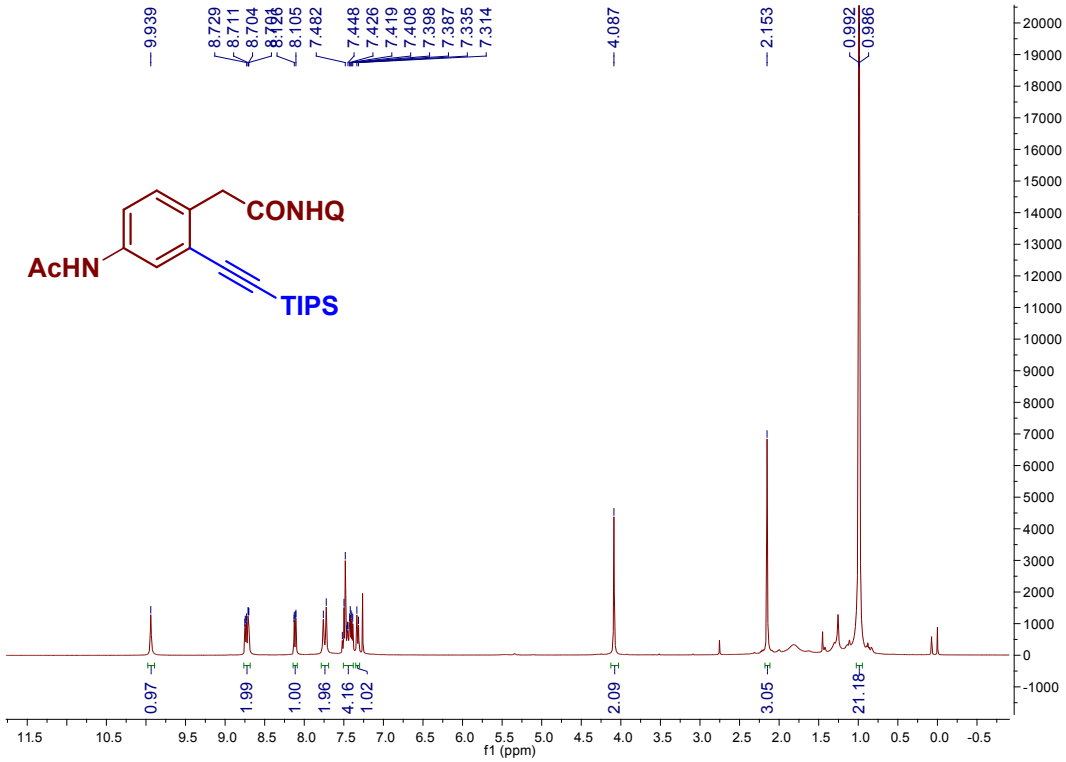

168.197
148.185
136.309
135.510
131.993
127.870
126.020
120.919
116.540
103.305
97.656
43.102
18.665
11.251
CONHQ
Br
TIPS
f1 (ppm)

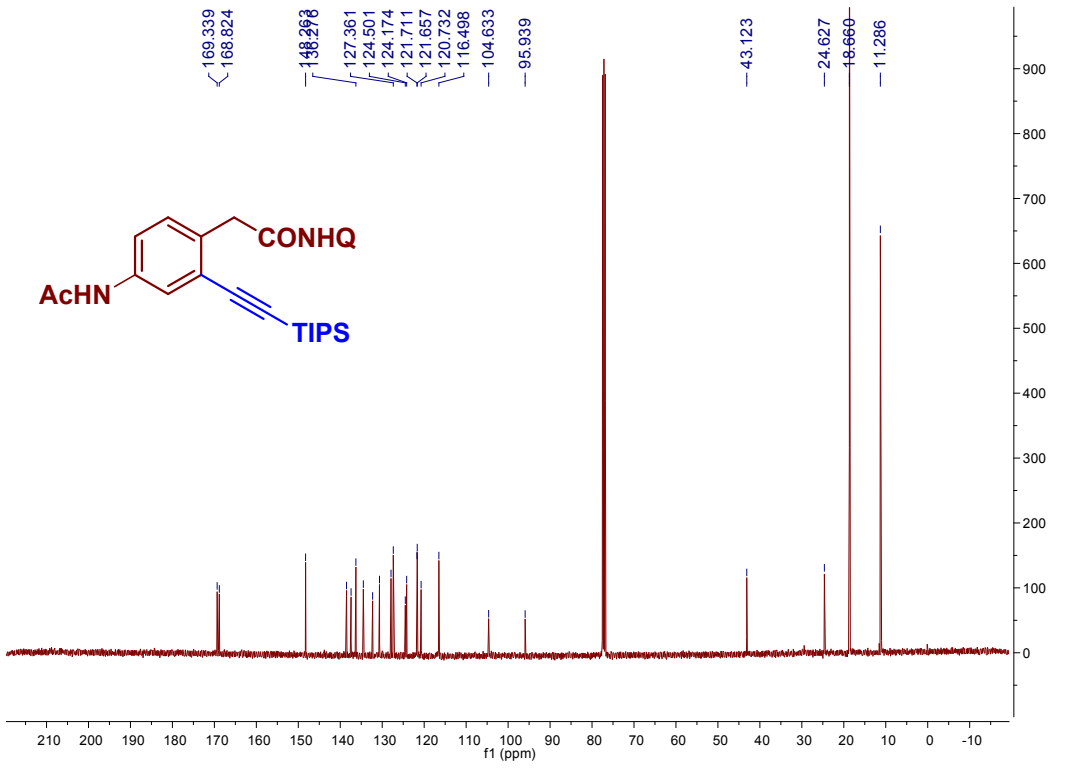
5o'


9.848
8.748
8.744
8.739
8.172
8.156
7.714
7.508
7.506
7.492
7.459
7.451
7.443
7.434
4.397
1.042
1.030
1.021
TIPS
CONHQ
Br
TIPS
0.89
2.10
1.00
2.08
2.12
1.01
2.11
42.06
f1 (ppm)

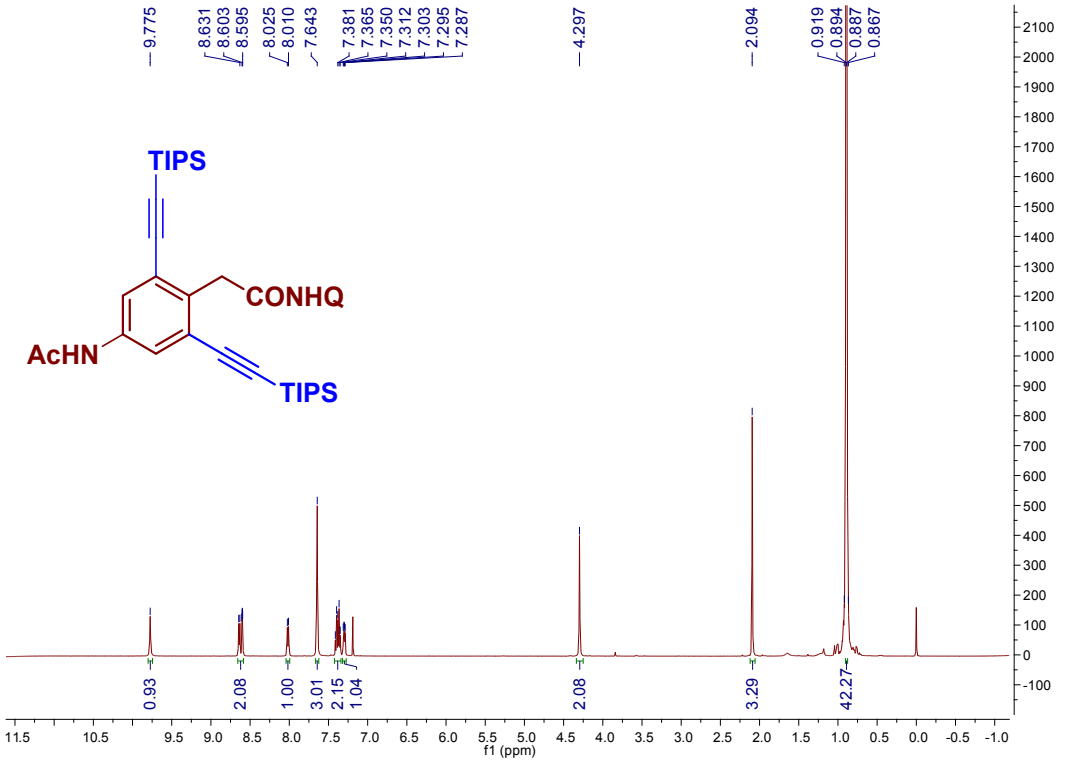

166.017
146.765
137.112
133.610
125.924
120.423
119.454
116.009
102.141
97.120
40.847
17.660
10.323
TIPS
CONHQ
Br
TIPS
f1 (ppm)

