Supporting Information for

Ti(O*i*Pr)$_4$/*n*BuLi: an attractive reagent system for [2+2+2] cyclotrimerisation reactions

Valentin A. Rassadin,[a] Emmanuel Nicolas,[b] Yvan Six[a]*

[a] Laboratoire de Synthèse Organique DCSO, UMR 7652 CNRS/École Polytechnique, 91128 Palaiseau Cedex (France). Fax: (+33) (0)1 6933 5972 ; E-mail: yvan.six@polytechnique.edu

[b] Laboratoire de Chimie Moléculaire LCM, UMR 9168 CNRS/École Polytechnique, 91128 Palaiseau Cedex (France).

Table of contents

1. General remarks

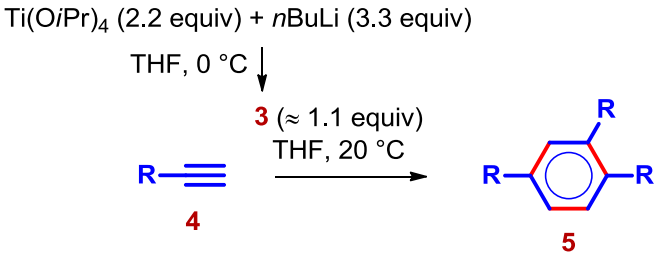
Titanium(IV) iso-propoxide (VERTEC® TIPT) was purchased from Alfa Aesar, distilled under reduced pressure (80 °C at 3 mbar) and stored under nitrogen for several months. Other commercial reagents were used as received, without purification. *n*BuLi was purchased from Sigma-Aldrich and titrated once a month according to a method described in the literature.[1] The commercially available compounds phenylacetylene, diphenylacetylene, 4-fluorophenylacetylene, 1-phenylpent-1-yn, hepta-1,6-diyne, octa-1,7-diyne, *p*-iodoanisole, 2-methylbenzaldehyde, 4-methylbenzaldehyde, pent-4-ynenitrile, hex-5-ynenitrile, propargyl bromide (80% solution in PhMe) and tosylamide were used as received. Tetrahydrofuran, diethyl ether, toluene and methanol for reactions were purified using a MB SPS-800 solvent purification system (MBRAUN). Petroleum ether (40−60 °C fraction, AnalaR Normapur®), EtOAc (AnalaR Normapur®), Et_2O (GPR Rectapur®), *n*-pentane (GPR Rectapur®) and CH_2Cl_2 (GPR Rectapur®) were purchased from VWR and used without purification. All the reactions were carried out under a stream of nitrogen. Concentration under reduced pressure was carried out using rotary evaporators at 40 °C.

Flash column chromatography was performed on Merck silica gel 60 (40–63 µm). NMR spectra were recorded with an AVANCE 400 Bruker spectrometer (^{1}H at 400.2 MHz, ^{13}C at 100.6 MHz). Chemical shifts δ are given in ppm, referenced to the peak of tetramethylsilane, defined at δ = 0.00 or the solvent peak [^{1}H NMR in $CDCl_3$: δ = 7.26 (residual $CHCl_3$ peak); ^{1}H NMR in DMSO-d_6: δ = 2.50 (residual DMSO-d_5 peak); ^{13}C NMR in $CDCl_3$: δ = 77.0; ^{13}C NMR in DMSO-d_6: δ = 39.5]. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, br = broad. Coupling constants *J* are given in Hz and are rounded to the closest multiple of 0.5. Infrared spectra were recorded with a Perkin-Elmer 2000 FT-IR spectrometer. Wavenumbers $\bar{\nu}_{max}$ are given in cm^{-1} and are rounded to the closest multiple of 5. Melting points were determined using a Stuart SMP40 apparatus. Low-resolution mass spectra were recorded on a Hewlett-Packard Quad GC-MS engine spectrometer *via* direct injection. High-resolution mass spectrometry was performed on a JEOL GC-mate II spectrometer.

1− W. G. Kofron, L. M. Baclawski, *J. Org. Chem.* **1976**, *41*, 1879–1880.

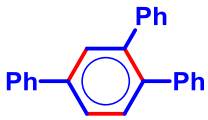
2. Experimental procedures

2.1. General procedure for the alkyne homocyclotrimerisation reactions (**GP1**)



*n*BuLi (2.0 M in hexanes, 3.3 mmol, 1.6 mL) was added slowly (5 min), at 0 °C, to a solution of Ti(O*i*Pr)$_4$ (2.2 mmol, 0.65 mL) in THF (8.0 mL). After 5 additional min of stirring at 0 °C, the reaction mixture was added dropwise to a solution of the terminal alkyne (1.0 mmol) in THF (5.0 mL), at 20 °C. After 20 min of stirring at the same temperature, 10% HCl aqueous solution (10 mL) was carefully added; the organic phase was separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure (P ≥ 25 mbar) to afford the crude product.

• The following [2+2+2] homocyclotrimerisation adducts were prepared according to **GP1**:

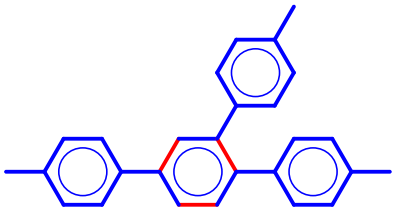


1,2,4-Triphenylbenzene (5a):[2] this product was isolated by flash column chromatography on silica gel (EtOAc/petroleum ether, gradient from 0 to 5%). Yield 86 mg (84%). Yellowish oil. R_f ≈ 0.1 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06–7.15 (m, 10 H, Ph), 7.25 (tt, *J* 7.5, 1.5, 1 H, Ph), 7.32–7.37 (m, 2 H, Ph), 7.40 (d,[3] *J* 8.0, 1 H, Ar), 7.52–7.59 (m, 4 H, Ar, Ph). ^{13}C NMR (101 MHz, $CDCl_3$): δ 126.1 ($C_{Ar}H$), 126.5 ($C_{Ph}H$), 126.6 ($C_{Ph}H$), 127.1 (2 C, $C_{Ph}H$), 127.4 ($C_{Ph}H$), 127.9 (2 C, $C_{Ph}H$), 127.9 (2 C, $C_{Ph}H$), 128.8 (2 C, $C_{Ph}H$), 129.4 ($C_{Ar}H$), 129.8 (2 C, $C_{Ph}H$), 129.9 (2 C, $C_{Ph}H$), 131.1 ($C_{Ar}H$), 139.5 (C_{Ar}), 140.3 (C_{Ar}), 140.5 (C_{Ar}), 141.0 (C_{Ar}), 141.1 (C_{Ar}), 141.4 (C_{Ar}).

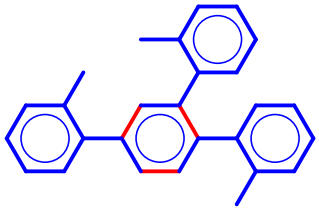
2− S. L. Kireev, V. A. Smit, B. I. Ugrak, O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.* **1991**, 2565–2571; *Russ. Chem. Bull.* **1991**, *40*, 2240–2246.

3− This signal is part of an AB system but is described as indicated for simplification purposes.

1,2,4-Tris(*p*-tolyl)benzene (5b):[4] this compound was isolated by flash column chromatography on silica gel (EtOAc/petroleum ether, gradient from 0 to 5%). Yield 86 mg (75%). Colourless oil. $R_f \approx 0.1$ (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 7.02–7.15 (m, 8 H, Tol[5]), 7.28 (br d,[6] *J* 8.0, 2 H, Tol), 7.48 (d,[3] *J* 8.0, 1 H, Ar), 7.57–7.66 (m, 4 H, Ar, Tol). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.1 (br, 3 C, CH_3), 125.7 ($C_{Ar}H$), 126.9 (2 C, $C_{Tol}H$), 128.6 (2 C, $C_{Tol}H$), 128.7 (2 C, $C_{Tol}H$), 129.2 ($C_{Ar}H$), 129.5 (2 C, $C_{Tol}H$), 129.67 (2 C, $C_{Tol}H$), 129.71 (2 C, $C_{Tol}H$), 131.1 ($C_{Ar}H$), 136.0 (C_{Ar}), 136.1 (C_{Ar}), 137.1 (C_{Ar}), 137.8 (C_{Ar}), 138.3 (C_{Ar}), 138.7 (C_{Ar}), 139.1 (C_{Ar}), 140.0 (C_{Ar}), 140.8 (C_{Ar}).



1,2,4-Tris(*o*-tolyl)benzene (5c):[7] this compound was isolated by flash column chromatography on silica gel (Et_2O/petroleum ether, gradient from 0 to 5%). Yield 79 mg (68%). Colourless oil. $R_f \approx 0.1$ (Et_2O/petroleum ether 5%). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 2.05–2.30 (m, 6 H, CH_3), 2.41 (s, 3 H, CH_3), 6.85–7.25 (m, 8 H, Ar), 7.25–7.34 (m, 4 H, Ar), 7.34–7.42 (m, 3 H, Ar). ^{1}H NMR (400 MHz, DMSO, 393 K):[8] δ 2.12 (s, 6 H, CH_3), 2.33 (s, 3 H, CH_3), 6.95–7.01 (m, 4 H, Ar), 7.04–7.12 (m, 4 H, Ar), 7.19 (m, 1 H, Ar), 7.23–7.39 (m, 6 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$, 293 K): δ 19.5–20.6 (br, 2 C, CH_3), 20.6 (CH_3), 124.8 (br, 2 C, $C_{Ar}H$), 125.8 ($C_{Ar}H$), 126.8 (2 C, $C_{Ar}H$), 127.3 ($C_{Ar}H$), 127.6 ($C_{Ar}H$), 129.8 (br, 2 C, $C_{Ar}H$), 129.9 (2 C, $C_{Ar}H$), 130.4 (2 C, $C_{Ar}H$), 131.4 (br, 2 C, $C_{Ar}H$), 135.4 (C_{Ar}), 135.6 (br, C_{Ar}), 135.7 (br, C_{Ar}), 139.2 (br, C_{Ar}), 140.3 (2 C, C_{Ar}), 141.5 (C_{Ar}). ^{13}C NMR (101 MHz, DMSO, 393 K): δ 18.9 (CH_3), 18.9 (CH_3), 19.1 (CH_3), 124.0 (2 C, $C_{Ar}H$), 125.1 ($C_{Ar}H$), 126.1 ($C_{Ar}H$), 126.1 ($C_{Ar}H$), 126.5 ($C_{Ar}H$), 126.7 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.9 (2 C, $C_{Ar}H$), 129.4 (br s, $C_{Ar}H$), 129.4 (br s, $C_{Ar}H$), 129.5 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 130.2 ($C_{Ar}H$), 134.1 (C_{Ar}), 134.4 (C_{Ar}), 134.5 (C_{Ar}), 138.3 (C_{Ar}), 139.5 (C_{Ar}), 139.5 (C_{Ar}), 139.8 (C_{Ar}), 139.9 (C_{Ar}), 140.4 (C_{Ar}). MS (EI): *m/z* 348 [$M^{+\bullet}$], 349. HRMS (EI): *m/z* calcd for $C_{27}H_{24}^{+\bullet}$ 348.1873 [$M^{+\bullet}$]; found: 348.1881.



4− O. V. Ozerov, B. O. Patrick, F. T. Ladipo, *J. Am. Chem. Soc.* **2000**, *122*, 6423–6431.

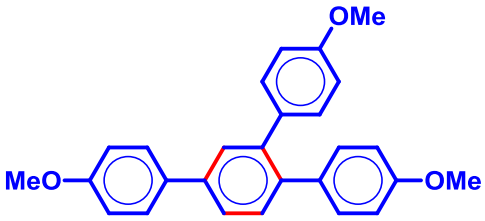
5− Tol = 4-methylphenyl.

6− This signal is part of an AA′BB′ system but is described as indicated for simplification purposes.

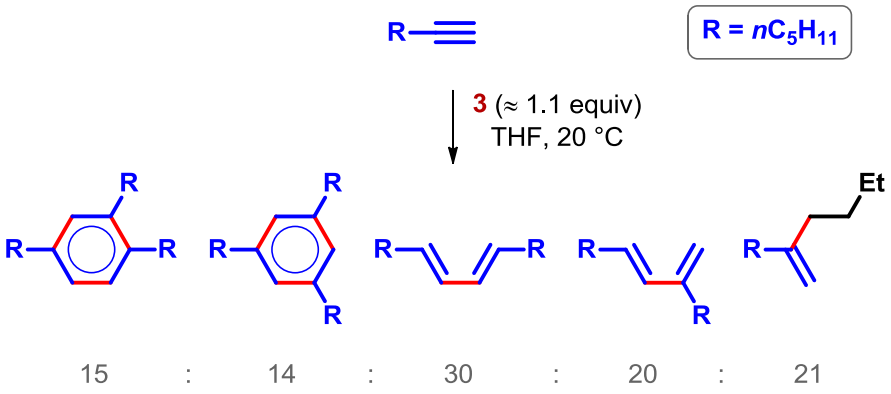
7− L. Xu, R. Yu, Y. Wang, J. Chen, Z. Yang, *J. Org. Chem.* **2013**, *78*, 5744–5750.

8− We warmly thank Alexander Yu. Ivanov, from the Research Resources Centre for Magnetic Resonance at St. Petersburg State University, Russia, for running the NMR analysis of this compound at 393 K.

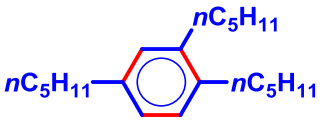
1,2,4-Tris(4-methoxyphenyl)benzene (5d):[9] this product was isolated by flash column chromatography on silica gel (EtOAc/petroleum ether, gradient from 0 to 10%). Yield 88 mg (67%). Colourless oil. R_f ≈ 0.1 (EtOAc/petroleum ether 5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.80–6.84 (m, 4 H, PMP[10]), 7.02 (br d,[6] J 8.5, 2 H, PMP), 7.11–7.17 (m, 4 H, PMP), 7.47 (d,[3] J 8.0, 1 H, Ar), 7.56–7.67 (m, 4 H, Ar, PMP). ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.1 (OCH_3), 55.1 (OCH_3), 55.3 (OCH_3), 113.4 (2 C, $C_{PMP}H$), 113.4 (2 C, $C_{PMP}H$), 114.2 (2 C, $C_{PMP}H$), 125.3 ($C_{Ar}H$), 128.1 (2 C, $C_{PMP}H$), 128.9 ($C_{Ar}H$), 130.8 (2 C, $C_{PMP}H$), 130.9 (2 C, $C_{PMP}H$), 131.0 ($C_{Ar}H$), 133.2 (C_{Ar}), 133.7 (C_{Ar}), 134.1 (C_{Ar}), 138.4 (C_{Ar}), 139.6 (C_{Ar}), 140.3 (C_{Ar}), 158.2 (*C*-OMe), 158.3 (*C*-OMe), 159.2 (*C*-OMe).



• The following products were formed in the reaction of hept-1-yne according to **GP1**. They were identified by ^{1}H and ^{13}C NMR analysis of the crude product.



1,2,4-Tripentylbenzene:[11] ^{1}H NMR (400 MHz, $CDCl_3$), characteristic signals: δ 2.54−2.63 (m, 6 H, Ar-CH_2), 6.97 (distorted d, J 2.0, 1 H, Ar), 7.01 (AB part of an ABX system, δ_A 6.95, δ_B 7.06, J_{AB} 7.5, J_{AX} 2.0, J_{BX} 0.0, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$), characteristic signals: δ 14.0 (3 C, CH_3), 22.6 (3 C, CH_2CH_3), 35.6 (Ar-CH_2), 35.8 (Ar-CH_2), 36.1 (Ar-CH_2), 125.7 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 129.2 ($C_{Ar}H$), 137.6 (C_{Ar}), 140.1 (C_{Ar}), 140.3 (C_{Ar}).

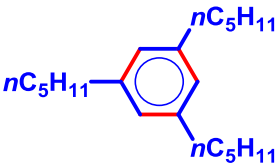


9− V. Cadierno, S. E. García-Garrido, J. Gimeno, *J. Am. Chem. Soc.* **2006**, *128*, 15094–15095.

10− PMP = 4-methoxyphenyl.

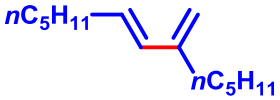
11− C. C. Eichman, J. P. Bragdon, J. P. Stambuli, *Synlett* **2011**, 1109−1112 (supporting information).

1,3,5-Tripentylbenzene:[11] ^{1}H NMR (400 MHz, $CDCl_3$), characteristic signals: δ 2.57 (t, J 7.5, 6 H, Ar-CH_2), 6.83 (s, 3 H, Ar) . ^{13}C NMR (101 MHz, $CDCl_3$), characteristic signals: δ 14.0 (3 C, CH_3), 22.6 (3 C, CH_2CH_3), 36.0 (3 C, Ar-CH_2), 125.8 (3 C, $C_{Ar}H$), 142.6 (3 C, C_{Ar}).

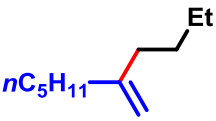


(6*E*,8*E*)-Tetradeca-6,8-diene:[12] ^{1}H NMR (400 MHz, $CDCl_3$), characteristic signals: δ 2.07 (q, J 7.0, 4 H, CH=CH-CH_2), 5.59 (m, 2 H, CH=CH-CH_2), 6.02 (m, 2 H, CH=CH-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.0 (2 C, CH_3), 22.6 (2 C, CH_2CH_3), 29.1 (2 C, CH_2), 31.5 (2 C, CH_2), 32.6 (2 C, CH_2), 130.4 (2 C, CH=CH), 132.3 (2 C, CH=CH).

(*E*)-8-Methylenetridec-6-ene:[13] ^{1}H NMR (400 MHz, $CDCl_3$), characteristic signals: δ 2.12 (br q, J 7.0, 2 H, CH_2-CH=CH), 2.21 (td, J 7.5, 1.0, 2 H, CH_2-C=CH_2), 4.86 (br s, 1 H, C=CH_2), 4.89 (br s, 1 H, C=CH_2), 5.73 (dt, J 16.0, 7.0, 1 H, CH_2-CH=CH), 6.07 (br d, J 16.0, 1 H, CH_2-CH=CH). ^{13}C NMR (101 MHz, $CDCl_3$), characteristic signals: δ 112.7 (C=CH_2), 130.1 (CH=CH), 132.1 (CH=CH), 146.6 (C=CH_2).



5-Methylenedecane:[14] ^{1}H NMR (400 MHz, $CDCl_3$), characteristic signal: δ 4.72 (br s, 2 H, C=CH_2). ^{13}C NMR (101 MHz, $CDCl_3$), characteristic signals: δ 108.3 (C=CH_2), 150.2 (C=CH_2).

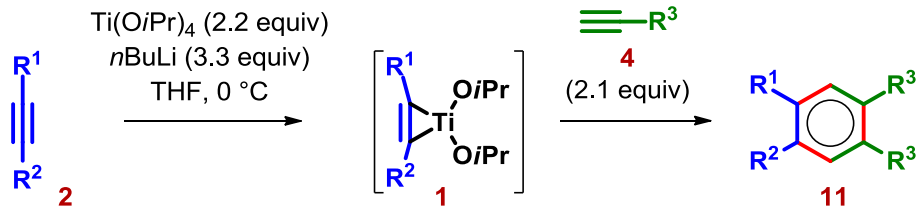


12− S. E. Denmark, Z. Wang, *Org. Lett.* **2001**, *3*, 1073−1076 (supporting information).

13− We could not find literature NMR data for this compound but the signals we observed are in excellent agreement with the data reported for a corresponding bis-deuteriated molecule (U. M. Dzhemilev, A. G. Ibragimov, L. O. Khafizova, L. R. Yakupova, L. M. Khalilov, *Zh. Org. Khim.* **2005**, *41*, 684−689; *Russ. J. Org. Chem.* **2005**, *41*, 667−672) and for the related compound (*E*)-2-butyl-1,3-decadiene (X. Qi, J. Montgomery, *J. Org. Chem.* **1999**, *64*, 9310−9313).

14− We could not find literature NMR data for this compound but the signals we observed are in excellent agreement with the data reported for the related molecule 2-butyloct-1-ene: G. Cahiez, O. Gager, V. Habiak, *Synthesis* **2008**, 2636−2644.

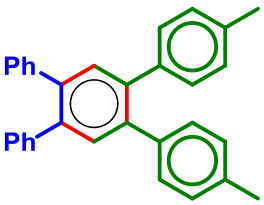
2.2. General procedure for the heterocyclotrimerisation of internal alkynes with terminal alkynes (**GP2**)



*n*BuLi (2.0 M in hexanes, 3.3 mmol, 1.6 mL) was added slowly (5 min), at 0 °C, to a solution of the internal alkyne (1.0 mmol) and Ti(O*i*Pr)$_4$ (2.2 mmol, 0.65 mL) in THF (10 mL). After 2 h of stirring at 0 °C, a solution of the terminal alkyne (2.1 mmol) in THF (1.0 mL) was added dropwise. The cold bath was then removed and stirring was continued for 1 h. 10% HCl aqueous solution (10 mL) was carefully added; the organic phase was separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure (P ≥ 25 mbar) to afford the crude product.

• The following [2+2+2] heterocyclotrimerisation adducts were prepared according to **GP2**:

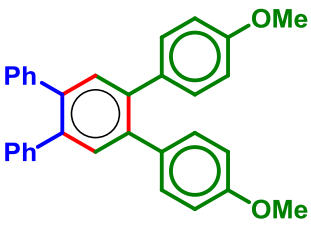
1,2,4,5-Tetraphenylbenzene (11a):[15] this product was isolated by flash column chromatography on silica gel (Et_2O/petroleum ether, gradient from 0 to 5%). Yield 0.18 g (48%). Colourless solid. M.p. 266.6–268.8 °C ($CHCl_3$/pentane). R_f ≈ 0.35 (EtOAc/petroleum ether 5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.24 (m, 20 H, Ph), 7.53 (s, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 126.6 (4 C, $C_{Ph}H$), 127.9 (8 C, $C_{Ph}H$), 129.9 (8 C, $C_{Ph}H$), 133.0 (2 C, $C_{Ar}H$), 139.6 (4 C, C_{Ar}), 140.9 (4 C, C_{Ar}).



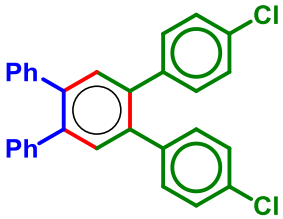
1,2-Diphenyl-4,5-bis(*p*-tolyl)benzene (11b): this compound was purified by recrystallisation of the crude product from Et_2O/pentane. Yield 82 mg (20%). Another pure sample was obtained by purification of the mother liquor by flash column chromatography on silica gel (Et_2O/petroleum ether, gradient from 0 to 5%). Yield 0.13 g (32%). Colourless solid. M.p. 213.2–214.5 °C (Et_2O/pentane). R_f ≈ 0.4 (EtOAc/petroleum ether 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 6 H, CH_3), 7.05 (br d,[6] *J* 7.5, 4 H, Tol[5]), 7.13 (br d,[6] *J* 7.5, 4 H, Tol), 7.21 (br s, 10 H, Ph),

15− J. A. Reed, C. L. Schilling, R. F. Tarvin, T. A. Rettig, J. K. Stil, *J. Org. Chem.* **1969**, *34*, 2188–2192.

7.50 (s, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.1 (2 C, CH_3), 126.5 (2 C, $C_{Ph}H$), 127.9 (4 C, $C_{Ph}H$), 128.7 (4 C, $C_{Tol}H$), 129.7 (4 C, $C_{Tol}H$), 129.9 (4 C, $C_{Ph}H$), 133.0 (2 C, $C_{Ar}H$), 136.2 (2 C, C_{Ar}), 138.1 (2 C, C_{Ar}), 139.4 (2 C, C_{Ar}), 139.5 (2 C, C_{Ar}), 141.0 (2 C, C_{Ar}). IR (CCl_4): $\bar{\nu}_{max}$ 3085 (w), 3060 (m), 3025 (m), 2955 (w), 2925 (m), 2870 (w), 1600 (w), 1515 (m), 1475 (s), 1445 (m), 1378 (m), 1185 (w), 1020 (w), 1010 (m). MS (positive CI, NH_3): *m/z* 411 [MH^+], 428 [$MH^+..NH_3$]. HRMS (EI): *m/z* calcd for $C_{32}H_{26}^{+\bullet}$ 410.2029 [$M^{+\bullet}$]; found: 410.2018.



1,2-Bis(4-methoxyphenyl)-4,5-diphenyl-benzene (11c): this product was isolated by flash column chromatography on silica gel (EtOAc/petroleum ether, gradient from 0 to 5%). Yield 0.24 g (54%). Yellowish solid. M.p. 200.1–200.8 °C (Et_2O/pentane). R_f ≈ 0.15 (EtOAc/petroleum ether 5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 6 H, OCH_3), 6.79 (br d,[6] *J* 8.5, 4 H, PMP[10]), 7.15 (br d,[6] *J* 8.5, 4 H, PMP), 7.22 (br s, 10 H, Ph), 7.48 (s, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.2 (2 C, OCH_3), 113.5 (4 C, $C_{PMP}H$), 126.5 (2 C, $C_{Ph}H$), 127.9 (4 C, $C_{Ph}H$), 129.9 (4 C, $C_{Ph}H$), 130.9 (4 C, $C_{PMP}H$), 132.9 (2 C, $C_{Ar}H$), 133.5 (2 C, C_{Ar}), 139.1 (2 C, C_{Ar}), 139.3 (2 C, C_{Ar}), 141.1 (2 C, C_{Ar}), 158.4 (2 C, *C*-OMe). IR (CCl_4): $\bar{\nu}_{max}$ 3080 (w), 3065 (m), 3030 (m), 2955 (m), 2935 (m), 2910 (w), 2835 (m), 1610 (s), 1515 (s), 1480 (s), 1295 (s), 1250 (s), 1175 (s), 1045 (s). MS (positive CI, NH_3): *m/z* 442, 443 [MH^+], 444, 460 [$MH^+..NH_3$], 461. HRMS (EI): *m/z* calcd for $C_{32}H_{26}O_2^{+\bullet}$ 442.1927 [$M^{+\bullet}$]; found: 442.1929.

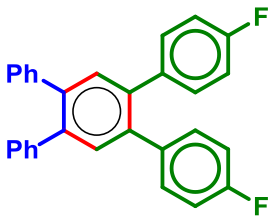


1,2-Bis(4-chlorophenyl)-4,5-diphenyl-benzene (11d): this compound was isolated by flash column chromatography on silica gel (Et_2O/petroleum ether, gradient from 0 to 5%). Yield 0.35 g (77%). Colourless solid, M.p. 231.5–232.6 °C (CH_2Cl_2/pentane). R_f ≈ 0.1 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (br d,[6] *J* 8.5, 4 H, PCP[16]), 7.19–7.25 (m, 14 H, Ph, PCP), 7.47 (s, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 126.8 (2 C, $C_{Ph}H$), 128.0 (4 C, $C_{Ph}H$), 128.4 (4 C, $C_{PCP}H$), 129.8 (4 C, $C_{Ph}H$), 131.1 (4 C, $C_{PCP}H$), 132.8 (2 C, $C_{Ar}H$), 133.0 (2 C, C_{Ar}), 138.3 (2 C, C_{Ar}), 139.1 (2 C, C_{Ar}), 140.2 (2 C, C_{Ar}), 140.6 (2 C, C_{Ar}). IR (CCl_4): $\bar{\nu}_{max}$ 3080 (w), 3060 (w), 3030 (w), 2955 (m), 2925 (s), 2855 (m), 1560 (s), 1555 (m), 1550 (m), 1545 (s), 1475 (s), 1375 (w), 1095 (s), 1015 (m), 1010 (m). MS (positive CI, NH_3): *m/z* 337, 417, 451 ([MH^+] with two ^{35}Cl), 452, 453 ([MH^+] with one ^{35}Cl and one ^{37}Cl), 454, 455([MH^+] with two ^{37}Cl). HRMS (EI): *m/z* calcd for $C_{30}H_{20}{}^{35}Cl_2^{+\bullet}$ 450.0937 [$M^{+\bullet}$]; found: 450.0946.

16− PCP = 4-chlorophenyl.

A colourless, plate shaped (dimensions: 0.400 × 0.280 × 0.080 mm) crystal of **11d** ($C_{30}H_{20}Cl_2$, MW = 451.36 g.mol^{-1}) was coated in Paratone-N oil and mounted on a loop. X-Ray diffraction data were collected at 150.0(1) K with a Bruker Apex II diffractometer, using an Mo-Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator. All data were measured using φ- and ω-scans, with θ values ranging from 2.38 to 30.27°. 17346 reflections were measured, among them 6321 were independent. The linear absorption coefficient was found to be 0.304 mm^{-1} after multi-scan corrections. The crystal structure was solved using *SIR*97[17] and refined using *SHELXL*2013.[18] The crystal was found to be triclinic, with P_{-1} space group, and cell dimensions a(Å) = 9.1872(4), b(Å) = 10.0783(4), c(Å) = 13.0004(5) and angles α(°) = 78.1390(19), β(°) = 73.1711(16), γ(°) = 87.3815(17), with a Z-value of 2, for a total volume V(Å^3) = 1127.45(8) and a calculated density of 1.330 g.cm^{-3}. After refinement, the Rint was found at 2.86%, the R_1 at 4.42 %, and the wR_2 at 13.12%, with a residual electron density of 0.055 e$^-$.Å^{-3} (highest peak 0.399, deepest hole −0.807). CCDC-986894 contains the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1,2-Bis(4-fluorophenyl)-4,5-diphenyl-benzene (11e): this compound was purified by recrystallisation of the crude product from CH_2Cl_2/petroleum ether. Yield 0.21 g (51%). Another pure sample was obtained by purification of the mother liquor by flash column chromatography on silica gel (EtOAc /petroleum ether, gradient from 0 to 10%). Yield 72 mg (17%).



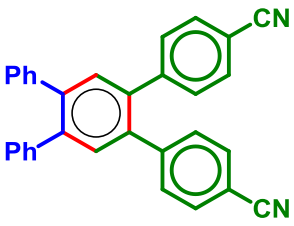
Colourless solid. M.p. 254.5–256.4 °C (CH_2Cl_2/pentane). R_f ≈ 0.3 (EtOAc/petroleum ether 5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (br t,[19] *J* 8.5, 4 H, C*H*CF), 7.15–7.25 (m, 14 H, Ph, C*H*CHCF), 7.48 (s, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 115.0 (d, *J* 21.5, 4 C, *C*HCF), 126.8 (2 C, $C_{Ph}H$), 128.0 (4 C, $C_{Ph}H$), 129.8 (4 C, $C_{Ph}H$), 131.4 (d, *J* 8.0, 4 C, *C*HCHCF), 132.9 (2 C, $C_{Ar}H$), 136.7 (d, *J* 3.5, 2 C, *C*CHCHCF), 138.6 (2 C, C_{Ar}), 139.9 (2 C, C_{Ar}), 140.7 (2 C, C_{Ar}), 161.9 (d, *J* 246.5, 2 C, *C*F). IR (CCl_4): $\bar{\nu}_{max}$ 3085 (w), 3060 (w), 3025 (w), 1600 (m), 1520 (m), 1510 (s), 1500 (m), 1475 (s), 1235 (s), 1225 (s), 1160 (s). MS (positive CI, NH_3): *m/z* 419 [MH^+], 420, 436 [MH^+..NH_3]. HRMS (EI): *m/z* calcd for $C_{30}H_{20}F_2^{+\bullet}$ 418.1528 [$M^{+\bullet}$]; found: 418.1542.

17− A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. J. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115−119.

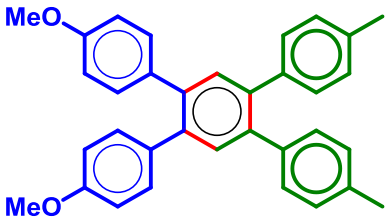
18− G. M. Sheldrick, *Acta Cryst.* **2008**, A*64*, 112−122.

19− This signal is the AA′ part of an AA′BB′X system but is described as indicated for simplification purposes.

4-[2-(4-Cyanophenyl)-4,5-diphenyl-phenyl]benzonitrile (11f): for the synthesis of this compound, the general procedure **GP2** was applied with the following changes: 4-ethynylbenzonitrile was used as a more dilute solution in THF (3.0 mL) and during work-up, the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The product was isolated by flash column chromatography on silica gel (EtOAc/petroleum ether, gradient from 0 to 20%). Yield 47 mg (11%). Yellowish solid. M.p. 270.5–271.8 °C (Et_2O/pentane). R_f ≈ 0.1 (EtOAc/petroleum ether 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.28 (m, 10 H, Ph), 7.31 (br d,[6] J 8.0, 4 H, PCNP[20]), 7.51 (s, 2 H, Ar), 7.57 (br d,[6] J 8.0, 4 H, PCNP). ^{13}C NMR (101 MHz, $CDCl_3$): δ 111.0 (2 C, *C*-CN), 118.6 (2 C, CN), 127.2 (2 C, $C_{Ph}H$), 128.2 (4 C, $C_{Ph}H$), 129.7 (4 C, $C_{Ph}H$), 130.5 (4 C, $C_{PCNP}H$), 132.1 (4 C, $C_{PCNP}H$), 132.9 (2 C, $C_{Ar}H$), 137.6 (2 C, C_{Ar}), 140.0 (2 C, C_{Ar}), 141.2 (2 C, C_{Ar}), 145.0 (2 C, C_{Ar}). IR (CCl_4): $\bar{\nu}_{max}$ 3085 (w), 3065 (w), 3030 (w), 2230 (s), 1610 (m), 1510 (w), 1475 (s), 1445 (w), 1010 (m), 905 (m). MS (positive CI, NH_3): *m/z* 433 [MH^+], 434, <u>451</u> [$MH^+..NH_3$], 452. HRMS (EI): *m/z* calcd for $C_{32}H_{20}N_2^{+\bullet}$ 432.1621 [$M^{+\bullet}$]; found: 432.1621.



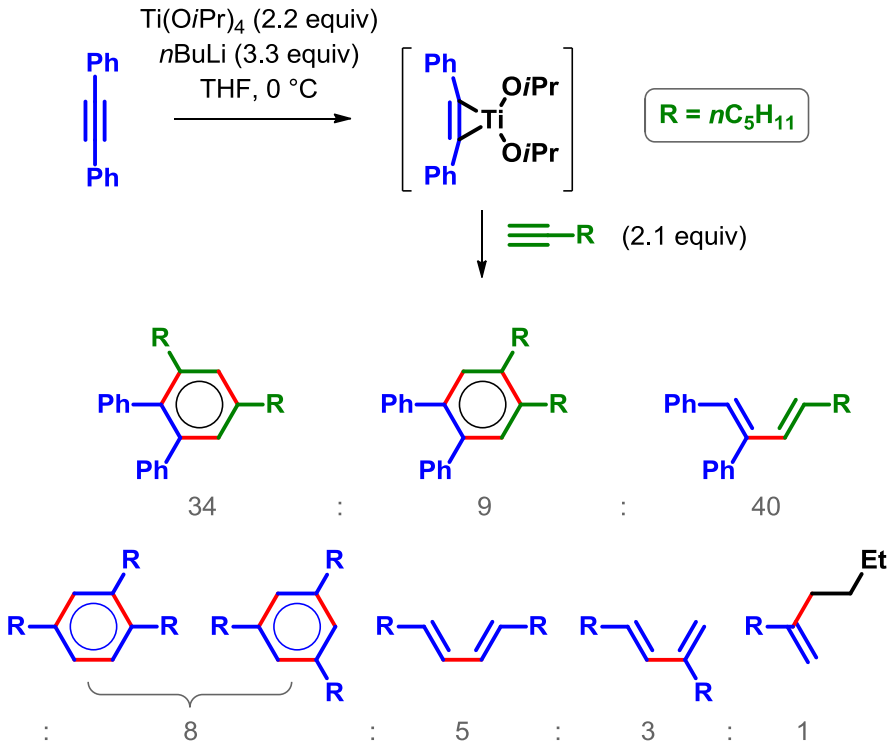
1,2-Bis(4-methoxyphenyl)-4,5-bis(*p*-tolyl)benzene (11g): this compound was purified by recrystallisation of the crude product from Et_2O/petroleum ether. Yield 93 mg (20%). Another pure sample was obtained by purification of the mother liquor by flash column chromatography on silica gel (EtOAc /petroleum ether, gradient from 0 to 10%). Yield 0.34 g (72%). Colourless solid. M.p. 237.4–239.5 °C (Et_2O/petroleum ether). R_f ≈ 0.15 (EtOAc/petroleum ether 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 6 H, $ArCH_3$), 3.77 (s, 6 H, OCH_3), 6.78 (br d,[6] J 8.5, 4 H, PMP[10]), 7.04 (br d,[6] J 8.0, 4 H, Tol[5]), 7.11–7.15 (m, 8 H, PMP, Tol), 7.46 (s, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.1 (2 C, $ArCH_3$), 55.1 (2 C, OCH_3), 113.4 (4 C, $C_{PMP}H$), 128.7 (4 C, $C_{Tol}H$), 129.7 (4 C, $C_{Tol}H$), 130.9 (4 C, $C_{PMP}H$), 132.9 (2 C, $C_{Ar}H$), 133.5 (2 C, C_{Ar}), 136.1 (2 C, C_{Ar}), 138.2 (2 C, C_{Ar}), 138.8 (2 C, C_{Ar}), 139.1 (2 C, C_{Ar}), 158.3 (2 C, *C*-OMe). IR (CCl_4): $\bar{\nu}_{max}$ 3025 (m), 3000 (m), 2955 (m), 2935 (m), 2925 (m), 2910 (m), 2865 (w), 2835 (m), 1610 (s), 1525 (s), 1515 (s), 1480 (s), 1465 (s), 1440 (m), 1295 (s), 1245 (s), 1175 (s), 1110 (m), 1040 (s), 1025 (m), 1005 (m), 910 (w). MS (positive CI, NH_3): *m/z* 470, <u>471</u> [MH^+], 472, 488 [$MH^+..NH_3$], 489. HRMS (EI): *m/z* calcd for $C_{34}H_{30}O^{+\bullet}$ 470.2240 [$M^{+\bullet}$]; found: 470.2238.



