

Regioselective Solvent-dependent Benzannulation of Conjugated Enynes

Florian Pünner, Gerhard Hilt*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Str., 35043 Marburg,
Germany

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Experimental

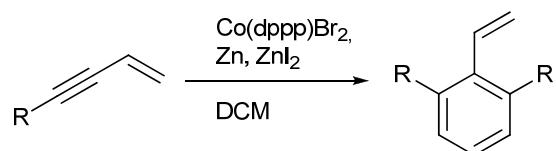
General

All experiments were carried out under an atmosphere of argon in dried flasks and absolute solvents. All used reagents and reactants were purchased and used as received or previously synthesized. The solvents were dried using common procedures. The cobalt catalysts were synthesized following known or adopted procedures.¹

General procedure for the synthesis of terminal 1,3-enynes (GP1)²

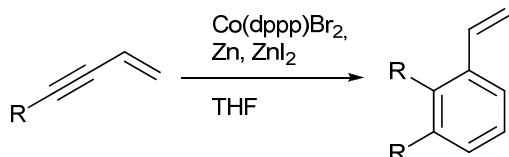
Copper (I) iodide (2.0 mol%) and tetrakis(triphenylphosphine)palladium (0.3 mol%) were dissolved in anhydrous and degassed diethylamine (0.5 mL/1.0 mmol alkyne) and cooled to 0 °C. Then alkyne (1.0 eq.) and 1 M vinyl bromide in tetrahydrofuran (1.1-1.4 eq.) were added and the mixture stirred at room temperature until complete conversion of the starting material. Water was added followed by extraction with *n*-pentane/diethyl ether (1:1). The organic layers were combined, washed with 1 M HCl and dried over magnesium sulfate. After evaporation of the solvent the crude product was purified by column chromatography.

General procedure for the synthesis of 2,6-disubstituted styrenes (GP2)



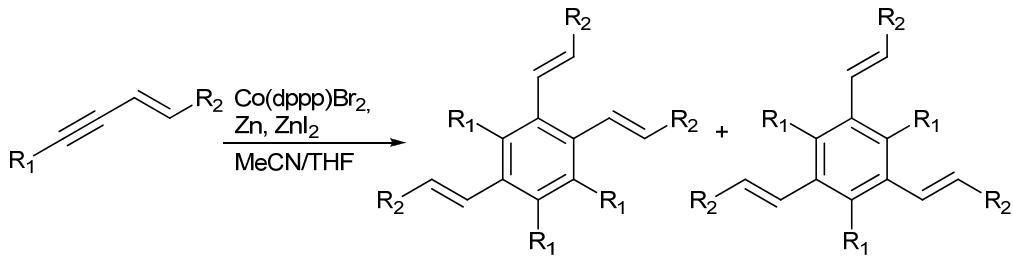
Cobaltdibromo(1,3-bis-(diphenylphosphino)propane) (10 mol%), zinc (20 mol%) and zinc iodide (20 mol%) were dissolved in 1 mL of dichloromethane and the enyne was added (0.5-1.0 mmol). The reaction mixture was stirred at room temperature until complete conversion was observed in GC/MS analysis. The mixture was filtered through a short pad of silica, the solvent was evaporated and the crude product was purified by column chromatography to give the desired styrenes.

General procedure for the synthesis of 2,3-disubstituted styrenes (GP3)



Cobaltdibromo(1,3-bis-(diphenylphosphino)propane) (10 mol%), zinc (20 mol%) and zinc iodide (20 mol%) were dissolved in 1 mL of tetrahydrofuran and the enyne was added (0.5-1.0 mmol). The reaction mixture was stirred at room temperature until complete conversion was observed in GC/MS analysis or TLC. The mixture was filtered through a short pad of silica, the solvent was evaporated and the crude product was purified by column chromatography to give the desired styrenes.

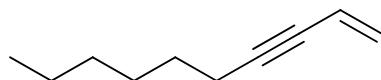
General procedure for the trimerisation of enynes (GP4)



Cobaltdibromo(1,3-bis-(diphenylphosphino)propane) (10 mol%), zinc (20 mol%) and zinc iodide (20 mol%) were dissolved in 1 mL of tetrahydrofuran or acetonitrile and the enyne was added (0.5-1.0 mmol). The reaction mixture was stirred at room temperature until complete conversion was observed in GC/MS analysis. The mixture was filtered through a short pad of silica, the solvent was evaporated and the crude product was purified by column chromatography to give the desired products.

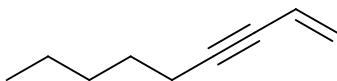
Synthesis of starting materials

Synthesis of dec-1-en-3-yne (1a)



The title compound was prepared according to GP1 using 1-octyne (2.00 g, 18.2 mmol, 1 eq.) and vinyl bromide (1.30 eq.) and was obtained after column chromatography with *n*-pentane as colorless oil (2.22 g, 16.3 mmol, 90%). ¹H NMR (300 MHz, CDCl₃): δ = 5.84-5.71 (m, 1 H), 5.54 (dd, *J* = 17.5, 2.3 Hz, 1 H), 5.37 (dd, *J* = 10.9, 2.2 Hz, 1 H), 2.29 (dd, *J* = 7.0, 1.8 Hz, 2 H), 1.58-1.47 (m, 2 H), 1.44-1.24 (m, 6 H), 0.89 (t, *J* = 6.5 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 125.3, 117.7, 91.2, 79.3, 31.3, 28.7, 28.6, 22.5, 19.3, 14.0. The analytical data are in accordance with the literature.³

Synthesis of non-1-en-3-yne (1b)



The title compound was prepared according to GP1 using 1-heptyne (1.1 mL, 8.38 mmol, 1 eq.) and vinyl bromide (1.20 eq.) and was obtained after column chromatography with *n*-pentane as

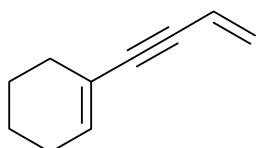
colorless oil (907 mg, 7.42 mmol, 89%). **¹H NMR (300 MHz, CDCl₃)**: δ = 5.78 (ddt, *J* = 17.5, 10.9, 2.1 Hz, 1 H), 5.54 (dd, *J* = 17.5, 2.3 Hz, 1 H), 5.37 (dd, *J* = 10.9, 2.3 Hz, 1 H), 2.29 (dd, *J* = 7.1, 2.0 Hz, 2 H), 1.59-1.48 (m, 2 H), 1.44-1.26 (m, 4 H), 0.90 (t, *J* = 6.9 Hz, 3 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 125.3, 117.7, 91.2, 79.3, 31.1, 28.4, 22.2, 19.3, 13.9. The analytical data are in accordance with the literature.⁴

Synthesis of (but-3-en-1-ynyl)trimethylsilane (**1c**)



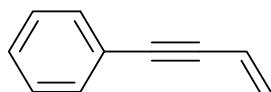
The title compound was prepared according to GP1 using ethynyltrimethylsilane (756 mg, 8.00 mmol, 1 eq.) and vinyl bromide (1.13 eq.) and was obtained after column chromatography with *n*-pentane as colorless oil (425 mg, 3.42 mmol, 43%). **¹H NMR (300 MHz, CDCl₃)**: δ = 5.82 (dd, *J* = 17.6, 10.8 Hz, 1 H), 5.69 (dd, *J* = 17.6, 2.6 Hz, 1 H), 5.50 (dd, *J* = 10.8, 2.6 Hz, 1 H), 0.19 (s, 9 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 127.9, 117.2, 103.7, 95.1, -0.2. The analytical data are in accordance with the literature.⁵

Synthesis of 1-(but-3-en-1-ynyl)cyclohex-1-ene (**1d**)



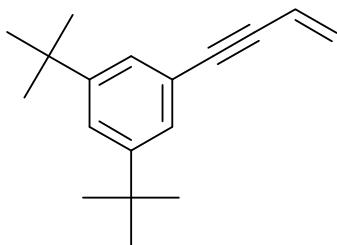
The title compound was prepared according to GP1 using 1-ethynylcyclohex-1-ene (940 μL, 7.99 mmol, 1 eq.) and vinyl bromide (1.25 eq.) and was obtained after column chromatography with *n*-pentane as colorless oil (921 mg, 6.97 mmol, 87%). **¹H NMR (300 MHz, CDCl₃)**: δ = 6.13-6.09 (m, 1 H), 5.90 (dd, *J* = 17.5, 11.1 Hz, 1 H), 5.58 (dd, *J* = 17.5, 2.2 Hz, 1 H), 5.41 (dd, *J* = 11.1, 2.2 Hz, 1 H), 2.17-2.07 (m, 4 H), 1.68-1.54 (m, 4 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 135.2, 125.6, 120.6, 117.4, 91.9, 85.5, 29.1, 25.7, 22.3, 21.5. **IR (film)**: 3098, 3007, 2928, 2858, 2831, 2186, 1832, 1607, 1448, 1436, 1411, 1347, 1291, 1270, 1218, 1136, 1074, 970, 917, 843, 799, 674, 581, 488, 454. **MS (EI)**: *m/z* (%) = 132 ([M⁺], 100), 117 (93), 103 (45), 91 (68), 78 (54). **HR-MS (EI)**: *m/z* (%) = calculated for C₁₀H₁₂: 132.0939; found: 132.0936.

Synthesis of (but-3-en-1-ynyl)benzene (1e)



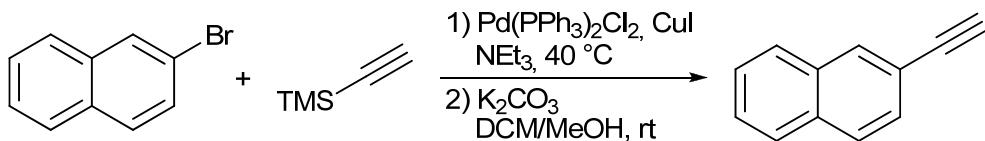
The title compound was prepared according to GP1 using phenylacetylene (940 mg, 1.6 mL, 14.6 mmol, 1 eq.) and vinyl bromide (1.30 eq.) and was obtained after column chromatography with *n*-pentane as colorless oil (1.82 g, 14.2 mmol, 95%). **¹H-NMR (300 MHz, CDCl₃)**: δ = 7.49-7.42 (m, 2 H), 7.35-7.29 (m, 3 H), 6.03 (dd, *J* = 17.5, 11.1 Hz, 1 H), 5.75 (dd, *J* = 17.5, 2.1 Hz, 1 H), 5.55 (dd, *J* = 11.1, 2.1 Hz, 1 H). **¹³C-NMR (75 MHz, CDCl₃)**: δ = 131.6, 128.3, 126.8, 123.1, 117.2, 90.0, 88.7. The analytical data are in accordance with the literature.⁶

Synthesis of 1,3-di-*tert*-butyl-5-(but-3-en-1-ynyl)benzene (1f)



The title compound was prepared according to GP1 using 1,3-di-*tert*-butyl-5-ethynylbenzene (1.71 g, 7.98 mmol, 1 eq.) and vinyl bromide (1.25 eq.) and was obtained after column chromatography with *n*-pentane as slightly yellow and highly viscose oil (1.77 g, 7.36 mmol, 92%). **¹H NMR (300 MHz, CDCl₃)**: δ = 7.39 (t, *J* = 1.8 Hz, 1 H), 7.31 (d, *J* = 1.8 Hz, 2 H), 6.04 (dd, *J* = 17.5, 11.1 Hz, 1 H), 5.74 (dd, *J* = 17.5, 2.2 Hz, 1 H), 5.53 (dd, *J* = 11.1, 2.2 Hz, 1 H), 1.32 (s, 18 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 150.8, 126.4, 125.8, 122.8, 122.1, 117.4, 91.2, 86.9, 34.8, 31.3. **IR (film)**: 3073, 2964, 2904, 2868, 2197, 1768, 1607, 1589, 1476, 1430, 1409, 1394, 1363, 1312, 1290, 1248, 1203, 1134, 1092, 988, 970, 913, 876, 735, 705, 539. **MS (EI)**: *m/z* (%) = 240 ([M⁺], 41), 225 (100), 165 (7). **HR-MS (EI)**: *m/z* (%) = calculated for C₁₈H₂₄: 240.1878; found: 240.1881.

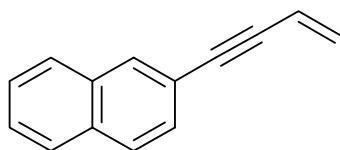
Synthesis of 2-ethynylnaphthalene⁷



A Schlenk flask was charged with 2-bromonaphthalene (1.04 g, 5.00 mmol, 1 eq.), bis(triphenylphosphine)palladium(II) dichloride (35.1 mg, 0.05 mmol, 0.01 eq.) and copper(I) iodide (9.5 mg, 0.05 mmol, 0.01 eq.) under argon atmosphere. The solids were then dissolved in triethylamine (5 mL). Ethynyltrimethylsilane (1.0 mL, 7.08 mmol, 1.42 eq.) was added and the mixture was stirred at 40 °C for 17 h. The insoluble compounds were removed by filtration, the solvent was removed under reduced pressure and the crude product was purified by column chromatography with *n*-pentane as solvent. The trimethyl(2-(naphthalene-6-yl)ethynyl)silane was dissolved in dichloromethane/methanol (50 mL each) and stirred with an excess of potassium carbonate at room temperature for 2 h. After complete conversion of the starting material the solution was filtered, the solvent was removed and the crude product was purified by column chromatography with *n*-pentane as solvent to give the desired compound as white solid (546 mg, 3.59 mmol, 72%). **¹H NMR (300 MHz, CDCl₃):** δ = 8.05 (s, 1 H), 7.86-7.77 (m, 3 H), 7.57-7.48 (m, 3 H), 3.17 (s, 1 H). **¹³C NMR (75 MHz, CDCl₃):** δ = 133.0, 132.8, 132.3, 128.5, 128.0, 127.8, 127.8, 126.9, 126.6, 119.4, 84.0, 77.4.

The analytical data are in accordance with the literature.⁷

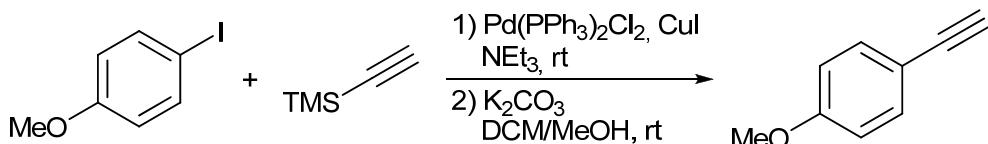
Synthesis of 2-(but-3-en-1-ynyl)naphthalene (1g)



The title compound was prepared according to GP1 using 2-ethynylnaphthalene (546 mg, 3.59 mmol, 1 eq.) and vinyl bromide (1.25 eq.) and was obtained after column chromatography with *n*-pentane as colorless oil (602 mg, 3.38 mmol, 94%). **¹H NMR (300 MHz, CDCl₃):** δ = 7.99 (s, 1 H), 7.84-7.76 (m, 3 H), 7.54-7.47 (m, 3 H), 6.09 (dd, *J* = 17.5, 11.1 Hz, 1 H), 5.80 (dd, *J* = 17.5, 2.1 Hz, 1 H), 5.59 (dd, *J* = 11.1, 2.1 Hz, 1 H). **¹³C NMR (75 MHz, CDCl₃):** δ = 133.0, 132.8, 131.4, 128.3, 128.0, 127.8, 127.7, 127.0, 126.7, 126.5, 120.4, 117.2, 90.4, 88.4. **IR (film):** 3053, 3009, 2203, 1838, 1600, 1499, 1411, 1362, 1223, 1129, 1074, 966, 917, 893, 855, 813, 741, 672,

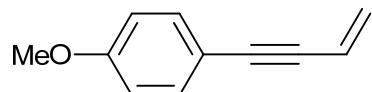
642, 608, 525, 470. **MS (EI):** m/z (%) = 178 ([M^+], 100), 152 (28), 76 (15). **HR-MS (EI):** m/z (%) = calculated for $C_{14}H_{10}$: 178.0783; found: 178.0791.

Synthesis of 1-ethynyl-4-methoxybenzene



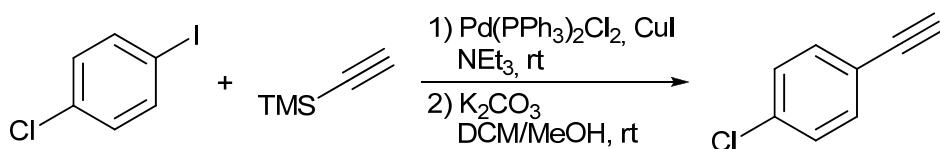
A Schlenk flask was charged with 1-iodo-4-methoxybenzene (1.17 g, 5.00 mmol, 1 eq.), bis(triphenylphosphine)palladium(II) dichloride (35.1 mg, 0.05 mmol, 0.01 eq.) and copper(I) iodide (9.5 mg, 0.05 mmol, 0.01 eq.) under argon atmosphere. The solids were then dissolved in triethylamine (5 mL). Ethynyltrimethylsilane (1.0 mL, 7.08 mmol, 1.42 eq.) was added and the mixture stirred at room temperature for 16 h. The insoluble compounds were removed by filtration, the solvent was removed under reduced pressure and the crude product was purified by column chromatography with *n*-pentane/diethyl ether as solvent. The (2-(4-methoxyphenyl)ethynyl)trimethylsilane was dissolved in dichloromethane/methanol (50 mL each) and stirred with an excess of potassium carbonate at room temperature for 2 h. After complete conversion of the starting material the solution was filtered, the solvent was removed and the crude product was purified by column chromatography with *n*-pentane as solvent to give the desired compound as slightly yellow oil (605 mg, 4.58 mmol, 92%). This compound was used without any analytical characterization (except GC/MS) for further transformation.

