Electronic Supplementary Material (ESI) for ChemComm.

Highly Effective Ni-Catalyzed Alkynylation of Unactivited (Hetero)arene C-H Bonds with Alkynes

Yue-Jin Liu,[a] Yan-Hua Liu,[a] Sheng-Yi Yan,[a] and Bing-Feng Shi*[a,b]

[a]Department of Chemistry, Zhejiang University, Hangzhou 310027, China

[b]State Key Laboratory of Bioorganic & Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Supporting Information

Table of Contents:

1. General Information

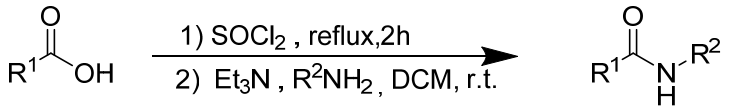
Trimethyacetonitrile was dried by Sodium, distilled under reduced pressure and stored under nitrogen. $Ni(OTf)_2$ was prepared by reported procedure.[1] The other materials and solvents were purchased from Aladdin and other commercial suppliers and used without additional purification. NMR spectra were recorded on a Bruke Avance operating for ^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, and ^{19}F NMR at 376 MHz, using TMS as internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal (77.16 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrumentor a low-resolution MS instrument using EI ionization.

2. Experimental Section

2.1 Praperation of Substrates

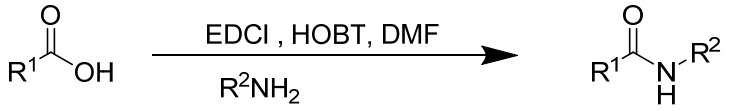
Compounds **1a-1e, 1g-1h, 1j-1m, 1o, 1q-1t, 1a-*d*$_5$, 4b** and **4d-4g** were known compounds.[2, 3] Compounds **1f, 1i, 1n, 1p, 1u, 1v** and **1ae** were prepared following **typical method A or method B**. [3]

General Procedure for the Preparation of Starting Materials (Method A):

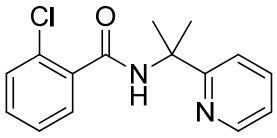


A solution of an acid (5 mmol) was refluxed in 5 mL $SOCl_2$ for 2h and cooled to RT. The excess of $SOCl_2$ was removed under vacuum to give corresponding acid choloride. The acid choloride was then re-dissolved in 5 mL dry CH_2Cl_2 and added dropwiseto a 20 mL dry CH_2Cl_2 solution containing amine (5 mmol) and Et_3N (10 mmol) at 0 ^oC. After stirring for 6h at ambient temperature, the resulting mixture was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.

General Procedure for the Preparation of Starting Materials (Method B):

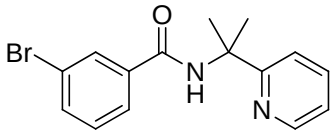


A mixture of amine (5 mmol), 6-bromohexanoic acid (5 mmol), EDCI (5.5 mmol) and HOBT (5.5 mmol) in anhydrous DMF (20 mL) was stirred at room temperature overnight. Water was added and the mixture was extracted with diethyl ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.



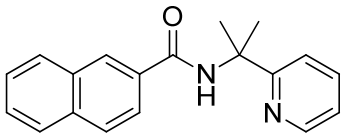
2-Chloro-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 1f

The title compound **1f** was prepared according to the general procedure (Method A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.0 Hz, 1H), 8.36 (br, 1H), 7.73 (td, *J* = 7.6, 2.0 Hz, 1H), 7.63 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.19 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 1H), 1.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.94, 164.34, 147.75, 137.25, 137.06, 130.99, 130.79, 129.75, 127.02, 122.04, 119.58, 57.63, 27.64; HRMS (EI-TOF) calcd for $C_{15}H_{15}N_2OCl$ (M^+): 274.0873, found: 274.0874.



3-bromo-N-(2-(pyridin-2-yl)propan-2-yl)benzamide **1i**

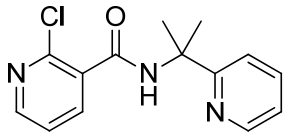
The title compound **1i** was prepared according to the general procedure (Method A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (br, 1H), 8.57 (d, *J* = 4.8 Hz, 1H), 8.05 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.77 (td, *J* = 8.0, 1.6 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.24 (dd, *J* = 7.6, 6.0 Hz, 1H), 1.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.84, 164.54, 147.71, 138.23, 137.47, 134.13, 130.49, 130.12, 125.64, 122.83, 122.18, 119.66, 56.88, 27.53.



N-(2-(pyridin-2-yl)propan-2-yl)-2-naphthamide 1l

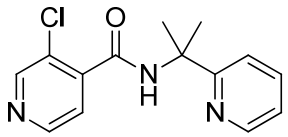
The title compound **1l** was prepared according to the general procedure (Method A). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (ddd, *J* = 4.4, 2.0, 0.8 Hz, 1H), 8.39 (m, 1H), 8.34 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.88 (m, 1H), 7.78 – 7.69 (m, 2H), 7.57 – 7.45

(m, 4H), 7.20 (ddd, J = 6.8, 5.6, 0.8 Hz, 1H), 1.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.89, 164.42, 147.67, 137.18, 135.94, 133.77, 130.35, 130.10, 128.22, 126.86, 126.22, 125.68, 124.86, 121.94, 119.49, 57.29, 27.67; HRMS (EI-TOF) calcd for $C_{15}H_{15}N_3O_3$ (M^+): 289.1419, found: 289.1425.



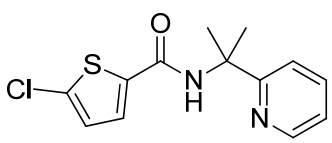
2-chloro-N-(2-(pyridin-2-yl)propan-2-yl)nicotinamide 1n

The title compound **1n** was prepared according to the general procedure (Method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (br, 1H), 8.48 (ddd, J = 6.8, 4.0, 1.6 Hz, 2H), 8.02 (dd, J = 7.6, 1.6 Hz, 1H), 7.76 (td, J = 8.0, 1.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 7.6, 4.8 Hz, 1H), 7.22 (ddd, J = 7.6, 4.8, 0.8 Hz, 1H), 1.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.12, 163.90, 150.50, 147.67, 139.00, 137.41, 133.20, 122.68, 122.20, 119.54, 57.75, 27.46.



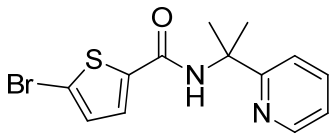
3-chloro-N-(2-(pyridin-2-yl)propan-2-yl)isonicotinamide 1p

The title compound **1p** was prepared according to the general procedure (Method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (br, 1H), 8.66 (d, J = 4.0 Hz, 1H), 8.57 (d, J = 4.8 Hz, 1H), 8.48 (d, J = 4.0 Hz, 1H), 7.76 (m, 1H), 7.54 (d, J = 4.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.23 (m, 1H), 1.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.67, 163.45, 150.46, 148.27, 147.59, 143.29, 137.49, 128.21, 123.26, 122.26, 119.52, 57.78, 27.46.



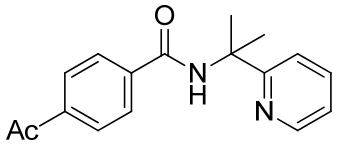
4-chloro-N-(2-(pyridin-2-yl)propan-2-yl)thiophene-2-carboxamide 1u

The title compound **1u** was prepared according to the general procedure (Method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (br, 1H), 8.54 (d, *J* = 4.8 Hz, 1H), 7.76 (td, *J* = 8.0, 1.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 4.0 Hz, 1H), 7.24 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 1H), 6.90 (d, *J* = 4.0 Hz, 1H), 1.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.30, 160.12, 147.64, 139.89, 137.51, 134.57, 126.92, 126.79, 122.23, 119.63, 56.98, 27.66; HRMS (EI-TOF) calcd for $C_{13}H_{13}ClN_2OS$ (M^+): 280.0437, found: 280.0436.



5-bromo-N-(2-(pyridin-2-yl)propan-2-yl)thiophene-2-carboxamide 1v

The title compound **1v** was prepared according to the general procedure (Method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (br, 1H), 8.55 (d, *J* = 4.8 Hz, 1H), 7.76 (td, *J* = 8.0, 1.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.24 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.04 (d, *J* = 4.0 Hz, 1H), 1.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 164.28, 160.03, 147.64, 142.76, 137.51, 130.60, 127.67, 122.23, 119.63, 117.20, 56.99, 27.65; HRMS (EI-TOF) calcd for $C_{13}H_{13}BrN_2OS$ (M^+): 323.9932, found: 323.9939.

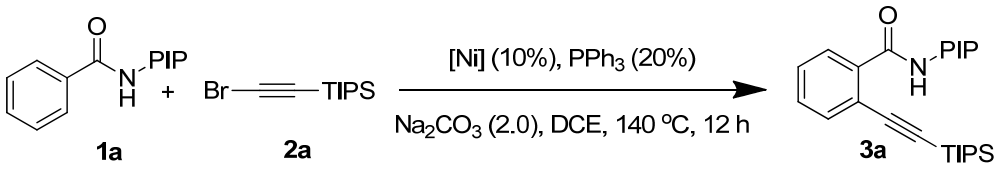


4-acetyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 1ae

The title compound **1ae** was prepared according to the general procedure (Method A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (br, 1H), 8.56 (d, *J* = 4.2 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.78 (td, *J* = 8.0, 1.7 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 1H), 2.65 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.76, 165.33, 164.53, 147.67, 140.16, 139.01, 137.55, 128.61, 127.45, 122.25, 119.72, 56.91, 27.53, 26.97.

2.2 Optimization of Reaction Conditions

Screening of Ni Salts

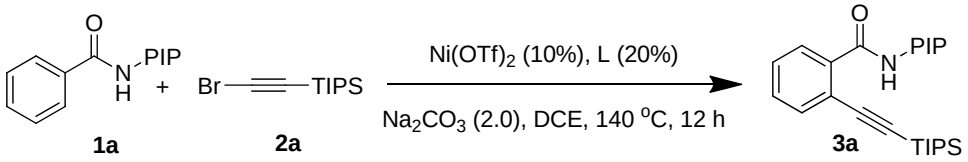


1a **2a** **3a**

Entry[a]	Ni (10%)	Yield[b] of 3a
1	$Ni(OTf)_2$	28%
2	$NiCl_2{\cdot}6H_2O$	trace
3	$NiBr_2$	N.D.
4	$NiCl_2$	trace
5	$(dppe)NiCl_2$	trace
6	$(dppp)NiCl_2$	trace
7	$(PPh_3)_2NiCl_2$	trace
8	$Ni(cod)_2$	trace
9	$(DME)NiCl_2$	trace
10	$NiCp_2$	trace
11	$Ni(acac)_2$	22%
12	$Ni(OAc)_2{\cdot}4H_2O$	trace

[a] The reactions were carried out **1a** (0.1 mmol), **2a** (0.2 mmol), [Ni] (0.01 mmol), DME (0.02 mmol), Na_2CO_3 (0.2 mmol), DCE (1 mL), N_2, 140°C. [b] Yield of ^1H NMR. N.D. = No Detection.

Screening of Ligands

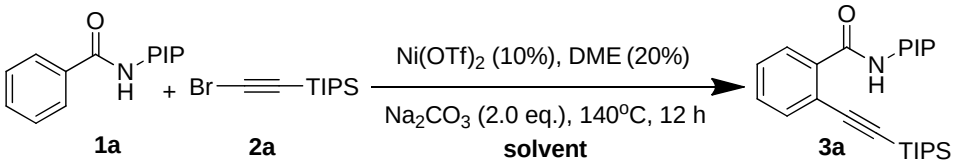


1a **2a** **3a**

Entry[a]	**L (20%)**	**Yield**[b] **of 3a**
1	BINAP	trace
2	PCy_3	trace
3	DPPM	8%
4	DPPP	trace
5	DPPB	trace
6	BPy	N.D.
7	1,10-Phen	N.D.
8	BDMAE	15%
9	DME	60%(mono:di=3:1)
10	TMEDA	25%

[a] The reactions were carried out **1a** (0.1 mmol), **2a** (0.2 mmol), $Ni(OTf)_2$ (0.01 mmol), Ligands (0.02 mmol), Na_2CO_3 (0.2 mmol), DCE (1 mL), N_2, 140°C. [b] Yield of ^1H NMR. N.D. = No Detection.

Screening of Solvents

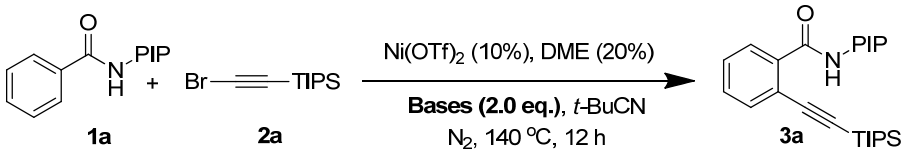


1a **2a** **3a**

Entry[a]	Solvent	Yield[b] of 3a
1	DMF	11%
2	DMSO	15%
3	1,4-dioxane	18%
4	Toluenel	trace
5	*o*-xylene	trace
6	Isobutyronitrile	75%(mono:di=4:1)
7	DME	5%
8	DCM	trace
9	Acetonitrile	trace
10	Butyronitrile	16%
11	Pivalonitrile	81%(mono:di=3:1)

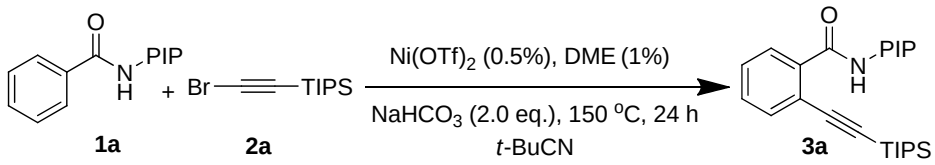
[a] The reactions were carried out **1a** (0.1 mmol), **2a** (0.2 mmol), $Ni(OTf)_2$ (0.01 mmol), DME (0.02 mmol), Na_2CO_3 (0.2 mmol), solvent (1.0 mL), N_2, 140°C, 12h. [b] Yield of ^1H NMR.

Screening of Bases



Entry[a]	Bases (2.0 eq.)	Yield[b] of 3a
1	Li_2CO_3	8%
2	Na_2CO_3	81%(mono:di=3:1)
3	K_2CO_3	N.D.
4	Cs_2CO_3	N.D.
5	$NaHCO_3$	99%(mono:di=1:2)
6	$KHCO_3$	90%(mono:di=1:3)
7	K_3PO_4	37%
8	K_2HPO_4	25%
9	KH_2PO_4	N.D.
10	NaOAc	N.D.

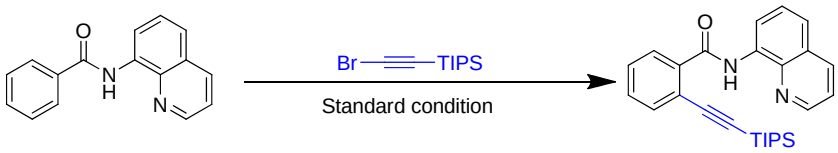
[a] The reactions were carried out **1a** (0.1 mmol), **2a** (0.2 mmol), $Ni(OTf)_2$ (0.01 mmol), DME (0.02 mmol), base (0.2 mmol), *t*-BuCN (1 mL), N_2, 140°C. [b] Yield of ^1H NMR. N.D. = No detection.



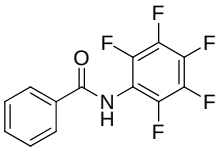
Entry[a]	Solvent	Yield[b] of 3a
1	0.5 mL	99%(mono:di=1:2.8)
2	2mL	83%(mono:di=2:1)
3	4 mL	79%(mono:di=1.5:1)
4	6mL	63%(mono:di=2:1)
5	8 mL	61%(mono:di=2:1)
6[c]	0.5 mL	99%(mono:di=32:1)

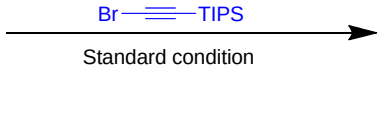
[a] The reactions were carried out **1a** (0.4 mmol), **2a** (0.8 mmol), $Ni(OTf)_2$ (0.002 mmol), DME (0.004 mmol), $NaHCO_3$ (0.8 mmol), *t*-BuCN (x mL), N_2, 150 °C, 24 h. [b] Yield of ^1H NMR. [c] **1a** (0.8 mmol), **2a** (0.4 mmol).

Screening of Directing Group

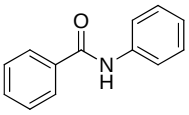


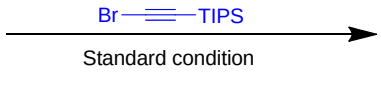
45%(mono)+27%(di)



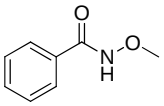


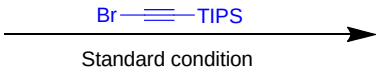
No Product





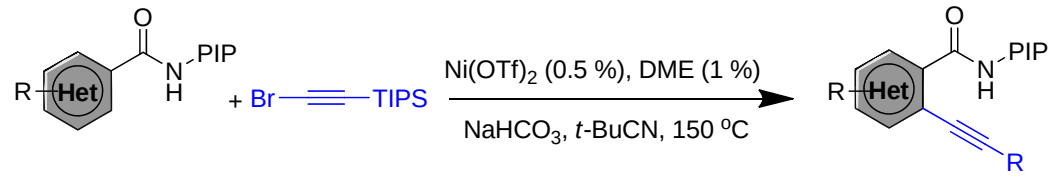
No Product



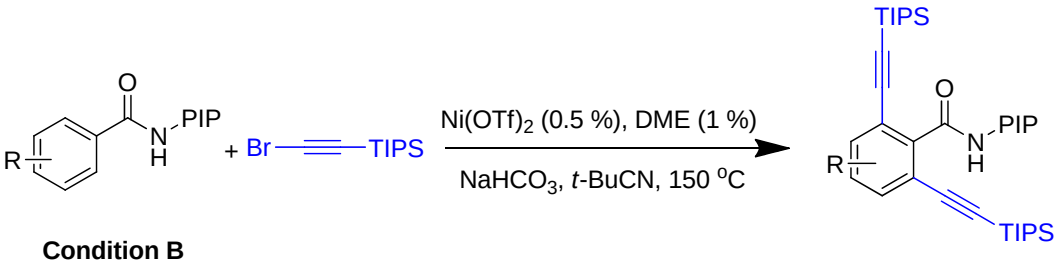


No Product

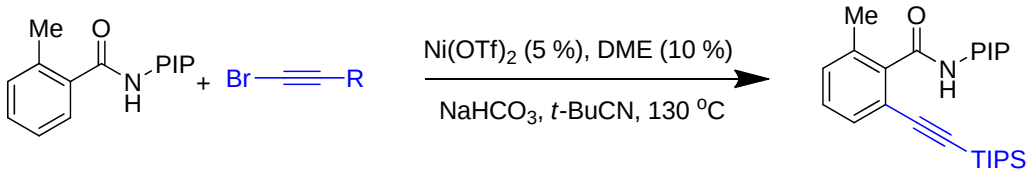
2.3 General Procedure for the Alkynylation



Condition A



Condition B



Condition C

Condtion A:

To an oven-dried 50 mL screw-capped vial was added substrate **1a** (x mmol), **2a** (y mmol), $Ni(OTf)_2$ (0.8 mg, 0.002 mmol), $NaHCO_3$ (67.2 mg, 0.8 mmol), DME (0.004 mmol) in *t*-BuCN (0.5 mL). The mixture was stirred for 24 h at 150 °C under N_2 followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.

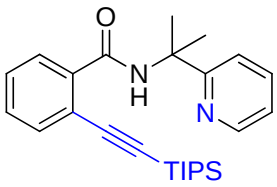
Condtion B:

To an oven-dried 50 mL screw-capped vial was added substrate **1a** (0.4 mmol), **2a** (1.6 mmol), $Ni(OTf)_2$ (0.8 mg, 0.002 mmol), $NaHCO_3$ (67.2 mg, 0.8 mmol), DME (0.004 mmol) in *t*-BuCN (0.5 mL). The mixture was stirred for 24 h at 150 °C under N_2 followed by cooling. The resulting mixture was filtered through a celite pad and

concentrated in *vacuo*. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.

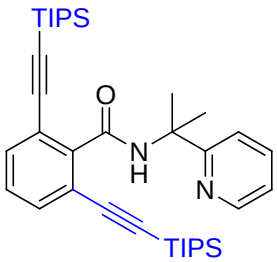
Condtion C:

To an oven-dried 50 mL screw-capped vial was added substrate **1a** (0.8 mmol), **2a** (0.4 mmol), $Ni(OTf)_2$ (0.8 mg, 0.002 mmol), $NaHCO_3$ (67.2 mg, 0.8 mmol), DME (0.004 mmol) in *t*-BuCN (0.5 mL). The mixture was stirred for 24 h at 130 °C under N_2 followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.



N-(2-(Pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3a

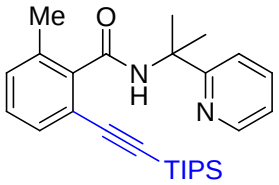
Following **Condition A: 1a** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.0 Hz, 1H), 8.40 (br, 1H), 7.80 (dd, *J* = 6.8, 3.6 Hz, 1H), 7.68 (td, *J* = 8.0, 2.0 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.15 (dd, *J* = 6.4, 4.8 Hz, 1H), 1.87 (s, 6H), 1.07–1.02 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.19, 164.57, 148.04, 137.75, 136.81, 134.72, 129.78, 129.13, 128.68, 121.62, 120.13, 119.36, 105.36, 97.33, 57.68, 27.76, 18.65, 11.30; **HRMS** (EI-TOF) calcd for $C_{26}H_{36}N_2OSi$ (M^+): 420.2597, found: 420.2599.



N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide **4a**

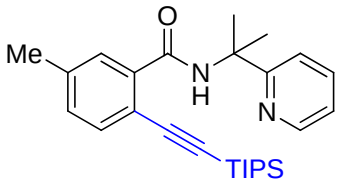
Following **Condition B: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.2 Hz, 1H), 8.41 (br, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.48 - 7.42 (m, 3H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.15

(dd, *J* = 6.4, 5.2 Hz, 1H), 1.92 (s, 6H), 1.03 – 0.97 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.03, 164.58, 147.41, 142.42, 137.13, 133.82, 128.18, 121.80, 121.59, 119.49, 104.25, 95.04, 57.29, 27.58, 18.74, 11.38; **HRMS** (EI-TOF) calcd for $C_{37}H_{56}N_2OSi_2$ (M^+): 600.3931, found: 600.3932.



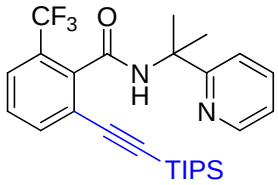
2-Methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamid 3b

Following **Condition A: 1b** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.8 Hz, 1H), 8.16 (br, 1H), 7.71 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 6.4 Hz, 1H), 7.21-7.15 (m, 3H), 2.37 (s, 3H), 1.92 (s, 6H), 1.02-0.97 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.60, 164.38, 147.47, 140.14, 137.00, 135.43, 131.23, 130.38, 128.14, 121.77, 120.48, 119.42, 105.06, 93.91, 57.13, 27.43, 19.33, 18.61, 11.27; **HRMS** (EI-TOF) calcd for $C_{27}H_{38}N_2OSi$ (M^+): 434.2753, found: 434.2755.



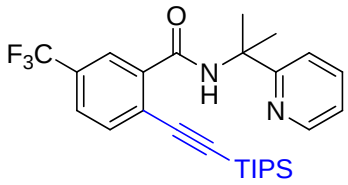
5-Methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamid e 3c

Following **Condition A: 1c** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 4.0, 0.8 Hz, 1H), 8.36 (br, 1H), 7.69–7.64 (m, 2H), 7.46 (dd, *J* = 8.0, 3.6 Hz, 2H), 7.19–7.13 (m, 2H), 2.36 (s, 3H), 1.86 (s, 6H), 1.07–1.02 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.36, 164.82, 148.25, 139.21, 137.41, 136.84, 134.87, 130.78, 129.97, 121.67, 119.49, 117.24, 105.78, 96.68, 57.87, 27.95, 21.46, 18.79, 11.47; **HRMS** (EI-TOF) calcd for $C_{27}H_{38}N_2OSi$ (M^+): 434.2753, found: 434.2752.



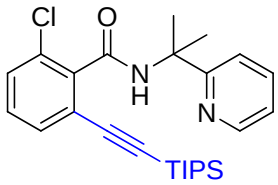
***N*-(2-(Pyridin-2-yl)propan-2-yl)-2-(trifluoromethyl)-6-((triisopropylsilyl)ethynyl) benzamide 3d**

Following **Condition A: 1d** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (br, 1H), 8.41 (d, *J* = 4.8 Hz, 1H), 7.75-7.71 (m, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.45-7.41 (m, 2H), 7.17 (dd, *J* = 6.8, 5.2 Hz, 1H), 1.91 (s, 6H), 1.03– 0.97 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.73, 164.25, 147.37, 138.76, 137.40, 137.29, 128.56, 127.98 (q, *J* = 31.7 Hz), 126.02 (q, *J* = 4.8 Hz), 123.65 (q, *J* = 272.7 Hz), 123.20, 121.98, 119.53, 103.41, 96.73, 57.49, 27.14, 18.71, 11.36; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 59.02; **HRMS** (EI-TOF) calcd for $C_{27}H_{35}F_3N_2OSi$ (M^+): 488.2471, found: 488.2474.



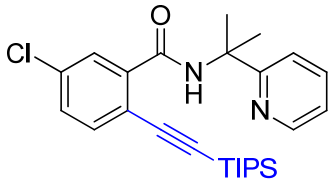
***N*-(2-(Pyridin-2-yl)propan-2-yl)-5-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl) benzamide 3e**

Following **Condition A: 1e** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (br, 1H), 8.50 (d, *J* = 4.4 Hz, 1H), 8.06 (s, 1H), 7.71 (td, *J* = 7.6, 1.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 7.2, 5.2 Hz, 1H), 1.89 (s, 6H), 1.06–0.99 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.14, 164.34, 148.08, 138.89, 137.10, 135.21, 130.59 (q, *J* = 33.0 Hz), 126.41-126.23 (m), 123.92, 123.69 (q, *J* = 270.8 Hz), 121.92, 119.54, 103.94, 100.56, 57.87, 27.69, 18.71, 11.37; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 62.96; **HRMS** (EI-TOF) calcd for $C_{27}H_{35}F_3N_2OSi$ (M^+): 488.2471, found: 488.2473.



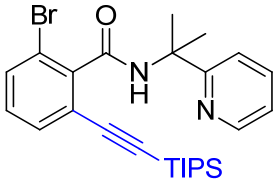
2-Chloro-*N*-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamide 3f

Following **Condition A: 1f** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.8 Hz, 1H), 8.30 (br, 1H), 7.72 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 7.2, 5.2 Hz, 1H), 1.92 (s, 6H), 1.06–0.98 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.78, 164.32, 147.51, 139.64, 137.24, 132.22, 131.61, 129.77, 129.30, 122.96, 121.97, 119.56, 103.57, 95.94, 57.55, 27.51, 18.74, 11.38; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}ClN_2OSi$ (M^+): 454.2207, found: 454.2209.



5-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3g

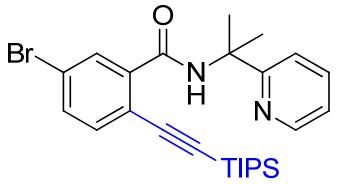
Following **Condition A: 1g** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.0 Hz, 1H), 8.46 (br, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.69 (td, *J* = 8.0, 1.6 Hz, 1H), 7.47 (dd, *J* = 14.8, 8.0 Hz, 2H), 7.33 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.17 (dd, *J* = 6.4, 4.8 Hz, 1H), 1.86 (s, 6H), 1.05 – 1.00 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.04, 164.42, 148.13, 139.56, 137.02, 135.97, 134.94, 130.00, 129.34, 121.85, 119.45, 118.76, 104.26, 98.51, 57.84, 27.74, 18.74, 11.39; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}ClN_2OSi$ (M^+): 454.2207, found: 454.2203.



2-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamide **3h**

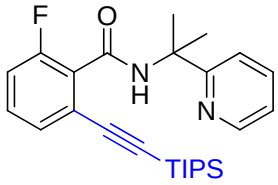
Following **Condition A: 1h** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.4 Hz, 1H), 8.35 (br, 1H), 7.72 (td, *J* = 8.0, 1.6 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.34 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 6.4, 4.8 Hz, 1H), 1.93 (s, 6H), 1.04 – 0.99 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 64.69,

164.15, 147.38, 139.55, 137.20, 132.11, 131.48, 129.68, 129.24, 122.83, 121.92, 119.47, 103.50, 95.80, 57.44, 27.41, 18.65, 11.28; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}BrN_2OSi$ (M^+): 498.1702, found: 498.1705.



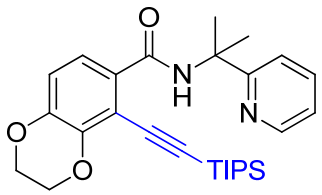
5-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide **3i**

Following **Condition A: 1i** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (br, 2H), 7.92 (d, *J* = 1.6 Hz, 1H), 7.69 (t, *J* = 6.8 Hz, 1H), 7.49 -7.40 (m, 3H), 7.16 (dd, *J* = 6.4, 5.2 Hz, 1H), 1.87 (s, 6H), 1.05 – 1.00 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.84, 164.25, 147.98, 139.63, 136.95, 135.94, 132.78, 132.06, 122.92, 121.77, 119.34, 119.11, 104.20, 98.55, 57.71, 27.61, 18.65, 11.27; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}BrN_2OSi$ (M^+): 498.1702, found: 498.1700.



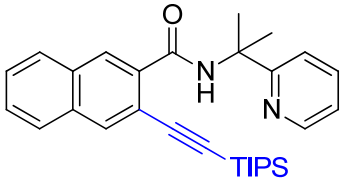
2-Fluoro-*N*-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamide 3g

Following **Condition A: 1g** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.2 Hz, 1H), 8.28 (br, 1H), 7.72 (td, *J* = 8.0, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.34–7.25 (m, 2H), 7.17 (dd, *J* = 6.8, 5.2 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 1.90 (s, 6H), 1.07–0.99 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.30, 162.77, 159.37 (d, *J* = 246.9 Hz), 147.60, 137.24, 130.01(d, *J* = 9.0 Hz), 129.79 (d, *J* = 3.2 Hz), 128.73 (d, *J* = 19.1 Hz), 123.26 (d, *J* = 5.0 Hz), 121.96, 119.52, 116.22 (d, *J* = 2.2 Hz), 103.39, 96.10, 57.62, 27.64, 18.73, 11.38; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 115.83; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}FN_2OSi$ (M^+): 438.2503, found: 438.2500.



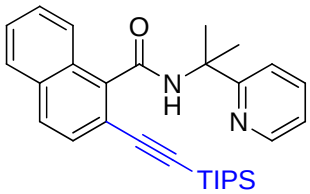
***N*-(2-(Pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine-6-carboxamide 3k**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.0 Hz, 1H), 8.35 (br, 1H), 7.64 (td, *J* = 7.6, 1.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.13 (dd, *J* = 6.8, 5.2 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 4.30 (m, 4H), 1.83 (s, 6H), 1.09-1.04 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.65, 164.98, 148.29, 145.97, 145.17, 136.73, 131.07, 122.37, 121.56, 119.46, 117.56, 110.06, 103.94, 100.18, 64.47, 64.20, 57.88, 28.07, 18.73, 11.46; **HRMS** (EI-TOF) calcd for $C_{28}H_{38}N_2O_3Si$ (M^+): 478.2652, found: 478.2655.



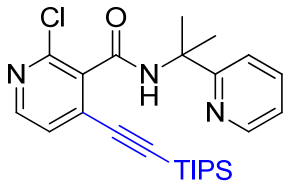
N-(2-(pyridin-2-yl)propan-2-yl)-3-((triisopropylsilyl)ethynyl)-2-naphthamide 3l

Following **Condition A: 1l** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 2H), 8.32 (br, 1H), 8.09 (s, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.68 (td, *J* = 8.0, 1.6 Hz, 1H), 7.54 - 7.48 (m, 3H), 7.15 (dd, *J* = 6.4, 5.2 Hz, 1H), 1.91 (s, 6H), 1.12 – 1.06 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.31, 164.74, 148.13, 136.90, 135.30, 134.48, 133.37, 132.45, 129.58, 128.73, 127.86, 127.50, 127.26, 121.71, 119.47, 117.44, 105.84, 96.49, 57.84, 27.89, 18.81, 11.47; **HRMS** (EI-TOF) calcd for $C_{30}H_{38}N_2OSi$ (M^+): 470.2753, found: 470.2759.



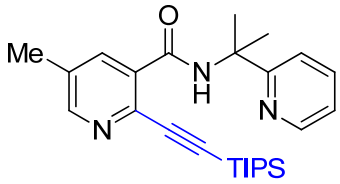
***N*-(2-(Pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)-1-naphthamide 3m**

Following **Condition A: 1m** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (br, 1H), 8.39 (d, *J* = 4.0 Hz, 1H), 8.04 (d, *J* = 6.8 Hz, 1H), 7.79 (m, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.71 (td, *J* = 8.0, 1.6 Hz, 1H), 7.50 (m, 4H), 7.14 (dd, *J* = 6.8, 5.2 Hz, 1H), 2.02 (s, 6H), 1.05-1.00 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.26, 164.31, 147.56, 138.64, 137.16, 133.03, 130.25, 129.79, 128.64, 127.99, 127.35, 126.91, 125.90, 121.92, 119.52, 117.88, 105.44, 95.77, 57.56, 27.64, 18.75, 11.39; **HRMS** (EI-TOF) calcd for $C_{30}H_{38}N_2OSi$ (M^+): 470.2753, found: 470.2757.



2-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-4-((triisopropylsilyl)ethynyl)nicotinamide 3n

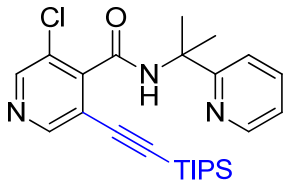
Following **Condition A: 1n** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (br, 1H), 8.44 (d, *J* = 4.0 Hz, 1H), 8.33 (d, *J* = 5.2 Hz, 1H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 4.8 Hz, 1H), 7.20 (dd, *J* = 6.4, 5.2 Hz, 1H), 1.92 (s, 6H), 1.10 – 1.00 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.87, 163.21, 148.95, 148.65, 147.41, 137.41, 134.73, 131.86, 126.20, 122.13, 119.50, 102.40, 101.00, 57.57, 27.33, 18.64, 11.23; **HRMS** (EI-TOF) calcd for $C_{25}H_{34}ClN_3OSi$ (M^+): 455.2160, found: 455.2158.



5-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)nicotinamide 3o

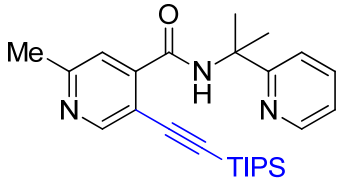
Following **Condition A: 1o** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55-8.48 (m, 3H), 7.86 (s, 1H), 7.71 (td, *J* = 8.0, 5.2 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 6.8, 4.8 Hz, 1H), 2.36 (s, 3H), 1.88 (s, 6H), 1.07-1.01 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.32, 164.34, 151.75, 148.05, 137.14, 137.07, 136.54,

134.23, 133.23, 121.88, 119.41, 104.53, 96.25, 57.80, 27.67, 18.75, 18.39, 11.44; **HRMS** (EI-TOF) calcd for $C_{26}H_{37}N_3OSi$ (M^+): 435.2706, found: 435.2711.



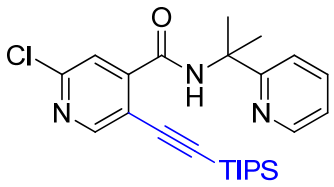
3-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide 3p

Following **Condition A: 1p** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (s, 2H), 8.52 (br, 1H), 8.44 (d, *J* = 4.0 Hz, 1H), 7.75 (td, *J* = 8.0, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.19 (m, 1H), 1.92 (s, 6H), 1.05 – 1.00 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.55, 162.33, 152.03, 148.54, 147.32, 145.16, 137.36, 128.38, 122.09, 119.38, 118.66, 99.93, 99.80, 57.62, 27.35, 18.57, 11.15; **HRMS** (EI-TOF) calcd for $C_{25}H_{34}ClN_3OSi$ (M^+): 455.2160, found: 455.2159.



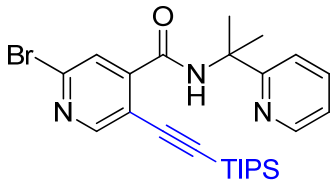
2-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide 3q

Following **Condition A: 1q** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.61 (br, 1H), 8.50 (d, *J* = 4.0 Hz, 1H), 7.71 (td, *J* = 8.0, 1.6 Hz, 1H), 7.50 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 6.4, 4.8 Hz, 1H), 2.58 (s, 3H), 1.88 (s, 6H), 1.07 – 1.01 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.43, 163.94, 158.52, 154.48, 147.88, 144.48, 136.95, 121.78, 121.64, 119.23, 113.47, 102.09, 99.41, 57.68, 27.46, 24.30, 18.54, 11.16; **HRMS** (EI-TOF) calcd for $C_{26}H_{38}N_3OSi$ $(M+H)^+$: 436.2784, found: 436.2794.



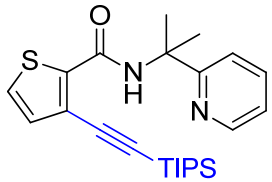
2-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide 3r

Following **Condition A: 1r** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (br, 1H), 8.55 (s, 1H), 8.49 (dd, *J* = 4.0, 0.8 Hz, 1H), 7.73 (td, *J* = 8.0, 1.6Hz, 1H), 7.64 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.20 (ddd, *J* = 7.6, 5.2, 0.8 Hz, 1H), 1.86 (s, 6H), 1.05– 0.99 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.85, 163.22, 155.03, 151.30, 148.00, 147.40, 137.31, 123.14, 122.13, 119.43, 115.79, 101.86, 100.67, 57.95, 27.54, 18.70, 11.33; **HRMS** (EI-TOF) calcd for $C_{25}H_{34}ClN_3OSi$ (M^+): 455.2160, found: 455.2161.



2-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide 3s

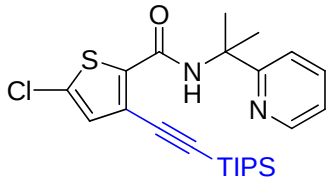
Following **Condition A: 1s** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (br, 1H), 8.52 (s, 1H), 8.49 (d, *J* = 4.0 Hz, 1H), 7.79 (s, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 6.4, 5.2 Hz, 1H), 1.87 (s, 6H), 1.05 – 1.00 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.62, 162.93, 155.01, 147.80, 146.89, 141.59, 137.21, 126.59, 122.02, 119.29, 116.00, 101.86, 100.53, 57.78, 27.37, 18.56, 11.15; **HRMS** (EI-TOF) calcd for $C_{25}H_{34}BrN_3OSi$ (M^+): 499.1655, found: 499.1657.



N-(2-(pyridin-2-yl)propan-2-yl)-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide 3t

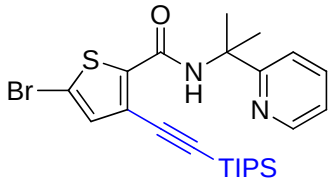
Following **Condition A: 1t** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.0 Hz, 1H), 8.14 (br, 1H), 7.64 (td, *J* = 7.6, 1.6 Hz, 1H), 7.45 (d, *J* =

8.0 Hz, 1H), 7.34 (d, *J* = 5.2 Hz, 1H), 7.14-7.11 (m, 2H), 1.83 (s, 6H), 1.12–1.06 (m, 21); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.51, 160.33, 148.61, 142.83, 136.61, 132.69, 128.64, 121.58, 120.09, 119.25, 101.04, 99.08, 58.19, 28.28, 18.71, 11.28; **HRMS** (EI-TOF) calcd for $C_{24}H_{34}N_2OSSi$ (M^+): 426.2161, found: 426.2165.



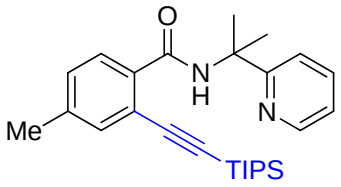
5-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide 3u

Following **Condition A: 1u** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.0 Hz, 1H), 8.06 (br, 1H), 7.65 (td, *J* = 8.0, 1.6 Hz,, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 7.2, 5.6 Hz, 1H), 6.94 (s, 1H), 1.81 (s, 6H), 1.10 – 1.05 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.35, 159.61, 148.74, 141.58, 136.75, 134.14, 131.29, 121.76, 119.62, 119.28, 100.13, 99.96, 58.33, 28.29, 18.75, 11.32; **HRMS** (EI-TOF) calcd for $C_{24}H_{33}ClN_2OSSi$ (M^+): 460.1771, found: 460.1777.



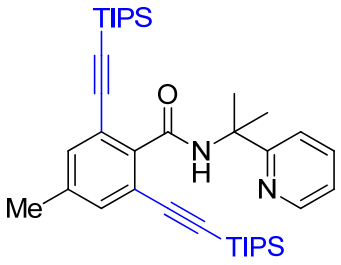
5-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide 3v

Following **Condition A: 1v** (0.4 mmol), **2a** (0.8 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.0 Hz, 1H), 8.05 (br, 1H), 7.65 (td, *J* = 8.0, 1.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.14 (td, *J* = 5.6, 1.6 Hz, 1H), 7.07 (s, 1H), 1.80 (s, 6H), 1.10 – 1.05 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.35, 159.54, 148.75, 144.35, 136.75, 134.90, 121.76, 120.48, 119.29, 116.98, 100.28, 99.69, 58.33, 28.29, 18.76, 11.33; **HRMS** (EI-TOF) calcd for $C_{24}H_{33}BrN_2OSSi$ (M^+): 504.1266, found: 504.1269.



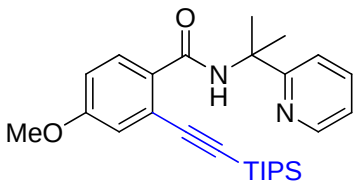
4-Methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamid e 3w

Following **Condition A: 1w** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.4 Hz, 1H), 8.35 (br, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.36 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.13 (dd, *J* = 6.8, 5.2 Hz, 1H), 2.35 (s, 3H), 1.85 (s, 6H), 1.08–1.03 (m, 21H);**^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.16, 164.87, 148.22, 140.18, 136.79, 135.18, 134.91, 129.77, 129.54, 121.62, 120.00, 119.45, 105.84 97.12, 57.82, 27.98, 21.12, 18.79, 11.45; **HRMS** (EI-TOF) calcd for $C_{27}H_{38}N_2OSi$ (M^+): 434.2753, found: 434.2752.



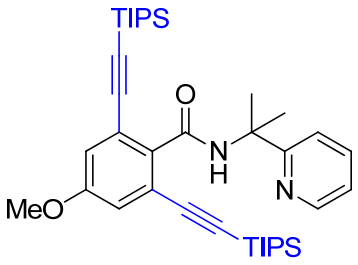
4-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benza mide 4w

Following **Condition B: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 4.0 Hz, 1H), 8.37 (br, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.28 (s, 2H), 7.14 (dd, *J* = 6.4, 5.2 Hz, 1H), 2.31 (s, 3H), 1.91 (s, 6H), 1.03 – 0.98 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.15, 164.60, 147.37, 139.92, 138.10, 137.08, 134.38, 121.75, 121.42, 119.47, 104.47, 94.41, 57.22, 27.55, 20.84, 18.72, 11.37; **HRMS** (EI-TOF) calcd for $C_{38}H_{58}N_2OSi_2$ (M^+): 614.4088, found: 614.4093.



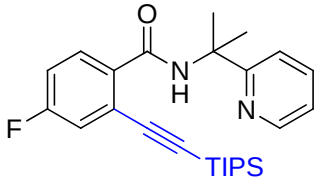
4-methoxy-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3x

Following **Condition A: 1x** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.0 Hz, 1H), 8.37 (br, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.67 (td, *J* = 8.0, 1.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.15 (dd, *J* = 7.2, 5.2 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.83 (s, 3H), 1.86 (s, 6H), 1.09–1.04 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.82, 164.72, 160.61, 148.32, 136.92, 131.63, 129.67, 121.68, 121.44, 119.74, 119.46, 114.63, 105.55, 97.88, 57.81, 55.50, 28.00, 18.72, 11.36; **HRMS** (EI-TOF) calcd for $C_{27}H_{38}N_2O_2Si$ (M^+): 450.2703, found: 450.2704.



4-methoxy-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4x

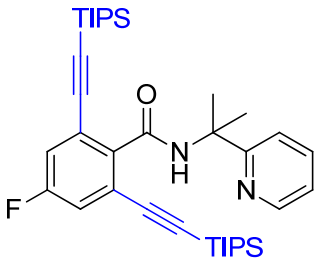
Following **Condition B: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.0 Hz, 1H), 8.38 (br, 1H), 7.70 (t, *J* = 6.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 7.0, 5.2 Hz, 1H), 7.00 (s, 2H), 3.81 (s, 3H), 1.92 (s, 6H), 1.04 – 0.98 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.86, 164.54, 158.60, 147.31, 137.06, 135.82, 122.75, 121.71, 119.42, 119.25, 104.22, 94.72, 57.12, 55.55, 27.47, 18.65, 11.30; **HRMS** (EI-TOF) calcd for $C_{38}H_{58}N_2O_2Si_2$ (M^+): 630.4037, found: 630.4036.



4-Fluoro-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3y

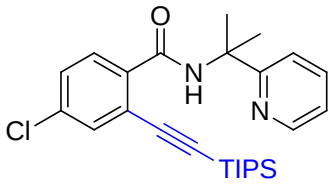
Following **Condition A: 1y** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.0 Hz, 1H), 8.38 (br, 1H), 7.80 (dd, *J* = 6.8, 4.0 Hz, 1H), 7.68 (td, *J* =

8.0, 1.6 Hz, 1H), 7.58–7.55 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.38–7.36 (m, 2H), 7.17–7.14 (m, 1H), 1.87 (s, 6H), 1.07–1.02 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.42, 164.65, 163.03 (d, *J* = 249.3 Hz), 148.19, 136.97, 134.36, 131.75 (d, *J* = 9.1 Hz), 122.38 (d, *J* = 9.7 Hz), 121.80, 121.07 (d, *J* = 22.9 Hz), 119.47, 116.30 (d, *J* = 21.3 Hz), 104.17, 98.99, 57.83, 27.84, 18.75, 11.41; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 110.89; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}FN_2OSi$ (M^+): 438.2503, found: 438.24503.



4-fluoro-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4y

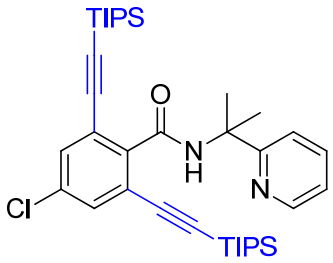
Following **Condition B:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (br, 1H), 8.42 (d, *J* = 4.4 Hz, 1H), 7.71 (td, *J* = 8.0, 1.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 3H), 1.93 (s, 6H), 1.03 – 0.98 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.21, 164.30, 161.21 (d, *J* = 247.2 Hz), 147.29, 139.06 (d, *J* = 3.2 Hz), 137.18, 123.56 (d, *J* = 10.2 Hz), 121.84, 120.52 (d, *J* = 22.5 Hz), 119.41, 103.05 (d, *J* = 2.7 Hz), 96.47, 57.19, 27.44, 18.62, 11.27; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 113.07; **HRMS** (EI-TOF) calcd for $C_{37}H_{57}FN_2OSi_2$ (M^+): 618.3837, found: 618.3842.



4-Chloro-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3z

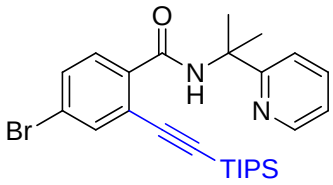
Following **Condition A:** **1z** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.4 Hz, 1H), 8.42 (br, 1H), 7.74-7.67(m, 2H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.16 (dd, *J* = 6.8, 5.2 Hz, 1H), 1.86 (s, 6H), 1.06-1.01 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.45, 164.53, 148.11, 137.04, 136.57, 135.76, 134.13, 130.73, 129.05, 121.94, 121.84, 119.48,

103.95, 99.02, 57.81, 27.78, 18.75, 11.41; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}ClN_2OSi$ (M^+): 454.2207, found: 454.2212.



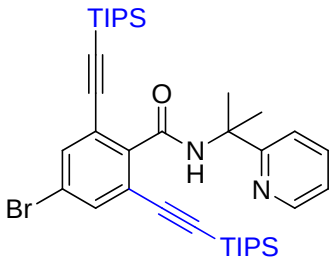
4-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4z

Following **Condition B:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (br, 1H), 8.41 (d, *J* = 4.4 Hz, 1H), 7.71 (t, *J* = 6.8 Hz, 1H), 7.44 - 7.41 (m, 3H), 7.16 (dd, *J* =7.2, 5.2 Hz, 1H), 1.92 (s, 6H), 1.03 – 0.98 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.07, 164.20, 147.26, 140.82, 137.20, 133.68, 133.21, 123.14, 121.85, 119.37, 102.81, 96.67, 57.19, 27.43, 18.63, 11.25; **HRMS** (EI-TOF) calcd for $C_{37}H_{55}ClN_2OSi_2$ (M^+): 634.3541, found: 634.3546.



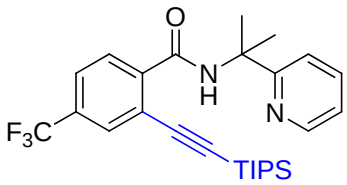
4-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3aa

Following **Condition A: 1aa** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.8 Hz, 1H), 8.44 (br, 1H), 7.71-7.63 (m, 3H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 7.2, 4.8 Hz, 1H), 1.86 (s, 6H), 1.06–1.01 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.50, 164.45, 148.06, 137.09, 136.99, 136.91, 131.91, 130.70, 123.77, 122.12, 121.80, 119.41, 103.75, 98.99, 57.75, 27.72, 18.72, 11.36; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}BrN_2OSi$ (M^+): 498.1702, found: 498.1705.



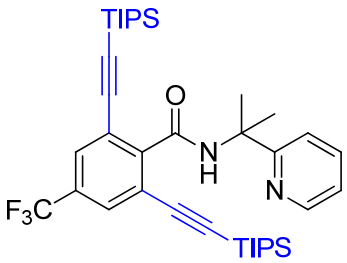
4-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4aa

Following **Condition B:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (br, 1H), 8.42 (d, *J* = 4.4 Hz, 1H), 7.71 (td, *J* = 7.6, 1.6 Hz, 1H), 7.59 (s, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 6.8, 5.2 Hz, 1H), 1.90 (s, 6H), 1.02–0.97 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.19, 164.36, 147.39, 141.28, 137.23, 136.12, 123.36, 121.89, 121.49, 119.45, 102.76, 96.88, 57.30, 27.53, 18.71, 11.35; **HRMS** (EI-TOF) calcd for $C_{37}H_{55}BrN_2OSi_2$ (M^+): 678.3036, found: 678.3034.



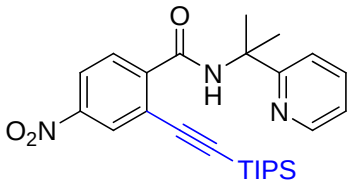
2-Methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamide 3ab

Following **Condition A:** **1ab** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (br, 1H), 8.48 (d, *J* = 4.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.71 (td, *J* = 7.86 1.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 6.8, 4.8 Hz, 1H), 1.88 (s, 6H), 1.06-1.01 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.41, 164.22, 147.88, 141.69, 137.07, 131.82 (q, *J* = 32.8 Hz), 131.26 (q, *J* = 2.8 Hz), 129.49, 127.48, 125.10 (q, *J* = 3.6 Hz), 123.41 (q, *J* = 270.9 Hz), 121.86, 121.20, 119.38, 103.48, 98.94, 57.68, 27.56, 18.63, 11.30; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 60.04; **HRMS** (EI-TOF) calcd for $C_{27}H_{35}F_3N_2OSi$ (M^+): 488.2471, found: 488.2474.



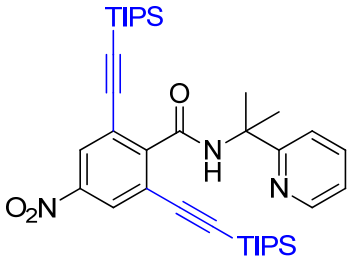
N-(2-(pyridin-2-yl)propan-2-yl)-4-(trifluoromethyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4ab

Following **Condition B:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (br, 1H), 8.32 (d, *J* = 4.0 Hz, 1H), 7.64 (td, *J* = 8.0, 1.2 Hz, 1H), 7.59 (s, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 6.4, 4.8 Hz, 1H), 1.85 (s, 6H), 0.95 – 0.90 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.89, 164.10, 147.30, 145.06, 137.31, 130.87 (q, *J* = 33.4 Hz), 130.02 (q, *J* = 3.0 Hz), 123.17 (q, *J* = 271.2 Hz), 122.63, 121.96, 119.40, 102.64, 97.33, 57.32, 27.50, 18.66, 11.30; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 63.12; **HRMS** (EI-TOF) calcd for $C_{38}H_{55}F_3N_2OSi_2$ (M^+): 688.3805, found: 688.3804.



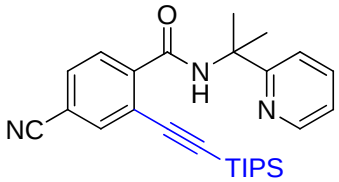
4-Nitro-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3ac

Following **Condition A: 1ac** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (br, 1H), 8.48 (d, *J* = 4.4Hz, 1H), 8.36 (d, *J* = 2.4 Hz, 1H), 8.18 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.74 (td, *J* = 8.0, 2.0 Hz, 1H), 7.46 (d, *J* = 8.10Hz, 1H), 7.20 (dd, *J* = 7.2, 5.6 Hz, 1H), 1.89 (s, 6H), 1.06–1.01(m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.94, 164.02, 148.20, 147.85, 144.22, 137.34, 130.08, 129.28, 123.15, 122.18, 122.09, 119.48, 102.55, 100.19, 57.79, 27.54, 18.69, 11.34; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}N_3O_3Si$ (M^+): 465.2448, found: 465.2446.



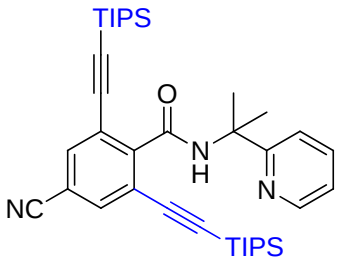
4-nitro-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4ac

Following **Condition B:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (br, 1H), 8.42 (d, *J* = 4.4 Hz, 1H), 8.26 (s, 2H), 7.76 (t, *J* = 8.0Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 6.4, 5.2 Hz, 1H), 1.95 (s, 6H), 1.05 – 1.00 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.16, 163.76, 147.18, 147.06, 147.00, 137.37, 127.79, 123.32, 122.00, 119.33, 101.78, 98.62, 57.32, 27.40, 18.56, 11.19; **HRMS** (EI-TOF) calcd for $C_{37}H_{55}N_3O_3Si_2$ (M^+): 645.3782, found: 645.3775.



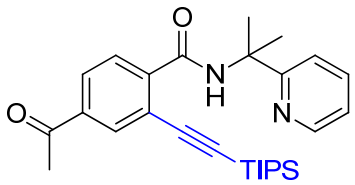
4-Cyano-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3ad

Following **Condition A:** **1ad** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (br, 1H), 8.48 (d, *J* = 4.4 Hz, 1H), 7.82 (dd, *J* = 4.5, 3.1 Hz, 2H), 7.83–7.81 (m, 2H), 7.73 (td, 8.0, 1.6 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.20 (dd, *J* = 7.6, 5.2 Hz, 1H), 1.88 (s, 6H), 1.05–1.00 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.03, 164.11, 147.90, 142.37, 138.10, 137.31, 131.56, 129.82, 122.06, 121.89, 119.51, 117.66, 113.90), 102.67, 100.26, 57.81, 27.59, 18.71, 11.35; **HRMS** (EI-TOF) calcd for $C_{27}H_{35}N_3OSi$ (M^+): 445.2549, found: 445.2551.



