Electronic Supplementary Material (ESI) for ChemComm.


*Supporting Information*

# Ru(II)-Catalyzed External Auxiliary Free Primary Amide Directed Inverse Sonogashira Reaction on (Hetero)Aryl-Amides

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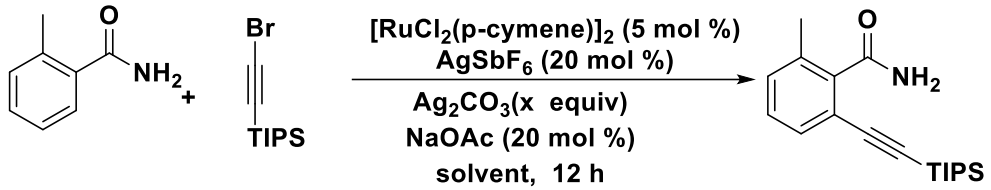
**General Consideration.** Unless otherwise noted, all reagents were purchased from a commercial supplier and used without further purification. All the benzamides were prepared by following the reported procedure in literature,[1]and TIPS-protocted bromoacetylene were purchased from Sigma Aldrich and Alfa Aeser. All the reactions were run in sealed tubes, and the indicated temperature was that of an oil bath. 1,2-dichloroethane was dried prior to use. $^{1}$H NMR spectra were recorded at 400 MHz and $^{13}$C{$^{1}$H} NMR spectra were recorded at 100 MHz, $CDCl_3$ and DMSO-$d_6$ were used as a solvent. Chemical shifts are reported in (δ) ppm referenced to $CDCl_3$ (δ 7.26), DMSO-$d_6$ (δ 2.50) for $^{1}$H NMR and $CDCl_3$ (δ 77.0), DMSO-$d_6$ (δ 39.5) for $^{13}$C NMR. The following abbreviations were used to explain multiplicities: (s, singlet; d, doublet; t, triplet; q, quartet; m, multiple, br, broad singlet), coupling constant (Hertz). Infrared spectra were recorded by FT-IR apparatus. High-resolution mass spectra (HRMS) spectra were obtained on ESI-TOF (electron spray ionization-time of flight) spectrometer and acetonitrile was used to dissolve the sample. Melting points were recorded with an automated melting point apparatus without correction. Column chromatography was performed on silica gel (100−200) mesh using ethyl acetate and hexanes as eluents in different ratios.

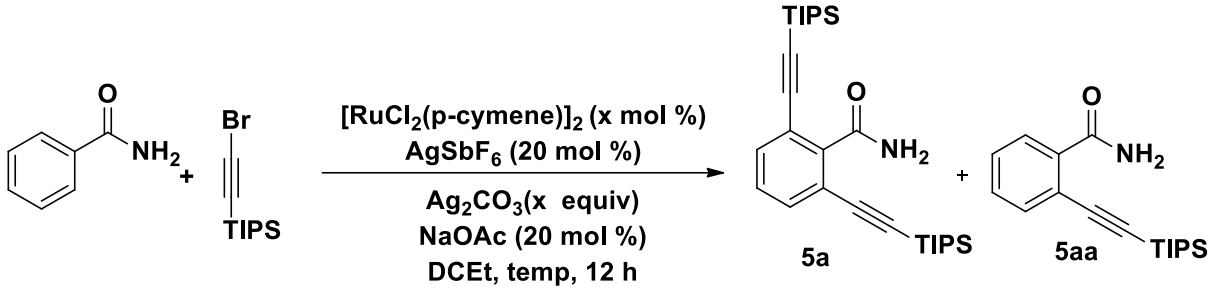
## 2. Table S1: Optimization table for mono-alkynylated arylamides




| entry | solvent | additive (1: 1) | temperature (°C) | yield (%)[b] |
|---|---|---|---|---|
| 1. | DCE | NaOAc : $AgSbF_6$ | 110 | 80 |
| 2. | Chloroform | NaOAc : $AgSbF_6$ | 110 | 60 |
| 3. | Toluene | NaOAc : $AgSbF_6$ | 110 | 18 |
| 4. | THF | NaOAc : $AgSbF_6$ | 110 | 38 |
| 5. | DCE | NaOAc : $AgSbF_6$ | 110 | 78[c] |
| 6. | DCE | NaOAc : $AgSbF_6$ | 110 | 75[d] |
| 7. | DCE | NaOAc : $AgSbF_6$ | 110 | 80[e] |
| 8. | DCE | NaOAc : $AgSbF_6$ | 110 | 72 |
| 9. | DCE | NaOAc : $AgSbF_6$ | rt | 16 |
| 10. | DCE | NaOAc : $AgSbF_6$ | 60 | 83 |
| 11. | DCE | NaOAc : $AgSbF_6$ | 80 | 75 |
| **12.** | **DCE** | NaOAc : $AgSbF_6$ | **60** | **96[f]** |
| 13. | DCE | NaOAc ÷ | 60 | 60 |
| 14. | DCE | – : $AgSbF_6$ | 60 | 30 |
| 15. | DCE | NaOAc : $AgSbF_6$ | 110 | 14[g] |
| 16. | DCE | NaOAc : $AgSbF_6$ | 110 | trace[h] |

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.22 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), additive (1:1) (20.0 mol %), $Ag_2CO_3$ (1.0 equiv), solvent (1.5 mL) at 110 °C for 12 h. [b]Isolated yield of product. [c]1.2 equiv of **2a** was used, [d]2.5 mol% of Ru catalyst was used. [e]0.5 equiv of $Ag_2CO_3$ was used. [f]2.5 mol% of Ru catalyst. 0.5 equiv of $Ag_2CO_3$ at 60° C was used. [g]Without $Ag_2CO_3$. [h]Without Ru catalyst.

**Table S2: Optimization table for di-alkynylated arylamides**




| entry | solvent | additive (1:1) | temperature (°C) | yield (%)[b] | |
|---|---|---|---|---|---|
| | | | | 5a | 5aa |
| 1. | DCE | NaOAc : $AgSbF_6$ | RT | 6 | 23 |
| 2. | DCE | NaOAc : $AgSbF_6$ | 60 | 52 | 19 |
| 3. | DCE | NaOAc : $AgSbF_6$ | 60 | 53 | 40[c] |
| 4. | DCE | NaOAc : $AgSbF_6$ | 110 | 92[c] | trace |
| 5 | DCE | NaOAc: - | 60 | - | 20[d] |
| 6. | DCE | - | 60 | - | 70[e] |

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), additive (20.0 mol %), $Ag_2CO_3$ (0.5 equiv), solvent (1.5 mL) for 12 hr. [b]Isolated yield of product. [c] 5.0 mol% of Ru catalyst, 1.0 equiv of $Ag_2CO_3$, 2.2 equiv of **2a** was used. [d]5.0 mol% of Ru catalyst, 1.0 equiv of NaOAc was used, [e]5.0 mol% of Ru catalyst, 1.0 equiv of $Ag_2CO_3$ was used.

## 3. General procedure for the synthesis of *ortho*-mono-alkynylated arylamide derivatives (GP-A, 3a-3g).

To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar was sequentially added benzamide (0.1 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene}]_2$ (2.5 mol %, 1.56 mg), NaOAc (20 mol %), $Ag_2CO_3$ (0.5 equiv). Then DCE (1.5 mL) was added followed by addition of 1-bromo-2-(triisopropylsilyl)acetylene (2.2 equiv) into reaction mixture. Subsequently, $AgSbF_6$ (20 mol %) was added under a nitrogen atmosphere and the reaction tube was flushed with nitrogen. The tube was tightly closed and placed in a preheated oil bath at 60 °C and was stirred for 12 h according to the conversion estimated by TLC. The reaction was monitored by TLC and after

completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite, and washed with DCM (20 mL x 3). The filtrate was concentrated and the product was purified by column chromatography on silica gel (100-200 mess) using ethyl acetate/hexanes as eluent.

**4. General procedure for the synthesis of *ortho*-di-alkynylated arylamide derivatives (GP-B, 5a-5z).**

To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar was sequentially added benzamide (0.1 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene}]_2$ (5 mol %, 3.05 mg), NaOAc (20 mol %), $Ag_2CO_3$ (1.0 equiv). Then DCE (1.5 mL) was added followed by addition of 1-bromo-2-(triisopropylsilyl)acetylene (2.2 equiv) into reaction mixture. Subsequently, $AgSbF_6$ (20 mol %) was added under a nitrogen atmosphere and the reaction tube was flushed with nitrogen. The tube was tightly closed and placed in a preheated oil bath at 110 $^oC$ and was stirred for 12 h according to the conversion estimated by TLC. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite and washed with DCM (20 mL x 3). The filtrate was concentrated and the product was purified by column chromatography on silica gel (100-200 mess) using ethyl acetate/hexanes as eluent.

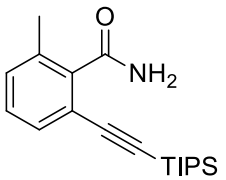
**5. General procedure for the synthesis of mono-alkynylated arylamide derivatives (GP-C, 5ab-5ag)**

To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar was sequentially added benzamide (0.1 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene}]_2$ (5 mol %, 3.05 mg), $Ag_2CO_3$ (1.0 equiv). Then DCE (1.5 mL) was added followed by addition of 1-bromo-2-(triisopropylsilyl)acetylene

(1.0 equiv) into reaction mixture. Subsequently, the reaction tube was flushed with nitrogen. The tube was tightly closed and placed in a preheated oil bath at 60 °C and was stirred for 12 h according to the conversion estimated by TLC. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite and washed with DCM (20 mL x 3). The filtrate was concentrated and the product was purified by column chromatography on silica gel (100-200 mess) using ethyl acetate/hexanes as eluent.

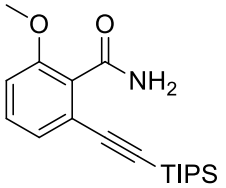
**5. Characterization of products:**

**2-Methyl-6-((triisopropylsilyl)ethynyl)benzamide (3a)**




Following GP-A, **3a** was isolated as white solid (30.2 mg, 96% yield); Mp 123-125 °C; $R_f$ (8:2 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3450, 3161, 2940, 2863, 2147, 1609, 1455, 1382, 1066, 1015 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.15 (m, 2H), 6.22 (s, 1H), 5.88 (s, 1H), 2.39 (s, 3H), 1.11 (s, 21H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.7, 138.8, 135.4, 130.5, 130.3, 128.8, 120.3, 104.2, 95.1, 19.5, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{29}NOSi$ $[M+ H]^+$ 316.2091 found 316.2096.

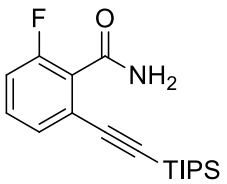
**2-Methoxy-6-((triisopropylsilyl)ethynyl)benzamide (3b)**




Following GP-A, **3b** was isolated as white solid (30.6 mg, 93% yield); Mp 122-123 °C; $R_f$ (7:3 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3491, 3118, 2938, 2863, 2144, 1678, 1571, 1464, 1383, 1279, 1074 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 5.93 (s, 1H), 5.82 (s, 1H, 3.82 (s, 3H), 1.08 (s, 21H).$^{13}C$ NMR (100 MHz, $CDCl_3$) δ

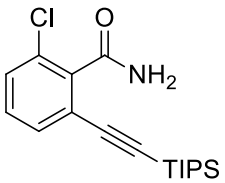
168.2, 156.1, 130.1, 128.3, 125.4, 122.2, 111.5, 103.6, 95.5, 56.0, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{29}NO_2Si$ $[M+H]^+$ 332.2040. found 332.2044.

**2-Fluoro-6-((triisopropylsilyl)ethynyl)benzamide (3c)**



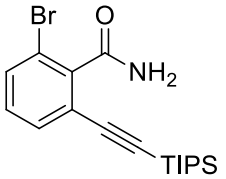

Following GP-A, **3c** was isolated as white solid (29.7 mg, 94% yield); Mp 99-101 $^oC$; $R_f$ (8:2 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3466, 3170, 2865, 2942, 2153, 1659, 1611, ,1456, 1397, 1366, 1234, 991 $cm^{-1}$.$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.12 – 7.06 (m, 1H), 6.31 (s, 1H), 6.01 (s, 1H), 1.12 (s, 21H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.7, 159.2(d, $^1J_{C-F}$ = 249.0 Hz), 130.9 (d, $^3J_{C-F}$ = 9.0 Hz), 129.2 (d, $^4J_{C-F}$ = 3.0 Hz), 126.49, 126.32, 123.0(d, $^4J_{C-F}$ = 4.0 Hz), 116.4 (d, $^2J_{C-F}$ = 22.0 Hz), 102.6 (d, $^4J_{C-F}$ = 4.0 Hz), 97.48, 18.58, 11.20. HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{26}FNOSi$ $[M+H]^+$ 320.1840 found 320.1835.

**2-Chloro-6-((triisopropylsilyl)ethynyl)benzamide (3d)**



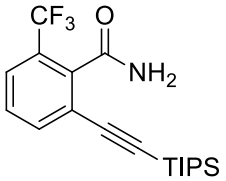

Following GP-A, **3d** was isolated as white solid (31.0 mg, 93% yield); Mp 123-125 $^oC$; $R_f$ (8:2 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3446, 3157, 2939, 2862, 2160, 1648, 1611, 1462, 1439, 1385, 1073 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.38 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.38 (s, 1H), 5.84 (s, 1H), 1.14 (s, 21H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.7, 138.4, 131.2, 130.9, 129.8, 129.6, 122.6, 102.5, 96.9, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{26}ClNOSi$ $[M+H]^+$ 336.1545 found 336.1551.

**2-Bromo-6-((triisopropylsilyl)ethynyl)benzamide (3e)**



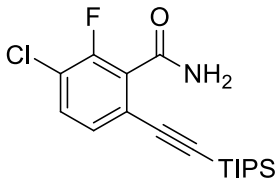

Following GP-A, **3e** was isolated as white solid(31.0 mg, 83% yield); Mp 147-148 $^{o}$C; $R_f$ (8:2 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3446, 3160, 2939, 2862, 2162, 1649, 1610, 1597, 1462, 1436, 1382, 1073 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 1H), 6.05 (s, 1H), 5.77 (s, 1H), 1.11 (s, 21H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.4, 140.4, 132.8, 131.7, 129.9, 122.6, 119.2, 102.6, 96.9, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{26}BrNOSi$ $[M+H]^+$ 380.1040 found 380.1047.

**2-(Trifluoromethyl)-6-((triisopropylsilyl)ethynyl)benzamide (3f)**




Following GP-A, **3f** was isolated as white solid (26 mg, 70% yield); Mp 103-105 $^{o}$C; $R_f$ (9:1 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3447, 3163, 2939, 2864, 2169, 1651, 1606, ,1463, 1390, 1320, 1169, 1119, 908 cm-$^{1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 6.15 (s, 1H), 5.79 (s, 1H), 1.12 (d, *J* = 2.9 Hz, 21H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.8, 137.5(q, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 136.2, 129.1, 127.7 (d, $^{2}J_{C\text{-}F}$ = 32.0 Hz), 125.8 (q, $^{3}J_{C\text{-}F}$ = 5.0 Hz), 123.1 (d, $^{1}J_{C\text{-}F}$ = 273.0 Hz), 122.7, 102.2, 97.7, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{26}F_3NOSi$ $[M+H]^+$ 370.1809. found 370.1814.

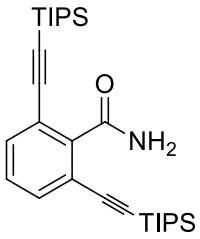
**3-Chloro-2-fluoro-6-((triisopropylsilyl)ethynyl)benzamide (3g)**




Following GP-A, **3g** was isolated as white solid (33.2 mg, 94% yield); Mp 95-97 $^{o}$C; $R_f$ (8:2 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3481, 3167, 2944, 2865, 2154, 1667, 1465, 1379, 1220, 1003, 816, 752 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.23 (m, 1H), 6.34 (s, 1H), 5.99 (s, 1H), 1.12 (d, *J* = 2.9 Hz, 21H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.5, 154.7 (d, $^{1}J_{C\text{-}F}$ = 251.0 Hz),

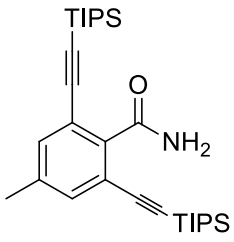
131.3, 129.4 (d, $^{4}J_{C\text{-}F}$ = 4.0 Hz), 127.9 (d, $^{2}J_{C\text{-}F}$ = 18.0 Hz), 122.2 (d, $^{2}J_{C\text{-}F}$ = 18.0 Hz),121.3 (d, $^{4}J_{C\text{-}F}$ = 4.0 Hz), 101.7 (d, $^{4}J_{C\text{-}F}$ = 4.0 Hz), 98.40, 18.56, 11.17. HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{26}ClFNOSi$ $[M+H]^{+}$ 354.1451 found 354.1456.

**2,6-Bis((triisopropylsilyl)ethynyl)benzamide (5a)**



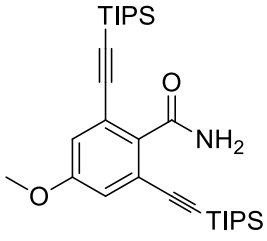

Following GP-B, **5a** was isolated as white solid (43 mg, 92% yield); Mp 113-115 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.5; IR(ATR): 3490, 3150, 2941, 2863, 2148, 1686, 1452, 1360, 1072, 982, 881, 752 $cm^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 1H), 5.79 (s, 1H), 5.75 (s, 1H),1.11 (s, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.7, 141.8, 132.6, 128.7, 121.1, 103.1, 95.9, 18.6, 11.2. HRMS (ESI-TOF*) m/z* calcd for $C_{29}H_{47}NOSi_2$ $[M+H]^{+}$ 482.3269 found 482.3275.

**4-Methyl-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5b)**




Following GP-B, **5b** was isolated as white solid (42 mg, 85% yield); Mp 151-153 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3490, 3139, 2940, 2863, 2148, 1686, 1459, 1361, 1018, 881, 669 $cm^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 2H), 5.79 (s, 1H), 5.76 (s, 1H), 2.30 (s, 3H), 1.10 (s, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.9, 139.1, 138.9, 133.3, 121.0, 103.4, 95.4, 20.7, 18.6, 11.3. HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{49}NOSi_2$ $[M+H]^{+}$ 496.3425 found 496.3439.

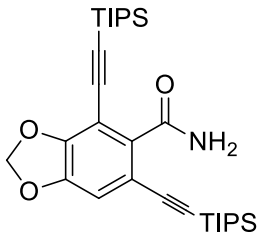
**4-Methoxy-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5c)**




Following GP-B, **5c** was isolated as white solid (43 mg, 85% yield); Mp 153-155 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3490,

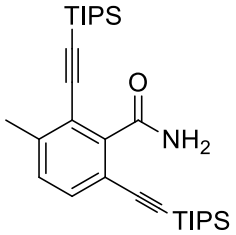
3128, 2940, 2863, 2151, 1685, 1459, 1358, 1323, 1163, 1007 $cm^{-1}$$^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 5.81 (s, 1H), 5.77 (s, 1H)3.81 (s, 3H), 1.10 (s, 42H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.7, 159.2, 134.7, 122.5, 118.3, 103.2, 95.8, 55.6, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{49}NO_2Si_2$ $[M+ H]^+$ 512.3375 found 512.3383.

**4,6-Bis((triisopropylsilyl)ethynyl)benzo[d][1,3]dioxole-5-carboxamide (5d)**



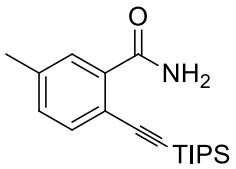

Following GP-B, **5d** was isolated as white solid (49.5 mg, 94% yield); Mp 128-130 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3486, 3129, 2941, 2863, 2158, 1682, 1459, 1381, 1342, 1224, 1070, 1030, 882. $cm^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.06 (s, 2H), 5.93 (s, 1H), 5.82 (s, 1H),1.10 (d, *J* = 6.3 Hz, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.3, 149.8, 147.7, 136.3, 114.8, 112.0, 103.4, 102.3, 100.5, 96.7, 94.2,18.6, 18.56, 11.2, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{47}NO_3Si_2$ $[M+ H]^+$ 526.3167 found 526.3172.

**3-Methyl-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5e)**



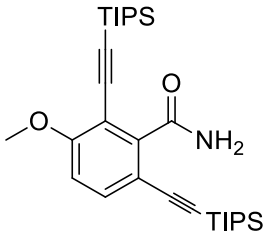

Following GP-B, **5e** was isolated as white solid (25 mg, 50% yield); Mp 110-112 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3485, 3148, 2940, 2863, 2151, 1682, 1603, 1462, 1381, 1359, 1073, 1017, 881 $cm^{-1}$.$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 5.84 (s, 1H), 5.75 (s, 1H), 2.46 (s, 3H), 1.11 (d, *J* = 6.6 Hz, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.4, 142.2, 141.6, 132.1, 129.9, 120.9, 118.3, 103.3, 101.6, 100.4, 94.8, 21.2, 18.6, 18.6, 11.3. HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{49}NOSi_2$ $[M+ H]^+$ 496.3425 found 496.3430.

**5-Methyl-2-((triisopropylsilyl)ethynyl)benzamide (5ee)**



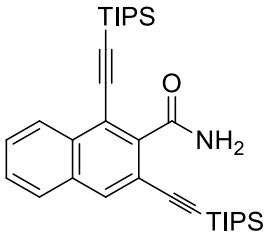

Following GP-B, **5ee** was isolated as white solid (11.5 mg, 37% yield); Mp 75-76 $^{o}$C; $R_f$ (8:2 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3423, 3139, 2941, 2864, 2145, 1679, 1601, 1460, 1416, 1354, 1209, 1018, 882 $cm^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.92 (s, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 9.5 Hz, 1H), 5.90 (s, 1H), 2.40 (s, 3H), 1.15 – 1.11 (m, 21H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.8, 139.5, 134.4, 133.8, 131.83, 131.0, 117.3, 105.9, 98.3, 21.4, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{29}NOSi$ $[M+H]^+$ 316.2091 found 316.2094.

**3-Methoxy-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5f)**




Following GP-B, **5f** was isolated as white solid (44.5 mg, 86% yield); Mp 108-110 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3486, 3146, 2941, 2864, 2151, 1680, 1464, 1364, 1278, 1057, 996, 881 $cm^{-1}$ .$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 5.95 (s, 1H), 5.76 (s, 1H), 3.87 (s, 3H), 1.11 (d, *J* = 6.0 Hz, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.8, 160.7, 143.6, 134.0, 113.0, 111.2, 110.8, 103.2, 100.7, 98.8, 93.5, 56.2, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{49}NO_2Si_2$ $[M+H]^+$ 512.3375 found 512.3381.

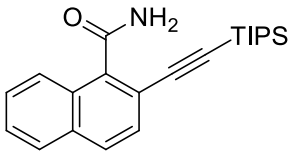
**1,3-Bis((triisopropylsilyl)ethynyl)-2-naphthamide (5g)**




Following GP-B, **5g** was isolated as white solid (32 mg, 62% yield); Mp 160-162 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3490, 3143, 2941, 2863, 2145, 1681, 1461, 1355, 1072, 1019, 881$cm^{-1}$.$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.3 Hz, 1H), 8.00 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.50 (m, 2H), 5.97 (s, 1H), 5.86 (s, 1H), 1.19 – 1.13 (m, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.3, 139.8, 133.3, 132.5, 128.3, 127.9, 127.7, 126.7, 118.8, 117.8, 103.5,

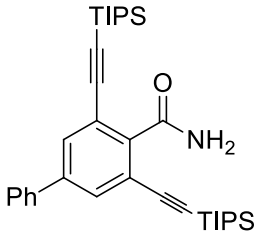
101.9, 100.9, 95.2, 18.7, 18.6, 11.3, 11.3. HRMS (ESI-TOF) *m/z* calcd for $C_{33}H_{49}NOSi_2$ $[M+H]^+$ 532.4325 found 532.3431.

**2-((Triisopropylsilyl)ethynyl)-1-naphthamide (5h)**



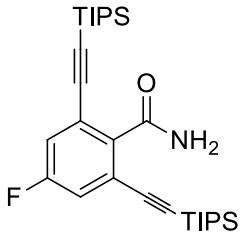

Following GP-B, **5h** was isolated as white solid (24.5 mg, 69% yield); Mp 168-170 $^oC$; $R_f$ (8.5:1.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3425, 3160, 2941, 2863, 2145, 1674, 1655, 1607, 1463, 1321, 1267, 1016, 993 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.81 (dd, *J* = 7.9, 4.9 Hz, 2H), 7.59 – 7.46 (m, 3H), 6.34 (s, 1H), 6.07 (s, 1H), 1.16 (s, 21H).$^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.1, 137.2, 132.8, 129.6, 129.3, 128.7, 127.9, 127.6, 127.1, 125.6, 117.9, 104.5, 96.9, 29.7, 18.7, 11.3.. HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{29}NOSi$ $[M+H]^+$ 352.2091 found 352.2096.

**3,5-Bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-carboxamide (5i)**



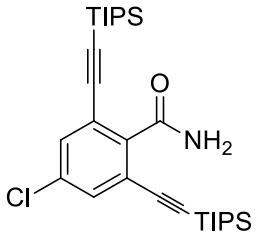

Following GP-B, **5i** was isolated as white solid (43 mg, 77% yield); Mp 194-196 $^oC$; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3494, 3147, 2941, 2863, 2156, 1682, 1584, 1460, 1366, 1072 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.36 (m, 3H), 5.85 (s, 1H), 5.79 (s, 1H), 1.13 (s, 42H).$^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.6, 142.1, 140.4, 138.8, 131.3, 128.9, 128.3, 127.1, 121.7, 103.2, 96.0, 18.6, 11.3..HRMS (ESI-TOF) *m/z* calcd for $C_{35}H_{51}NOSi_2$ $[M+H]^+$ 558.3582 found 558.3583.

**4-Fluoro-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5j)**



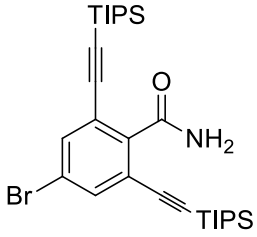

Following GP-B, **5j** was isolated as white solid (43 mg, 86% yield); Mp 124-126 °C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3489, 3146, 2942, 2864, 2165, 1686, 1580, 1462, 1359, 1141, 1009, 881 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.7 Hz, 2H), 5.76 (s, 2H), 1.11 (s, 42H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.0, 161.7(d, $^1J_{C-F}$ = 248.0 Hz), 138.4 (d, $^4J_{C-F}$ = 3.0 Hz),, 123.3(d, $^3J_{C-F}$ = 11.0 Hz), 119.7 (d, $^2J_{C-F}$ = 23.0 Hz), 102.0 (d, $^4J_{C-F}$ = 3.0 Hz), 97.5, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{46}FNOSi_2$ $[M+ H]^+$ 500.3175 found 500.3184.

**4-Chloro-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5k)**



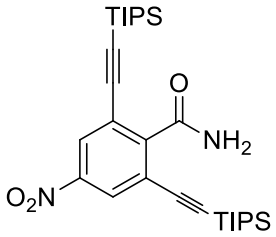

Following GP-B, **5k** was isolated as white solid (33 mg, 64% yield); Mp 142-144 °C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3469, 3145, 2940, 2863, 2160, 1659, 1559, 1462, 1369, 1072, 1005, 881 $cm^{-1}$.$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 2H), 5.78 (s, 2H), 1.10 (d, *J* = 2.1 Hz, 42H).$^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.9, 140.2, 134.5, 132.3, 122.7, 101.8, 97.7, 18.6, 11.20. HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{46}ClNOSi_2$ $[M+ H]^+$ 516.2879 found 516.2888.

**4-Bromo-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5l)**



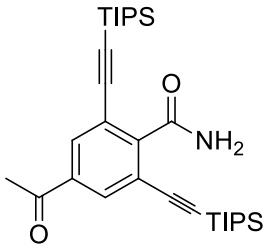

Following GP-B, **5l** was isolated as white solid (48.4 mg, 87% yield); Mp 170-172 °C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3469, 3145, 2940, 2863, 2153, 1660, 1556, 1462, 1390, 1370, 1004, 855 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 2H), 5.84 (s, 1H), 5.79 (s,1H). 1.10 (d, *J* = 2.3 Hz, 42H).$^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.9, 140.6, 135.1, 122.8, 122.3, 101.6, 97.8, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{46}BrNOSi_2$ $[M+ H]^+$ 560.2374 found 560.2381.

**4-Nitro-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5m)**



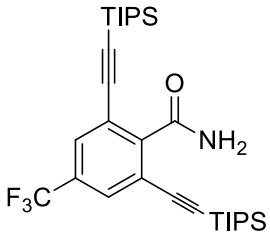

Following GP-B, **5m** was isolated as white solid (40 mg, 76% yield); Mp 143-145 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3453, 3144, 2943, 2864, 2157, 1693, 1527, 1461, 1344, 1005, 881 cm$^{-1}$.$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 2H), 5.86 (s, 1H), 5.81 (s, 1H), 1.11 (d, *J* = 3.6 Hz, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.9, 147.5, 146.8, 126.7, 122.9, 100.7, 99.7, 18.5, 11.1. HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{46}N_2O_3Si_2$ [M+ H]$^+$ 527.3120 found 527.3129.

**4-Acetyl-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5n)**




Following GP-B, **5n** was isolated as white solid (43 mg, 82% yield); Mp 170-172 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3406, 3178, 2942, 2864, 2157, 1682, 1461, 1354, 1308, 1200, 1012, 882 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 5.79 (s, 2H), 2.61 (s, 3H), 1.12 (s, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.3, 167.9, 145.4, 137.2, 131.9, 121.9, 102.1, 97.5, 26.8, 18.6, 11.3. HRMS (ESI-TOF) *m/z* calcd for $C_{31}H_{49}NO_2Si_2$ [M+ H]$^+$ 524.3375 found 524.3387.

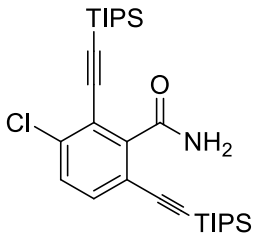
**4-(Trifluoromethyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5o)**




Following GP-B, **5o** was isolated as white solid (48.7 mg, 89% yield); Mp 158-159 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3492, 3127, 2944, 2865, 2150, 1693, 1458, 1411, 1345, 1168, 1127, 1003, 881 cm$^{-1}$.$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 2H), 5.79 (s, 2H),

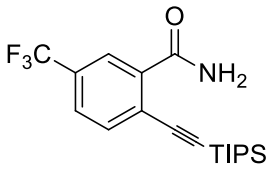
1.11 (d, $J$ = 2.7 Hz, 42H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.56, 144.72, 131.5 (d, $^2J_{C\text{-}F}$ = 33.0 Hz), 128.9 (q, $^3J_{C\text{-}F}$ = 5.0 Hz), 122.9 (d, $^1J_{C\text{-}F}$= 271.0 Hz), 122.2, 101.6, 98.3, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{46}F_3NOSi_2$ $[M+H]^+$ 550.3143 found 550.3157.

.**3-Chloro-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5p)**



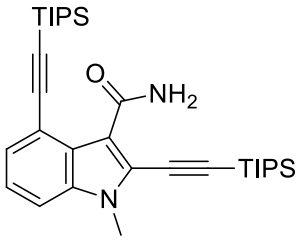

Following GP-B, **5p** was isolated as white solid ( 26.2 mg, 48% yield); Mp 125-127 ºC; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3483, 3147, 2941, 2864, 2151, 1682, 1462, 1352, 1207, 1073, 1015, 991, 881 $cm^{-1}$ . $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H), 5.99 (s, 1H), 5.76 (s, 1H), 1.11 (d, $J$ = 9.2 Hz, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.2, 143.5, 136.9, 132.9, 129.7, 121.0, 119.5, 102.8, 102.1, 99.3, 96.9, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{46}ClOSi_2$ $[M+H]^+$ 516.2879 found 516.2896.

**3-(Trifluoromethyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5q)**



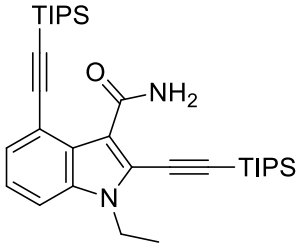

Following GP-B, **5q** was isolated as Yellow viscous liquid (22 mg, 60% yield); $R_f$ (9:1 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3441, 3177, 2944, 2866, 2169, 1682, 1602, 1462, 1318, 1172, 1130, 1092, 881 $cm^{-1}$.$^1$H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.78 (s, 1H), 7.62 (s, 2H), 6.19 (s, 1H), 1.07 (d, $J$ = 5.4 Hz, 21H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.2, 134.92, 134.9, 130.9 (d, $^2J_{C\text{-}F}$ = 33.0 Hz), 127.7 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 127.4 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 123.71, 123.4 (d, $^1J_{C\text{-}F}$ = 271.0 Hz), 104.2, 102.6, , 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{26}F_3NOSi$ $[M+H]^+$ 370.1809 found 370.1813..

**1-Methyl-2,4-bis((triisopropylsilyl)ethynyl)-1H-indole-3-carboxamide (5r)**



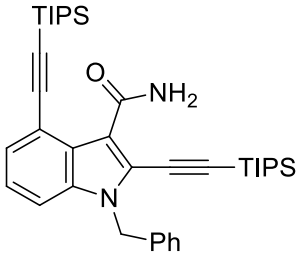

Following GP-B, **5r** was isolated as white solid (43 mg, 83% yield); Mp 190-192 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3479, 3158, 2939, 2862, 2152, 1670, 1603, 1462, 1434, 1279, 992, 880 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 1H), 7.25 – 7.14 (m, 2H), 6.74 (s, 1H), 5.53 (s, 1H), 3.77 (s, 3H), 1.1 (d, *J* = 11.2 Hz, 42H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.0, 137.0, 129.2, 125.6, 123.3, 114.9, 110.5, 105.9, 104.5, 96.9, 96.1, 30.9, 18.7, 18.6, 11.4, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{32}H_{50}N_2OSi_2$ [M+ H]$^+$ 535.3534 found 535.3541.

**1-ethyl-2,4-bis((triisopropylsilyl)ethynyl)-1H-indole-3-carboxamide (5s)**




Following GP-B, **5s** was isolated as white solid (35.6 mg, 65% yield); Mp 169-171 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3484, 3168, 2940, 2863, 2149, 1674, 1608, 1463, 1438, 1381, 1342, 1264, 863 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.75 (s, 1H), 5.61 (s, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.16 (dd, *J* = 8.9, 3.3 Hz, 42H).). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.2, 135.9, 129.1, 124.5, 123.6, 123.3, 116.1, 115.2, 110.4, 105.9, 104.2, 96.9, 95.9, 39.5, 18.7, 18.6, 14.9, 11.4, 11.3. HRMS (ESI-TOF) *m/z* calcd for $C_{33}H_{52}N_2OSi_2$ [M+ H]$^+$ 549.3691 found 549.3696.

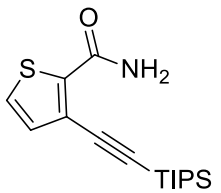
**1-benzyl-2,4-bis((triisopropylsilyl)ethynyl)-1H-indole-3-carboxamide (5t)**




Following GP-B, **5t** was isolated as white solid (38.4 mg, 63% yield); Mp 149-150 $^{o}$C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3487, 3148, 2940, 2863, 2157, 1671, 1608, 1461, 1444, 1413, 1280,

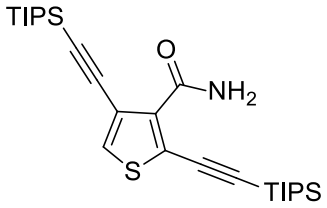
1071, 995, 881 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.1 Hz, 1H), 7.27 – 7.08 (m, 7H), 6.79 (s, 1H), 5.64 (s, 1H), 5.51 (s, 2H), 1.18 – 1.05 (m, 42H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.0, 136.6, 136.2, 129.3, 128.7, 127.6, 126.5, 125.2, 123.6, 116.6, 115.2, 111.1, 105.7, 104.8, 97.1, 96.0, 48.1, 18.7, 18.6, 11.4, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{38}H_{54}N_2OSi_2$ $[M+H]^+$ 611.3847 found 611.3852.

**3-((Triisopropylsilyl)ethynyl)thiophene-2-carboxamide (5u)**



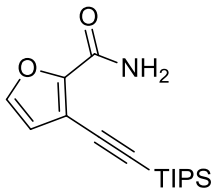

Following GP-B, **5u** was isolated as white solid (24.5 mg, 82% yield); Mp 123-125 °C; $R_f$ (8.5:1.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3434, 3142, 2940, 2863, 2147, 1656, 1601, 1457, 1427, 1386, 1125, 993 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.44 (d, *J* = 5.1 Hz, 1H), 7.14 (d, *J* = 5.1 Hz, 1H), 5.97 (s, 1H), 1.12 (d, *J* = 4.7 Hz, 21H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 162.8, 141.2, 132.1, 129.8, 121.6, 100.9, 99.8, 18.6, 11.1. HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{25}NOSSi$ $[M+H]^+$ 308.1499 found 308.1506.

**2,4-Bis((triisopropylsilyl)ethynyl)thiophene-3-carboxamide (5v)**



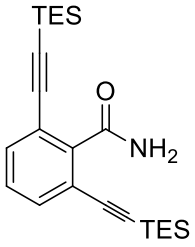

Following GP-B, **5v** was isolated as white solid (38.2 mg, 80% yield); Mp 165-167 °C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3441, 3147, 2942, 2863, 2140, 1681, 1610, 1504, 1460, 1383, 1329, 1042, 994, 880 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.02 (s, 1H), 5.72 (s, 1H), 1.11 (t, *J* = 4.0 Hz, 42H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 162.8, 137.9, 131.2, 126.7, 121.6, 103.5, 100.2, 97.5, 95.2, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{27}H_{45}NOSSi_2$ $[M+H]^+$ 488.2833 found 488.2845.

