Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2018

SUPPORTING INFORMATION

Transition Metal-Free Coupling of Terminal Alkynes and Hypervalent Iodine Based Alkyne-Transfer Reagents to Access Unsymmetrical 1,3-Diynes

Johannes Schörgenhumer and Mario Waser*

Institute of Organic Chemistry, Johannes Kepler University Linz,
Altenbergerstraße 69, 4040 Linz, Austria.
Tel: +43 732 2468 5411; Fax: +43 732 2468 5402.
E-mail: mario.waser@jku.at

1. General Information:

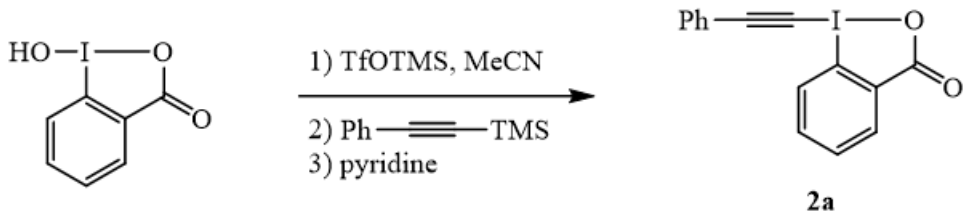
^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer. All NMR spectra were referenced on the solvent peak. Mass spectra were obtained using an Agilent LC/MSD Trap SL.

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. THF was distilled from Na under Ar atmosphere prior to use. All reactions were performed under Ar-atmosphere.

2. Preparation of EBX reagents:

All used Ethynyl-benziodoxolones were prepared from 2-iodosylbenzoic acid and TMS-alkynes following known procedures[1]. The starting materials were synthesised according to literature[1,2].

1-[2-(Phenyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (2a)



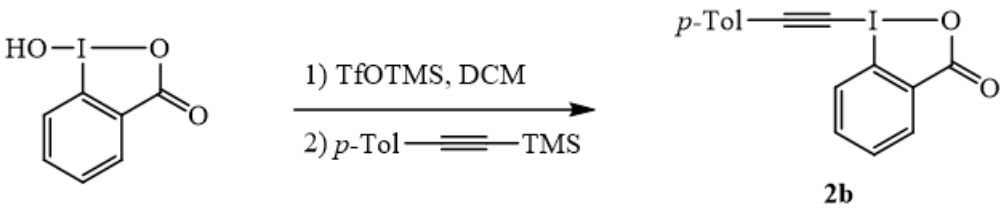
2a

2-Iodosylbenzoic acid (500.4 mg, 1.89 mmol) was taken up in MeCN (10 mL) and while rapid stirring, trimethylsilyl trifluoromethanesulfonate (363 µL, 1.98 mmol) was slowly added at room temperature, which resulted in the immediate formation of a yellow solution, which was then stirred at room temperature for 30 min. Then, the addition of trimethylsilyl(phenylethynyl)silane (346.3 mg, 1.99 mmol) followed and the mixture was stirred for 30 min at room temperature, before adding pyridine (170 µL, 2.11 mmol) and stirring for another 10 min. The solvent was then removed under reduced pressure and the resulting residue was taken up in DCM (10 mL). After washing with 1M aqueous HCl (10 mL), the aqueous layer was extracted once with DCM (10 mL). The organic phases were then washed with a saturated solution of $NaHCO_3$ (15 mL), dried over Na_2SO_4 and filtrated. The crude product obtained by evaporation of the solvent was then recrystallised from MeCN and dried *in vacuo* to afford the targeted Phenyl-EBX reagent **2a** as colourless powder in 66% yield

[1] D. F. González, J. P. Brand, R. Mondière, J. Waser, *Adv. Synth. Catal.* **2013**, *355*, 1631-1639
[2] H. Huang, G. Zhang, L. Gong, S. Zhang, Y. Cheng, *J. Am. Chem. Soc.* **2014**, *136*, 2280-2283

(433.4 mg, 1.24 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 8.44-8.41 (m, 1H), 8.27-8.24 (m, 1H), 7.79-7.76 (m, 2H), 7.61 (d, J = 7.5 Hz, 2H), 7.50-7.42 (m, 3H); Spectroscopic data are in accordance to literature[1].

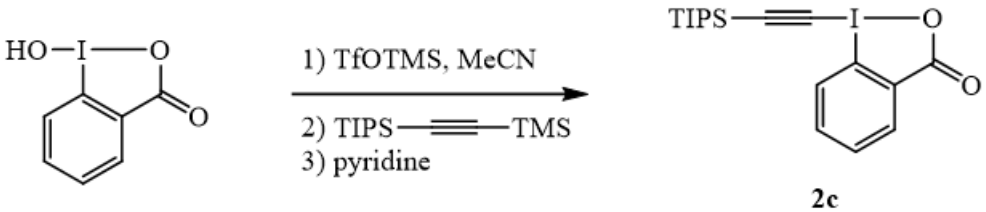
1-[2-(4-Methylphenyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (2b)



2b

2-Iodosylbenzoic acid (505.0 mg, 1.91 mmol) was taken up in DCM (5 mL) and while stirring rapidly, trimethylsilyl trifluoromethanesulfonate (363 µL, 1.98 mmol) was slowly added at room temperature, which resulted in the immediate formation of a yellow suspension. The mixture was stirred for 1 h before adding trimethyl((4-methylphenyl)ethynyl)silane (374.2 mg, 1.99 mmol). After stirring overnight at room temperature, the organic phase was washed twice with a saturated solution of $NaHCO_3$ (5 mL), then dried over Na_2SO_4, filtrated and evaporated. The crude product was then recrystallised from MeCN and dried *in vacuo* to give the Tolyl-EBX reagent **2b** as colourless solid in 43% yield (293.5 mg, 0.81 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 8.43-8.40 (m, 1H), 8.26-8.23 (m, 1H), 7.78-7.74 (m, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H); Spectroscopic data are in accordance to literature[3].

1-[2-(Tri*iso*-propylsilyl)ethinyl]-1,2-benziodoxol-3(1*H*)-one (2c)



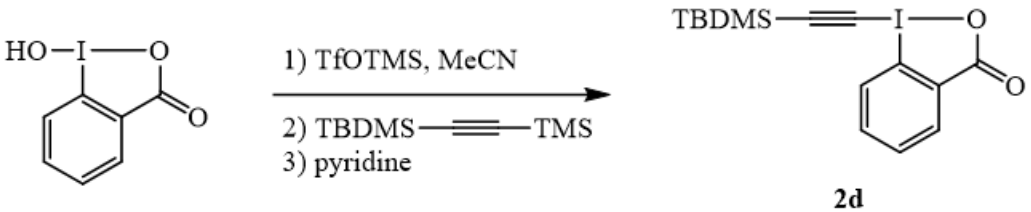
2c

2-Iodosylbenzoic acid (1000.2 mg, 3.79 mmol) was taken up in MeCN (20 mL) and while rapid stirring, trimethylsilyl trifluoromethanesulfonate (764 µL, 4.17 mmol) was slowly added at room temperature, which resulted in the immediate formation of a yellow solution, which was then stirred at room temperature for 30 min. Then, the addition of tri*iso*-propyl((trimethylsilyl)ethynyl)silane (1062.2 mg, 4.17 mmol) followed and the mixture was stirred for 30 min at room temperature, before adding pyridine (338 µL, 4.20 mmol) and stirring

[3] M. J. Bouma, B. Olofsson, *Chem. Eur. J.* **2012**, *18*, 14242-14245

for another 15 min. The solvent was then removed under reduced pressure and the resulting residue was taken up in DCM (20 mL). After washing with 1M aqueous HCl (20 mL), the aqueous layer was extracted once with DCM (20 mL). The organic phases were then washed twice with a saturated solution of $NaHCO_3$ (15 mL), dried over Na_2SO_4 and filtrated. The crude product obtained by evaporation of the solvent was then recrystallised from MeCN and dried *in vacuo* to afford the TIPS-EBX reagent **2c** as colourless crystals in 55% yield (890.2 mg, 2.08 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 8.44-8.41 (m, 1H), 8.31-8.27 (m, 1H), 7.78-7.74 (m, 2H), 1.18-1.15 (m, 21H); Spectroscopic data are in accordance to literature[1].

1-[2-(*tert*-Butyldimethylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (2d)

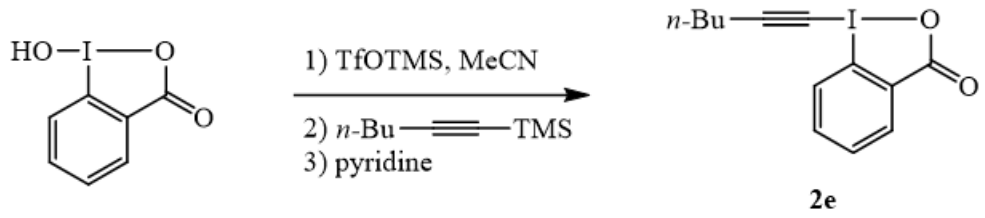


2d

2-Iodosylbenzoic acid (503.7 mg, 1.91 mmol) was taken up in MeCN (10 mL) and while rapid stirring, trimethylsilyl trifluoromethanesulfonate (382 µL, 2.08 mmol) was slowly added at room temperature, which resulted in the immediate formation of a yellow solution, which was then stirred at room temperature for 30 min. Then, the addition of *tert*-butyldimethyl((trimethylsilyl)ethynyl)silane (445,3 mg, 2.09 mmol) followed and the mixture was stirred for 30 min at room temperature, before adding pyridine (170 µL, 2.11 mmol) and stirring for another 10 min. The solvent was then removed under reduced pressure and the resulting residue was taken up in DCM (10 mL). After washing with 1M aqueous HCl (10 mL), the aqueous layer was extracted once with DCM (10 mL). The organic phases were then washed with a saturated solution of $NaHCO_3$ (15 mL), dried over Na_2SO_4 and filtrated. The crude product obtained by evaporation of the solvent was then purified by column chromatography (silica gel; DCM/MeOH = 20/1) and dried *in vacuo* to afford the targeted TBDMS-EBX reagent **2d** as colourless, crystalline solid in 72% yield (530.3 mg, 1.37 mmol). R_f = 0.30 (DCM/MeOH = 20/1); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 8.43-8.40 (m, 1H), 8.24-8.20 (m, 1H), 7.78-7.73 (m, 2H), 1.02 (s, 9H), 0.25 (s, 6H); Spectroscopic data are in accordance to literature[4].

[4] J.P. Brand, C. Chevalley, R. Scopelliti, J. Waser, *Chem. Eur. J.* **2012**, *18*, 5655-5666

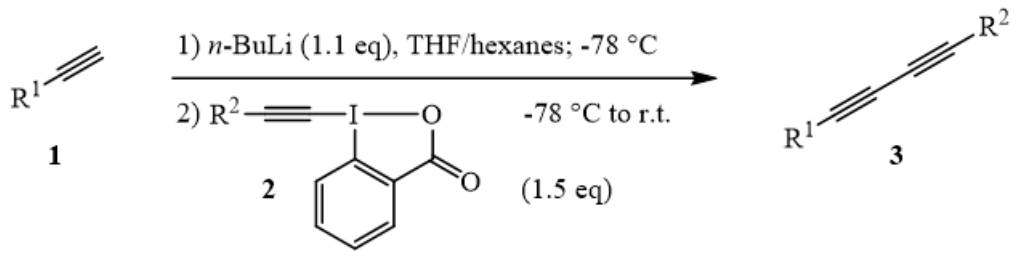
1-[2-(*n*-Butyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (2e)



2e

2-Iodosylbenzoic acid (514.6 mg, 1.95 mmol) was taken up in MeCN (10 mL) and while rapid stirring, trimethylsilyl trifluoromethanesulfonate (392 µL, 2.14 mmol) was slowly added at room temperature, which resulted in the immediate formation of a yellow solution, which was then stirred at room temperature for 30 min. Then, the addition of hex-1-yn-1-yltrimethylsilane (330,0 mg, 2.14 mmol) followed and the mixture was stirred for 30 min at room temperature, before adding pyridine (170 µL, 2.11 mmol) and stirring for another 10 min. The solvent was then removed under reduced pressure and the resulting residue was taken up in DCM (10 mL). After washing with 1M aqueous HCl (10 mL), the aqueous layer was extracted once with DCM (10 mL). The organic phases were then washed with a saturated solution of $NaHCO_3$ (15 mL), dried over Na_2SO_4 and filtrated. The crude product obtained by evaporation of the solvent was then purified by column chromatography (silica gel; DCM/MeOH = 20/1) and dried *in vacuo* to afford the targeted Butyl-EBX reagent as slightly yellow coloured solid in 26% yield (162.9 mg, 0.50 mmol). R_f = 0.35 (DCM/MeOH = 20/1); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 8.42-8.39 (m, 1H), 8.19-8.16 (m, 1H), 7.79-7.71 (m, 2H), 2.60 (t, J = 7.0 Hz, 2H), 1.69-1.62 (m, 2H), 1.55-1.43 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H); Spectroscopic data are in accordance to literature[4].

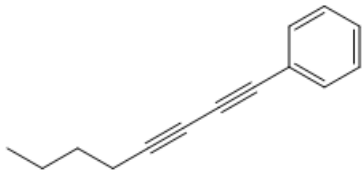
3. Dimerization of terminal alkynes:



General Procedure: 140 µL (0.22 mmol, 1.1 eq.) of a solution of *n*-BuLi (1.6 M in hexane) were added to a solution of the corresponding terminal alkyne **1** (0.20 mmol, 1.0 eq.) in dry THF (1 mL) at -78 °C. After stirring for 2 h, the corresponding ethynyl-benziodoxolone **2** (0.30 mmol, 1.5 eq.) was added in one portion. The mixture was allowed to reach room

temperature over 3 h while stirring rapidly. The resulting suspension was quenched with 2 mL of a saturated solution of $NaHCO_3$ and extracted three times with 5 mL dichloromethane. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel) to afford the targeted diyne **3** in the reported yield.

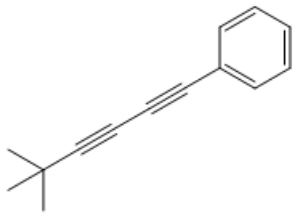
Octa-1,3-diyn-1-ylbenzene (3a)



3a

Following the general procedure, hex-1-yne (23 µL, 0.20 mmol) was reacted with Phenyl-EBX reagent **2a** (103.0 mg, 0.30 mmol) to afford the diyne **3a** as colourless oil in 87% yield (31.7 mg, 0.17 mmol). $R_f = 0.43$ (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.47 (d, J = 7.3 Hz, 2H), 7.36-7.26 (m, 3H), 2.37 (t, J = 6.8 Hz, 2H), 1.62-1.52 (m, 2H), 1.50-1.40 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 132.6, 128.9, 128.5, 122.3, 85.0, 74.8, 74.5, 65.2, 30.4, 22.1, 19.4, 13.7; MS(ESI): *m/z* calcd for $C_{14}H_{14}$: 182.11 $[M]^+$; found: 182.13. Analytical data are in accordance to literature[5].

(5,5-Dimethylhexa-1,3-diyn-1-yl)benzene (3b)



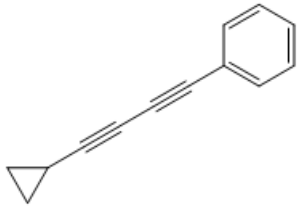
3b

Following the general procedure, 3,3-dimethylbut-1-yne (25 µL, 0.20 mmol) was reacted with Phenyl-EBX reagent **2a** (105.7 mg, 0.30 mmol) to afford the diyne **3b** as colourless oil in 81% yield (29.5 mg, 0.16 mmol). $R_f = 0.50$ (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.48-7.45 (m, 2H), 7.37-7.29 (m, 3H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$,

[5] X. Li, X. Xie, N. Sung, Y. Liu, *Angew. Chem. Int. Ed.* **2017**, *56*, 6994-6998

298 K): δ / ppm = 132.6, 128.9, 128.5, 122.3, 92.4, 76.1, 74.2, 63.9, 30.7, 28.4; MS(ESI): *m/z* calcd for $C_{14}H_{14}$: 182.11 $[M]^+$; found: 182.10. Analytical data are in accordance to literature[6].