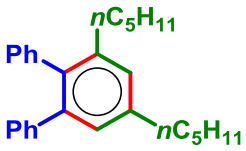
20− PCNP = 4-cyanophenyl.

1,2,4-Triphenyl-5-propyl-benzene (11h): this product was isolated by flash column chromatography on silica gel (petroleum ether). Yield 69 mg (20%). Yellowish oil. $R_f \approx 0.1$ (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J 7.5, 3 H, CH_2CH_3), 1.58 (sext, J 7.5, 2 H, CH_2CH_3), 2.64 (m, 2 H, $CH_2CH_2CH_3$), 7.12–7.52 (m, 17 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.1 (CH_3), 24.5 (CH_2CH_3), 34.9 (CH_2Ar), 126.3 ($C_{Ph}H$), 126.4 ($C_{Ph}H$), 126.8 ($C_{Ph}H$), 127.8 (2 C, $C_{Ph}H$), 127.9 (2 C, $C_{Ph}H$), 128.1 (2 C, $C_{Ph}H$), 129.3 (2 C, $C_{Ph}H$), 129.9 (2 C, $C_{Ph}H$), 129.9 (2 C, $C_{Ph}H$), 131.6 ($C_{Ar}H$), 132.3 ($C_{Ar}H$), 137.8 (C_{Ar}), 139.3 (C_{Ar}), 139.4 (C_{Ar}), 141.1 (C_{Ar}), 141.2 (C_{Ar}), 141.5 (C_{Ar}), 141.5 (C_{Ar}). IR (CCl_4): $\bar{\nu}_{max}$ 3080 (m), 3060 (m), 3025 (m), 2960 (s), 2870 (m), 2360 (w), 2340 (w), 1600 (m), 1495 (m), 1475 (s), 1465 (m), 1445 (m), 1380 (w), 1075 (m), 1025 (m), 1010 (m). MS (positive CI, NH_3): m/z 348 [MH^+], 366 [$MH^+..NH_3$], 367. HRMS (EI): m/z calcd for $C_{27}H_{24}^{+\bullet}$ 348.1873 [$M^{+\bullet}$]; found: 348.1880.

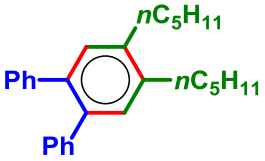
• The following products were formed in the reaction of diphenylbenzene and hept-1-yne according to **GP2**. They were identified by ^{1}H and ^{13}C NMR analyses of the crude product and of partially purified products.



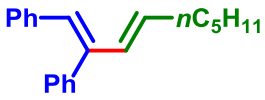
1,5-Dipentyl-2,3-diphenyl-benzene: ^{1}H NMR (400 MHz, $CDCl_3$), characteristic signals: δ 0.78 (t, *J* 7.0, 3 H, C*H*$_3$), 0.92 (t, *J* 7.0, 3 H, C*H*$_3$), 2.45 (m, 2 H, Ar-C*H*$_2$), 2.65 (m, 2 H, Ar-C*H*$_2$), 7.00–7.22 (m, 12 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$), characteristic signals: δ 13.9 (CH_3), 14.1 (CH_3), 22.3 (*C*H$_2$CH$_3$), 22.6 (*C*H$_2$CH$_3$), 33.7 (Ar-*C*H$_2$), 35.7 (Ar-*C*H$_2$), 125.8 ($C_{Ph}H$), 126.0 ($C_{Ph}H$), 127.3 (2 C, $C_{Ph}H$), 127.4 (2 C, $C_{Ph}H$), 127.7 ($C_{Ar}H$), 128.3 ($C_{Ar}H$), 129.8 (2 C, $C_{Ph}H$), 130.8 (2 C, $C_{Ph}H$), 137.5 (C_{Ar}), 140.1 (C_{Ar}), 141.1 (C_{Ar}), 141.6 (C_{Ar}), 141.7 (C_{Ar}), 142.4 (C_{Ar}).



1,2-Dipentyl-4,5-diphenyl-benzene:[21] ^{1}H NMR (400 MHz, $CDCl_3$), characteristic signals: δ 0.92 (t, *J* 7.0, 6 H, C*H*$_3$), 1.70 (m, 4 H, C*H*$_2$), 2.67 (t, *J* 7.0, 4 H, Ar-C*H*$_2$), 7.00–7.22 (m, 12 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$), characteristic signals: δ 14.1 (2 C, CH_3), 22.6 (2 C, *C*H$_2$CH$_3$), 32.4 (2 C, Ar-*C*H$_2$), 126.1 (2 C, $C_{Ph}H$), 127.7 (4 C, $C_{Ph}H$), 129.9 (4 C, $C_{Ph}H$), 131.4 (2 C, $C_{Ar}H$), 137.8 (2 C, C_{Ar}), 139.9 (2 C, C_{Ar}), 141.7 (2 C, C_{Ar}).



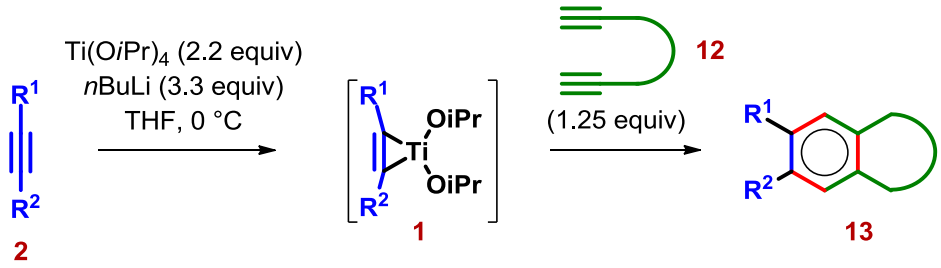
[(*E*,1*Z*)-1-Benzylideneoct-2-enyl]benzene:[22] ^{1}H NMR (400 MHz, $CDCl_3$), characteristic signals: δ 0.87 (t, *J* 7.0, 3 H, C*H*$_3$), 2.09 (tdd, *J* 7.5, 7.0, 1.0, 2 H, CH=CH-C*H*$_2$), 5.31 (dt, *J* 15.5, 7.0, 1 H, CH=C*H*-CH$_2$), 6.41 (br d, *J* 15.5, 1 H, C*H*=CH-CH$_2$), 6.48 (br s, 1 H, C*H*-Ph), 6.82–6.87 (m, 2 H, Ph), 7.00–7.40 (m, 8 H, Ph). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.0 (CH_3), 22.5 (*C*H$_2$CH$_3$), 29.0 (*C*H$_2$), 31.5 (*C*H$_2$), 33.0 (CH=CH-*C*H$_2$), 126.4 ($C_{Ph}H$), 127.1 ($C_{Ph}H$), 127.8 (2 C, $C_{Ph}H$), 128.7 (2 C, $C_{Ph}H$), 128.9 (*C*H-Ph), 129.2 (2 C, $C_{Ph}H$), 129.6 (2 C, $C_{Ph}H$), 134.4 (CH=*C*H-CH$_2$), 135.3 (*C*H=CH-CH$_2$), 137.2, 138.9, 141.8 (*C*-Ph, C_{Ph}).



21− We could not find literature NMR data for this compound but the signals we observed are in good agreement with the data reported for the related molecules 1,2-dipropyl-4,5-diphenyl-benzene [M. Danz, G. Hilt, *Adv. Synth. Catal.* **2011**, *353*, 303−308 (supporting information)] and 1,2-dihexyl-4,5-diphenyl-benzene (H. Meier, B. Rose, *J. Prakt. Chem.* **1998**, *340*, 536−543).

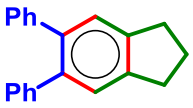
22− We could not find literature NMR data for this compound but the signals we observed are in excellent agreement with the data reported for the related molecule (1*Z*,3*E*)-1,2-diphenyldeca-1,3-diene: A. Ogata, M. Nemoto, K. Kobayashi, A. Tsubouchi, T. Takeda, *J. Org. Chem.* **2007**, *72*, 3816−3822 (supporting information).

2.3. General procedure for the heterocyclotrimerisation of internal alkynes with α,ω-diynes (**GP3**)



*n*BuLi (2.0 M in hexanes, 3.3 mmol, 1.6 mL) was slowly added to a solution of the internal alkyne substrate (1.0 mmol) and Ti(O*i*Pr)$_4$ (2.2 mmol, 0.65 mL) in THF (10 mL) at 0 °C, over 5 min. After 2 h of stirring at the same temperature, a solution of the diyne (1.25 mmol) in THF (1.0 mL) was added dropwise. The cold bath was removed and stirring was continued for 1 h. 10% HCl aqueous solution (10 mL) was carefully added; the organic phase was separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure (P ≥ 25 mbar) to afford the crude product.

• The following [2+2+2] heterocyclotrimerisation adducts were prepared according to **GP3**:



5,6-Diphenyl-2,3-dihydro-1*H*-indene (13a):[23] this product was isolated by flash column chromatography on silica gel (petroleum ether). Yield 0.21 g (77%). Yellowish solid. M.p. 119.5–120.8 °C (Et_2O/pentane). R_f ≈ 0.3 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (quint, J 7.5, 2 H, $CH_2CH_2CH_2$), 3.00 (t, J 7.5, 4 H, $CH_2CH_2CH_2$), 7.16 (m, 10 H, Ph), 7.30 (s, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.6 ($CH_2CH_2CH_2$), 32.6 (2 C, $CH_2CH_2CH_2$), 126.1 (2 C, $C_{Ph}H$), 126.5 (2 C, $C_{Ar}H$), 127.7 (4 C, $C_{Ph}H$), 130.0 (4 C, $C_{Ph}H$), 138.7 (2 C, C_{Ar}), 142.0 (2 C, C_{Ar}), 143.6 (2 C, C_{Ar}). IR (CCl_4): $\bar{\nu}_{max}$ 3085 (w), 3060 (w), 3025 (m), 2955 (s), 2890 (w), 2870 (w), 2845 (m), 1600 (w), 1495 (w), 1475 (s), 1440 (m), 1400 (w), 1075 (w), 1020 (w), 1030 (w). MS (positive CI, NH_3): *m/z* 270, 288 [MH^+..NH_3], 289. HRMS (EI): *m/z* calcd for $C_{21}H_{18}N^{+\bullet}$ 270.1403 [$M^{+\bullet}$]; found: 270.1403.

23− R. L. Hillard III, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1977**, *99*, 4058–4069.

6,7-Diphenyl-1,2,3,4-tetrahydronaphthalene (13b):[24] this compound was isolated by flash column chromatography on silica gel (petroleum ether). Yield 83 mg (30%). Colourless solid. M.p. 119.4–121.6 °C (pentane). R_f ≈ 0.15 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85 (m, 4 H, $CH_2CH_2CH_2CH_2$), 2.84 (m, 4 H, $CH_2CH_2CH_2CH_2$), 7.09–7.21 (m, 12 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.3 (2 C, $ArCH_2CH_2$), 29.1 (2 C, $ArCH_2CH_2$), 126.2 (2 C, $C_{Ph}H$), 127.8 (4 C, $C_{Ph}H$), 129.9 (4 C, $C_{Ph}H$), 131.3 (2 C, $C_{Ar}H$), 136.5 (2 C, C_{Ar}), 137.9 (2 C, C_{Ar}), 141.6 (2 C, C_{Ar}). IR (CCl_4): $\bar{\nu}_{max}$ 3080 (w), 3065 (m), 3030 (m), 2930 (s), 2890 (w), 2860 (m), 2840 (m), 1600 (w), 1495 (w), 1480 (s), 1145 (m), 1435 (m), 1400 (w), 1355 (w), 1075 (w), 990 (w), 925 (w), 910 (w). MS (positive CI, NH_3): *m/z* 284, 285, 302 [$MH^+..NH_3$], 303. HRMS (EI): *m/z* calcd for $C_{22}H_{20}^{+\bullet}$ 284.1560 [$M^{+\bullet}$]; found: 284.1559.

5,6-Diphenyl-2-tosylisoindoline (13c): this product was isolated by flash column chromatography on silica gel (EtOAc/petroleum ether, gradient from 0 to 15%). Yield 0.17 g (49%). Colourless solid. M.p. 168.5–169.1 °C (Et_2O/pentane). R_f ≈ 0.15 (EtOAc/petroleum ether 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3 H, CH_3), 4.69 (s, 4 H, CH_2), 7.02–7.06 (m, 4 H, Ph), 7.15–7.19 (m, 6 H, Ph), 7.21 (s, 2 H, Ar), 7.33 (br d,[6] *J* 8.0, 2 H, Ts), 7.81 (br d,[6] *J* 8.0, 2 H, Ts). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.5 (CH_3), 53.5 (2 C, CH_2), 124.6 (2 C, $C_{Ar}H$), 126.6 (2 C, $C_{Ar}H$), 127.6 (2 C, $C_{Ar}H$), 127.9 (4 C, $C_{Ph}H$), 129.7 (4 C, $C_{Ph}H$), 129.8 (2 C, $C_{Ar}H$), 133.6 (C-SO_2), 135.4 (2 C, C_{Ar}), 140.5 (2 C, C_{Ar}), 140.8 (2 C, C_{Ar}), 143.7 (C-Me). IR (CCl_4): $\bar{\nu}_{max}$ 3085 (w), 3065 (m), 3030 (m), 2955 (w), 2920 (w), 2850 (w), 1600 (m), 1495 (m), 1480 (s), 1470 (s), 1360 (s), 1305 (m), 1185 (m), 1170 (s), 1100 (s), 1065 (s), 1020 (m). MS (positive CI, NH_3): *m/z* 268, 426 [MH^+], 427. HRMS (EI): *m/z* calcd for $C_{27}H_{23}NO_2S^{+\bullet}$ 425.1444 [$M^{+\bullet}$]; found: 425.1446.

5-Phenyl-6-propyl-2,3-dihydro-1*H*-indene (13d): this compound was isolated by flash column chromatography on silica gel (petroleum ether). Yield 0.19 g (81%). Yellowish oil. R_f ≈ 0.4 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (t, *J* 7.5, 3 H, CH_3), 1.47 (sext, *J* 7.5, 2 H, CH_3CH_2), 2.09 (quint, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 2.50 (m, 2 H, $CH_3CH_2CH_2$), 2.90 (t, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 2.93 (t, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 7.06 (s, 1 H, Ar), 7.15 (s, 1 H, Ar), 7.25–7.33 (m, 3 H, Ph), 7.34–7.40 (m, 2 H, Ph). ^{13}C NMR (101

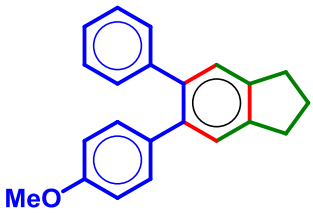
24− V. Gandon, D. Leca, T. Aechtner, K. P. C. Vollhardt, M. Malacria, C. Aubert, *Org. Lett.* **2004**, *6*, 3405–3407.

MHz, $CDCl_3$): δ 14.1 (CH_3), 24.8 (CH_2), 25.5 (CH_2), 32.5 (CH_2), 32.7 (CH_2), 35.1 (CH_2), 125.0 ($C_{Ar}H$), 125.9 ($C_{Ar}H$), 126.4 ($C_{Ph}H$), 127.9 (2 C, $C_{Ph}H$), 129.4 (2 C, $C_{Ph}H$), 137.9 (C_{Ar}), 139.9 (C_{Ar}), 141.4 (C_{Ar}), 142.7 (C_{Ar}), 143.3 (C_{Ar}). IR (KBr, thin film): $\bar{\nu}_{max}$ 3055 (w), 3025 (w), 3010 (w), 2955 (s), 2930 (s), 2870 (m), 2845 (m), 1600 (w), 1480 (m), 1465 (w), 1455 (w), 1440 (w), 1375 (w), 1070 (w), 880 (w). MS (EI): *m/z* 178, 179, 207, 208, 236 [$M^{+\bullet}$], 237. HRMS (EI): *m/z* calcd for $C_{18}H_{20}^{+\bullet}$ 236.1560 [$M^{+\bullet}$]; found: 236.1567.

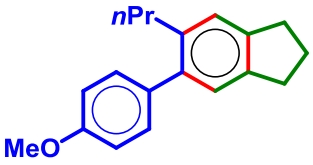
6-Phenyl-7-propyl-1,2,3,4-tetrahydronaphthalene (13e): this product was isolated by flash column chromatography on silica gel (petroleum ether). Yield 65 mg (26%). Yellowish oil. $R_f \approx 0.3$ (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, *J* 7.5, 3 H, CH_3CH_2), 1.47 (sext, *J* 7.5, 2 H, CH_3CH_2), 1.76–1.85 (m, 4 H, $CH_2CH_2CH_2CH_2$), 2.48 (m, 2 H, $CH_3CH_2CH_2$), 2.70–2.83 (m, 4 H, $CH_2CH_2CH_2CH_2$), 6.91 (s, 1 H, Ar), 6.98 (s, 1 H, Ar), 7.26–7.33 (m, 3 H, Ph), 7.33–7.40 (m, 2 H, Ph). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.1 (CH_3), 23.4 (2 C, CH_2), 24.6 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 34.8 (CH_2), 126.4 ($C_{Ph}H$), 127.9 (2 C, $C_{Ph}H$), 129.3 (2 C, $C_{Ph}H$), 129.8 ($C_{Ar}H$), 130.6 ($C_{Ar}H$), 134.3 (C_{Ar}), 136.1 (C_{Ar}), 137.2 (C_{Ar}), 139.3 (C_{Ar}), 142.2 (C_{Ar}). IR (KBr, thin film): $\bar{\nu}_{max}$ 3055 (w), 3025 (w), 3000 (w), 2955 (s), 2925 (s), 2860 (m), 1600 (w), 1485 (m), 1450 (m), 1440 (m), 1375 (w), 1070 (w). MS (EI): *m/z* 139, 179, 221, 250 [$M^{+\bullet}$]. HRMS (EI): *m/z* calcd for $C_{19}H_{22}^{+\bullet}$ 250.1716 [$M^{+\bullet}$]; found: 250.1724.

5,6-Bis(4-methoxyphenyl)-2,3-dihydro-1*H*-indene (13f) and 5-(4-methoxyphenyl)-6-phenyl-2,3-dihydro-1*H*-indene (13g): these compounds were isolated by flash column chromatography on silica gel (petroleum ether). Yields **13f**: 98 mg (30%); **13g**: 0.18 g (61%).

13f: Yellowish solid. M.p. 101.5–102.5 °C (pentane). $R_f \approx 0.2$ (EtOAc/petroleum ether 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (quintet, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 2.96 (t, *J* 7.5, 4 H, $CH_2CH_2CH_2$), 3.74 (s, 6 H, OCH_3), 6.73 (br d,[6] *J* 8.5, 4 H, PMP[10]), 7.04 (br d,[6] *J* 8.5, 4 H, PMP), 7.25 (s, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.6 ($CH_2CH_2CH_2$), 32.6 (2 C, $CH_2CH_2CH_2$), 55.1 (2 C, OCH_3), 113.2 (4 C, $C_{PMP}H$), 126.4 (2 C, $C_{Ar}H$), 130.9 (4 C, $C_{PMP}H$), 134.5 (2 C, C_{Ar}), 138.1 (2 C, C_{Ar}), 143.3 (2 C, C_{Ar}), 157.9 (2 C, *C*-OMe).
IR (CCl_4): $\bar{\nu}_{max}$ 3035 (w), 3000 (w), 2955 (s), 2935 (m), 2910 (m), 2835 (m), 1610 (s), 1515 (s), 1480 (s), 1465 (m), 1440 (m), 1290 (s), 1245 (s), 1175 (s), 1105 (w), 1050 (m), 1040 (m), 1030 (m). MS (positive CI, NH_3): *m/z* 330, 331 [MH^+], 332, 348 [$MH^+..NH_3$], 349. HRMS (EI): *m/z* calcd for $C_{23}H_{22}O_2^{+\bullet}$ 330.1614 [$M^{+\bullet}$]; found: 330.1614.



13g: Yellow oil. R_f ≈ 0.35 (EtOAc/petroleum ether 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (quintet, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 2.96 (t, *J* 7.5, 4 H, $CH_2CH_2CH_2$), 3.72 (s, 3 H, OCH_3), 6.71 (br d,[6] *J* 8.5, 2 H, PMP[10]), 7.03 (br d,[6] *J* 8.5, 2 H, PMP), 7.10–7.21 (m, 5 H, Ph), 7.27 (br s, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.6 ($CH_2CH_2CH_2$), 32.6 ($CH_2CH_2CH_2$), 32.6 ($CH_2CH_2CH_2$), 55.0 (OCH_3), 113.2 (2 C, $C_{PMP}H$), 126.0 ($C_{Ph}H$), 126.4 ($C_{Ar}H$), 126.5 ($C_{Ar}H$), 127.8 (2 C, $C_{Ph}H$), 129.9 (2 C, $C_{Ph}H$), 130.9 (2 C, $C_{PMP}H$), 134.3 (C_{Ar}), 138.2 (C_{Ar}), 138.6 (C_{Ar}), 142.2 (C_{Ar}), 143.3 (C_{Ar}), 143.6 (C_{Ar}), 158.0 (*C*-OMe). IR (CCl_4): $\bar{\nu}_{max}$ 3065 (w), 3020 (w), 2955 (m), 2935 (m), 2910 (w), 2870 (w), 2845 (w), 2835 (w), 1610 (m), 1515 (s), 1480 (s), 1440 (w), 1290 (w), 1245 (s), 1175 (m), 1050 (w), 1035 (w). MS (positive CI, NH_3): *m/z* 300, 301 [MH^+], 302, 318 [$MH^+..NH_3$], 319. HRMS (EI): *m/z* calcd for $C_{22}H_{20}O^{+\bullet}$ 330.1509 [$M^{+\bullet}$]; found: 330.1506.

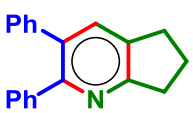


5-(4-Methoxyphenyl)-6-propyl-2,3-dihydro-1*H*-indene (13h): this product was isolated by flash column chromatography on silica gel (Et_2O/petroleum ether, gradient from 0 to 10%). Yield 72 mg (27%). **13d** was isolated as a side product (52 mg, 22%). **13h:** Yellowish oil. R_f ≈ 0.25 (Et_2O/petroleum ether 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, *J* 7.5, 3 H, CH_3), 1.48 (m, 2 H, CH_3CH_2), 2.08 (quint, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 2.51 (m, 2 H, $CH_3CH_2CH_2$), 2.89 (t, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 2.92 (t, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 3.82 (s, 3 H, OCH_3), 7.05 (s, 1 H, Ar), 7.06 (AA′BB′ system,[25] δ_A 6.91, δ_B 7.20, *N* 8.5, *L* 8.0, *K* 5.0 [*M* could not be measured accurately], 4 H, PMP[10]), 7.14 (s, 1 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.1 (CH_2CH_3), 24.7 (CH_2), 25.5 (CH_2), 32.5 (CH_2), 32.7 (CH_2), 35.2 (CH_2), 55.2 (OCH_3), 113.3 (2 C, $C_{PMP}H$), 125.0 ($C_{Ar}H$), 126.0 ($C_{Ar}H$), 130.3 (2 C, $C_{PMP}H$), 135.0 (C_{Ar}), 138.1 (C_{Ar}), 139.5 (C_{Ar}), 141.4 (C_{Ar}), 143.1 (C_{Ar}), 158.3 (*C*-OMe). IR (KBr, thin film): $\bar{\nu}_{max}$ 3035 (w), 3005 (w), 2955 (s), 2935 (s), 2870 (m), 2840 (m), 1610 (m), 1575 (w), 1515 (s), 1585 (s), 1465 (m), 1440 (m), 1290 (m), 1245 (s), 1175 (m), 1110 (w), 1040 (m). MS (EI): *m/z* 162, 209, 237, 266 [$M^{+\bullet}$], 267. HRMS (EI): *m/z* calcd for $C_{19}H_{22}O^{+\bullet}$ 266.1665 [$M^{+\bullet}$]; found: 266.1675.

25− H. Günther, *Angew. Chem.*, **1972**, *84*, 907–920; *Angew. Chem. Int. Ed.*, **1972**, *11*, 861–874.

2.4. Syntheses of substituted pyridines

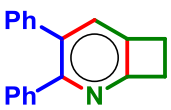
2,3-Diphenyl-6,7-dihydro-5*H*-cyclopenta[b]pyridine (14): *n*BuLi (2.0 M in hexanes, 3.3 mmol, 1.6 mL) was added, over 5 min at 0 °C, to a solution of diphenylacetylene (1.0 mmol, 0.18 g) and Ti(O*i*Pr)$_4$ (2.2 mmol, 0.65 mL) in THF (10 mL). After 2 h of stirring at 0 °C, a solution of hex-5-ynenitrile (1.25 mmol, 0.13 mL) in THF (1.0 mL) was added dropwise. The cold bath was removed and stirring was continued for 1 h. Saturated NH_4Cl aqueous solution (10 mL) was then carefully added. The organic phase was separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure (P ≥ 25 mbar). Purification of the crude product by flash column chromatography on silica gel (EtOAc/petroleum ether, gradient from 10 to 20%) yielded pure 2,3-Diphenyl-6,7-dihydro-5*H*-cyclopenta[b]pyridine **14** (0.15 g, 59%).



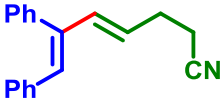
14: Colourless solid. M.p. 163.8–164.5 °C (CH_2Cl_2/pentane). R_f ≈ 0.15 (EtOAc/petroleum ether 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.21 (quint, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 3.03 (t, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 3.13 (t, *J* 7.5, 2 H, $CH_2CH_2CH_2$), 7.11–7.35 (m, 10 H, Ph), 7.54 (s, 1 H, py). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.3 ($CH_2CH_2CH_2$), 30.4 (N-C-$CH_2CH_2CH_2$), 34.2 (N-C-CH_2CH_2), 126.7 (CH, $C_{Ph}H$), 127.2 (CH, $C_{Ph}H$), 127.7 (2 C, $C_{Ph}H$), 128.1 (2 C, $C_{Ph}H$), 129.6 (2 C, $C_{Ph}H$), 129.9 (2 C, $C_{Ph}H$), 133.6 (C_{Ar}), 134.4 ($C_{py}H$), 135.5 (C_{Ar}), 140.6 (C_{Ar}), 140.6 (C_{Ar}), 155.3 (C-N), 164.5 (C-N). IR (CCl_4): $\bar{\nu}_{max}$ 3085 (w), 3060 (m), 3035 (w), 2961 (m), 2900 (w), 2850 (w), 1600 (m), 1550 (w), 1530 (m), 1450 (s), 1425 (s), 1400 (s), 1200 (m), 1075 (w), 1025 (m). MS (positive CI, NH_3): *m/z* 272 [MH^+], 273. HRMS (EI): *m/z* calcd for $C_{20}H_{17}N^{+\bullet}$ 271.1356 [$M^{+\bullet}$]; found: 271.1355.

3,4-Diphenyl-2-azabicyclo[4.2.0]octa-1,3,5-triene (15) and (4*E*,6*Z*)-6,7-Diphenylhepta-4,6-dienenitrile (16): *n*BuLi (2.0 M in hexanes, 3.3 mmol, 1.6 mL) was added, over 5 min at 0 °C, to a solution of diphenylacetylene (1.0 mmol, 0.18 g) and Ti(O*i*Pr)$_4$ (2.2 mmol, 0.65 mL) in THF (10 mL). After 2 h of stirring at 0 °C, a solution of pent-4-ynenitrile (1.25 mmol, 0.11 mL) in THF (1.0 mL) was added dropwise. The cold bath was removed and stirring was continued for 1 h. Then 10% NH_3 aqueous solution (10 mL) was then carefully added. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure (P ≥ 25 mbar). Purification of the crude product by flash column chromatography on silica gel (EtOAc/petroleum

ether, gradient from 10 to 50%) yielded a 55:45 mixture of 3,4-diphenyl-2-azabicyclo[4.2.0]octa-1,3,5-triene (**15**) and (4*E*,6*Z*)-6,7-diphenylhepta-4,6-dienenitrile (**16**) (54 mg). The two compounds could be separated easily by acid-base extraction. Yields **15**: 25 mg (10%); **16**: Yield 21 mg (8%).



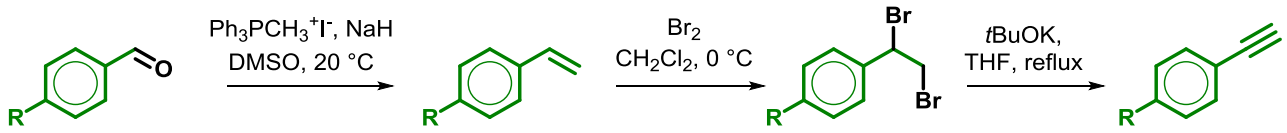
15: Yellowish solid. M.p. 134.5–135.6 °C (Et_2O) $R_f \approx 0.1$ (EtOAc/petroleum ether 10%). $R_f \approx 0.5$ (EtOAc/petroleum ether 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.19 (br t, *J* 4.5, 2 H, CH_2), 3.51 (br t, *J* 4.5, 2 H, CH_2), 7.10–7.15 (m, 2 H, Ph), 7.17–7.32 (m, 8 H, Ph), 7.35 (s, 1 H, py). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.7 (CH_2), 35.0 (CH_2), 126.7 ($C_{Ph}H$ r), 127.2 ($C_{Ph}H$), 127.7 (2 C, $C_{Ph}H$), 128.1 (2 C, $C_{Ph}H$), 129.8 (2 C, $C_{Ph}H$), 130.0 (2 C, $C_{Ph}H$), 132.1 ($C_{py}H$), 135.9 (C_{Ar}), 138.5 (C_{Ar}), 140.8 (C_{Ar}), 141.1 (C_{Ar}), 157.0 (C-N), 162.8 (C-N). IR (CCl_4): $\bar{\nu}_{max}$ 3085 (w), 3060 (w), 3035 (w), 2975 (w), 29440 (m), 1600 (w), 1585 (w), 1570 (w), 1495 (w), 1450 (m), 1415 (s), 1380 (s), 1175 (m), 1075 (w), 1025 (w), 907 (s). MS (positive CI, NH_3): *m/z* 258 [MH^+], 259. HRMS (EI): *m/z* calcd for $C_{19}H_{15}N^{+\bullet}$ 257.1199 [$M^{+\bullet}$]; found: 257.1206.



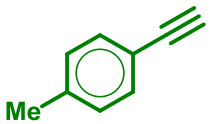
16: Colourless oil. $R_f \approx 0.1$ (EtOAc/petroleum ether 10%), $R_f \approx 0.6$ (EtOAc/petroleum ether 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35–2.51 (m, 4 H, CH_2CH_2), 5.24 (dt, *J* 15.5, 7.5, 1 H, CH_2CH=CH), 6.55 (d, *J* 15.5, 1 H, CH_2CH=C*H*), 6.57 (s, 1 H, C*H*Ph), 6.83–6.90 (m, 2 H, Ph), 7.02–7.47 (m, 8 H, Ph). ^{13}C NMR (101 MHz, $CDCl_3$): δ 17.4 (CH_2CN), 28.6 (CH_2CH_2CN), 119.1 (CN), 126.9 ($C_{Ph}H$), 127.4 ($C_{Ph}H$), 127.9 (2 C, $C_{Ph}H$), 128.1 (CH_2CH=CH), 128.8 (2 C, $C_{Ph}H$), 129.3 (2 C, $C_{Ph}H$), 129.4 (2 C, $C_{Ph}H$), 131.2 (CH-Ph), 136.5 (C), 138.1 (C), 138.3 (CH_2CH=CH), 140.5 (C). MS (positive CI, NH_3): *m/z* 260 [MH^+], 277 [MH^+..NH_3], 278. HRMS (EI): *m/z* calcd for $C_{19}H_{17}N^{+\bullet}$ 259.1356 [$M]^{+\bullet}$; found: 259.1353. *Note:* **16** is not stable; it polymerised after 2 days of standing at 20 °C.

2.5. Synthesis of the starting alkynes

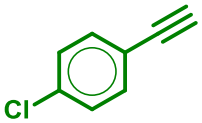
• 1-Ethynyl-4-methylbenzene (4b) and 1-chloro-4-ethynylbenzene



The styrene intermediates were prepared according to a published protocol.[26] Bromination was then carried out with Br_2 in CH_2Cl_2 at 0 °C, followed by double hydro-bromo-elimination with *t*BuOK in refluxing THF.[27] The crude products were purified by Kugelrohr distillation.

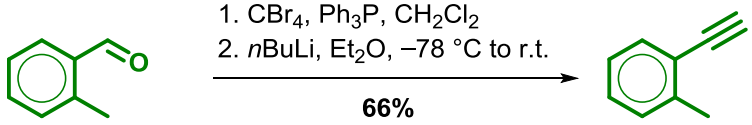


4b:[28] Yield 3.0 g (83%, over 3 steps). Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3 H, CH_3), 3.03 (s, 1 H, C≡C*H*), 7.12 (br d,[6] *J* 8.0, 2 H, Ar), 7.38 (br d,[6] *J* 8.0, 2 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.4 (CH_3), 76.4 (C≡*C*H), 83.8 (*C*≡CH), 119.0 (*C*-C≡CH), 129.0 (2 C, $C_{Ar}H$), 132.0 (2 C, $C_{Ar}H$), 138.9 (*C*-Me).



1-Chloro-4-ethynylbenzene:[29] Yield 11.7 g (76%, over 3 steps). Colourless solid, mp 45.4–47.8 °C (Et_2O/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.10 (s, 1 H, C≡CH), 7.35 (AA′BB′ system,[25] δ_A 7.29, δ_B 7.41, *N* 8.5, *L* 7.5, *K* 4.5 [M could not be measured accurately], 4 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 78.1 (C≡*C*H), 82.5 (*C*≡CH), 120.6 (*C*-C≡CH), 128.7 (2 C, $C_{Ar}H$), 133.3 (2 C, $C_{Ar}H$), 134.9 (*C*-Cl).

• 1-Ethynyl-2-methylbenzene (4c)



A solution of CBr_4 (50.0 mmol, 16.7 g) in CH_2Cl_2 (50.0 mL) was slowly added to a solution of Ph_3P (100 mmol, 26.2 g) in CH_2Cl_2 (50.0 mL) at 0 °C. After 5 min of stirring at 0 °C, a solution of 2-methylbenzaldehyde (25.0 mmol, 3.00 g) in CH_2Cl_2 (10.0 mL) was added and the reaction mixture was stirred overnight at r.t. Saturated $NaHCO_3$ aqueous solution (30.0 mL) was then added

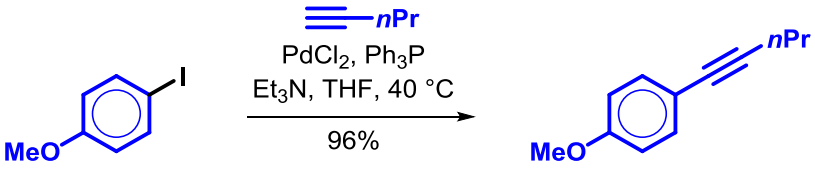
26− M. Yasuda, K. Harano, K. Kanematsu, *J. Org. Chem.* **1980**, *45*, 659–664.
27− H. O. House, N. I. Ghali, J. L. Haack, D. VanDerveer, *J. Org. Chem.* **1980**, *45*, 1807–1817.
28− E. Negishi, M. Kotora, C. Xu, *J. Org. Chem.* **1997**, *62*, 8957–8960.
29− A. Miersch, G. Hilt, *Chem. Eur. J.* **2012**, *18*, 9798–9801.

and the mixture was concentrated under reduced pressure. The residue was diluted with petroleum ether (100 mL) and the resulting suspension was filtered, washed with H_2O (100 mL), dried over anhydrous $MgSO_4$, filtered again and concentrated under reduced pressure (P ≥ 25 mbar) to afford 1-(2,2-dibromovinyl)-2-methylbenzene (6.80 g) which was engaged in the next step without purification.