**2-((Triisopropylsilyl)ethynyl)furan-3-carboxamide (5w)**



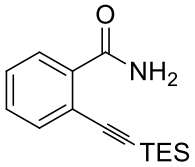

Following GP-B, **5w** was isolated white solid (9.5 mg, 33% yield); Mp 74-76 $^{o}$C; $R_f$ (8.5:1.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3429, 3179, 2942, 2864, 2159, 1672, 1612, 1461, 1424, 1345, 1261, 1212, 1071, 995 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 1.5 Hz, 1H), 7.02 (s, 1H), 6.55 (d, *J* = 1.5 Hz, 1H), 5.84 (s, 1H), 1.12 (d, *J* = 4.4 Hz, 21H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.1, 148.4, 144.6, 114.8, 110.6, 101.36, 97.4, 29.7, 18.6, 11.13. HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{25}NO_2Si$ $[M+ H]^+$ 292.1727 found 292.1728.

**2,6-bis((triethylsilyl)ethynyl)benzamide (5x)**




Following GP-B, **5x** was isolated as viscous liquid (6 mg, 15% yield); $R_f$ (9.5: 1.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3442, 3183, 2931, 2863, 2150, 1691, 1665 ,1453, 1352, 1264, 1179, 1104, 895 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.16 (m, 1H), 5.74 (d, *J* = 5.2 Hz, 2H), 1.01 – 0.89 (m, 18H), 0.64 – 0.54 (m, 12H). $^{13}$C NMR (126 MHz) δ 168.7, 141.9, 132.7, 132.7, 132.7, 128.8, 121.0, 102.60, 97.1, 29.7, 7.4, 4.3. HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{35}NOSi_2$ $[M+ H]^+$ 398.2330 found 398.2329.

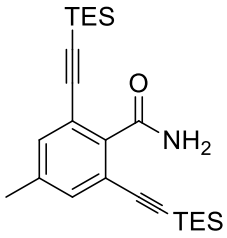
**2-((Triethylsilyl)ethynyl)benzamide (5xx)**




Following GP-B, **5xx** was isolated as yellow solid (14 mg, 54% yield); Mp 76-78 $^{o}$C; $R_f$ (8:2 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3371, 3184, 2915, 2850, 2153, 1729, 1642, ,1469, 1424, 1393, 1260, 1179, 1104, 847 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 6.1, 3.2 Hz, 1H), 7.92 – 7.77 (m, 1H), 7.57 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.44 (dd, *J* = 5.2, 3.9 Hz, 2H), 6.16 (s, 1H), 1.05 (t, *J* = 7.9 Hz, 9H), 0.71 (q, *J* = 7.9

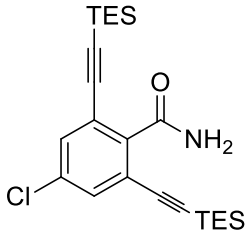
Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.7, 134.3, 134.2, 131.0, 130.5, 129.1, 120.1, 105.0, 100.1, 7.5, 4.2. HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{21}NOSi[M+H]^+$ 260.1465 found 260.1469.

**4-Methyl-2,6-bis((triethylsilyl)ethynyl)benzamide (5y)**



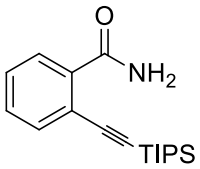

Following GP-B, **5y** was isolated as yellow solid (11 mg, 33% yield); Mp 125-127 °C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3487, 3228, 2955, 2915, 2158, 1729, 1683, 1455, 1362, 1261, 1178, 1016, 862 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 2H), 5.75 (s, 1H), 5.67 (s, 1H), 2.23 (s, 3H), 0.96 (t, *J* = 7.9 Hz, 18H), 0.59 (q, *J* = 7.9 Hz, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.8, 139.1, 138.9, 133.4, 120.9, 102.9, 96.6, 20.7, 7.5, 4.3. HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{37}NOSi_2[M+Na]^+$ 434.2306 found 434.2306.

**4-Chloro-2,6-bis((triethylsilyl)ethynyl)benzamide (5z)**




Following GP-B, **5z** was isolated as yellow solid (8 mg, 22% yield); Mp 112-114 °C; $R_f$ (9.5:0.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3467, 3248, 2915, 28, 2155, 1730, 1661, 1562, 1457, 1395, 1369, 1262, 1179, 1007, 867 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 2H), 5.77 (s, 2H), 1.02 (t, *J* = 7.9 Hz, 18H), 0.66 (q, *J* = 7.9 Hz, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.79, 140.24, 134.59, 132.35, 122.63, 101.26, 98.80, 7.42, 4.20. HRMS (ESI-TOF) m/z calcd for $C_{23}H_{34}ClNOSi_2[M+H]^+$ 432.1940 found 432.1942.

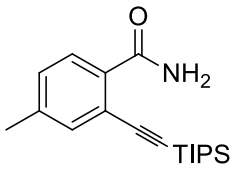
**2-((Triisopropylsilyl)ethynyl)benzamide (5ab)**




Following GP-C, **5ab** was isolated as viscous liquid (70%, yield); $R_f$ (8:2 Hexane /Ethyl acetate) = 0.5; IR(ATR): 3440, 3196, 2941, 2863, 2158, 1664,

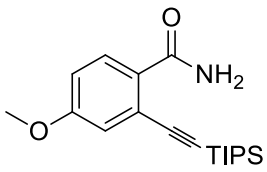
1462, 1384, 1116, 1014, 994, 880 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.89 (s, 1H), 7.63 – 7.55 (m, 1H), 7.50 – 7.38 (m, 2H), 6.02 (s, 1H), 1.13 (d, *J* = 4.4 Hz, 21H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 167.6, 134.4, 134.1, 131., 130.5, 129.0, 120.3, 105.7, 99.2, 29.7, 18.6, 11.2, .HRMS (ESI-TOF) m/z calcd for $C_{18}H_{27}NOSi$ $[M+ H]^+$ 302.1935 found 302.1934.

**4-methyl-2-((triisopropylsilyl)ethynyl)benzamide (5ac)**



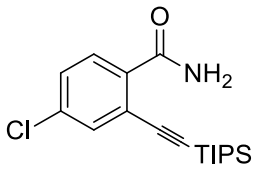

Following GP-C, **5ac** was isolated as white solid (13.3 mg, 40% yield); Mp 109-111 °C; $R_f$ (8.5:1.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3435, 3136, 2945, 2866, 2143, 1675, 1600, 1463, 1366, 1013, 884, 669 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.94 (s, 1H), 7.37 (s, 1H), 7.25 (d, *J* = 7.1 Hz, 1H), 5.88 (s, 2H), 2.37 (s, 3H), 1.13 (d, *J* = 4.2 Hz, 21H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.6, 141.6, 134.7, 131.3, 130.7, 130.0, 120.1, 106.0, 98.7, 21.0, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{29}NOSi$ $[M+ H]^+$ 316.2091 found 316.2094.

**4-Methoxy-2-((triisopropylsilyl)ethynyl)benzamide (5ad)**



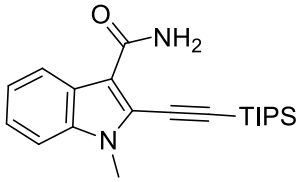

Following GP-C, **5ad** was isolated as white solid (15 mg, 48% yield); Mp 69-71 °C; $R_f$ (8.0:2.0 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3435, 3136, 2945, 2863, 2153, 1661, 1584, 1463, 1417, 1323, 1284, 1164, 1032 $cm^{-1.1}$ $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 1H), 7.86 (s, 1H), 6.96 (d, *J* = 2.6 Hz, 1H), 6.90 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.83 (s, 1H), 3.79 (s, 3H), 1.09 – 1.04 (m, 21H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 167.3, 161.3, 132.8, 126.5, 121.7, 119.1, 114.8, 105.8, 99.1, 55.5, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{29}NO_2Si$ $[M+ H]^+$ 332.2040 found 332.2048.

**4-Chloro-2-((triisopropylsilyl)ethynyl)benzamide (5ae)**



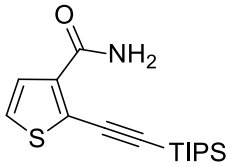

Following GP-C, **5ae** was isolated as white solid (23.3 mg, 70% yield); Mp 93-95 $^{o}$C; $R_f$ (8.5:1.5 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3438, 3140, 2920, 2866, 2150, 1679, 1585, 1459, 1402, 1359, 1075, 1017, 880 $cm^{-1}$.$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.77 (s, 1H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.35 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.03 (s, 1H), 1.06 (d, *J* = 4.8 Hz, 21H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.6, 137.2, 133.7, 132.5, 132.1, 129.3, 121.8, 104.2, 100.9, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{26}ClNOSi$ $[M+ H]^+$ 336.1545 found 336.1546.

**1-Methyl-2-((triisopropylsilyl)ethynyl)-1H-indole-3-carboxamide (5af)**




Following GP-C, **5ar** was isolated as white solid (22.6 mg, 64% yield); Mp 126-128 $^{o}$C; $R_f$ (7:3 Hexane /Ethyl acetate) = 0.4; IR(ATR); 3480, 3158, 2940, 2863, 2150, 1672, 1603, 1462, 1270, 880 $cm^{-1}$.$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.20 (m, 2H), 7.09 (s, 1H), 5.52 (s, 1H), 3.79 (s, 3H), 1.10 (d, *J* = 5.8 Hz, 21H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.9, 136.8, 126.3, 124.5, 123.1, 122.4, 122.2, 113.4, 109.3, 106.6, 97.0, 31.0, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{30}N_2OSi$ $[M+ H]^+$ 355.2200 found 355.2220 .

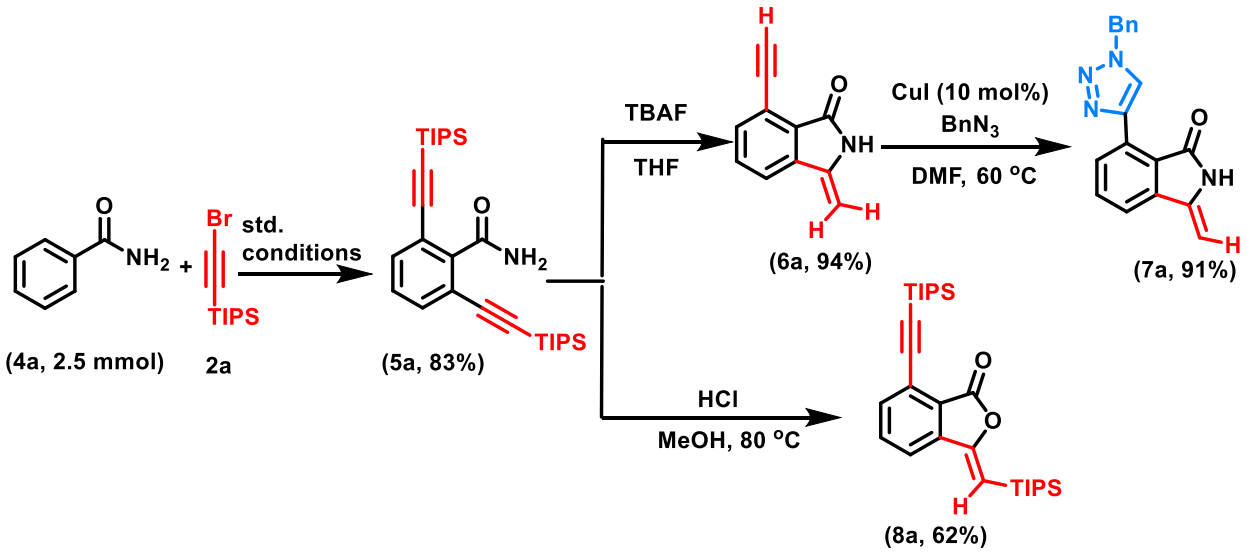
**2-((Triisopropylsilyl)ethynyl)thiophene-3-carboxamide (5ag)**



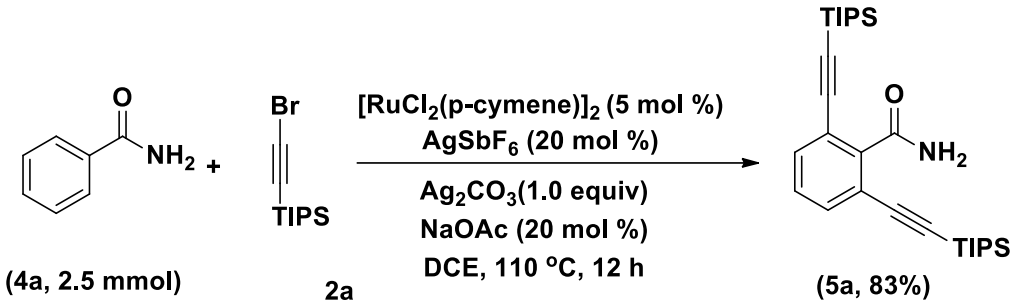

Following GP-C, **5av** was isolated as white solid (19 mg, 62% yield); Mp 70-72 $^{o}$C; $R_f$ (7:3 Hexane /Ethyl acetate) = 0.4; IR(ATR): 3440, 3145, 2940, 2863, 2140, 1679, 1507, 1459, 1379, 1329, 1040, 880 $cm^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 5.3 Hz, 1H), 7.43 (s, 1H), 7.19 (d, *J* = 5.3 Hz, 1H), 5.79 (s, 1H), 1.12 (d, *J* = 5.1 Hz, 21H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.5, 138.7, 129.4, 126.0, 123.6, 104.6,

98.2, 18.6, 11.2. HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{25}NOSSi$ [M+ H]$^+$ 308.1499 found 308.1523 .

## 6. Scale up synthesis and derivatization



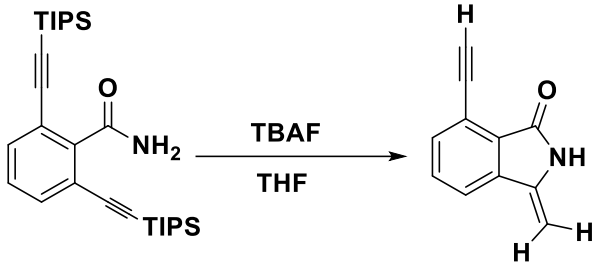

**Procedure for scale-up synthesis**




To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar was sequentially added benzamide (2.5 mmol, 1.0 equiv), [$RuCl_2$(*p*-cymene]$_2$ (5 mol %, 76.5 mg), NaOAc (20 mol % 41 mg), $Ag_2CO_3$ (1.0 equiv, 689 mg). Then DCE (20 mL) was added followed by addition of 1-bromo-2- (triisopropylsilyl)acetylene (5.5 mmol, 2.2 equiv) into reaction mixture. Subsequently, $AgSbF_6$ (20 mol %, 172 mg) was added under a nitrogen atmosphere and the reaction tube was flushed with nitrogen. The tube was tightly closed and placed in a preheated oil bath at 110$^o$C

and was stirred for 12 h according to the conversion estimated by TLC. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite, and washed with DCM (20 mL x 3). The filtrate was concentrated and the product was purified by column chromatography on silica gel (100-200 mess) using ethyl acetate/hexanes as eluent. The desired product was isolated in 83% yield (1g).

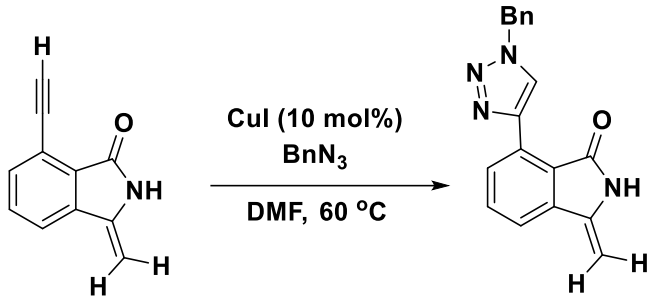
**Procedure for the Synthesis 7-Ethynyl-3-methyleneisoindolin-1-one, 6a (*via* deprotection of TIPS group)**




By following a reported procedure,[2] one equivalent of alkynylamide(0.20 mmol) was dissolved in anhydrous THF at rt. Tetrabutylammonium fluoride (1.1–3 equiv) was added and the reaction was allowed to stir at the room temperature until TLC analysis indicated reaction completion (5 min–12 h). Saturated $NH_4Cl_{(aq)}$ was added to the solution, and the organic phase was extracted with $Et_2O$, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford **6a** (32 mg, 94% yield). Charred at 192$^oC$; $R_f$ (8.5:1.5 Hexane /Ethyl acetate) = 0.4. IR(ATR): 3237, 2962, 2107, 1708, 1653, 1474, 1361, 1277, 1118, 847 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.67 – 7.44 (m, 3H), 5.13 (d, *J* = 1.6 Hz, 1H), 4.91 (d, *J* = 1.9 Hz, 1H), 3.45 (s, 1H). $^{13}C$ NMR (100

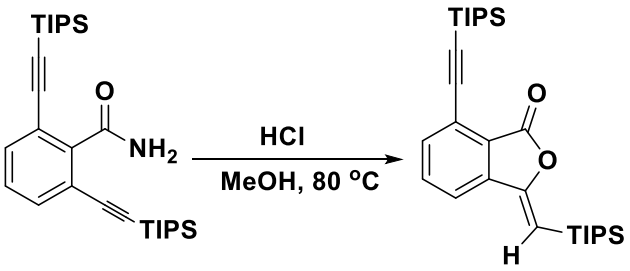
MHz, $CDCl_3$) δ 167.1, 138.8, 137.8, 134.8, 131.8, 129.8, 120.6, 118.7, 90.8, 83.6, 79.4. HRMS (ESI-TOF) m/z calcd for $C_{11}H_7NO$ $[M+ Na]^+$ 192.0420 found 192.0421.

**Procedure for the Synthesis 7-(1-Benzyl-1H-1,2,3-triazol-4-yl)-3-methyleneisoindolin-1-one(7a)**




By following a reported procedure,[3] To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar (0.2 mmol) followed by CuI(10 mol%), $BnN_3$ ( 0.4 mmol) and DMF (1 mL). The Reaction tube was sealed and the reaction mixture was stirred at 60 $^oC$ for 14 h after which it was diluted with water (5 mL) and extracted by ethyl acetate (5 mL x 3). The organic phase was combined and washed with aqueous HCl (1.0 N, 5 mL) and brine (5 mL) concentrated in vaccum. The residue was purified by column chromatography on silica gel to afford **7a** (55 mg, 91%). Mp 208-210 $^oC$; $R_f$ (8:2 Hexane /Ethyl acetate)= 0.4; IR(ATR): 3145, 2922, 2105, 1706, 1644, 1455, 1370, 1257, 1224, 1119, 1051, 815 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO) δ 10.75 (s, 1H), 9.22 (s, 1H), 8.39 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.47 – 7.38 (m, 5H), 5.79 (s, 2H), 5.41 (s, 1H), 4.95 (d, *J* = 0.8 Hz, 1H). $^{13}C$ NMR (100 MHz, DMSO) δ 167.7, 142.1, 139.7, 138.4, 136.1, 132.3, 128.8, 128.2, 128.1, 127.9, 126.6, 124.4, 120.1, 90.1, 52.9. HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{14}N_4O$ $[M+ Na]^+$ 325.1060 found 325.1062

**Synthesis (Z)-7-((triisopropylsilyl)ethynyl)-3 ((triisopropylsilyl)methylene)isobenzofuran-1(3H)-one (8a)**

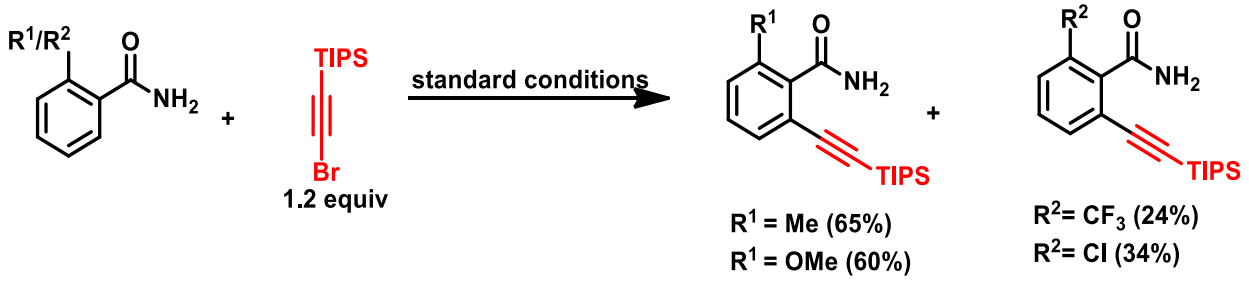



By following a reported procedure.[2] To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar, alkynylated amide ( 0.20 mmol) and 1.25 M HCl in MeOH (2 mL) were added. The mixture was stirred for 24 hrs at 80 °C (bath temperature) followed by cooling to room temperature. The mixture was concentrated in vacuo followed by the addition of EtOAc (15 mL) and saturated aq. $NaHCO_3$ (10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine solution (10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated in vaccum. The residue was purified by column chromatography on silica gel to afford 8**a** (58.5 mg, 62% yield). Mp 100-102$^oC$; $R_f$ (Hexane ) = 0.8; IR(ATR): 2940, 2863, 2147, 1785, 1641, 1588, 1460, 1237, 972 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.4, 4.1 Hz, 1H), 7.62 (d, *J* = 3.7 Hz, 2H), 5.56 (s, 1H), 1.20 – 1.06 (m, 42H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.3, 155.7, 139.8, 134.8, 133.5, 124.6, 121.7, 120.3, 100.9, 100.7, 100.5, 18.8, 18.6, 11.6, 11.3. HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{46}O_2Si_2$ $[M+H]^+$ 483.3109 found 483.3111.

**8. Procedure for Intermolecular Competition Experiment.**

To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar was sequentially electron withdrawing benzamide (0.1 mmol, 1.0 equiv), electron donating benzamide (0.1 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene}]_2$ (2.5 mol %), NaOAc (20 mol %), $Ag_2CO_3$ (0.5 equiv). Then DCE

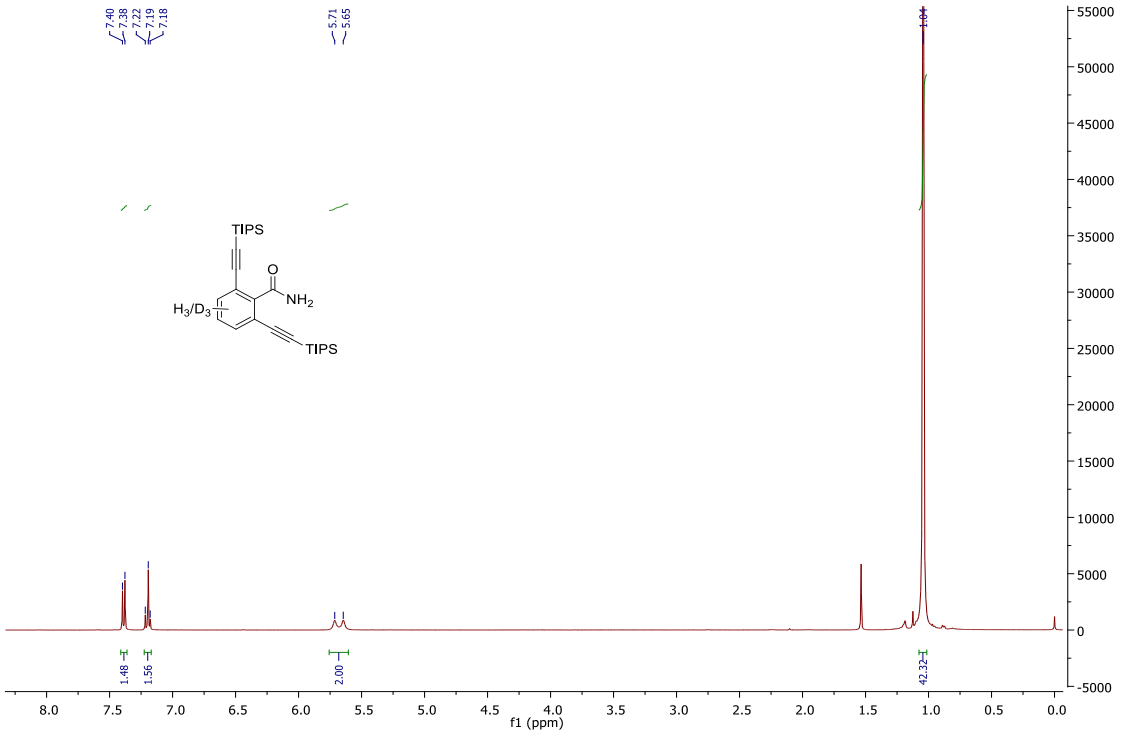
(1.5 mL) was added followed by addition of 1-bromo-2- (triisopropylsilyl)acetylene (1.2 equiv) into reaction mixture. Subsequently, $AgSbF_6$ (20 mol %) was added under a nitrogen atmosphere and the reaction tube was flushed with nitrogen. The tube was tightly closed and placed in a preheated oil bath at 60 $^oC$ and was stirred for 12h according to the conversion estimated by TLC. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite, and washed with DCM (20 mL x 3). The filtrate was concentrated and the product was purified by column chromatography using silica gel (100-200 mess) using ethyl acetate/hexanes as eluent.




**9. Procedure for Intermolecular Competition Experiment between (1a and 1a-$D_5$)**.

To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar was sequentially added benzamide (0.1 mmol, 1.0 equiv), deuterated benzamide (**1a-$D_5$**) (0.1 mmol, 1.0 equiv) $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), NaOAc (20 mol %), $Ag_2CO_3$ (1.0 equiv). Then DCE (1.5 mL) was added followed by addition of 1-bromo-2-(triisopropylsilyl)acetylene (2.2 equiv) into reaction mixture. Subsequently, $AgSbF_6$ (20 mol %) was added under a nitrogen atmosphere and the reaction tube was flushed with nitrogen. The tube was tightly closed and placed in a preheated oil bath and was stirred for 2h. After completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite,

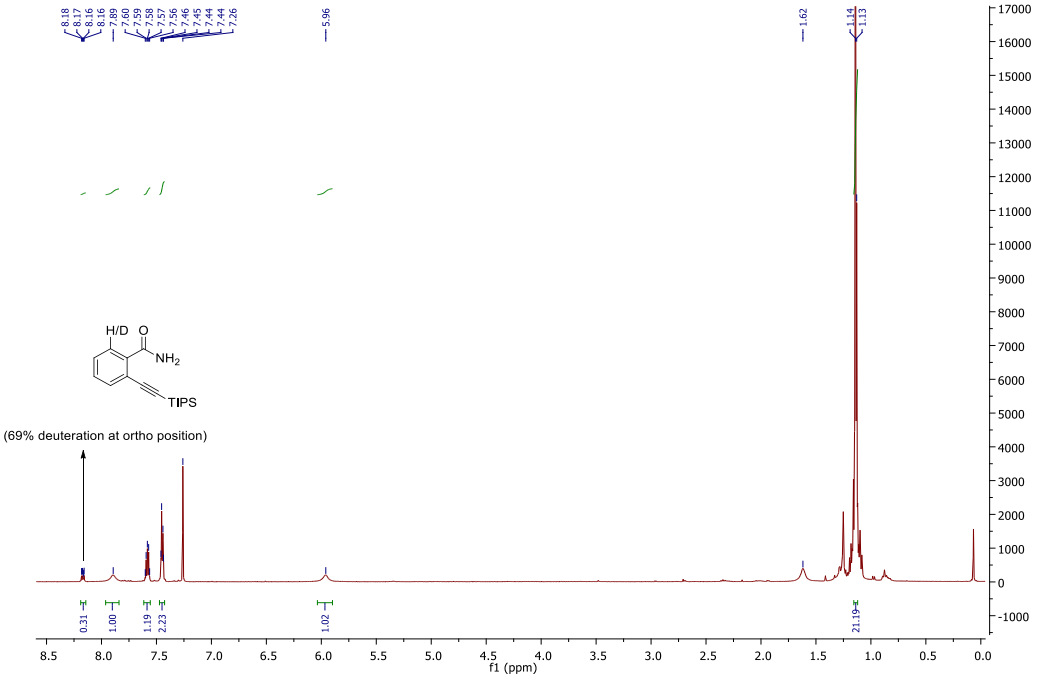
and washed with DCM (20 mL x 3). The filtrate was concentrated and the product was purified by column chromatography using silica gel (100-200 mess) using ethyl acetate/hexanes as eluent to give 62% of the product in combined yield. The ratio of **5a** and **5a-D$_3$** was determined by $^1$H NMR analysis, found to be $k_H/k_D \approx 2.84:1$




**10. Procedure for H/D exchange experiment with TIPS-protected Bromoacetylene in CD$_3$COOD:**

To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar was sequentially added benzamide (0.1 mmol, 1.0 equiv), [RuCl$_2$(*p*-cymene]$_2$ (5 mol %, 7.6 mg), NaOAc (20 mol %), $Ag_2CO_3$ (1.0 equiv). Then, DCE (1.5 mL) was added followed by addition of 1-bromo-2-(triisopropylsilyl)acetylene (2.2 equiv) and $CD_3COOD$ (150 µL) into reaction mixture. Subsequently, $AgSbF_6$ (20 mol %) was added under a nitrogen atmosphere and the reaction tube was flushed with nitrogen. The tube was tightly closed and placed in a preheated oil bath and

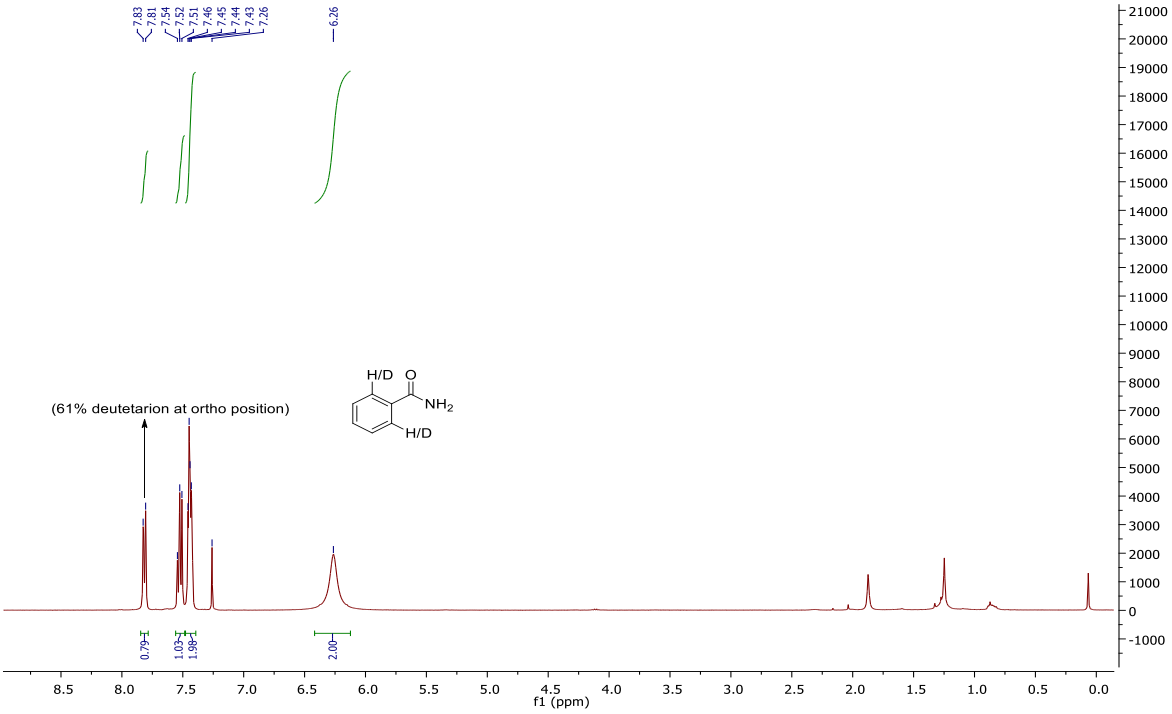
was stirred for 12. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite, and washed with DCM (20 mL x 3). The filtrate was concentrated and the product was purified by column chromatography using silica gel (100-200 mess) using ethyl acetate/hexanes as eluent. The amount of deuterium incorporation was determined by $^1$H NMR analysis. The di-alkynylated product was observed in 41% along with 24% mono-alkynylated product. The amount of deuterium incorporation in mono-alkynylated product was found to be 69%.




**11. Procedure for H/D exchange experiment without TIPS-protected Bromoacetylene in $CD_3COOD$.**

To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar was sequentially added benzamide (0.1 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene}]_2$ (5 mol %, 3.05 mg), NaOAc (20 mol %), $Ag_2CO_3$ (1.0 equiv). Then DCE (2.0 mL) was added followed by addition of

$CD_3COOD$ (150 µL) into reaction mixture. Subsequently, $AgSbF_6$ ( 20 mol %) was added under a nitrogen atmosphere and the reaction tube was flushed with nitrogen. The tube was tightly closed and placed in a preheated oil bath and was stirred for 12h. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite, and washed with DCM (20 mL x 3). The filtrate was concentrated and the product was purified by column chromatography on silica gel (100-200 mess) using ethyl acetate/hexanes as eluent to give 61% of *ortho*-deuterated starting material. The amount of deuterium incorporation was determined by $^1H$ NMR analysis.




**12. Procedure for radical inhibition experiment:**

To a clean oven-dried 15 mL sealed tube equipped with magnetic stir bar was sequentially added benzamide (0.1 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene}]_2$ (5 mol %,), NaOAc (20 mol %), $Ag_2CO_3$ (1.0 equiv) and TEMPO/BHT (0.15 mmol 1.5 equiv). Then DCE (1.5 mL) was added followed

by addition of 1-bromo-2- (triisopropylsilyl)acetylene (2.2 equiv) into reaction mixture. Subsequently, $AgSbF_6$ (20 mol %) was added under a nitrogen atmosphere and the reaction tube was flushed with nitrogen. The tube was tightly closed and placed in a preheated oil bath and was stirred for 12h. The reaction was monitored by TLC and after completion, the reaction mixture was cooled to room temperature, and diluted with DCM (10 mL), then filtered through a short pad of celite, and washed with DCM (20 mL x 3). The filtrate was concentrated and the product was purified by column chromatography using silica gel (100-200 mess) using ethyl acetate/hexanes as eluent. The desired product **5a** was obtained in 52% and 46% yield respectively, with TEMPO and BHT along with mono-alkynylated products.

## 13. References


1. (a) Moorthy, J. N.; Singhal, N. Facile and highly selective conversion of nitriles to amides via Indirect acid-catalyzed hydration using TFA or AcOH−$H_2SO_4$. *J. Org.Chem.* **2005**, *70*, 1926-1929; (b) Veisi, H.; Maleki, B.; Hamelian, M.; Ashrafi, S. S. Chemoselective hydration of nitriles to amides using hydrated ionic liquid (IL) Tetrabutylammonium hydroxide (TBAH) as a green catalyst. *RSC Adv.* **2015**, *5*, 6365-6371.

2. Ano, Y.; Tobisu, M.; Chatani, N., Palladium-Catalyzed Direct *ortho*-Alkynylation of Aromatic Carboxylic Acid Derivatives. *Org. Lett*. **2012**, *14*, 354-357.

