Electronic Supplementary Material (ESI) for ChemComm.

A Straightforward Alkynylation of Li and Mg Metalated Heterocycles with Sulfonylacetylenes

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Supporting Information

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General Methods. NMR spectra were acquired on a Bruker 300 spectrometer, running at 300 and 75 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm). ^{13}C NMR spectra were acquired on a broad band decoupled mode. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or $KMnO_4$ dip. Purification of reaction products was carried out by flash chromatography (FC) using silica gel Merck-60. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected.

Materials. Sulfones **1a**,[1] **1b**,[1] **1c**,[1] **1d**,[3] **1e**,[3] **1f**,[3] **1g,**[3] **1h**[2] and **1i**[3] were synthesized following reported procedures. Diisopropylamine was dried by distillation over KOH. Comercially available anhydrous tetrahydrofuran (THF) and ethyl ether (Et_2O) were dried over 4Å molecular sieves.[2] All commercial reagents were purchased by Aldrich and used as received.

General Procedure A: Synthesis of Alkynes from Organolithium Compounds.

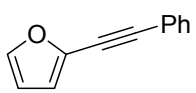
A solution of the alkynyl sulfone (0.2 mmol) in THF (1 mL) or Et_2O (1 mL) was added to a solution of the organolithium reagent (0.4 mmol, freshly prepared by direct metallation with *n*-BuLi, or *t*-BuLi) in THF (1.0 mL) or Et_2O (1.0 mL), under an argon atmosphere. After 15 min, the reaction mixture was quenched with a sat aq solution of NH_4Cl (1 mL) and diluted with Et_2O (1.0 mL). The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography (FC) using the appropriate mixture of solvents.

General Procedure B: Synthesis of Alkynes from Grignard Reagents.

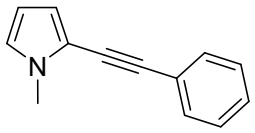
A solution of 1,2-dibromoethane (0.9 mmol) in THF (1 mL) was added over Mg (0.9 mmol) contained in a flask under argon atmosphere, and the solution stirred until bubble evolution ceased. Then the reaction mixture was cooled (0 ºC) and a solution of organolithium compound (0.3 mmol, freshly prepared by direct metallation with *n*-BuLi, *s*-BuLi or *t*-BuLi) in THF (3mL) was added. The reaction was warmed to room temperature over 10 min and a solution of the corresponding alkynyl sulfone (0.1 mmol) in THF (1 mL) was added. When the

[1] Nair, V., Augustine, A., Suja, T. D. *Synthesis* **2002**, 2259-2265
[2] Williams, D. B. G., Lawton, M. *J. Org. Chem.* **2010**, *75*, 8351-8354.

reaction was finished (followed by TLC) the mixture was quenched with a sat aq solution of NH_4Cl (1 mL) and diluted with Et_2O (1 mL). The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography (FC) using the appropriate mixture of solvents.

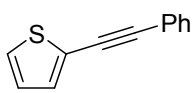


2-(Phenylethynyl)furan (3Aa). The title compound was obtained from sulfone **1a** and furan following general procedure A (89% yield) and general procedure B (96% yield). The organolithium was prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of furan in THF (1 mL). After purification by FC (hexane-AcOEt 15:1), compound **3Aa** was obtained as a yellow oil. Data for **3Aa** are in agreement with those described in the literature.[3] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.54 (m, 2H), 7.44 (s, 1H), 7.35 (t, *J* = 3.2 Hz, 3H), 6.66 (d, *J* = 3.3 Hz, 1H), 6.44-6.42 (m, 1H).



1-Methyl-2-(phenylethynyl)-1H-pyrrole (3Ba). The title compound was obtained from sulfone **1a** (0.20 mmol) and *N*-methylpyrrol (0.8 mmol) following general procedure A. The organolithium was prepared by addition of *n*-BuLi (0.80 mmol, 2.5 M in hexanes) to a cold solution (-78 ºC) of *N*-methylpyrrol (0.80 mmol) in THF (2 mL). After purification by FC (hexane-AcOEt 99:1), compound **3Ba** was obtained as a brown oil (69 % yield). Data for **3Ba** are in agreement with those described in the literature.[4] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.47 (m, 2H), 7.40-7.28 (m, 3H), 6.69 (dd, *J* = 2.7, 1.7 Hz, 1H), 6.50 (dd, *J* = 3.75,1.65 Hz, 1H), 6.13 (dd, *J* = 3.66, 2.73 Hz,

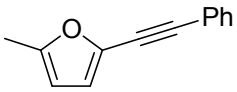
1H), 3.75 (s, 3H).



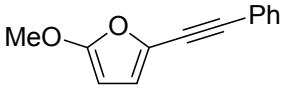
2-(Phenylethynyl)thiophene (3Ca). The title compound was obtained from sulfone **1a** and thiophene following general procedure A (87 % yield) and general procedure B (82 % yield). The organolithium was previously prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of thiophene in THF (1 mL). After

[3] A. Orita, N. Yoshioka, P. Struwe, A. Braier, A. Beckmann, J. Otera, *Chem. Eur. J.* **1999**, *5*, 1355.
[4] a) A. Minato, K. Tamao, T. Hayashi, K. Suzuki, M. Kumada, *Tetrahedron Letters* **1981**, *22*, 5319; b) B. E. Moulton, A. C. Whitwood, A. K. Duhme-Klair, J. M. Lynam, I. J. S. Fairlamb, *J. Org. Chem.* **2011**, *76*, 5320.

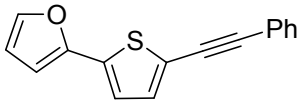
purification by FC (hexane-AcOEt 15:1), compound **3Ca** was obtained as a yellow solid. Data for **3Ca** are in agreement with those described in the literature.[5] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.50 (m, 2H), 7.35-7.33 (m, 3H), 7.30-7.28 (m, 2H), 7.01 (dd, *J* = 4.9, 3.9 Hz, 1H).



2-Methyl-5-(phenylethynyl)furan (3Da). The title compound was obtained from sulfone **1a** and 2-methylfuran following general procedure A. The organolithium was prepared by addition of *n*-BuLi (0.40 mmol, 2.5 M in hexanes) to a cold solution (-78 ºC) of 2-methylfuran (0.40 mmol) in THF (1 mL). After purification by FC (hexane-AcOEt 15:1), compound **3Da** was obtained as a brown oil (84 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.42 (m, 2H), 7.27-7.25 (m, 3H), 6.48 (d, *J* = 3.2 Hz, 1H), 5.95-5.94 (dd, *J*= 3.2, 1.0, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, CDCl3) δ 153.8, 135.4, 131.3, 128.4, 128.3, 122.6, 116.5, 107.2, 92.9, 79.8, 13.9.;TOF MS EI+: calcd for $C_{13}H_{10}O$ $[M]^+$ 182.0732, found 182.0724.



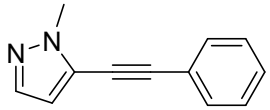
2-Methoxy-5-(phenylethynyl)furan (3Ea). The title compound was obtained from sulfone **1a** and 2-methoxyfuran following general procedure A. The organolithium was prepared by addition of *n*-BuLi (0.40 mmol, 2.5 M in hexanes) to a cold solution (-78 ºC) of 2-methoxyfuran (0.40 mmol) in THF (1 mL). After purification by FC (hexane-AcOEt 9:1), compound **3Ea** was obtained as a brown oil (86 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.40 (m, 2H), 7.26-7.24 (m, 3H), 6.49 (d, *J* = 3.4 Hz, 1H), 5.13 (d, *J*= 3.4 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 131.8, 131.1, 128.3, 128.4, 122.7, 117.7, 92.5, 81.8, 79.8, 57.8. TOF MS EI+: calcd for $C_{12}H_7O_3Na$ $[M+Na-CH_3]^+$ 206.0871, found 206.0798.



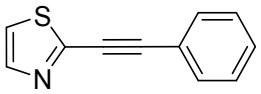
2-(5-(Phenylethynyl)thiophen-2-yl)furan (3Fa). The title compound was obtained from sulfone **1a** and 2-(thiophen-2-yl)furan following general procedure A. The organolithium was prepared by addition of *n*-BuLi (0.20 mmol, 2.5 M in hexanes) to a cold solution (-78 ºC) of 2-(thiophen-2-yl)furan (0.20 mmol) in THF (1 mL). After purification by FC (hexane-AcOEt 8:1), compound **3Fa** was obtained as a brown oil (60 % yield). Data for **3Fa** are in agreement with those described in the literature.[6] ^{1}H NMR (300

[5] K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, S. Lee, *J. Org. Chem.* **2010**, *75*, 6244.

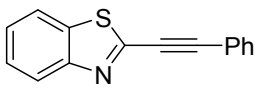
MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 7.35-7.34 (m, 1H), 7.28-7.26 (m, 3H), 7.12 (d, *J*= 3.8 Hz, 1H), 7.06 (d, *J*= 3.8 Hz, 1H), 6.46 (d, *J*= 3.4 Hz, 1H), 6.38 (dd, *J*= 3.4, 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 142.1, 135.0, 132.6, 131.4, 128.5, 128.4, 122.9, 122.3, 121.8, 111.8, 105.9, 94.1, 82.7; TOF MS EI+: calcd for $C_{16}H_{10}OS$ $[M]^+$ 250.0452, found 250.0452.



1-Methyl-5-(phenylethynyl)-1H-pyrazole (3Ga). The title compound was obtained from sulfone **1a** and 1-methyl-1H-pyrazole following general procedure A. The organolithium was prepared by addition of *n*-BuLi (0.50 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of 1-methyl-1H-pyrazole (0.50 mmol) in Et_2O (1 mL). After purification by FC (hexane-AcOEt 15:1), compound **3Ga** was obtained as a yellow solid (96 % yield). MP = 41-43 ºC. ^1H NMR (300 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.34 (d, *J*= 2.0 Hz 1H), 7.26-7-23 (m, 3H), 6.35 (d, *J*= 2.0 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 131.5, 129.0, 128.5, 125.6, 122.1, 110.1, 96.5, 77.6, 37.3; TOF MS EI+: calcd for $C_{12}H_{10}N_2$ $[M]^+$ 182.0844, found 182.0840.



2-(Phenylethynyl)thiazole (3Ha). The title compound was obtained from sulfone **1a** and thiazole following general procedure A (65% yield) and general procedure B (87% yield). The organolithium was prepared by addition of *n*-BuLi (0.50 mmol, 2.5 M in hexanes) to a cold solution (-78 ºC) of thiazole (0.50 mmol) in THF (1 mL). After purification by FC (hexane-AcOEt 9:1), compound **3Ha** was obtained as a brown solid. Data for **3Ha** are in agreement with those described in the literature.[7] ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J*= 3.3 Hz, 1H), 7.56-7.48 (m, 2H), 7.30-7.29 (m, 4H); ^{13}C NMR (75 MHz, CDCl3) δ 148.9, 143.6, 132.0, 129.5, 128.5, 121.5, 120.7, 93.9, 82.3; TOF MS EI+: calcd for $C_{11}H_7NS$ $[M]^+$ 185.0299, found 185.0291.



2-(Phenylethynyl)benzo[d]thiazole (3Ia). The title compound was obtained from sulfone **1a** and 1,3-benzothiazole following general procedure A. The organolithium was previously prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of 1,3-benzothiazole in THF (1 mL). After purification by

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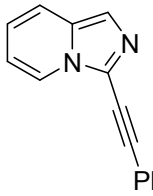
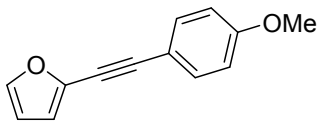
[6] M. Martínez, M. Peña-López, J. Pérez, L. Sarandeses, *Org. Biomol. Chem*., **2012**, *10*, 3892.
[7] S. Saleh, M. Picquet, P. Meunier, J. Hierso, *Tetrahedron* **2009**, *65,* 7146.

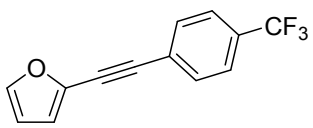
FC (hexane-AcOEt 15:1), compound **3Ia** was obtained as a yellow oil (64 % yield). Data for **3Ia** are in agreement with those described in the literature.[8] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.53 (td, *J* = 7.2, 1.0 Hz, 1H), 7.45-7.39 (m, 4H).



3-(Phenylethynyl)-3,8a-dihydroimidazo[1,5-a]pyridine (3Ja): The title compound was obtained from sulfone **1a** and 1 imidazo[1,5-a]pyridine following general procedure A. The organolithium was previously prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of imidazo[1,5-a]pyridine in THF (1 mL). After purification by FC (hexane-AcOEt 15:1), compound **3Ja** was obtained as a brown solid (90 % yield). Data for **3Ja** are in agreement with those described in the literature.[9] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (dd, *J*= 7.0, 1.0 Hz, 1H) 7.54-7.51 (m, 2H), 7.42-7.39 (m, 2H), 7.31-7.27 (m, 3H) 6.75 (ddd, *J*= 9.1, 6.5, 1.0 Hz, 1H), 6.64 (td, *J*= 6.9, 1.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl3) δ 131.6, 131.2, 128.9, 128.5, 122.7, 122.5, 122.2, 121.4, 120.4, 118.5, 113.7, 95.7, 78.3; TOF MS EI+: calcd for $C_{15}H_{10}N_2$ $[M]^+$ 218.0844, found 218.0834.



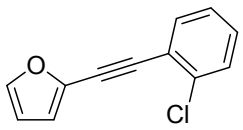
2-(4-Methoxyphenylethynyl)furan (3Ac). The title compound was obtained from sulfone **1c** and furan following general procedure A. The organolithium was prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of furan in THF (1 mL). After purification by FC (hexane-AcOEt 15:1), compound **3Ac** was obtained as a brown oil (58 % yield). Data for **3Ac** are in agreement with those described in the literature.[10] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 1.0 Hz, 1H), 6.87 (d *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 3.0 Hz, 1H), 6.41 (dd, *J* = 3.0, 1.0 Hz, 1H), 3.83 (s, 3H).



2-(4-(Trifluoromethyl)phenylethynyl)furan (3Ad). The title compound was obtained from sulfone **1c** and furan following general procedure A. The organolithium was prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of furan in THF (1 mL). After purification by FC (hexane-AcOEt 15:1), compound **3Ad** was obtained as a yellow oil (95 %

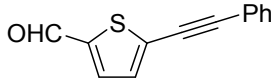
[8]B. Pacheco Berciano, S. Lebrequier, F. Besselièvre, S. Piguel, *Org. Lett.* **2010,** *12*, 4038.
[9] F. Shibahara, Y. Dohke, T. Murai, *J.Org.Chem.* **2012**, *77*, 5381.
[10] M. L. N. Rao, D. N. Jadhav, P. Dasgupta *Org. Lett.* **2010**, *9,* 2048.

yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (s, 4H), 7.46 (d, *J* = 2.0 Hz, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.45 (dd, *J* = 3.4, 2.0 Hz, 1H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 136.6, 131.5, 130.3 (q, $J_{C\text{-}F}$ = 32.6 Hz), 126.2, 125.3 (q, J_C = 3.7 Hz), 123.9 (q, $J_{C\text{-}F}$ = 270.4), 116.2, 111.2, 91.9, 81.7; TOF MS EI+: calcd for $C_{13}H_7OF_3$ $[M]^+$ 236.0449, found 236.0448.