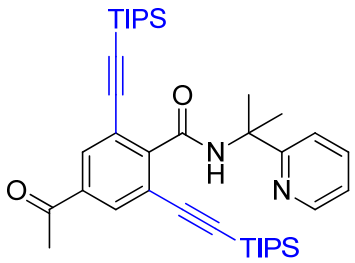
4-Cyano-*N*-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4ad

Following **Condition B:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (br, 1H), 8.42 (d, *J* = 4.8 Hz, 1H), 7.74 (td, *J* = 7.6, 1.2 Hz, 1H), 7.71 (s, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 7.6, 5.2 Hz, 1H), 1.91 (s, 6H), 1.06–0.97 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.40, 164.06, 147.35, 145.50, 137.38, 136.42, 123.25, 122.04, 119.44, 117.17, 112.99, 101.88, 98.61, 57.44, 27.52, 18.68, 11.32; **HRMS** (EI-TOF) calcd for $C_{38}H_{55}N_3OSi_2$ (M^+): 625.3884, found: 625.3882.



4-acetyl-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3ae

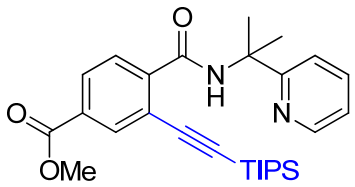
Following **Condition A:** **1ae** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (br, 1H), 8.49 (d, *J* = 4.0 Hz, 1H), 8.10 (s, 1H), 7.92 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.71 (td, *J* = 8.0, 1.2 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 6.4, 4.8 Hz, 1H), 2.63 (s, 3H), 1.89 (s, 6H), 1.13 – 1.01 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.93, 165.71, 164.29, 147.95, 142.19, 137.77, 137.07, 134.44, 129.35, 128.13, 121.87, 120.94, 119.41, 104.10, 98.23, 57.72, 27.63, 26.82, 18.70, 11.35; **HRMS** (EI-TOF) calcd for $C_{28}H_{38}N_2O_2Si$ (M+): 462.2703, found: 462.2712.



4-acetyl-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide

4ae

Following Condition B: ^{1}H NMR (400 MHz, CDCl3) δ 8.58 (br, 1H), 8.41 (d, J = 4.4 Hz, 1H), 8.00 (s, 2H), 7.73 (t, J = 6.8 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.17 (dd, J = 6.4, 5.2 Hz, 1H), 2.62 (s, 3H), 1.94 (s, 6H), 1.05 – 0.99 (m, 42H); 13C NMR (100 MHz, CDCl3) δ 196.39, 165.20, 164.13, 147.27, 145.69, 137.25, 136.71, 133.16, 122.26, 121.90, 119.38, 103.14, 96.42, 57.27, 27.49, 26.78, 18.66, 11.29; HRMS (EI-TOF) calcd for $C_{39}H_{58}N_2O_2Si_2$ (M+): 642.4037, found: 642.4036.

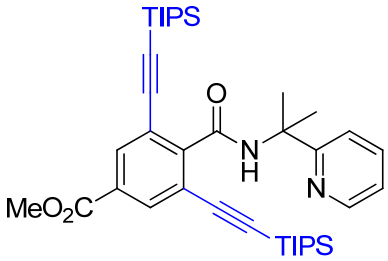


Methyl

4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)-3-((triisopropylsilyl)ethynyl)benzoate

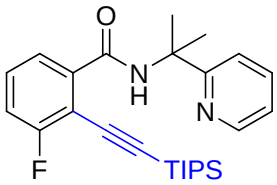
3af

Following **Condition A: 1af** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (br, 1H), 8.49 (d, *J* = 4.8 Hz, 1H), 8.20 (d, *J* = 1.6 Hz, 1H), 8.00 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.71 (td, *J* = 8.0, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.16 (m, 1H), 3.94 (s, 3H), 1.89 (s, 6H), 1.07 – 1.01 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.91, 165.76, 164.30, 147.95, 142.18, 137.05, 135.73, 131.29, 129.39, 129.11, 121.84, 120.71, 119.41, 104.05, 98.07, 57.71, 52.50, 27.62, 18.69, 11.34; **HRMS** (EI-TOF) calcd for $C_{28}H_{38}N_2O_3Si_2$ (M^+): 478.2652, found: 478.2659.



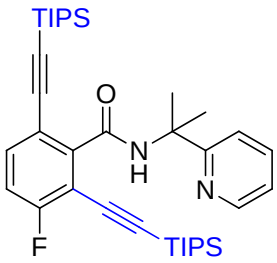
methyl 4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)-3,5-bis((triisopropylsilyl)ethynyl)benzoate 4af

Following **Condition B:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (br, 1H), 8.41 (d, *J* = 4.0 Hz, 1H), 8.10 (s, 2H), 7.73 (t, *J* = 6.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 6.4, 4.8 Hz, 1H), 3.95 (s, 3H), 1.94 (s, 6H), 1.04 – 0.99 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.46, 165.23, 164.12, 147.25, 145.64, 137.22, 134.40, 130.19, 122.05, 121.87, 119.36, 103.09, 96.24, 57.25, 52.55, 27.46, 18.63, 11.26; **HRMS** (EI-TOF) calcd for $C_{39}H_{58}N_2O_3Si_2$ (M^+): 658.3986, found: 658.3988.



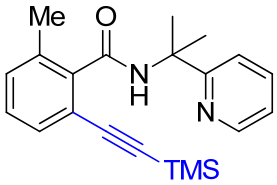
3-Fluoro-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3ag

Following **Condition A:** **1ag** (0.8 mmol), **2a** (0.4 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.8 Hz, 1H), 8.45 (br, 1H), 7.69 (td, *J* = 8.0, 1.6 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.33 (td, *J* = 8.0, 5.6 Hz, 1H), 7.18-7.13 (m, 2H), 1.87 (s, 6H), 1.07–1.02 (m, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.34 (d, *J* = 2.9 Hz), 164.52, 164.23 (d, *J* = 251.1 Hz), 162.98, 148.10, 140.31, 137.02, 129.69 (d, *J* = 8.5 Hz), 124.56 (d, *J* = 3.3 Hz), 121.83, 119.47, 116.91 (d, *J* = 11.8 Hz), 109.55 (d, *J* = 17.2 Hz, 2H), 104.09 (d, *J* = 4.8 Hz), 97.49, 57.81, 27.76, 18.67, 11.37; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 107.44; **HRMS** (EI-TOF) calcd for $C_{26}H_{35}FN_2OSi$ (M^+): 438.2503, found: 438.2499.



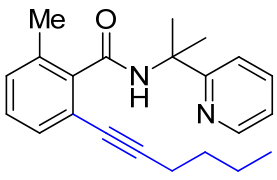
3-Fluoro-*N*-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4ag

Following **Condition B:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (br, 1H), 8.43 (d, *J* = 4.0 Hz, 1H), 7.71 (td, *J* = 8.0, 1.6 Hz, 1H), 7.46–7.42 (m, 2H), 7.16 (dd, *J* = 6.4, 4.8 Hz, 1H), 7.02 (t, *J* = 8.4 Hz, 1H), 1.92 (s, 6H), 1.03–0.97 (m, 42H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.84 (d, *J* = 2.4 Hz), 164.40, 163.42 (d, *J* = 254.6 Hz), 147.42, 144.40, 137.22, 135.20 (d, *J* = 8.3 Hz), 121.90, 119.48, 117.52 (d, *J* = 4.1 Hz), 115.72 (d, *J* = 22.3 Hz), 110.88, 103.32, 101.87 (d, *J* = 4.4 Hz), 96.62, 94.61, 57.37, 27.56, 18.73, 18.70, 11.40, 11.34; **^{19}H NMR** (376 MHz, $CDCl_3$) δ 105.83; **HRMS** (EI-TOF) calcd for $C_{37}H_{55}FN_2OSi_2$ (M^+): 618.3837, found: 618.3839.



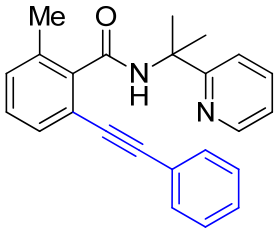
2-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-6-((trimethylsilyl)ethynyl)benzamide 5a

Following **Condition C:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.0 Hz, 1H), 8.11 (br, 1H), 7.72 (td, *J* = 8.0, 1.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.21 – 7.17 (m, 3H), 2.38 (s, 3H), 1.92 (s, 6H), 0.10 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.63, 164.46, 147.64, 140.44, 137.15, 135.64, 130.74, 130.63, 128.34, 121.95, 120.22, 119.61, 103.04, 97.41, 57.30, 27.60, 19.50, -0.08; **HRMS** (EI-TOF) calcd for $C_{21}H_{26}N_2OSi$ (M^+): 350.1814, found: 350.1822.



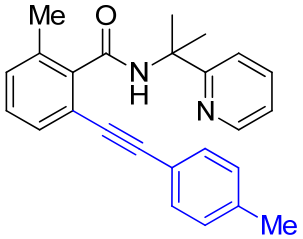
2-(hex-1-yn-1-yl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5b

Following **Condition C:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 1H), 7.98 (br, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.19 -7.16 (m, 2H), 7.11 (d, *J* = 7.2 Hz, 1H), 2.37 (s, 3H), 2.31 (t, *J* = 7.2 Hz, 2H), 1.91 (s, 6H), 1.50 – 1.43 (m, 2H), 1.39 -1.33 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.23, 164.56, 147.69, 140.49, 137.15, 135.35, 129.92, 129.68, 128.32, 121.93, 121.18, 119.63, 93.59, 78.70, 57.30, 30.76, 27.65, 22.13, 19.44, 19.40, 13.70; **HRMS** (EI-TOF) calcd for $C_{22}H_{26}N_2O$ (M^+): 334.2045, found: 334.2047.



2-methyl-6-(phenylethynyl)-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5c

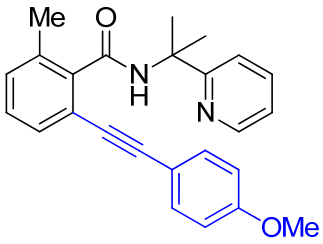
Following **Condition C:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.4 Hz, 1H), 8.09 (br, 1H), 7.64 (td, *J* = 8.0, 1.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.26 – 7.23 (m, 4H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.16 – 7.13 (m, 1H), 2.42 (s, 3H), 1.91 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.92, 164.44, 147.70, 140.53, 137.16, 135.57, 131.67, 130.54, 129.97, 128.49, 128.32, 123.34, 121.95, 120.42, 119.63, 92.22, 87.69, 57.44, 27.70, 19.45; **HRMS** (EI-TOF) calcd for $C_{24}H_{22}N_2O$ (M^+): 354.1732, found: 354.1732.



2-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-6-(p-tolylethynyl)benzamide 5d

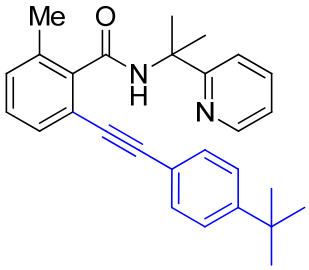
Following **Condition C:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.8 Hz, 1H), 8.08 (br, 1H), 7.64 (td, *J* = 8.0, 1.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.12 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 1.90 (s, 6H); **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 167.96, 164.41, 147.67, 140.40, 138.44, 137.12, 135.50, 131.53, 130.33, 129.90, 129.07, 128.44, 121.91, 120.57, 120.23, 119.61, 92.43, 87.00, 57.41, 27.68, 21.56, 19.42; **HRMS** (EI-TOF) calcd for $C_{25}H_{24}N_2O$ (M^+): 368.1889, found: 368.1896.



2-((4-methoxyphenyl)ethynyl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5e

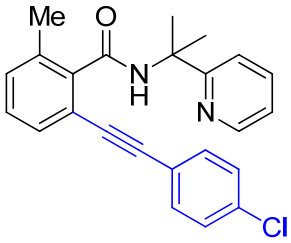
Following **Condition C:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.4 Hz, 1H), 8.06 (br, 1H), 7.64 (td, *J* = 8.0, 1.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.17 – 7.13 (m, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 2.41 (s, 3H), 1.90 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.01, 164.42, 159.65, 147.68, 140.33, 137.12, 135.46, 133.09, 130.19, 129.80, 128.44, 121.92, 120.70, 119.61, 115.44, 113.95, 92.27, 86.35, 57.41, 55.35, 27.69, 19.42; **HRMS** (EI-TOF) calcd for $C_{25}H_{24}N_2O_2$ (M^+): 384.1838, found: 384.1836.



2-((4-(tert-butyl)phenyl)ethynyl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5f

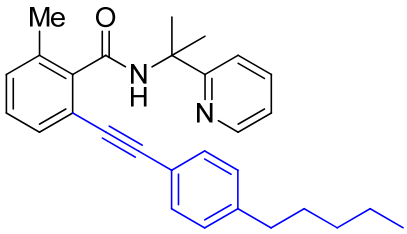
Following **Condition C:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.8 Hz, 1H), 8.08 (br, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.11 (m, 2H), 2.41 (s, 3H), 1.91 (s, 6H), 1.28 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.97, 164.40, 151.56, 147.67, 140.34, 137.11, 135.47, 131.37, 130.30, 129.97,

128.43, 125.29, 121.90, 120.59, 120.26, 119.61, 92.41, 87.02, 57.41, 34.83, 31.24, 27.70, 19.41; **HRMS** (EI-TOF) calcd for $C_{28}H_{30}N_2O$ (M^+): 410.2358, found: 410.2359.



2-((4-chlorophenyl)ethynyl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5g

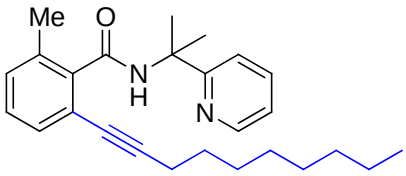
Following **Condition C:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.4 Hz, 1H), 8.14 (br, 1H), 7.67 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.23 – 7.19 (m, 3H), 7.16 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.42 (s, 3H), 1.90 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.85, 164.39, 147.68, 140.65, 137.24, 135.59, 134.35, 132.86, 130.78, 129.90, 128.69, 128.53, 122.03, 121.87, 120.11, 119.62, 91.02, 88.68, 57.41, 27.66, 19.43; **HRMS** (EI-TOF) calcd for $C_{24}H_{21}ClN_2O$ (M^+): 388.1342, found: 388.1342.



2-methyl-6-((4-pentylphenyl)ethynyl)-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5h

Following **Condition C:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.4 Hz, 1H), 8.07 (br, 1H), 7.62 (td, *J* = 8.0, 1.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.90 (s, 6H), 1.61 - 1.52 (m, 2H), 1.32 – 1.26 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.94, 164.40, 147.66, 143.46, 140.36, 137.10, 135.47, 131.53, 130.30, 129.91, 128.42, 128.39, 121.88, 120.58, 120.41, 119.60, 92.48, 87.01, 57.41, 35.92, 31.50,

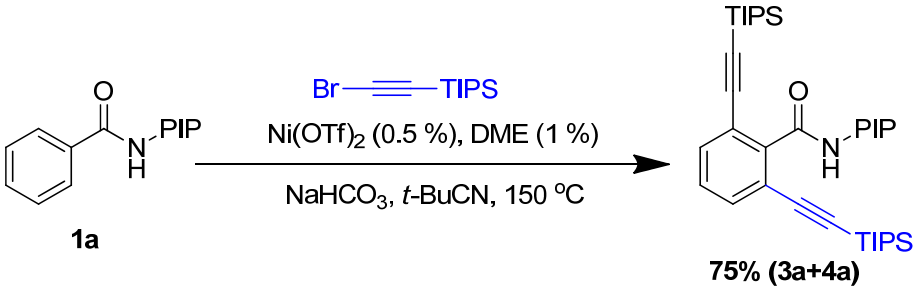
30.95, 27.68, 22.58, 19.40, 14.09; **HRMS** (EI-TOF) calcd for $C_{29}H_{32}N_2O$ (M^+): 424.2515., found: 424.2514.



2-(dec-1-yn-1-yl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5i

Following **Condition C:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.0 Hz, 1H), 7.98 (br, 1H), 7.72 (td, *J* = 8.0, 1.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 1H), 2.37 (s, 3H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.91 (s, 6H), 1.51 – 1.44 (m, 2H), 1.27 – 1.21 (m, 10H), 0.86 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.19, 164.54, 147.69, 140.48, 137.08, 135.30, 129.89, 129.65, 128.29, 121.89, 121.16, 119.57, 93.64, 78.66, 57.29, 31.94, 29.22, 29.20, 29.07, 28.69, 27.64, 22.74, 19.69, 19.40, 14.20; **HRMS** (ESI-TOF) calcd for $C_{26}H_{35}N_2O$ $(M+H)^+$: 391.2744, found: 391.2747.

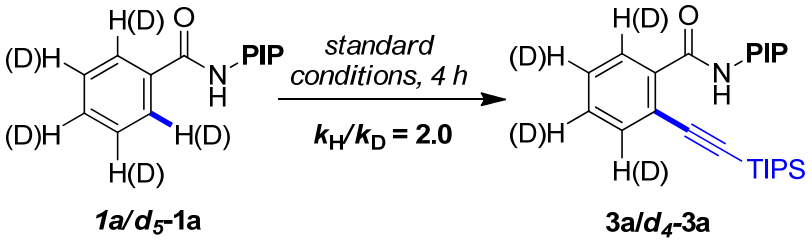
2.4 Gram-scale Reaction



To an oven-dried 100 mL screw-capped vial was added substrate **1a** (6.0 mmol), **2a** (12.0 mmol), $Ni(OTf)_2$ (0.03 mmol), $NaHCO_3$ (12 mmol), DME (0.06 mmol) in *t*-BuCN (6 mL). The mixture was stirred for 36 h at 150 °C under N_2 followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The residue was purified by chromatography on silica gel using hexane/EtOAc as the eluent to afford the product **3a** (1.436 g, 57%) and **4a** (657.9 mg, 18%).

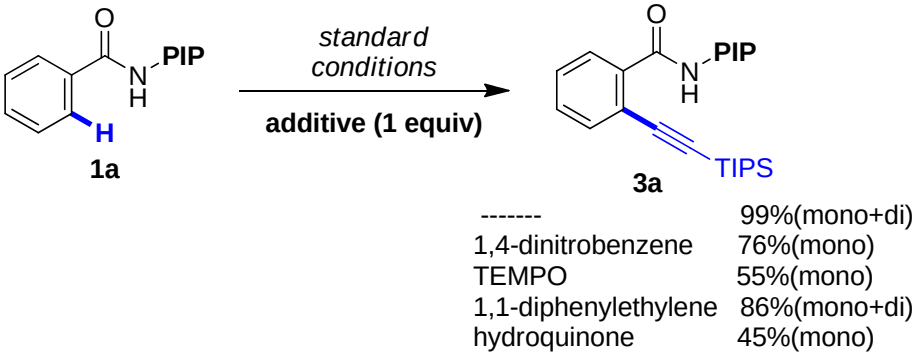
2.5 Mechanistic Investigation

Intrermolecular Competition KIE



To an oven-dried 50 mL screw-capped vial was added substrate **1a** (0.4 mmol), **2a** (0.8 mmol), $Ni(OTf)_2$ (0.8 mg, 0.002 mmol), $NaHCO_3$ (67.2 mg, 0.8 mmol), DME (0.004 mmol) in *t*-BuCN (0.5 mL). The mixture was stirred for 4 h at 150 °C under N_2 followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product. The ratio of product **3a/*d*$_4$-3a** was analyzed by ^{1}H NMR.

Radical Scavenger Reactions



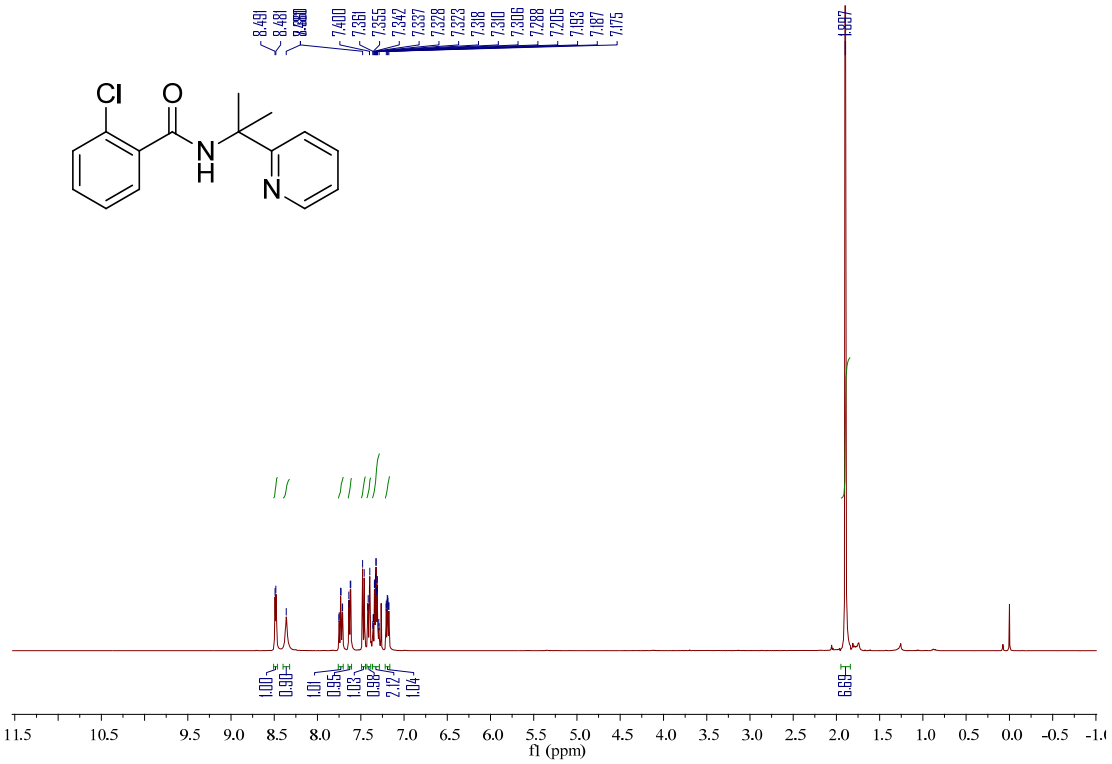
To an oven-dried 50 mL screw-capped vial was added substrate **1a** (0.4 mmol), **2a** (0.8 mmol), $Ni(OTf)_2$ (0.8 mg, 0.002 mmol), $NaHCO_3$ (67.2 mg, 0.8 mmol), additives (0.4 mmol), DME (0.004 mmol) in *t*-BuCN (0.5 mL). The mixture was stirred for 24 h at 150 °C under N_2 followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The yield of product **3a** was analyzed by ^{1}H NMR.

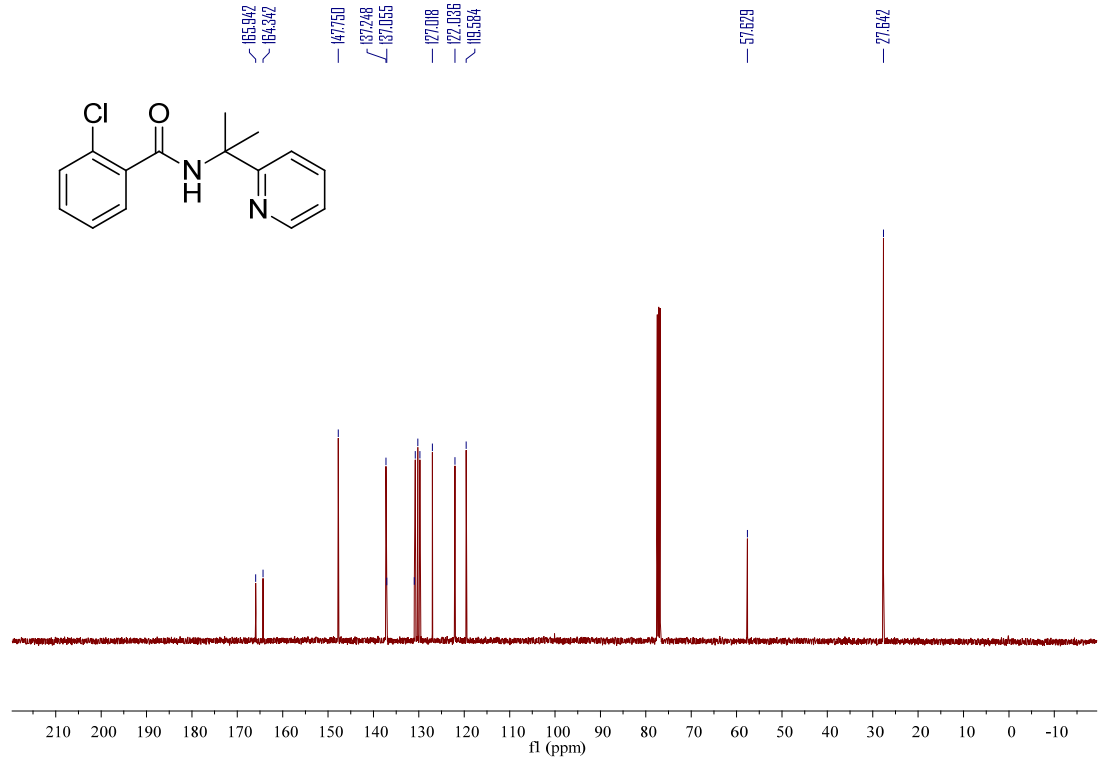
3. References:

1. Y. Aihara, N. Chatani, *J. Am. Chem. Soc.* 2013, **135**, 5308.
2. F-J. Chen, G. Liao, X. Li, J. Wu, B-F. Shi, *Org. Lett.* **DOI:** 10.1021/ol5027156
3. **X.** Li, Y-H. Liu, Yan-Hua, W-J. Gu, B. Li, F-J. Chen, B-F. Shi, *Org. Lett.* 2014**, 16**, 3904.

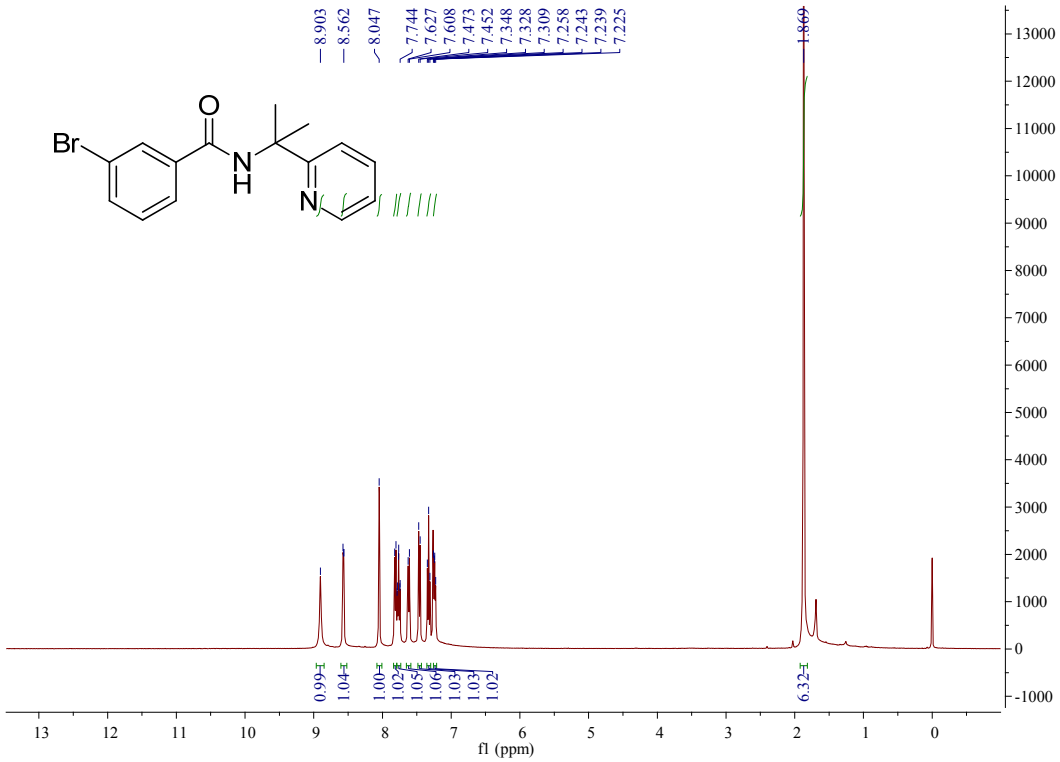
4. NMR Spectra

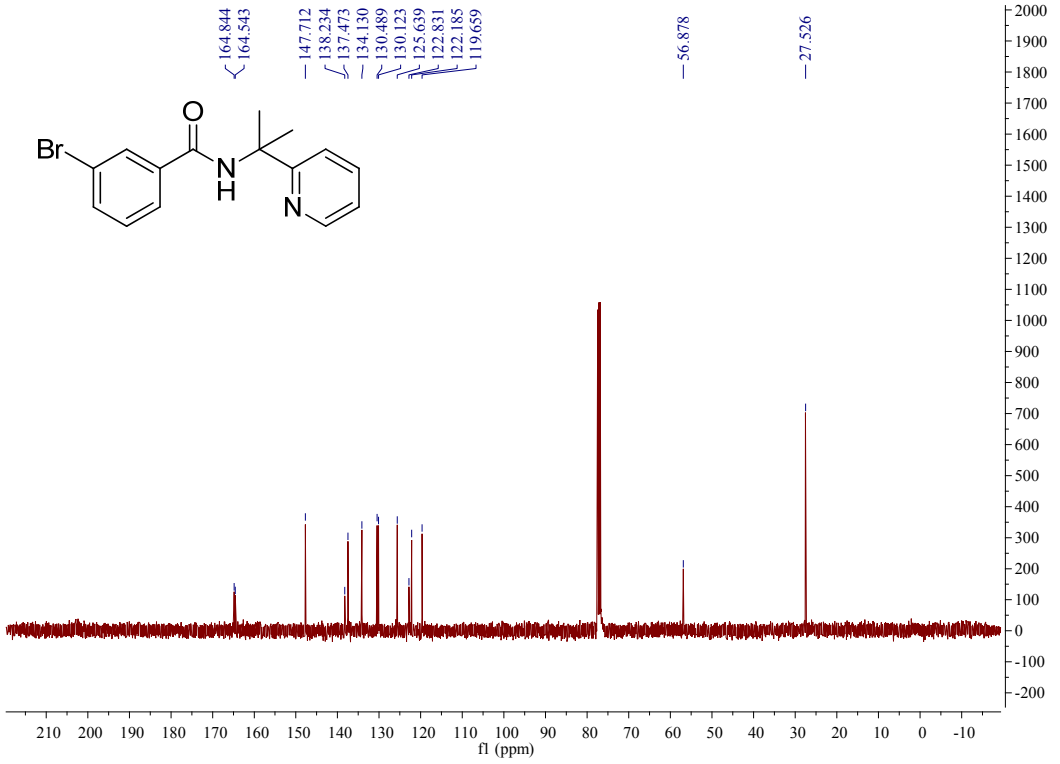
1f



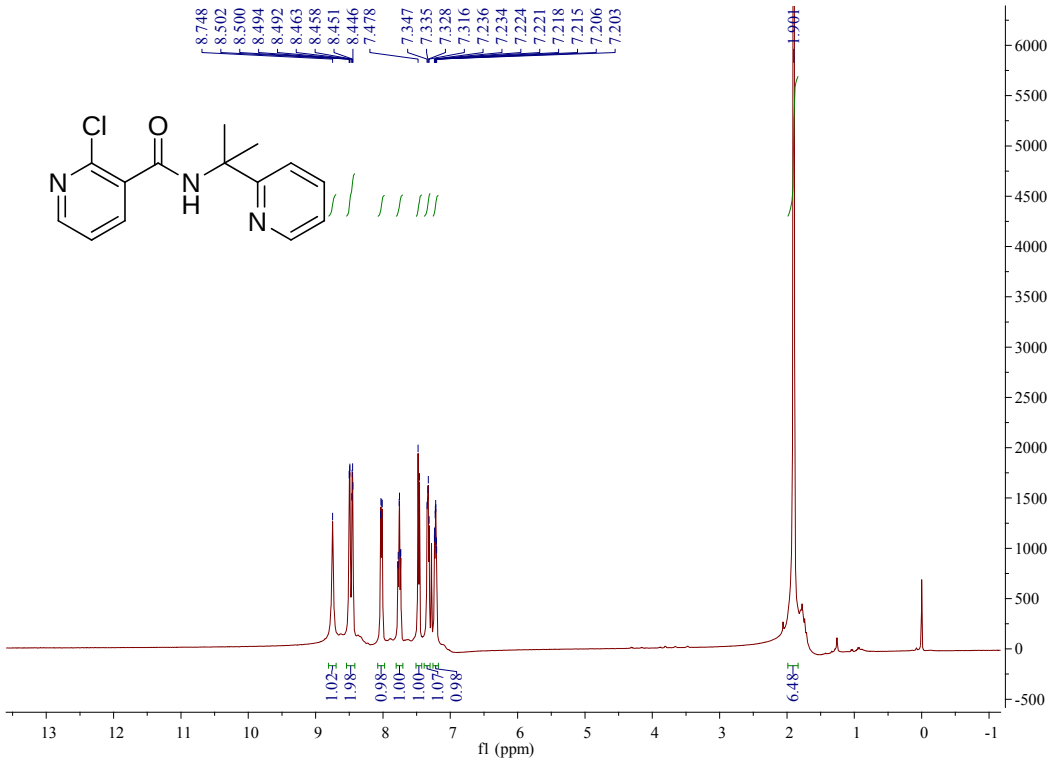


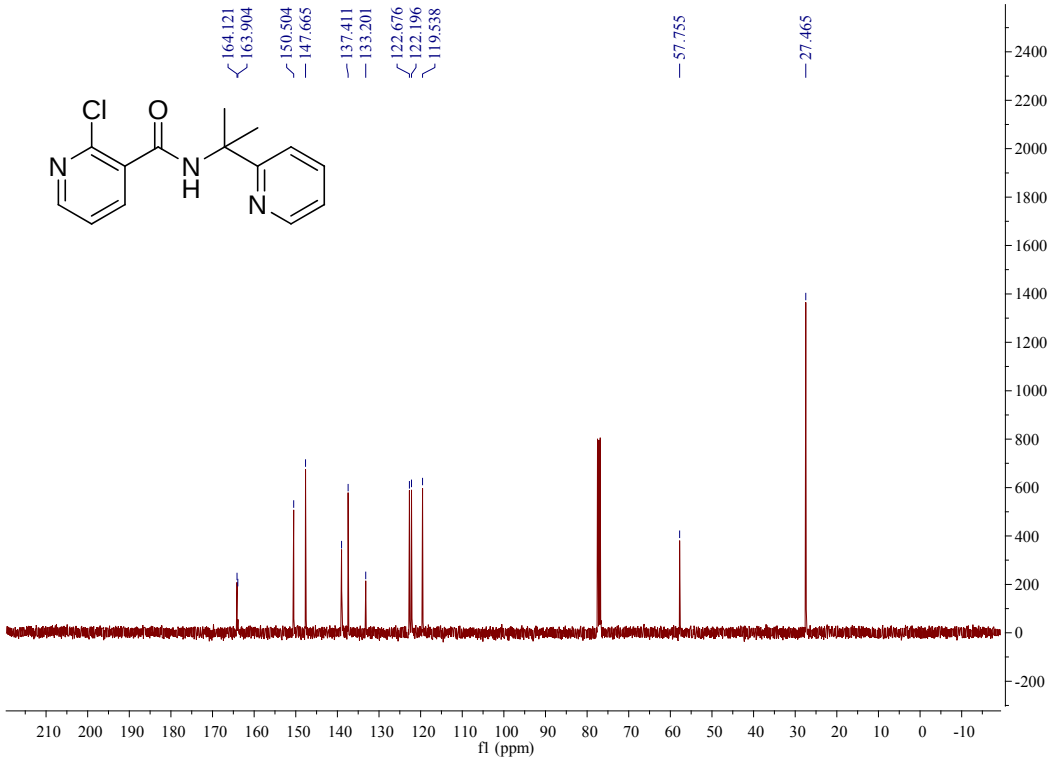
1i


8.903
8.562
8.047
7.744
7.627
7.608
7.473
7.452
7.348
7.328
7.309
7.258
7.243
7.239
7.225
1.869
Br
O
N
H
N
0.99
1.04
1.00
1.02
1.05
1.06
1.03
1.03
1.02
6.32
fl (ppm)

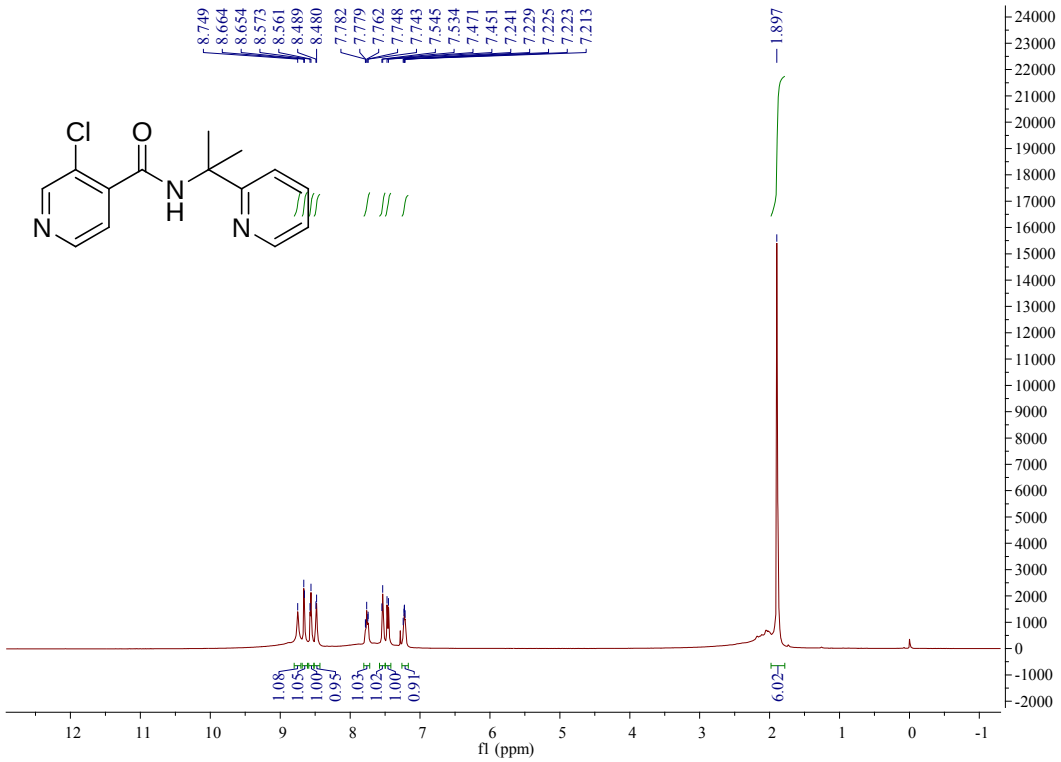

164.844
164.543
147.712
138.234
137.473
134.130
130.489
130.123
125.639
122.831
122.185
119.659
56.878
27.526
Br
O
N
H
N
fl (ppm)

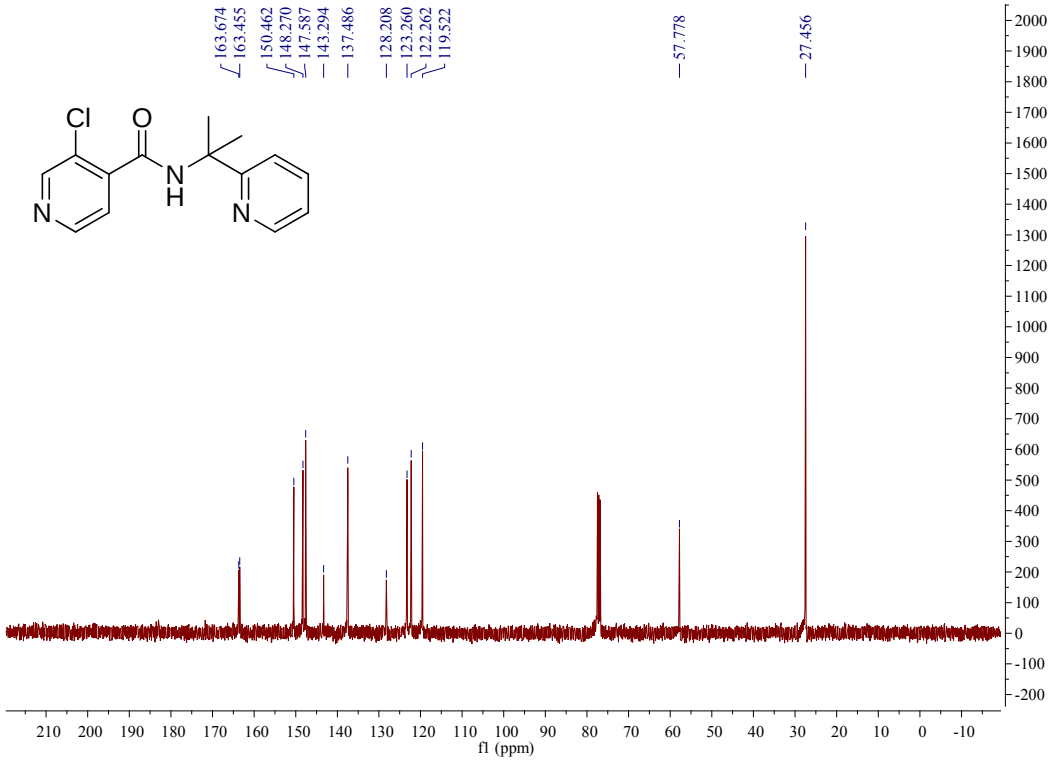
1n


8.748
8.502
8.500
8.494
8.492
8.463
8.458
8.451
8.446
7.478
7.347
7.335
7.328
7.316
7.236
7.234
7.224
7.221
7.218
7.215
7.206
7.203
1.901
Cl
O
N
N
H
N
1.02
1.98
0.98
1.00
1.00
1.07
0.98
6.48
fl (ppm)


164.121
163.904
150.504
147.665
137.411
133.201
122.676
122.196
119.538
57.755
27.465
Cl
O
N
N
H
N
fl (ppm)

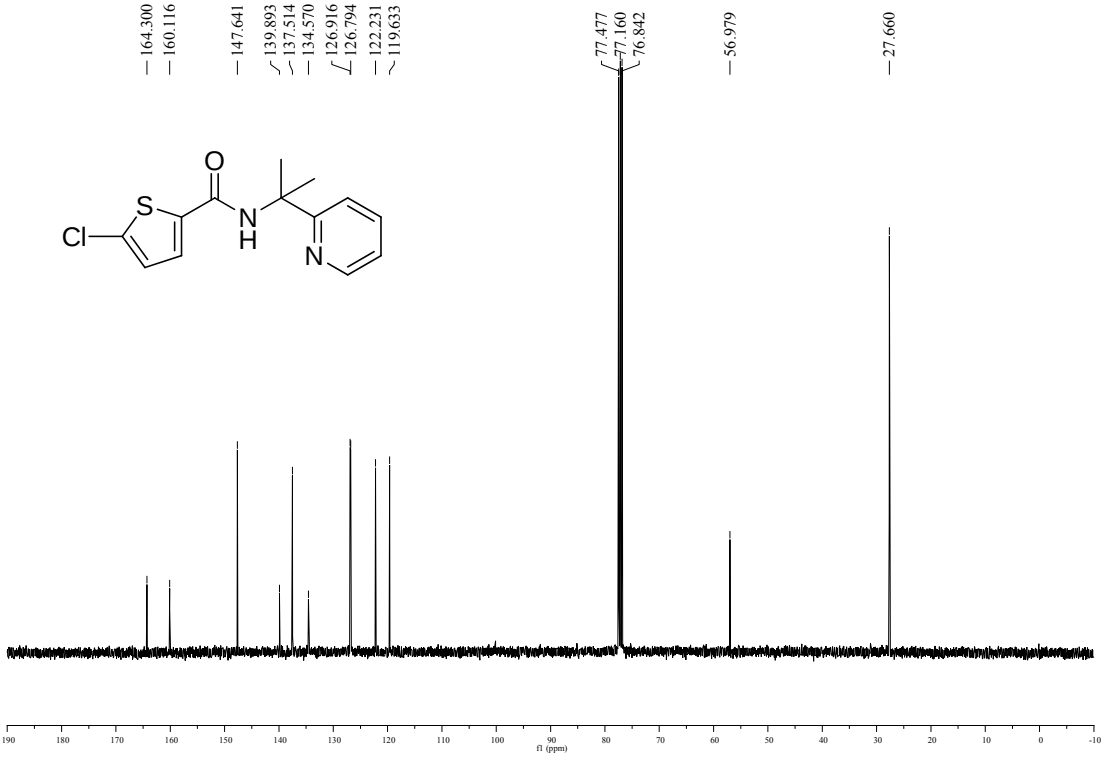
1p


8.749
8.664
8.654
8.573
8.561
8.489
8.480
7.782
7.779
7.762
7.748
7.743
7.545
7.534
7.471
7.451
7.241
7.229
7.225
7.223
7.213
1.897
Cl
O
N
H
N
N
1.08
1.05
1.00
0.95
1.03
1.02
1.00
0.91
6.02
f1 (ppm)

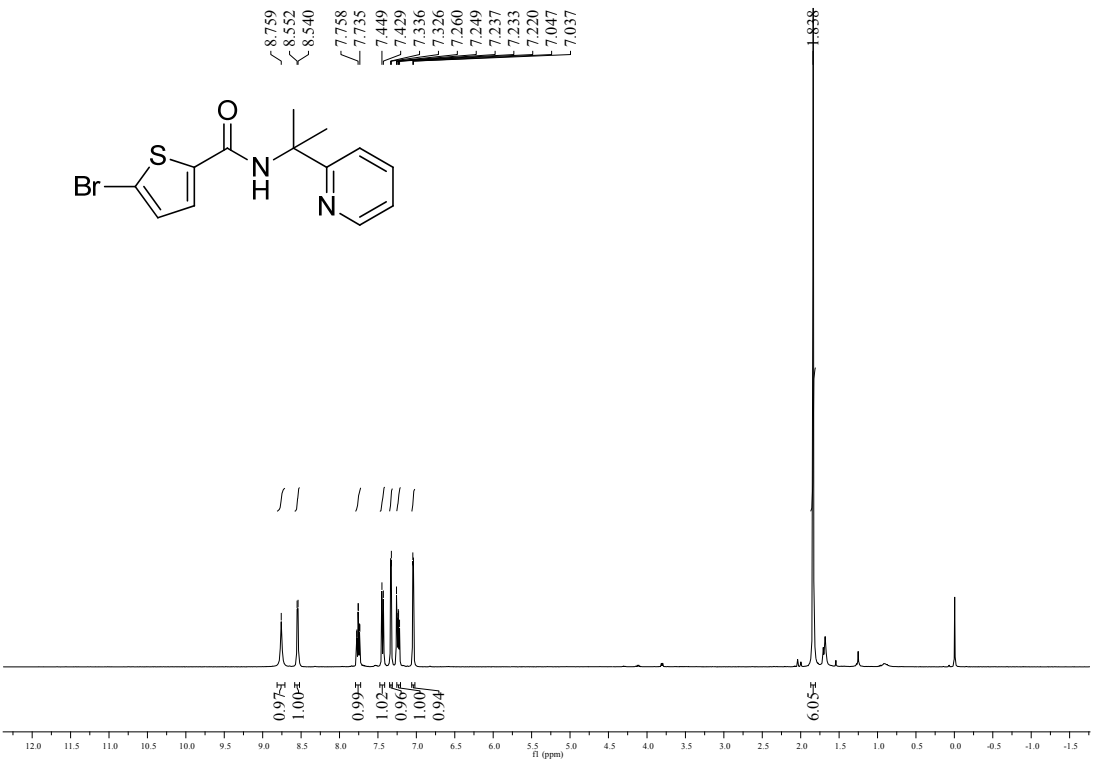

163.674
163.455
150.462
148.270
147.587
143.294
137.486
128.208
123.260
122.262
119.522
57.778
27.456
Cl
O
N
H
N
N
f1 (ppm)

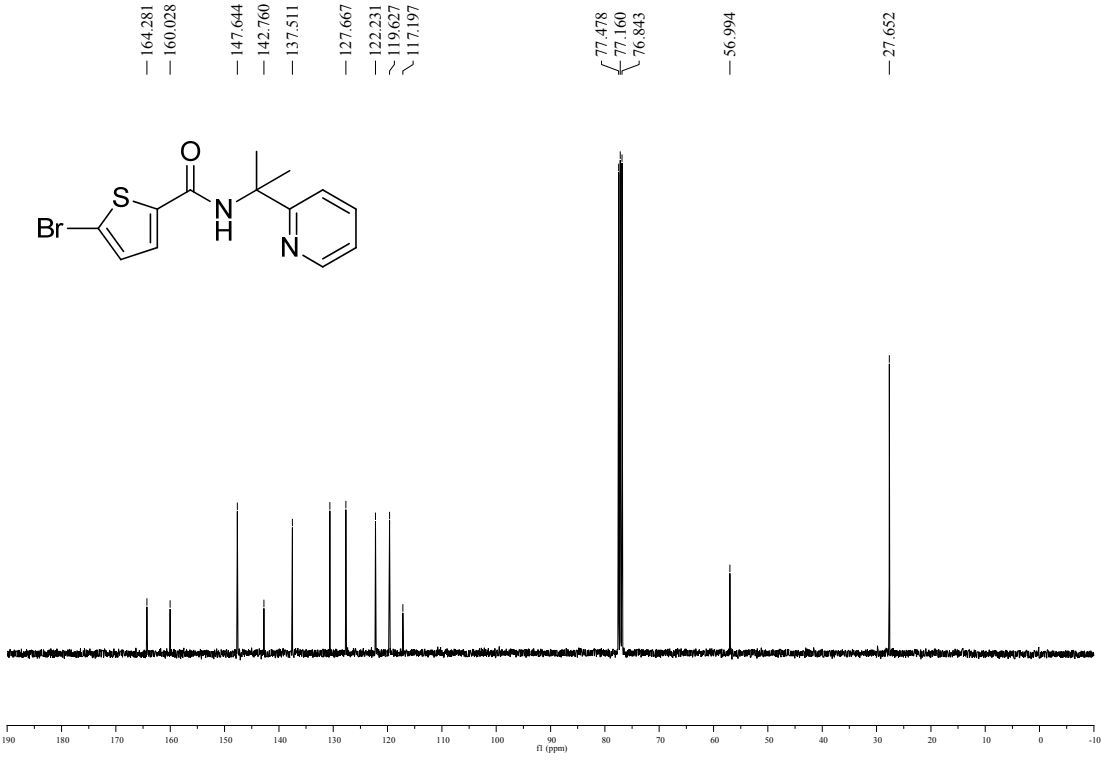
1u


8.759
8.550
8.538
7.759
7.736
7.260
7.231
6.906
6.896
1.837
O
S
Cl
N
H
N
1.01
1.00
1.05
0.97
6.10
f1 (ppm)

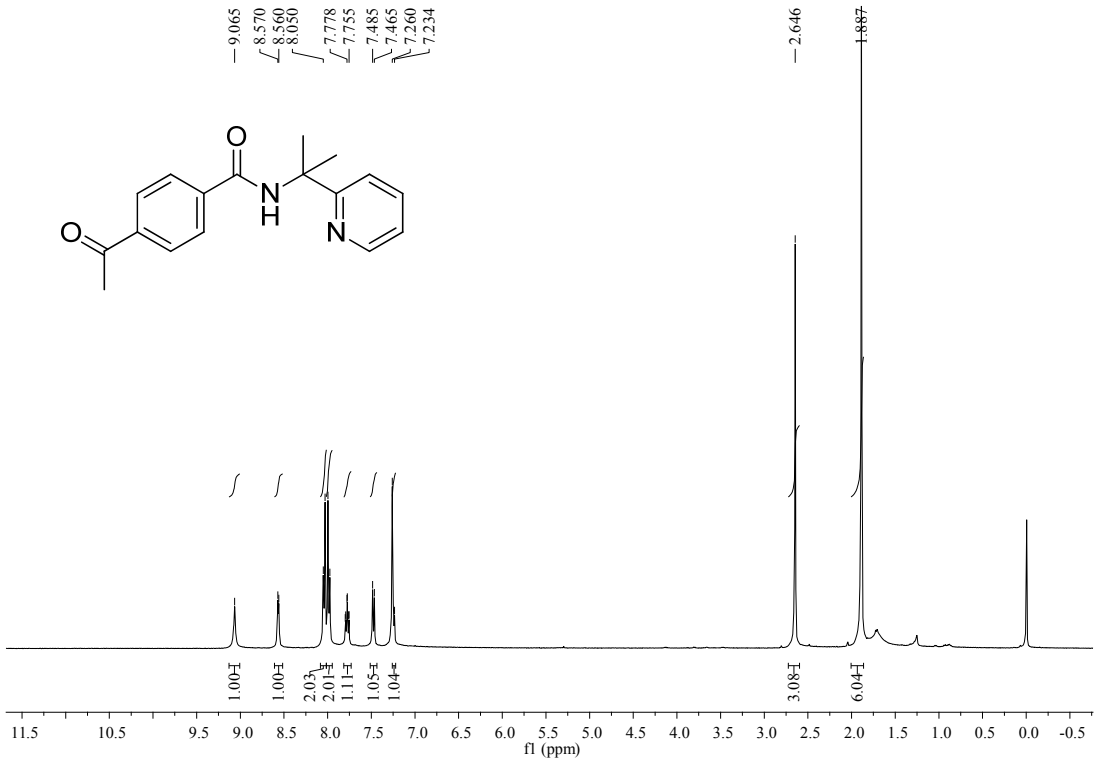

164.300
160.116
147.641
139.893
137.514
134.570
126.916
126.794
122.231
119.633
77.477
77.160
76.842
56.979
27.660
O
S
Cl
N
H
N
f1 (ppm)

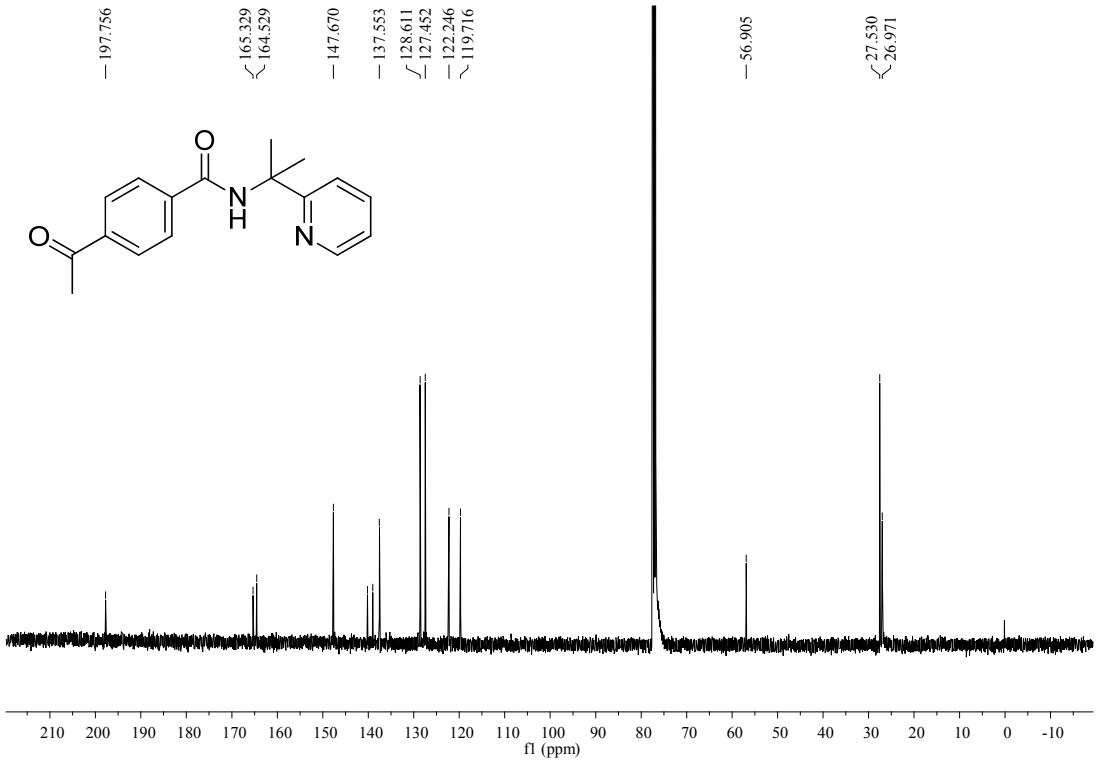
1v


8.759
8.552
8.540
7.758
7.735
7.449
7.429
7.336
7.326
7.260
7.249
7.237
7.233
7.220
7.047
7.037
1.838
O
S
N
H
Br
N
0.97
1.00
0.99
1.02
0.96
1.00
0.94
6.05
f1 (ppm)