A solution of *n*BuLi in hexanes (2.10 M, 25.0 mmol, 11.9 mL) was slowly added to a solution of 1-(2,2-dibromovinyl)-2-methylbenzene (10.0 mmol, 2.75 g) in Et_2O (30.0 mL) at –78 °C. The cooling bath was removed and stirring was continued for 60 min. Saturated NH_4Cl aqueous solution (15.0 mL) was then carefully added. The organic phase was separated and the aqueous layer was extracted with Et_2O (10.0mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure (P ≥ 25 mbar). The crude product was purified by Kugelrohr distillation to afford pure 1-ethynyl-2-methylbenzene **4c** (0.76 g, 66%).

4c:[30] Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3 H, CH_3), 3.33 (s, 1 H, C≡C*H*), 7.19 (m, 1 H, Ar), 7.17–7.32 (m, 2 H, Ar), 7.52 (m, 1 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.6 (CH_3), 80.9 (C≡*C*H), 82.5 (*C*≡CH), 121.9 (*C*-C≡CH), 125.5 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 129.4 ($C_{Ar}H$), 132.5 ($C_{Ar}H$), 140.7 (*C*-Me).

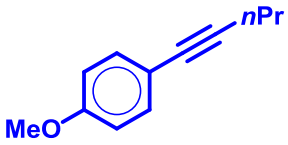
• Typical procedure for Sonogashira cross-coupling reaction (TP1): 1-methoxy-4-(pent-1-yn-1-yl)benzene



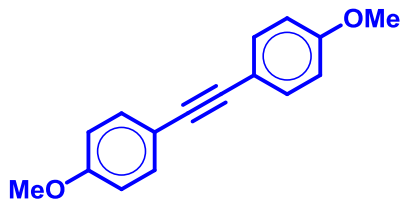
A mixture of 4-iodoanisole (25 mmol, 5.9 g), $PdCl_2$ (0.5 mmol, 90 mg), CuI (0.5 mmol, 96 mg), Ph_3P (1.0 mmol, 0.26 g) and pent-1-yne (38 mmol, 2.6 g) in Et_3N (10 mL) and THF (50 mL) was stirred at 40 °C during 12 h. After cooling, the reaction mixture was concentrated under reduced pressure (P ≥ 60 mbar). The residue was diluted with petroleum ether (0.10 L). 5% HCl aqueous solution (30 mL) was added and the mixture was filtered through celite. The organic phase was separated, washed with water (3 × 30 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure (P ≥ 25 mbar). Purification of the crude product by by Kugelrohr distillation yielded pure 1-methoxy-4-(pent-1-yn-1-yl)benzene (4.2 g, 96%).

30− S. Bhunia, S. Ghorpade, D. B. Huple, R. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 2939–2942.

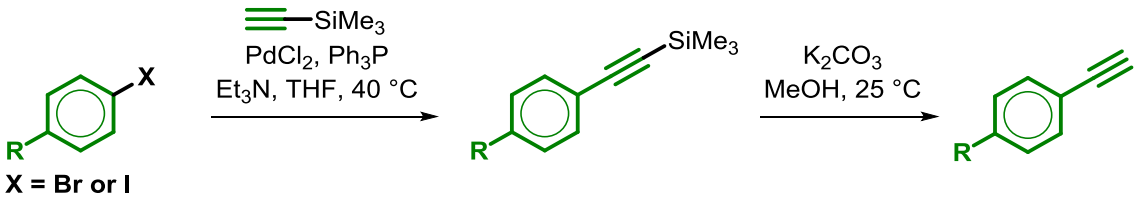
1-Methoxy-4-(pent-1-yn-1-yl)benzene:[31]. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (t, J 7.0, 3 H, CH_3CH$_2$), 1.61 (sext, J 7.0, 2 H, CH$_3$CH_2), 2.36 (t, J 7.0, 2 H, ArCH_2), 3.77 (s, 3 H, OCH$_3$), 7.06 (AA′BB′ system,[25] δ_A 6.80, δ_B 7.32, N 9.0, L 8.0, K 5.0 [M could not be measured accurately], 4 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.5 (*C*H$_3$CH$_2$), 21.4 (CH$_2$), 22.3 (CH$_2$), 55.2 (OCH$_3$), 80.4 (Ar-*C*≡C), 88.5 (C≡*C*-*n*Pr), 113.8 (2 C, C$_{Ar}$H), 116.3 (*C*$_{Ar}$-C≡C), 132.8 (2 C, C$_{Ar}$H), 159.0 (*C*-OMe).



1,2-Bis(4-methoxyphenyl)ethyne:[32] this compound was prepared in a similar manner as in **TP1**, from 4-iodoanisole (14 mmol, 3.2 g) and 1-ethynyl-4-methoxybenzene (15 mmol, 2.0 g). The crude product was purified by flash column chromatography (EtOAc/petroleum ether, gradient from 5 to 10%), followed by recrystallization from Et$_2$O/petroleum ether. Yield 1.34 g (82%). Yellow solid. M.p. 143.7–144.9 °C (Et$_2$O/petroleum ether). $R_f \approx 0.3$ (EtOAc/petroleum ether 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 6 H, OCH$_3$), 7.16 (AA′BB′ system,[25] δ_A 6.87, δ_B 7.45, N 9.0, L 8.5, K 4.5 [M could not be measured accurately], 4 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.3 (2 C, OCH$_3$), 87.9 (2 C, C≡C), 113.9 (4 C, C$_{Ar}$H), 115.7 (2 C, *C*$_{Ar}$-C≡C), 132.9 (4 C, C$_{Ar}$H), 159.4 (2 C, *C*-OMe).



- **General procedure for Sonogashira cross-coupling followed by cleavage of the trimethylsilyl group (GP4)**



The Sonogashira cross-coupling reaction was carried out analogously to **TP1**. Purification of the crude product by flash column chromatography on silica gel (typically, EtOAc/petroleum ether, gradient from 0 to 10%) yielded the pure trimethylsilyl-protected arylacetylene intermediate.

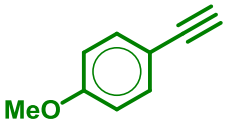
K_2CO_3 (50 mmol, 6.9 g) was added to a solution of this Sonogashira reaction product (40 mmol) in anhydrous MeOH (30 mL) at 25 °C. After 2 h of stirring, the reaction mixture was concentrated

31− C. Fen, T. Loh, *Chem. Commun.*, **2010**, *46*, 4779–4781.

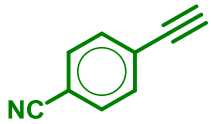
32− W. Zhang, S. Kraft, J. S. Moore, *J. Am. Chem. Soc.* **2004**, *126*, 329–335.

under reduced pressure (P ≥ 80 mbar). The residue was diluted with pentane (50 mL), washed with water (3 × 30 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure (P ≥ 80 mbar). The crude product was purified by Kugelrohr distillation.

The following arylacteylenes were prepared according to **GP4**:

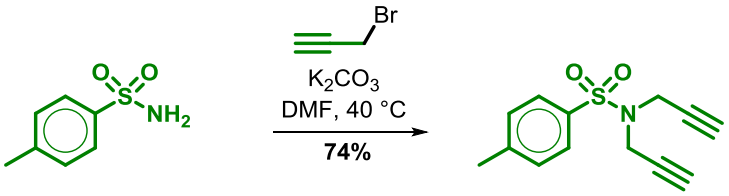


1-Ethynyl-4-methoxybenzene (4d):[33] this compound was prepared from 4-iodoanisole. Yield 4.5 g (68% over 2 steps). Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.00 (s, 1 H, C≡CH), 3.81 (s, 3 H, OCH_3), 7.14 (AA′BB′ system,[25] δ_A 6.84, δ_B 7.43, *N* 9.0, *L* 8.5, *K* 5.0 [*M* could not be measured accurately], 4 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.2 (OCH_3), 75.8 (C≡*C*H), 83.6 (*C*≡CH), 113.9 (2 C, $C_{Ar}H$), 114.1 (*C*-C≡CH), 133.5 (2 C, $C_{Ar}H$), 159.9 (*C*-OMe).



4-Ethynylbenzonitrile:[34] this molecule was prepared from 4-bromobenzonitrile. Yield 0.85 g (42% over 2 steps). Colourless solid. M.p. 157.3–158.1 °C (Et_2O/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.30 (s, 1 H, C≡CH), 7.59 (AA′BB′ system,[25] δ_A 7.57, δ_B 7.61, *N* 8.0 [*L*, *K*, *M* could not be measured accurately], 4 H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 81.5 (C≡*C*H), 81.8 (*C*≡CH), 112.3 (*C*-CN), 118.3 (CN), 127.0 (*C*-C≡CH), 132.0 (2 C, $C_{Ar}H$), 132.7 (2 C, $C_{Ar}H$).

• 4-Methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide



A mixture of *p*-$TsNH_2$ (31 mmol, 5.2 g), anhydrous K_2CO_3 (92 mmol, 13 g) and propargyl bromide (80% solution in PhMe, 70 mmol, 10.5 g) in DMF (20 mL) was stirred at 40 °C for 2 h. After cooling, the solvent was removed under reduced pressure and the residue was dissolved in a mixture of CH_2Cl_2 (0.10 L) and 10% HCl aqueous solution (0.10 L). The organic phase was separated,

33− D. F. Taber, S. Bai, P. Guo, *Tet. Lett.* **2008**, *49*, 6904–6906.

washed with 3% HCl aqueous solution (5 × 50 mL) and H_2O (0.10 L), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure (P ≥ 25 mbar). The crude product was recrystallized from Et_2O/pentane to give pure 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (5.6 g, 74%).

4-Methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide:[35] Colourless solid. M.p. 56.4–57.5 °C (Et_2O/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (t, *J* 2.5, 2 H, C≡CH), 2.42 (s, 3 H, CH_3), 4.16 (d, *J* 2.5, 4 H, CH_2), 7.30 (br d,[6] *J* 8.5, 2 H, H-Ar), 7.71 (br d,[6] *J* 8.5, 2 H, H-Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.6 (CH_3) 36.2 (2 C, CH_2), 74.1 (2 C, C≡*C*H), 76.1 (2 C, *C*≡CH), 127.8 (2 C, $C_{Ar}H$), 129.6 (2 C, $C_{Ar}H$), 135.0 (C-SO_2), 144.0 (*C*-Me).

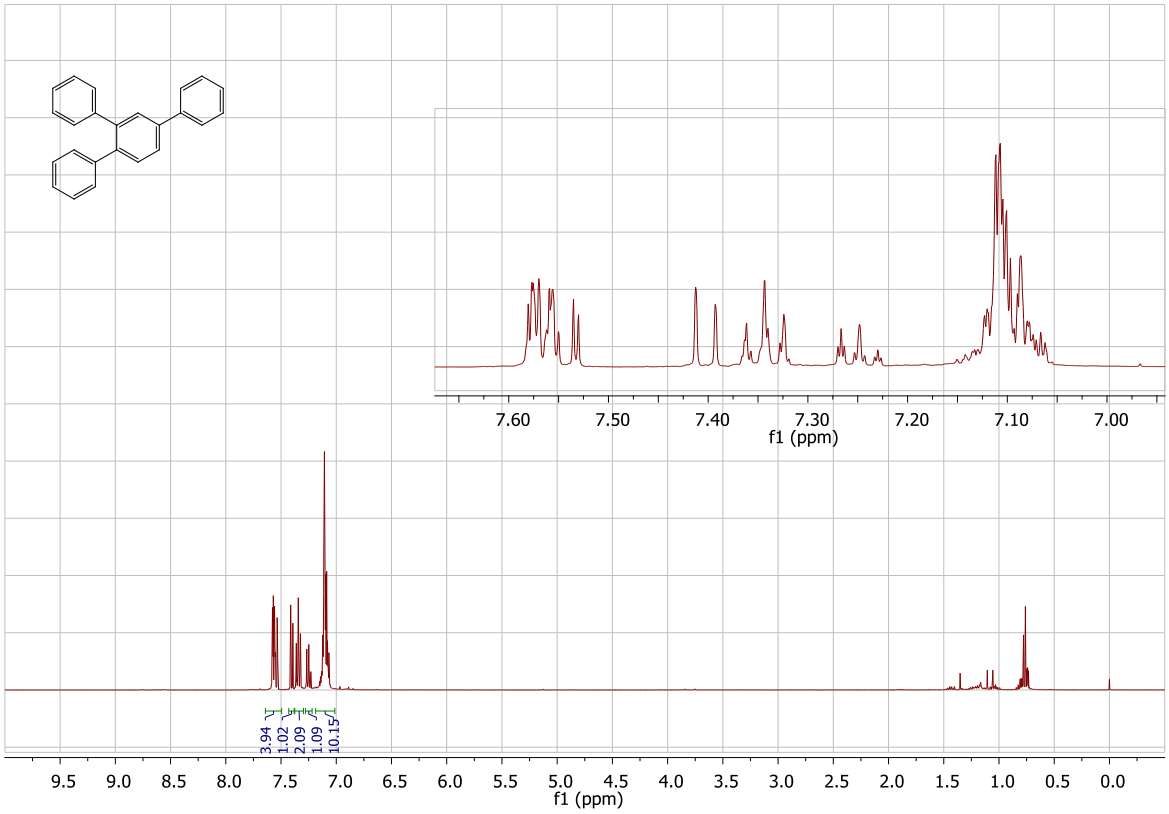
34− B. K. Blackburn, A. Lee, M. Baier, B. Kohl, A. G. Olivero, R. Matamoros, K. D. Robarge, R. S. McDowell, *J. Med. Chem.* **1997**, *40*, 717–729.

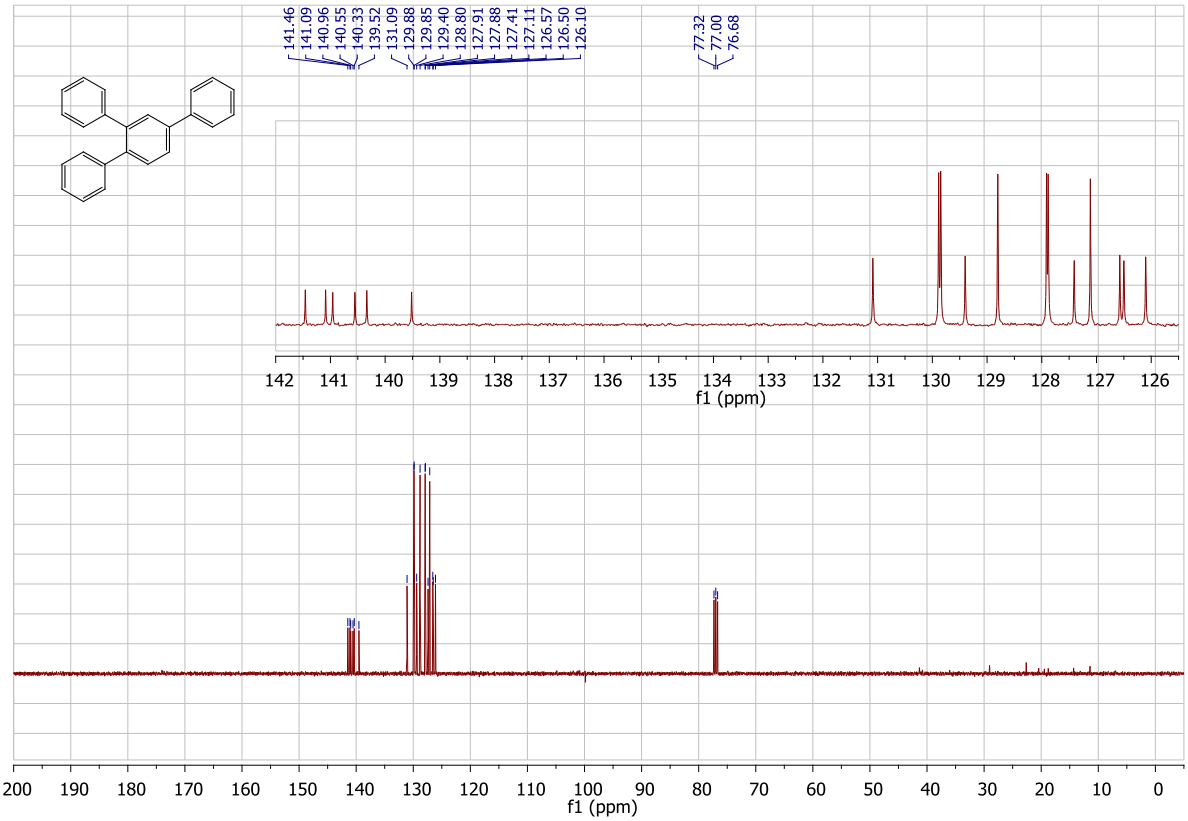
35− W. Oppolzer, A. Pimm, B. Stammen, W. E. Hume, *Helvetica Chimica Acta* **1997**, *80*, 623–639.

3. NMR spectra

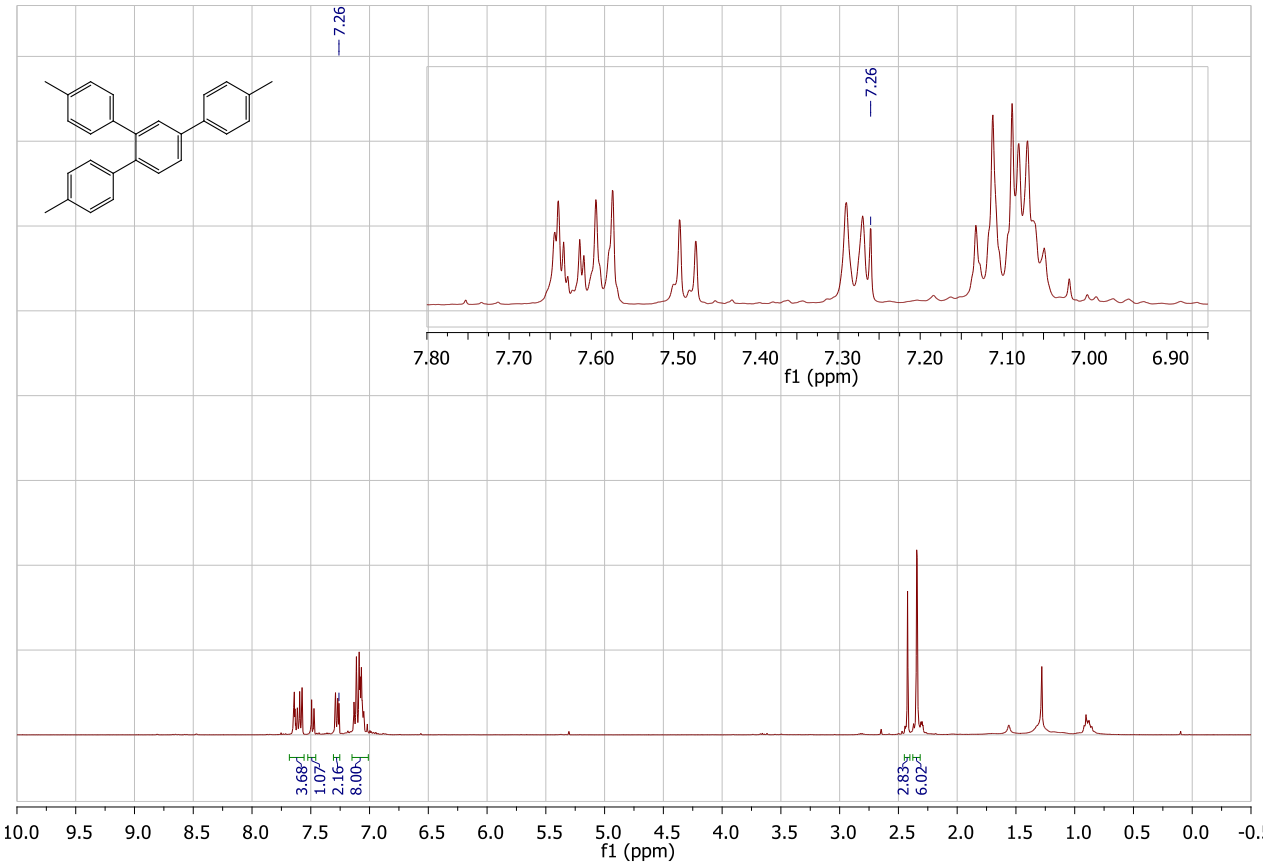
3.1. Spectra of compounds ***5a–d***

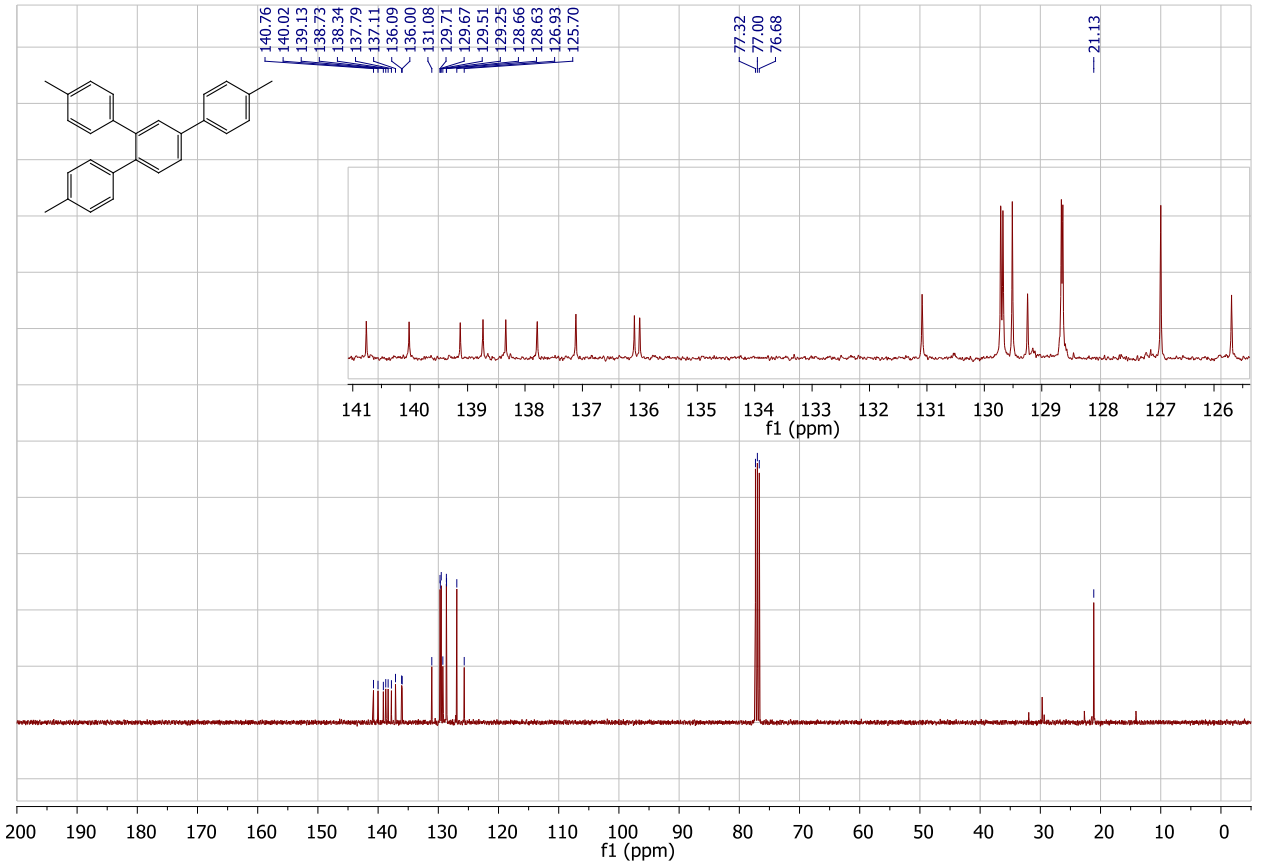
1,2,4-Triphenylbenzene (**5a**)



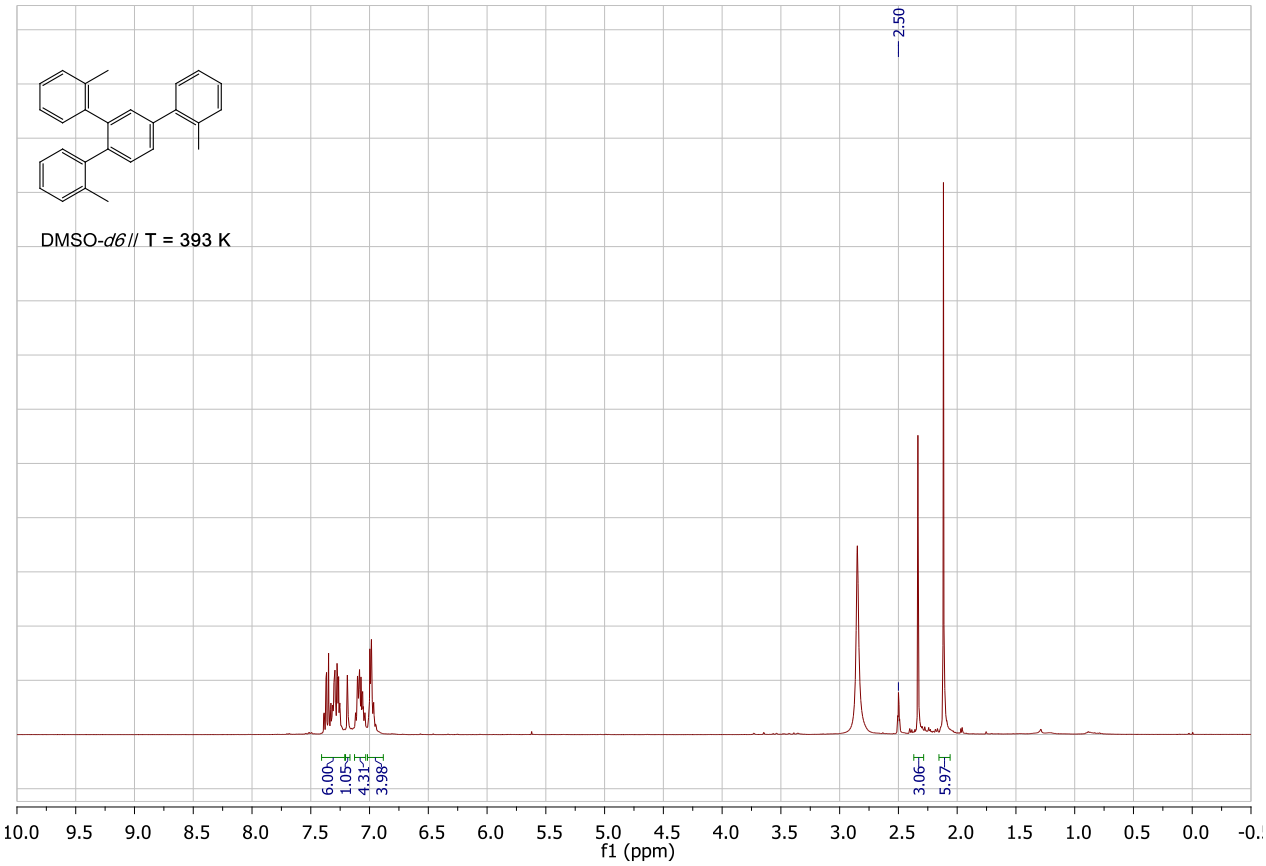


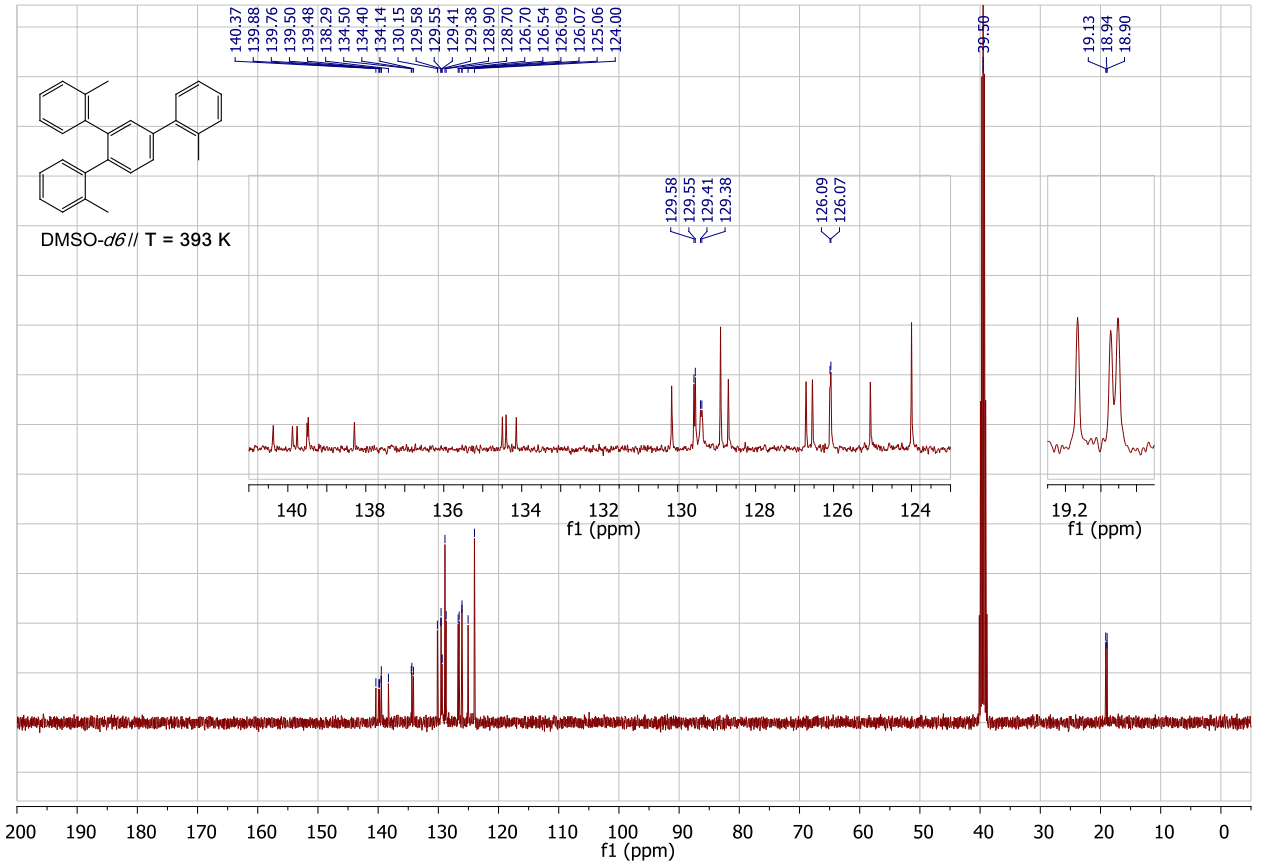
1,2,4-Tris(p-tolyl)benzene (**5b**)



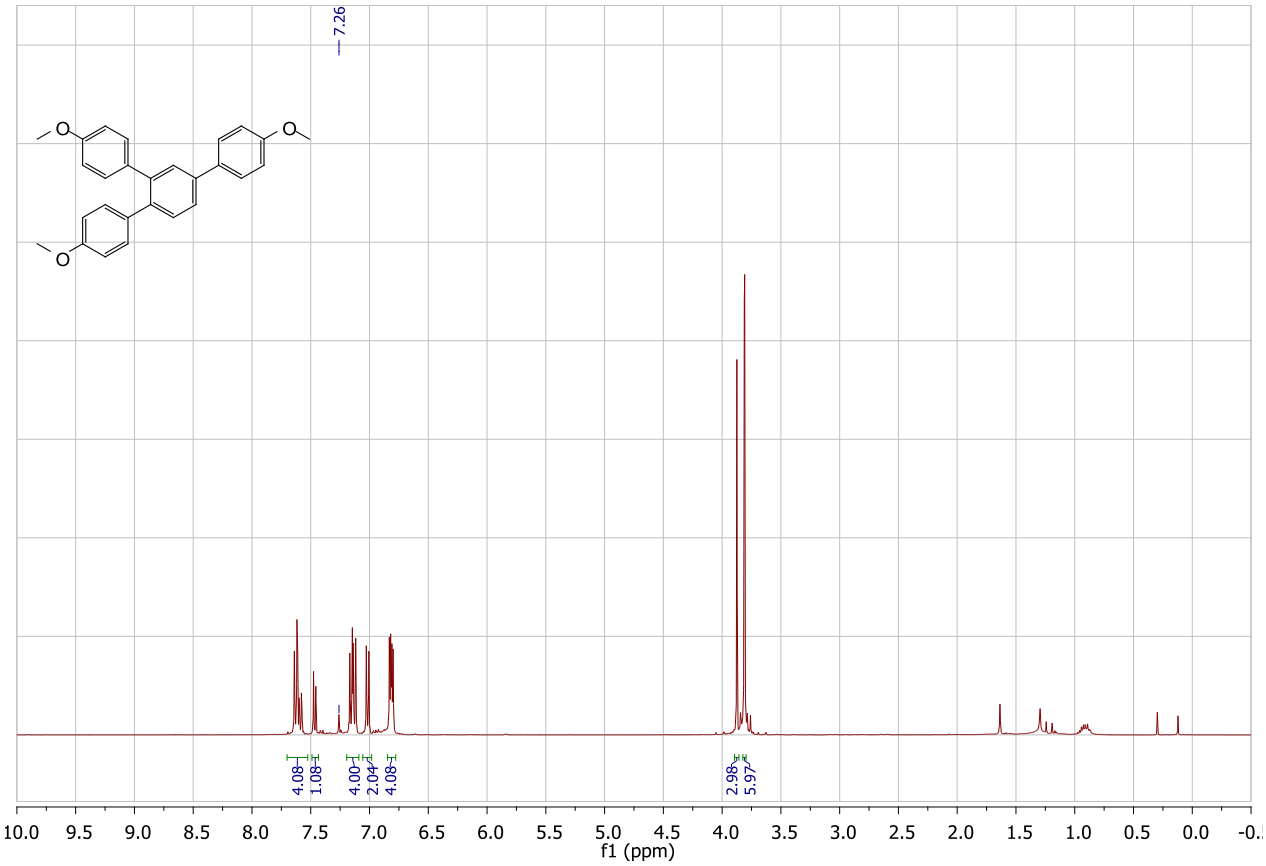


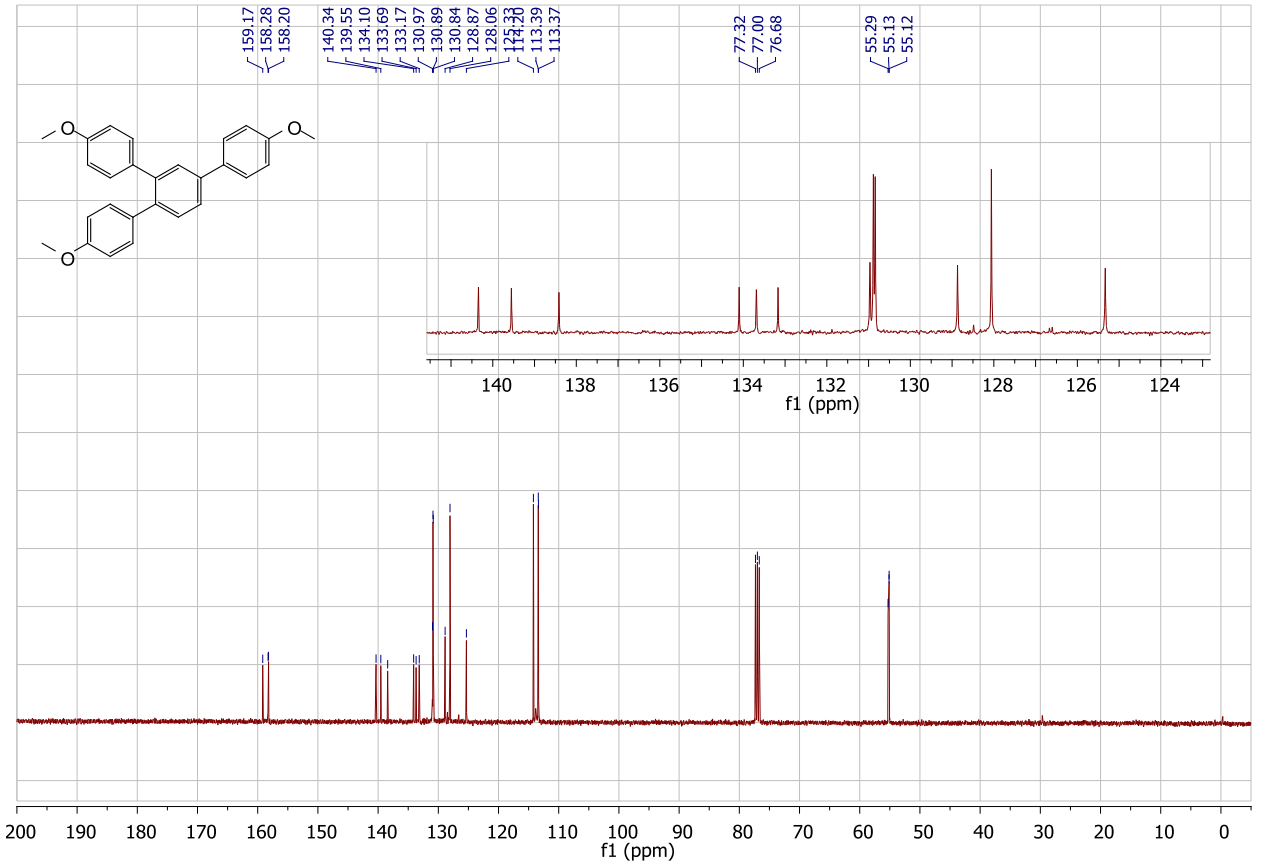
1,2,4-Tris(*o*-tolyl)benzene (**5c**)