2-(2-Chlorophenylethynyl)furan (3Ae). The title compound was obtained from sulfone **1e** and furan following general procedure A. The organolithium was prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of furan in THF (1 mL). After purification by FC (hexane-AcOEt 15:1), compound **3Ae** was obtained as a brown oil (76 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.0 Hz, 1H), 7.38-7.34 (m, 2H), 7.24-7.15 (m, 3H), 6.65 (d, *J* = 3.0 Hz, 1H), 6.38-6.37 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 136.8, 135.7, 133.1, 129.6, 129.3, 126.5, 122.4, 116.0, 111.1, 90.0, 84.3; TOF MS EI+: calcd for $C_{13}H_7OF_3$ $[M]^+$ 236.0449, found 236.0449.

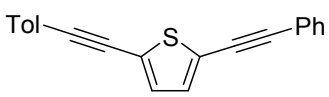
2-(Triisopropylsilylethynyl)furan (3Ag). The title compound was obtained from sulfone **1g** and furan following general procedure A. The organolithium was prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of furan in THF (1 mL). After purification by FC (hexane-AcOEt 15:1), compound **3Ag** was obtained as a brown oil (54 % yield). Data for **3Ag** are in agreement with those described in the literature.[11] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (s, 1H), 6.59 (d, *J* = 3.3 Hz, 1H), 6.36 (d, *J* = 3.3 Hz, 1H), 1.17-1.06 (m, 21H).



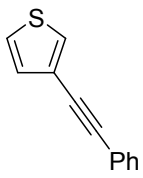
5-(Phenylethynyl)thiophene-2-carbaldehyde (5). To a cold solution (-78 ºC) of 2-(phenylethynyl)thiophene **3Ca** (0.2 mmol) in THF (1 mL), *n*-BuLi (0.2 mmol, 2.5 M in hexanes) was added and the mixture stirred for 10 min. Then the mixture was wormed up to room temperature, and dried DMF (1.0 mmol) was added. The reaction mixture was stirred until disappearance of **3Ca** (followed by TLC). The reaction mixture was quenched with a sat aq solution of NH_4Cl (1 mL) and diluted with Et_2O (1 mL). The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. After purification

[11] Y. Li, J. P. Brand, J. Waser *Angew. Chem. Int. Ed.* **2013**, *52*, 6743.

by FC (hexane-AcOEt 8:1), compound **5** was obtained as a brown solid (75 % yield). Data for **5** are in agreement with those described in the literature.[12] ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.87 (s, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.56-7.53 (m, 2H), 7.40-7.36 (m, 3H), 7.31 (d, *J* = 4.0 Hz, 1H).

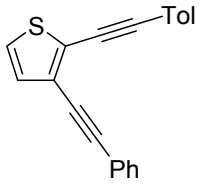


2-(Phenylethynyl)-5-(p-tolylethynyl)thiophene (4Cab). To a cold solution (-78 ºC) of 2-(phenylethynyl)thiophene **3Ca** (0.2 mmol) in THF (1 mL), *n*-BuLi (0.2 mmol, 2.5 M in hexanes) was added and the mixture stirred for 10 min. Then the mixture was warmed up to room temperature, and sulfone **1b** (0.3 mmol) in THF (0.7 mL) was added. The reaction mixture was stirred until disappearance of **3Ca** (followed by TLC). The reaction mixture was quenched with a sat aq solution of NH_4Cl (1 mL) and diluted with Et_2O (1 mL). The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. After purification by FC (hexane), compound **4Cab** was obtained as a yellow solid (52 % yield). MP = 103-105 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.51 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37-7.35 (m, 3H), 7.18-7.13 (m, 4H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 131.8, 131.6, 131.4, 129.2, 128.6, 128.4, 125.0, 124.4, 122.7, 119.5, 94.3, 94.0, 82.4, 81.7, 21.6; TOF MS EI+: calcd for $C_{21}H_{14}S$ $[M]^+$ 298.0816, found 298.0818.

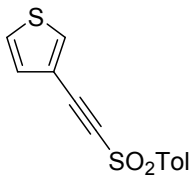


3-(Phenylethynyl)thiophene (3Ka). The title compound was obtained from sulfone **1a** and 3-bromothiophene following general procedure A (99 % yield). The organolithium was previously prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (-78 ºC) of thiophene in THF (1 mL). This compound was also obtained from sulfone **1h** and phenylmagnesium bromide (0.2 mmol, 3M in Et_2O) following general procedure A (89% yield). After purification by FC (hexane-AcOEt 10:1), compound **3Ka** was obtained as a white solid. Data for **3Ka** are in agreement with those described in the literature.[13] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.42 (m, 3H), 7.27-7.20 (m, 4H), 7.12 (dd, *J* = 1.2, 5.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.6, 129.9, 128.6, 128.4, 128.2, 125.4, 123.3, 122.3, 88.9, 84.5.

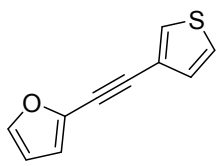
[12] A. Orita, F. Ye, G. Babu, T. Ikemoto, J. Otera, *Can. J. Chem.* **2005**, *83*, 716.
[13] C. W. D. Gallop, M.-T. Chen, O. Navarro, *Org. Lett.* **2014**, *16*, 3724.



3-(Phenylethynyl)-2-(*p*-tolylethynyl)thiophene (4Kab). To a cold solution (-78 ºC) of 3-(phenylethynyl)thiophene **3Ka** (0.2 mmol) in THF (1 mL), *n*-BuLi (0.2 mmol, 2.5 M in hexanes) was added and the mixture stirred for 10 min. Then the mixture is warmed up to room temperature, and sulfone **1b** (0.3 mmol) in THF (0.7 mL) was added. The reaction mixture was stirred until disappearance of **3Ka** (followed by TLC). The reaction mixture was quenched with a sat aq solution of NH_4Cl (1 mL) and diluted with Et_2O (1 mL). The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. After purification by FC (hexane), compound **4Kab** was obtained as a yellow oil (57 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.55 (m, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.36-7.34 (m, 3H), 7.21-7.16 (m, 3H), 7.12-7.09 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 131.6, 131.4, 129.5, 129.2, 128.4, 126.6, 126.4, 125.8, 123.2, 119.8, 97.9, 93.5, 84.1, 81.4, 21.6; TOF MS EI+: calcd for $C_{21}H_{14}S$ $[M]^+$ 298.0816, found 298.0812.



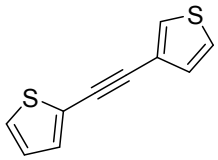
3-(Tosylethynyl)thiophene (1i): The title compound was obtained following the experimental procedure described in the literature.[14] After purification by FC (hexane-AcOEt 6:1), compound **1i** was obtained as a brown solid (50 % yield). Mp = 96-98 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 3.0 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 3.0, 5.1 Hz, 1H), 7.14 (d, *J* = 5.1 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 138.9, 134.5, 130.0, 129.7, 127.5, 126.5, 117.2, 88.6, 85.6, 21.7. TOF MS EI+: calcd for $C_{13}H_{10}O_2S_2$ $[M]^+$ 262.0135, found 262.0135.



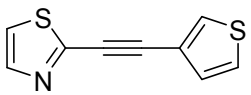
2-(Thiophen-3-ylethynyl)furan (3Mi). The title compound was obtained from sulfone **1i** and furan following general procedure B. The organolithium was prepared by addition of *n*-BuLi (0.42 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of furan in THF (1 mL). After purification by FC (hexane-AcOEt 6:1), compound **3Mi** was obtained as a brown oil (67 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 3.0 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.30 (dd, *J* = 3.0, 5.0 Hz, 1H), 7.19 (d, *J* = 5.0 Hz, 1H), 6.64 (d, *J* = 3.3 Hz, 1H), 6.42 (dd, *J* = 3.3, 2.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 137.1, 129.7, 129.3, 125.5, 121.3, 115.1, 111.0, 84.4, 78.9; TOF MS EI+: calcd for $C_{10}H_6OS$ $[M]^+$ 174.0139, found 174.0143.

[14] Nair, V., Augustine, A., Suja, T. D. *Synthesis* **2002**, 2259.

2-(Thiophen-3-ylethynyl)thiophene (3Ni). The title compound was obtained from sulfone **1h**

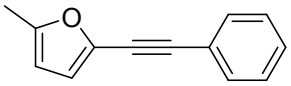


(0.2 mmol) in THF (1mL), and 2-thyenylmagnesium bromide (0.4 mmol, 1 M in THF) following the general procedure A. After purification by FC (hexane-AcOEt 10:1), compound **3Ni** was obtained as a white solid (72 % yield). MP = 92-94 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, *J* = 3.0 Hz, 1H), 7.36-7.30 (m, 1H), 7.23 (d, *J* = 6.0 Hz, 1H), 7.05 (dd, *J* = 3.0, 6.0 Hz, 1H): ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.8, 129.7, 128.7, 127.1, 127.0, 125.4, 123.3, 121.9, 88.17, 82.1; TOF MS EI+: calcd for $C_{10}H_6S_2$ $[M]^+$ 189.9911, found 189.9918.



2-(thiophen-3-ylethynyl)thiazole (3Oi). The title compound was obtained from sulfone **1i** and thiazole following general procedure B, but heating the final mixture a 50 ºC. The organolithium was prepared by addition of *n*-BuLi (0.50 mmol, 2.5 M in hexanes) to a cold solution (0 ºC) of thiazole (0.50 mmol) in THF (1 mL). After purification by FC (hexane-AcOEt 6:1), compound **3Oi** was obtained as a brown solid (89 % yield). MP = 73-75 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 3.0 Hz, 1H), 7.60-7.58 (m, 1H), 7.29 (d, *J* = 3.0 Hz, 1H), 7.25 (dd, *J* = 2.9, 5.0 Hz, 1H), 7.19-7.16 (m, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 143.5, 130.8, 129.7, 125.8, 120.6, 120.5, 89.3, 81.9; TOF MS EI+: calcd for $C_9H_5NS_2$ $[M]^+$ 190.9863, found 190.9861.

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



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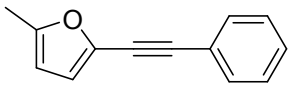