Synthesis of 1-(but-3-en-1-ynyl)-4-methoxybenzene (1h)



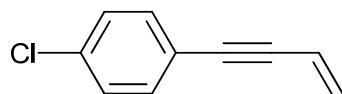
The title compound was prepared according to GP1 using 1-ethynyl-4-methoxybenzene (604 mg, 4.57 mmol, 1 eq.) and vinyl bromide (1.20 eq.) and was obtained after column chromatography with *n*-pentane/diethyl ether (50:1) as yellow oil (718 mg, 4.54 mmol, 99%). **1H NMR (300 MHz, CDCl₃):** δ = 7.39 (d, J = 8.9 Hz, 2 H), 6.85 (d, J = 8.9 Hz, 2 H), 6.01 (dd, J = 17.5, 11.1 Hz, 1 H), 5.70 (dd, J = 17.5, 2.2 Hz, 1 H), 5.50 (dd, J = 11.1, 2.2 Hz, 1 H), 3.81 (s, 3 H). **^{13}C NMR (75 MHz, CDCl₃):** δ = 159.7, 133.1, 126.1, 117.5, 115.3, 114.1, 90.1, 87.0, 55.4. The analytical data are in accordance with the literature.⁸

Synthesis of 1-ethynyl-4-chlorobenzene



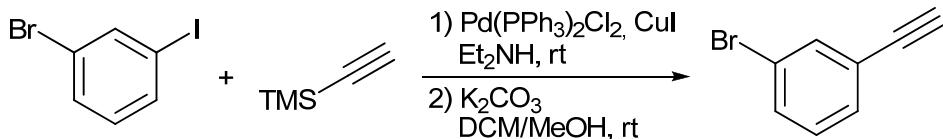
A Schlenk flask was charged with bis(triphenylphosphine)palladium(II) dichloride (35.1 mg, 0.05 mmol, 0.01 eq.) and copper(I) iodide (9.5 mg, 0.05 mmol, 0.01 eq.) under argon atmosphere. The solids were then dissolved in triethylamine (5 mL). Ethynyltrimethylsilane (1.0 mL, 7.08 mmol, 1.47 eq.) and 1-chloro-4-iodobenzene (1.19 g, 5.00 mmol, 1 eq.) were added and the mixture was stirred at room temperature for 16 h. The insoluble compounds were removed by filtration through a short pad of silica with *n*-pentane, the solvent was removed under reduced pressure and the crude product (2-(4-chlorophenyl)ethynyl)trimethylsilane was dissolved in dichloromethane/methanol (50 mL each) and was stirred with an excess of potassium carbonate at room temperature for 2 h. After complete conversion of the starting material the solution was filtered, the solvent was removed and the crude product was purified by column chromatography with *n*-pentane as solvent to give the desired compound as colorless crystals (609 mg, 4.46 mmol, 89%). ¹H NMR (300 MHz, CDCl₃): δ = 7.42 (d, *J* = 8.6 Hz, 2 H), 7.30 (d, *J* = 8.7 Hz, 2 H), 3.11 (s, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 134.9, 133.5, 128.7, 120.6, 82.5, 78.1. The analytical data are in accordance with the literature.⁹

Synthesis of 1-(but-3-en-1-ynyl)-4-chlorobenzene (1i)



The title compound was prepared according to GP1 using 1-ethynyl-4-chlorobenzene (609 mg, 4.46 mmol, 1 eq.) and vinyl bromide (1.19 eq.) and was obtained after column chromatography with *n*-pentane as colorless oil (588 mg, 1.10 mmol, 82%). ¹H NMR (300 MHz, CDCl₃): δ = 7.37 (d, *J* = 8.8 Hz, 2 H), 7.29 (d, *J* = 8.8 Hz, 2 H), 6.01 (dd, *J* = 17.5, 11.1 Hz, 1 H), 5.74 (dd, *J* = 17.5, 2.1 Hz, 1 H), 5.57 (dd, *J* = 11.1, 2.1 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 134.3, 132.8, 128.7, 127.3, 121.6, 116.9, 89.0, 88.8. IR (film): 3097, 3010, 1899, 1843, 1646, 1586, 1485, 1399, 1264, 1090, 1012, 967, 919, 822, 740, 673, 578, 519, 480, 410. MS (EI): *m/z* (%) = 162 ([M⁺], 100), 127 (75), 75 (23), 63 (27). HR-MS (EI): *m/z* (%) = calculated for C₁₀H₇Cl: 162.0236; found: 162.0230.

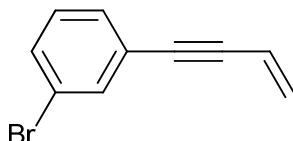
Synthesis of 1-bromo-3-ethynylbenzene



A Schlenk flask was charged with bis(triphenylphosphine)palladium(II) dichloride (105 mg, 0.15 mmol, 0.05 eq.) and copper(I) iodide (28.6 mg, 0.15 mmol, 0.05 eq.) under argon atmosphere. The solids were then dissolved in diethylamine (10 mL) and tetrahydrofuran (5 mL). Ethynyltrimethylsilane (707 mg, 7.20 mmol, 1.2 eq.) and 1-bromo-3-iodobenzene (1.70 g, 6.00 mmol, 1 eq.) were added and the mixture was stirred at room temperature for 3 h. The insoluble compounds were removed by filtration through a short pad of silica with *n*-pentane, the solvent was removed under reduced pressure and the crude product (2-(3-bromophenyl)ethynyl)trimethylsilane was dissolved in dichloromethane/methanol (50 mL each) and was stirred with an excess of potassium carbonate at room temperature for 1 h. After complete conversion of the starting material the solution was filtered, the solvent was removed and the crude product was purified by column chromatography with *n*-pentane as solvent to give the desired compound as colorless oil (580 mg, 3.20 mmol, 53%). **$^1\text{H NMR}$ (300 MHz, CDCl_3)**: δ = 7.64 (t, J = 1.7 Hz, 1 H), 7.51-7.46 (m, 1 H), 7.44-7.40 (m, 1 H), 7.19 (t, J = 7.9 Hz, 1 H), 3.12 (s, 1 H). **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)**: δ = 134.9, 132.0, 130.7, 129.7, 124.1, 122.1, 82.0, 78.5.

The analytical data are in accordance with the literature.¹⁰

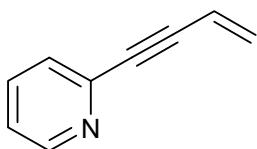
Synthesis of 1-bromo-3-(but-3-en-1-ynyl)benzene (1j)



The title compound was prepared according to GP1 using 1-bromo-3-ethynylbenzene (580 mg, 3.20 mmol, 1 eq.) and vinyl bromide (1.25 eq.) and was obtained after column chromatography with *n*-pentane as colorless oil (615 mg, 2.97 mmol, 93%). **$^1\text{H NMR}$ (300 MHz, CDCl_3)**: δ = 7.60 (t, J = 1.7 Hz, 1 H), 7.44 (ddd, J = 8.0, 2.0, 1.1 Hz, 1 H), 7.37 (dt, J = 7.7, 1.2 Hz, 1 H), 7.18 (t, J = 7.9 Hz, 1 H), 6.01 (dd, J = 17.5, 11.1 Hz, 1 H), 5.76 (dd, J = 17.5, 2.1 Hz, 1 H), 5.58 (dd, J = 11.1, 2.1 Hz, 1 H). **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)**: δ = 134.3, 131.4, 130.1, 129.7, 127.7, 125.2, 122.1, 116.8, 89.3, 88.3. **IR (film)**: 3062, 3008, 1848, 1592, 1552, 1470, 1404, 1291, 1071, 996,

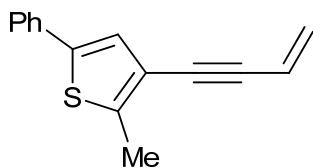
919, 878, 778, 746, 676, 553, 505, 435. **MS (EI):** m/z (%) = 206/208 ([M⁺], 62), 127 (100), 101 (20), 75 (22), 63 (19). **HR-MS (EI):** m/z (%) = calculated for C₁₀H₇Br: 205.9731; found: 205.9727.

Synthesis of 2-(but-3-en-1-ynyl)pyridine (1k)



The title compound was prepared according to GP1 using 2-ethynylpyridine (309 mg, 3.00 mmol, 1 eq.) and vinyl bromide (1.20 eq.) and was obtained after filtration through a short pad of silica with *n*-pentane/diethyl ether (2:3) and short path distillation (4 mbar, 100 °C) as yellow oil (269 mg, 2.08 mmol, 69%). The product slowly decomposes under aerobic conditions. **¹H NMR (300 MHz, CDCl₃):** δ = 8.58-8.54 (m, 1 H), 7.62 (dt, J = 7.7, 1.8 Hz, 1 H), 7.41 (d, J = 7.8 Hz, 1 H), 7.19 (ddd, J = 7.6, 4.9, 1.1 Hz, 1 H), 6.01 (dd, J = 17.6, 11.0 Hz, 1 H), 5.83 (dd, J = 17.6, 2.2 Hz, 1 H), 5.62 (dd, J = 11.0, 2.2 Hz, 1 H). **¹³C NMR (75 MHz, CDCl₃):** δ = 150.0, 143.3, 136.0, 128.8, 126.9, 122.7, 116.5, 89.0, 87.7. **IR (film):** 3051, 3006, 2971, 2196, 1858, 1630, 1581, 1461, 1426, 1361, 1268, 1206, 1149, 1087, 1045, 968, 925, 775, 737, 675, 627, 557, 531, 401. **MS (EI):** m/z (%) = 129 ([M⁺], 100), 102 (22), 79 (24), 51 (23). **HR-MS (ESI+):** m/z (%) = calculated for C₉H₇N+H⁺: 130.0651; found: 130.0652.

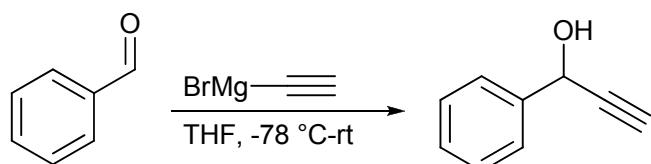
Synthesis of 3-(but-3-en-1-ynyl)-2-methyl-5-phenylthiophene (1l)



The title compound was prepared according to GP1 using 3-ethynyl-2-methyl-5-phenylthiophene (793 mg, 4.00 mmol, 1 eq.) and vinyl bromide (1.25 eq.) and was obtained after column chromatography with *n*-pentane/diethyl ether (50:1) as white solid (853 mg, 3.80 mmol, 95%). **¹H NMR (300 MHz, CDCl₃):** δ = 7.56-7.51 (m, 2 H), 7.41-7.33 (m, 2 H), 7.31-7.24 (m, 1 H), 7.18 (s, 1 H), 6.06 (dd, J = 17.5, 11.1 Hz, 1 H), 5.73 (dd, J = 17.5, 2.1 Hz, 1 H), 5.54 (dd, J = 11.1, 2.1 Hz, 1 H), 2.55 (s, 3 H). **¹³C NMR (75 MHz, CDCl₃):** δ = 143.1, 140.3, 133.9, 128.9, 127.5, 126.3, 125.5, 125.1, 120.6, 117.2, 90.3, 84.7, 14.5. **IR (film):** 3090, 3008, 2915, 2846,

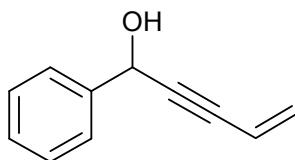
2194, 1812, 1593, 1494, 1456, 1133, 960, 903, 838, 751, 683, 541, 461. **HR-MS (EI):** m/z (%) = calculated for C₁₅H₁₂S: 224.0660; found: 224.0660.

Synthesis of 1-phenylprop-2-yn-1-ol



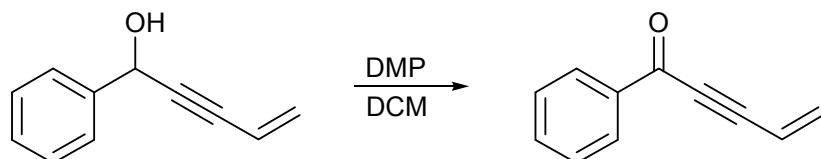
To a solution of benzaldehyde (888 mg, 8.37 mmol, 1 eq.) in tetrahydrofuran (5 mL) ethynylmagnesium bromide 0.5 M in THF (20 mL, 10.0 mmol, 1.19 eq.) was added dropwise at -78°C . The solution was slowly warmed to room temperature and stirred for 1.5 h. Saturated ammonium chloride solution was added and extracted with diethyl ether. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The title compound was obtained as slightly yellow oil (1.16 g, 8.11 mmol, 97%). **¹H-NMR (300 MHz, CDCl₃):** δ = 7.59-7.53 (m, 2 H), 7.44-7.32 (m, 3 H), 5.48 (d, J = 1.9 Hz, 1 H), 2.68 (d, J = 2.2 Hz, 1 H), 2.29 (bs, 1 H). **¹³C-NMR (75 MHz, CDCl₃):** δ = 140.0, 128.7, 128.6, 126.5, 83.5, 74.8, 64.4. The analytical data are in accordance with the literature.¹¹

Synthesis of 1-phenylpent-4-en-2-yn-1-ol



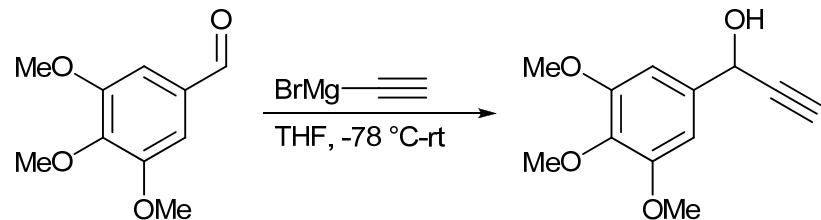
The title compound was prepared according to GP1 using 1-phenylprop-2-yn-1-ol (1.07 g, 8.10 mmol, 1 eq.) and vinyl bromide (1.23 eq.) and was obtained after column chromatography with *n*-pentane/diethyl ether (5:1 \rightarrow 3:1 \rightarrow 1:1) as yellow oil (1.13 g, 7.15 mmol, 88%). **¹H NMR (300 MHz, CDCl₃):** δ = 7.57-7.53 (m, 2 H), 7.43-7.31 (m, 3 H), 5.88 (ddd, J = 17.6, 10.9, 1.8 Hz, 1 H), 5.71 (dd, J = 17.6, 2.3 Hz, 1 H), 5.59 (dd, J = 6.1, 1.3 Hz, 1 H), 5.54 (dd, J = 10.9, 2.3 Hz, 1 H), 2.30-2.23 (m, 1 H). **¹³C NMR (75 MHz, CDCl₃):** δ = 140.5, 128.6, 128.4, 127.8, 126.6, 116.5, 89.3, 85.3, 65.0. **IR (film):** 3062, 3031, 2875, 1634, 1600, 1492, 1451, 1409, 1268, 1189, 1151, 1037, 973, 921, 831, 727, 695, 633, 544. **MS (EI):** m/z (%) = 157 ([M⁺-H], 16), 129 (100), 115 (48), 77 (33), 51 (28). **HR-MS (EI):** m/z (%) = calculated for C₁₁H₁₀O: 158.0732; found: 158.0731.

Synthesis of 1-phenylpent-4-en-2-yn-1-one (**1m**)



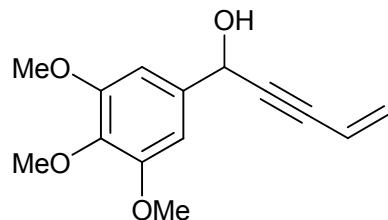
1-Phenylpent-4-en-2-yn-1-ol (1.11 g, 7.02 mmol, 1 eq.) was dissolved in dichloromethane (150 mL) at 0 °C and Dess-Martin periodinane (7.44 g, 17.5 mmol, 2.50 eq.) was added. The reaction mixture was stirred at room temperature for 1.5 h and then the solvent was removed under reduced pressure. Sodium bicarbonate solution was added and then extracted with diethyl ether, dried over magnesium sulfate, the solvent removed and the crude product purified by column chromatography with *n*-pentane/diethyl ether (8:1) as eluent to give the title compound as slightly yellow oil (870 mg, 5.57 mmol, 79%). ¹H NMR (300 MHz, CDCl₃): δ = 8.15 (dd, *J* = 8.4, 1.4 Hz, 2 H), 7.62 (tt, *J* = 7.4, 1.4 Hz, 1 H), 7.53-7.46 (m, 2 H), 6.07 (d, *J* = 5.8 Hz, 1 H), 6.06 (d, *J* = 7.4 Hz, 1 H), 5.88 (dd, *J* = 7.4, 5.8 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 177.9, 136.7, 134.1, 133.1, 129.6, 128.6, 115.3, 91.2, 87.0. The analytical data are in accordance with the literature.¹²

Synthesis of 1-(3,4,5-trimethoxyphenyl)prop-2-yn-1-ol



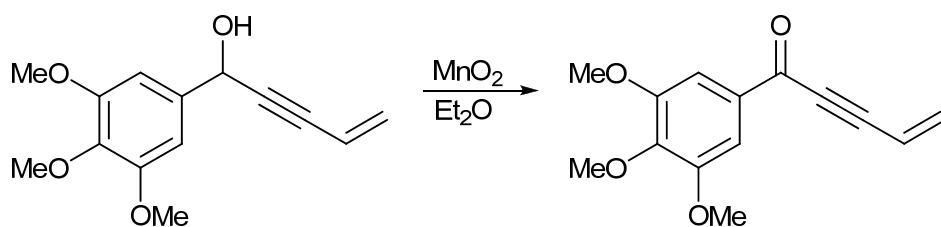
To a solution of 3,4,5-trimethoxybenzaldehyde (1.20 g, 6.12 mmol, 1 eq.) in tetrahydrofuran (5 mL) ethynylmagnesium bromide 0.5 M in THF (15 mL, 7.5 mmol, 1.23 eq.) was added dropwise at -78 °C. The solution was slowly warmed to room temperature and was stirred for 2 h. Saturated ammonium chloride solution was added and extracted with diethyl ether. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The title compound was obtained as slightly yellow oil (1.33 g, 6.00 mmol, 98%). ¹H NMR (300 MHz, CDCl₃): δ = 6.77 (s, 2 H), 5.39 (bs, 1 H), 3.86 (s, 6 H), 3.82 (s, 3 H), 2.67 (d, *J* = 2.2 Hz, 1 H), 2.58 (bs, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 153.3, 138.0, 135.7, 103.6, 83.4, 74.7, 64.4, 60.8, 56.1. The analytical data are in accordance with the literature.¹³

Synthesis of 1-(3,4,5-trimethoxyphenyl)pent-4-en-2-yn-1-ol



The title compound was prepared according to GP1 using (1-(3,4,5-trimethoxyphenyl)prop-2-yn-1-ol (1.33 g, 6.00 mmol, 1 eq.) and vinyl bromide (1.25 eq.) and was obtained after column chromatography with *n*-pentane/diethyl ether (2:1 → 1:1 → 1:2) as orange oil (1.41 g, 5.70 mmol, 95%). **¹H NMR (300 MHz, CDCl₃)**: δ = 6.77 (s, 2 H), 5.87 (ddd, *J* = 17.6, 11.0, 1.7 Hz, 1 H), 5.70 (dd, *J* = 17.5, 2.2 Hz, 1 H), 5.54 (dd, *J* = 10.9, 2.5 Hz, 1 H), 5.54-5.50 (m, 1 H), 3.88 (s, 6 H), 3.84 (s, 3 H), 2.42-2.29 (m, 1 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 153.4, 138.0, 136.2, 127.9, 116.5, 103.7, 89.1, 85.3, 65.1, 60.8, 56.1. **IR (film)**: 2939, 2836, 1593, 1503, 1458, 1418, 1328, 1231, 1121, 1043, 1000, 923, 843, 778, 733, 701, 528. **MS (EI)**: *m/z* (%) = 248 ([M⁺], 84), 196 (24), 169 (32), 115 (31), 79 (100), 51 (38). **HR-MS (ESI+)**: *m/z* (%) = calculated for C₁₄H₁₆O₄+Na⁺: 271.0946; found: 271.0943.

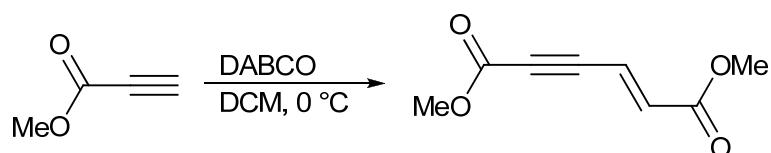
Synthesis of 1-(3,4,5-trimethoxyphenyl)pent-4-en-2-yn-1-one (1n)¹⁴



1-(3,4,5-Trimethoxyphenyl)pent-4-en-2-yn-1-ol (1.40 g, 5.64 mmol, 1 eq.) was dissolved in diethyl ether (100 mL) and manganese(IV) oxide (1.96 g, 22.6 mmol, 4.00 eq.) was added. The reaction mixture was stirred at room temperature for 30 min. Then another 4.00 eq. of manganese(IV) oxide were added. Then the mixture was stirred for another 60 min at room temperature and then filtered through celite. Evaporation of the solvent gave the title compound as pale orange solid (1.06 g, 4.30 mmol, 76%). **¹H NMR (300 MHz, CDCl₃)**: δ = 7.40 (s, 2 H), 6.05 (d, *J* = 7.3 Hz, 1 H), 6.04 (d, *J* = 5.9 Hz, 1 H), 5.87 (dd, *J* = 7.3, 5.9 Hz, 1 H), 3.93 (s, 3 H), 3.92 (s, 6 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 176.7, 153.1, 143.7, 132.4, 131.9, 115.3, 107.0, 90.9, 86.9, 61.0, 56.3. **IR (neat)**: 2941, 2837, 2198, 1635, 1581, 1499, 1459, 1413, 1327, 1219,

1181, 1123, 1065, 1001, 942, 860, 820, 772, 740, 677. **MS (EI):** m/z (%) = 246 ([M⁺], 100), 231 (34), 203 (20), 175 (23). **HR-MS (ESI+):** m/z (%) = calculated for C₁₄H₁₄O₄+Na⁺: 269.0790; found: 269.0785.

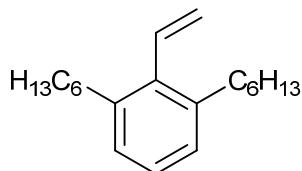
Synthesis of (*E*)-dimethyl hex-2-en-4-ynedioate (**1o**)¹⁵



To a stirred solution of methyl propiolate (900 μ L, 10.1 mmol, 1 eq.) in dichloromethane (20 mL) at 0 °C 1,4-diaza-bicyclo[2.2.2]octane (11.2 mg, 0.10 mmol, 0.01 eq.) was added and the mixture was stirred for 5 minutes. The solvent was evaporated and the residue was purified by column chromatography with *n*-pentane/diethyl ether (7:1) to give the desired compound as white solid (841 mg, 5.00 mmol, 99%). **¹H NMR (300 MHz, CDCl₃):** δ = 6.79 (d, J = 16.0 Hz, 1 H), 6.47 (d, J = 16.0 Hz, 1 H), 3.82 (s, 3 H), 3.79 (s, 3 H). **¹³C NMR (75 MHz, CDCl₃):** δ = 165.1, 153.5, 135.1, 121.7, 86.7, 81.8, 53.0, 52.3. **IR (neat):** 3071, 3025, 2960, 2853, 2224, 2193, 1711, 1618, 1437, 1253, 1166, 1097, 996, 963, 872, 830, 745, 718, 583, 496, 434. **HR-MS (EI):** m/z (%) = calculated for C₈H₈O₄: 168.0423; found: 168.0422.

Synthesis of 2,6-disubstituted styrenes

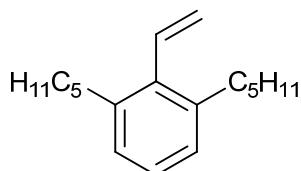
Synthesis of 1,3-dihexyl-2-vinylbenzene (**2a**)



The title compound was prepared according to GP2 using dec-1-en-3-yne (68.1 mg, 0.5 mmol) and was obtained after column chromatography with *n*-pentane as colorless oil (50.3 mg, 0.37 mmol, 74%). In this case 10 mol% cobalt catalyst and 20 mol% zinc powder and zinc iodide were applied. Reaction time: 24 h. **¹H NMR (300 MHz, CDCl₃):** δ = 7.13 (dd, J = 8.5, 6.4 Hz, 1 H), 7.06-7.02 (m, 2 H), 6.76 (dd, J = 17.9, 11.4 Hz, 1 H), 5.51 (dd, J = 11.4, 2.2 Hz, 1 H), 5.22 (dd, J = 17.9, 2.2 Hz, 1 H), 2.65-2.58 (m, 4 H), 1.59-1.48 (m, 4 H), 1.40-1.25 (m, 12 H), 0.90 (t, J

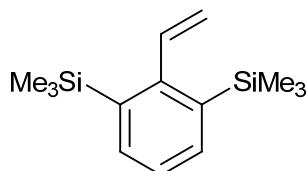
= 6.8 Hz, 6 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 140.7, 137.5, 135.0, 126.7, 126.5, 119.2, 33.8, 31.7, 31.1, 29.4, 22.6, 14.1. **IR (film)**: 3080, 3061, 2956, 2927, 2857, 1924, 1847, 1632, 1593, 1577, 1460, 1406, 1378, 1301, 1166, 1114, 1036, 992, 921, 788, 760, 725, 665, 581, 418. **MS (EI)**: *m/z (%)* = 272 ([M⁺], 27), 187 (31), 145 (93), 131 (100), 117 (36). **HR-MS (EI)**: *m/z (%)* = calculated for C₂₀H₃₂: 272.2504; found: 272.2493.

Synthesis of 1,3-dipentyl-2-vinylbenzene (2b)



The title compound was prepared according to GP2 using non-1-en-3-yne (122 mg, 1.0 mmol) and was obtained after column chromatography with *n*-pentane as colorless oil (81.8 mg, 0.33 mmol, 67%). In this case 5 mol% cobalt catalyst and 10 mol% zinc powder and zinc iodide were applied. Reaction time: 40 h. **¹H NMR (300 MHz, CDCl₃)**: δ = 7.13 (dd, *J* = 8.5, 6.4 Hz, 1 H), 7.06-7.02 (m, 2 H), 6.76 (dd, *J* = 17.9, 11.5 Hz, 1 H), 5.51 (dd, *J* = 11.4, 2.2 Hz, 1 H), 5.23 (dd, *J* = 17.9, 2.2 Hz, 1 H), 2.66-2.58 (m, 4 H), 1.60-1.50 (m, 4 H), 1.38-1.29 (m, 8 H), 0.90 (t, *J* = 6.8 Hz, 6 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 140.7, 137.5, 135.0, 126.7, 126.5, 119.2, 33.8, 31.9, 30.8, 22.5, 14.0. **IR (film)**: 3080, 3061, 2957, 2928, 2859, 1924, 1852, 1632, 1577, 1460, 1406, 1378, 1301, 1166, 1111, 1036, 992, 922, 791, 759, 729, 666, 421. **MS (EI)**: *m/z (%)* = 244 ([M⁺], 41), 229 (19), 215 (29), 173 (46), 159 (44), 145 (58), 131 (100), 117 (44), 91 (23). **HR-MS (EI)**: *m/z (%)* = calculated for C₁₈H₂₈: 244.2190; found: 244.2191.

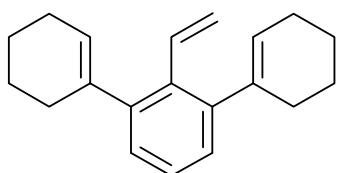
Synthesis of 1,3-bis(trimethylsilyl)-2-vinylbenzene (2c)



The title compound was prepared according to GP2 using (but-3-en-1-ynyl)trimethylsilane (124 mg, 1.0 mmol) and was obtained after column chromatography with *n*-pentane as white solid (37.5 mg, 0.15 mmol, 30%). In this case 10 mol% cobalt catalyst and 20 mol% zinc powder and zinc iodide were applied. Reaction time: 140 h. **¹H NMR (300 MHz, CDCl₃)**: δ = 7.56 (d, *J*

= 7.4 Hz, 2 H), 7.27 (t, J = 7.5 Hz, 1 H), 7.14 (dd, J = 17.7, 11.2 Hz, 1 H), 5.48 (dd, J = 11.2, 2.1 Hz, 1 H), 5.21 (dd, J = 17.7, 2.1 Hz, 1 H), 0.30 (s, 18 H). **^{13}C NMR (75 MHz, CDCl_3):** δ = 152.8, 141.0, 137.8, 135.1, 125.4, 120.4, 0.8. **IR (film):** 3042, 2952, 2897, 1550, 1410, 1368, 1244, 1201, 1150, 1120, 1078, 992, 930, 827, 742, 684, 617, 412. **MS (EI):** m/z (%) = 248 ([M^+], 6), 233 (100), 215 (21), 159 (18), 145 (22), 73 (80). **HR-MS (EI):** m/z (%) = calculated for $\text{C}_{14}\text{H}_{24}\text{Si}_2$: 248.1417; found: 248.1410.

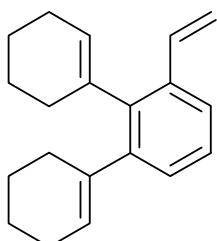
Synthesis of 1,3-dicyclohexenyl-2-vinylbenzene (2d)



The title compound was prepared according to GP2 using 1-(but-3-en-1-ynyl)cyclohex-1-ene (66.1 mg, 0.5 mmol) and was obtained after column chromatography with *n*-pentane as colorless oil (12.8 mg, 0.048 mmol, 19%). In this case 5 mol% cobalt catalyst and 10 mol% zinc powder and zinc iodide were applied. Reaction time: 48 h. **^1H NMR (300 MHz, CDCl_3):** δ = 7.12 (dd, J = 8.1, 6.9 Hz, 1 H), 6.99 (d, J = 7.4 Hz, 2 H), 6.74 (dd, J = 17.9, 11.6 Hz, 1 H), 5.63-5.59 (m, 2 H), 5.58 (dd, J = 17.9, 2.1 Hz, 1 H), 5.26 (dd, J = 11.6, 2.1 Hz, 1 H), 2.22-2.12 (m, 8 H), 1.74-1.62 (m, 8 H). **^{13}C NMR (75 MHz, CDCl_3):** δ = 144.1, 139.8, 135.2, 133.1, 127.7, 126.5, 126.1, 117.6, 30.1, 25.5, 23.2, 22.1. **IR (film):** 3062, 2956, 2903, 2867, 1593, 1470, 1426, 1397, 1361, 1307, 1247, 1202, 1139, 1026, 992, 903, 873, 813, 754, 716, 650, 587. **MS (EI):** m/z (%) = 264 ([M^+], 51), 221 (61), 207 (100), 179 (48), 165 (70). **HR-MS (EI):** m/z (%) = calculated for $\text{C}_{20}\text{H}_{24}$: 264.1878; found: 264.1883.

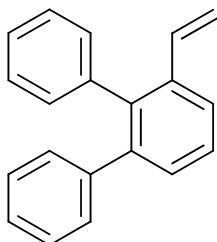
Synthesis of 2,3-disubstituted styrenes

Synthesis of 1,2-dicyclohexenyl-3-vinylbenzene (3a)



The title compound was prepared according to GP3 using 1-(but-3-en-1-ynyl)cyclohex-1-ene (132 mg, 1.0 mmol) and was obtained after column chromatography with *n*-pentane as white solid (51.6 mg, 0.20 mmol, 39%). Reaction time: 220 h. **1H NMR (300 MHz, CDCl₃)**: δ = 7.46 (dd, *J* = 7.8, 1.0 Hz, 1 H), 7.17 (t, *J* = 7.7 Hz, 1 H), 7.04 (dd, *J* = 7.5, 1.2 Hz, 1 H), 6.89 (dd, *J* = 17.6, 11.0 Hz, 1 H), 5.64 (dd, *J* = 17.6, 1.3 Hz, 1 H), 5.56-5.46 (m, 2 H), 5.19 (dd, *J* = 11.0, 1.3 Hz, 1 H), 2.35-2.02 (m, 8 H), 1.78-1.58 (m, 8 H). **13C NMR (75 MHz, CDCl₃)**: δ = 144.1, 141.5, 139.0, 136.4, 136.1, 135.5, 128.0, 127.5, 126.3, 125.8, 123.2, 113.6, 30.9, 30.8, 25.6, 25.5, 23.3, 23.1, 22.2. **IR (neat)**: 2926, 2855, 2200, 1444, 914, 804, 756. **MS (EI)**: *m/z* (%) = 264 ([M⁺], 17), 221 (31), 207 (100), 179 (38), 165 (68), 152 (32). **HR-MS (EI)**: *m/z* (%) = calculated for C₂₀H₂₄: 264.1878; found: 264.1867.