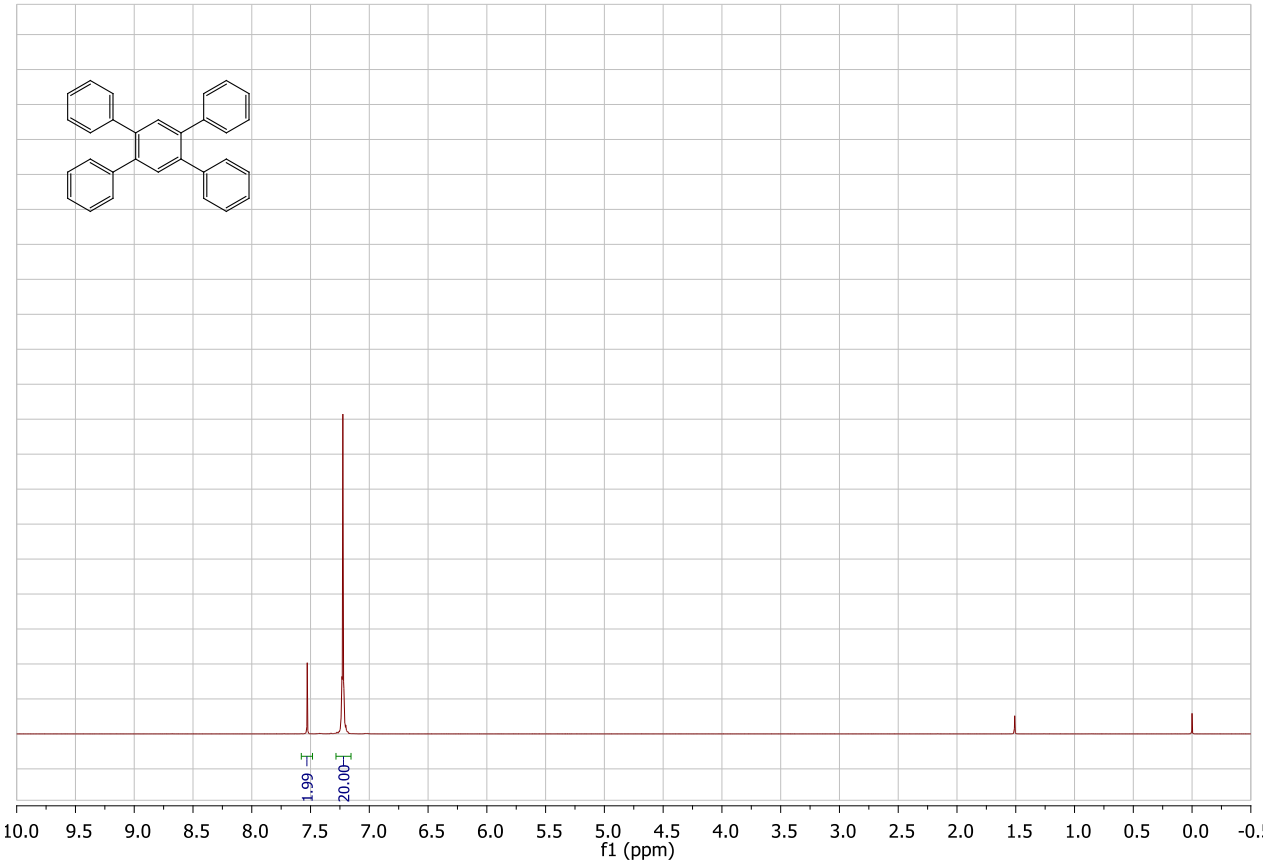
1,2,4-Tris(4-methoxyphenyl)benzene (**5d**)

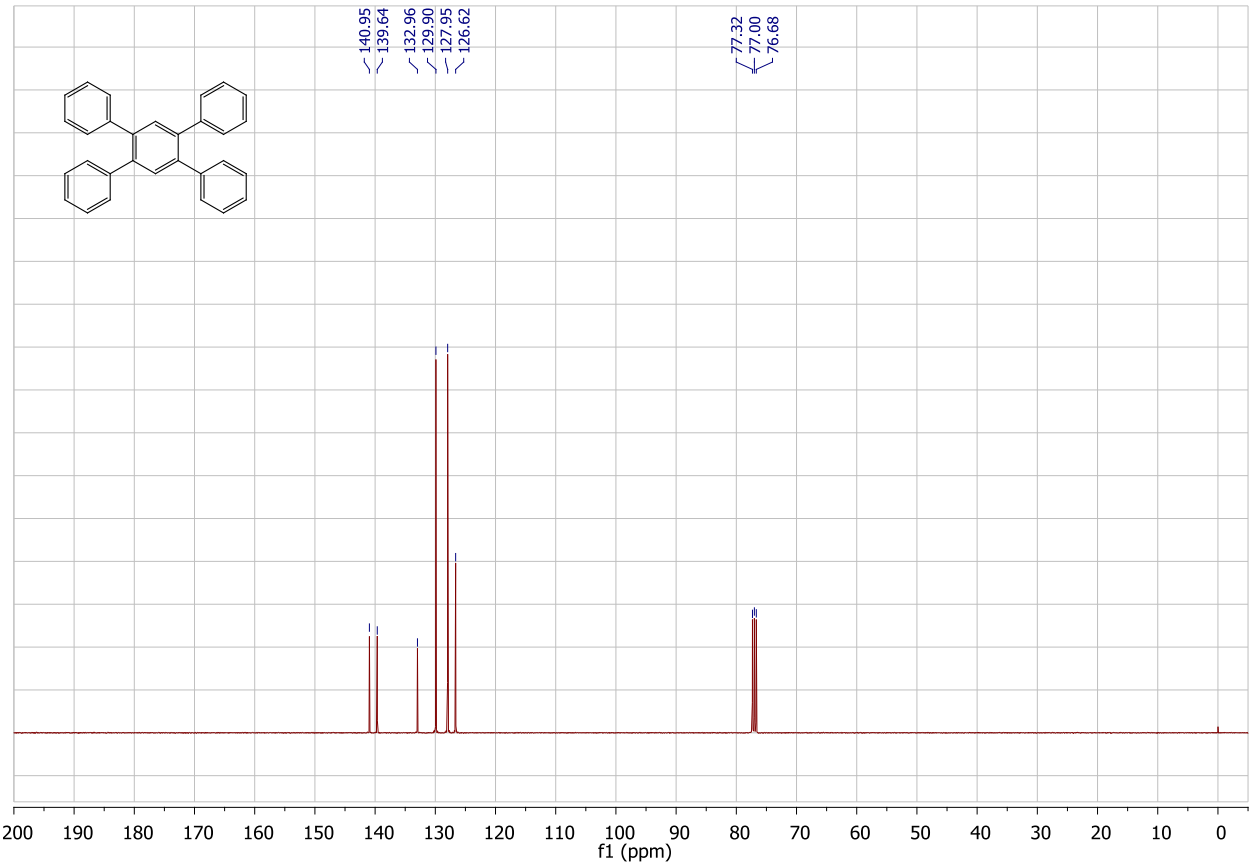




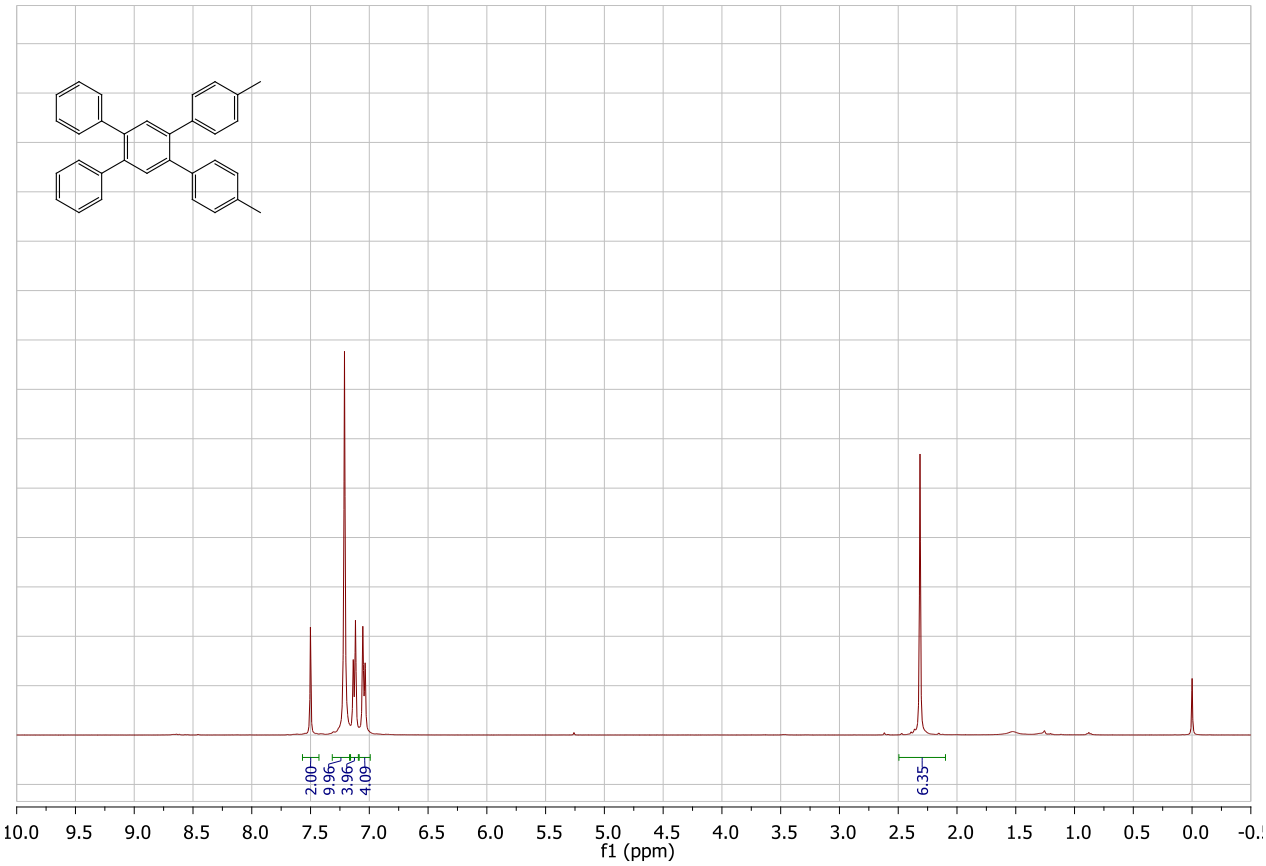
3.2. Spectra of compounds ***11a−h***

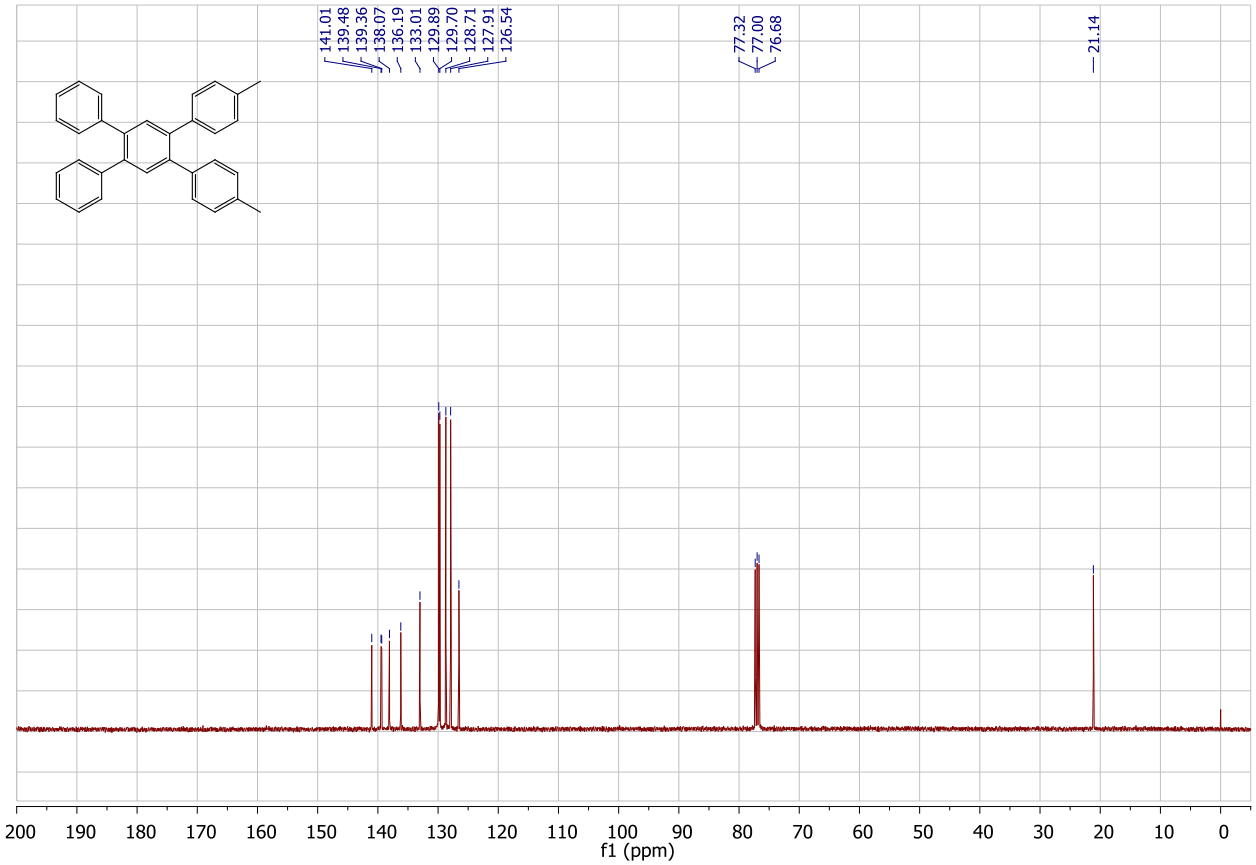
1,2,4,5-Tetraphenylbenzene (**11a**)



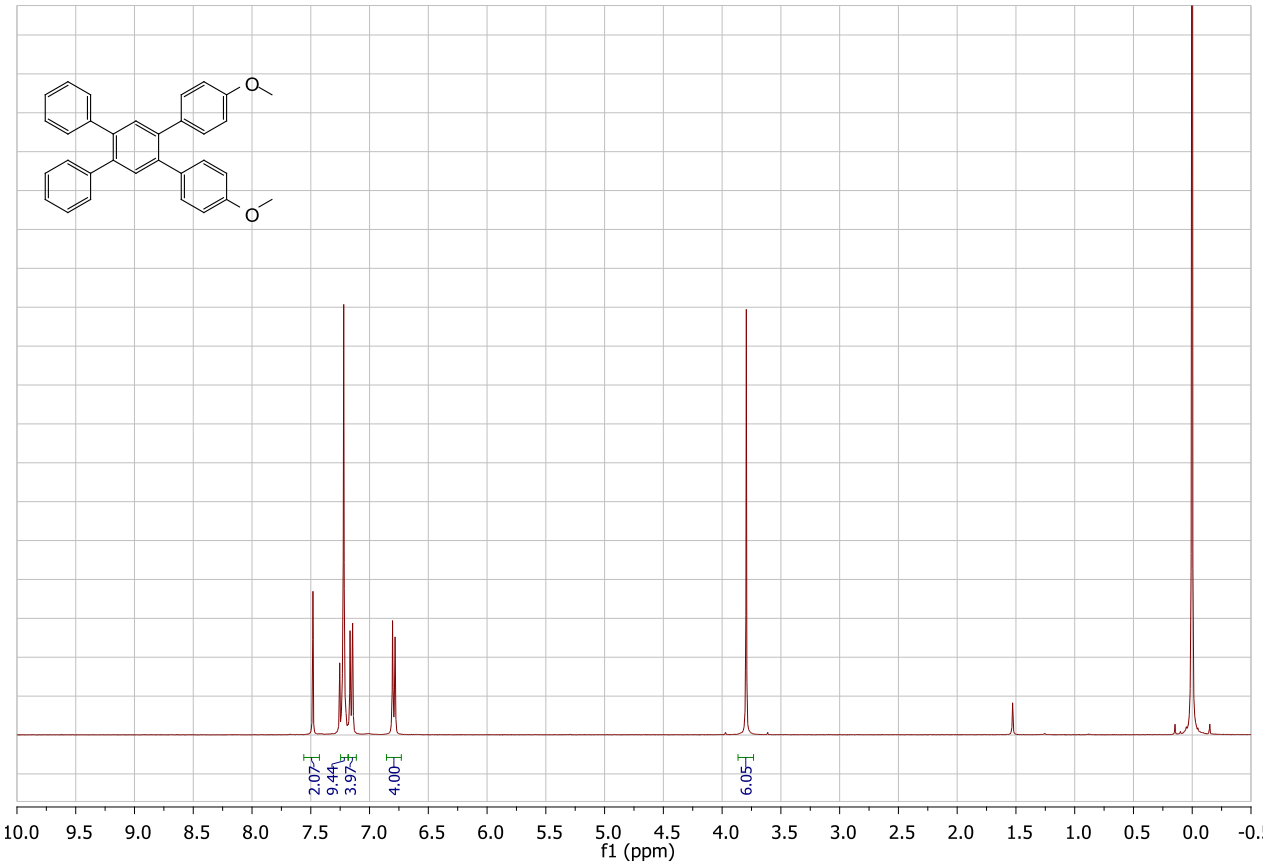


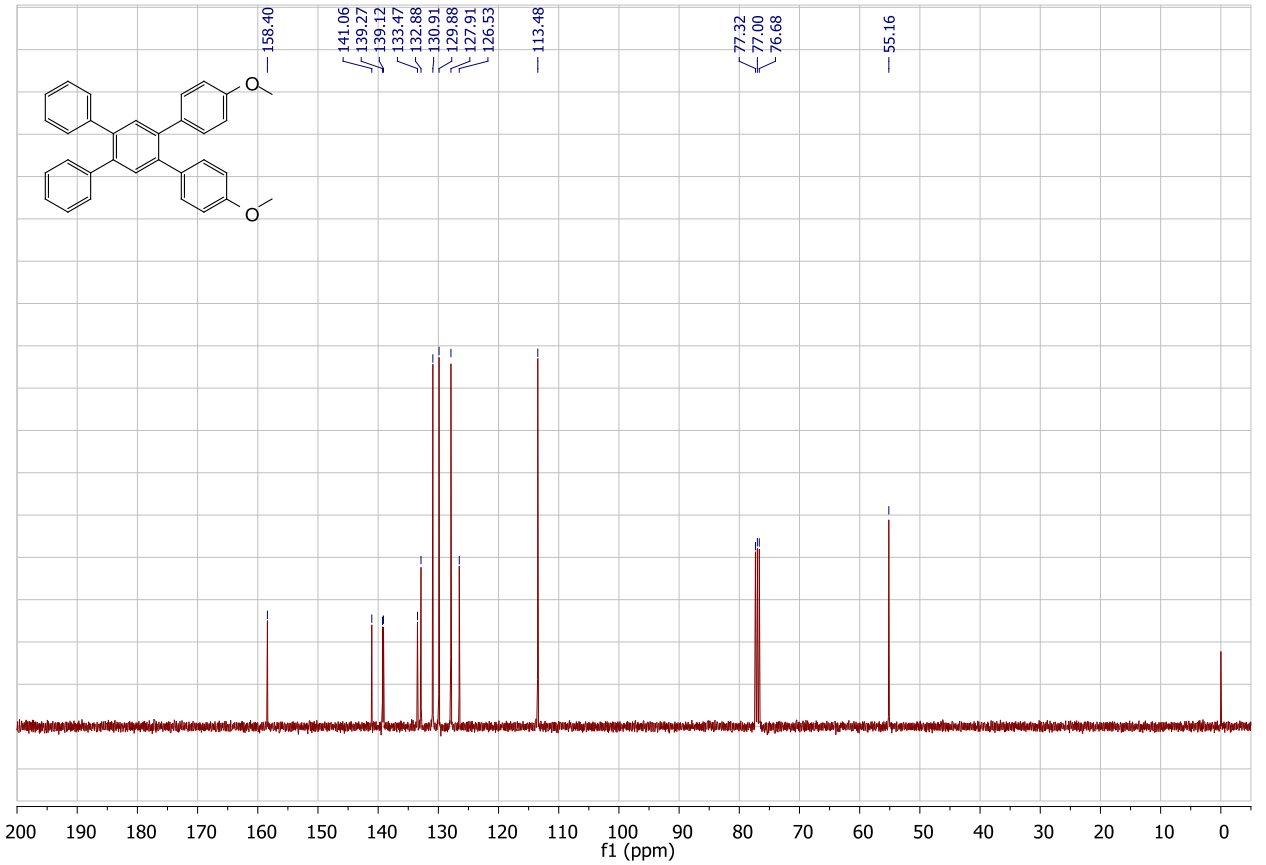
1,2-Diphenyl-4,5-bis(p-tolyl)benzene (**11b**)



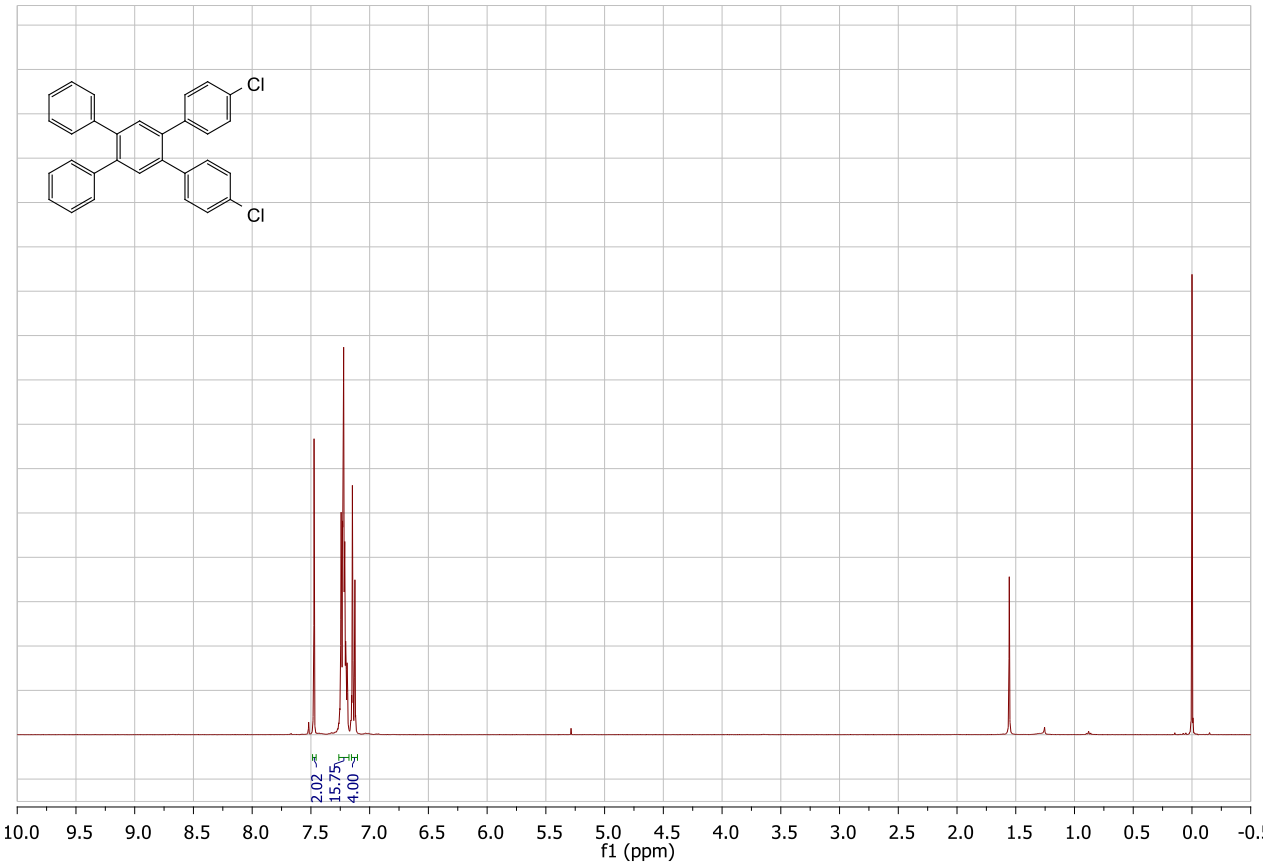


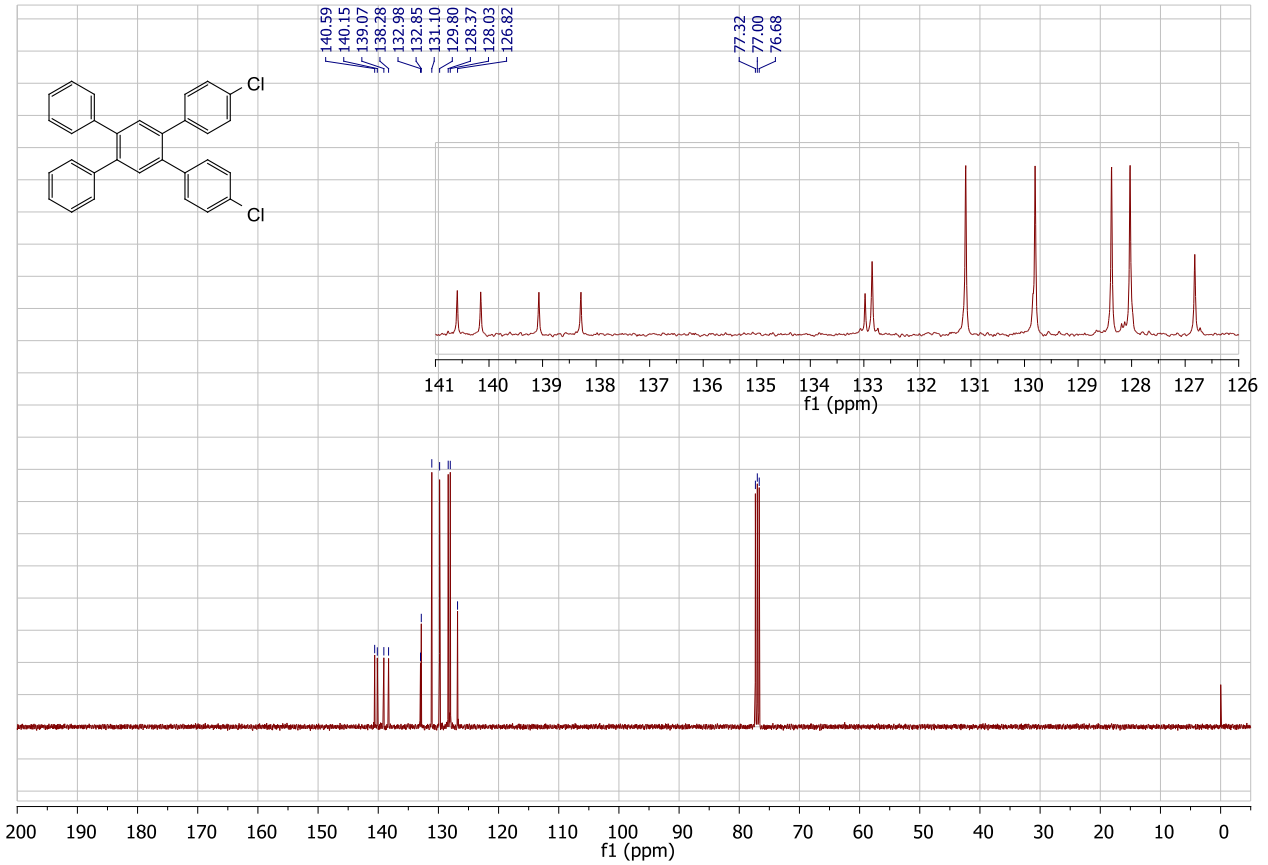
1,2-Bis(4-methoxyphenyl)-4,5-diphenyl-benzene (**11c**)



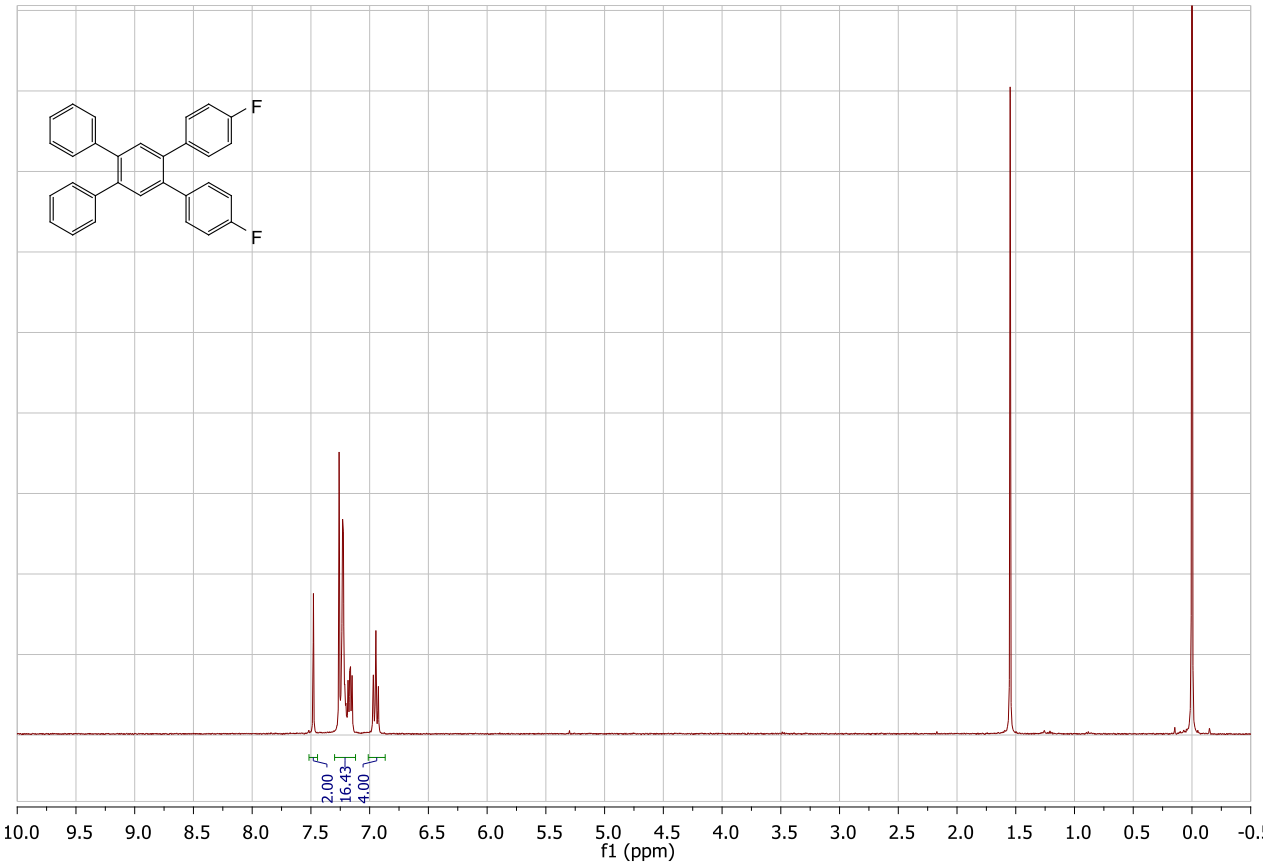


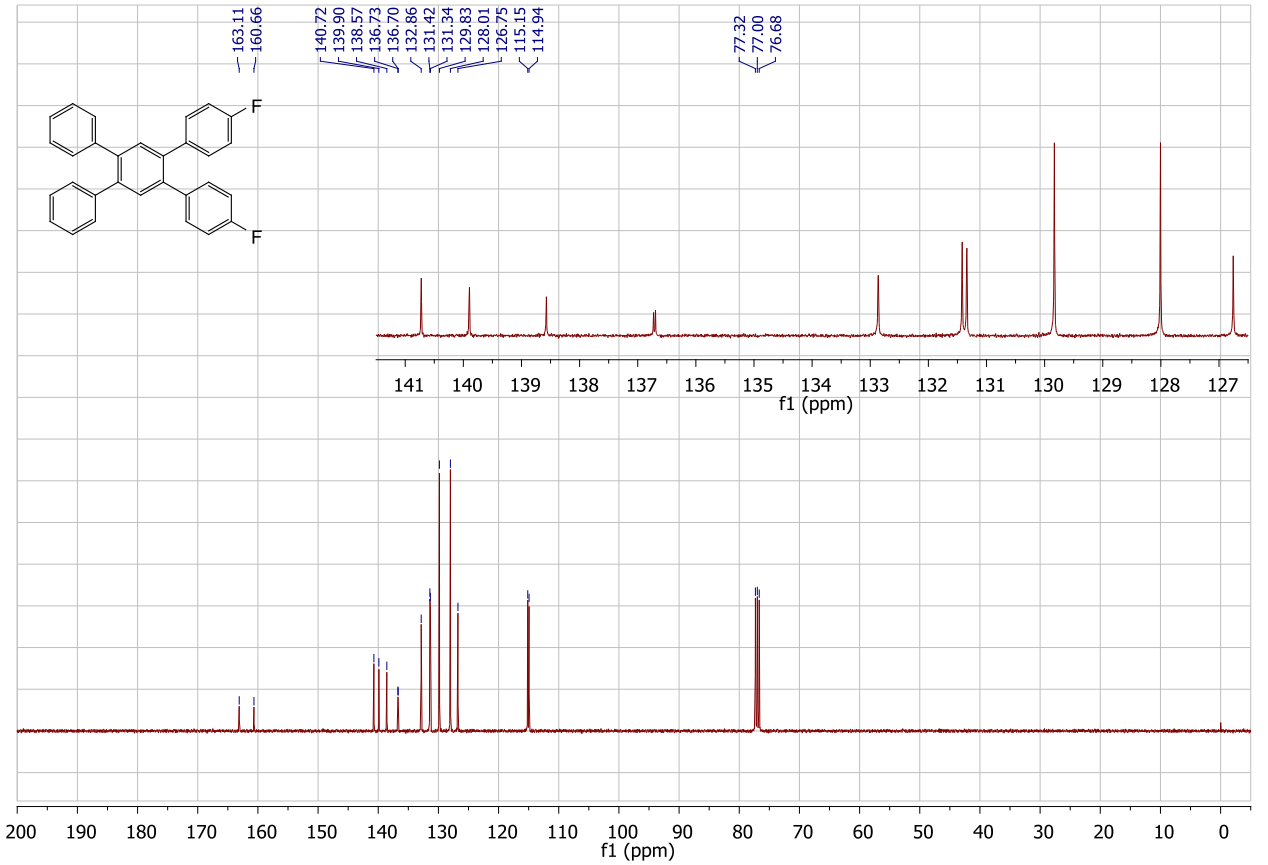
1,2-Bis(4-chlorophenyl)-4,5-diphenyl-benzene (**11d**)