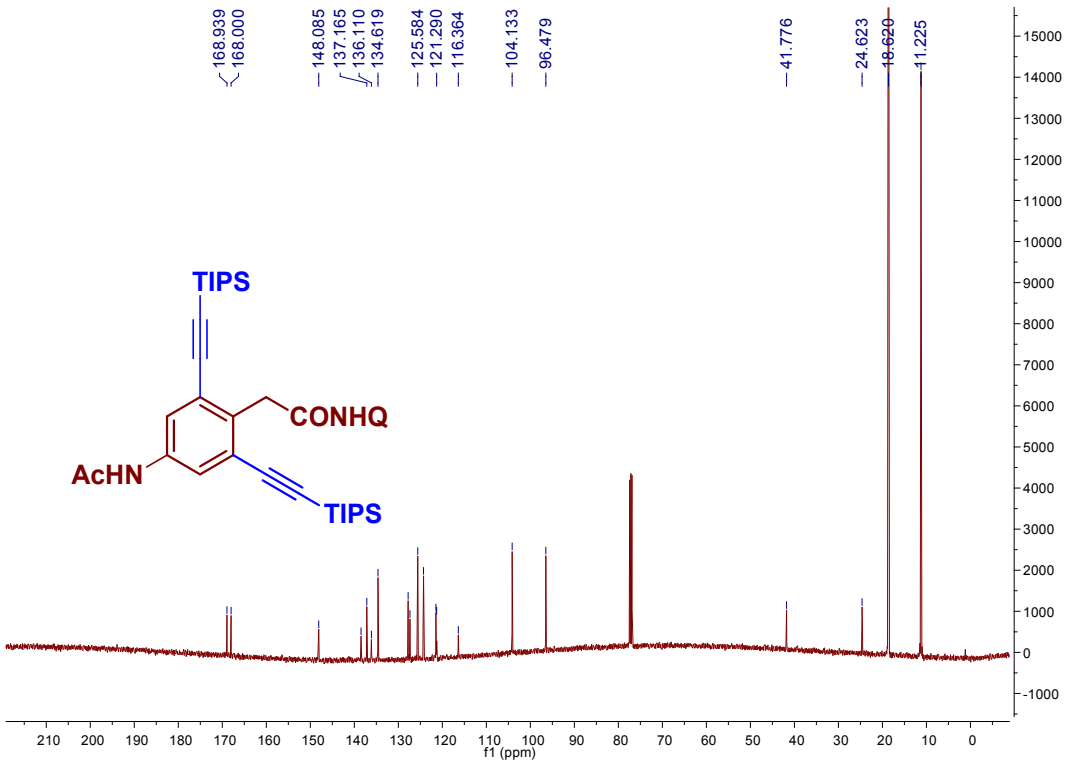
5p


9.939
8.729
8.711
8.704
8.126
8.105
7.482
7.448
7.426
7.419
7.408
7.398
7.387
7.335
7.314
4.087
2.153
0.992
0.986
CONHQ
AcHN
TIPS
0.97
1.99
1.00
1.96
4.16
1.02
2.09
3.05
21.18
f1 (ppm)

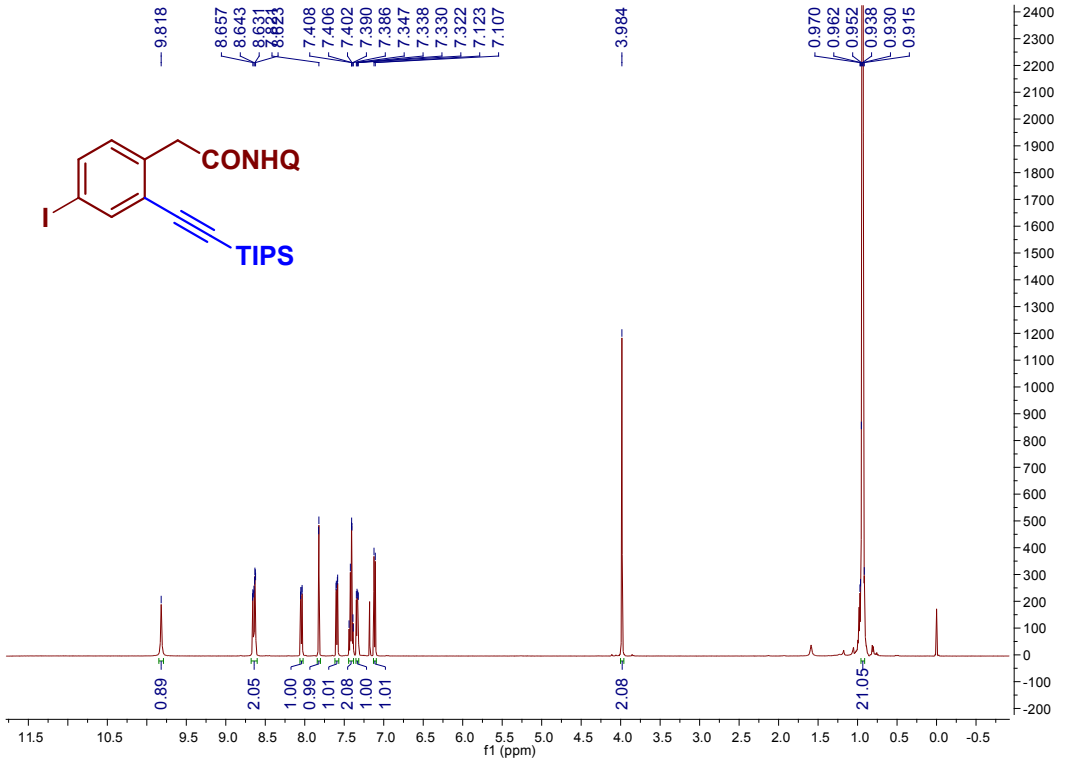

169.339
168.824
148.293
135.276
127.361
124.501
124.174
121.711
121.657
120.732
116.498
104.633
95.939
43.123
24.627
18.660
11.286
CONHQ
AcHN
TIPS
f1 (ppm)

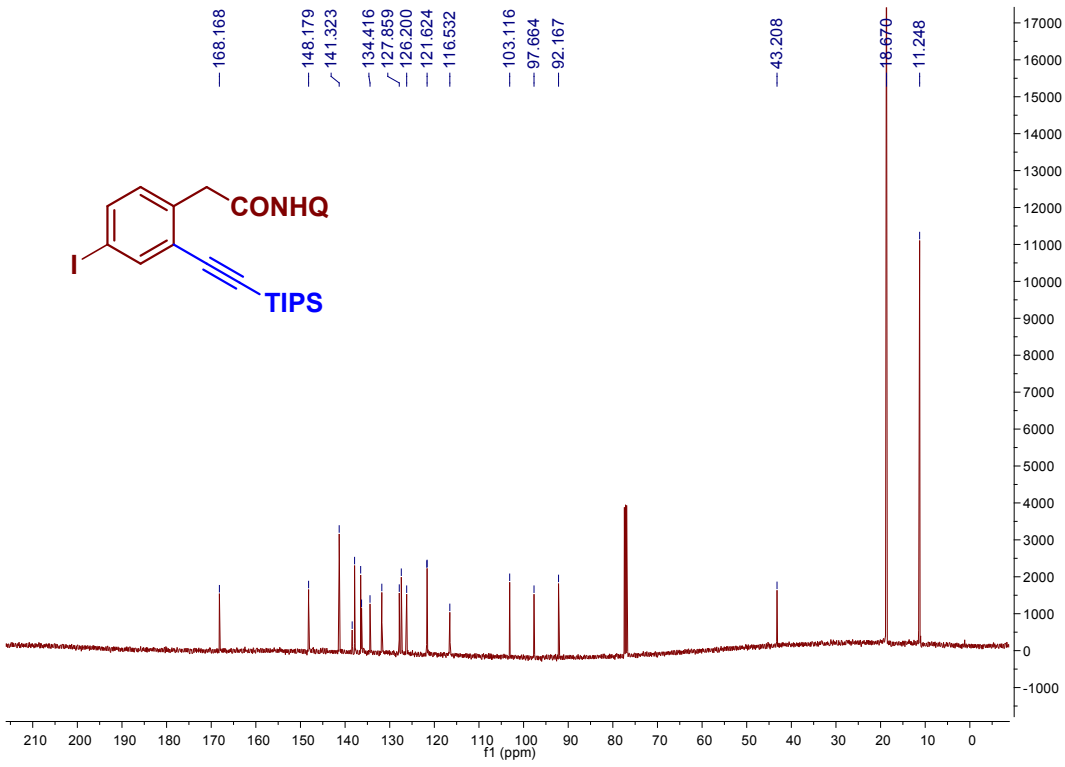
5p'