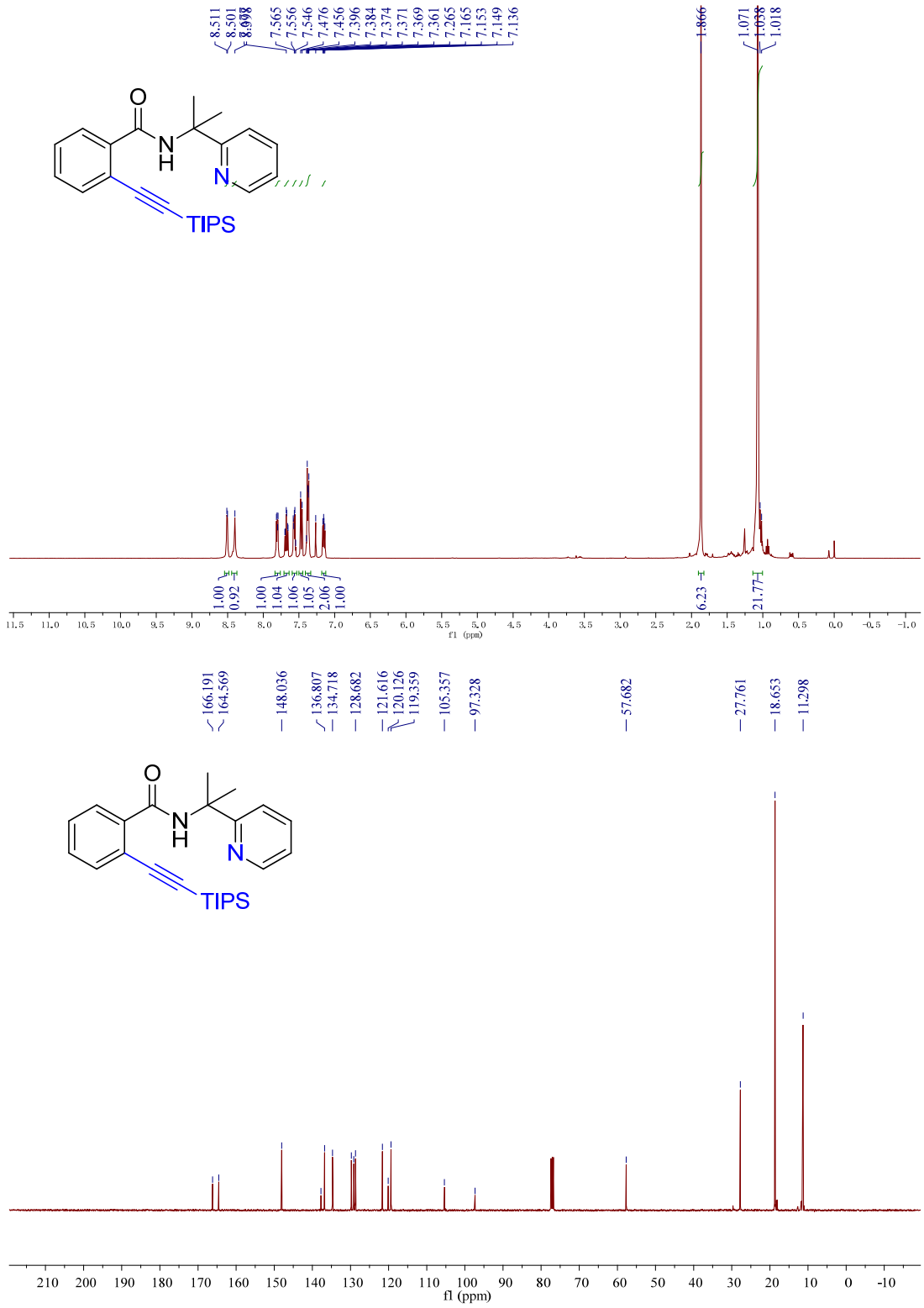

164.281
160.028
147.644
142.760
137.511
127.667
122.231
119.627
117.197
77.478
77.160
76.843
56.994
27.652
O
S
N
H
Br
N
f1 (ppm)

1ae

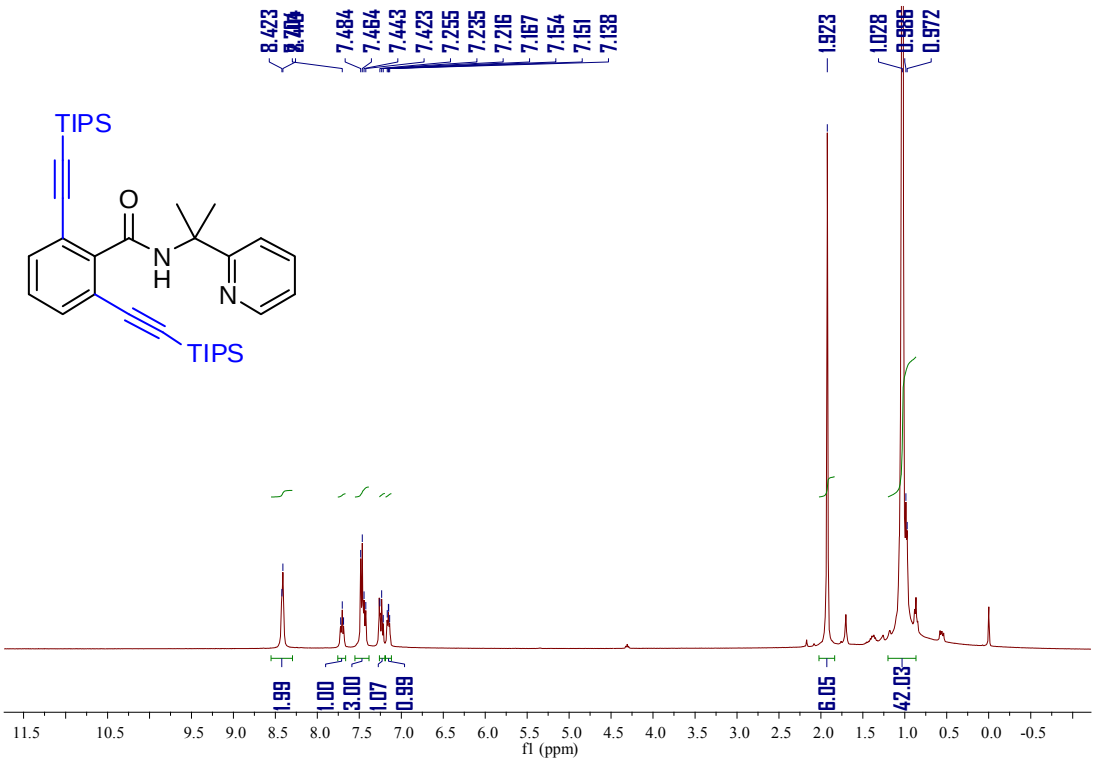

9.065
8.570
8.560
8.050
7.778
7.755
7.485
7.465
7.260
7.234
2.646
1.887
1.00
1.00
2.03
2.01
1.11
1.05
1.04
3.08
6.04
f1 (ppm)

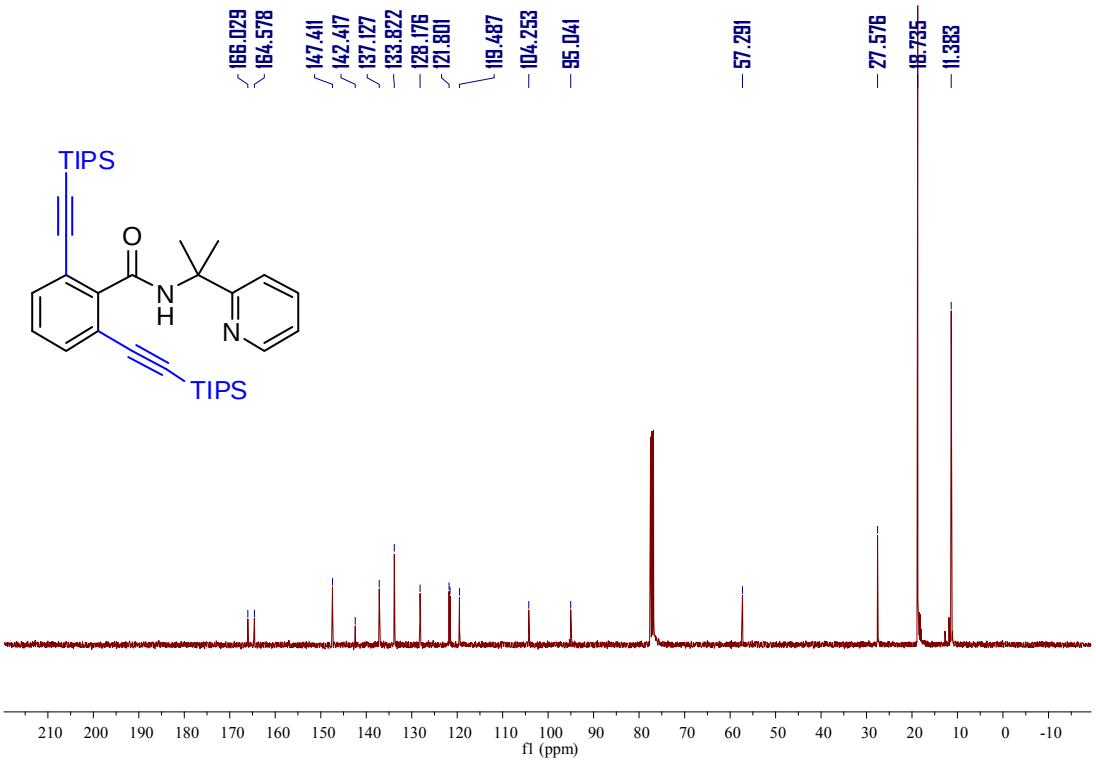

197.756
165.329
164.529
147.670
137.553
128.611
127.452
122.246
119.716
56.905
27.530
26.971
f1 (ppm)

3a

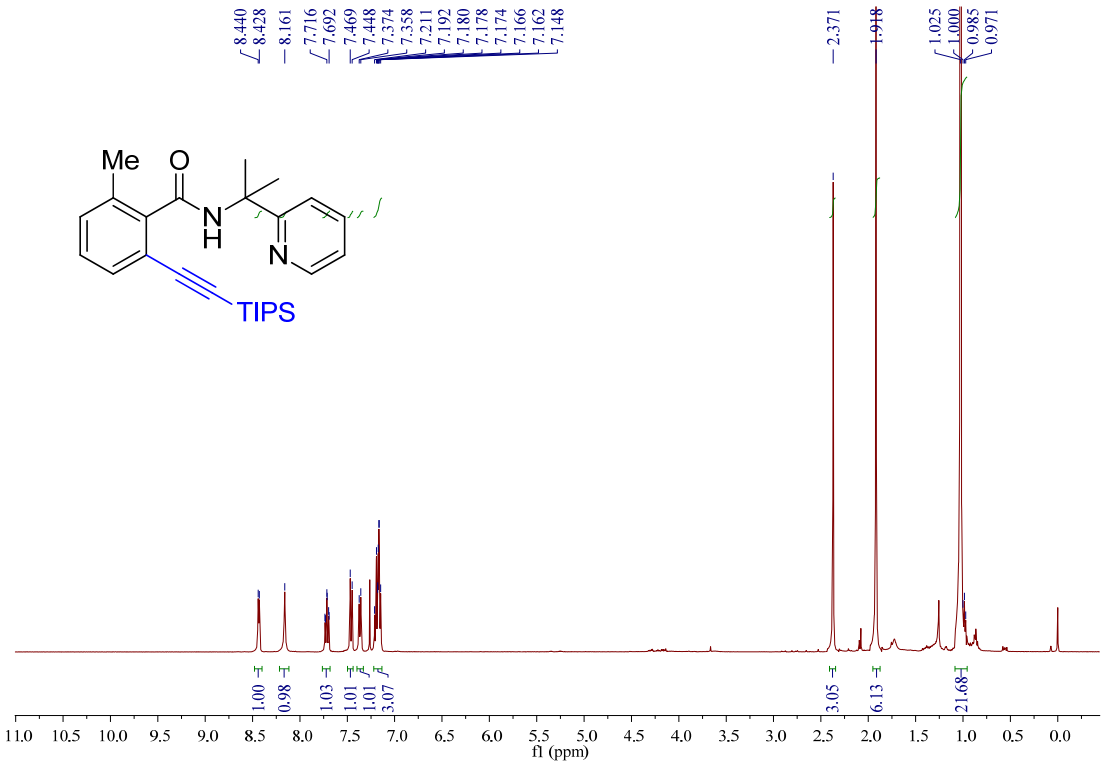

8.511
8.501
7.565
7.556
7.546
7.476
7.456
7.396
7.384
7.374
7.371
7.369
7.361
7.265
7.165
7.153
7.149
7.136
1.866
1.071
1.038
1.018
O
N
H
N
TIPS
1.00
0.92
1.00
1.04
1.06
1.05
2.06
1.00
6.23
21.77
f1 (ppm)
166.191
164.569
148.036
136.807
134.718
128.682
121.616
120.126
119.359
105.357
97.328
57.682
27.761
18.653
11.298
O
N
H
N
TIPS
f1 (ppm)

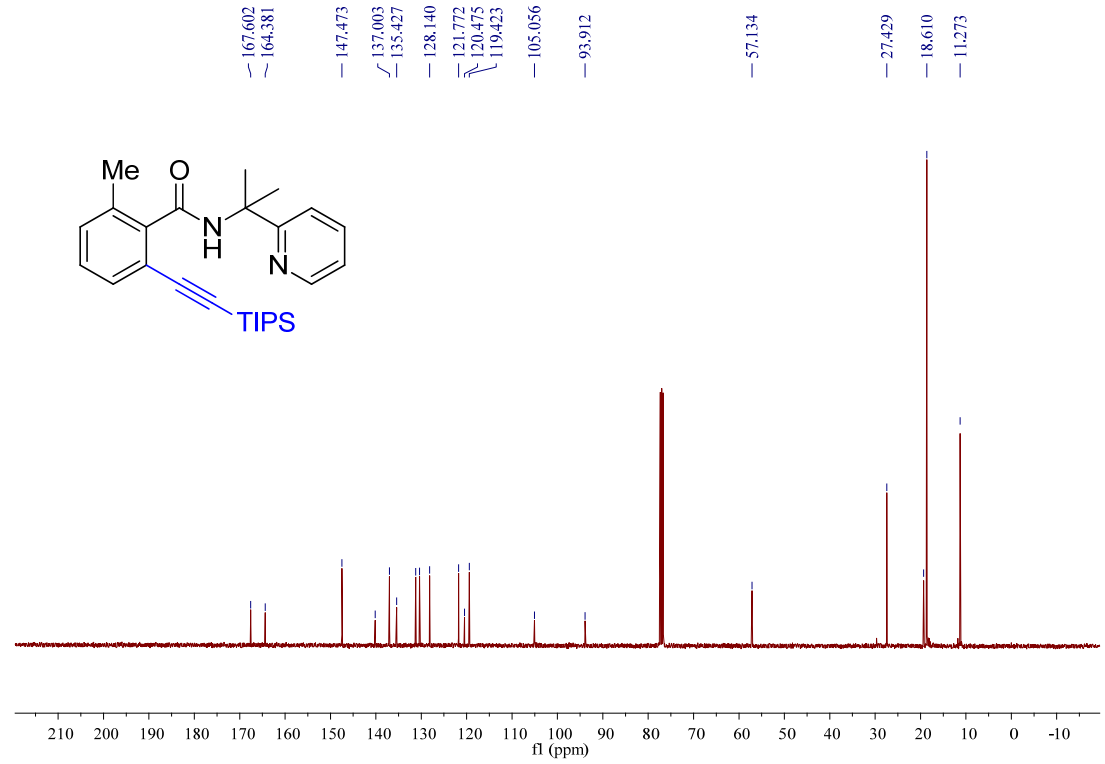
4a


8.423
7.484
7.464
7.443
7.423
7.255
7.235
7.216
7.167
7.154
7.151
7.138
1.923
1.028
0.972
TIPS
O
N
H
N
TIPS
1.99
1.00
3.00
1.07
0.99
6.05
42.03
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

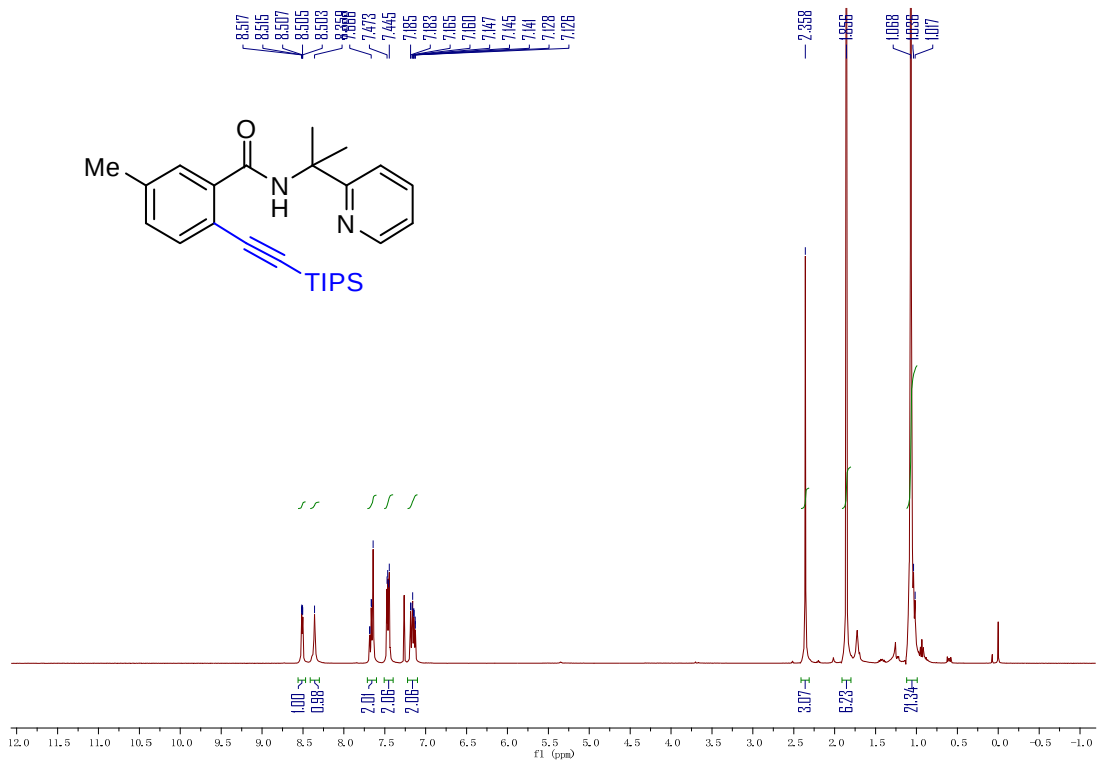

166.029
164.578
147.411
142.417
137.127
133.822
128.176
121.801
119.487
104.253
95.041
57.291
27.576
18.735
11.383
TIPS
O
N
H
N
TIPS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

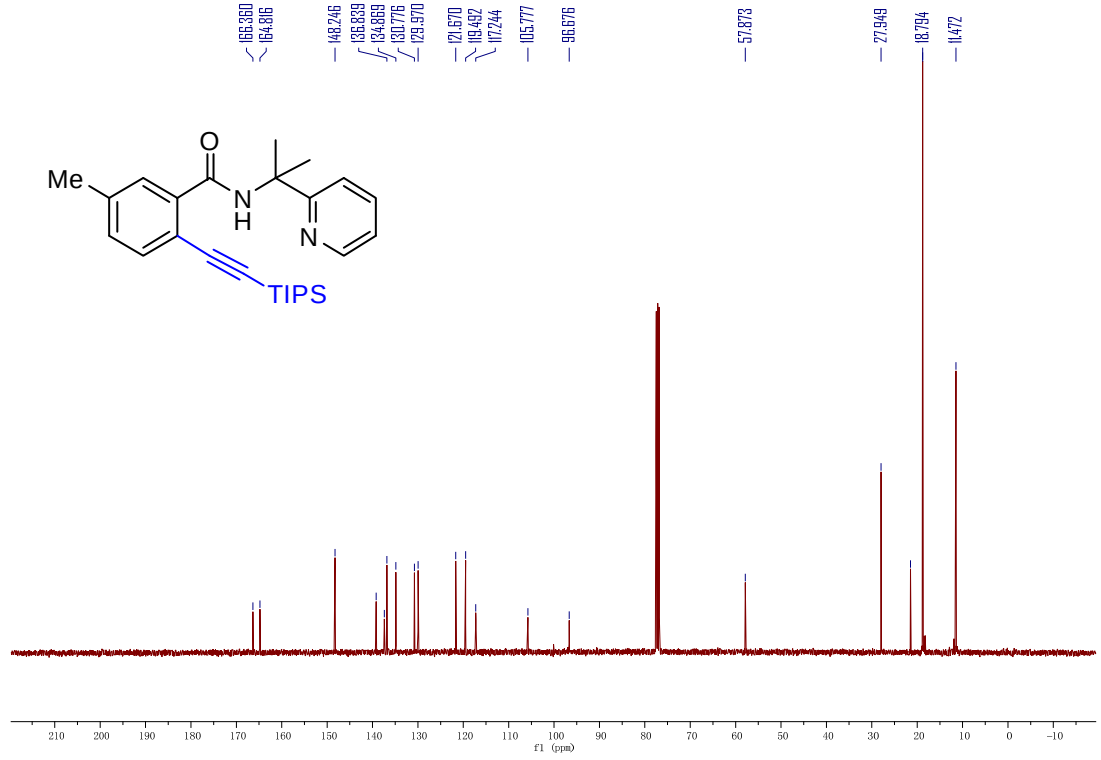
3b


8.440
8.428
8.161
7.716
7.692
7.469
7.448
7.374
7.358
7.211
7.192
7.180
7.178
7.174
7.166
7.162
7.148
2.371
1.918
1.025
1.000
0.985
0.971
Me
O
N
H
N
TIPS
1.00
0.98
1.03
1.01
1.01
3.07
3.05
6.13
21.68
f1 (ppm)

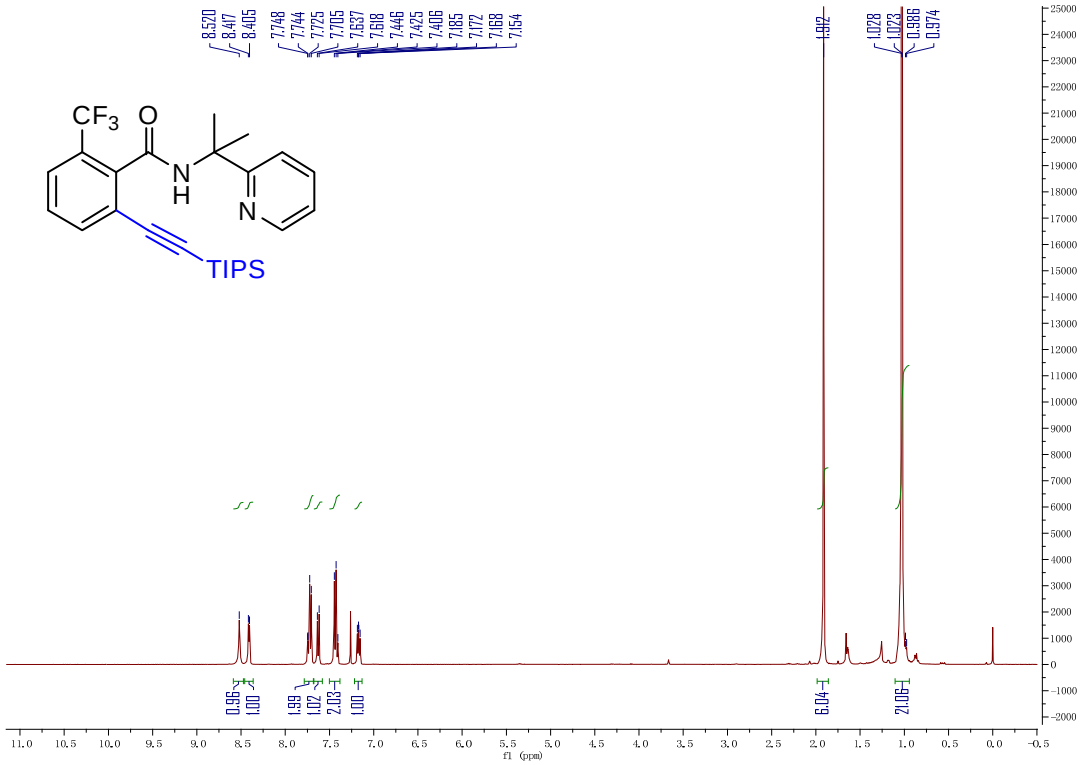

167.602
164.381
147.473
137.003
135.427
128.140
121.772
120.475
119.423
105.056
93.912
57.134
27.429
18.610
11.273
Me
O
N
H
N
TIPS
f1 (ppm)

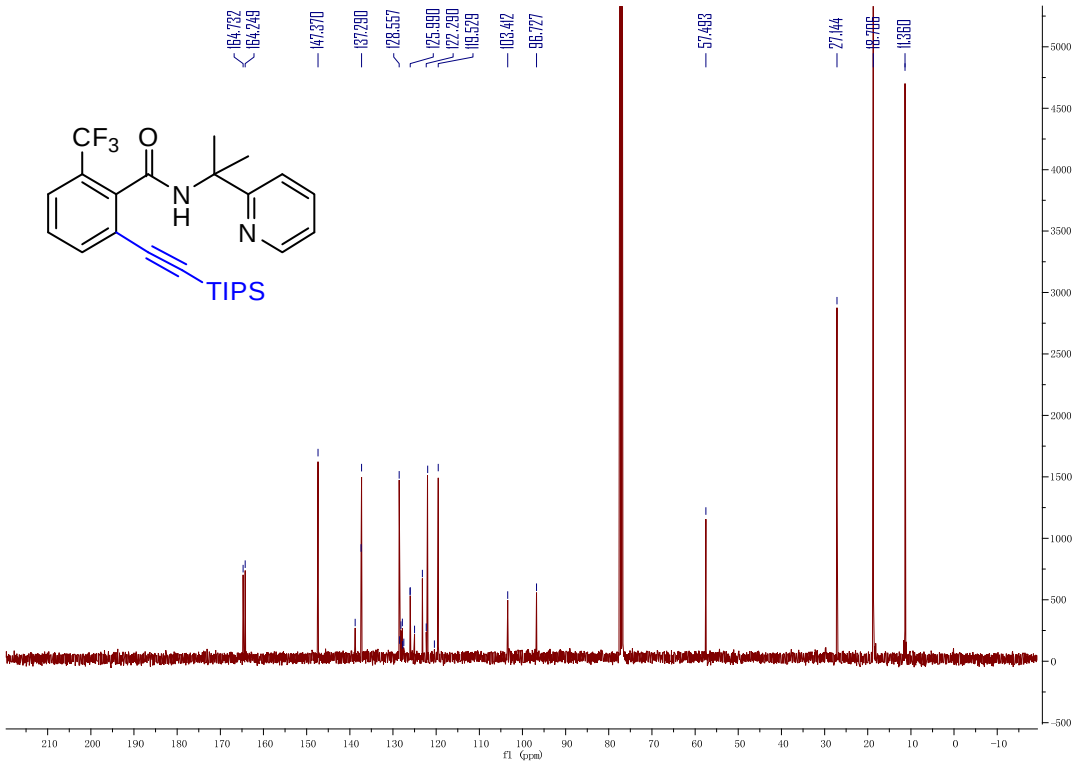
3c

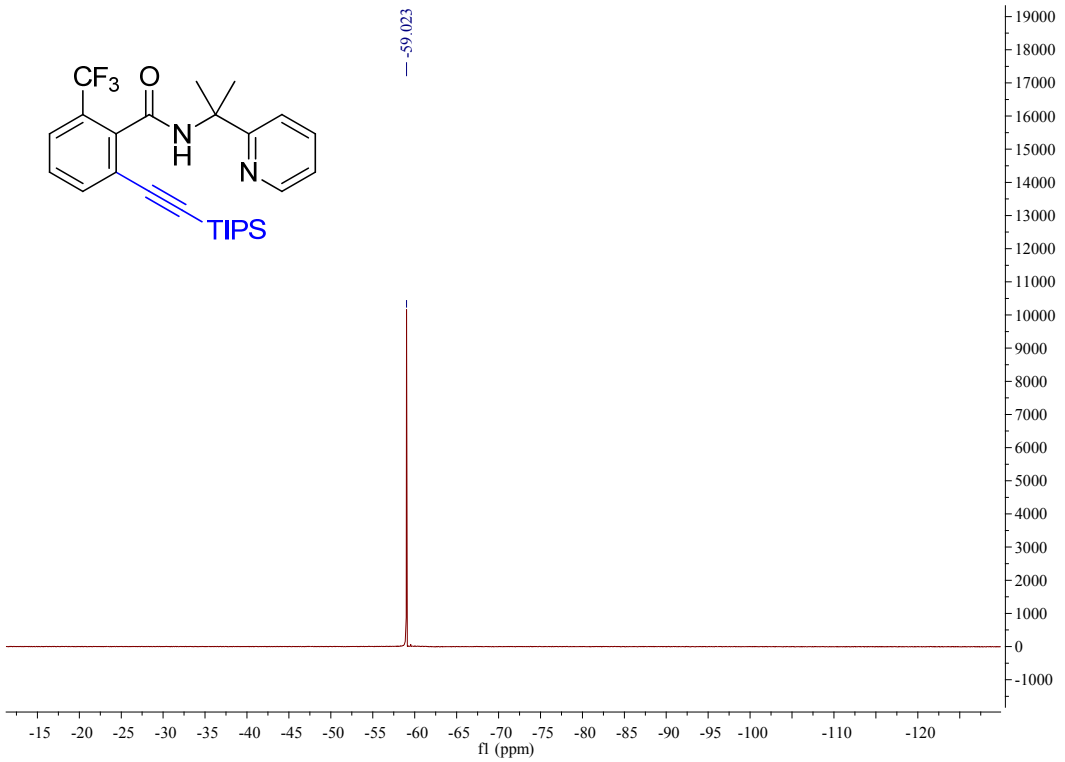

8.517
8.515
8.507
8.505
8.503
7.473
7.445
7.185
7.183
7.165
7.160
7.147
7.145
7.141
7.128
7.126
2.358
1.955
1.068
1.017
Me
O
N
H
N
TIPS
1.00
0.98
2.01
2.06
2.06
3.07
6.23
21.34
f1 (ppm)


166.380
164.816
148.246
136.833
134.869
130.776
129.970
121.670
119.432
117.244
105.777
96.676
57.873
27.949
18.794
11.472
Me
O
N
H
N
TIPS
f1 (ppm)

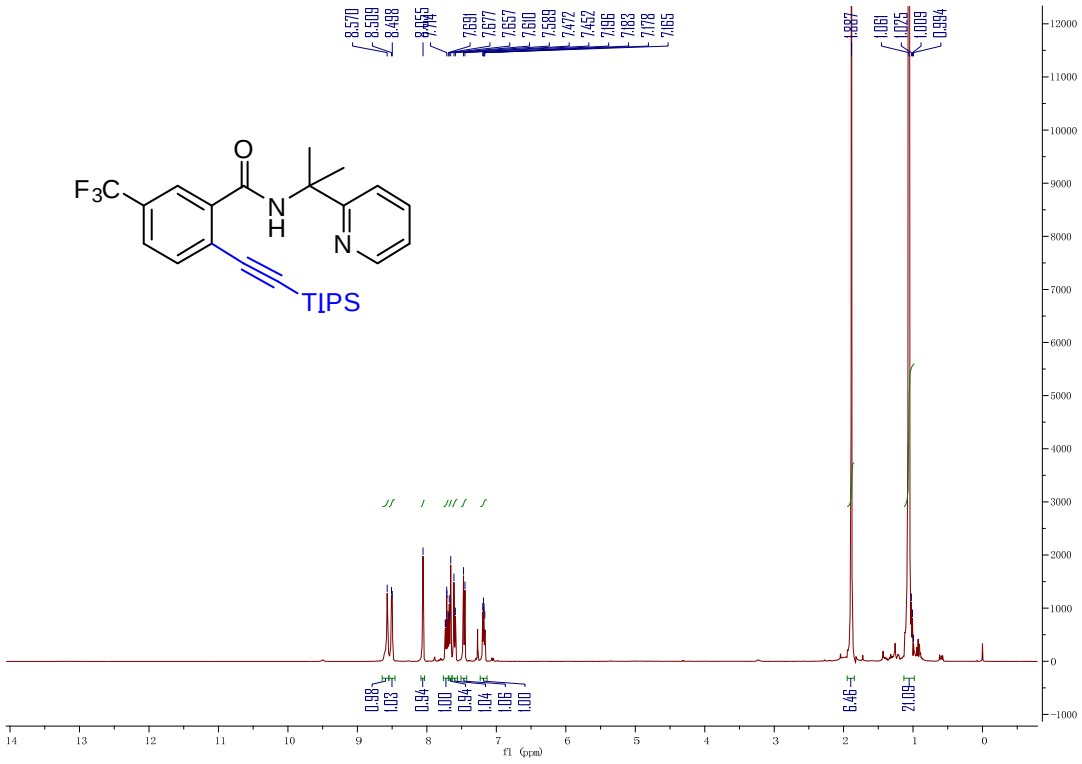
3d

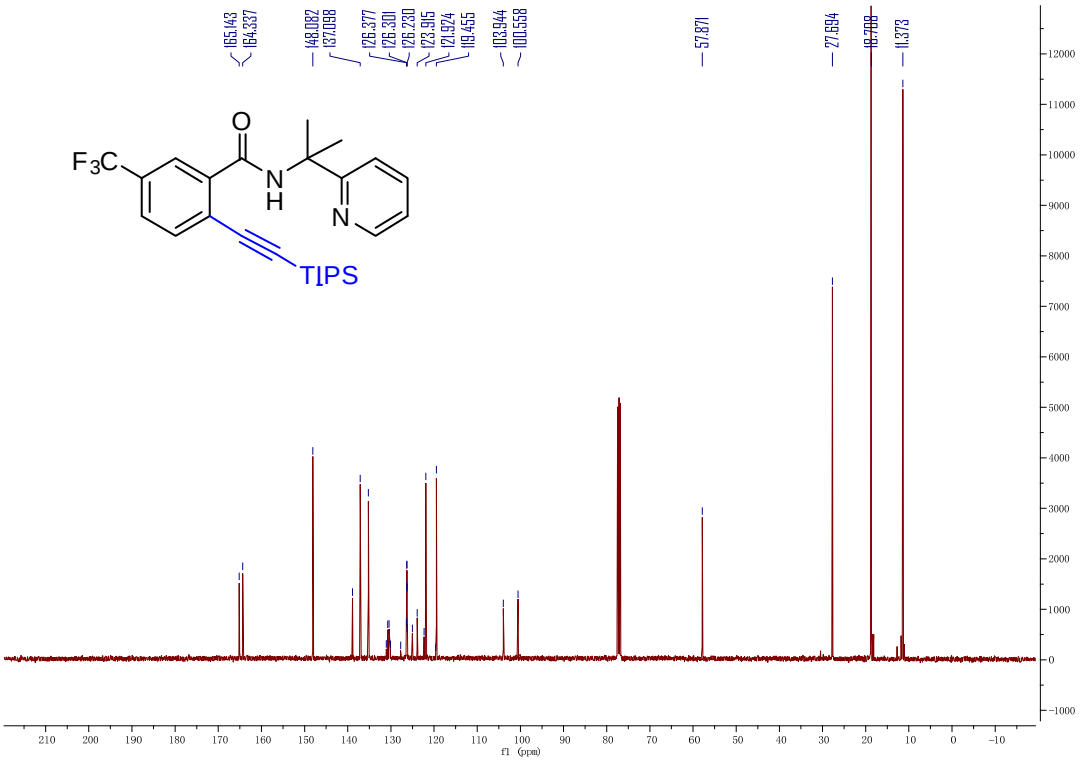

8.520
8.417
8.405
7.748
7.744
7.725
7.705
7.637
7.618
7.446
7.425
7.406
7.185
7.172
7.168
7.154
4.892
1.028
1.023
0.986
0.974
CF3
O
N
H
N
TIPS
0.96
1.00
1.93
1.02
2.03
1.00
6.04
21.06
f1 (ppm)

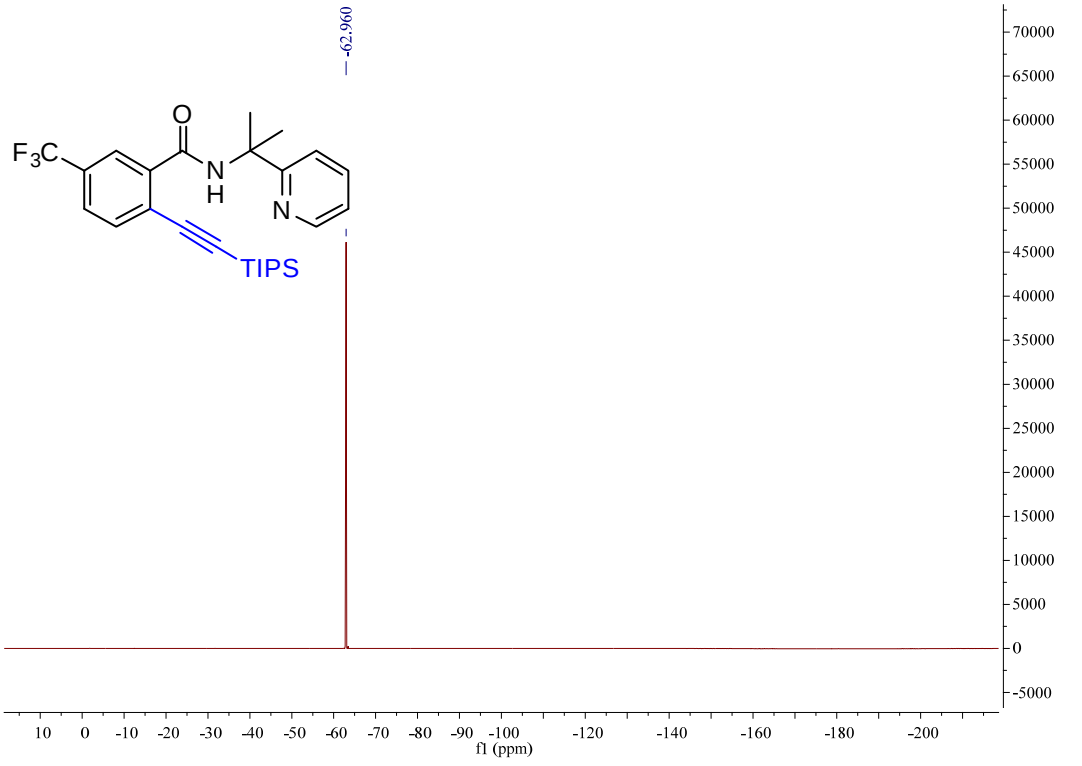

164.732
164.249
147.370
137.290
128.557
125.990
122.290
119.529
103.412
96.727
57.493
27.144
18.788
11.360
CF3
O
N
H
N
TIPS
f1 (ppm)



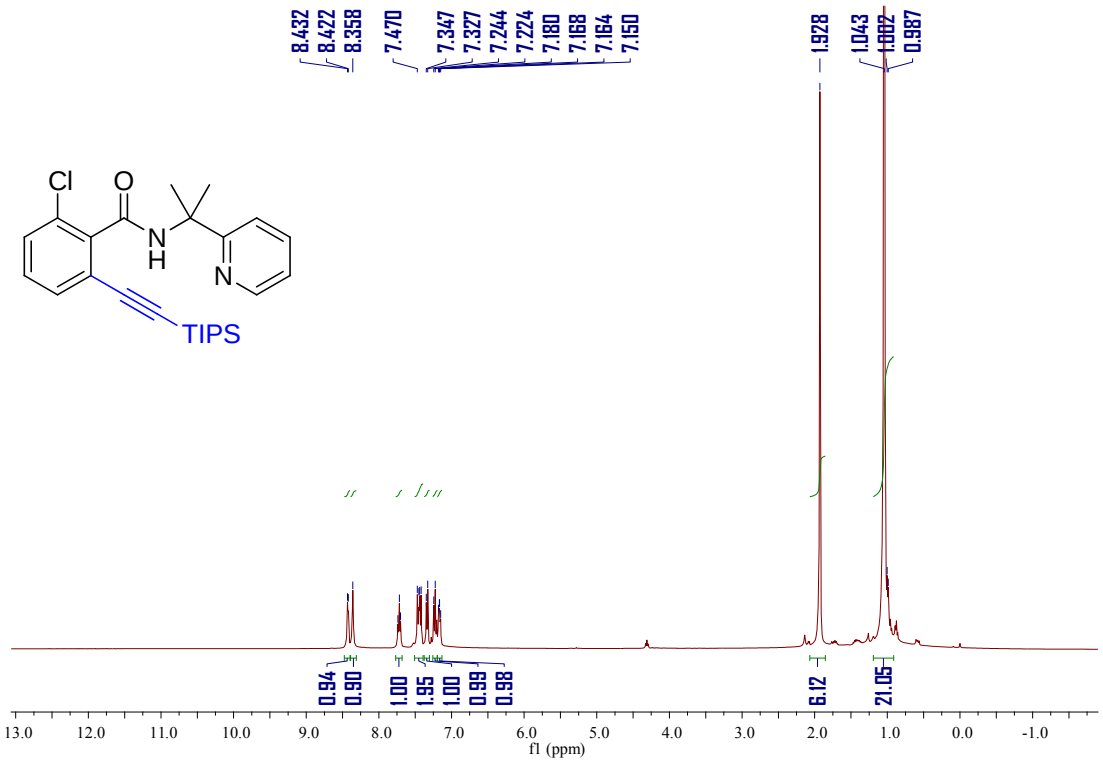
3e

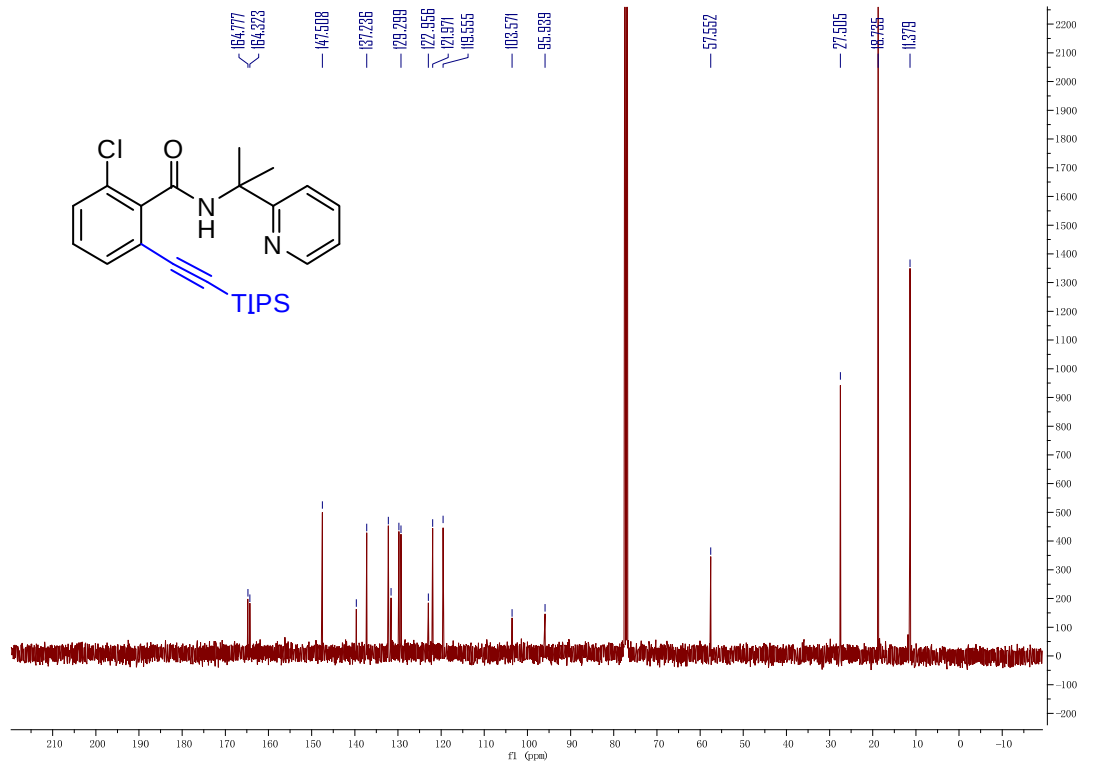



165.143
164.337
148.082
137.058
126.377
126.310
126.230
123.915
121.924
119.455
103.944
100.558
57.871
27.694
18.788
11.373
F3C
O
N
H
N
TIPS
f1 (ppm)

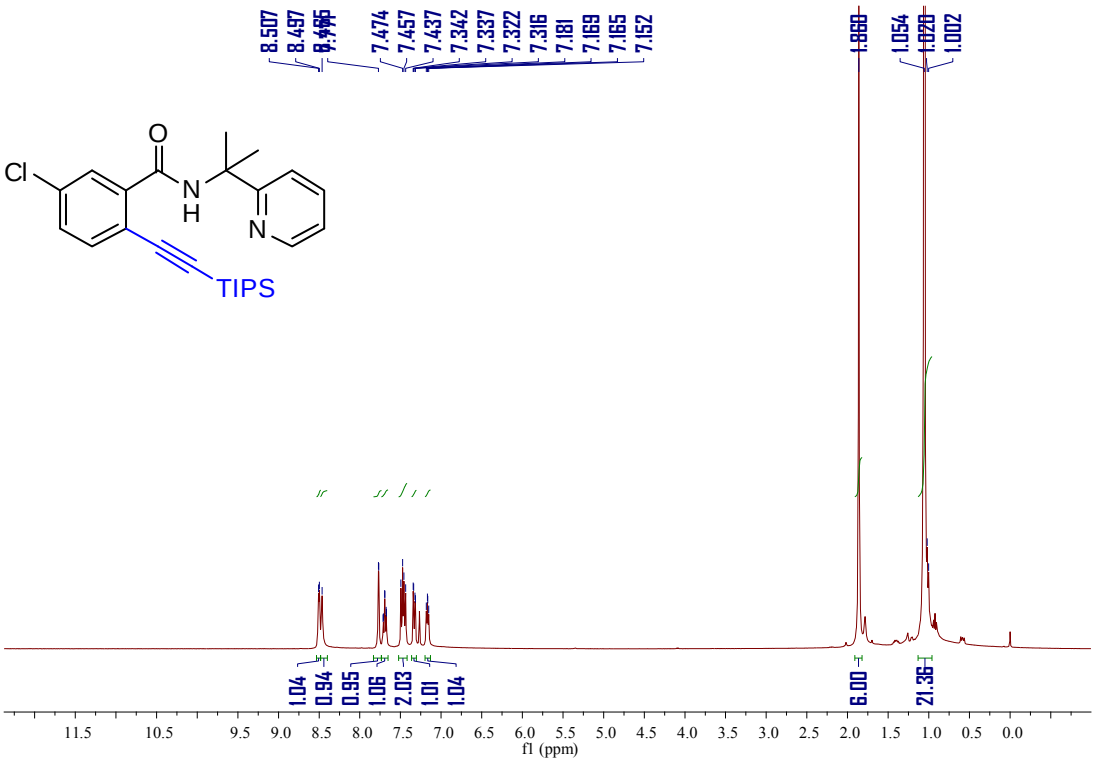

-62.960
F3C
O
N
H
N
TIPS
f1 (ppm)

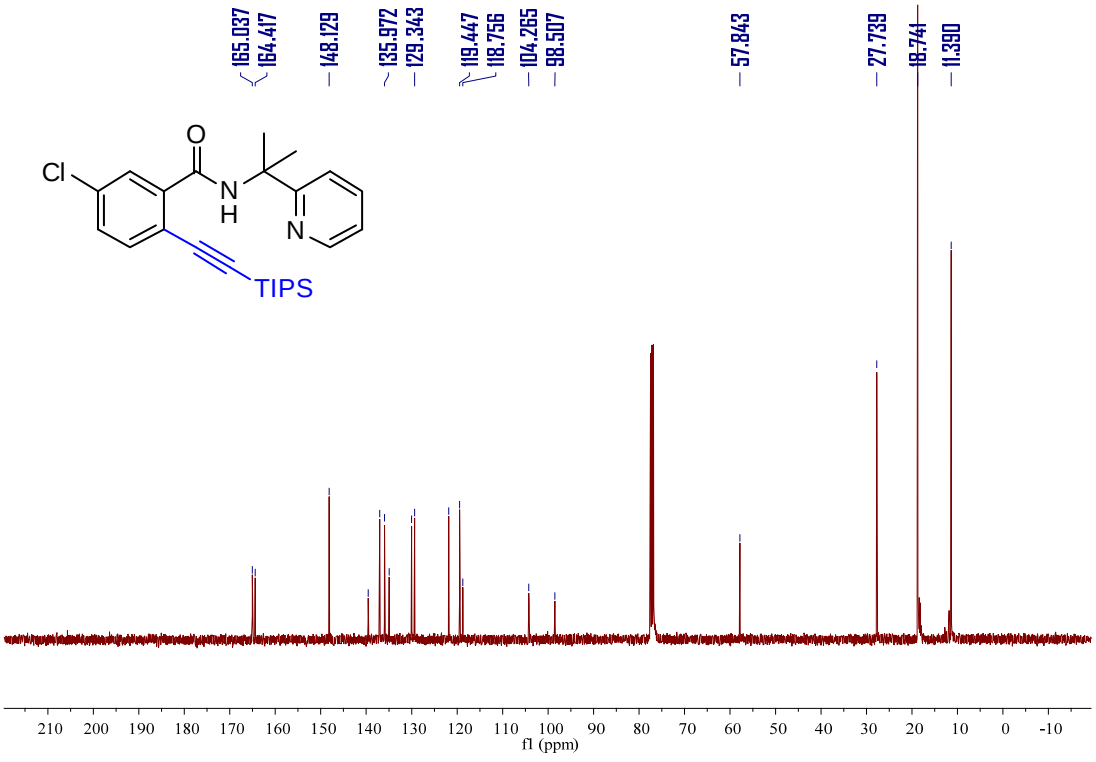
3f


8.432
8.422
8.358
7.470
7.347
7.327
7.244
7.224
7.180
7.168
7.164
7.150
1.928
1.043
1.002
0.987
Cl
O
N
H
N
TIPS
0.94
0.90
1.00
1.95
1.00
0.99
0.98
6.12
21.05
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

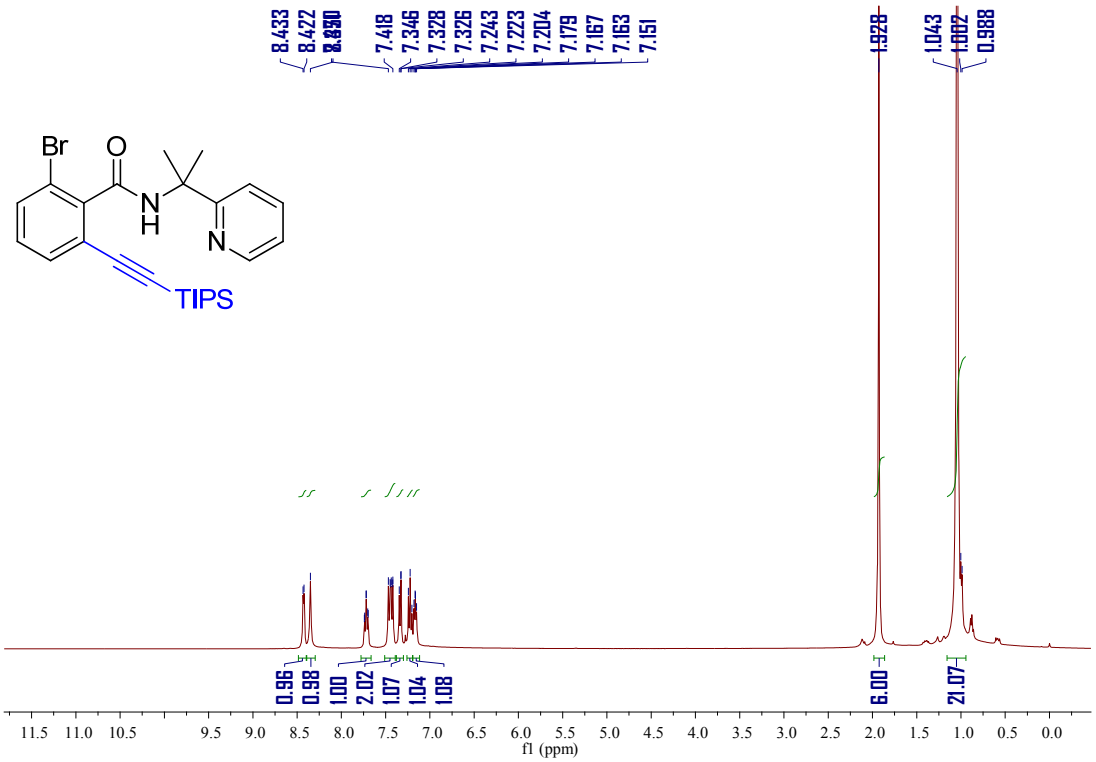

164.777
164.473
147.508
137.236
129.289
122.956
121.971
119.555
103.571
95.939
57.552
27.505
18.726
11.379
Cl
O
N
H
N
TIPS
f1 (ppm)

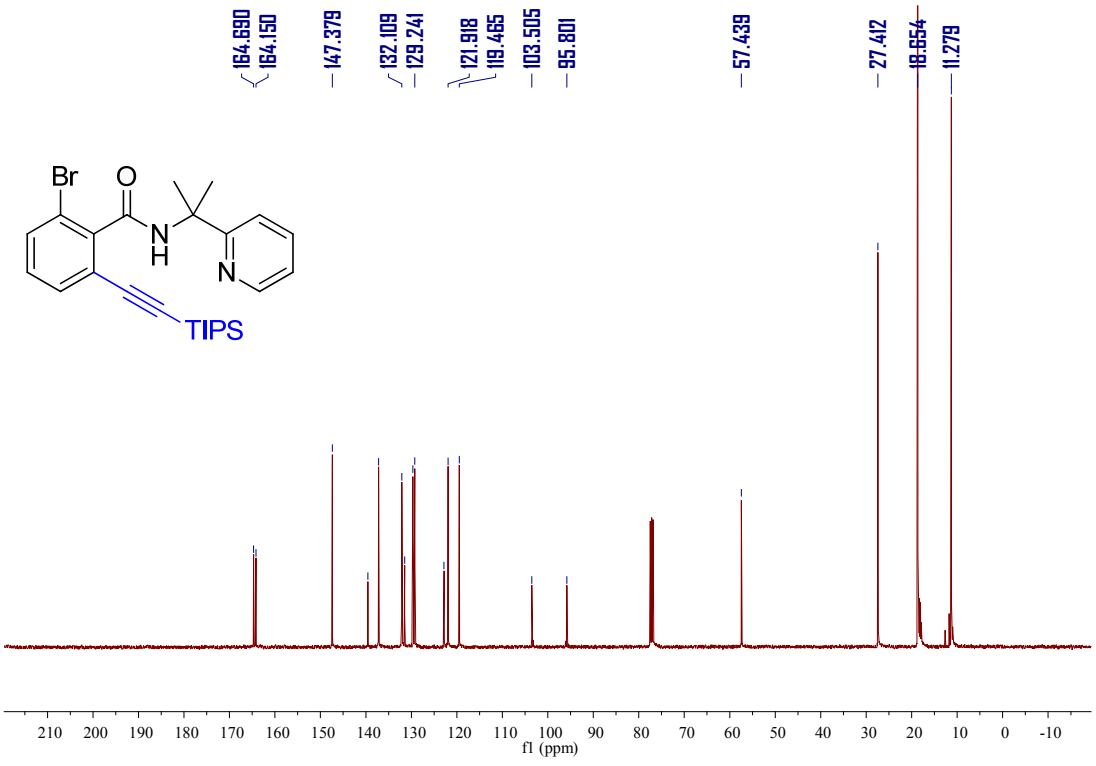
3g


8.507
8.497
7.474
7.457
7.437
7.342
7.337
7.322
7.316
7.181
7.169
7.165
7.152
1.868
1.054
1.028
1.002
Cl
O
N
H
N
TIPS
1.04
0.94
0.95
1.06
2.03
1.01
1.04
6.00
21.36
f1 (ppm)