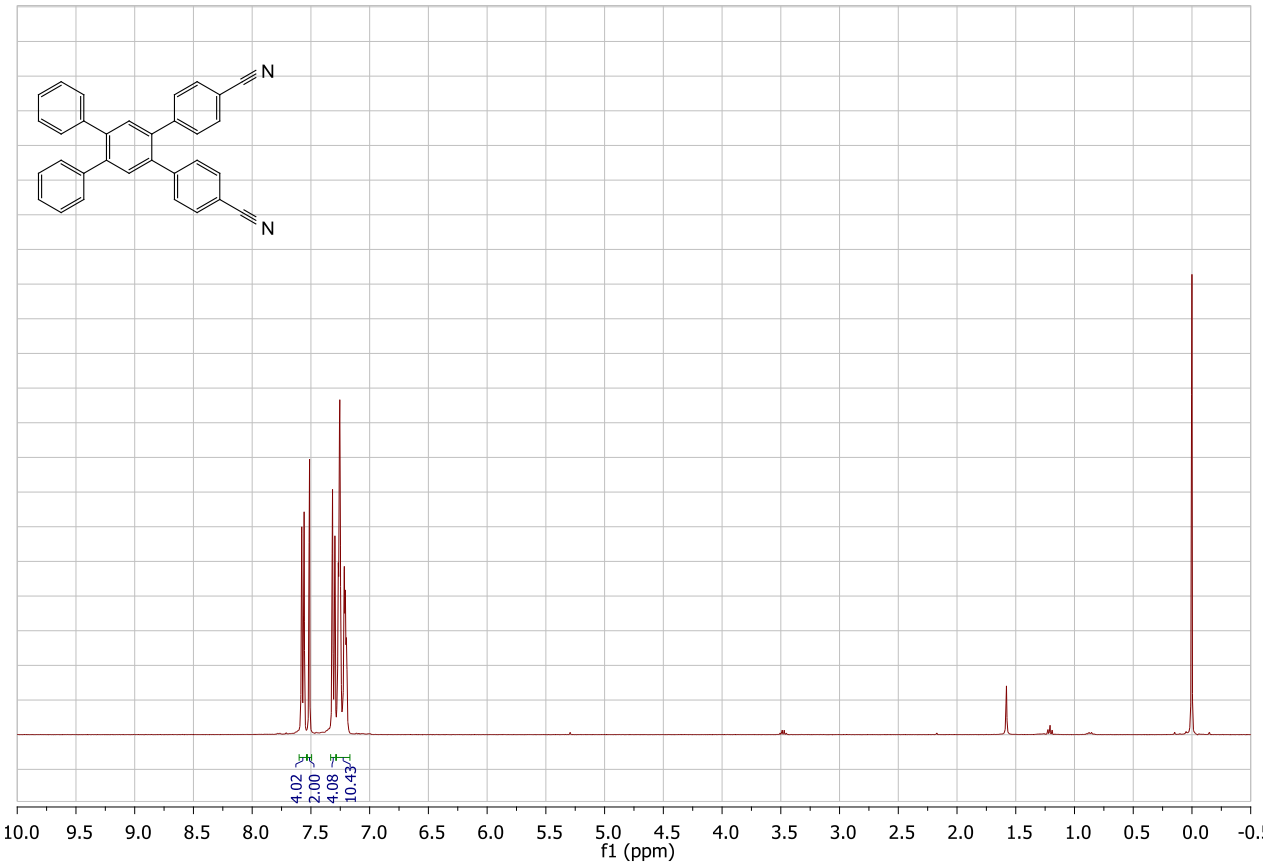


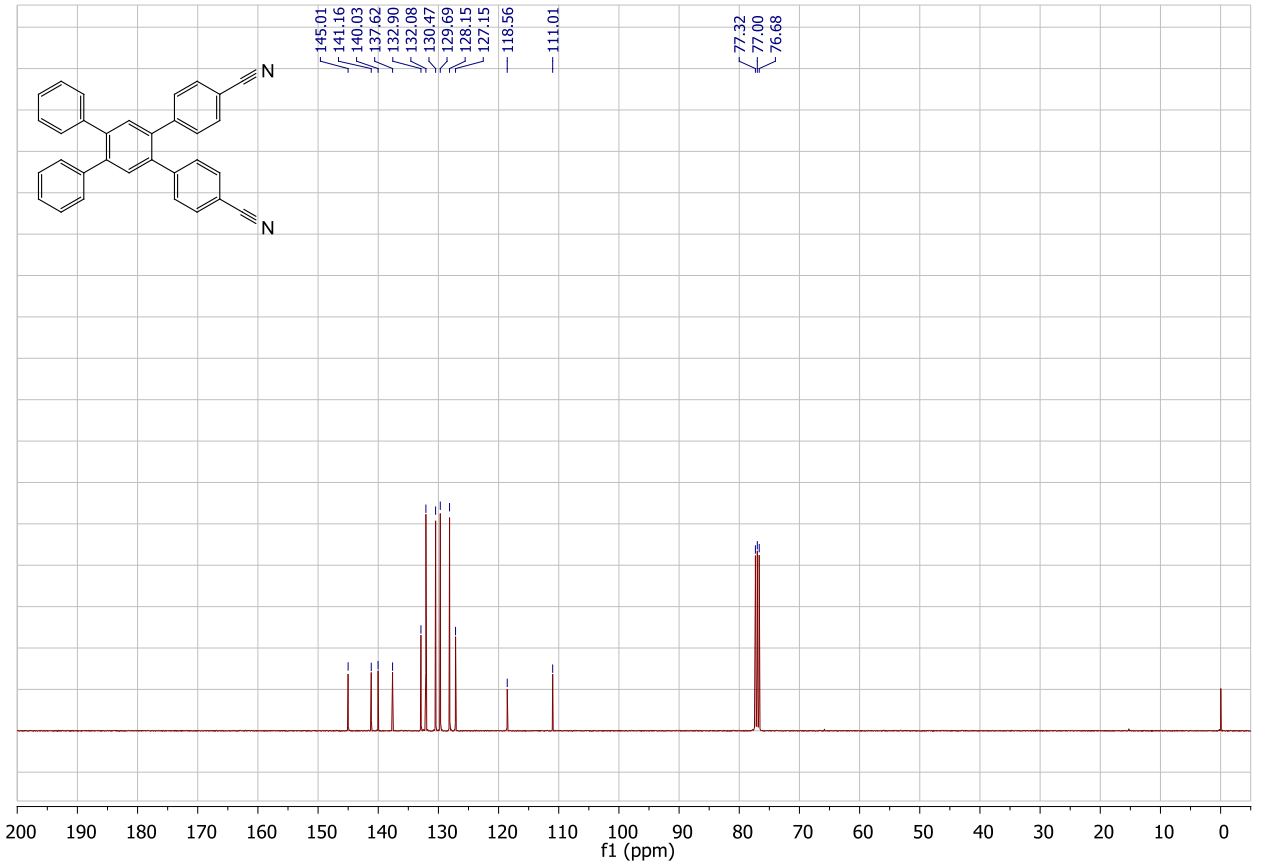
1,2-Bis(4-fluorophenyl)-4,5-diphenyl-benzene (**11e**)



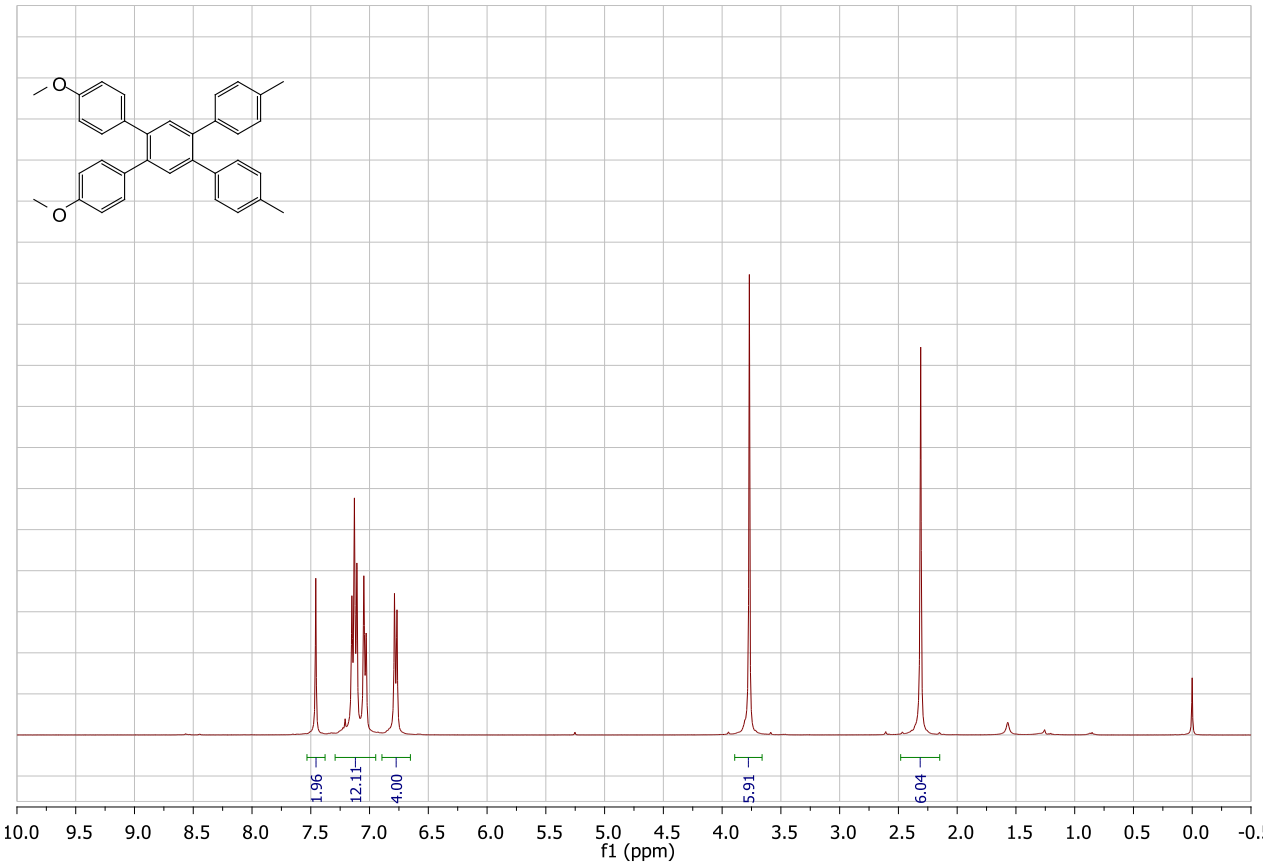


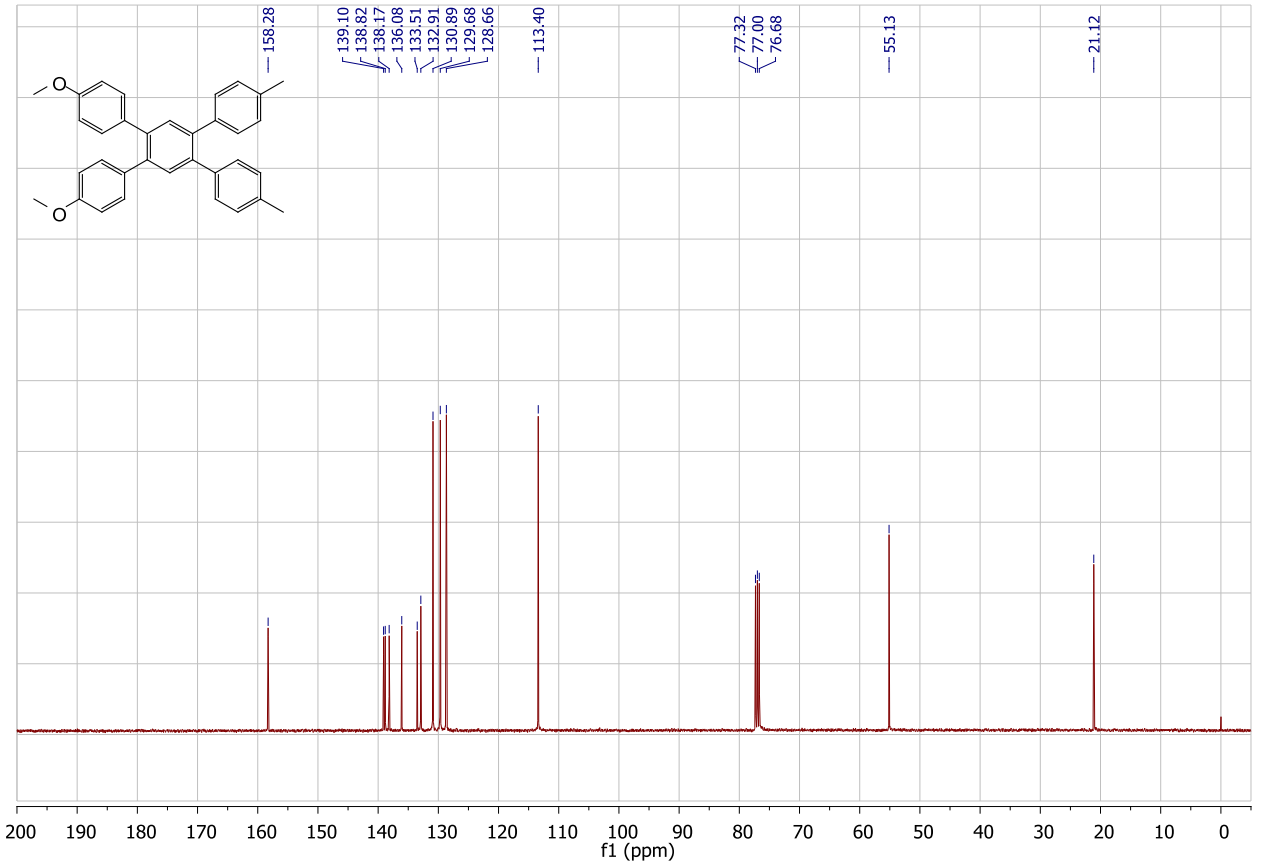
4-[2-(4-Cyanophenyl)-4,5-diphenyl-phenyl]benzonitrile (**11f**)



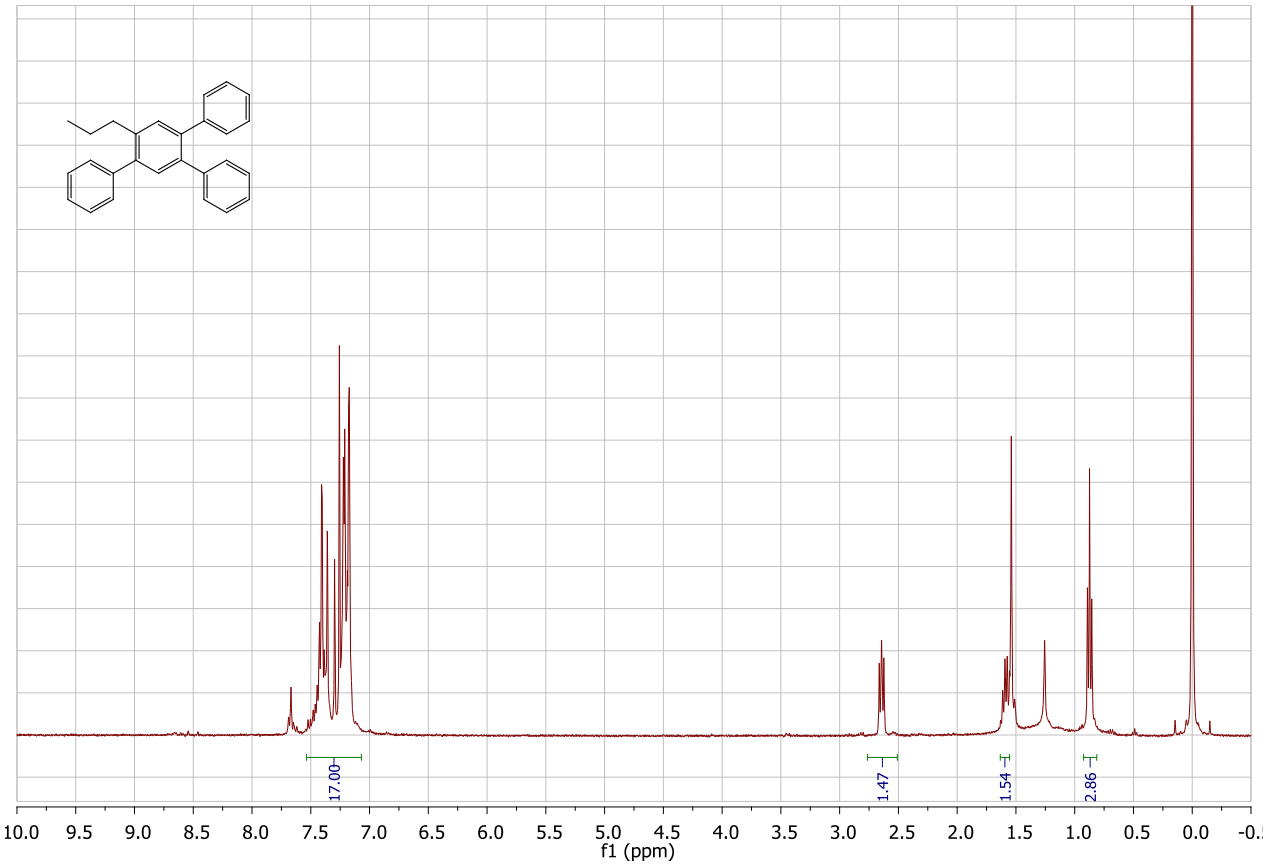


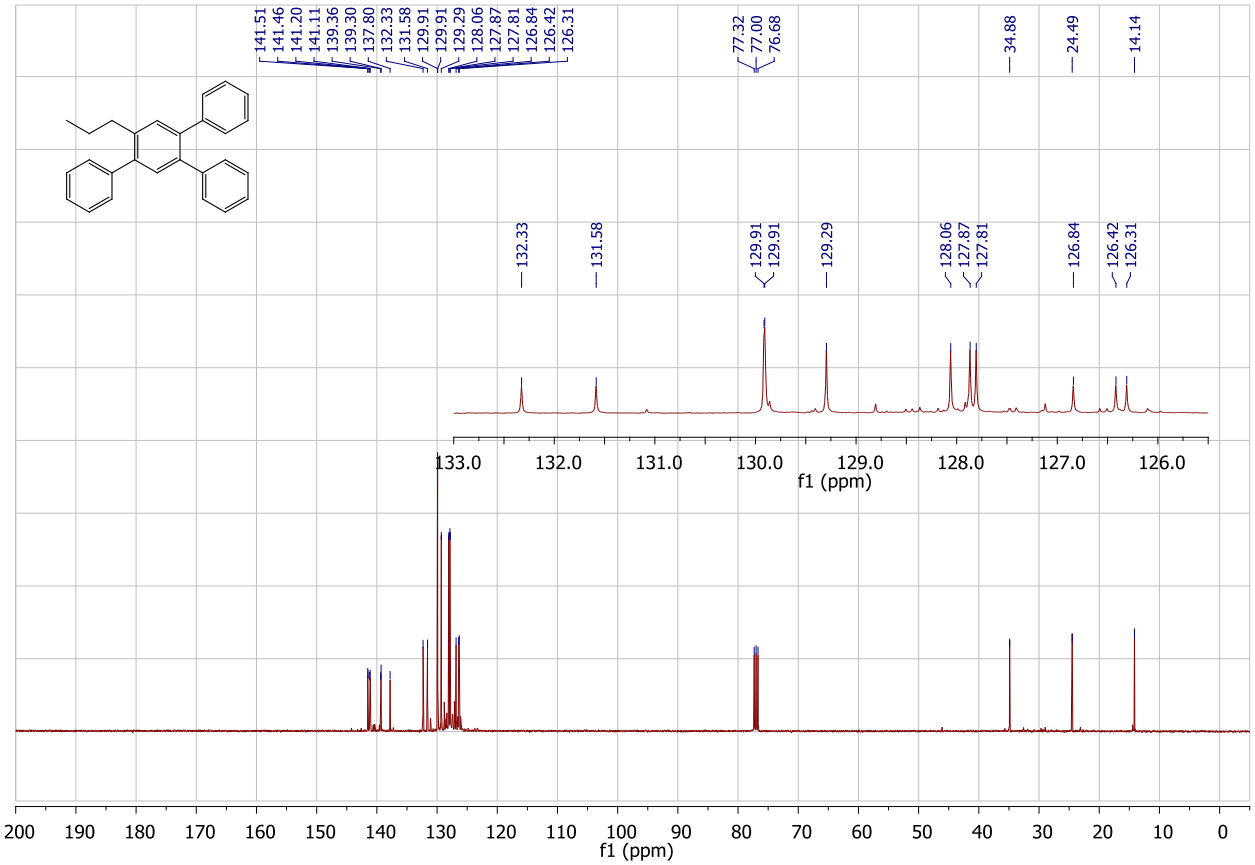
1,2-Bis(4-methoxyphenyl)-4,5-bis(p-tolyl)benzene (**11g**)





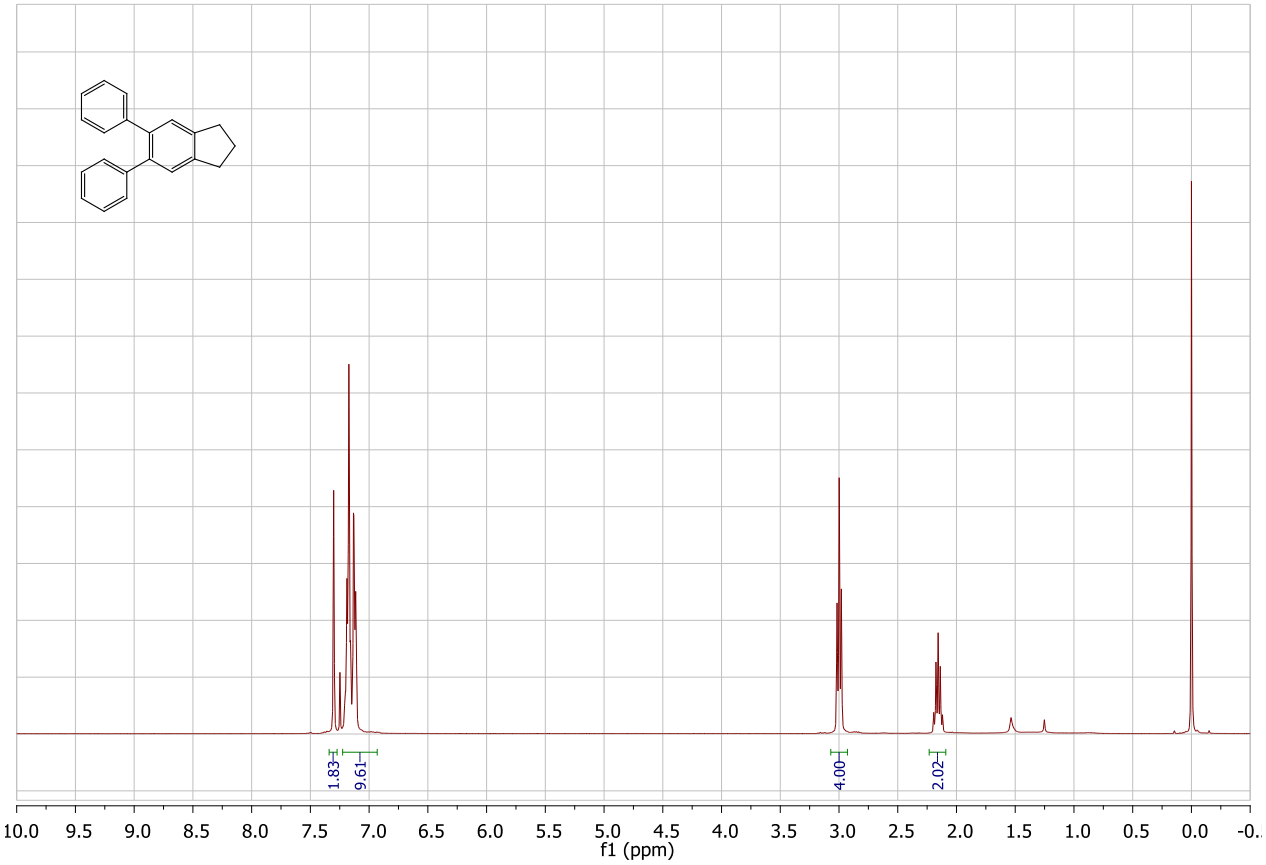
1,2,4-Triphenyl-5-propyl-benzene (**11h**)

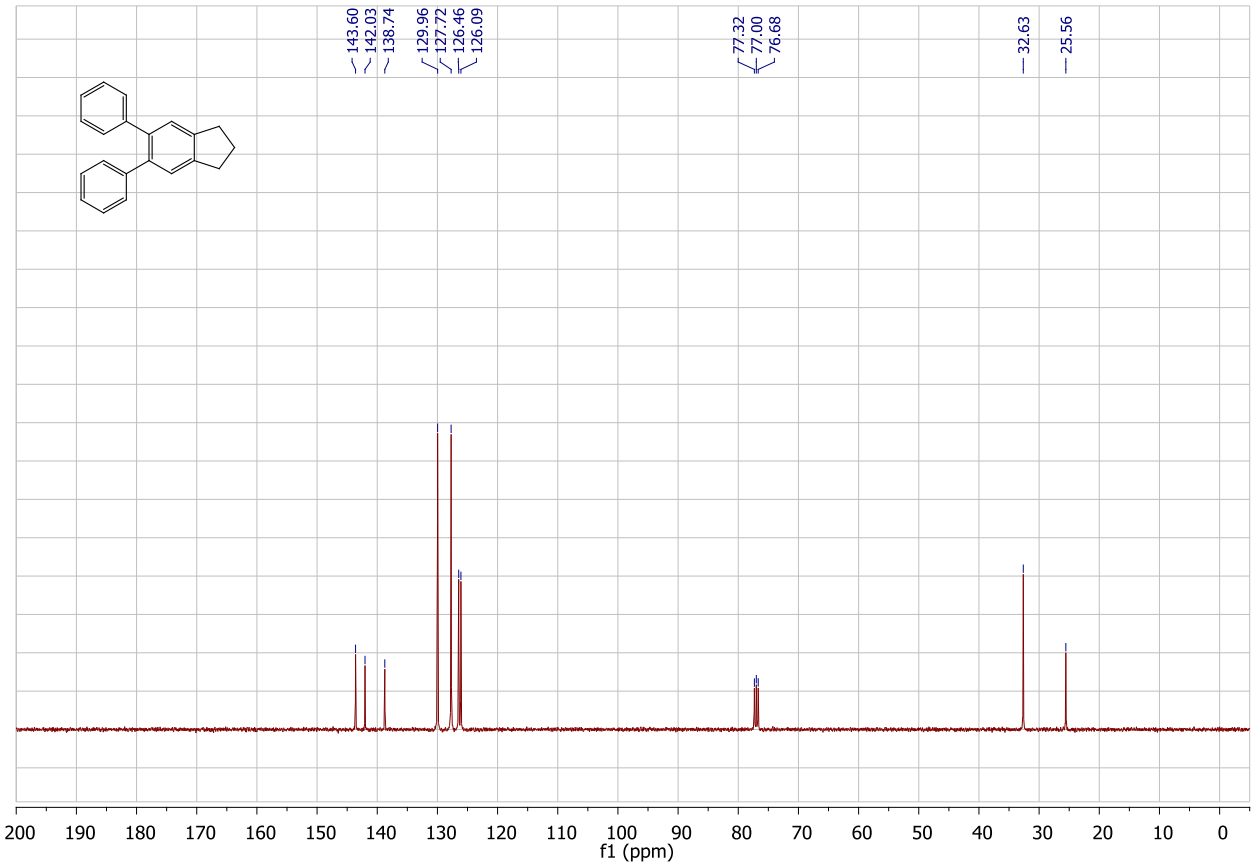




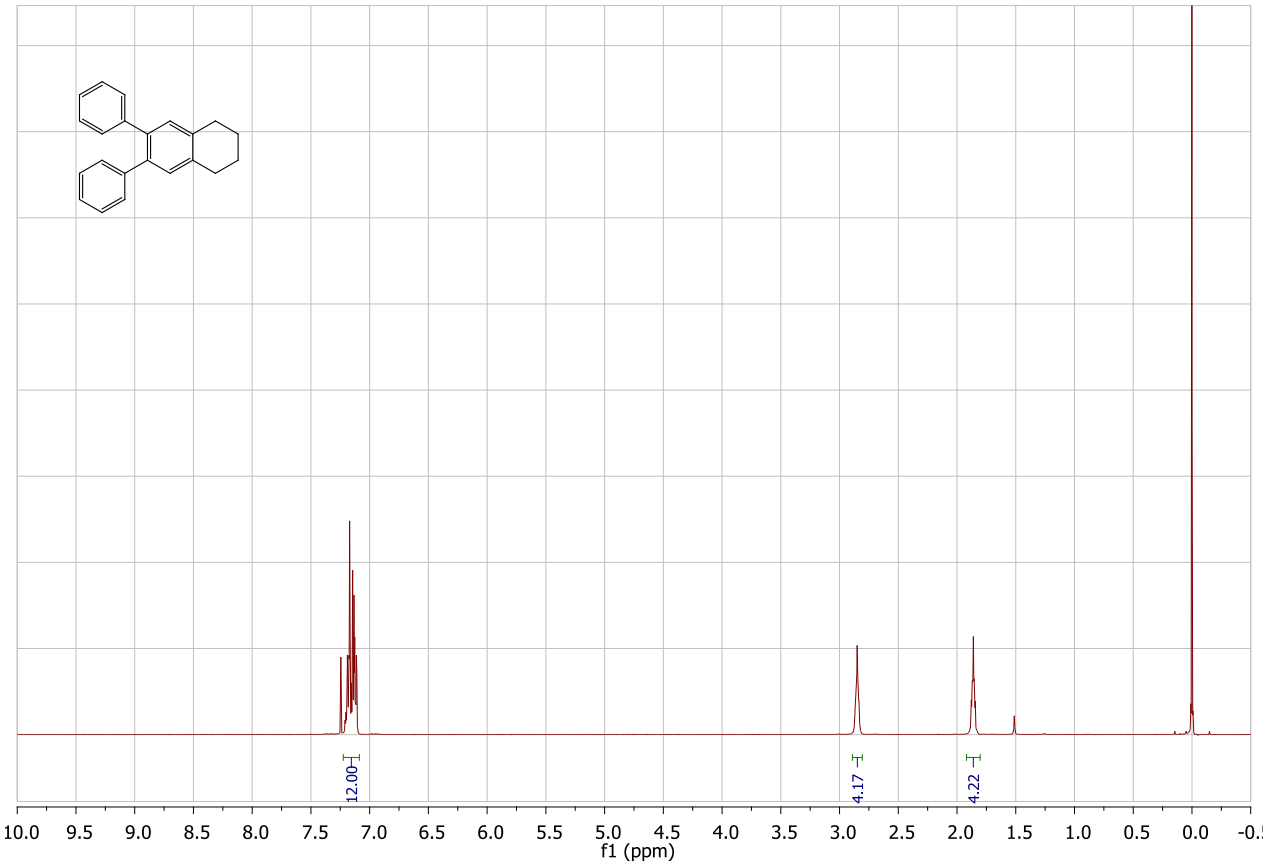
*3.3. Spectra of compounds **13a–h** and compounds **14–16***

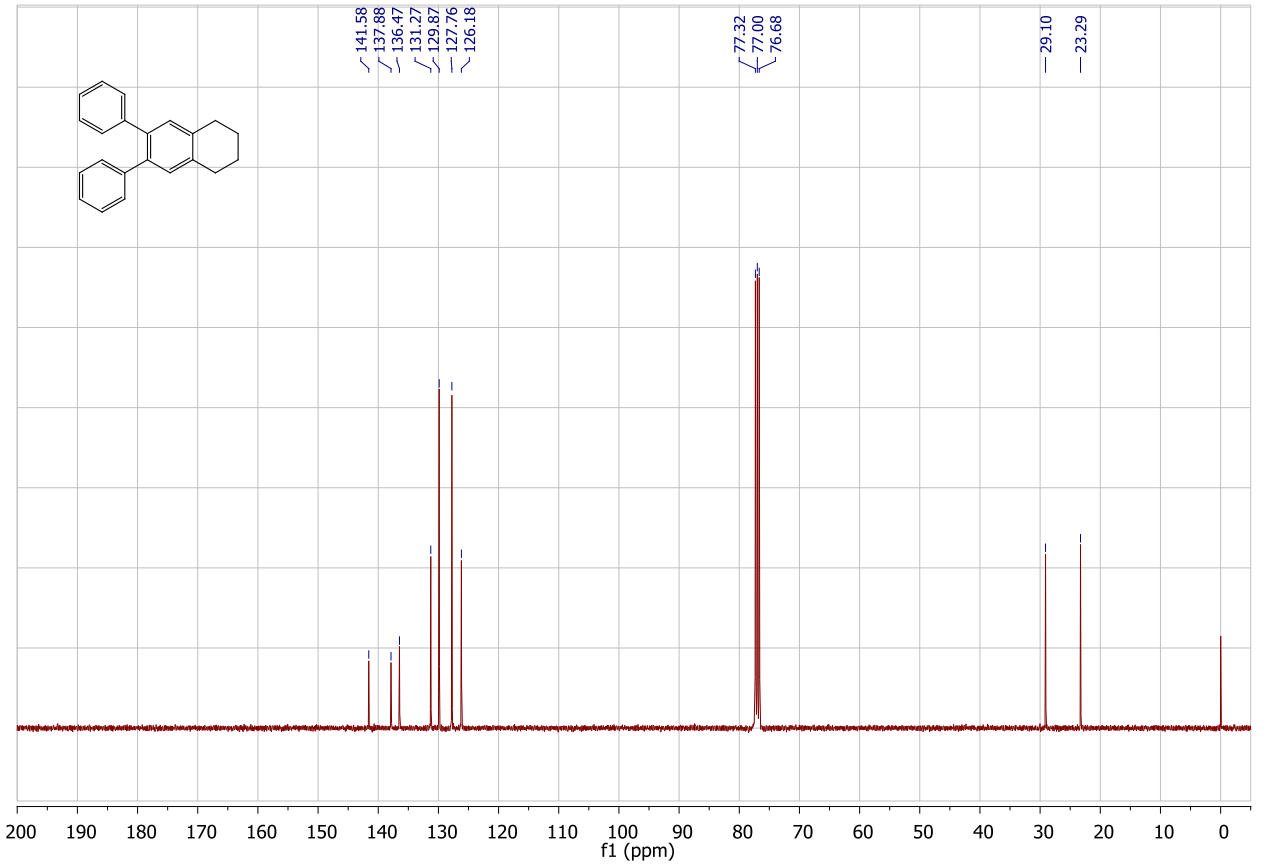
5,6-Diphenyl-2,3-dihydro-1H-indene (**13a**)