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## 14. NMR Data

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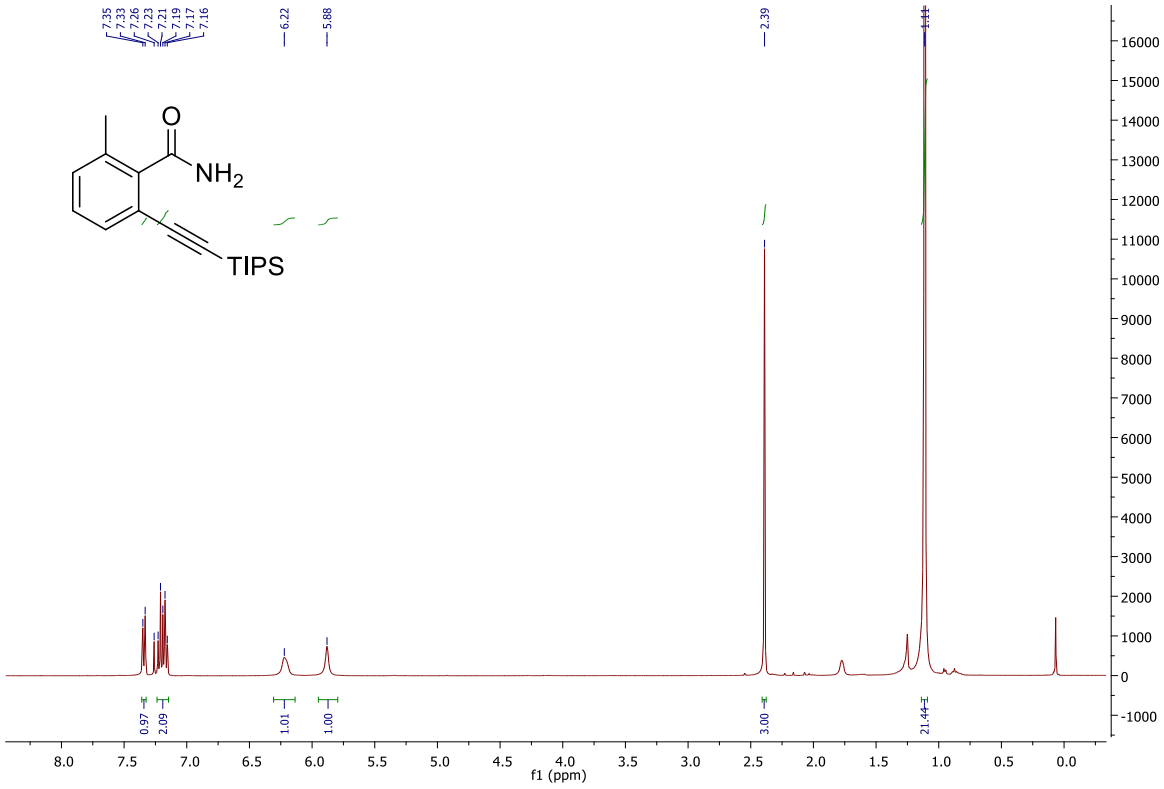


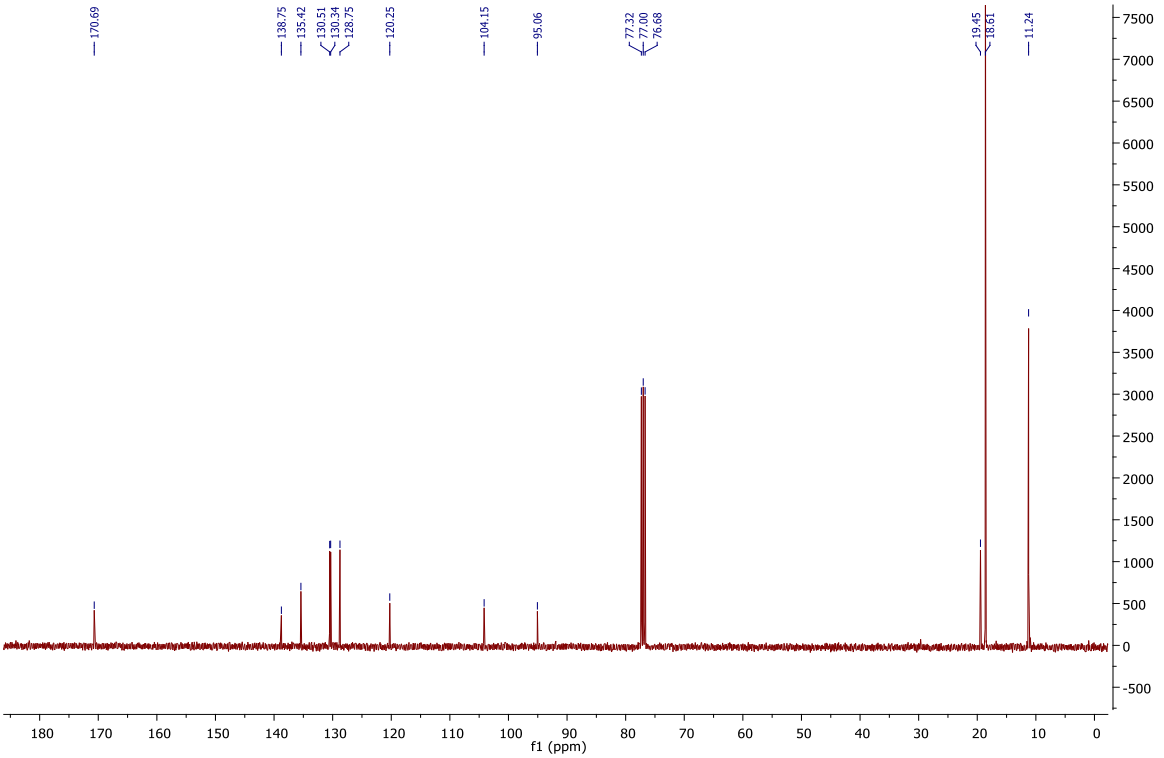

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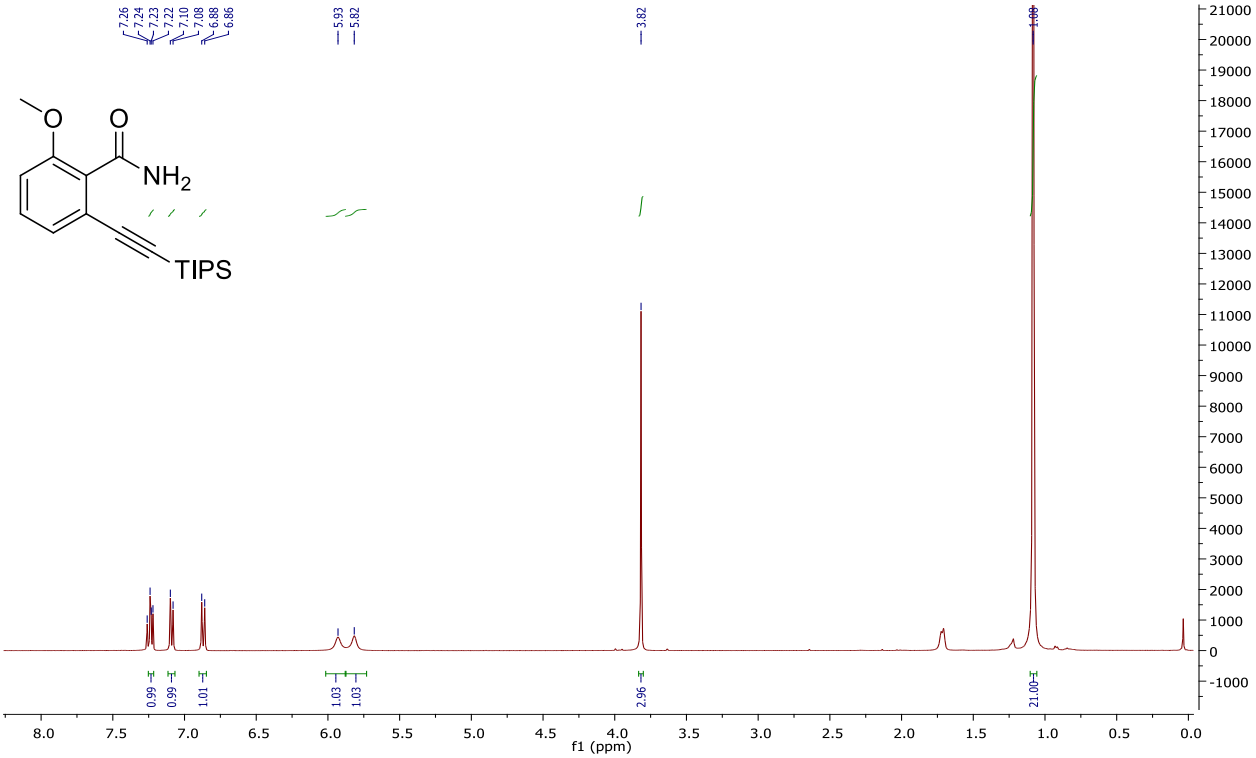


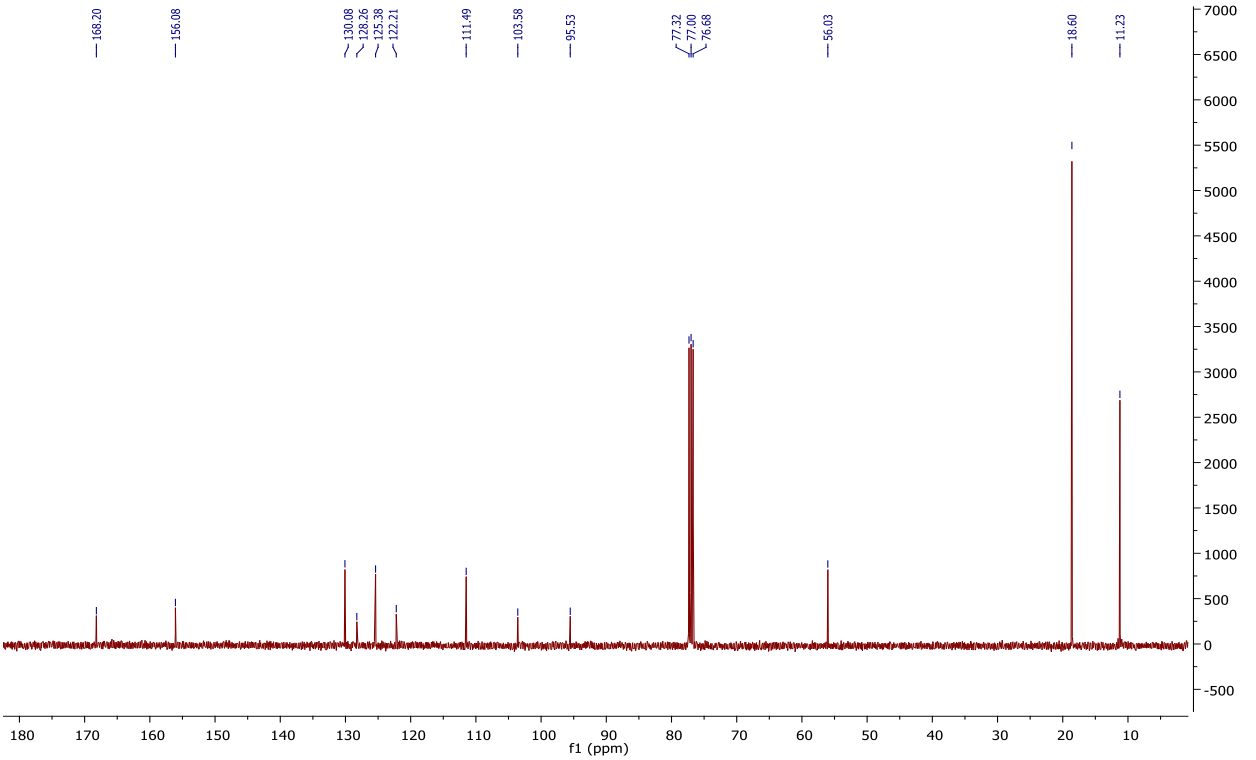

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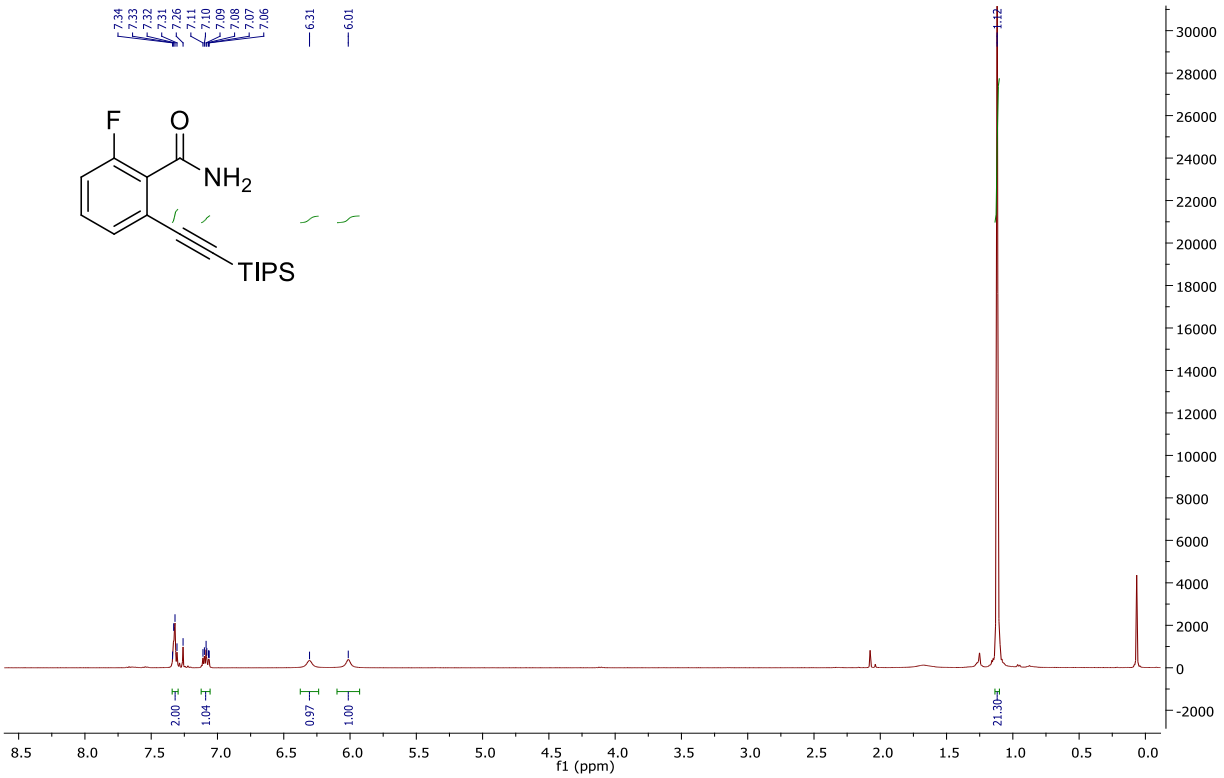


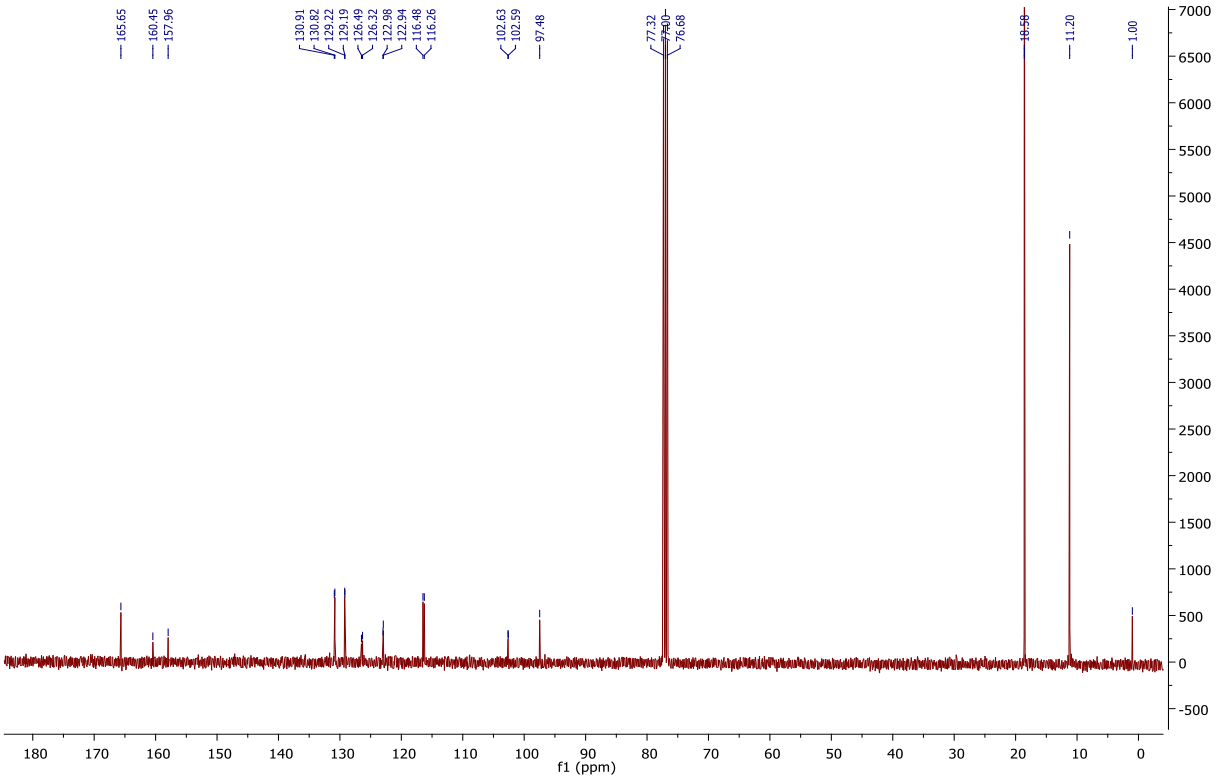

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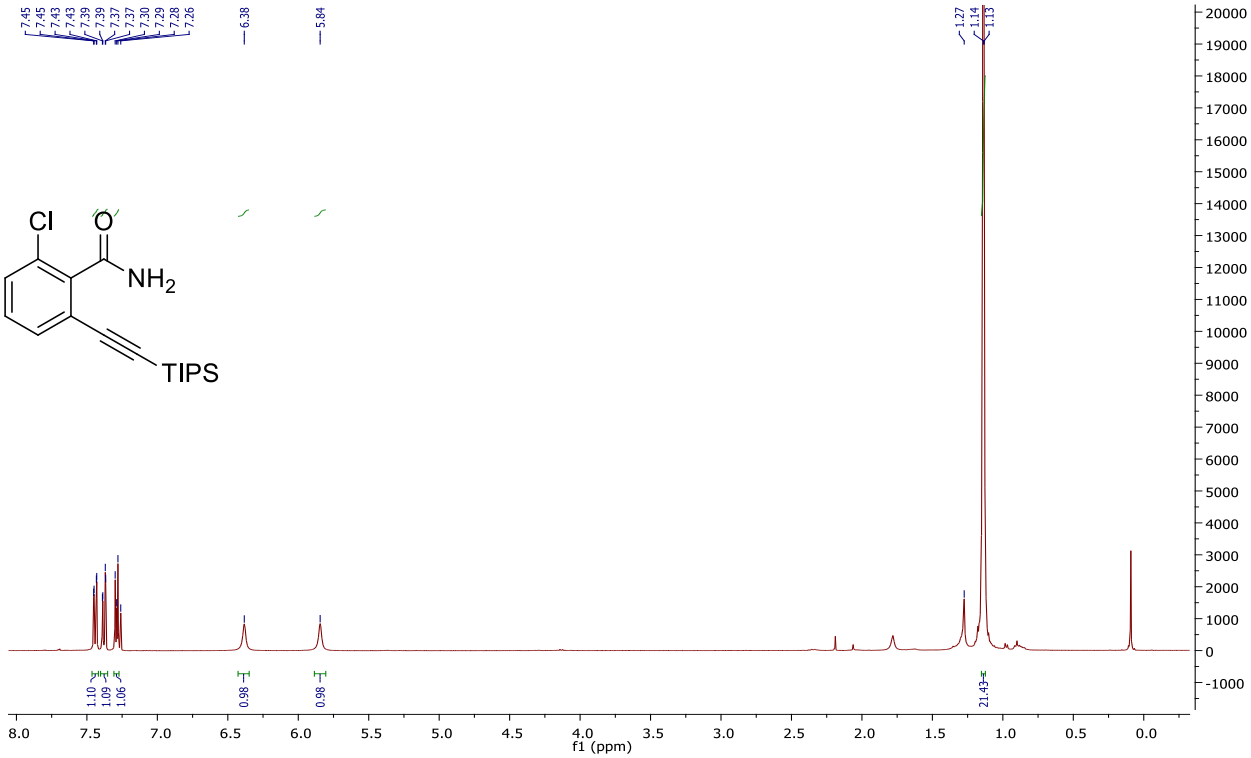


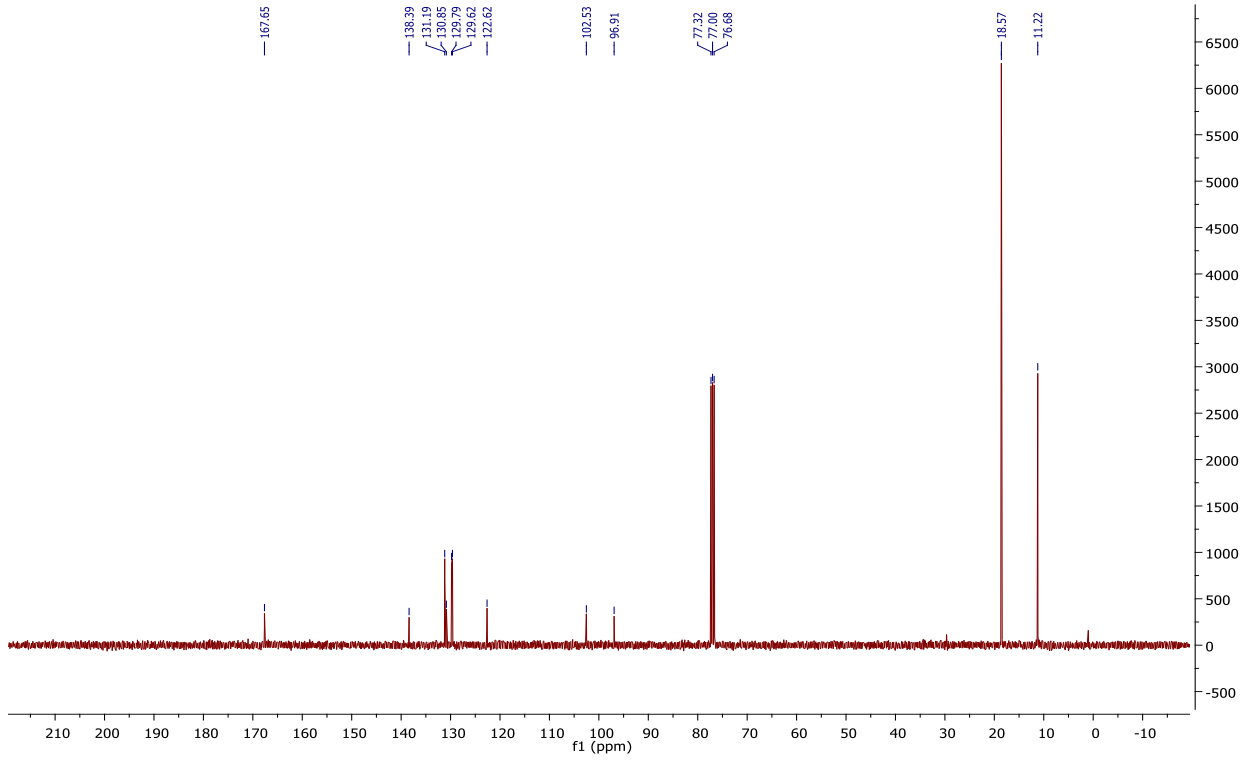

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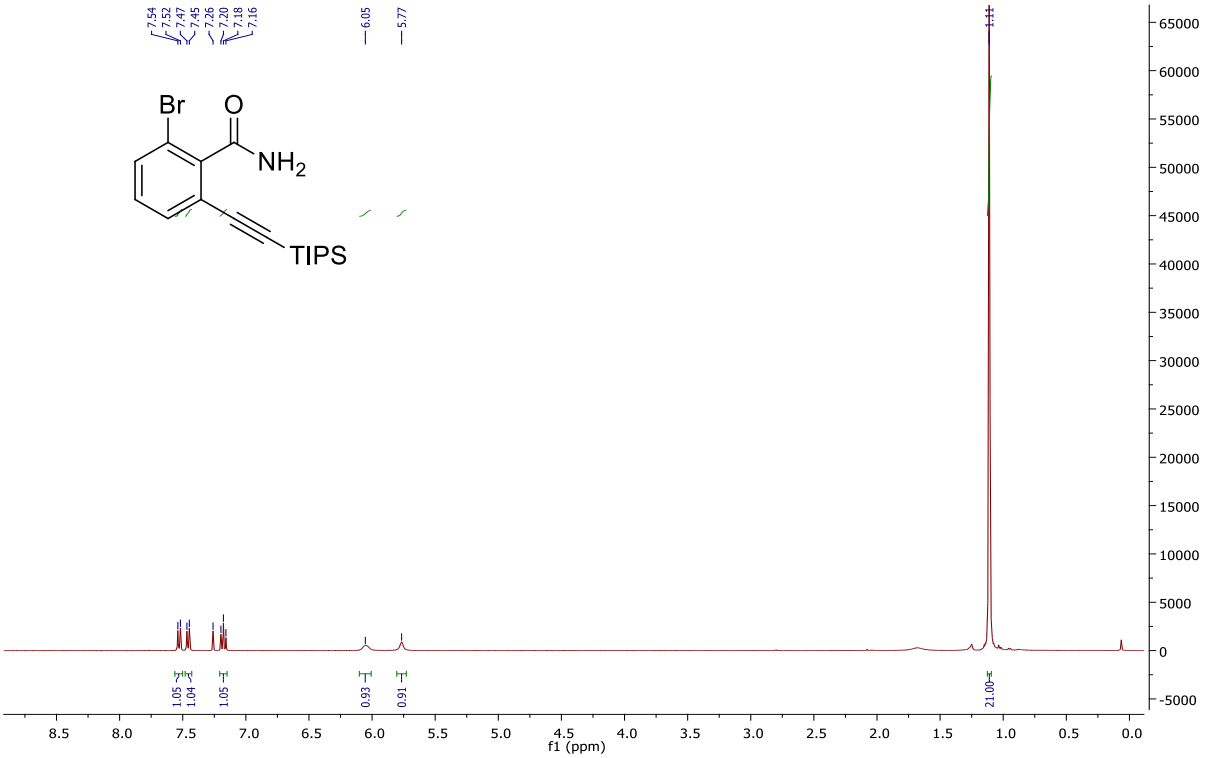


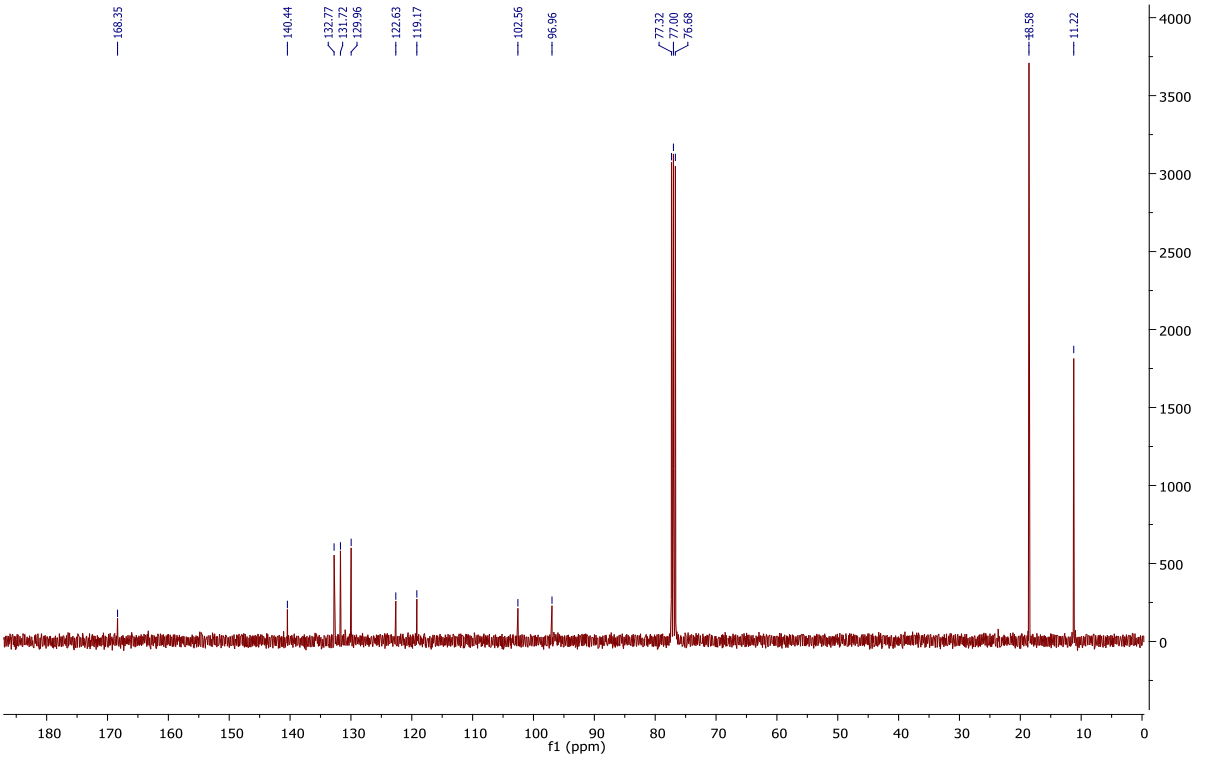

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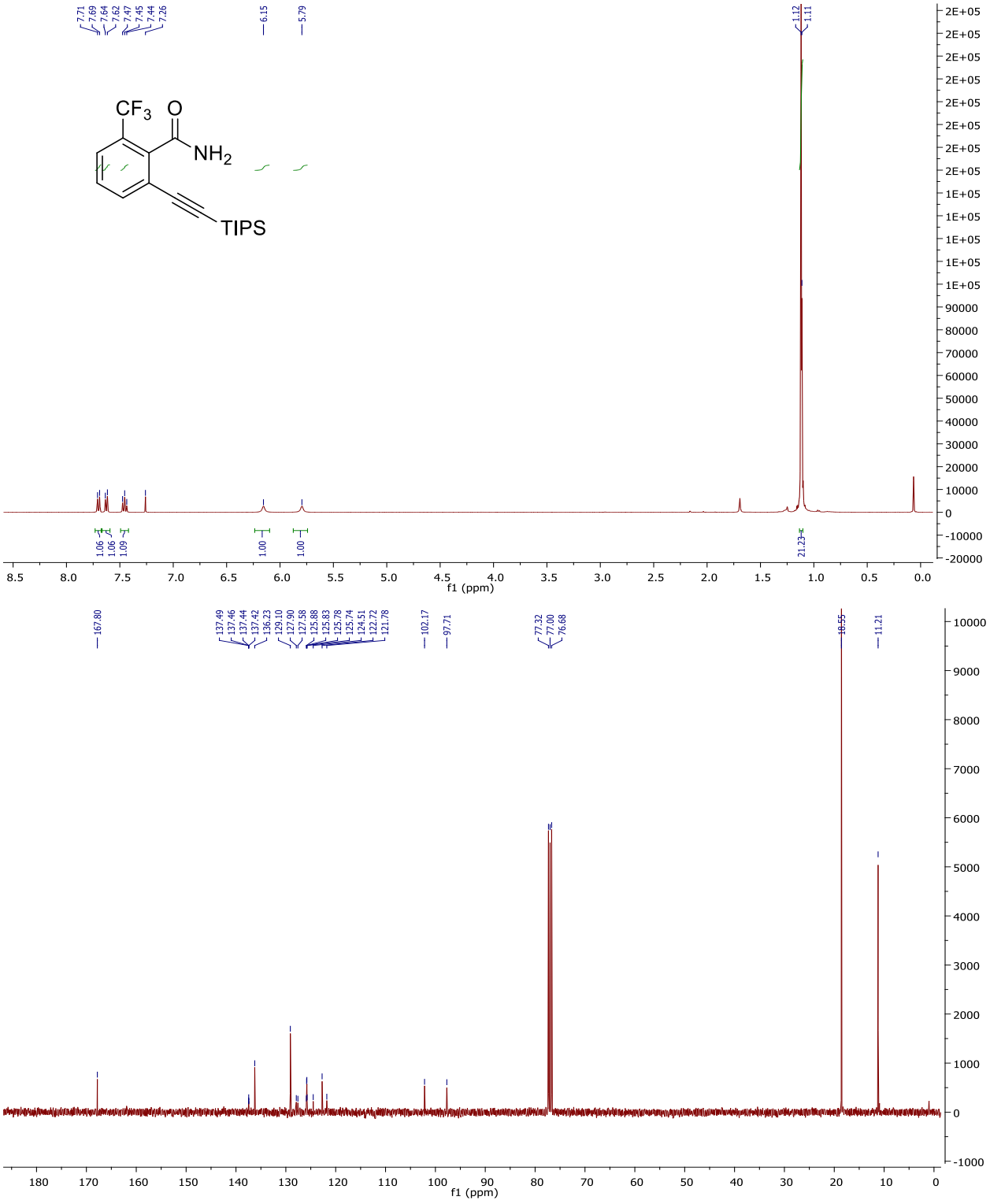

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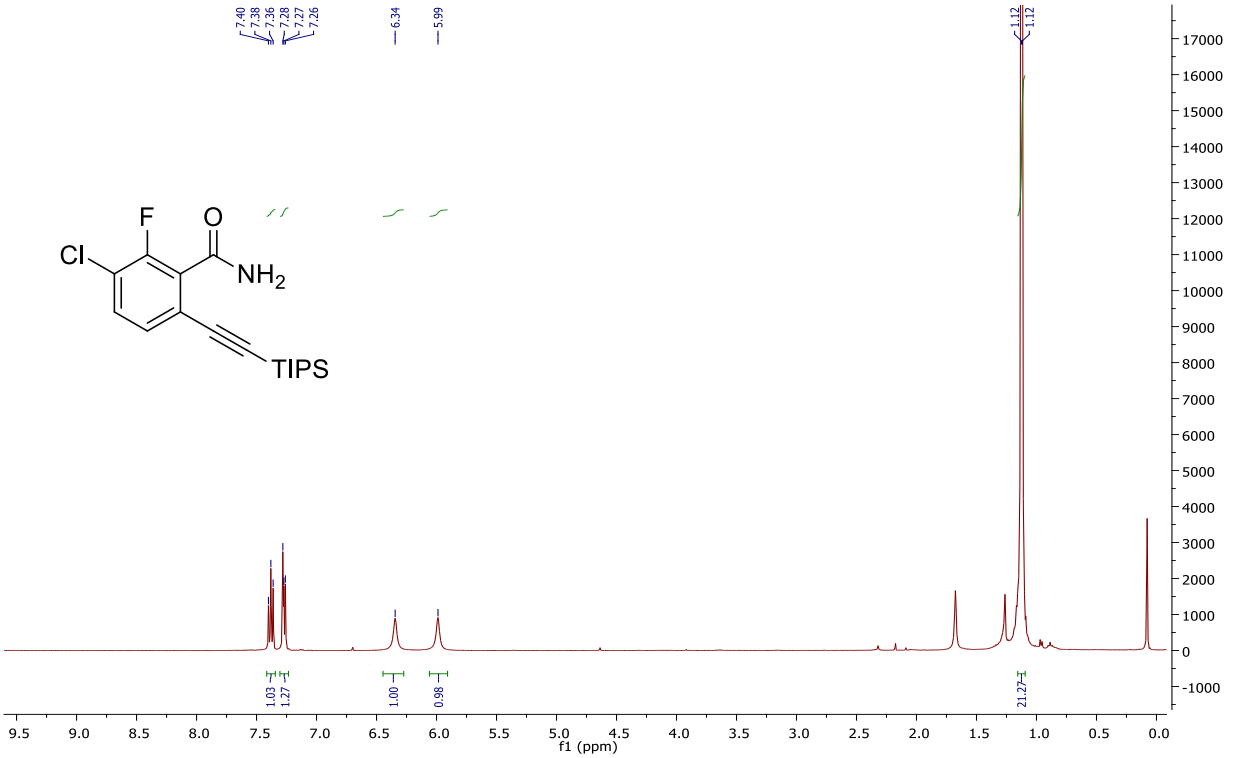


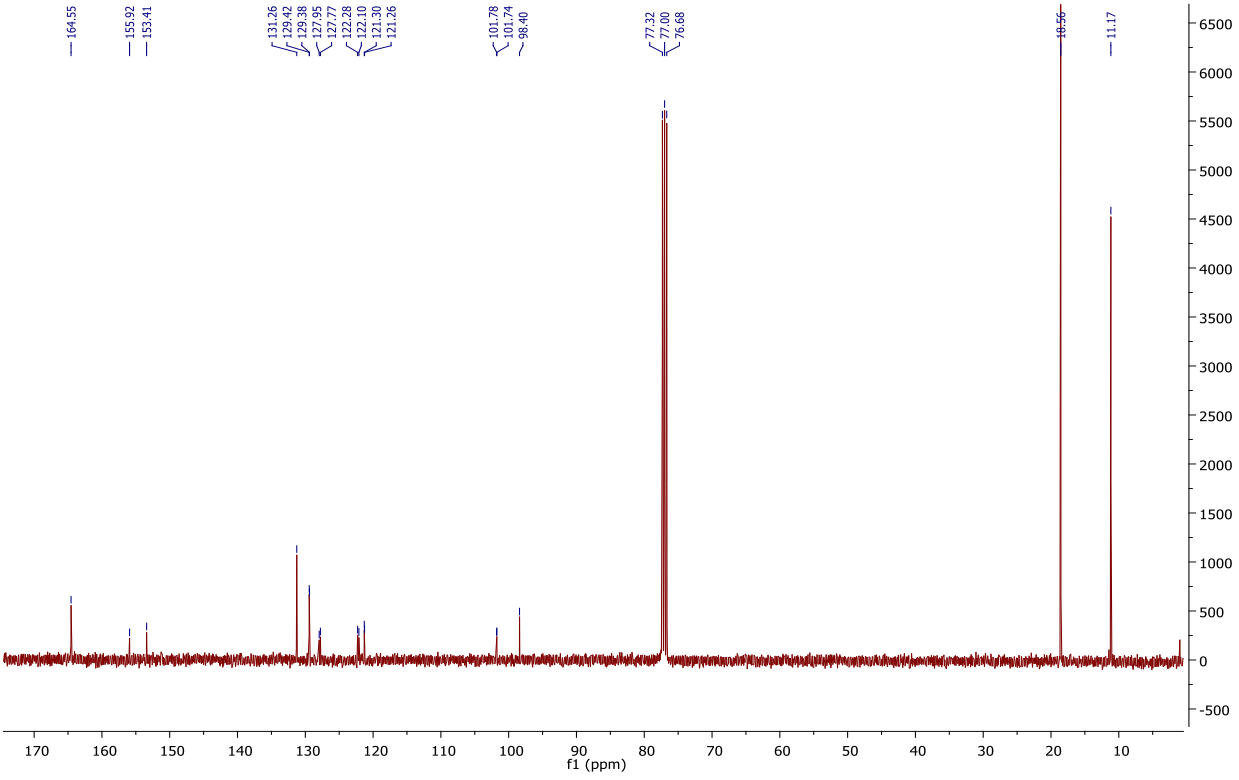

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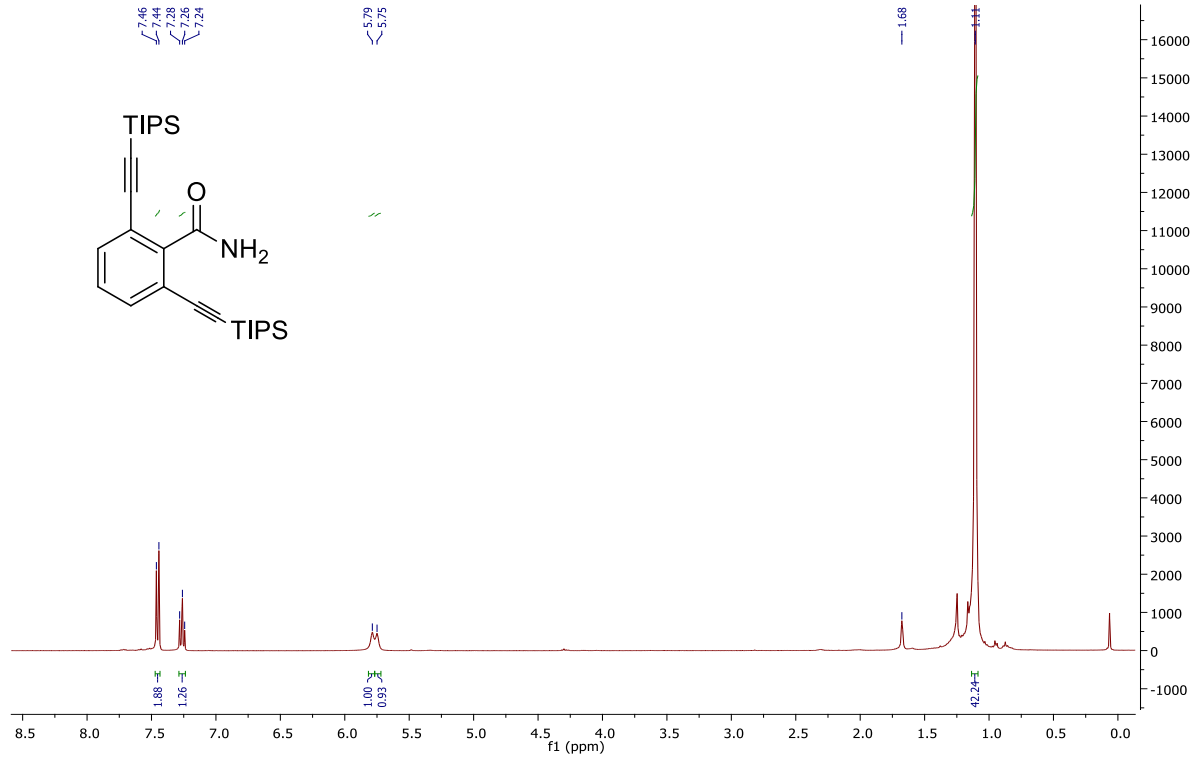