9.775
8.631
8.603
8.595
8.025
8.010
7.643
7.381
7.365
7.350
7.312
7.303
7.295
7.287
4.297
2.094
0.919
0.894
0.887
0.867
TIPS
CONHQ
AcHN
TIPS
0.93
2.08
1.00
3.01
2.15
1.04
2.08
3.29
42.27
f1 (ppm)

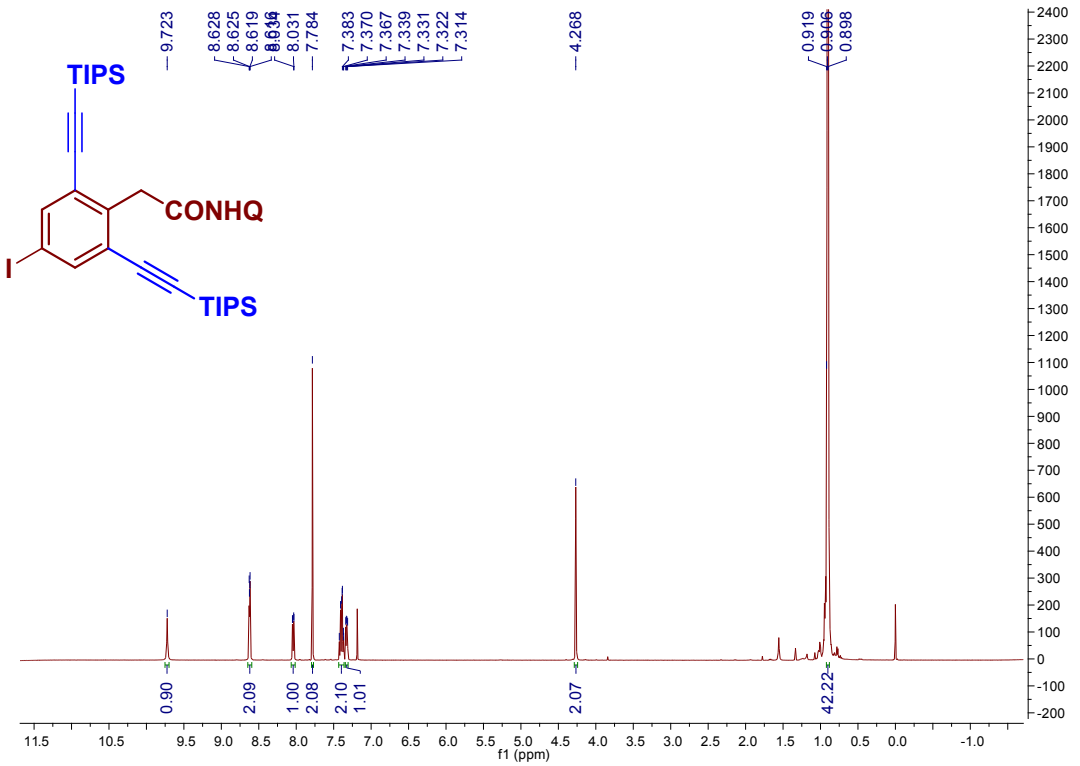

168.939
168.000
148.085
137.165
136.110
134.619
125.584
121.290
116.364
104.133
96.479
41.776
24.623
18.620
11.225
TIPS
CONHQ
AcHN
TIPS
f1 (ppm)

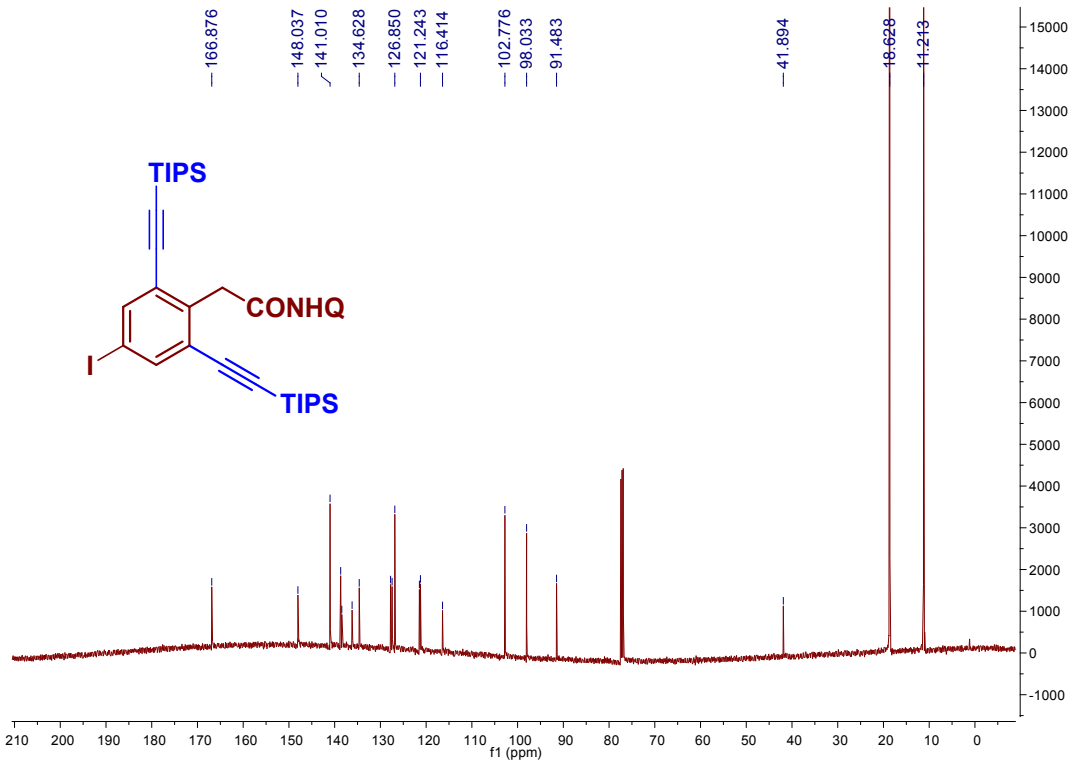
5q


9.818
8.657
8.643
8.631
8.623
7.408
7.406
7.402
7.390
7.386
7.347
7.338
7.330
7.322
7.123
7.107
3.984
0.970
0.962
0.952
0.938
0.930
0.915
CONHQ
I
TIPS
0.89
2.05
1.00
0.99
1.01
2.08
1.00
1.01
2.08
21.05
f1 (ppm)