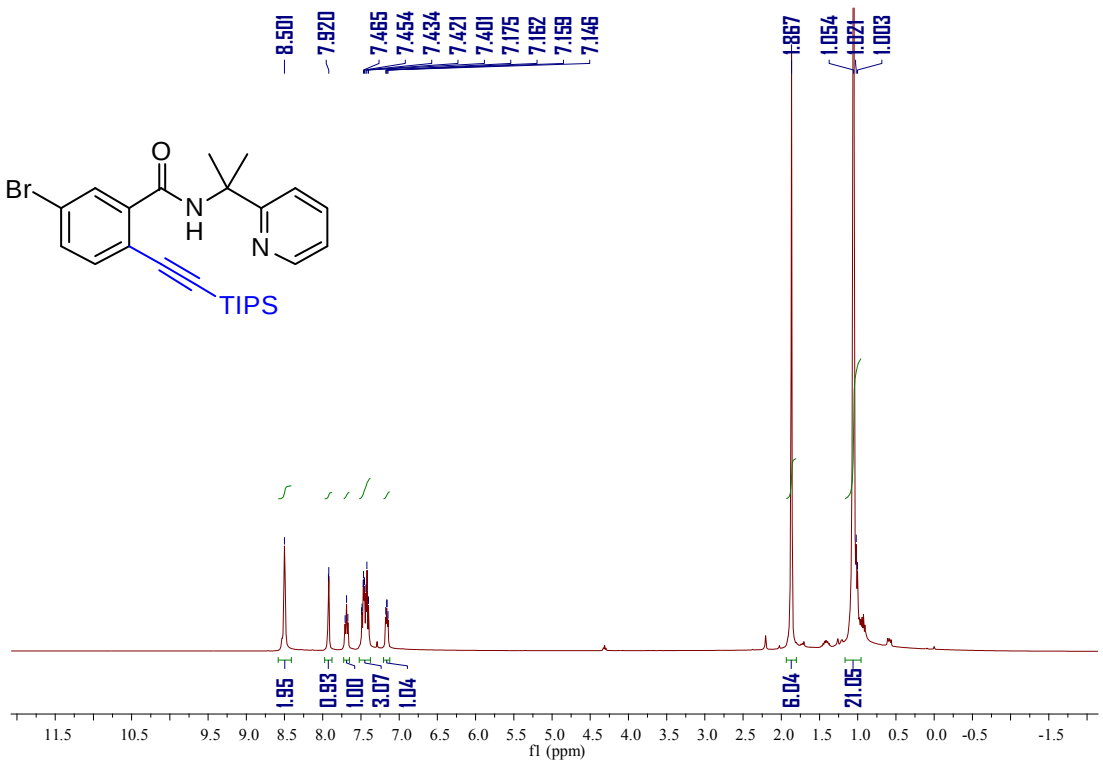

165.037
164.417
148.129
135.972
129.343
119.447
118.756
104.265
98.507
57.843
27.739
18.741
11.390
Cl
O
N
H
N
TIPS
f1 (ppm)

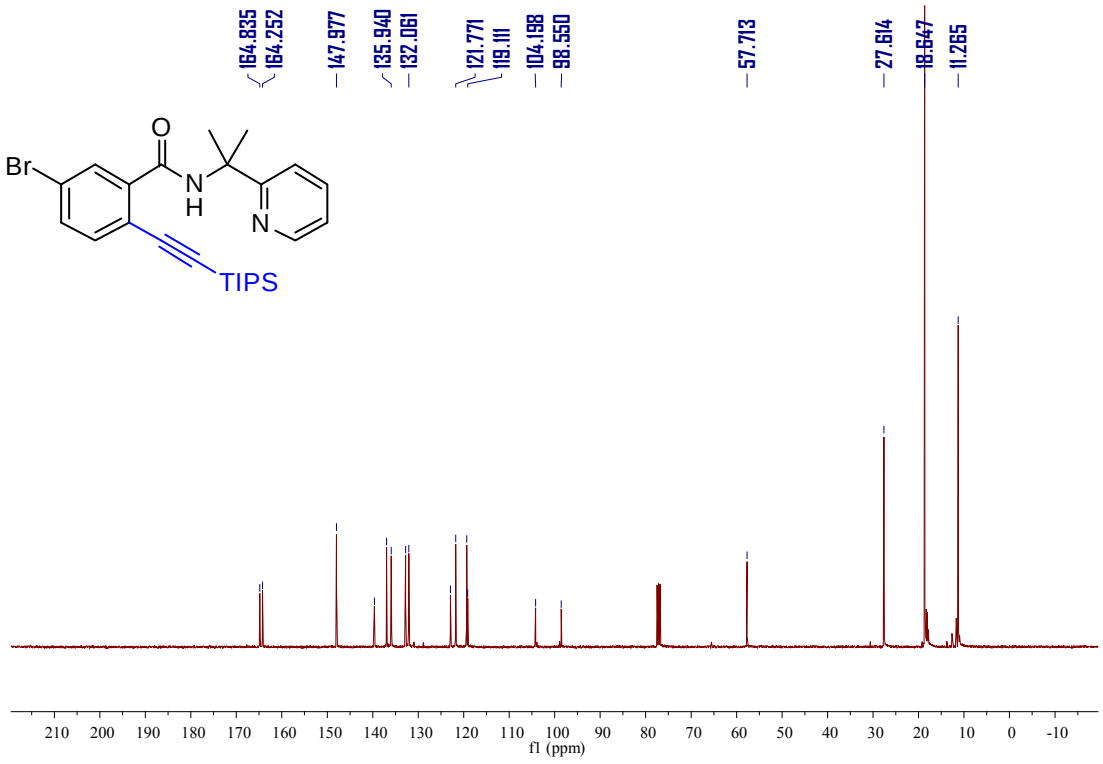
3h


8.433
8.422
7.418
7.346
7.328
7.326
7.243
7.223
7.204
7.179
7.167
7.163
7.151
1.928
1.043
0.988
Br
O
N
H
N
TIPS
0.96
0.98
1.00
2.02
1.07
1.04
1.08
6.00
21.07
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

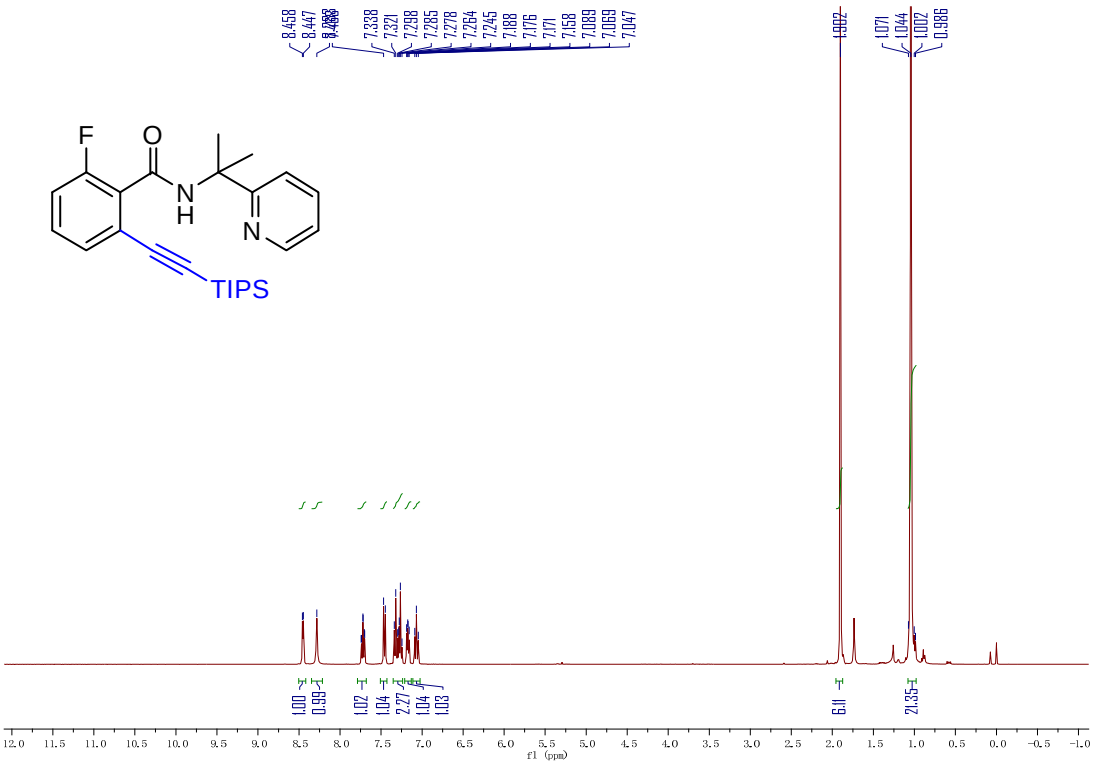

164.690
164.150
147.379
132.109
129.241
121.918
119.485
103.505
95.801
57.439
27.412
18.654
11.279
Br
O
N
H
N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

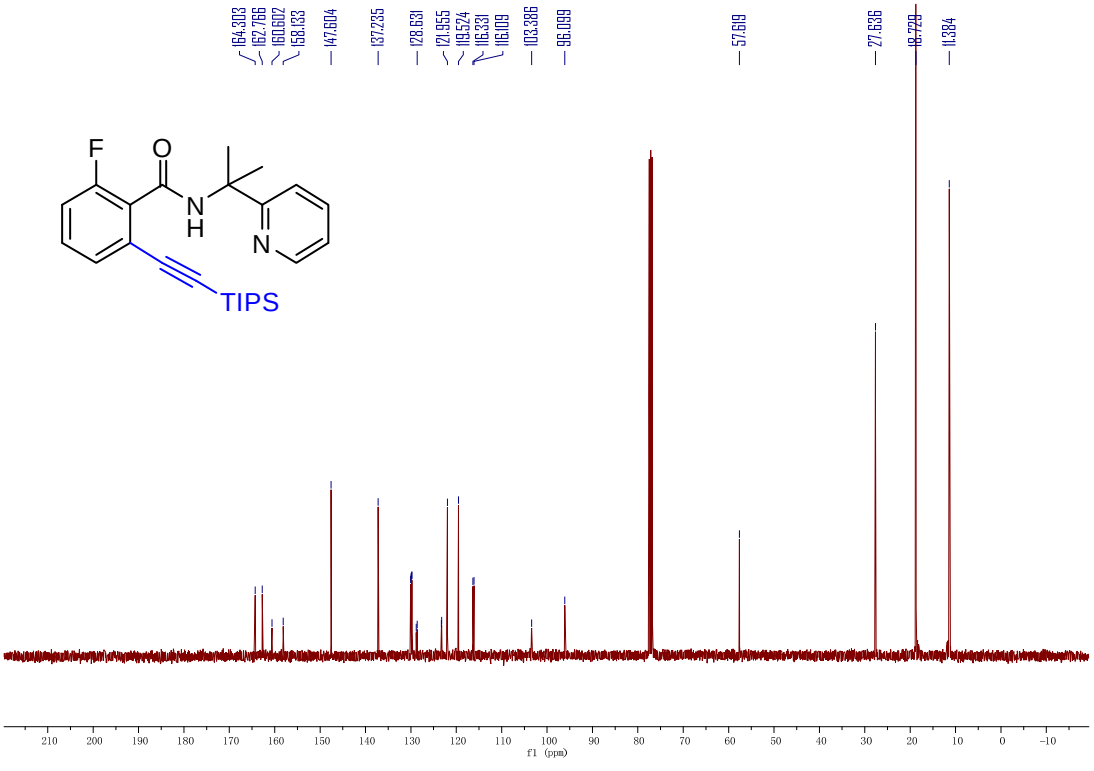
3i

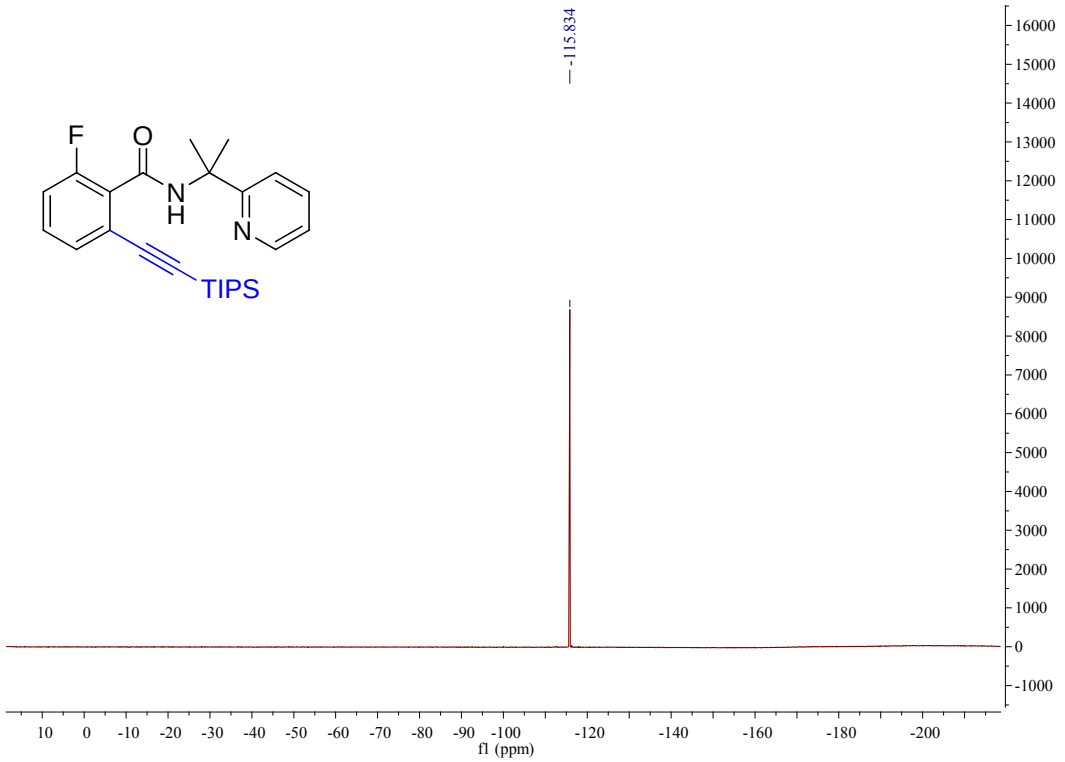

8.501
7.920
7.465
7.454
7.434
7.421
7.401
7.175
7.162
7.159
7.146
1.867
1.054
1.021
1.003
Br
O
N
H
N
TIPS
1.95
0.93
1.00
3.07
1.04
6.04
21.05
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
f1 (ppm)


164.835
164.252
147.977
135.940
132.061
121.771
119.111
104.198
98.550
57.713
27.614
18.647
11.265
Br
O
N
H
N
TIPS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

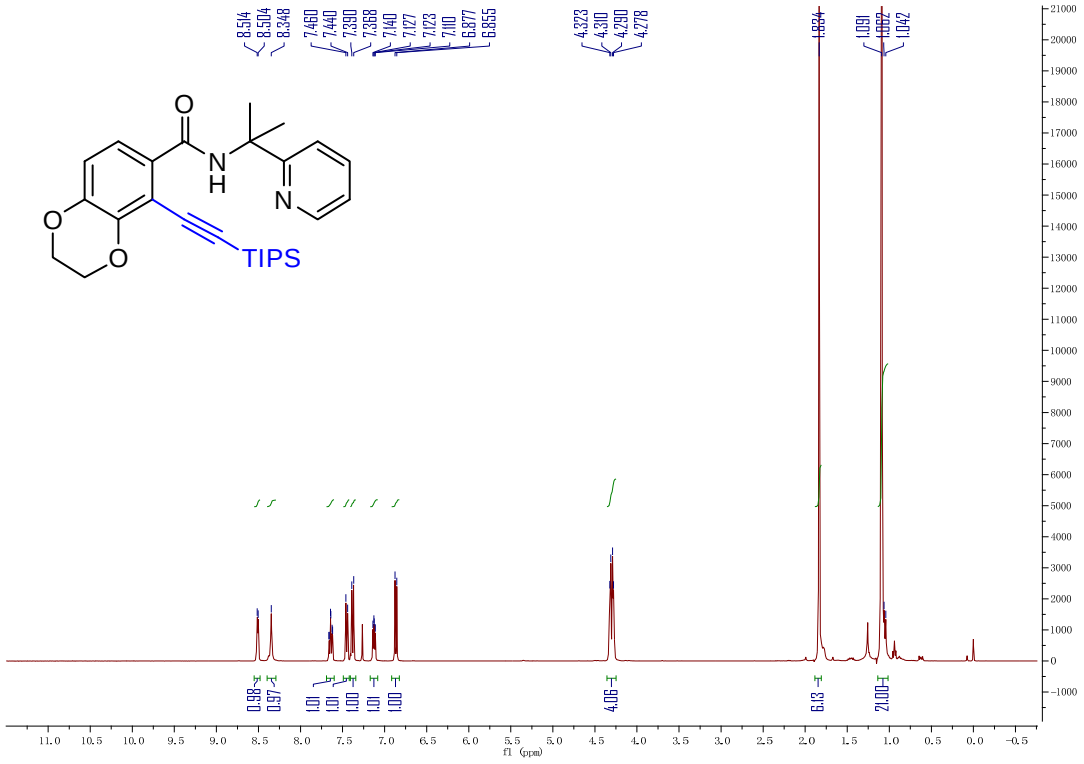
3j

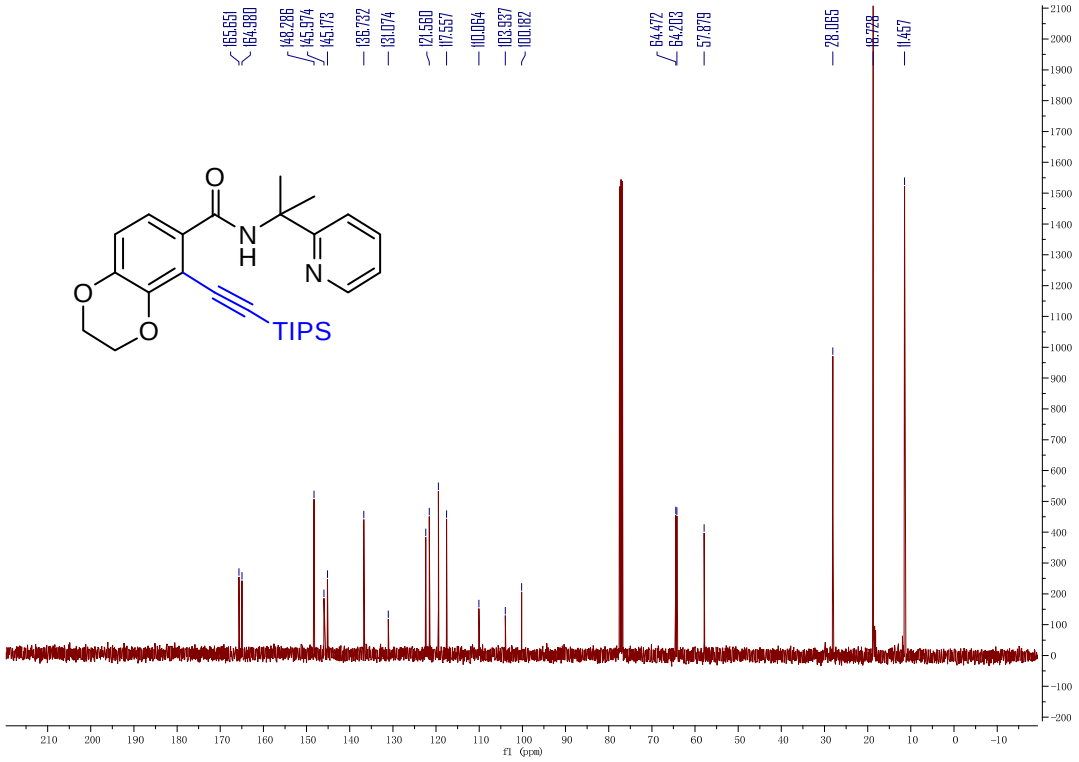

F
O
N
H
N
TIPS
8.458
8.447
7.338
7.321
7.298
7.285
7.278
7.264
7.245
7.188
7.176
7.171
7.158
7.089
7.069
7.047
1.982
1.071
1.044
1.002
0.986
1.00
0.99
1.02
1.04
2.27
1.04
1.03
6.11
21.35
f1 (ppm)


F
O
N
H
N
TIPS
164.303
162.766
160.602
158.133
147.604
137.235
128.631
121.955
119.524
116.331
116.109
103.386
96.099
57.619
27.636
18.729
11.384
f1 (ppm)

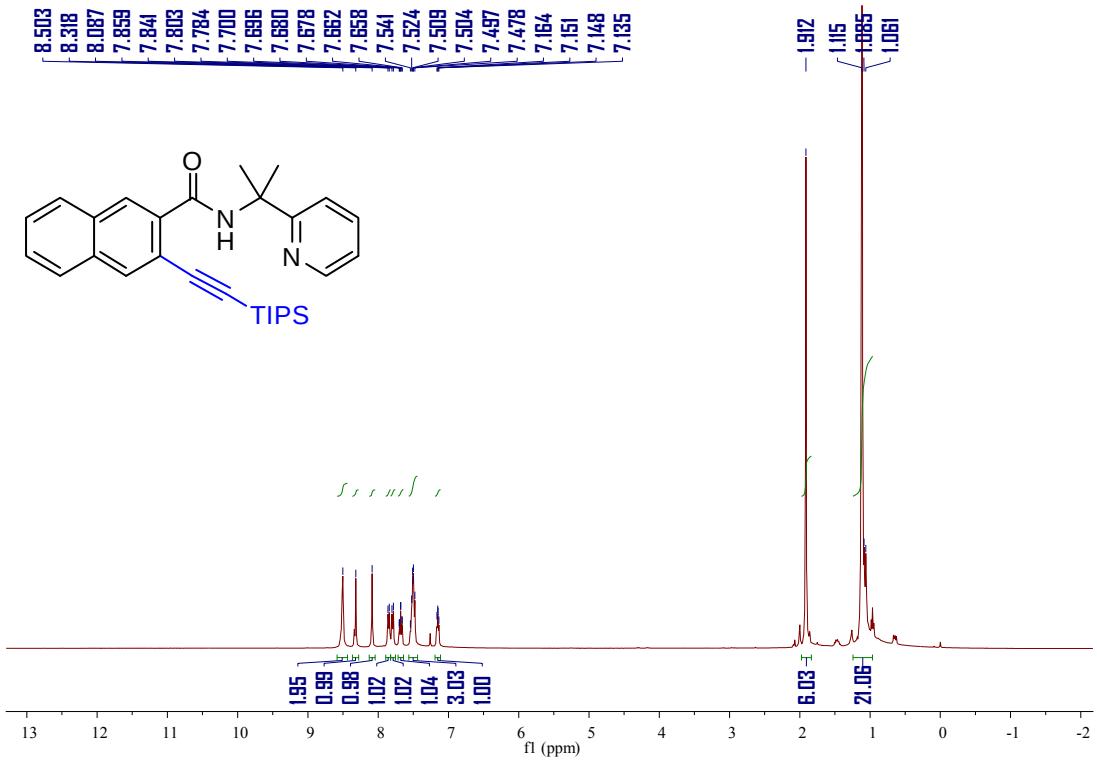

F
O
N
H
N
TIPS
-115.834
f1 (ppm)

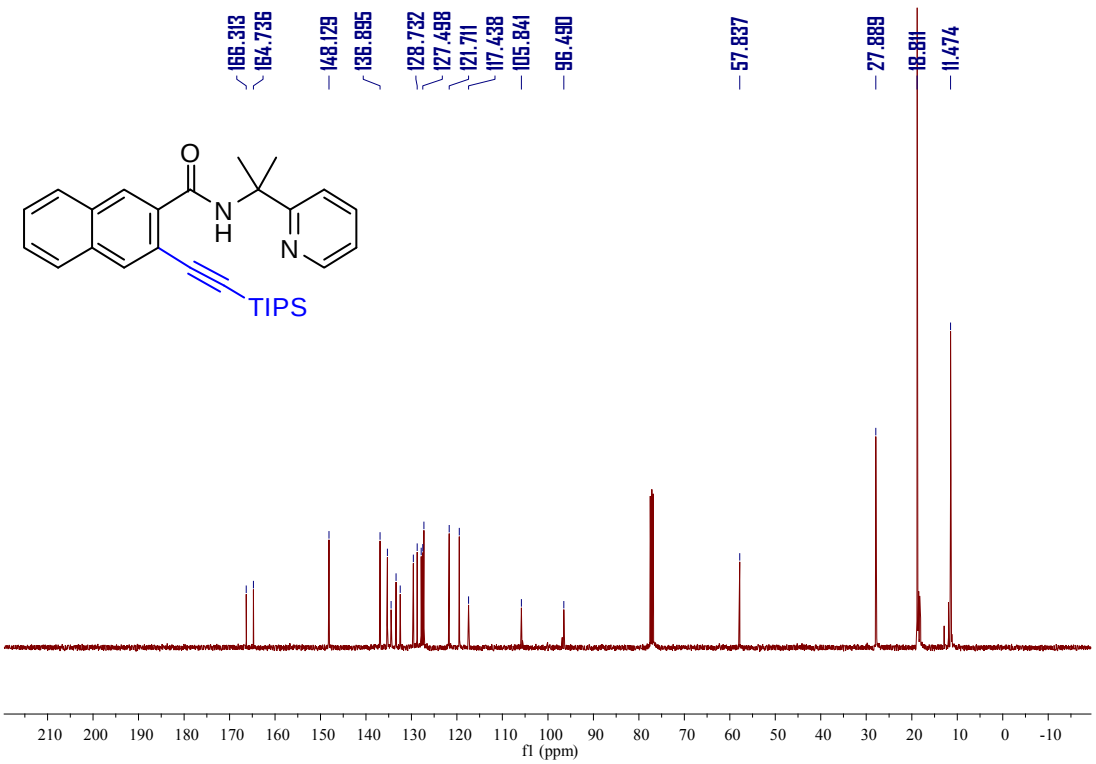
3k


8.514
8.504
8.348
7.460
7.440
7.390
7.368
7.140
7.127
7.123
7.110
6.877
6.855
4.323
4.310
4.290
4.278
1.934
1.091
1.062
1.042
O
N
H
N
O
O
TIPS
0.98
0.97
1.01
1.01
1.00
1.00
1.01
1.00
4.06
6.13
21.00
f1 (ppm)

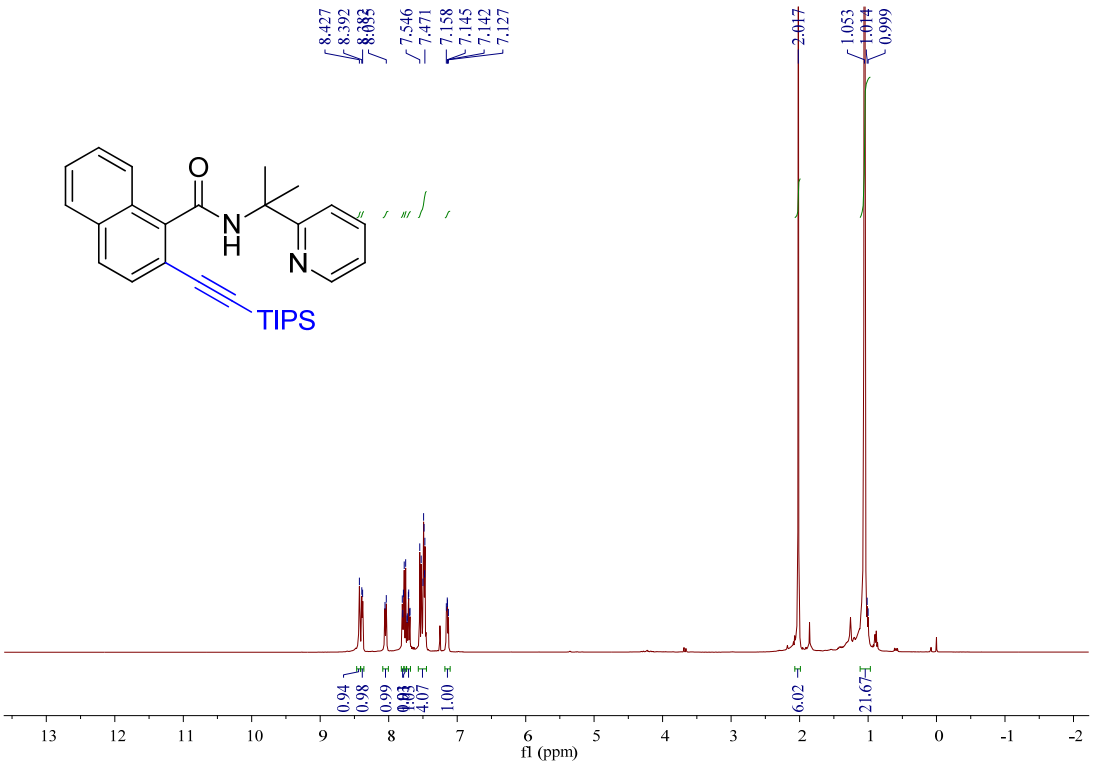

155.651
154.980
148.286
145.974
145.173
136.732
131.074
121.580
117.557
110.064
103.937
100.182
64.472
64.203
57.879
28.065
18.728
11.457
TIPS
f1 (ppm)

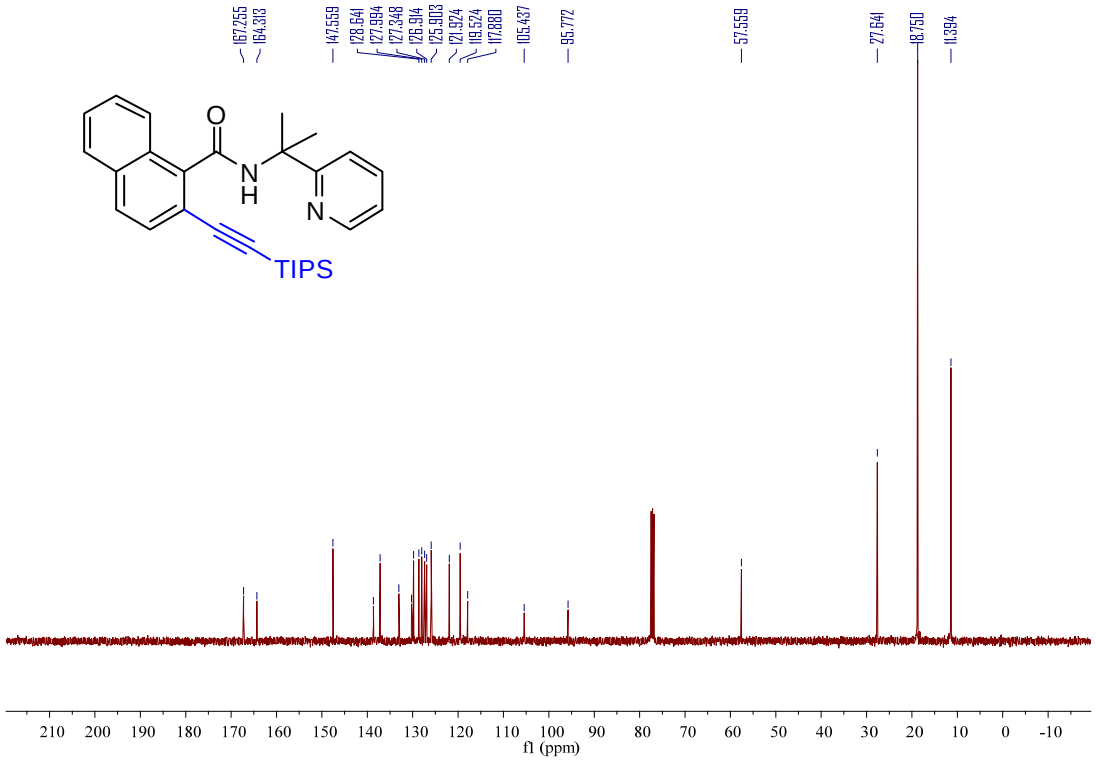
3l


8.503
8.318
8.087
7.859
7.841
7.803
7.784
7.700
7.696
7.680
7.678
7.662
7.658
7.541
7.524
7.509
7.504
7.497
7.478
7.164
7.151
7.148
7.135
1.912
1.115
1.085
1.061
1.95
0.99
0.98
1.02
1.02
1.04
3.03
1.00
6.03
21.06
TIPS
f1 (ppm)

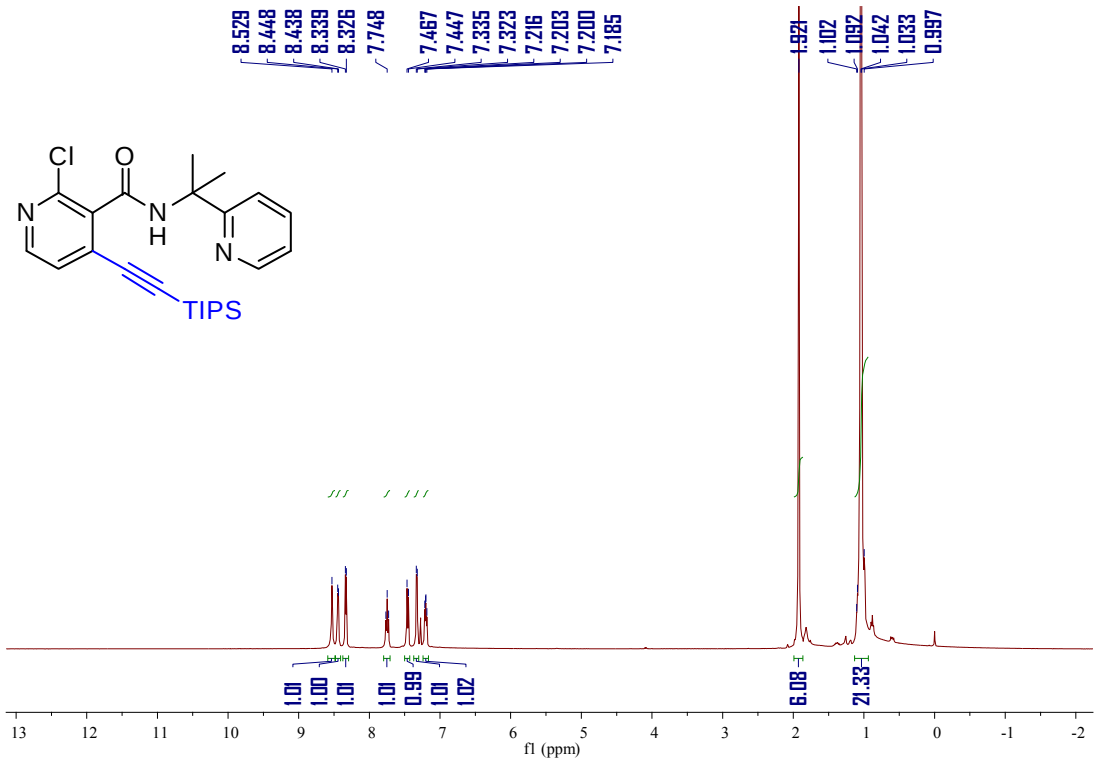

166.313
164.736
148.129
136.895
128.732
127.458
121.711
117.438
105.841
96.490
57.837
27.889
18.811
11.474
O
N
H
N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

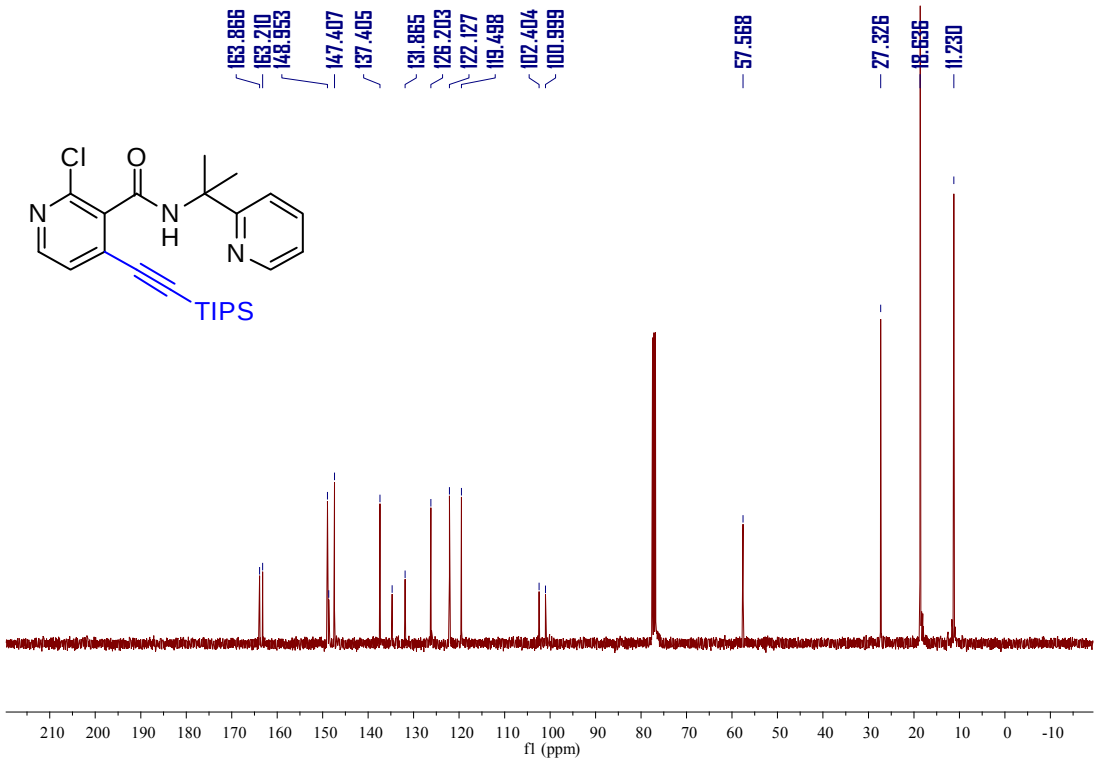
3m


8.427
8.392
7.546
7.471
7.158
7.145
7.142
7.127
2.017
1.053
1.014
0.999
O
N
H
N
TIPS
0.94
0.98
0.99
4.07
1.00
6.02
21.67
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

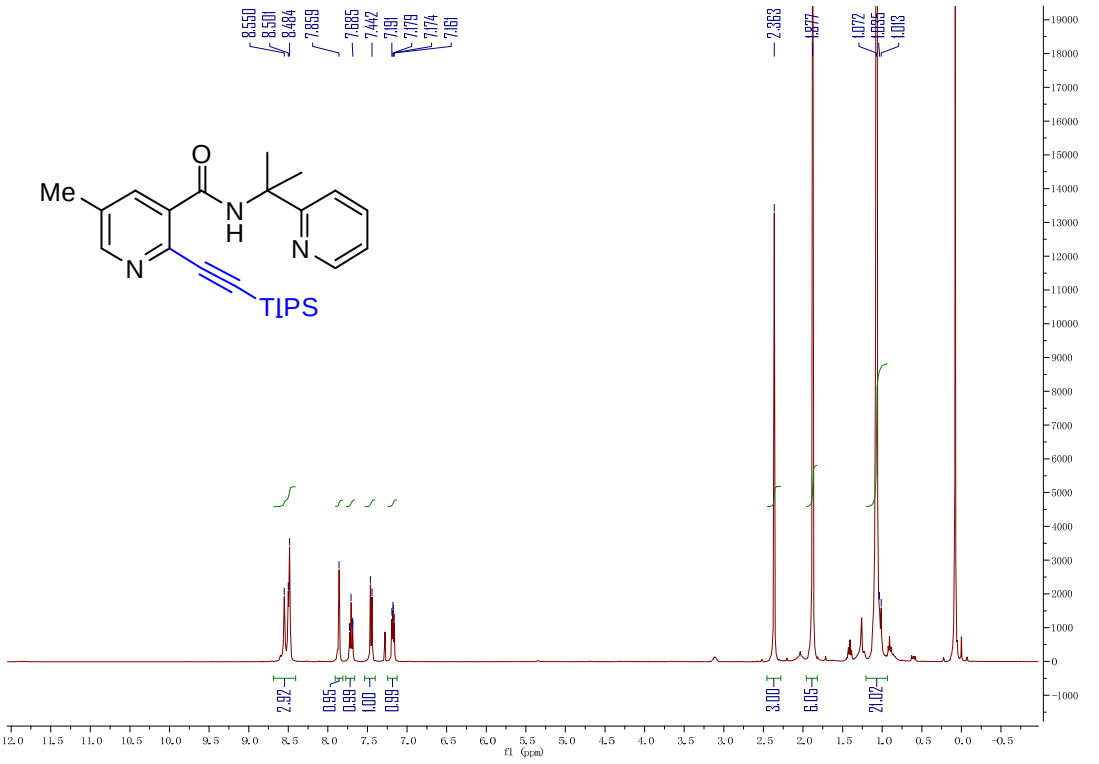

167.255
164.313
147.559
128.641
127.994
127.348
126.914
125.903
121.924
119.524
117.880
105.437
95.772
57.559
27.641
18.750
11.394
O
N
H
N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

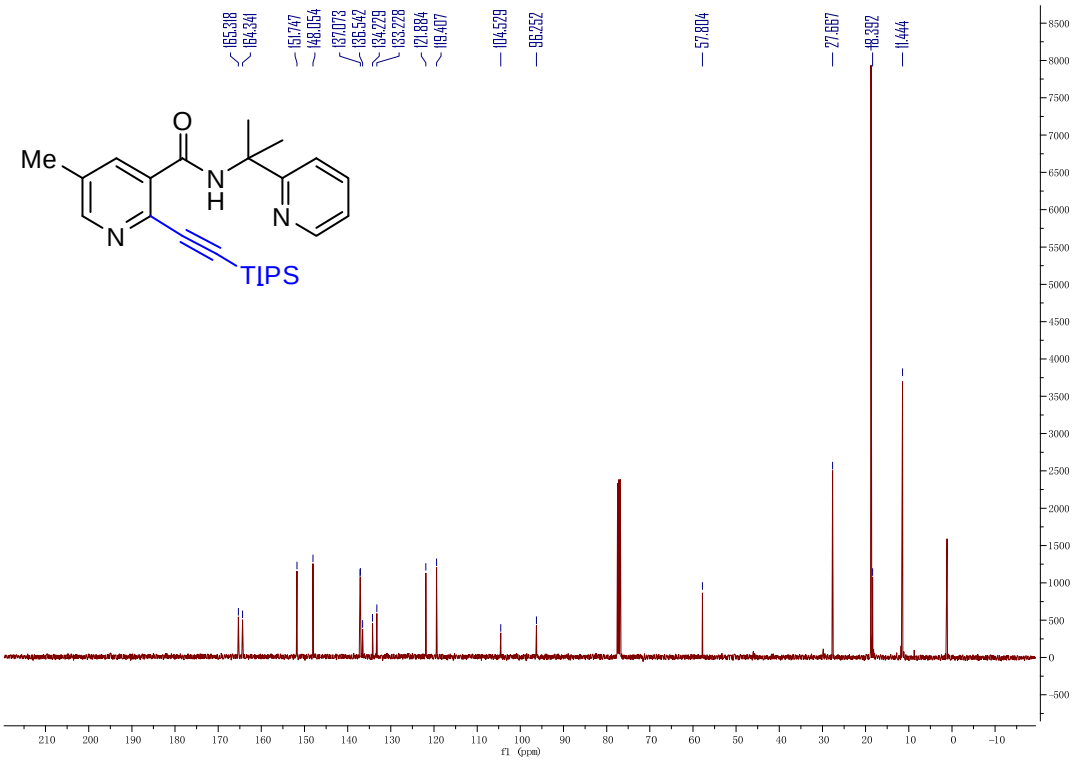
3n


8.529
8.448
8.438
8.339
8.326
7.748
7.467
7.447
7.335
7.323
7.216
7.203
7.200
7.185
1.921
1.102
1.092
1.042
1.033
0.997
Cl
O
N
H
N
N
TIPS
1.01
1.00
1.01
1.01
0.99
1.01
1.02
6.08
21.33
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

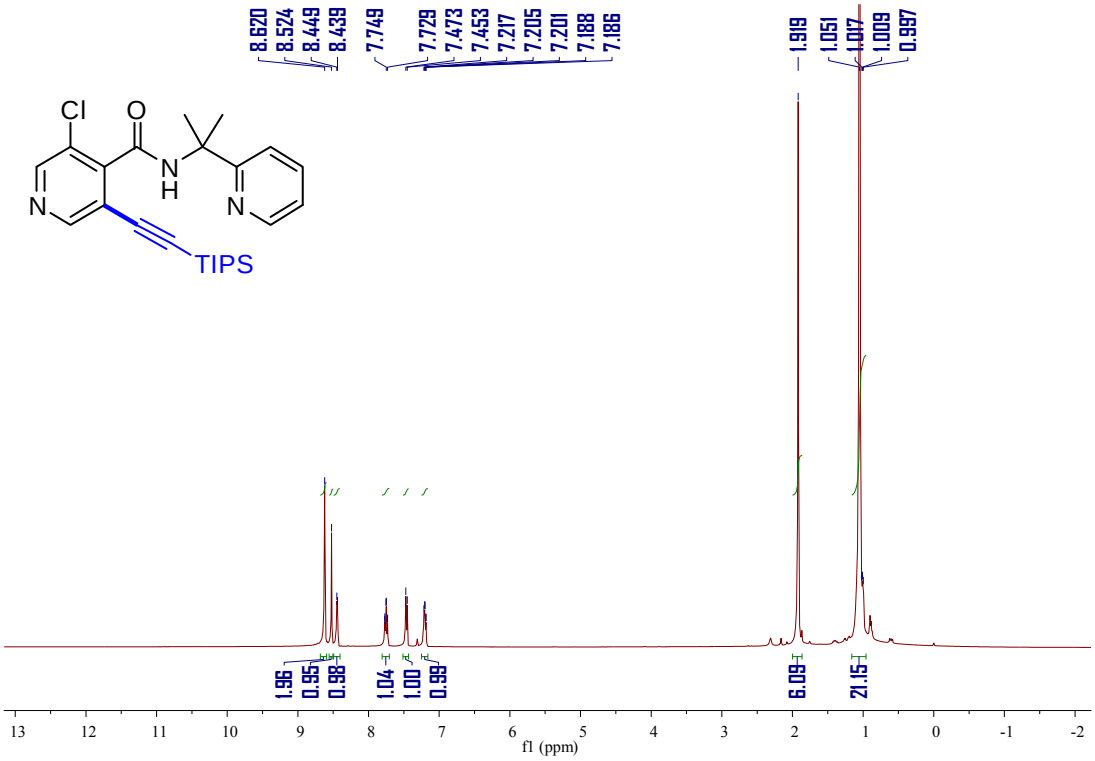

163.866
163.210
148.953
147.407
137.405
131.865
126.203
122.127
119.498
102.404
100.999
57.568
27.326
18.636
11.230
Cl
O
N
N
H
N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

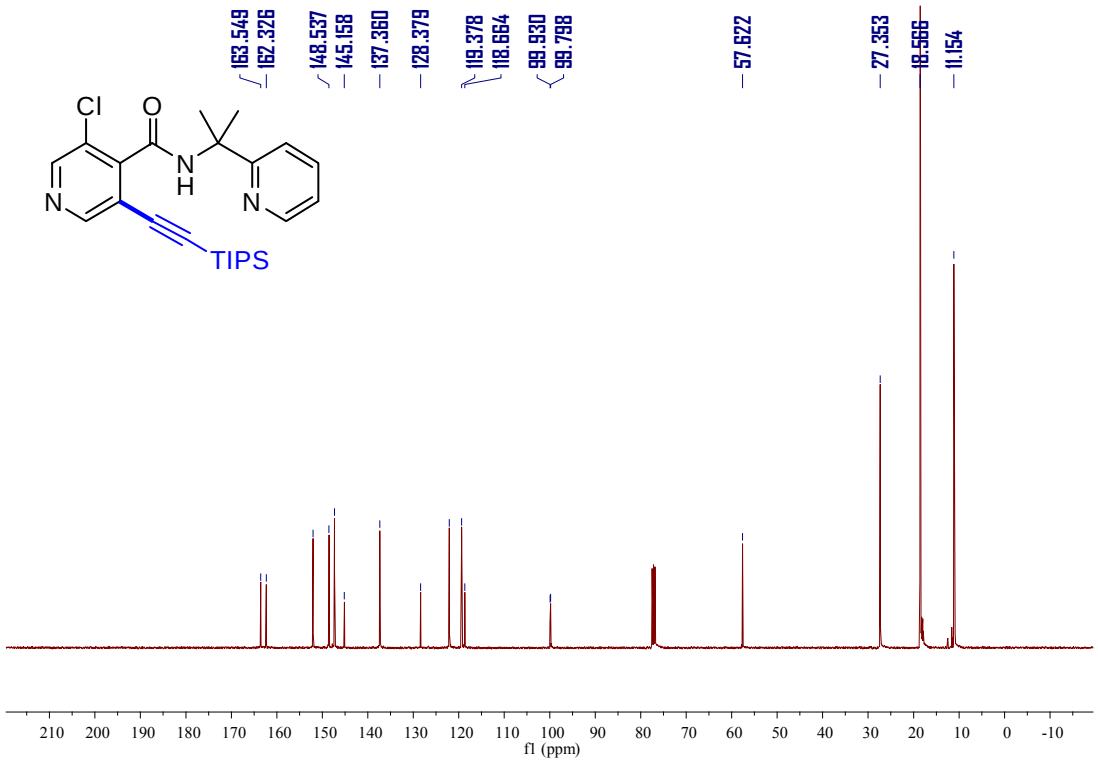
3o


8.550
8.501
8.494
7.859
7.685
7.442
7.191
7.179
7.174
7.161
2.383
1.977
1.072
1.035
1.013
O
Me
N
H
N
N
TIPS
2.87
0.95
0.99
1.00
0.99
3.00
6.05
21.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

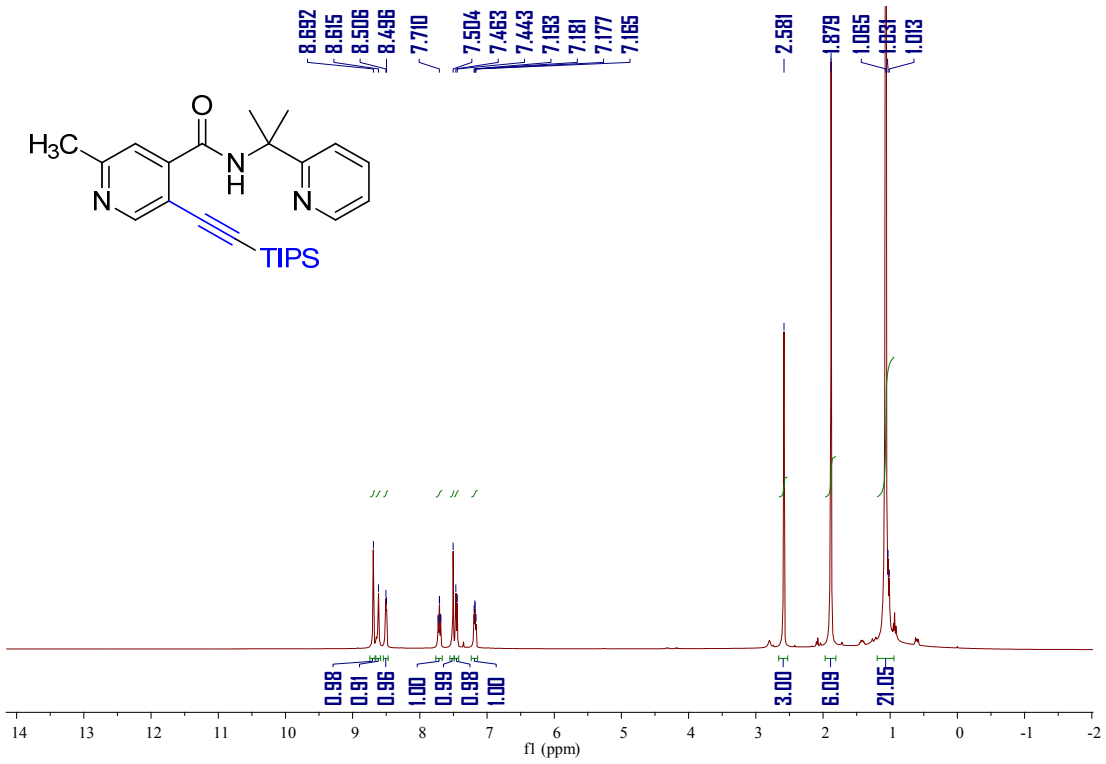

165.318
164.341
151.747
148.054
137.073
136.542
134.229
133.228
121.884
119.407
104.529
96.252
57.804
27.667
18.392
11.444
Me
O
N
H
N
N
TIPS
f1 (ppm)

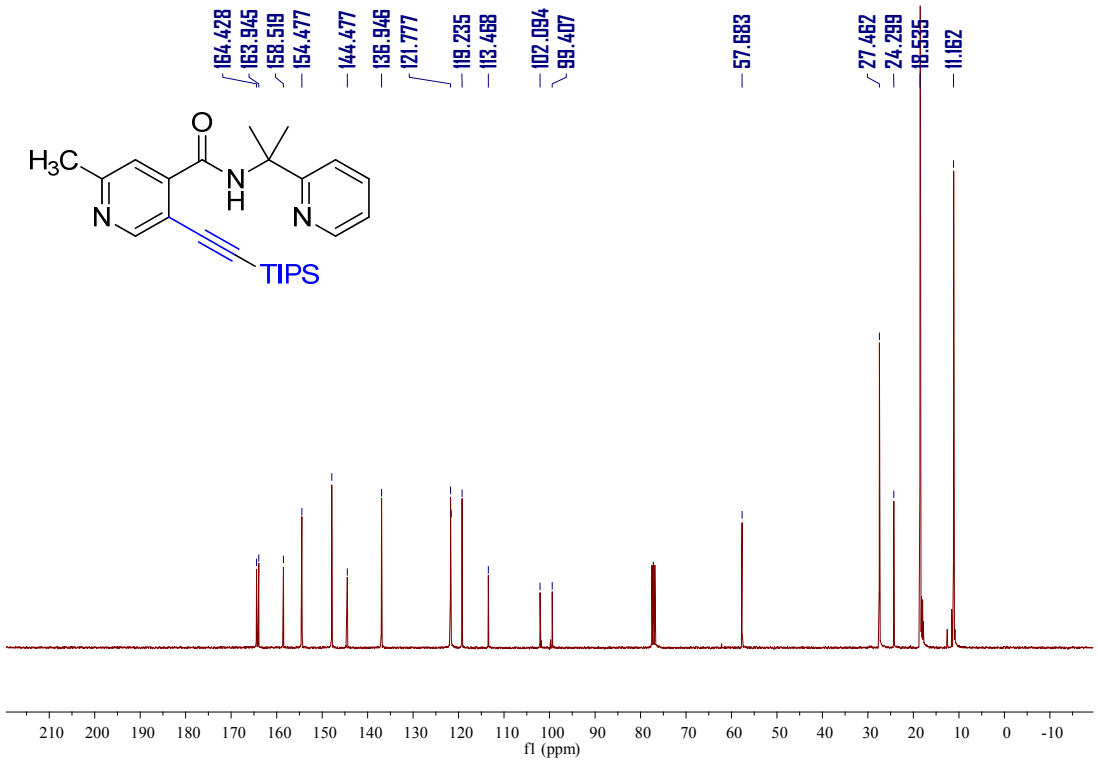
3p


8.620
8.524
8.449
8.439
7.749
7.729
7.473
7.453
7.217
7.205
7.201
7.188
7.186
1.919
1.051
1.017
1.009
0.997
Cl
O
N
H
N
N
TIPS
1.96
0.95
0.98
1.04
1.00
0.99
6.09
21.15
f1 (ppm)

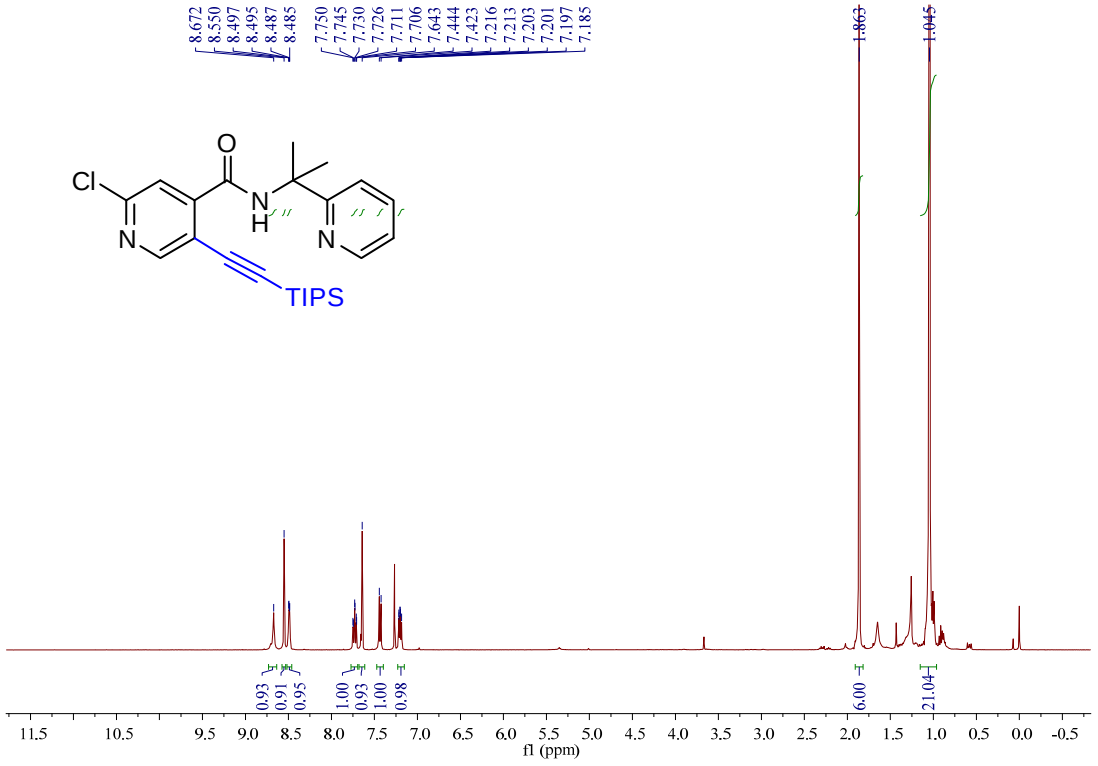

163.549
162.326
148.537
145.158
137.360
128.379
119.378
118.664
99.930
99.798
57.622
27.353
18.566
11.154
Cl
O
N
H
N
N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