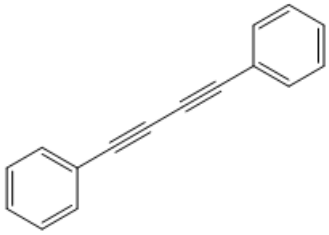
(Cyclopropylbuta-1,3-diyn-1-yl)benzene (3c)



3c

Following the general procedure, ethynylcyclopropane (17 µL, 0.19 mmol) was reacted with Phenyl-EBX reagent **2a** (105.6 mg, 0.30 mmol) to afford the diyne **3c** as colourless oil in 83% yield (26.2 mg, 0.16 mmol). R_f = 0.38 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.48-7.45 (m, 2H), 7.36-7.28 (m, 3H), 1.45-1.36 (m, 1H), 0.92-0.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 132.7, 128.9, 128.5, 122.3, 88.0, 74.7, 74.3, 60.5, 9.2, 0.5; MS(ESI): *m/z* calcd for $C_{13}H_{10}$: 166.08 $[M]^+$; found: 166.11. Analytical data are in accordance to literature[5].

1,4-Diphenylbuta-1,3-diyne (3d)

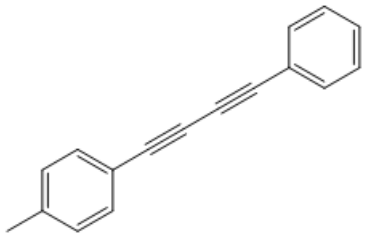


3d

Following the general procedure, phenylacetylene (22 µL, 0.20 mmol) was reacted with Phenyl-EBX reagent **2a** (103.3 mg, 0.30 mmol) to afford the diyne **3d** as colourless solid in 90% yield (35.7 mg, 0.18 mmol). R_f = 0.45 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.56-7.52 (m, 4H), 7.39-7.33 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 132.5, 129.2, 128.5, 121.8, 81.6, 73.9; MS(ESI): *m/z* calcd for $C_{16}H_{10}$: 202.08 $[M]^+$; found: 202.10. Analytical data are in accordance to literature[7].

[6] K. Fang, M. Xie, Z. Zhang, P. Ning, G. Shu, *Tetrahedron Lett.* **2013**, *54*, 3819-3821
[7] Merkul E., Urselmann D., Müller T. J. J., *Eur. J. Org. Chem.*, **2011**, 238–242

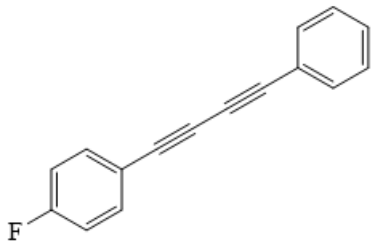
1-Methyl-4-(phenylbuta-1,3-diyn-1-yl)benzene (3e)



3e

Following the general procedure, *p*-tolylacetylene (25 µL, 0.20 mmol) was reacted with Phenyl-EBX reagent **2a** (107.1 mg, 0.31 mmol) to afford the diyne **3e** as colourless solid in 69% yield (29.8 mg, 0.14 mmol). R_f = 0.40 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.54 (d, J = 6.5 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 7.36-7.30 (m, 3H), 7.15 (d, J = 7.7 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 132.5, 129.2, 128.5, 121.8, 81.6, 73.9; MS(ESI): *m/z* calcd for $C_{17}H_{12}$: 216.09 $[M]^+$; found: 216.13. Analytical data are in accordance to literature[5].

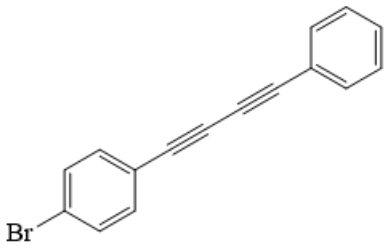
1-Fluoro-4-(phenylbuta-1,3-diyn-1-yl)benzene (3f)



3f

Following the general procedure, 4-fluorophenylacetylene (23 µL, 0.20 mmol) was reacted with Phenyl-EBX reagent **2a** (104.5 mg, 0.30 mmol) to afford the diyne **3f** as colourless solid in 59% yield (25.8 mg, 0.12 mmol). R_f = 0.36 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.54-7.49 (m, 4H), 7.40-7.32 (m, 3H), 7.04 (t, J = 8.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 163.1 (d, $^1J_{C\text{-}F}$ = 250.8 Hz), 134,7 (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 132.7, 129.4, 128.6, 121.8, 116.2, 115.9, 81.7, 80.6, 74.0, 73.8; ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -108.6; MS(ESI): *m/z* calcd for $C_{16}H_9F$: 220.07 $[M]^+$; found: 220.13. Analytical data are in accordance to literature[5].

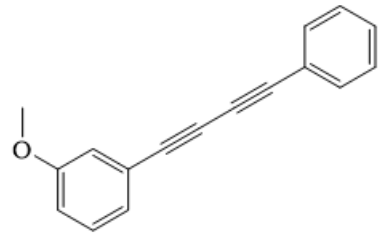
1-Bromo-4-(phenylbuta-1,3-diyn-1-yl)benzene (3g)



3g

Following the general procedure, 4-bromophenylacetylene (36.2 mg, 0.19 mmol) was reacted with Phenyl-EBX reagent **2a** (101.5 mg, 0.29 mmol) to afford the diyne **3g** as colourless solid in 54% yield (28.8 mg, 0.10 mmol). R_f = 0.55 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.53 (d, J = 7.2 Hz, 2H), 7.49-7.45 (m, 2H), 7.39-7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 134.0, 132.6, 131.9, 129.5, 128.6, 123.8, 121.9, 120.9, 82.3, 80.5, 75.2, 73.8; MS(ESI): *m/z* calcd for $C_{16}H_9Br$: 279.99 $[M]^+$; found: 280.07. Analytical data are in accordance to literature[5].

1-Methoxy-3-(phenylbuta-1,3-diyn-1-yl)benzene (3h)

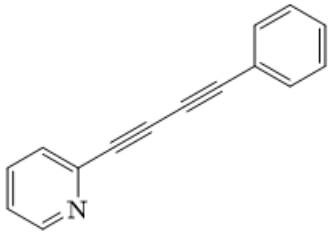


3h

Following the general procedure, 3-methoxyphenylacetylene (26 µL, 0.20 mmol) was reacted with Phenyl-EBX reagent **2a** (107.1 mg, 0.31 mmol) to afford the diyne **3h** as colourless solid in 48% yield (21.9 mg, 0.09 mmol). R_f = 0.15 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.57 (d, J = 7.4 Hz, 2H), 7.42-7.36 (m, 3H), 7.31-7.28 (m, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.09 (s, 1H), 6.97 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 159.5, 132.7, 129.7, 129.4, 128.6, 125.2, 122.9, 121.9, 117.2, 116.2, 81.7, 81.6, 74.0, 73.8, 55.5; MS(ESI): *m/z* calcd for $C_{17}H_{12}O$: 232.09 $[M]^+$; found: 232.13. Analytical data are in accordance to literature[8].

[8] A. Sagadevan, P.-C. Lyu, K. C. Hwang, *Green Chem.* **2016**, *18*, 4526-4530

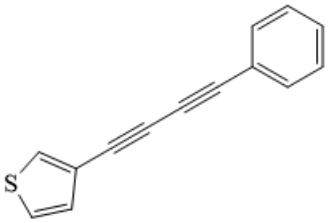
2-(Phenylbuta-1,3-diyn-1-yl)pyridine (3i)



3i

Following the general procedure, 2-ethynylpyridine (20 µL, 0.19 mmol) was reacted with Phenyl-EBX reagent **2a** (102.3 mg, 0.29 mmol) to afford the diyne **3i** as colourless solid in 91% yield (35.8 mg, 0.18 mmol). R_f = 0.43 (DCM); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 8.61 (d, J = 4.7 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.56-7.51 (m, 3H), 7.39-7.34 (m, 3H), 7.31-7.28 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 150.5, 142,5, 136.3, 132.8, 129.7, 128.6, 128.2, 123.6, 121.5, 82.6, 80.3, 73.9, 73.7; MS(ESI): *m/z* calcd for $C_{15}H_{10}N$: 204.08 $[M+H]^+$; found: 204.03. Analytical data are in accordance to literature[5].

3-(Phenylbuta-1,3-diyn-1-yl)thiophene (3j)

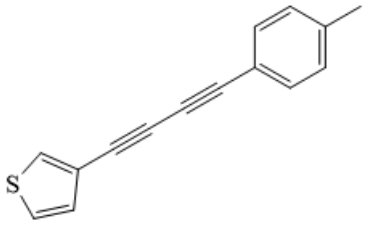


3j

Following the general procedure, 3-ethynylthiophene (21 µL, 0.20 mmol) was reacted with Phenyl-EBX reagent **2a** (105.6 mg, 0.30 mmol) to afford the diyne **3j** as colourless solid in 66% yield (27.5 mg, 0.13 mmol). R_f = 0.35 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.59 (s, 1H), 7.54-7.51 (m, 2H), 7.37-7.28 (m, 4H), 7.19-7.17 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 132.6, 131.4, 130.3, 129.3, 128.6, 125.7, 121.9, 121.0, 81.7, 81.5, 74.1, 73.7; MS(ESI): *m/z* calcd for $C_{14}H_9S$: 209.04 $[M+H]^+$; found: 209.10. Analytical data are in accordance to literature[9].

[9] N. Mukherjee, D. Kundu, B. C. Ranu, *Chem. Commun.* **2014**, *50*, 15784-15787

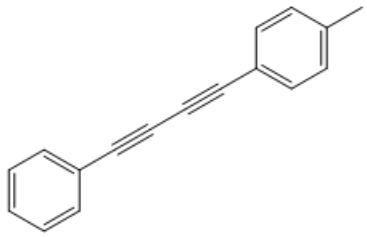
3-(*p*-Tolylbuta-1,3-diyn-1-yl)thiophene (3k)



3k

Following the general procedure, 3-ethynylthiophene (21 µL, 0.20 mmol) was reacted with Tolyl-EBX reagent **2b** (108.7 mg, 0.30 mmol) to afford the diyne **3k** as colourless solid in 92% yield (40.0 mg, 0.18 mmol). R_f = 0.33 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.59-7.58 (m, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.30-7.27 (m, 1H), 7.18-7.13 (m, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 139.6, 132.5, 131.2, 130.3, 129.4, 125.7, 121.1, 118.9, 81.7, 76.5, 73.6, 73.4, 21.8; MS(ESI): *m/z* calcd for $C_{15}H_{11}S$: 223.06 $[M+H]^+$; found: 223.13.

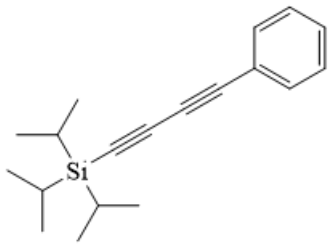
1-Methyl-4-(phenylbuta-1,3-diyn-1-yl)benzene (3e‘)



3e'

Following the general procedure, phenylacetylene (23 µL, 0.21 mmol) was reacted with Tolyl-EBX reagent **2b** (109.3 mg, 0.30 mmol) to afford the diyne **3e'** as colourless solid in 73% yield (32.4 mg, 0.15 mmol). Analytical data are identical to **3e** (see above).

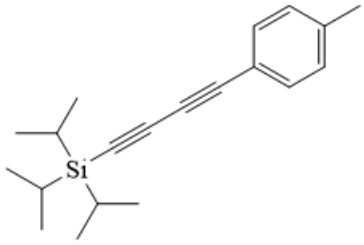
Tri*iso*propyl(phenylbuta-1,3-diyn-1-yl)silane (3l)



3l

Following the general procedure, ethynyltri*iso*propylsilane (46 µL, 0.20 mmol) was reacted with Phenyl-EBX reagent **2a** (108.7 mg, 0.30 mmol) to afford the diyne **3l** as colourless oil in 49% yield (27.1 mg, 0.10 mmol). R_f = 0.68 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.55-7.50 (m, 2H), 7.38-7.29 (m, 3H), 1.09-1.07 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 132.7, 129.4, 128.5, 121.7, 89.6, 88.0, 75.7, 74.8, 18.7, 11.5; MS(ESI): *m/z* calcd for $C_{19}H_{26}Si$: 282.18 $[M]^+$; found: 282.18. Analytical data are in accordance to literature[5].

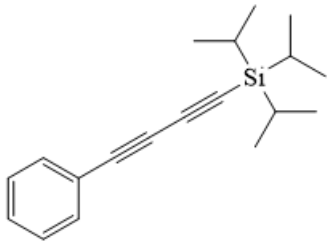
Tri*iso*propyl(*p*-tolylbuta-1,3-diyn-1-yl)silane (3m)



3m

Following the general procedure, ethynyltri*iso*propylsilane (46 µL, 0.20 mmol) was reacted with Tolyl-EBX reagent **2b** (108.9 mg, 0.30 mmol) to afford the diyne **3m** as colourless oil in 51% yield (30.2 mg, 0.10 mmol). R_f = 0.65 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.40 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 2.35 (s, 3H), 1.11 (s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 139.8, 132.8, 129.3, 118.5, 89.8, 87.5, 76.0, 74.2, 21.8, 18.7, 11.5; MS(ESI): *m/z* calcd for $C_{20}H_{28}Si$: 296.20 $[M]^+$; found: 296.23. Analytical data are in accordance to literature[10].

Tri*iso*propyl(phenylbuta-1,3-diyn-1-yl)silane (3l')

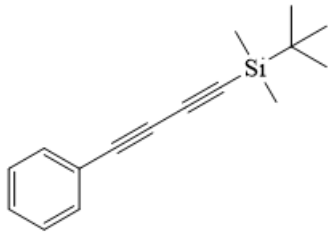


3l'

[10] S. Banerjee, N. T. Patil, *Chem. Commun.* **2017**, *53*, 7937-7940

Following the general procedure, phenylacetylene (18 µL, 0.16 mmol) was reacted with TIPS-EBX reagent **2c** (102.8 mg, 0.24 mmol) to afford the diyne **3l'** as colourless oil in 86% yield (39.0 mg, 0.14 mmol). Analytical data are identical to **3l** (see above).

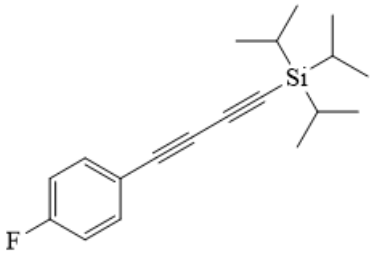
***tert*-Butyldimethyl(phenylbuta-1,3-diyn-1-yl)silane (3n)**



3n

Following the general procedure, phenylacetylene (22 µL, 0.20 mmol) was reacted with TBDMS-EBX reagent **2d** (120,4 mg, 0.31 mmol) to afford the diyne **3n** as colourless solid in 41% yield (19.8 mg, 0.08 mmol). R_f = 0.35 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.55-7.52 (m, 2H), 7.38-7.32 (m, 3H), 0.98 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 132.7, 129.4, 128.6, 122.0, 89.8, 88.6, 76.4, 74.1, 26.2, 17.3, -4.5; MS(ESI): *m/z* calcd for $C_{16}H_{20}Si$: 240.13 $[M]^+$; found: 240.17. Analytical data are in accordance to literature[11].

((4-Fluorophenyl)buta-1,3-diyn-1-yl)tri*iso*propylsilane (3o)



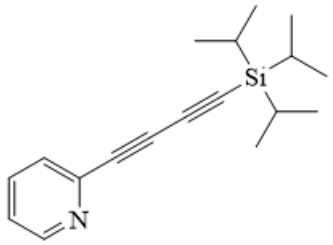
3o

Following the general procedure, 4-fluorophenylacetylene (18 µL, 0.16 mmol) was reacted with TIPS-EBX reagent **2c** (102.9 mg, 0.24 mmol) to afford the diyne **3o** as colourless oil in 75% yield (35.8 mg, 0.12 mmol). R_f = 0.60 (heptanes); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 7.52-7.47 (m, 2H), 7.01 (t, J = 8.5 Hz, 2H), 1.11 (s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 163.2 (d, $^1J_{C\text{-}F}$ = 251.8 Hz), 134,9 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 117.8 (d, $^4J_{C\text{-}}$

[11] J. P. Marino, H. N. Nguyen, *J. Org. Chem.* **2002**, *67*, 6841-6844

$_F$ = 3.7 Hz), 116.0 (d, $^2J_{C-F}$ = 22.3 Hz), 89.5, 88.1, 74.6, 18.7, 11.4; ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -108.6; MS(ESI): *m/z* calcd for $C_{19}H_{25}FSi$: 300.17 $[M]^+$; found: 300.25. Analytical data are in accordance to literature[10].