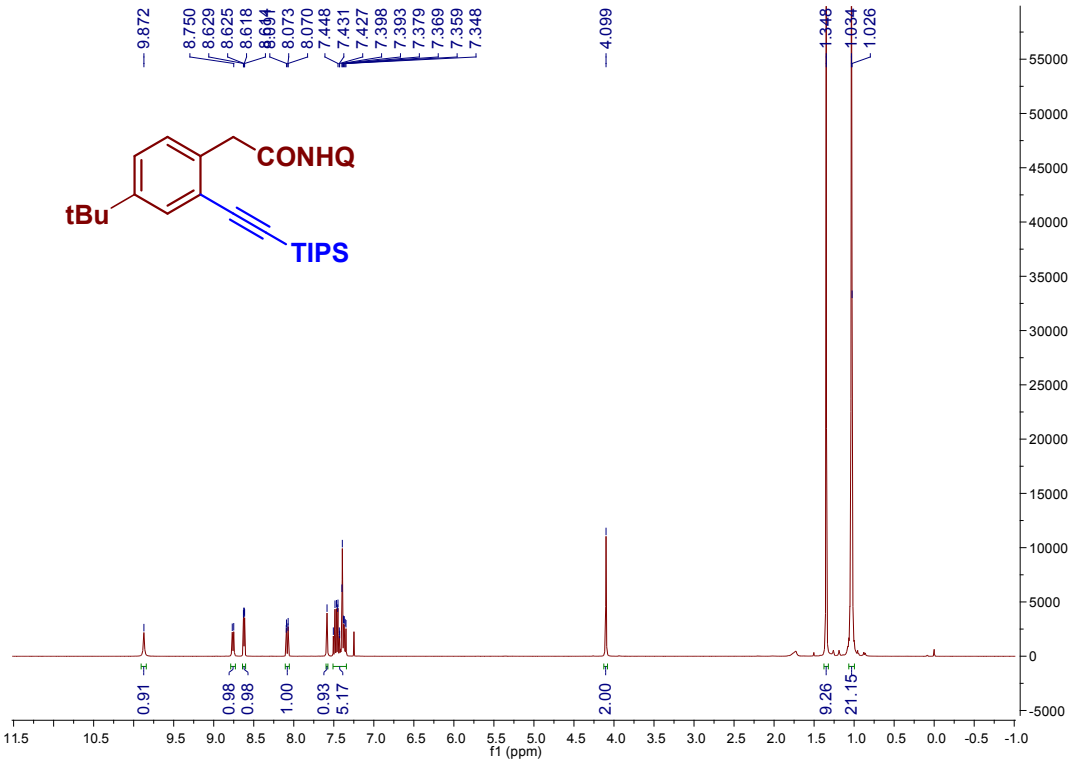

168.168
148.179
141.323
134.416
127.859
126.200
121.624
116.532
103.116
97.664
92.167
43.208
18.670
11.248
CONHQ
I
TIPS
f1 (ppm)

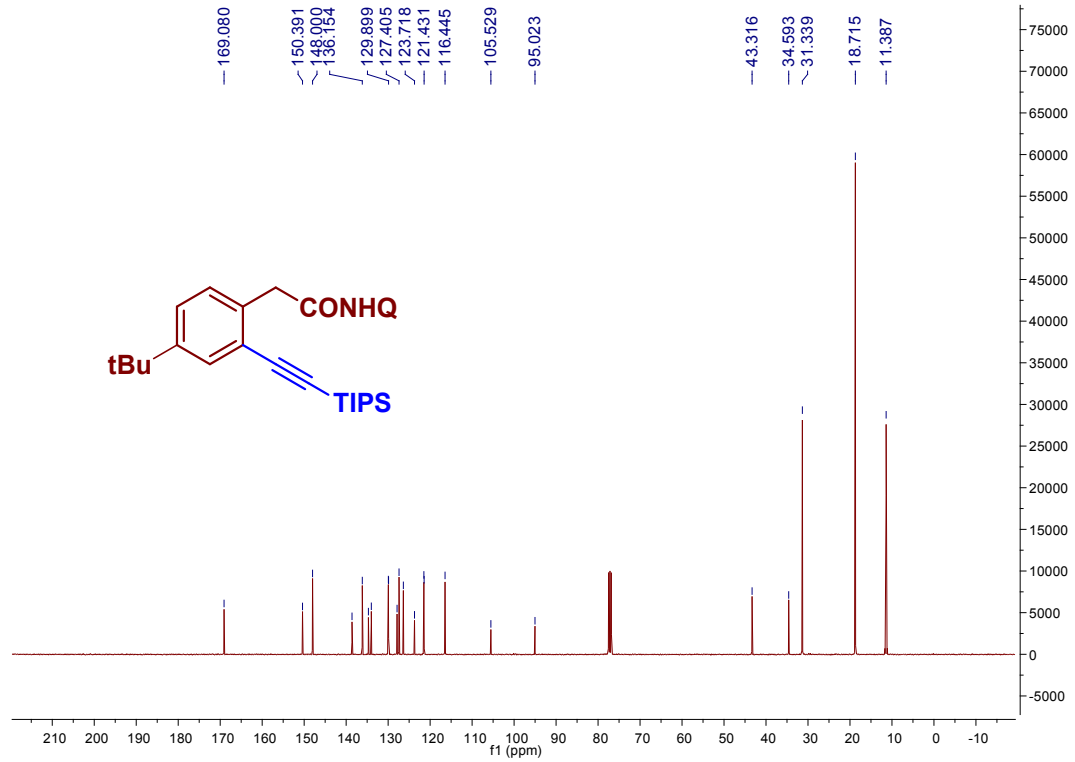
5q'


TIPS
CONHQ
I
TIPS
9.723
8.628
8.625
8.619
8.034
8.031
7.784
7.383
7.370
7.367
7.339
7.331
7.322
7.314
4.268
0.919
0.906
0.898
0.90
2.09
1.00
2.08
2.10
1.01
2.07
42.22
f1 (ppm)

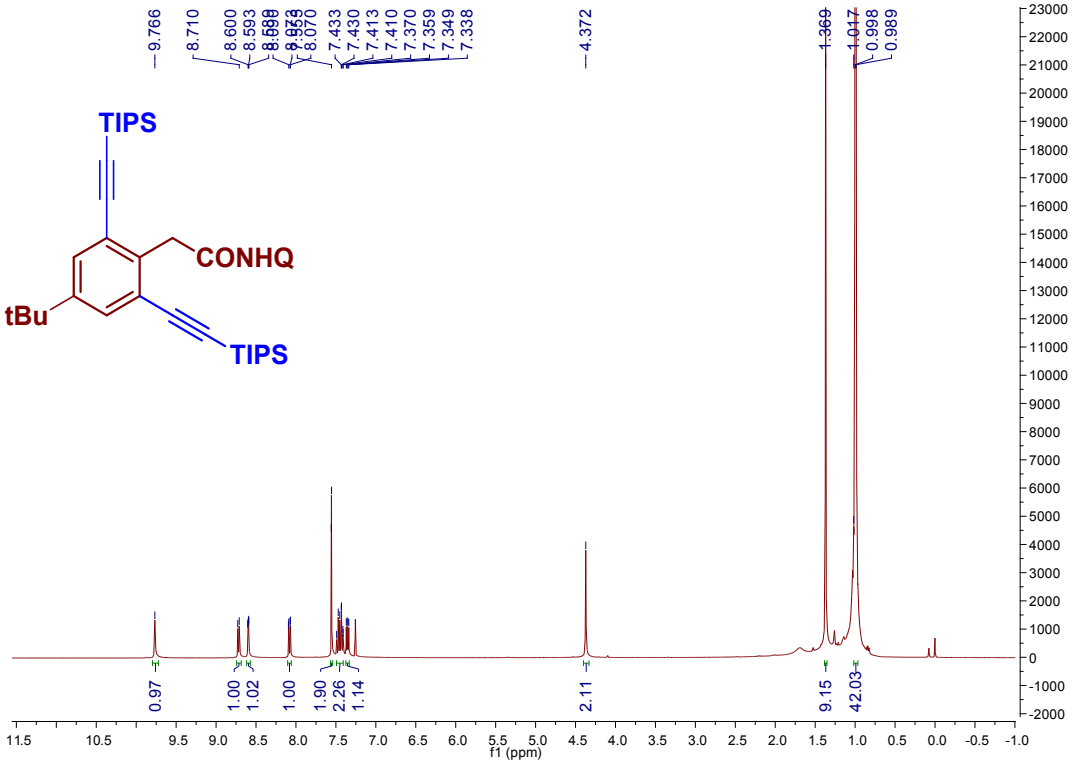

TIPS
CONHQ
I
TIPS
166.876
148.037
141.010
134.628
126.850
121.243
116.414
102.776
98.033
91.483
41.894
18.628
11.213
f1 (ppm)