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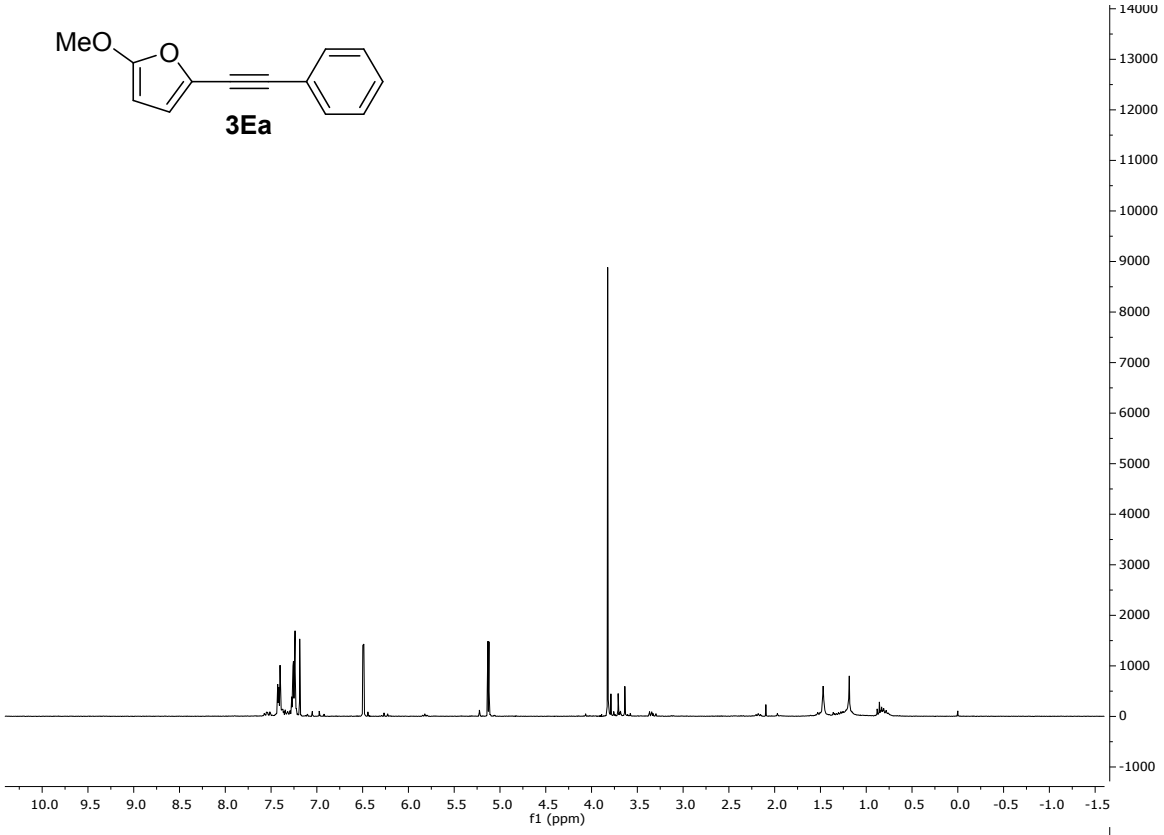
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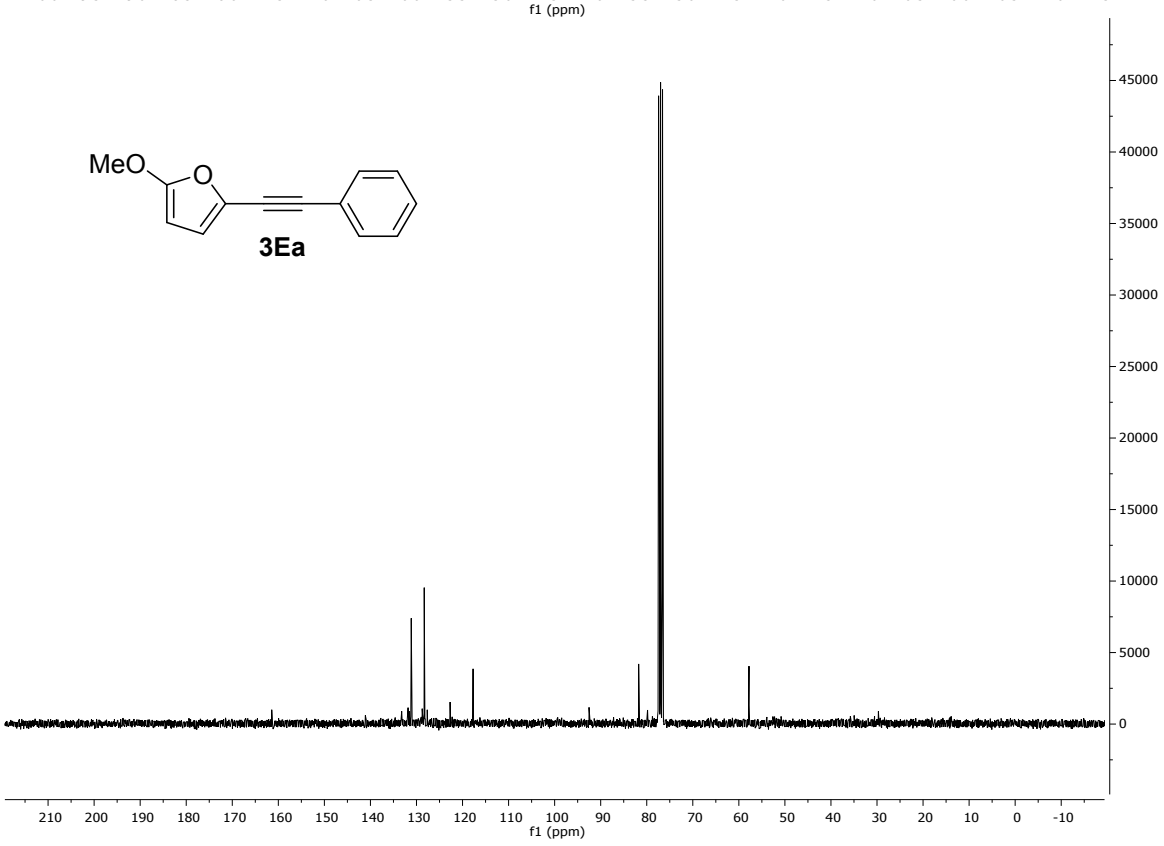
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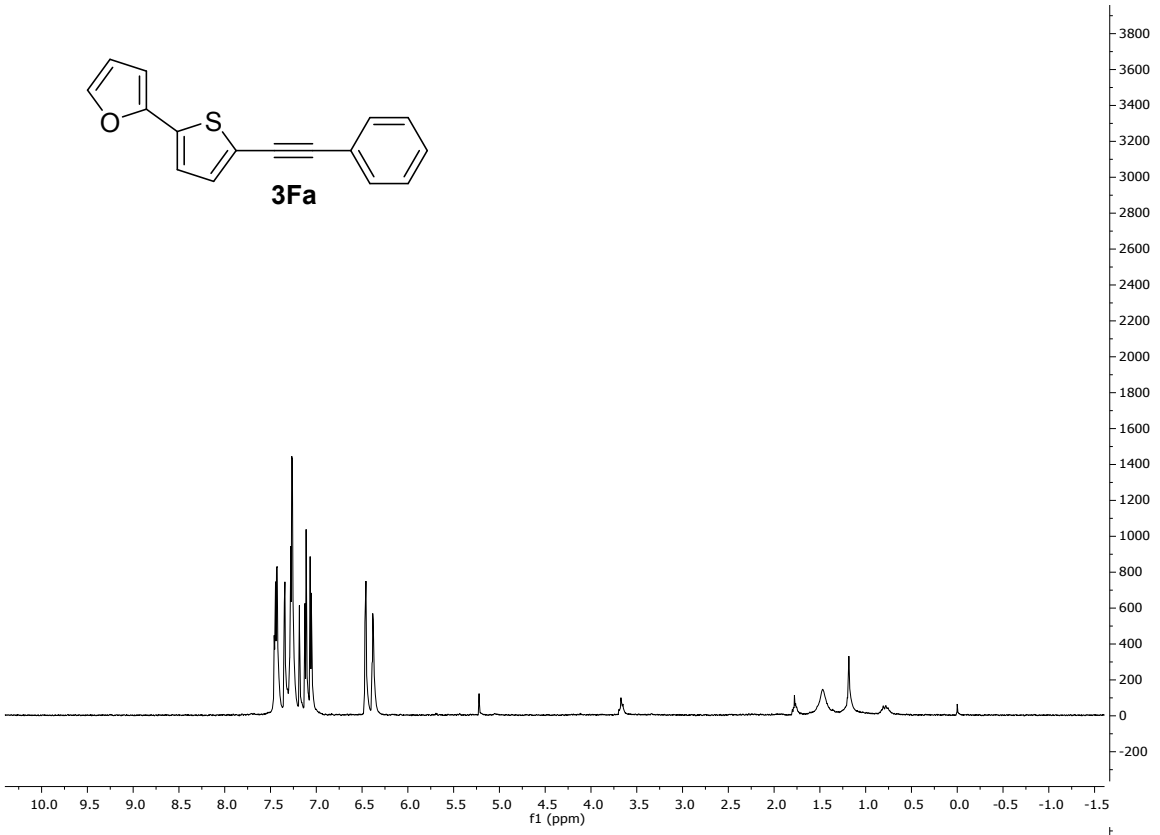
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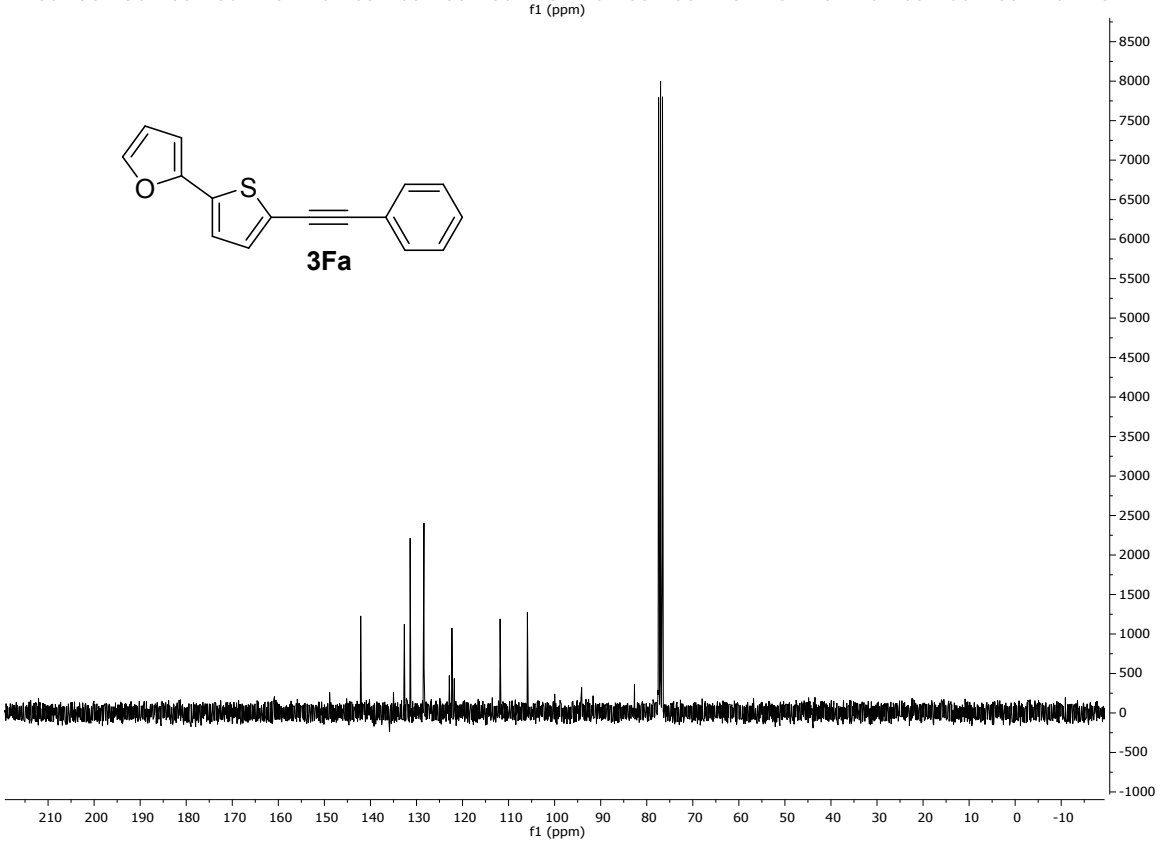
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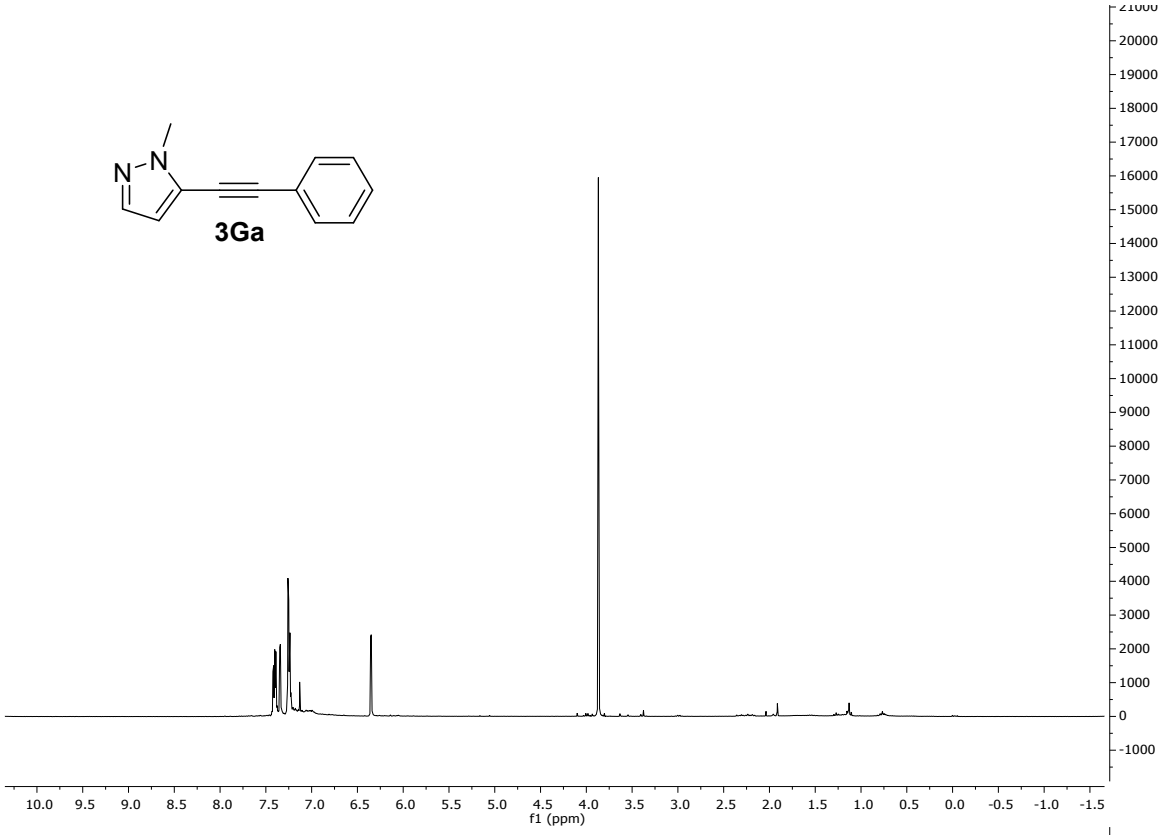