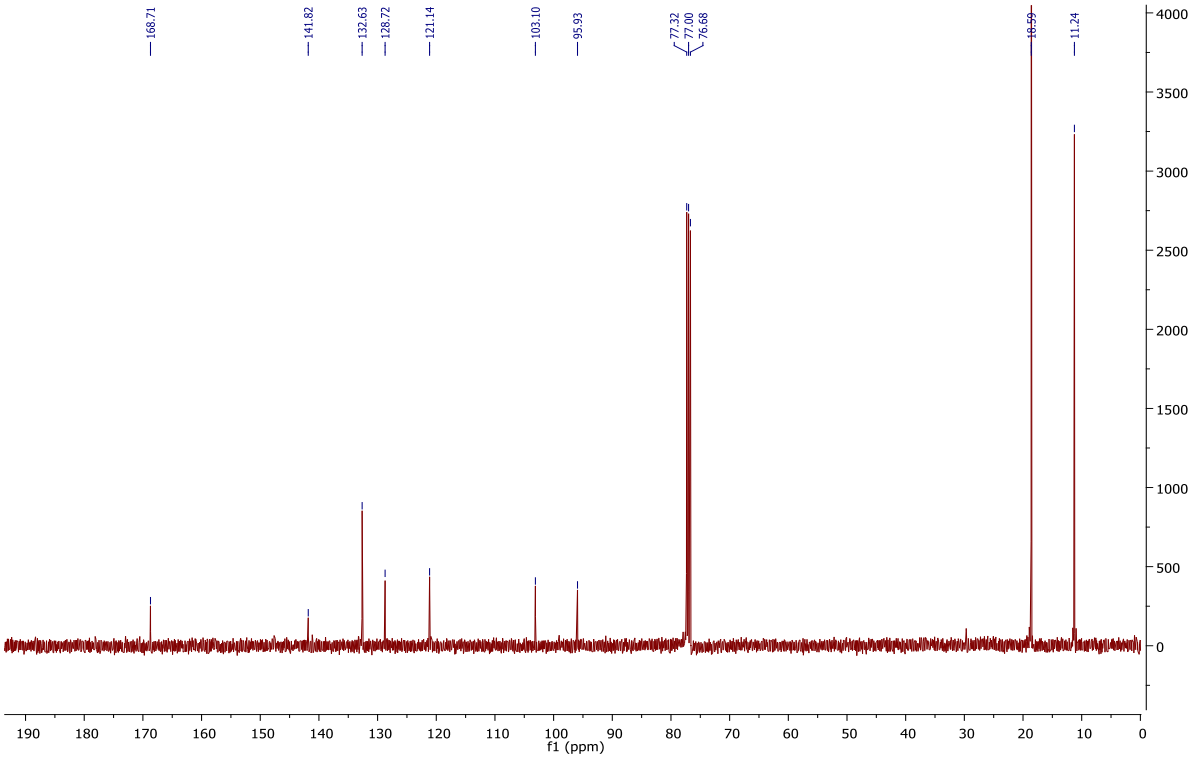

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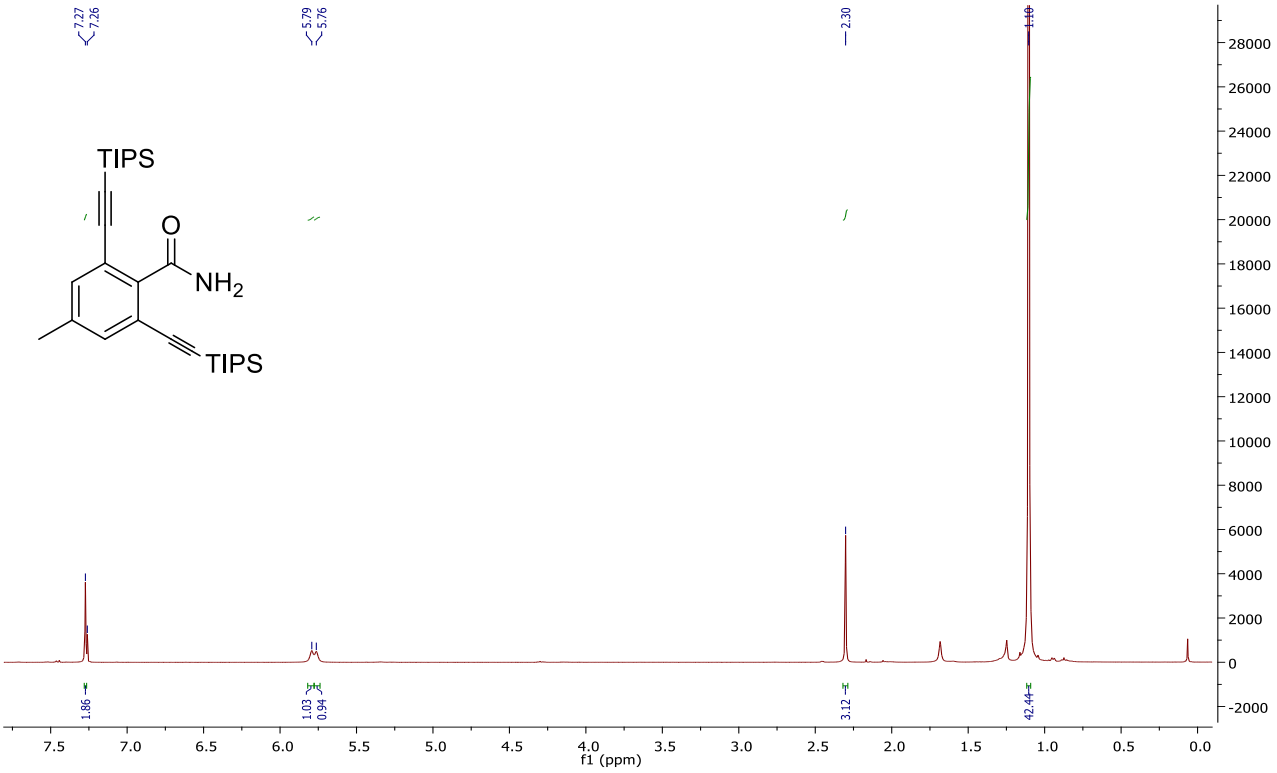


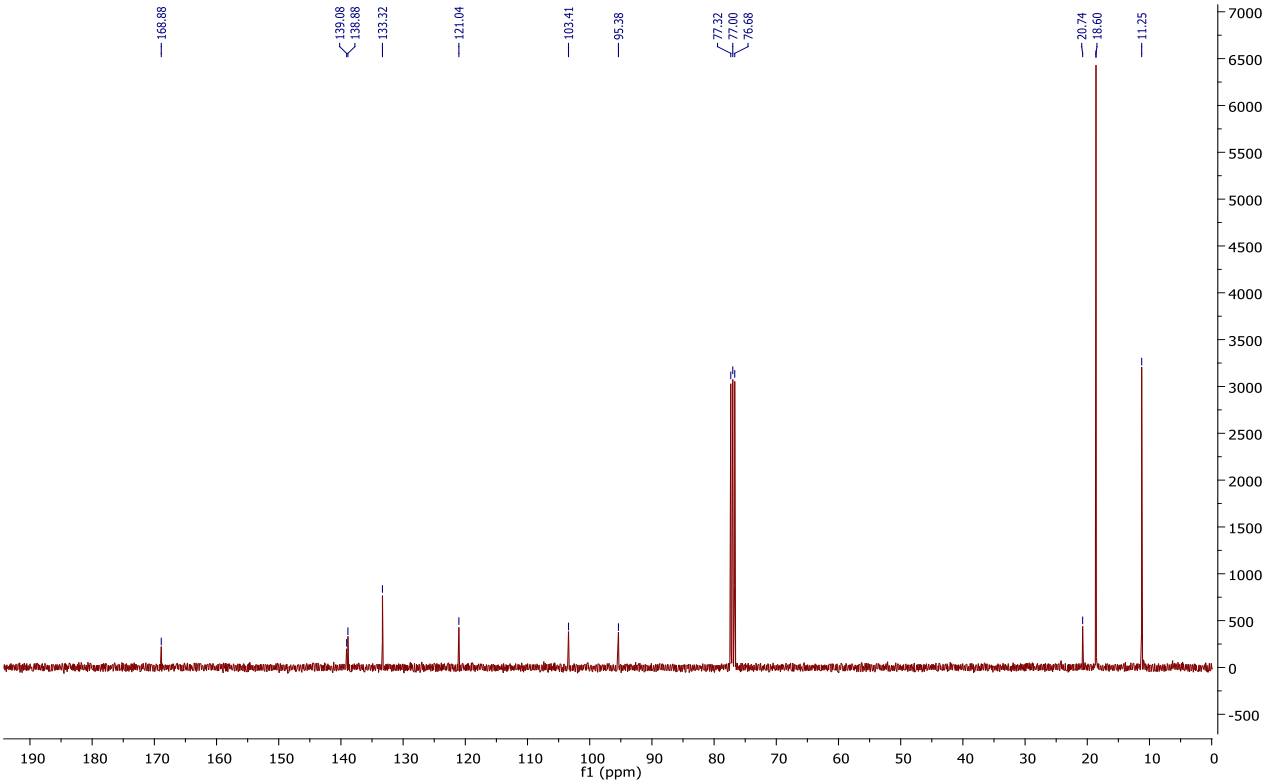

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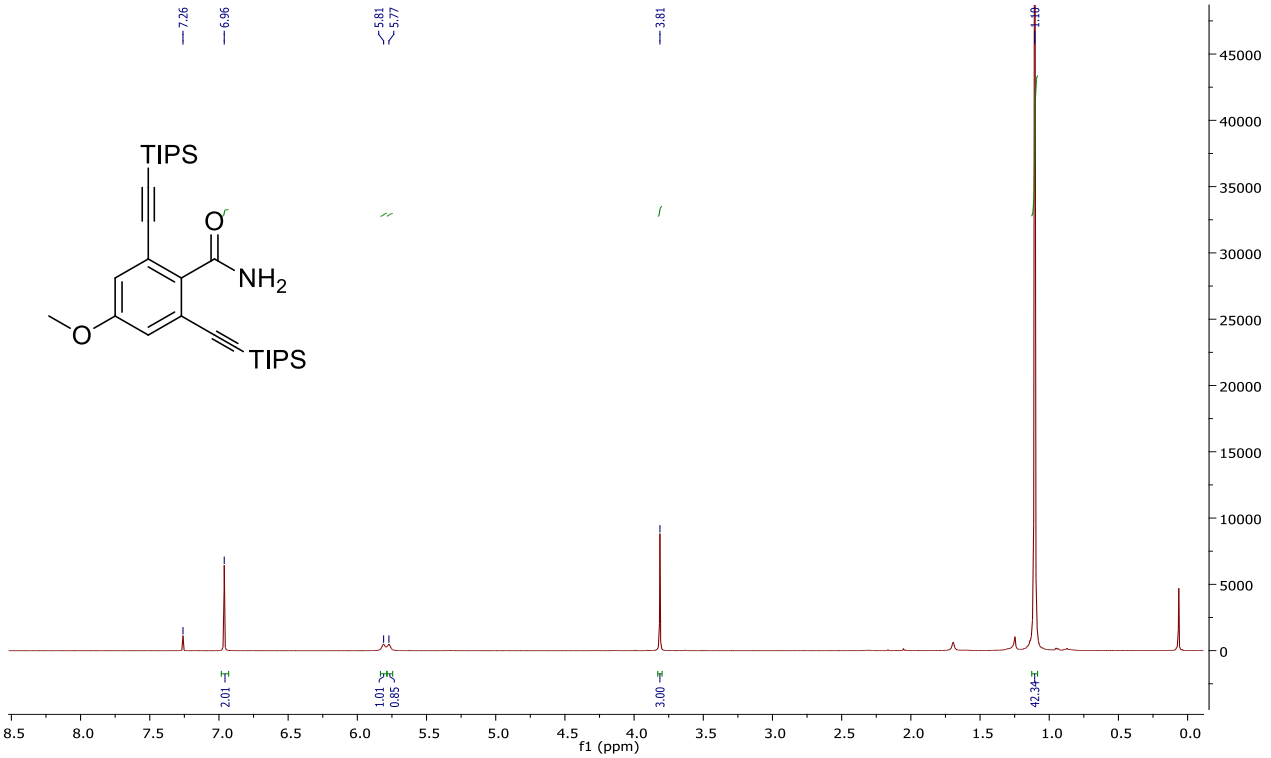


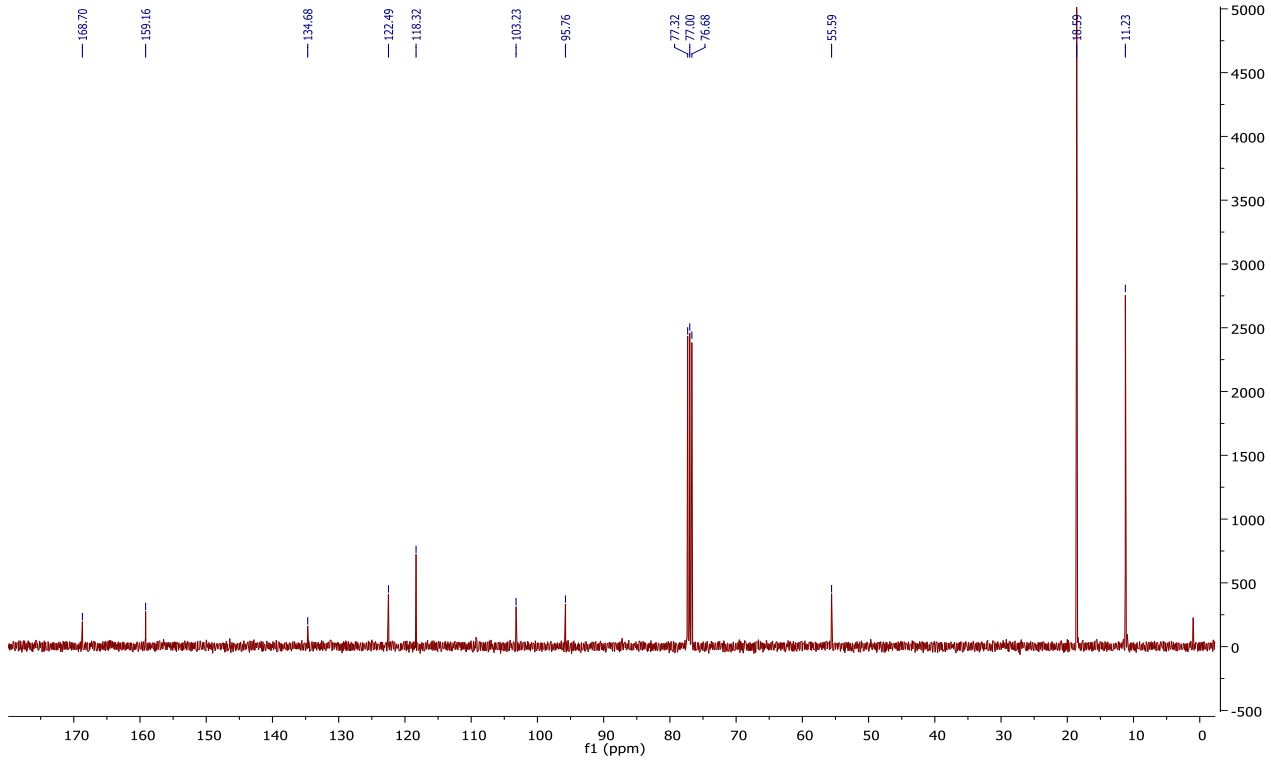

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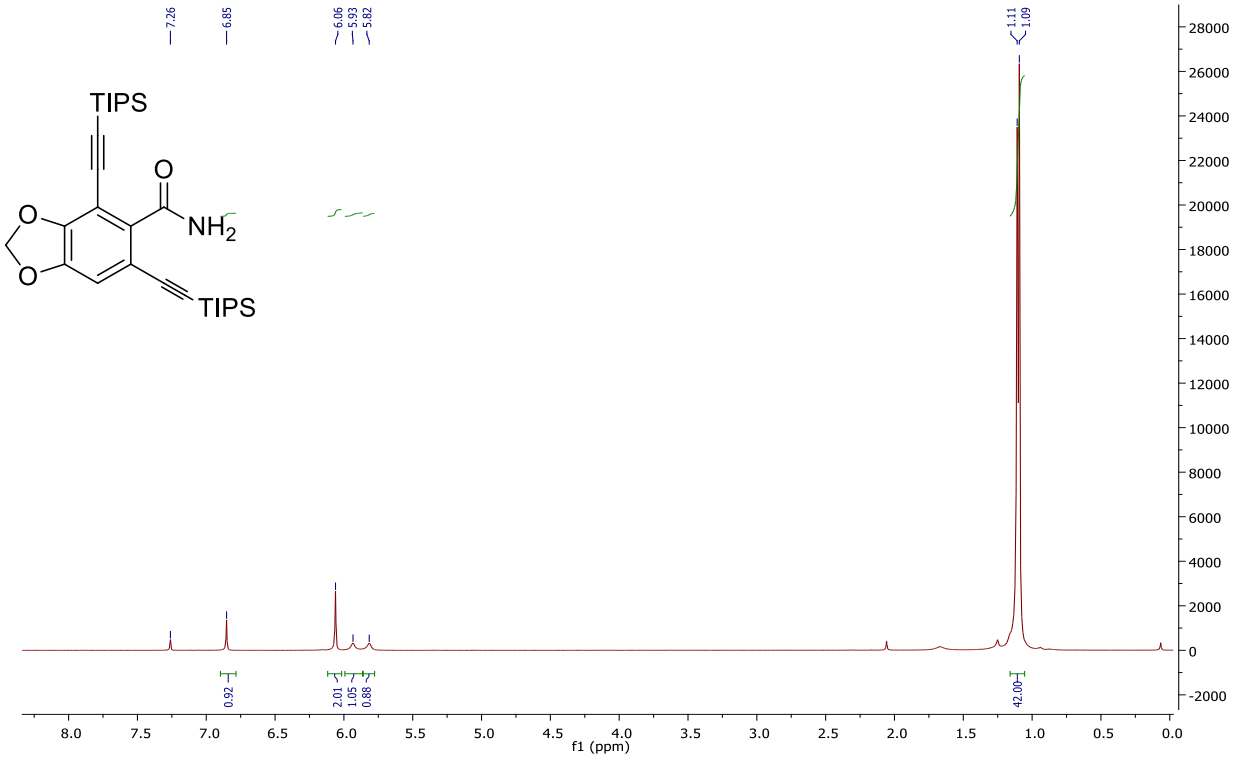


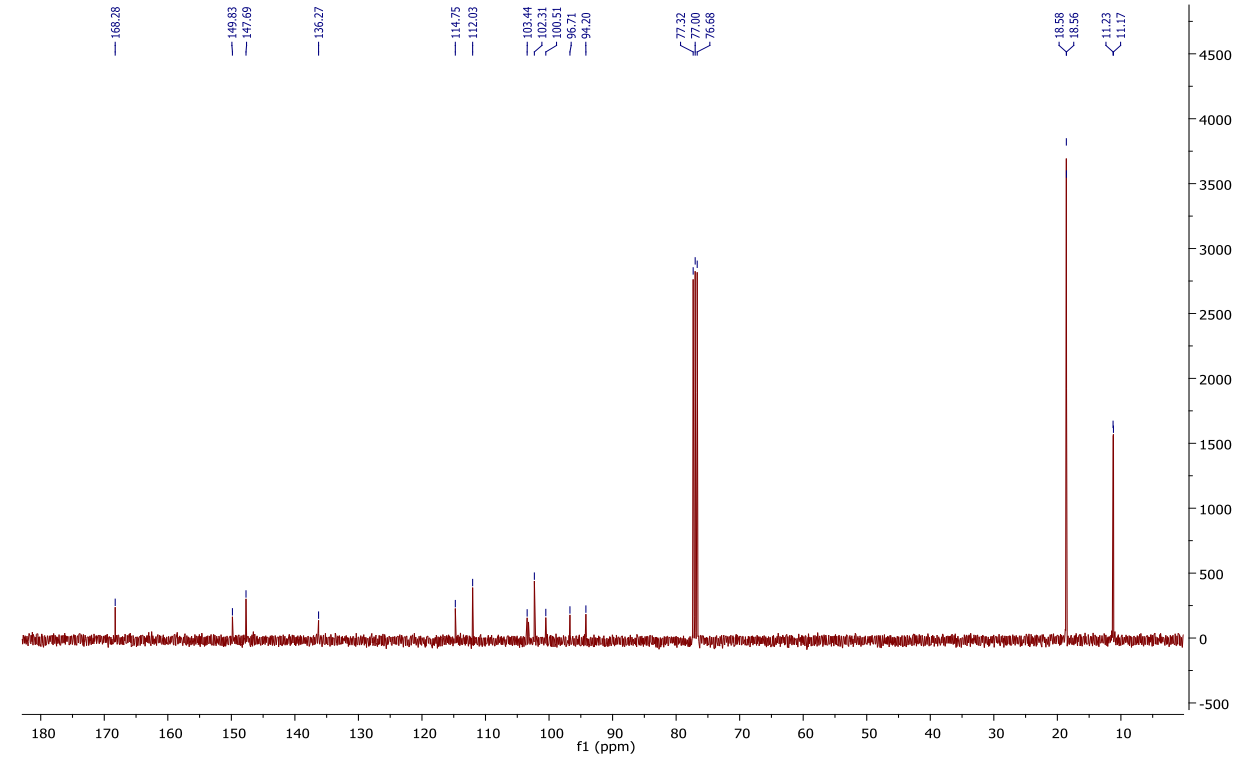

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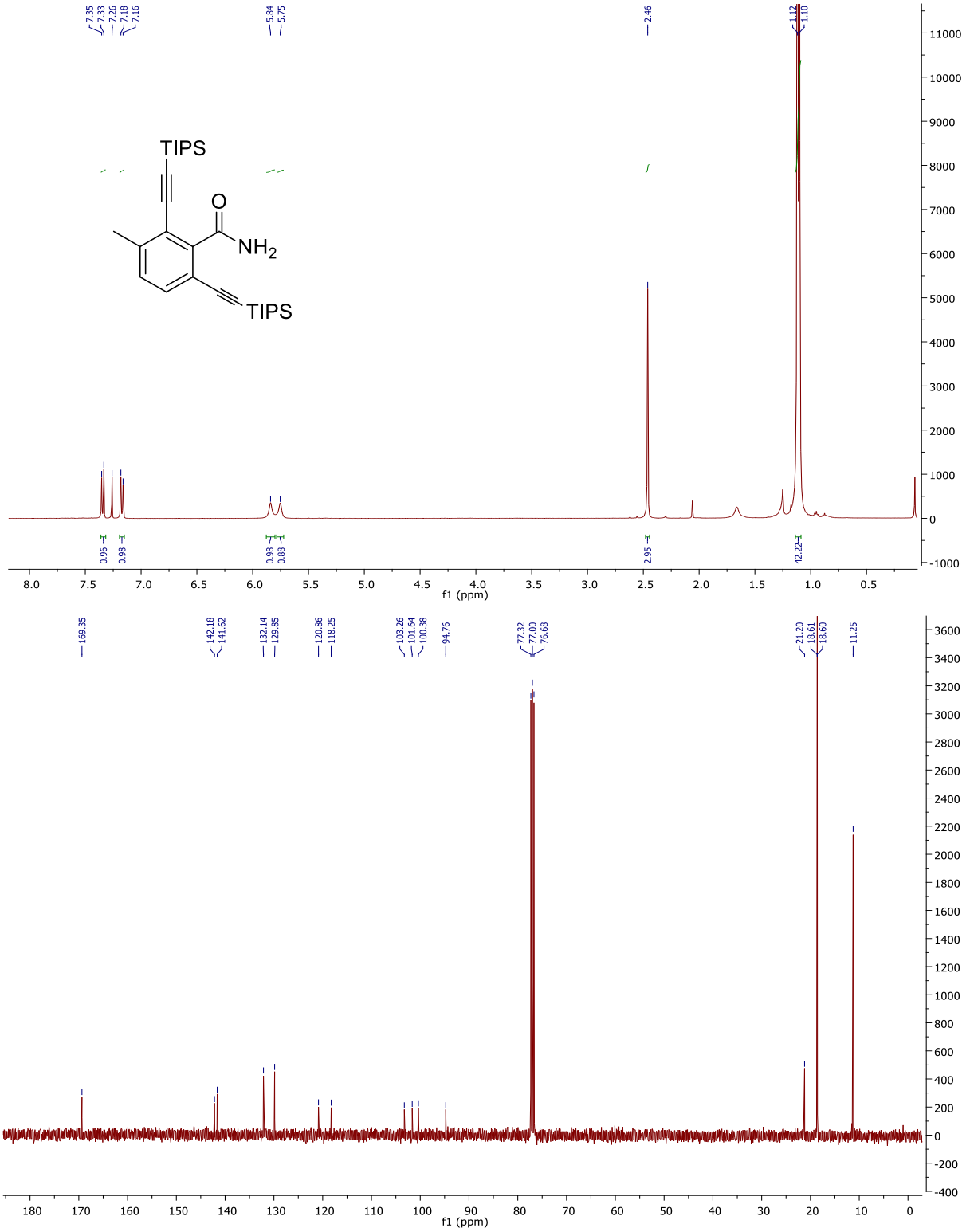

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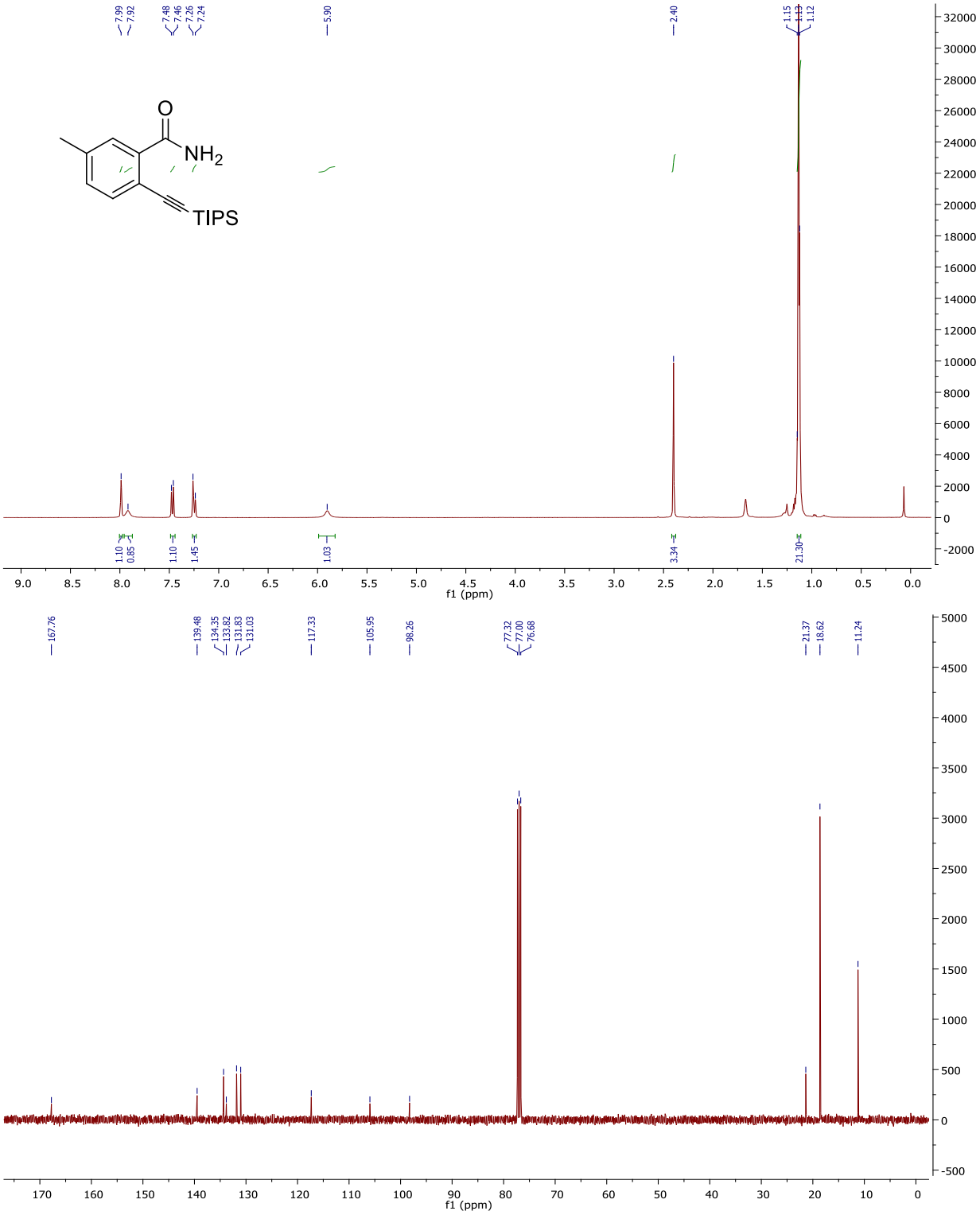

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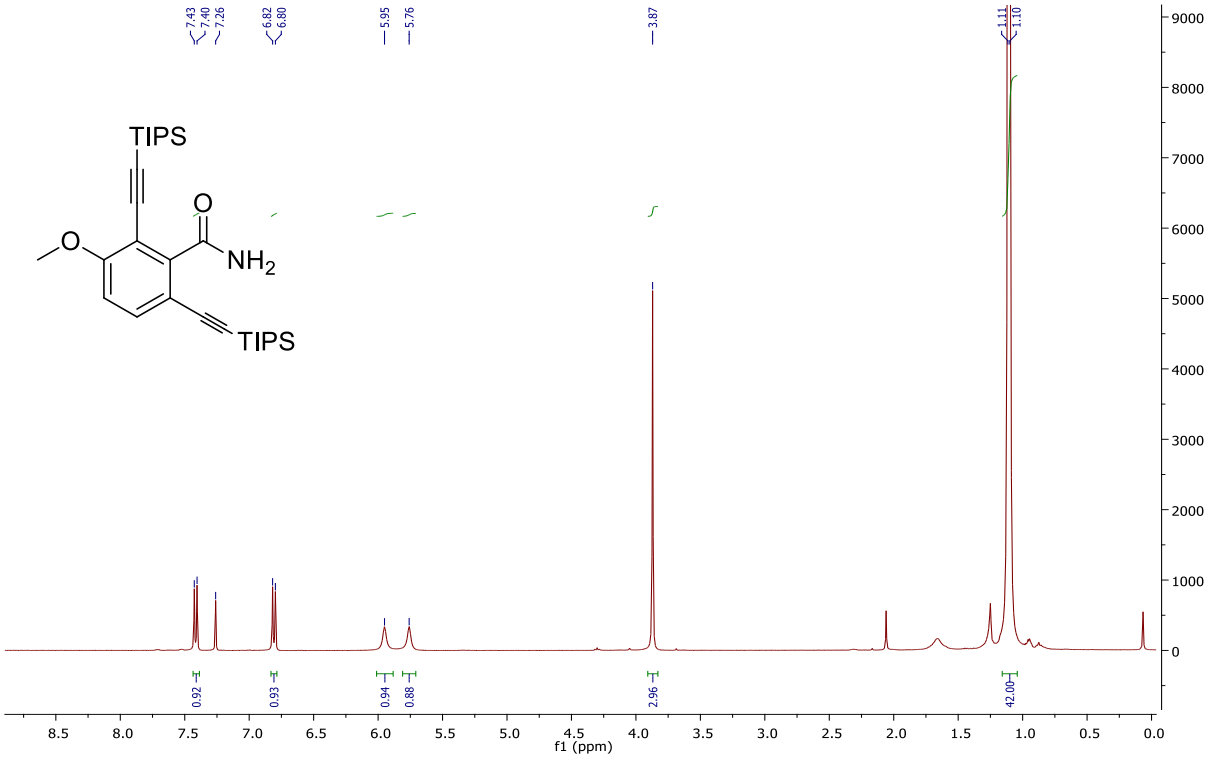


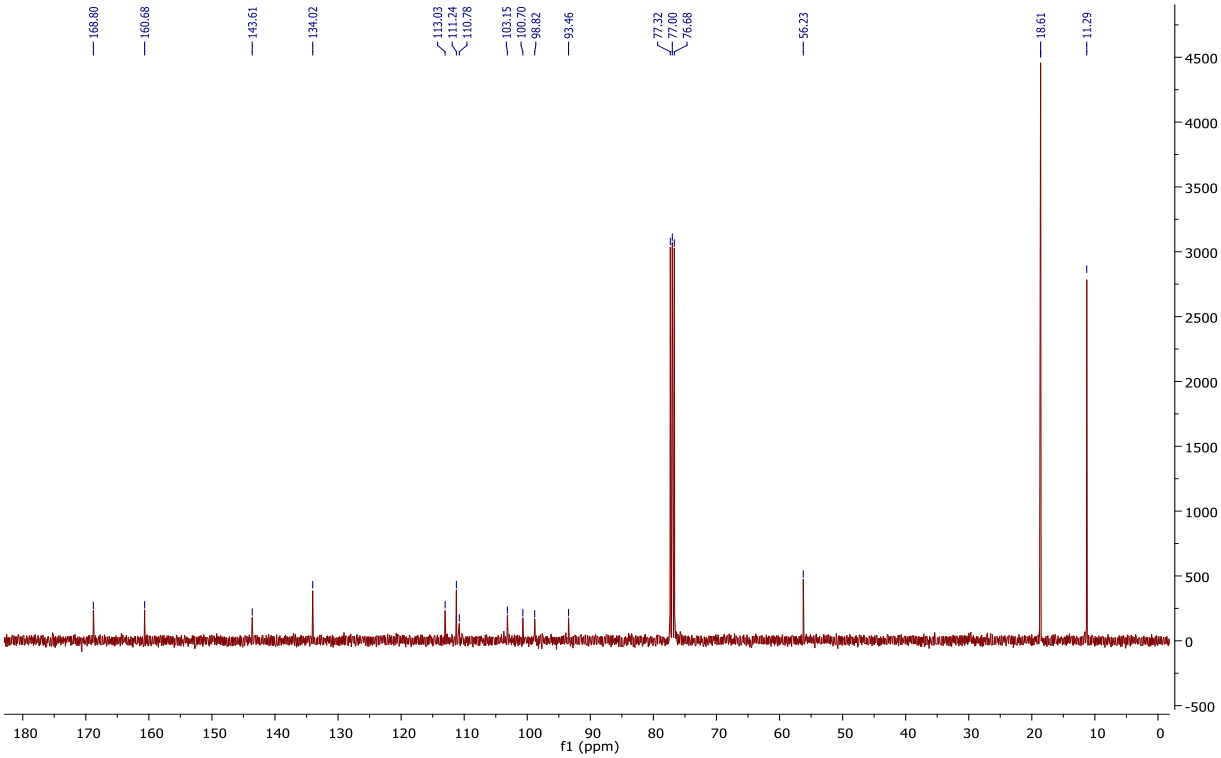

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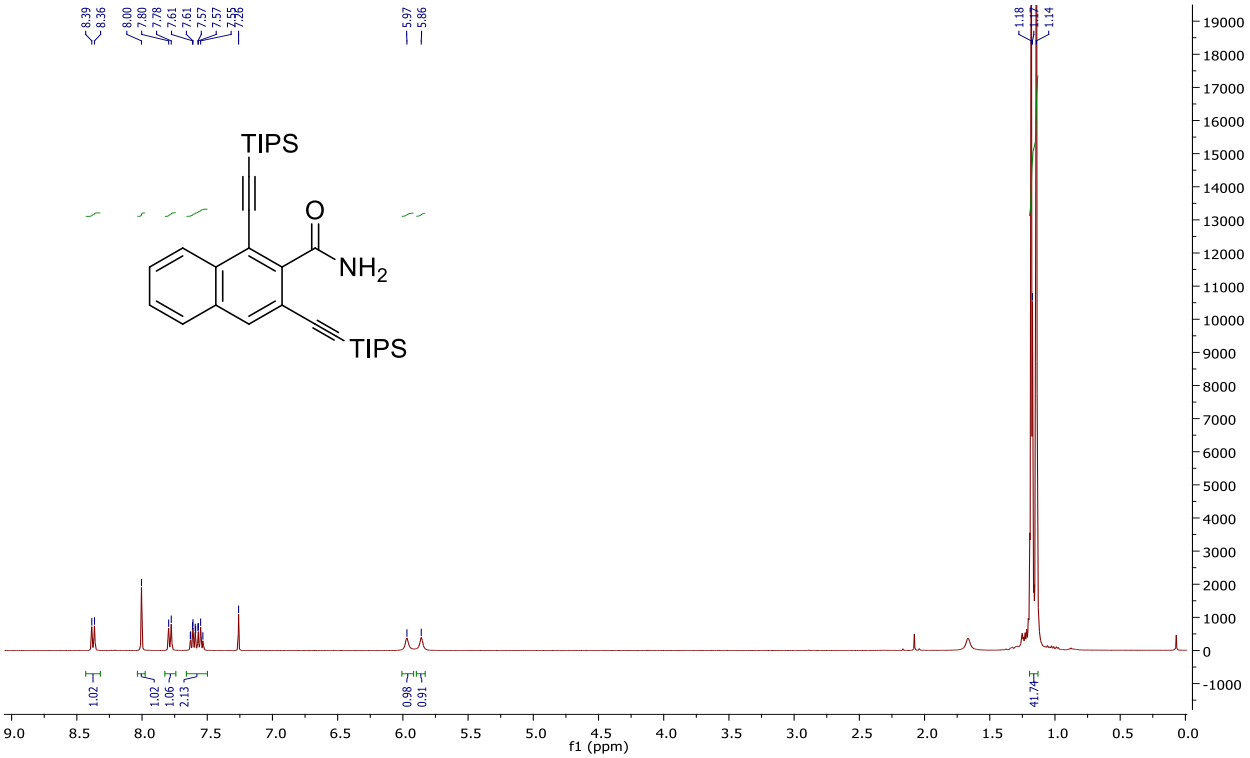