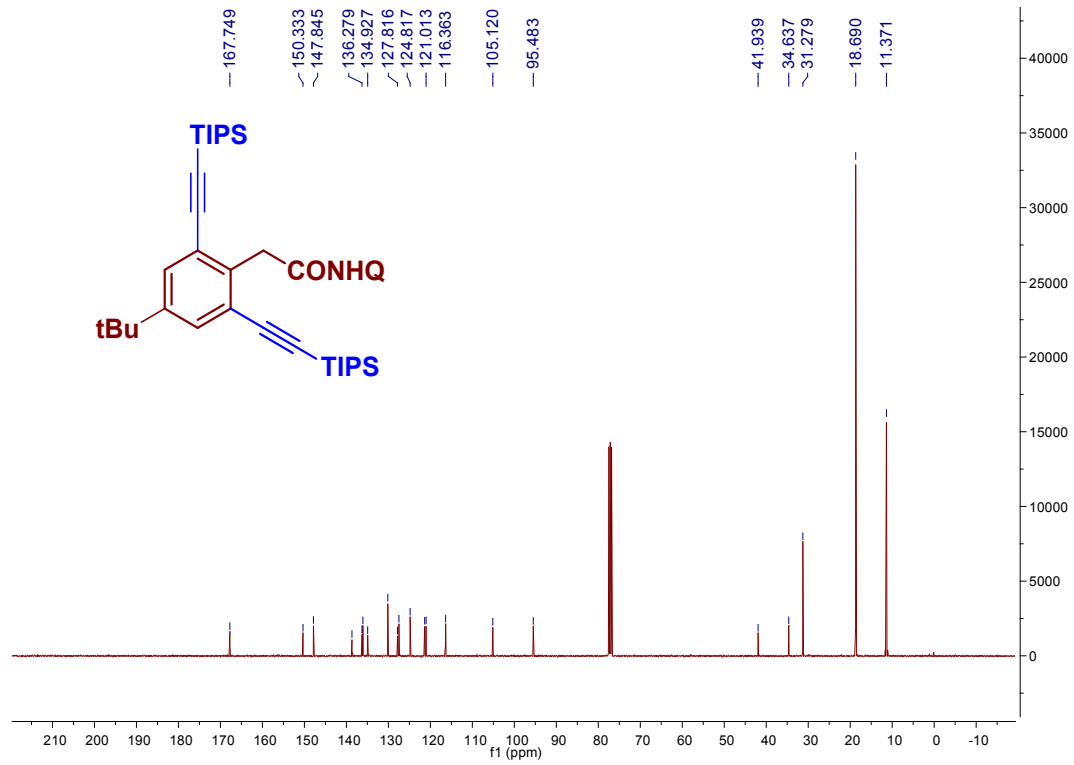
5r


9.872
8.750
8.629
8.625
8.618
8.073
8.070
7.448
7.431
7.427
7.398
7.393
7.379
7.369
7.359
7.348
4.099
1.348
1.034
1.026
CONHQ
tBu
TIPS
0.91
0.98
0.98
1.00
0.93
5.17
2.00
9.26
21.15
f1 (ppm)

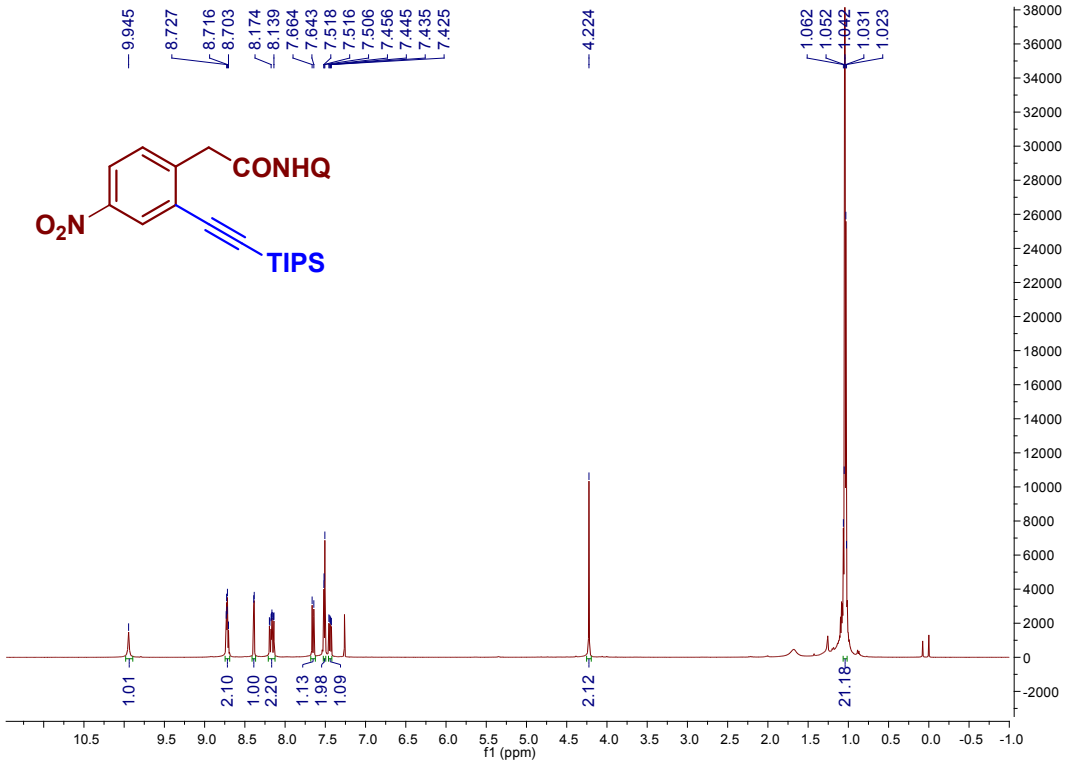

169.080
150.391
148.000
136.154
129.899
127.405
123.718
121.431
116.445
105.529
95.023
43.316
34.593
31.339
18.715
11.387
CONHQ
tBu
TIPS
f1 (ppm)

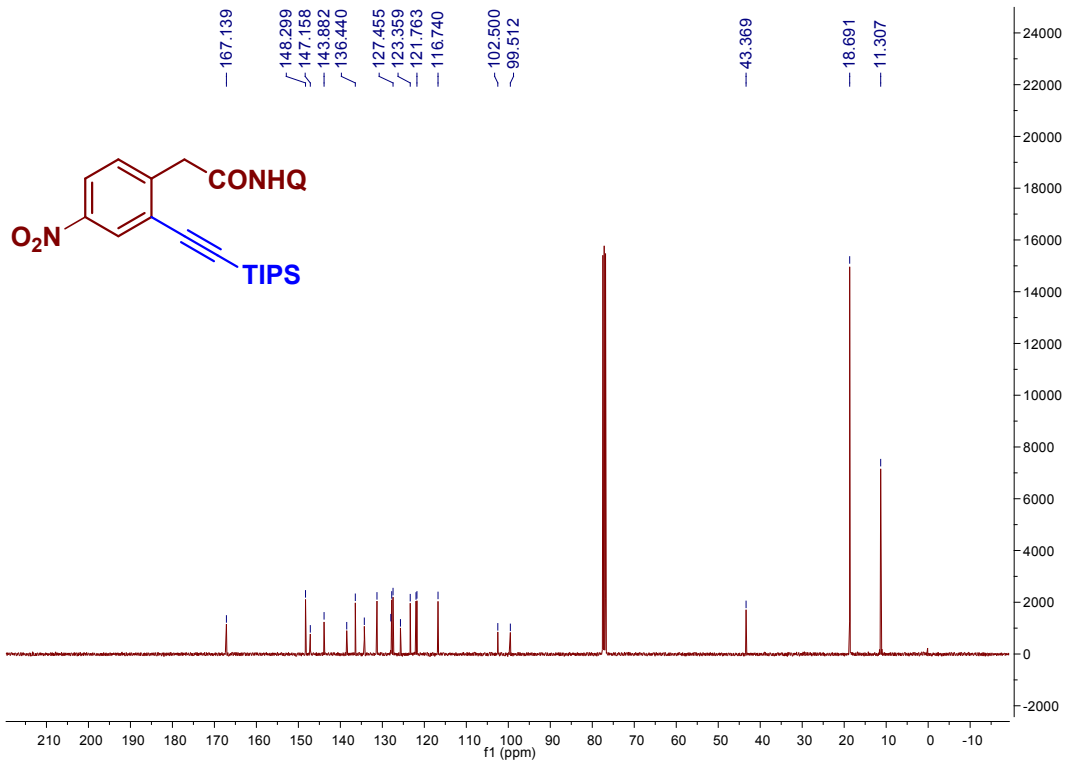
5r'