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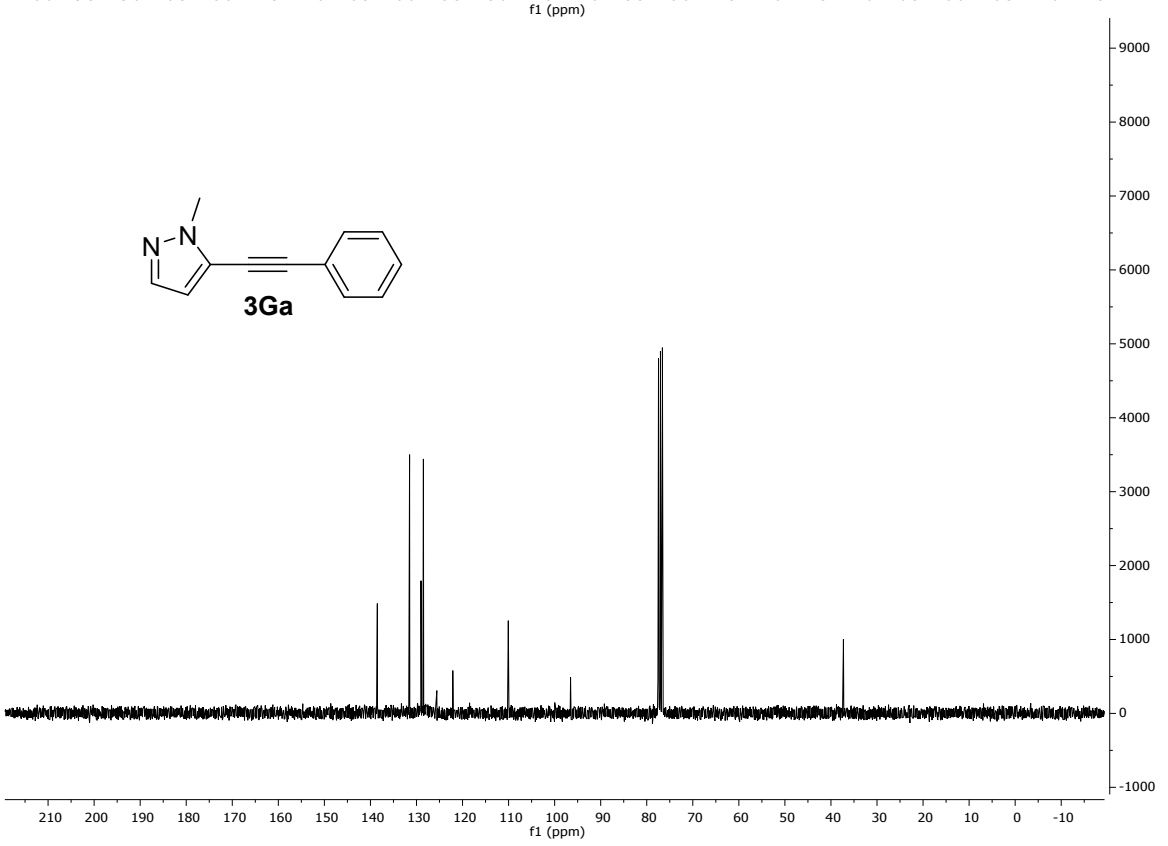
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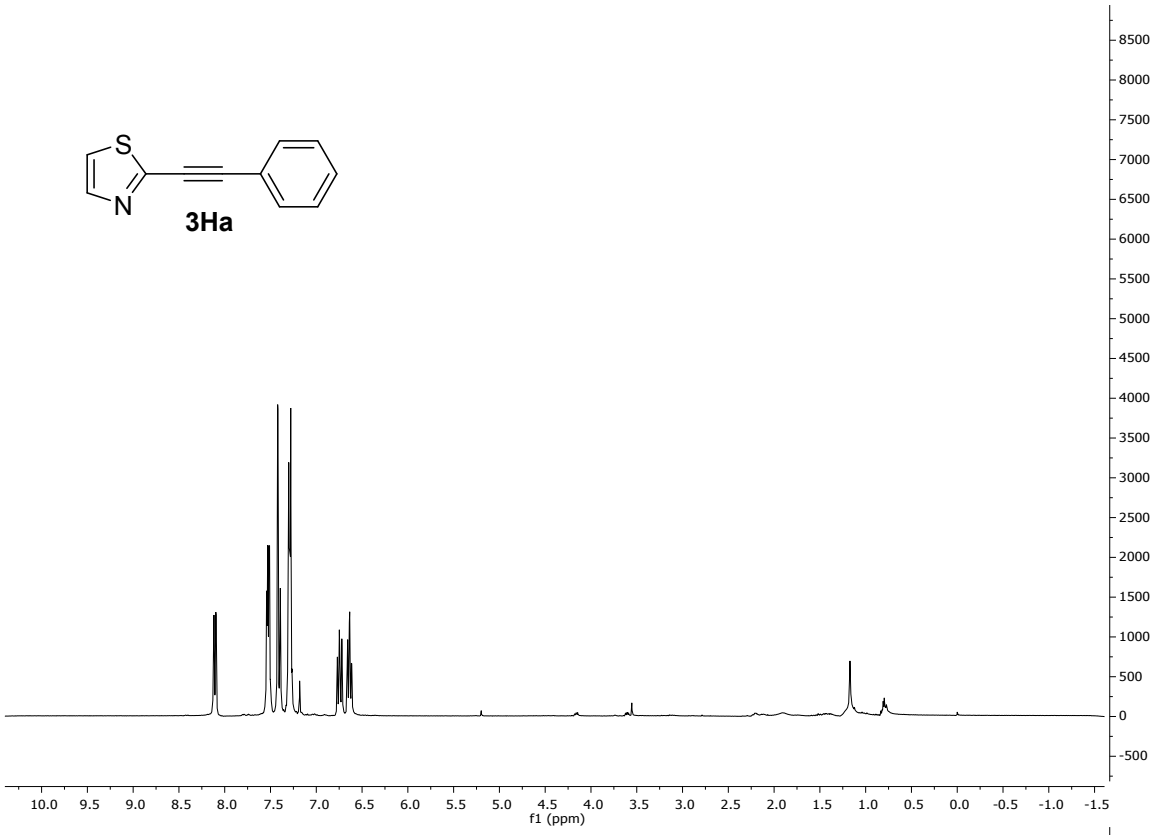
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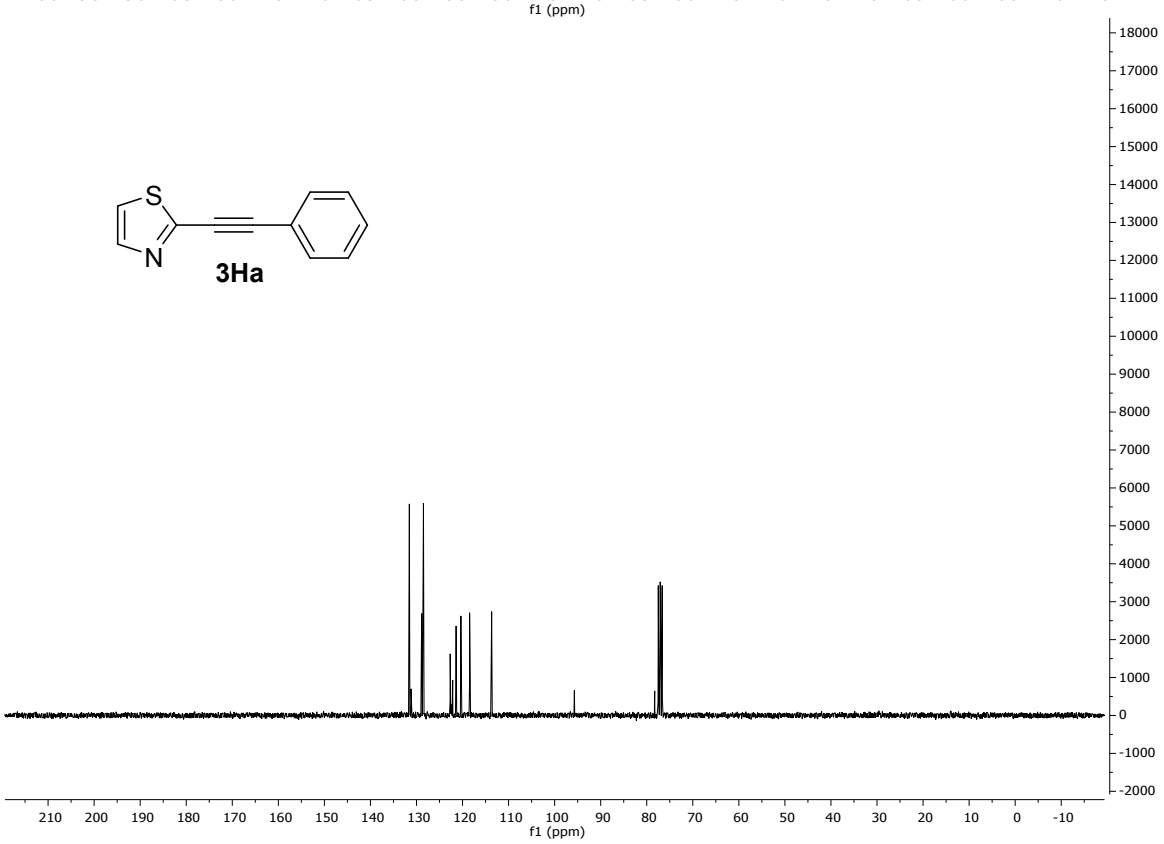
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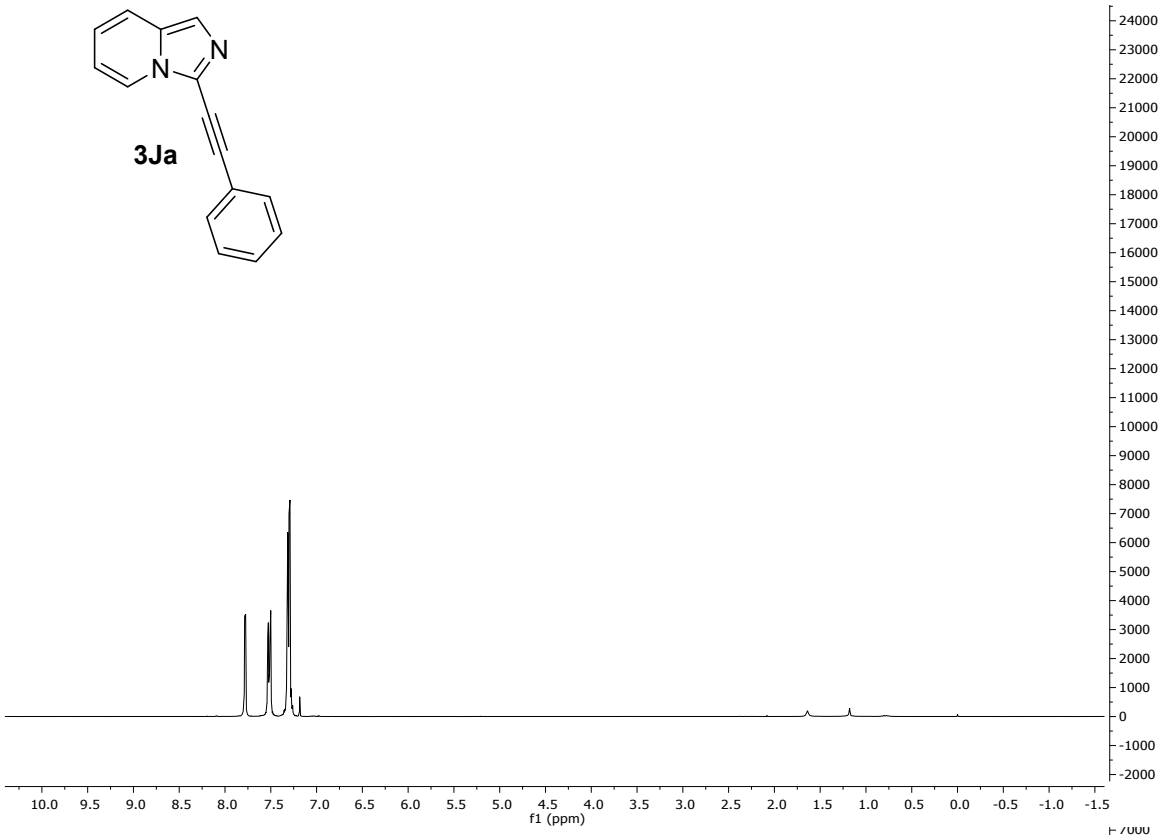
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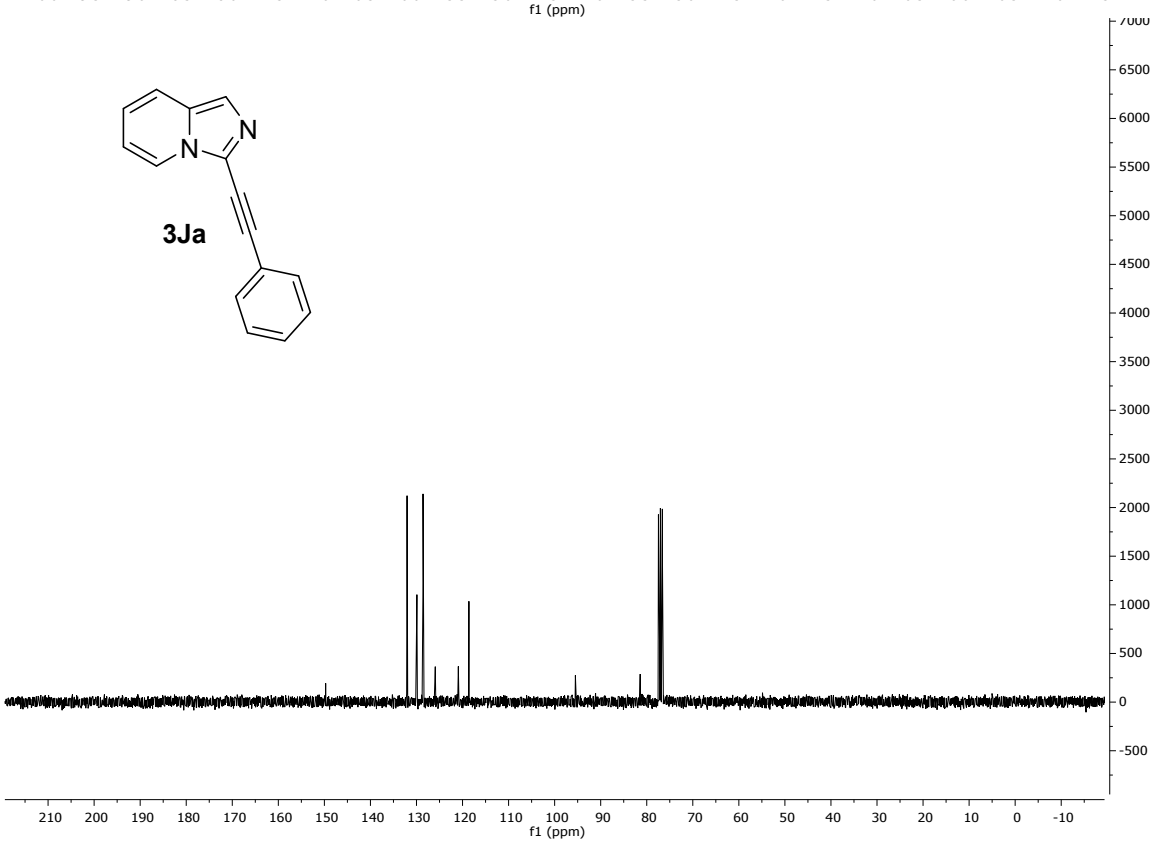