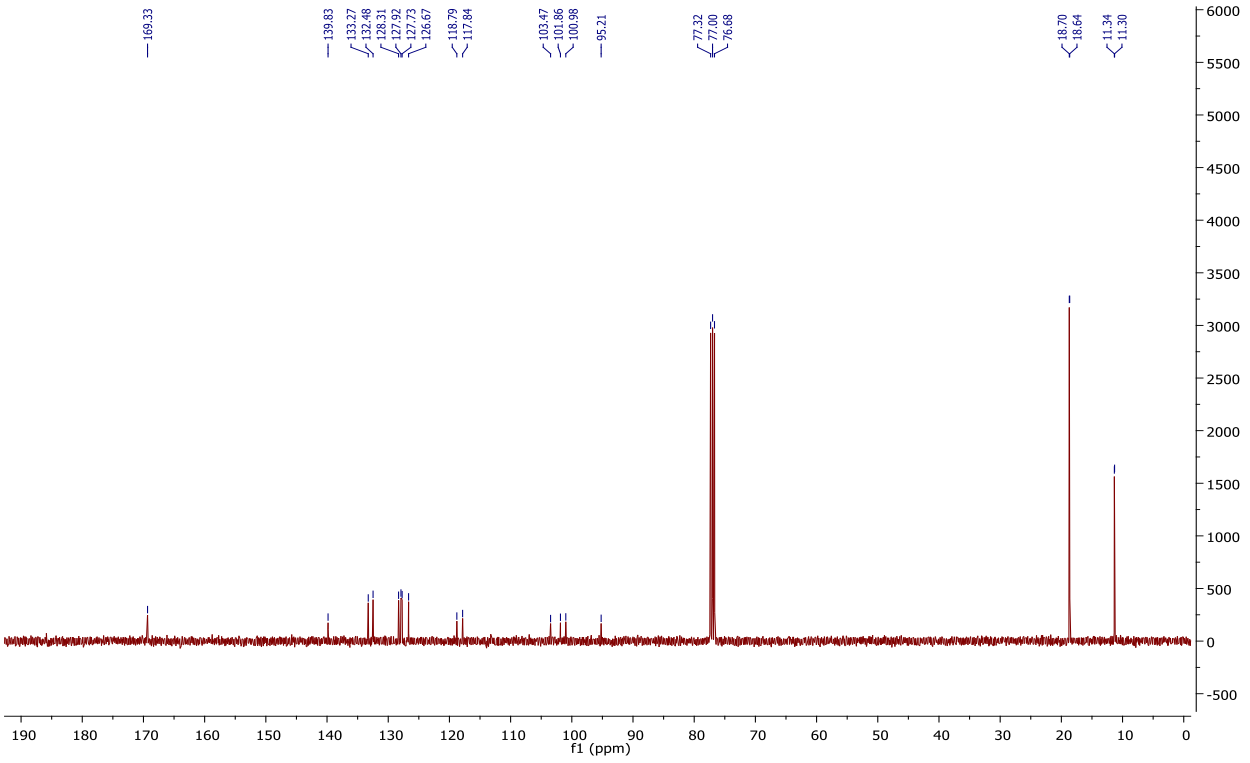

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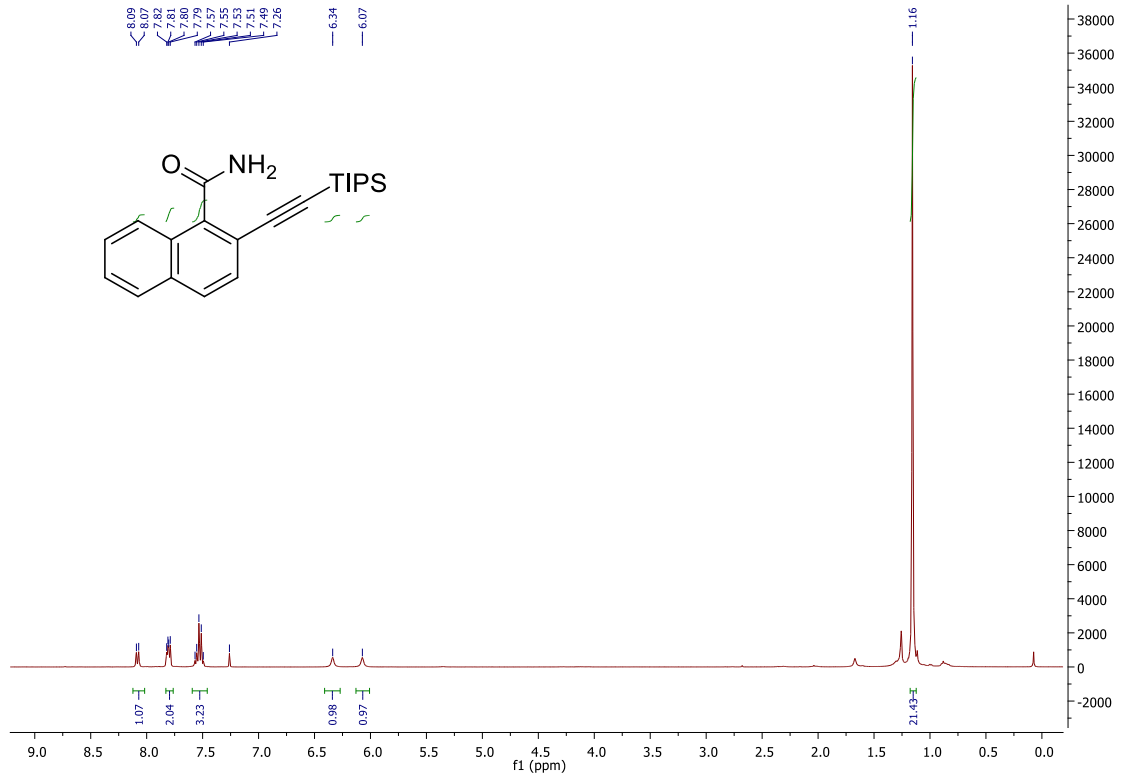


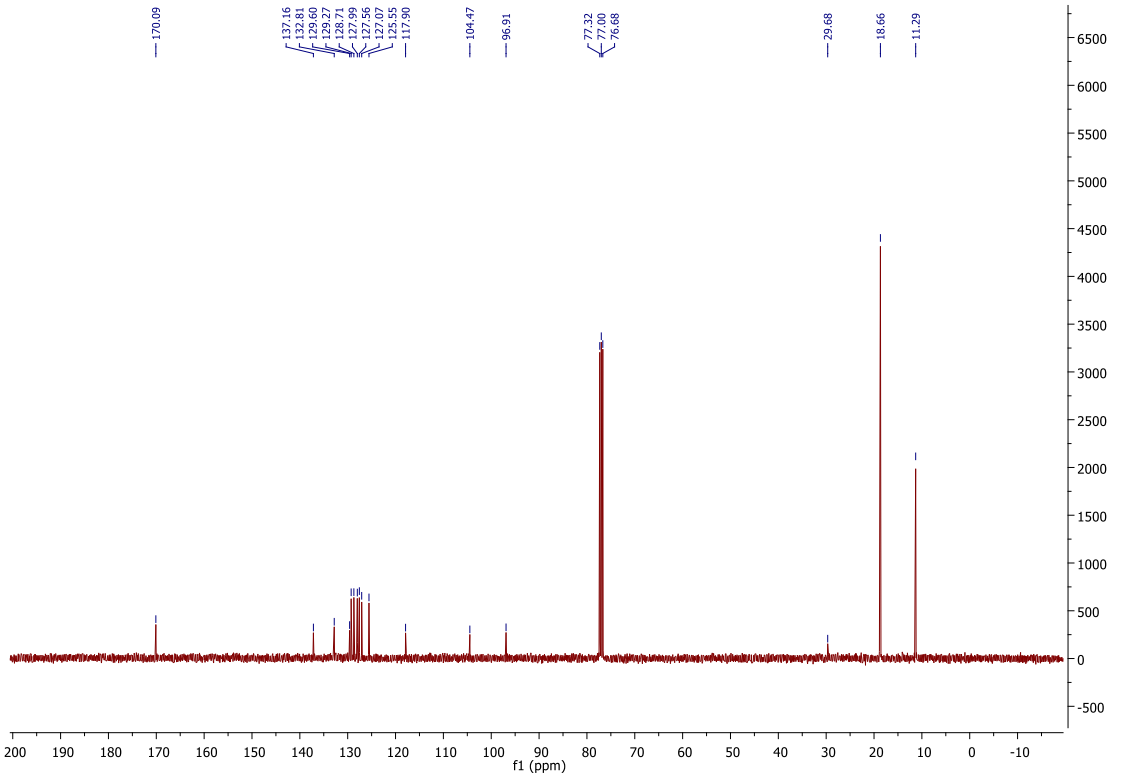

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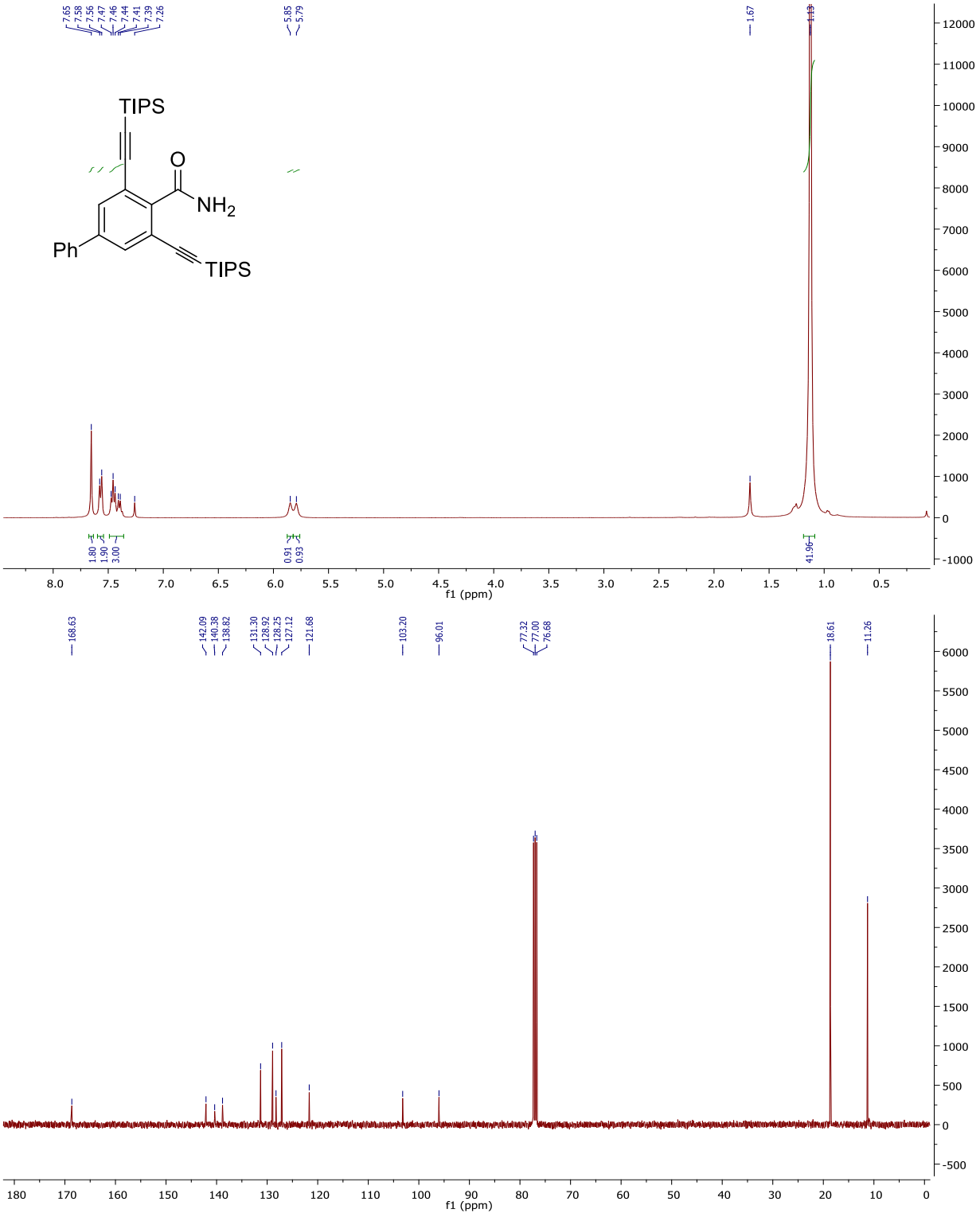
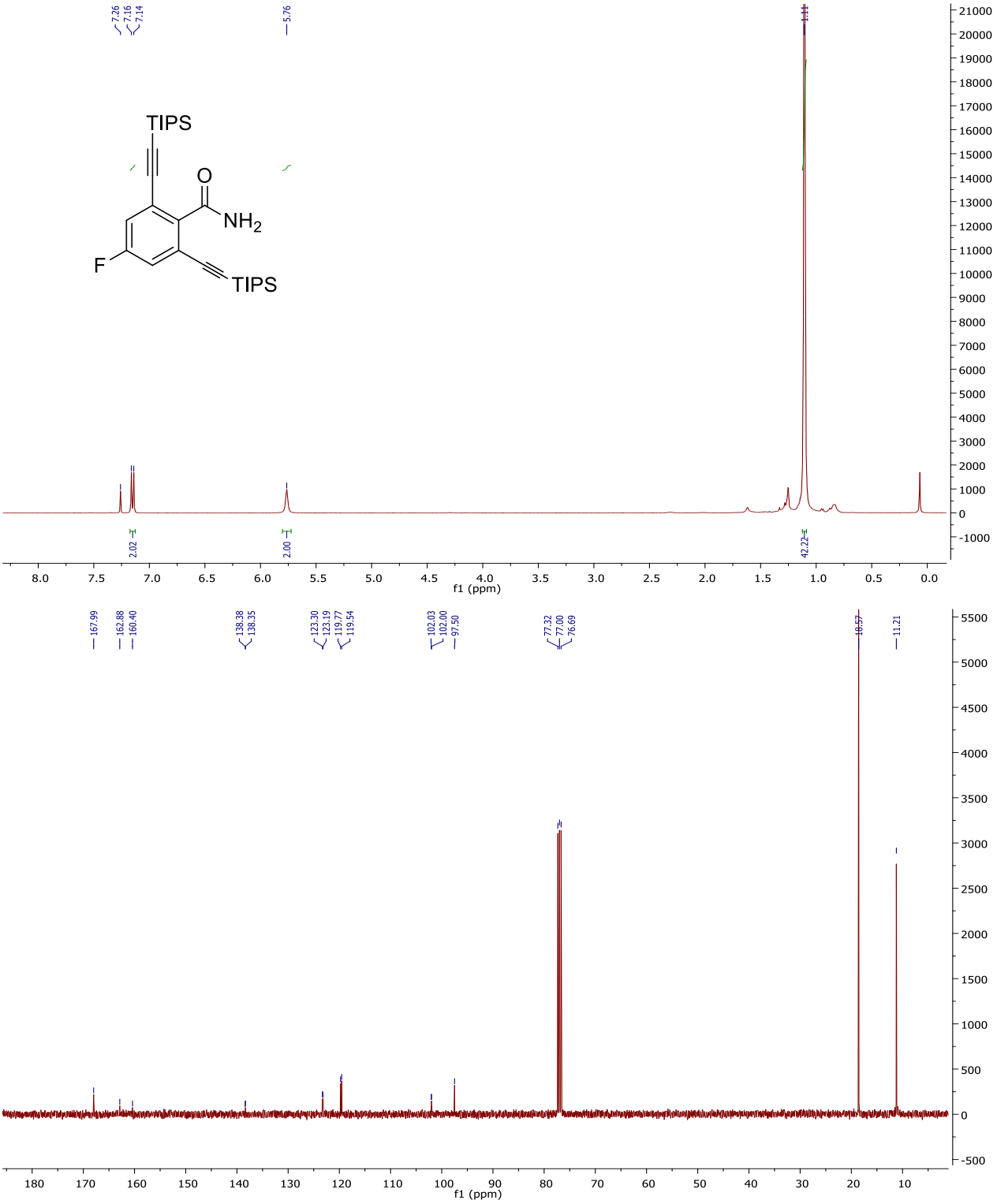
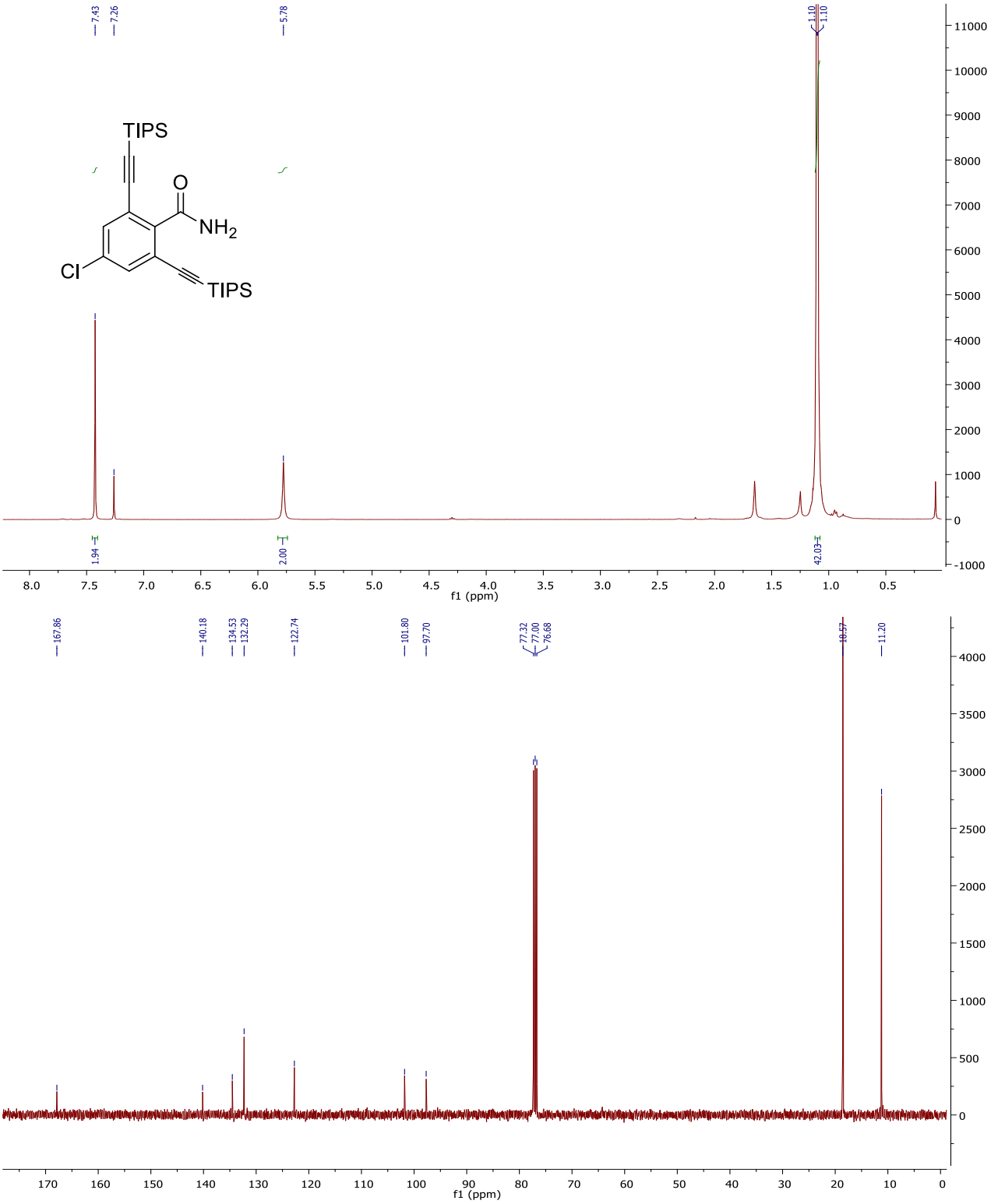


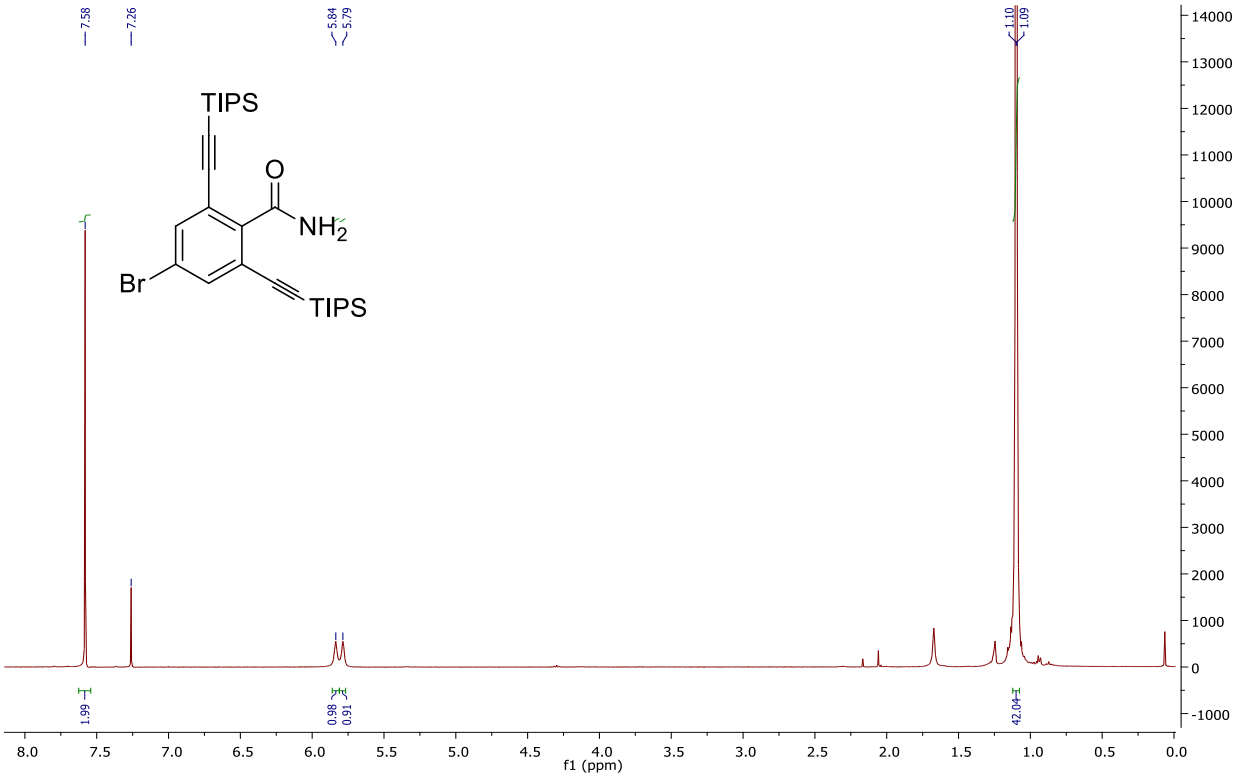
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5j in $CDCl_3$**

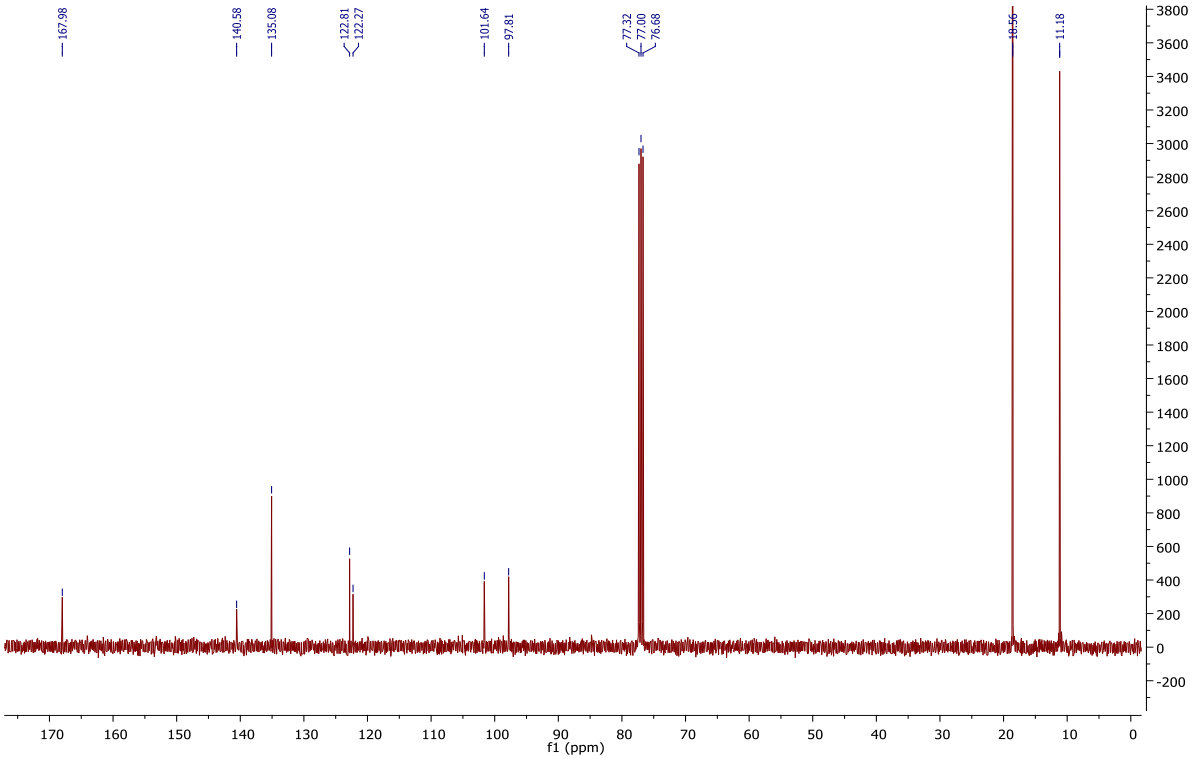


**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5k in $CDCl_3$**

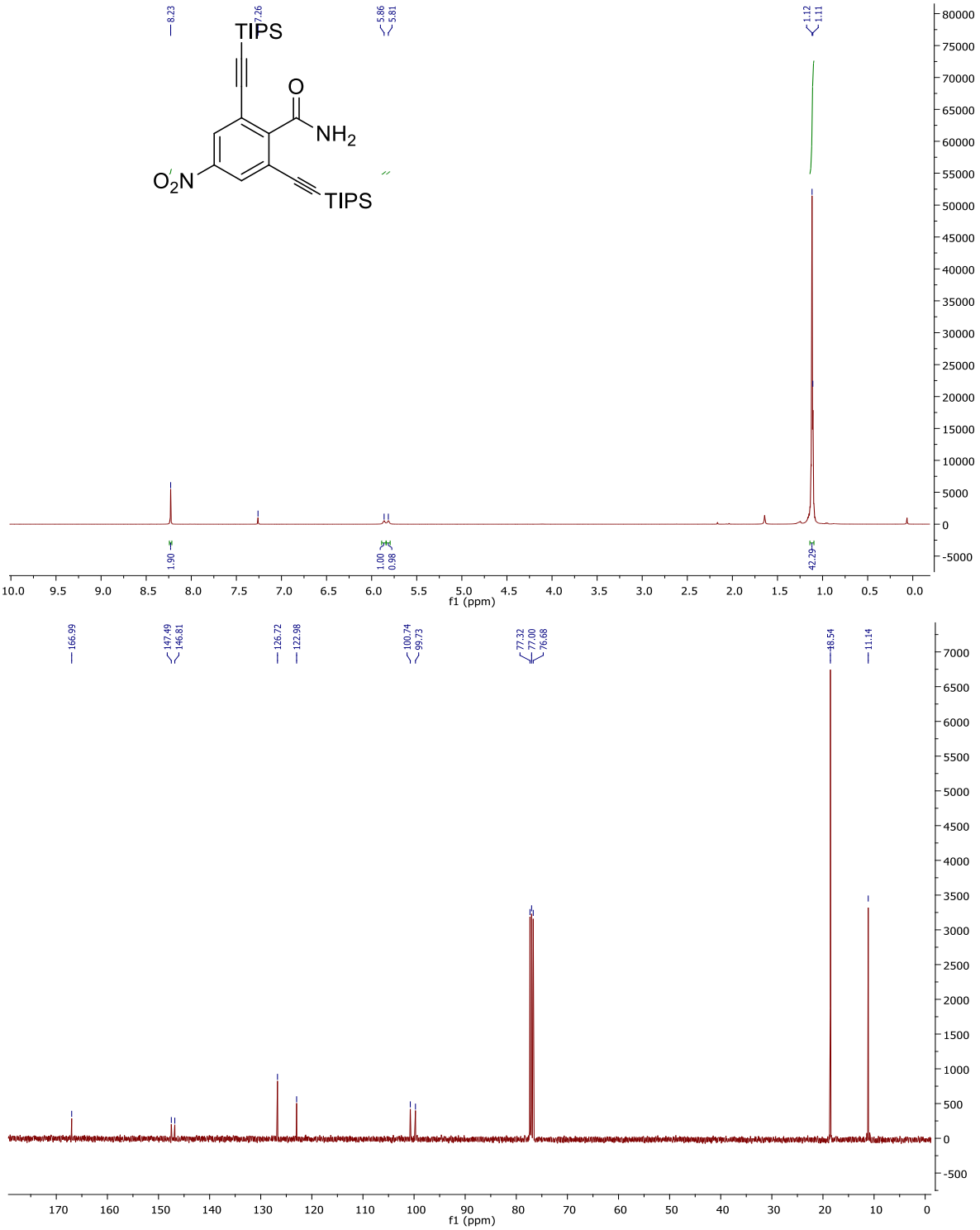


**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5l in $CDCl_3$**

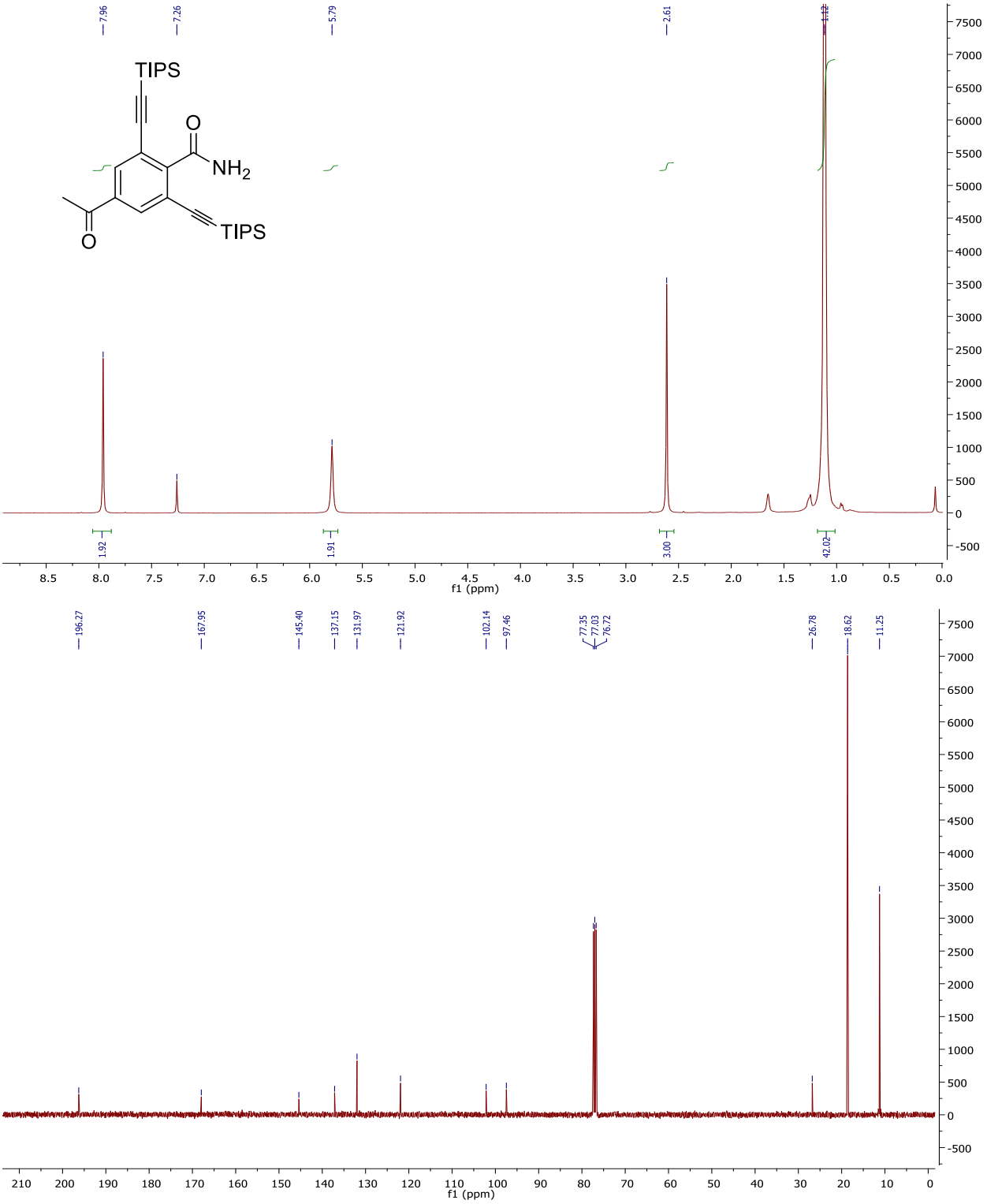


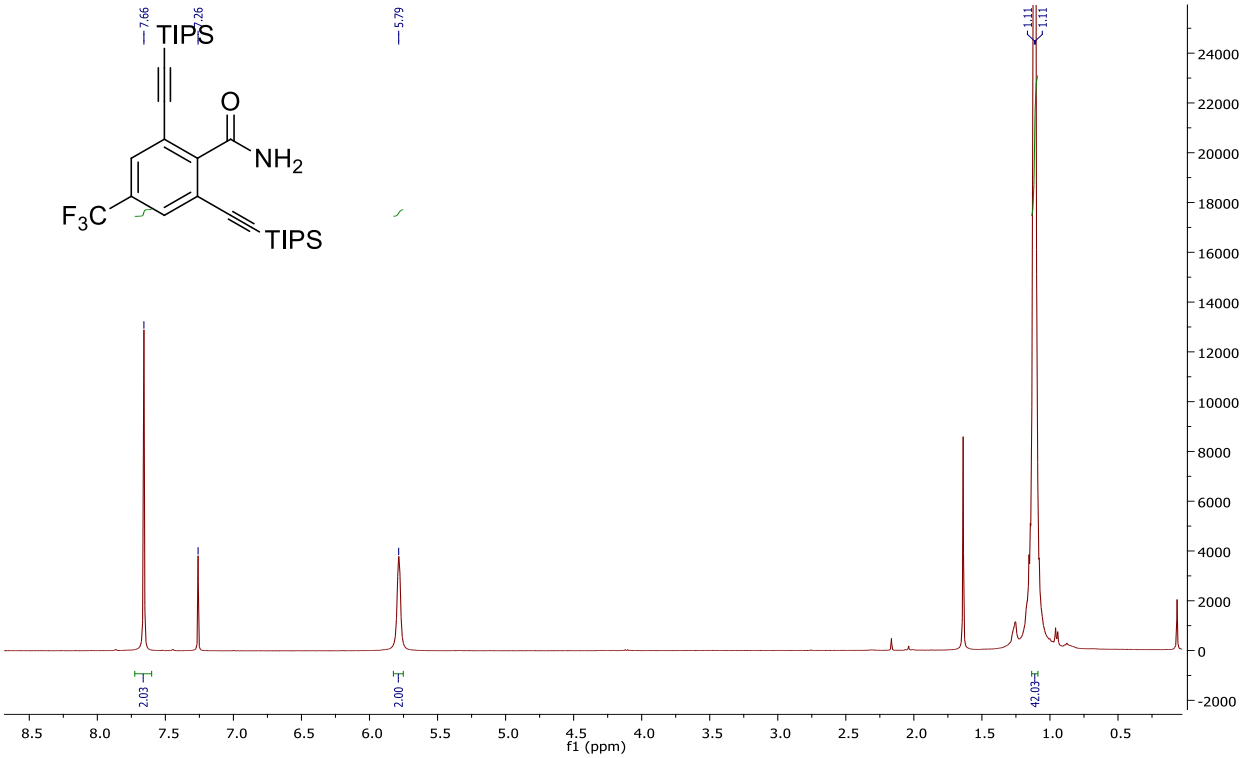
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5m in $CDCl_3$**