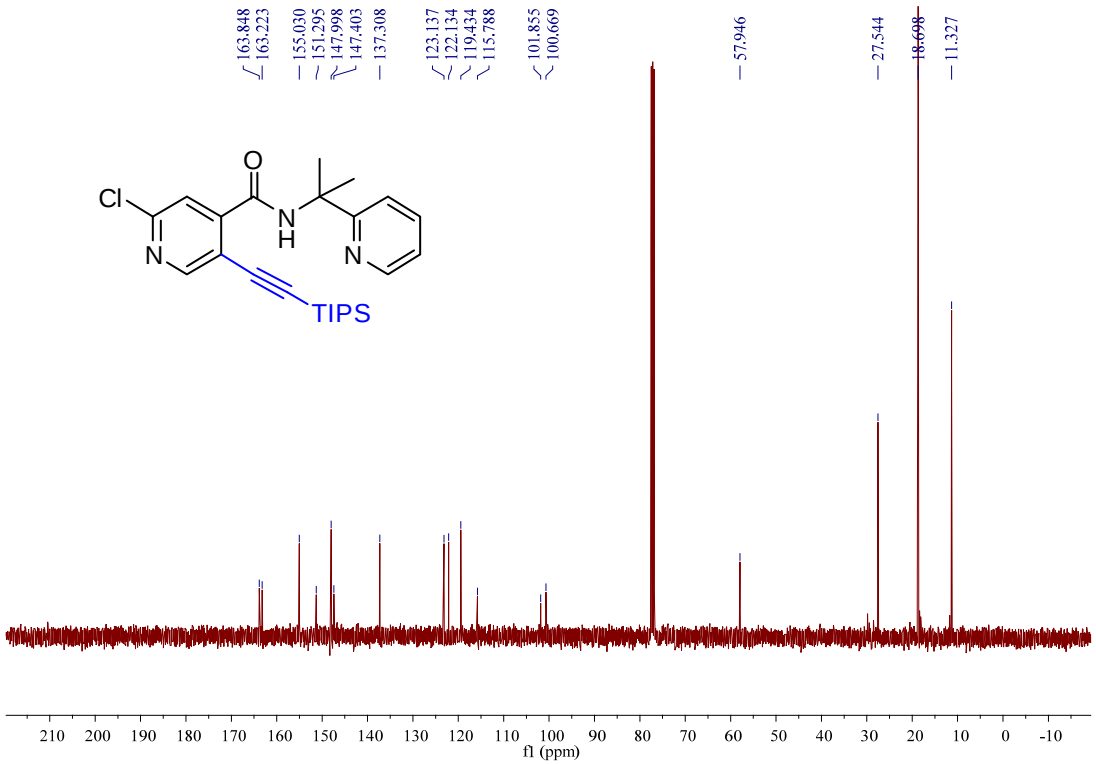
3q


8.692
8.615
8.506
8.496
7.710
7.504
7.463
7.443
7.193
7.181
7.177
7.165
2.581
1.879
1.065
1.031
1.013
H3C
O
N
H
N
N
TIPS
0.98
0.91
0.96
1.00
0.99
0.98
1.00
3.00
6.09
21.05
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

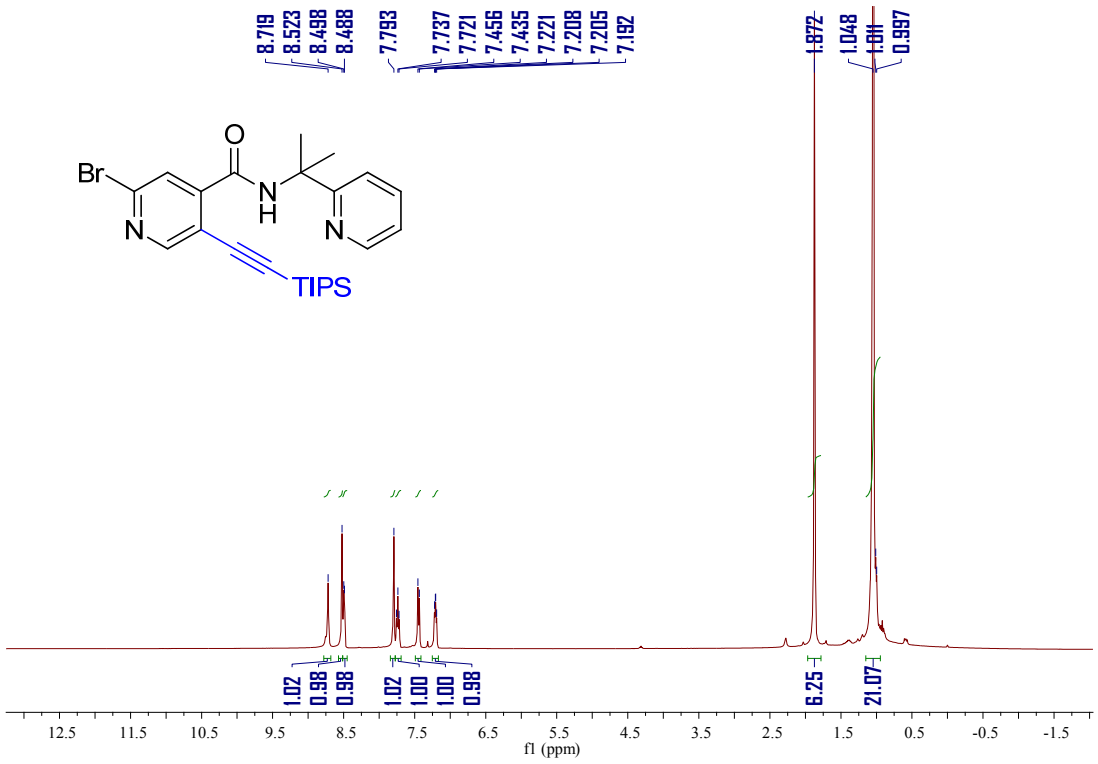

164.428
163.945
158.519
154.477
144.477
136.946
121.777
119.235
113.468
102.094
99.407
57.683
27.462
24.299
18.535
11.162
H3C
O
N
H
N
N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

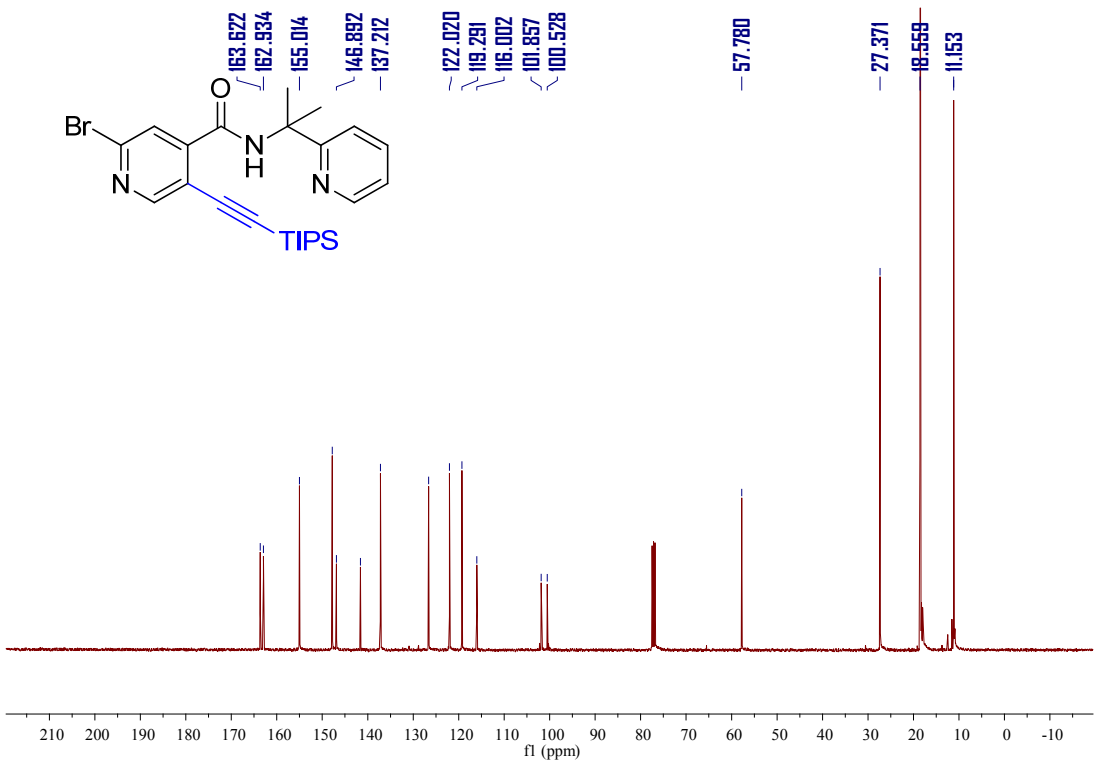
3r


8.672
8.550
8.497
8.495
8.487
8.485
7.750
7.745
7.730
7.726
7.711
7.706
7.643
7.444
7.423
7.216
7.213
7.203
7.201
7.197
7.185
1.863
1.045
Cl
O
N
H
N
N
TIPS
0.93
0.91
0.95
1.00
0.93
1.00
0.98
6.00
21.04
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

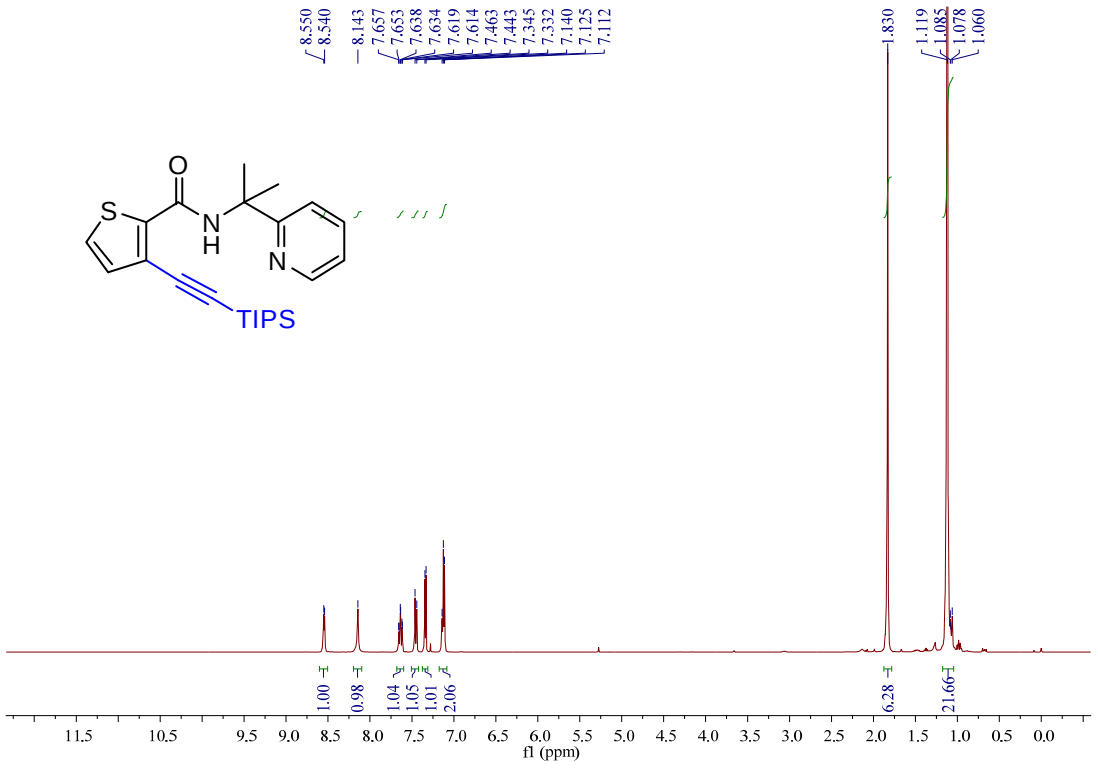

163.848
163.223
155.030
151.295
147.998
147.403
137.308
123.137
122.134
119.434
115.788
101.855
100.669
57.946
27.544
18.698
11.327
Cl
O
N
H
N
N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

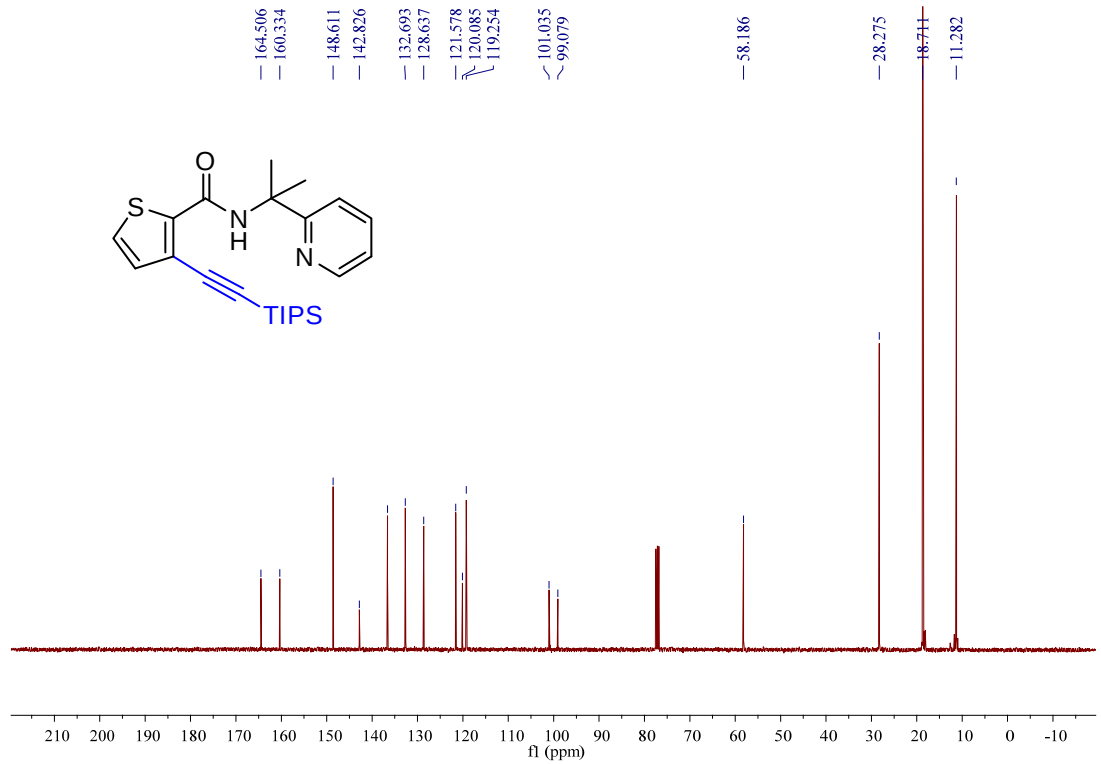
3s


8.719
8.523
8.498
8.488
7.793
7.737
7.721
7.456
7.435
7.221
7.208
7.205
7.192
1.872
1.048
1.011
0.997
Br
O
N
H
N
N
TIPS
1.02
0.98
0.98
1.02
1.00
1.00
0.98
6.25
21.07
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
f1 (ppm)

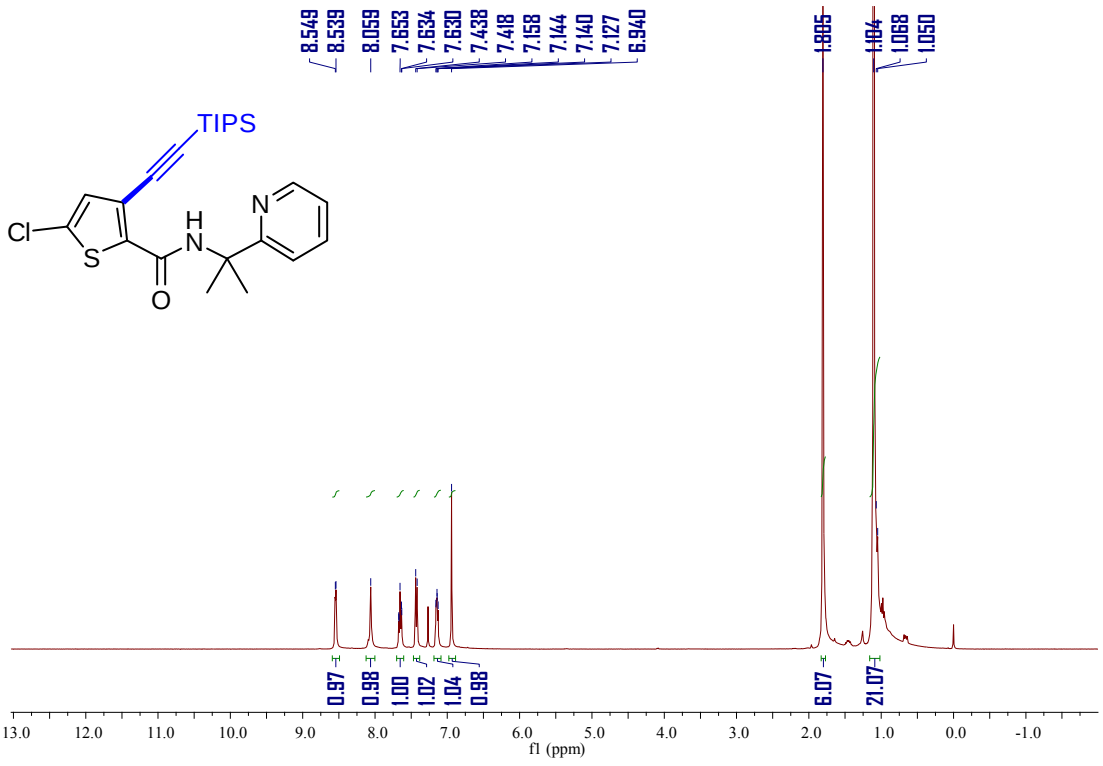

163.622
162.934
155.014
146.892
137.212
122.020
119.291
116.002
101.857
100.528
57.780
27.371
18.559
11.153
Br
O
N
H
N
N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

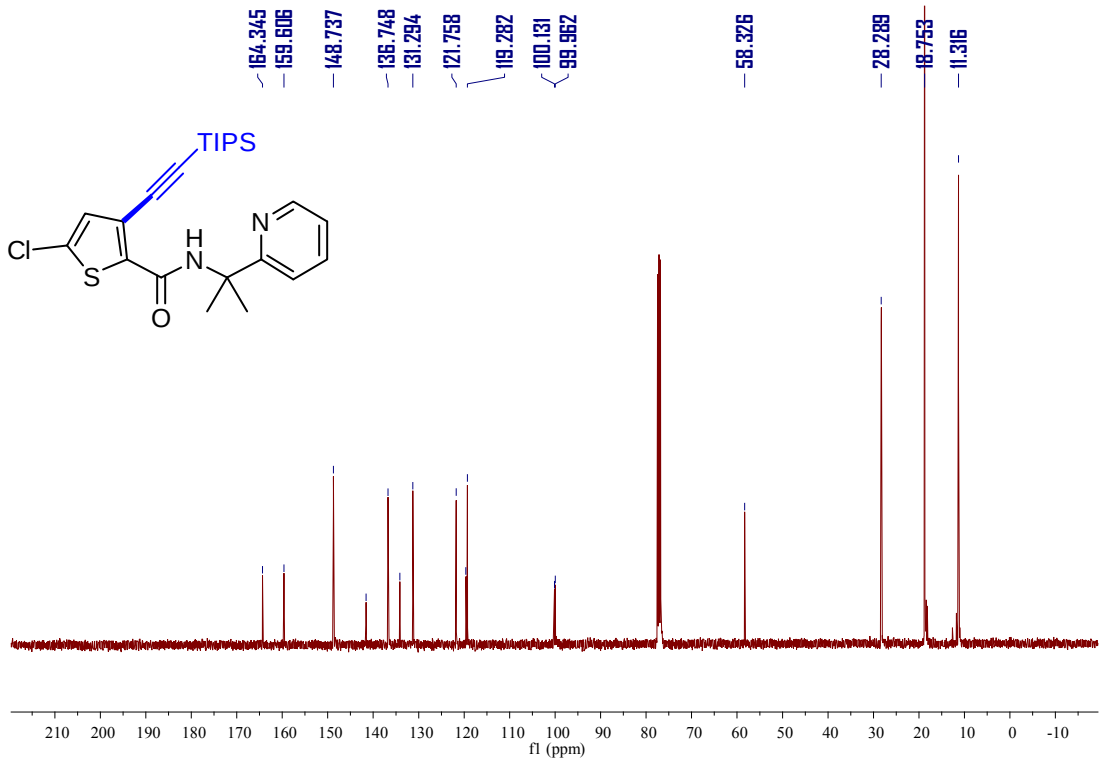
3t


8.550
8.540
8.143
7.657
7.653
7.638
7.634
7.619
7.614
7.463
7.443
7.345
7.332
7.140
7.125
7.112
1.830
1.119
1.085
1.078
1.060
O
S
N
H
N
TIPS
1.00
0.98
1.04
1.05
1.01
2.06
6.28
21.66
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

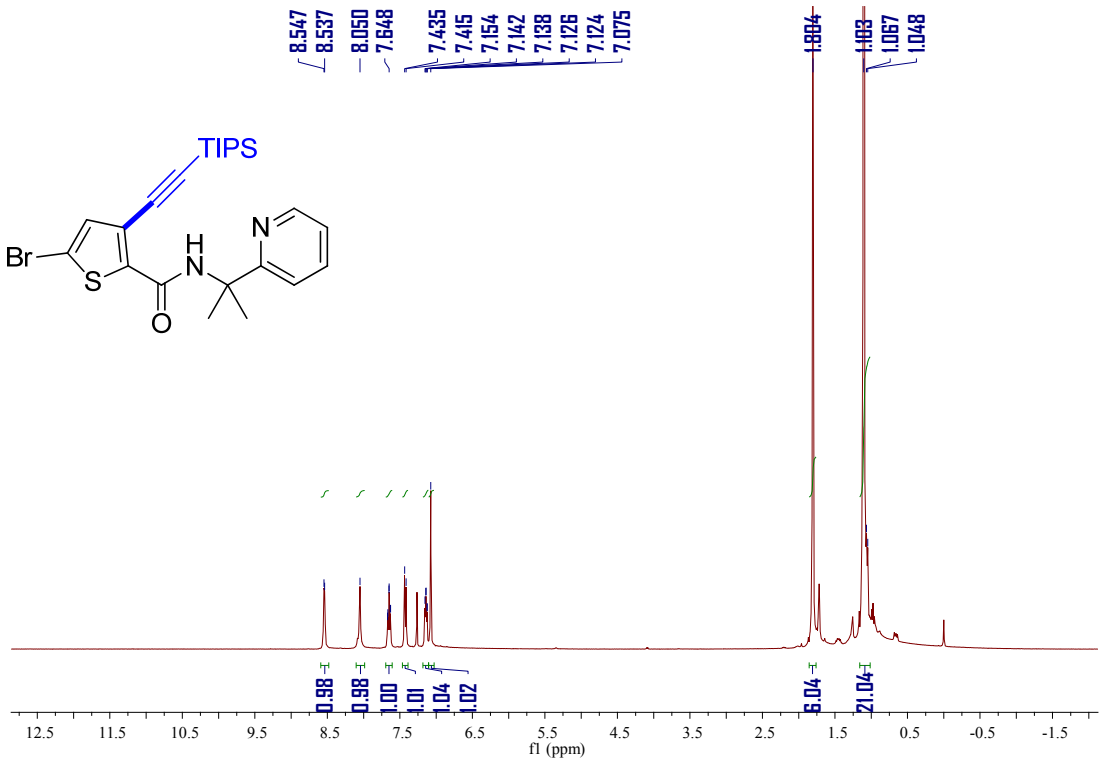

164.506
160.334
148.611
142.826
132.693
128.637
121.578
120.085
119.254
101.035
99.079
58.186
28.275
18.711
11.282
O
S
N
H
N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

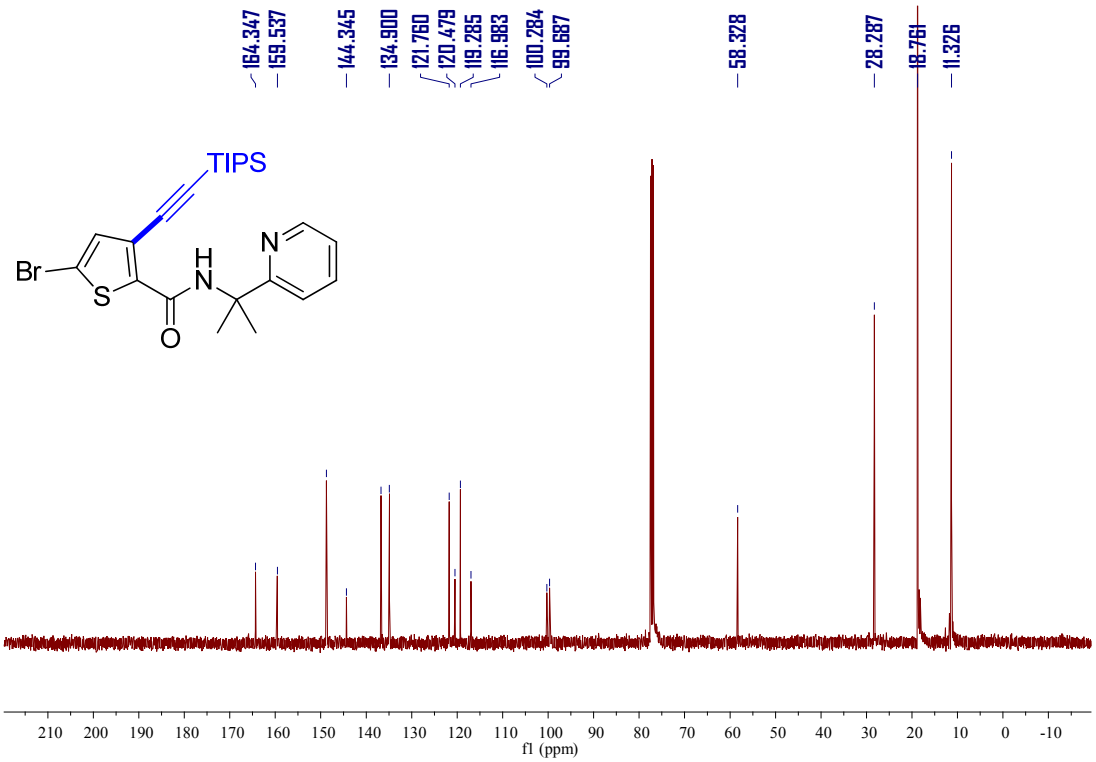
3u


8.549
8.539
8.059
7.653
7.634
7.630
7.438
7.418
7.158
7.144
7.140
7.127
6.940
1.885
1.104
1.068
1.050
TIPS
Cl
S
H
N
N
O
0.97
0.98
1.00
1.02
1.04
0.98
6.07
21.07
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

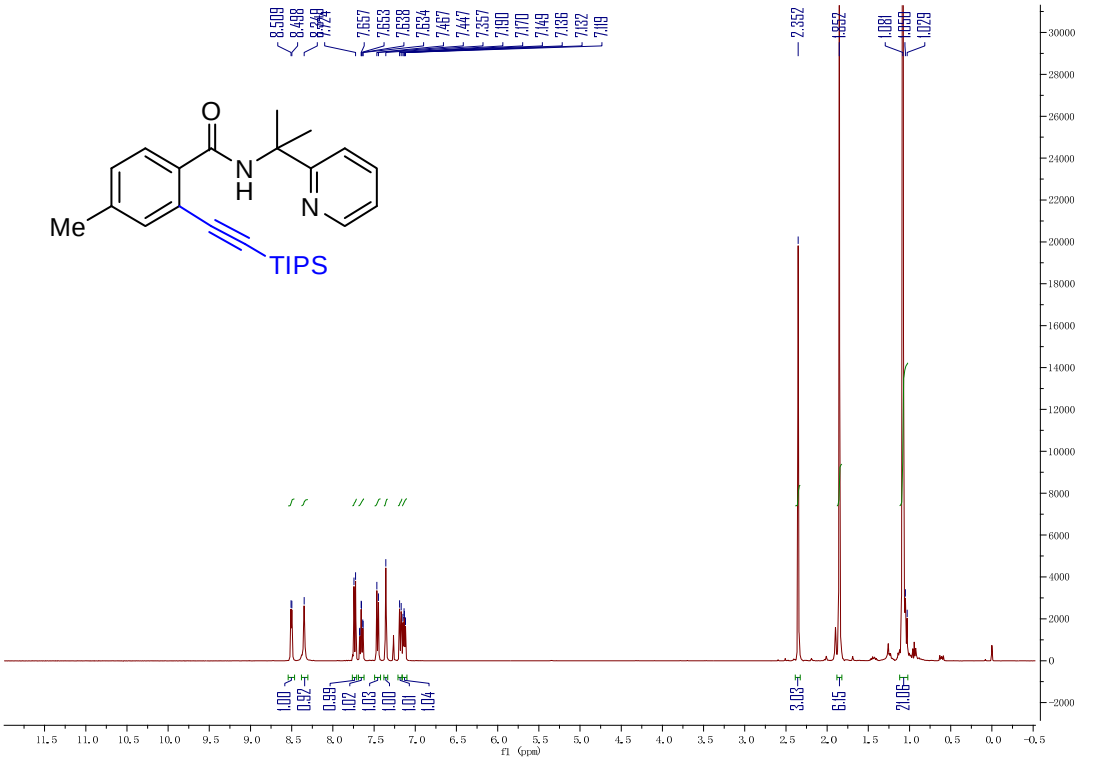

164.345
159.606
148.737
136.748
131.294
121.758
119.282
100.131
99.962
58.326
28.289
18.753
11.316
TIPS
Cl
S
H
N
N
O
f1 (ppm)

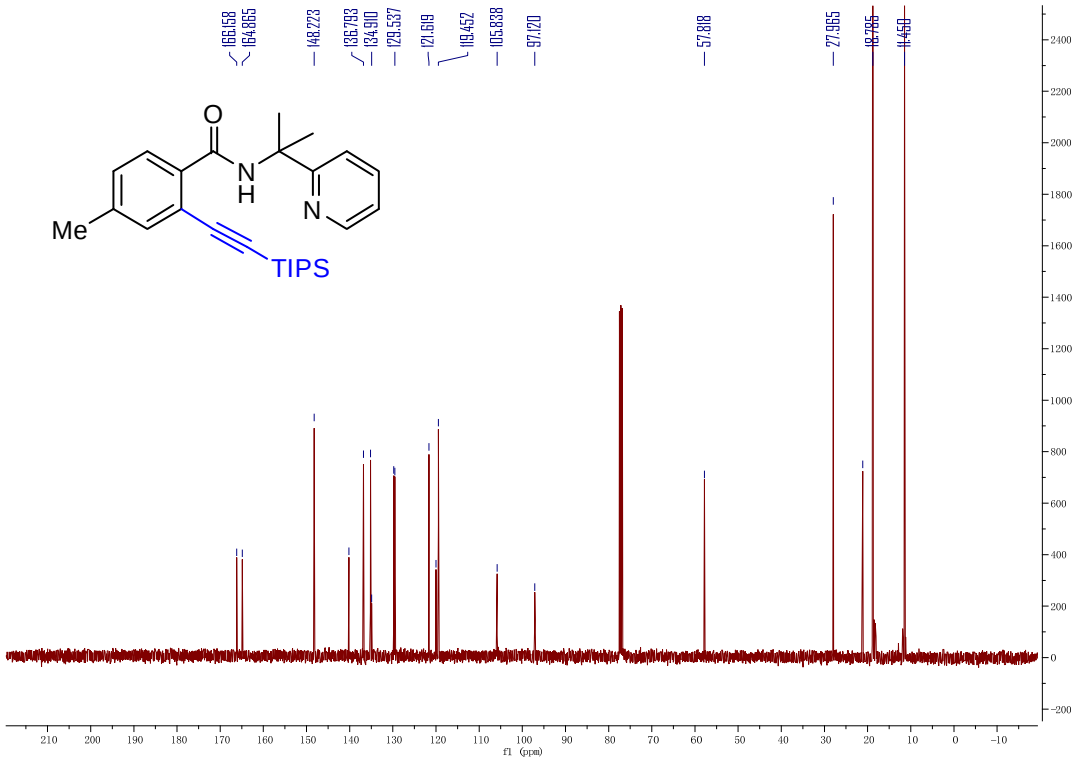
3v


8.547
8.537
8.050
7.648
7.435
7.415
7.154
7.142
7.138
7.126
7.124
7.075
1.884
1.103
1.067
1.048
TIPS
Br
S
H
N
N
O
0.98
0.98
1.00
1.01
1.04
1.02
6.04
21.04
f1 (ppm)

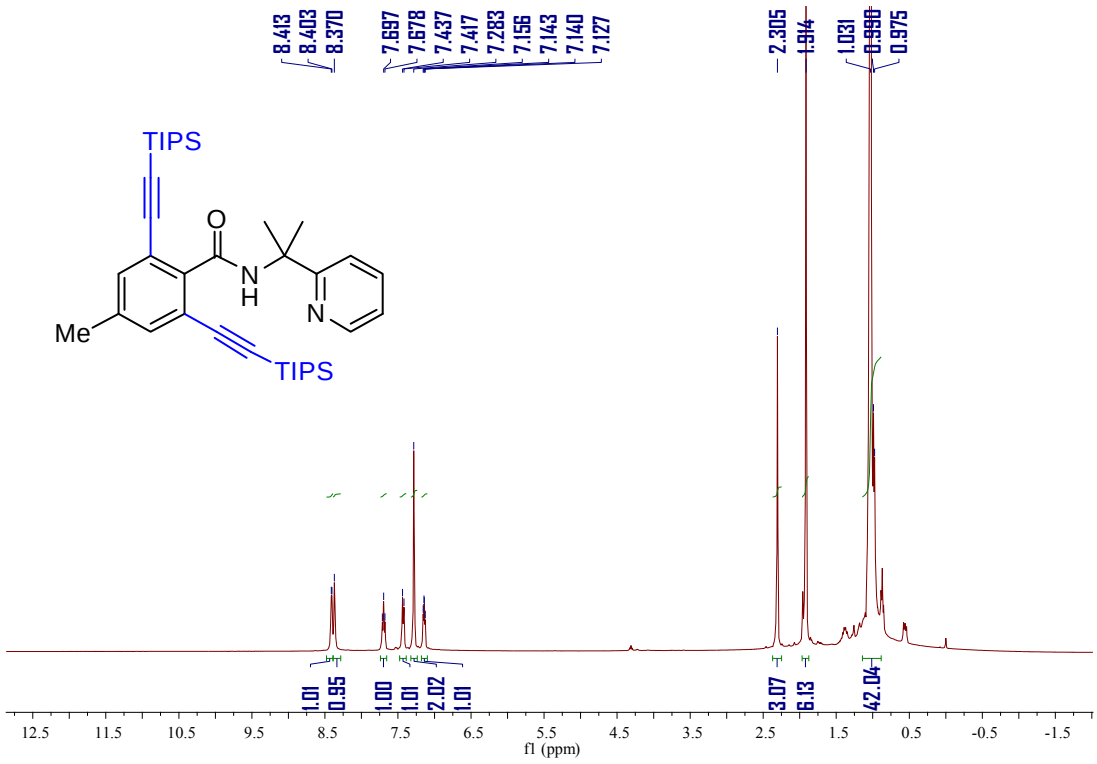

164.347
159.537
144.345
134.900
121.760
120.479
119.285
116.983
100.284
99.687
58.328
28.287
18.761
11.326
TIPS
Br
S
H
N
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

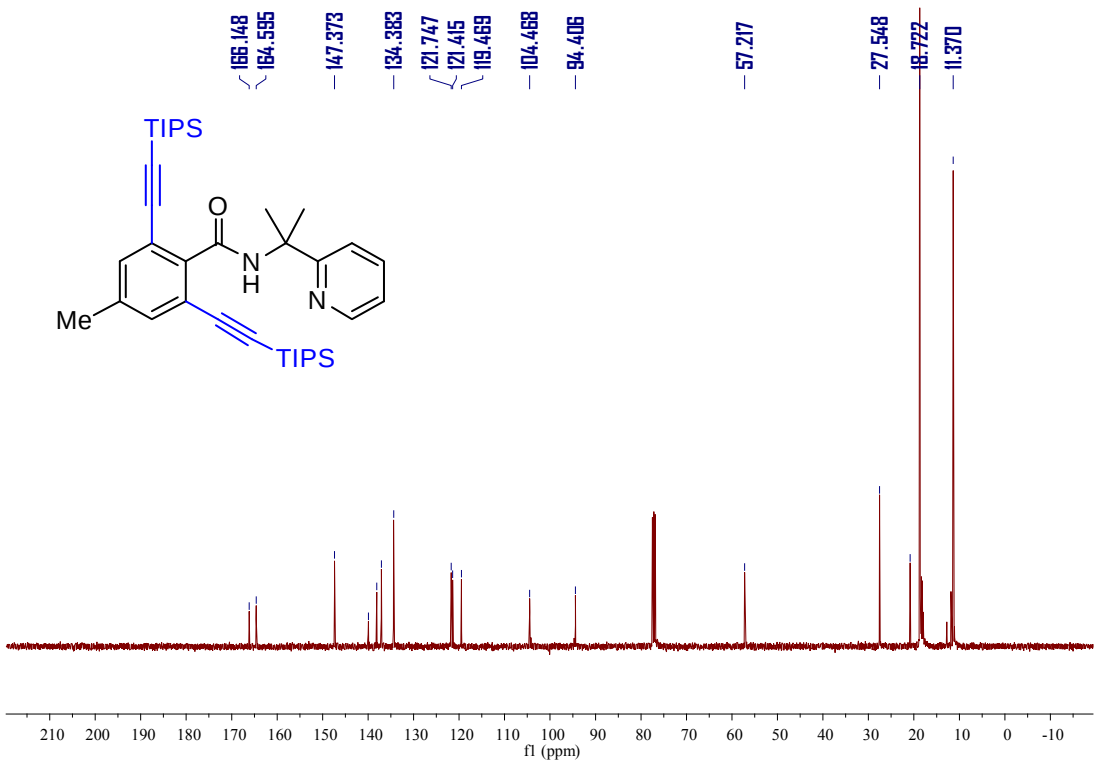
3w


8.509
8.498
7.657
7.653
7.638
7.634
7.467
7.447
7.357
7.190
7.170
7.149
7.136
7.132
7.119
2.352
1.362
1.081
1.060
1.029
O
N
H
N
Me
TIPS
1.00
0.92
0.99
1.02
1.03
1.00
1.01
1.04
3.03
6.15
21.06
f1 (ppm)

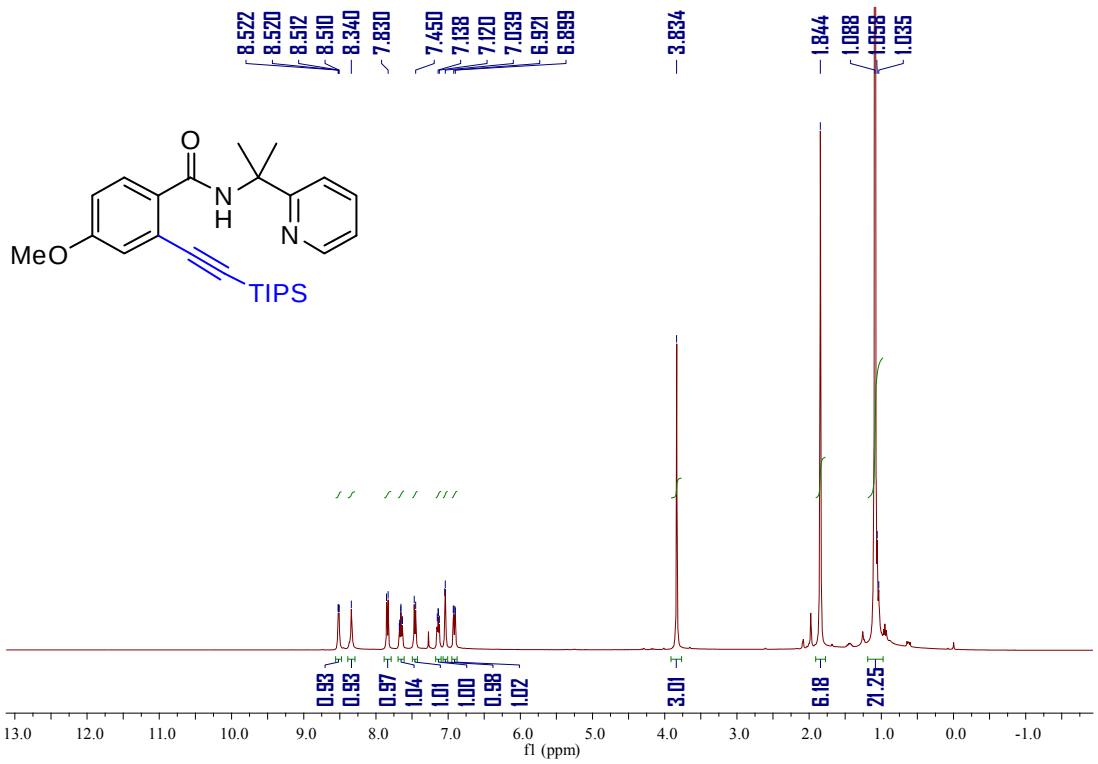

166.158
164.865
148.223
136.793
134.910
129.537
121.619
119.452
105.838
97.120
57.818
27.965
18.766
11.450
O
N
H
N
Me
TIPS
f1 (ppm)

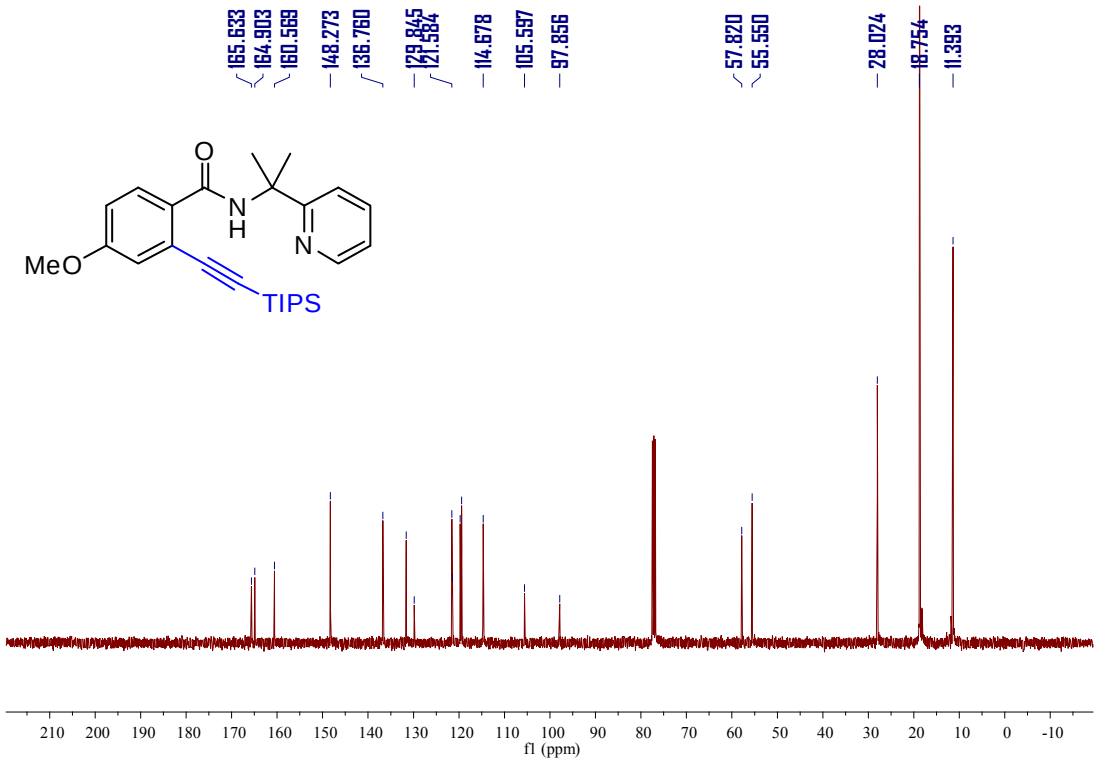
4w


8.413
8.403
8.370
7.697
7.678
7.437
7.417
7.283
7.156
7.143
7.140
7.127
2.305
1.914
1.031
0.988
0.975
TIPS
O
N
H
N
Me
TIPS
1.01
0.95
1.00
1.01
2.02
1.01
3.07
6.13
42.04
f1 (ppm)

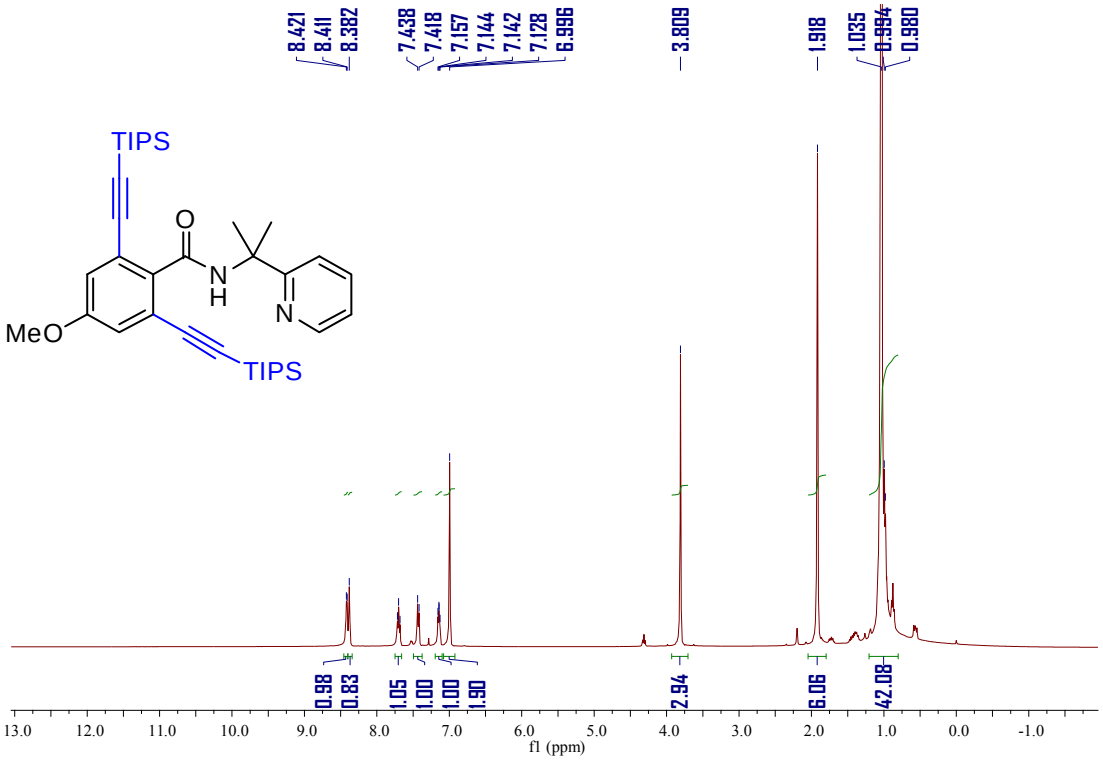

166.148
164.595
147.373
134.383
121.747
121.415
119.469
104.468
94.406
57.217
27.548
18.722
11.370
TIPS
O
N
H
N
Me
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

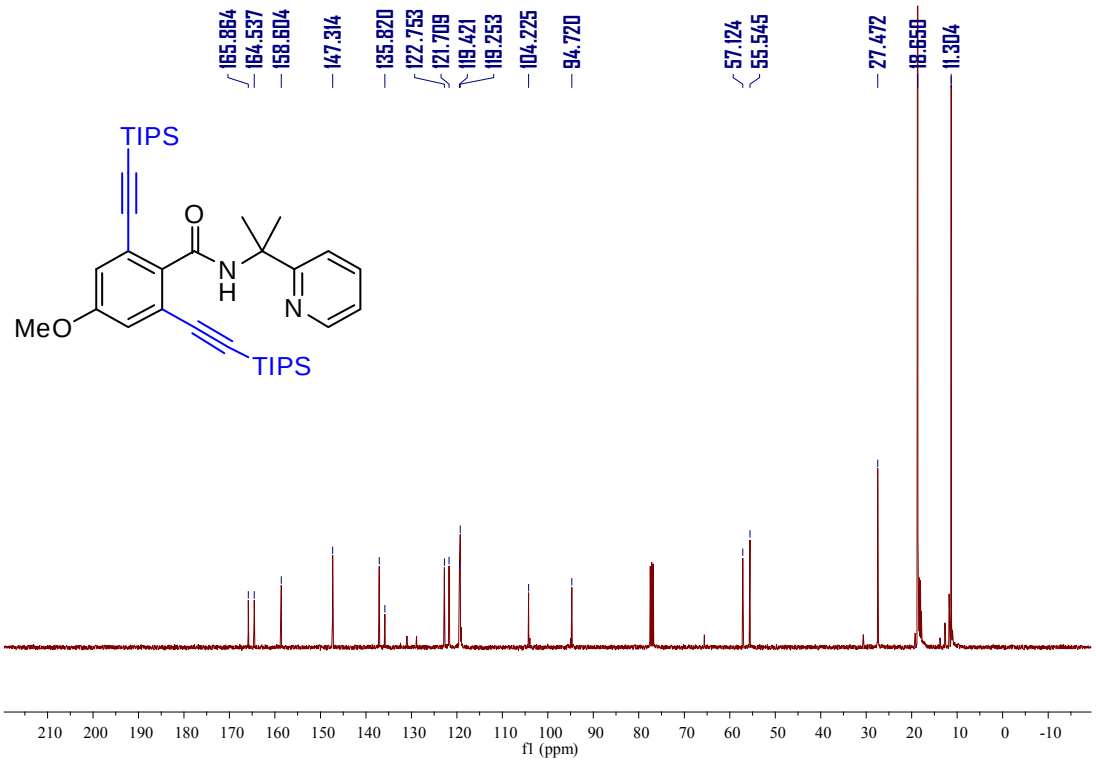
3x


8.522
8.520
8.512
8.510
8.340
7.830
7.450
7.138
7.120
7.039
6.921
6.899
3.834
1.844
1.088
1.058
1.035
O
N
H
N
MeO
TIPS
0.93
0.93
0.97
1.04
1.01
1.00
0.98
1.02
3.01
6.18
21.25
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

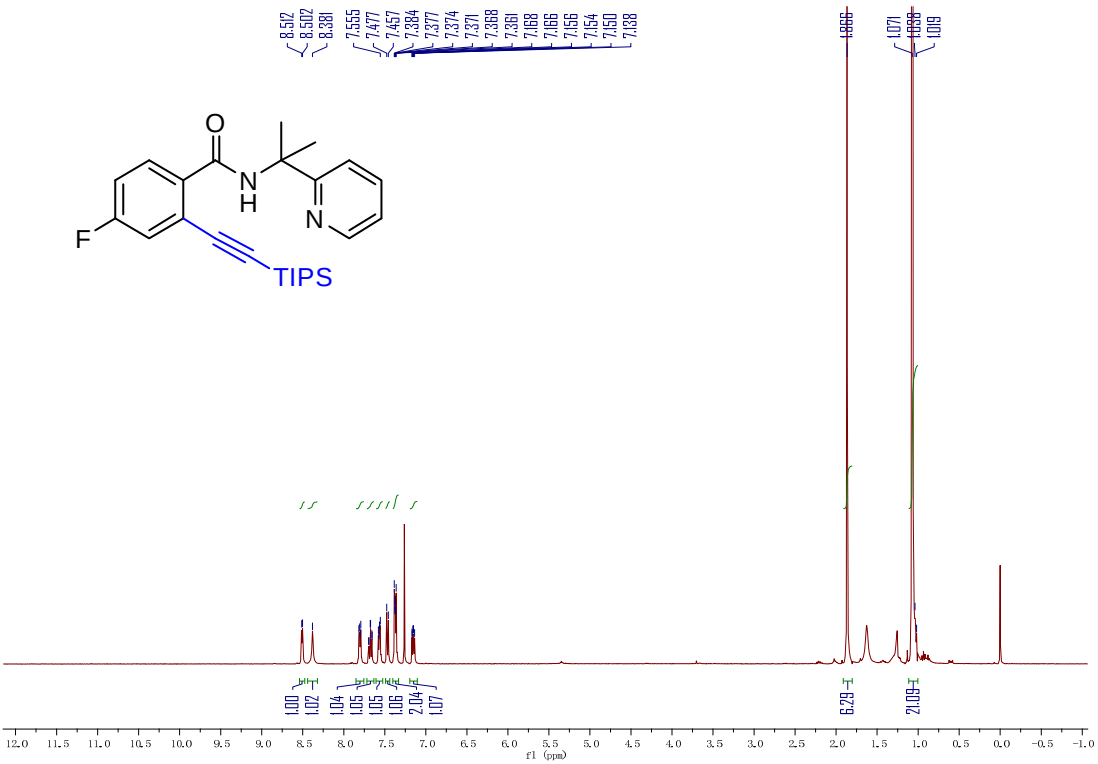

165.633
164.903
160.569
148.273
136.760
128.845
121.584
114.678
105.597
97.856
57.820
55.550
28.024
19.754
11.393
O
N
H
N
MeO
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

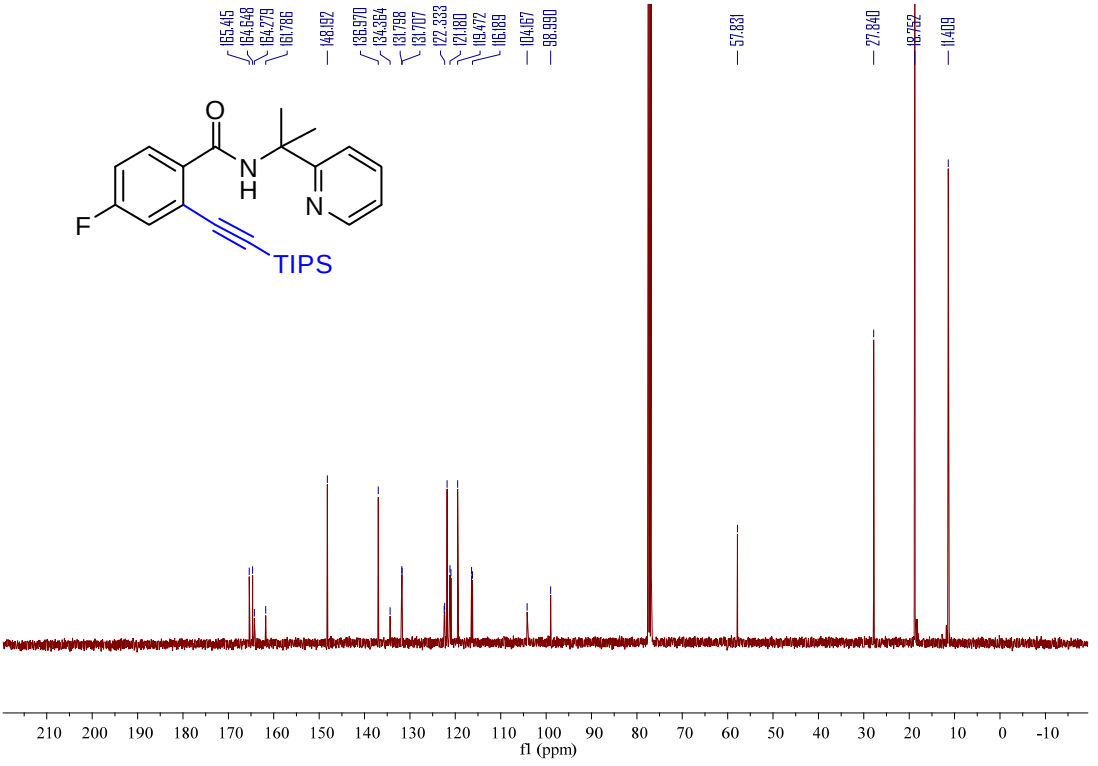
4x

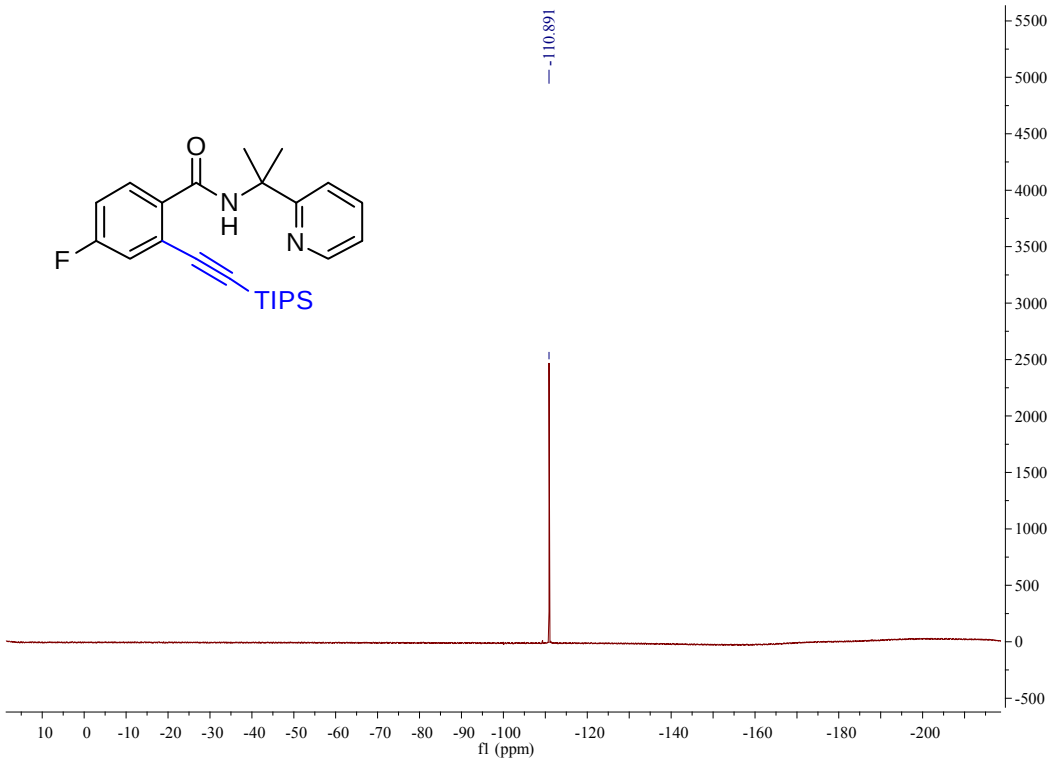

8.421
8.411
8.382
7.438
7.418
7.157
7.144
7.142
7.128
6.996
3.809
1.918
1.035
0.994
0.980
TIPS
O
N
H
N
MeO
TIPS
0.98
0.83
1.05
1.00
1.00
1.90
2.94
6.06
42.08
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