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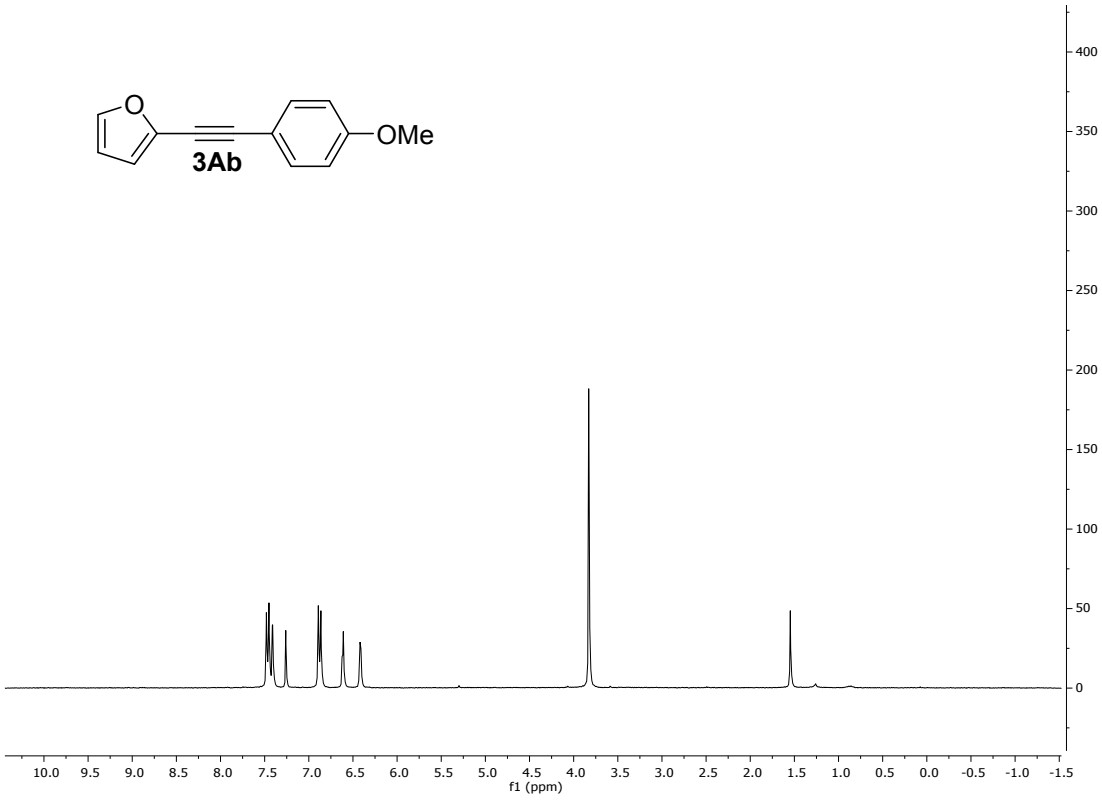
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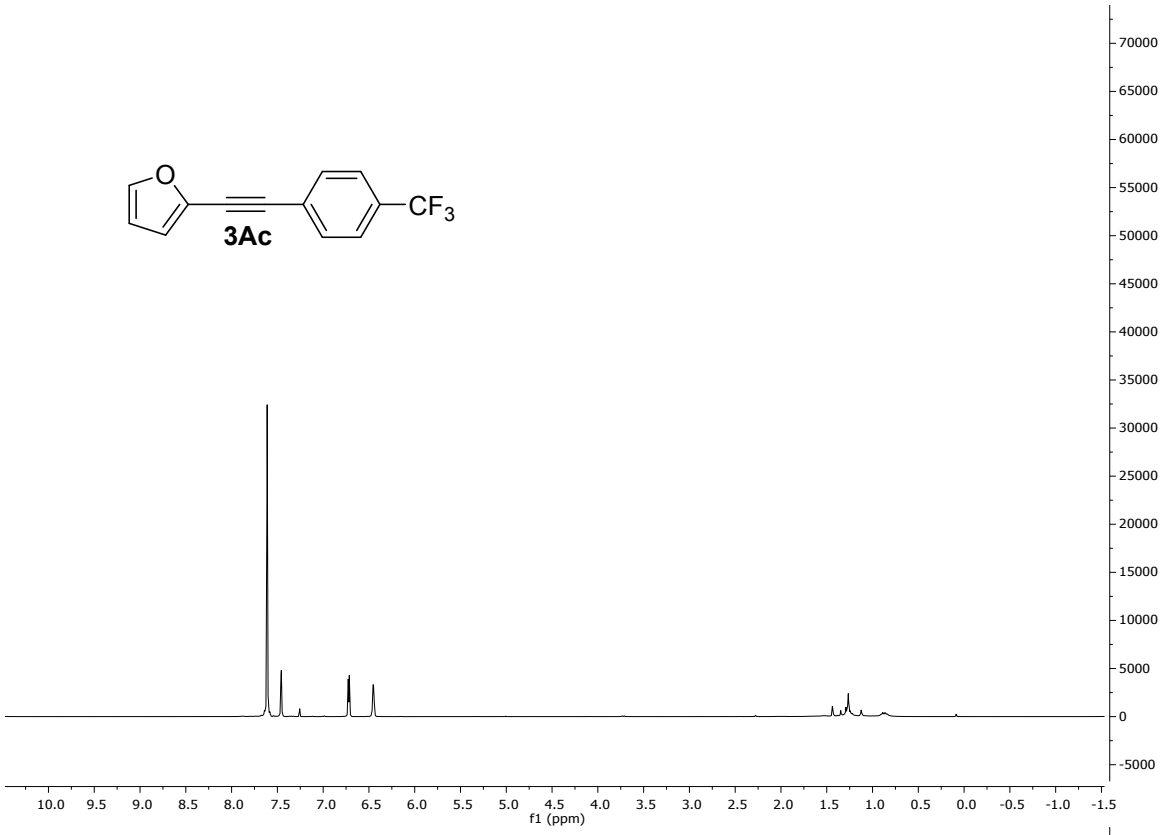
f1 (ppm)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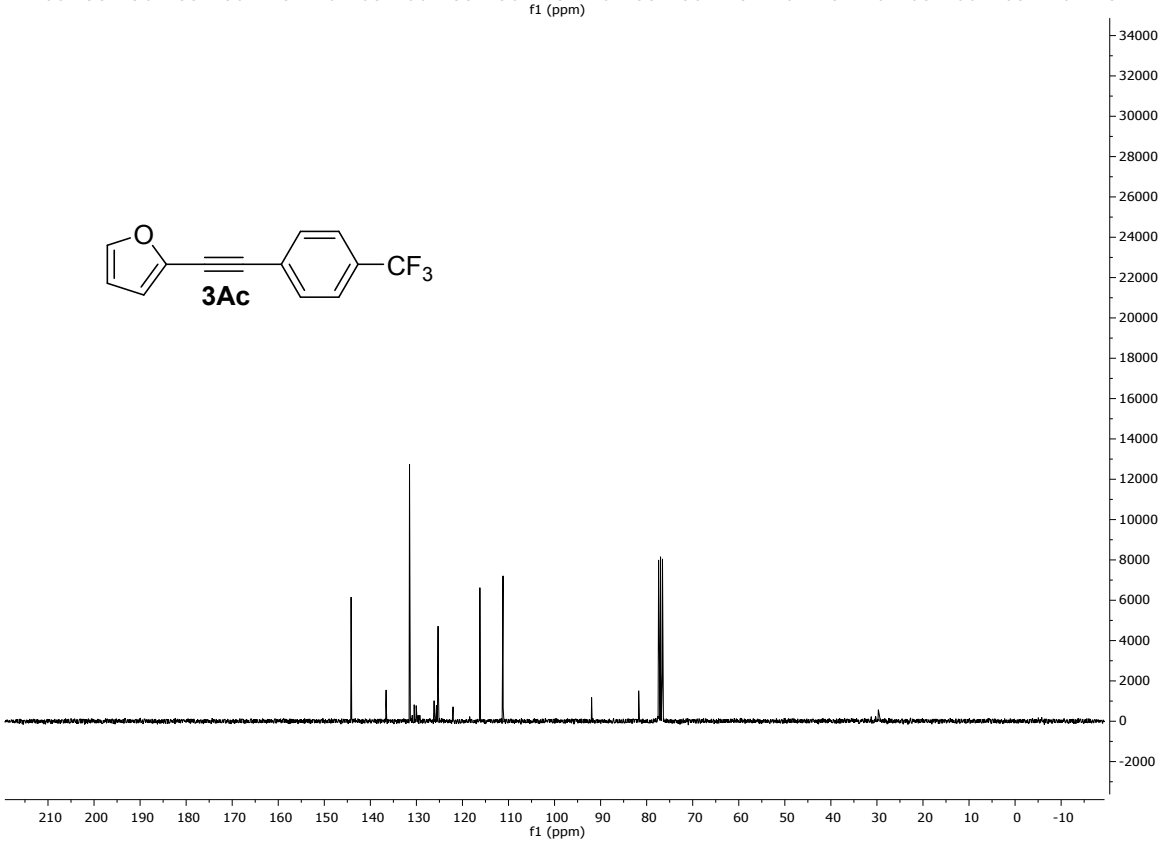
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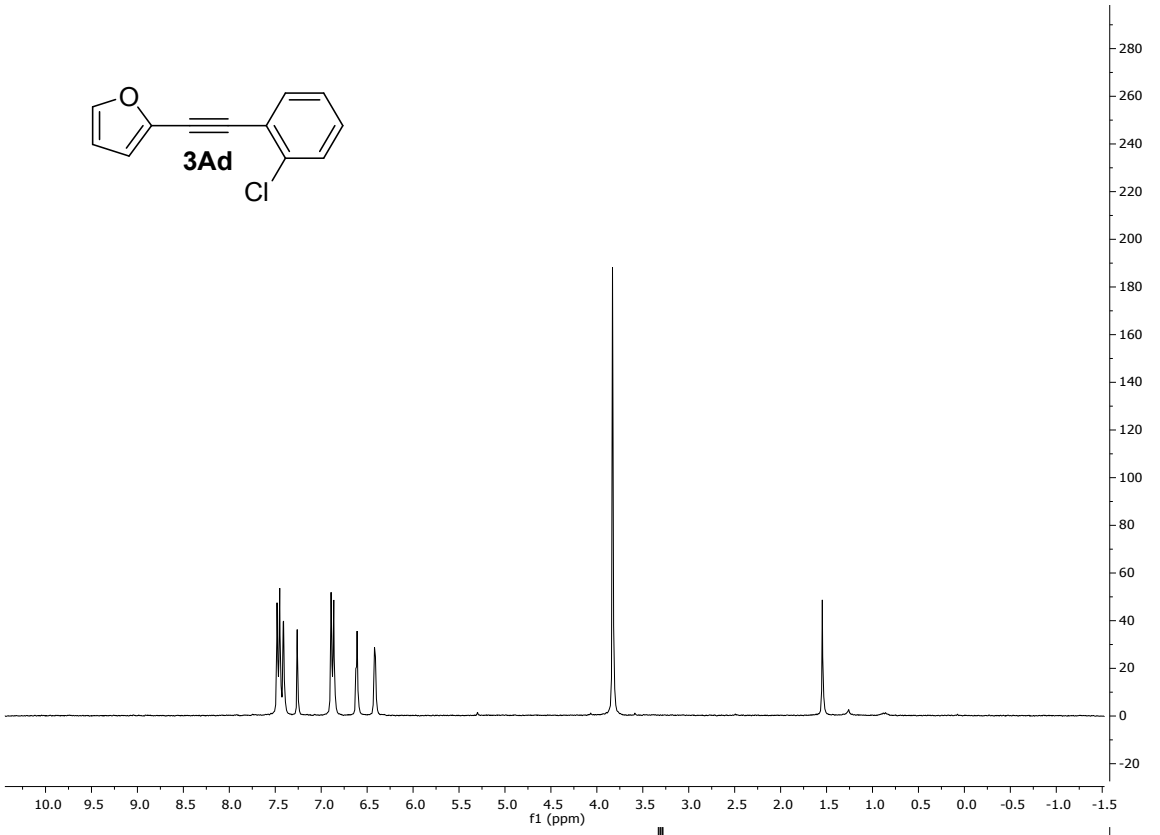
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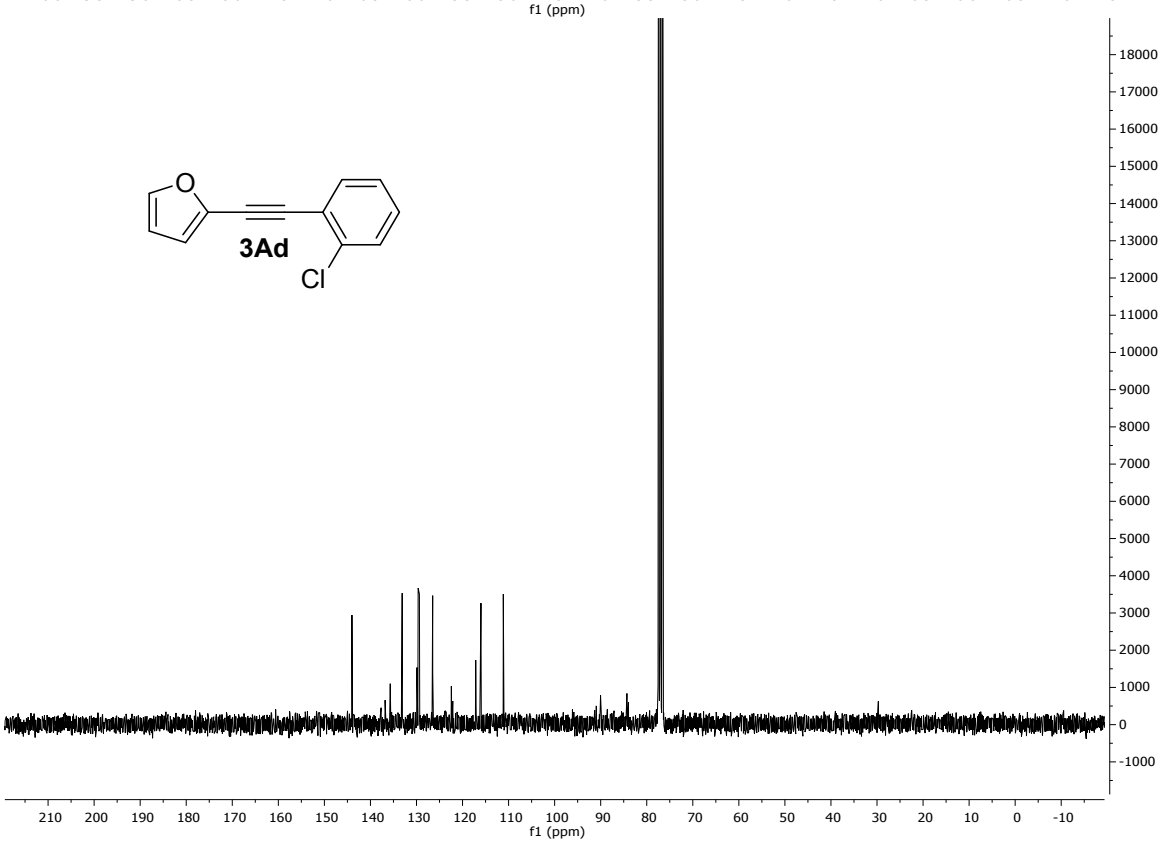