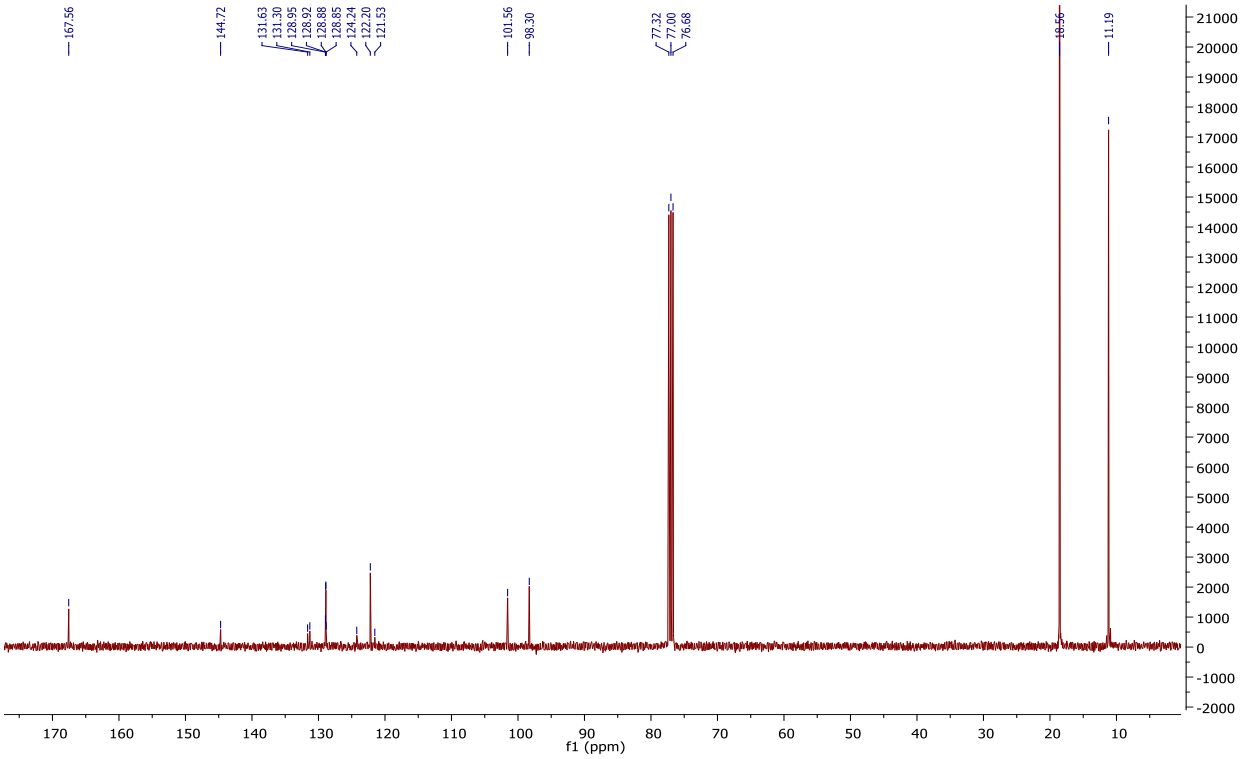


**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5n in $CDCl_3$**

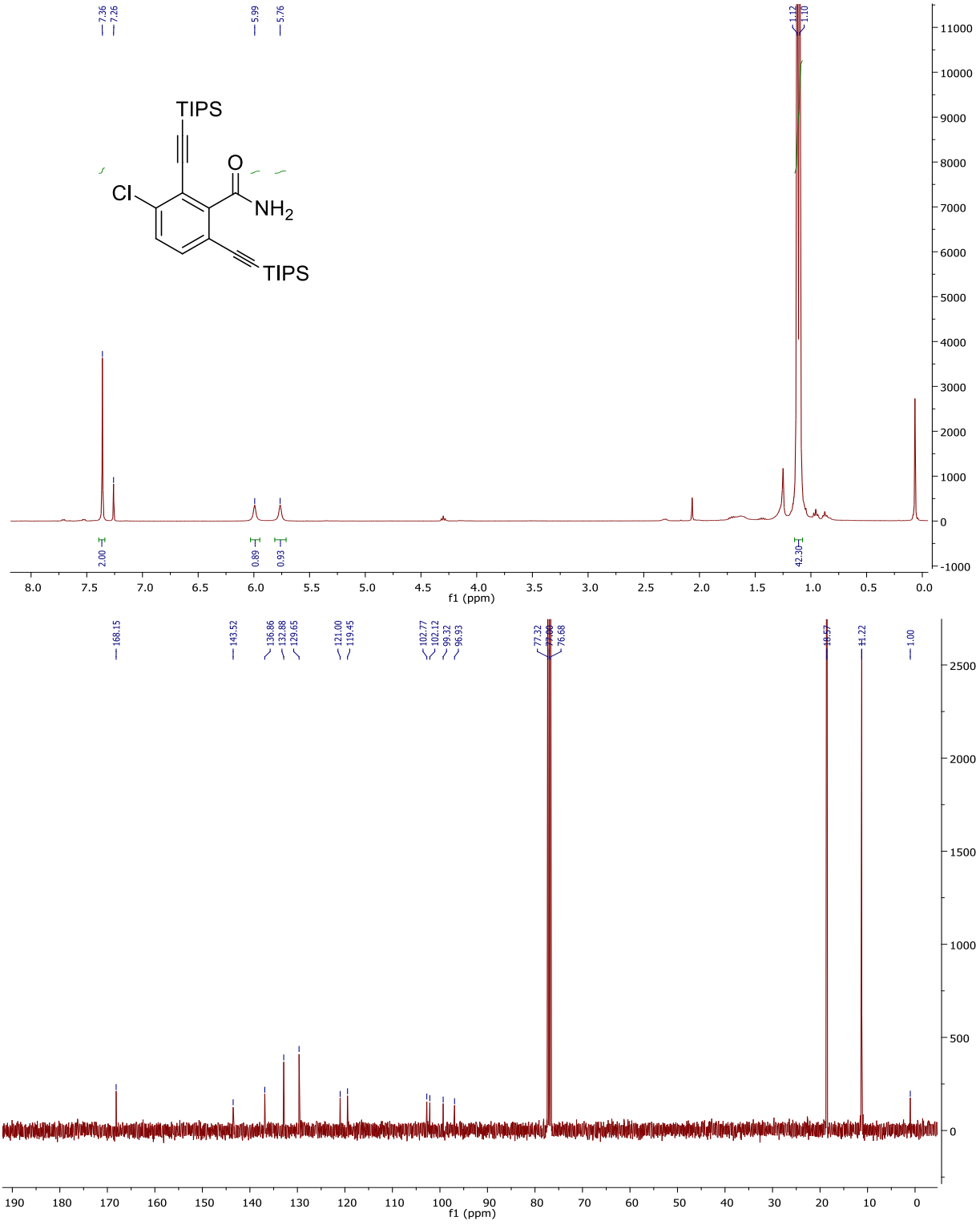


**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5o in $CDCl_3$**

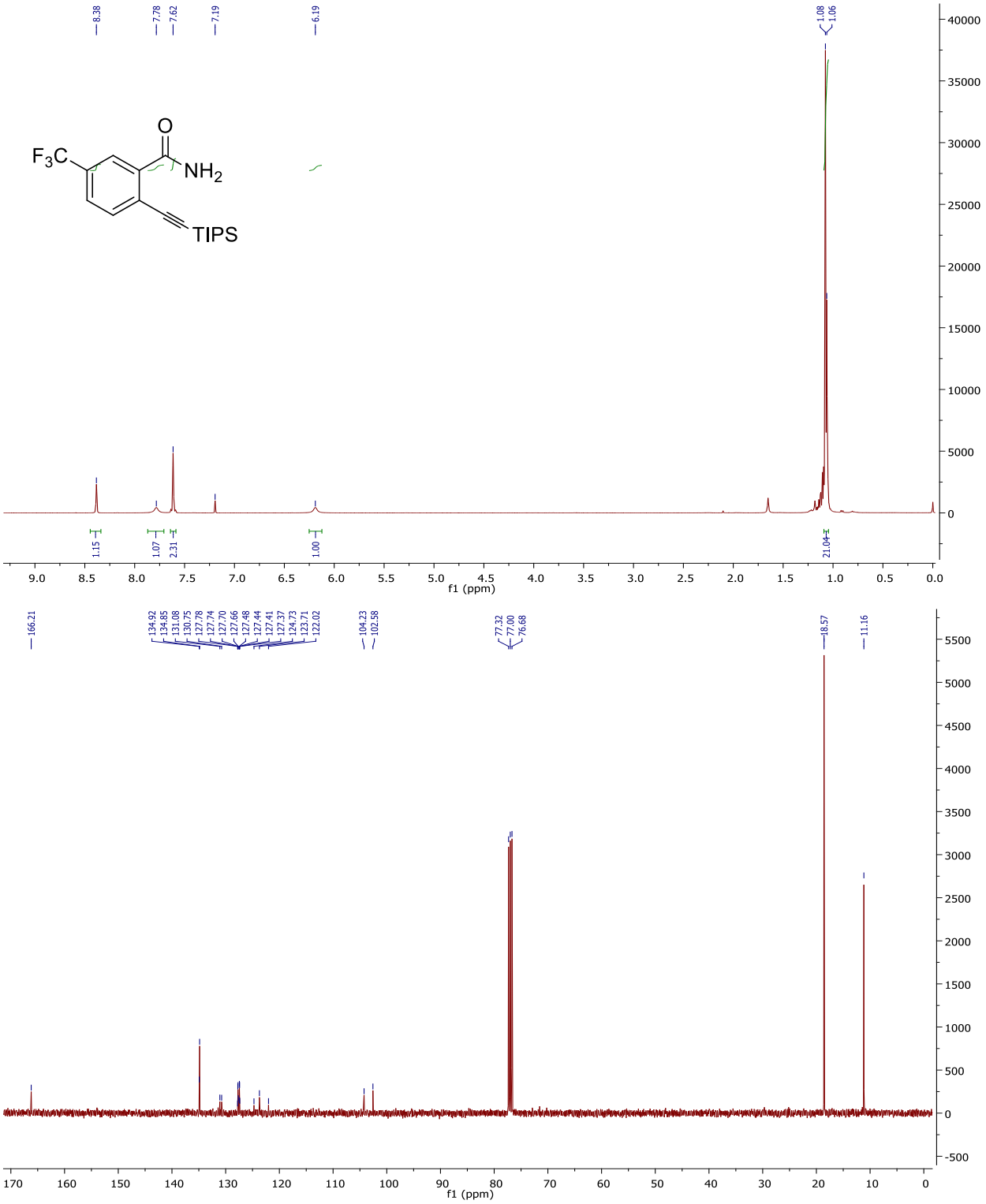


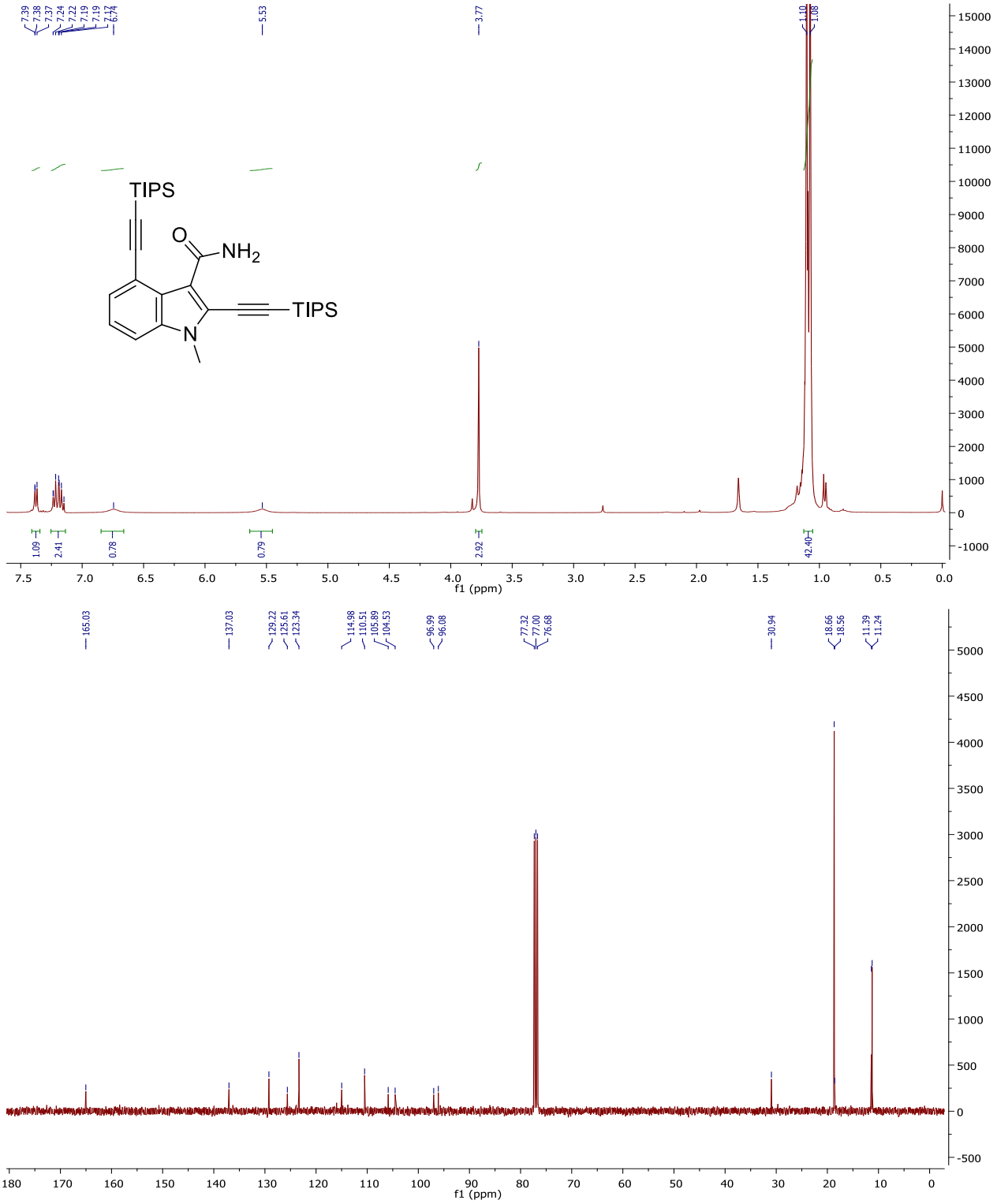
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5p in $CDCl_3$**



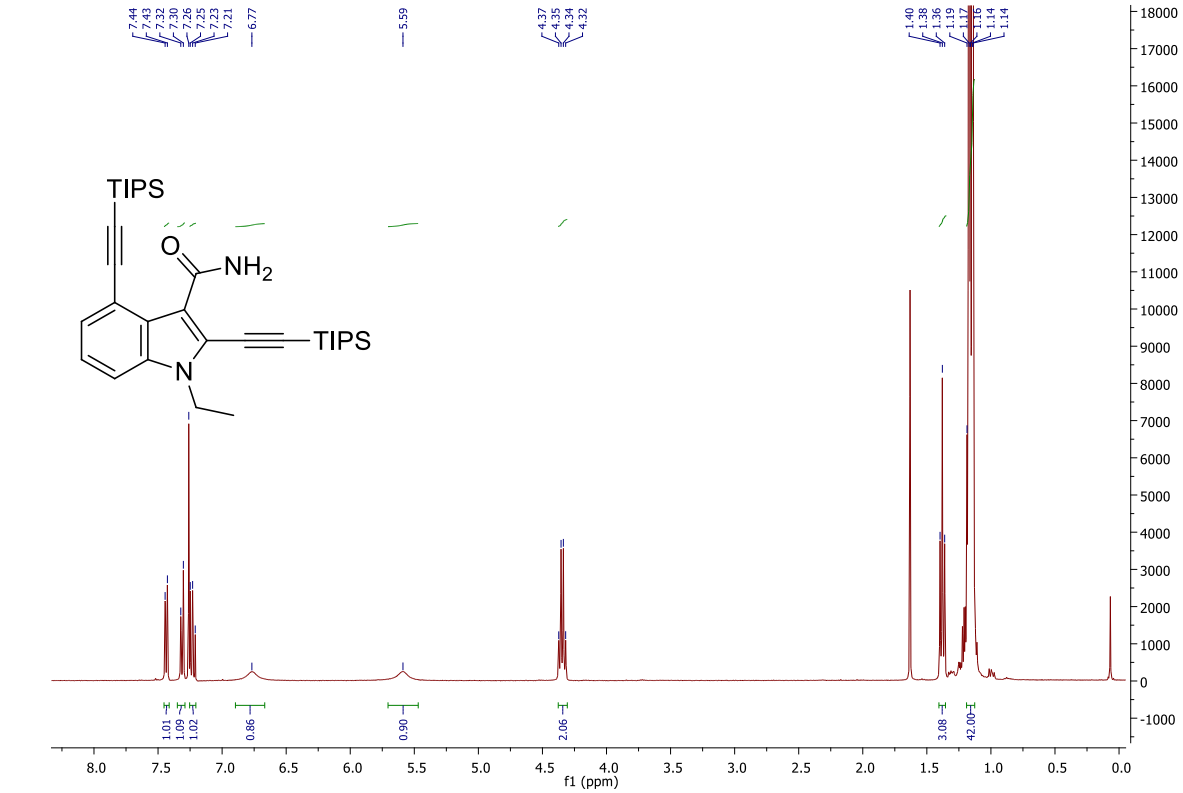
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5q in $CDCl_3$**

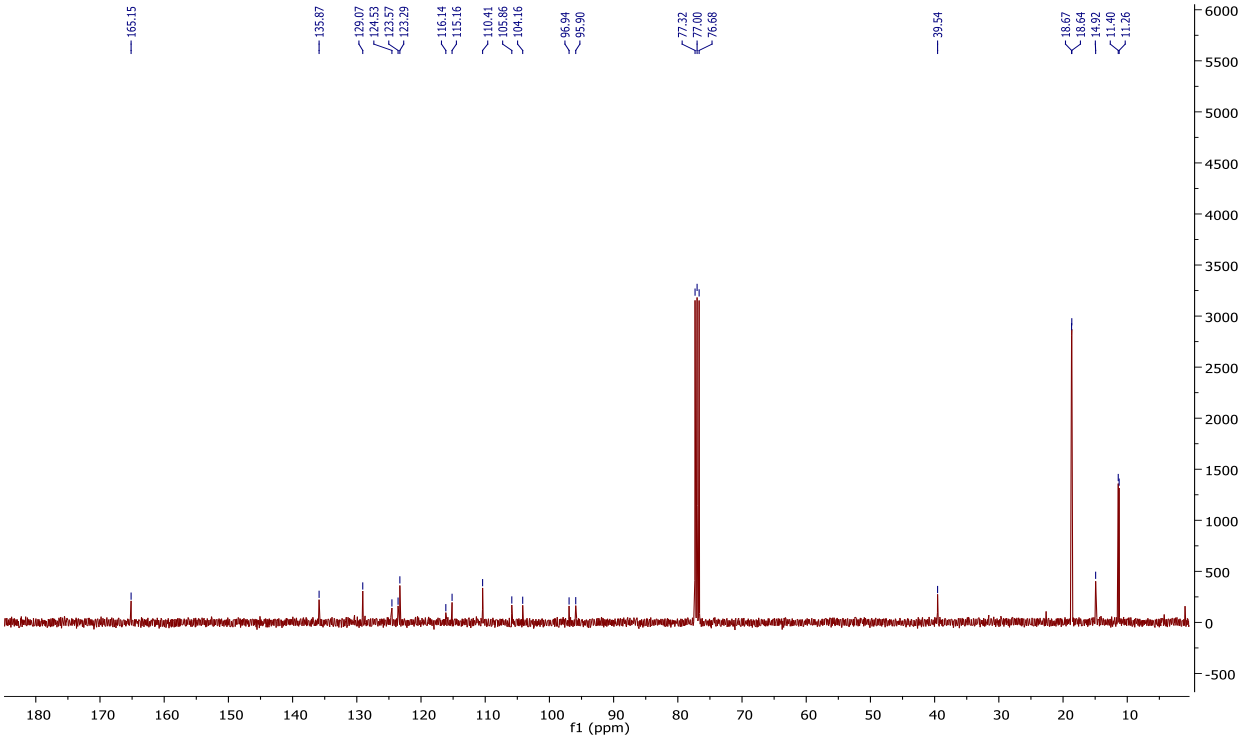


**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5r in $CDCl_3$**

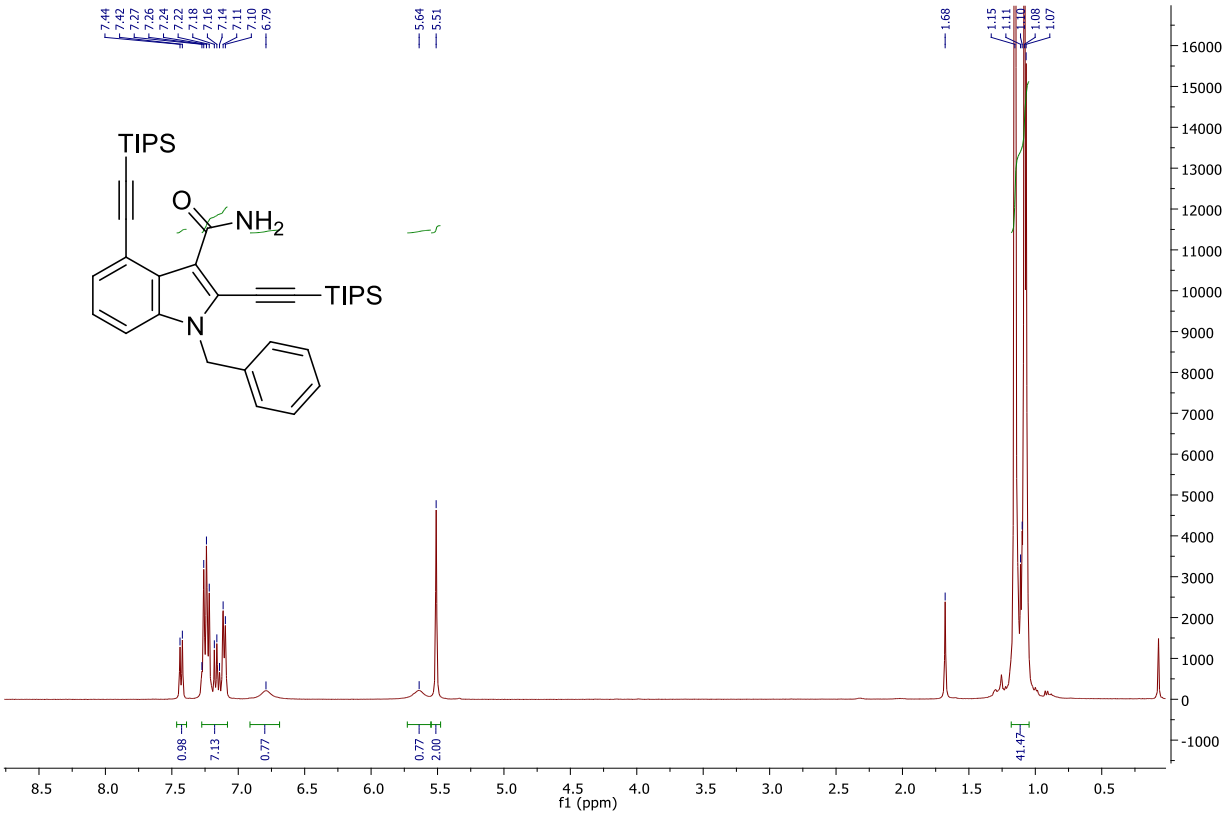


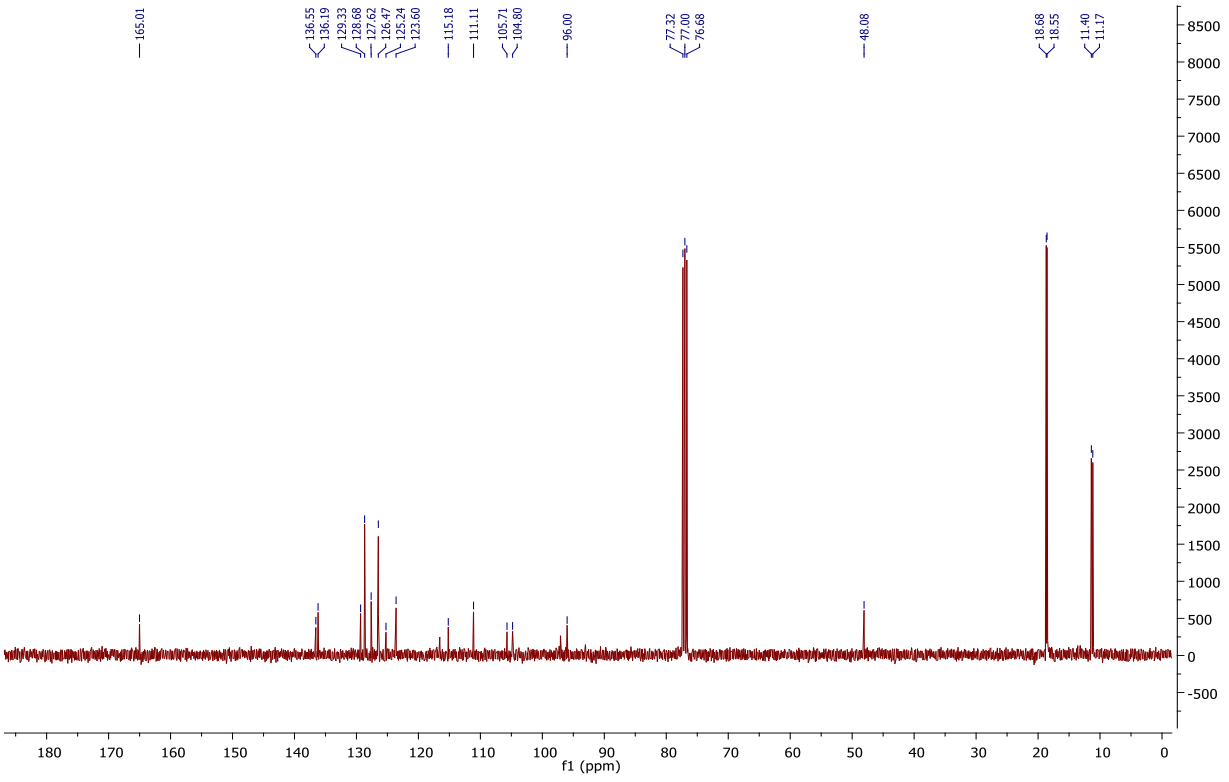
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5s in $CDCl_3$**



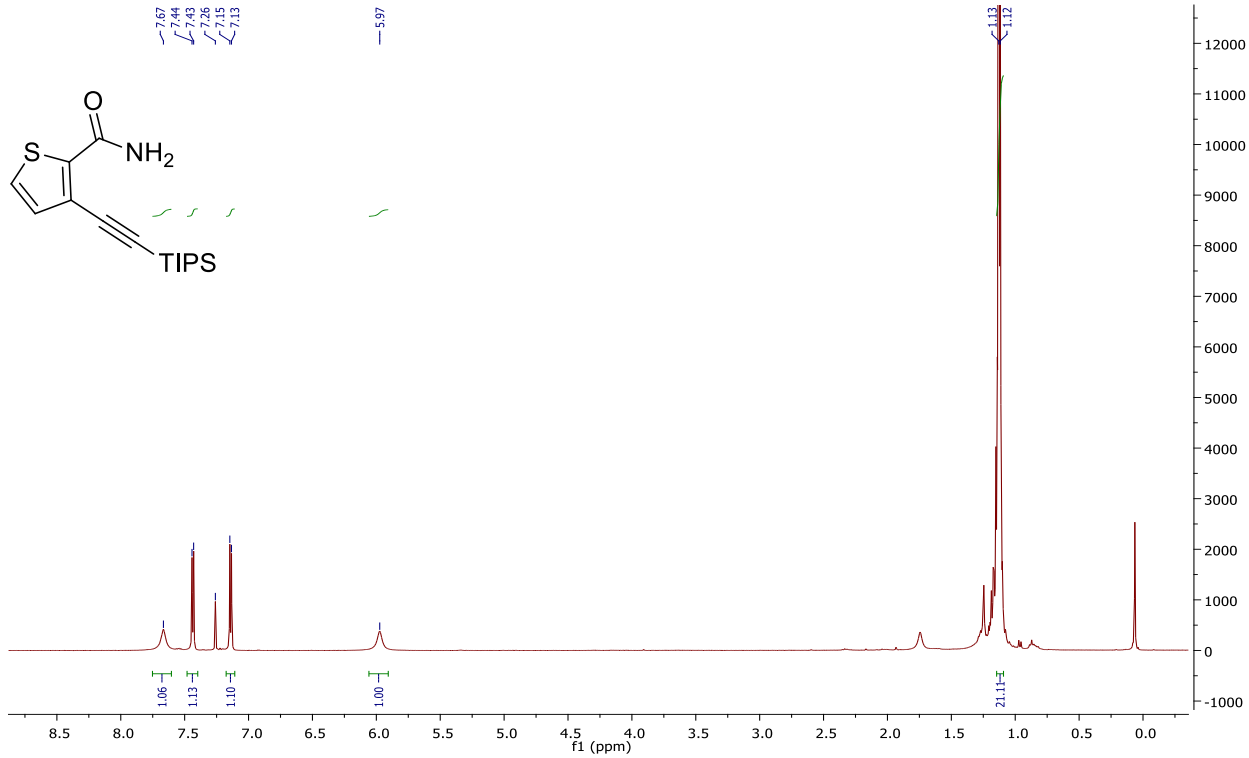



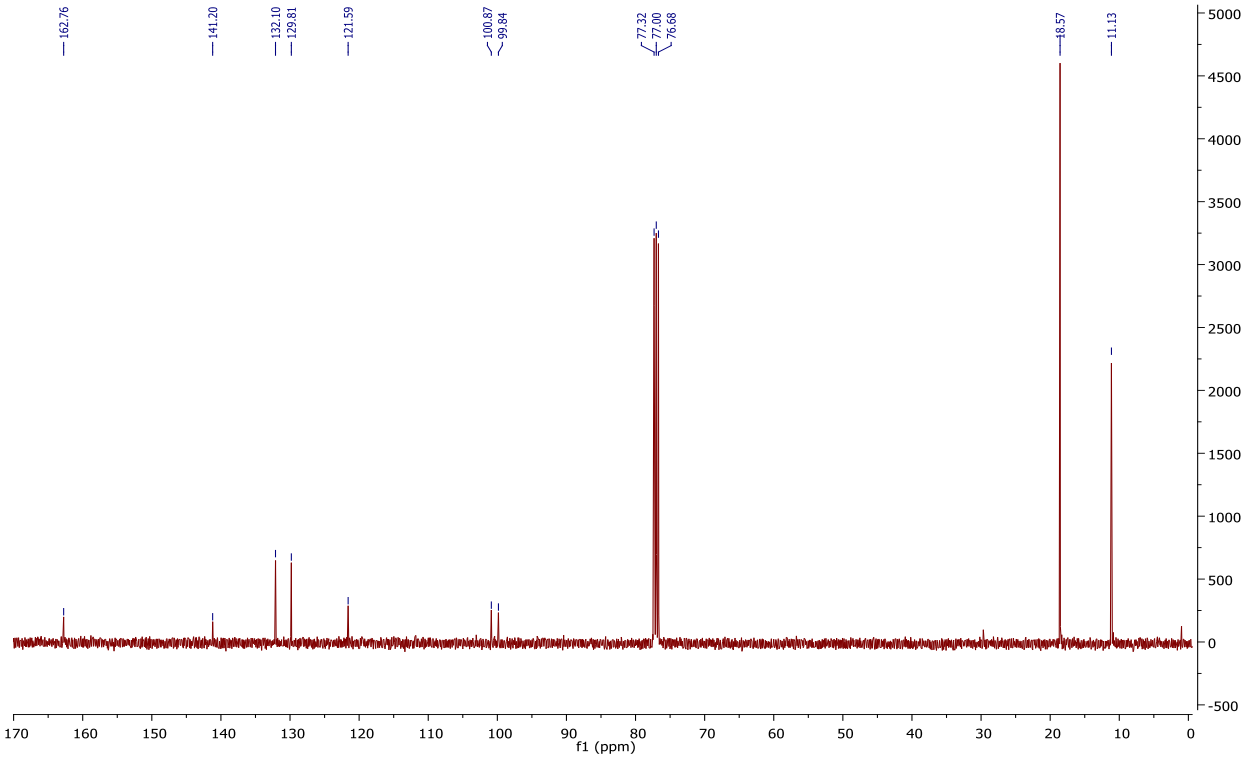
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5t in $CDCl_3$**



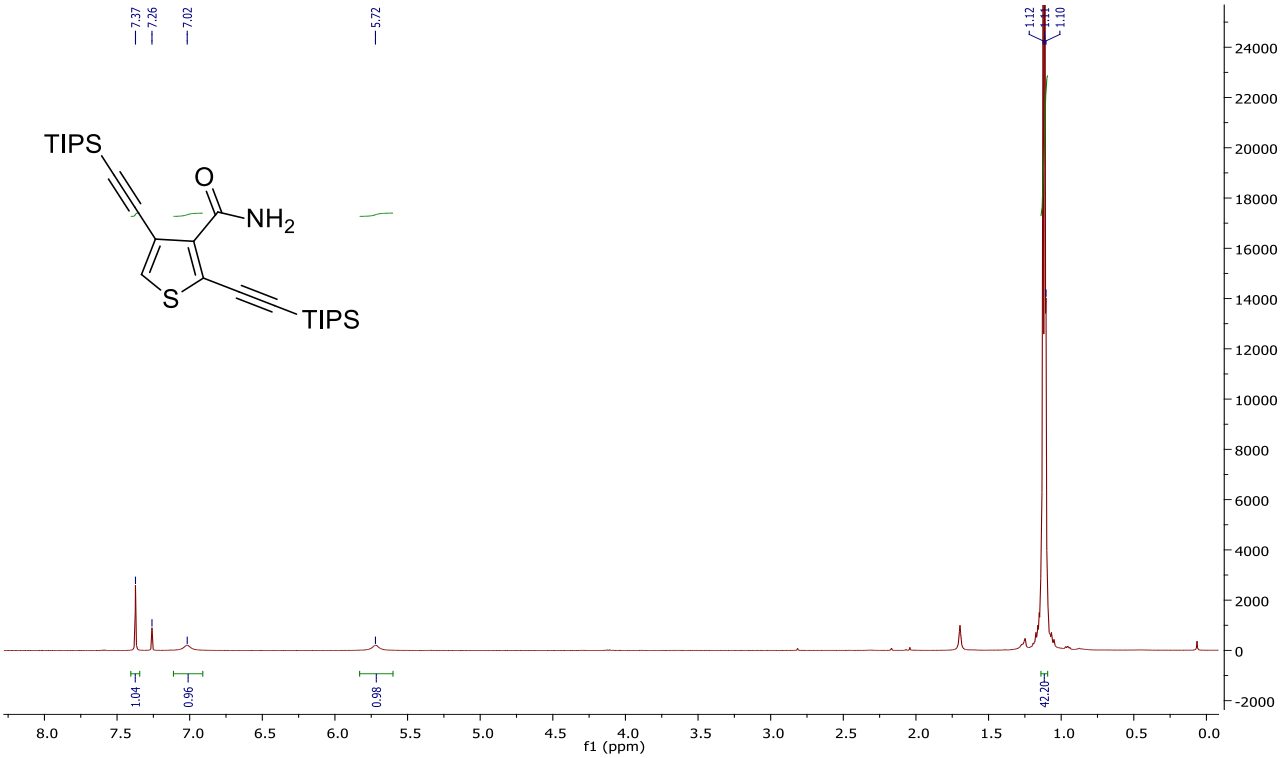



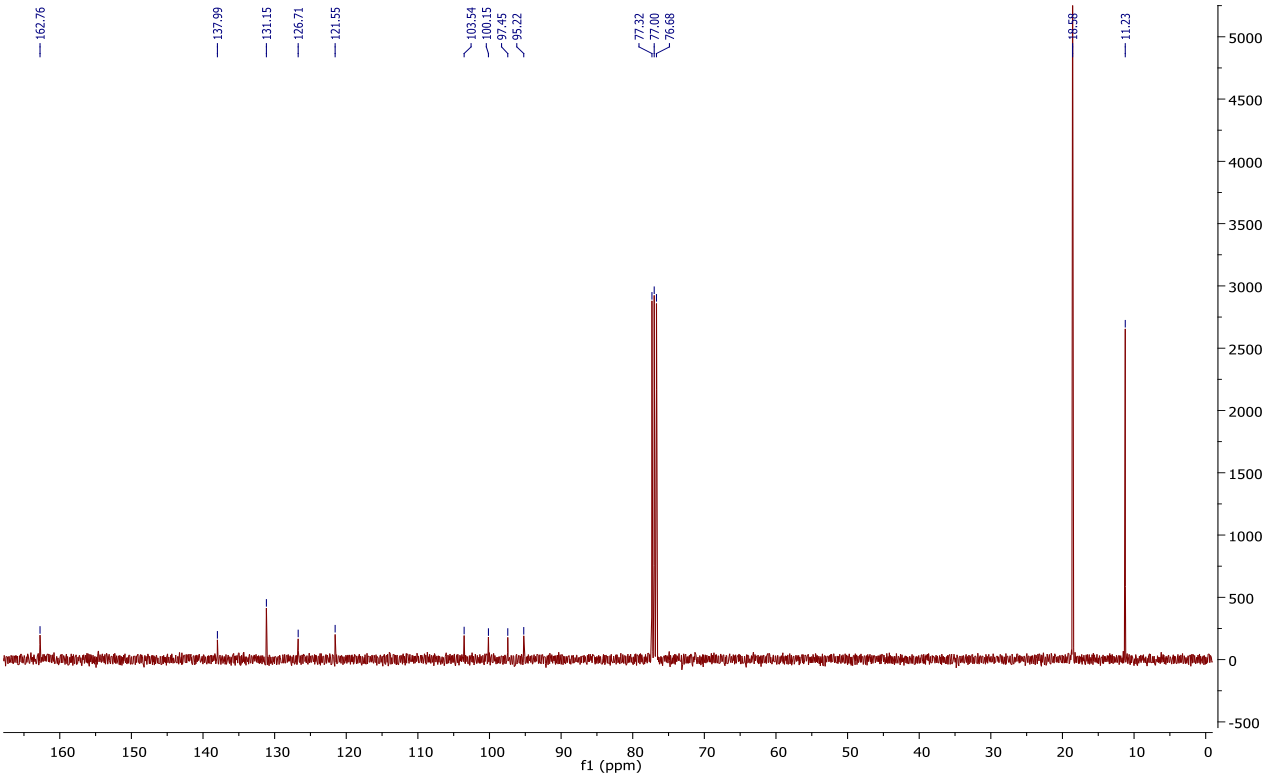
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5u in $CDCl_3$**