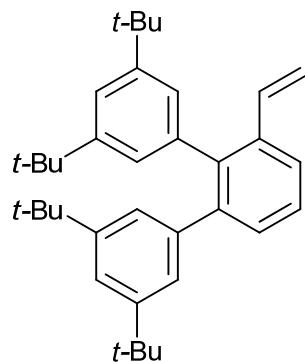
Synthesis of 1,2-diphenyl-3-vinylbenzene (6)



The title compound was prepared according to GP3 using (but-3-en-1-ynyl)benzene (128 mg, 1.0 mmol) and was obtained after column chromatography with *n*-pentane and recrystallization from *n*-pentane as pale yellow solid (76.9 mg, 0.30 mmol, 60%). Reaction time: 44 h. **1H NMR (300 MHz, CDCl₃)**: δ = 7.69 (dd, *J* = 7.7, 1.3 Hz, 1 H), 7.43 (t, *J* = 7.7 Hz, 1 H), 7.35 (dd, *J* = 7.6, 1.5 Hz, 1 H), 7.25-7.02 (m, 10 H), 6.55 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.70 (dd, *J* = 17.5, 1.4 Hz, 1 H), 5.15 (dd, *J* = 11.0, 1.3 Hz, 1 H). **13C NMR (75 MHz, CDCl₃)**: δ = 141.9, 141.7, 139.4, 139.1, 136.9, 136.2, 131.1, 129.8, 129.6, 127.5, 127.5, 127.4, 126.5, 126.1, 124.5, 114.7. **IR**:

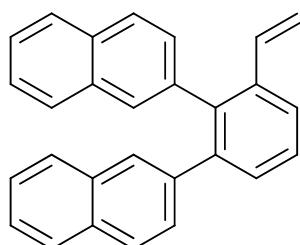
(KBr): 3064, 3021, 1617, 1575, 1492, 1459, 1438, 1408, 1175, 1079, 1068, 1028, 995, 918, 816, 772, 763, 748, 702, 614, 599, 564, 508, 460, 418. **MS (EI):** m/z (%) = 256 ([M⁺], 100), 239 (62), 215 (53), 178 (29), 120 (35). **HR-MS (EI):** m/z (%) = calculated for C₂₀H₁₆: 256.1252; found: 256.1238.

Synthesis of 1,2-di(3,5-di-*tert*-butylphenyl)-3-vinylbenzene (3b)



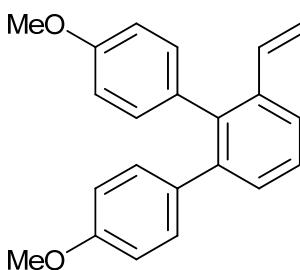
The title compound was prepared according to GP3 using 1,3-di-*tert*-butyl-5-(but-3-en-1-ynyl)benzene (120 mg, 0.5 mmol) and was obtained after column chromatography with *n*-pentane as white solid (103 mg, 0.21 mmol, 86%). In this case 15 mol% cobalt catalyst and 30 mol% zinc powder and zinc iodide were applied. Reaction time: 48 h. **¹H NMR (300 MHz, CDCl₃):** δ = 7.68 (dd, J = 5.4, 3.8 Hz, 1 H), 7.44-7.40 (m, 2 H) 7.16-7.14 (m, 2 H), 6.86 (dd, J = 3.2, 1.9 Hz, 4 H), 6.70 (dd, J = 17.5, 11.0 Hz, 1 H), 5.70 (dd, J = 17.5, 1.5 Hz, 1 H), 5.16 (dd, J = 11.0, 1.4 Hz, 1 H), 1.14 (s, 36 H). **¹³C NMR (75 MHz, CDCl₃):** δ = 149.8, 149.5, 143.2, 141.1, 140.5, 137.7, 137.0, 136.8, 129.5, 127.1, 126.3, 124.5, 124.4, 119.7, 119.6, 114.4, 34.6, 31.4, 31.4. **IR (KBr):** 3088, 3053, 3017, 2923, 2854, 2834, 1625, 1570, 1437, 1339, 1133, 991, 915, 841, 799, 762, 724, 676, 607, 550. **HR-MS (EI):** m/z (%) = calculated for C₃₆H₄₈: 480.3756; found: 480.3745.

Synthesis of 2-(2-(naphthalen-3-yl)-3-vinylphenyl)naphthalene (3c)



The title compound was prepared according to GP3 using 2-(but-3-en-1-ynyl)naphthalene (178 mg, 1.0 mmol) and was obtained after column chromatography with *n*-pentane and recrystallization from *n*-pentane/methanol as pale yellow solid (135 mg, 0.38 mmol, 76%). In this case 5 mol% cobalt catalyst and 10 mol% zinc powder and zinc iodide were applied. Reaction time: 26 h. **¹H NMR (300 MHz, CDCl₃)**: δ = 7.79-7.60 (m, 8 H), 7.51-7.36 (m, 7 H), 7.19 (dd, *J* = 8.5, 1.4 Hz, 1 H), 7.10 (dd, *J* = 8.5, 1.5 Hz, 1 H), 6.55 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.74 (dd, *J* = 17.5, 1.0 Hz, 1 H), 5.14 (dd, *J* = 11.0, 1.1 Hz, 1 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 141.8, 139.4, 139.2, 137.3, 136.6, 136.3, 133.1, 132.8, 132.0, 131.8, 130.2, 130.1, 129.3, 128.4, 128.2, 128.0, 127.9, 127.6, 127.6, 127.5, 127.1, 126.8, 125.9, 125.8, 125.6, 124.8, 114.8. **IR (neat)**: 3049, 2921, 2853, 1597, 1501, 1452, 1129, 989, 949, 908, 855, 812, 744, 531, 474, 403. **MS (EI)**: *m/z* (%) = 356 ([M⁺], 100), 339 (36), 326 (12), 265 (21), 228 (18), 170 (10). **HR-MS (EI)**: *m/z* (%) = calculated for C₂₈H₂₀: 356.1565; found: 356.1552.

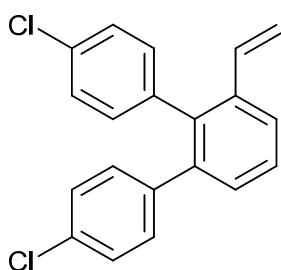
Synthesis of 1,2-di(4-methoxyphenyl)-3-vinylbenzene (3d)



The title compound was prepared according to GP3 using 1-(but-3-en-1-ynyl)-4-methoxybenzene (158 mg, 1.0 mmol) and was obtained after column chromatography with *n*-pentane/diethyl ether (10:1) as white solid (61.3 mg, 0.19 mmol, 39%). Reaction time: 48 h. **¹H NMR (300 MHz, CDCl₃)**: δ = 7.65 (dd, *J* = 7.6, 1.5 Hz, 1 H), 7.39 (7, *J* = 7.6 Hz, 1 H), 7.33 (dd, *J* = 7.6, 1.5 Hz, 1 H), 7.02-6.94 (m, 4 H), 6.78 (d, *J* = 8.7 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 6.57 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.68 (dd, *J* = 17.5, 1.3 Hz, 1 H), 5.15 (dd, *J* = 11.0, 1.3 Hz, 1 H), 3.80 (s, 3 H),

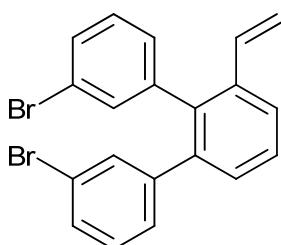
3.76 (s, 3 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 158.1, 157.9, 141.6, 139.0, 137.2, 136.5, 134.3, 132.2, 131.5, 130.8, 129.6, 127.2, 124.3, 114.4, 113.0, 55.1. **IR (neat)**: 3000, 2951, 2834, 1698, 1511, 1454, 1290, 1243, 1176, 1106, 1033, 995, 912, 826, 759, 560. **MS (EI)**: *m/z* (%) = 316 ([M⁺], 100), 285 (48), 253 (36), 239 (35). **HR-MS (ESI+)**: *m/z* (%) = calculated for C₂₂H₂₀O₂+H⁺: 317.1536; found: 317.1534.

Synthesis of 1,2-di(4-chlorophenyl)-3-vinylbenzene (3e)



The title compound was prepared according to GP3 using 1-(but-3-en-1-ynyl)-4-chlorobenzene (163 mg, 1.0 mmol) and was obtained after column chromatography with *n*-pentane as white solid (107 mg, 0.33 mmol, 66%). Reaction time: 18 h. **¹H NMR (300 MHz, CDCl₃)**: δ = 7.68 (dd, *J* = 7.8, 1.1 Hz, 1 H), 7.43 (t, *J* = 7.7 Hz, 1 H), 7.31 (dd, *J* = 7.6, 1.3 Hz, 1 H), 7.22 (d, *J* = 8.5 Hz, 2 H), 7.15 (d, *J* = 8.6 Hz, 2 H), 6.97 (d, *J* = 8.4 Hz, 4 H), 6.48 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.70 (dd, *J* = 17.5, 1.2 Hz, 1 H), 5.18 (dd, *J* = 11.0, 1.2 Hz, 1 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 140.5, 139.8, 137.9, 137.3, 137.1, 135.7, 132.8, 132.5, 132.3, 131.0, 129.5, 128.0, 127.9, 127.8, 125.1, 115.4. **IR (neat)**: 3058, 1910, 1587, 1488, 1448, 1391, 1260, 1174, 1086, 999, 922, 809, 750, 686, 609, 571, 477. **MS (EI)**: *m/z* (%) = 324 ([M⁺], 34), 289 (59), 254 (100), 126 (65). **HR-MS (EI)**: *m/z* (%) = calculated for C₂₀H₁₄Cl₂: 324.0473; found: 324.0474.

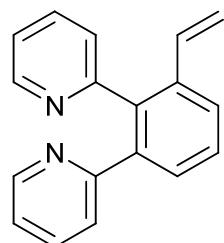
Synthesis of 1,2-di(3-bromophenyl)-3-vinylbenzene (3f)



The title compound was prepared according to GP3 using 1-(but-3-en-1-ynyl)-3-bromobenzene (104 mg, 0.5 mmol) and was obtained after column chromatography with *n*-pentane as colorless

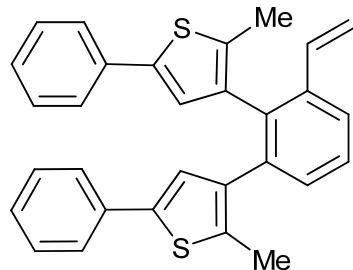
oil (67.0 mg, 0.16 mmol, 65%). Reaction time: 24 h. **¹H NMR (300 MHz, CDCl₃)**: δ = 7.68 (dd, *J* = 7.8, 1.1 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.36 (ddd, *J* = 8.0, 1.9, 1.1 Hz, 1 H), 7.33-7.22 (m, 4 H), 7.10 (t, *J* = 7.8 Hz, 1 H), 7.02 (t, *J* = 7.7 Hz, 1 H), 6.97-6.88 (m, 2 H), 6.49 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.71 (dd, *J* = 17.4, 1.2 Hz, 1 H), 5.20 (dd, *J* = 11.0, 1.2 Hz, 1 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 143.2, 140.9, 140.2, 137.6, 136.9, 135.5, 133.8, 132.6, 129.9, 129.6, 129.5, 129.4, 129.2, 129.1, 128.4, 128.0, 125.1, 121.8, 121.8, 115.6. **IR (film)**: 3059, 2955, 2922, 2863, 1590, 1557, 1450, 1398, 1289, 1254, 1099, 1068, 1022, 991, 912, 889, 815, 782, 755, 726, 696, 672, 618, 574, 434. **MS (EI)**: *m/z* (%) = 414 ([M⁺], 10), 335 (13), 254 (100), 239 (13), 226 (12). **HR-MS (EI)**: *m/z* (%) = calculated for C₂₀H₁₄Br₂: 411.9462; found: 411.9455.

Synthesis of 2-(2-(pyridin-2-yl)-6-vinylphenyl)pyridine (3g)



The title compound was prepared according to GP3 using 2-(but-3-en-1-ynyl)pyridine (129 mg, 1.0 mmol) and was obtained after column chromatography with *n*-pentane/diethyl ether/triethylamine (33:66:1) as pale brown solid (51.7 mg, 0.20 mmol, 40%). The product decomposes slowly under aerobic conditions. In this case 15 mol% cobalt catalyst and 30 mol% zinc powder and zinc iodide were applied. Reaction time: 26 h. **¹H NMR (300 MHz, CDCl₃)**: δ = 8.60 (d, *J* = 4.9 Hz, 1 H), 8.50 (d, *J* = 4.8 Hz, 1 H), 7.73 (dd, *J* = 7.7, 0.9 Hz, 1 H), 7.59 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.47 (dt, *J* = 7.7, 1.8 Hz, 1 H), 7.33 (ddd, *J* = 7.8, 7.7, 1.8 Hz, 1 H), 7.11 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1 H), 7.04-6.98 (m, 2 H), 6.86 (d, *J* = 7.9 Hz, 1 H), 6.51 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.70 (dd, *J* = 17.4, 1.2 Hz, 1 H), 5.16 (dd, *J* = 11.0, 1.1 Hz, 1 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 159.1, 158.5, 149.0, 148.8, 140.6, 138.0, 136.9, 135.6, 135.1, 129.4, 128.4, 126.3, 125.7, 124.8, 121.5, 121.1, 115.4. **IR (film)**: 3050, 3004, 1852, 1579, 1468, 1420, 1287, 1147, 1090, 1022, 987, 922, 828, 781, 750, 600, 549, 404. **MS (EI)**: *m/z* (%) = 257 ([M⁺-H], 100), 251 (9), 191 (11), 128 (20). **HR-MS (ESI+)**: *m/z* (%) = calculated for C₁₈H₁₄N₂+H⁺: 259.1230; found: 259.1228.

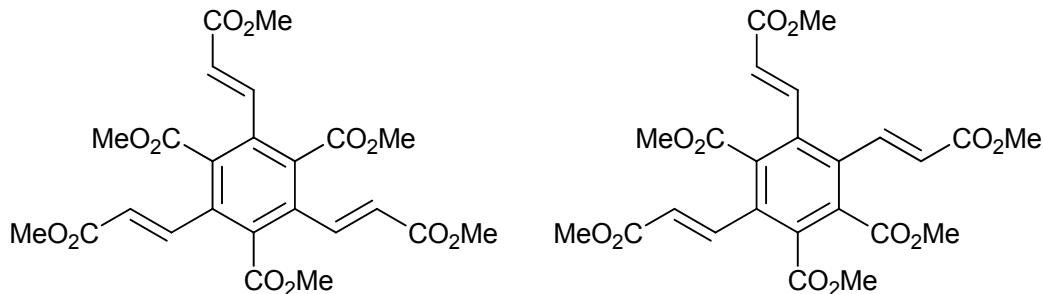
Synthesis of 2-methyl-3-(2-(2-methyl-5-phenylthiophen-3-yl)-6-vinylphenyl)-5-phenylthiophene (3h)



The title compound was prepared according to GP3 using 3-(but-3-en-1-ynyl)-2-methyl-5-phenylthiophene (112 mg, 0.5 mmol) and was obtained after column chromatography with *n*-pentane/diethyl ether (25:1) as yellow solid (61.8 mg, 0.14 mmol, 55%). In this case 20 mol% cobalt catalyst and 40 mol% zinc and zinc iodide were applied. The conversion was incomplete but with higher amounts of catalyst (up to 50 mol% cobalt catalyst) no higher yields were obtained. Reaction time: 96 h. **¹H NMR (300 MHz, CDCl₃)**: δ = 7.71 (dd, *J* = 7.7, 0.9 Hz, 1 H), 7.51-7.16 (m, 12 H), 6.96 (s, 1 H), 6.77 (s, 1 H), 6.70 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.77 (dd, *J* = 17.5, 1.0 Hz, 1 H), 5.23 (dd, *J* = 11.0, 1.0 Hz, 1 H), 2.32 (s, 3 H), 2.05 (s, 3 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 139.5, 139.0, 138.9, 137.7, 137.2, 136.6, 136.1, 135.7, 134.9, 134.7, 134.6, 129.8, 128.8, 128.8, 128.7, 127.5, 127.0, 126.9, 126.4, 125.9, 125.5, 125.3, 124.2, 114.9, 14.0, 13.9. **IR (neat)**: 3057, 3019, 2910, 1765, 1700, 1594, 1499, 1469, 1404, 1362, 1335, 1303, 1229, 1158, 1121, 1025, 993, 954, 908, 840, 813, 753, 687, 598, 538, 465. **HR-MS (APCI)**: *m/z* (%) = calculated for C₃₀H₂₄S₂+H⁺: 449.1392; found: 449.1390.

Synthesis of cyclotrimerisation products

Synthesis of trimethyl 2,4,6-tris((E)-2-(methoxycarbonyl)vinyl)benzene-1,3,5-tricarboxylate (**8a**) and trimethyl 3,5,6-tris((E)-2-(methoxycarbonyl)vinyl)benzene-1,2,4-tricarboxylate (**9a**)



Using GP2 (*E*)-dimethyl hex-2-en-4-yne dioate (75.0 mg, 0.45 mmol, 1 eq.) was stirred with 10 mol% cobalt catalyst and 20 mol% zinc powder and zinc iodide for 48 h at room temperature in dichloromethane. After passing the solution through a short pad of silica with diethyl ether and column chromatography with *n*-pentane/diethyl ether (1:1) as eluent, the symmetric isomer (**8a**) was obtained as white solid (10.3 mg, 0.020 mmol, 14%) and the unsymmetric (**9a**) as white solid (25.8 mg, 0.051 mmol, 34%).

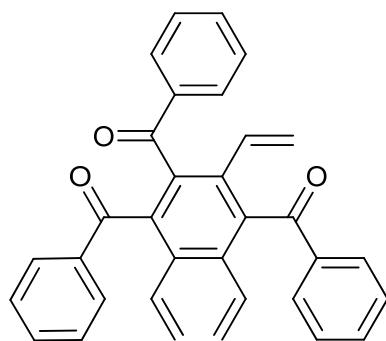
Yield of the isolated isomers in different solvents: The Reaction in acetonitrile and tetrahydrofuran were conducted with 1.0 mmol of the enyne, 10 mol% cobalt catalyst and 20 mol% zinc powder and zinc iodide.

solvent	amount of catalyst	time / h	8a	9a
DCM	10 mol%	48	14%	34%
THF	10 mol%	168	20%	50%
MeCN	10 mol%	26	13%	19%

Analytical data of the symmetric isomer (**8a**): **1H NMR** (300 MHz, CDCl₃): δ = 7.71 (d, *J* = 16.2 Hz, 3 H), 6.10 (d, *J* = 16.2 Hz, 3 H), 3.84 (s, 9 H), 3.79 (s, 9 H). **13C NMR** (75 MHz, CDCl₃): δ = 166.7, 165.5, 139.4, 133.4, 133.3, 126.0, 53.0, 52.1. **IR (neat)**: 2957, 1723, 1650, 1554, 1440, 1320, 1238, 1180, 1129, 1050, 980. **HR-MS (EI)**: *m/z* (%) = calculated for C₂₄H₂₄O₁₂: 504.1268; found: 504.1243.

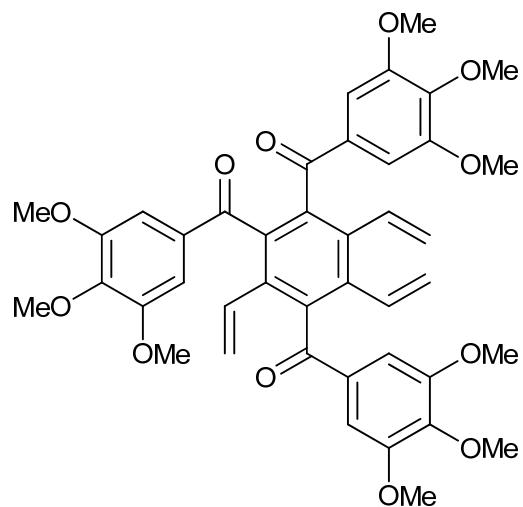
Analytical data of the unsymmetrical isomer (**9a**): **¹H NMR (300 MHz, CDCl₃)**: δ = 7.77 (d, *J* = 16.2 Hz, 1 H), 7.70 (d, *J* = 16.2 Hz, 1 H), 7.63 (d, *J* = 16.2 Hz, 1 H), 6.11 (d, *J* = 16.3 Hz, 1 H), 6.05 (d, *J* = 16.2 Hz, 1 H), 6.04 (d, *J* = 16.2 Hz, 1 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.81 (s, 3 H), 3.79 (s, 6 H), 3.78 (s, 3 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 166.9, 166.7, 166.1, 165.6, 165.5, 165.4, 139.8, 139.6, 139.6, 135.3, 134.8, 134.0, 133.7, 133.2, 131.7, 127.0, 126.9, 125.5, 53.1, 53.0, 52.1, 52.0. **IR (neat)**: 3002, 2954, 1718, 1645, 1436, 1327, 1273, 1172, 1068, 1032, 979, 938, 880, 739. **HR-MS (ESI+)**: *m/z* (%) = calculated for C₂₄H₂₄O₁₂+Na⁺: 527.1160; found: 527.1159.

Synthesis of (3,5,6-trivinylbenzene-1,2,4-triyl)tris(phenylmethanone) (**9b**)



Using GP4 1-phenylpent-4-en-2-yn-1-one (78.1 mg, 0.5 mmol, 1 eq.) was stirred with 5 mol% cobalt catalyst and 10 mol% zinc powder and zinc iodide for 75 h at room temperature in tetrahydrofuran. After passing the solution through a short pad of silica with diethyl ether and column chromatography with *n*-pentane/diethyl ether (3:1) as eluent, the title compound was obtained as single isomer as yellow oil (26.4 mg, 0.056 mmol, 34%). **¹H NMR (300 MHz, CDCl₃)**: δ = 7.81-7.30 (m, 15 H), 6.62-6.48 (m, 2 H), 6.31 (dd, *J* = 17.6, 11.5 Hz, 1 H), 5.44-5.18 (m, 5 H), 5.04 (dd, *J* = 11.5, 0.6 Hz, 1 H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 197.9, 197.6, 197.4, 139.2, 139.1, 137.6, 137.5, 137.4, 137.2, 135.8, 134.7, 133.8, 133.6, 133.3, 133.0, 132.6, 131.7, 129.7, 129.6, 129.5, 128.8, 128.4, 124.1, 123.5, 123.4. **IR (film)**: 3060, 2924, 1666, 1594, 1449, 1394, 1316, 1289, 1234, 1173, 965, 936, 733, 693. **HR-MS (ESI+)**: *m/z* (%) = calculated for C₃₃H₂₄O₃+H⁺: 469.1804; found: 469.1800.

Synthesis of (3,5,6-trivinylbenzene-1,2,4-triyl)tris((3,4,5-trimethoxyphenyl)methanone) (9c)



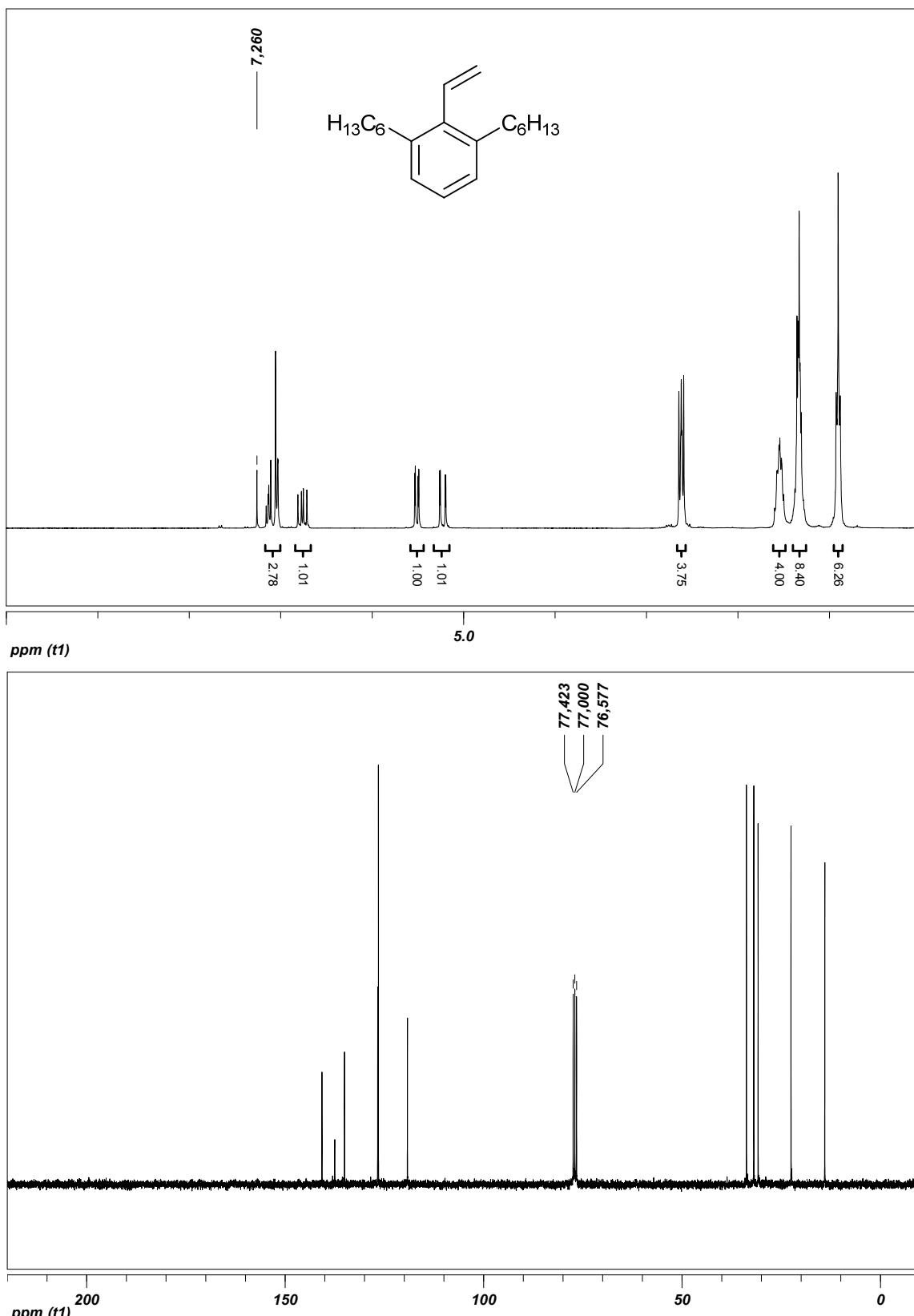
Using GP4 1-(3,4,5-trimethoxyphenyl)pent-4-en-2-yn-1-one (123 mg, 0.5 mmol, 1 eq.) was stirred with 5 mol% cobalt catalyst and 10 mol% zinc powder and zinc iodide for 22 h at room temperature in tetrahydrofuran. After passing the solution through a short pad of silica with diethyl ether/dichloromethane and column chromatography with *n*-pentane/dichloromethane/diethyl ether (2:2:1) as eluent, the title compound was obtained as single isomer as orange solid (40.4 mg, 0.055 mmol, 33%). **1H NMR (300 MHz, CDCl₃)**: δ = 7.03 (s, 2 H), 6.94 (s, 4 H), 6.61 (dd, *J* = 18.0, 11.4 Hz, 1 H), 6.60 (dd, *J* = 17.7, 11.6 Hz, 1 H), 6.37 (dd, *J* = 17.6, 11.5 Hz, 1 H), 5.45-5.29 (m, 4 H), 5.24 (dd, *J* = 17.6, 0.6 Hz, 1 H), 5.13 (dd, *J* = 11.5, 0.6 Hz, 1 H), 3.94 (s, 3 H), 3.89 (s, 3 H), 3.87 (s, 3 H), 3.84 (s, 6 H), 3.79 (s, 6 H), 3.78 (s, 6 H). **13C NMR (75 MHz, CDCl₃)**: δ = 196.6, 196.2, 195.8, 153.3, 152.9, 143.8, 143.3, 143.2, 139.0, 138.9, 137.3, 135.8, 134.7, 133.7, 132.9, 132.6, 132.5, 132.3, 132.2, 131.8, 123.4, 123.2, 107.8, 107.6, 107.5, 107.0, 61.0, 60.9, 56.5, 56.4, 56.3. **IR (neat)**: 2939, 2836, 1662, 1580, 1499, 1457, 1411, 1324, 1229, 1119, 995, 933, 853, 769, 732, 699, 523. **HR-MS (ESI+)**: *m/z* (%) = calculated for C₄₂H₄₂O₁₂+Na⁺: 761.2574; found: 761.2568.

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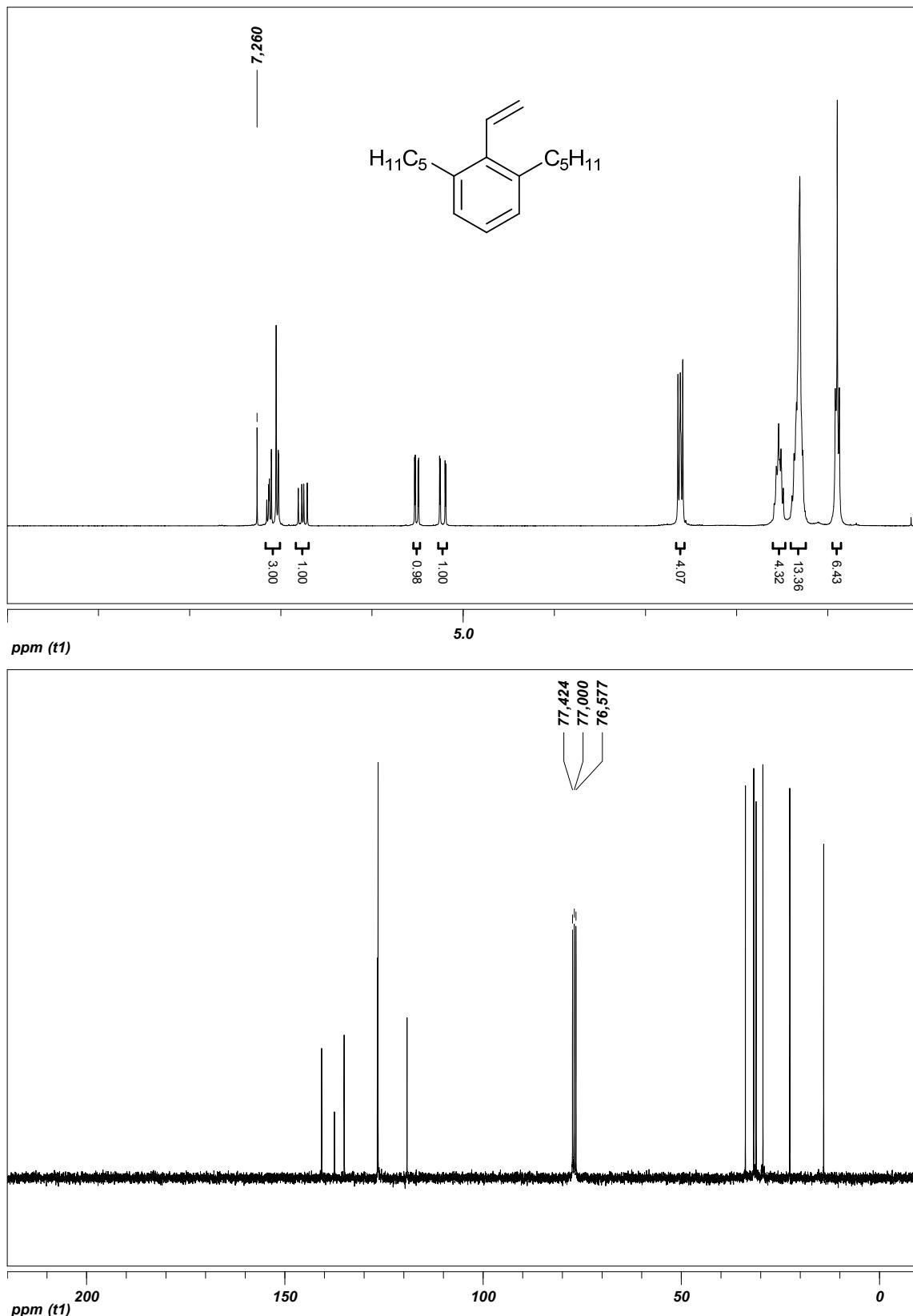
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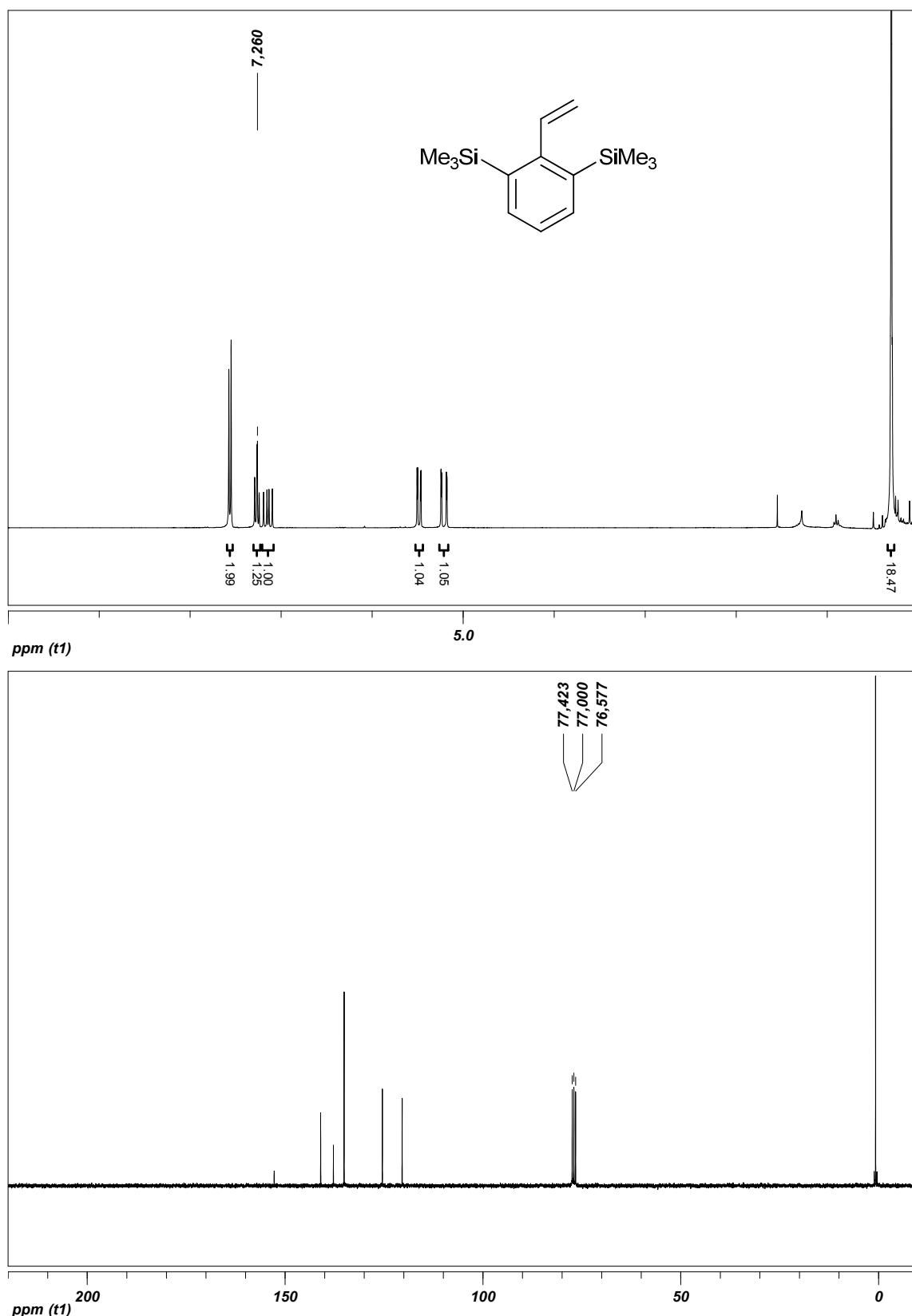
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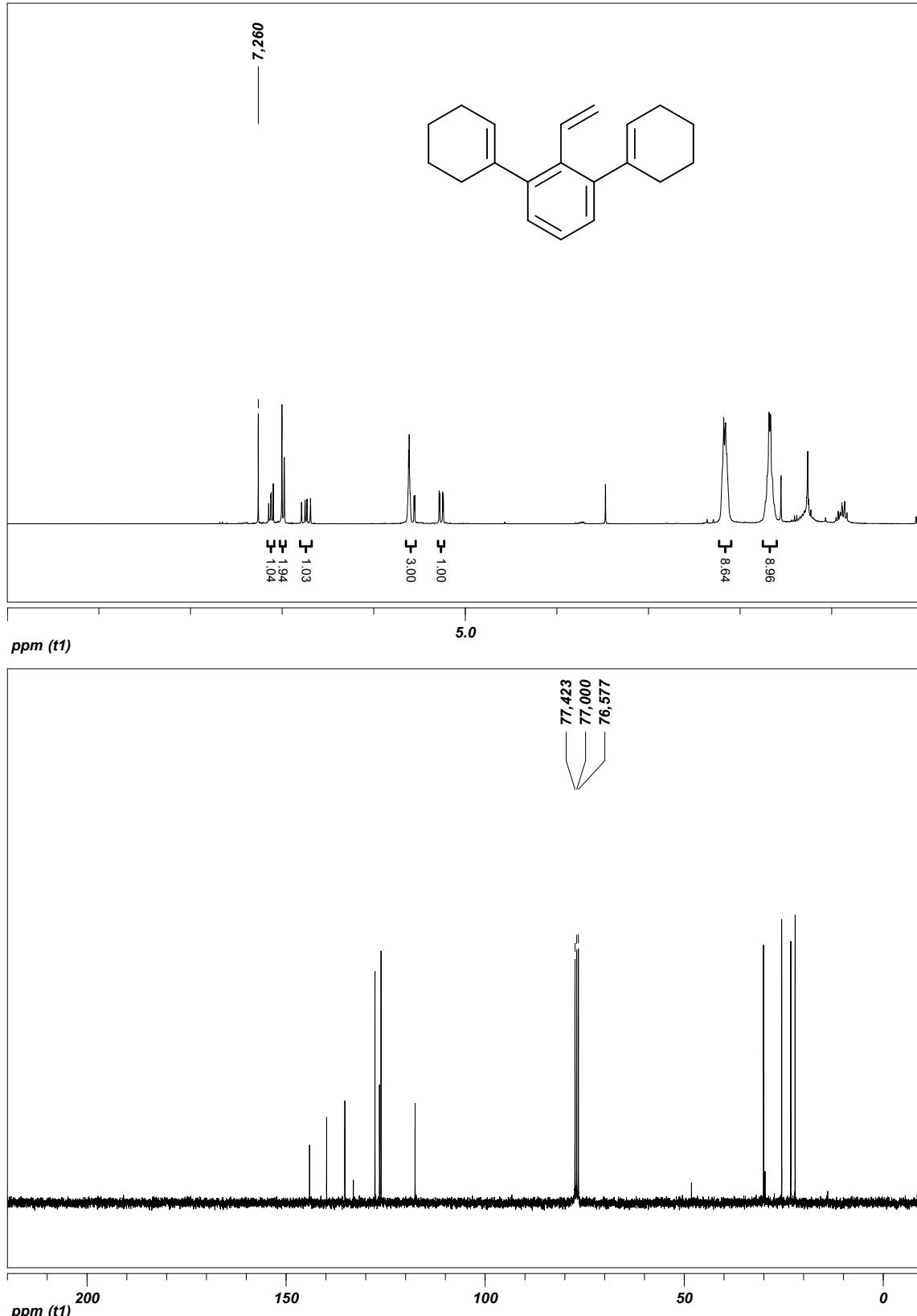
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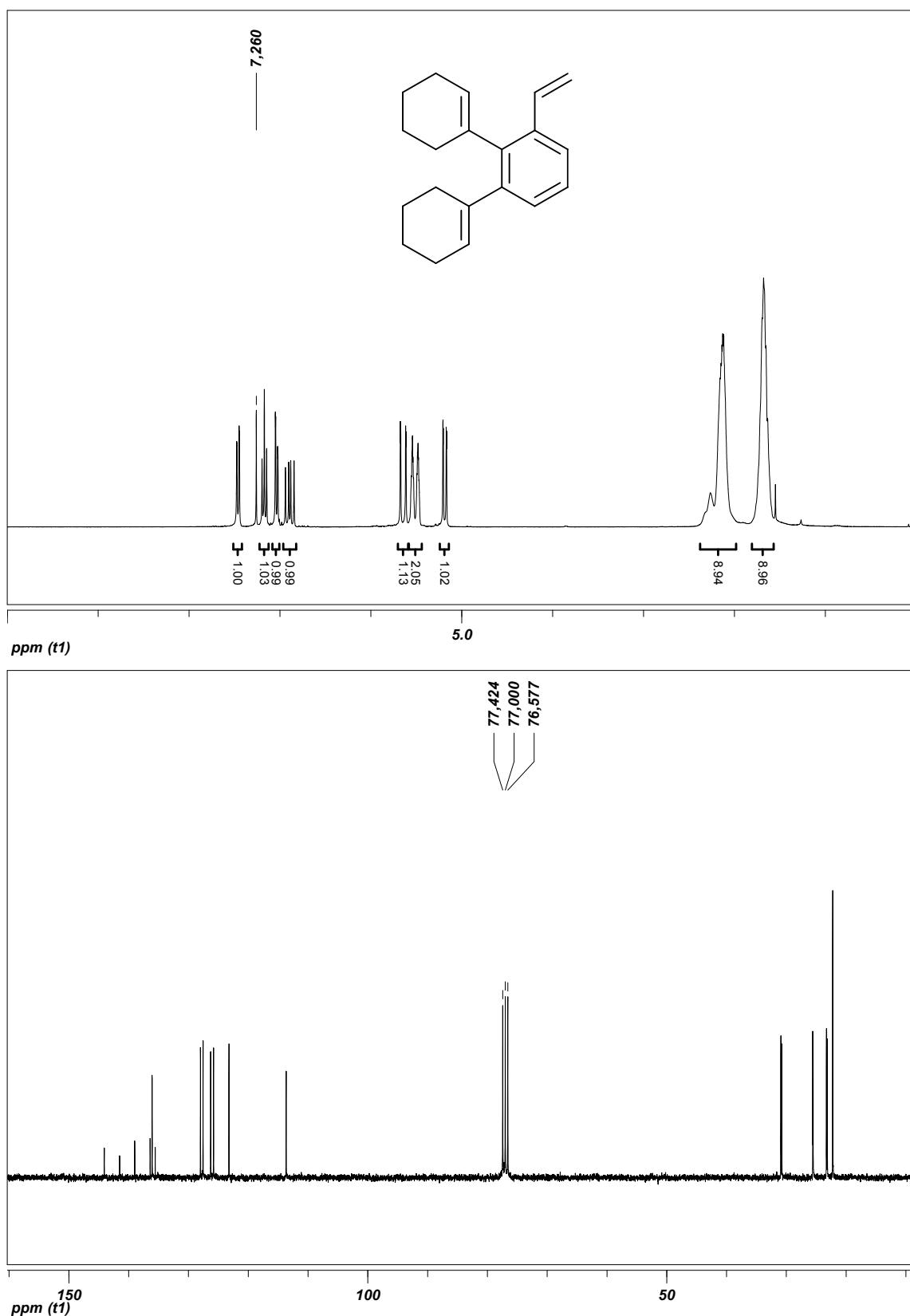
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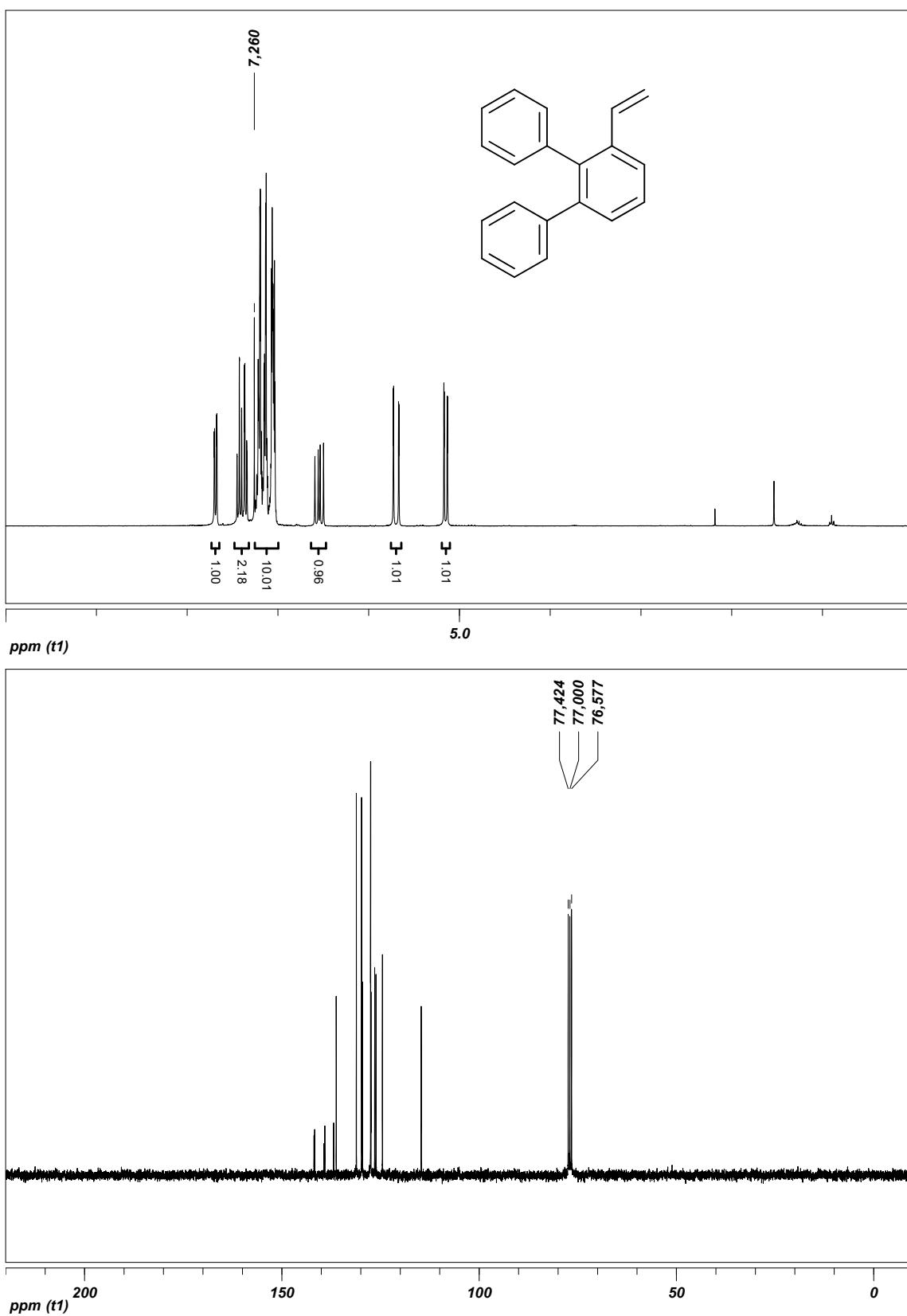
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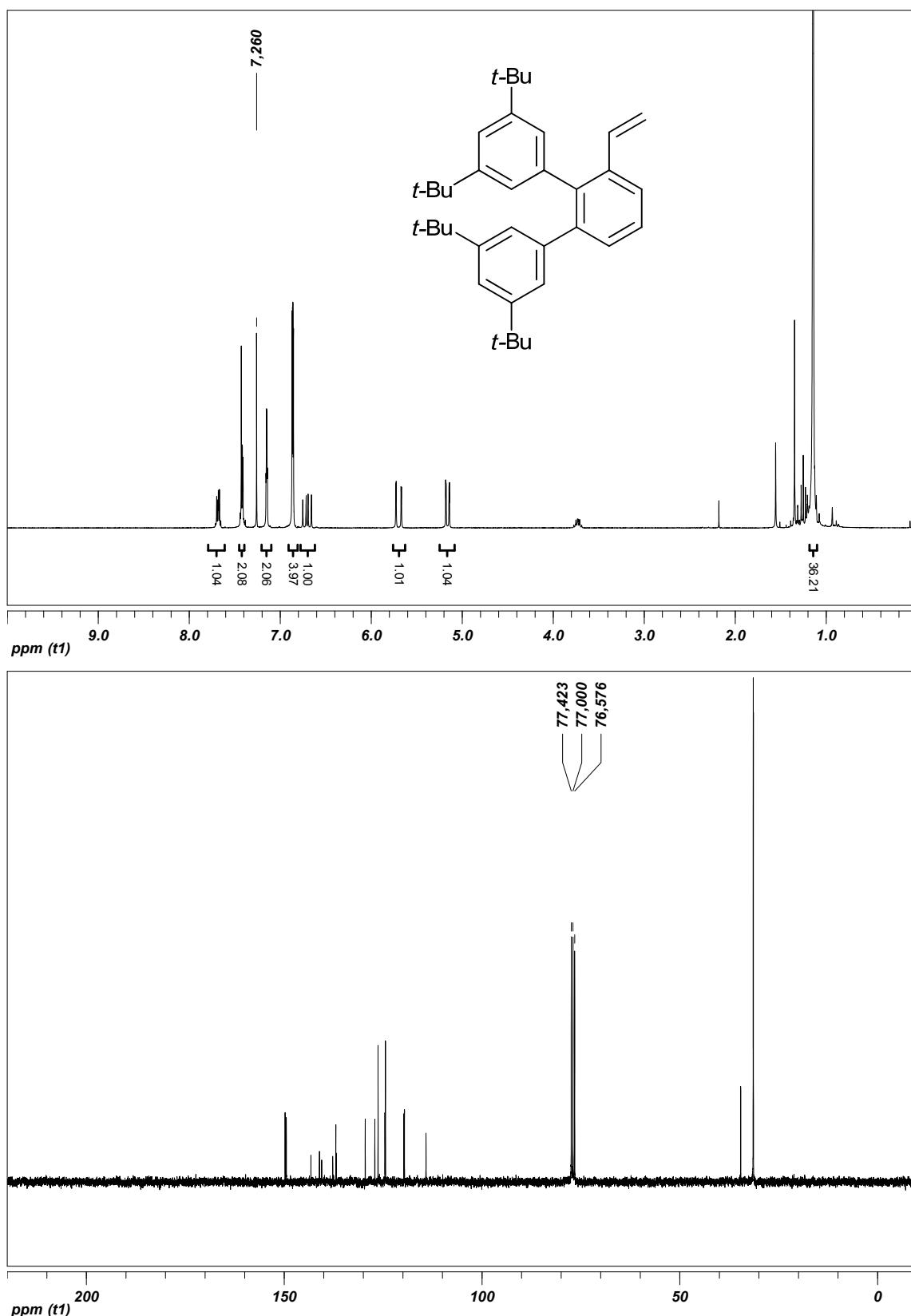
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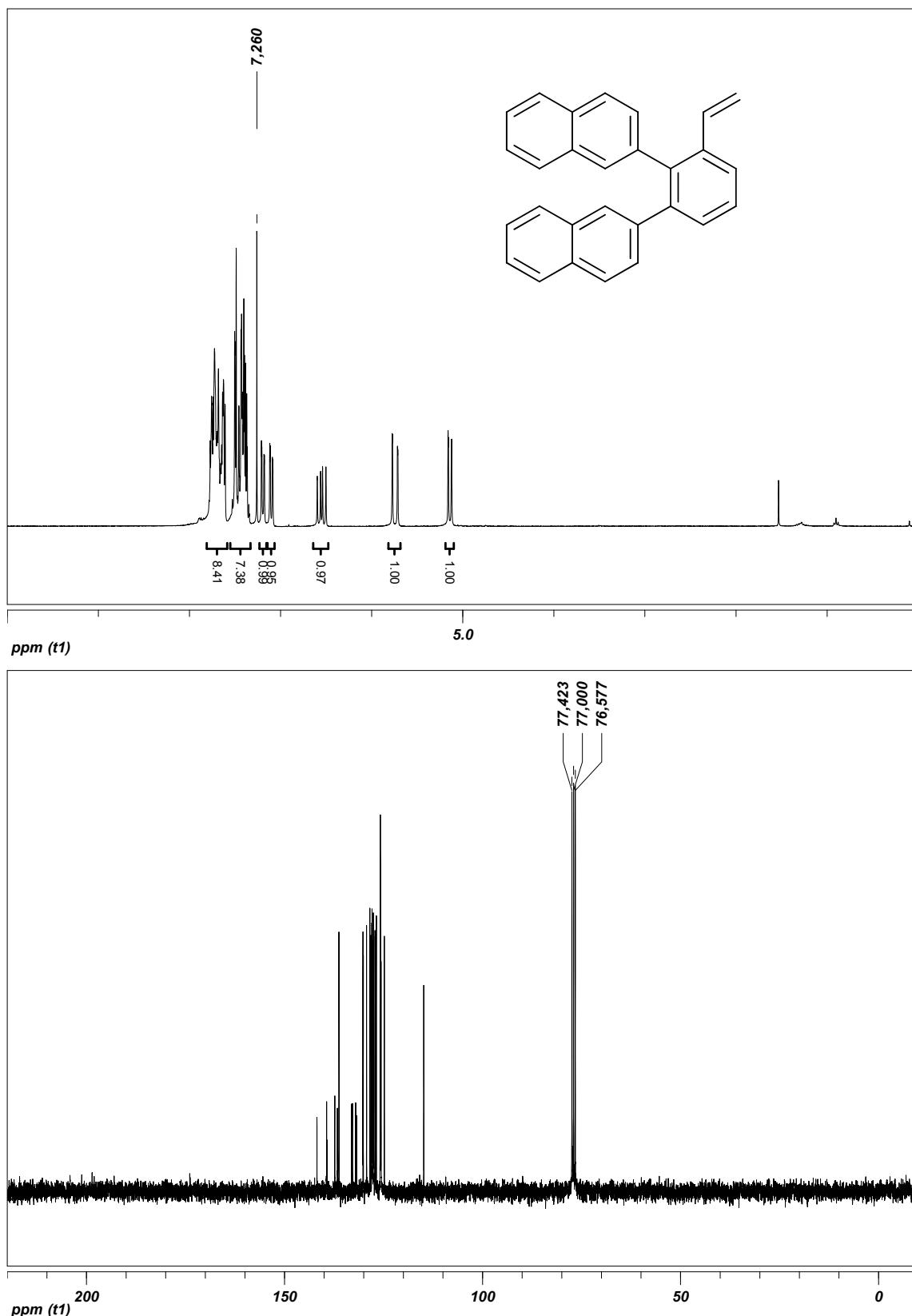
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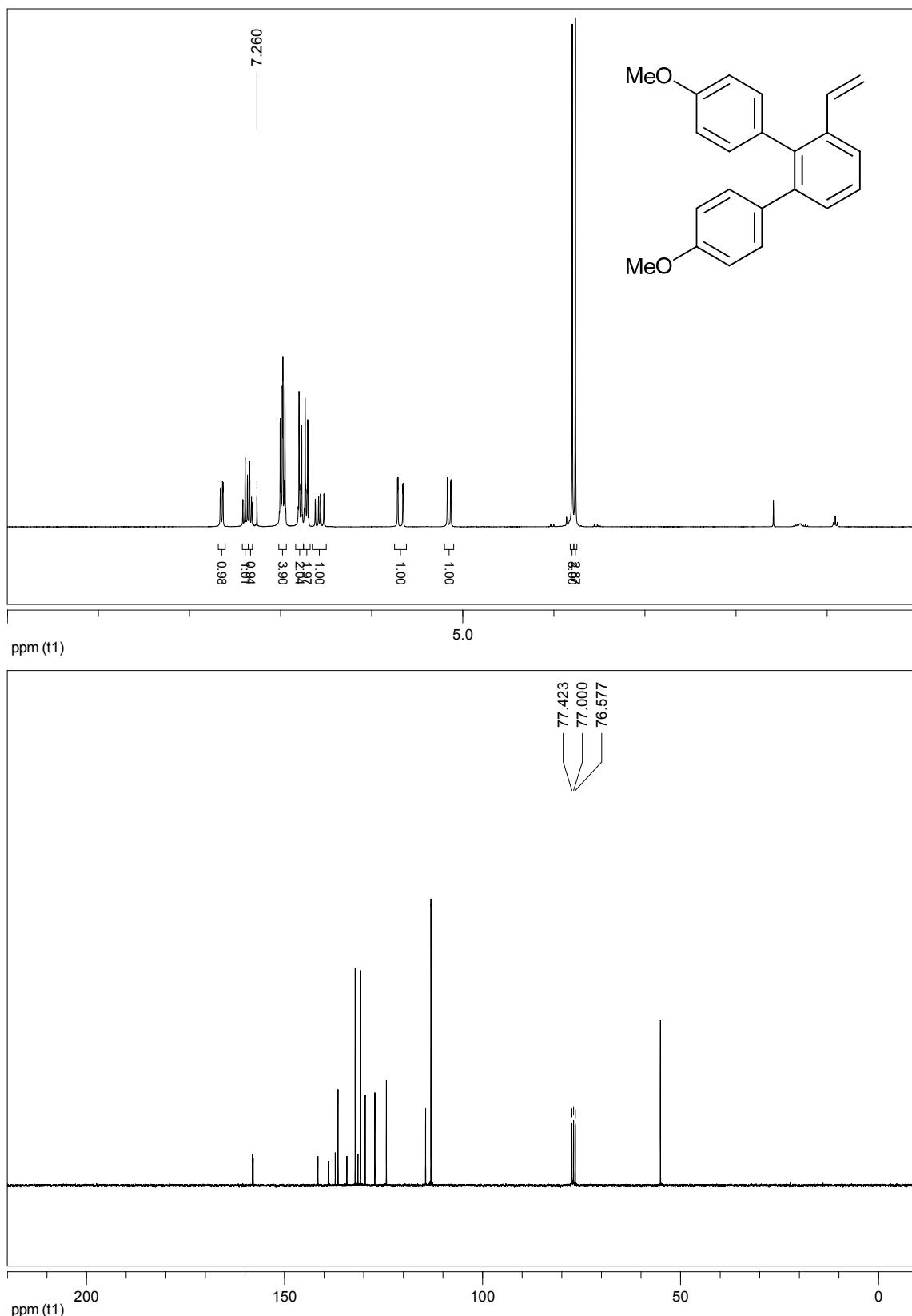
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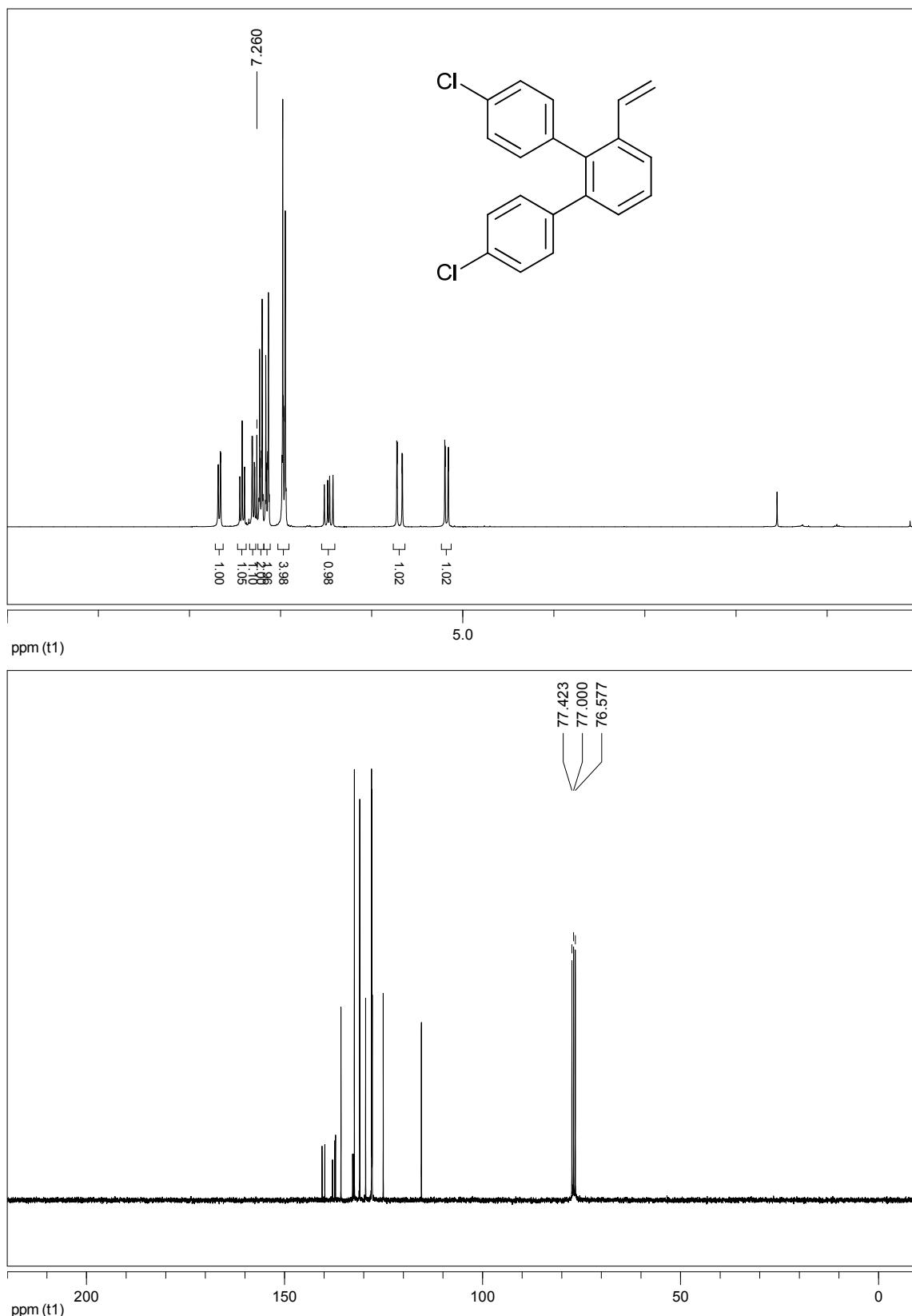
3c



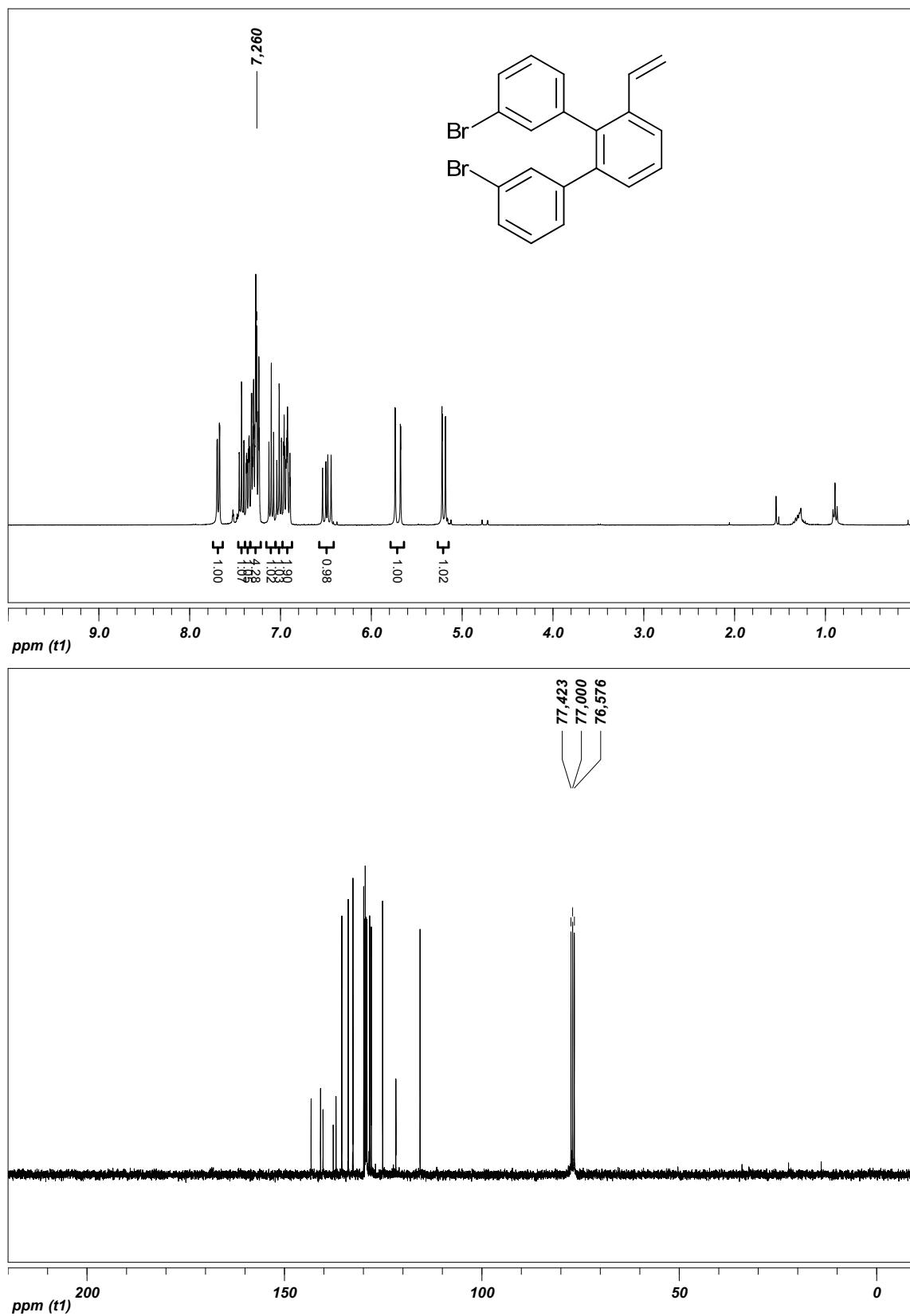
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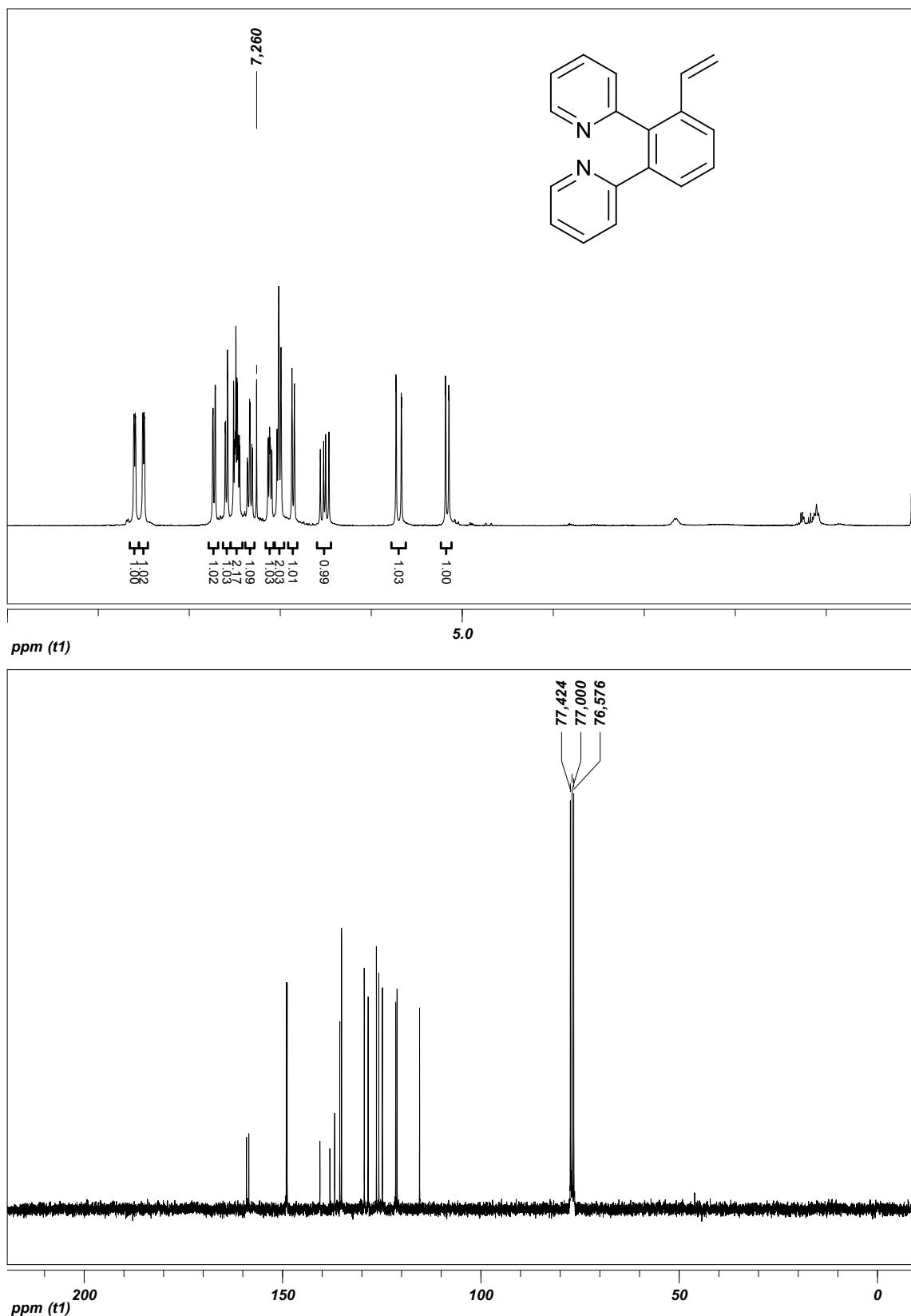
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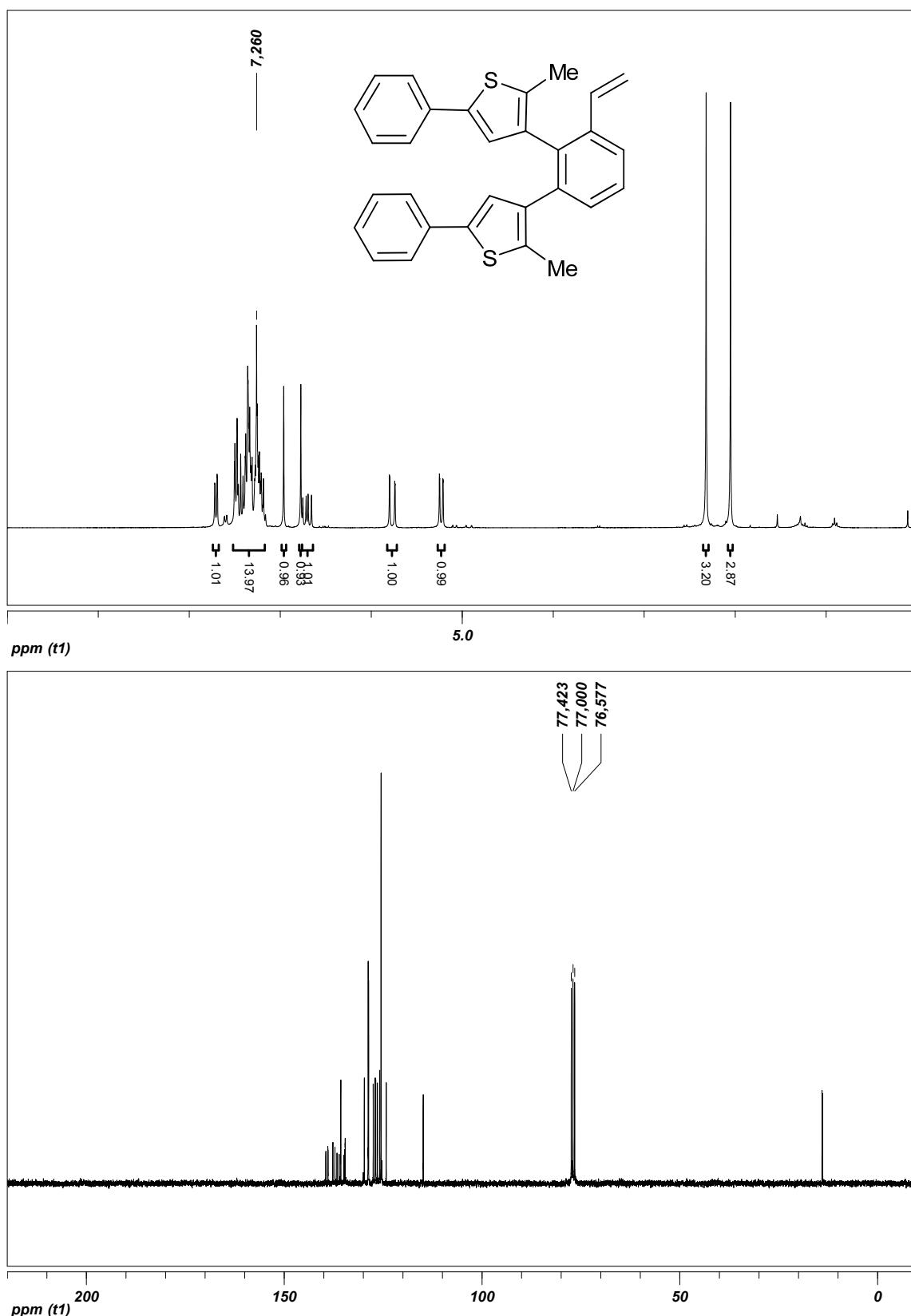
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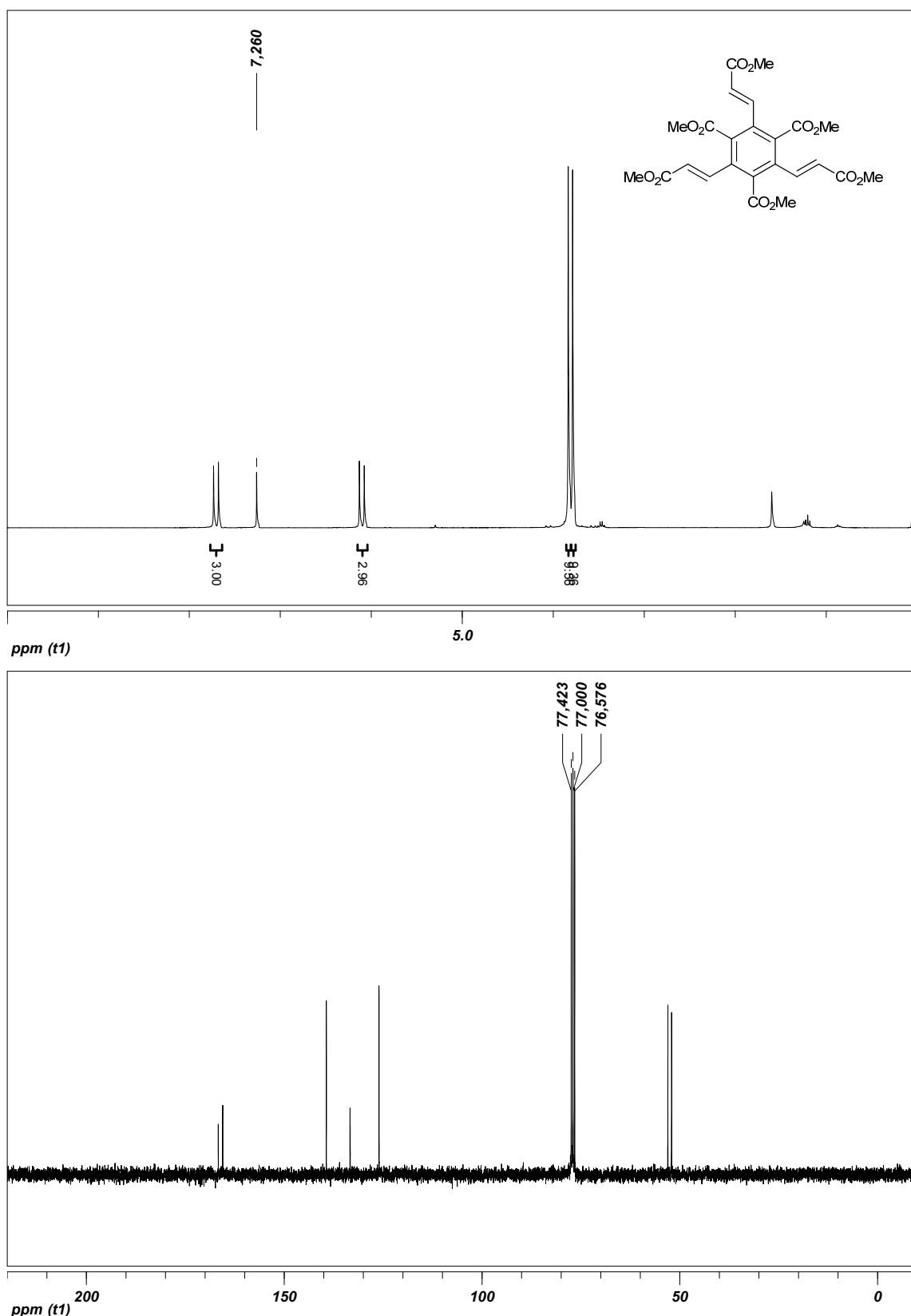
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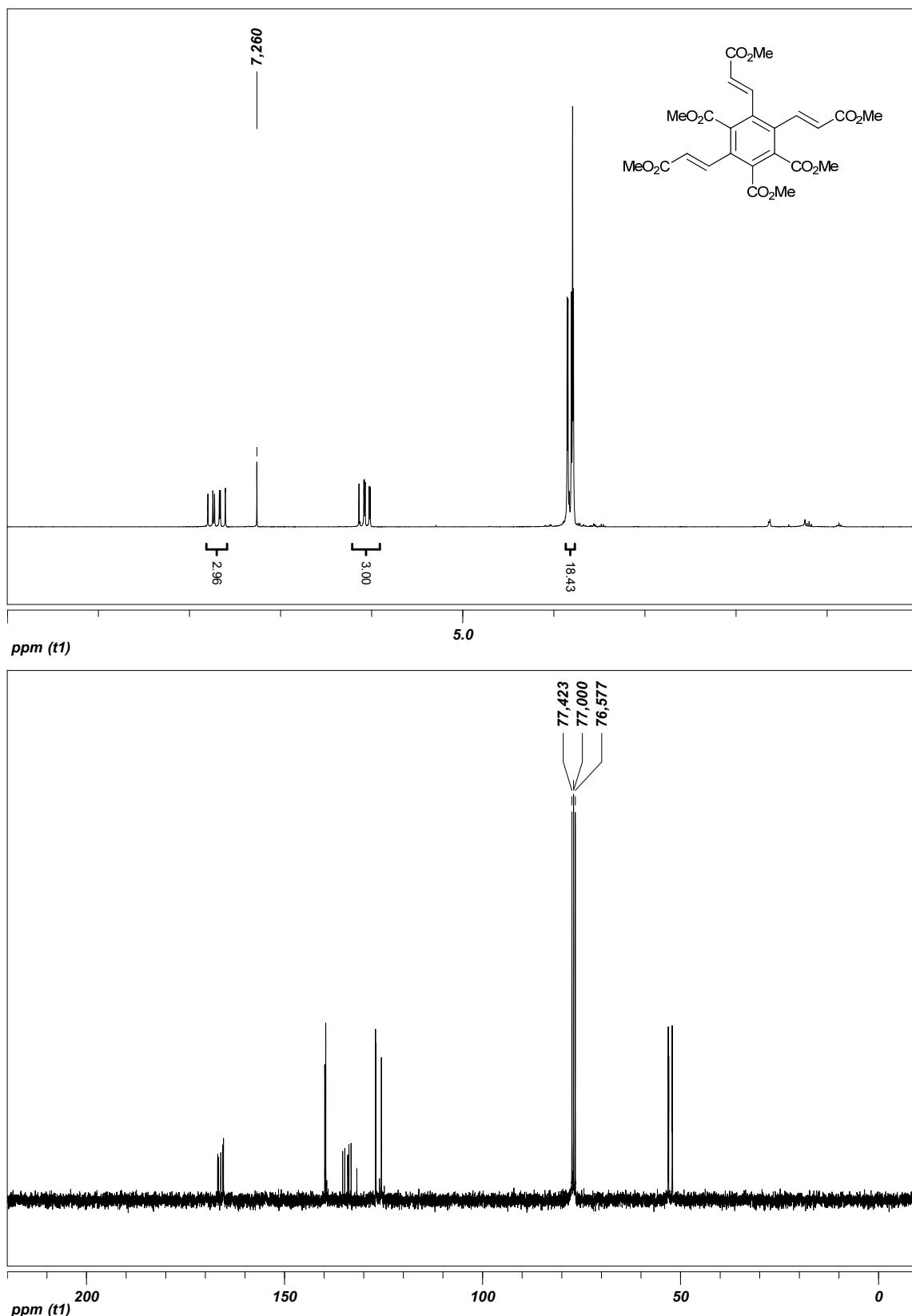
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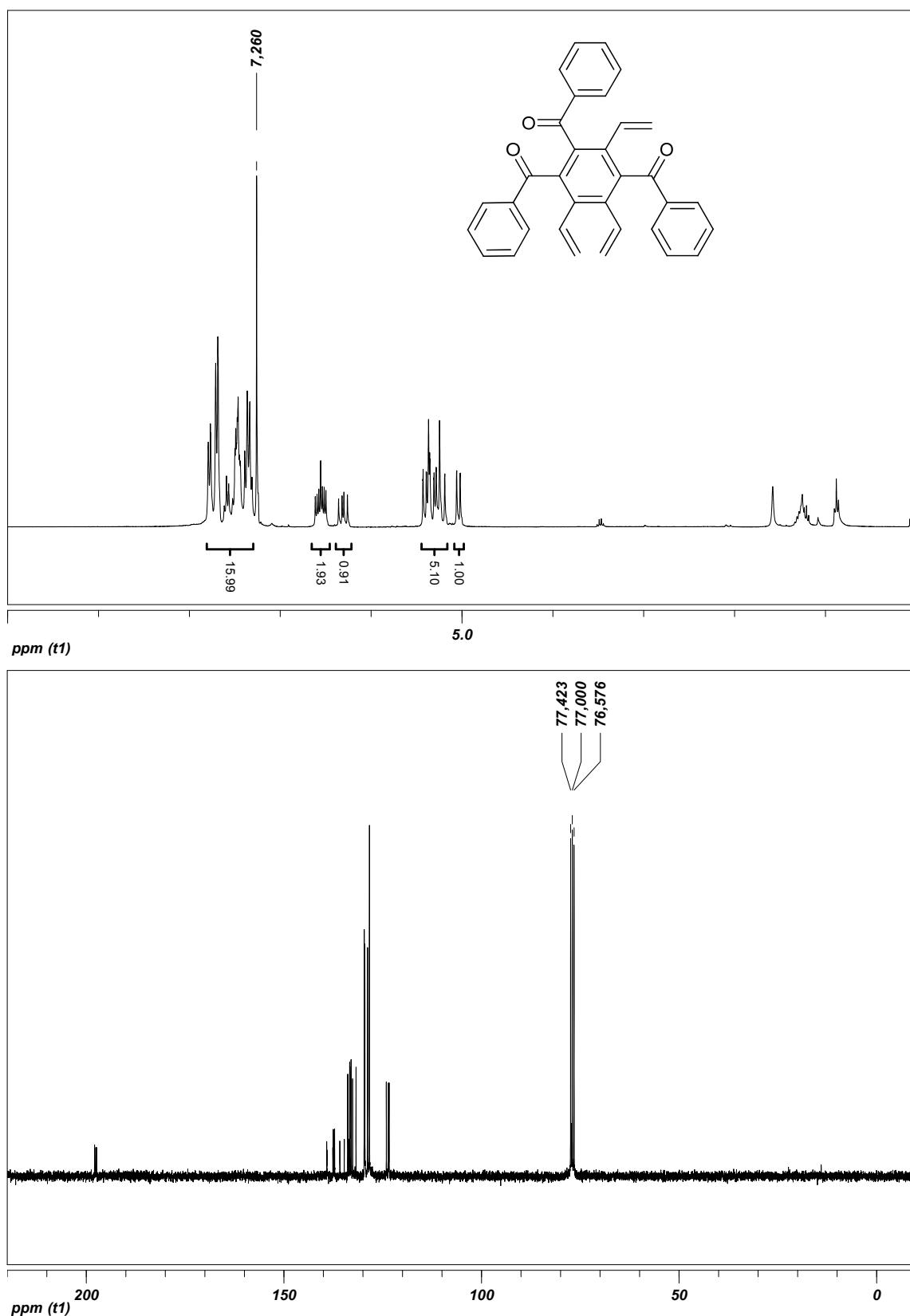
8a



9a



9b



9c