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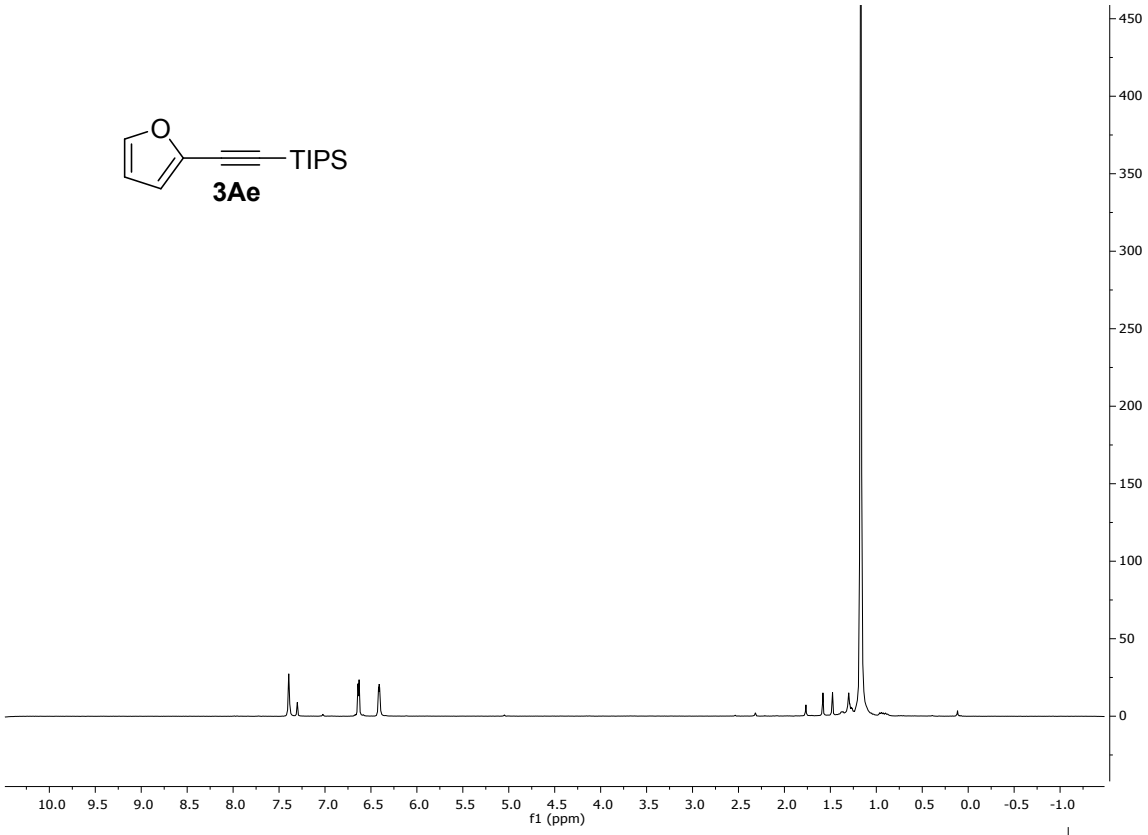
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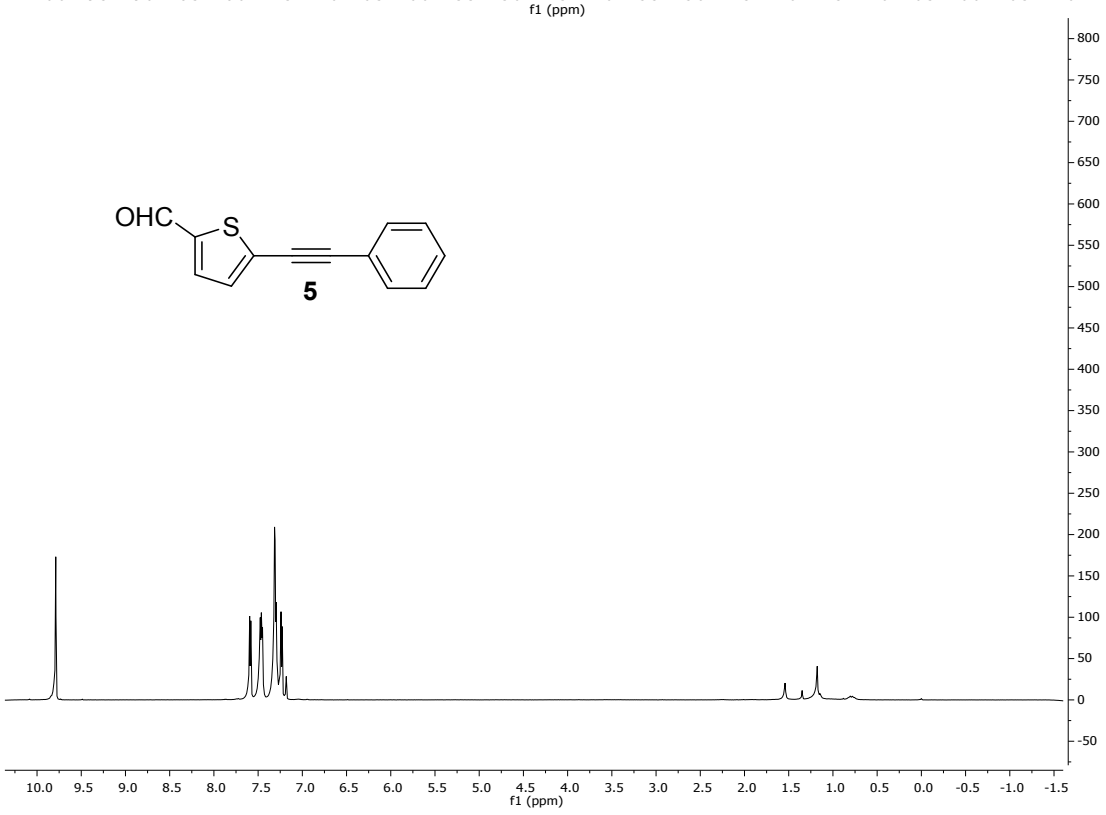
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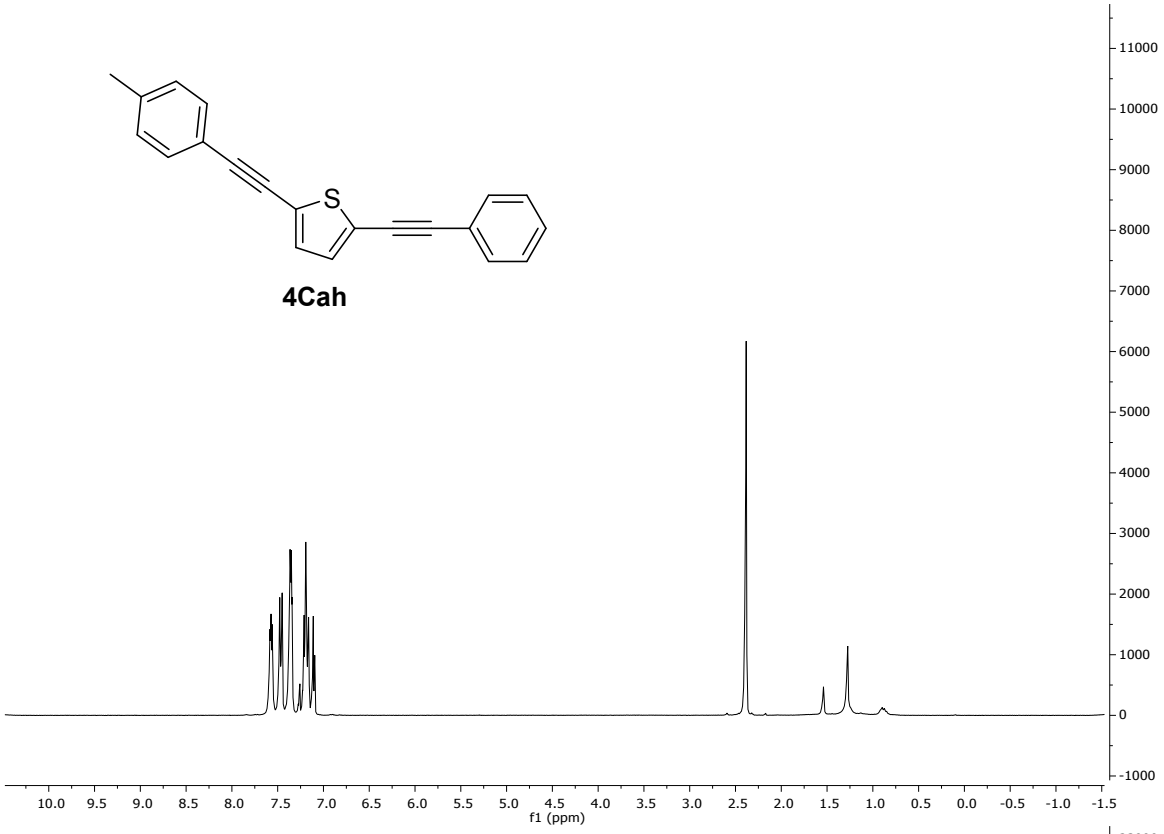
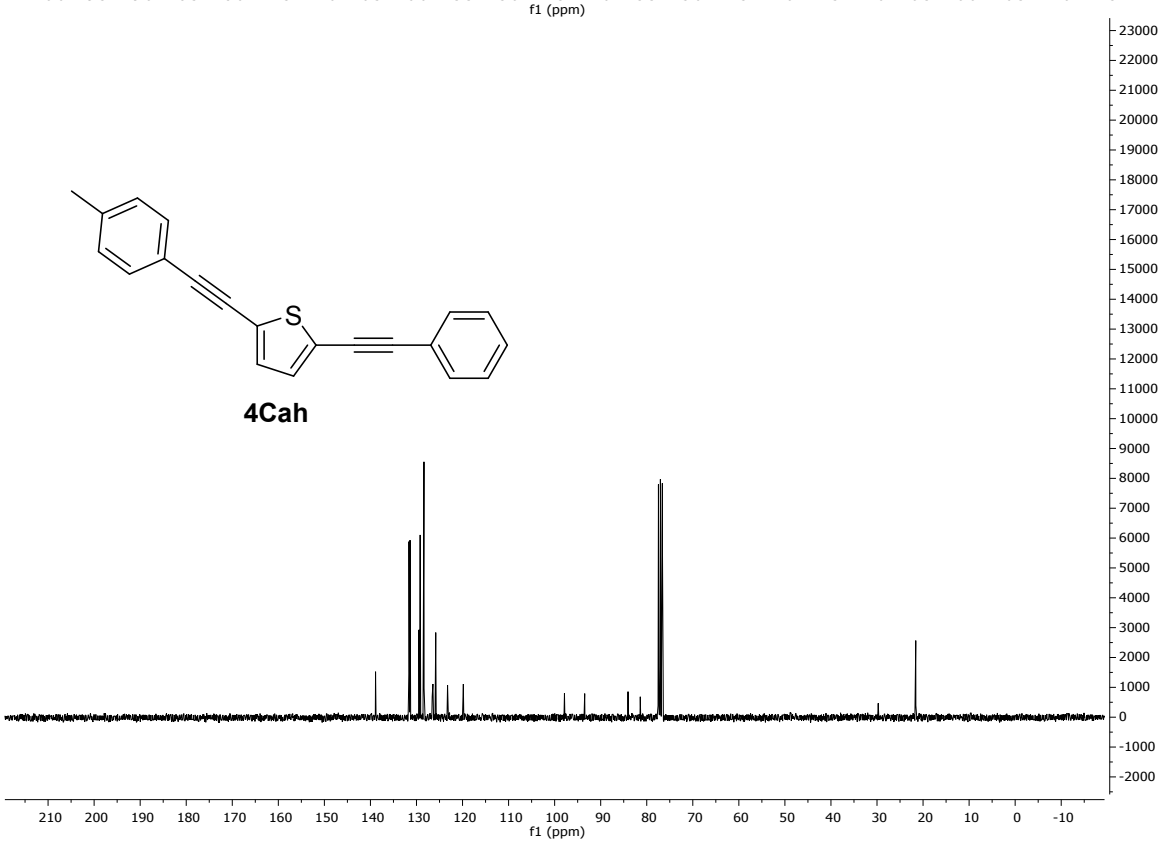
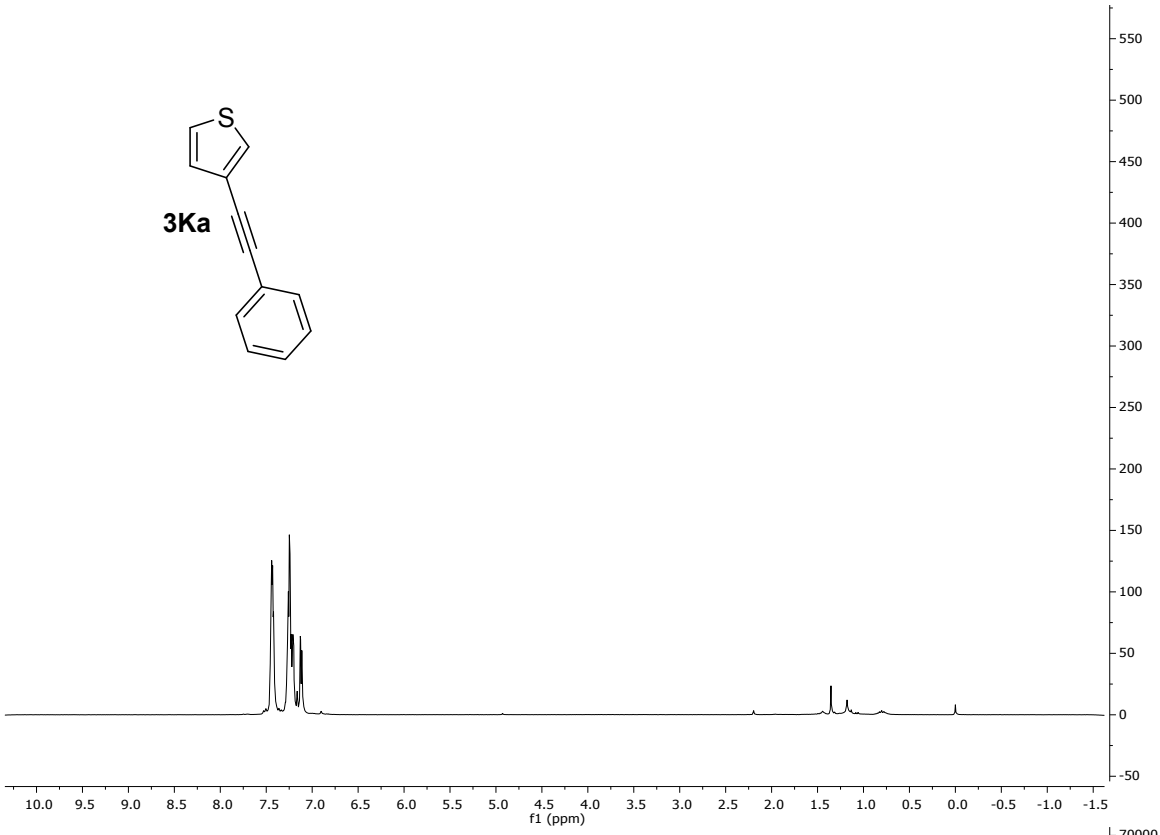
0
-50
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

