

Regiodivergent Hydroallylation of 1,3-Diynes Controlled by Nickel and Palladium Catalysts

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S1. General methods and materials

The liquid-state NMR was recorded on a 400 or 500 MHz spectrometer. Chemical shifts were reported in ppm. ^1H NMR spectra were referenced to CDCl_3 (7.26 ppm), and ^{13}C -NMR spectra were referenced to CDCl_3 (77.0 ppm). All ^{13}C NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz.

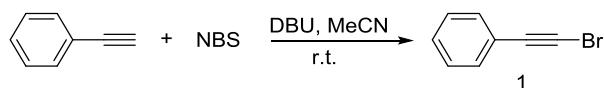
High resolution mass spectrometry: Mass spectra were recorded with Agilent 1290-6545XT Ultra-High performance liquid chromatography-quadrupole time-of-flight mass spectrometer using electron spray ionization

All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Solvents were treated prior to use according to the standard methods. If there is no special description, the reagents used in the experiment are commercial analytical pure. The 1,3-diyne were prepared according to corresponding literature procedures.^[1,2]

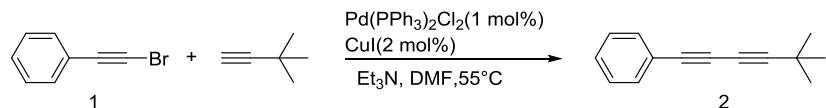
References:

- [1] Shi, W.; Lei, A. *Tetrahedron Lett.* **2014**, *55*, 2763-2772.
- [2] Burghart, J.; Brückner, R. *Eur. J. Org. Chem.* **2011**, 150–165.

S2. Typical procedure for the preparation of 1,3-diyne



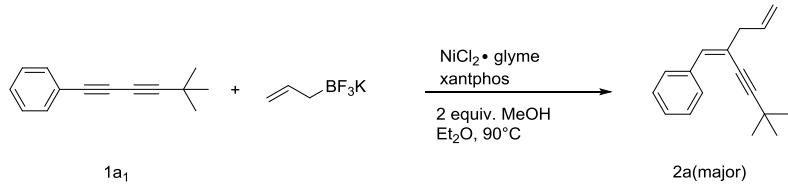
To a solution of alkyne (5.0 mmol, 1.0 equiv) in MeCN (10 mL) were added NBS (5.5 mmol, 1.1 equiv) and DBU (5.5 mmol, 1.1 equiv). The mixture was stirred at room temperature for 20 min. Then, the reaction mixture was quenched with water and extracted with CH_2Cl_2 (3×15 mL), dried over anhydrous Na_2SO_4 . The combined organic layers were concentrated under reduced pressure, and the crude product was purified by flash chromatography (petroleum ether) to give alkynyl bromide **1**.



To a flame-dried round-bottom flask under N_2 , alkynyl bromide **1** (5 mmol, 1.0 equiv), $\text{PdCl}_2(\text{PPh}_3)_2$ (1 mol%) and CuI (2 mol%) were dissolved in 5 mL Et_3N and 3,3-dimethyl-1-butyne (12 mmol, 2.4 equiv) were dissolved in 5 mL DMF and the reaction mixture was stirred under N_2 at 55°C for 12h. After the starting material was consumed completely which was detected by TLC, the reaction mixture was diluted with 20 mL dichloromethane, then washed with

saturated NaCl aqueous solution, dried over anhydrous Na₂SO₄. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel with petroleum ether to afford the alkynylation products **2**. The trimethyl(phenylbuta-1,3-diyne-1-yl)silane is synthesized in a similar way.

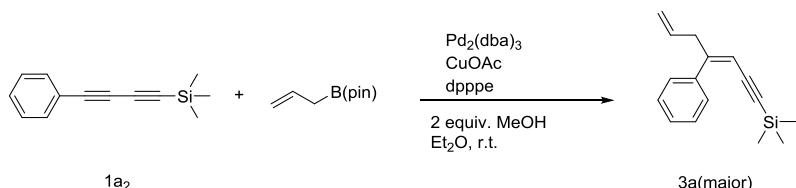
S3. General procedure for 1,3-diyne hydroallylation



In a nitrogen filled pressure resistant reaction tube, NiCl₂·glyme (0.02mmol, 10 mol%), potassium allyltrifluoroborate (0.3mmol, 1.5 equiv), xantphos (0.02mmol, 10 mol%), Et₂O (2 mL), 1,3-diyne 1a₁ (0.2 mmol, 1.0 equiv) and MeOH (0.4 mmol, 2.0 equiv) were successively added into the pressure resistant reaction tube under the protection of nitrogen atmosphere, and stirred at 90°C under N₂ atmosphere for 3 days. When the reaction was completed, the solvent was removed in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product.

Scale-up experiments of 2a: In a nitrogen filled pressure resistant reaction tube, NiCl₂·glyme (0.2mmol, 10 mol%), potassium allyltrifluoroborate (3.0mmol, 1.5 equiv), xantphos (0.2mmol, 10 mol%), Et₂O (15 mL), 1,3-diyne 1a₁ (2.0mmol, 1.0 equiv, 364mg) and MeOH (4.0mmol, 2.0 equiv) were successively added into the pressure resistant reaction tube under the protection of nitrogen atmosphere, and stirred at 90°C under N₂ atmosphere for 5 days. When the reaction was completed, the solvent was removed in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford 386mg of 2a in 86% yield.

A small number of samples of crude products were used for NMR detection to obtain the selectivity of the reaction.



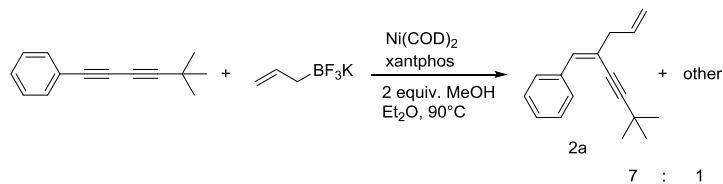
In a nitrogen filled schlenk tube, Pd₂(dba)₃ (0.005mmol, 2.5 mol%), CuOAc (0.02 mmol, 10 mol%), dpppe (0.01mmol, 5 mol%), Et₂O (2 mL), 1,3-diyne 1a₂ (0.2 mmol, 1.0 equiv), allylboronic acid pinacol ester (0.3 mmol, 1.5 equiv) and MeOH (0.4 mmol, 2.0 equiv) were successively added into the schlenk tube under the protection of nitrogen atmosphere, and stirred at room temperature under N₂ atmosphere for 3 days. When the reaction was completed, the solvent was removed in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product.

Scale-up experiments of 3a: In a nitrogen filled schlenk tube, Pd₂(dba)₃ (0.05mmol, 2.5 mol%), CuOAc (0.2 mmol, 10 mol%), dpppe (0.1mmol, 5 mol%), Et₂O (15 mL), 1,3-diyne 1a₂ (2.0mmol,

1.0 equiv, 397mg), allylboronic acid pinacol ester (3.0mmol, 1.5 equiv) and MeOH (4.0mmol, 2.0 equiv) were successively added into the schlenk tube under the protection of nitrogen atmosphere, and stirred at room temperature under N₂ atmosphere for 5 days. When the reaction was completed, the solvent was removed in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford 394mg of 3a in 82% yield.

A small number of samples of crude products were used for NMR detection to obtain the selectivity of the reaction.

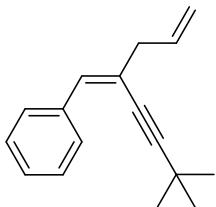
S4. Control experiment with Ni(0)



In a argon filled pressure resistant reaction tube, $\text{Ni}(\text{COD})_2$ (0.02mmol, 10 mol%), potassium allyltrifluoroborate (0.3mmol, 1.5 equiv), xantphos (0.02mmol, 10 mol%), Et_2O (2 mL), 1,3-diyne 1a₁ (0.2 mmol, 1.0 equiv) and MeOH (0.4 mmol, 2.0 equiv) were successively added into the pressure resistant reaction tube under the protection of argon atmosphere, and stirred at 90°C under argon atmosphere for 3 days. We have obtained the main product 2a in 32% yield (Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxy-benzene as internal standard) with poor selectivity of 7:1 (determined by ¹H NMR).

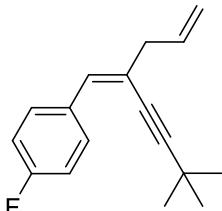
S5. Analytical data for compounds

(Z)-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)benzene (2a)



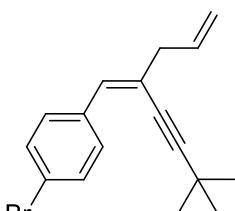
colorless liquid (82%, 37 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.33-7.29 (m, 2H), 7.24-7.21 (m, 1H), 6.46 (s, 1H), 5.95 (ddt, *J* = 17.1, 10.1, 6.8 Hz, 1H), 5.18-5.12 (m, 1H), 5.11-5.08 (m, 1H), 3.02 (dd, *J* = 6.8, 1.2 Hz, 2H), 1.31 (s, 9H); **¹³C NMR** (125 MHz, CDCl₃) δ 136.9, 135.6, 132.9, 128.2, 127.9, 127.4, 121.1, 116.3, 105.8, 79.1, 43.9, 30.8, 28.4. **HRMS** (ESI) m/z Calculated for C₁₇H₂₁⁺ [M+H]⁺ : 225.1638, found: 225.1631.

(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)-4-fluorobenzene (2b)



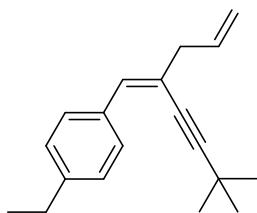
colorless liquid (73%, 35 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.81 (dd, *J* = 8.5, 5.7 Hz, 2H), 6.98 (dd apparent t, *J* = 8.6 Hz, 2H), 6.41 (s, 1H), 5.93 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.15-5.08 (m, 2H), 3.00 (d, *J* = 6.8 Hz, 2H), 1.30 (s, 9H); **¹³C NMR** (125 MHz, CDCl₃) δ 160.8 (d, *J* = 247.3 Hz), 134.5, 132.07 (d, *J* = 3.1 Hz), 130.5, 128.7 (d, *J* = 7.8 Hz), 119.7, 115.3, 113.7 (d, *J* = 21.7 Hz), 104.8, 77.8, 42.7, 29.7, 28.6. **HRMS** (ESI) m/z Calculated for C₁₇H₂₀F⁺ [M+H]⁺ : 243.1544, found: 243.1539.

(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)-4-bromobenzene (2c)



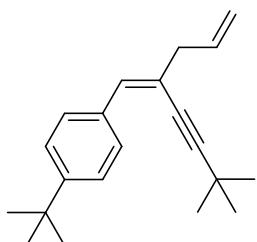
colorless liquid (76%, 46 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.70 (d, *J* = 8.46 Hz, 2H), 7.42 (d, *J* = 8.59 Hz, 2H), 6.38 (s, 1H), 5.92 (ddt, *J* = 17.2, 10.1, 6.7 Hz, 1H), 5.15-5.08 (m, 2H), 3.01 (d, *J* = 6.8, 2H), 1.30 (s, 9H); **¹³C NMR** (125 MHz, CDCl₃) δ 135.8, 135.3, 131.5, 131.0, 129.7, 122.0, 121.0, 116.5, 106.7, 78.9, 43.8, 30.7, 28.4. **HRMS** (ESI) m/z Calculated for C₁₇H₂₀Br⁺ [M+H]⁺ : 303.0743, found: 303.0737.

(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)-4-ethylbenzene (2d)



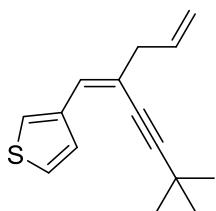
colorless liquid (87%, 44 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.43 (s, 1H), 5.94 (ddt, *J* = 17.1, 10.0, 6.9 Hz, 1H), 5.13 (d, *J* = 16.9 Hz, 1H), 5.08 (d, *J* = 10.1 Hz, 1H), 3.01 (d, *J* = 5.9, 2H), 2.63 (d, *J* = 7.6, 2H), 1.31 (s, 9H), 1.23(t, *J* = 7.5, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 143.6, 135.8, 134.4, 132.8, 128.2, 127.4, 119.9, 116.1, 105.6, 79.3, 43.9, 30.8, 28.6, 28.4, 15.48. **HRMS** (ESI) m/z Calculated for C₁₉H₂₅⁺ [M+H]⁺ : 253.1951, found: 253.1944.

(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)-4-tert-butylbenzene (2e)



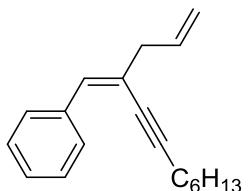
colorless liquid (84%, 47 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.42 (s, 1H), 5.93 (ddt, *J* = 17.2, 10.1, 6.8 Hz, 1H), 5.14-5.06(m, 2H), 3.00 (d, *J* = 6.7, 2H), 1.31 (s, 18H); **¹³C NMR** (125 MHz, CDCl₃) δ 150.5, 135.8, 134.1, 132.6, 127.9, 124.8, 120.0, 116.1, 105.7, 79.3, 43.9, 34.6, 31.3, 30.9, 28.4. **HRMS** (ESI) m/z Calculated for C₂₁H₂₉⁺ [M+H]⁺ : 281.2264, found: 281.2255.

(Z)-3-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)thiophene (2f)



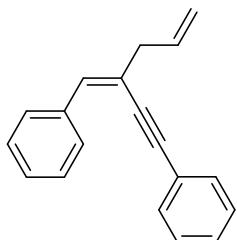
colorless liquid (83%, 38 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.70 (s, 1H), 7.57 (d, *J* = 4.9, 1H), 7.24-7.23 (m, 1H), 6.49 (s, 1H), 5.92 (ddt, *J* = 17.2, 10.1, 6.8 Hz, 1H), 5.13 (d, *J* = 17.1 Hz, 1H), 5.08 (d, *J* = 9.8 Hz, 1H), 2.99 (d, *J* = 6.7 Hz, 2H), 1.32 (s, 1H); **¹³C NMR** (125 MHz, CDCl₃) δ 138.8, 135.6, 127.8, 126.9, 124.4, 123.1, 119.9, 116.2, 106.0, 79.5, 43.3, 30.8, 28.4. **HRMS** (ESI) m/z Calculated for C₁₅H₁₉S⁺ [M+H]⁺ : 231.1202, found: 231.1194.

(Z)-(2-allyldec-1-en-3-ynyl)benzene (2g)



colorless liquid (47%, 25 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.32-7.29 (m, 2H), 7.24-7.21 (m, 1H), 6.47 (s, 1H), 5.95 (ddt, *J* = 17.0, 10.1, 6.7 Hz, 1H), 5.15 (d, *J* = 17.0 Hz, 1H), 5.10 (d, *J* = 10.1 Hz, 1H), 3.03 (d, *J* = 6.6 Hz, 2H), 2.43 (t, *J* = 6.9 Hz, 2H), 1.62-1.55 (m, 2H), 1.47-1.42 (m, 2H), 1.34-1.28 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 136.8, 135.7, 133.1, 128.1, 128.0, 127.4, 121.0, 116.3, 97.9, 80.5, 43.9, 31.4, 28.6, 28.6, 22.5, 19.8, 14.0. **HRMS** (ESI) m/z Calculated for C₁₉H₂₅⁺ [M+H]⁺ : 253.1951, found: 253.1943.

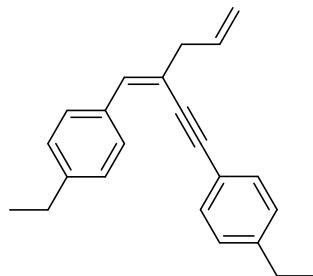
(Z)-(2-allylbut-1-en-3-yne-1,4-diyl)dibenzene (2h)



colorless solid (81%, 40 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.48-7.46 (m, 2H), 7.37-7.32 (m, 5H), 7.28-7.24 (m, 1H), 6.61 (s, 1H), 6.01 (ddt, *J* = 17.1, 10.1, 6.7 Hz, 1H), 5.22 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.15 (dd, *J* = 10.1, 1.1 Hz, 1H), 3.15 (dd, *J* = 6.8, 1.1 Hz, 2H); **¹³C NMR**

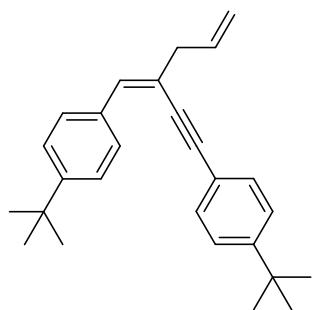
NMR (125 MHz, CDCl₃) δ 136.7, 135.4, 134.8, 131.5, 128.4, 128.3, 128.32, 128.2, 127.8, 123.5, 120.2, 116.7, 96.02, 89.5, 43.3. **HRMS** (ESI) m/z Calculated for C₁₉H₁₇⁺ [M+H]⁺ : 245.1325, found: 245.1318.

(Z)-4,4'-(2-allylbut-1-en-3-yne-1,4-diyl)bis(ethylbenzene) (2i)



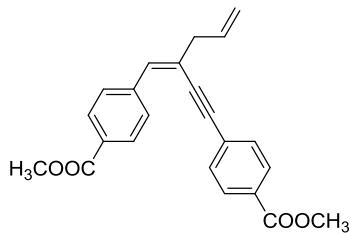
colorless solid (81%, 49 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.20-7.17 (m, 4H), 6.57 (s, 1H), 6.02 (ddt, *J* = 17.2, 10.2, 6.6 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.14 (d, *J* = 9.9 Hz, 1H), 3.14 (d, *J* = 6.6 Hz, 2H), 2.69-2.64 (m, 4H), 1.26-1.23 (m, 6H); **¹³C NMR** (125 MHz, CDCl₃) δ 143.6, 143.0, 134.6, 133.3, 133.2, 130.4, 127.4, 126.9, 126.6, 119.7, 118.2, 115.4, 95.1, 88.1, 42.4, 27.8, 27.6, 14.4, 14.3. **HRMS** (ESI) m/z Calculated for C₂₃H₂₅⁺ [M+H]⁺ : 301.1951, found: 301.1944.

(Z)-4,4'-(2-allylbut-1-en-3-yne-1,4-diyl)bis(tert-butylbenzene) (2j)



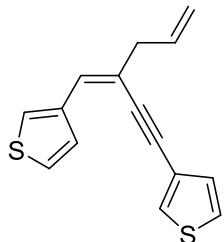
colorless solid (79%, 56 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.39-7.37 (m, 4H), 6.57 (s, 1H), 6.01 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 5.13 (d, *J* = 10.1 Hz, 1H), 3.13 (d, *J* = 6.6 Hz, 2H), 1.33 (s, 18H); **¹³C NMR** (125 MHz, CDCl₃) δ 151.5, 150.8, 135.7, 134.2, 134.0, 131.2, 128.2, 125.3, 125.1, 120.6, 119.4, 116.4, 96.2, 89.2, 43.5, 34.8, 34.6, 31.2, 31.1. **HRMS** (ESI) m/z Calculated for C₂₇H₃₃⁺ [M+H]⁺ : 357.2577, found: 357.2571.

dimethyl 4,4'-(2-allylbut-1-en-3-yne-1,4-diyil)(Z)-dibenzoate (2k)



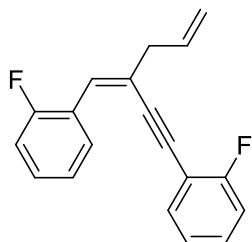
colorless solid (68%, 48 mg); **¹H NMR** (500 MHz, CDCl₃) δ 8.04-8.01 (m, 4H), 7.89 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 6.69 (s, 1H), 5.9 (ddt, J = 17.0, 10.1, 6.8 Hz, 1H), 5.26-5.22 (m, 1H), 5.19-5.17 (m, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.18 (dd, J = 6.6, 1.0 Hz, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 165.7, 165.4, 139.8, 133.7, 133.7, 131.4, 130.4, 128.58, 128.52, 128.2, 127.3, 126.6, 121.6, 116.3, 95.0, 90.9, 51.2, 51.0, 42.2. **HRMS** (ESI) m/z Calculated for C₂₃H₂₁O₄⁺ [M+H]⁺ : 361.1434, found: 361.1427.

(Z)-3,3'-(2-allylbut-1-en-3-yne-1,4-diyil) dithiophene (2l)



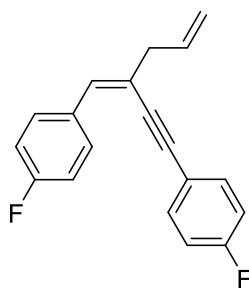
colorless solid (80%, 51 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.74 (s, 1H), 7.63 (d, J = 4.8 Hz, 1H), 7.49 (s, 1H), 7.32-7.31 (m, 1H), 7.29-7.28 (m, 1H), 7.17 (d, J = 4.7 Hz, 1H), 6.64 (s, 1H), 5.98 (ddt, J = 17.1, 9.9, 6.9 Hz, 1H), 5.21 (d, J = 17.1 Hz, 1H), 5.14 (d, J = 10.1 Hz, 1H), 3.11 (d, J = 6.6 Hz, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 138.6, 135.4, 129.6, 128.8, 128.5, 127.8, 125.5, 124.9, 124.0, 122.4, 118.9, 116.7, 91.4, 89.4, 42.6. **HRMS** (ESI) m/z Calculated for C₁₅H₁₃S₂⁺ [M+H]⁺ : 257.0453, found: 257.0447.

(Z)-2,2'-(2-allylbut-1-en-3-yne-1,4-diyil)bis(fluorobenzene) (2m)



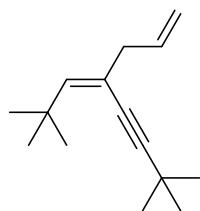
colorless solid (71%, 40 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.45-7.33 (m, 1H), 7.30-7.15 (m, 3H), 7.11-6.94 (m, 4H), 6.80 (s, 1H), 5.98-5.90 (m, 1H), 5.18-5.08 (m, 2H), 3.12 (d, *J* = 6.9 Hz, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 162.7 (d, *J* = 254.7 Hz), 161.2 (d, *J* = 251.4 Hz), 134.0, 132.3, 130.0 (d, *J* = 7.5 Hz), 129.1 (d, *J* = 8.0 Hz), 128.3 (d, *J* = 8.5 Hz), 127.7, 125.5 (d, *J* = 6.6 Hz), 123.3 (d, *J* = 11.3 Hz), 123.0 (d, *J* = 3.6 Hz), 122.9 (d, *J* = 3.6 Hz), 122.6 (d, *J* = 3.6 Hz), 116.0, 114.5 (d, *J* = 20.3 Hz), 114.1 (d, *J* = 22.1 Hz), 93.0, 88.8, 42.3. **HRMS** (ESI) m/z Calculated for C₁₉H₁₅F₂⁺ [M+H]⁺ : 281.1136, found: 281.1131.