9.766
8.710
8.600
8.593
8.070
7.433
7.430
7.413
7.410
7.370
7.359
7.349
7.338
4.372
1.369
1.017
0.998
0.989
TIPS
CONHQ
tBu
TIPS
0.97
1.00
1.02
1.00
1.90
2.26
1.14
2.11
9.15
42.03
f1 (ppm)

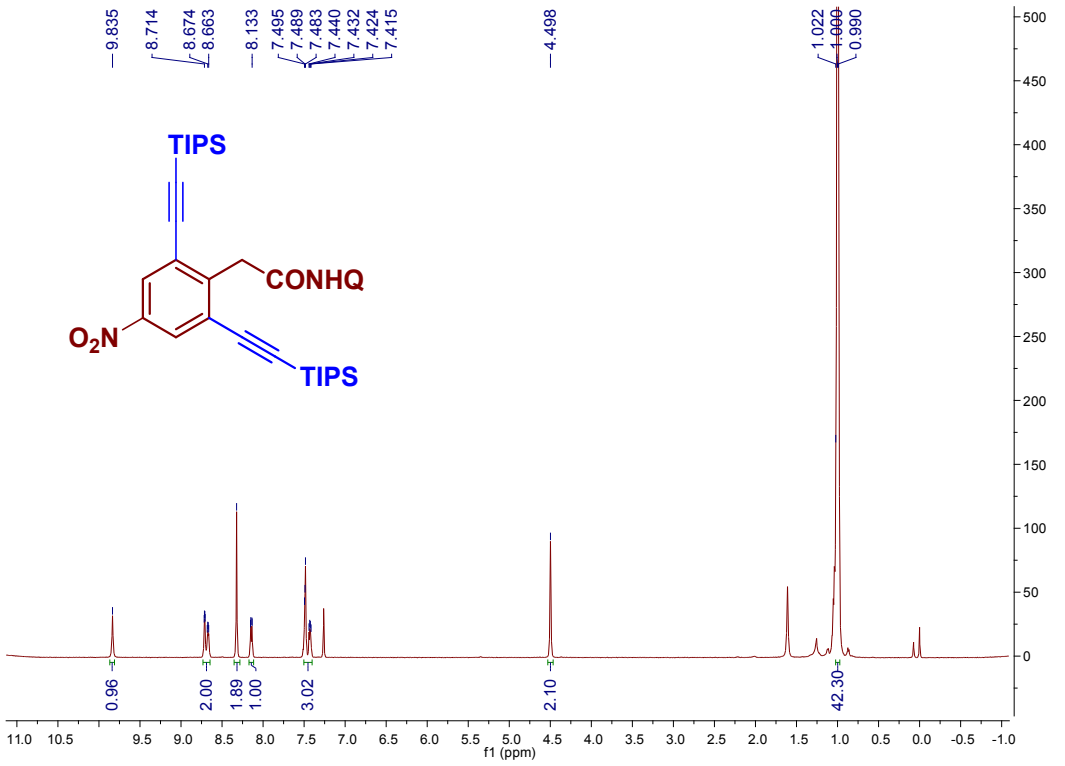

167.749
150.333
147.845
136.279
134.927
127.816
124.817
121.013
116.363
105.120
95.483
41.939
34.637
31.279
18.690
11.371
TIPS
CONHQ
tBu
TIPS
f1 (ppm)

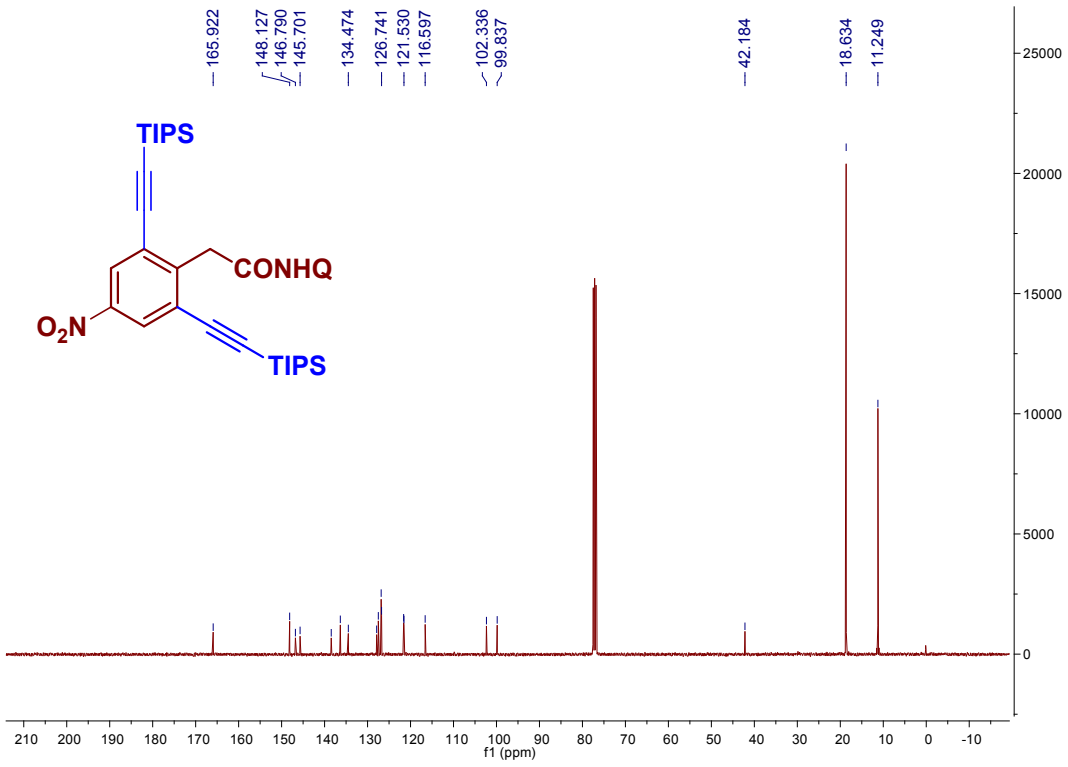
5s


9.945
8.727
8.716
8.703
8.174
8.139
7.664
7.643
7.518
7.516
7.506
7.456
7.445
7.435
7.425
4.224
1.062
1.052
1.042
1.031
1.023
CONHQ
O2N
TIPS
1.01
2.10
1.00
2.20
1.13
1.98
1.09
2.12
21.18
f1 (ppm)

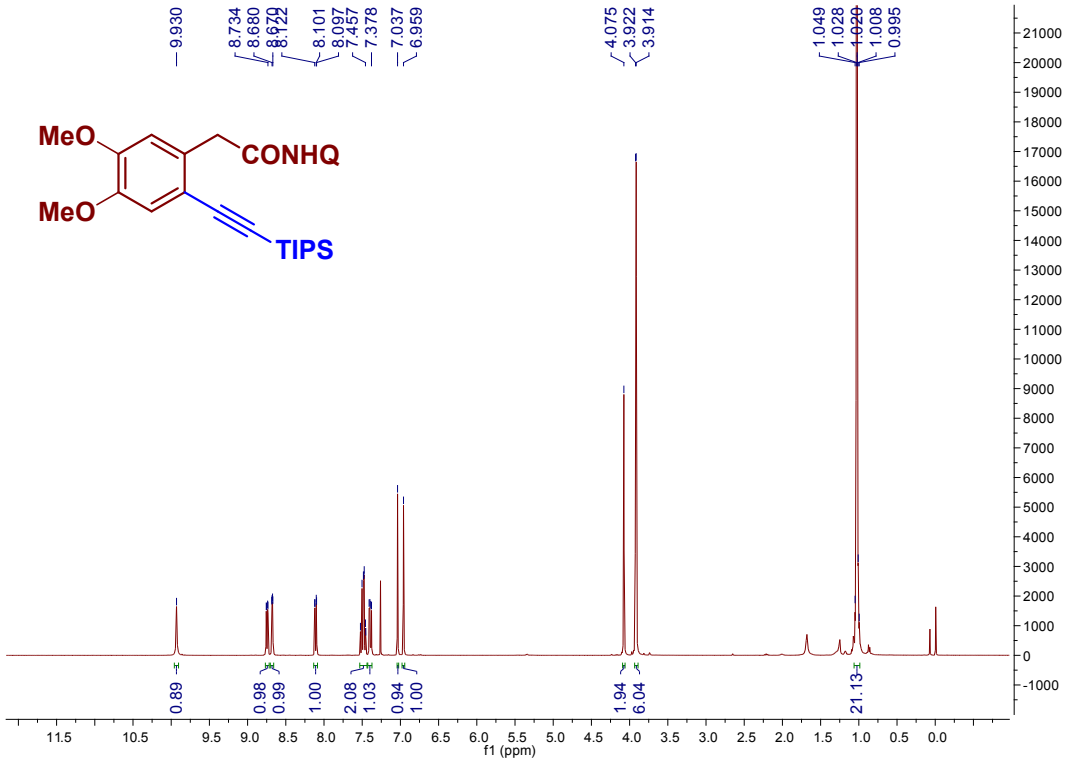

167.139
148.299
147.158
143.882
136.440
127.455
123.359
121.763
116.740
102.500
99.512
43.369
18.691
11.307
CONHQ
O2N
TIPS
f1 (ppm)