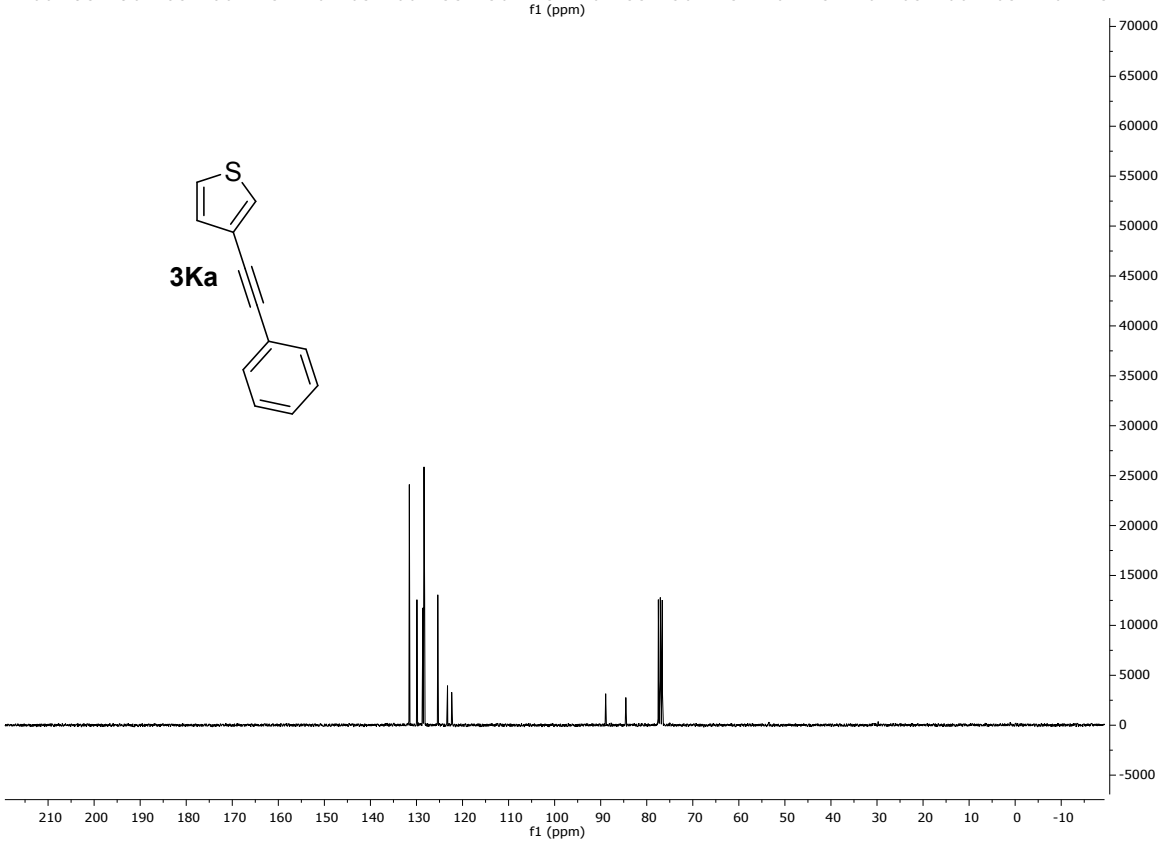

S
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

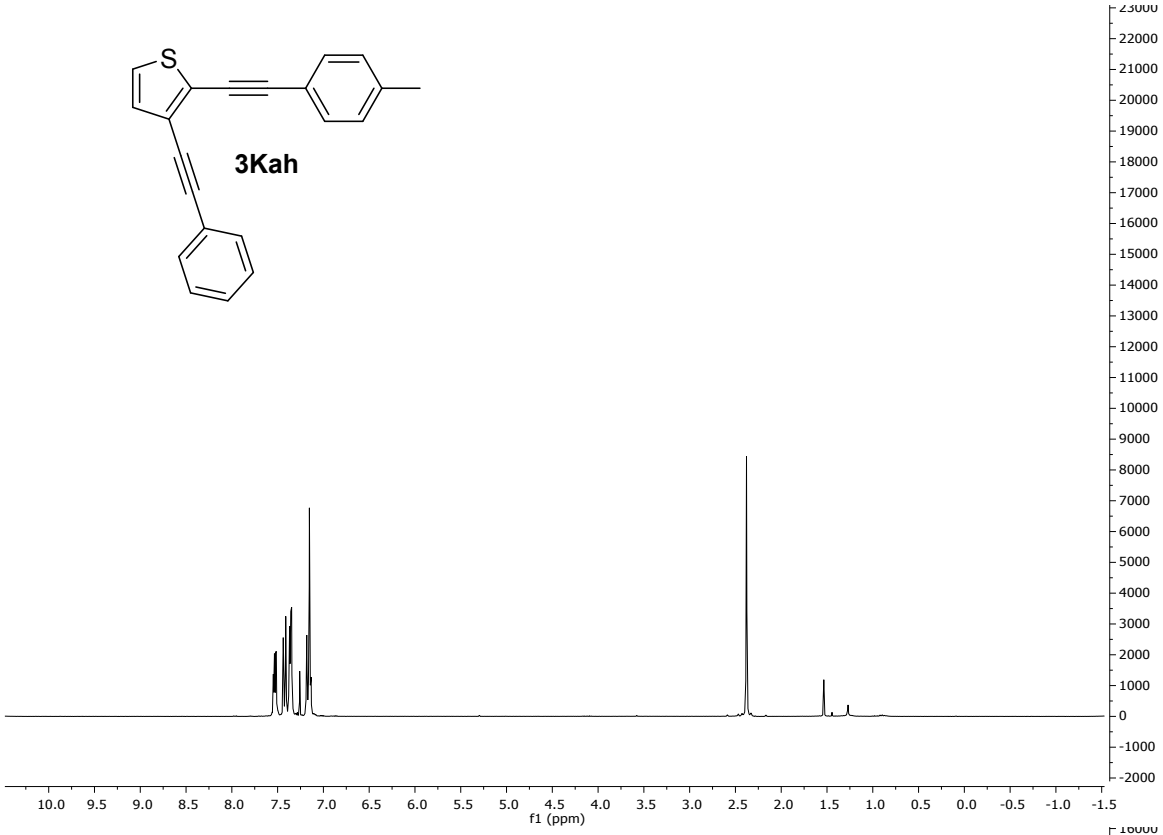
4Cah

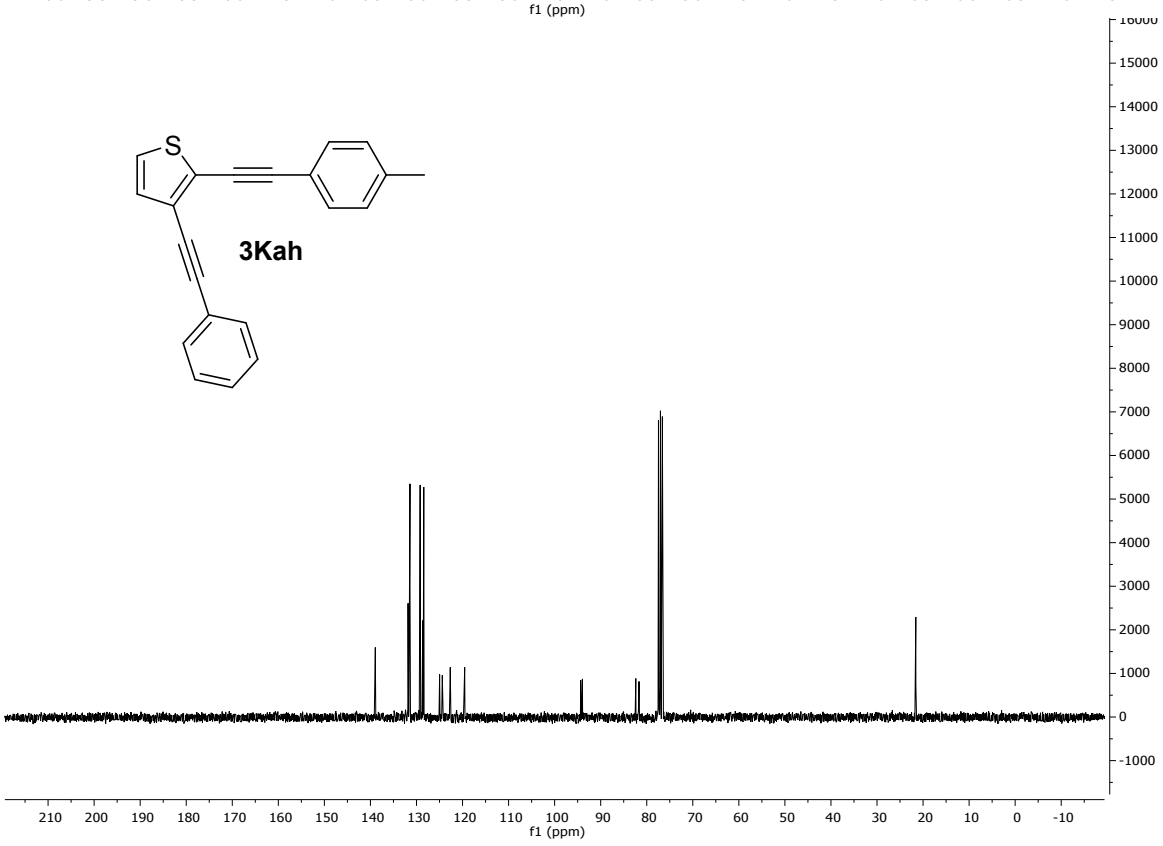

S
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

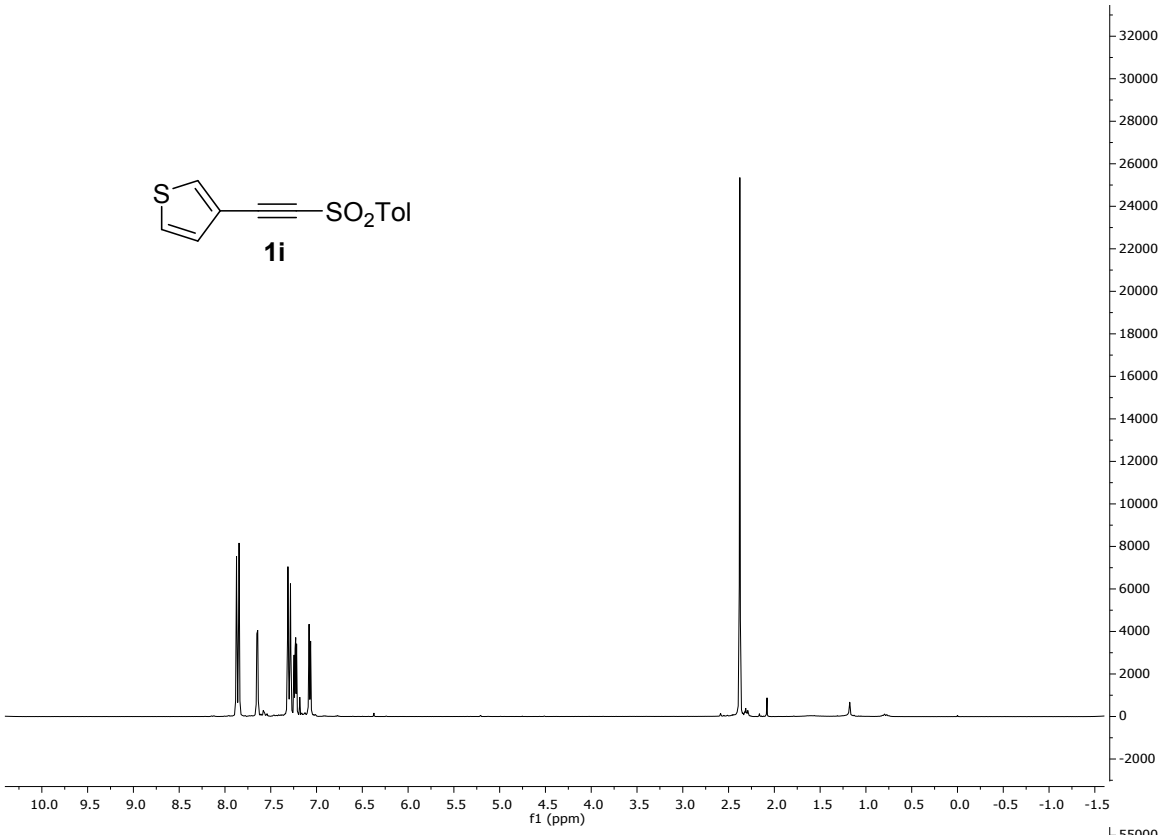
4Cah

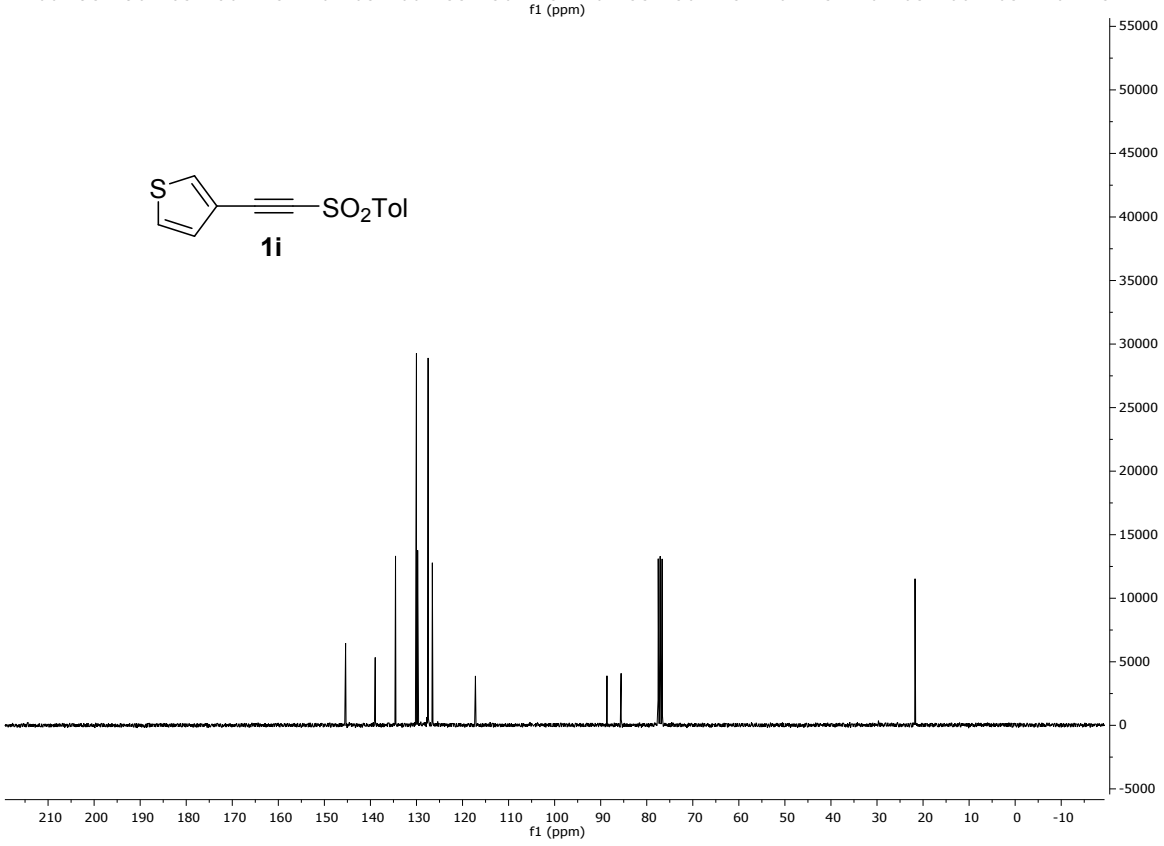

S
3Ka
550
500
450
400
350
300
250
200
150
100
50
0
-50
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