(Z)-4,4'-(2-allylbut-1-en-3-yne-1,4-diyI)bis(fluorobenzene) (2n)



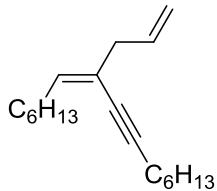
colorless solid (75%, 42 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.82 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.43 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.06-7.02 (m, 4H), 6.58 (s, 1H), 5.99 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1H), 5.23-5.15 (m, 2H), 3.13 (d, *J* = 6.6 Hz, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 162.4 (d, *J* = 250.1 Hz), 162.2 (d, *J* = 250.1 Hz), 135.2, 133.6, 133.3 (d, *J* = 8.3 Hz), 132.8 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 7.8 Hz), 119.8, 119.4 (d, *J* = 3.5 Hz), 116.8, 115.7 (d, *J* = 22.2 Hz), 115.1 (d, *J* = 21.3 Hz), 94.8, 88.9, 43.1. **HRMS** (ESI) m/z Calculated for C₁₉H₁₅F₂⁺ [M+H]⁺ : 281.1136, found: 281.1132.

(Z)-4-(2,2-dimethylpropylidene)-7,7-dimethyloct-1-en-5-yne (2o)



colorless solid (78%, 32 mg); **¹H NMR** (500 MHz, CDCl₃) δ 5.85 (ddt, *J* = 17.1, 10.0, 6.8 Hz, 1H), 5.55 (s, 1H), 5.06-4.99 (m, 2H), 5.85 (dd, *J* = 6.8, 1.1Hz, 2H), 1.24 (s, 9H), 1.17 (s, 9H); **¹³C NMR** (125 MHz, CDCl₃) δ 144.6, 135.4, 118.1, 114.4, 103.6, 77.1, 32.0, 31.8, 29.7, 29.5, 28.9. **HRMS** (ESI) m/z Calculated for C₁₅H₂₅⁺ [M+H]⁺ : 205.1951, found: 205.1945.

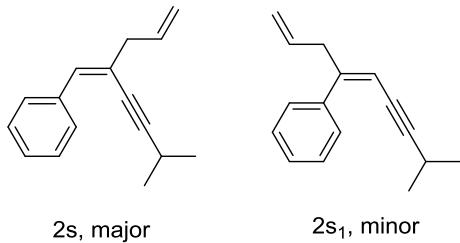
(Z)-8-allylhexadec-7-en-9-yne (2p)



colorless liquid (83%, 52 mg); **¹H NMR** (500 MHz, CDCl₃) δ 5.86 (ddt, *J* = 17.1, 10.1, 6.7 Hz, 1H), 5.60 (t, *J* = 7.3 Hz, 1H), 5.08-5.01 (m, 2H), 2.82 (d, *J* = 6.6 Hz, 2H), 2.34 (t, *J* = 6.9 Hz, 2H), 2.25-2.21 (m, 2H), 1.54-1.49 (m, 2H), 1.45-1.25 (m, 14H), 0.90-0.87 (m, 6H); **¹³C NMR** (125 MHz, CDCl₃) δ 136.8, 136.2, 121.4, 115.7, 94.4, 79.1, 41.7, 31.7, 31.3, 30.4, 29.1, 28.9, 28.92, 28.5, 22.6, 22.5, 19.5, 14.1, 14.0. **HRMS** (ESI) m/z Calculated for C₁₉H₃₃⁺ [M+H]⁺ : 261.2577, found: 261.2569.

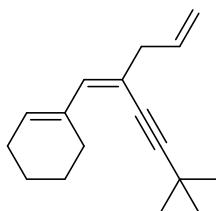
(Z)-(2-allyl-5-methylhex-1-en-3-yn-1-yl)benzene (2s)

(Z)-(8-methylnona-1,4-dien-6-yn-4-yl)benzene (2s₁) (2s and 2s₁ cannot be isolated)



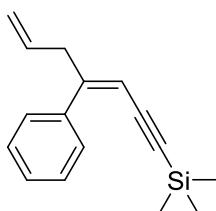
colorless liquid (72%, 32 mg); **¹H NMR** (500 MHz, CDCl₃) **2s**: δ 7.83-7.81 (m, 2H), 7.47-7.45 (m, 2H), 7.24-7.20 (m, 1H), 6.46 (s, 1H), 5.94 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.17-5.03 (m, 2H), 3.02 (dd, *J* = 6.8, 1.1 Hz, 2H), 2.83-2.75 (m, 1H), 1.23 (d, *J* = 6.9, 6H); **2s₁**: δ 7.61-7.59 (m, 2H), δ 7.29-7.26 (m, 3H), 5.80 (ddt, *J* = 17.1, 10.0, 6.8 Hz, 1H), 5.60 (s, 1H), 5.17-5.03 (m, 2H), 3.22-3.21 (m, 2H), 2.63-2.57 (m, 1H), 1.10 (d, *J* = 6.8, 6H); **¹³C NMR** (125 MHz, CDCl₃) **2s+2s₁**: δ 136.8, 135.6, 133.0, 132.4, 128.7, 128.3, 128.1, 127.9, 127.6, 127.5, 127.4, 122.1, 120.9, 116.9, 116.3, 107.3, 103.0, 89.7, 79.7, 43.8, 41.4, 22.8, 22.4, 21.5, 21.3.

(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3-yn-1-yl)cyclohex-1-ene (2t)



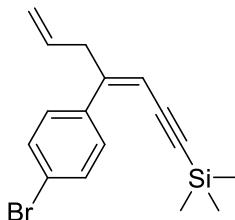
colorless liquid (36%, 17 mg); **¹H NMR** (500 MHz, CDCl₃) δ 5.90-5.89 (m, 1H), 5.76 (ddt, J = 17.2, 10.2, 6.6 Hz, 1H), 5.28 (s, 1H), 5.05-5.00 (m, 2H), 2.91 (dd, J = 6.7, 1.2 Hz, 2H), 2.13-2.08 (m, 4H), 1.66-1.63 (m, 2H), 1.61-1.56 (m, 2H), 1.22 (s, 9H); **¹³C NMR** (425 MHz, CDCl₃) δ 137.8, 136.0, 129.9, 126.6, 116.2, 104.7, 91.1, 77.9, 40.5, 30.9, 30.5, 27.5, 25.4, 22.9, 22.1. **HRMS** (ESI) m/z Calculated for C₁₇H₂₅⁺ [M+H]⁺ : 229.1951, found: 229.1958.

(Z)-trimethyl(4-phenylhepta-3,6-dien-1-ynyl)silane (3a)



colorless liquid (81%, 41 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.62 (d, J = 7.6 Hz, 2H), 7.35-7.28 (m, 3H), 5.81 (ddt, J = 17.1, 10.2, 6.7 Hz, 1H), 5.63 (s, 1H), 5.11-5.05 (m, 2H), 3.23 (dd, J = 6.6, 1.2 Hz, 2H), 0.11 (s, 9H); **¹³C NMR** (125 MHz, CDCl₃) δ 152.1, 139.2, 135.4, 128.2, 127.9, 117.5, 107.1, 104.1, 98.07, 41.7, -0.003. **HRMS** (ESI) m/z Calculated for C₁₆H₂₁BrSi⁺ [M+H]⁺ : 241.1407, found: 241.1401.

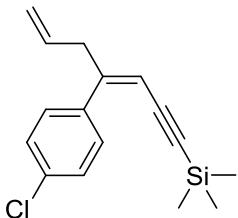
(Z)-(4-(4-bromophenyl)hepta-3,6-dien-1-ynyl)trimethylsilane (3b)



colorless solid (82%, 52 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.51 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 5.80-5.72 (m, 1H), 5.65 (s, 1H), 5.09-5.06 (m, 2H), 3.19 (d, J = 6.4 Hz, 2H), 0.12 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 149.2, 136.8, 133.8, 129.8, 128.6, 120.9, 116.5, 106.5, 102.4,

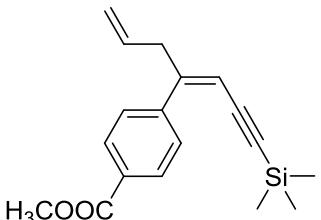
97.7, 40.3, -0.003. **HRMS** (ESI) m/z Calculated for $C_{16}H_{20}BrSi^+$ $[M+H]^+$: 319.0512, found: 319.0507.

(Z)-(4-(4-chlorophenyl)hepta-3,6-dien-1-ynyl)trimethylsilane (3c)



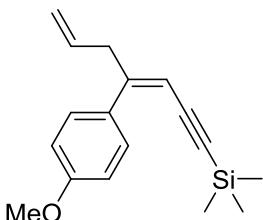
colorless solid (81%, 44 mg); **¹H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, $J = 8.8$ Hz, 2H), 7.30 (d, $J = 8.7$ Hz, 2H), 5.7 (ddt, $J = 17.1, 10.3, 6.6$ Hz, 1H), 5.65 (s, 1H), 5.10-5.06 (m, 2H), 3.23 (dd, $J = 6.4, 1.1$ Hz, 2H), 0.13 (s, 9H); **¹³C NMR** (100 MHz, $CDCl_3$) δ 150.5, 137.6, 135.1, 133.9, 129.6, 128.2, 117.8, 107.7, 103.7, 98.9, 41.6, -0.003. **HRMS** (ESI) m/z Calculated for $C_{16}H_{20}ClSi^+$ $[M+H]^+$: 275.1017, found: 275.1011.

(Z)-methyl 4-(1-(trimethylsilyl)hepta-3,6-dien-1-yn-4-yl)benzoate (3d)



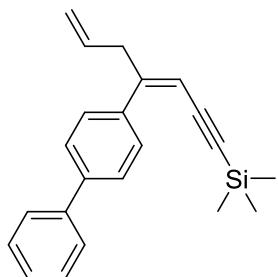
colorless solid (71%, 42 mg); **¹H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, $J = 8.3$ Hz, 2H), 7.67 (d, $J = 8.3$ Hz, 2H), 5.7 (ddt, $J = 17.3, 10.2, 6.5$ Hz, 1H), 5.71 (s, 1H), 5.10-5.06 (m, 2H), 3.92 (s, 3H), 3.23 (d, $J = 6.5$ Hz, 2H), 0.11 (s, 9H); **¹³C NMR** (100 MHz, $CDCl_3$) δ 167.1, 150.8, 143.9, 134.9, 129.3, 128.5, 128.3, 117.9, 108.7, 103.5, 99.4, 52.4, 41.6, -0.003. **HRMS** (ESI) m/z Calculated for $C_{18}H_{23}O_2Si^+$ $[M+H]^+$: 299.1462, found: 299.1458.

(Z)-(4-(4-methoxyphenyl)hepta-3,6-dien-1-ynyl)trimethylsilane (3e)



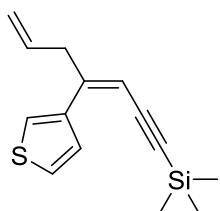
colorless liquid (62%, 33 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.64 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.80 (ddt, *J* = 17.2, 10.1, 6.6 Hz, 1H), 5.57 (s, 1H), 5.10-5.04 (m, 2H), 3.82 (s, 3H), 3.21 (d, *J* = 6.4 Hz, 2H), 0.14 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 159.5, 151.1, 135.6, 131.4, 129.5, 117.3, 113.2, 105.6, 104.5, 97.8, 55.4, 41.6, -0.003. **HRMS** (ESI) m/z Calculated for C₁₇H₂₃OSi⁺ [M+H]⁺ : 271.1518, found: 271.1514.

(Z)-(4-(biphenyl-4-yl)hepta-3,6-dien-1-ynyl)trimethylsilane (3f)



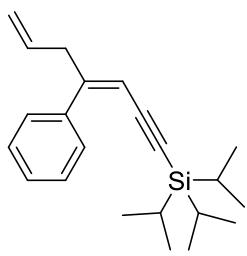
colorless solid (76%, 48 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.46-7.43 (m, 2H), 7.36-7.34 (m, 2H), 5.8 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.67 (s, 1H), 5.14-5.08 (m, 2H), 3.28 (dd, *J* = 6.5, 1.1 Hz, 2H), 0.14 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 151.2, 140.9, 138.0, 135.4, 128.9, 128.6, 127.5, 127.2, 126.8, 126.6, 117.6, 107.1, 104.2, 98.5, 41.6, -0.003. **HRMS** (ESI) m/z Calculated for C₂₂H₂₅Si⁺ [M+H]⁺ : 317.1720, found: 317.1714.

(Z)-trimethyl(4-(thiophen-3-yl)hepta-3,6-dien-1-ynyl)silane (3g)



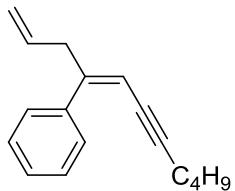
colorless liquid (80%, 39 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.81 (s, 1H), 7.72 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.27-7.25 (m, 1H), 5.8 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1H), 5.57 (s, 1H), 5.13-5.08 (m, 2H), 3.22 (dd, *J* = 6.6, 1.2 Hz, 2H), 0.20 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 144.9, 140.0, 135.6, 127.6, 124.8, 124.5, 117.5, 105.6, 104.8, 100.2, 41.6, -0.003. **HRMS** (ESI) m/z Calculated for C₁₄H₁₉SSi⁺ [M+H]⁺ : 247.0971, found: 247.0964.

(Z)-triisopropyl(4-phenylhepta-3,6-dien-1-ynyl)silane (3h)



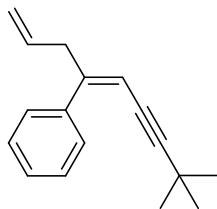
colorless liquid (81%, 52 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.60-7.58 (m, 2H), 7.32-7.29 (m, 2H), 7.26-7.25 (m, 1H), 7.27-7.25 (m, 1H), 5.7 (ddt, *J* = 17.2, 10.1, 6.8 Hz, 1H), 5.67 (s, 1H), 5.11-5.06 (m, 2H), 3.22 (dd, *J* = 6.8, 1.3 Hz, 2H), 0.99 (s, 21H); **¹³C NMR** (100 MHz, CDCl₃) δ 151.6, 139.3, 135.1, 127.9, 127.8, 127.7, 117.3, 107.2, 105.2, 94.1, 41.6, 18.5, 11.2. **HRMS** (ESI) m/z Calculated for C₂₂H₃₃Si⁺ [M+H]⁺ : 325.2346, found: 325.2341.

(Z)-undeca-1,4-dien-6-yn-4-ylbenzene (3i)



colorless liquid (42%, 30 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.47 (d, *J* = 6.5 Hz, 2H), 7.40 (d, *J* = 6.4 Hz, 2H), 7.32-7.26 (m, 1H), 5.79 (ddt, *J* = 17.1, 10.0, 6.6 Hz, 1H), 5.51 (s, 1H), 5.11-5.08 (m, 2H), 2.87 (d, *J* = 6.93 Hz, 2H), 2.40 (t, *J* = 7.8 Hz, 2H), 1.51-1.43 (m, 2H), 1.41-1.34 (m, 2H), 0.94 (t, *J* = 6.6 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 154.9, 135.3, 132.5, 128.7, 128.3, 128.2, 127.6, 117.9, 105.6, 92.2, 40.5, 33.0, 21.9, 19.2, 13.5. **HRMS** (ESI) m/z Calculated for C₁₇H₂₁⁺ [M+H]⁺ : 225.1638, found: 225.1631.

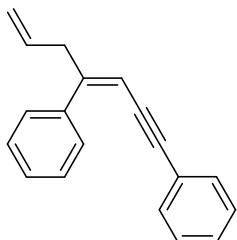
(Z)-(8,8-dimethylnona-1,4-dien-6-yn-4-yl)benzene (3j)



colorless liquid (62%, 38 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.33-7.30 (m, 2H), 7.27-7.25 (m, 1H), 5.8 (ddt, *J* = 17.2, 10.1, 6.6 Hz, 1H), 5.60 (s, 1H), 5.09-5.03 (m, 2H), 3.21 (dd, *J* = 6.6, 1.3 Hz, 2H), 1.16 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 148.5, 139.4, 135.6,

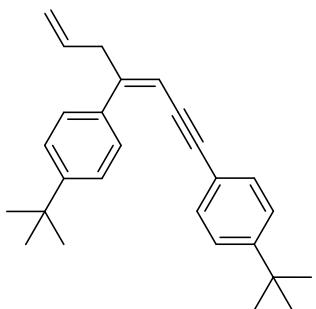
127.9, 127.6, 127.5, 116.9, 107.4, 101.5, 77.6, 41.4, 30.7, 28.1. **HRMS** (ESI) m/z Calculated for C₁₇H₂₁⁺ [M+H]⁺: 225.1638, found: 225.1632.

(Z)-hepta-3,6-dien-1-yne-1,4-diylbenzene (3k)



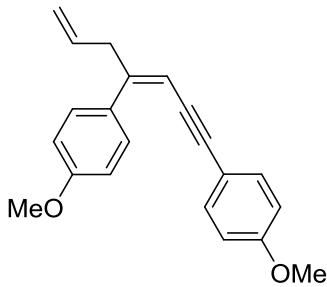
colorless solid (84%, 41 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.40-7.36 (m, 2H), 7.32-7.24 (m, 6H), 5.89-5.83 (m, 1H), 5.81 (s, 1H), 5.14-5.08 (m, 2H), 3.29 (d, *J* = 6.7 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 150.7, 139.4, 135.2, 131.3, 128.2, 128.0, 127.9, 127.87, 127.85, 123.7, 117.2, 106.9, 92.0, 88.4, 41.7. **HRMS** (ESI) m/z Calculated for C₁₉H₁₇⁺ [M+H]⁺: 245.1325, found: 245.1318.

(Z)-4,4'-(hepta-3,6-dien-1-yne-1,4-diyl)bis(tert-butylbenzene) (3l)



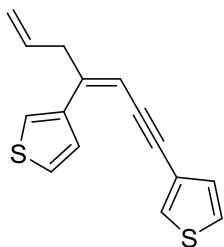
colorless solid (77%, 55 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.39-7.37 (m, 4H), 6.57 (s, 1H), 6.01 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 5.13 (d, *J* = 10.1 Hz, 1H), 3.13 (d, *J* = 6.6 Hz, 2H), 1.33 (s, 18H); **¹³C NMR** (100 MHz, CDCl₃) δ 151.5, 150.8, 135.7, 134.2, 134.0, 131.2, 128.2, 125.3, 125.1, 120.6, 119.4, 116.4, 96.2, 89.2, 43.5, 34.8, 34.6, 31.2, 31.1. **HRMS** (ESI) m/z Calculated for C₂₇H₃₃⁺ [M+H]⁺: 357.2577, found: 357.2571.

(Z)-4,4'-(hepta-3,6-dien-1-yne-1,4-diyl)bis(methoxybenzene) (3m)



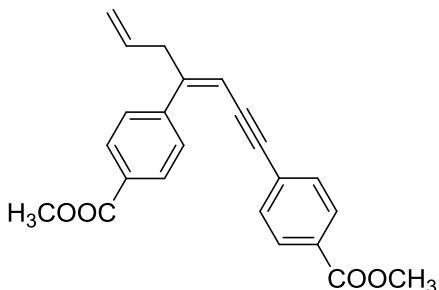
colorless solid (68%, 41 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.8 (d, *J* = 8.5 Hz, 2H), 6.7 (d, *J* = 8.7 Hz, 2H), 5.7 (ddt, *J* = 17.1, 10.1, 6.7 Hz, 1H), 5.68 (s, 1H), 5.06-4.99 (m, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 3.19 (d, *J* = 6.5 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 159.2, 158.2, 147.7, 134.6, 133.0, 131.6, 130.7, 128.3, 115.9, 113.1, 112.9, 112.1, 104.8, 86.4, 54.2, 40.6. **HRMS** (ESI) m/z Calculated for C₂₁H₂₁O₂⁺ [M+H]⁺ : 305.1536, found: 305.1531.

(Z)-3,3'-(hepta-3,6-dien-1,4-diyl)dithiophene (3n)



colorless solid (83%, 42 mg); **¹H NMR** (500 MHz, CDCl₃) δ 7.79 (d, *J* = 2.99 Hz, 1H), 7.72 (d, *J* = 5.16 Hz, 1H), 7.41 (d, *J* = 3.01 Hz, 1H), 7.30-7.289 (m, 1H), 7.282-7.26 (m, 1H), 7.10 (d, *J* = 5.13 Hz, 1H), 5.9 (ddt, *J* = 17.3, 10.3, 6.5 Hz, 1H), 5.75 (s, 1H), 5.17-5.10 (m, 2H), 3.28 (dd, *J* = 6.7, 1.1 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 143.5, 140.0, 135.6, 129.5, 128.0, 127.4, 125.3, 124.5, 124.2, 122.7, 117.2, 105.4, 89.2, 88.4, 41.5. **HRMS** (ESI) m/z Calculated for C₁₅H₁₃S₂⁺ [M+H]⁺ : 257.0543, found: 257.0536.