165.864
164.537
158.604
147.314
135.820
122.753
121.709
119.421
119.253
104.225
94.720
57.124
55.545
27.472
18.658
11.304
TIPS
O
N
H
N
MeO
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

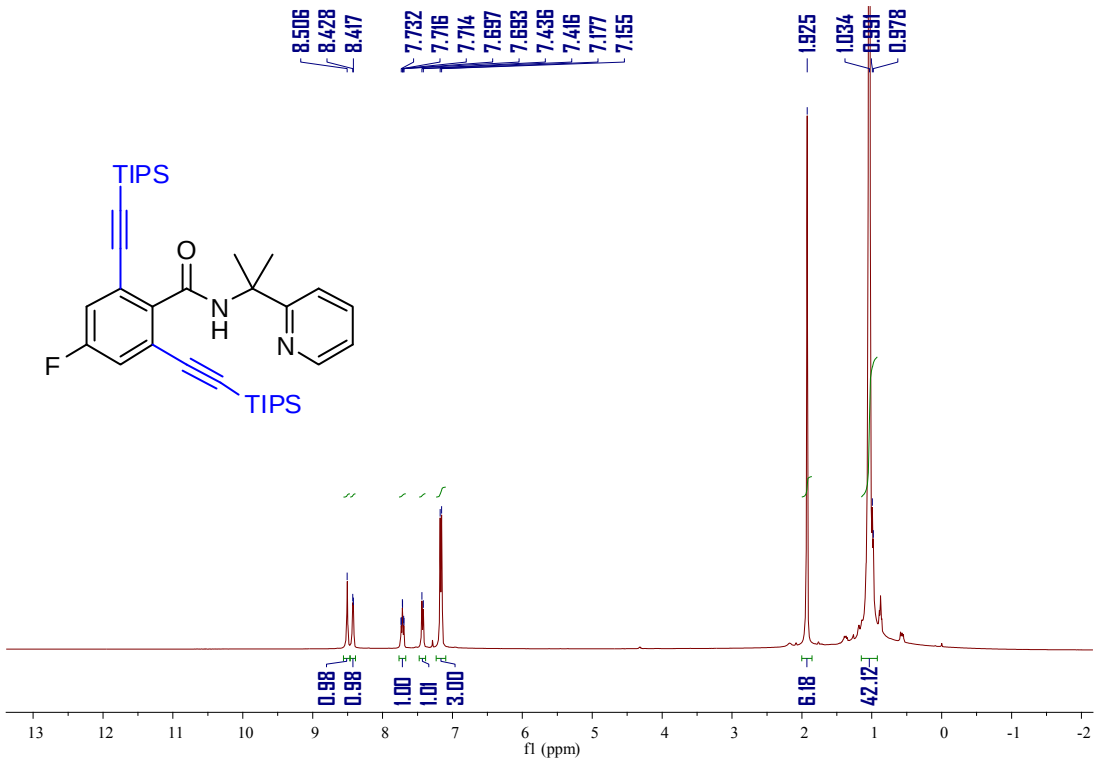
3y

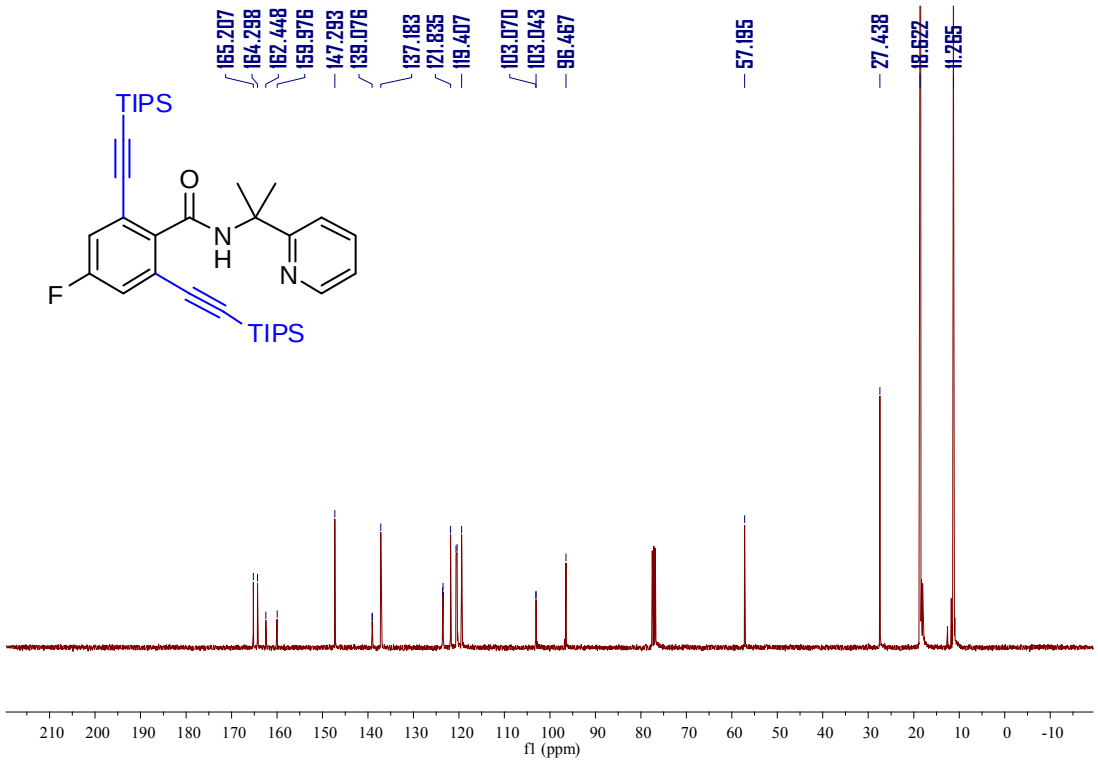

8.512
8.502
8.381
7.555
7.477
7.457
7.384
7.377
7.374
7.371
7.368
7.361
7.168
7.166
7.156
7.154
7.150
7.138
1.866
1.071
1.038
1.019
O
N
H
N
F
TIPS
1.00
1.02
1.04
1.05
1.05
1.06
2.04
1.07
6.29
21.09
f1 (ppm)

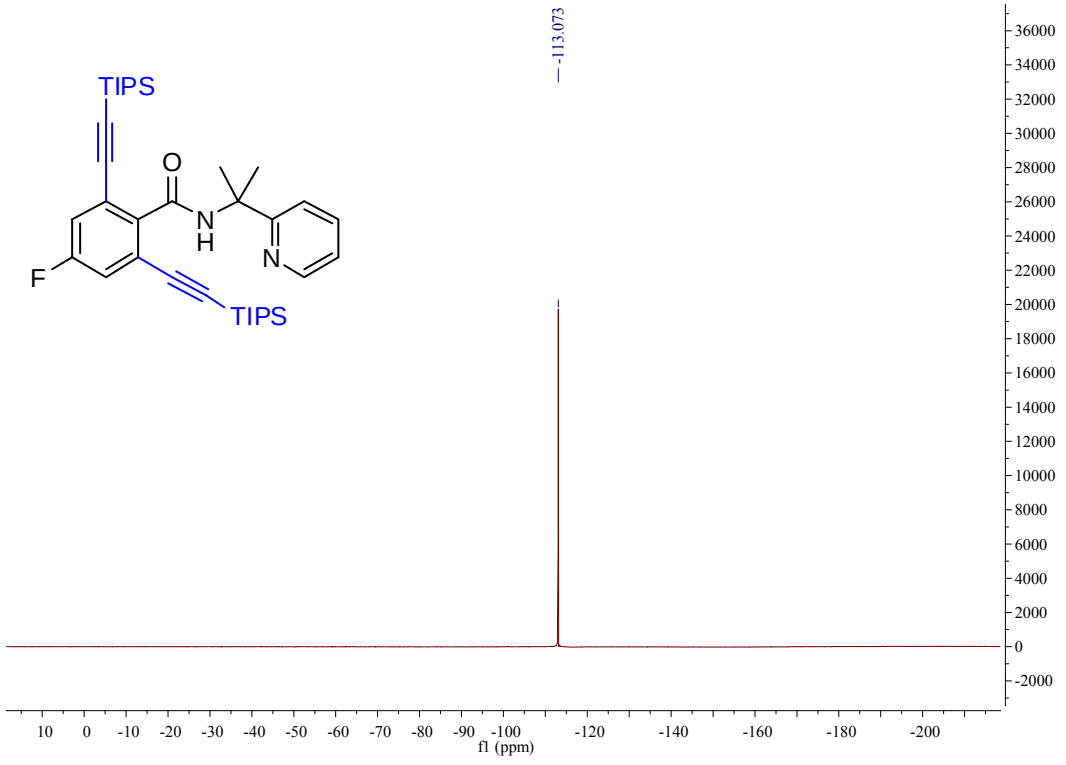

165.445
164.648
164.279
161.786
148.192
136.970
134.384
131.798
131.707
122.333
121.180
119.472
116.183
104.167
98.990
57.831
27.840
18.752
11.409
O
N
H
N
F
TIPS
f1 (ppm)


-110.891
O
N
H
N
F
TIPS
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

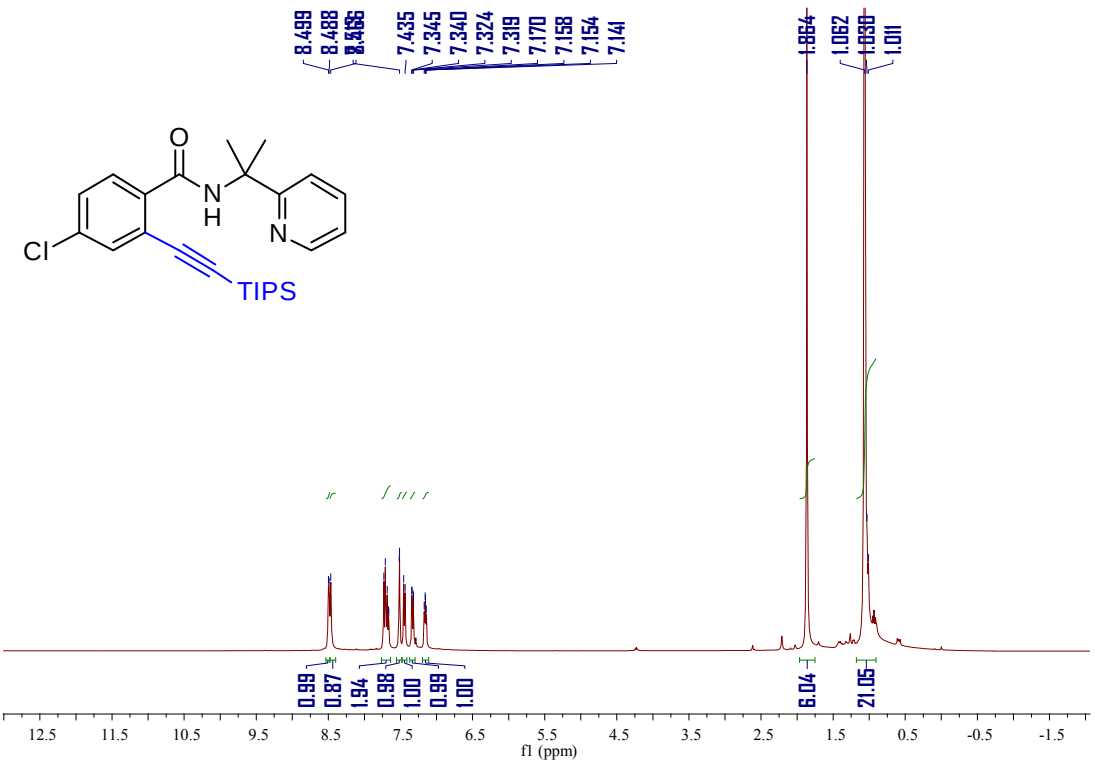
4y

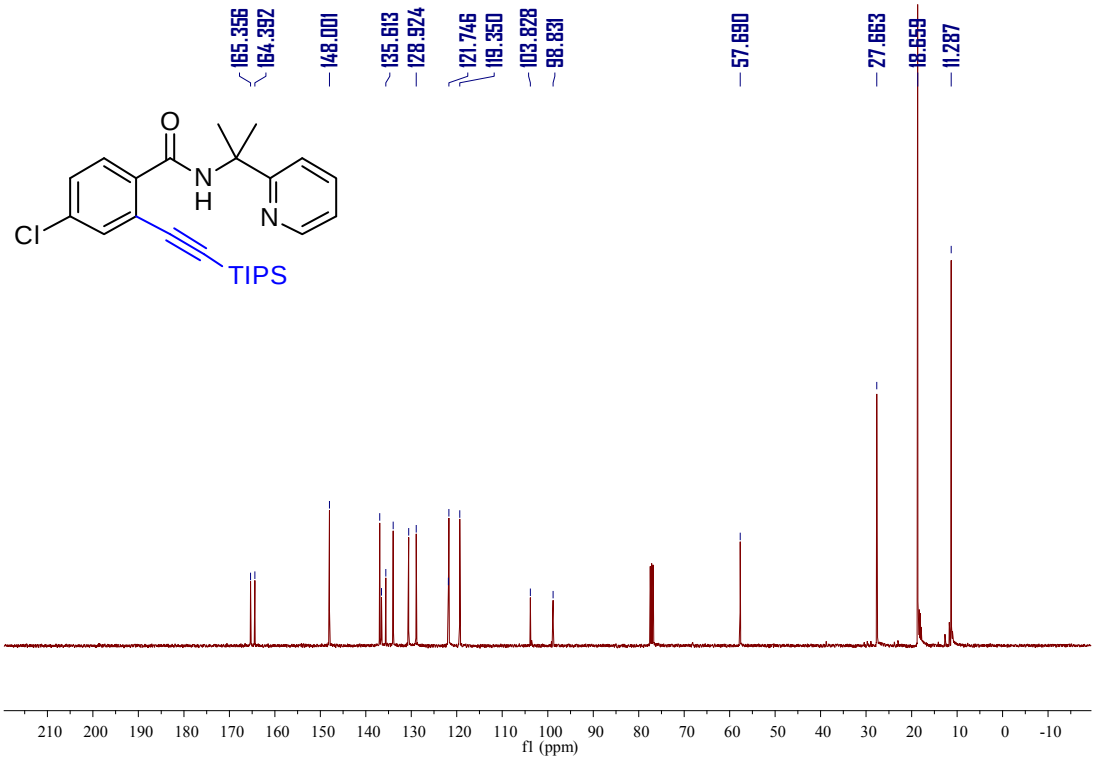

8.506
8.428
8.417
7.732
7.716
7.714
7.697
7.683
7.436
7.416
7.177
7.155
1.925
1.034
0.991
0.978
TIPS
O
N
H
N
F
TIPS
0.98
0.98
1.00
1.01
3.00
6.18
42.12
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


165.207
164.298
162.448
159.976
147.293
139.076
137.183
121.835
119.407
103.070
103.043
96.467
57.195
27.438
18.622
11.265
TIPS
TIPS
F
O
N
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

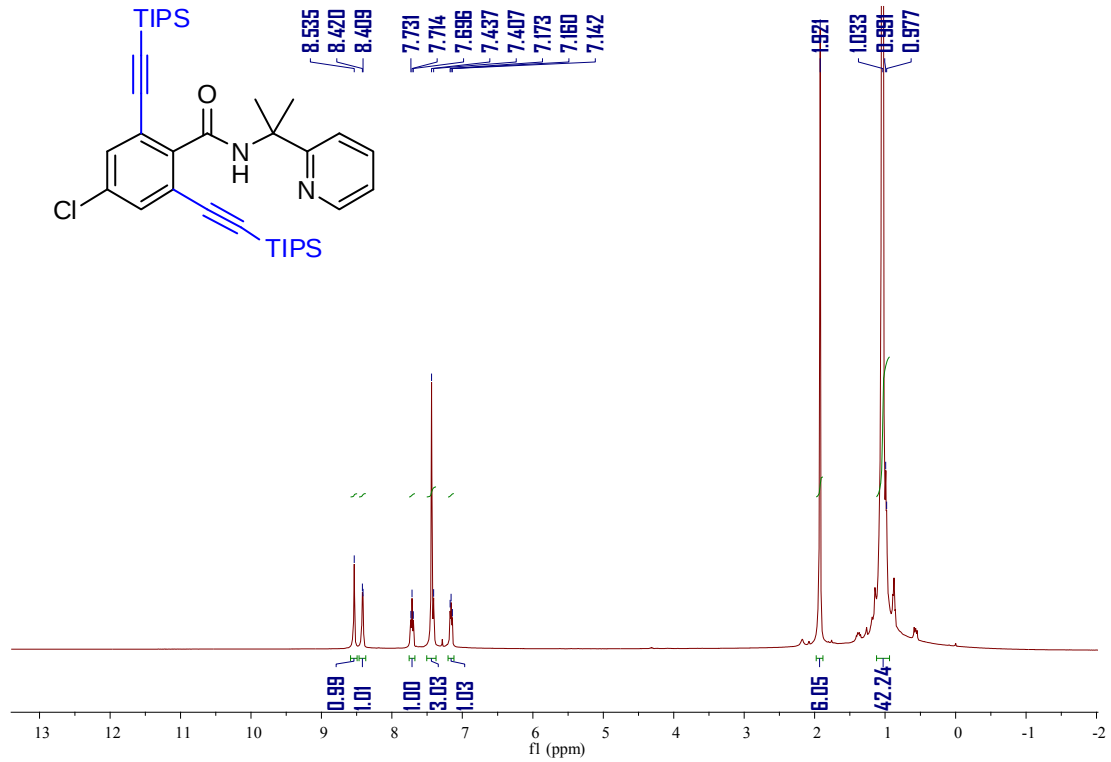

-113.073
TIPS
TIPS
F
O
N
H
N
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

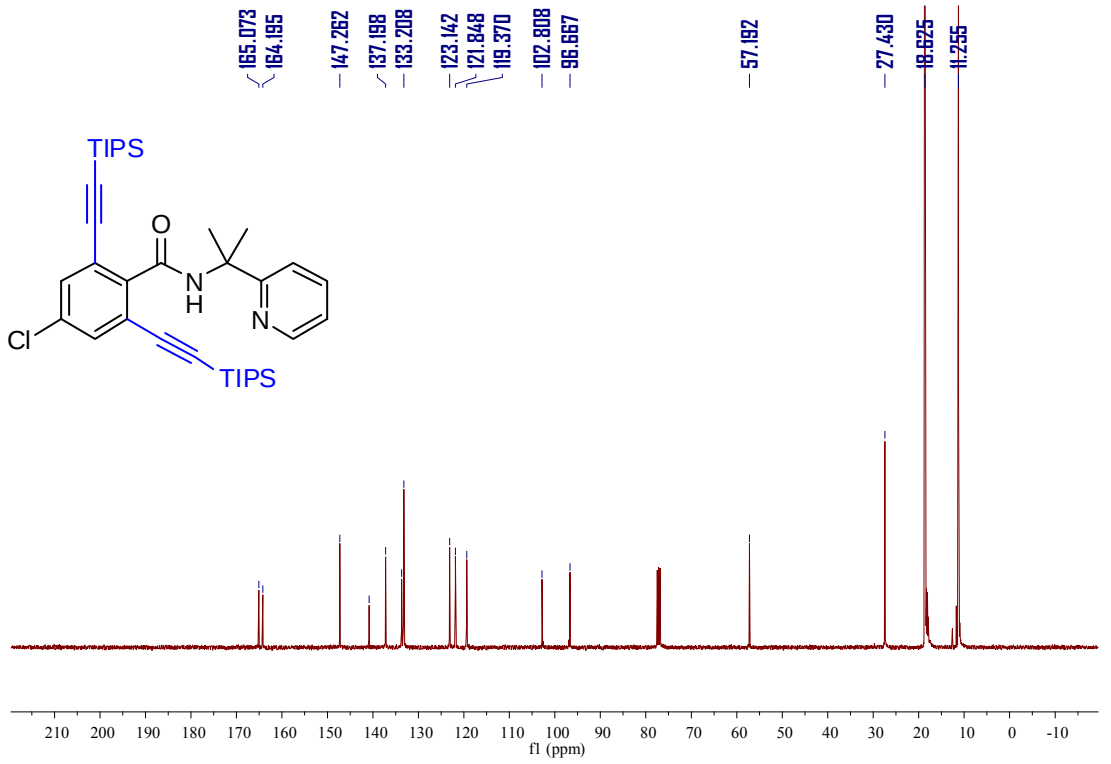
3z


8.499
8.488
7.435
7.345
7.340
7.324
7.319
7.170
7.158
7.154
7.141
1.864
1.062
1.038
1.011
O
N
H
N
Cl
TIPS
0.93
0.87
1.94
0.98
1.00
0.99
1.00
6.04
21.05
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

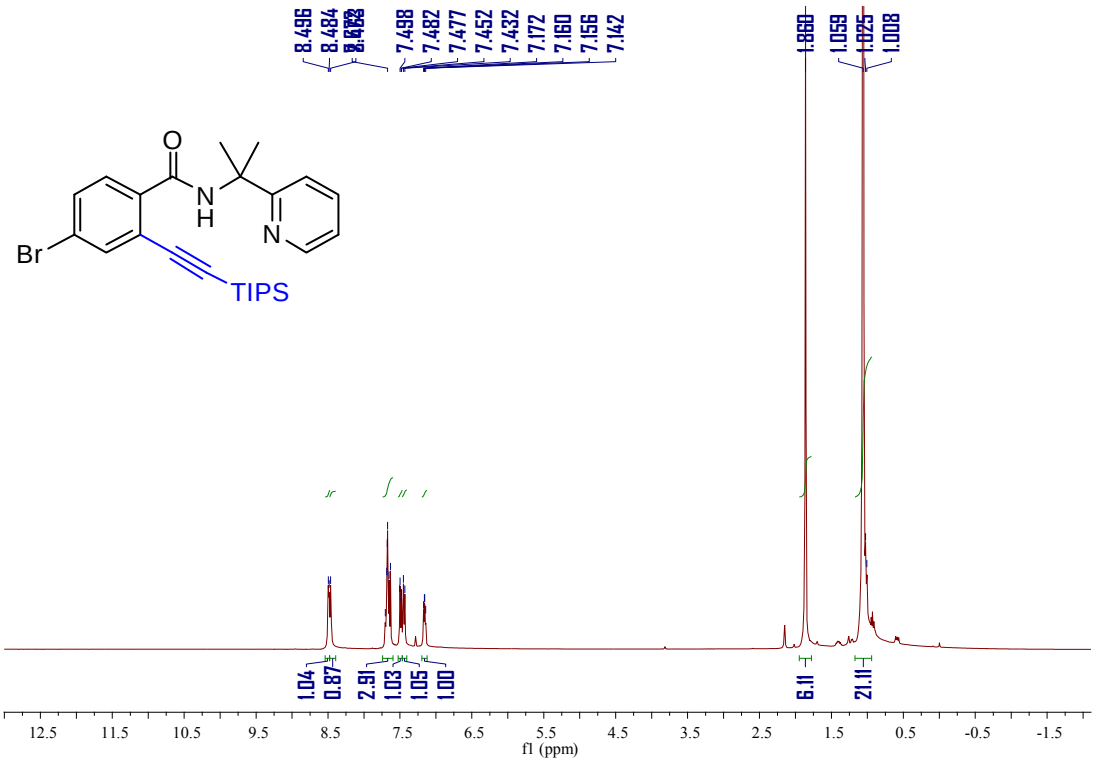

165.356
164.392
148.001
135.613
128.924
121.746
119.350
103.828
98.831
57.690
27.663
18.659
11.287
O
N
H
N
Cl
TIPS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

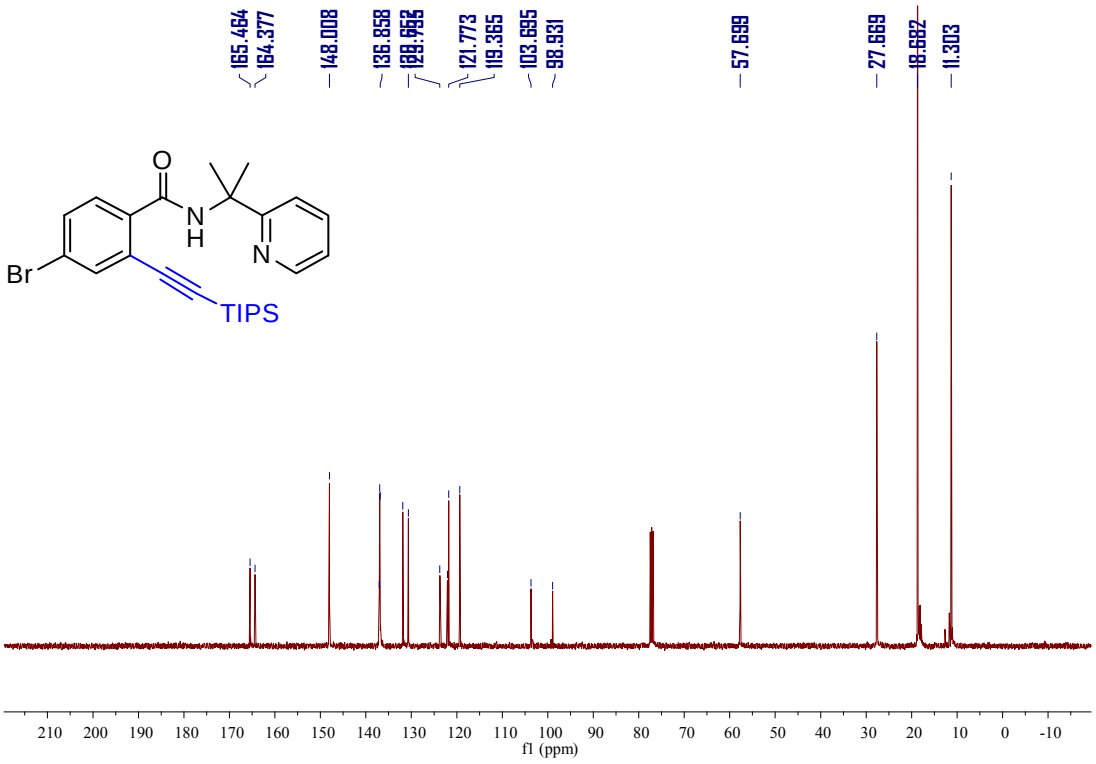
4z


TIPS
O
N
H
N
Cl
TIPS
8.535
8.420
8.409
7.731
7.714
7.696
7.437
7.407
7.173
7.160
7.142
1.921
1.033
0.977
0.99
1.01
1.00
3.03
1.03
6.05
42.24
fl (ppm)

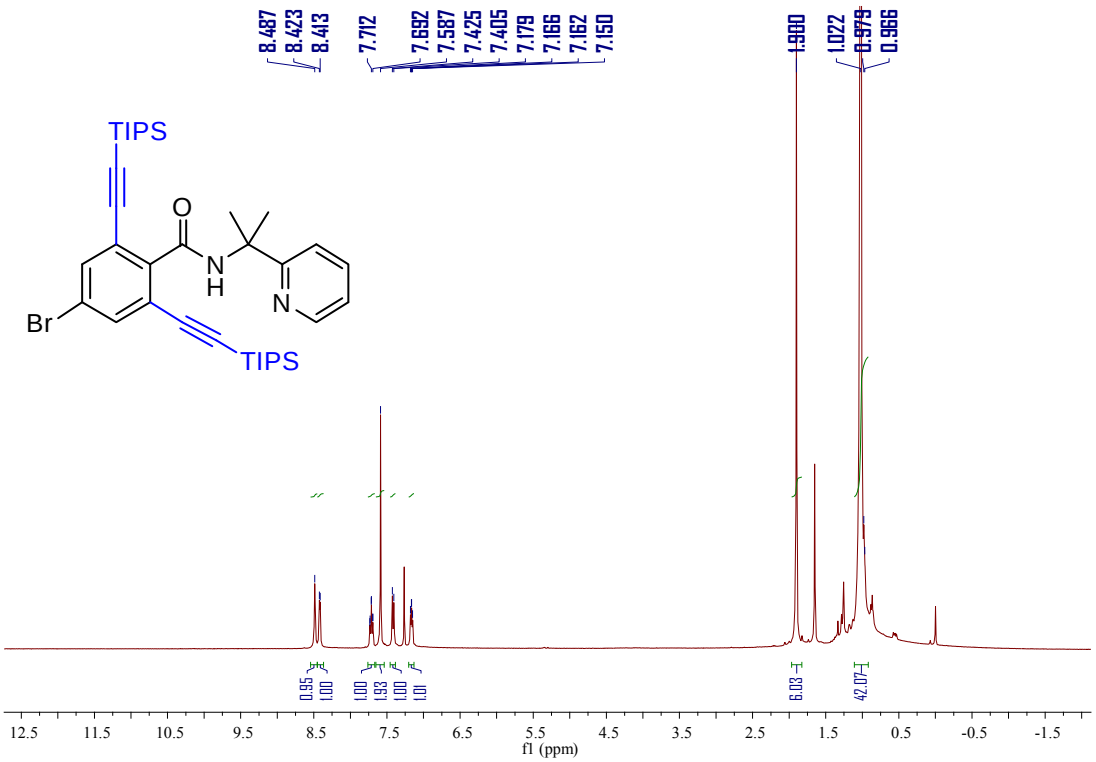

TIPS
O
N
H
N
Cl
TIPS
165.073
164.195
147.262
137.198
133.208
123.142
121.848
119.370
102.808
96.667
57.192
27.430
18.625
11.255
fl (ppm)

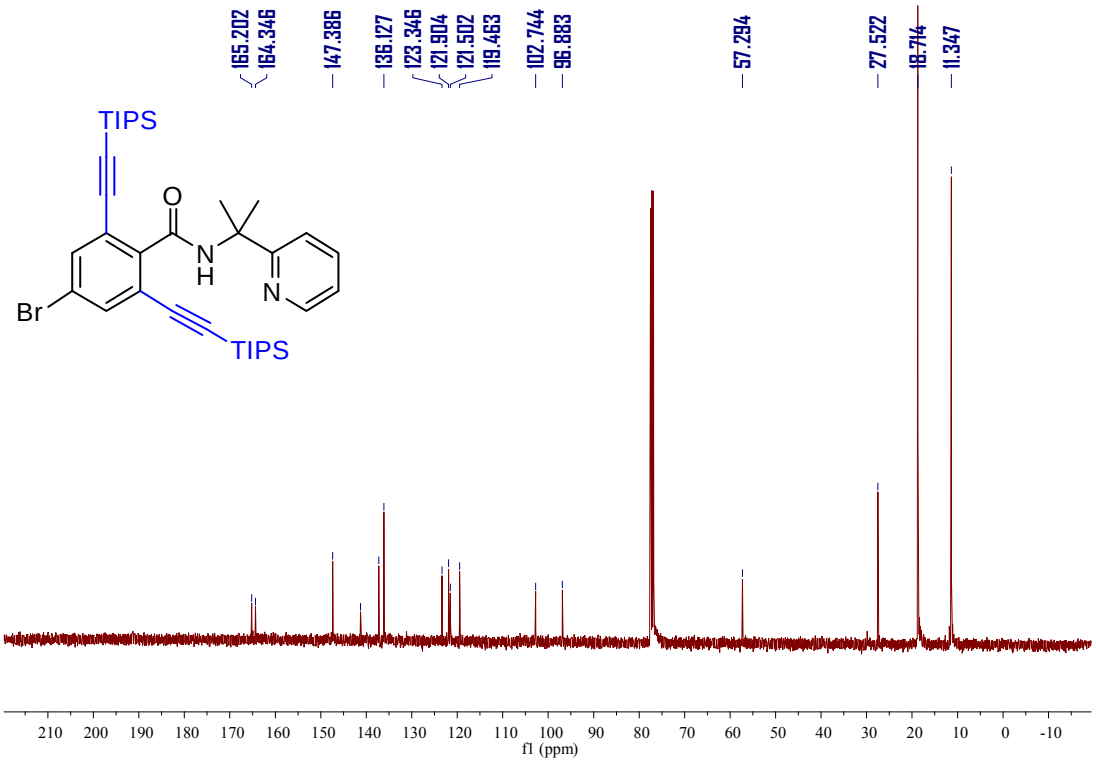
3aa


8.496
8.484
7.498
7.482
7.477
7.452
7.432
7.172
7.160
7.156
7.142
1.860
1.059
1.025
1.008
O
N
H
N
Br
TIPS
1.04
0.87
2.91
1.03
1.05
1.00
6.11
21.11
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

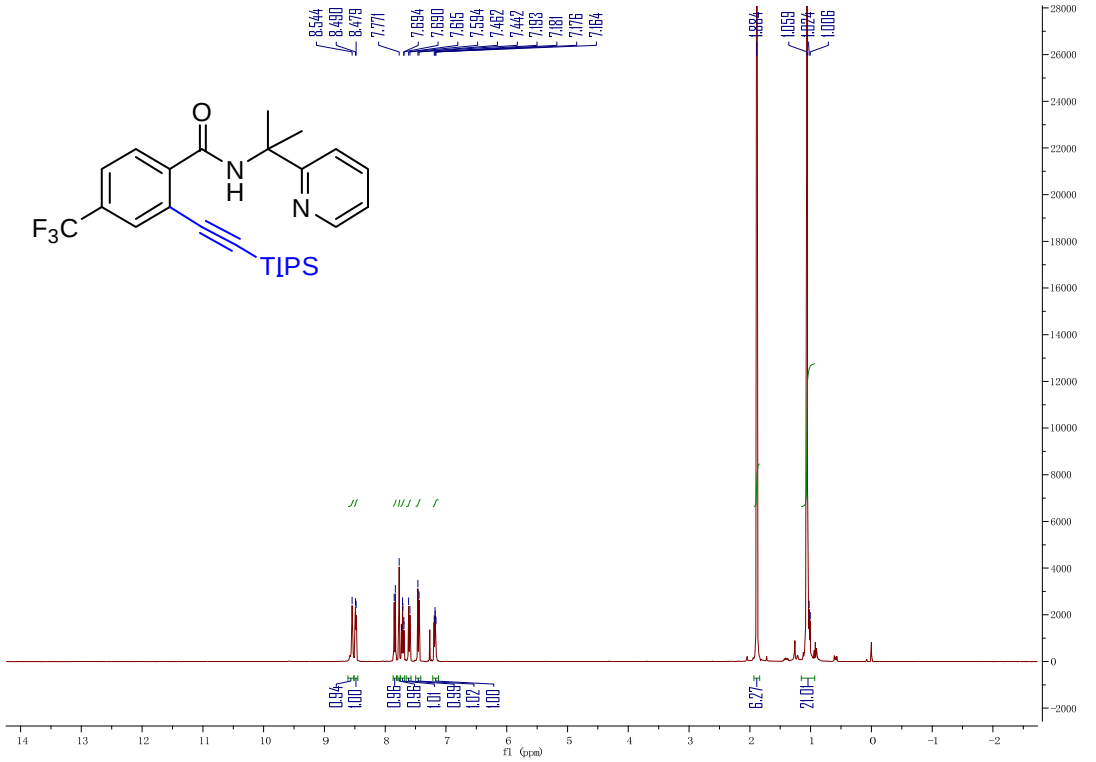

165.464
164.377
148.008
136.858
121.773
119.365
103.685
98.931
57.699
27.669
18.682
11.303
O
N
H
N
Br
TIPS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

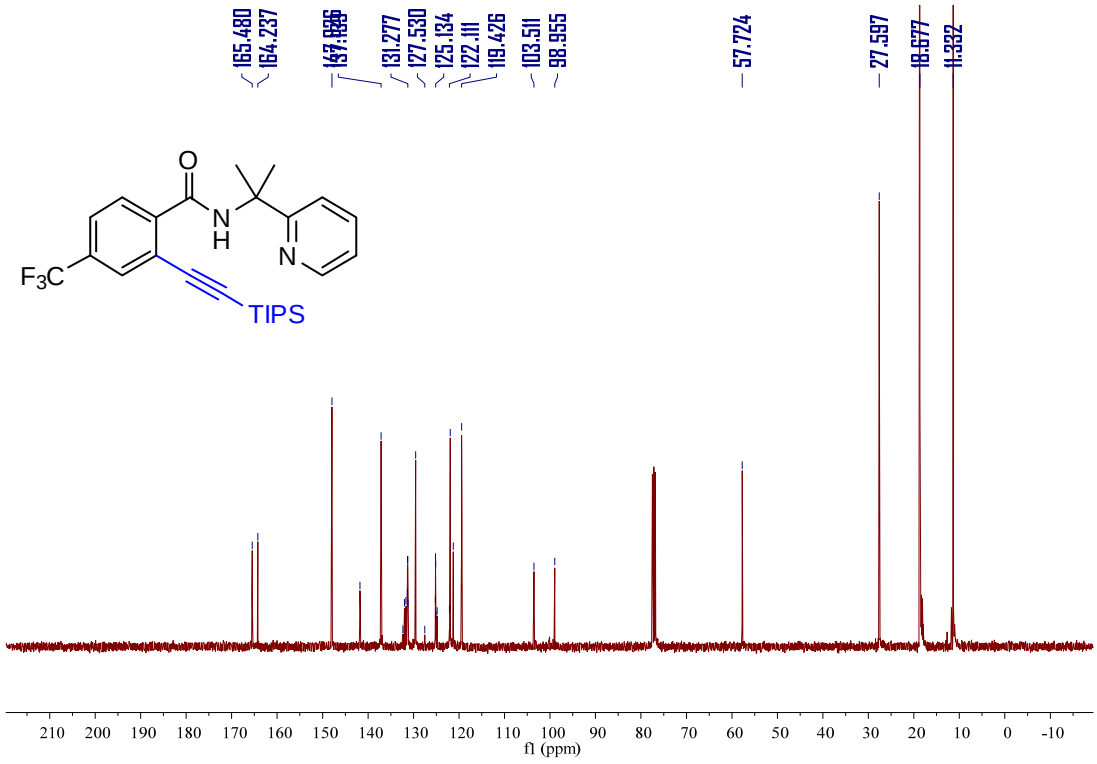
4aa

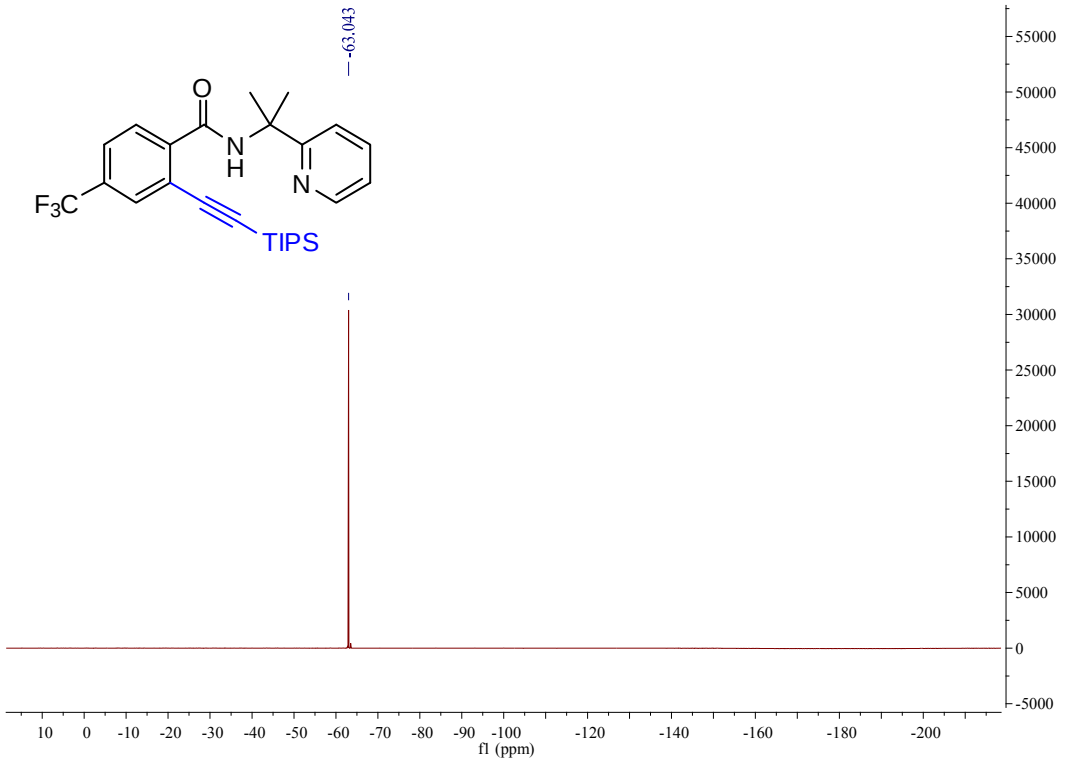

8.487
8.423
8.413
7.712
7.692
7.587
7.425
7.405
7.179
7.166
7.162
7.150
1.900
1.022
0.973
0.966
TIPS
O
N
H
N
Br
TIPS
0.95
1.00
1.00
1.93
1.00
1.01
6.03
42.07
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)


165.202
164.346
147.386
136.127
123.346
121.904
121.502
119.463
102.744
96.883
57.294
27.522
18.714
11.347
TIPS
O
N
H
N
Br
TIPS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

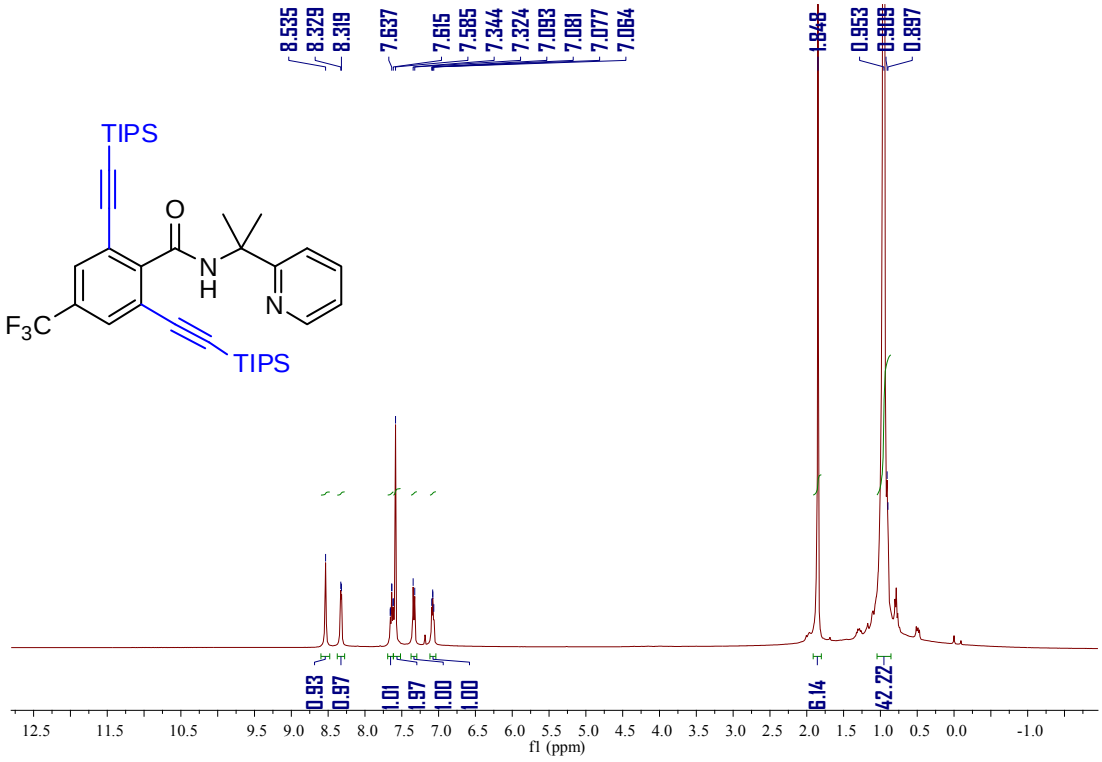
3ab

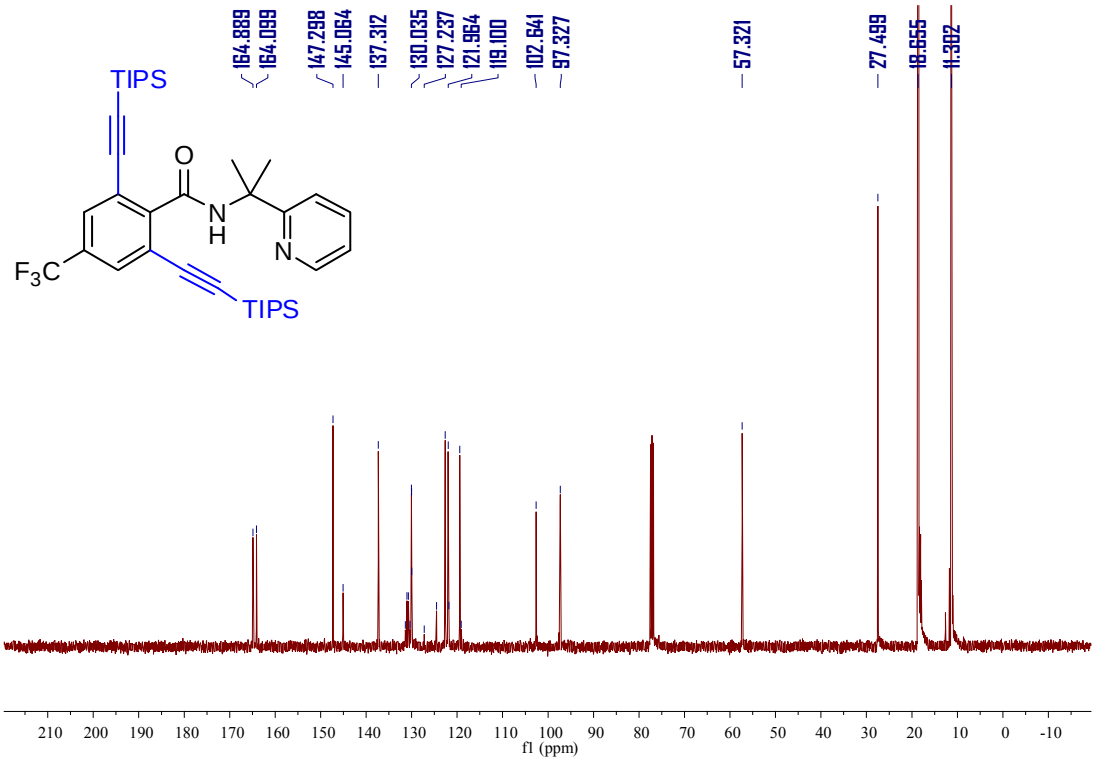

8.544
8.490
8.479
7.771
7.694
7.690
7.615
7.594
7.462
7.442
7.193
7.181
7.176
7.164
1.884
1.059
1.024
1.006
0.94
1.00
0.96
0.96
1.01
0.99
1.02
1.00
6.27
21.09
O
N
H
N
F3C
TIPS
f1 (ppm)

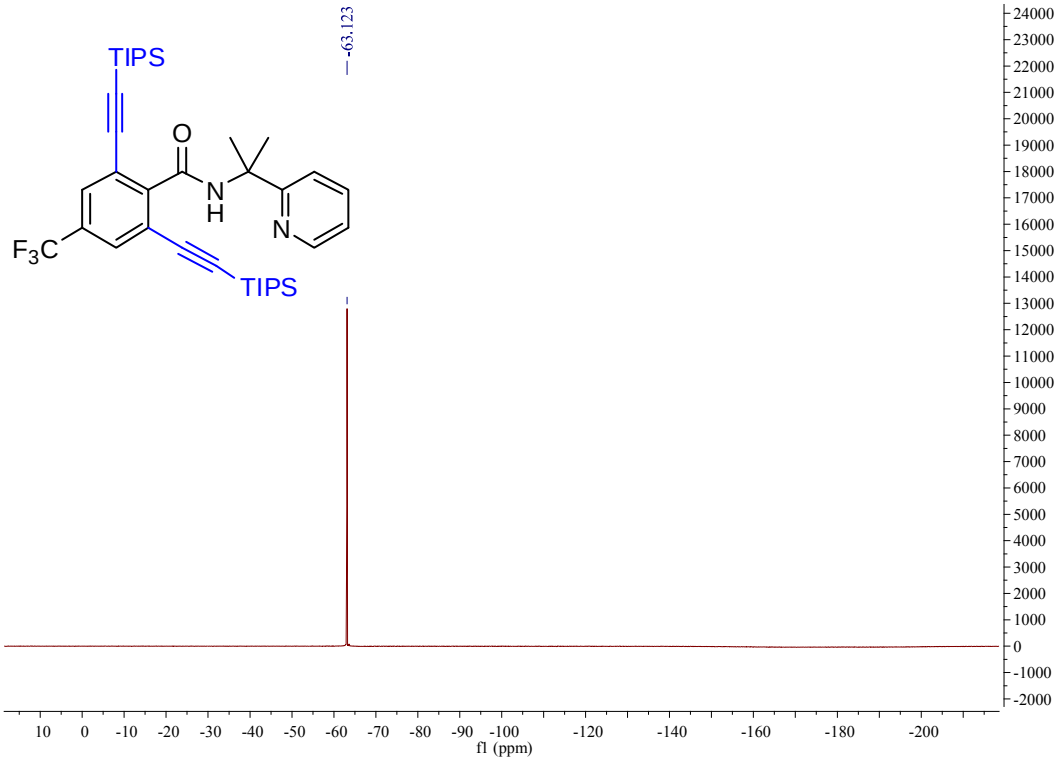

165.480
164.237
147.886
147.139
131.277
127.530
125.134
122.111
119.426
103.511
98.955
57.724
27.597
18.677
11.332
O
N
H
N
F3C
TIPS
f1 (ppm)


-63.043
O
N
H
N
F3C
TIPS
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

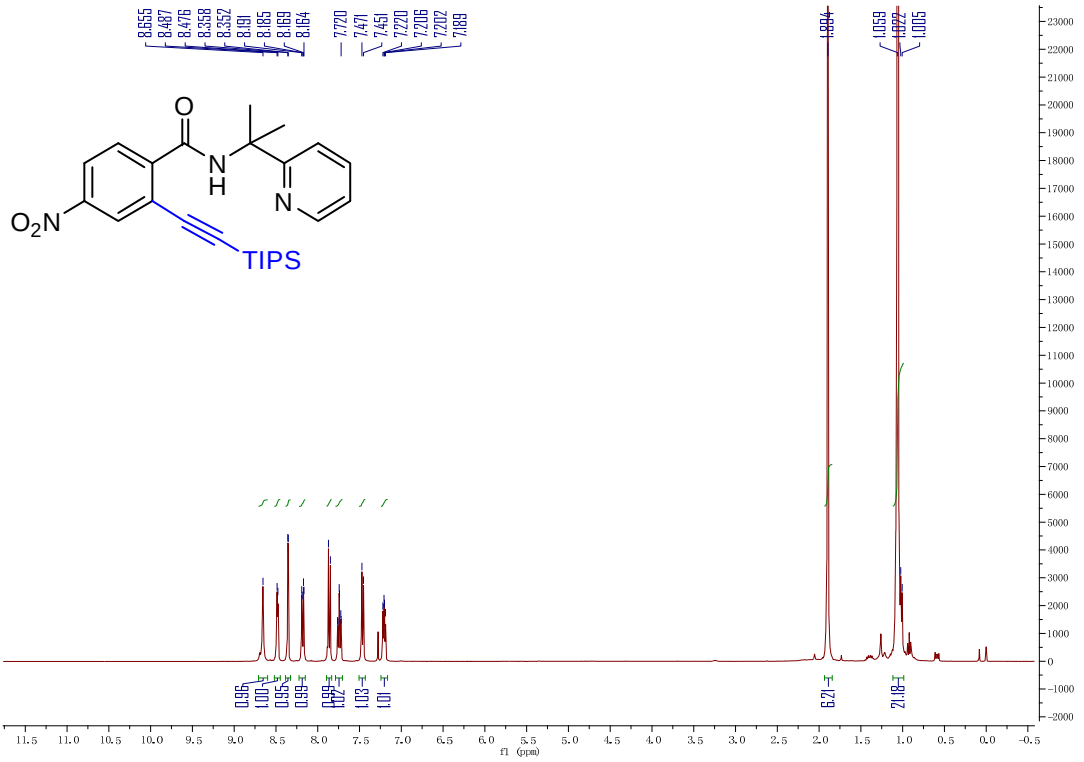
4ab

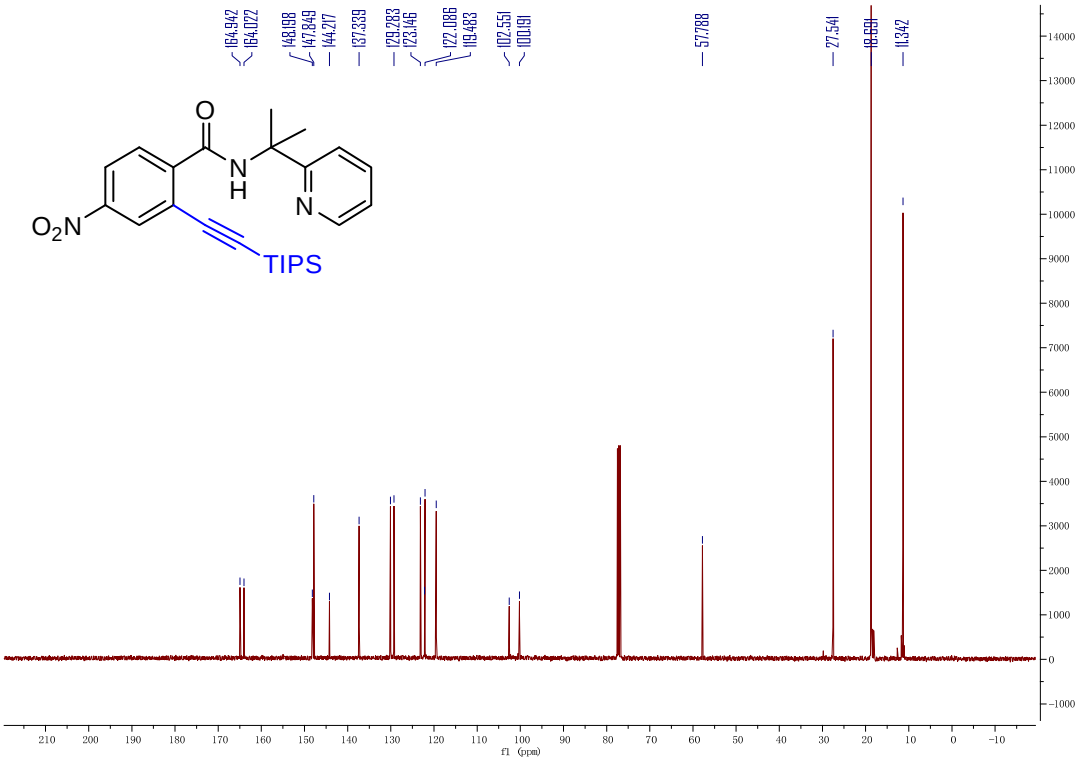

8.535
8.329
8.319
7.637
7.615
7.585
7.344
7.324
7.093
7.081
7.077
7.064
1.848
0.953
0.869
0.897
TIPS
O
N
H
N
F3C
TIPS
0.93
0.97
1.01
1.97
1.00
1.00
6.14
42.22
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)