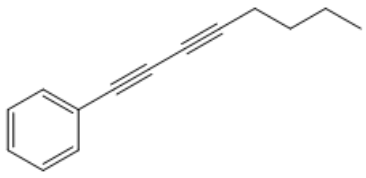
2-((Tri*iso*propylsilyl)buta-1,3-diyn-1-yl)pyridine (3p)



3p

Following the general procedure, 2-ethynylpyridine (17 µL, 0.16 mmol) was reacted with TIPS-EBX reagent **2c** (104.6 mg, 0.24 mmol) to afford the diyne **3p** as slightly yellow coloured oil in 73% yield (33.9 mg, 0.12 mmol). R_f = 0.35 (heptanes/EtOAc = 5/1); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ / ppm = 8.58 (d, *J* = 4.8 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.28-7.24 (m, 1H), 1.10 (s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 150.5, 142.3, 136.3, 128.2, 123.6, 89.8, 89.2, 74.5, 74.3, 18.7, 11.4; MS(ESI): *m/z* calcd for $C_{18}H_{26}NSi$: 284.18 $[M+H]^+$; found: 284.18. Analytical data are in accordance to literature[9].

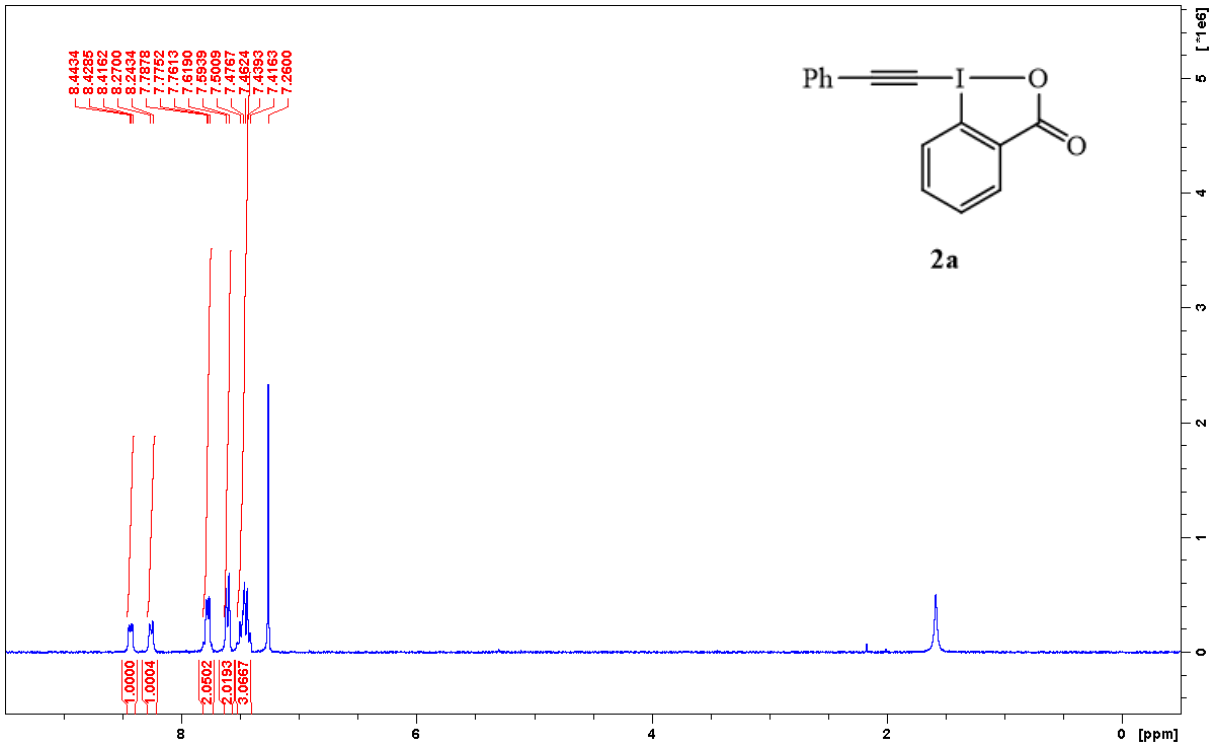
Octa-1,3-diyn-1-ylbenzene (3a‘)

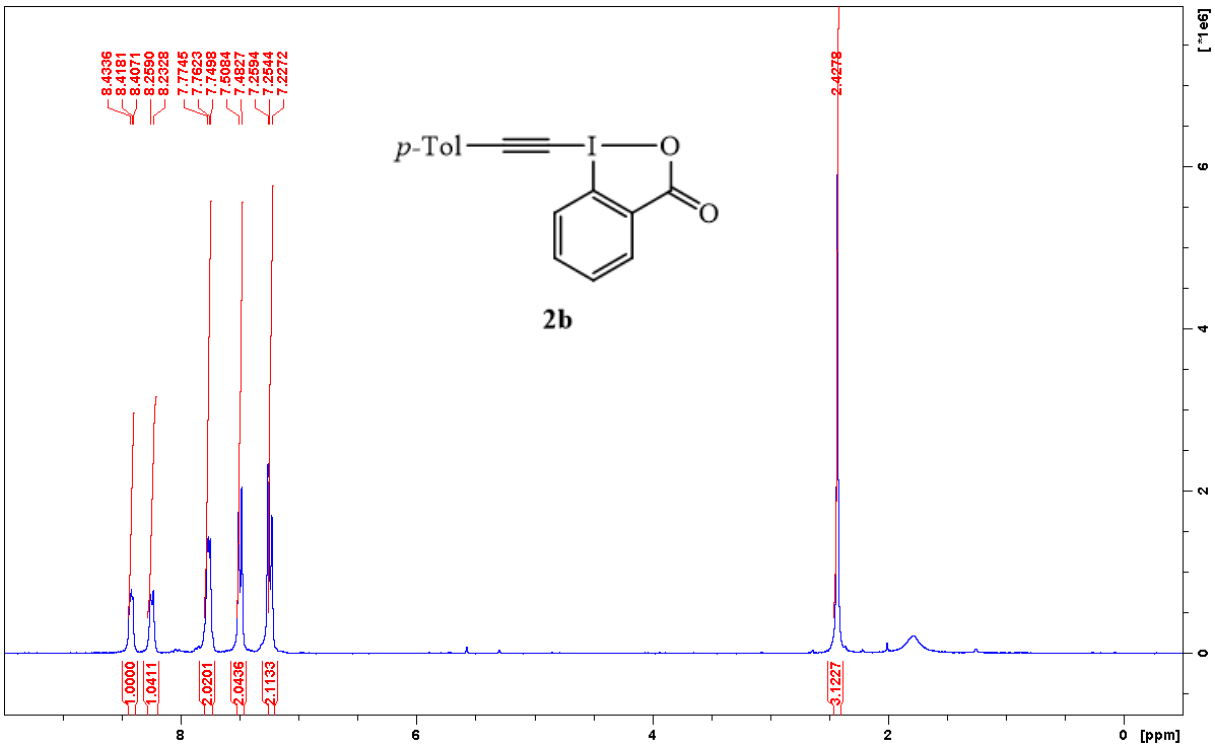


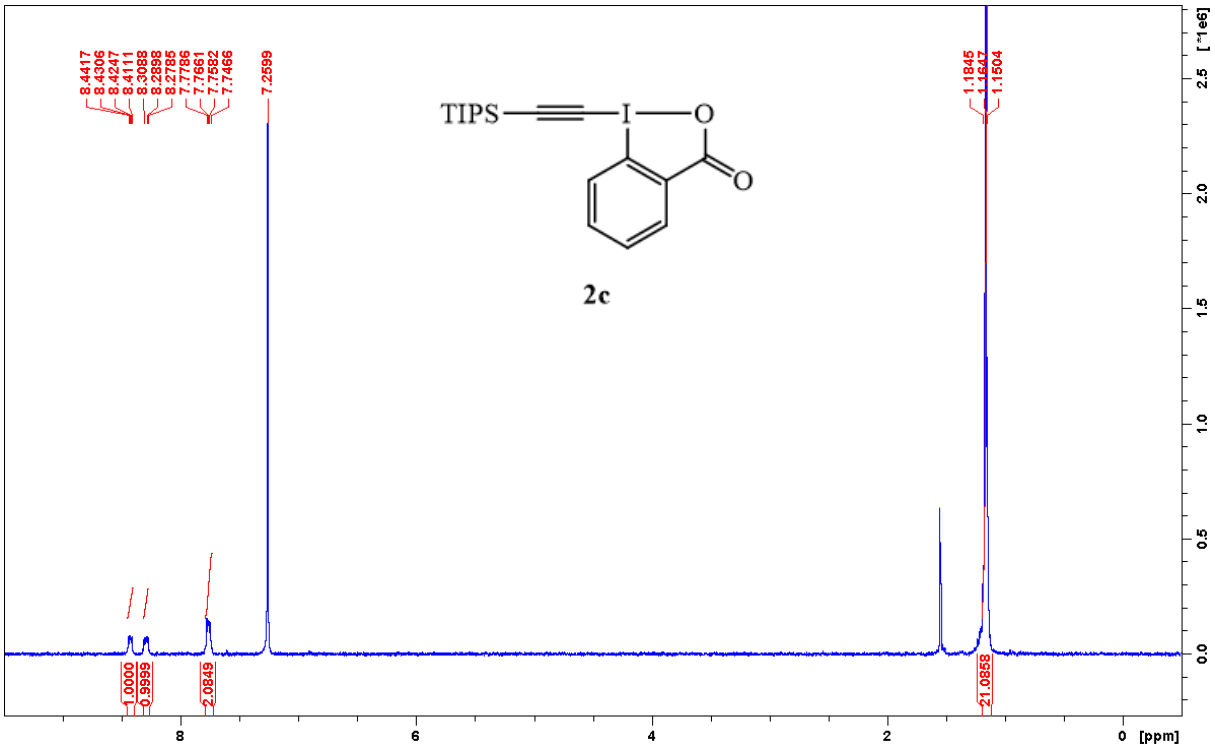
3a'

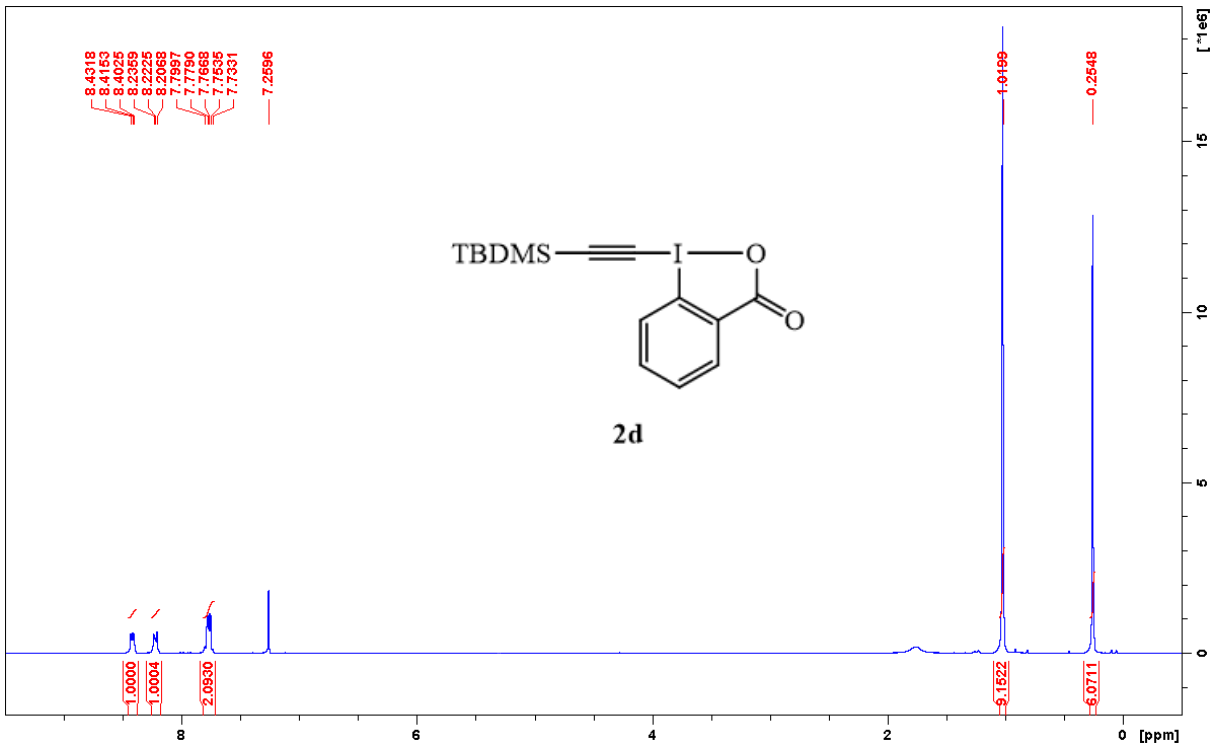
Following the general procedure, phenylacetylene (18 µL, 0.16 mmol) was reacted with Butyl-EBX reagent **2e** (89.9 mg, 0.27 mmol) to afford the diyne **3a’** as colourless solid in 73% yield (21.6 mg, 0.12 mmol). Analytical data are identical to **3a** (see above).

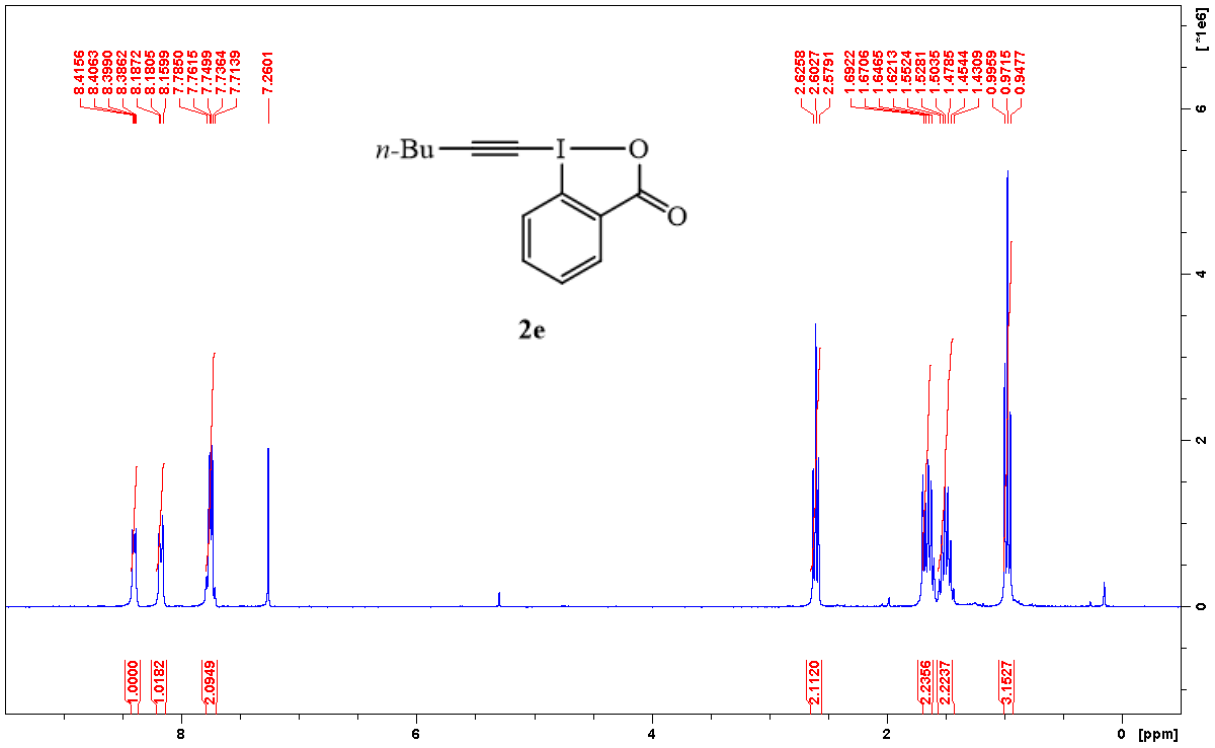
4. Selected NMR spectra:

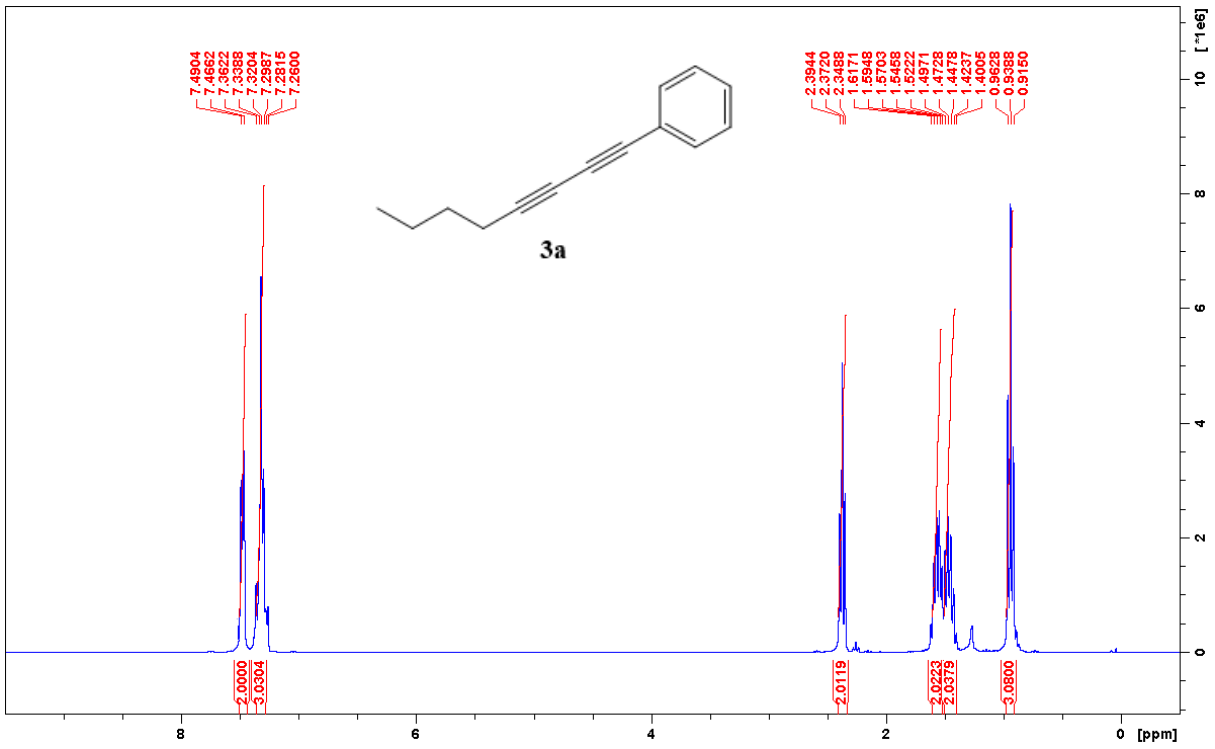


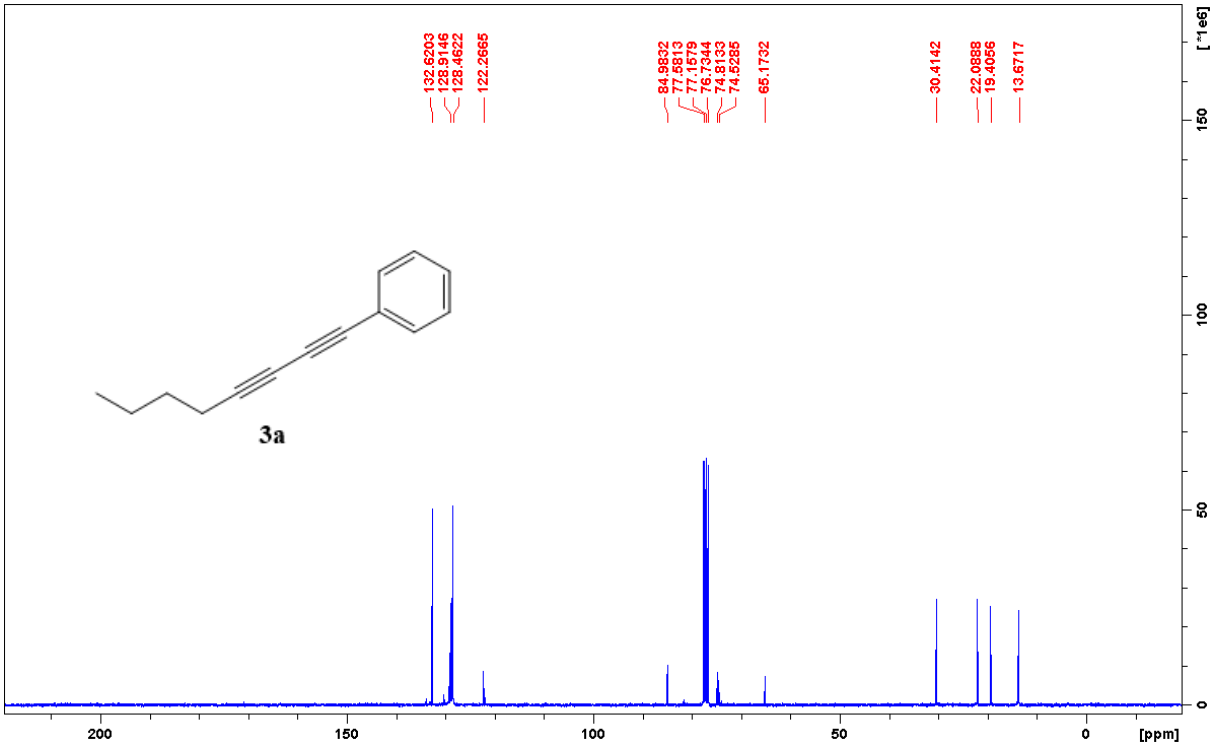


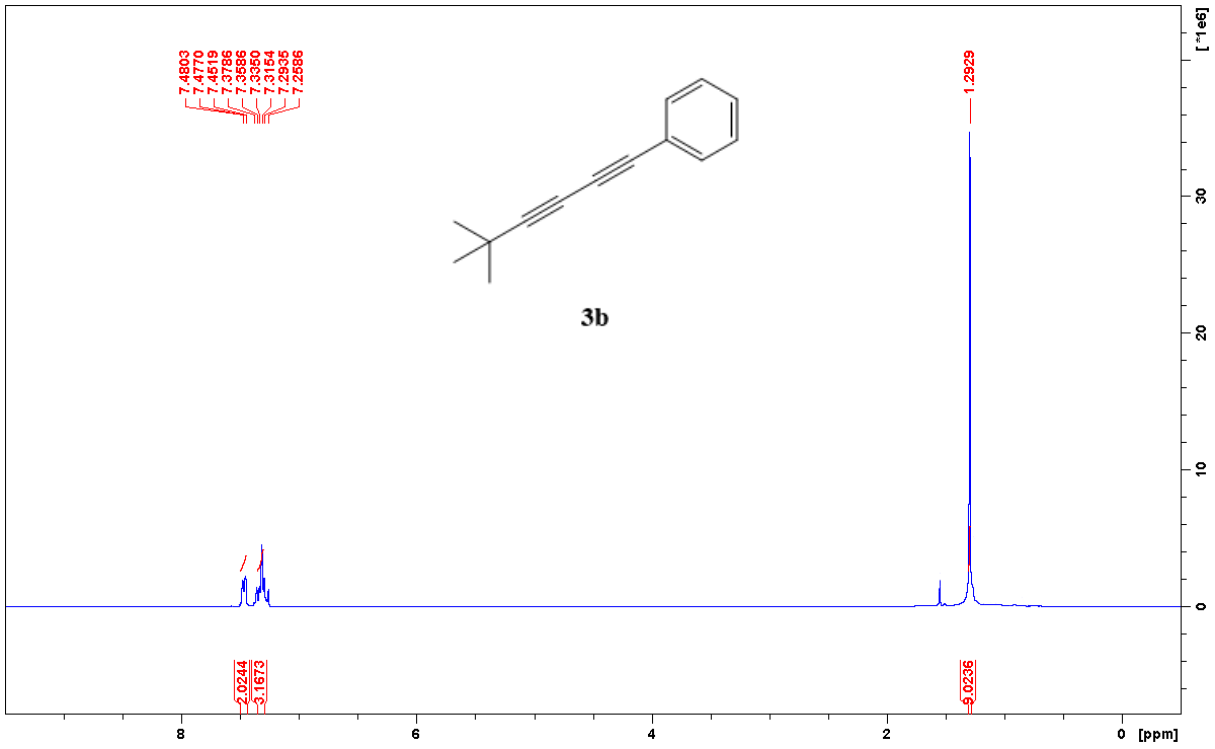

8.4417
8.4306
8.4247
8.4111
8.3088
8.2898
8.2785
7.7786
7.7661
7.7582
7.7466
7.2599
1.1845
1.1647
1.1504
TIPS
I
O
O
2c
1.0000
0.9999
2.0849
21.0858
8
6
4
2
0 [ppm]
0.0
0.5
1.0
1.5
2.0
2.5 [*1e6]

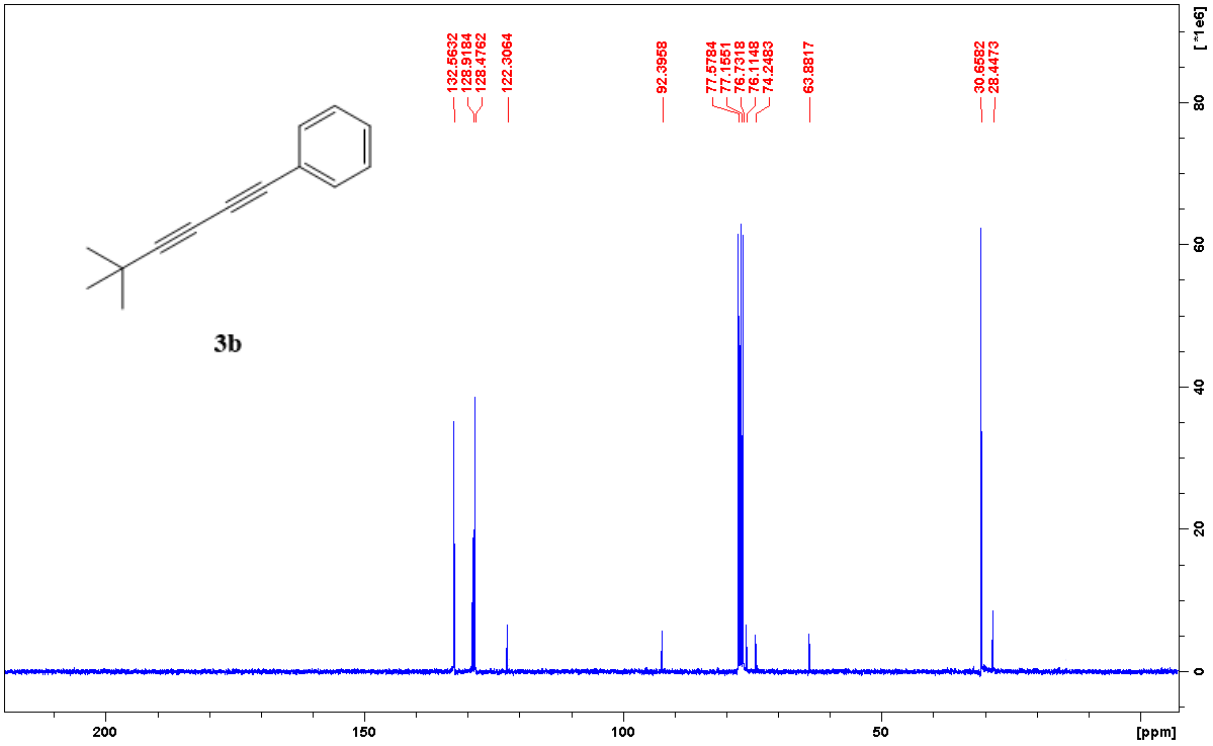

8.4318
8.4183
8.4025
8.2359
8.2225
8.2068
7.7997
7.7790
7.7668
7.7535
7.7331
7.2596
1.0199
0.2548
TBDMS
I
O
O
2d
1.0000
1.0004
2.0930
9.1522
6.0711
8
6
4
2
0 [ppm]
0
5
10
15 [*1e6]

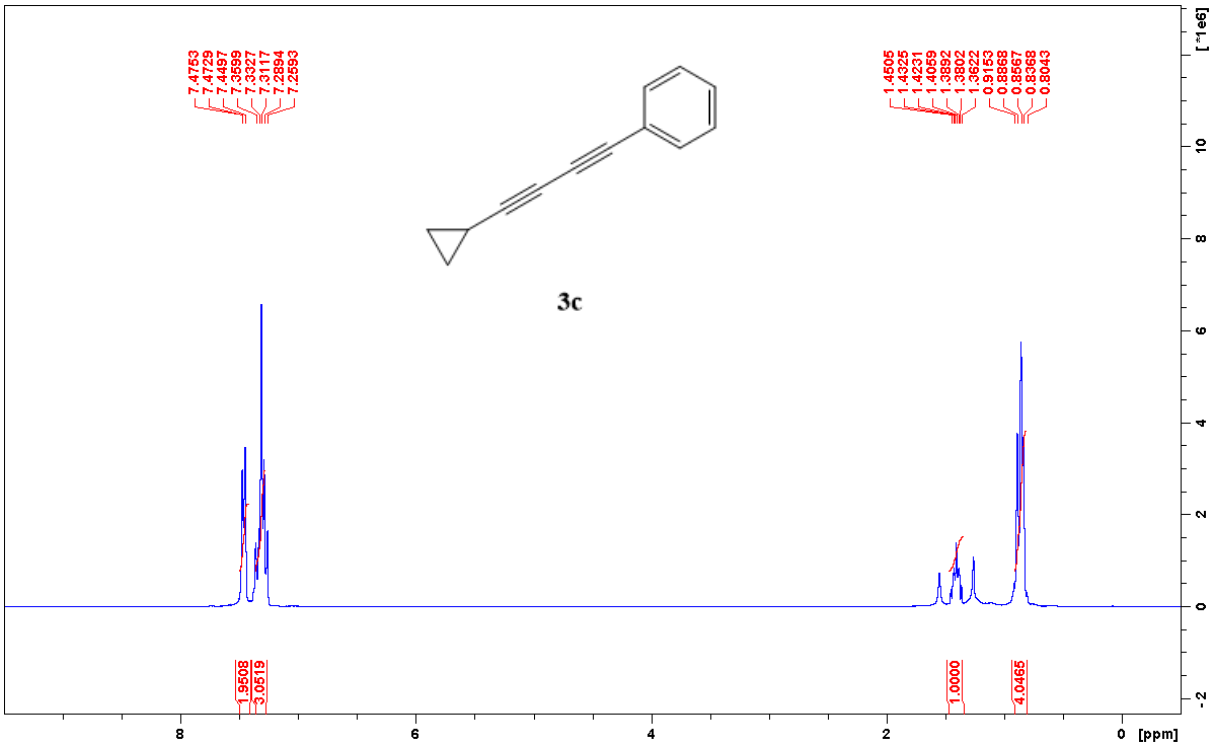

8.4156
8.4063
8.3990
8.3862
8.1872
8.1805
8.1599
7.7880
7.7615
7.7489
7.7364
7.7139
7.2601
2.6258
2.6027
2.5791
1.6922
1.6706
1.6465
1.6213
1.5524
1.5261
1.5035
1.4785
1.4544
1.4369
0.9959
0.9715
0.9477
n-Bu
I
O
O
2e
1.0000
1.0182
2.0949
2.1120
2.2356
2.2237
3.1527
8
6
4
2
0
[ppm]
[*1e6]

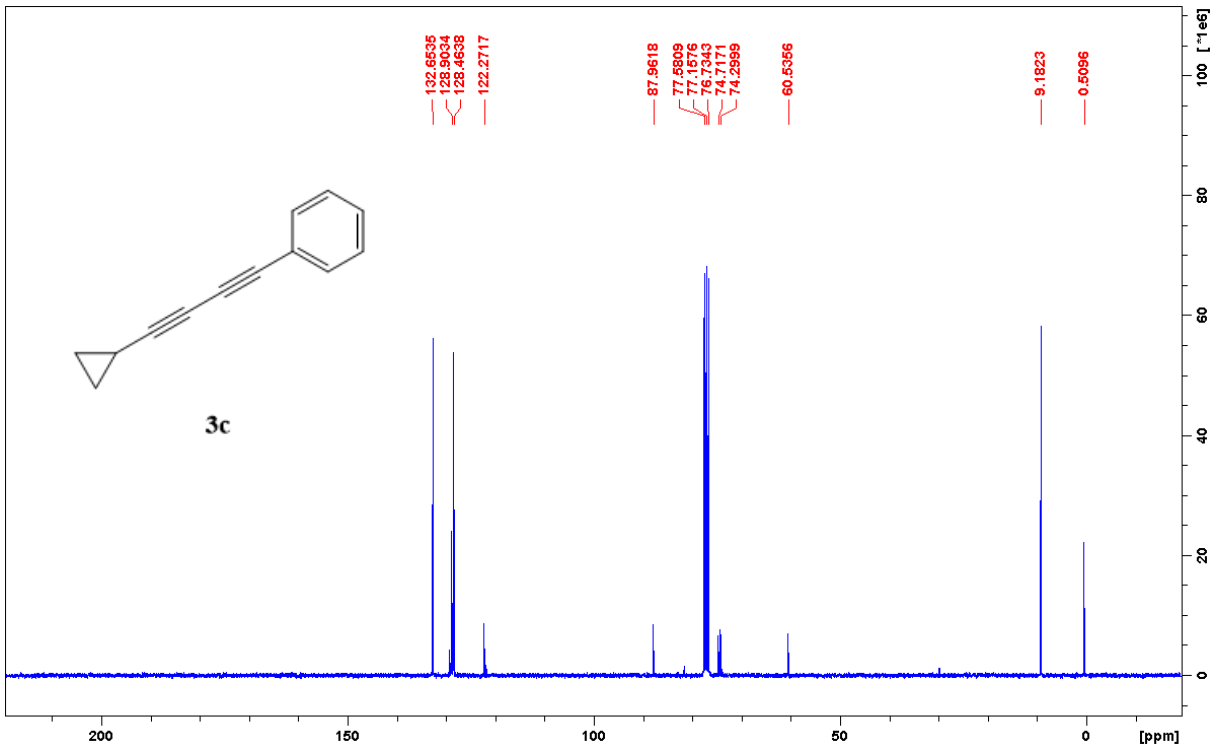

7.4904
7.4662
7.3622
7.3388
7.3204
7.2987
7.2815
7.2600
2.3944
2.3720
2.3488
1.6171
1.5948
1.5703
1.5488
1.5222
1.4971
1.4728
1.4478
1.4237
1.4006
0.9628
0.9388
0.9150
3a
2.0000
3.0304
2.0119
2.0223
2.0379
3.0800
8
6
4
2
0
[ppm]
[*1e6]

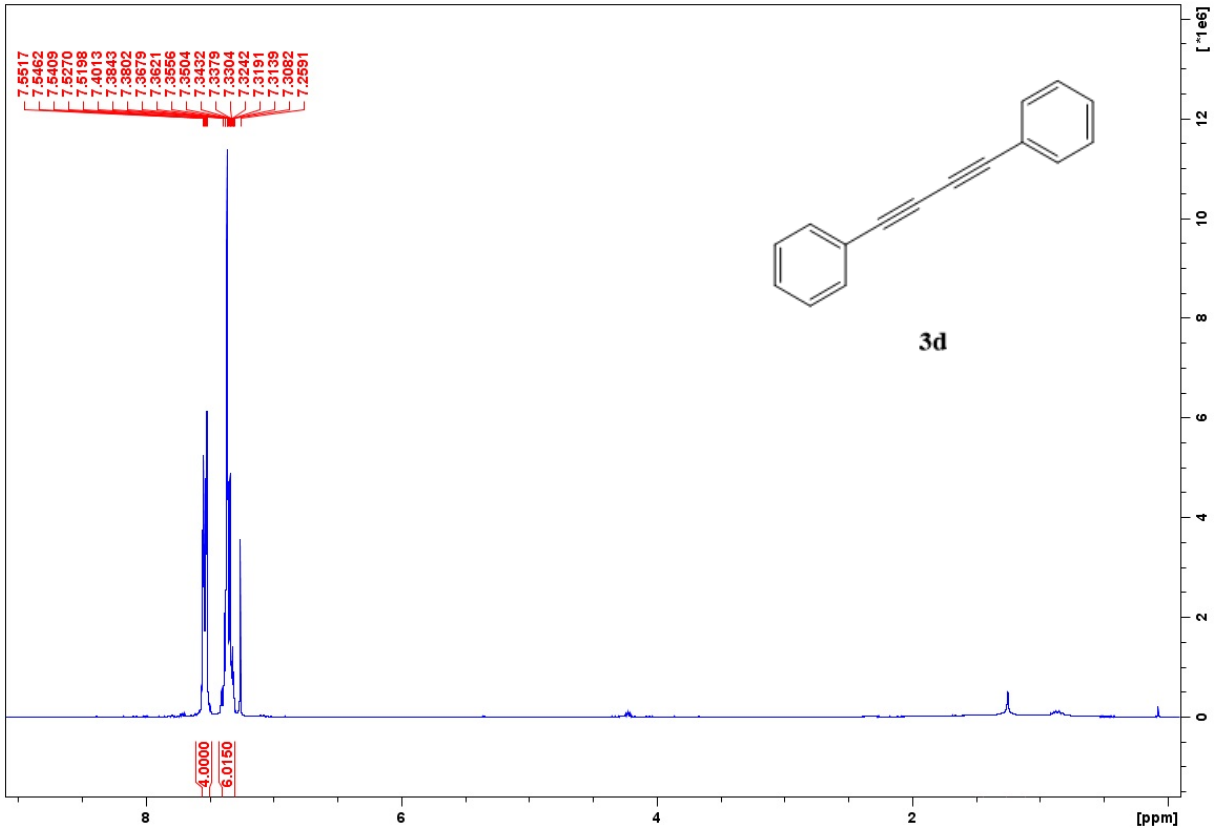

132.6203
128.9146
128.4622
122.2665
84.9832
77.5813
77.1579
76.7344
74.8133
74.5285
65.1732
30.4142
22.0888
19.4056
13.6717
3a
[*1e6]
150
100
50
0
200
150
100
50
0
[ppm]

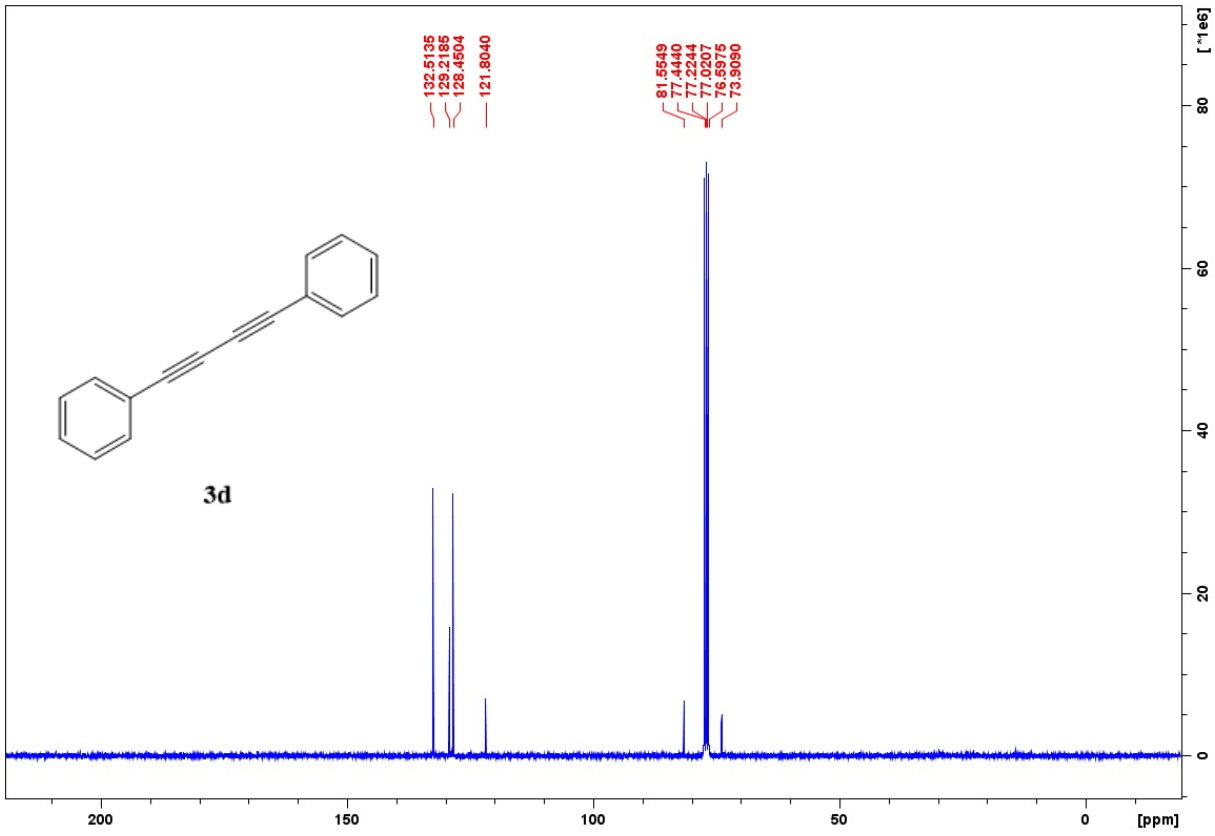

7.4803
7.4770
7.4519
7.3786
7.3586
7.3350
7.3154
7.2935
7.2586
1.2929
3b
[*1e6]
30
20
10
0
2.0244
3.1673
9.0236
8
6
4
2
0
[ppm]

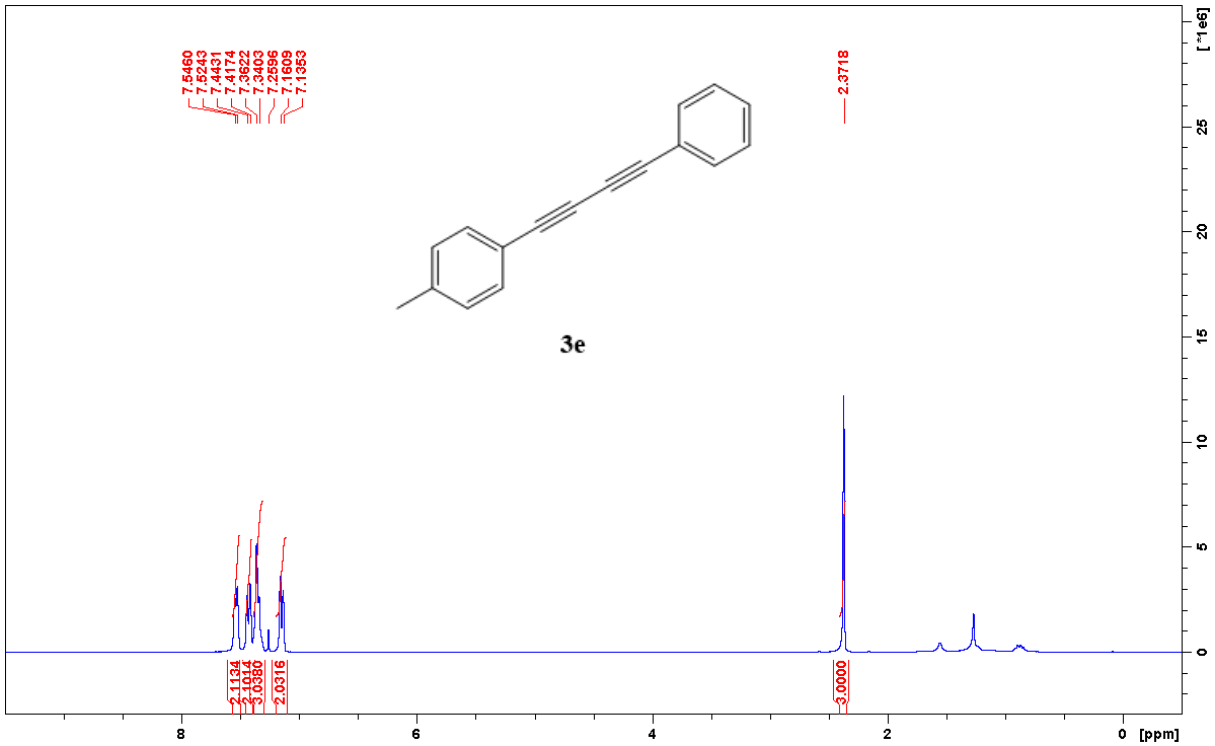

132.5632
128.9184
128.4762
122.3064
92.3958
77.5784
77.1651
76.7318
76.1148
74.2483
63.8817
30.6582
28.4473
3b
[*1e6]
200
150
100
50
[ppm]

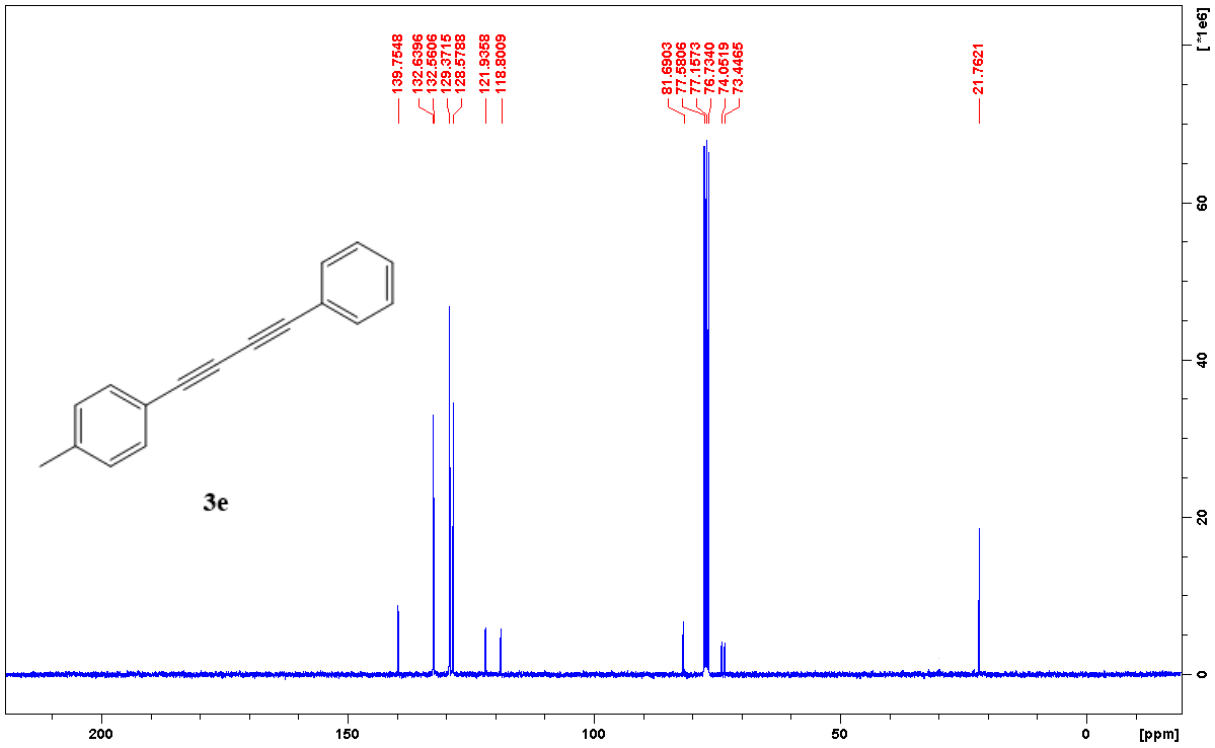

7.4753
7.4729
7.4497
7.3599
7.3327
7.3117
7.2894
7.2593
1.4505
1.4325
1.4231
1.4059
1.3892
1.3802
1.3622
0.9153
0.8868
0.8567
0.8368
0.8043
3c
1.9508
3.0519
1.0000
4.0465
[*1e6]
8
6
4
2
0
[ppm]

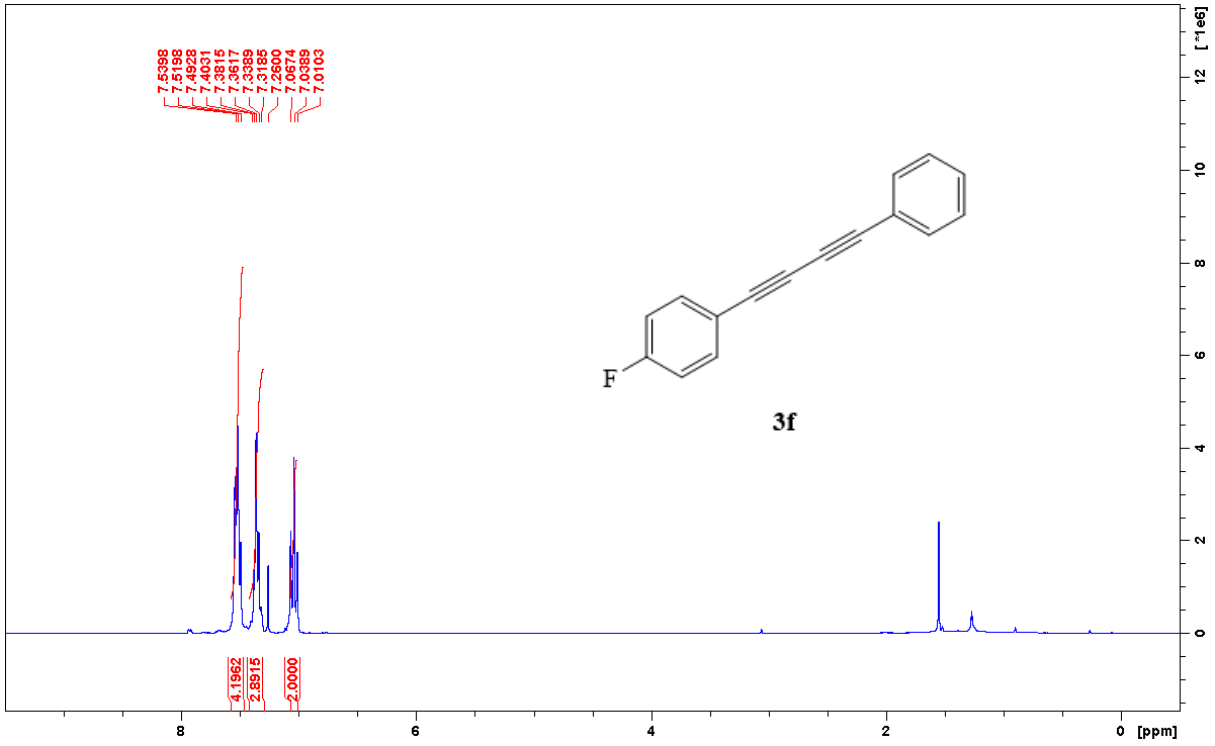

132.6535
128.9034
128.4638
122.2717
87.9618
77.5809
77.1576
76.7343
74.7171
74.2999
60.5356
9.1823
0.5096
3c
[*1e6]
[ppm]

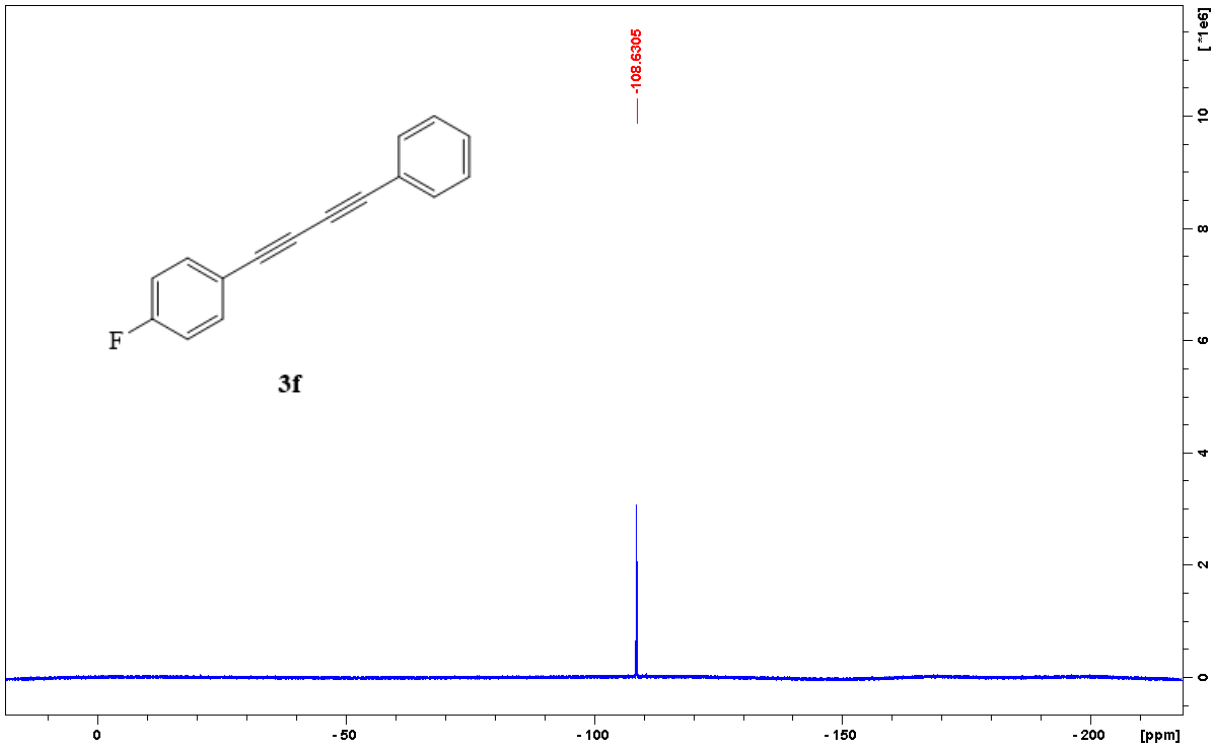

7.5517
7.5462
7.5409
7.5270
7.5198
7.4013
7.3843
7.3802
7.3679
7.3621
7.3556
7.3504
7.3432
7.3379
7.3304
7.3242
7.3191
7.3139
7.3082
7.2591
4.0000
6.0150
3d
[*1e6]
[ppm]

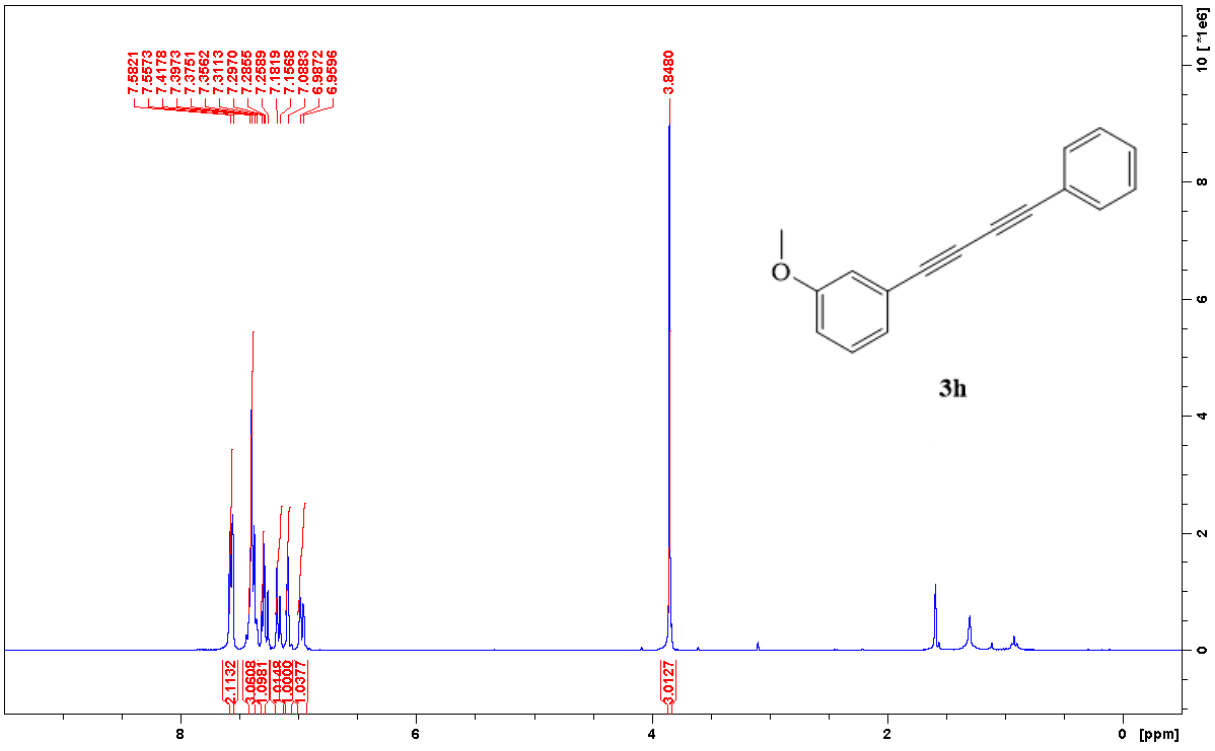

132.5135
129.2185
128.4504
121.8040
81.5549
77.4440
77.2244
77.0207
76.5975
73.9090
3d
[*1e6]
200
150
100
50
0
[ppm]

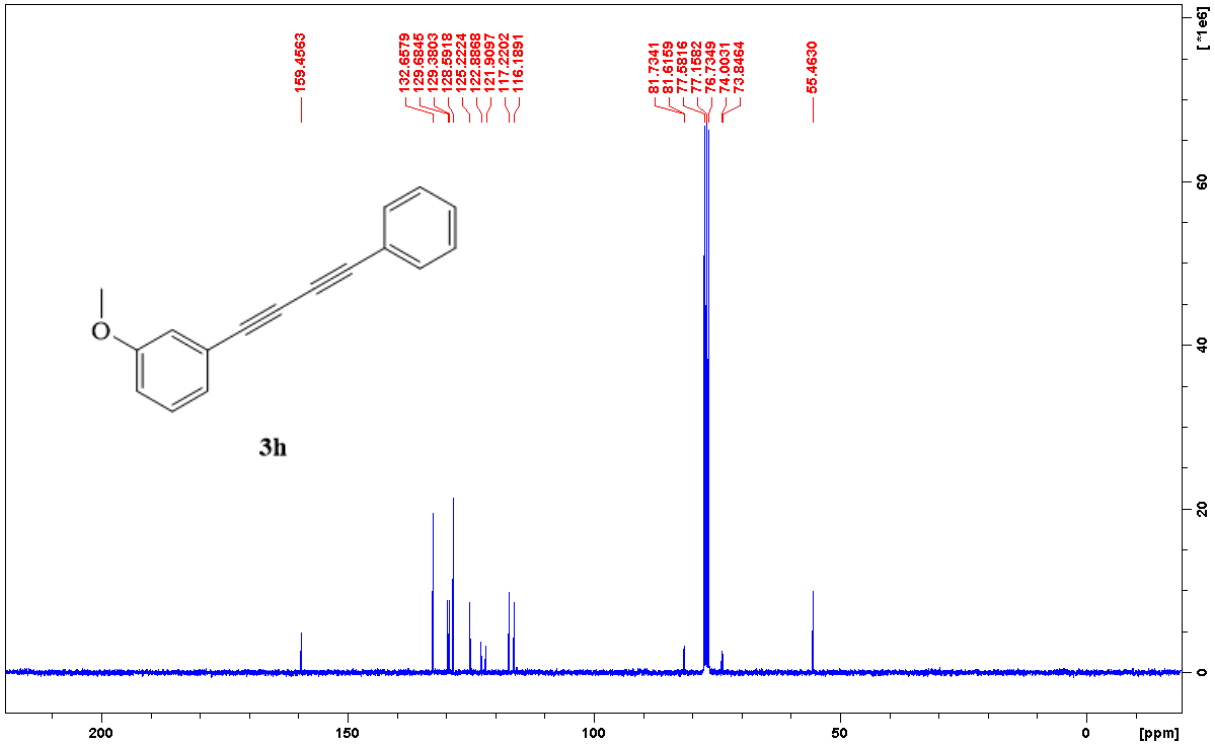

7.5460
7.5243
7.4431
7.4174
7.3622
7.3403
7.2596
7.1609
7.1353
2.3718
3e
2.1134
2.1014
3.0380
2.0316
3.0000
[*1e6]
8
6
4
2
0
[ppm]

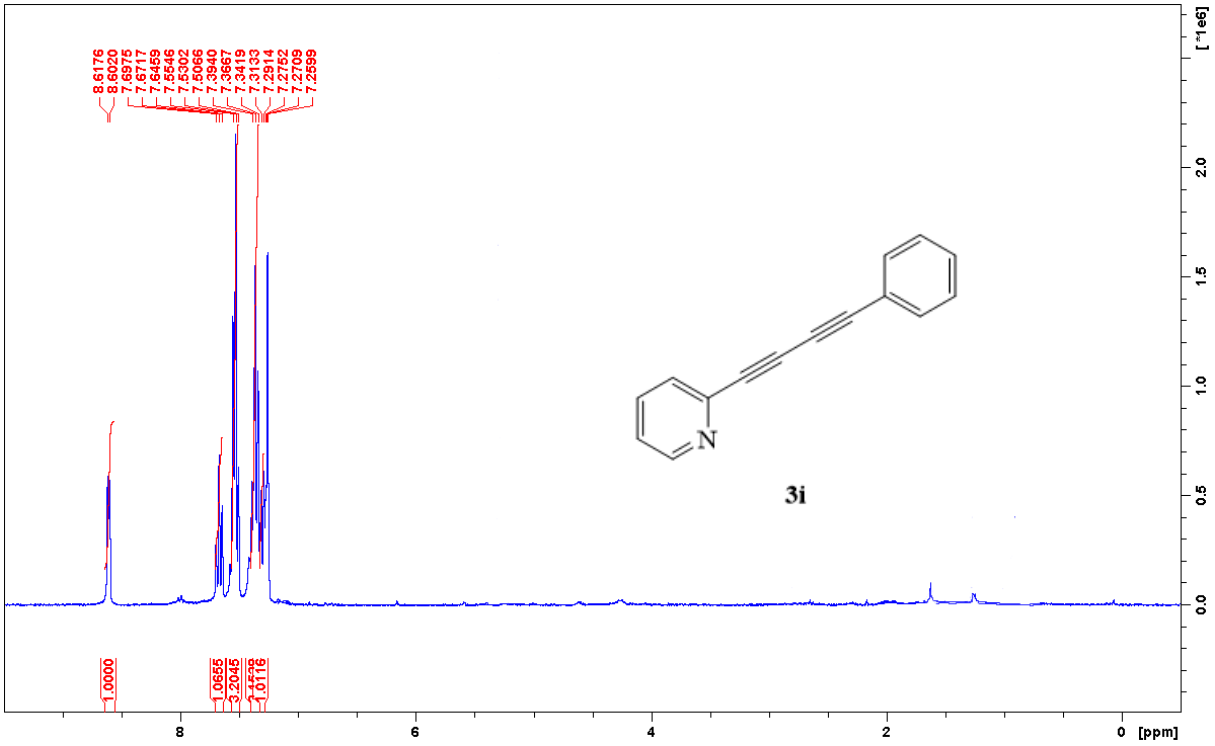

139.7548
132.6396
132.5606
129.3715
128.5788
121.9358
118.8009
81.6903
77.5806
77.1573
76.7340
74.0519
73.4465
21.7621
3e
200
150
100
50
0
[ppm]
[*1e6]

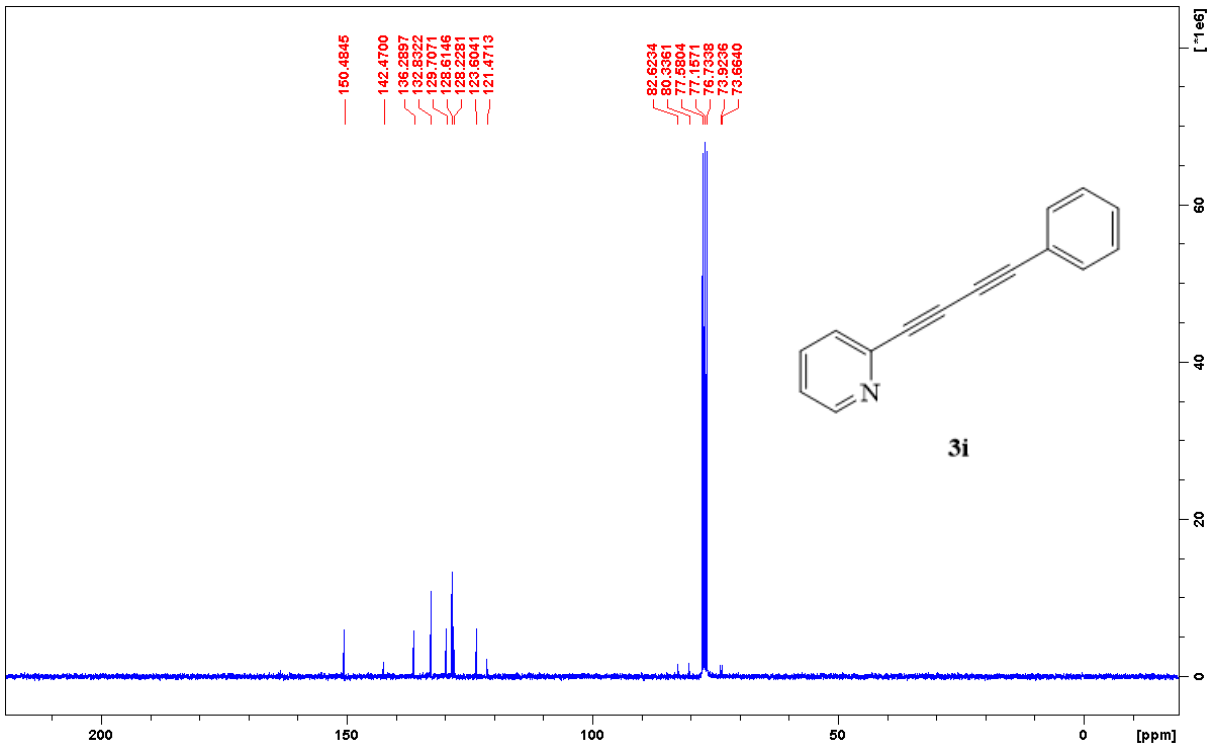

7.5398
7.5198
7.4928
7.4031
7.3815
7.3617
7.3389
7.3185
7.2600
7.0674
7.0389
7.0103
F
3f
4.1962
2.8915
2.0000
8
6
4
2
0
[ppm]
[*1e6]

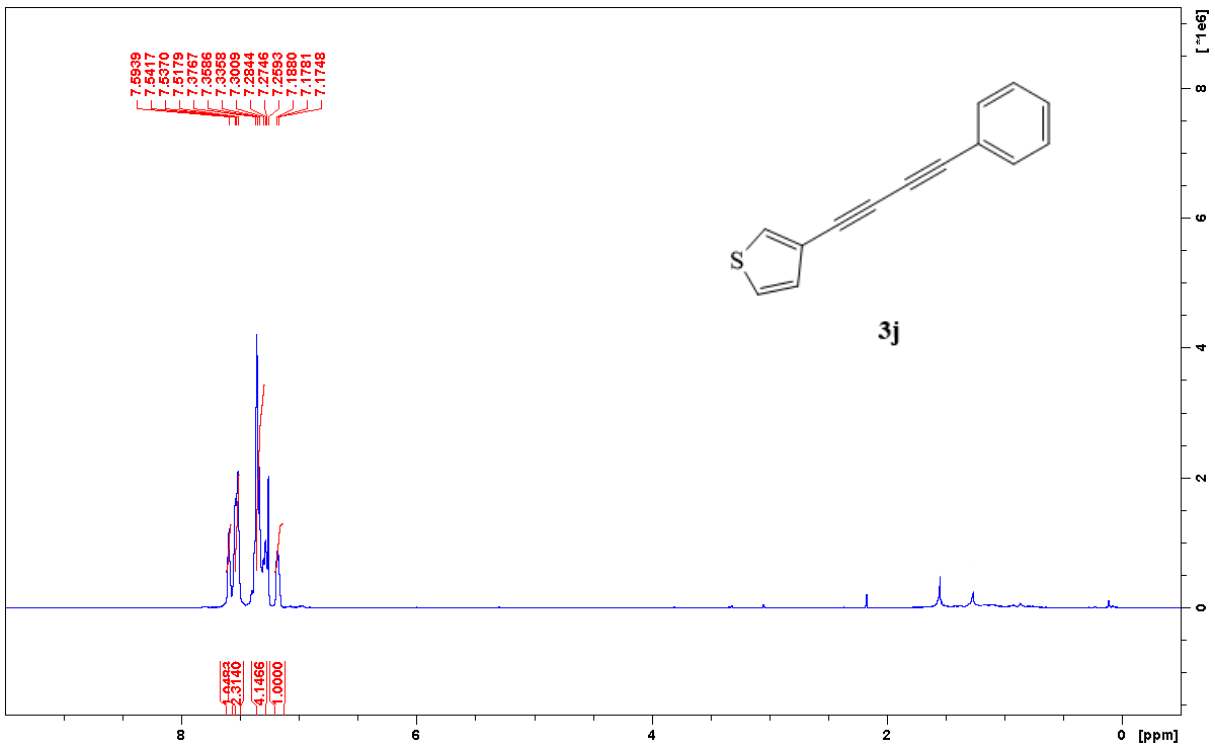

-108.6305
F
3f
0
-50
-100
-150
-200
[ppm]

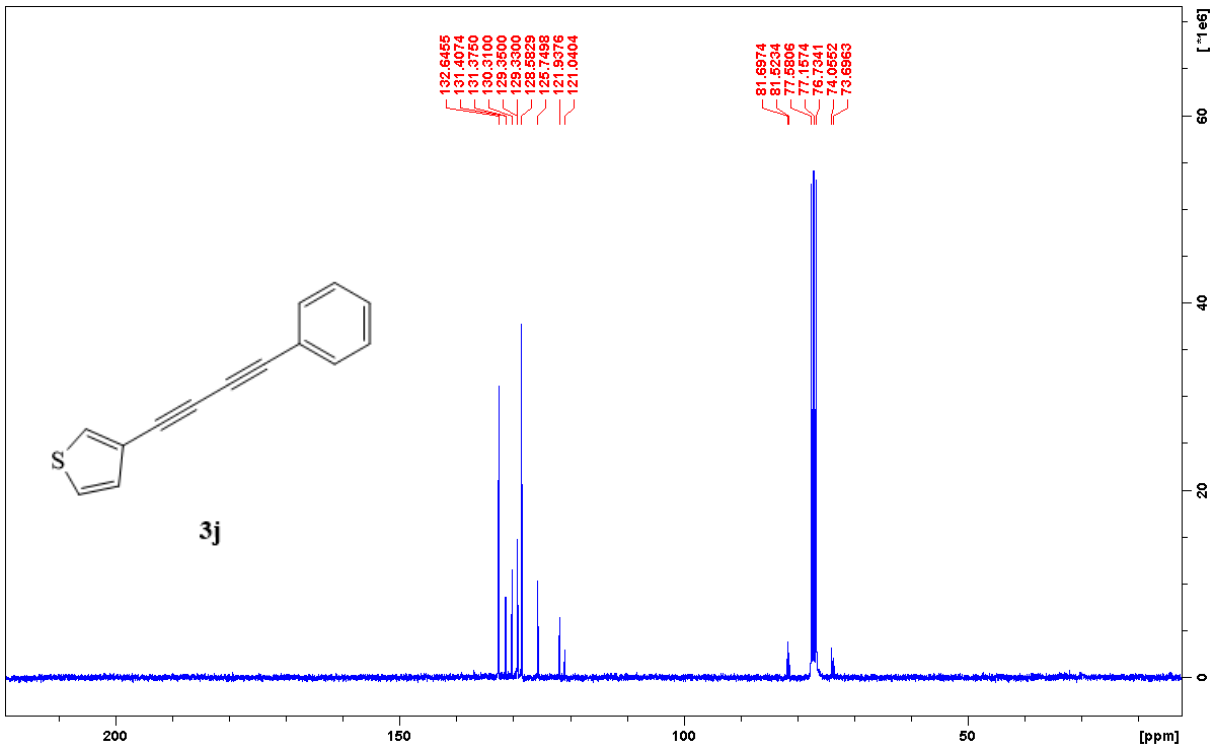

7.5821
7.5573
7.4178
7.3973
7.3751
7.3562
7.3113
7.2970
7.2855
7.2589
7.1819
7.1568
7.0883
6.9872
6.9596
3.8480
O
3h
2.1132
3.0608
3.0681
1.0040
1.0000
1.0377
3.0127
8
6
4
2
0
[ppm]

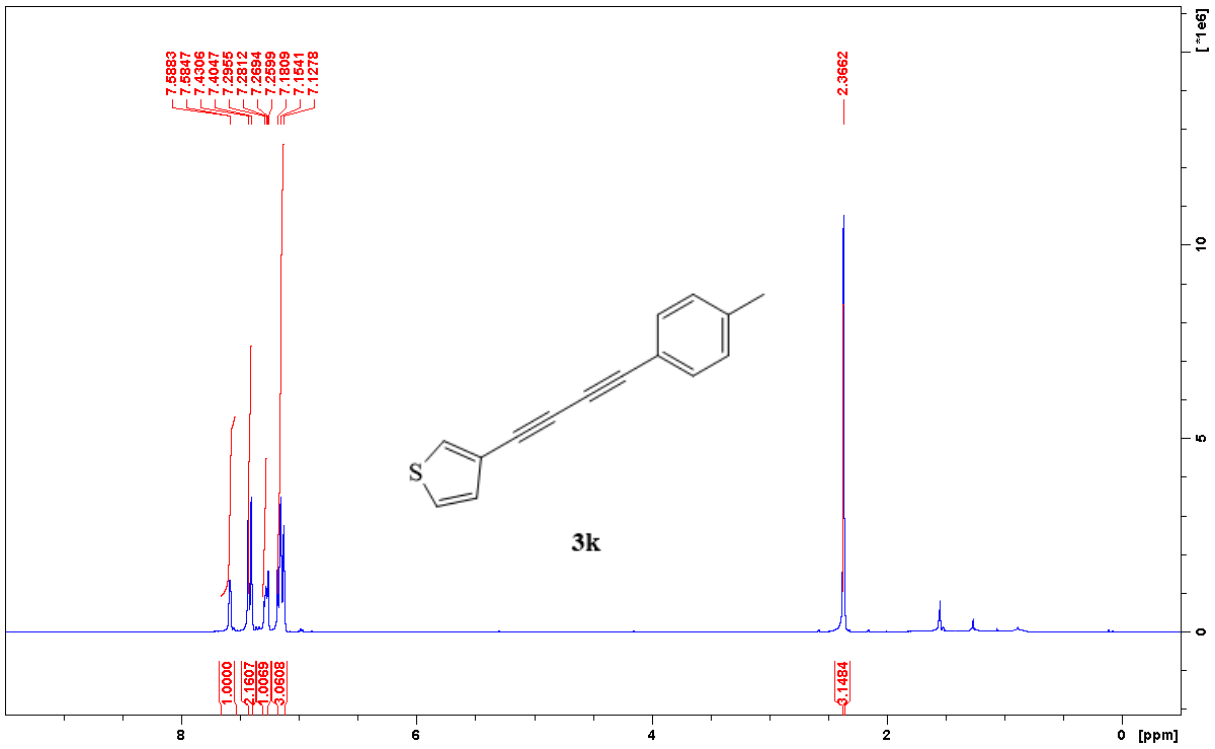

159.4563
132.6579
129.6845
129.3803
128.5918
125.2224
122.8868
121.9097
117.2202
116.1891
81.7341
81.6159
77.5816
77.1582
76.7349
74.0021
73.8464
55.4630
O
3h
200
150
100
50
0
[ppm]
[*1e6]
60
40
20
0

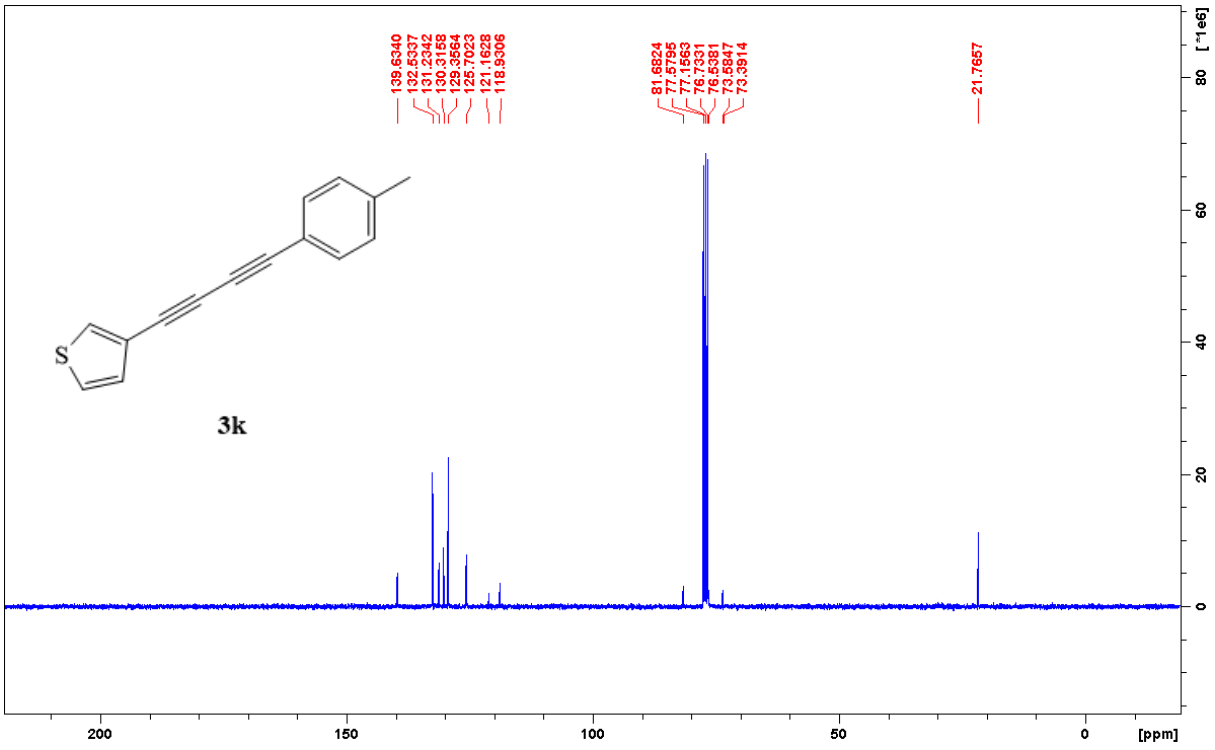

8.6176
8.6020
7.6875
7.6717
7.6459
7.5546
7.5302
7.5066
7.3940
7.3667
7.3419
7.3133
7.2914
7.2752
7.2709
7.2599
N
3i
1.0000
1.0655
3.2045
1.0116
1.0116
8
6
4
2
0
[ppm]
[*1e6]
2.0
1.5
1.0
0.5
0.0

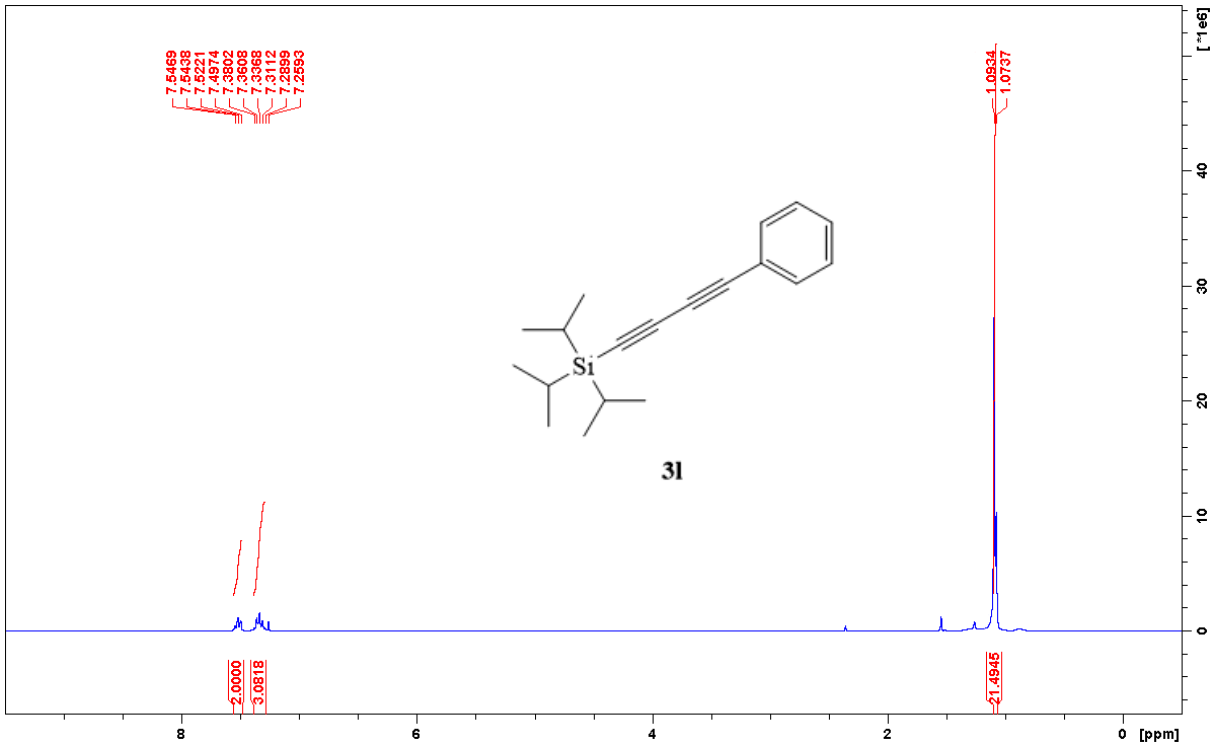

150.4845
142.4700
136.2897
132.8522
129.7071
128.6146
128.2281
123.6941
121.4713
82.6234
80.3361
77.5804
77.1571
76.7338
73.9236
73.6640
N
3i
[*1e6]
60
40
20
0
200
150
100
50
0
[ppm]

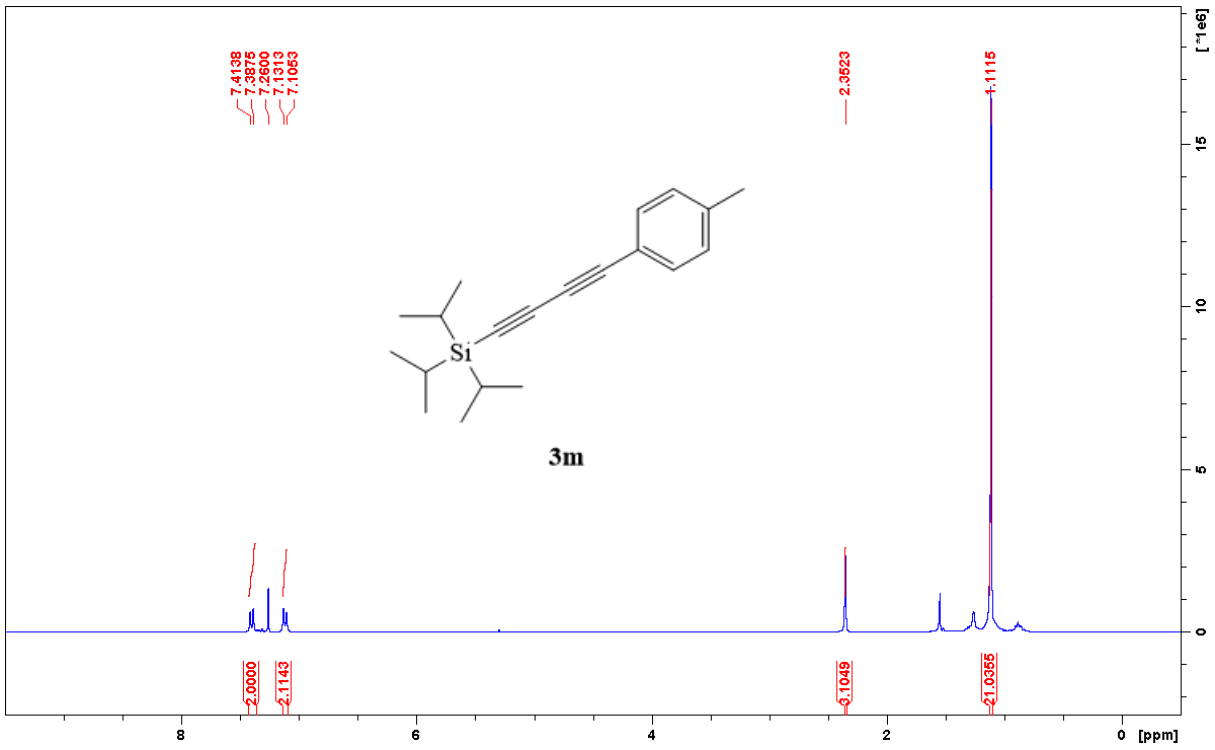

7.5939
7.5417
7.5370
7.5179
7.3767
7.3586
7.3368
7.3099
7.2844
7.2746
7.2593
7.1880
7.1781
7.1748
S
3j
1.0000
[*1e6]
8
6
4
2
0
8
6
4
2
0
[ppm]

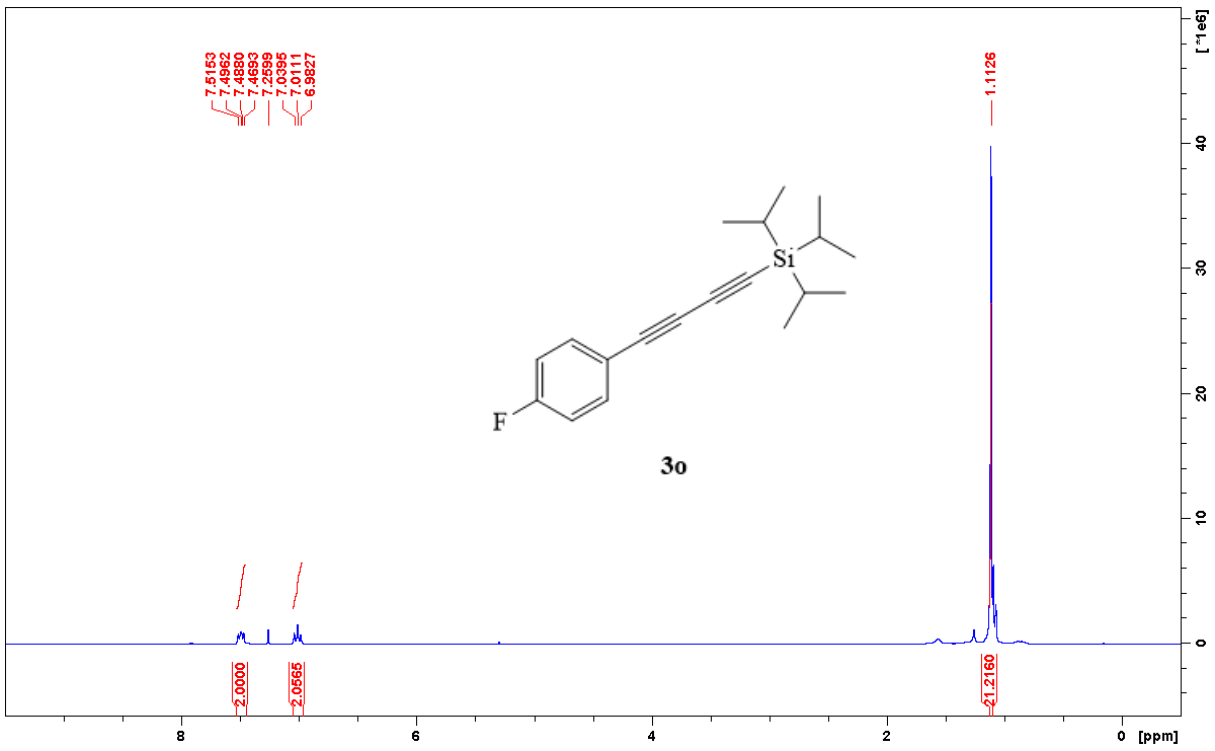

132.6455
131.4074
131.3750
130.3100
129.3500
129.3300
128.5529
125.7498
121.9376
121.0404
81.6974
81.5234
77.5806
77.1574
76.7341
74.0552
73.6963
S
3j
[*1e6]
60
40
20
0
200
150
100
50
[ppm]

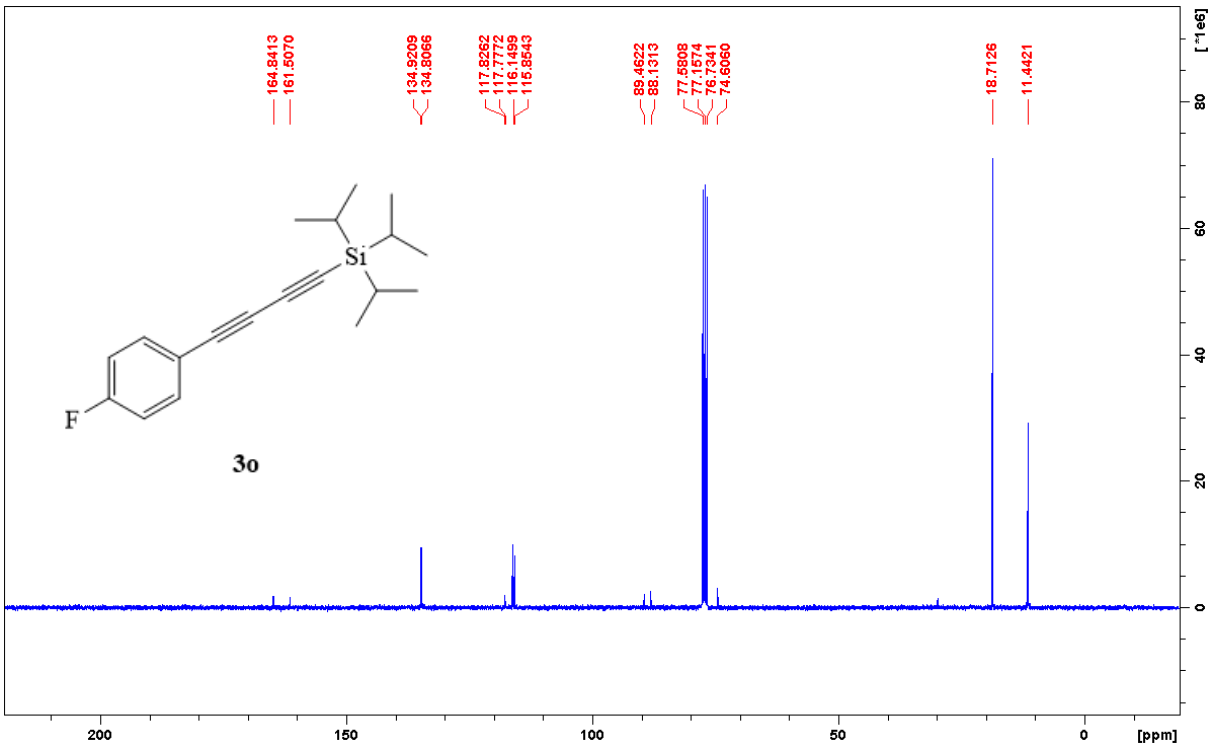

7.5883
7.5847
7.4306
7.4047
7.2955
7.2812
7.2694
7.2599
7.1809
7.1541
7.1278
2.3662
S
3k
[*1e6]
10
5
0
1.0000
2.1607
1.0069
3.0608
0.1484
8
6
4
2
0
[ppm]

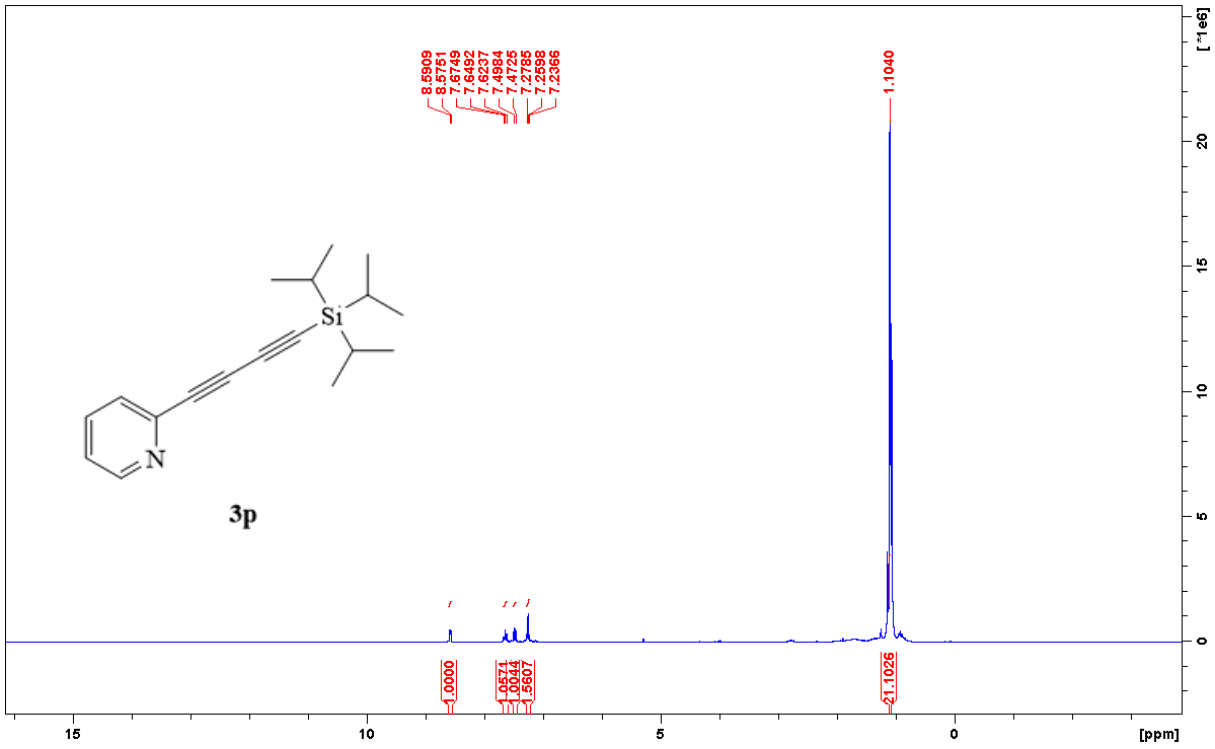

139.6340
132.5337
131.2342
130.3158
129.3564
125.7023
121.1628
118.9306
81.6824
77.5795
77.1563
76.7331
76.5381
73.5847
73.3914
21.7657
S
3k
200
150
100
50
0
[ppm]
[1e6]

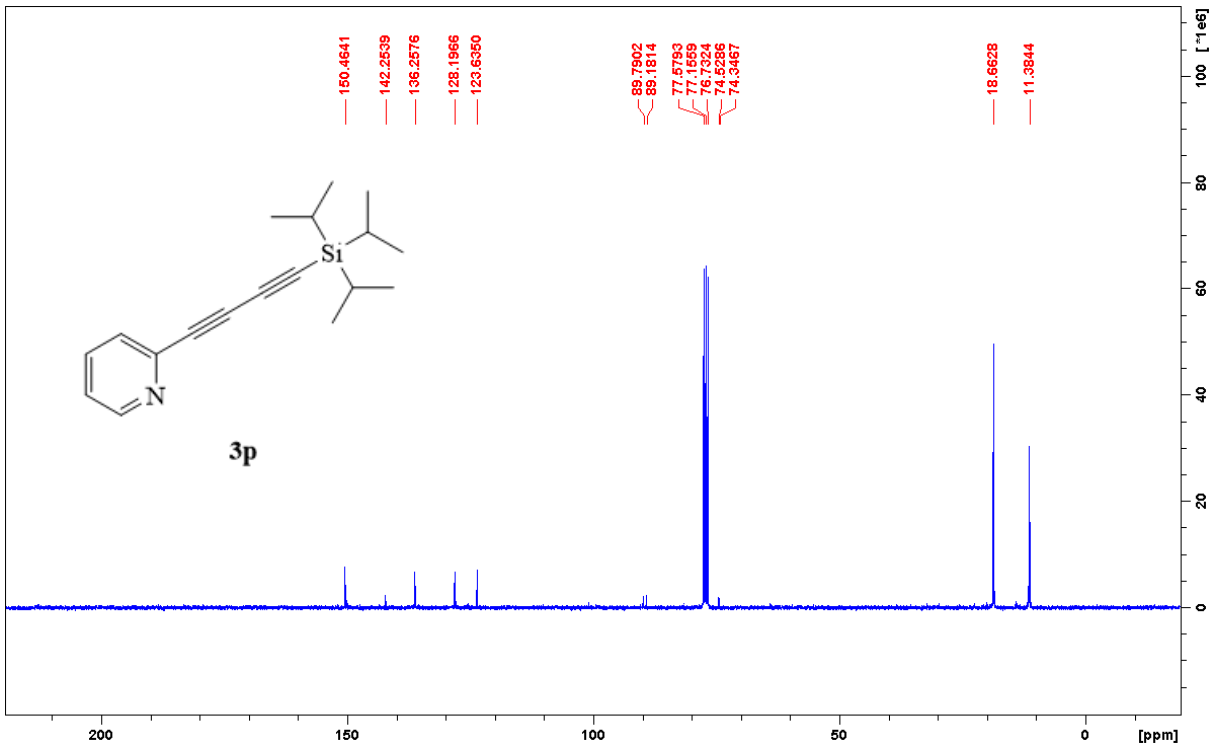

7.5469
7.5438
7.5221
7.4974
7.3802
7.3608
7.3368
7.3112
7.2899
7.2593
1.0934
1.0737
Si
3l
2.0000
3.0818
21.4945
8
6
4
2
0
[ppm]
[1e6]


7.4138
7.3875
7.2600
7.1313
7.1053
2.3523
1.1115
Si
3m
2.0000
2.1143
3.1049
21.0355
8
6
4
2
0
[ppm]
[*1e6]


7.5153
7.4962
7.4880
7.4693
7.2599
7.0395
7.0111
6.9827
1.1126
Si
F
3o
2.0000
2.0565
21.2160
8
6
4
2
0
[ppm]
[*1e6]


164.8413
161.5070
134.9209
134.8066
117.8262
117.7772
116.1499
115.8543
89.4622
88.1313
77.5898
77.1574
76.7341
74.6060
18.7126
11.4421
Si
F
3o
200
150
100
50
0
[ppm]


8.5909
8.5751
7.6749
7.6492
7.6237
7.4984
7.4725
7.2785
7.2598
7.2366
1.1040
Si
N
3p
1.0000
1.0671
1.0044
1.5607
21.1026
15
10
5
0
[ppm]


150.4641
142.2539
136.2576
128.1966
123.6350
89.7902
89.1814
77.5793
77.1559
76.7324
74.5286
74.3467
18.6628
11.3844
Si
N
3p
200
150
100
50
0
[ppm]
100
80
60
40
20
0
[*1e6]