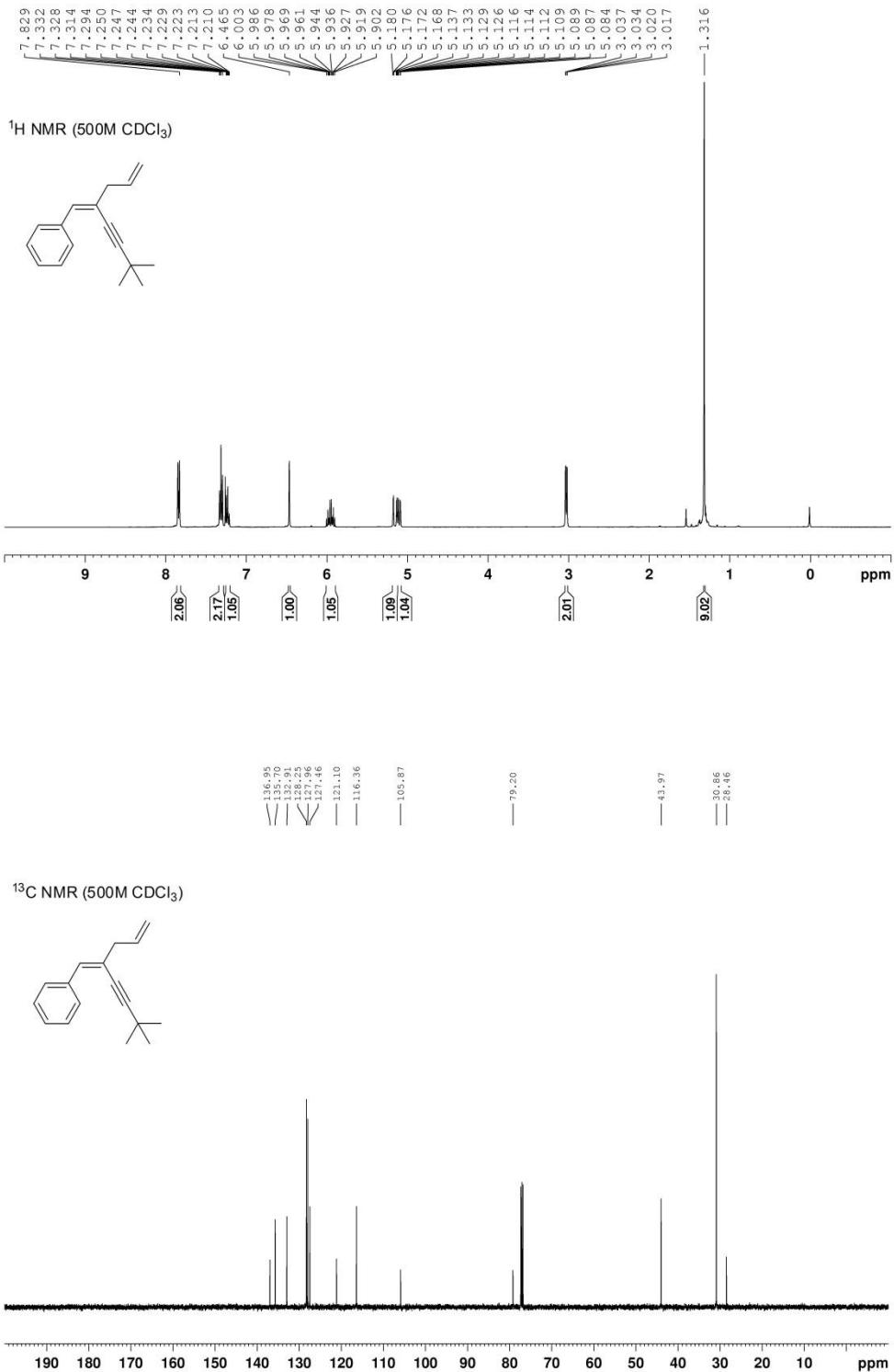
(Z)-dimethyl 4,4'-(hepta-3,6-dien-1,4-diyl)dibenzoate (3o)



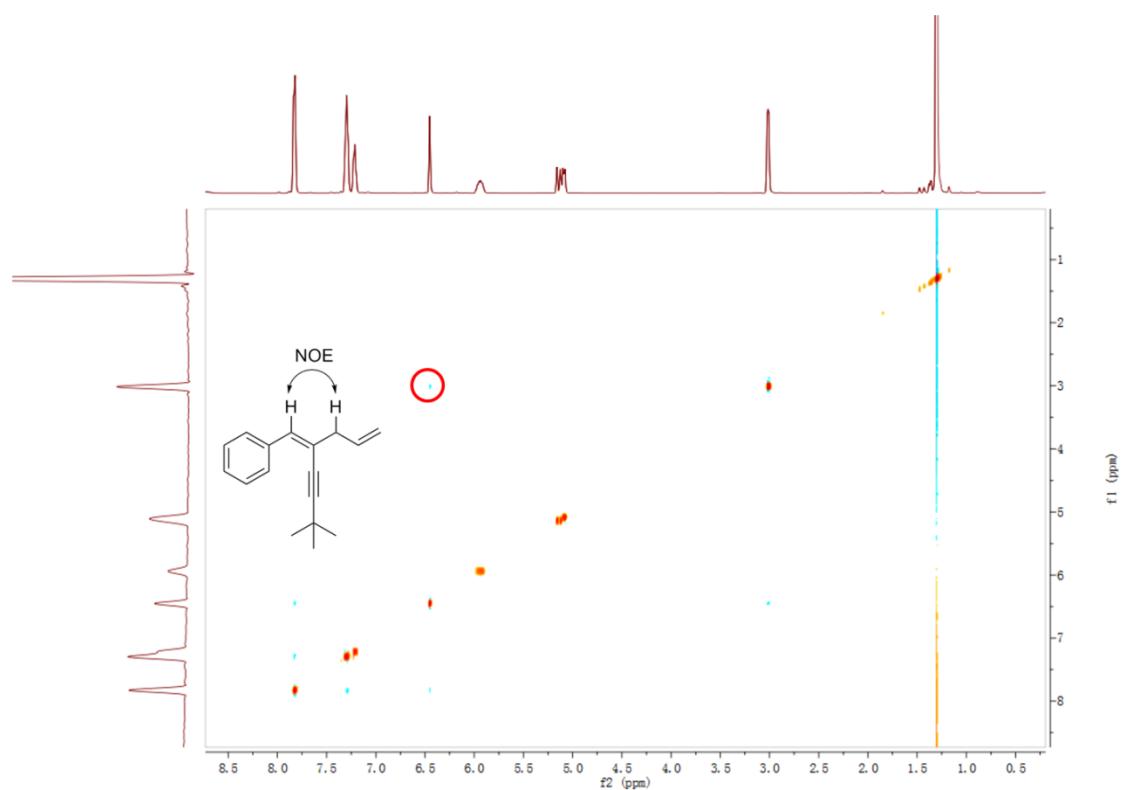
colorless solid (74%, 53 mg); **¹H NMR** (500 MHz, CDCl₃) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.91 (s, 1H), 5.8 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1H), 5.15-5.11 (m, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 3.31 (d, *J* = 6.7 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 165.8, 165.5, 150.0, 142.9, 133.5, 130.4, 130.1, 128.7, 128.4, 128.2, 127.3, 127.0, 124.9, 116.8, 107.0, 89.7, 51.18, 51.14, 40.5. **HRMS** (ESI) m/z Calculated for C₂₃H₂₁O₄⁺ [M+H]⁺: 361.1434, found: 361.1428.

S5. NMR spectra

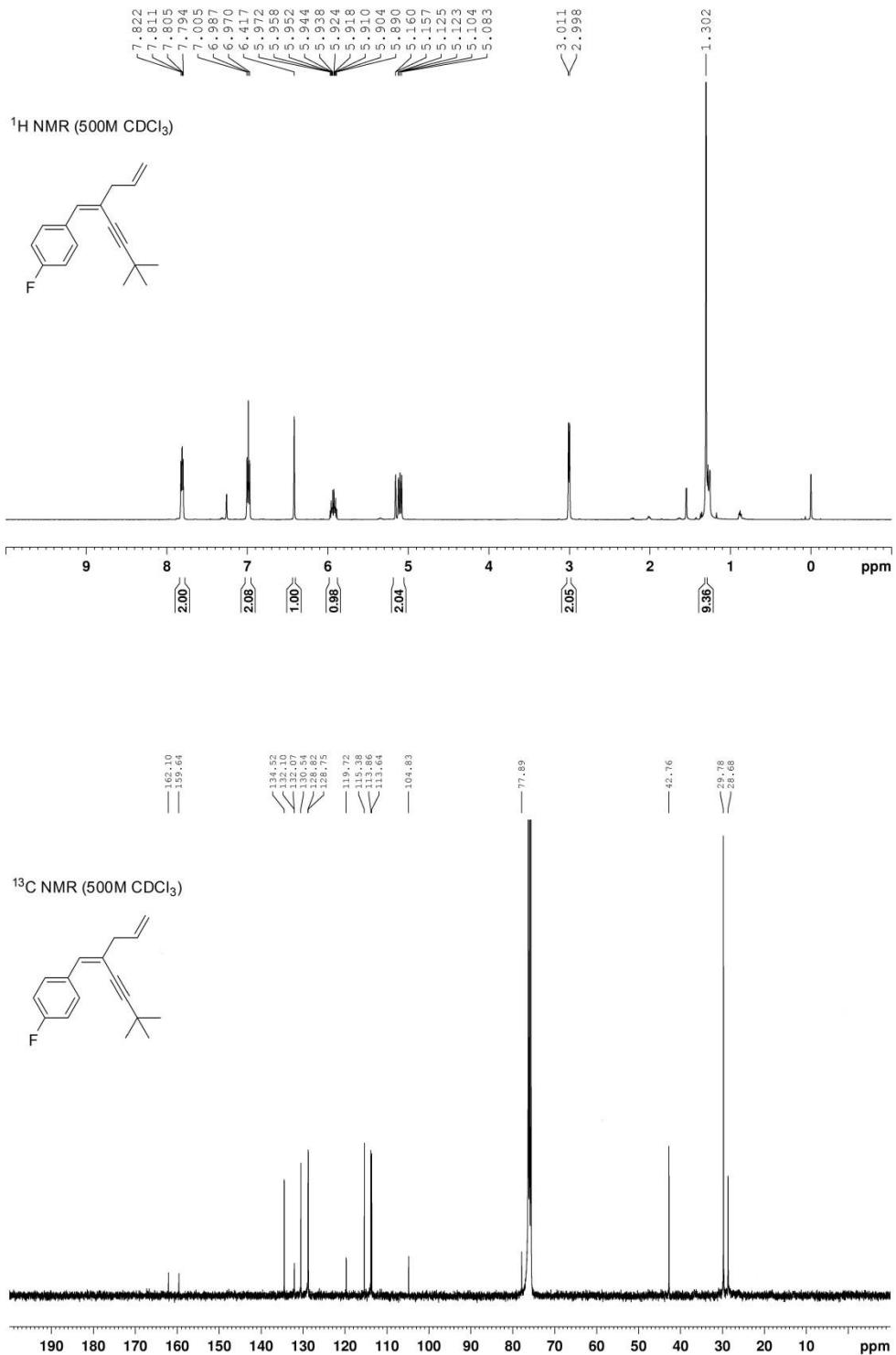
(Z)-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)benzene (2a)



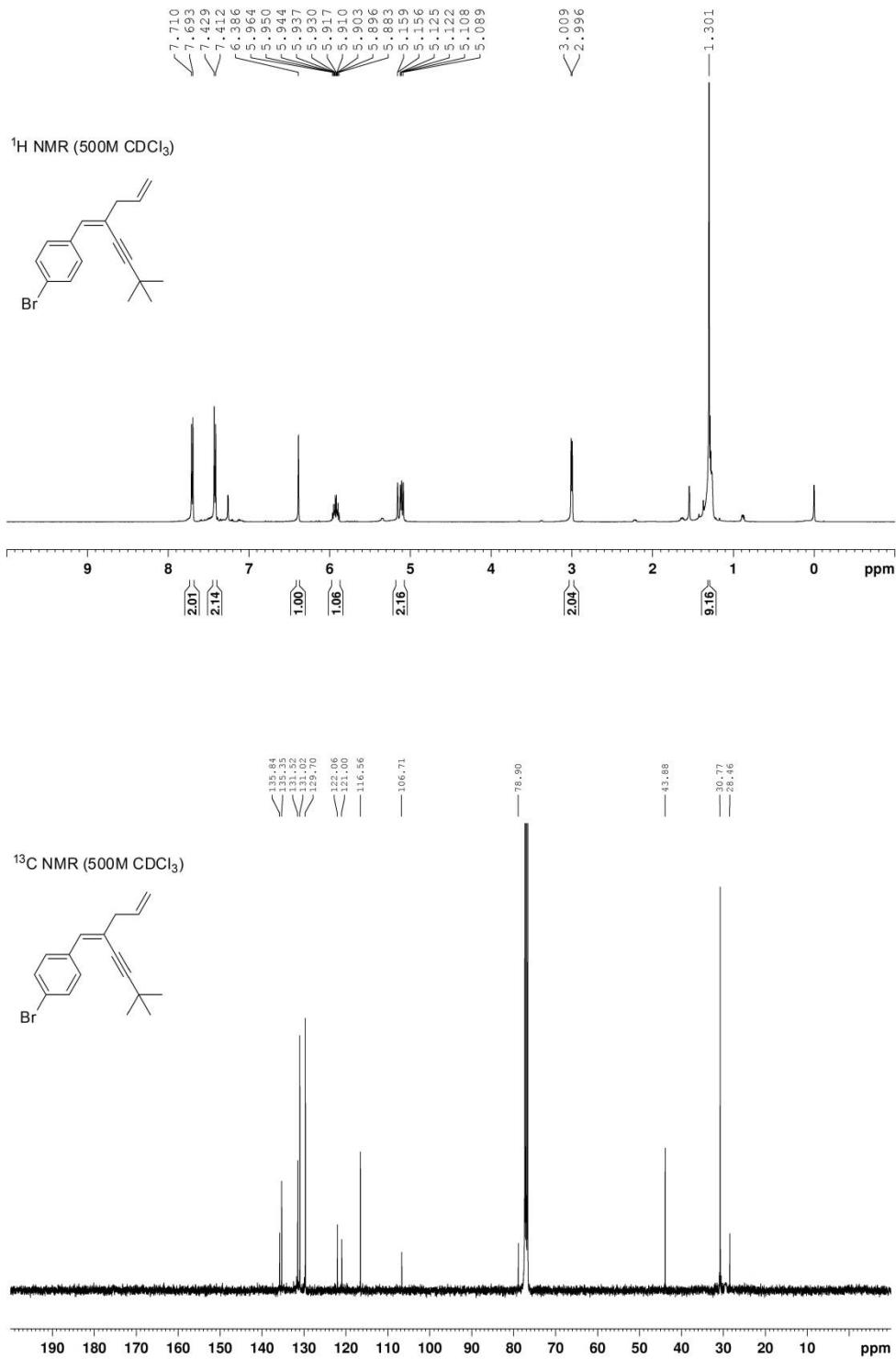
(Z)-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)benzene (NOE of 2a)



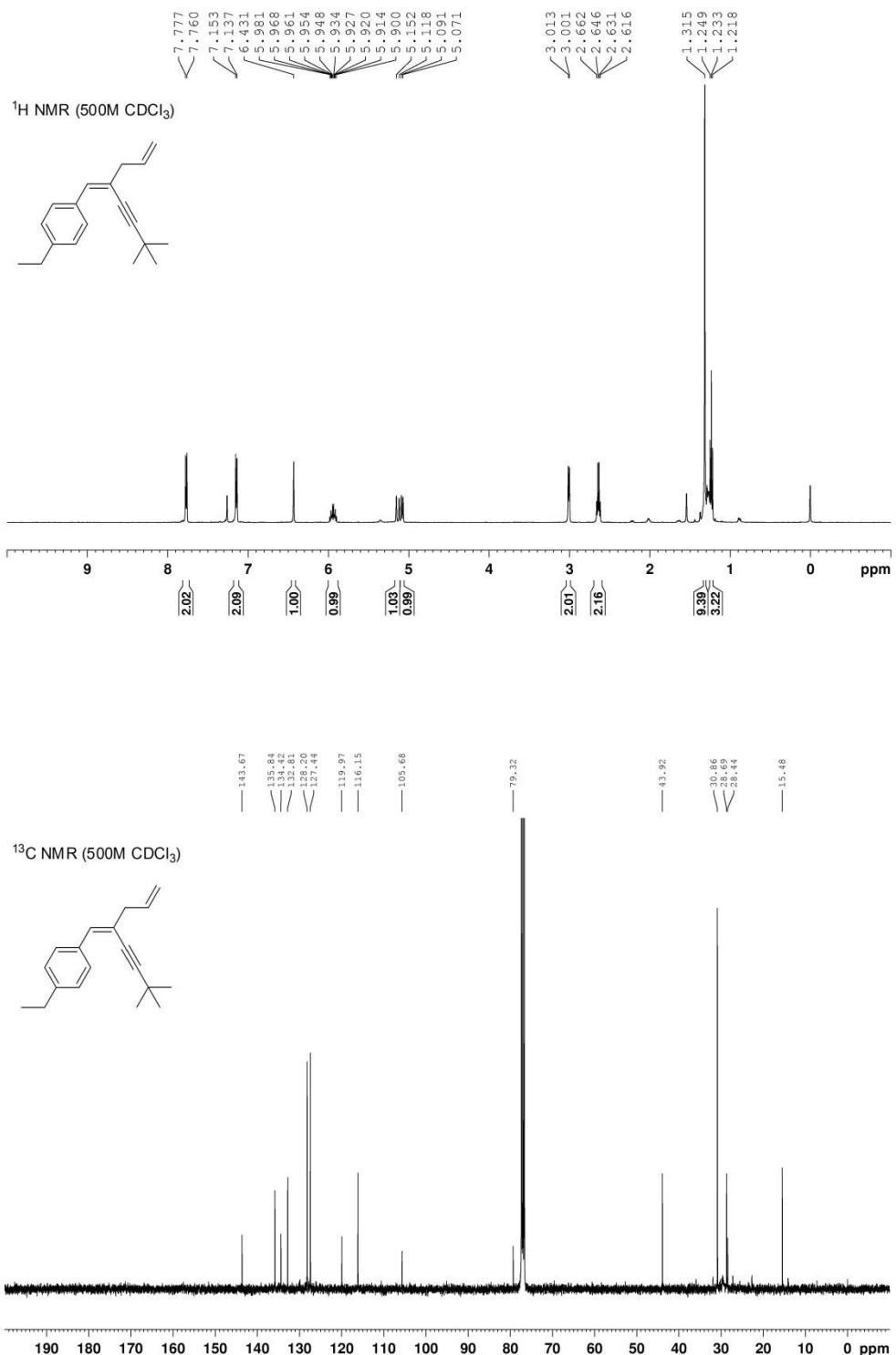
(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)-4-fluorobenzene (2b)



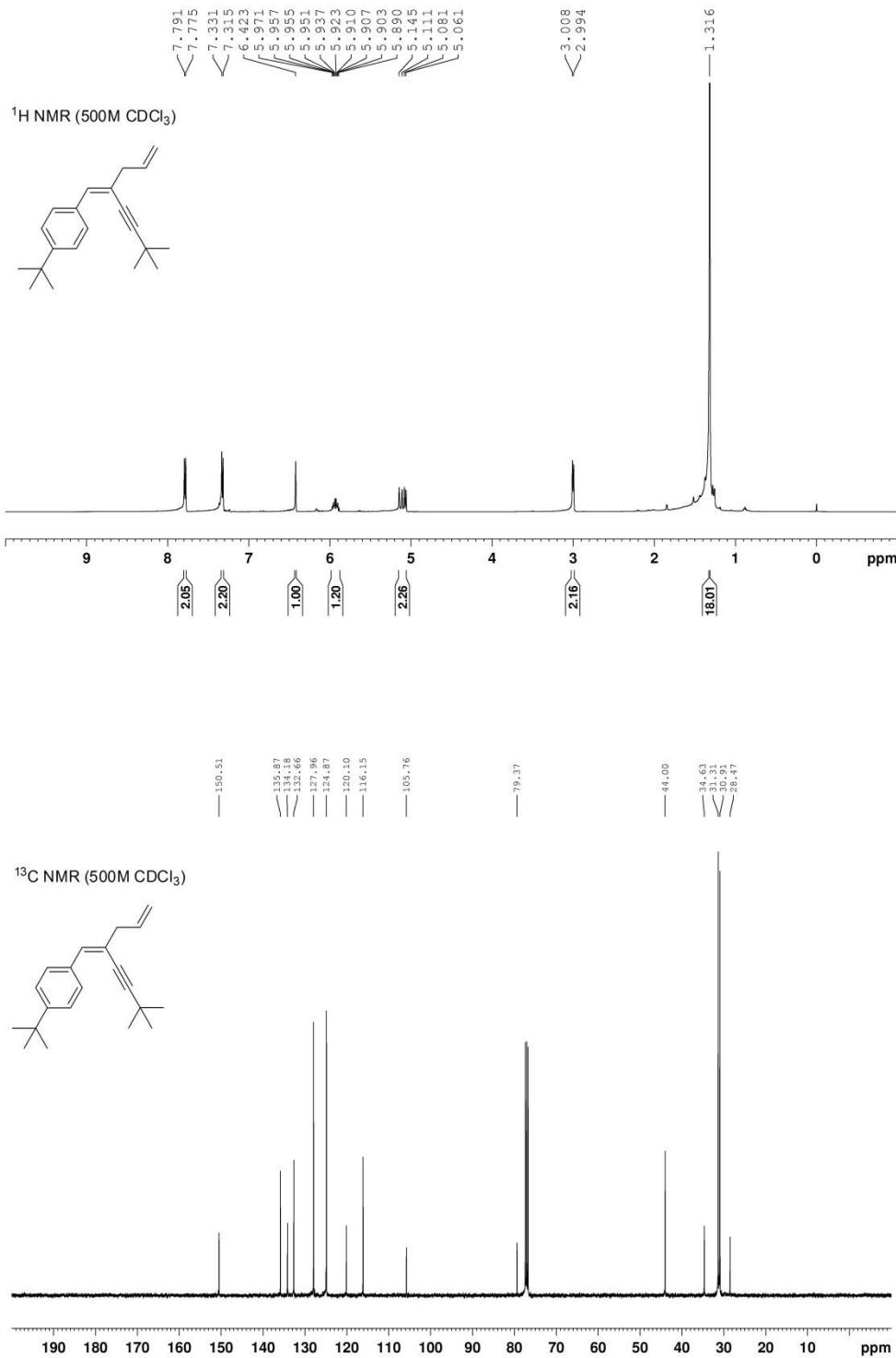
(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)-4-bromobenzene (2c)