TIPS
O
N
H
N
F3C
TIPS
164.889
164.099
147.298
145.064
137.312
130.035
127.237
121.964
119.100
102.641
97.327
57.321
27.499
18.655
11.362
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

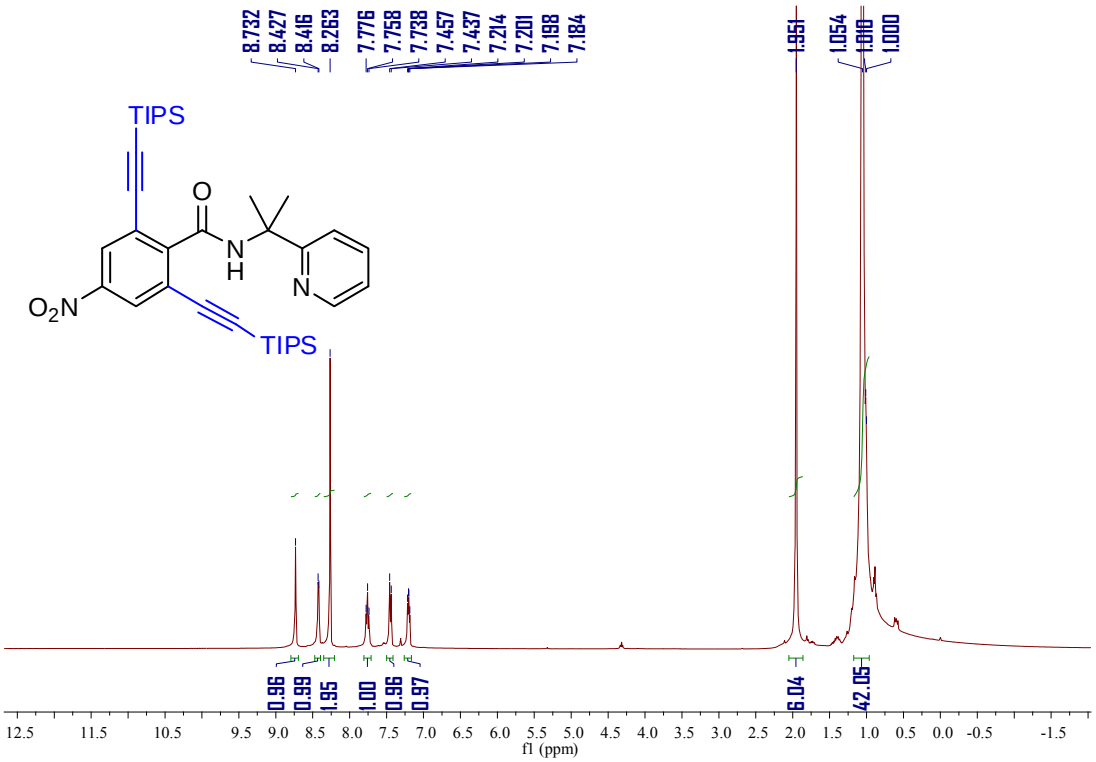

TIPS
O
N
H
N
F3C
TIPS
-63.123
24000 23000 22000 21000 20000 19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000 -2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

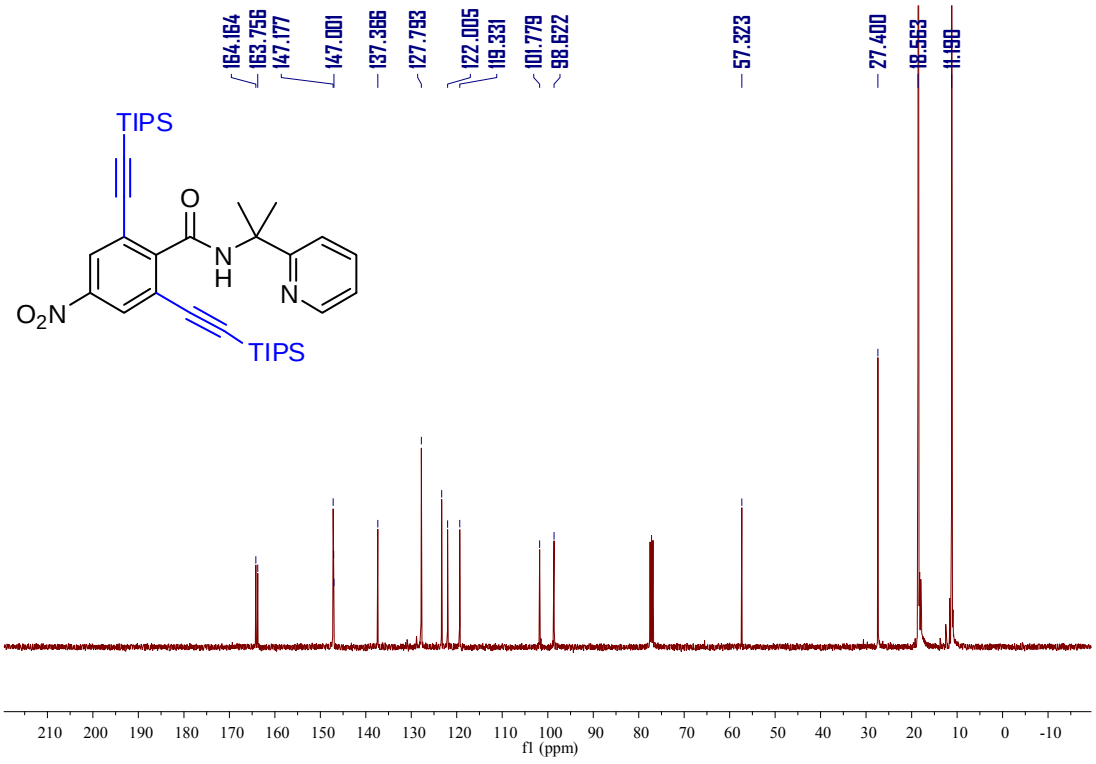
3ac


8.555
8.487
8.476
8.358
8.352
8.191
8.185
8.169
8.164
7.720
7.471
7.451
7.220
7.206
7.202
7.189
1.884
1.059
1.022
1.005
O
N
H
N
O_2N
TIPS
0.96
1.00
0.95
0.99
0.99
1.02
1.03
1.01
6.21
21.18
f1 (ppm)

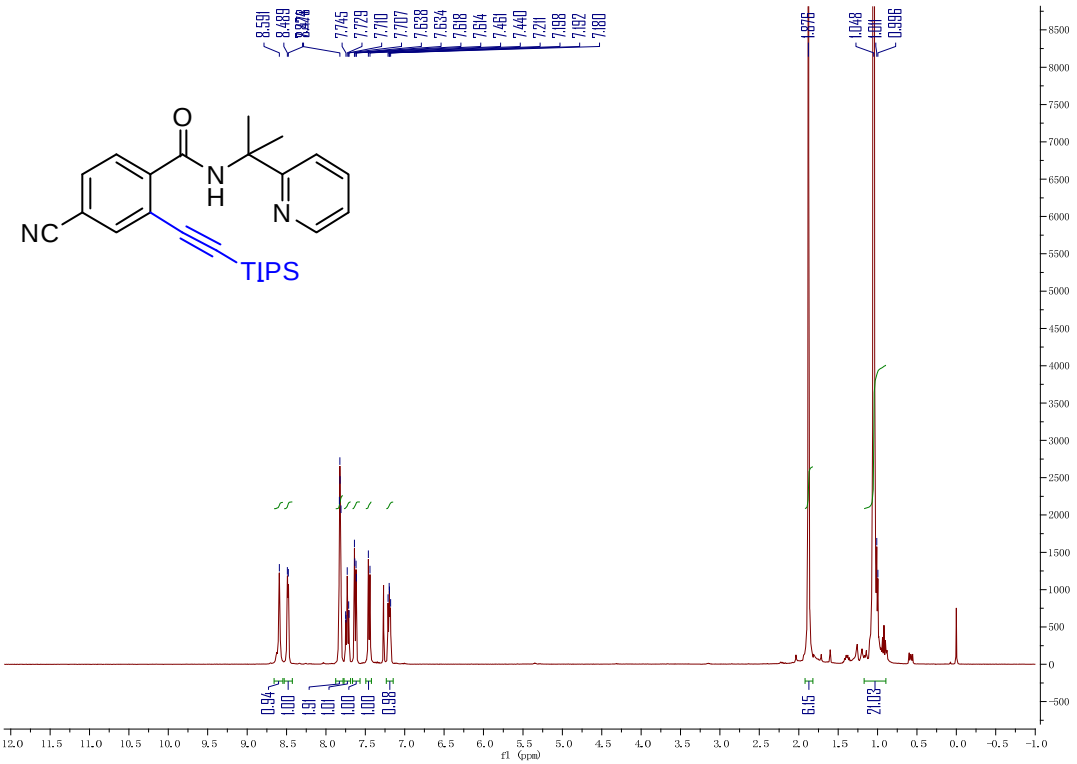

164.942
164.072
148.198
147.849
144.217
137.339
129.283
123.146
122.088
119.483
102.551
100.191
57.788
27.541
18.691
11.342
O
N
H
N
O_2N
TIPS
f1 (ppm)

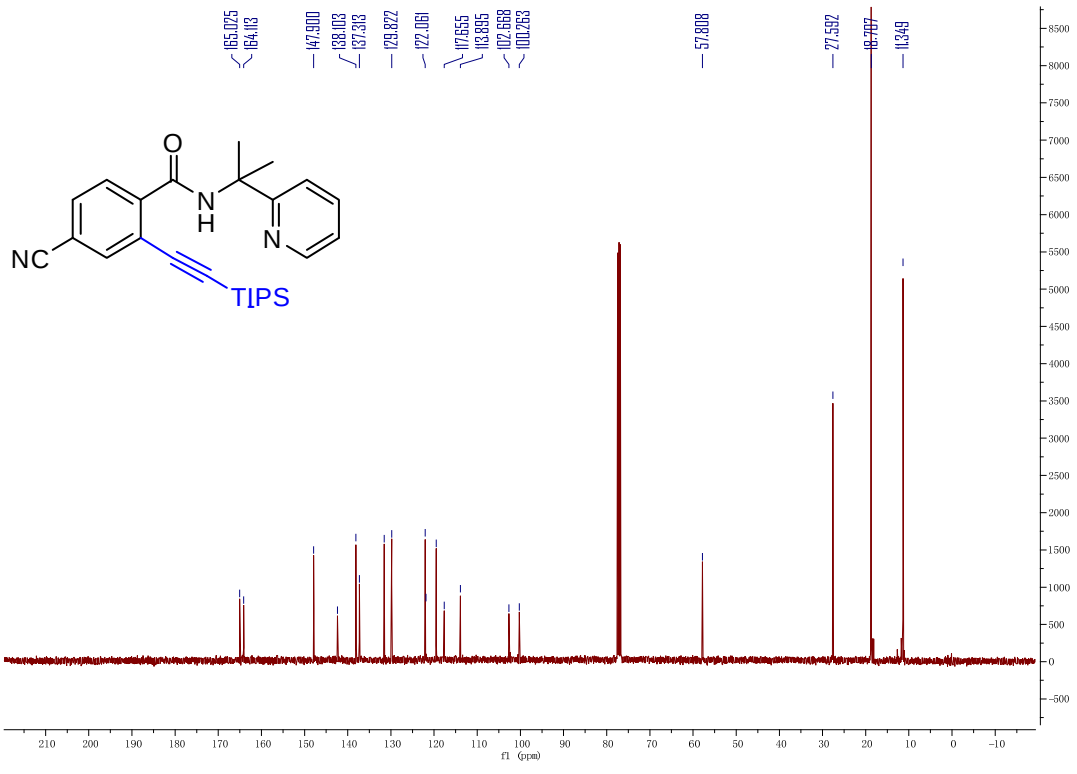
4ac


8.732
8.427
8.416
8.263
7.776
7.758
7.738
7.457
7.437
7.214
7.201
7.198
7.184
1.951
1.054
1.018
1.000
TIPS
O
N
H
N
O2N
TIPS
0.96
0.99
1.95
1.00
0.96
0.97
6.04
42.05
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)

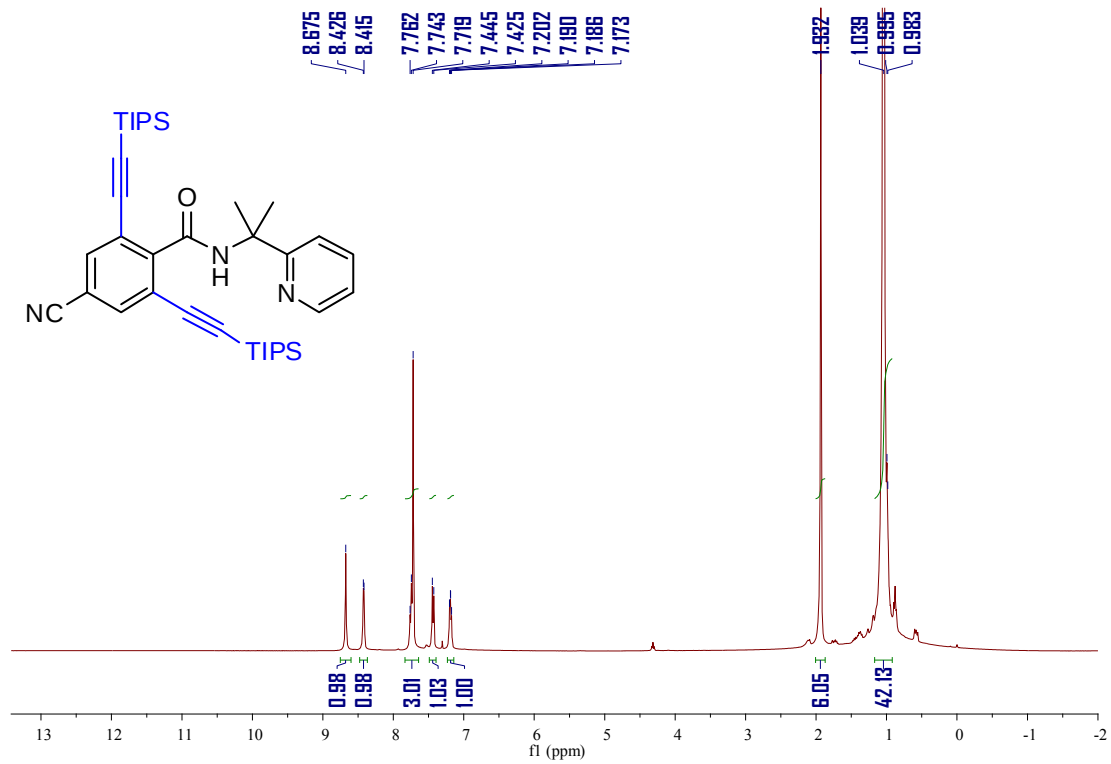

164.164
163.756
147.177
147.001
137.366
127.783
122.005
119.331
101.779
98.622
57.323
27.400
18.563
11.190
TIPS
O
N
H
N
O2N
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

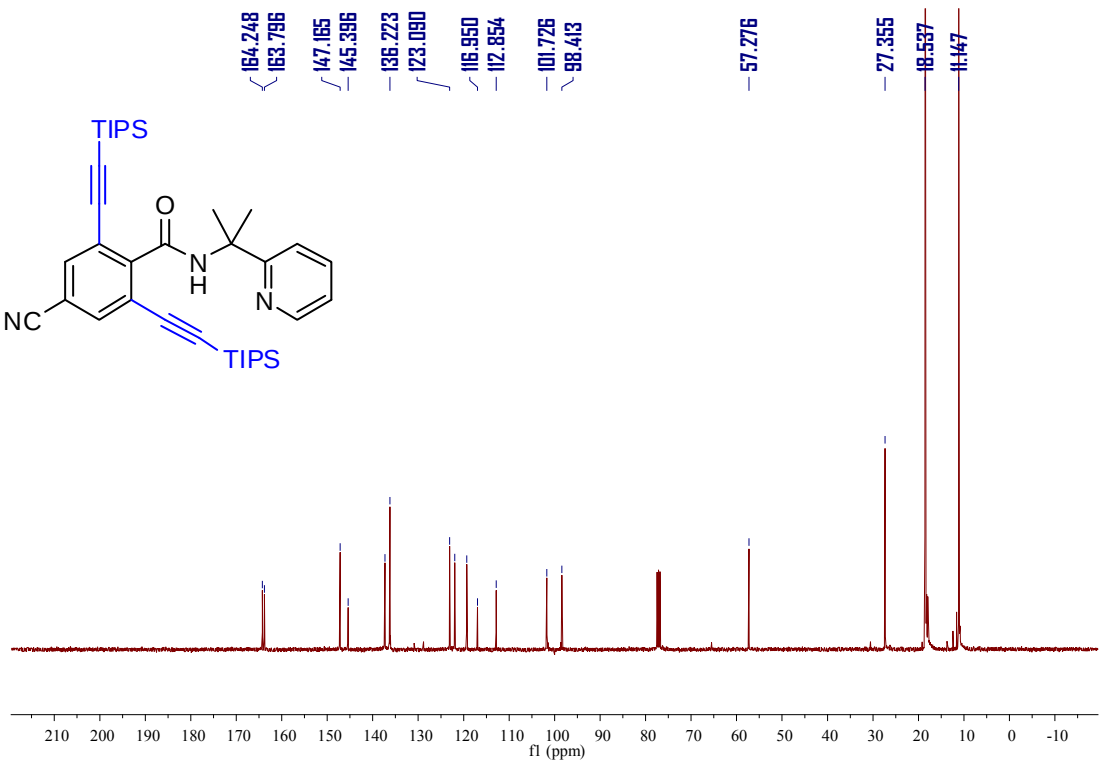
3ad


8.591
8.489
7.745
7.729
7.710
7.707
7.638
7.634
7.618
7.614
7.461
7.440
7.211
7.198
7.192
7.180
1.876
1.048
1.031
0.996
O
N
H
N
NC
TIPS
0.94
1.00
1.91
1.91
1.00
1.00
0.98
6.15
21.09
f1 (ppm)

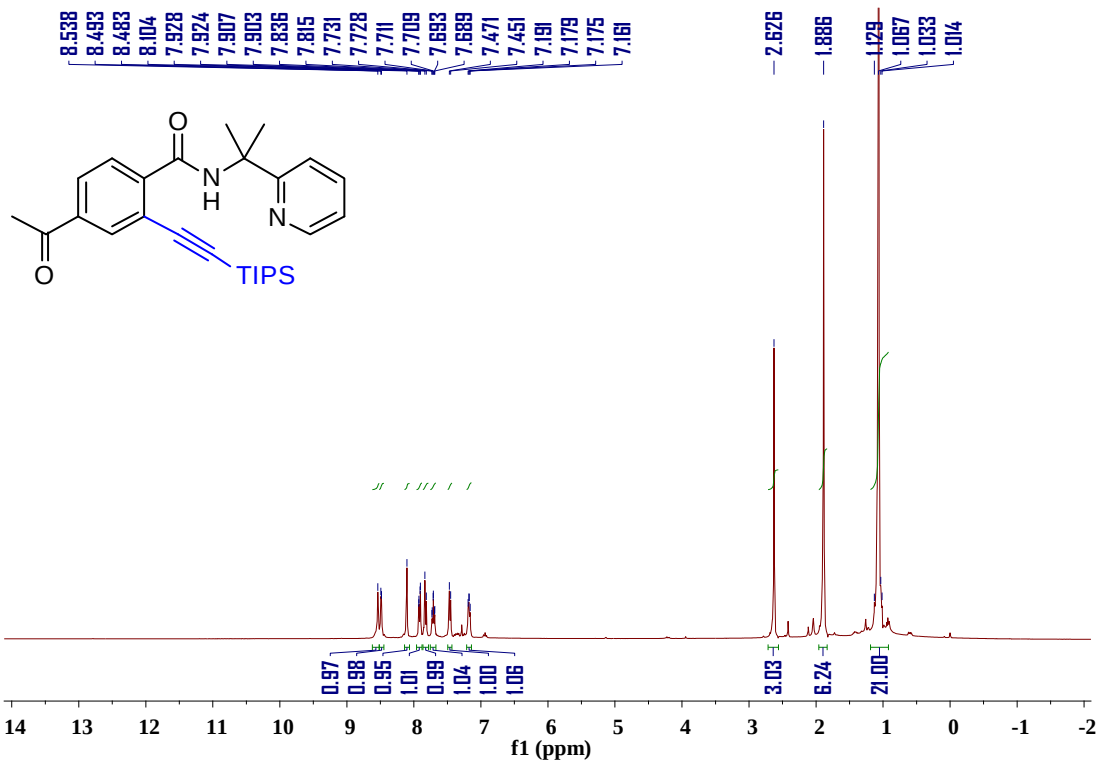

165.1025
164.113
147.900
138.103
137.393
129.872
122.061
117.655
113.895
102.668
100.263
57.808
27.592
18.787
11.349
O
N
H
N
NC
TIPS
f1 (ppm)

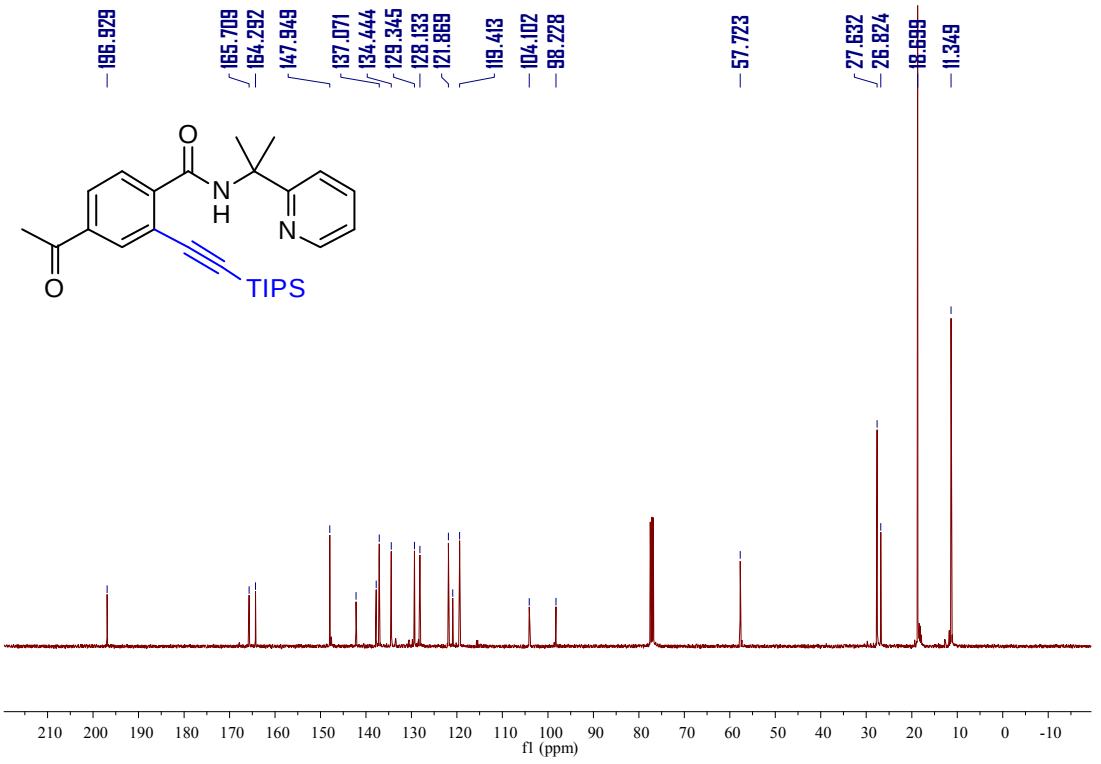
4ad


8.675
8.426
8.415
7.762
7.743
7.719
7.445
7.425
7.202
7.190
7.186
7.173
1.932
1.039
1.000
0.983
TIPS
O
N
H
N
NC
TIPS
0.98
0.98
3.01
1.03
1.00
6.05
42.13
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

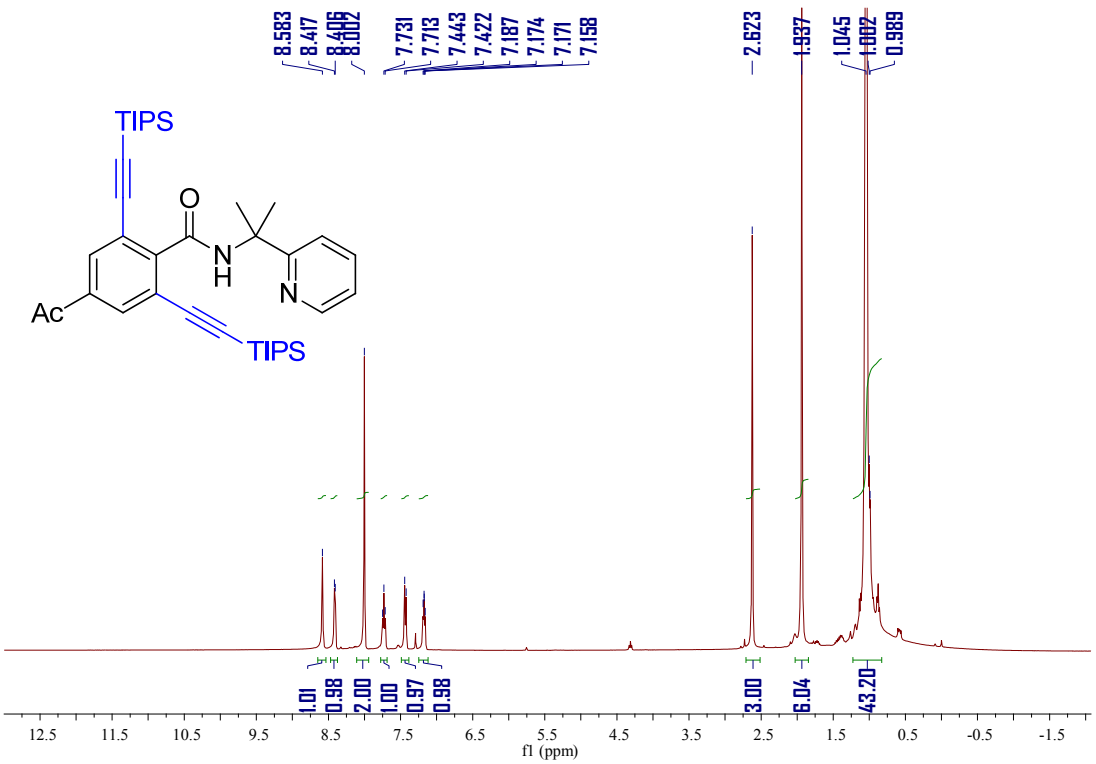

164.248
163.796
147.165
145.396
136.223
123.090
116.950
112.854
101.726
98.413
57.276
27.355
18.537
11.147
TIPS
O
N
H
N
NC
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

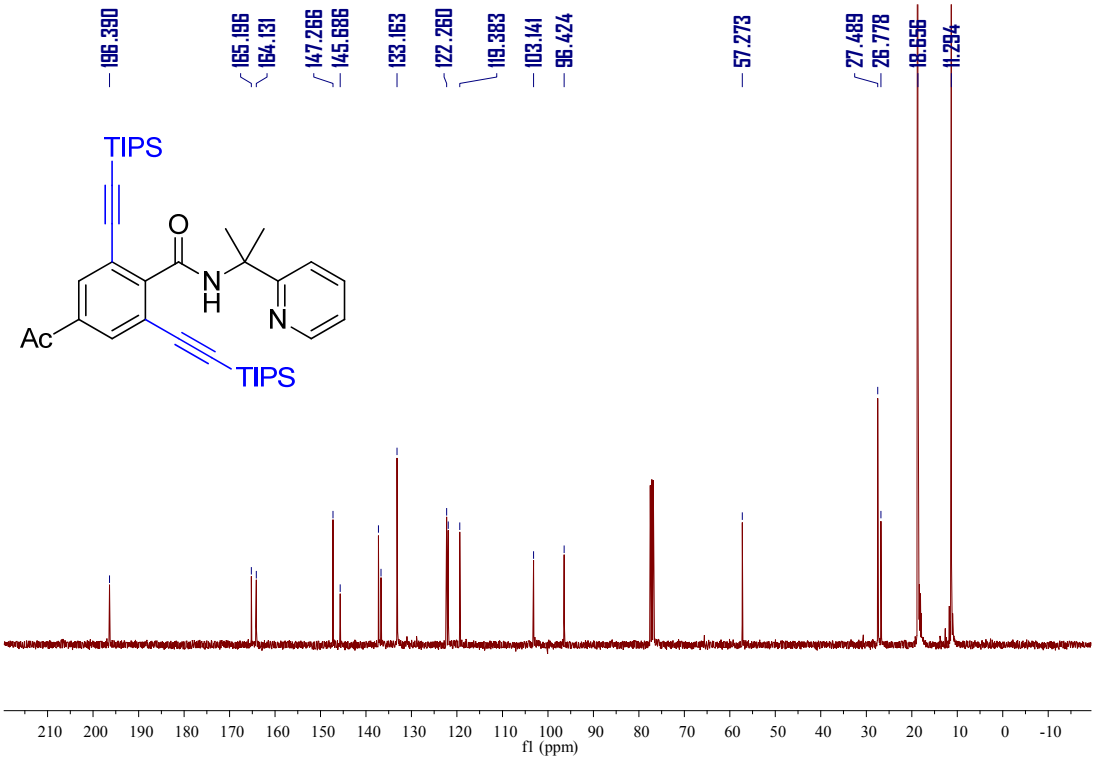
3ae


8.538
8.493
8.483
8.104
7.928
7.924
7.907
7.903
7.836
7.815
7.731
7.728
7.711
7.709
7.693
7.689
7.471
7.451
7.191
7.179
7.175
7.161
2.626
1.886
1.129
1.067
1.033
1.014
O
N
H
N
O
TIPS
0.97
0.98
0.95
1.01
0.99
1.04
1.00
1.06
3.03
6.24
21.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

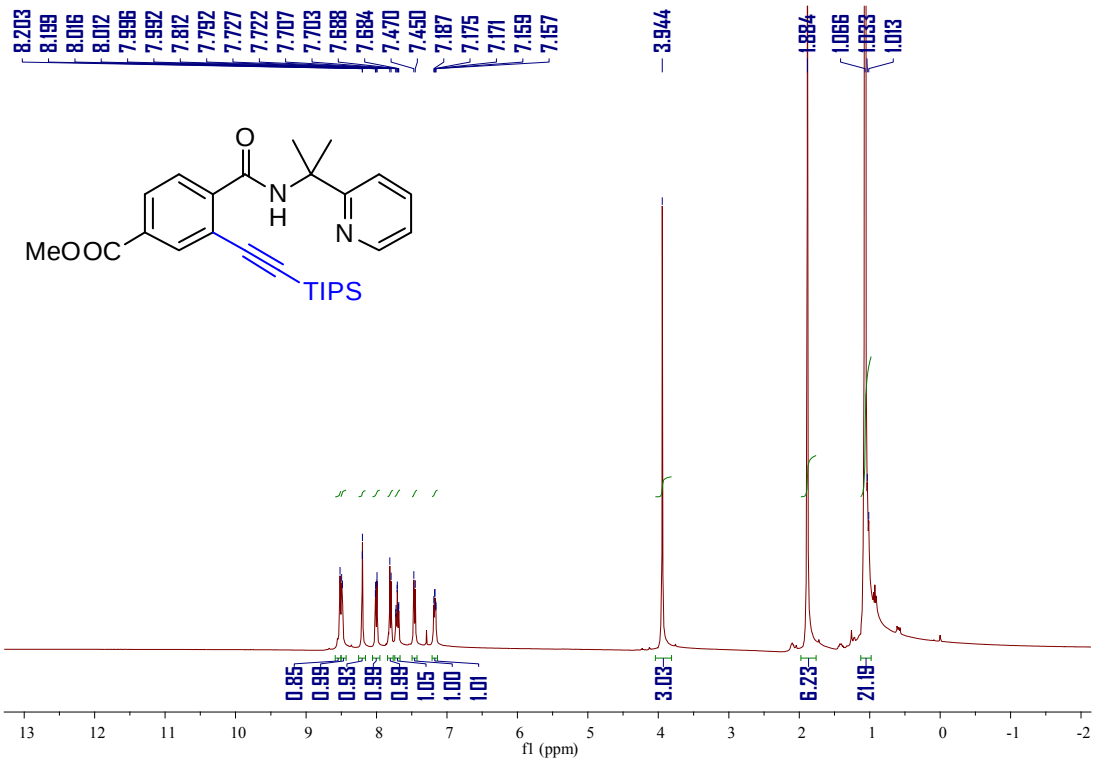

196.929
165.709
164.292
147.949
137.071
134.444
129.345
128.133
121.869
119.413
104.102
98.228
57.723
27.632
26.824
18.699
11.349
O
N
H
N
O
TIPS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

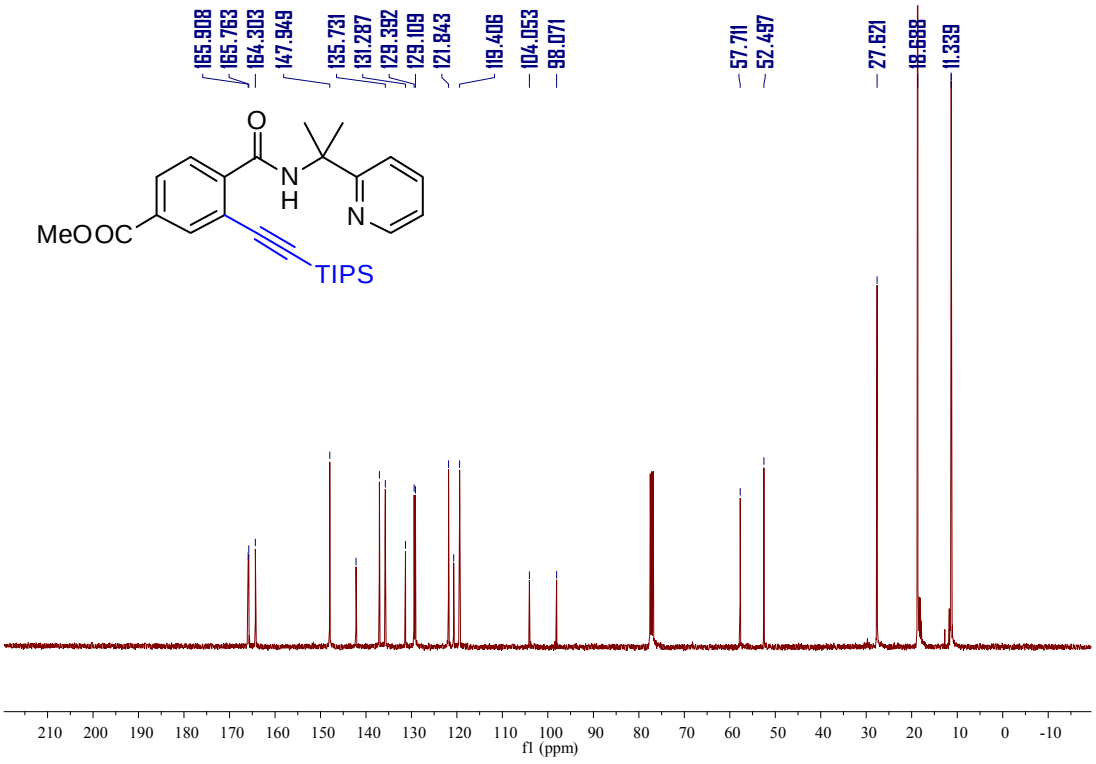
4ae


8.583
8.417
8.406
8.002
7.731
7.713
7.443
7.422
7.187
7.174
7.171
7.158
2.623
1.937
1.045
1.002
0.989
TIPS
O
N
H
N
Ac
TIPS
1.01
0.98
2.00
1.00
0.97
0.98
3.00
6.04
43.20
f1 (ppm)

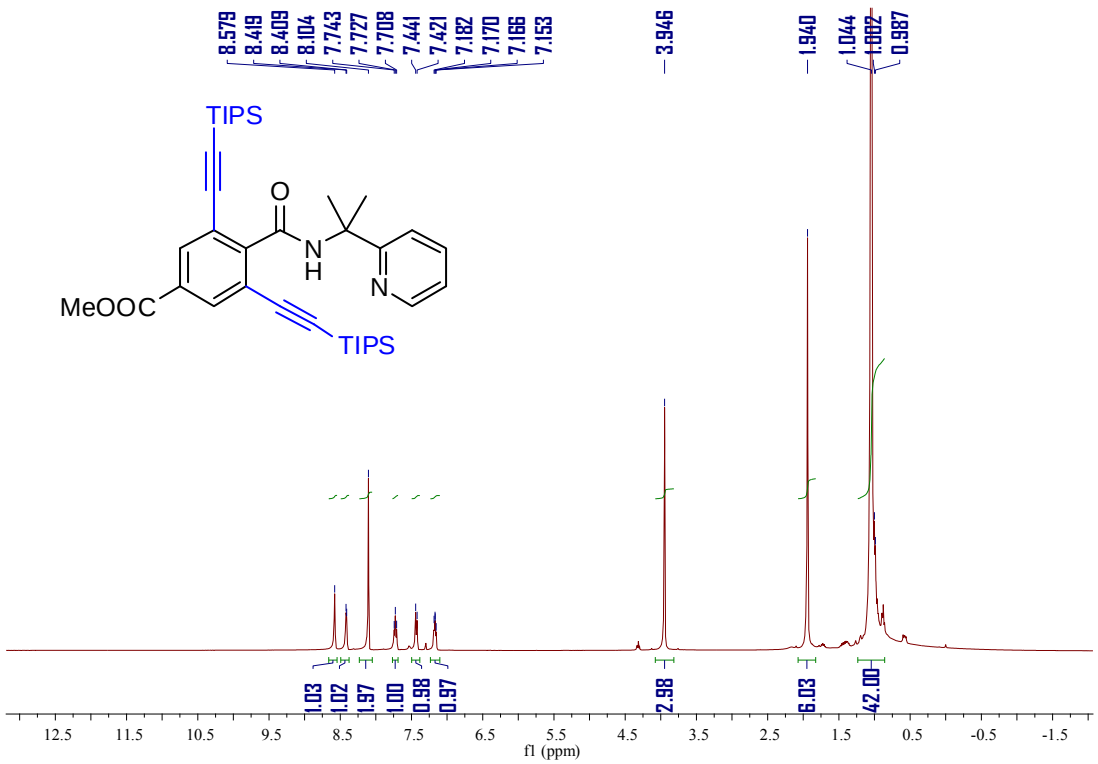

196.390
165.196
164.131
147.266
145.686
133.163
122.260
119.383
103.141
96.424
57.273
27.489
26.778
18.656
11.294
TIPS
O
N
H
N
Ac
TIPS
f1 (ppm)

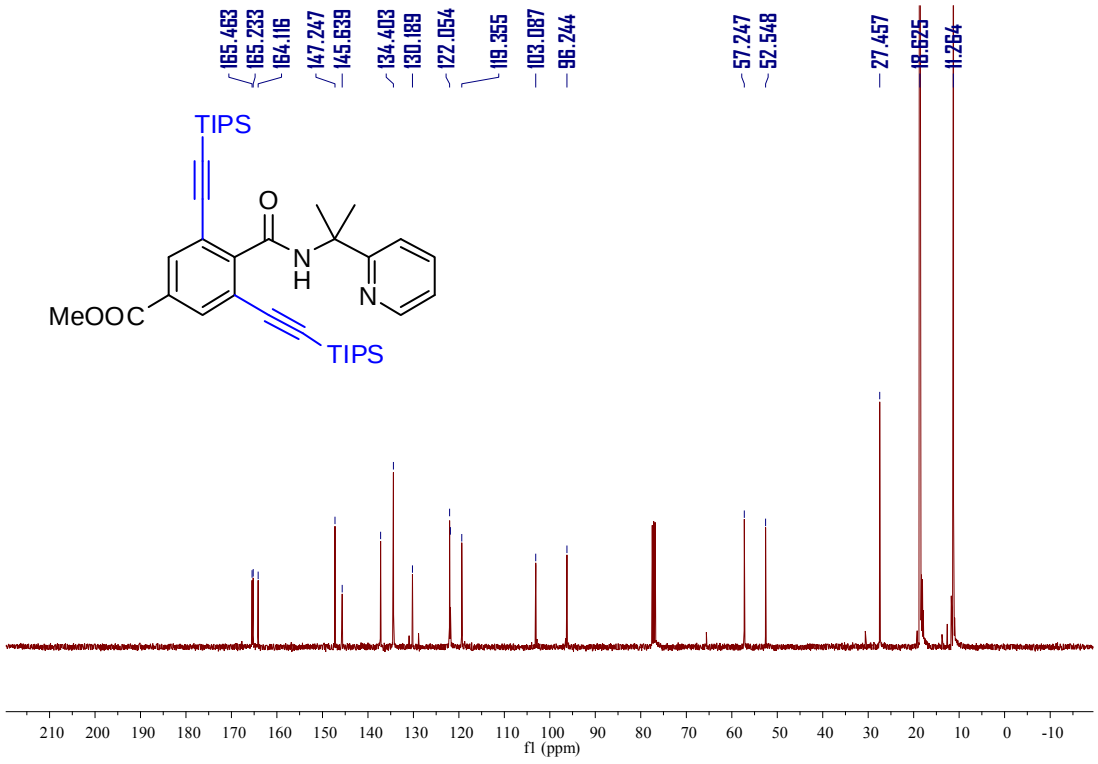
3af


8.203
8.199
8.016
8.012
7.996
7.992
7.812
7.792
7.727
7.722
7.707
7.703
7.688
7.684
7.470
7.450
7.187
7.175
7.171
7.159
7.157
3.944
1.884
1.066
1.033
1.013
O
N
H
N
MeOOC
TIPS
0.85
0.99
0.93
0.99
0.99
1.05
1.00
1.01
3.03
6.23
21.19
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

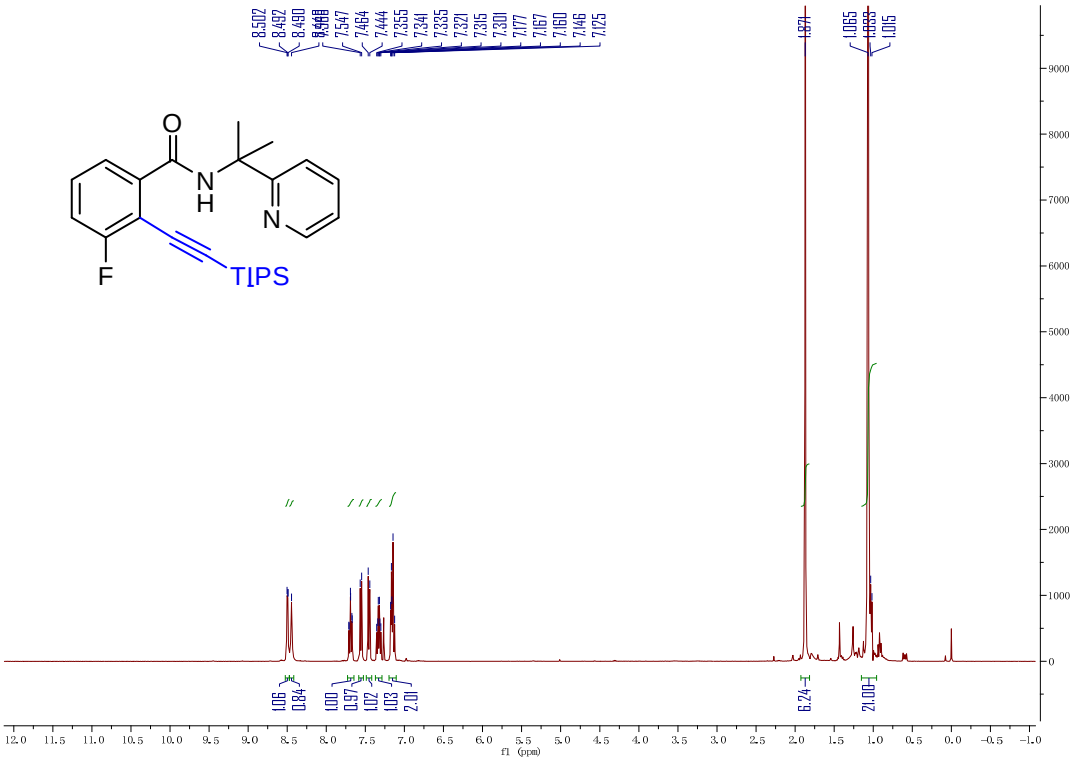

165.908
165.763
164.303
147.949
135.731
131.287
129.382
129.109
121.843
119.406
104.053
98.071
57.711
52.497
27.621
18.688
11.339
O
N
H
N
MeOOC
TIPS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

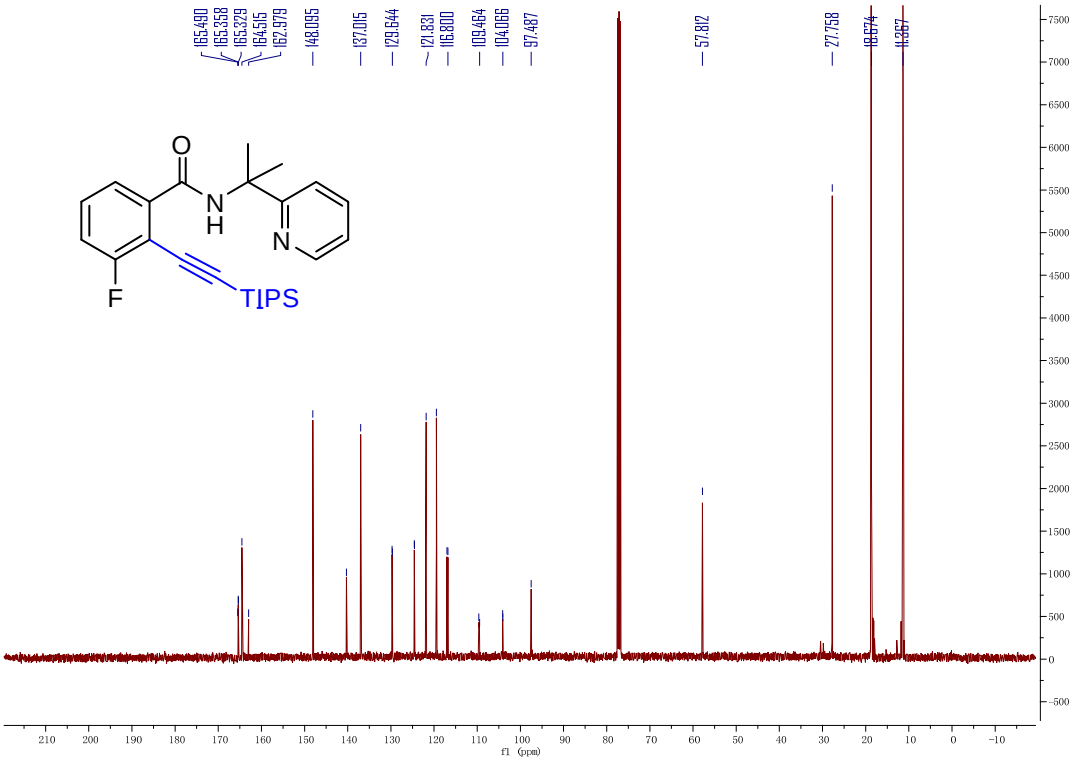
4af

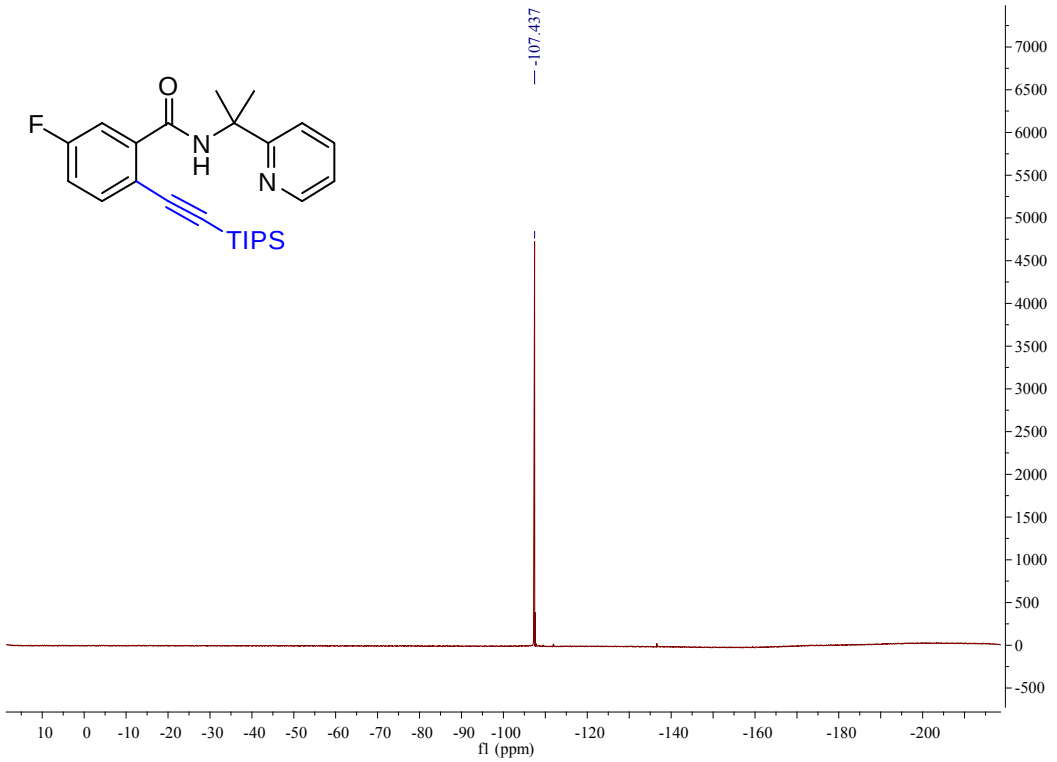

8.579
8.419
8.409
8.104
7.743
7.727
7.708
7.441
7.421
7.182
7.170
7.166
7.153
3.946
1.940
1.044
1.002
0.987
TIPS
O
N
H
N
MeOOC
TIPS
1.03
1.02
1.97
1.00
0.98
0.97
2.98
6.03
42.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)


165.463
165.233
164.116
147.247
145.639
134.403
130.189
122.054
119.355
103.087
96.244
57.247
52.548
27.457
18.625
11.264
TIPS
O
N
H
N
MeOOC
TIPS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

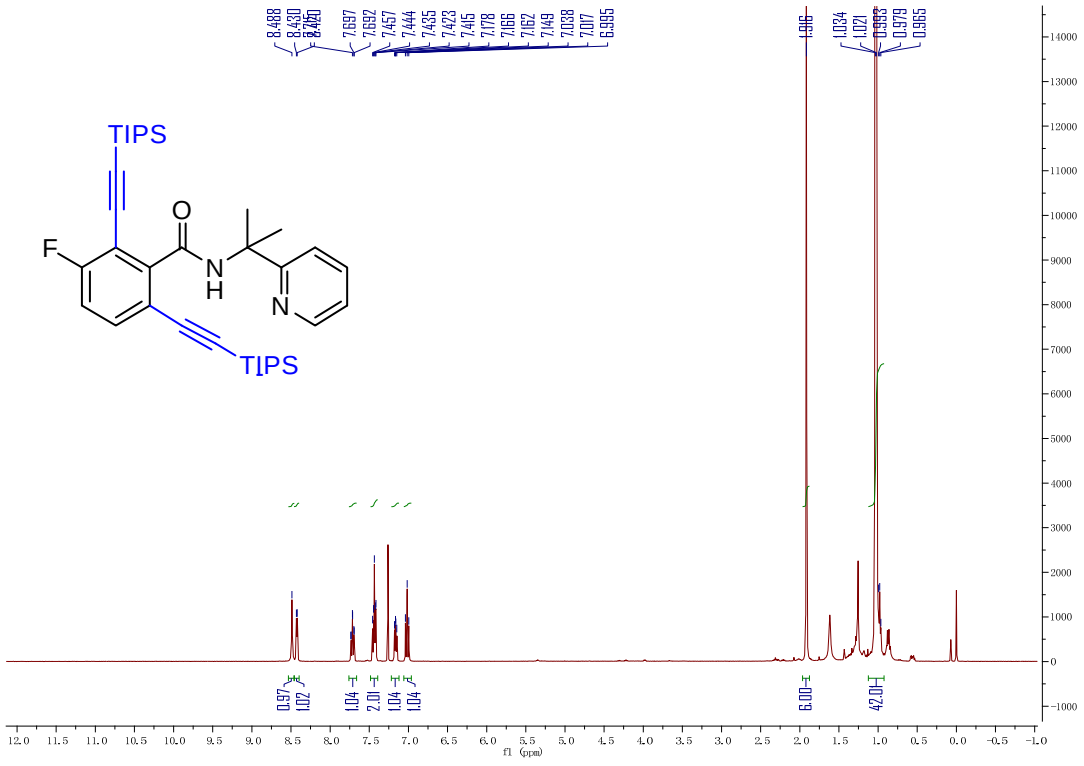
3ag

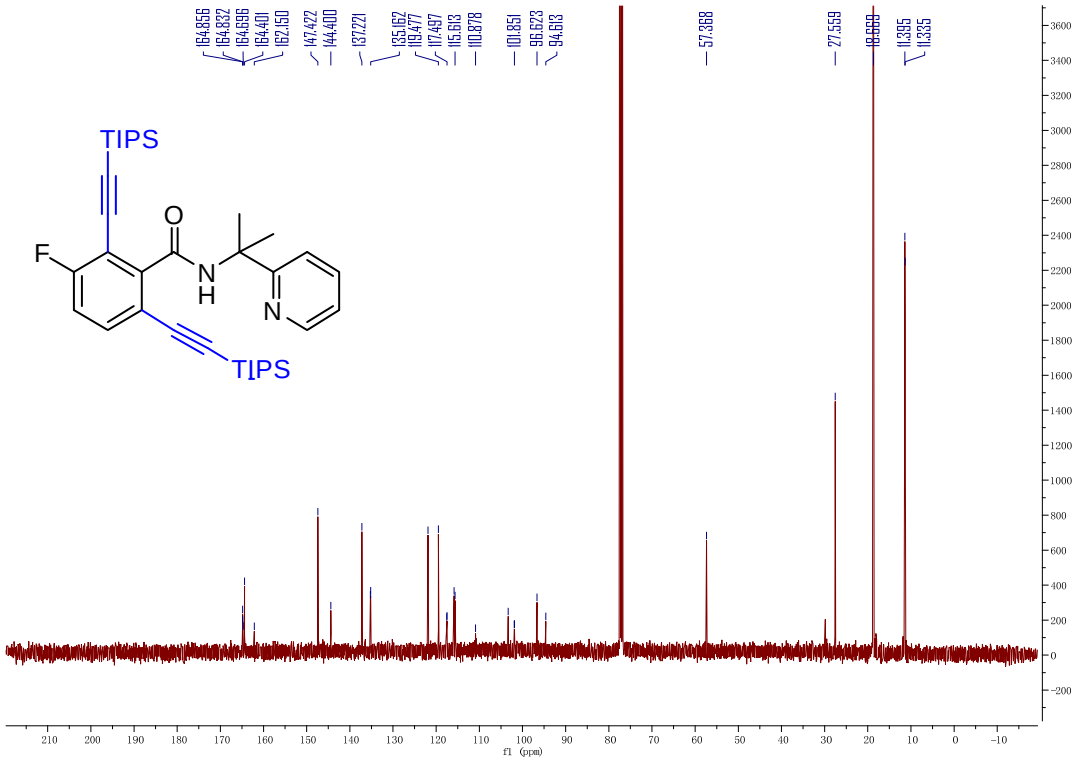

8.502
8.492
8.490
7.547
7.464
7.444
7.355
7.341
7.335
7.321
7.315
7.301
7.177
7.167
7.160
7.146
7.125
1.971
1.065
1.033
1.015
O
N
H
N
F
TIPS
1.06
0.84
1.00
0.97
1.02
1.03
2.01
6.24
21.00
f1 (ppm)

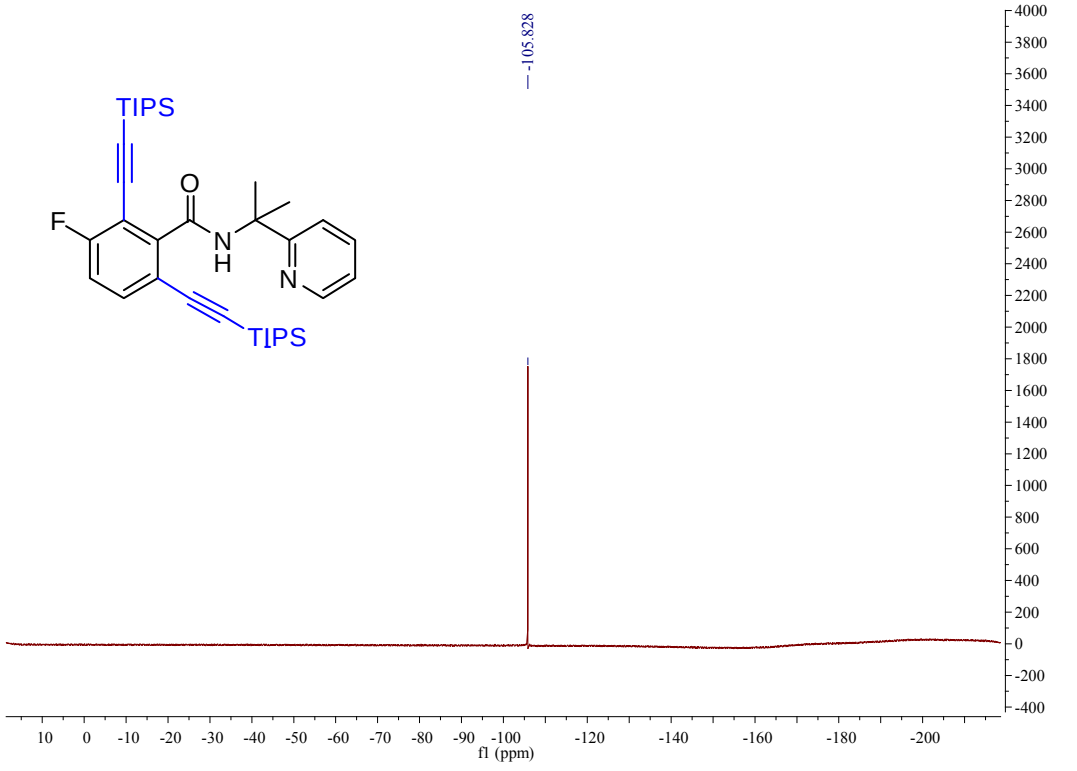

165.490
165.358
165.229
164.515
162.979
148.095
137.015
129.644
121.831
116.800
109.464
104.066
97.487
57.812
27.758
18.674
14.287
O
N
H
N
F
TIPS
f1 (ppm)


F
O
N
H
N
TIPS
-107.437
f1 (ppm)

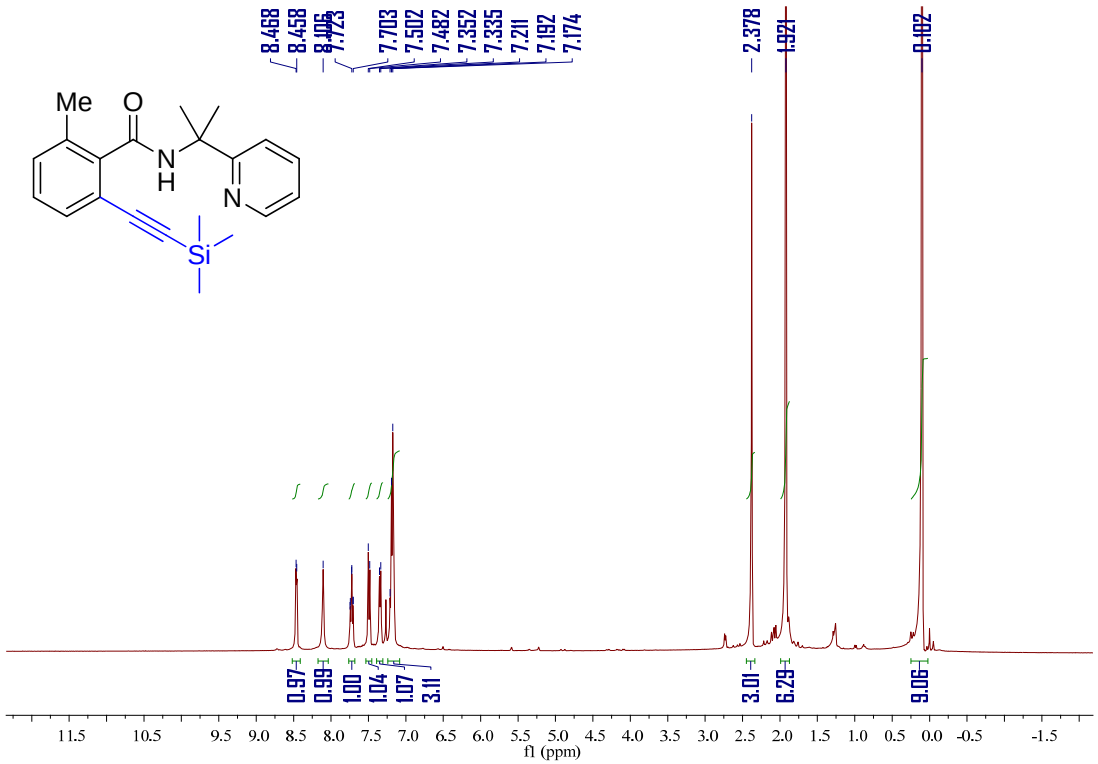
4ag

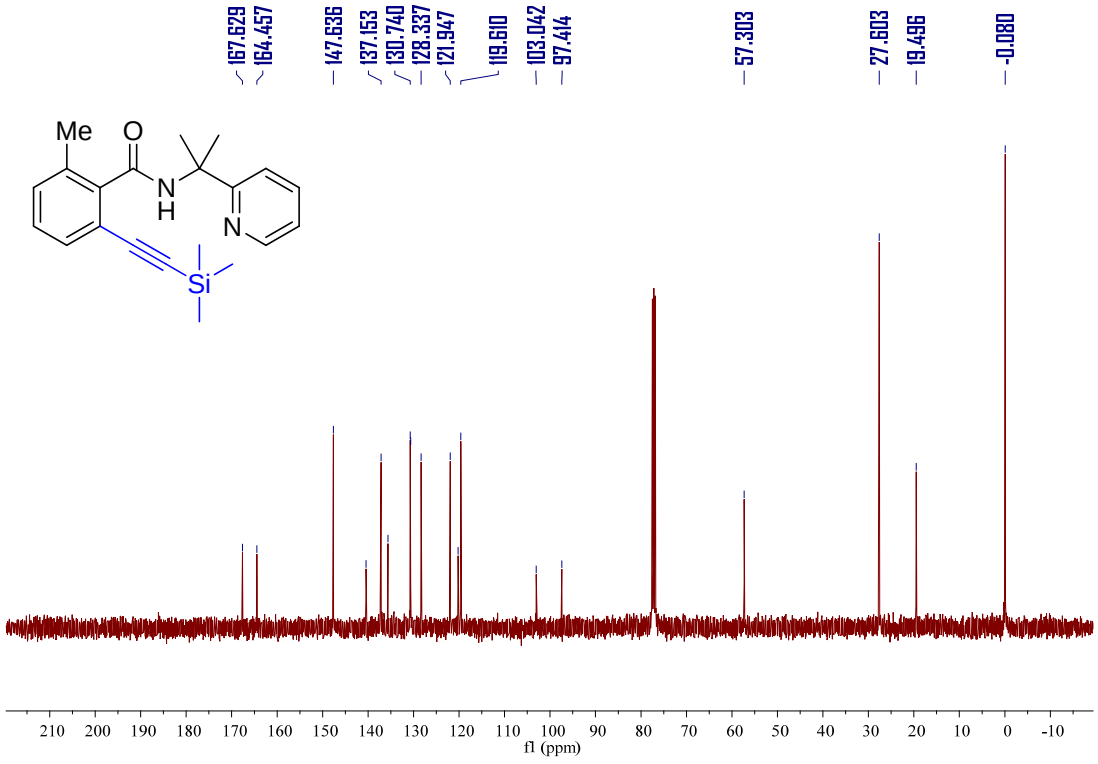

TIPS
F
O
N
H
N
TIPS
8.488
8.430
7.697
7.692
7.457
7.444
7.435
7.423
7.415
7.178
7.166
7.162
7.149
7.038
7.017
6.995
1.946
1.034
1.021
0.979
0.965
0.97
1.02
1.04
2.01
1.04
1.04
6.00
42.01
f1 (ppm)


164.856
164.832
164.696
164.401
162.150
147.422
144.400
137.221
135.162
119.477
117.497
115.613
110.878
101.851
96.623
94.613
57.388
27.559
18.668
11.395
11.335
TIPS
TIPS
F
O
N
H
N
f1 (ppm)

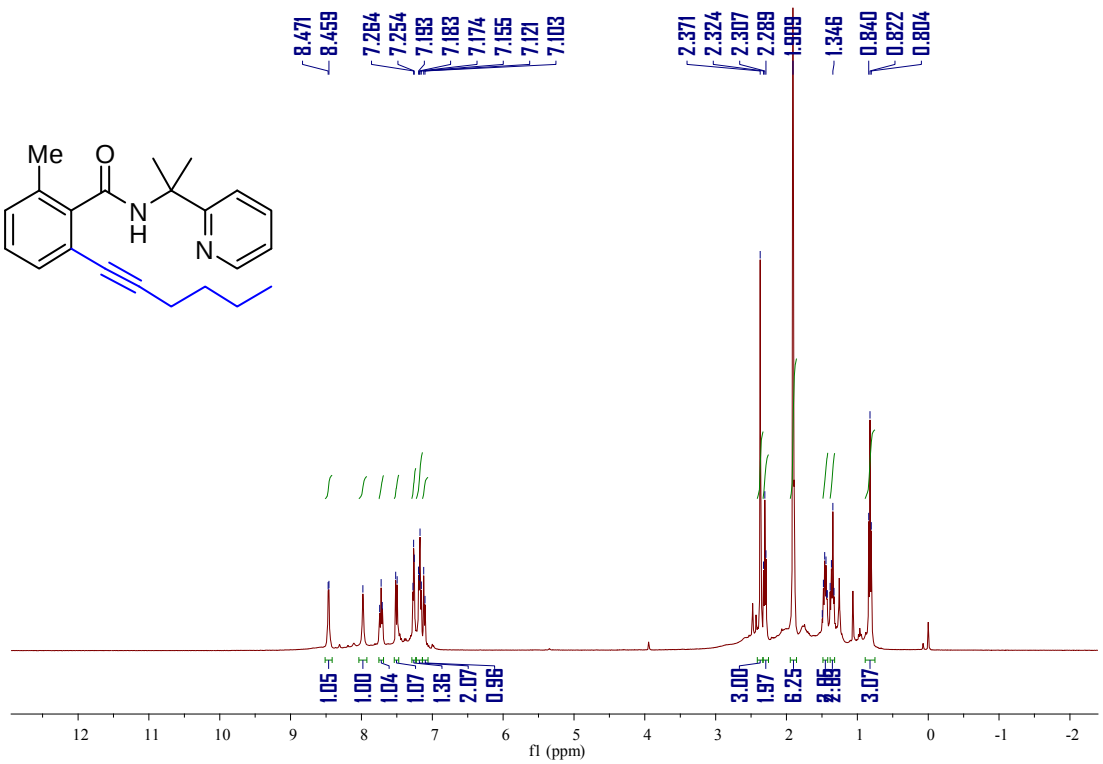

-105.828
TIPS
TIPS
F
O
N
H
N
f1 (ppm)

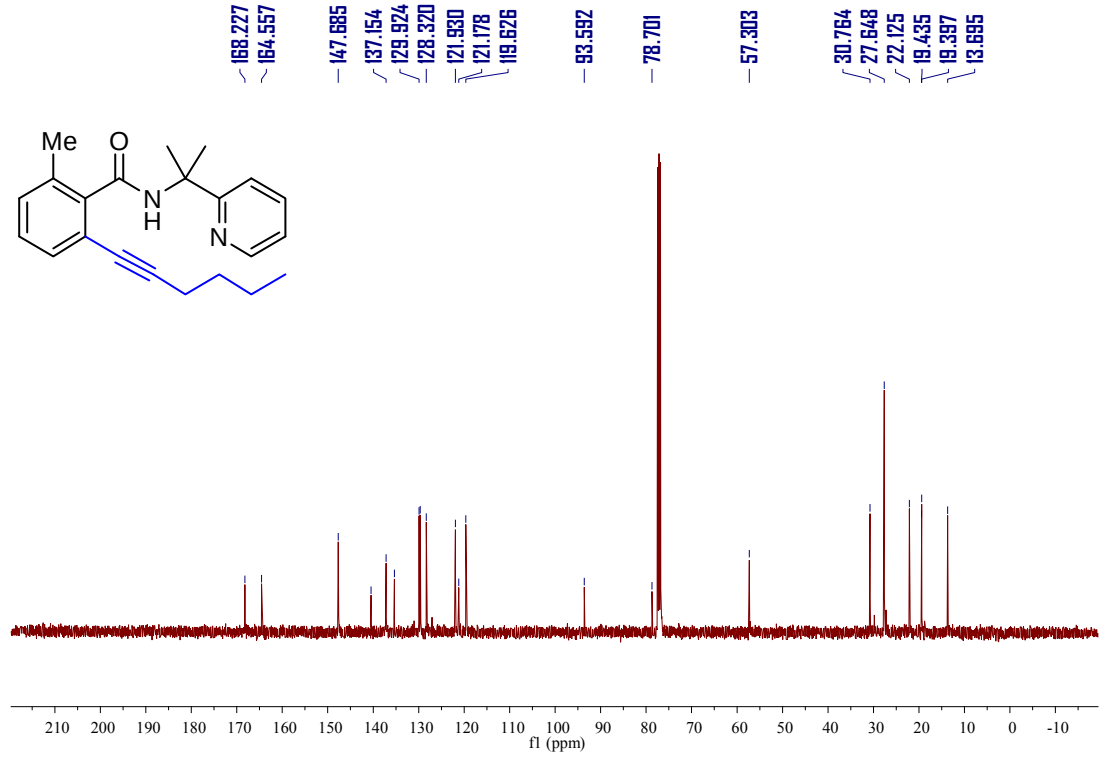
5a


8.468
8.458
7.723
7.703
7.502
7.482
7.352
7.335
7.211
7.192
7.174
2.378
1.921
8.182
Me
O
N
H
N
Si
0.97
0.99
1.00
1.04
1.07
3.11
3.01
6.29
9.06
fl (ppm)

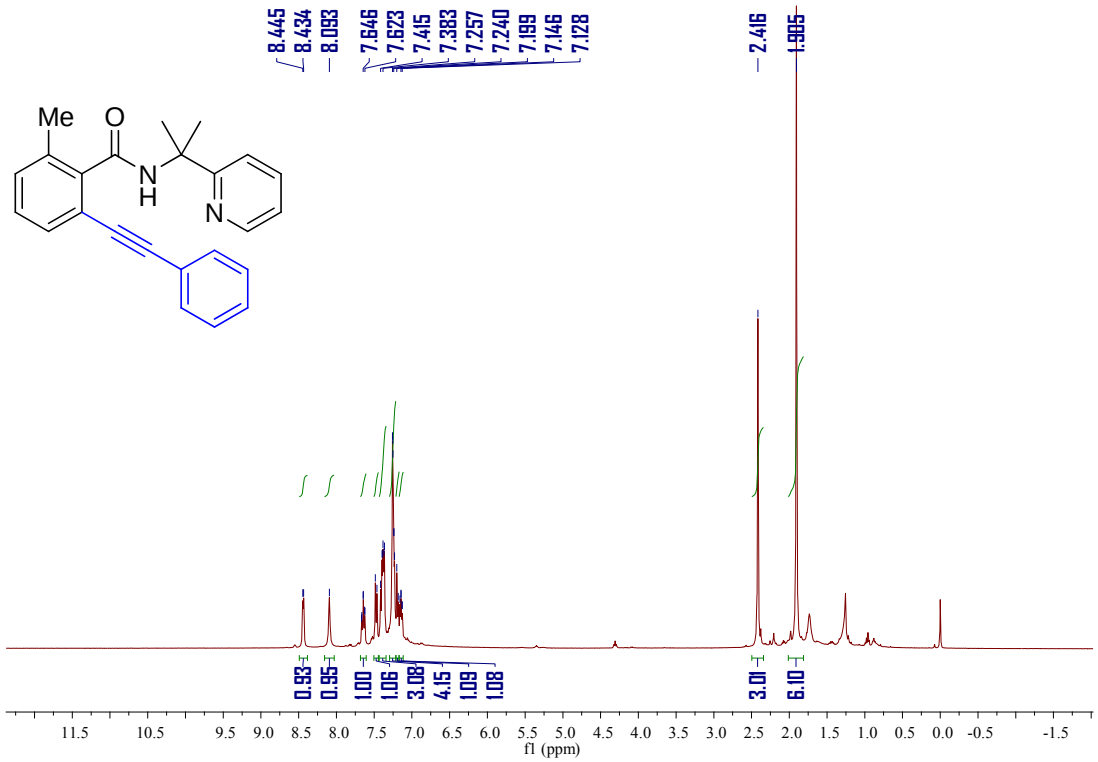

167.629
164.457
147.636
137.153
130.740
128.337
121.947
119.610
103.042
97.414
57.303
27.603
19.496
-0.080
Me
O
N
H
N
Si
fl (ppm)

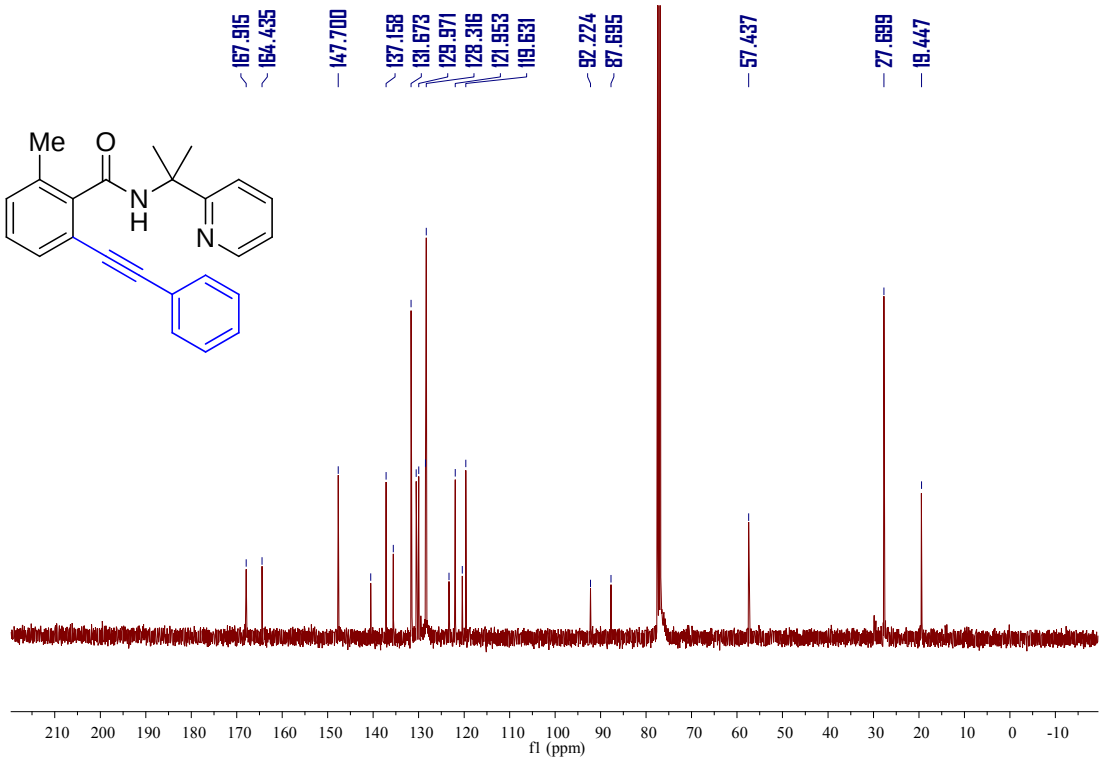
5b


8.471
8.459
7.264
7.254
7.193
7.183
7.174
7.155
7.121
7.103
2.371
2.324
2.307
2.289
1.988
1.346
0.840
0.822
0.804
Me
O
N
H
N
1.05
1.00
1.04
1.07
1.36
2.07
0.96
3.00
1.97
6.25
3.07
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

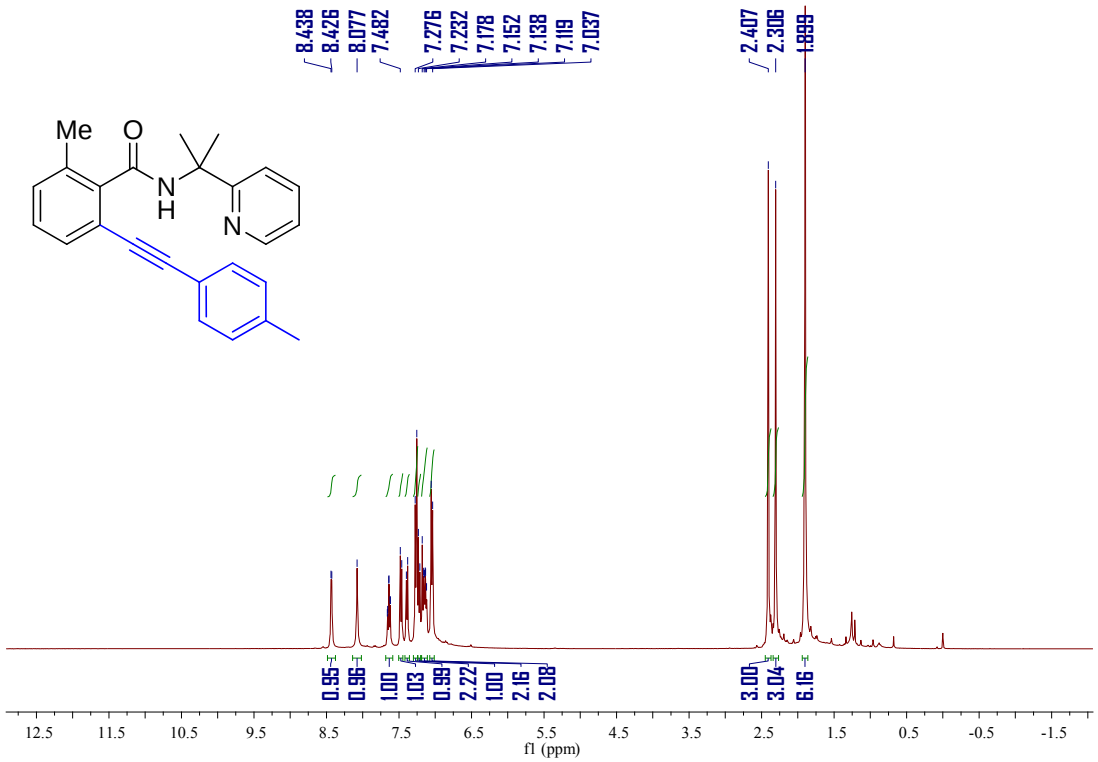

168.227
164.557
147.685
137.154
129.924
128.320
121.930
121.178
119.626
93.592
78.701
57.303
30.764
27.648
22.125
19.435
19.397
13.695
Me
O
N
H
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

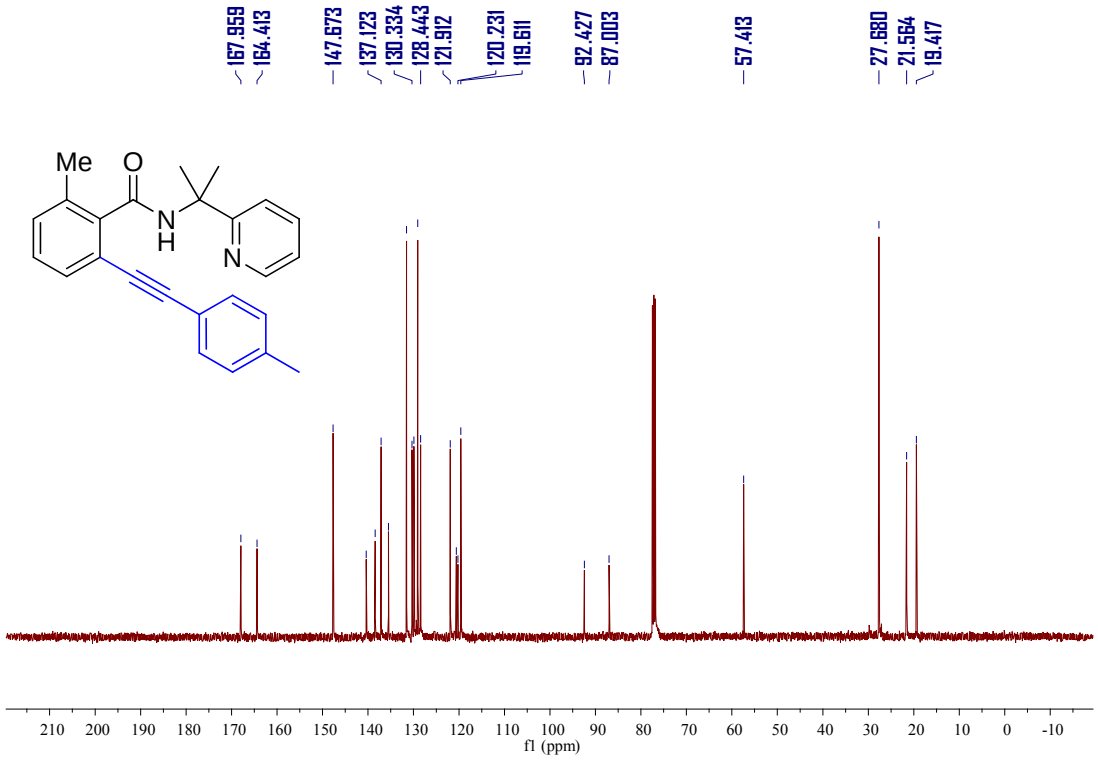
5c


8.445
8.434
8.093
7.646
7.623
7.415
7.383
7.257
7.240
7.199
7.146
7.128
2.416
1.985
Me
O
N
H
N
0.93
0.95
1.00
1.06
3.08
4.15
1.09
1.08
3.01
6.10
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)

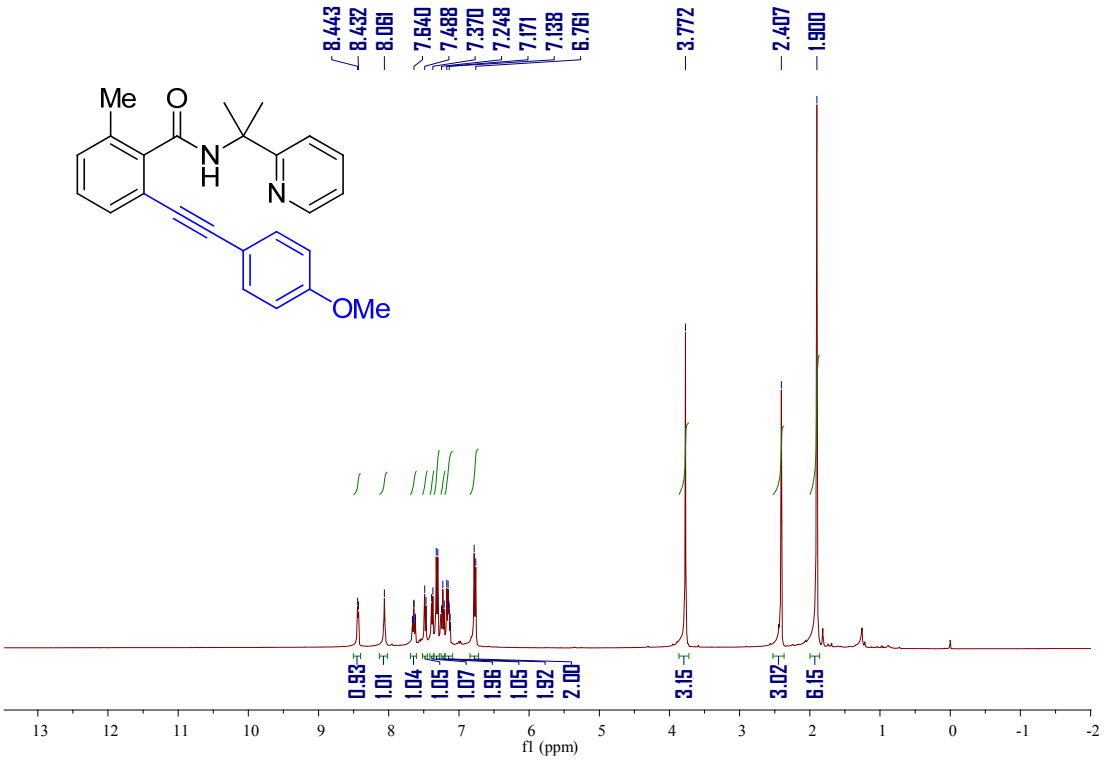

167.915
164.435
147.700
137.158
131.673
129.971
128.316
121.953
119.631
92.224
87.695
57.437
27.899
19.447
Me
O
N
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

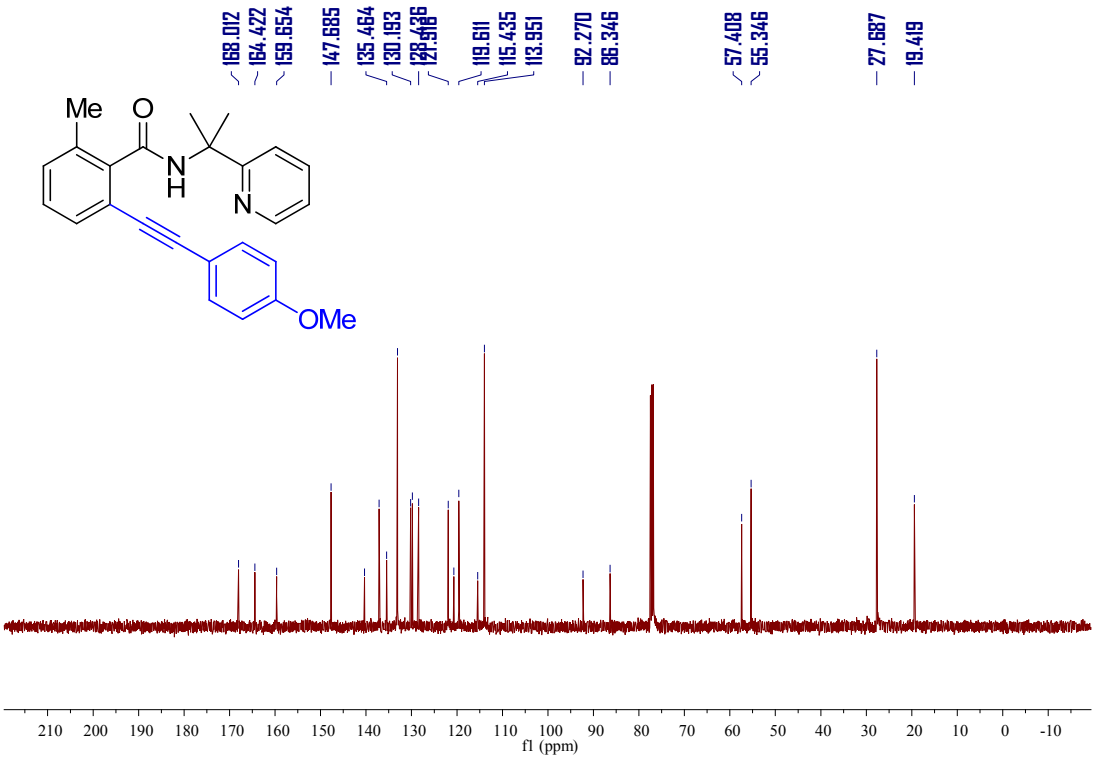
5d


8.438
8.426
8.077
7.482
7.276
7.232
7.178
7.152
7.138
7.119
7.037
2.407
2.306
1.893
Me
O
N
H
N
0.95
0.96
1.00
1.03
0.99
2.22
1.00
2.16
2.08
3.00
3.04
6.16
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

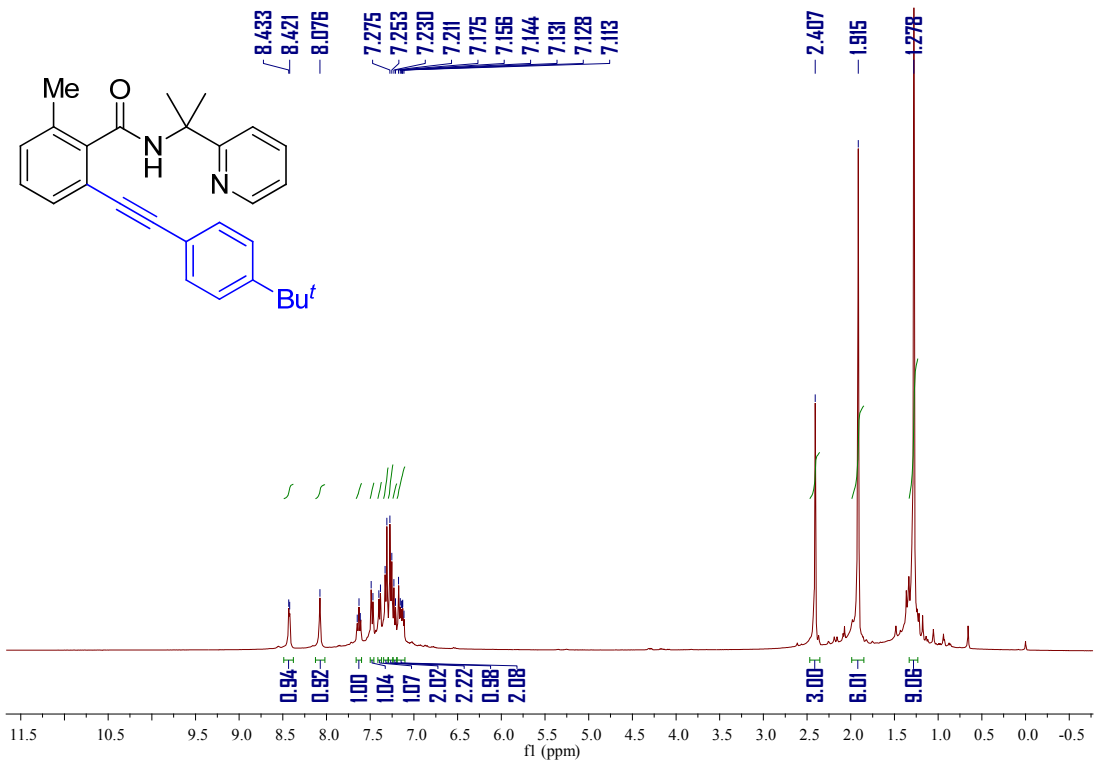

167.959
164.413
147.673
137.123
131.334
128.443
121.912
120.231
119.611
92.427
87.003
57.413
27.680
21.564
19.417
Me
O
N
H
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

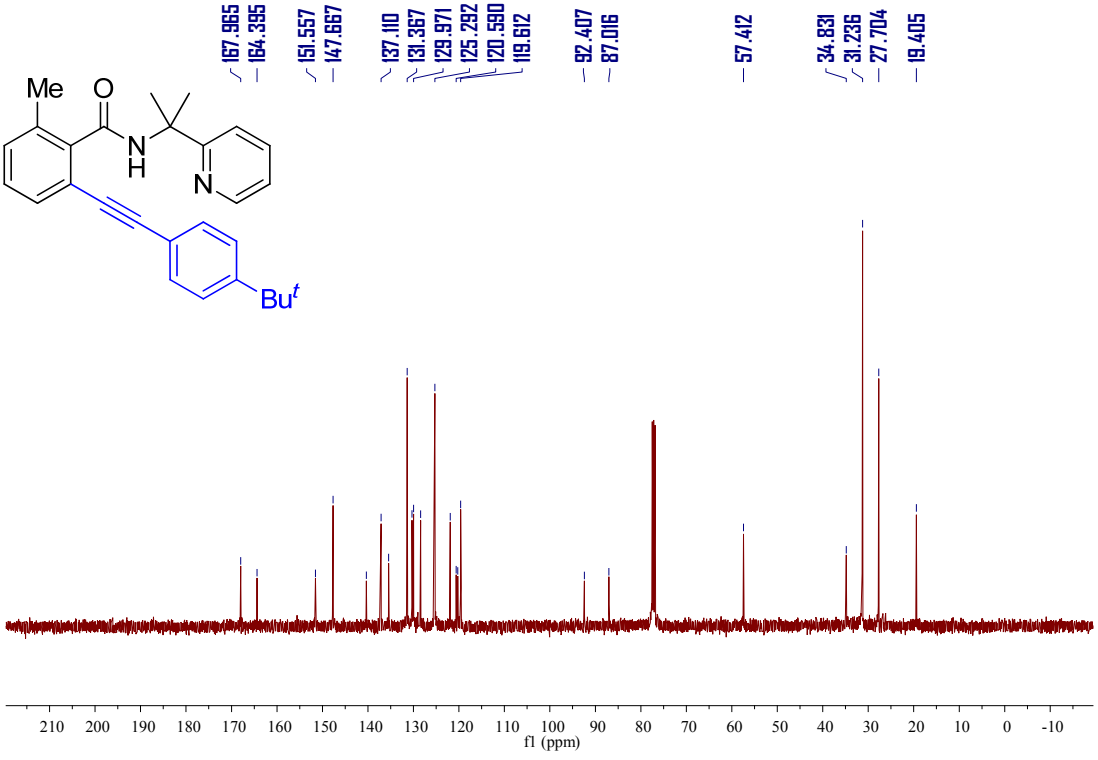
5e


8.443
8.432
8.061
7.640
7.488
7.370
7.248
7.171
7.138
6.761
3.772
2.407
1.900
Me
O
N
H
N
OMe
0.93
1.01
1.04
1.05
1.07
1.96
1.05
1.92
2.00
3.15
3.02
6.15
f1 (ppm)

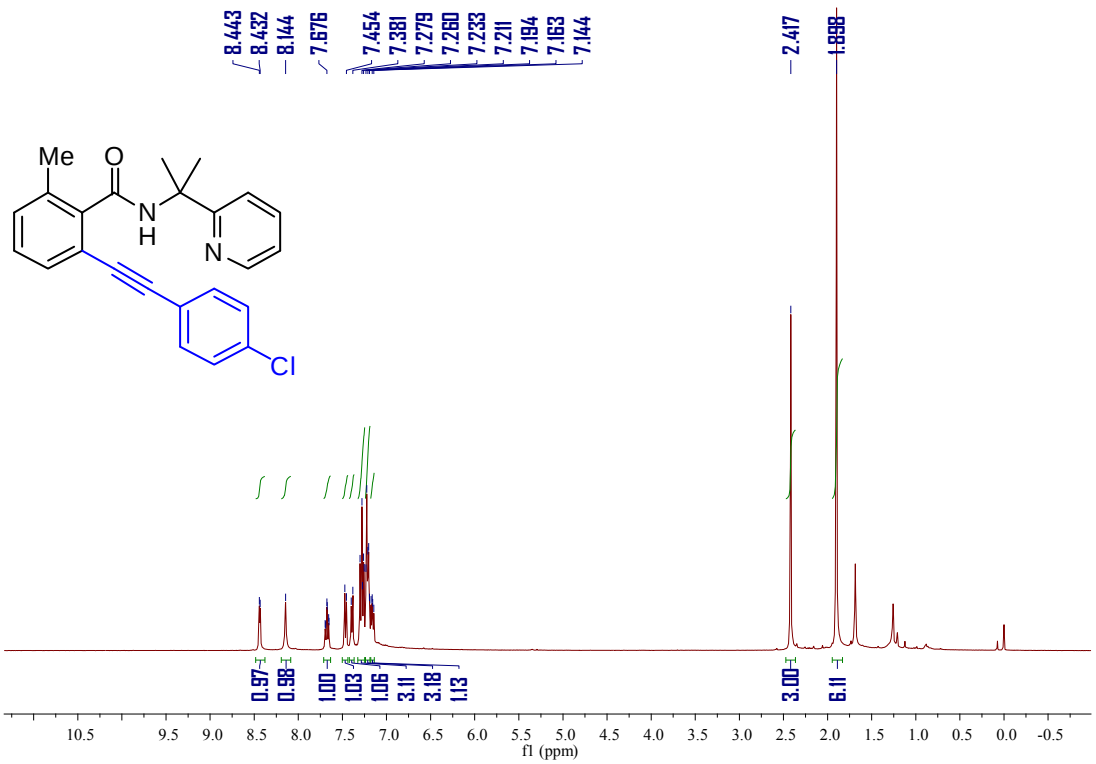

168.012
164.422
159.654
147.685
135.464
130.193
128.436
121.918
119.611
115.435
113.951
92.270
86.346
57.408
55.346
27.687
19.419
Me
O
N
H
N
OMe
f1 (ppm)

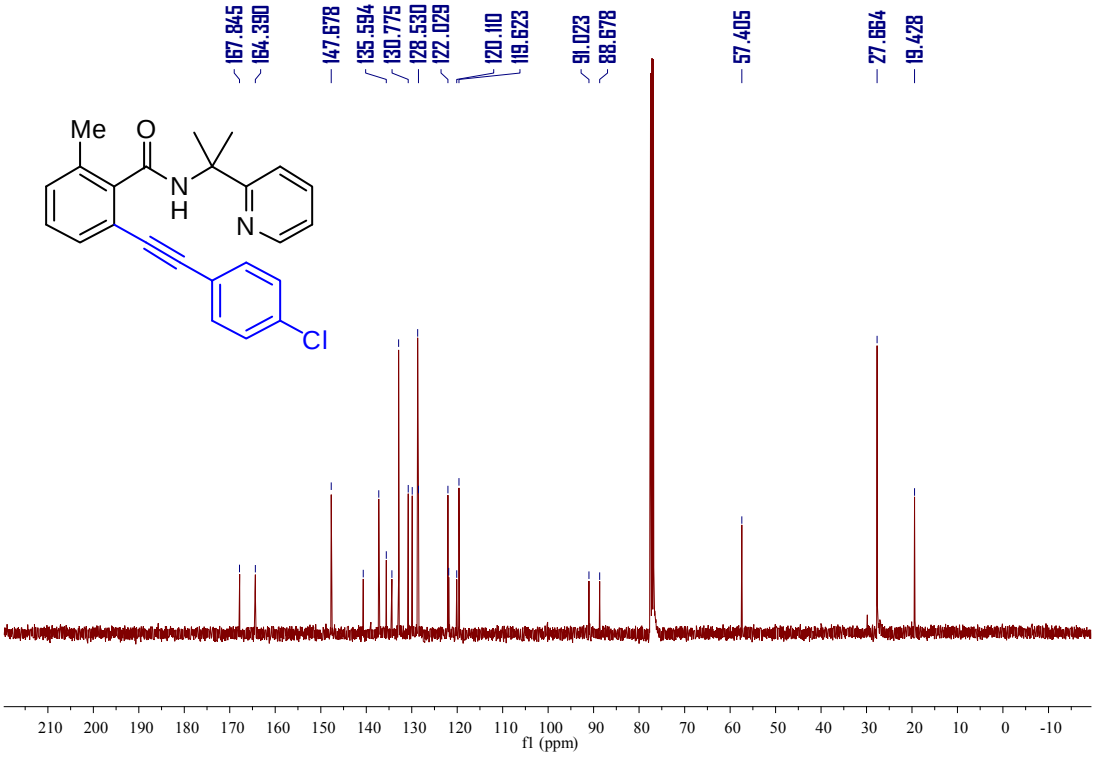
5f


8.433
8.421
8.076
7.275
7.253
7.230
7.211
7.175
7.156
7.144
7.131
7.128
7.113
2.407
1.915
1.278
Me
O
N
H
N
Bu^t
0.94
0.92
1.00
1.04
1.07
2.02
2.22
0.98
2.08
3.00
6.01
9.06
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

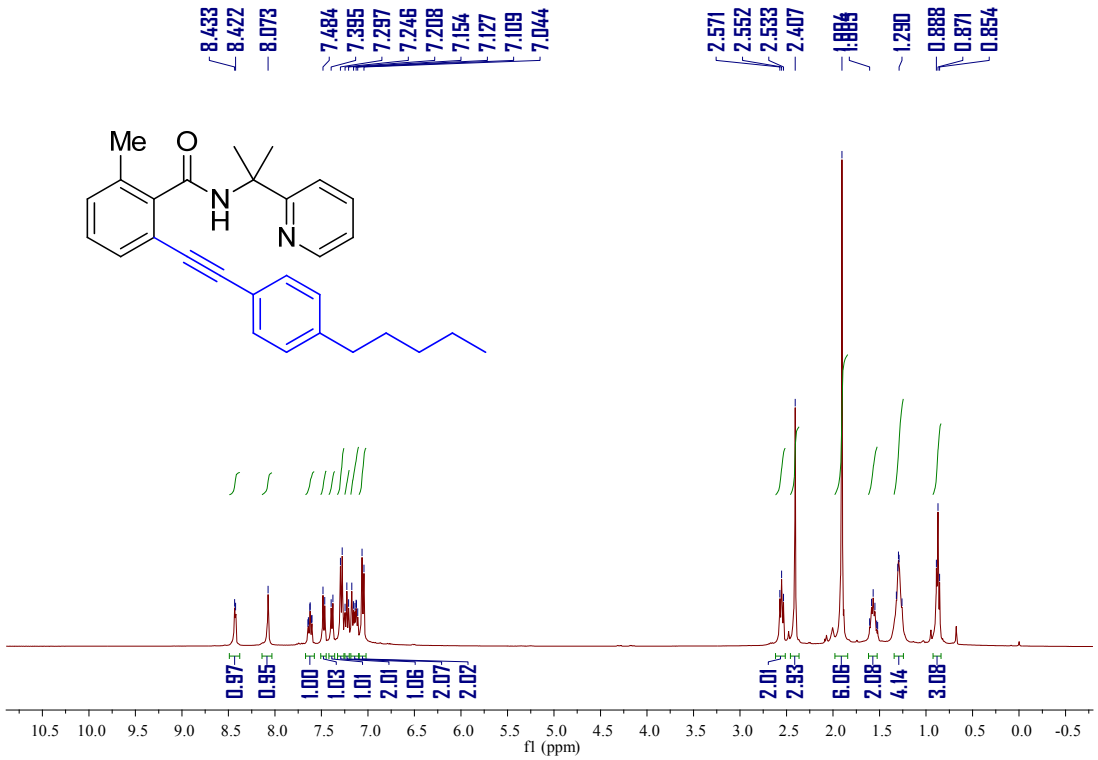

167.965
164.395
151.557
147.667
137.110
131.367
129.971
125.282
120.590
119.612
92.407
87.016
57.412
34.831
31.236
27.704
19.405
Me
O
N
H
N
Bu^t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

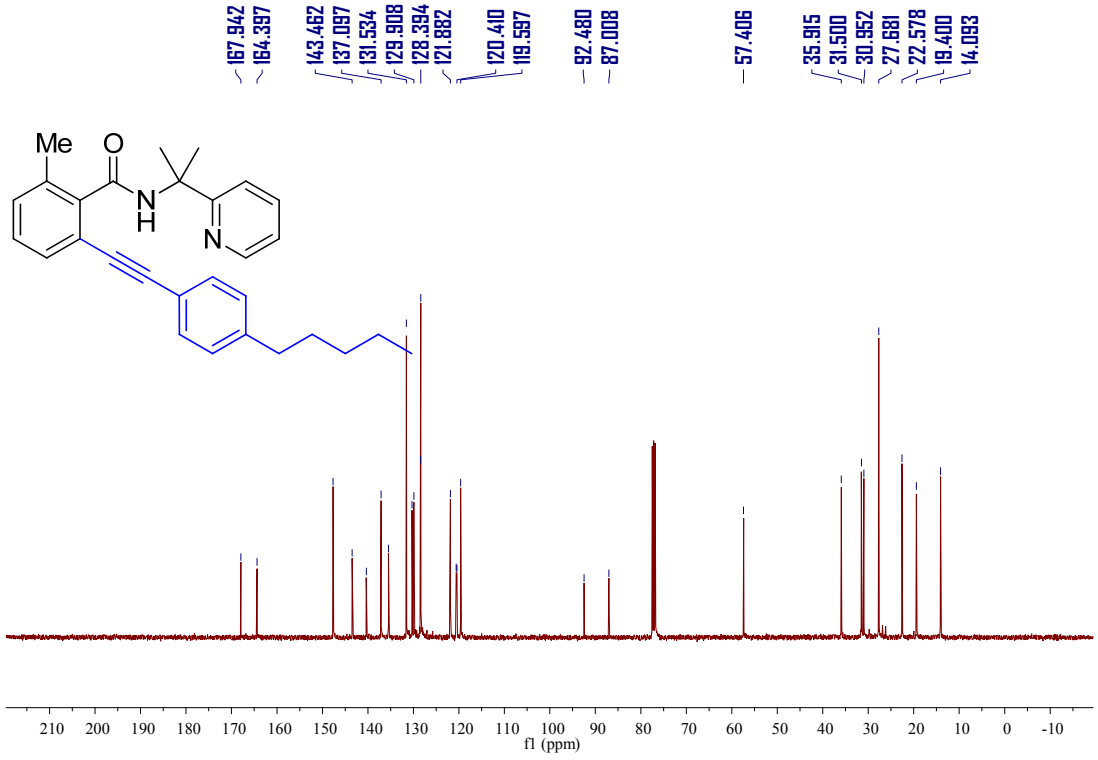
5g


8.443
8.432
8.144
7.676
7.454
7.381
7.279
7.260
7.233
7.211
7.194
7.163
7.144
2.417
1.888
Me
O
N
H
N
Cl
0.97
0.98
1.00
1.03
1.06
3.11
3.18
1.13
3.00
6.11
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

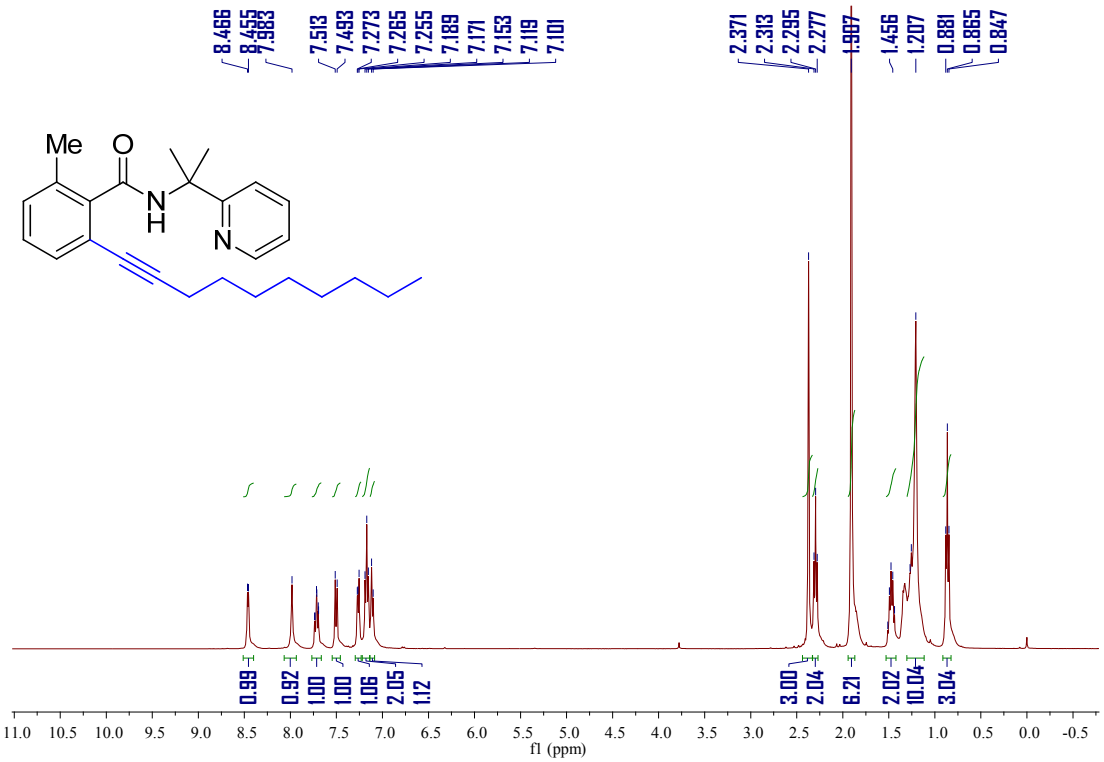

167.845
164.390
147.678
135.594
130.775
128.530
122.029
120.110
119.623
91.023
88.678
57.405
27.664
19.428
Me
O
N
H
N
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

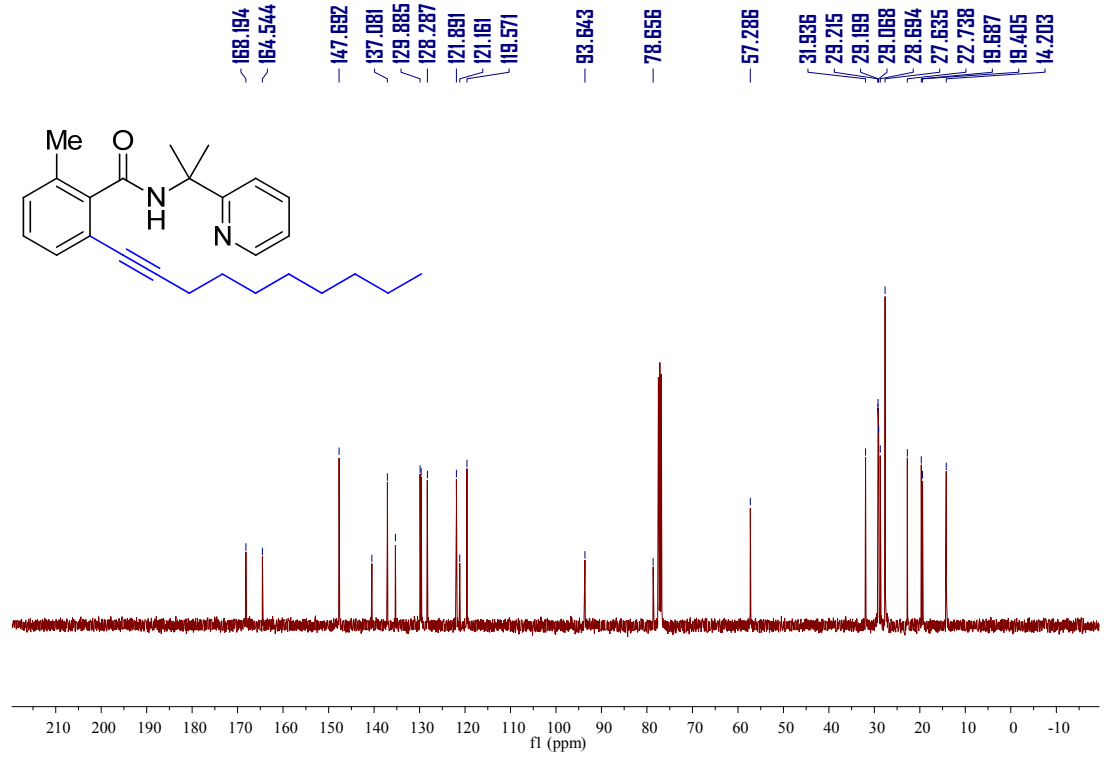
5h


8.433
8.422
8.073
7.484
7.395
7.297
7.246
7.208
7.154
7.127
7.109
7.044
2.571
2.552
2.533
2.407
1.290
0.888
0.871
0.854
Me
O
N
H
N
0.97
0.95
1.00
1.03
1.01
2.01
1.06
2.07
2.02
2.01
2.93
6.06
2.08
4.14
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.942
164.397
143.462
137.097
131.534
129.908
128.394
121.882
120.410
119.597
92.480
87.008
57.406
35.915
31.500
30.952
27.681
22.578
19.400
14.093
Me
O
N
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5i


8.466
8.455
7.983
7.513
7.493
7.273
7.265
7.255
7.189
7.171
7.153
7.119
7.101
2.371
2.313
2.295
2.277
1.987
1.456
1.207
0.881
0.865
0.847
Me
O
N
H
N
0.99
0.92
1.00
1.00
1.06
2.05
1.12
3.00
2.04
6.21
2.02
10.04
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


168.194
164.544
147.692
137.081
129.885
128.287
121.891
121.161
119.571
93.643
78.656
57.286
31.936
29.215
29.199
29.068
28.694
27.635
22.738
19.687
19.405
14.203
Me
O
N
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)