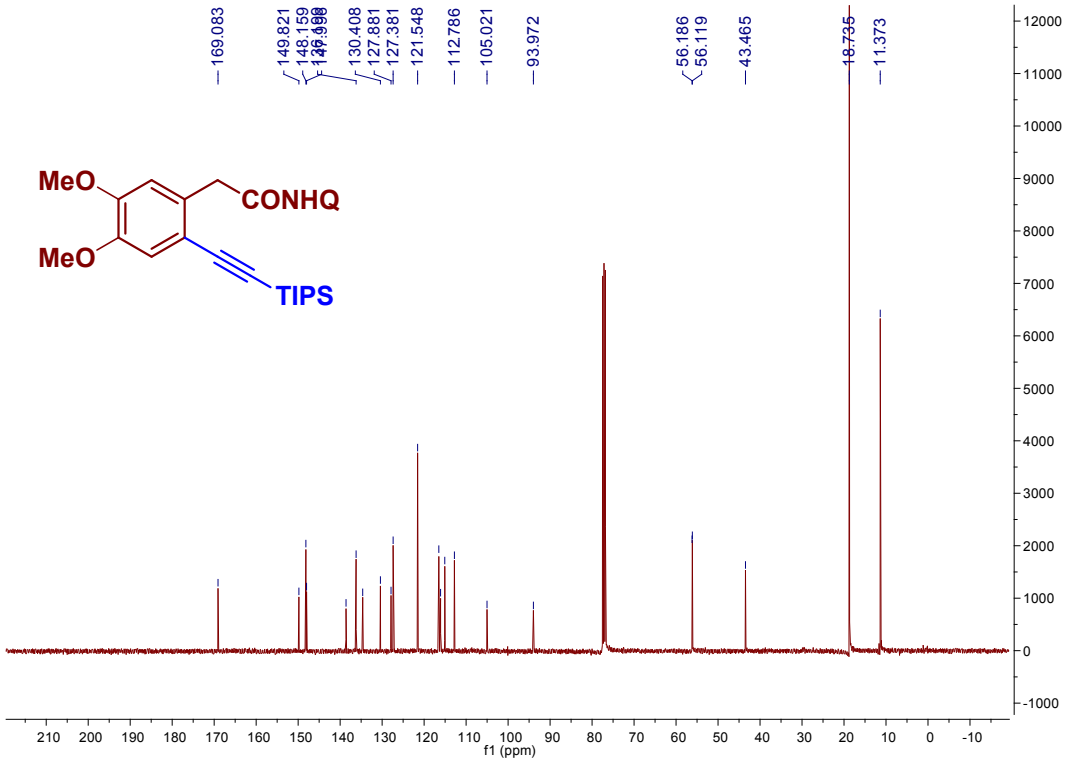
5s'


9.835
8.714
8.674
8.663
8.133
7.495
7.489
7.483
7.440
7.432
7.424
7.415
4.498
1.022
1.000
0.990
TIPS
CONHQ
O2N
TIPS
0.96
2.00
1.89
1.00
3.02
2.10
42.30
f1 (ppm)

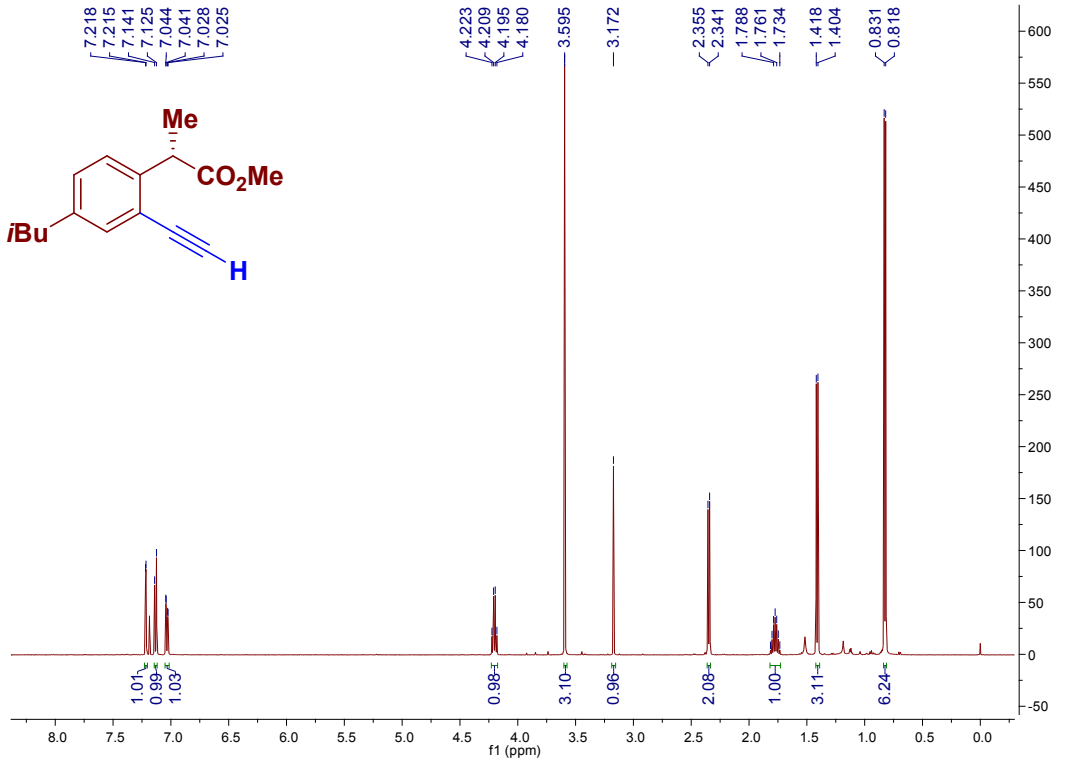

165.922
148.127
146.790
145.701
134.474
126.741
121.530
116.597
102.336
99.837
42.184
18.634
11.249
TIPS
CONHQ
O2N
TIPS
f1 (ppm)