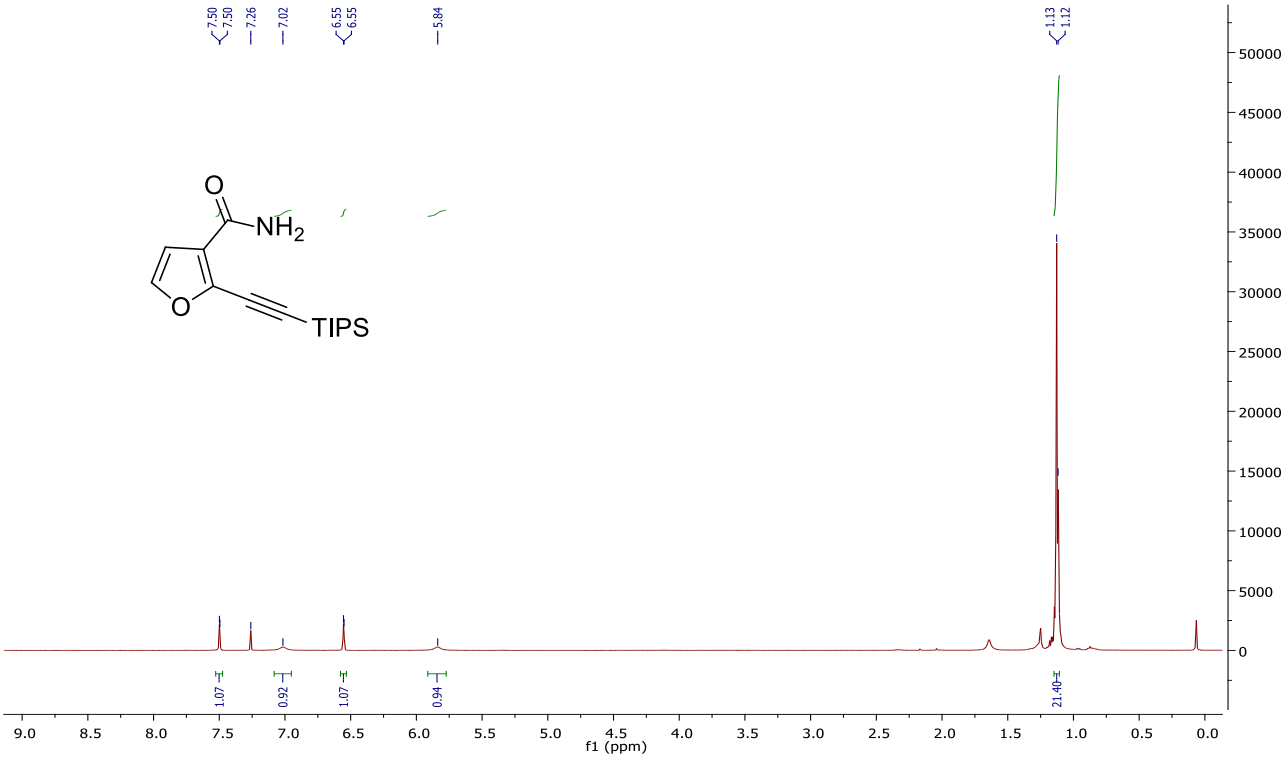



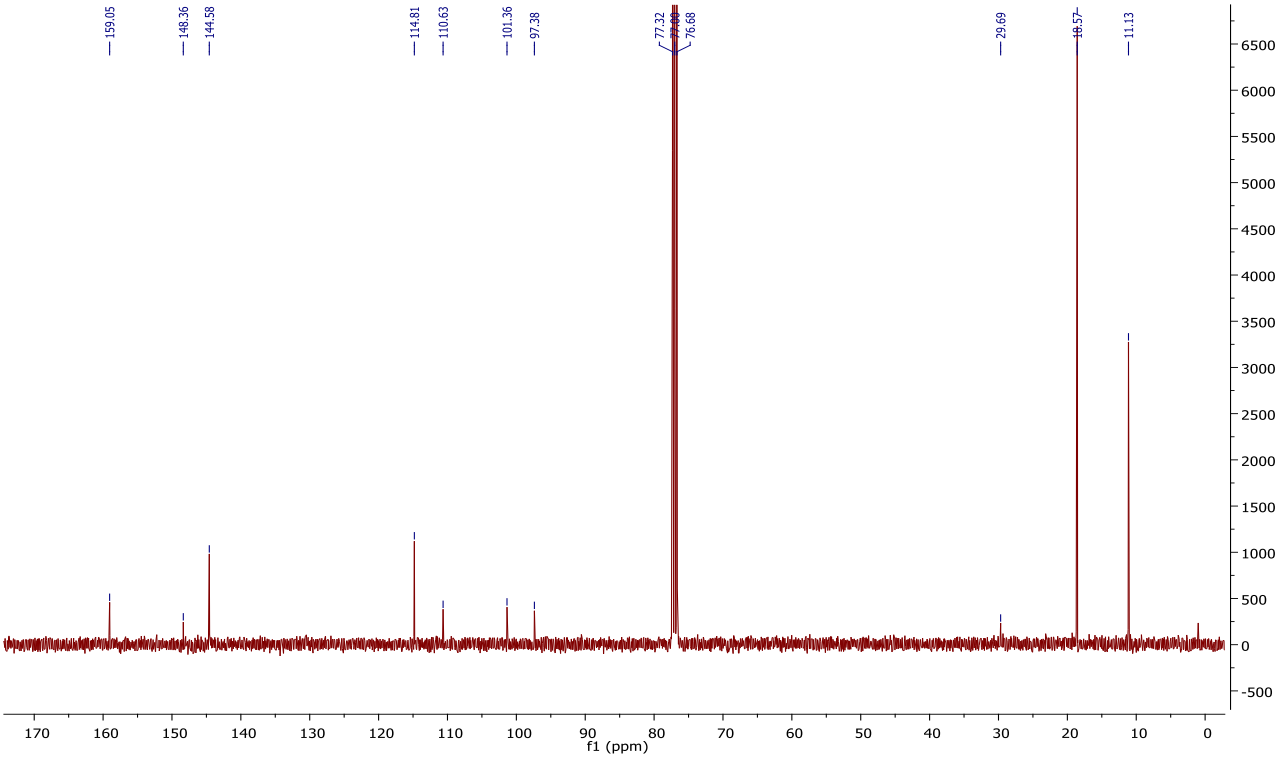
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5v in $CDCl_3$**



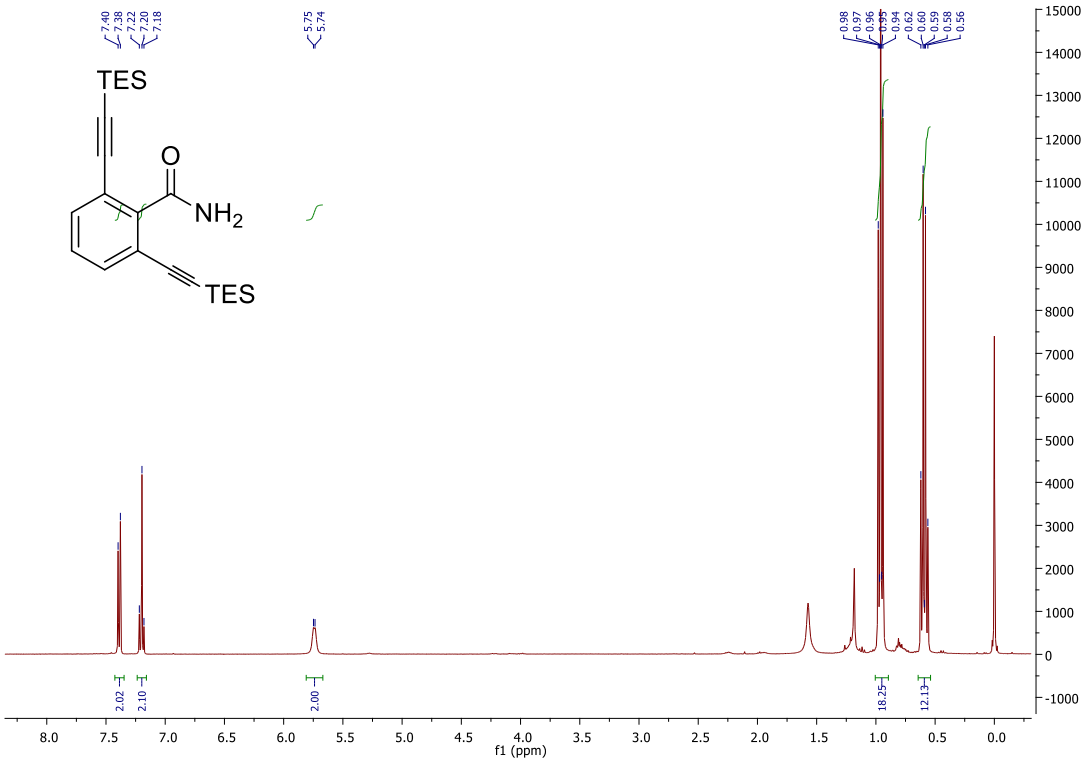



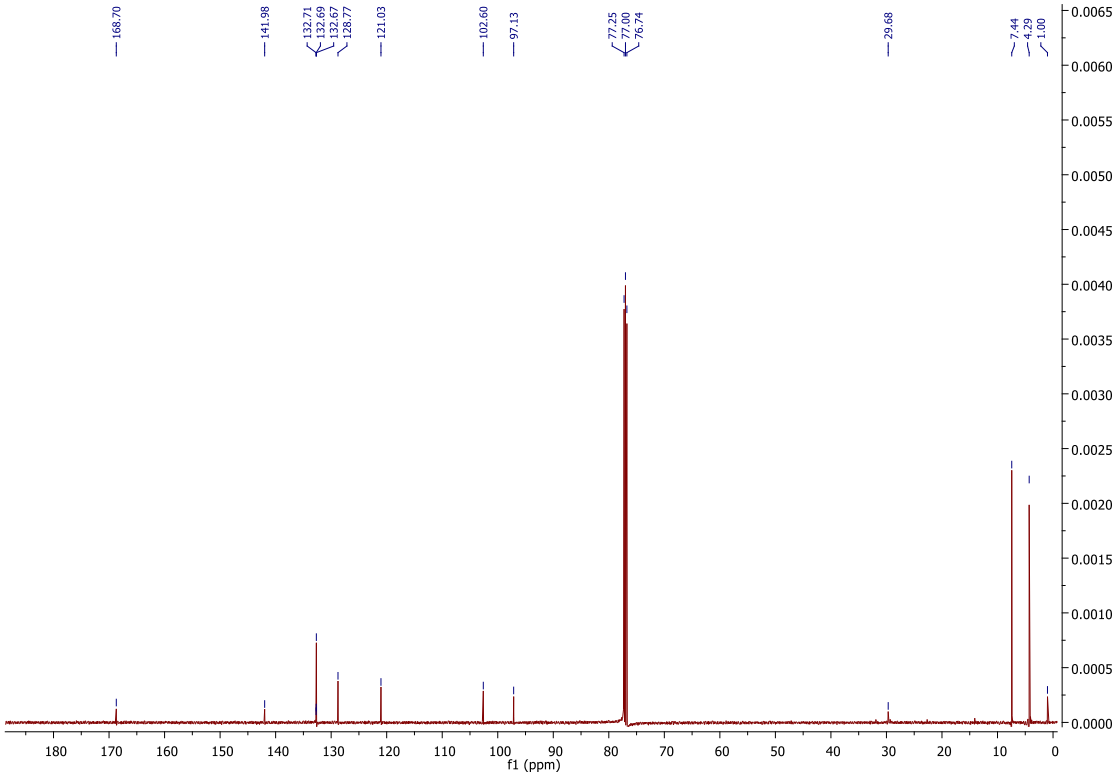
**$^{1}H$(400 MHz) and $^{13}C\{^{1}H\}$(100 MHz) spectra of 5w in $CDCl_3$**



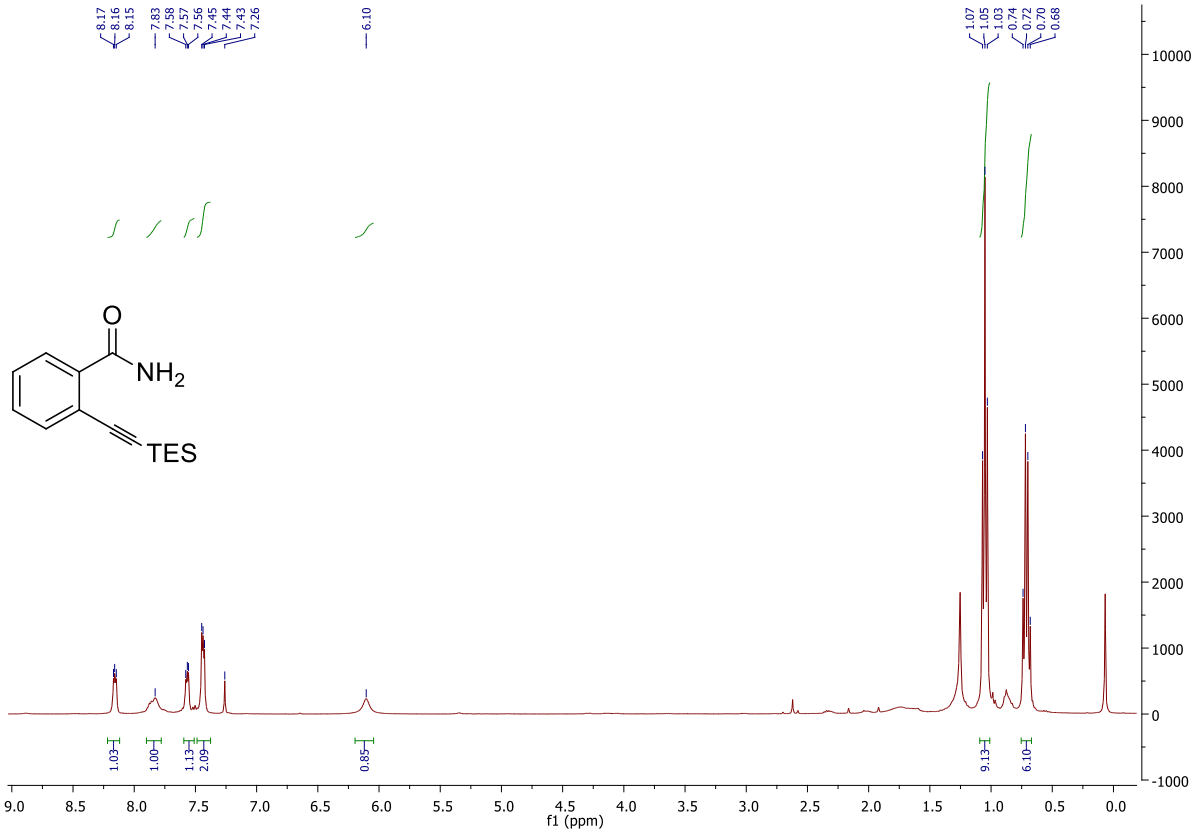



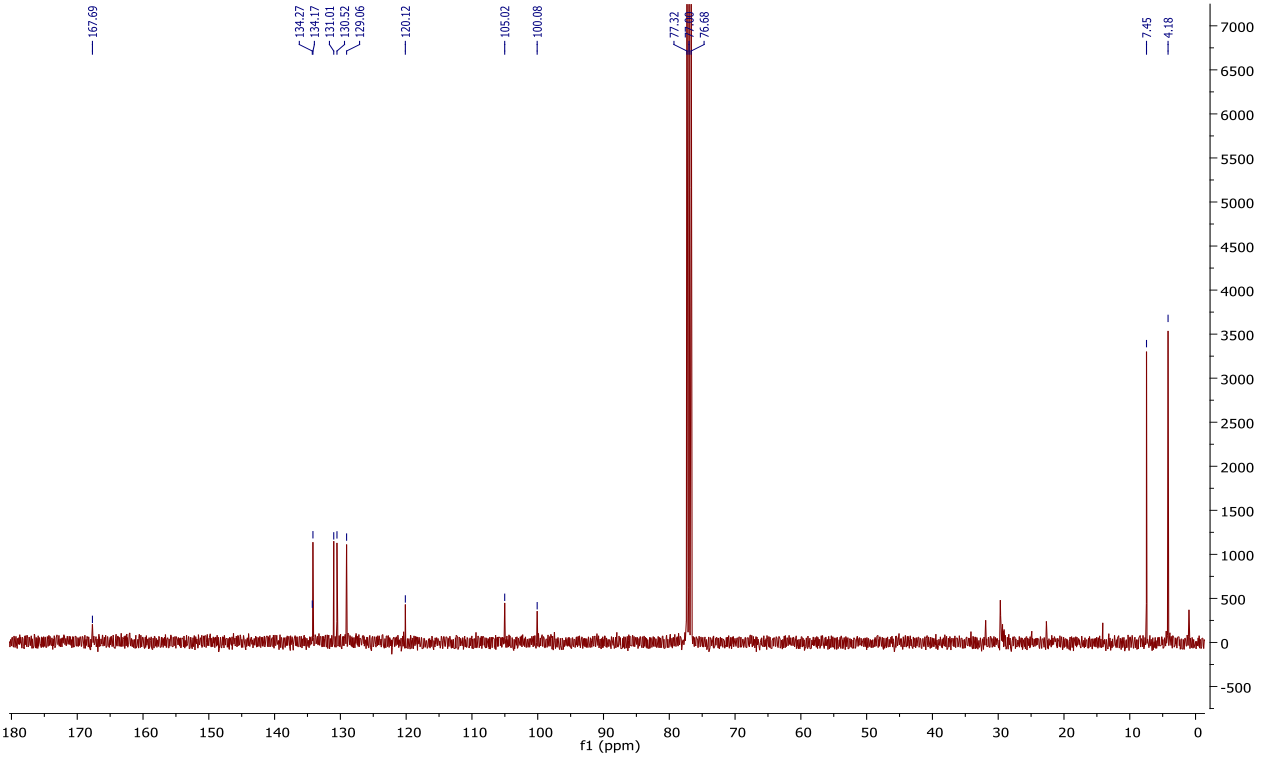
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5x in $CDCl_3$**



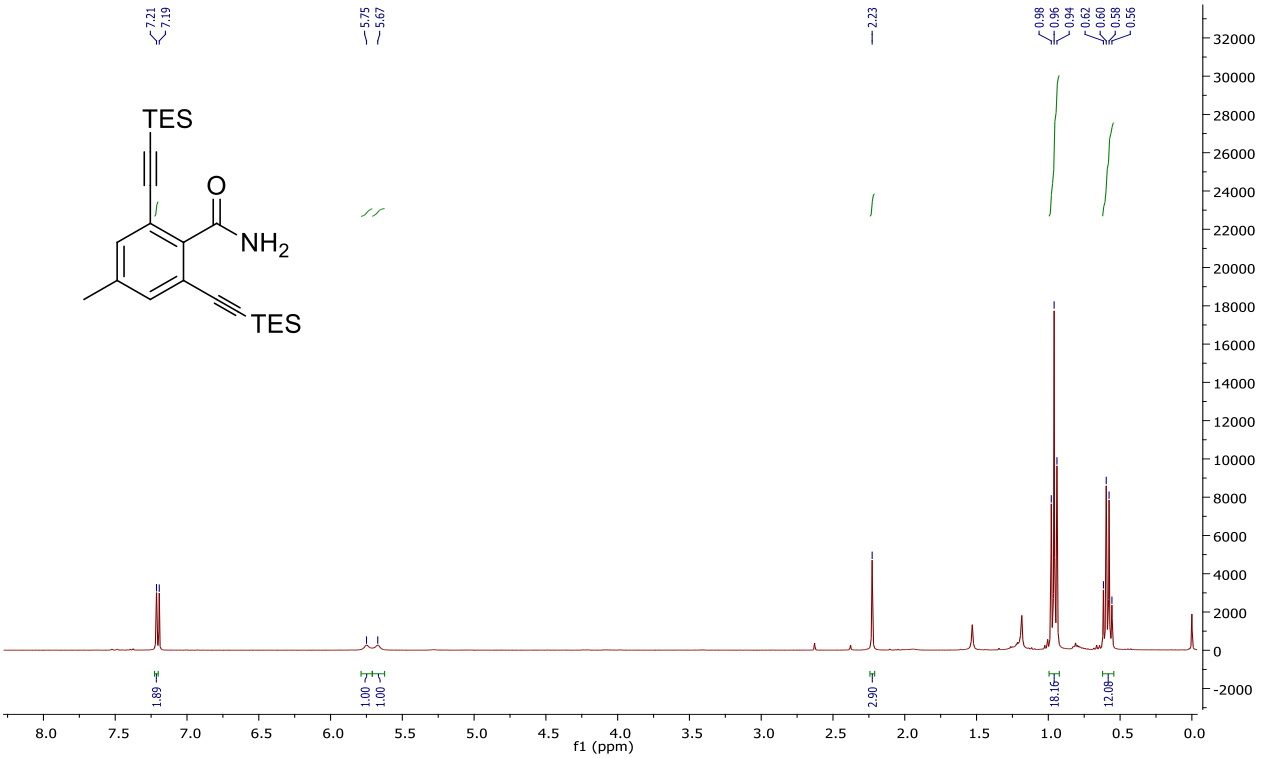



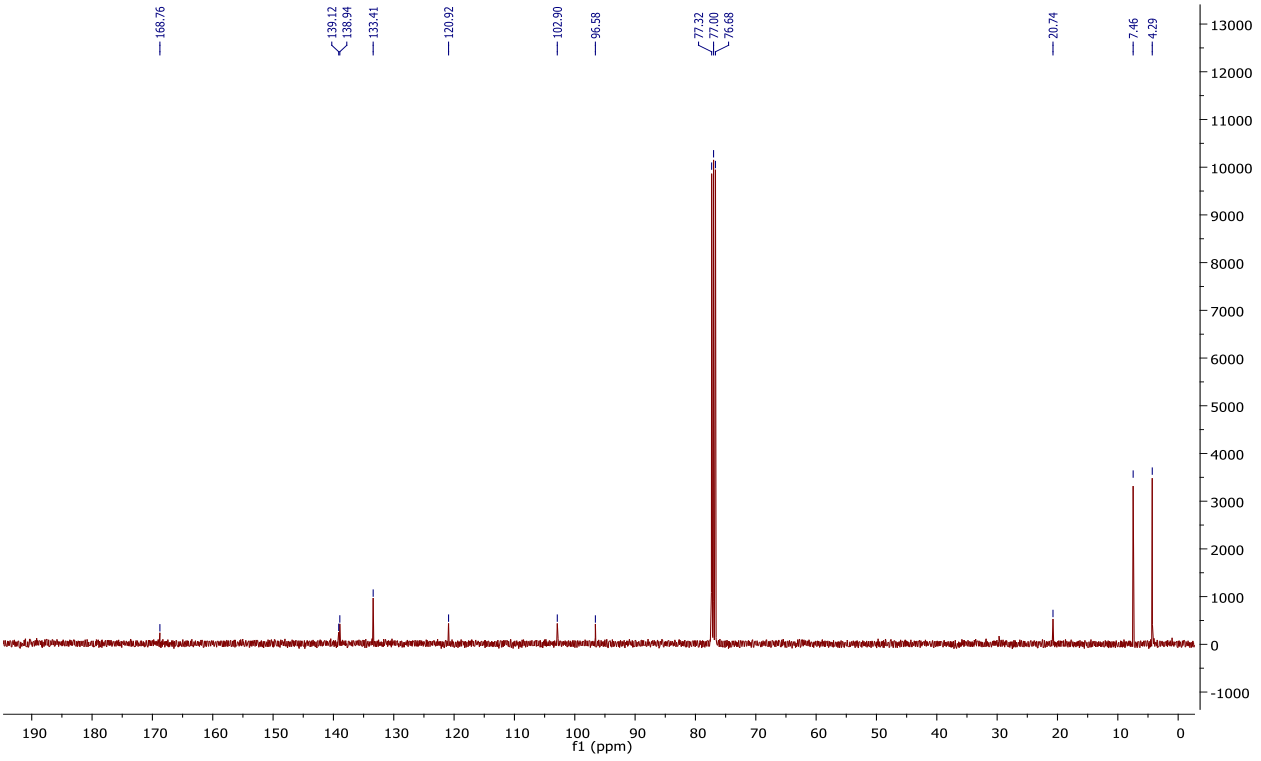
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5xx in $CDCl_3$**



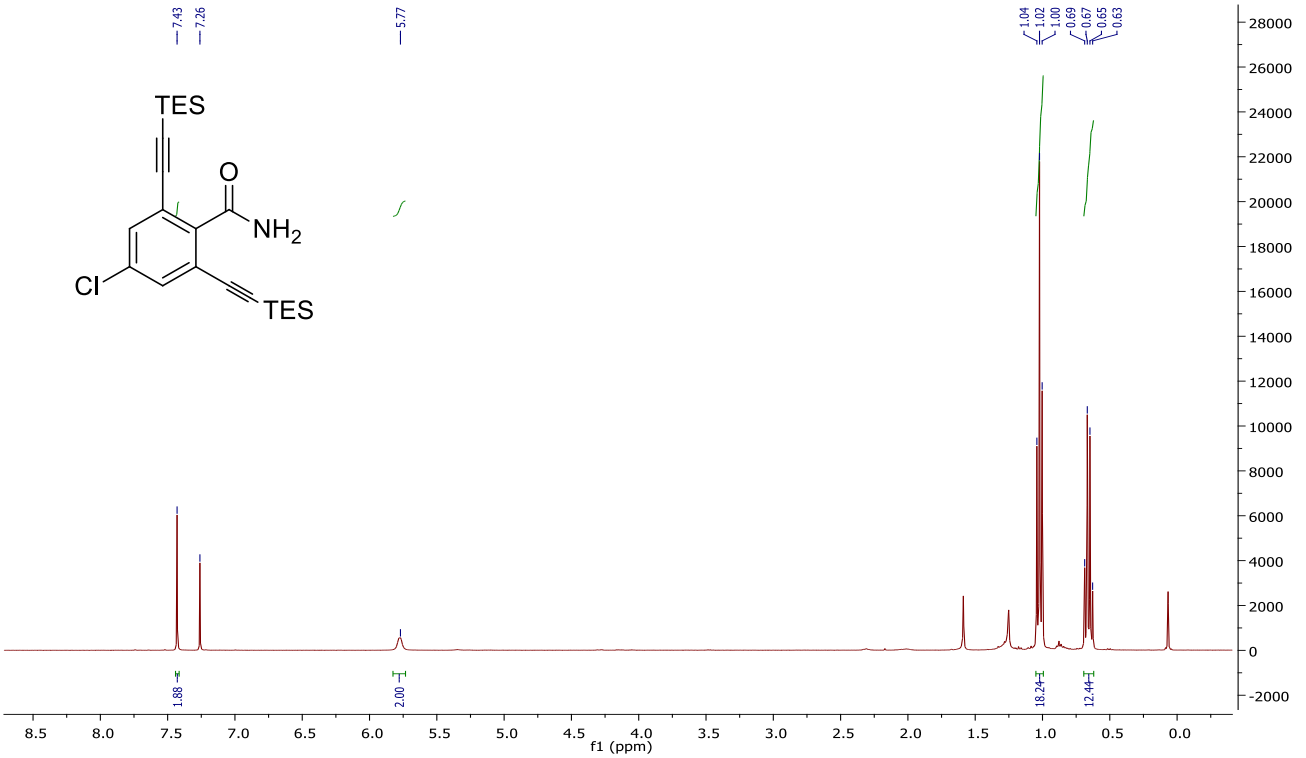



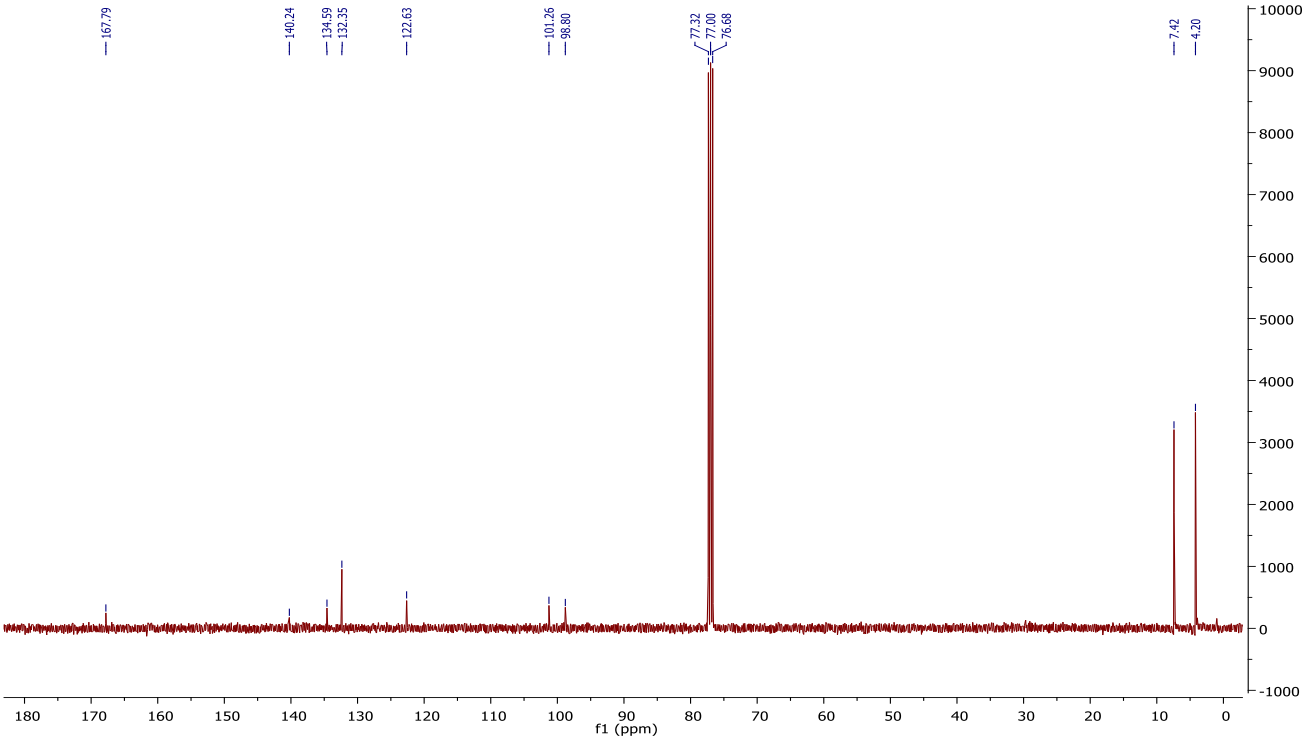
**$^{1}H$(400 MHz) and $^{13}C\{^{1}H\}$(100 MHz) spectra of 5y in $CDCl_3$**



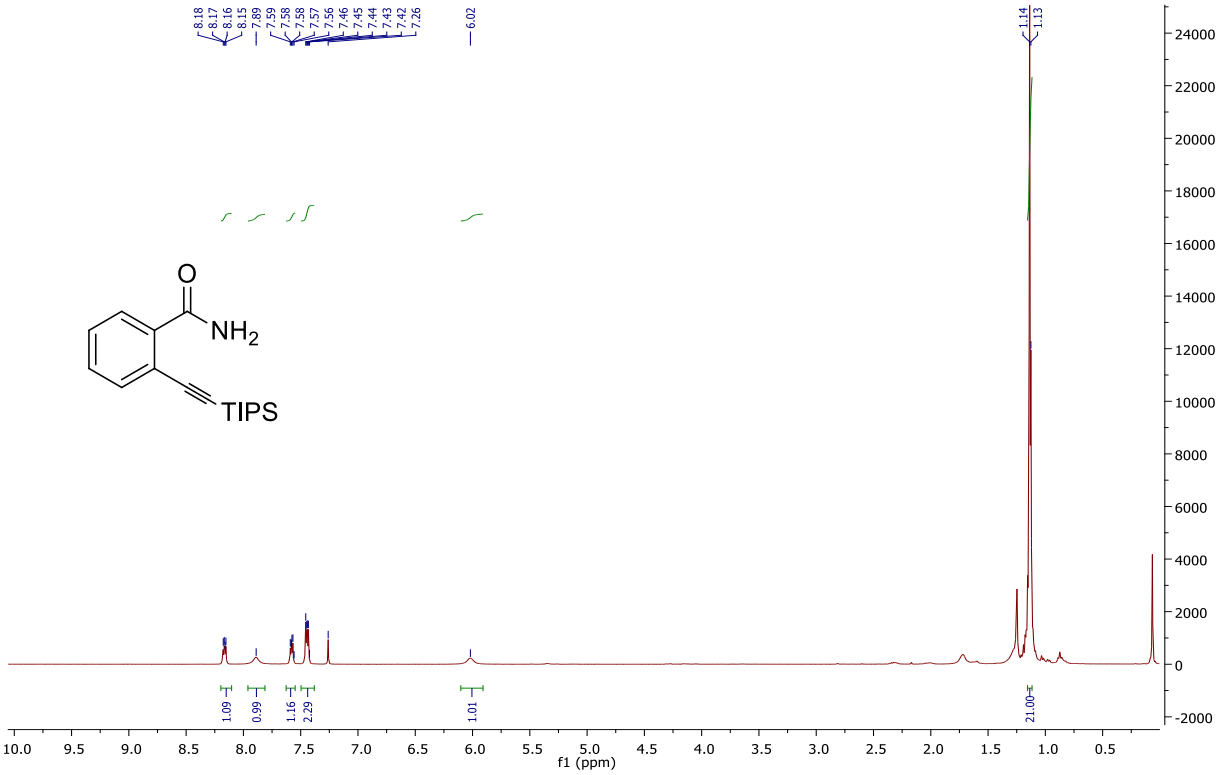



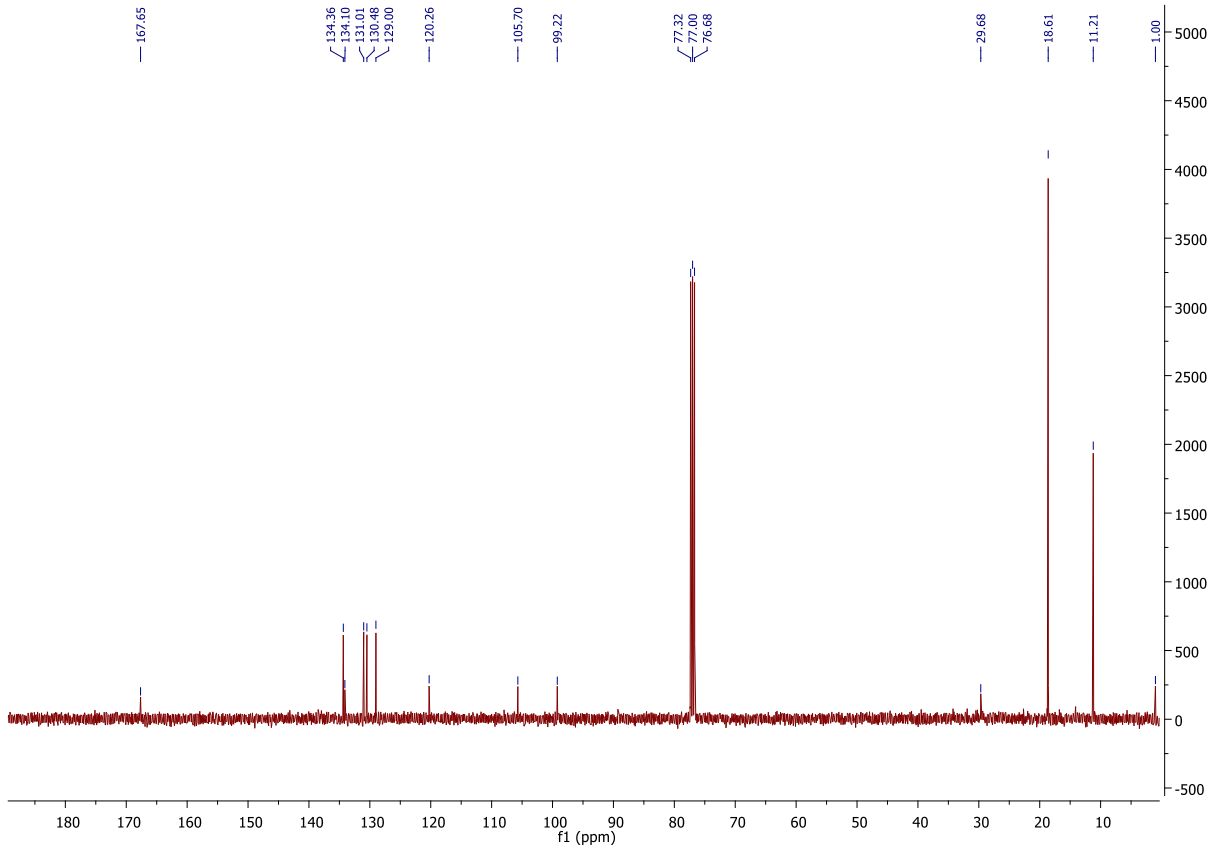
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5z in $CDCl_3$**