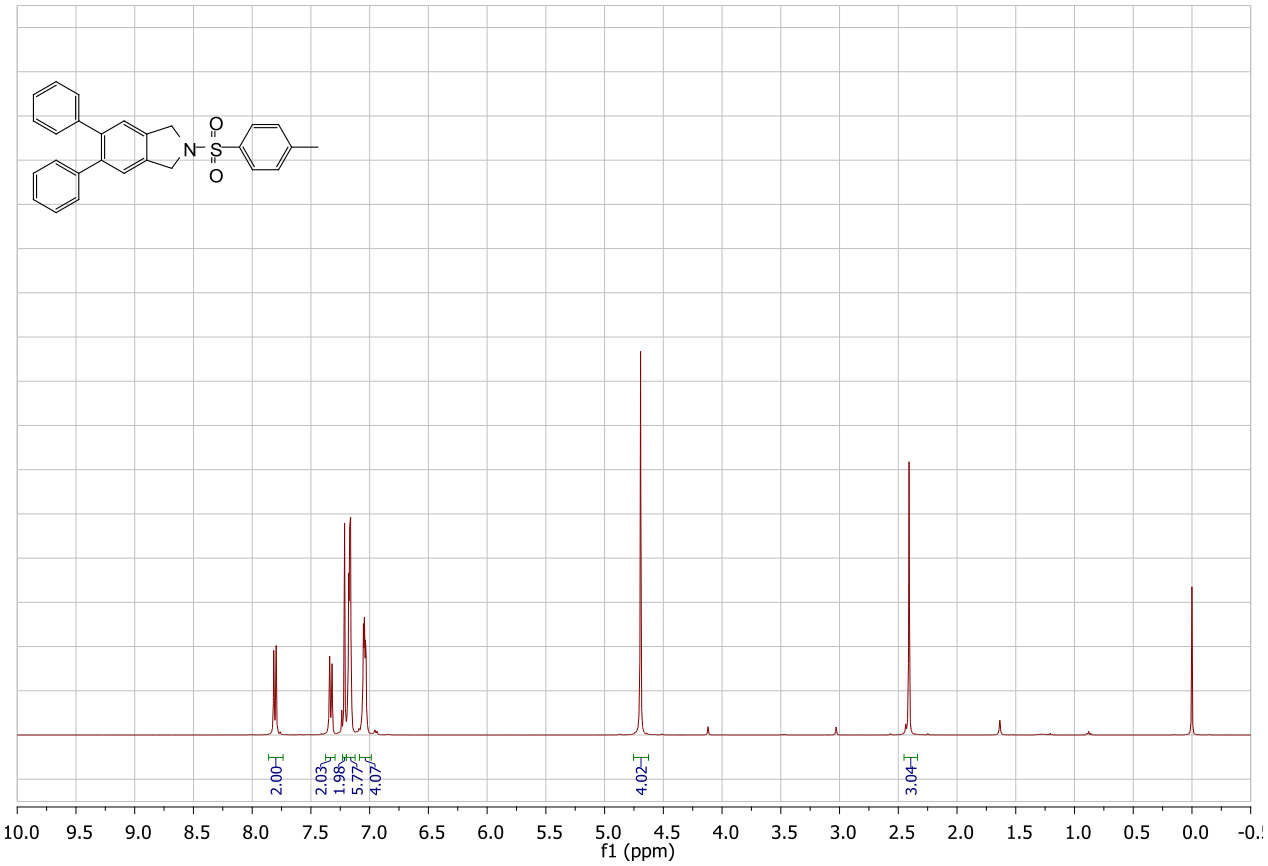


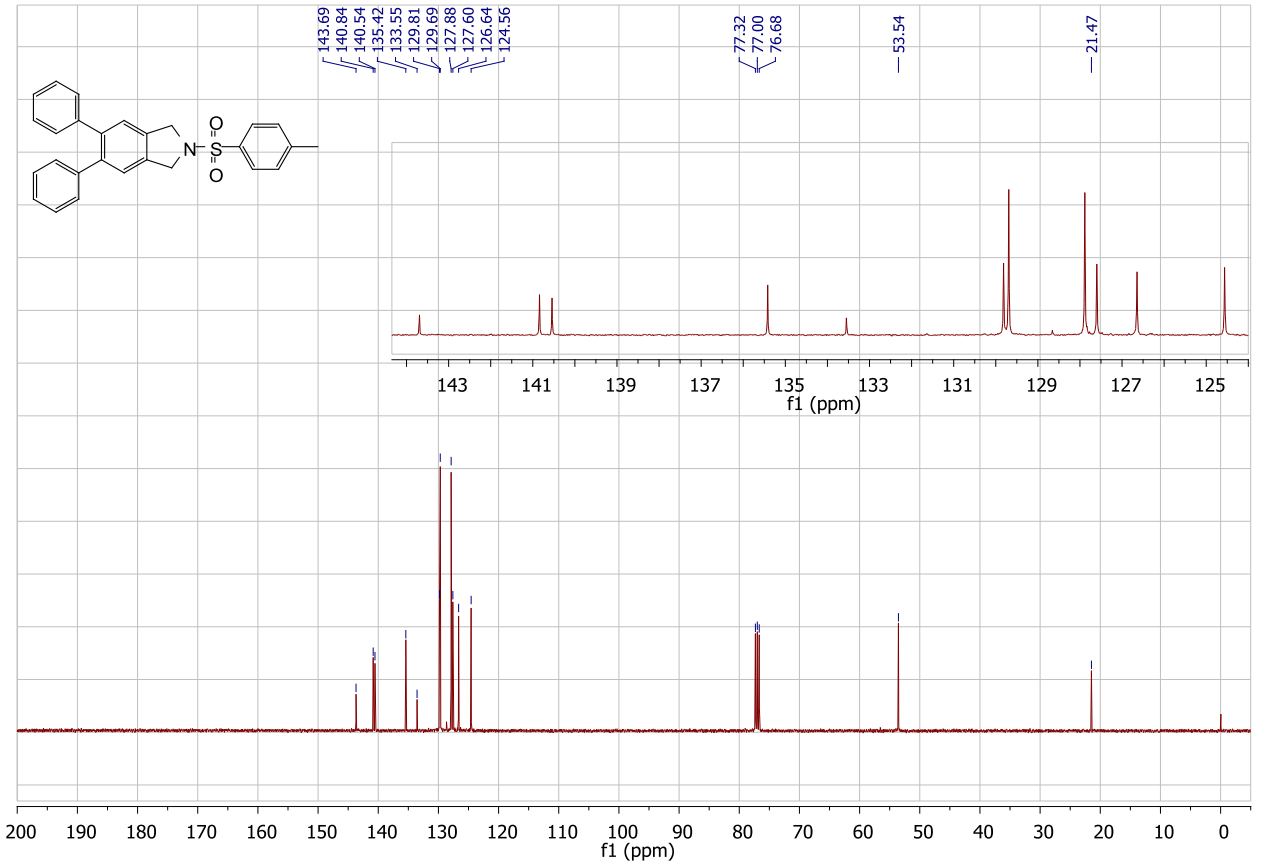
6,7-Diphenyl-1,2,3,4-tetrahydronaphthalene (**13b**)



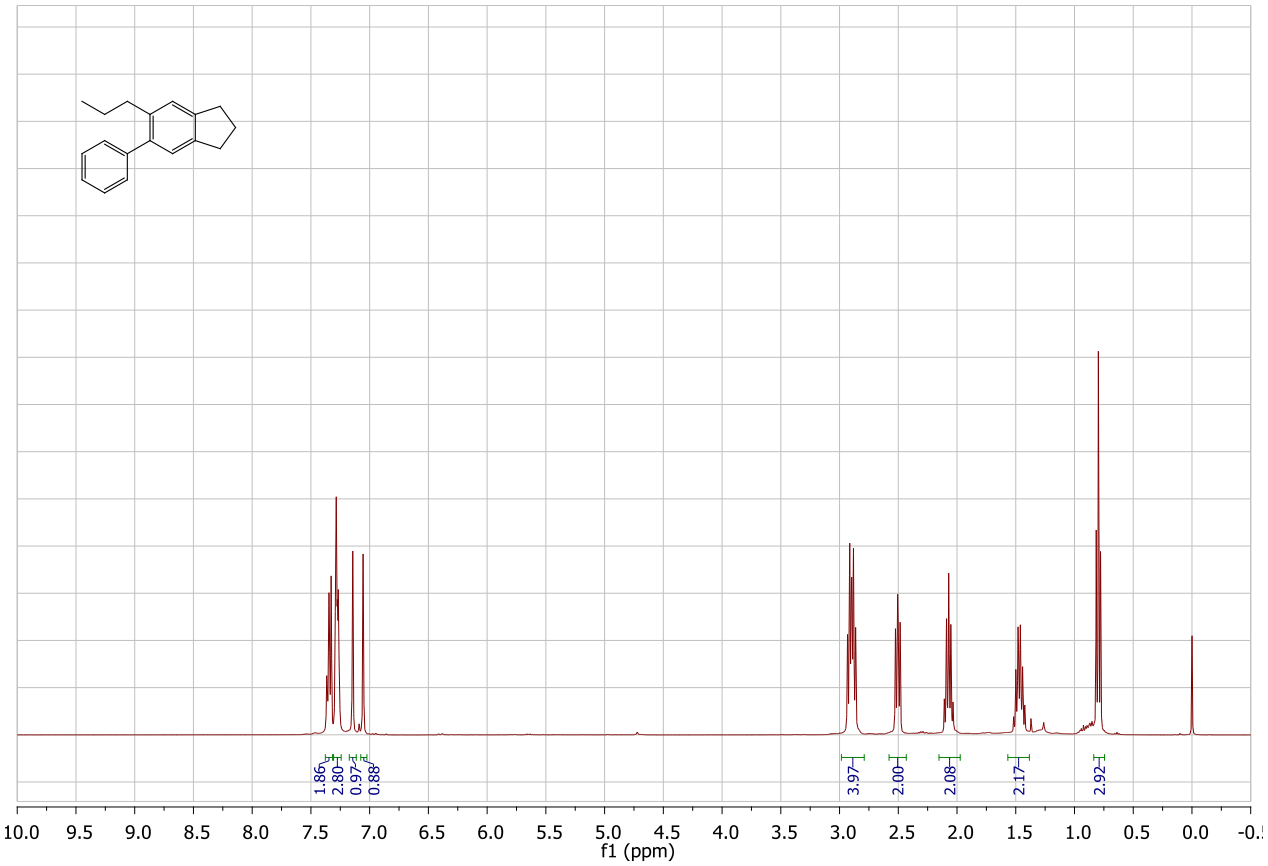


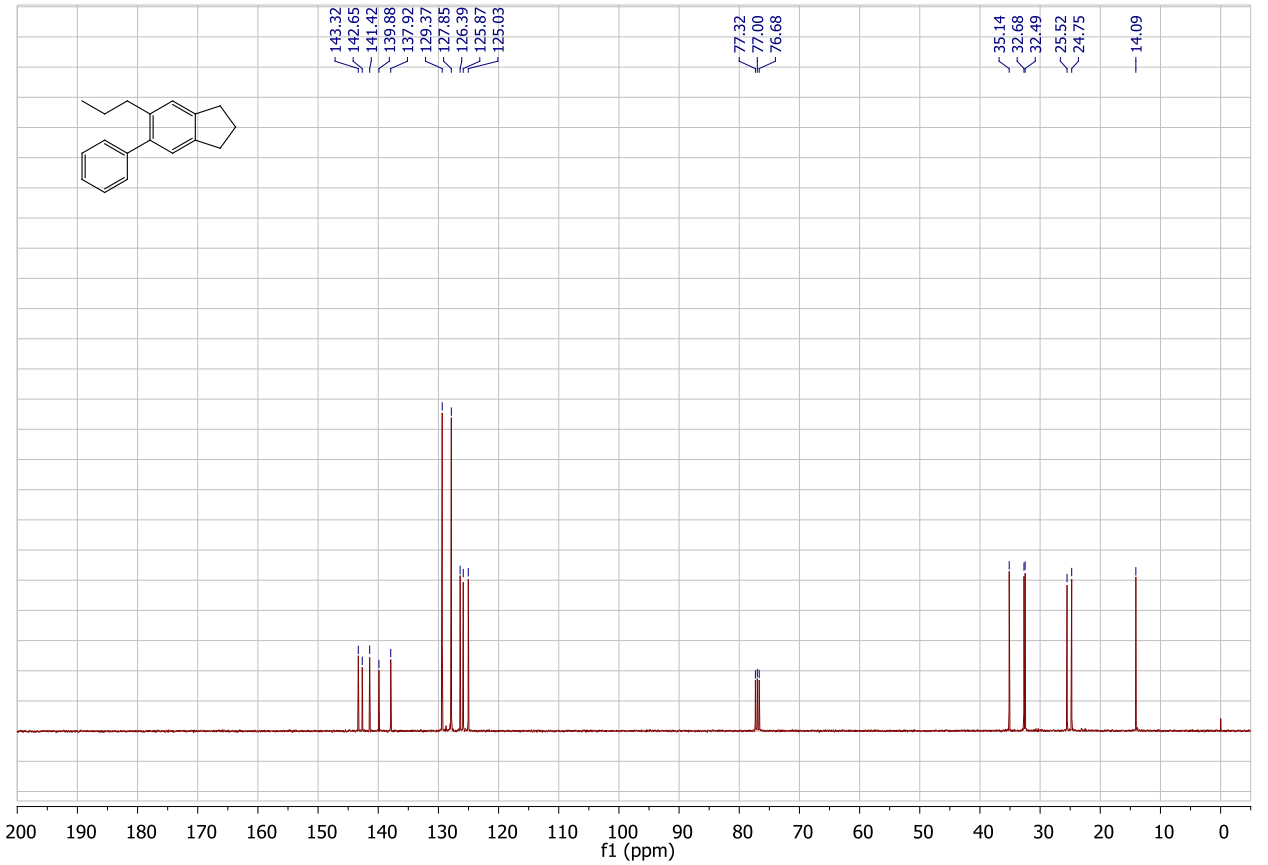
5,6-Diphenyl-2-tosylisoindoline (**13c**)



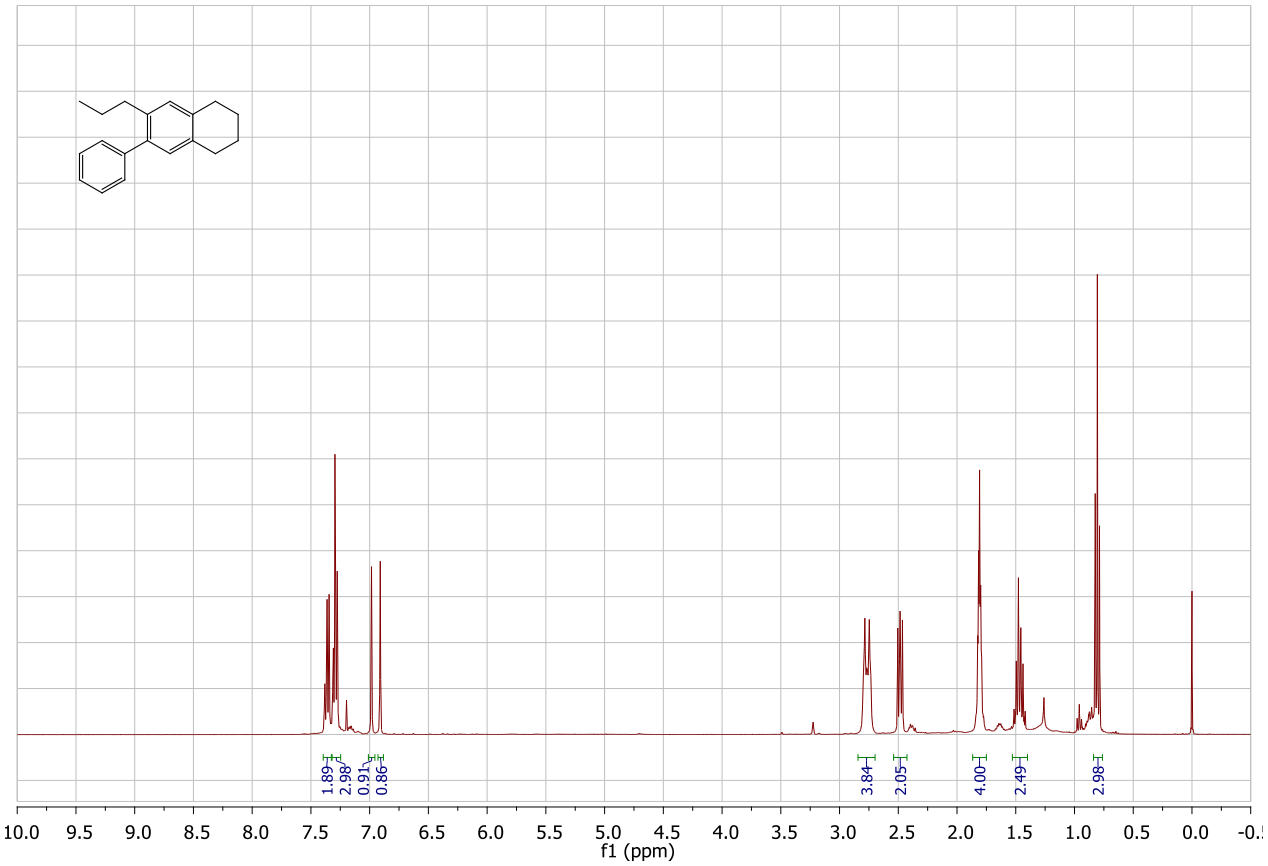


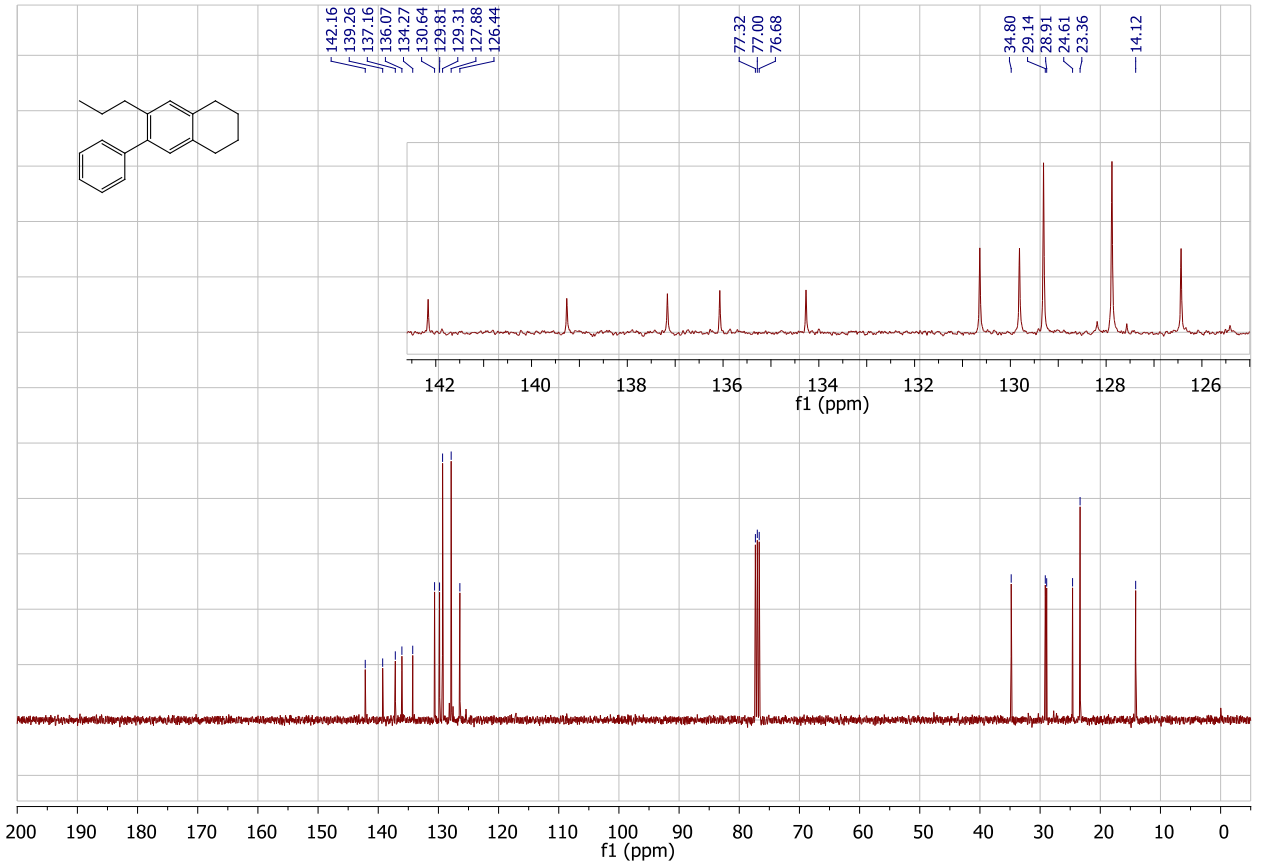
5-Phenyl-6-propyl-2,3-dihydro-1H-indene (**13d**)



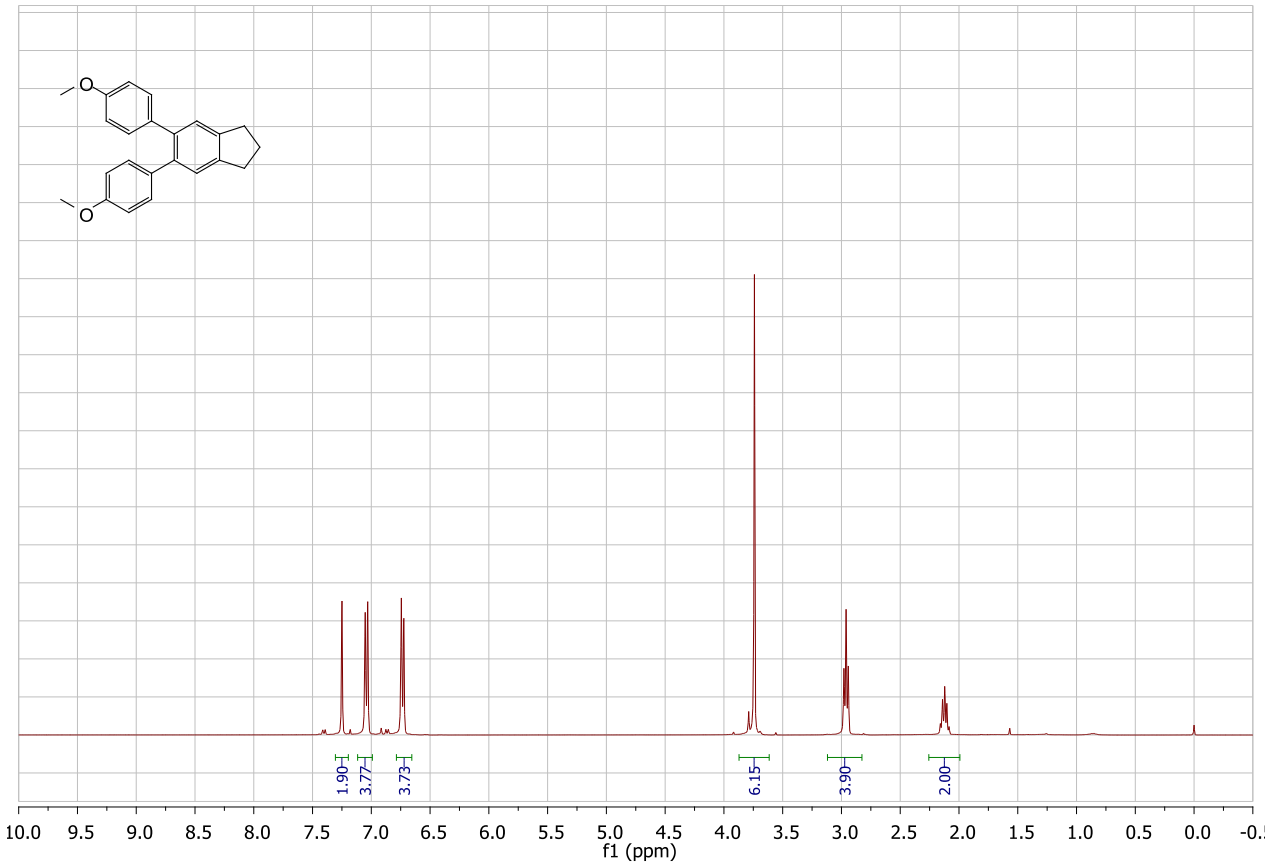


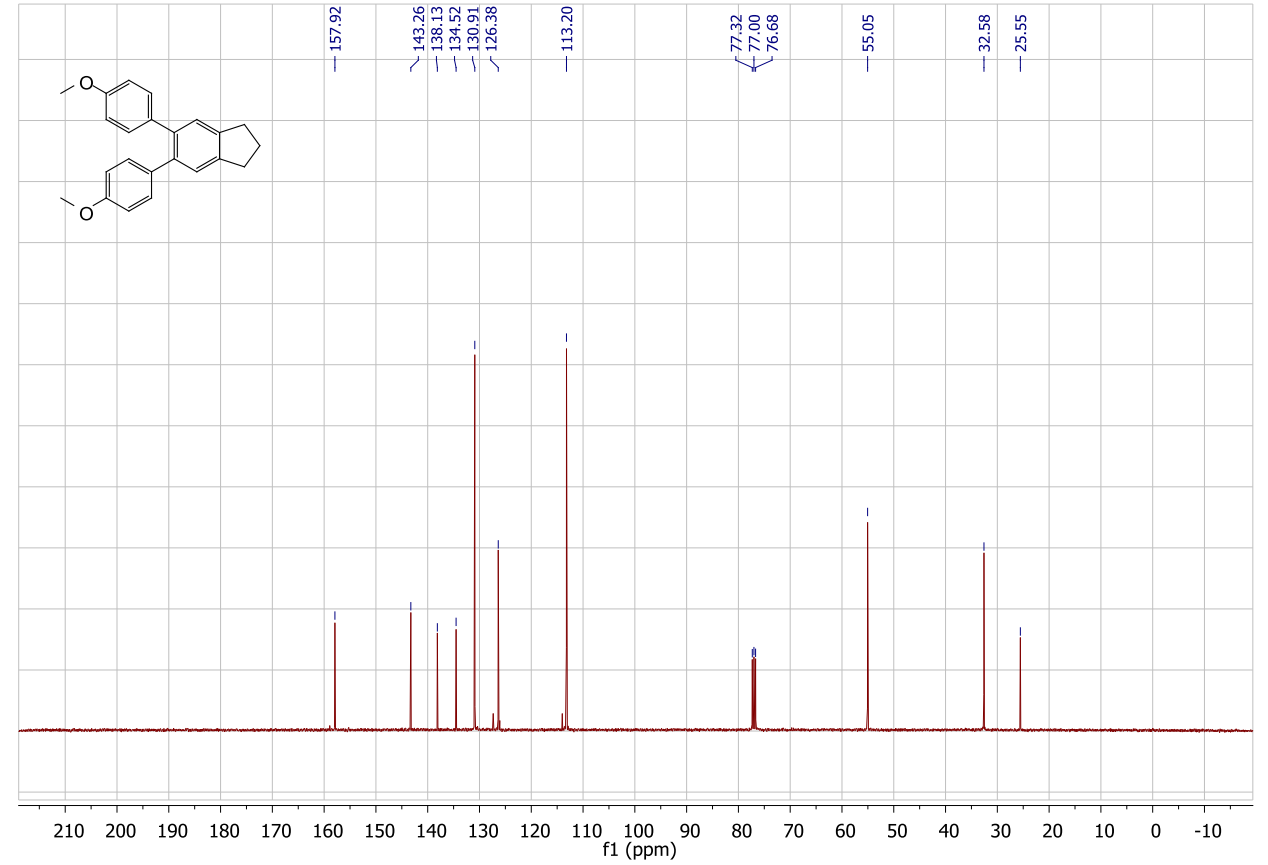
6-Phenyl-7-propyl-1,2,3,4-tetrahydronaphthalene (**13e**)



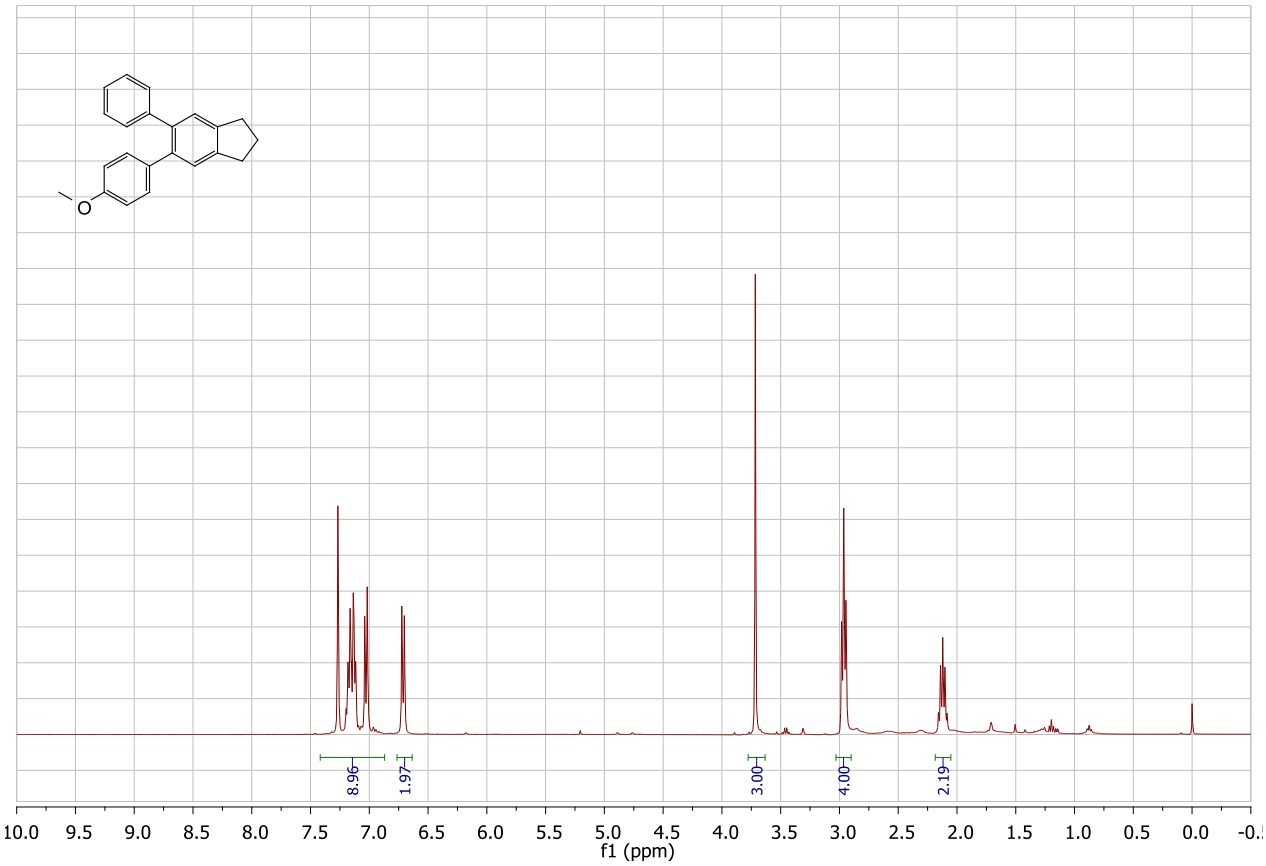


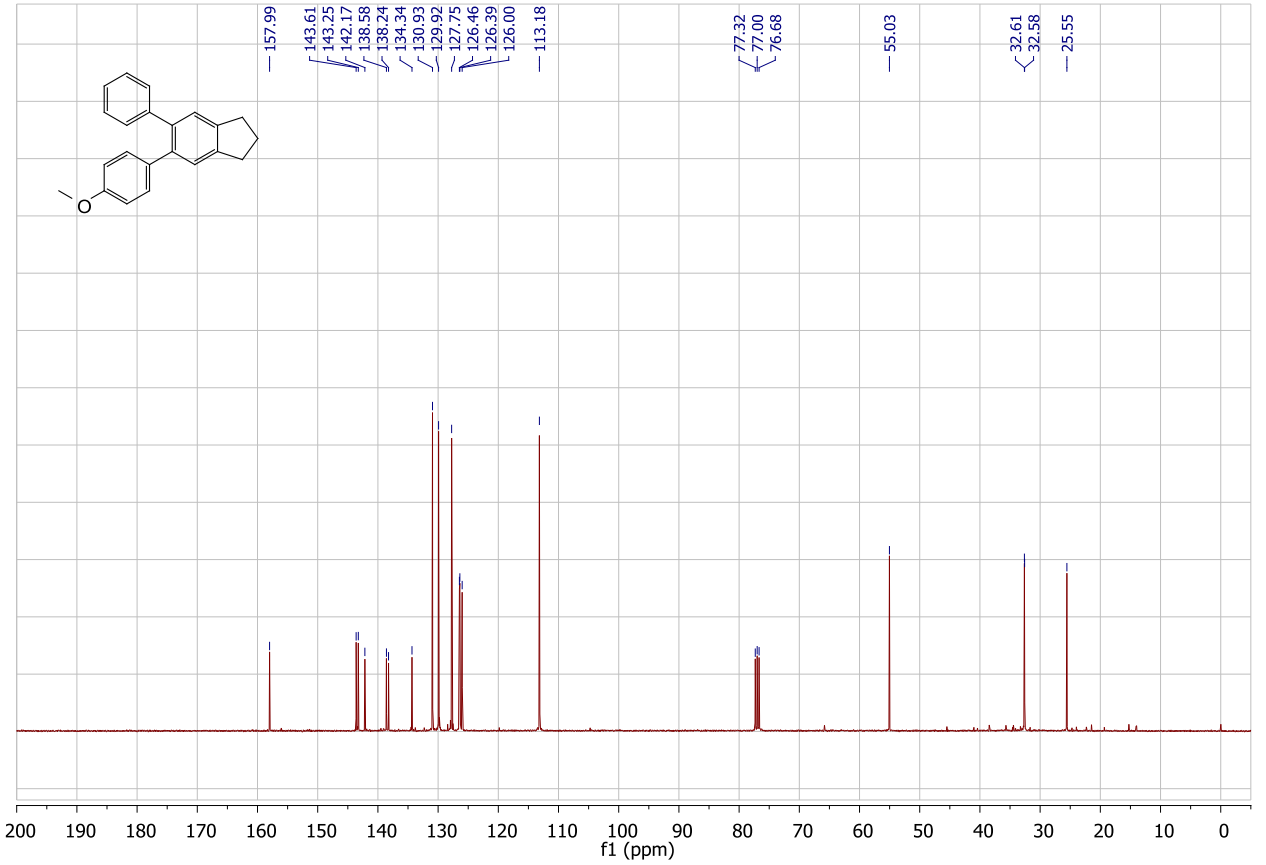
5,6-Bis(4-methoxyphenyl)-2,3-dihydro-1H-indene (**13f**)