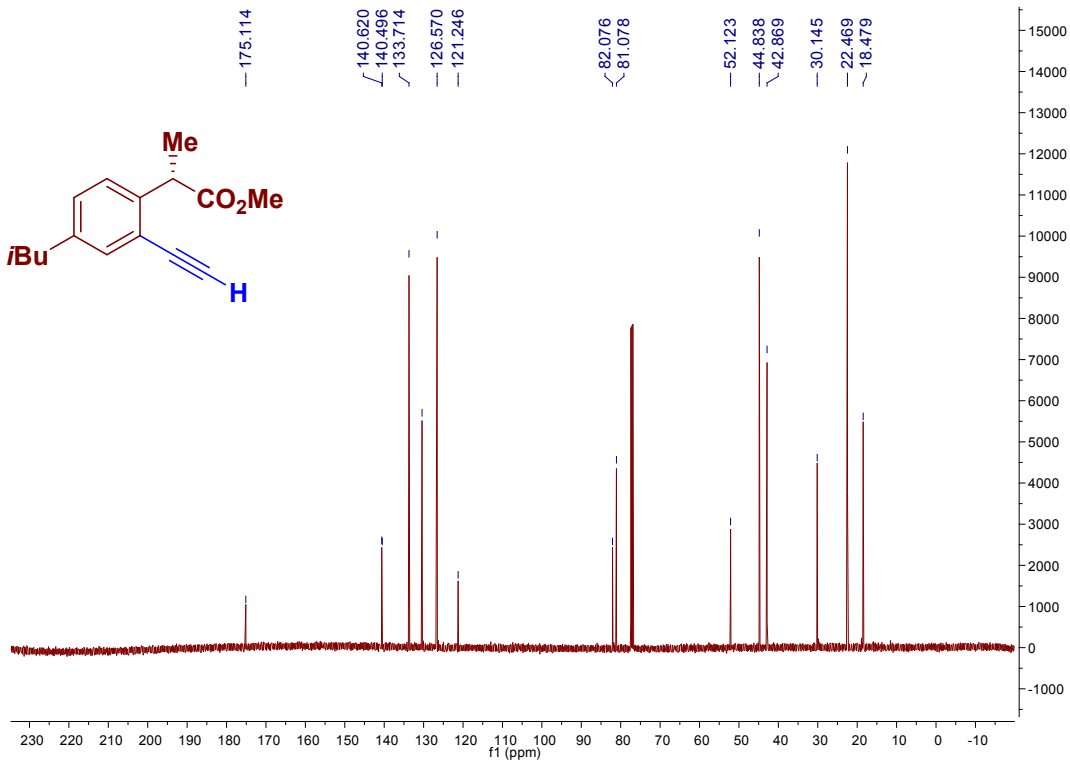
5t


9.930
8.734
8.680
8.670
8.122
8.101
8.097
7.457
7.378
7.037
6.959
4.075
3.922
3.914
1.049
1.028
1.020
1.008
0.995
MeO
MeO
CONHQ
TIPS
0.89
0.98
0.99
1.00
2.08
1.03
0.94
1.00
1.94
6.04
21.13
f1 (ppm)

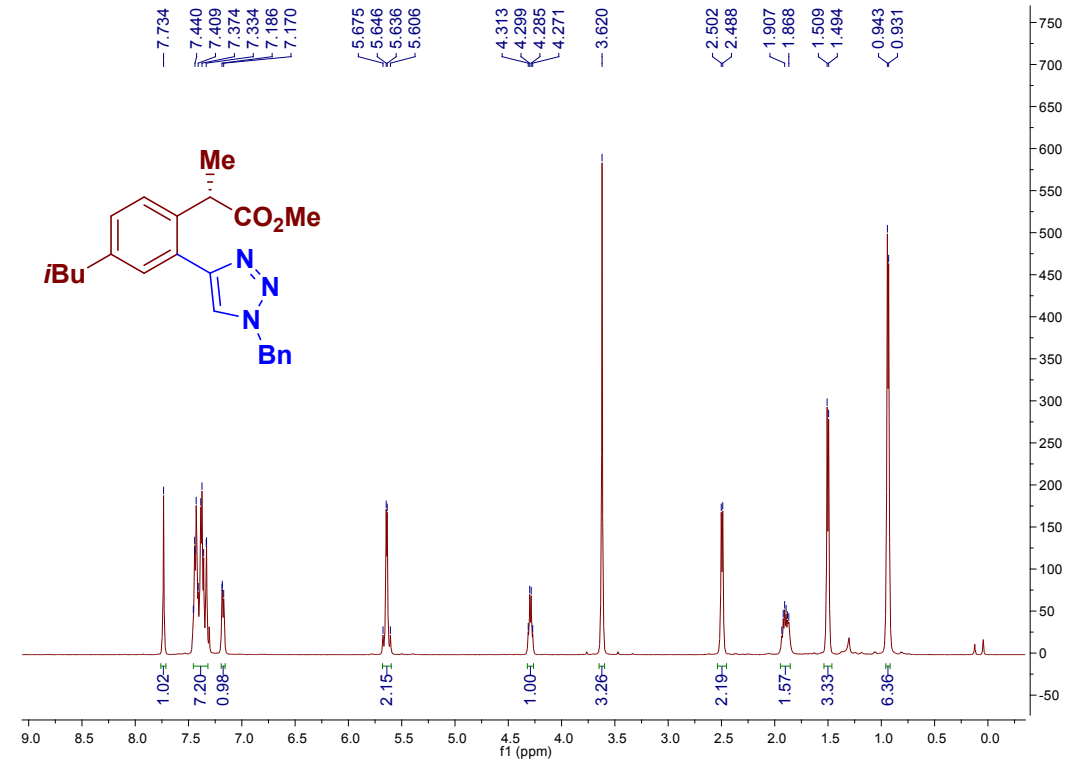

169.083
149.821
148.159
130.408
127.881
127.381
121.548
112.786
105.021
93.972
56.186
56.119
43.465
18.735
11.373
MeO
MeO
CONHQ
TIPS
f1 (ppm)

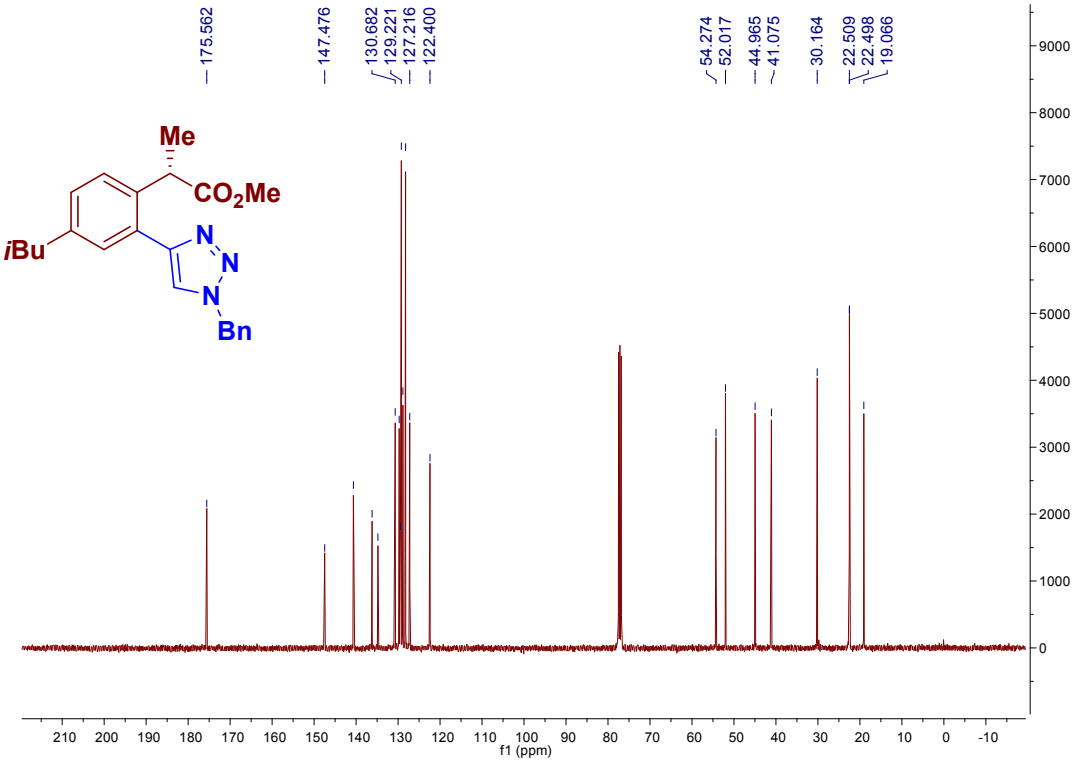
3ac


7.218
7.215
7.141
7.125
7.044
7.041
7.028
7.025
4.223
4.209
4.195
4.180
3.595
3.172
2.355
2.341
1.788
1.761
1.734
1.418
1.404
0.831
0.818
Me
CO2Me
iBu
H
1.01
0.99
1.03
0.98
3.10
0.96
2.08
1.00
3.11
6.24
f1 (ppm)


175.114
140.620
140.496
133.714
126.570
121.246
82.076
81.078
52.123
44.838
42.869
30.145
22.469
18.479
Me
CO2Me
iBu
H
f1 (ppm)

3ad


7.734
7.440
7.409
7.374
7.334
7.186
7.170
5.675
5.646
5.636
5.606
4.313
4.299
4.285
4.271
3.620
2.502
2.488
1.907
1.868
1.509
1.494
0.943
0.931
Me
CO2Me
iBu
N
N
N
Bn
1.02
7.20
0.98
2.15
1.00
3.26
2.19
1.57
3.33
6.36
f1 (ppm)


175.562
147.476
130.682
129.221
127.216
122.400
54.274
52.017
44.965
41.075
30.164
22.509
22.498
19.066
Me
CO2Me
iBu
N
N
N
Bn
f1 (ppm)