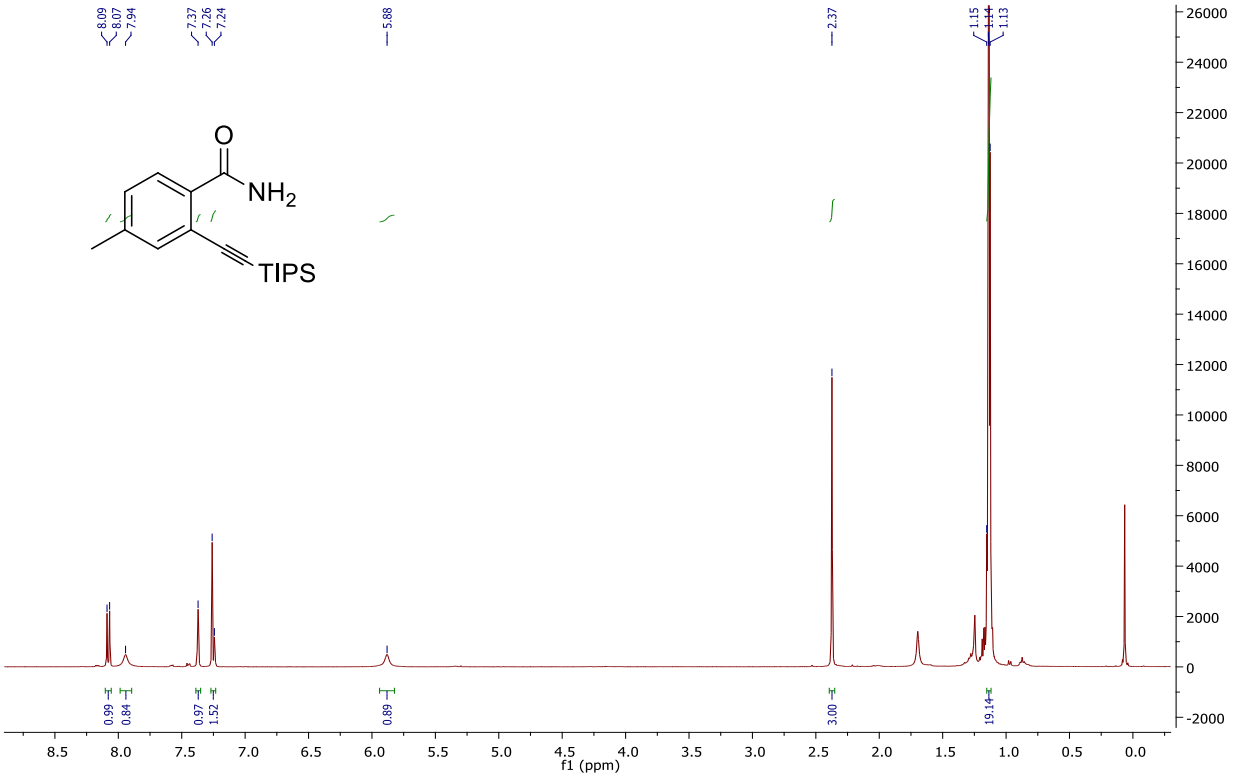



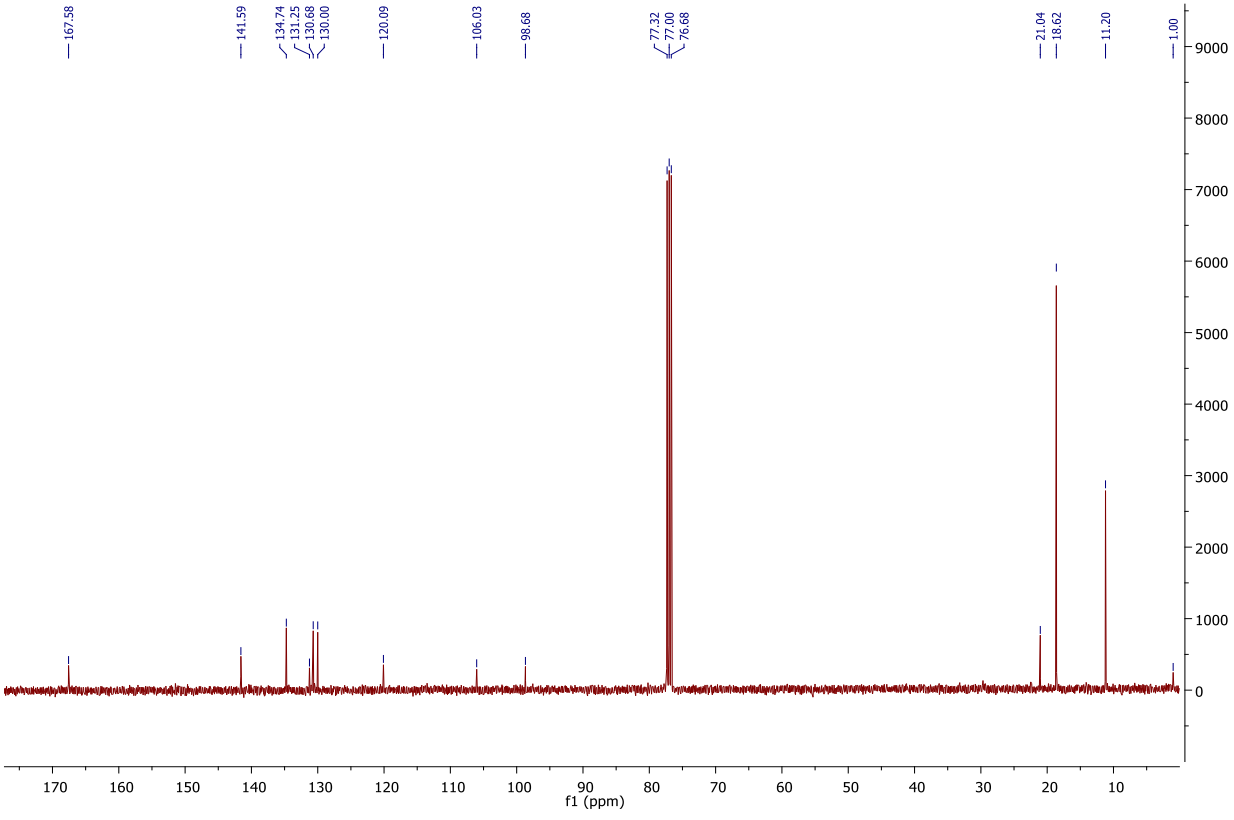
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5ab in $CDCl_3$**



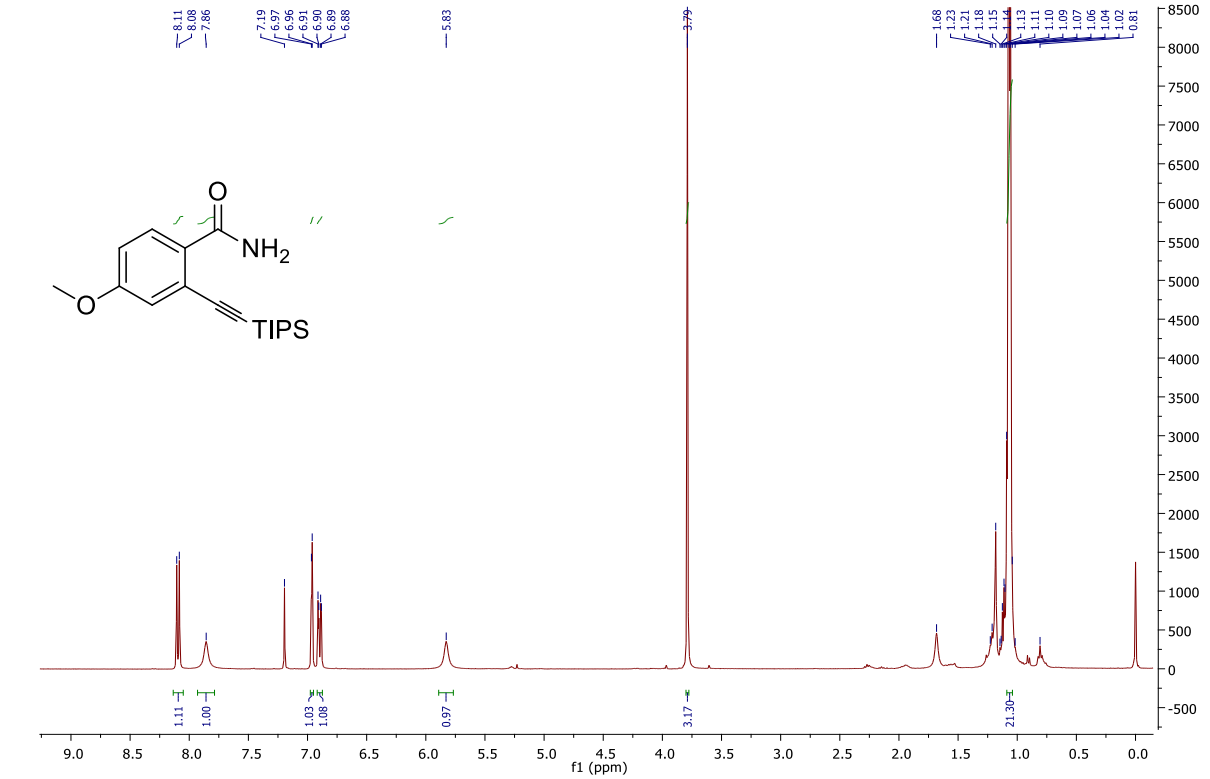



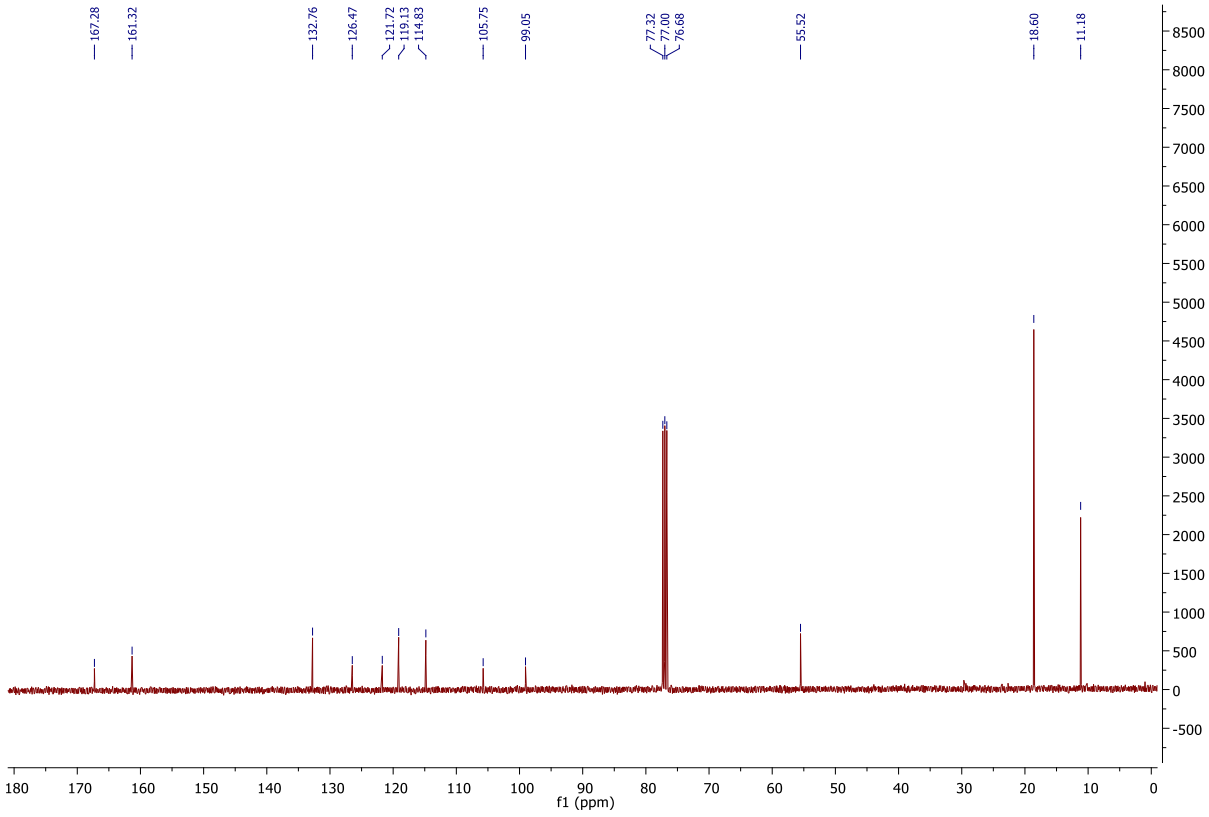
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5ac in $CDCl_3$**



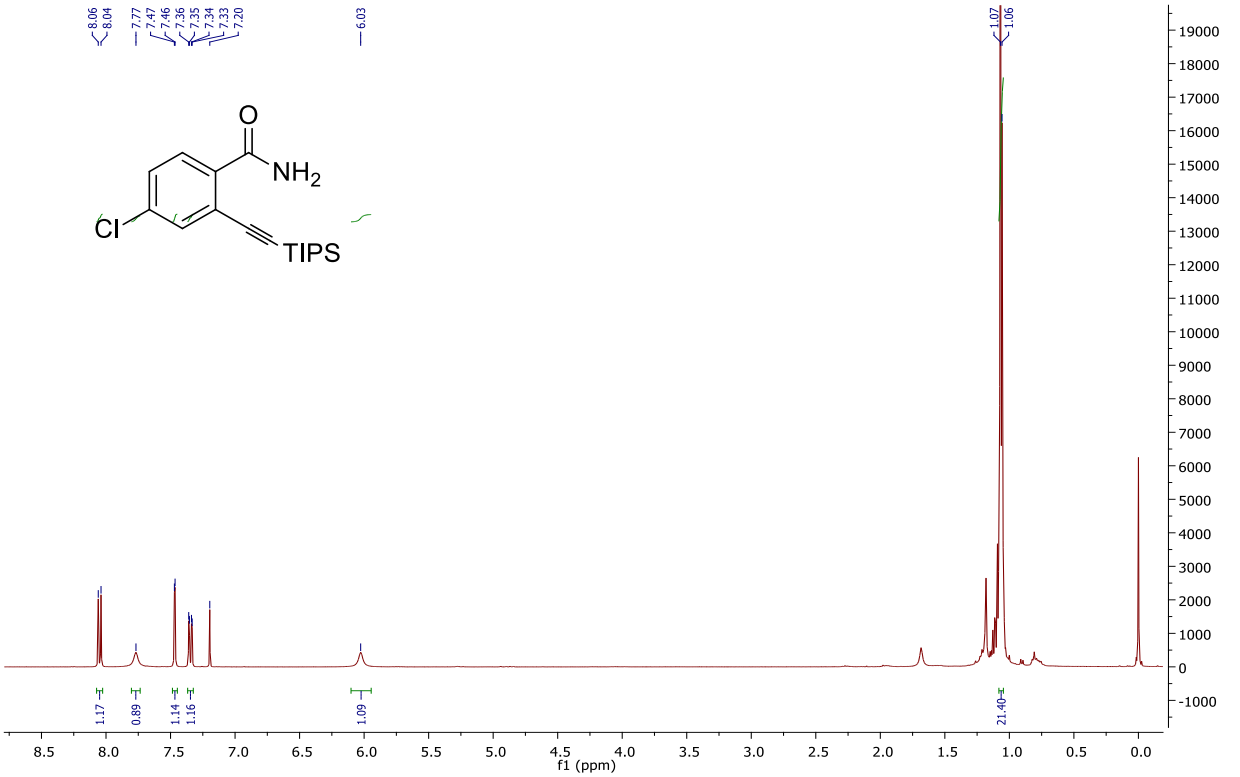



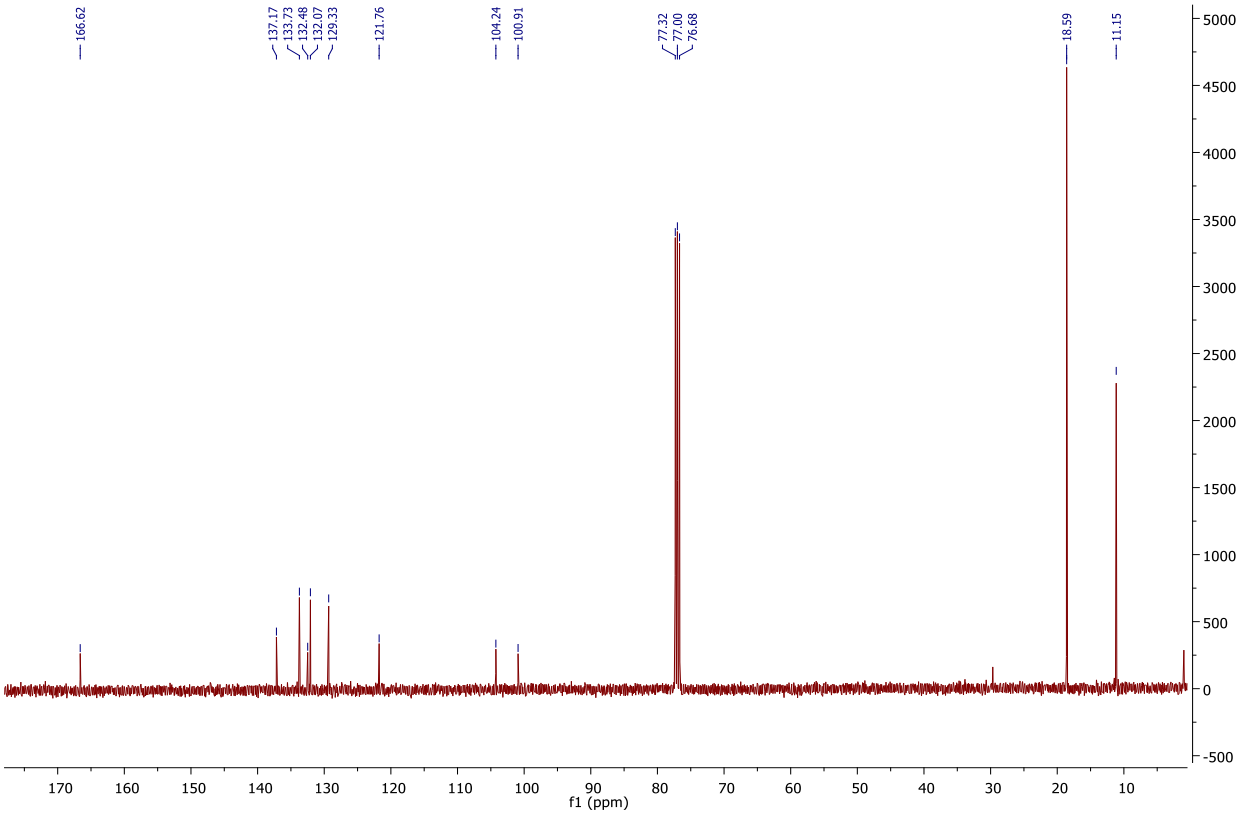
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5ad in $CDCl_3$**



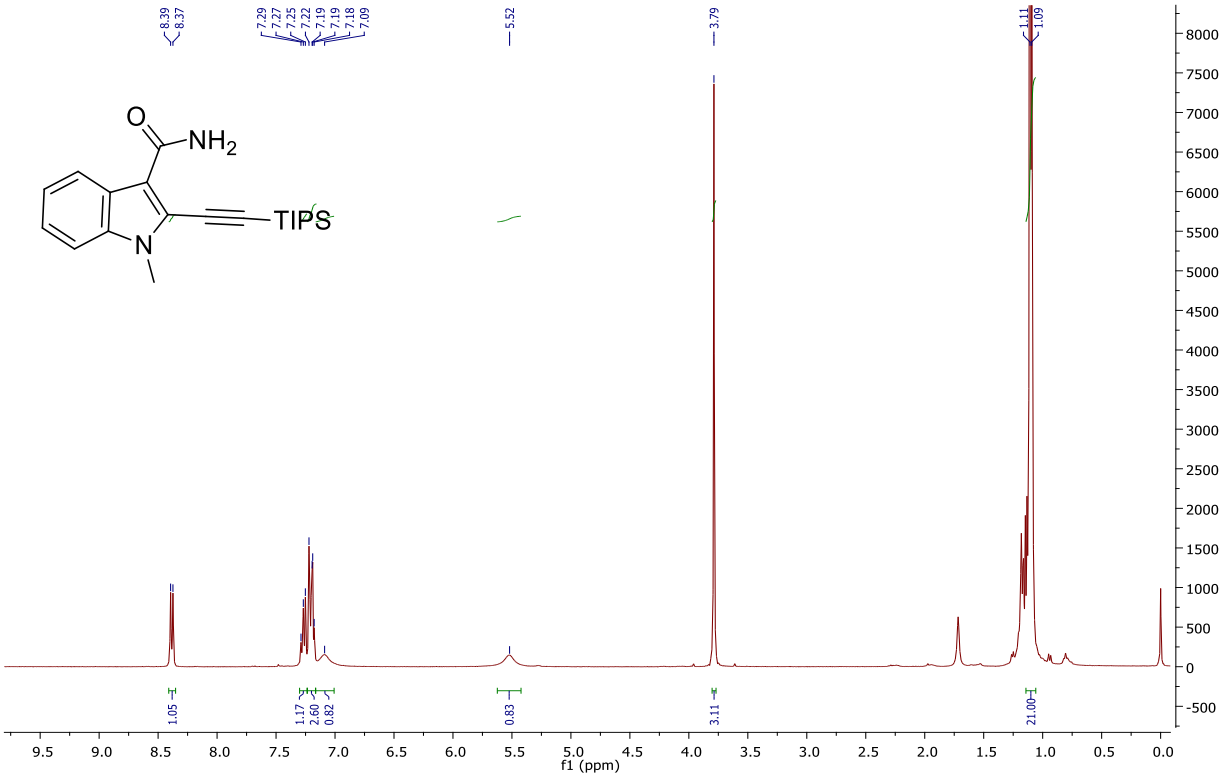



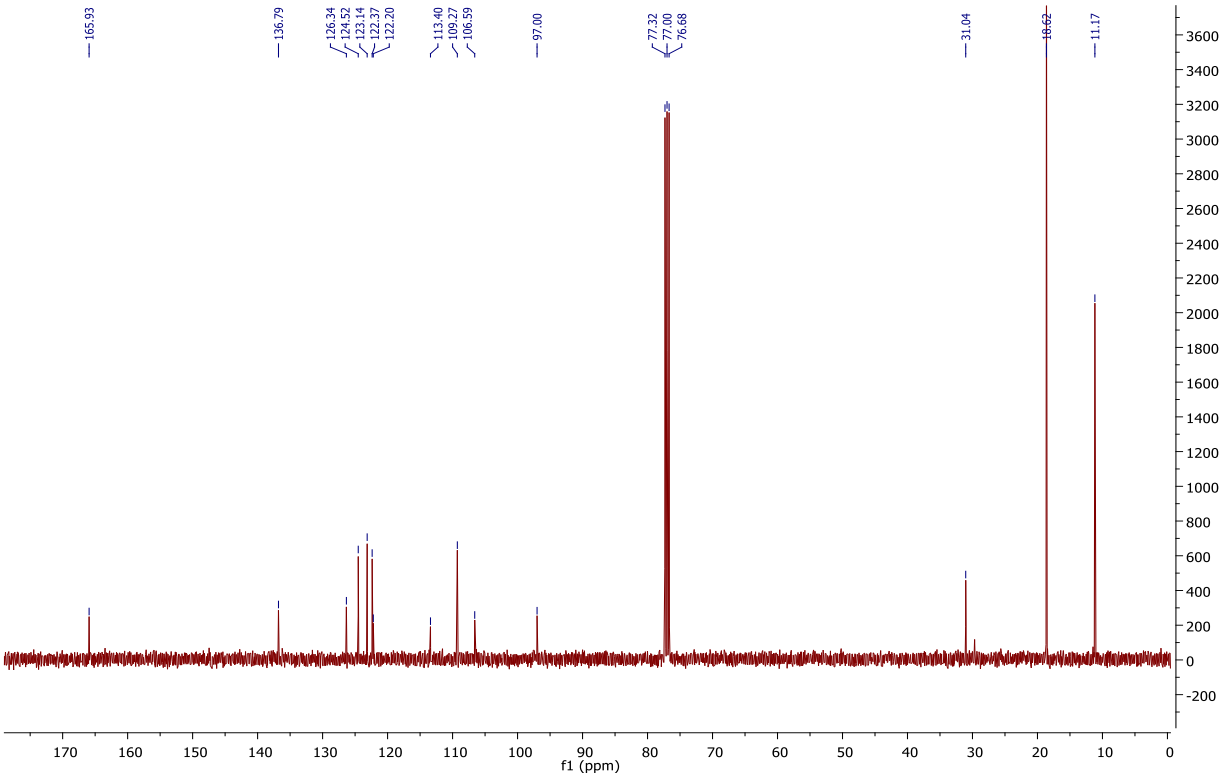
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5ae in $CDCl_3$**



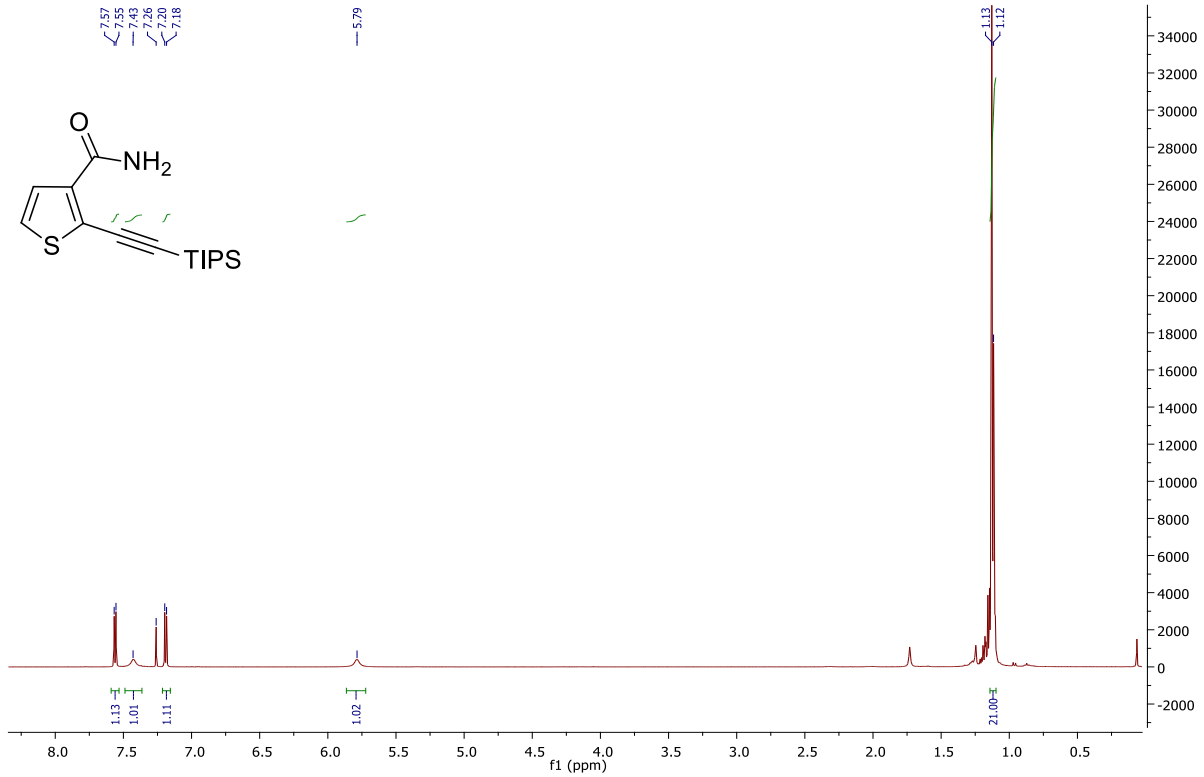



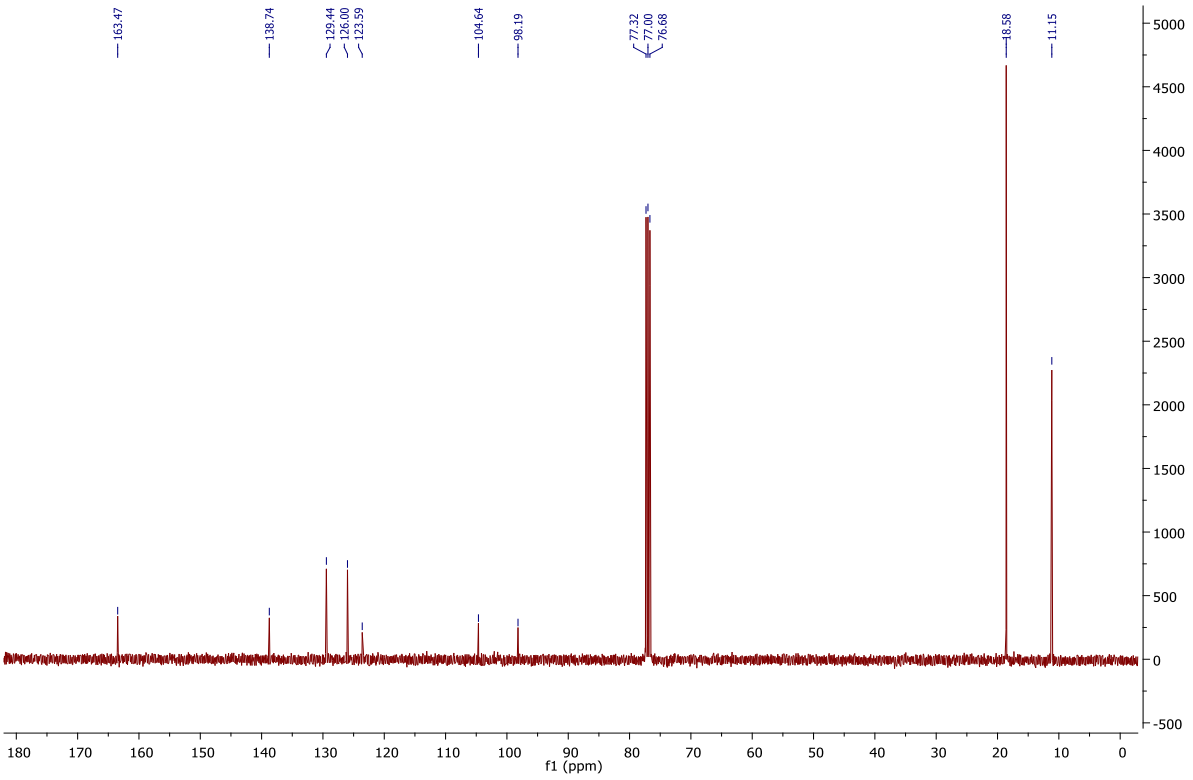
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5af in $CDCl_3$**



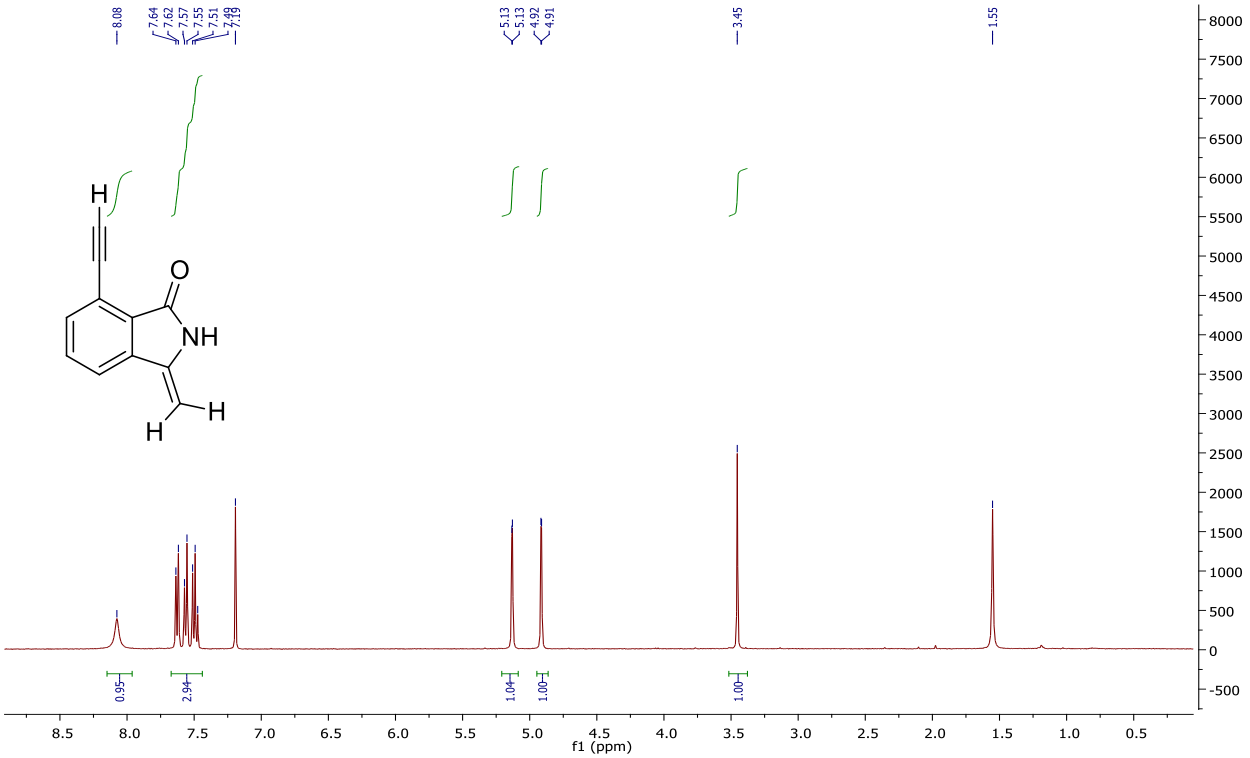



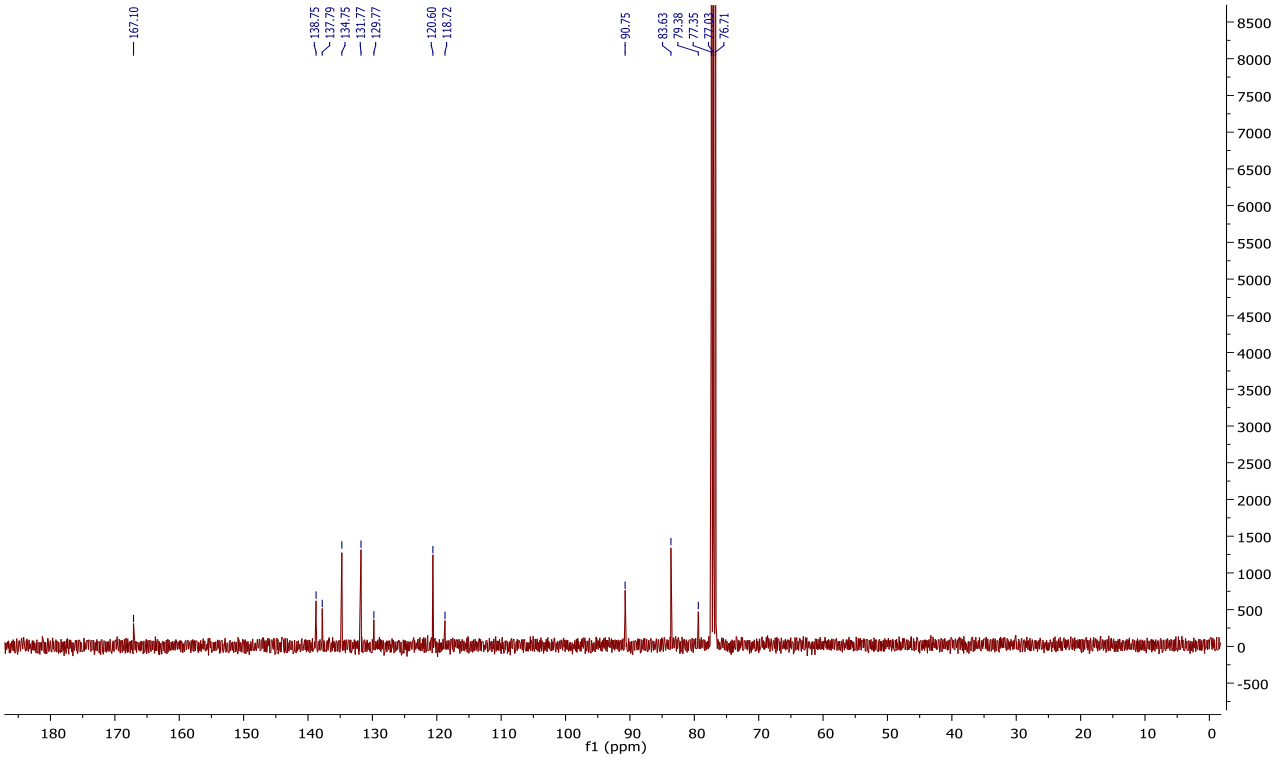
**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 5ag in $CDCl_3$**



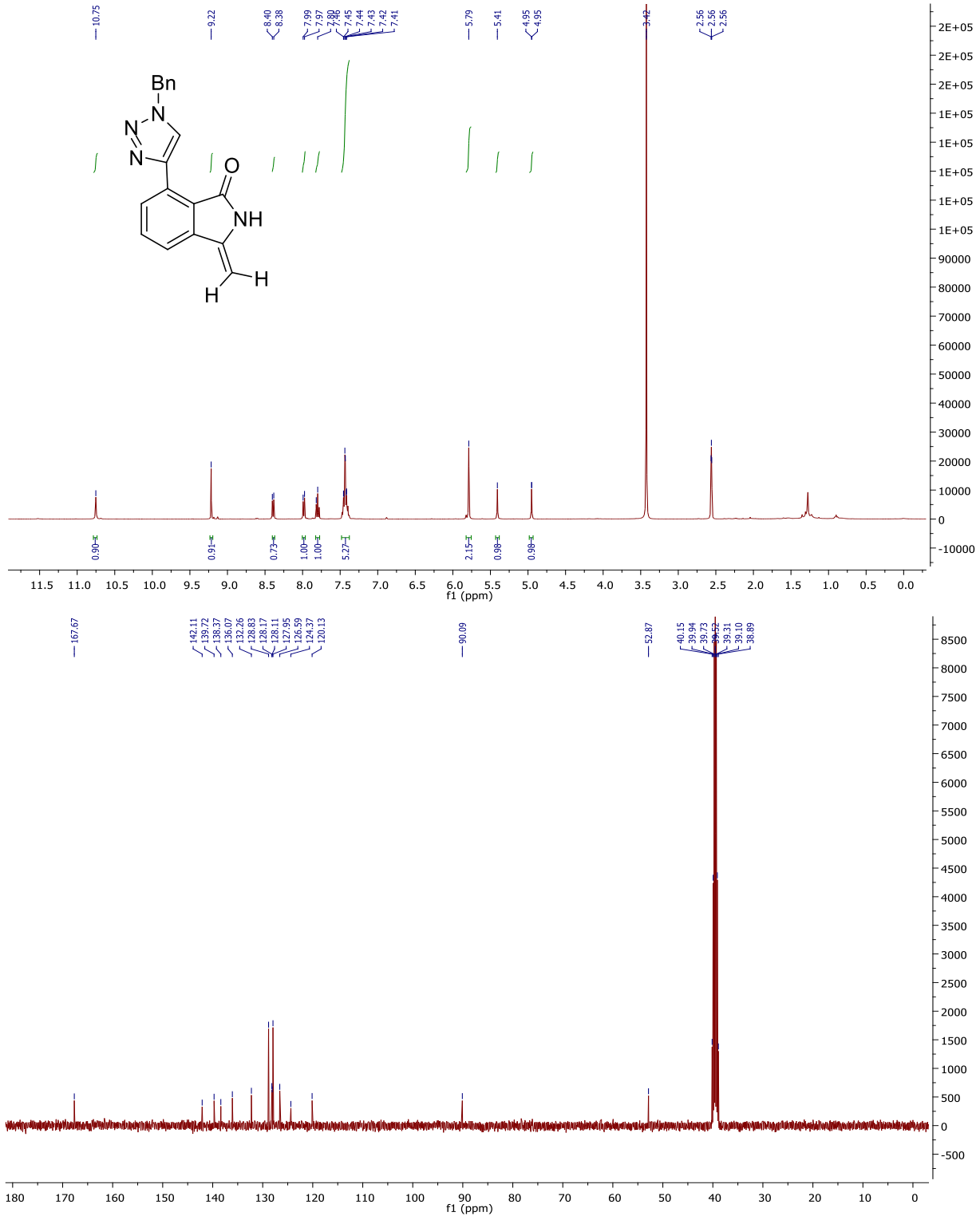



## $^{1}H$(400 MHz) and $^{13}C\{^{1}H\}$(100 MHz) spectra of 6a in $CDCl_3$



**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 7a in DMSO**



**$^{1}$H(400 MHz) and $^{13}$C{$^{1}$H}(100 MHz) spectra of 8a in $CDCl_3$**