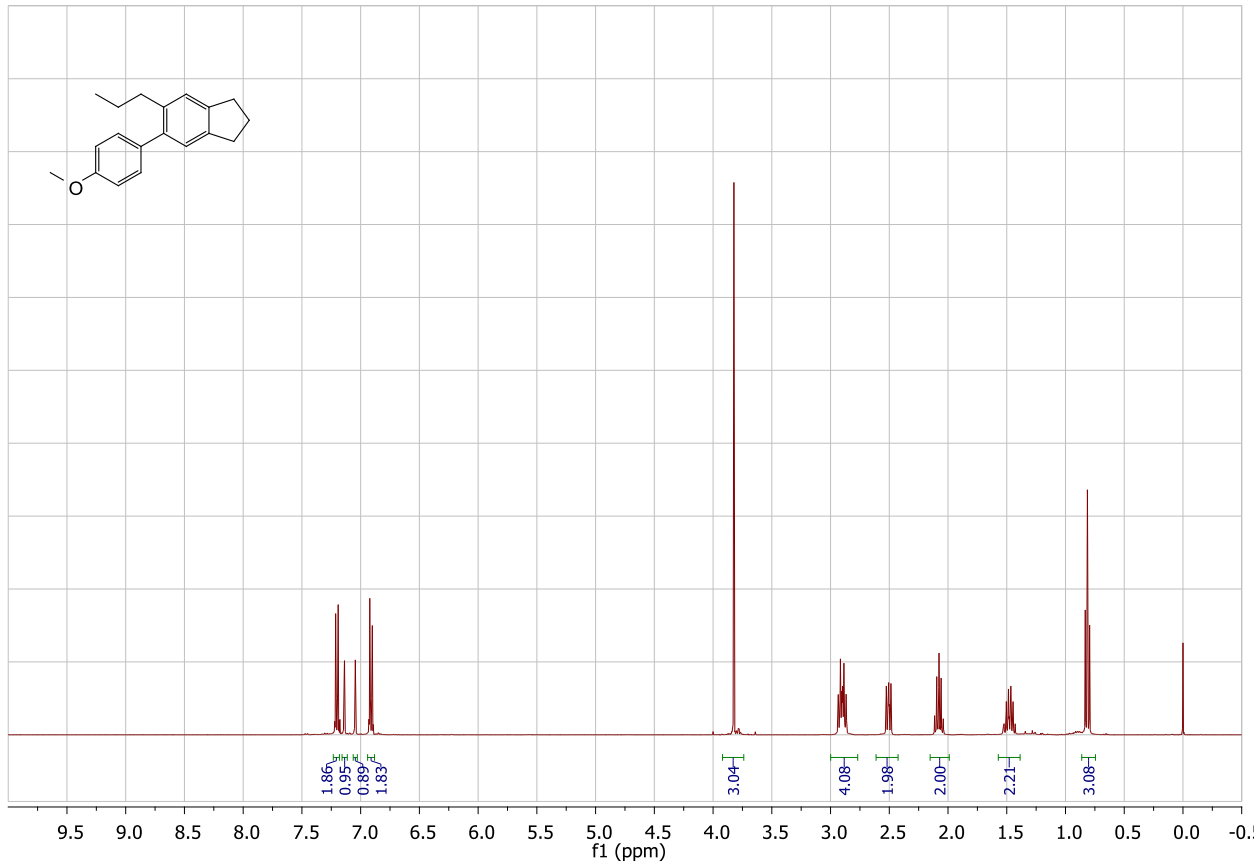


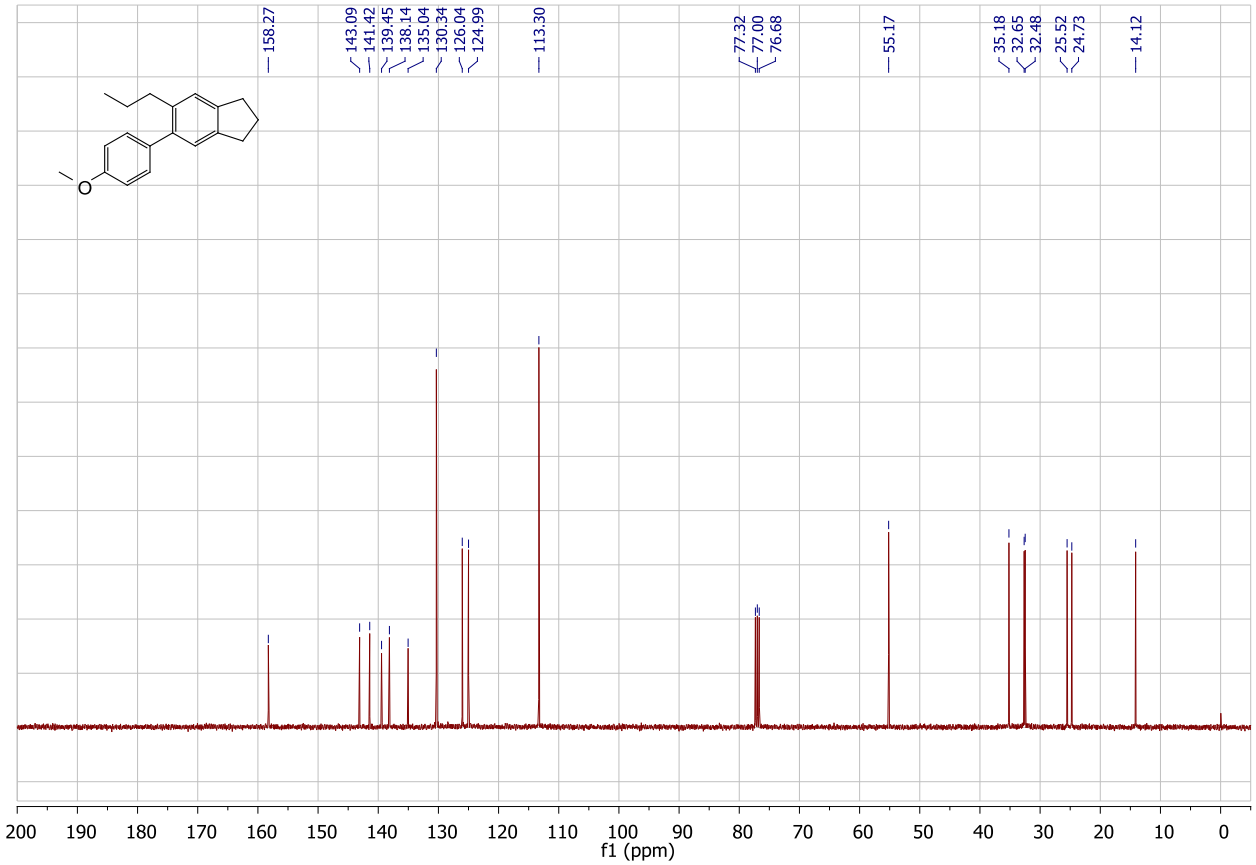
5-(4-Methoxyphenyl)-6-phenyl-2,3-dihydro-1H-indene (**13g**)



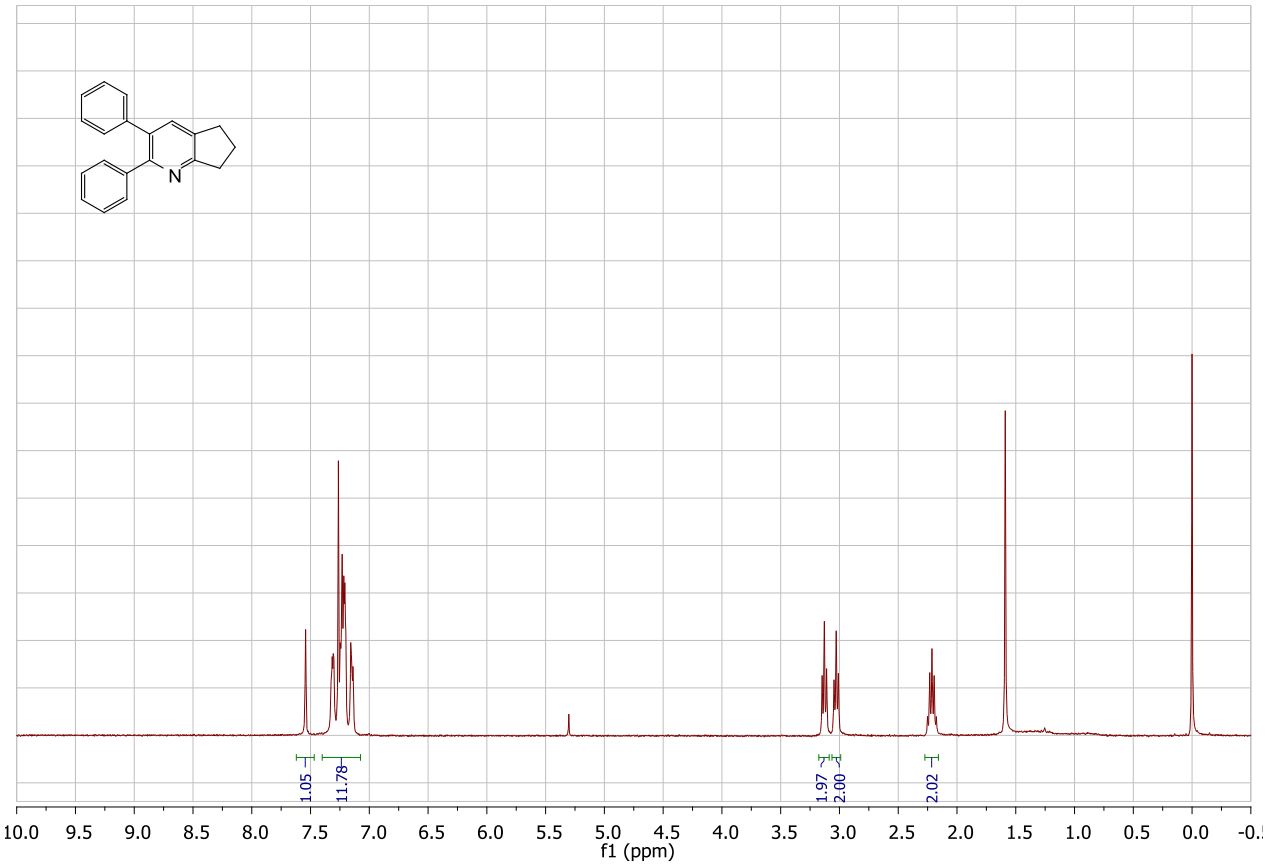


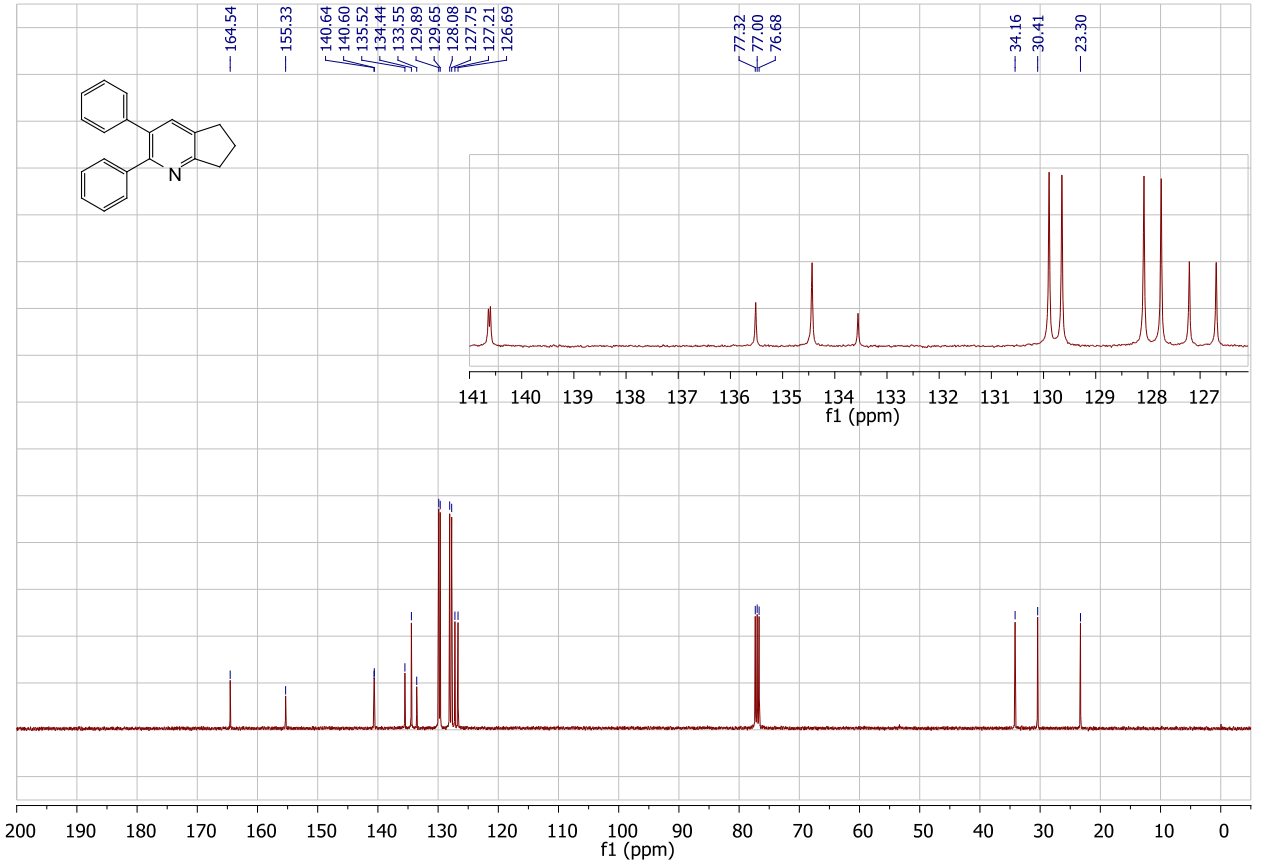
5-(4-Methoxyphenyl)-6-propyl-2,3-dihydro-1H-indene (**13h**)



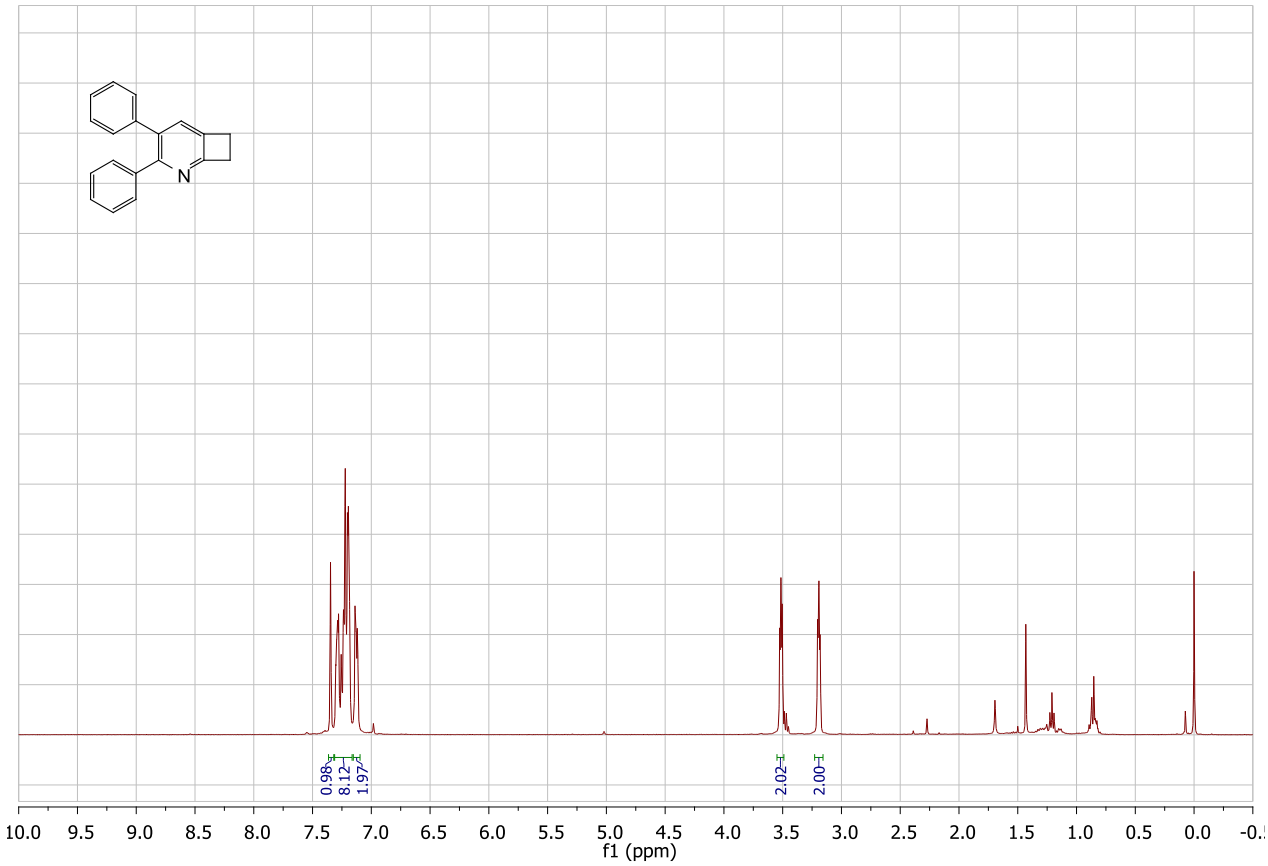


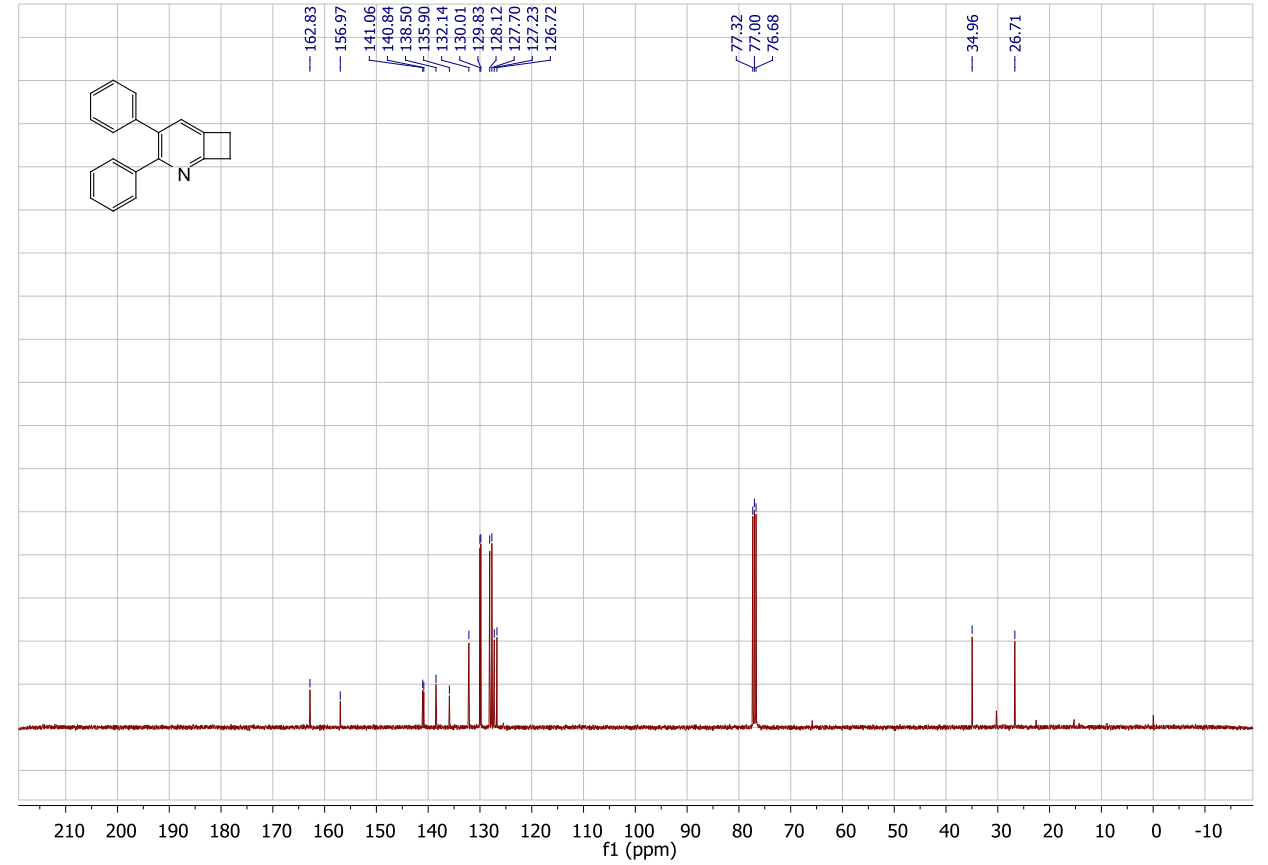
2,3-Diphenyl-6,7-dihydro-5H-cyclopenta[b]pyridine (**14**)



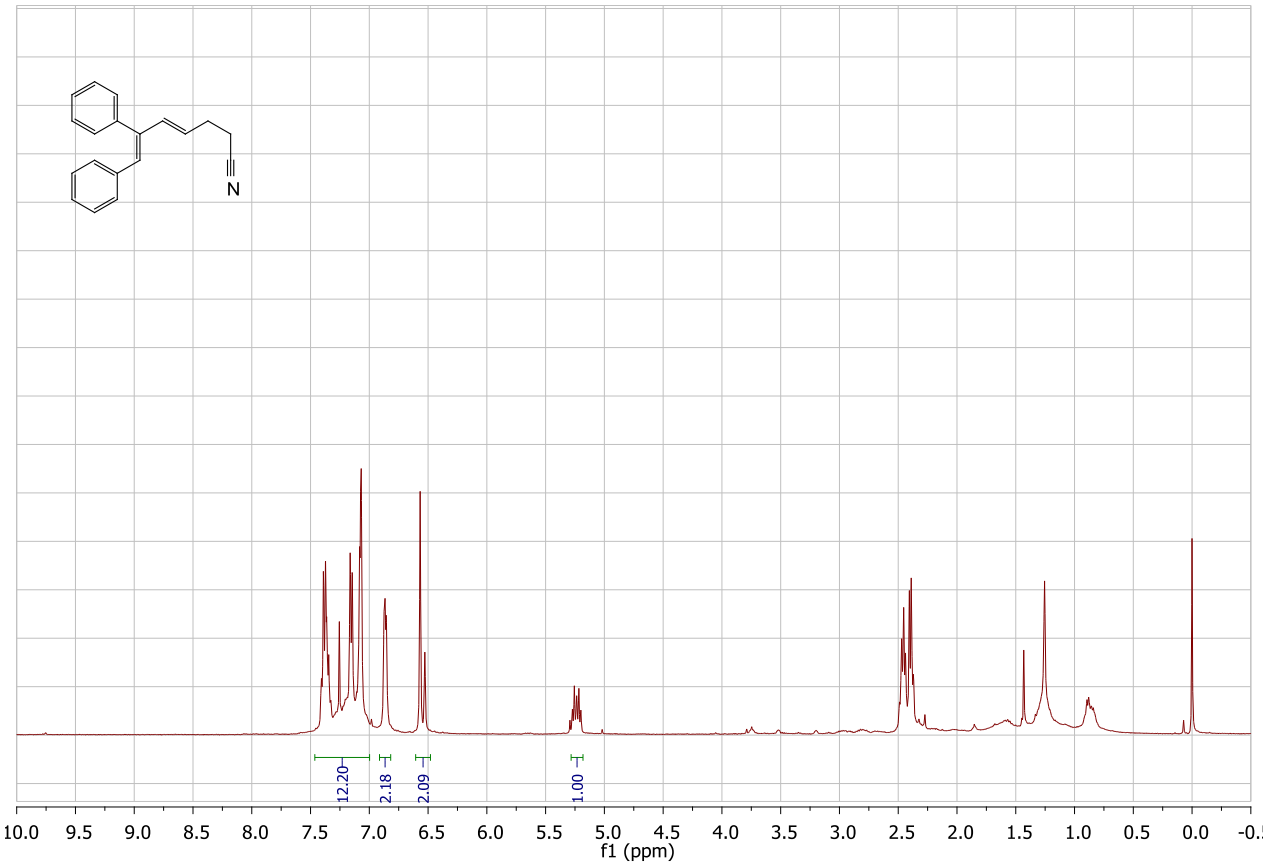


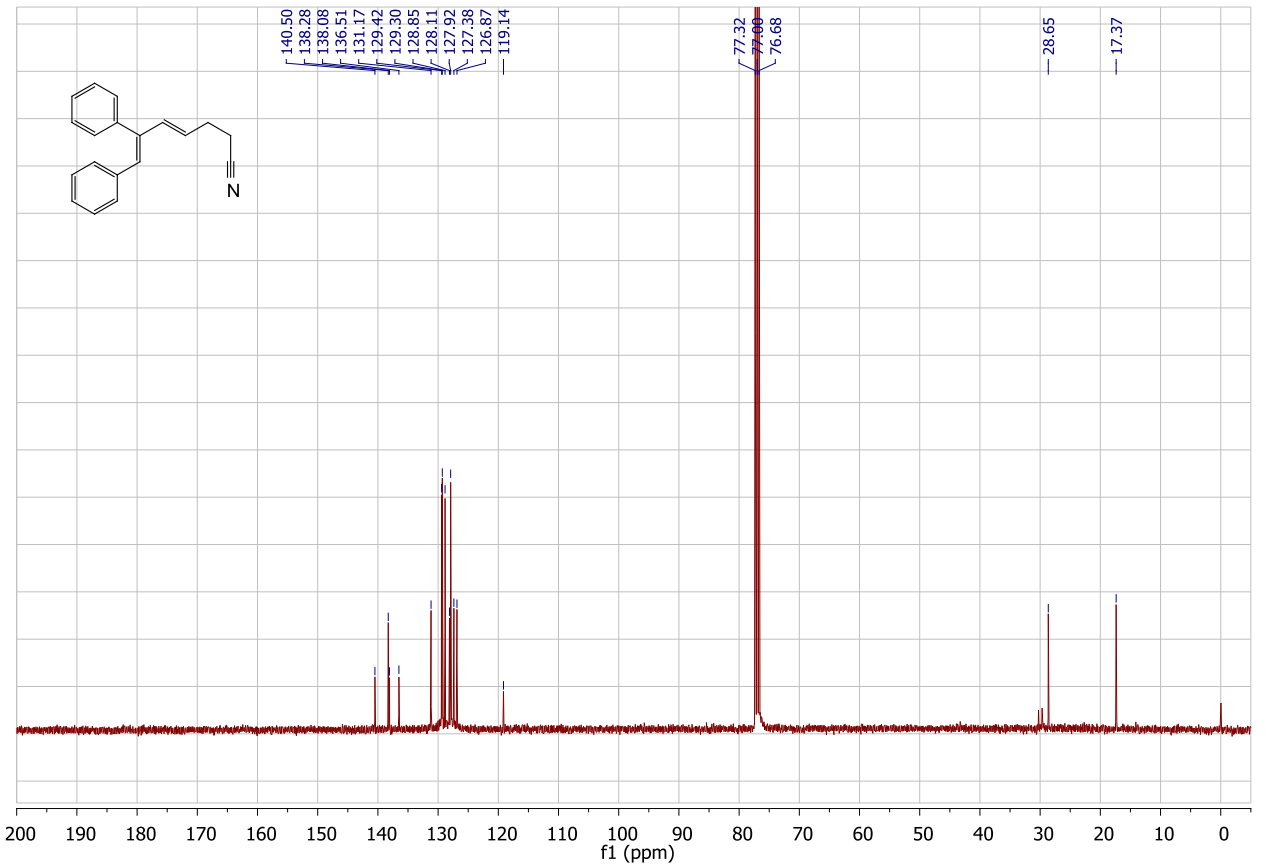
3,4-Diphenyl-2-azabicyclo[4.2.0]octa-1,3,5-triene (**15**)





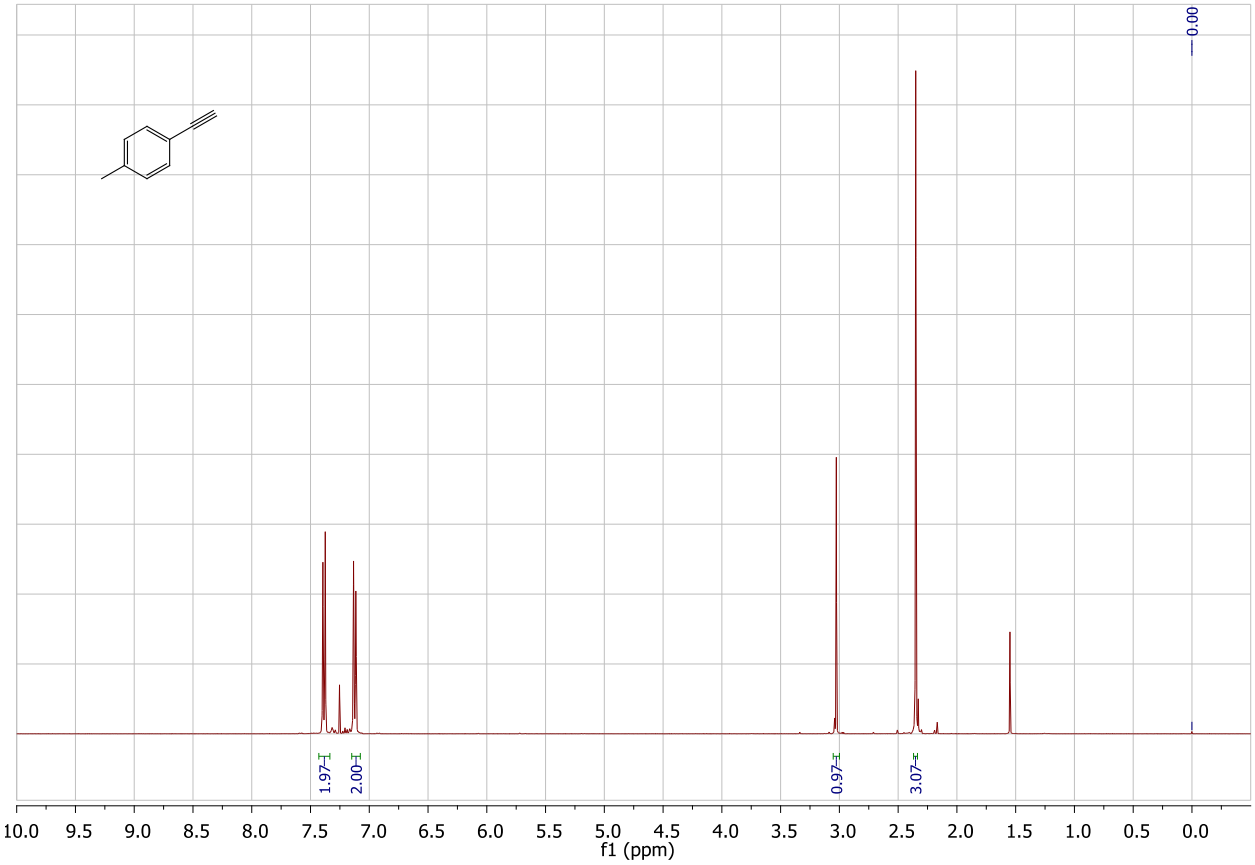
(4*E*, 6*Z*)-6,7-Diphenylhepta-4,6-dienenitrile (**16**)

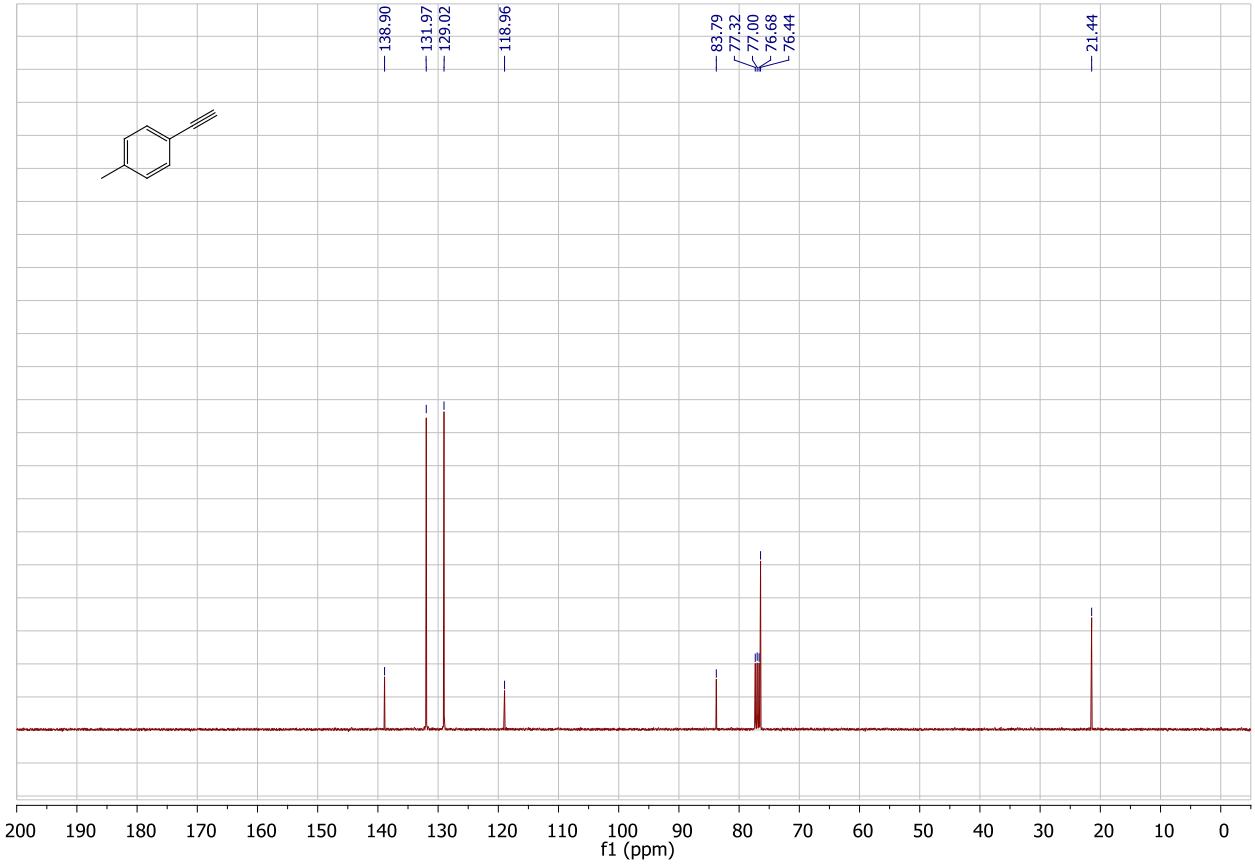




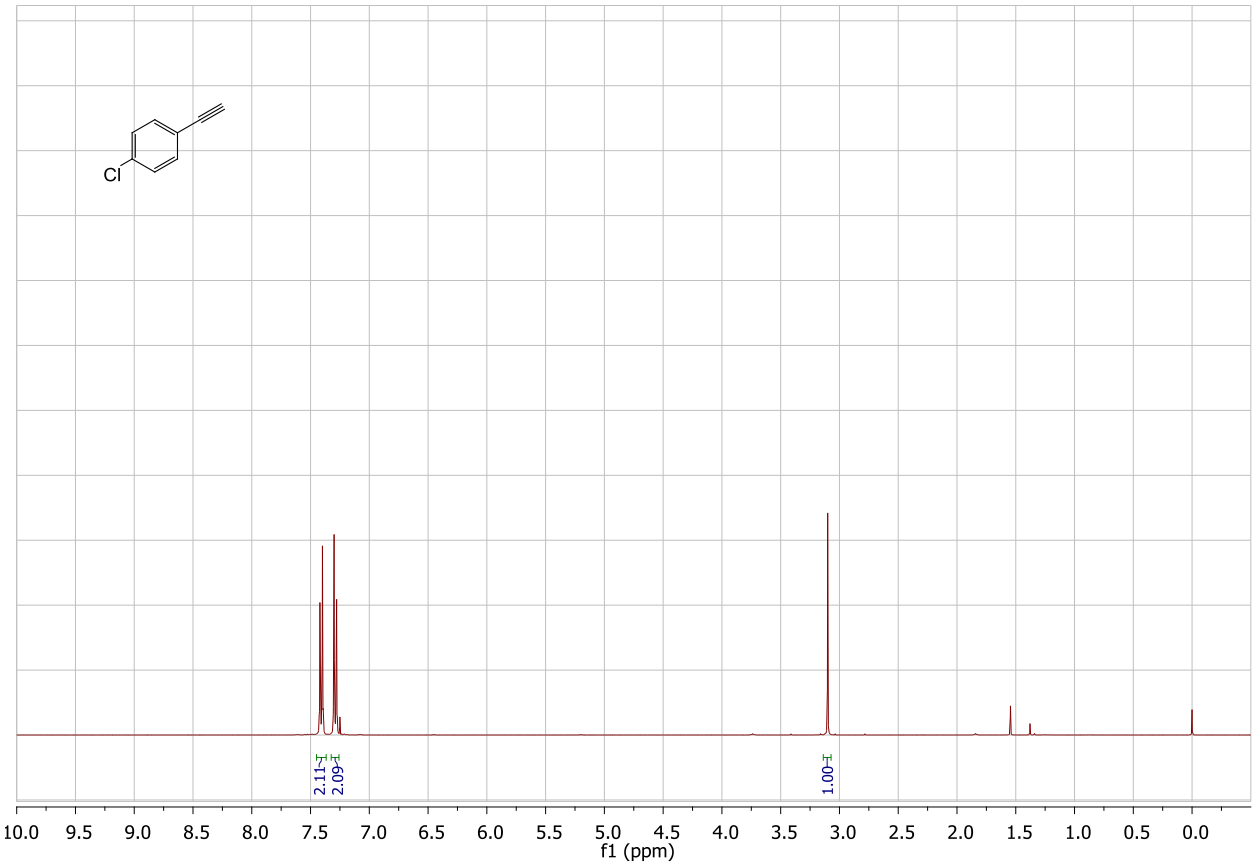
3.4. Spectra of the starting alkynes

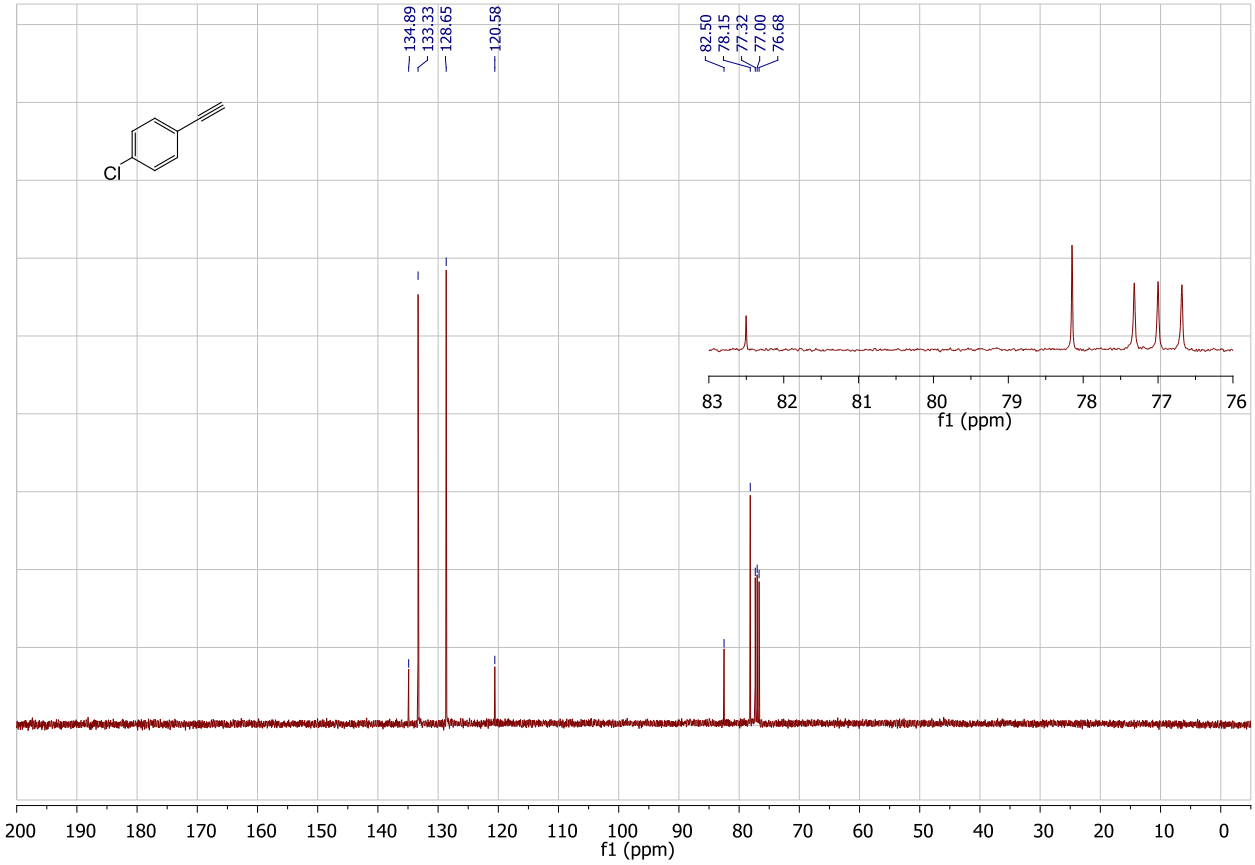
1-Ethynyl-4-methylbenzene (**4b**)