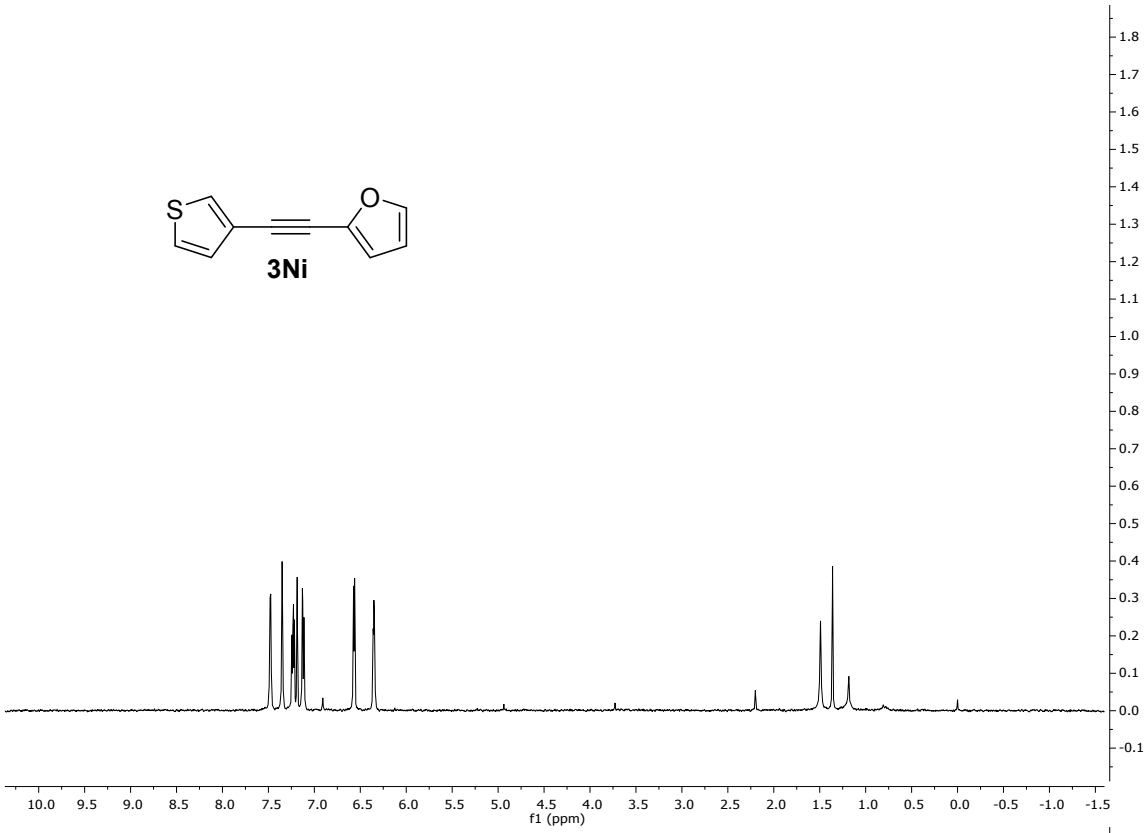

S
3Ka
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

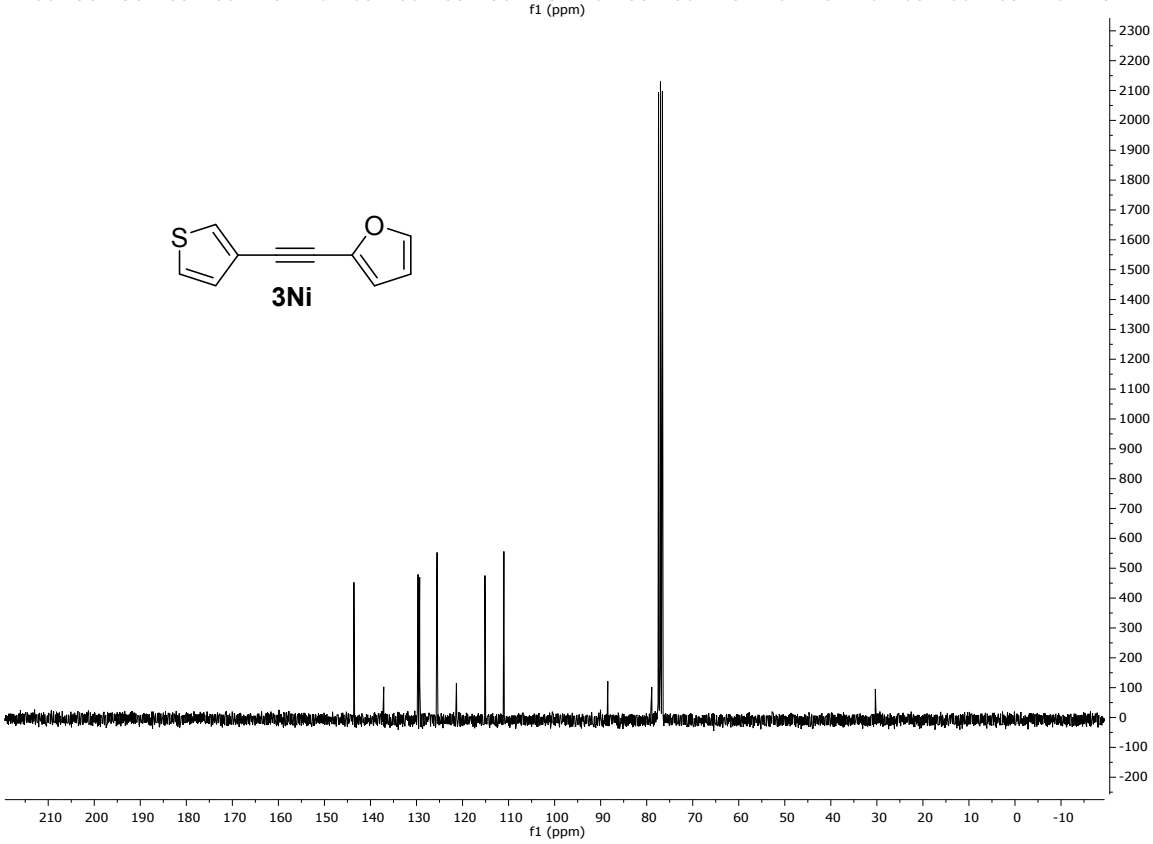

S
3Kah
f1 (ppm)

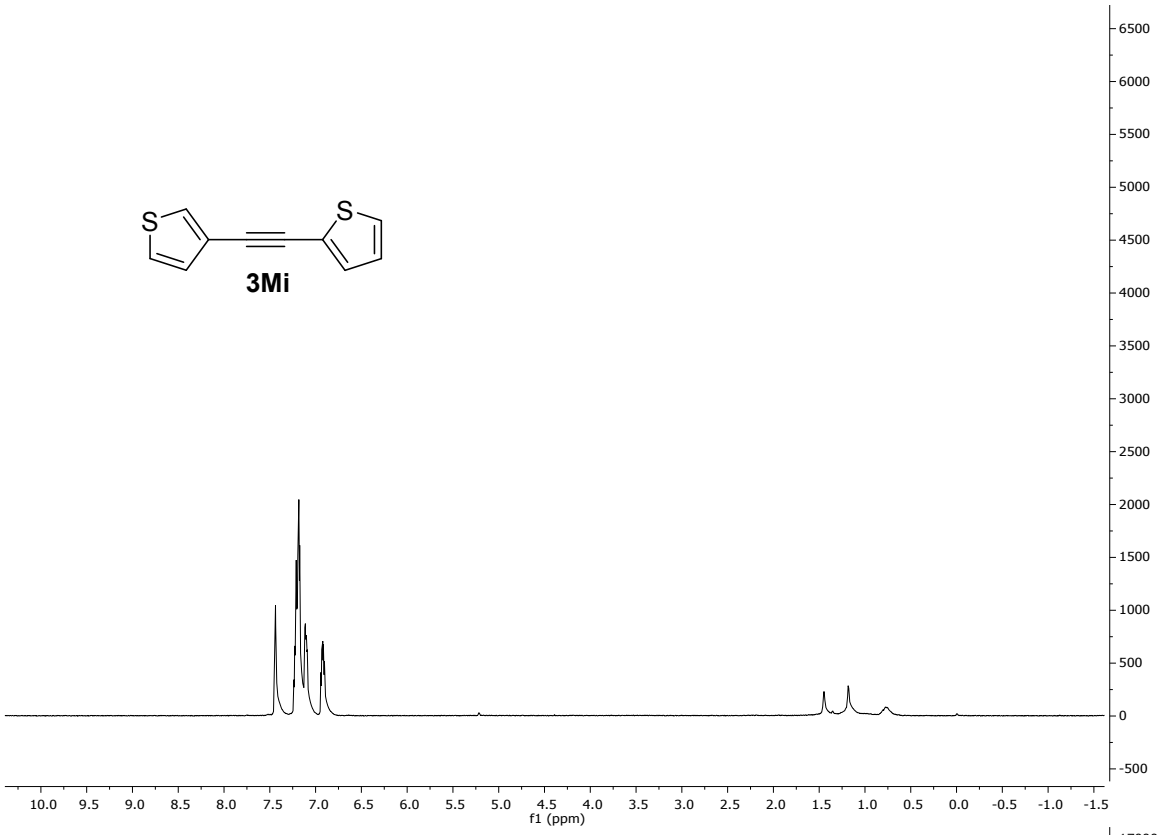

S
3Kah
f1 (ppm)

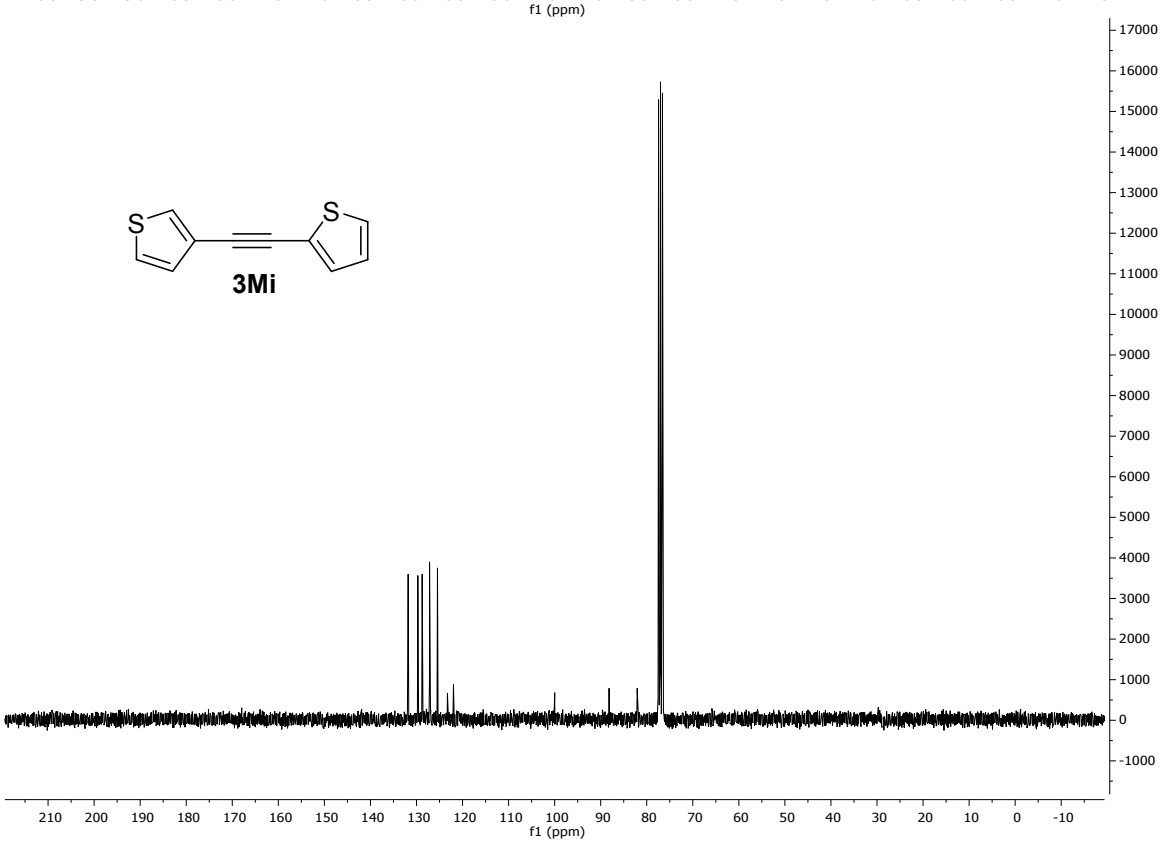

S
SO2Tol
1i
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

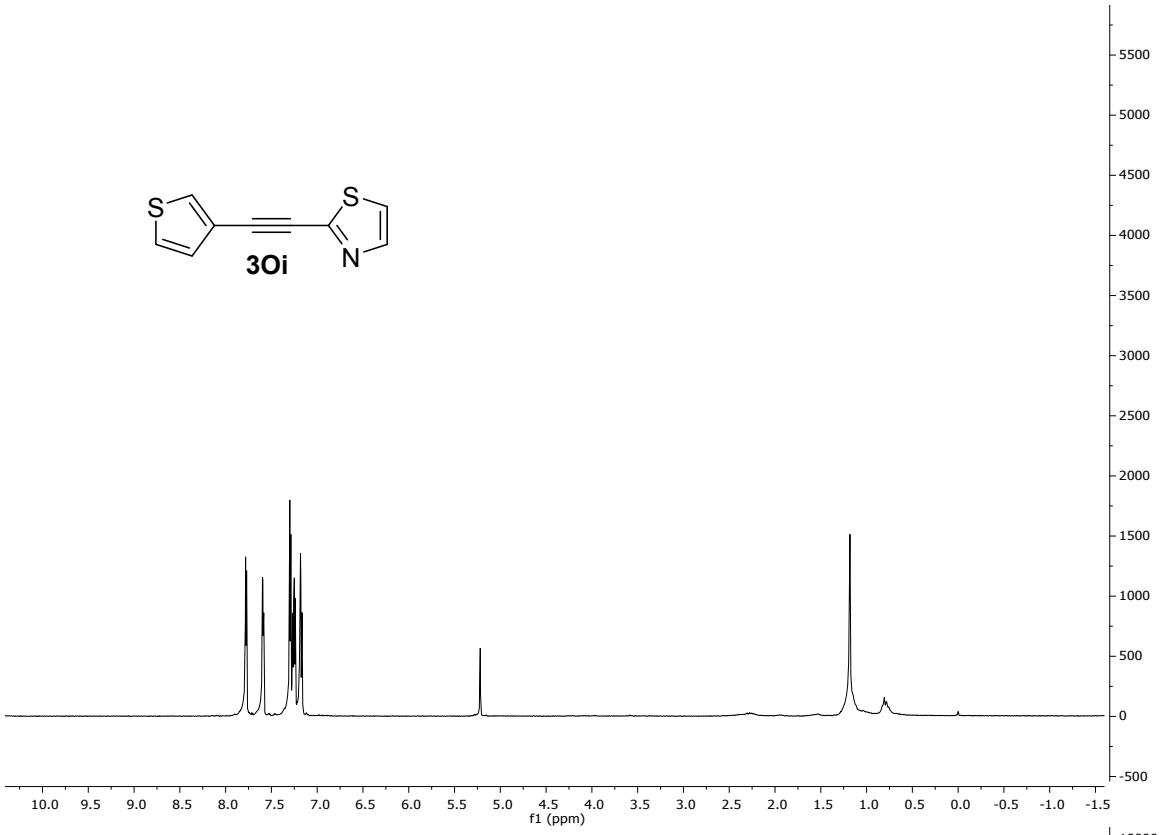

S
SO2Tol
1i
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

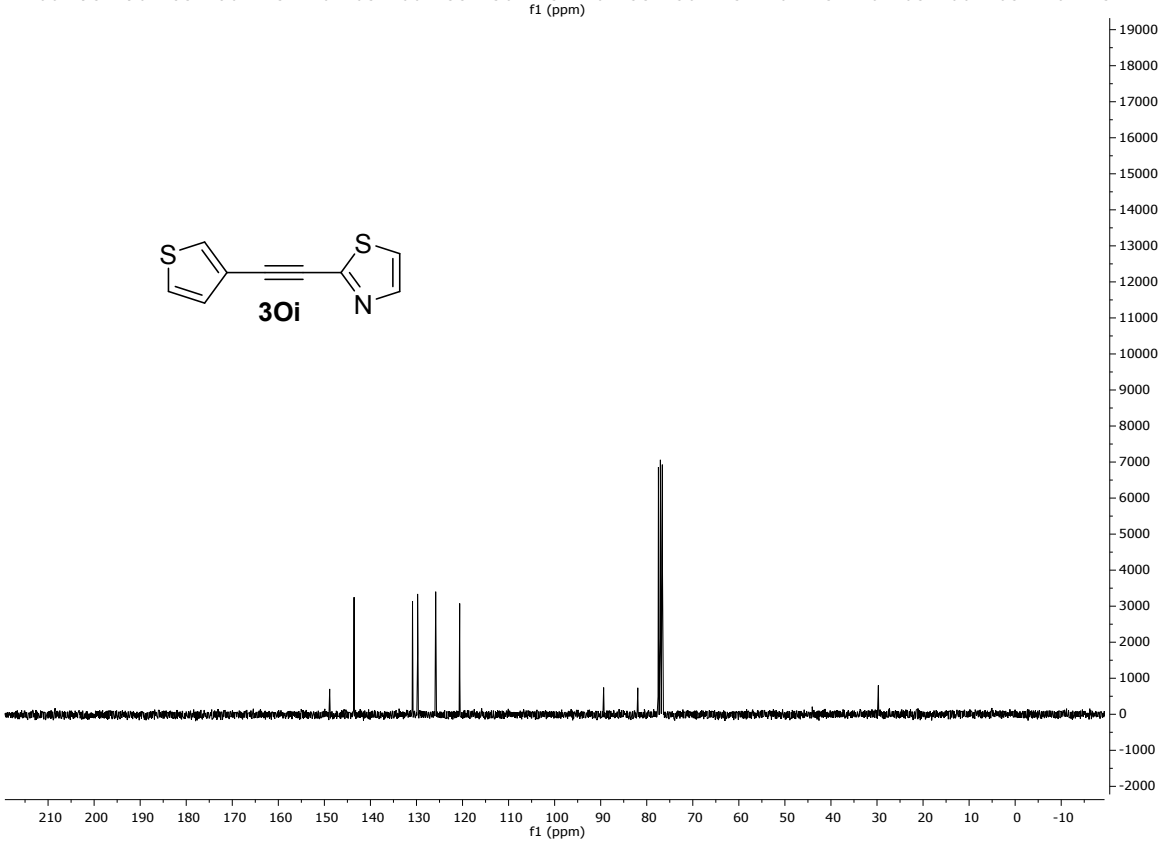

S
O
3Ni
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


S
O
3Ni
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
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)


S
S
3Mi
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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 -1.0 -1.5
f1 (ppm)


S
S
3Mi
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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)


S
S
N
3Oi
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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 -1.0 -1.5
f1 (ppm)


S
S
N
3Oi
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
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)