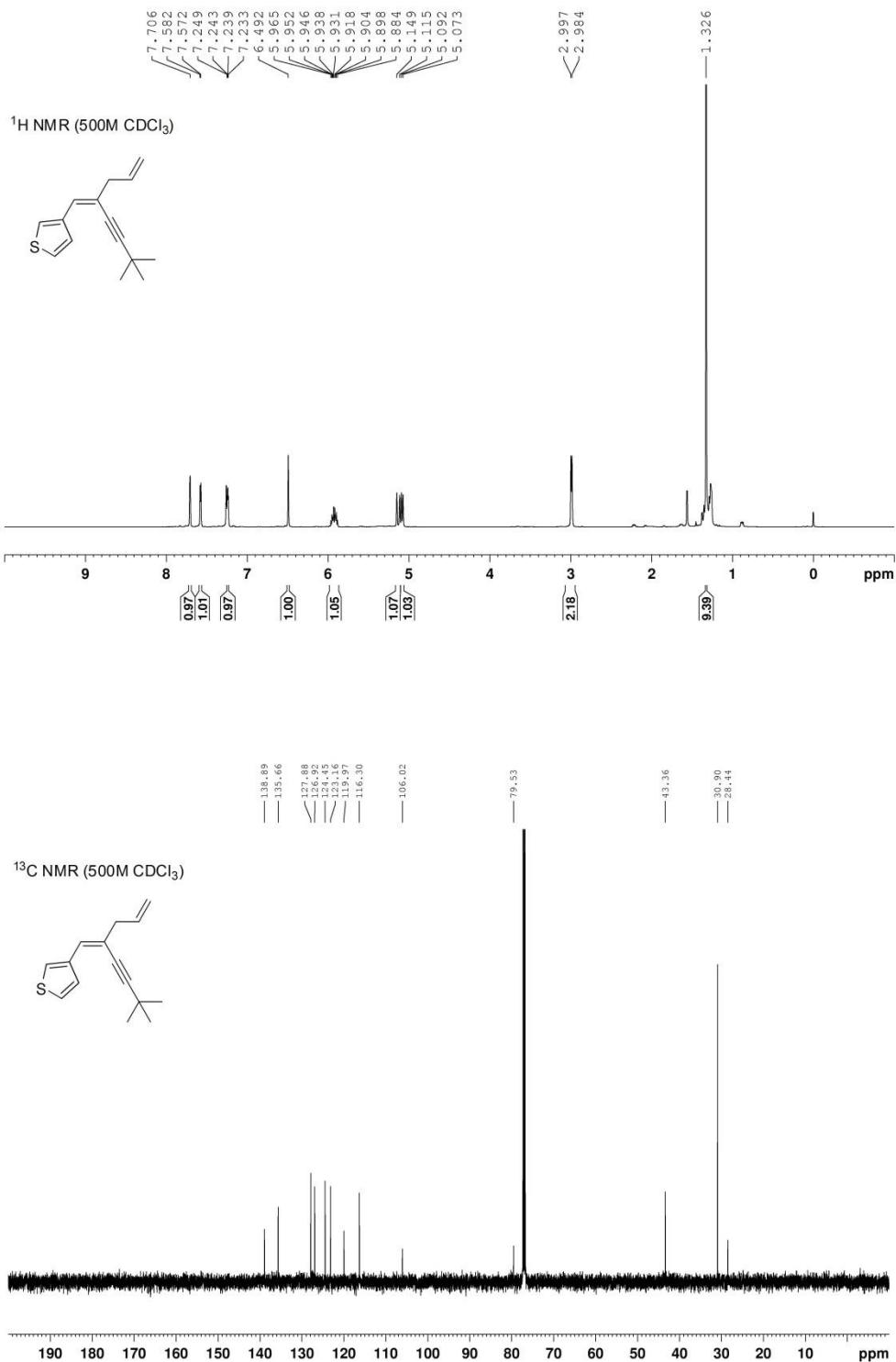
(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3ynyl)-4-ethylbenzene (2d)



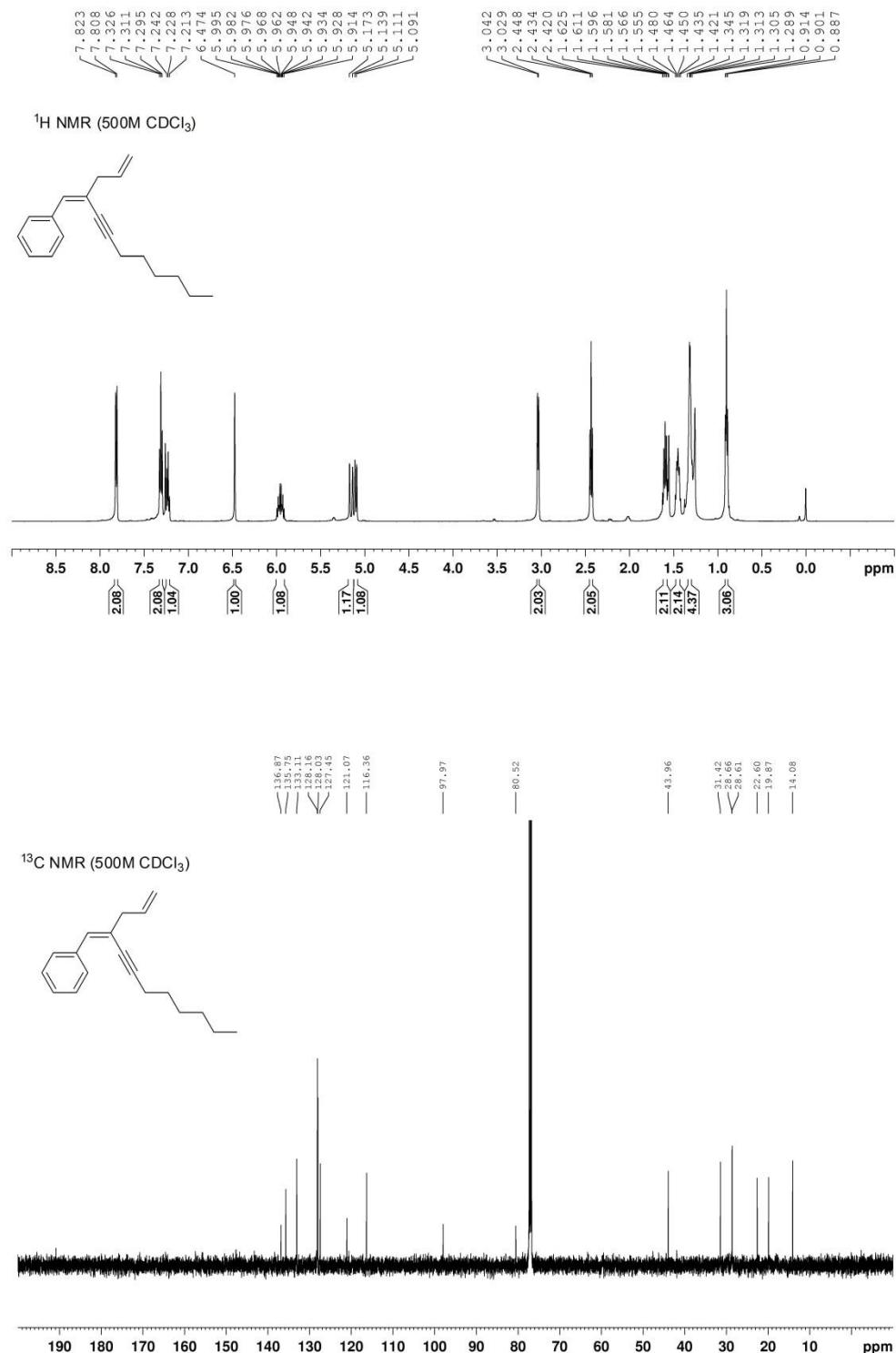
(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3ynyl)-4-tert-butylbenzene (2e)



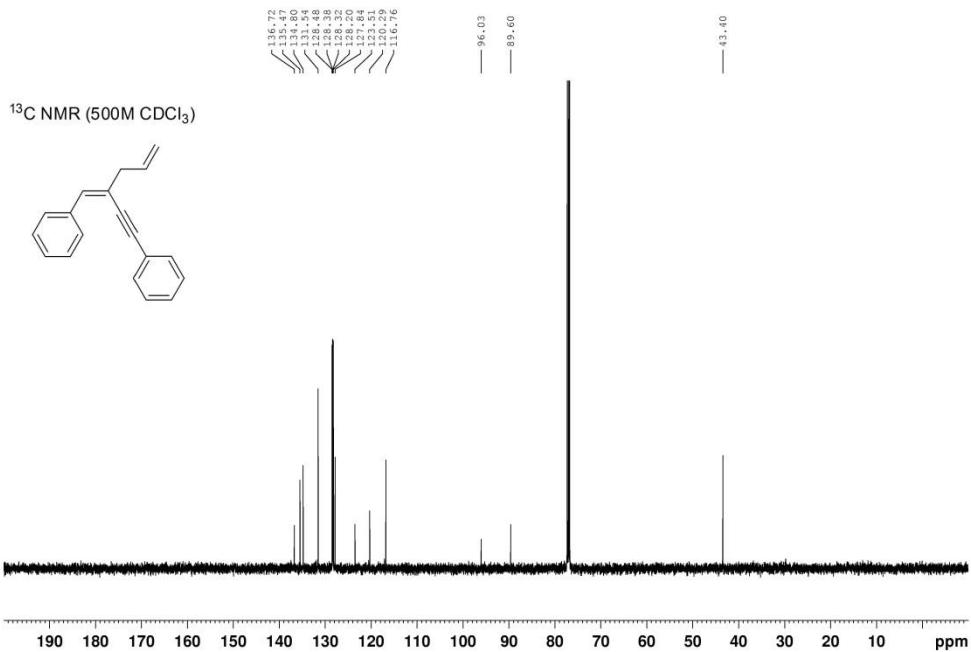
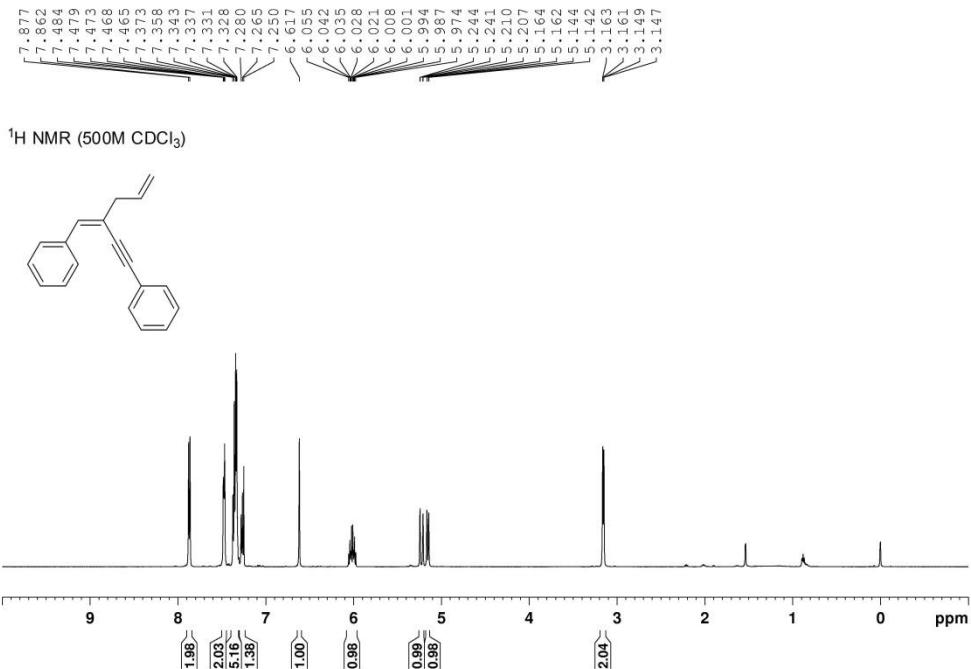
(Z)-3-(2-allyl-5,5-dimethylhex-1-en-3-ynyl)thiophene (2f)



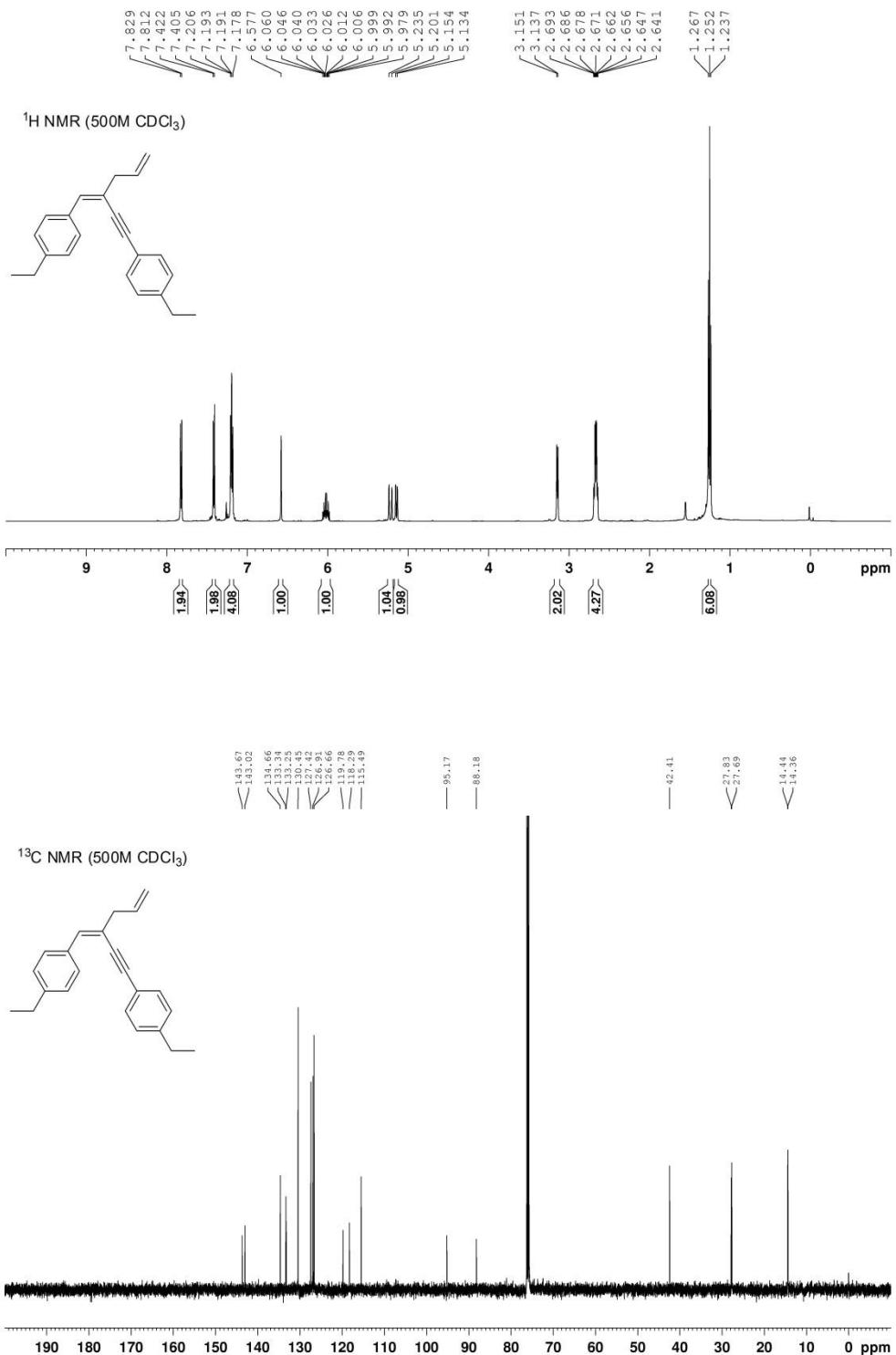
(Z)-(2-allyldec-1-en-3-yynyl)benzene (2g)



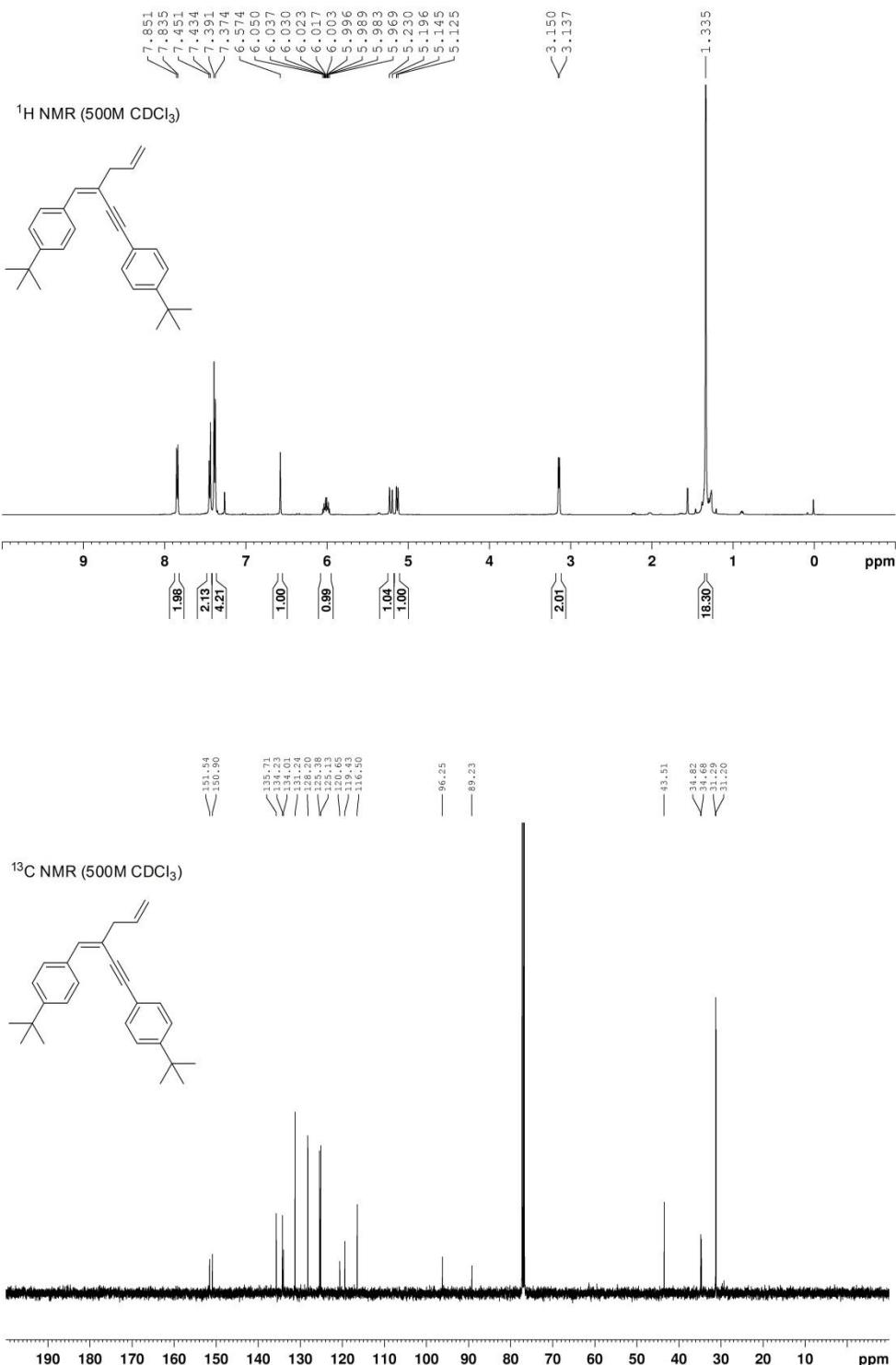
(Z)-(2-allylbut-1-en-3-yne-1,4-diyl)dibenzene (2h)



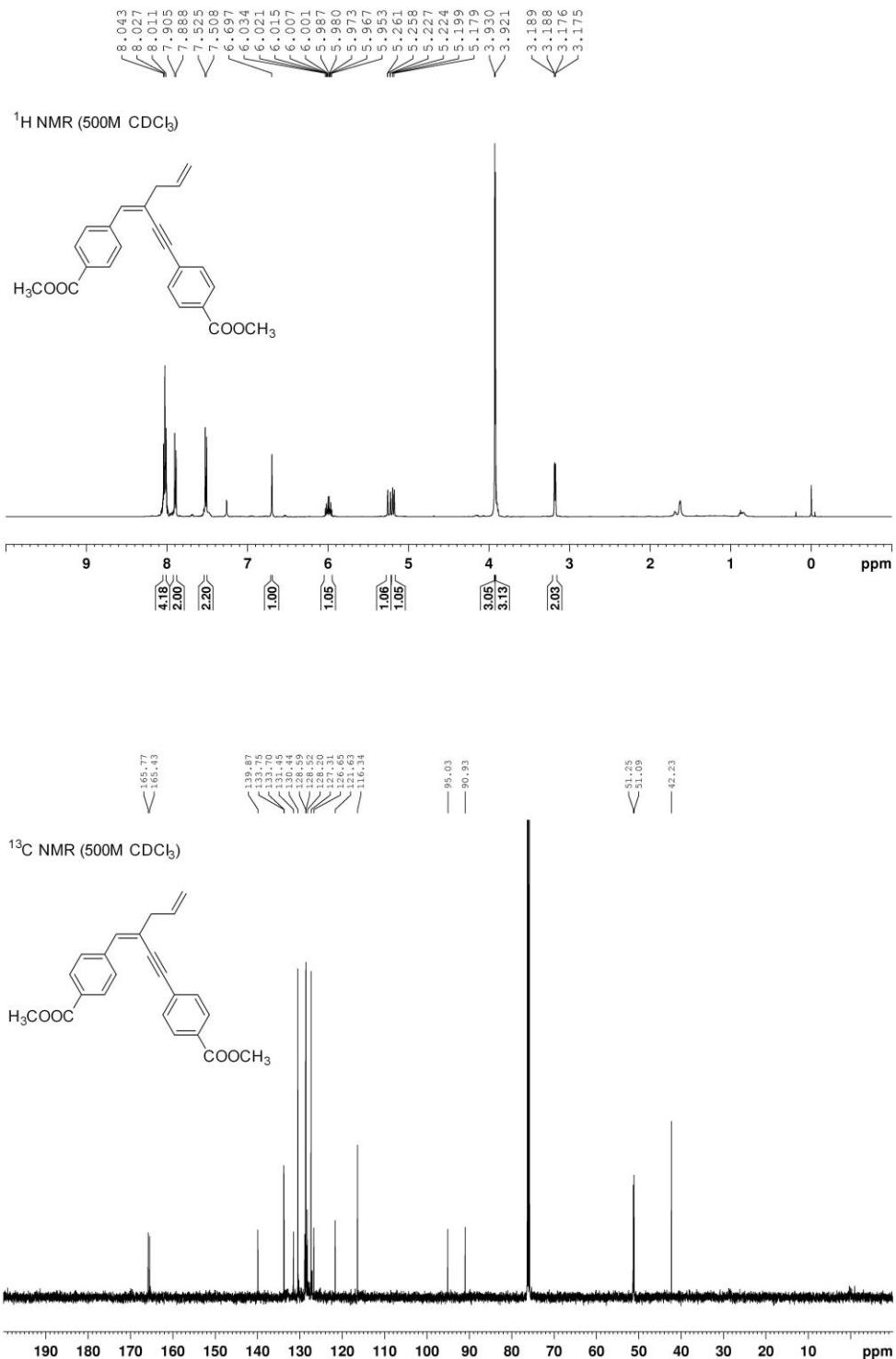
(Z)-4,4'-(2-allylbut-1-en-3-yne-1,4-diyl)bis(ethylbenzene) (2i)



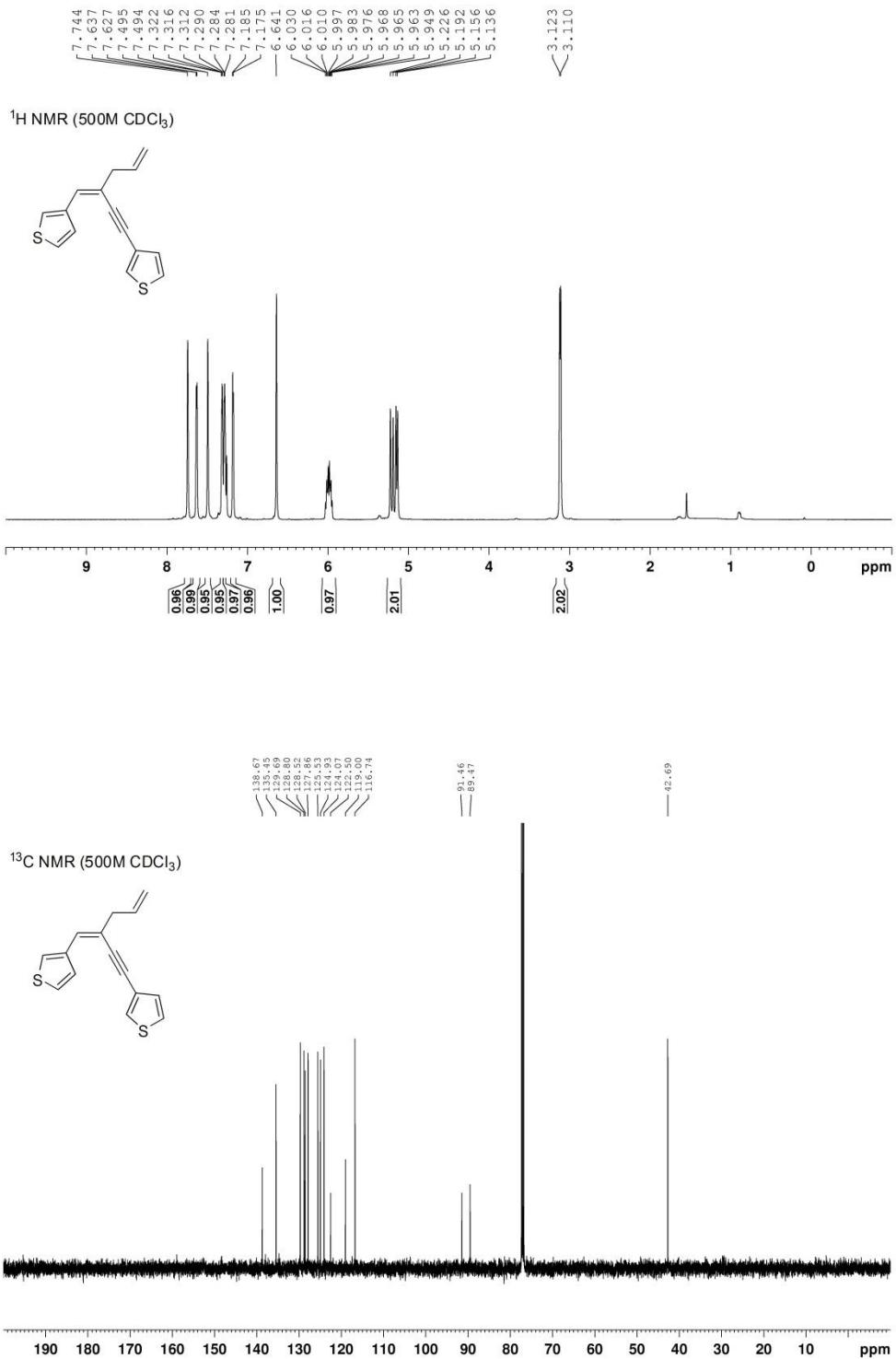
(Z)-4,4'-(2-allylbut-1-en-3-yne-1,4-diyl)bis(tert-butylbenzene) (2j)



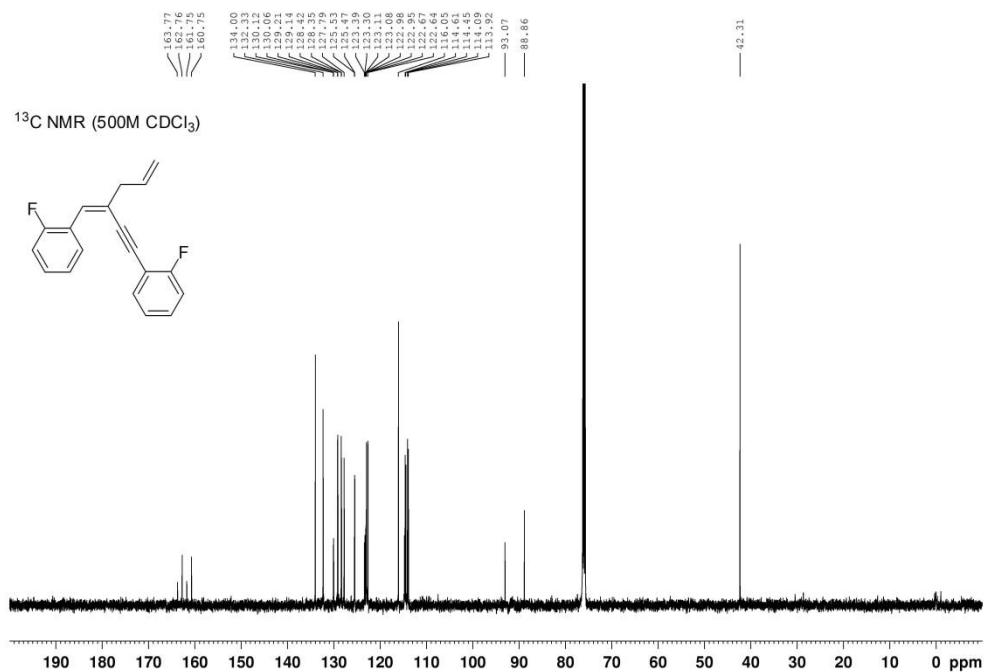
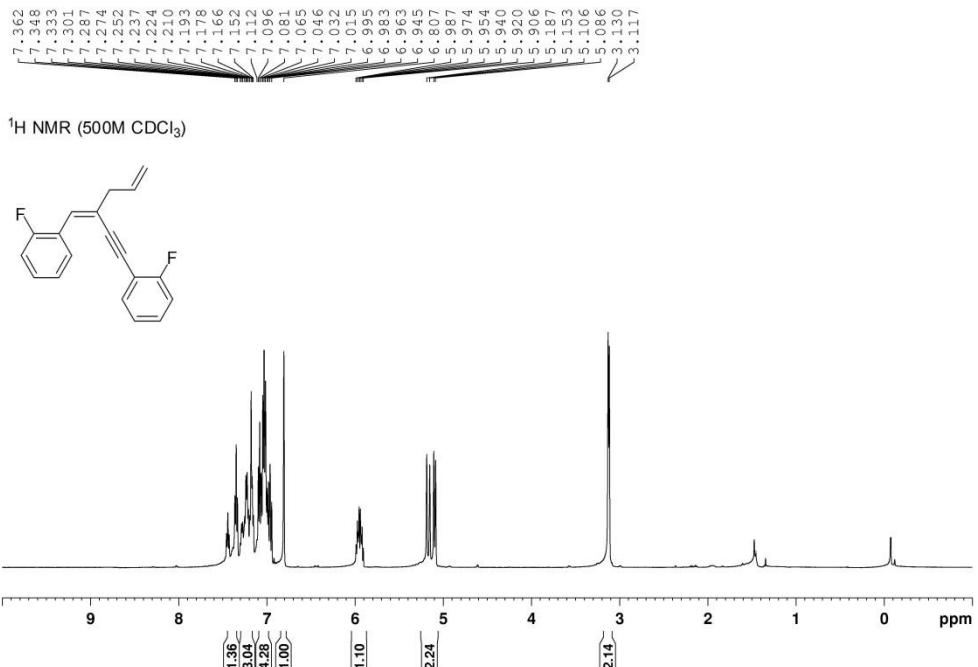
dimethyl 4,4'-(2-allylbut-1-en-3-yne-1,4-diy)(Z)-dibenzoate (2k)



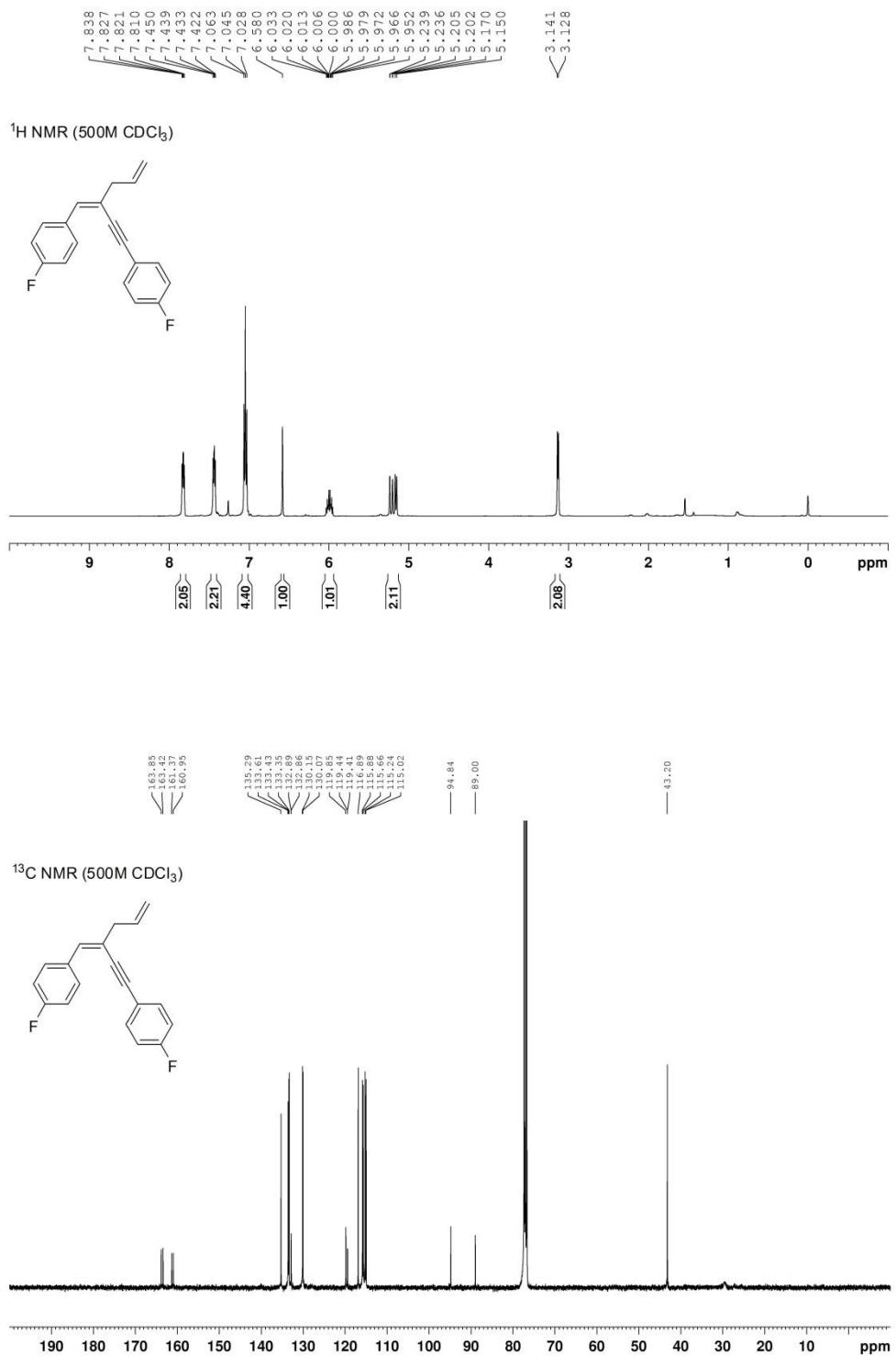
(Z)-3,3'-(2-allylbut-1-en-3-yne-1,4-diyil)dithiophene (2l)



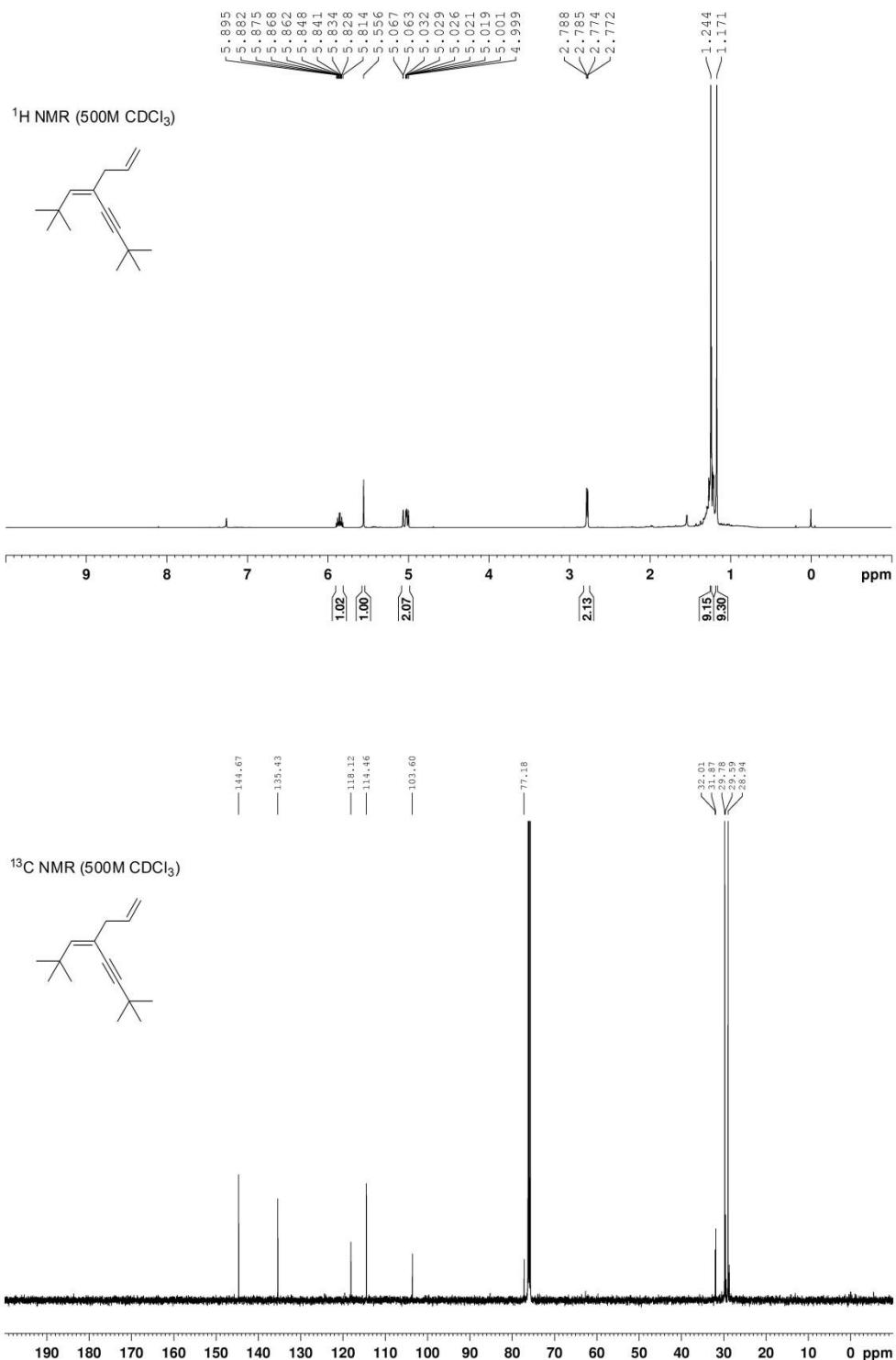
(Z)-2,2'-(2-allylbut-1-en-3-yne-1,4-diyl)bis(fluorobenzene) (2m)



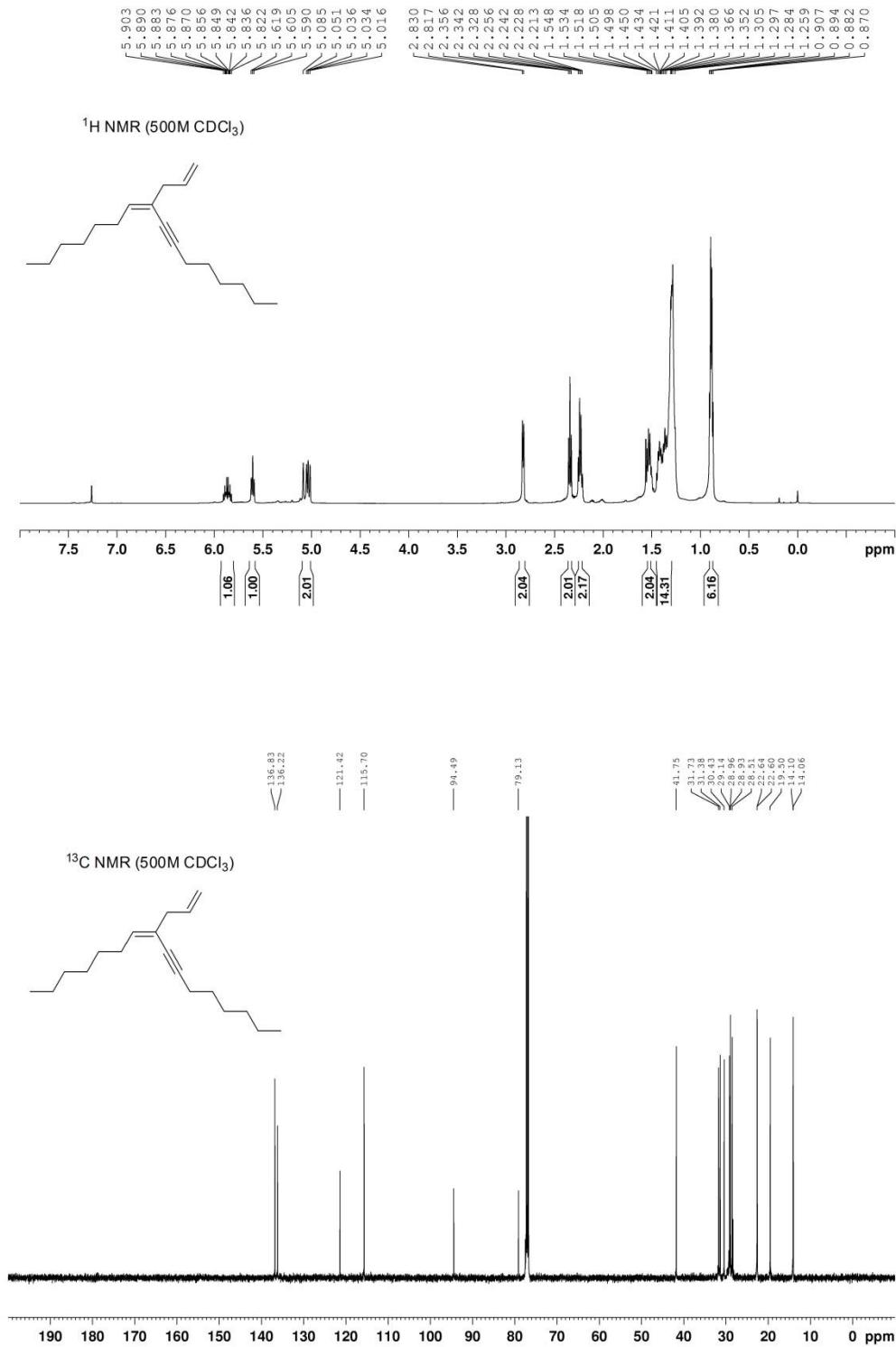
(Z)-4,4'-(2-allylbut-1-en-3-yne-1,4-diyl)bis(fluorobenzene) (2n)



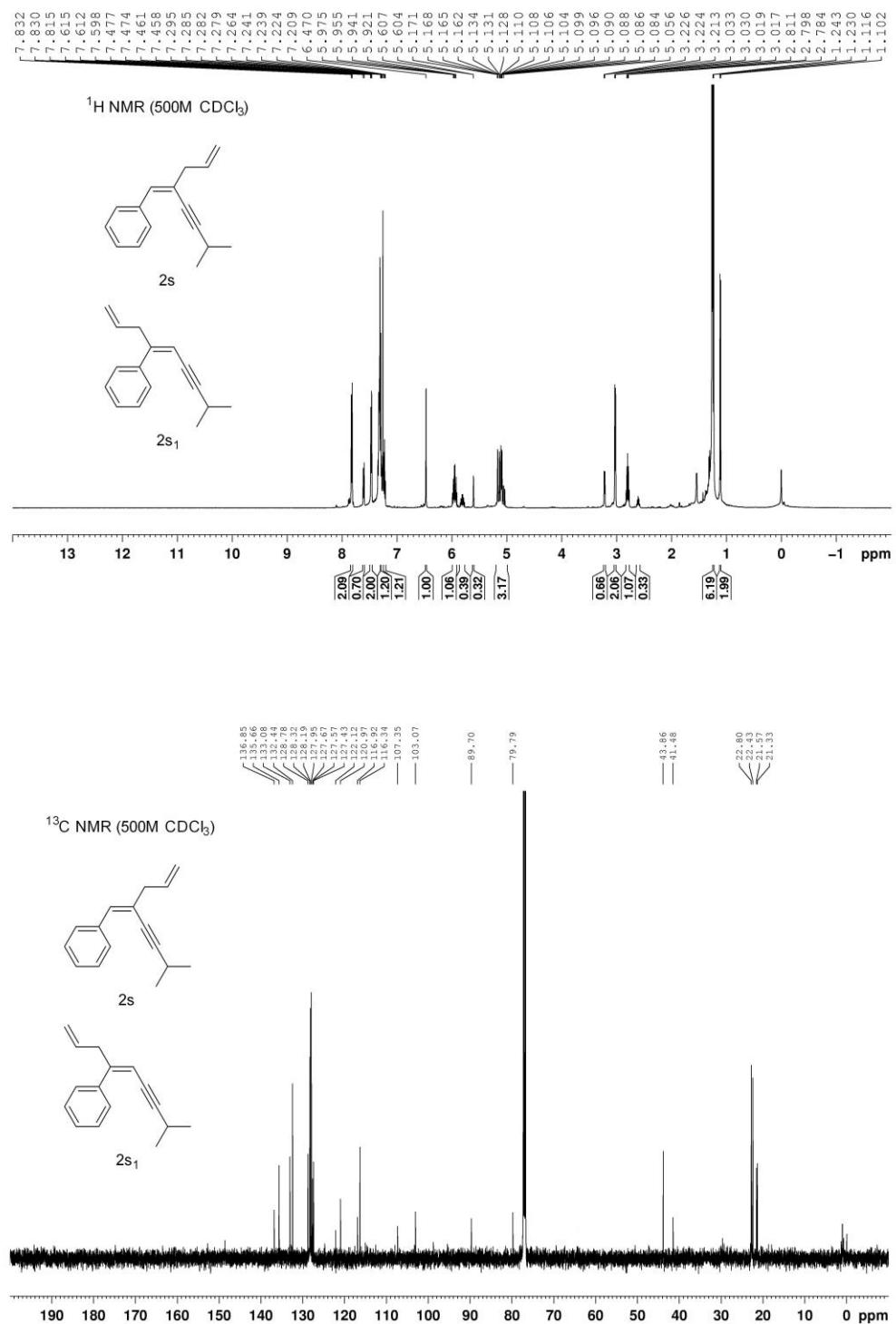
(Z)-4-(2,2-dimethylpropylidene)-7,7-dimethyloct-1-en-5-yne (2o)



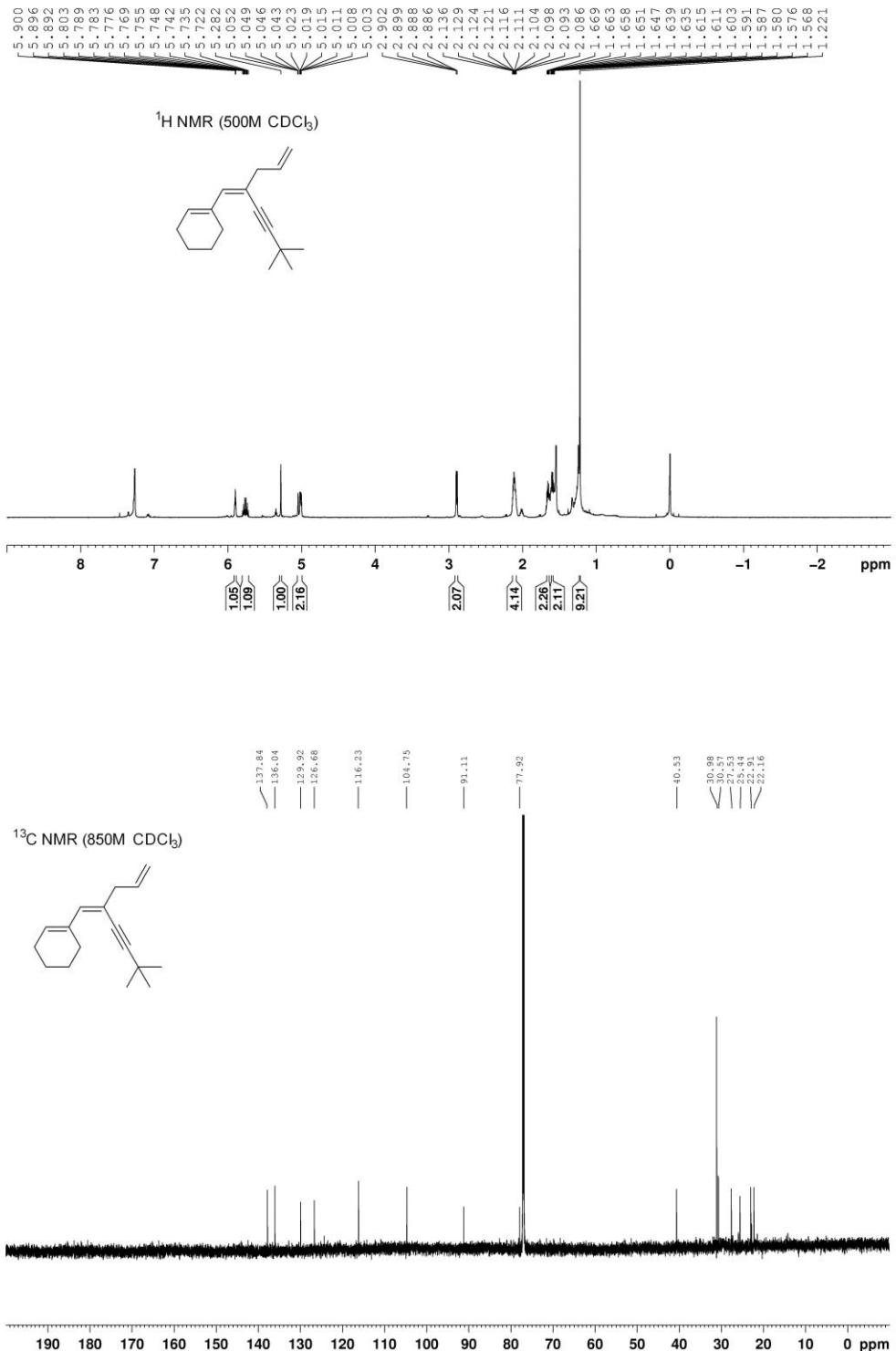
(Z)-8-allylhexadec-7-en-9-yne (2p)



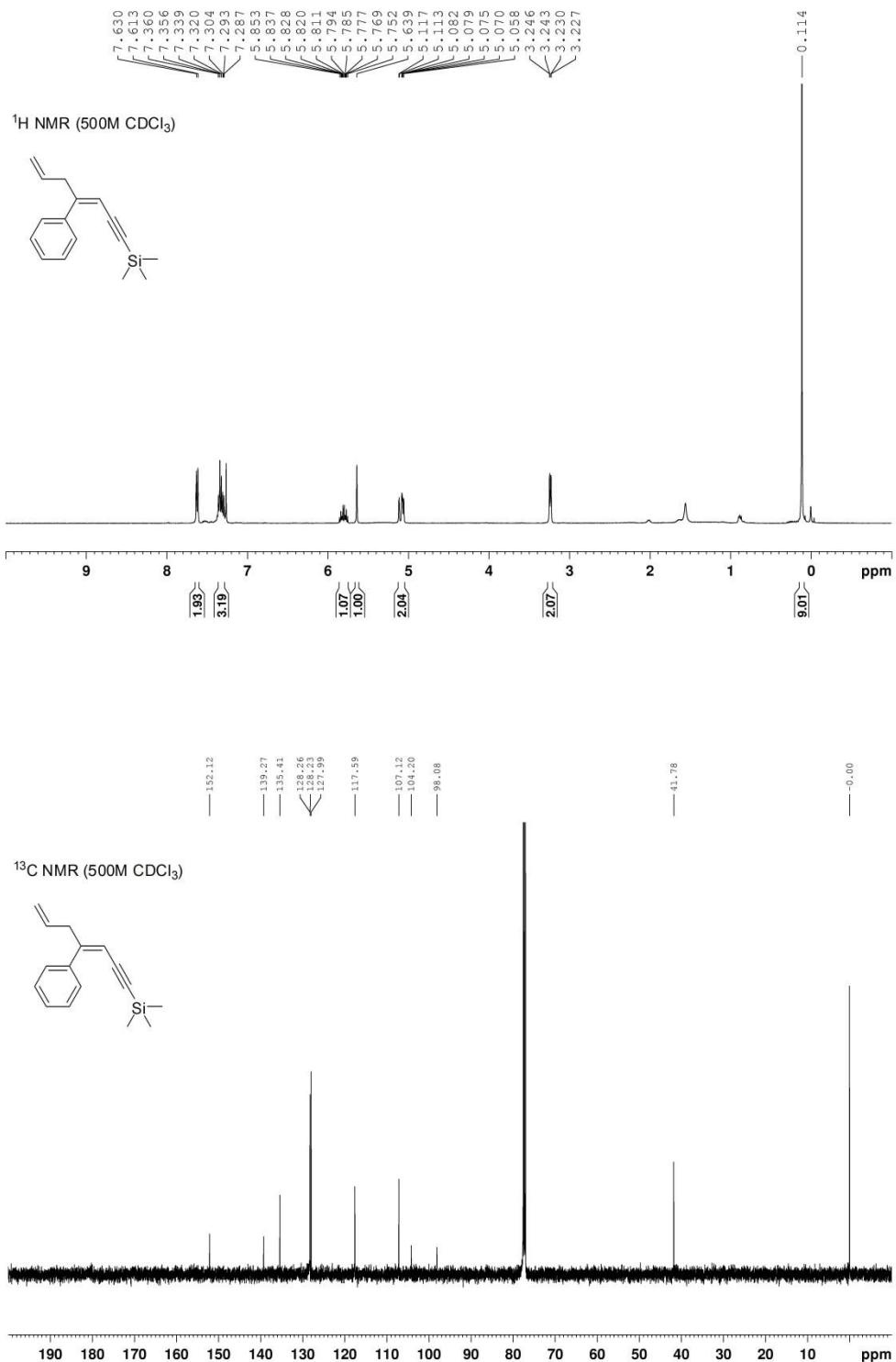
(Z)-(2-allyl-5-methylhex-1-en-3-yn-1-yl)benzene (2s)



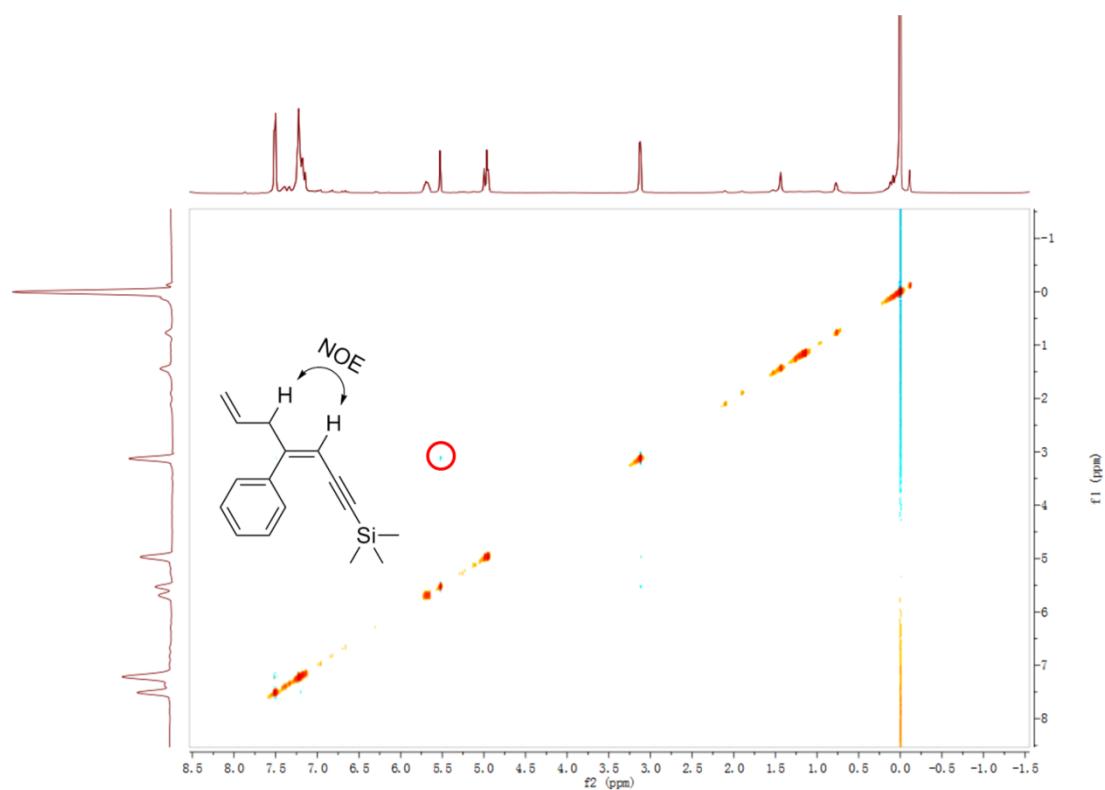
(Z)-1-(2-allyl-5,5-dimethylhex-1-en-3-yn-1-yl)cyclohex-1-ene(2t)



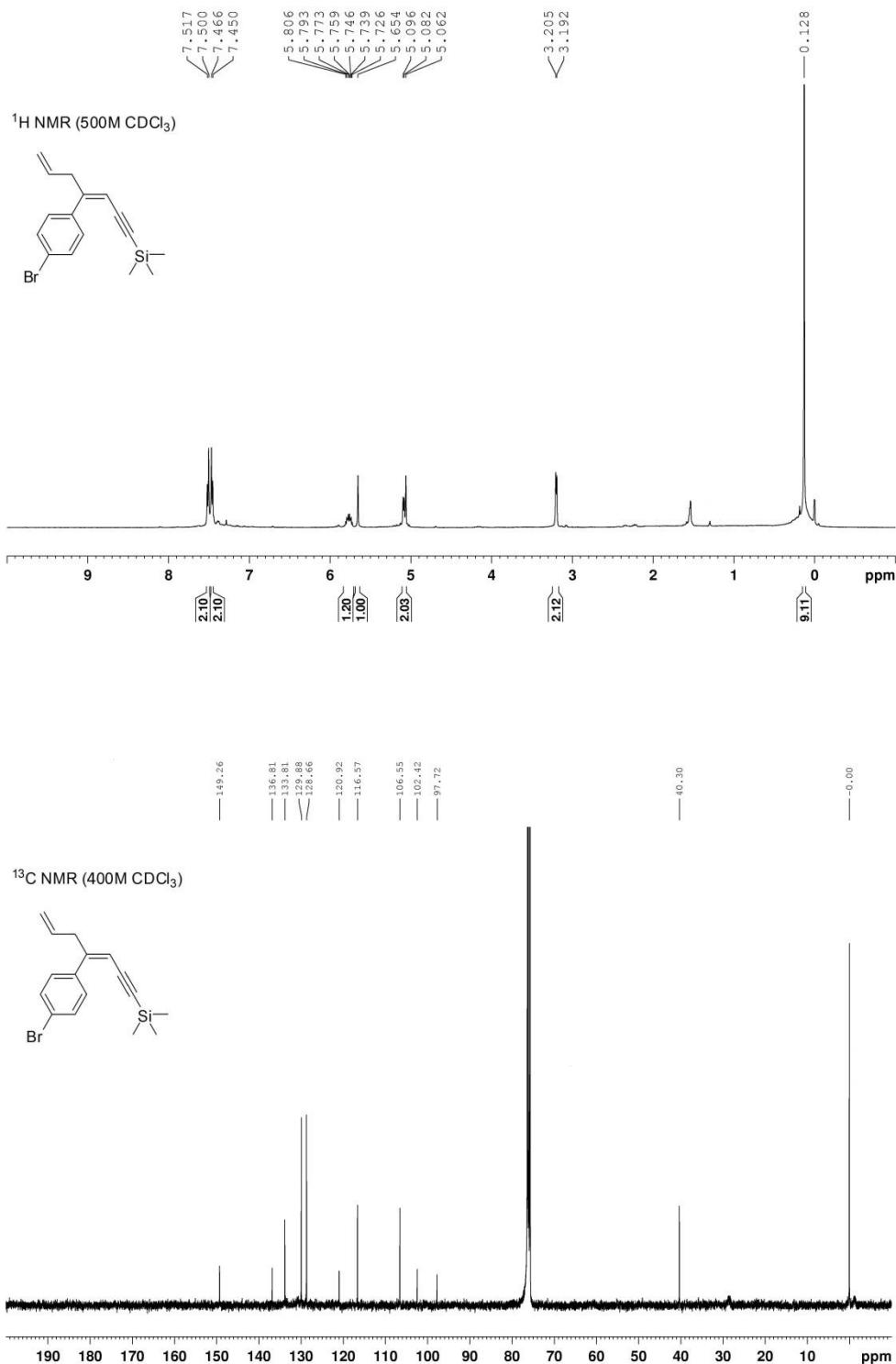
(Z)-trimethyl(4-phenylhepta-3,6-dien-1-ynyl)silane (3a)



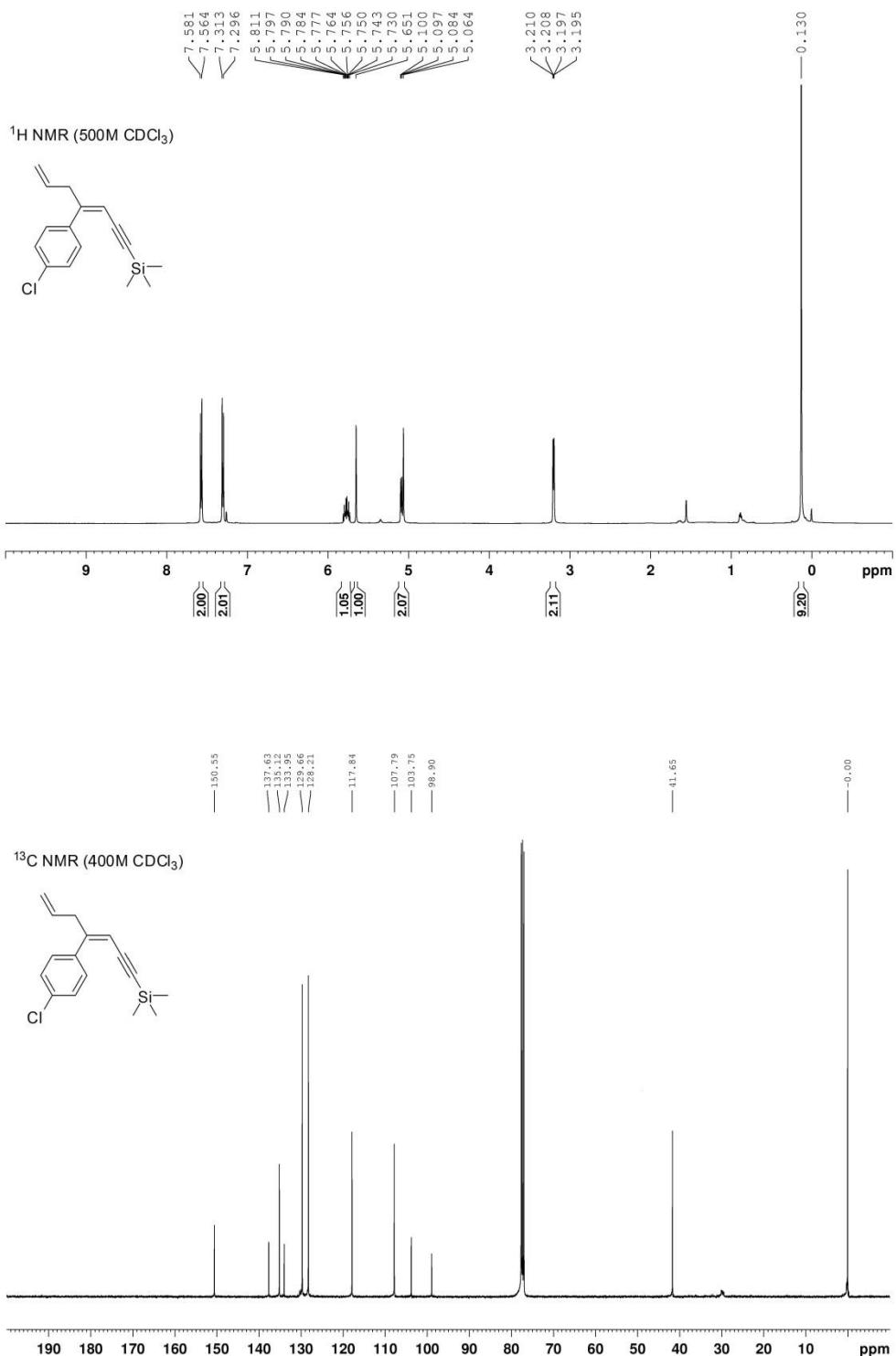
(Z)-trimethyl(4-phenylhepta-3,6-dien-1-ynyl)silane (NOE of 3a)



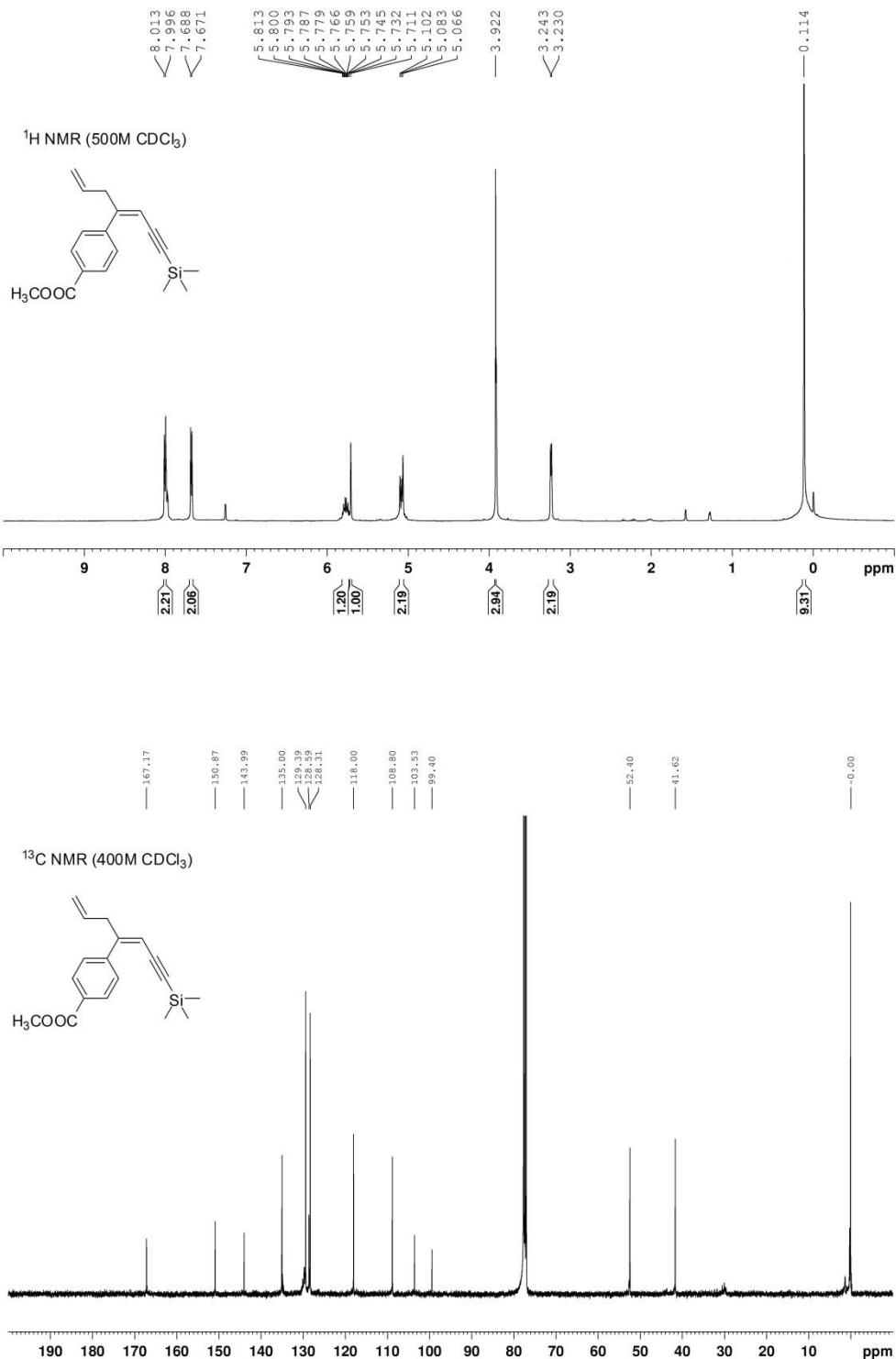
(Z)-(4-(4-bromophenyl)hepta-3,6-dien-1-ynyl)trimethylsilane (3b)



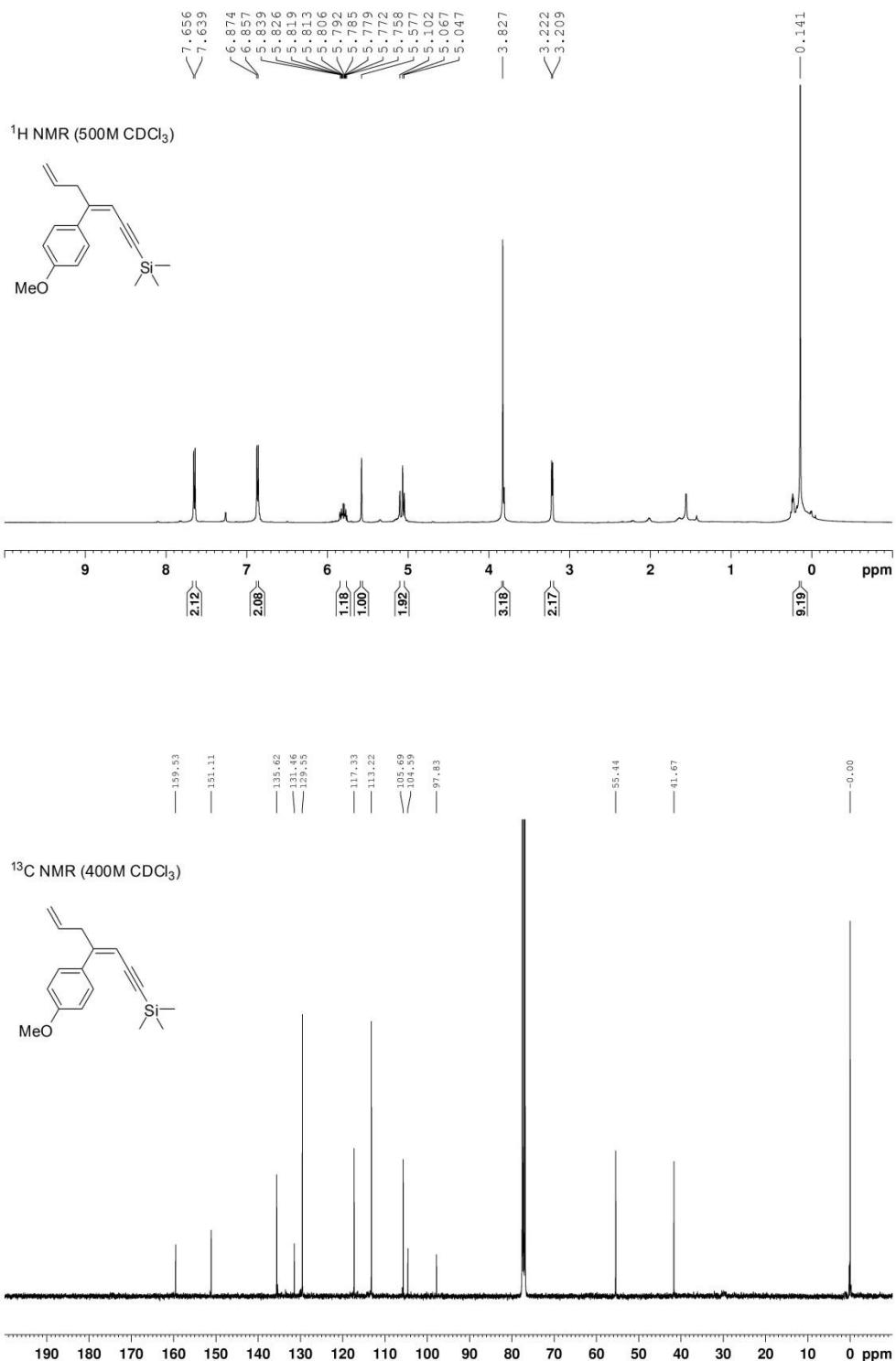
(Z)-(4-(4-chlorophenyl)hepta-3,6-dien-1-ynyl)trimethylsilane (3c)



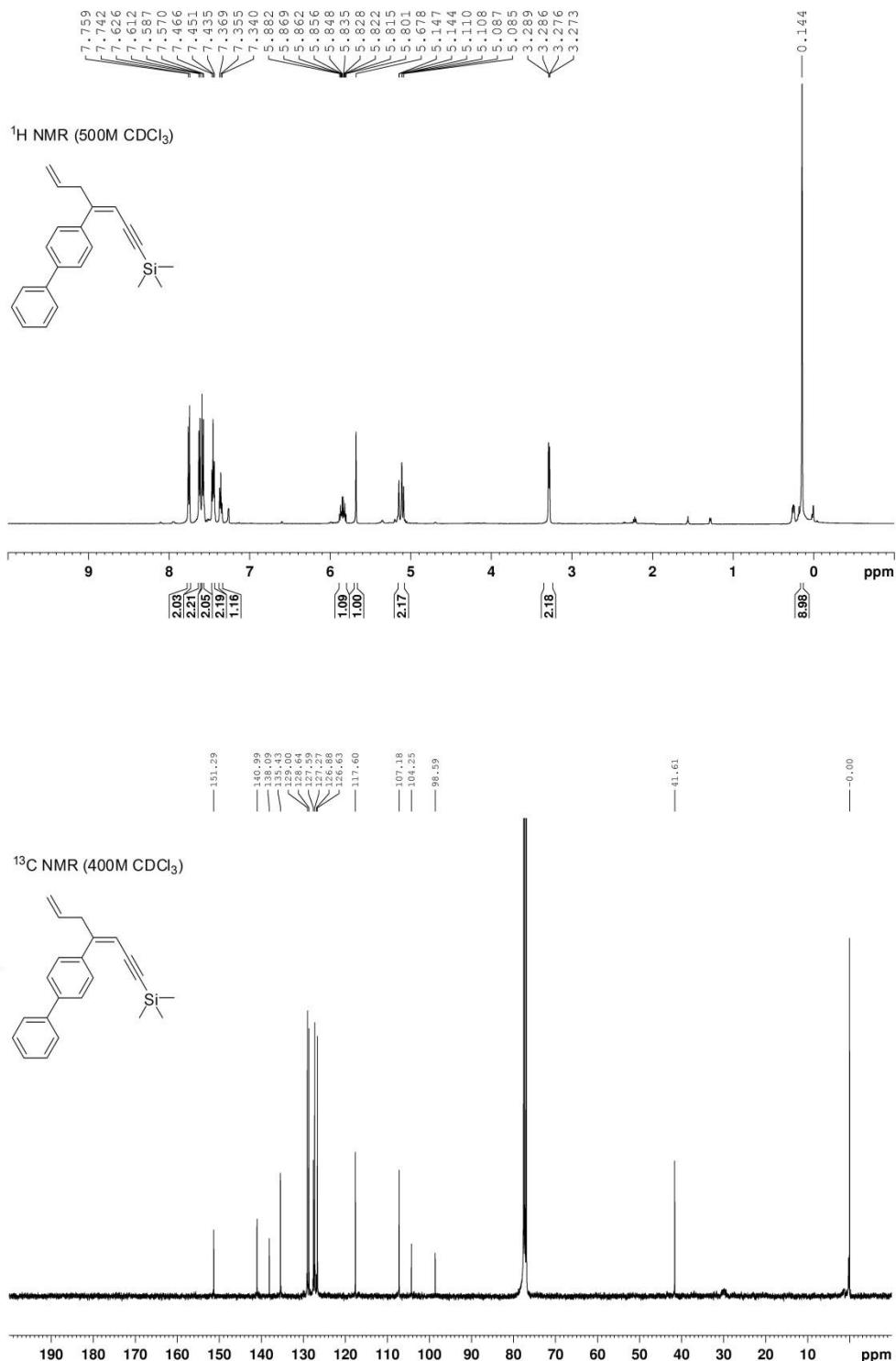
(Z)-methyl 4-(1-(trimethylsilyl)hepta-3,6-dien-1-yn-4-yl)benzoate (3d)



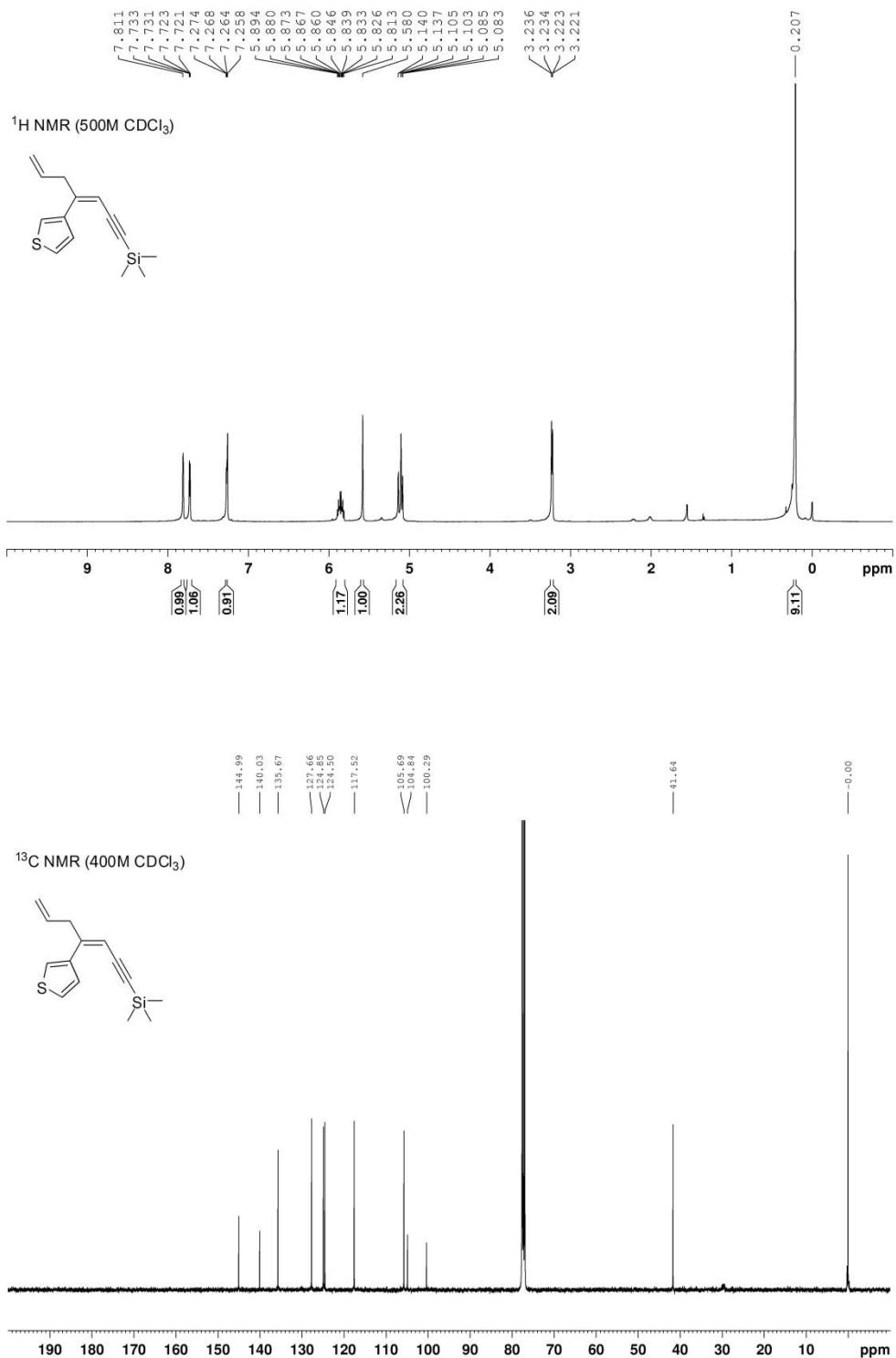
(Z)-(4-(4-methoxyphenyl)hepta-3,6-dien-1-ynyl)trimethylsilane (3e)



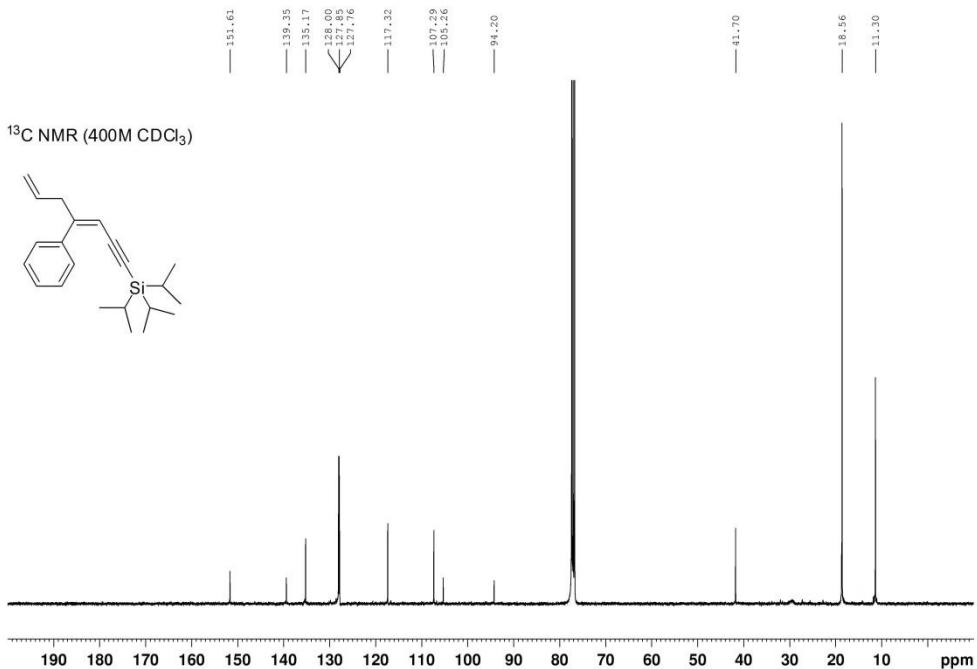
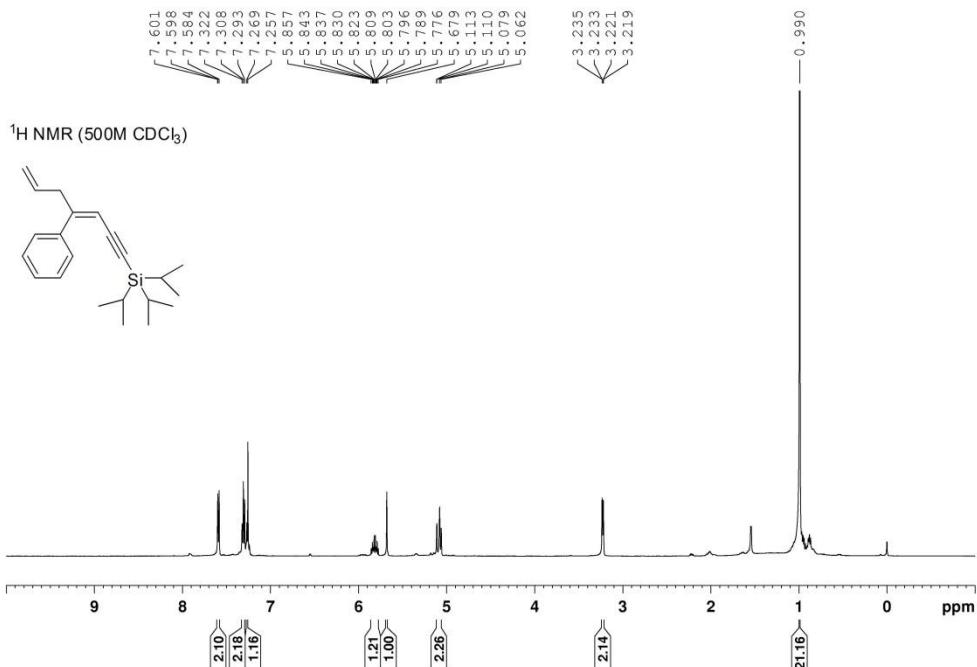
(Z)-(4-(biphenyl-4-yl)hepta-3,6-dien-1-yanyl)trimethylsilane (3f)



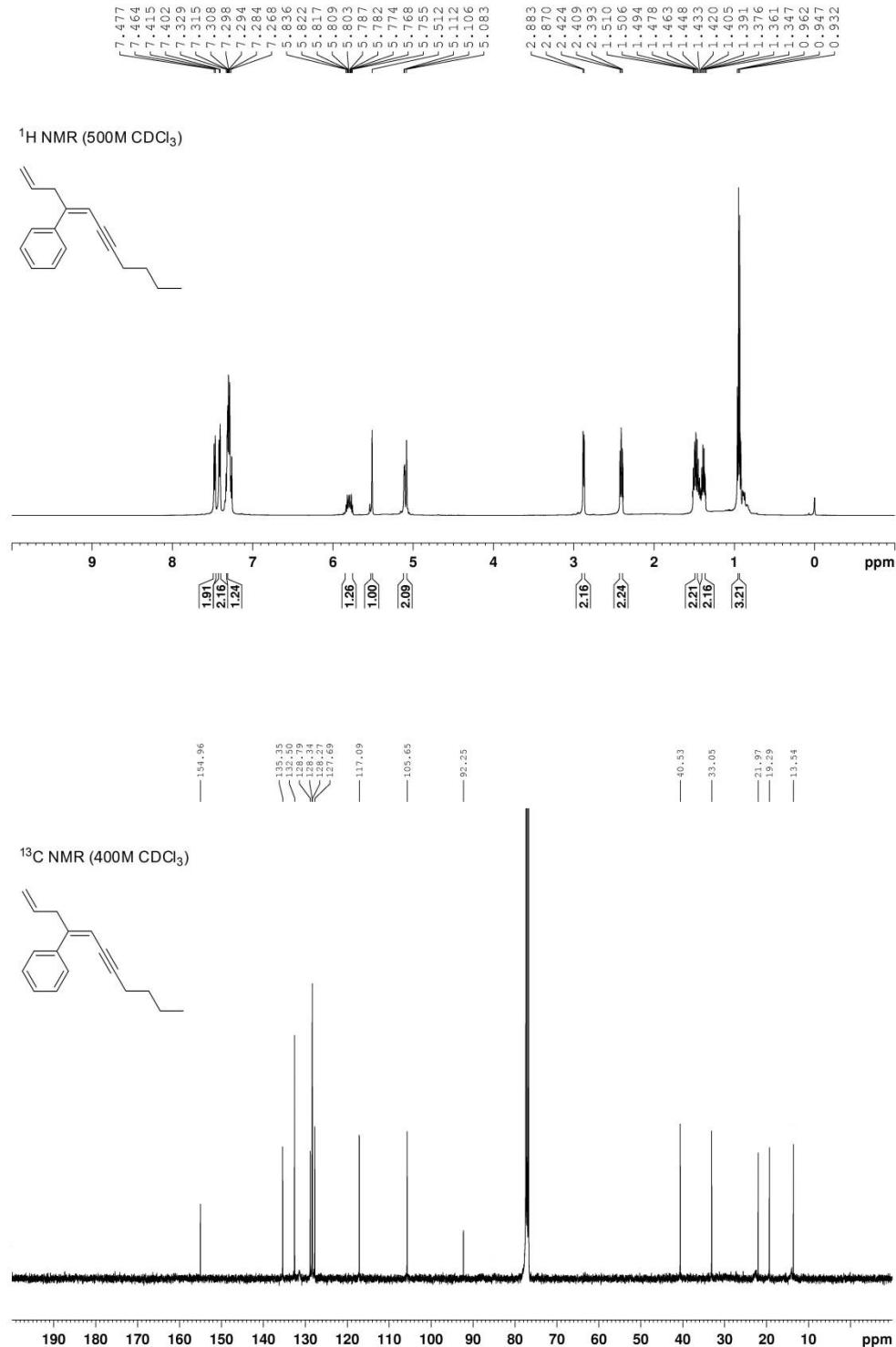
(Z)-trimethyl(4-(thiophen-3-yl)hepta-3,6-dien-1-ynyl)silane (3g)



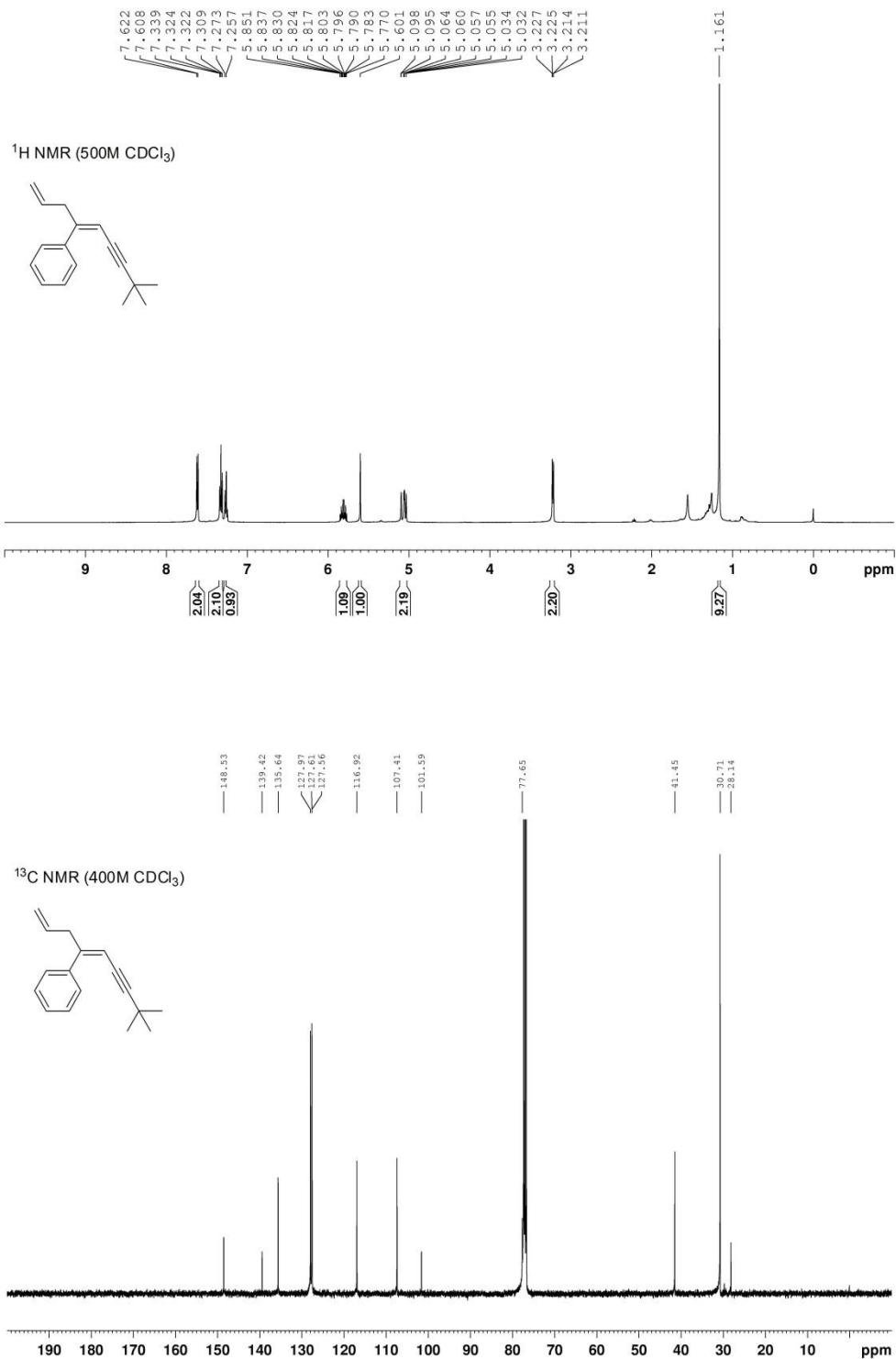
(Z)-triisopropyl(4-phenylhepta-3,6-dien-1-ynyl)silane (3h)



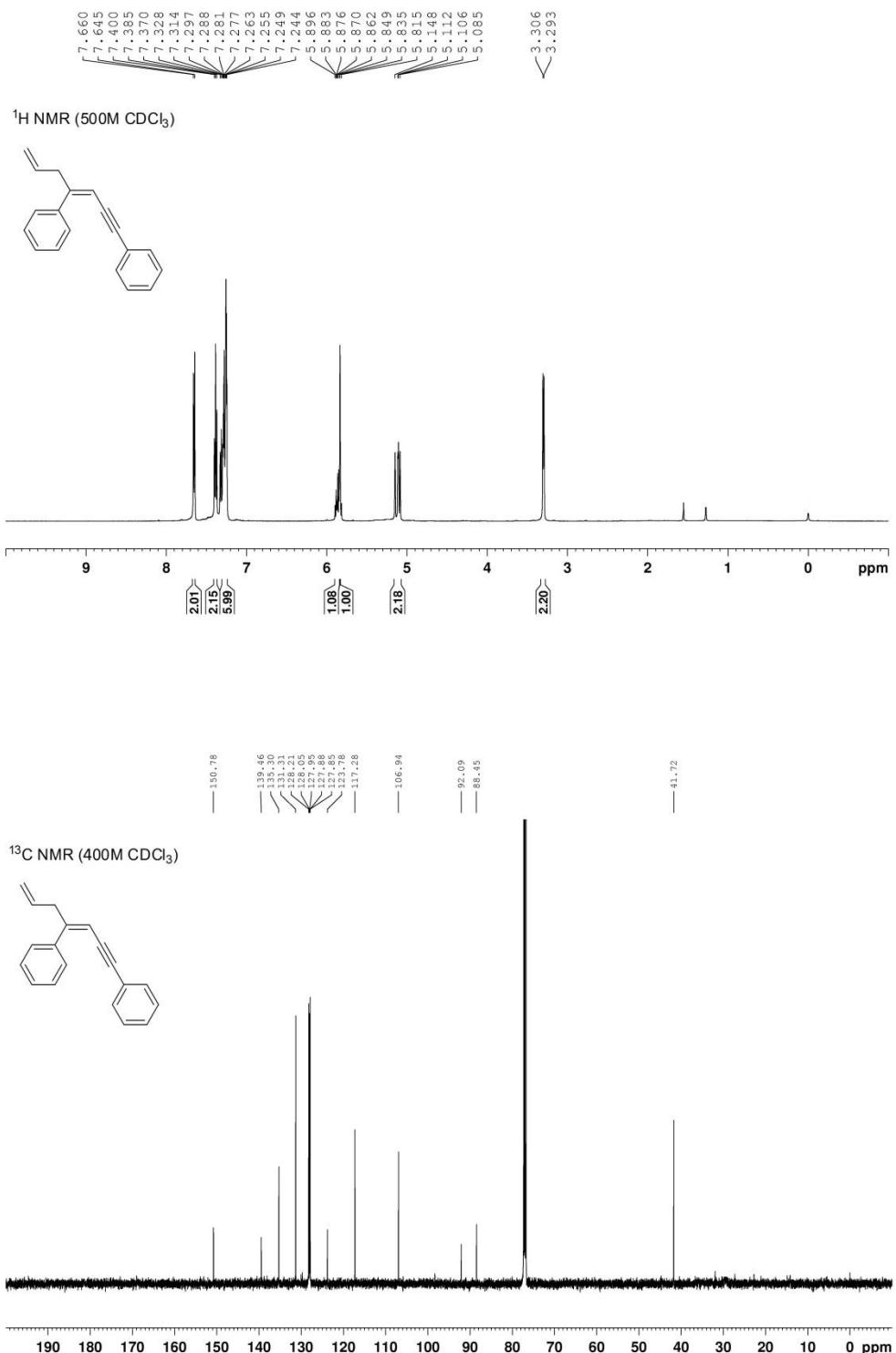
(Z)-undeca-1,4-dien-6-yn-4-ylbenzene (3i)



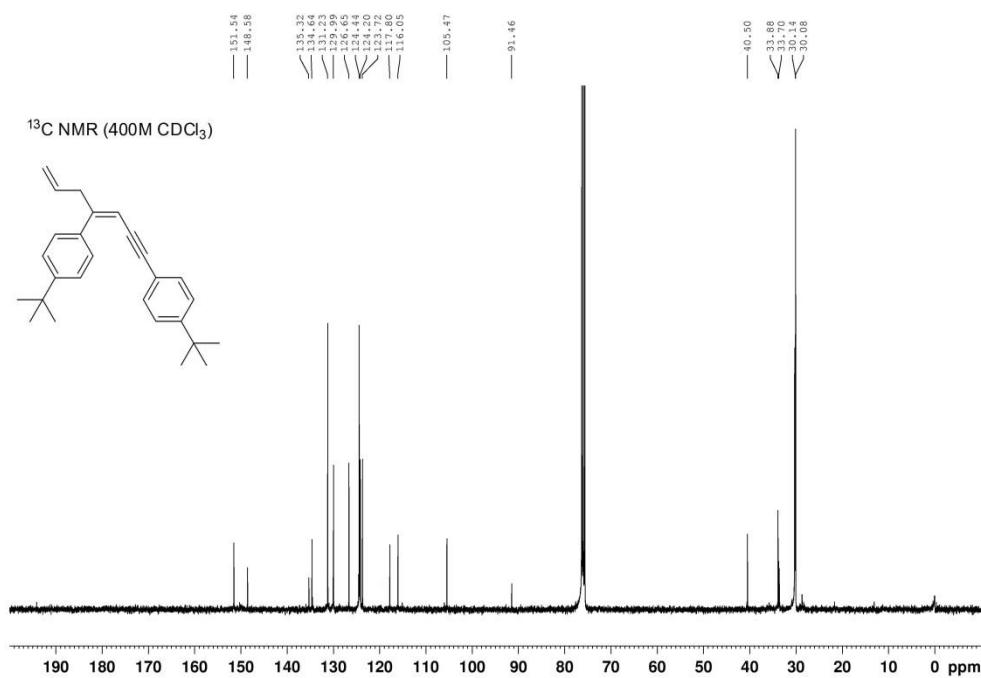
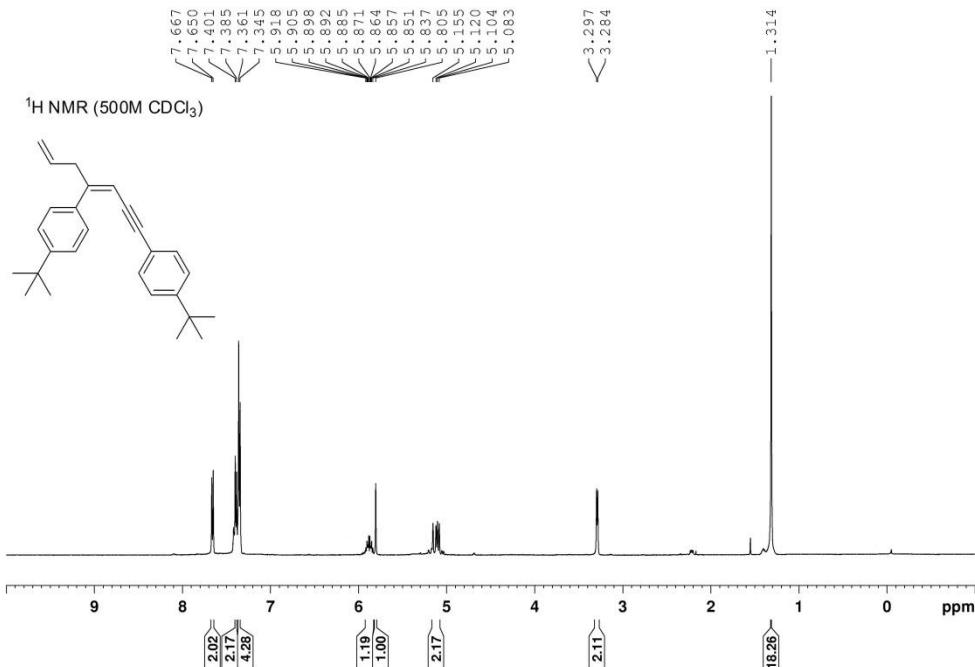
(Z)-(8,8-dimethylnona-1,4-dien-6-yn-4-yl)benzene (3j)



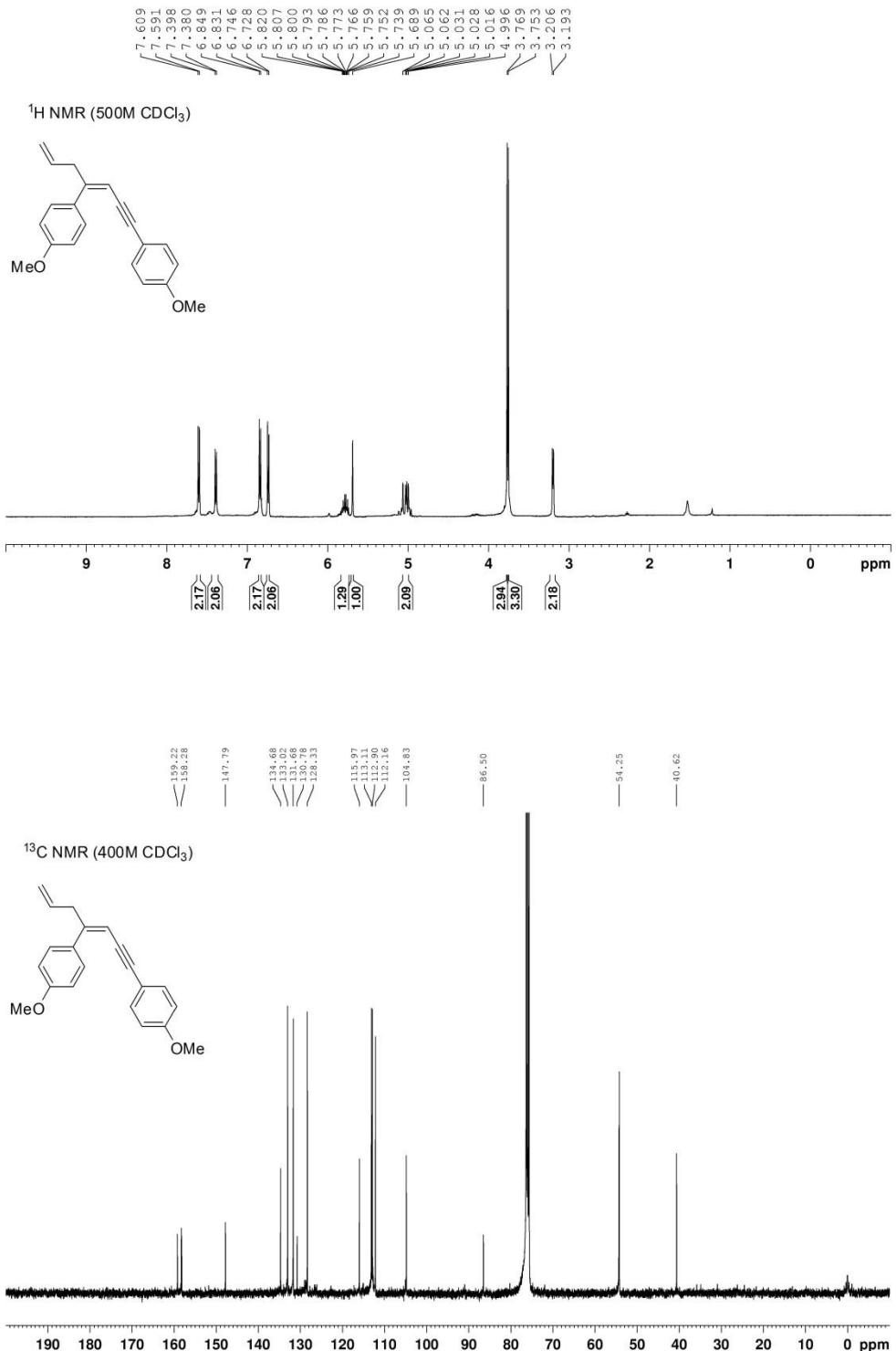
(Z)-hepta-3,6-dien-1-yne-1,4-diylbenzene (3k)



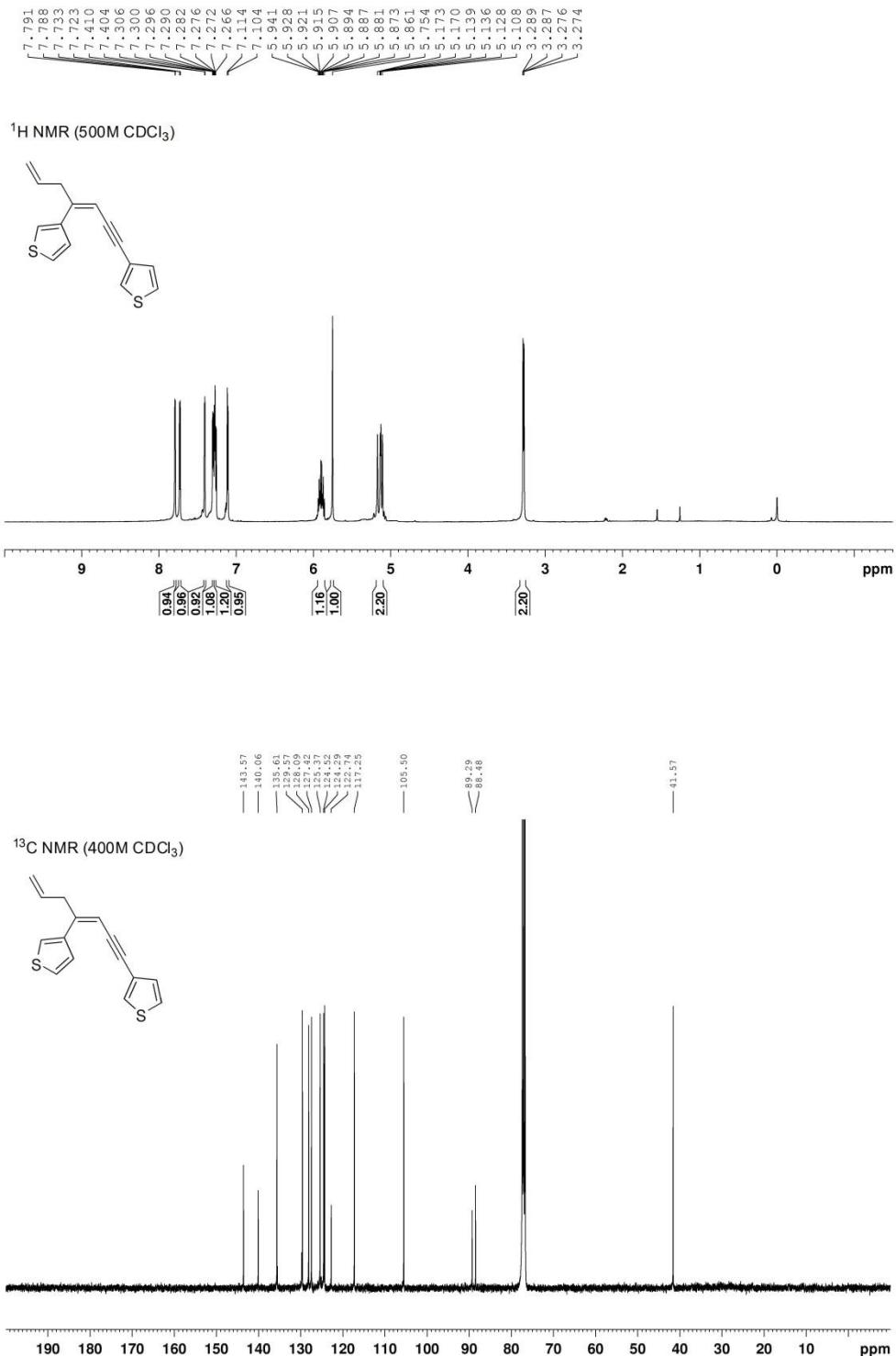
(Z)-4,4'-(hepta-3,6-dien-1-yne-1,4-diyl)bis(tert-butylbenzene) (3l)



(Z)-4,4'-(hepta-3,6-dien-1-yne-1,4-diyl)bis(methoxybenzene) (3m)



(Z)-3,3'-(hepta-3,6-dien-1-yne-1,4-diyl)dithiophene (3n)



(Z)-dimethyl 4,4'-(hepta-3,6-dien-1-yne-1,4-diyl)dibenzoate (3o)