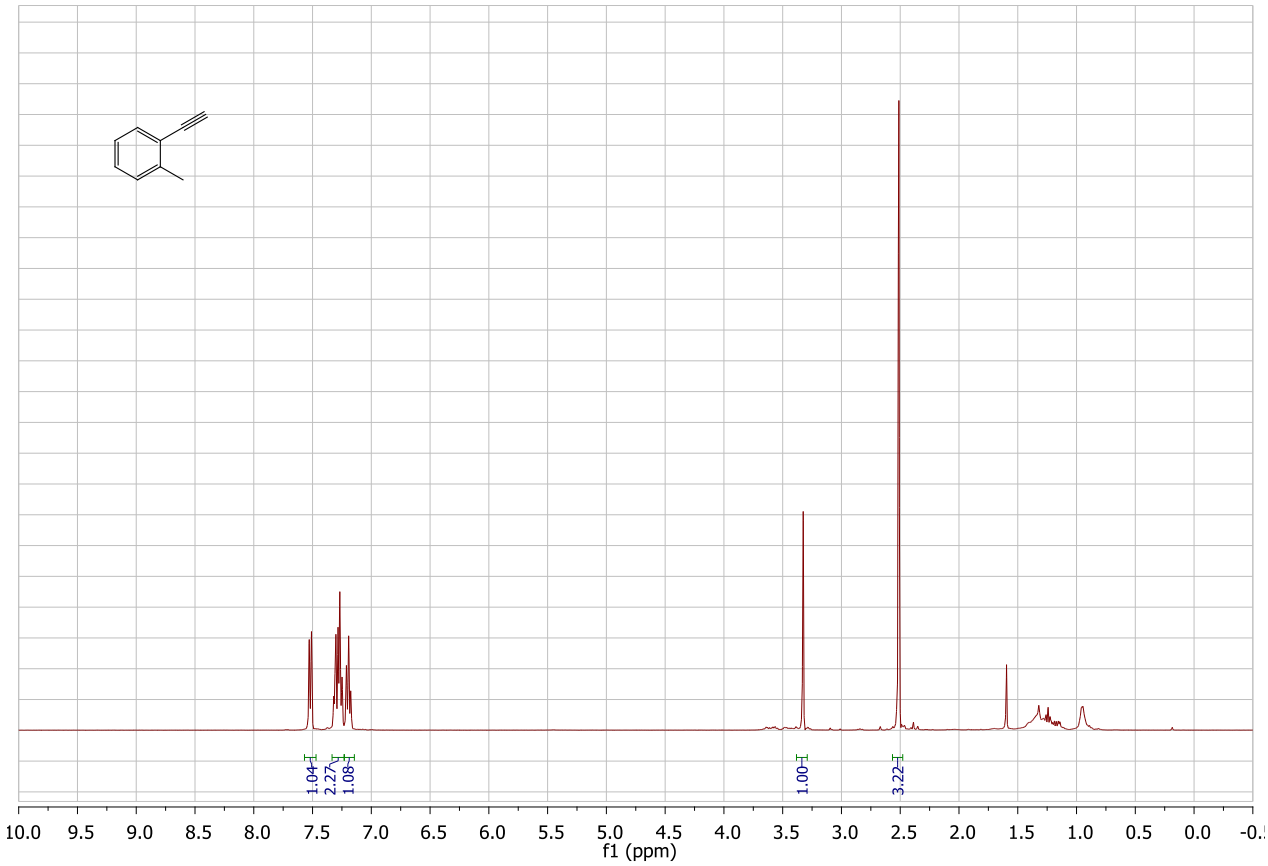


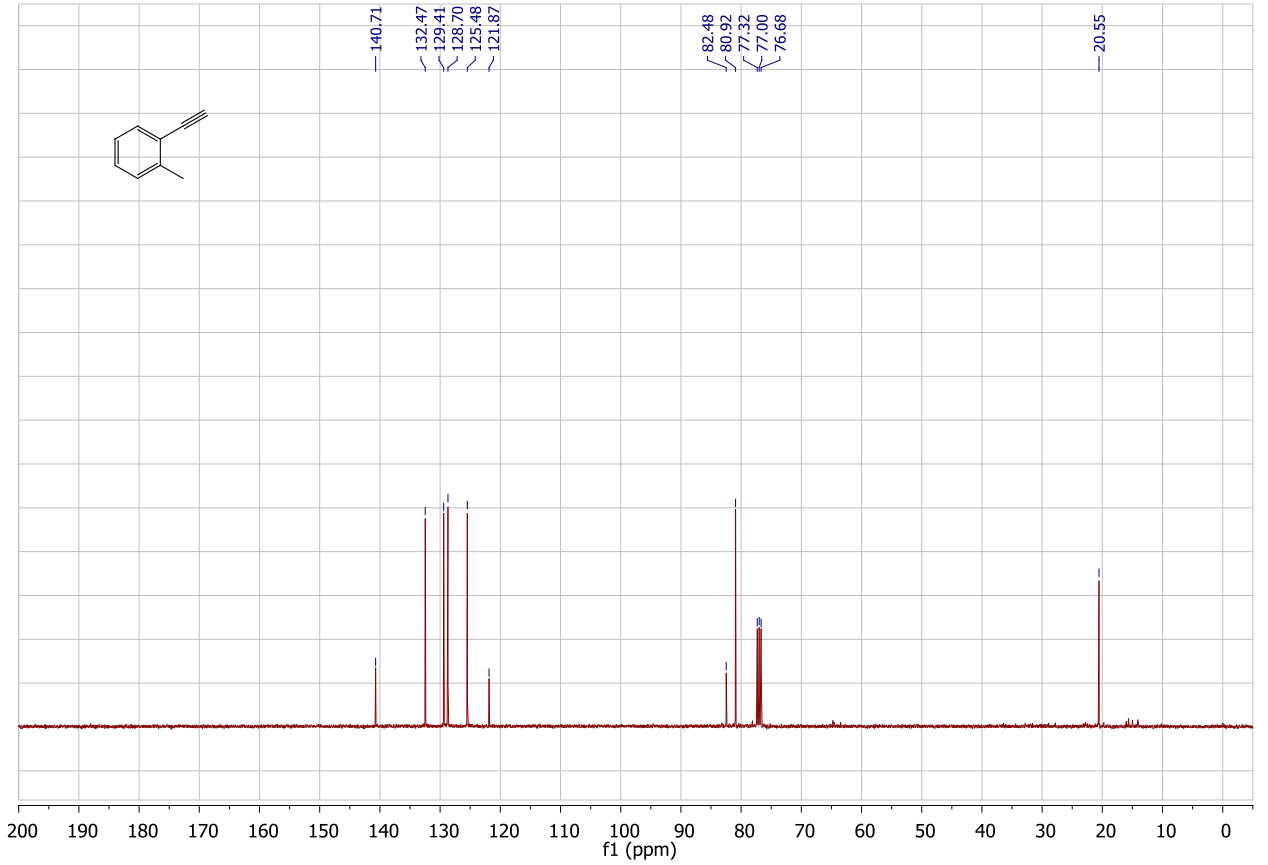
1-Chloro-4-ethynylbenzene



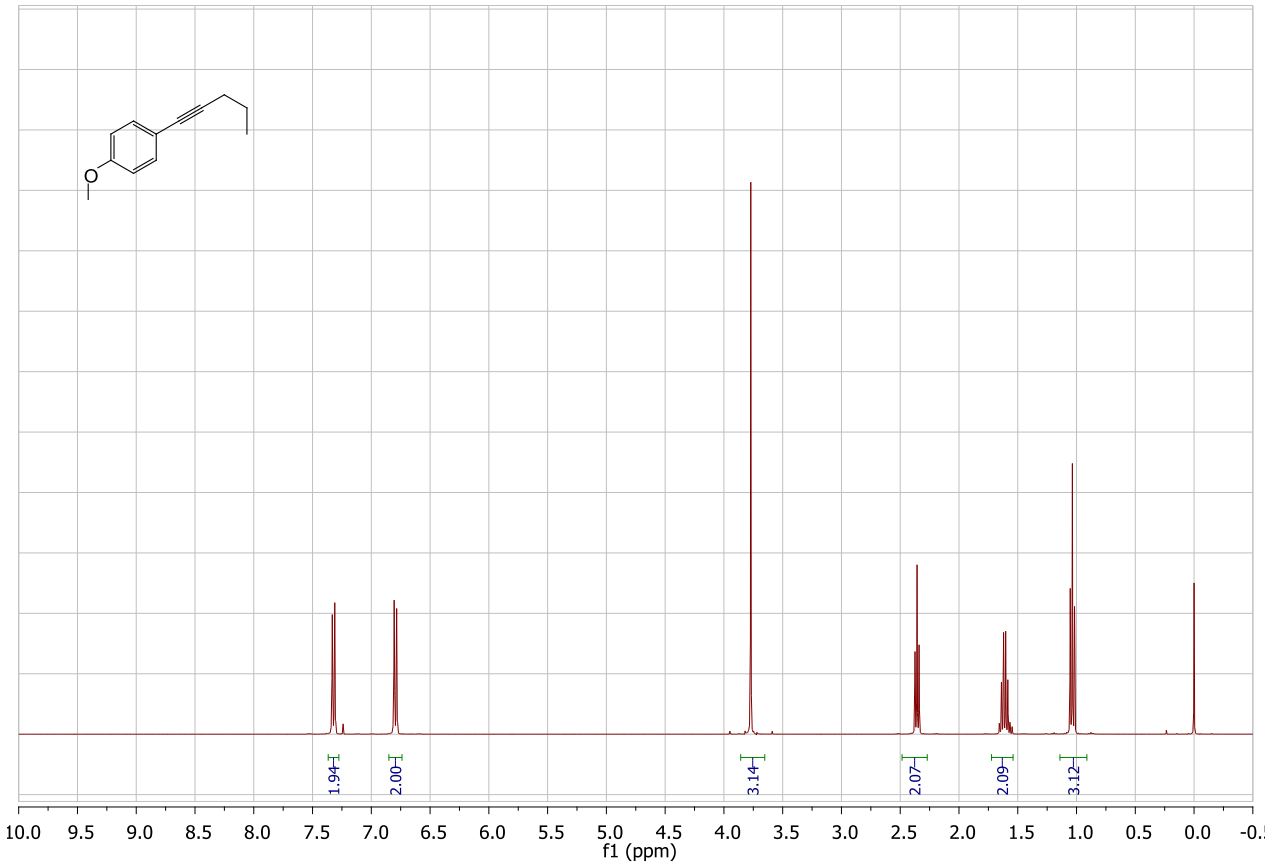


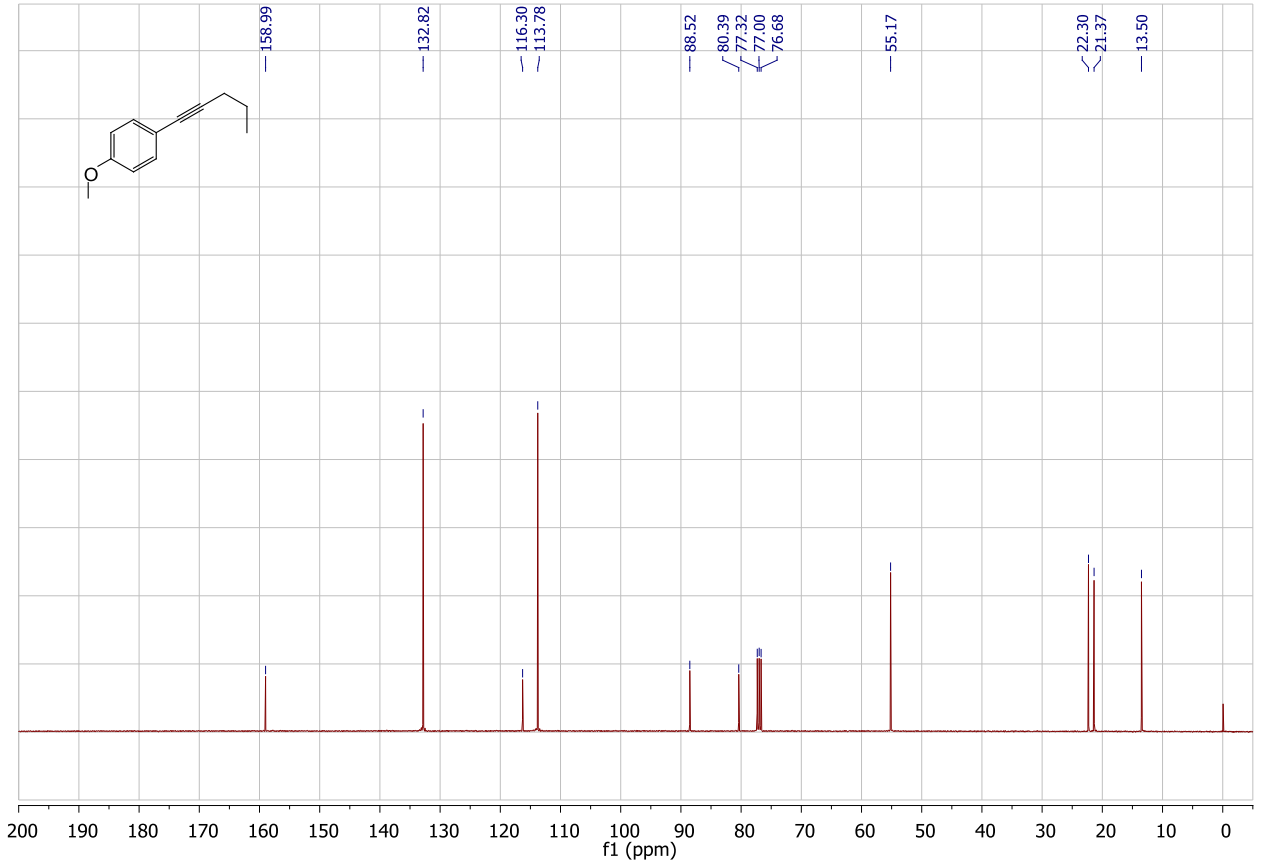
1-Ethynyl-2-methylbenzene (**4c**)



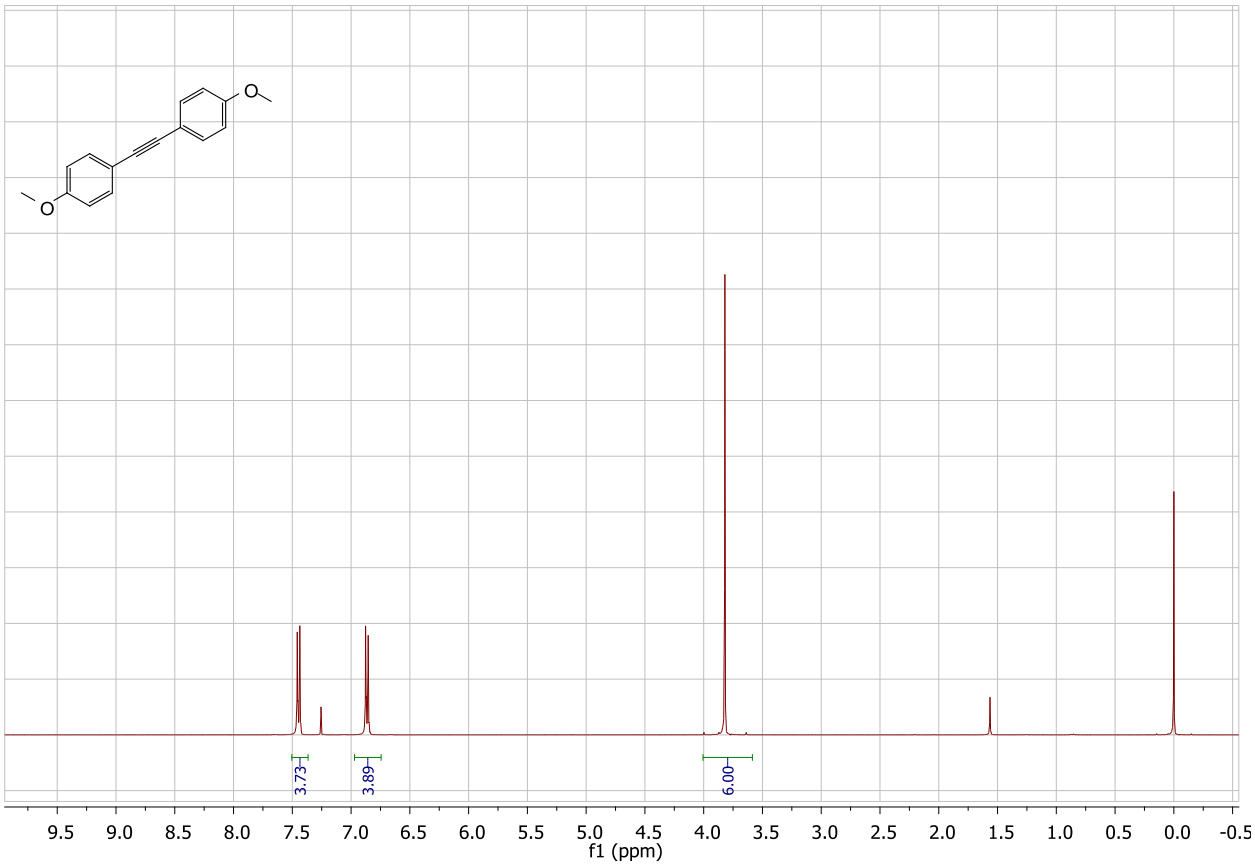


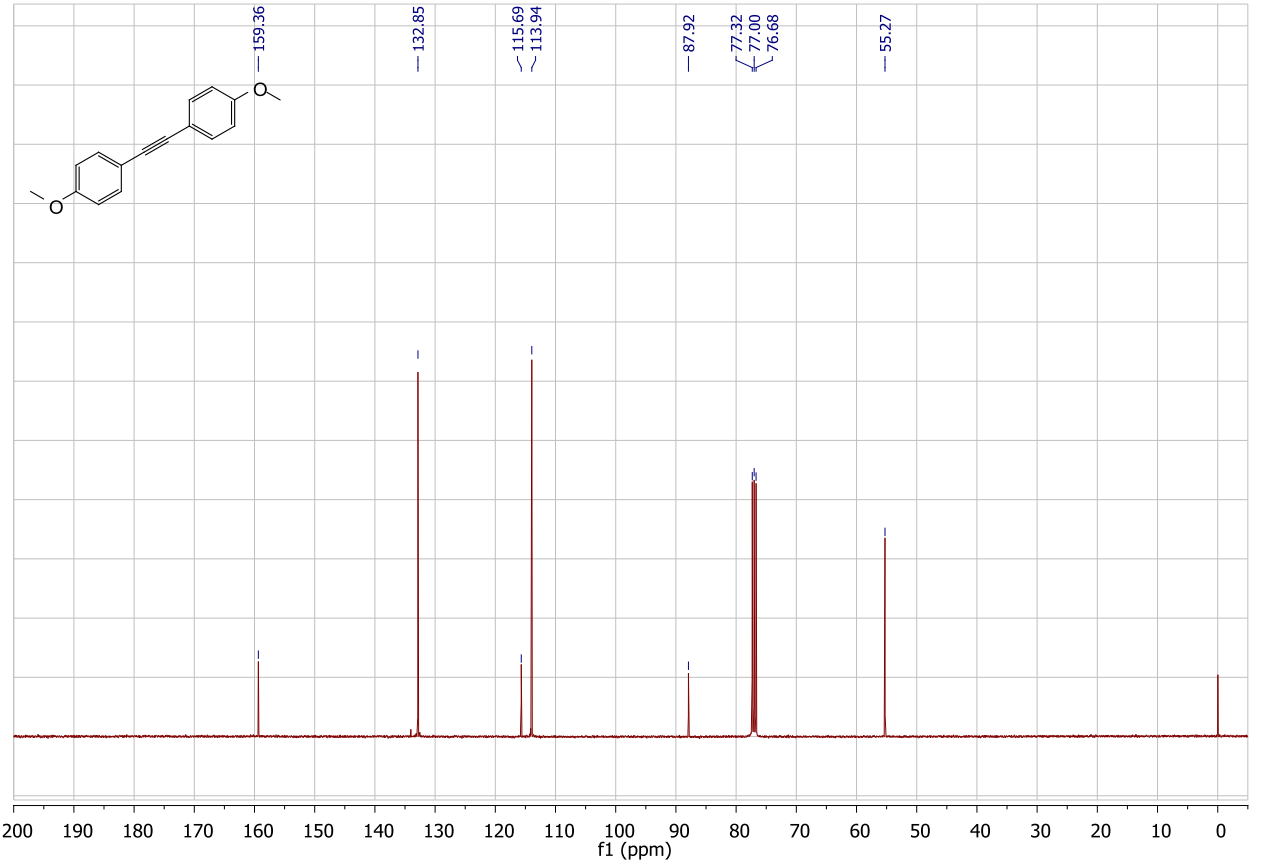
1-Methoxy-4-(pent-1-yn-1-yl)benzene



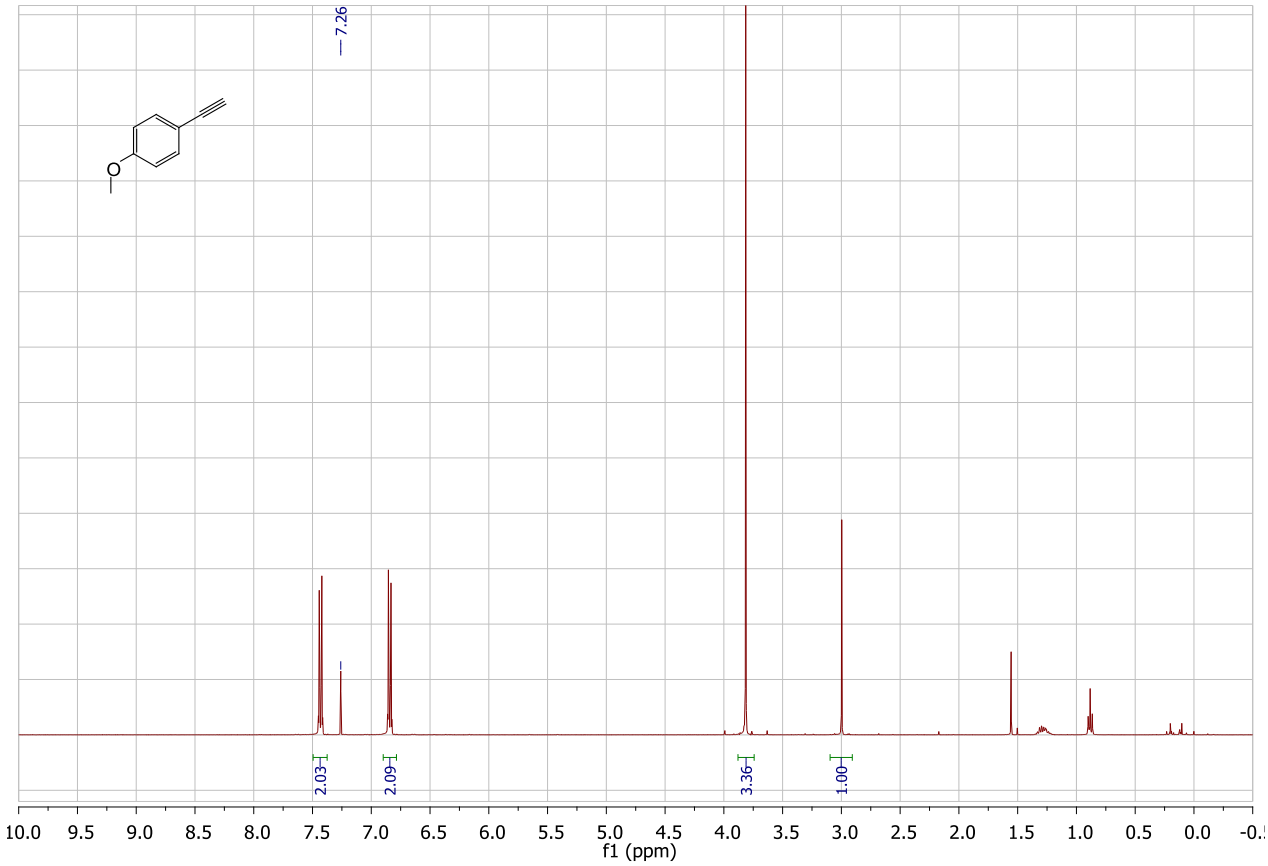


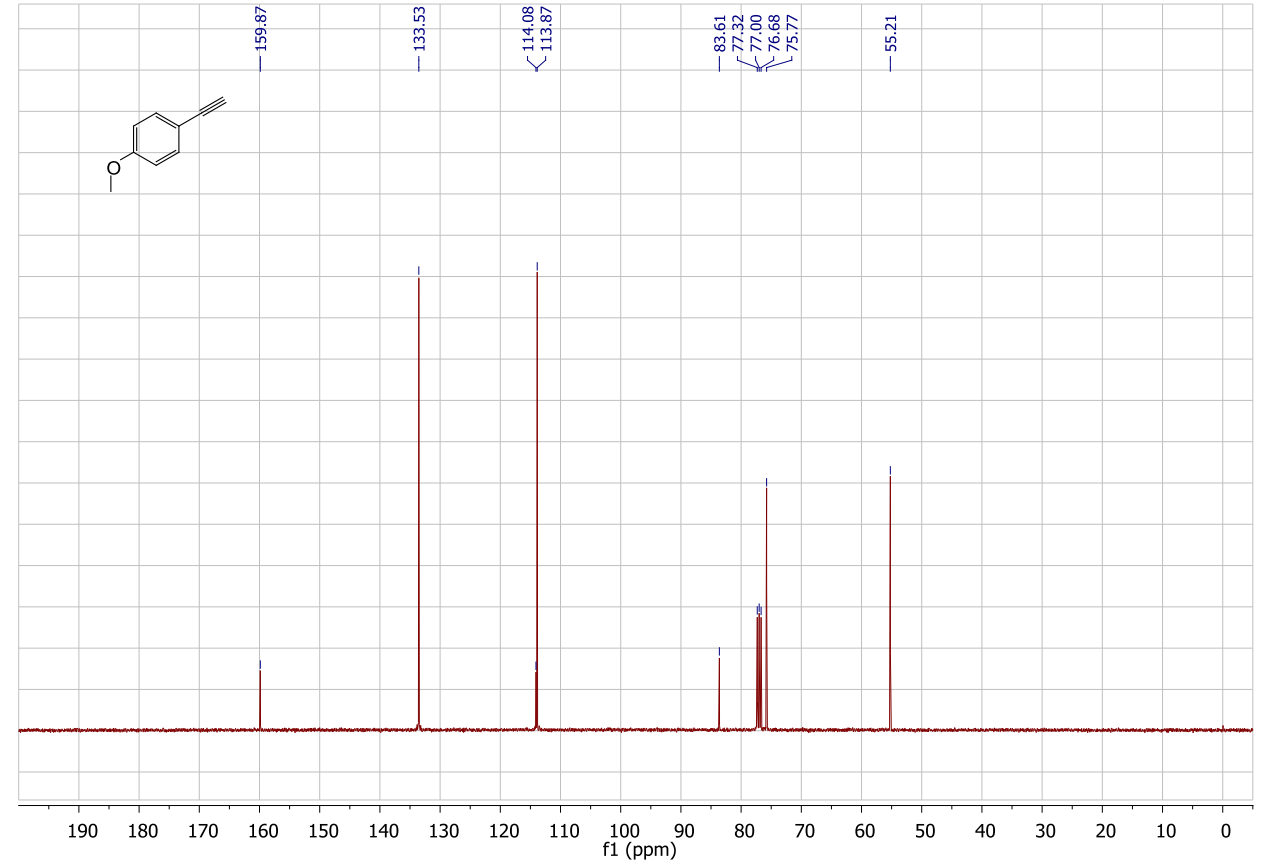
1,2-Bis(4-methoxyphenyl)ethyne



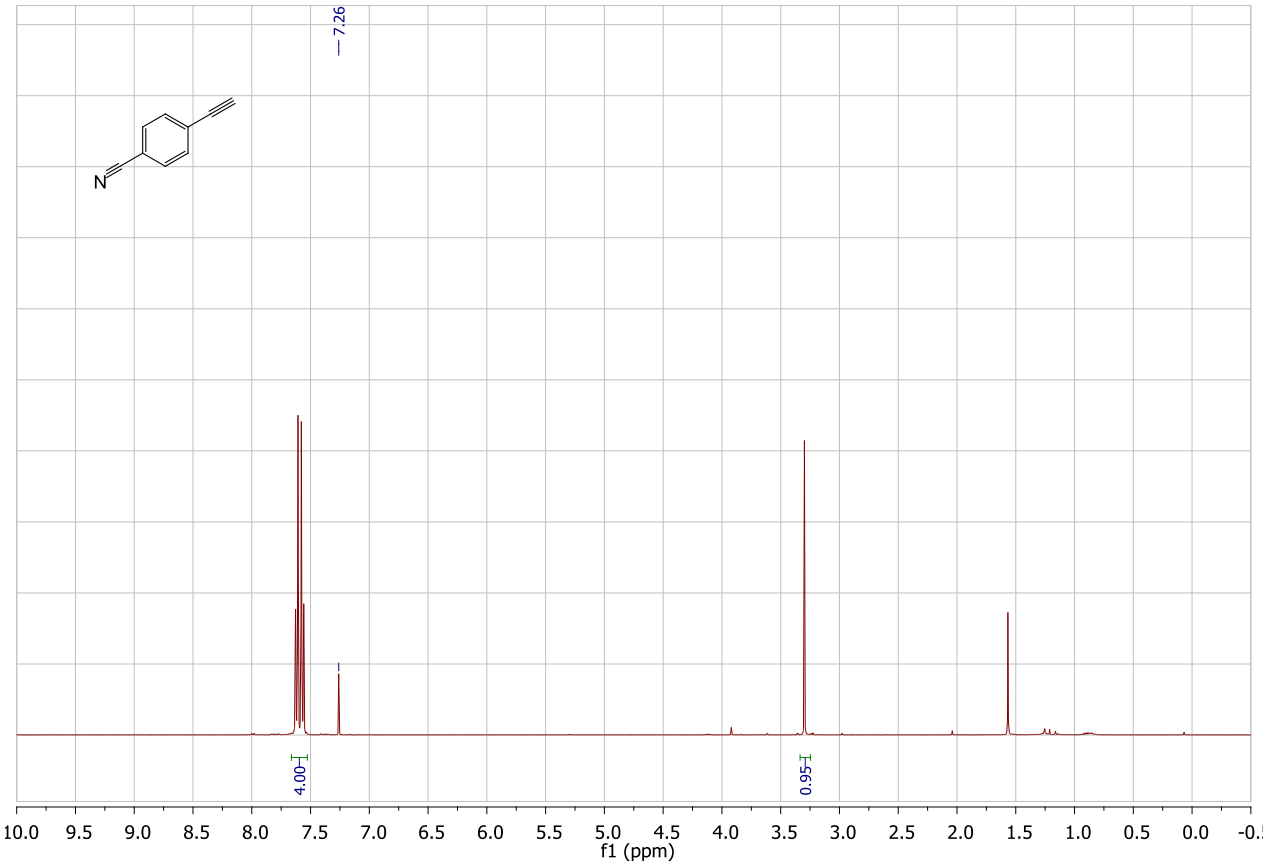


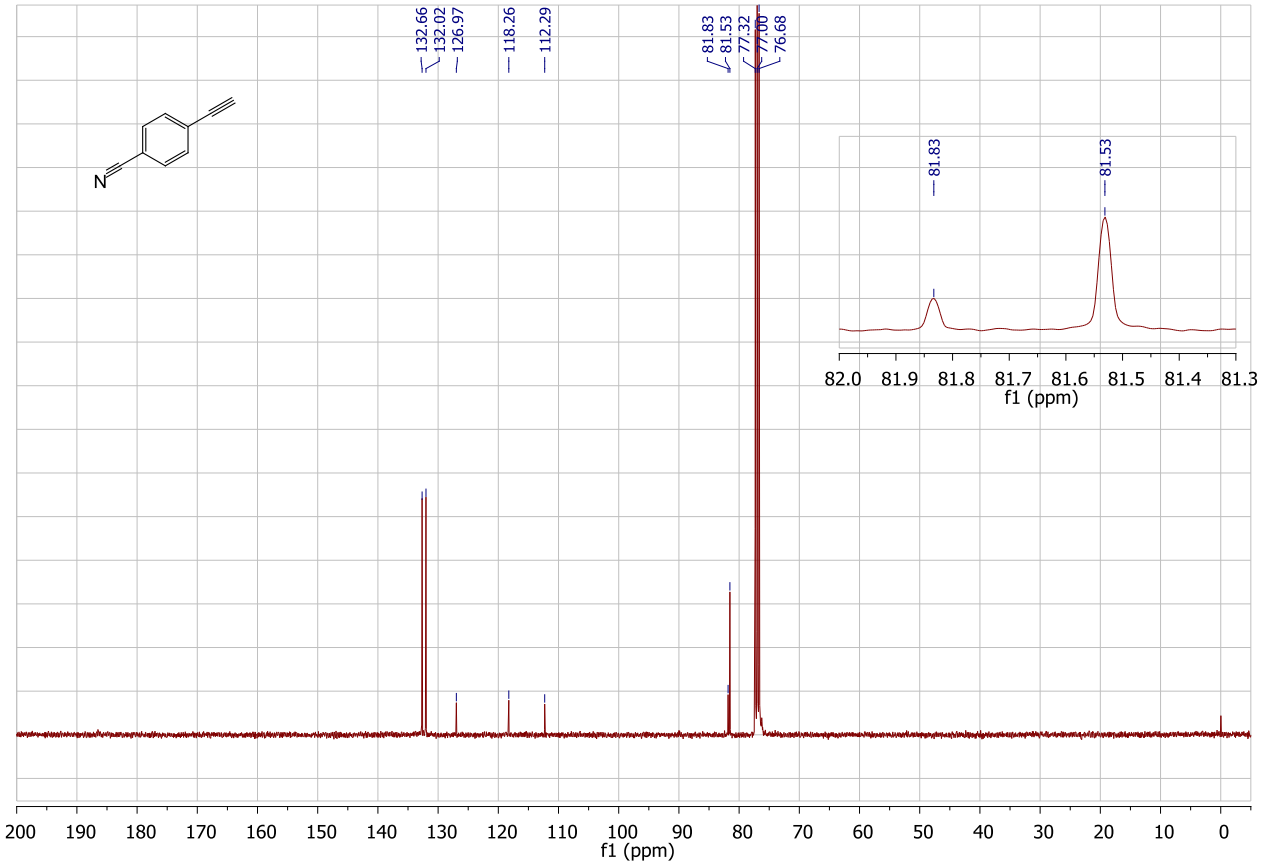
1-Ethynyl-4-methoxybenzene (**4d**)





4-Ethynylbenzonitrile





4-Methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide