Ene-yne Cross-Metathesis for the Preparation of 2,3-Diaryl-1,3-dienes

Meriem K. Abderrezak, [1,2] Zahia Kabouche, [1] Christian Bruneau, [2*] Cédric Fischmeister [2,*]

[1] Université Frères Mentouri Constantine, Department of Chemistry, Laboratory of Therapeutic Substances Obtention (LOST), Chaabet Ersas Campus, 25000 Constantine, Algeria; abderrezakmk@gmail.com (M.K.A.); zahiakabouche@gmail.com (Z.K.)

[2] UMR6226 CNRS, Institut des Sciences Chimiques de Rennes, Université de Rennes 1, Organometallics: Materials and Catalysis, Centre for Catalysis and Green Chemistry, Campus de Beaulieu, 35042 Rennes Cedex, France ; christian.bruneau@univ-rennes1.fr (C.B.)

* Correspondence: cedric.fischmeister@univ-rennes1.fr (C.F.); Tel.: +33-2 23 23 59 98

Supplementary Materials

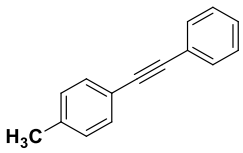
1) General information

All reagents for the synthesis of alkynes were purchased from commercial sources and used as received. Ethylene was purchased from Air Liquide (N35 grade). Toluene and dichloromethane were dried on a MBraun Solvent Purification System. Dimethyl carbonate and triethylamine were distilled and stored over molecular sieves prior to use. NMR spectra were recorded on Bruker Avance (300 MHz or 400 MHz) instruments. Low Resolution mass (LRMS) spectra were obtained on a QP2010 GC/MS apparatus from Shimadzu.

2) Alkyne syntheses

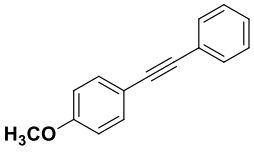
A degassed Schlenk tube was loaded with phenylacetylene (0.3 g, 2.94 mmol, 1.1 equiv.), arylhalide (1 equiv., 2.67 mmol), $PdCl_2(PPh_3)_2$ (1 mol%), PPh_3 (2 mol%) and 20 mL of Et_3N. After 5 min stirring at room temperature, CuI (1 mol%) was added and the reaction mixture was stirred at 60 °C for 17 h. The reaction mixture was allowed to cool down to room temperature and filtrated. The filtrate was washed with 50 mL of diethylether. The organic phase was successively washed with 20 mL of saturated NH_4Cl, 20 mL of 1 N HCl, 20 mL of 1N KOH and 20 mL of brine. The organic phase was then dried with $MgSO_4$, filtrated and concentrated to dryness. The product was purified by column chromatography on silica gel using heptane/ethyl acetate mixtures as eluent.

- 1-Methyl-4-(phenylethynyl)benzene **1b**



1b was synthesized according to the general procedure employing 1-iodo-4-methylbenzene and obtained as a yellow solid in 90% yield. NMR data are consistent with reported data.[1]
^{1}H (400 MHz, $CDCl_3$) δ ppm = 7.57-7.54 (m, 2H), 7.47 (d, 2H, 8.0 Hz), 7.38-7.34 (m, 3H), 7.19-7.17 (m, 2H), 2.39 (s, 3H).
^{13}C (100 MHz, $CDCl_3$) δ ppm = 138.9, 131.7, 131.6, 129.2, 128.4, 128.2, 123.6, 120.3, 89.7, 88.8, 21.6 ppm.
LRMS calculated for $C_{15}H_{12}$ $[M]^{+\cdot}$ 192, measured 192.

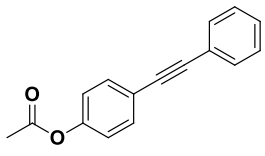
- 1-Methoxy-4-(phenylethynyl)benzene **1c**



1c was synthesized according to the general procedure employing 1-iodo-4-methoxybenzene and obtained as a yellow solid in 90% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.53-7.46 (m, 4H), 7.36-7.30, (m, 3H), 6.90-6.86, (m, 2H), 3.83, (s, 3 H).
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 159.7, 133.2, 131.6, 128.4, 128.0, 123.7, 115.5, 114.1, 89.5, 88.2, 55.5.
LRMS calculated for $C_{15}H_{12}O$ $[M]^{+\cdot}$ 208, measured 208.

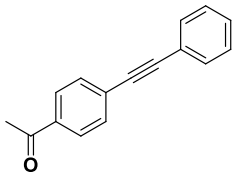
[1] G. C. E. Raja, F. M. Irudayanathan, H. -S. Kim, H.-S.; J. Kim, S. J. Lee, *Org. Chem*. **2016**, *81*, 5244−5249.
[2] Y. Miao, A. Dupé, C. Bruneau, C. Fischmeister, *Eur. J. Org. Chem*, **2014**, 5071-5077.

- 4-(2-phenylethynyl)phenyl)acetate **1d**



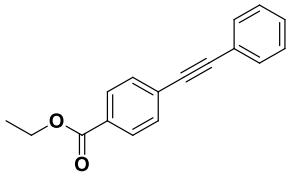
1d was synthesized according to the general procedure employing 4-bromophenylacetate and obtained as a white solid in 83% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.56–7.52 (m, 4 H), 7.37–7.33 (m, 3 H), 7.12 (d, 8.2 Hz, 2H), 2.31 (s, 3 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm = 169.1, 150.5, 132.7, 131.4, 128.3, 128.3, 123.2, 121.7, 121.0, 89.6, 88.5, 21.1.
LRMS calculated for $C_{16}H_{12}O_2$ $[M]^{+\cdot}$ 236; measured 236.

- 1-(4-(2-phenylethynyl)phenyl)ethanone **1e**



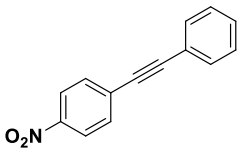
1e was synthesized according to the general procedure employing 4-bromoacetophenone and obtained as a white solid in 79% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.94 (d, 8.1 Hz, 2H), 7.63 (d, 8.1 Hz, 2H), 7.58–7.53 (m, 2H), 7.40–7.35 (m, 3H), 2.62 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm = 197.2, 136.3, 131.7, 131.4, 128.8, 128.6, 128.5, 128.4, 122.9, 92.9, 88.8, 26.8.
LRMS calculated for $C_{16}H_{12}O$ $[M]^{+\cdot}$ 220; measured 220.

- Ethyl 4-(phenylethynyl)benzoate **1f**



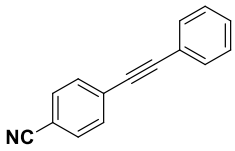
1f was synthesized according to the general procedure employing ethyl 4-bromobenzoate and obtained as a white solid in 80% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, CDCl3) δ ppm = 8.04 (d, 8.1 Hz, 2H), 7.58 (d, 8.1 Hz, 2H), 7.56- 7.54 (m, 2H), 7.37- 7.35 (m, 3H), 4.39 (q, 7.1 Hz, 2H), 1.40 (t, 7.1 Hz, 3H).
^{13}C NMR (101 MHz, CDCl3) δ ppm = 166.0, 131.7, 131.4, 129.8, 129.4, 128.8, 128.4, 127.8, 122.7, 92.3, 88.7, 61.1, 14.3.
LRMS calculated for $C_{17}H_{14}O_2$[M]$^{+\cdot}$250 ; measured 250.

- 1-Nitro-4-(phenylethynyl)benzene **1g**



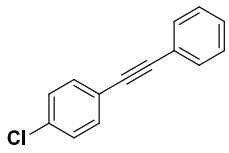
1g was synthesized according to the general procedure employing 4-iodonitrobenzene and obtained as a yellow solid in 68% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 8.23 (d, 8.7 Hz, 2H), 7.67 (m, 2H), 7.56 (m, 2H), 7.43-7.39 (m, 3H).
^{13}C NMR (100 MHz $CDCl_3$): δ ppm = 147.0, 132.3, 131.7, 130.2, 129.2, 128.4, 123.5, 122.0, 94.6, 87.4.
LRMS calculated for $C_{14}H_9NO_2$[M] $^{+\cdot}$ 223; measured 223.

- 4-phenylethynylbenzonitrile **1h**



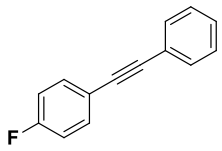
1h was synthesized according to the general procedure employing 4-bromobenzonitrile and obtained as a white solid in 82% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.63 (d, 8.4 Hz, 2H), 7.62 (d, 8.4 Hz, 2H), 7.59–7.52 (m, 2H), 7.38–7.35 (m, 3H).
^{13}C NMR (100 MHz, CDCl3) δ ppm = 132.1, 132.0, 131.8, 129.1, 128.5, 128.2, 122.2, 118.5, 111.5, 93.8, 87.7.
LRMS calculated for $C_{15}H_9N$ [M]$^{+\cdot}$ 203; measured 203.

- 1-Chloro-(4-phenylethynyl)benzene **1i**



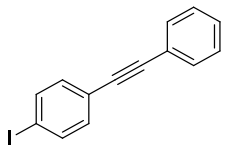
1i was synthesized according to the general procedure employing 4-iodochlorobenzene and obtained as a white solid in 75% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.57-7.53, (m, 2H), 7.49-7.46, (m, 2H), 7.38-7.32 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 134.4, 133.0, 131.7, 128.8, 128.8, 128.5, 123.1, 121.9, 90.5, 88.4.
LRMS calculated for $C_{14}H_9{}^{35}Cl$ [M]+· 212, measured 212.

- 1-Fluoro-(4-phenylethynyl)benzene **1j**



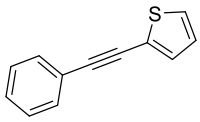
1j was synthesized according to the general procedure employing 4-bromofluorobenzene and obtained as a white solid in 80% yield. NMR data are consistent with reported data.[3]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.54-7.50 (m, 4H), 7.37-7.34 (m, 3H), 7.07-7.03 (m, 2H).
RMN ^{13}C (100 MHz, $CDCl_3$) δ ppm = 163.7 (d, J_{C-F} = 249,6 Hz), 133.5 (d, J_{C-F} = 8.0 Hz), 132.5, 131.6, 129.2, 128.5, 123.1, 115.7 (d, J_{C-F} = 22,4 Hz), 89.5, 88.3.
LRMS calculated for $C_{14}H_9F$ $[M]^{+\cdot}$ 196, measured 196.

- 1-Iodo-(4-phenylethynyl)benzene **1k**



1k was synthesized according to the general procedure employing 1,4-diiodobenzene and obtained as a white solid in 80% yield. NMR data are consistent with reported data.[3]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.71- 7.67, (m, 2H), 7.55-7.51, (m, 2H), 7.37- 7.33, (m, 3H), 7.27- 7.24, (m, 2H).
^{13}C (100 MHz, $CDCl_3$) δ ppm = 137.7, 133.3, 131.8, 128.7, 128.6, 123.0, 122.8, 94.3, 91.0, 88.7 ppm.
LRMS calculated for $C_{14}H_9I$ $[M]^{+\cdot}$ 304, measured 304.

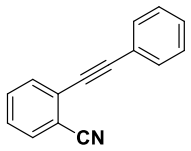
- 2-(phenylethynyl)thiophene **1l**



1l was synthesized according to the general procedure employing 2-bromothiophene and obtained as a white solid in 98% yield. NMR data are consistent with reported data.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.56-7.51, (m, 2H), 7.38-7.35, (m, 3H), 7.30- 7.29 (m, 2H), 7.03- 7.00, (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 132.0, 131.6, 128.6, 128.3, 127.4, 127.2, 123.5, 123.1, 93.2, 82.8. LRMS calculated for $C_{12}H_8S$ $[M]^{+\cdot}$ 184, measured 184.

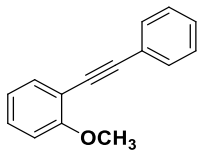
[3] S. Wang, M. Wang, L. Wang, B. Wang, P. Li, J. Yiang, *Tetrahedron*, **2011**, *67*, 4800-4806.

- 2-phenylethynylbenzonitrile **1m**



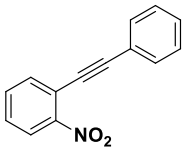
1m was synthesized according to the general procedure employing 2-bromobenzonitrile and obtained as a yellowish liquid in 78% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.69- 7.67 (d, 1H), 7.64-7.60 (m, 3H), 7.57-7.55 (m, 1H), 7.43-7.41 (m, 1H), 7.39-7.35 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 132.6, 132.3, 132.1, 132.0, 129.2, 128.4, 128.2, 127.2, 122.0, 117.5, 115.3, 96.0, 85.6.
LRMS calculated for $C_{15}H_9N$ $[M]^{+\cdot}$ 203, measured 203.

- 1-Methoxy-2-(phenylethynyl)benzene **1n**



1n was synthesized according to the general procedure employing 1-iodo-2-methoxybenzene and obtained as a yellow solid in 98% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.58-7.55 (m, 2H), 7.51 (bd, 7.6 Hz, 1H), 7.37-7.29 (m, 4H), 6.96-6.90 (m, 2H), 3.92 (s, 3 H).
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 159.9, 133.5, 131.6, 129.7, 128.2, 128.0, 123.5, 120.4, 112.4, 110.7, 93.4, 85.7, 55.8.
LRMS calculated for $C_{15}H_{12}O$ $[M]^{+\cdot}$ 208, measured 208.

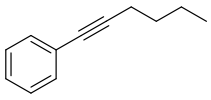
- 1-Nitro-2-(phenylethynyl)benzene **1o**



1o was synthesized according to the general procedure employing 2-bromonitrobenzene and obtained as a reddish liquid in 73% yield. NMR data are consistent with reported data.[4]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 8.08 (m, 1H), 7.72 (m, 1H), 7.60 (m, 3H), 7.47 (m, 1H) 7.38 (m, 3H).
^{13}C NMR (100 MHz $CDCl_3$) δ ppm = 148.0, 134.6, 134.2, 132.3, 129.1, 128.4, 128.3, 127.6, 123.1, 112.4, 93.2, 85.7.
LRMS calculated for $C_{14}H_9NO_2$ $[M]^{+\cdot}$ 223 ; measured 223.

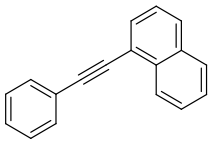
[4] K. Karami, N. Haghighat Naeini, *Turk. J. Chem.*, **2015**, 39, 1199

- Hex-1-ynyl-1-benzene **1p**



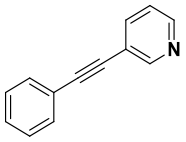
1p was synthesized according to the general procedure employing 1-hexyne and iodobenzene. **1p** was obtained as a light yellow liquid in 70% yield. NMR data are consistent with reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.41- 7.39 (m, 2H), 7.30- 7.25 (m, 3H), 2.41 (t, 6.8 Hz, 2H), 1.63-1.58 (m, 2H), 1.55-1.44 (m, 2H), 0.96 (t, 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 131.7, 128.3, 127.5, 124.2, 90.4, 80.7, 30.8, 22.2, 19.3, 13.8.
LRMS calculated for $C_{14}H_{18}$ $[M]^{+\cdot}$ 158, measured 158.

- 1-(phenylethynyl) naphtalène **1q**



1q was synthesized according to the general procedure employing 1-bromonaphtalene and obtained as light yellow liquid in 87% yield. NMR data are consistent with reported data.[5]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 8.47 (d, 8.3 Hz, 1H), 7.85 (m, 2H), 7.79 (d, 7.0 Hz, 1H), 7.69-7.66 (m, 2H), 7.64-7.60 (dd, 11.1 Hz, 4.0 Hz, 1H), 7.57 (dd, 11.0, 3.9 Hz, 1H), 7.50-7.46 (m, 1H), 7.42-7.37 (m, 3H).
LRMS calculated for $C_{18}H_{12}$ $[M]^{+\cdot}$ 228, measured 228.

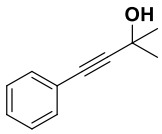
- 3-(phenylethynyl)pyridine **1r**



1r was synthesized according to the general procedure employing 3-bromopyridine and obtained as yellow solid in 85% yield. NMR data are consistent with reported data.[6]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 8.77 (d, 1.4 Hz, 1H), 8.56-8.54 (m, 1H), 7.82-7.81 (m, 1H), 7.55-7.54 (m, 2H), 7.38-7.36 (m, 3H), 7.30-7.27 (m, 1H).

[5] T. Takeda, Y. Tobe, *Chem. Commun*, **2012**, 48, 7841
[6] H. Huang, H. Jiang, K. Chen, H. Liu, *J. Org. Chem.*, **2008**, *73*, 9061

- 2-methyl-4-phenylbut-3-yn-2-ol **1s**

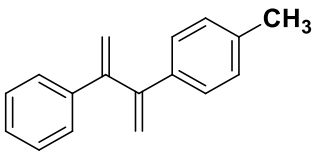


1s was synthesized according to a modified procedure employing bromobenzene (3.23 mmol, 1 equiv.) and 2-methylbut-3-yn-2-ol (1.2 eq, 3.56 mmol) in the presence of $PdCl_2(PPh_3)_2$ (6 mol%), PPh_3(12 mol% mmol) and CuI (0.003 mol%) in 15 mL of Et_3N. The reaction mixture was heated at 80 °C for 14 h. **1r** obtained as light orange liquid in 85% yield. NMR data are consistent with reported data.[7]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.42-7.39 (m, 2H), 7.30-7.29 (m, 3H), 1.62 (s, 6H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 131.5, 128.3, 128.2, 122.6, 93.6, 81.9, 65.4, 31.3 ppm.
LRMS calculated for $C_{11}H_{12}O$ $[M]^{+\cdot}$ 160, measured 160.

3) 2,3-diarylbutadiene syntheses

A dry 22 mL Parr reactor was loaded with 0.1 g of alkyne derivative, 2 mol% of Hoveyda **II** catalyst, 2 mL of dry toluene and 10 µL of *n*-tetradecane as GC internal standard. The reactor was flushed with ethylene for 2 min and then pressurised with 3 bar of ethylene (Air Liquide, N35 grade). The reactor was heated in an oil bath (T bath = 100 °C) for the mentioned duration. After cooling to r.t., the reactor was depressurized and the solvent evaporated. The products were purified by column chromatography on silica gel using heptane/ethyl acetate mixtures as eluent.

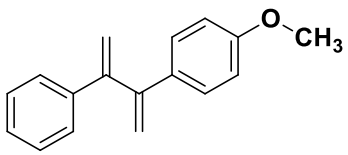
- 1-methyl-4-(3-phenylbuta-1,3-dien-2-yl)benzene **2b**



White solid, Y= 91%. NMR data are consistent with reported data.[8]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.53-7.50 (m, 2H), 7.40-7.32 (m, 5H), 7.19-7.17 (d, *J*= 7.9 Hz, 2H,), 5.66 (d, *J*= 1.7 Hz, 1H), 5.64 (d, *J*= 1.7 Hz, 1H), 5.44 (d, *J*= 1.7 Hz, 1H), 5.40 (d, *J*= 1.7Hz, 1H), 2.40 (s, 3H).
^{13}C RMN (101 MHz, $CDCl_3$): δ ppm= 150.1, 149.8, 140.3, 137.4, 137.3, 129.0, 128.2, 127.6, 127.5, 127.4, 116.2, 115.6, 21.2.
LRMS calculated for $C_{17}H_{16}$ $[M]^{+\cdot}$ 220, measured 220.

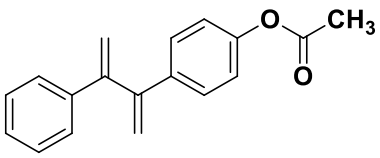
[7] J. Cheng, Y. Sun, F. Wang, M. Guo, J. Xu, Y. Pan, *J. Org. Chem.,* **2004**, *69*, 5428–5432
[8] Z. Ikeda, K. Oshima, S. Matsubara, *Org. Lett*. **2005**, *7*, 4859-4861.

- 1-methoxy-4-(3-phenylbuta-1,3-dien-2-yl)benzene **2c**



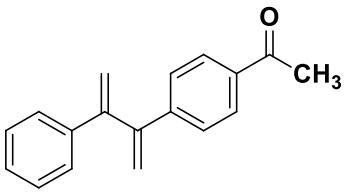
Colorless oil, Y = 98%. NMR data were consistent with reported data.[9]
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.47-7.44 (m, 2H), 7.40-7.37 (m,2H) 7.34- 7.24 (m, 3H), 6.87-6.83 (m, 2H), 5.61 (d, 1.7 Hz, 1H), 5.54 (d, 1.7 Hz, 2H), 5.39 (d, 1.7 Hz, 1H), 5.30 (d, 1.7 Hz, 1H), 3.80 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.2, 150.1, 149.2, 140.3, 132.7, 128.6, 128.3, 127.5, 127.6, 116.1, 114.7, 113.6, 55.2.
LRMS calculated for $C_{17}H_{16}O$ $[M]^{+\cdot}$ 236, measured 236.

- 4-(3-phenylbuta-1,3-dien-2-yl)phenyl)acetate **2d**



White solid, Y = 91%.
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.43-7.38 (m, 4H), 7.29-7.24 (m, 3H), 7.03- 7.00 (m, 2H), 5.58-5.56 (m 2H), 5.33- 5.32 (m, 2H), 2.28 (s, 3H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm = 169.5, 150.2, 149.7, 149.0, 140.0, 137.9, 128.6, 128.3, 127.7, 127.5, 121.3, 116.7, 116.6, 21.3.
LRMS calculated for $C_{18}H_{16}O_2$ $[M]^{+\cdot}$ 264, measured 264.

- 1-(4-(3-phenylbuta-1,3-dien-2-yl)phenyl)ethanone **2e**

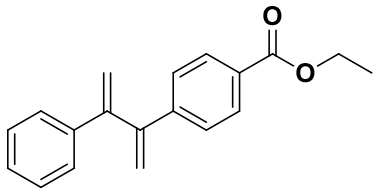


Beige product, Y = 91%. NMR data are consistent with reported data.[10]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.87-7.85 (m, 2H), 7.49-7.47 (m, 2H), 7.39-7.36 (m, 2H), 7.29-7.29(m, 3H), 5.65 (d, *J*= 1.3 Hz, 1H), 5.59 (d, *J*=1.4Hz, 1H), 5.45 (d, *J*= 1.3, 1H), 5.34 (d, *J*=1.3 Hz, 1H), 2.56 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm = 197.7, 149.4, 149.1, 144.9, 139.8, 136.2, 128.5, 128.4, 127.8, 127.7, 122.5, 118.2, 116.39, 26.7.

---

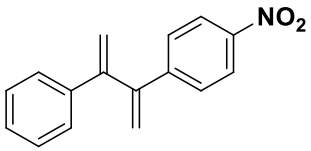
[9] H. Jiang, L. He, X. Li, H. Chen, W. Wu, W. Fu, *Chem. Commun*., **2013**, *49*, 9218-9220.
[10] H.-M. Chang, C.-H. Cheng, *J. Org. Chem*., **2000**, *65*, 1767-1773.

- Ethyl-4-(3-phenylbuta-1,3-dien-2-yl)benzoate **2f**



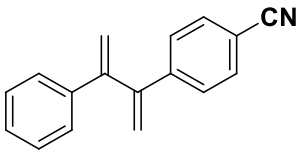
Colourless liquid, Y = 99%.
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 8.00-7.98 (d, *J*= 8.5 Hz, 2H), 7.55-7.46 (m, 2H), 7.42-7.39 (m, 3H), 7.32-7.27 (m, 2H), 5.64(d, *J*= 1.4 Hz, 1H), 5.59 (d, *J*= 1.5Hz, 1H), 5.44 (d, *J*= 1.4 Hz, 1H), 5.35 (d, *J*= 1.5 Hz, 1H), 4.36 (q, *J*= 7.1 Hz, 2H), 1.37 (t, *J*= 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ ppm = 166.4, 149.5, 149.2, 144.7, 139.8, 129.6, 129.5, 128.3, 127.8, 127.5, 118.0, 116.8, 60.9, 14.4.
LRMS calculated for $C_{19}H_{18}O_2$ $[M]^{+\cdot}$ 278, measured 278.
Elemental analysis calculated for $C_{19}H_{18}O_2$: C 81.99, H 6.52. Measured C 81.87, H 6.55.

- 2-(4-nitrophenyl)-3-phenyl-1,3-butadiene **2g**



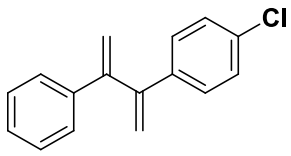
Yellow oil, Y= 97%.
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 8.12-8.10 (m, 2H), 7.54-7.51 (m, 2H), 7.38- 7.35 (m, 2H), 7.31-7.26 (m, 3H), 5.7-7.69 (d, J=1.0 Hz, 1H), 5.63 (d, J=1.3Hz, 1H), 5.55 (d, J=1.0 Hz, 1H), 5.37 (d, J=1.3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 148.9, 148.2, 147.2, 146.7, 139.3, 128.5, 128.3, 128.1, 127.4, 123.7, 119.5, 117.2
LRMS calculated for $C_{16}H_{13}NO_2$ $[M]^{+\cdot}$ 251, measured 251.
Elemental analysis calculated for $C_{16}H_{13}NO_2$ C 76.48%, H 5.21%, measured C 76.78%, H 5.19%

- 4-(3-phenylbutadien-2-yl)benzonitrile **2h**



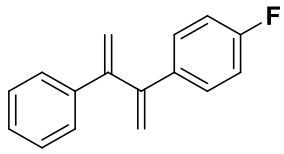
White solid, Y= 92%
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.57 (d, *J*= 8.2 Hz, 2H), 7.50 (d, *J=8.3* Hz, 2H), 7.38 (d, *J*= 7.7 Hz, 2H), 7.33-7.29 (m, 3H), 5.64 (bs, 1H), 5.60 (bs, 1H), 5.50 (bs, 1H), 5.33 (bs, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 148.9, 148.5, 144.7, 139.4, 132.2, 128.4, 128.14, 128.0, 127.42, 118.9, 118.8, 117.1, 111.2.
LRMS calculated for $C_{17}H_{13}N$ $[M]^{+\cdot}$ 231, measured 231.
Elemental analysis calculated for $C_{17}H_{13}N$ C 88.28%, H 5.67%, measured C 88.51%, H 5.72%

- 1-Chloro-4-(3-phenylbuta-1,3-dien-2-yl)benzene **2i**



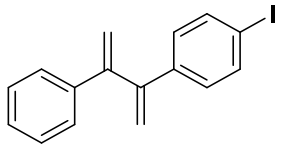
Colourless oil, Y= 90%
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.45-7.42 (m, 2H), 7.40-7.27 (m, 7H), 5.61 (d, 1.5 Hz, 1H), 5.59 (d, 1.5 Hz, 1H), 5.41 (d, 1.5 Hz, 1H), 5.39 (d, 1.5 Hz, 1H).
^{13}C (101 MHz, $CDCl_3$) δ ppm = 149.6, 148.8, 139.9, 138.7, 133.5, 128.9, 128.5, 128.3, 127.7, 127.5, 116.9, 116.7.
LRMS calculated $C_{16}H_{13}{}^{35}Cl$ $[M]^{+\cdot}$ 240, measured 240 (56%); $C_{16}H_{13}{}^{37}Cl$ $[M]^{+\cdot}$ 242, measured 242 (19%).
Elemental analysis calculated for $C_{16}H_{13}Cl$: C 79.83%, H 5.44%, measured C 80.33%, H 5.44%

- 1-fluoro-4-(3-phenylbuta-1,3-dien-2-yl)benzene **2j**



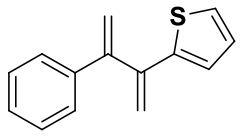
White solid, Y = 92%
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.48-7.37 (m, 4H), 7.35-7.27 (m, 3H), 7.03-6.95 (m, 2H), 5.60 (d, *J*= 1.5 Hz, 1H), 5.55 (d, *J*= 1.4 Hz, 1H), 5.37 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm = 163.7, 161.2, 149.9 (d, $J_{C\text{-}F}$=92 Hz), 139.8, 136.4 (d, $J_{C\text{-}F}$= 3.3 Hz) 129.3, 128.1, 127.4, 127.3, 116.5, 116.1, 115.2 (d, $J_{C\text{-}F}$= 21 Hz).
LRMS calculated $C_{16}H_{13}F$ $[M]^{+\cdot}$ 224, measured 224
Elemental analysis calculated for $C_{16}H_{13}F$: C 85.69 %, H 5.84%. Measured C 85.89%, H 5.59%

- 1-Iodo-4-(3-phenylbuta-1,3-dien-2-yl)benzene **2k**



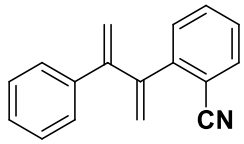
Colourless oil, Y= 91%.
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm= 7.64-7.61 (m, 2H), 7.42-7.39 (m, 2H), 7.33- 7.25 (m, 3H), 7.18-7.15 (m, 2H), 5.59 (d, 1.5 Hz, 1H), 5.58 (d, 1.5 Hz, 1H), 5.39 (d, 1.5 Hz, 1H), 5.36 (d, 1.5 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm = 149.4, 149.0, 139.8, 139.7, 137.4, 129.4, 128.3, 127.8, 127.5, 116.9, 116.7, 93.4.
LRMS calculated for $C_{16}H_{13}I$ $[M]^{+\cdot}$ 332, measured 332
Elemental analysis calculated for $C_{16}H_{13}I$: C 57.85 %, H 3.94%. Measured C 57.62%, H 3.86%

- 2-(3-phenylbuta-1,3-dien-2-yl)thiophene **2l**



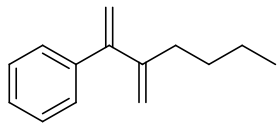
Colourless solid, 60%.
^{1}H NMR (400 MHz, $CDCl_3$) : δ ppm =7.49-7.46 (m, 2H,), 7.37-7.24 (m, 3H), 7.16 (dd, *J*= 4.7, 1.5Hz, 1H) 6.88 (m, 2H), 5.67 (d, *J*= 1.4 Hz, 1H), 5.62 (d, *J*= 1.4 Hz, 1H), 5.46 (d, *J*= 1.4 Hz, 1H), 5.24 (d, *J*= 1.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) : δ ppm= 149.2, 143.9, 143.3, 139.7, 128.4, 127.8, 127.4, 127.1, 126.3, 124.9, 115.8, 115.0.
LRMS calculated for $C_{14}H_{12}S$ $[M]^{+\cdot}$ 212, measured 212.
Elemental analysis calculated for $C_{14}H_{12}S$: C 79.20%, H 5.70%, S 15.10. Measured C 79.28%, H 5.58%, S 14.65.

- 2-(3-phenylbutadien-2-yl)benzonitrile **2m**



Light yellow oil, 18%.
RMN 1H (400 MHz, $CDCl_3$) δ ppm= 7.69- 7.67 (dd, *J*= 7.7, 0.9 Hz, 1H), 7.60-7.56 (m, 1H), 7.46-7.43 (m, 3H), 7.40-7.27 (m, 4H), 5.50 (s, 1H), 5.47 (s, 1H), 5.38 (s, 1H), 5.02 (s, 1H).
RMN 13C (101 MHz, $CDCl_3$): δ ppm= 149.6, 147.1, 145.2, 140.3, 133.3, 132.5, 130.16, 128.5, 128.3, 127.9, 127.8, 121.4, 118.3, 118.3, 112.3.
LRMS calculated for $C_{16}H_{13}CN$ $[M]^{+\cdot}$ 231, measured 231.

- (3-methylenhept-1-en-2-yl)benzene **2p**



Colourless oil, Y= 97%. NMR data are consistent with reported data.[11]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm =7.37-7.29 (m, 5H), 5.28 (d, *J*= 1.5 Hz, 1H), 5.19 (bs, 1H), 5.08 (d, *J*= 2.0 Hz, 1H), 4.96 (d, *J*=2.0 Hz, 1H), 2.27 (t, *J*=11.0, 2H), 1.56-1.48 (m, 2H), 1.41-1.30 (m, 2H), 0.90 (t, *J*= 9.2Hz, 3H).
^{13}C (101 MHz, $CDCl_3$) δ ppm= 150.8, 149.3, 141.4, 128.2, 128.1, 127.3, 115.3, 113.5, 34.3, 30.5, 22.5, 14.1.
HRMS calculated for $C_{16}H_{22}$ $[M]^{+\cdot}$ 186, measured 186

[11] Y. Zou, L. Qin, X. Ren, Y. Lu, Y. Li, J. Zhou, *Chem. Eur. J.*, **2013**, *19*, 3504-3511.

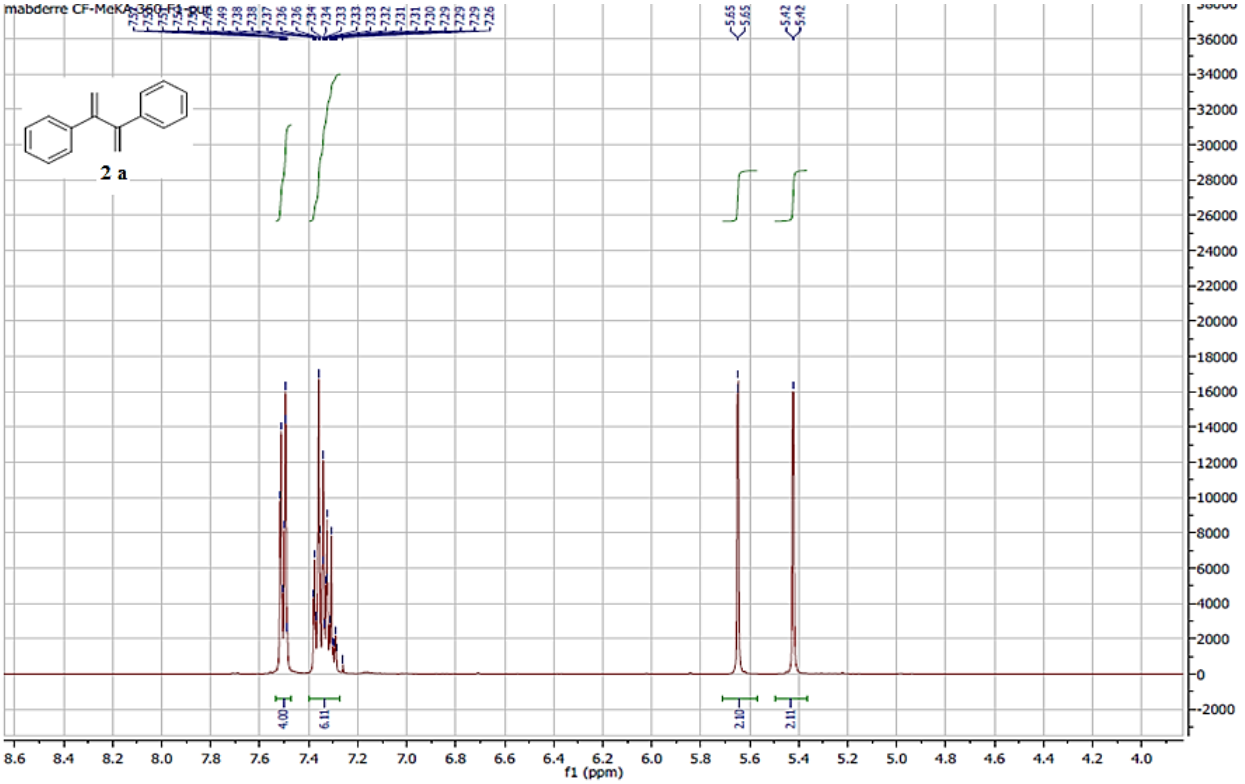


Figure S1: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 1,3-diphenylebutadiene **(2a)**

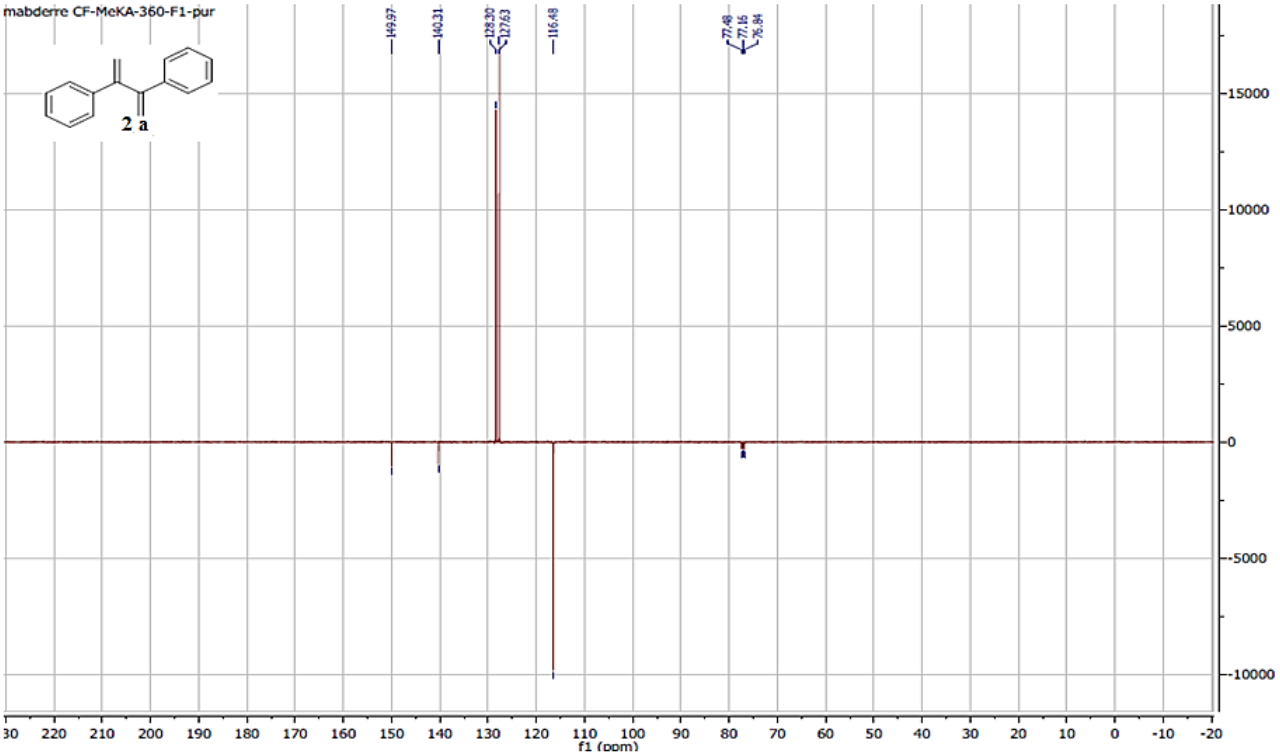


Figure S2: ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 1,3-diphenylebutadiene **(2a)**

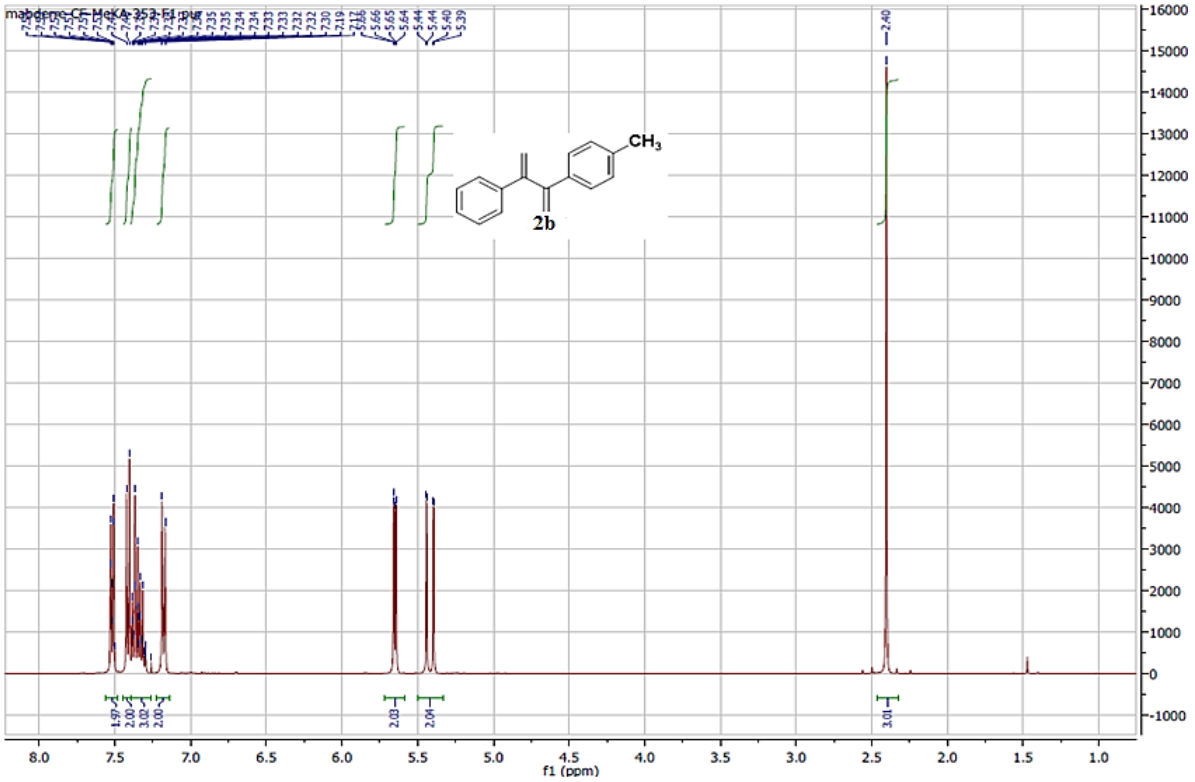


Figure S3: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 1-methyl-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2b)**

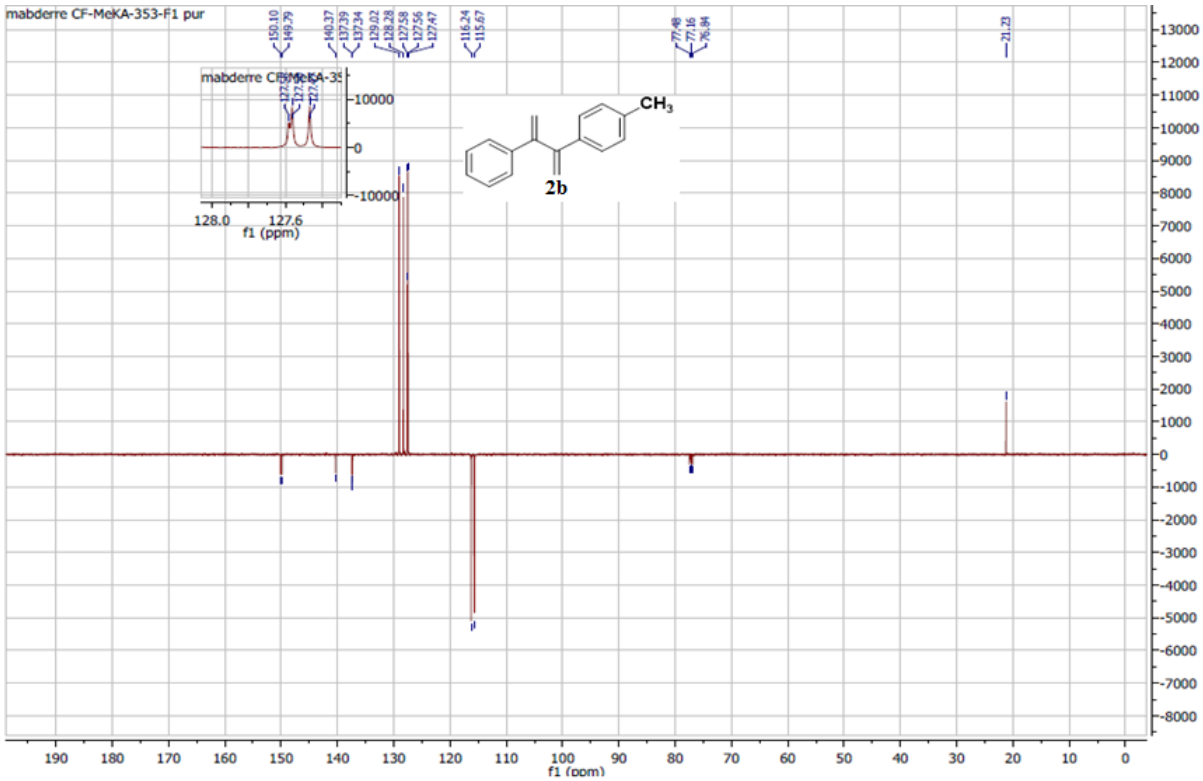


Figure S4: ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 1-methyl-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2b)**

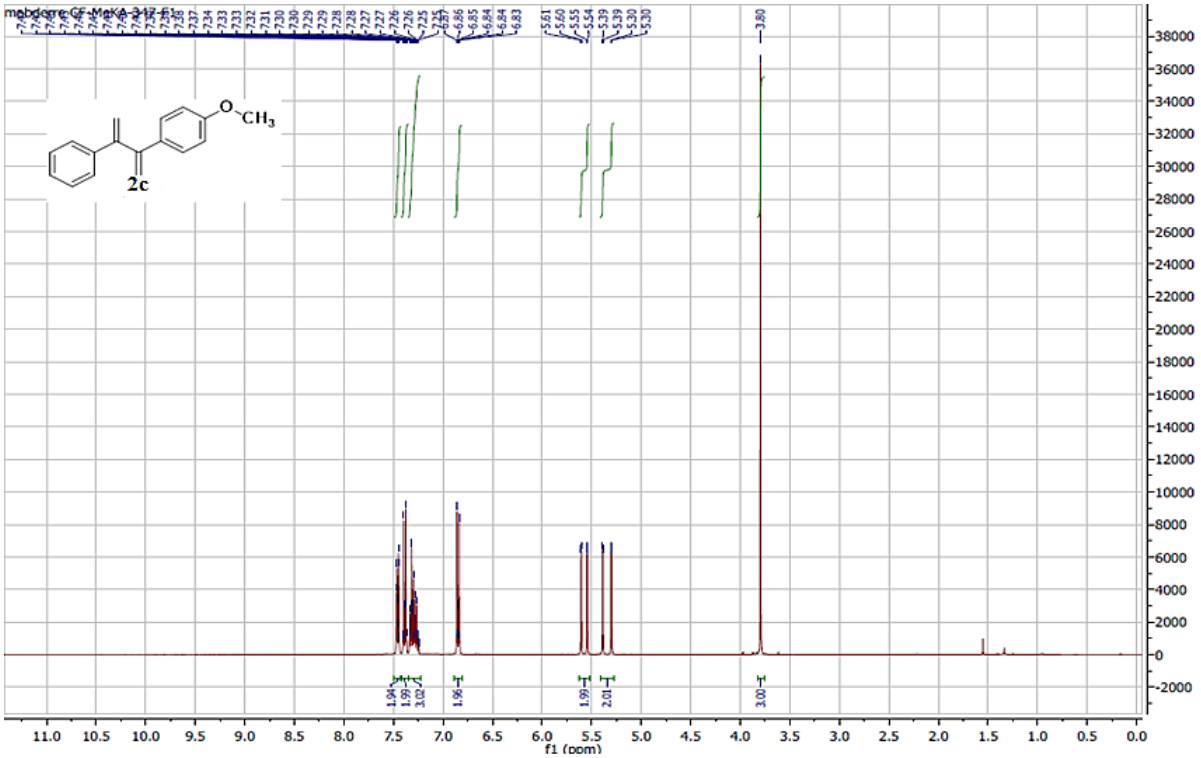


Figure S5: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 1-methoxy-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2c)**

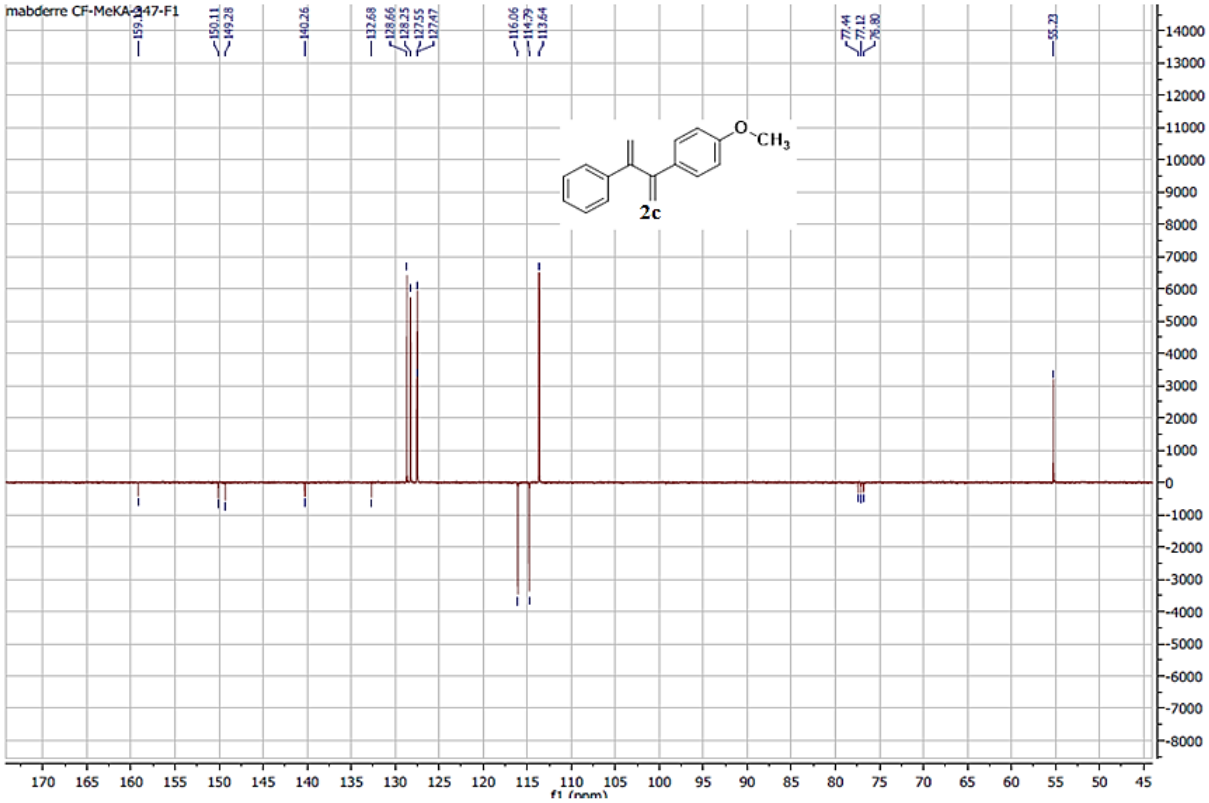


Figure S6: ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 1-methoxy-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2c)**

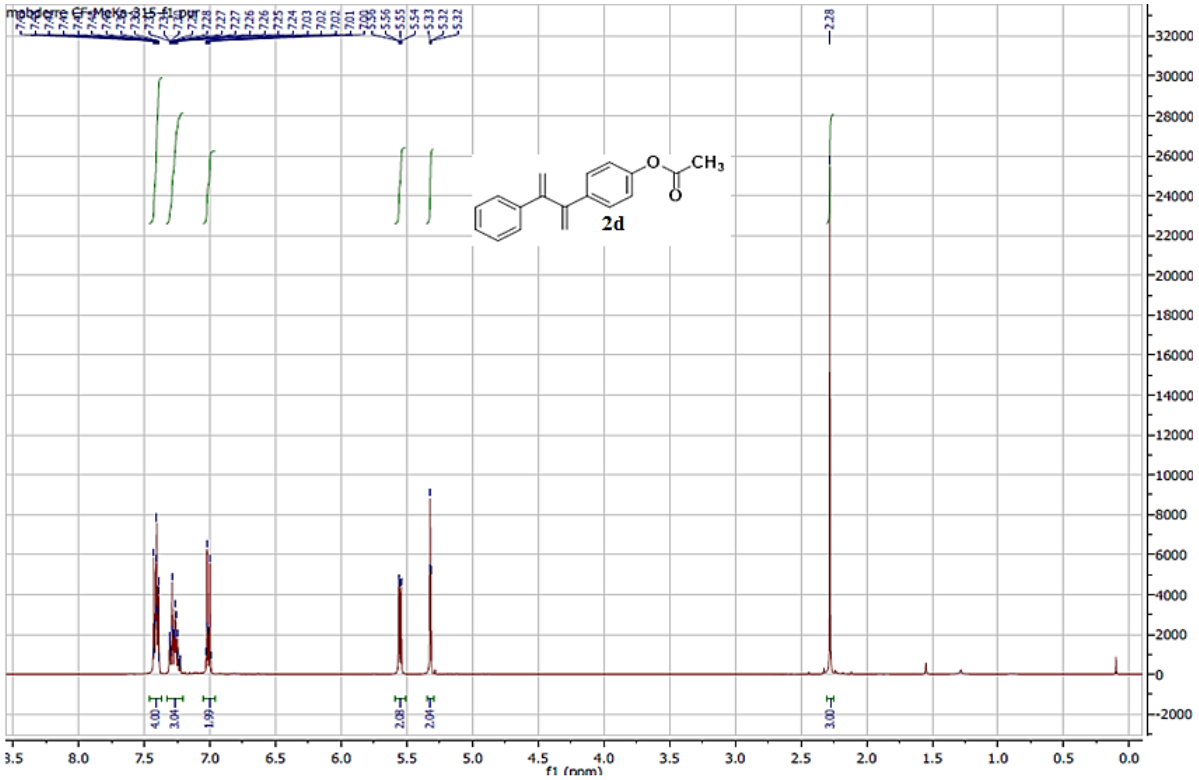


Figure S7: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 4-(3-phenylbuta-1,3-dien-2-yl)phenyl)acetate **(2d)**

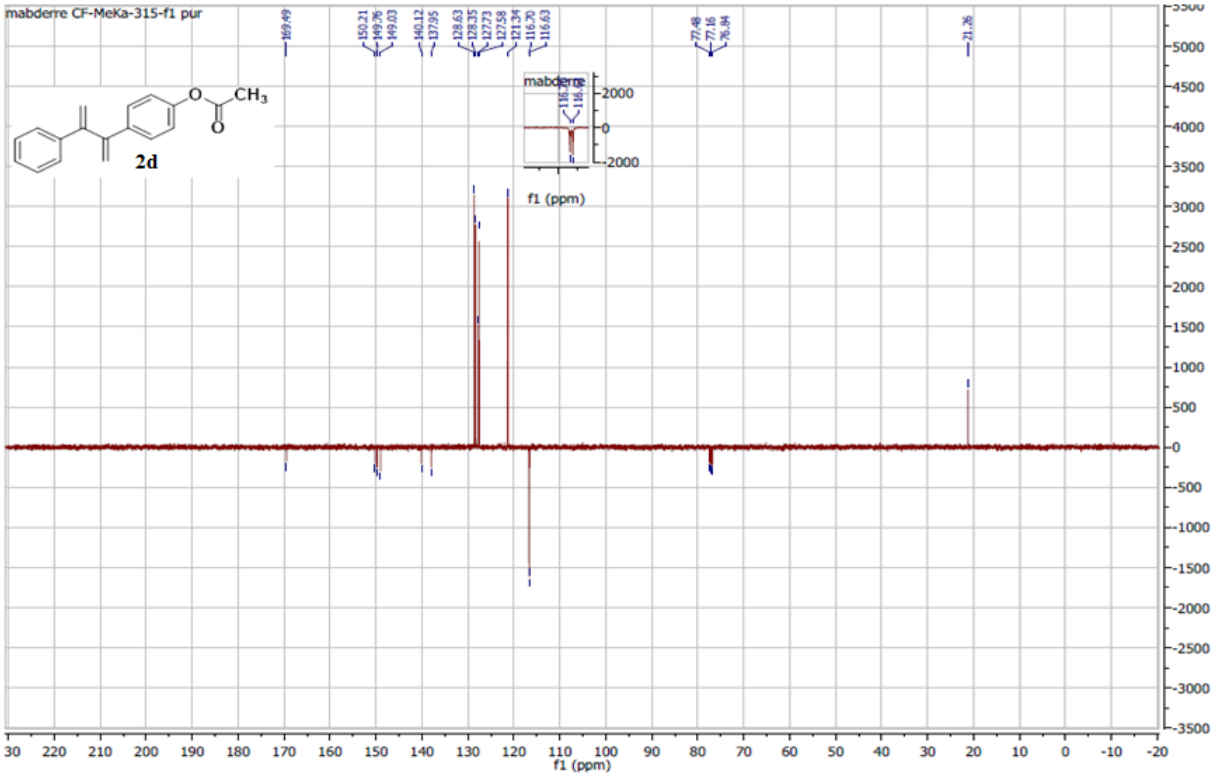


Figure S8: ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 4-(3-phenylbuta-1,3-dien-2-yl)phenyl)acetate **(2d)**

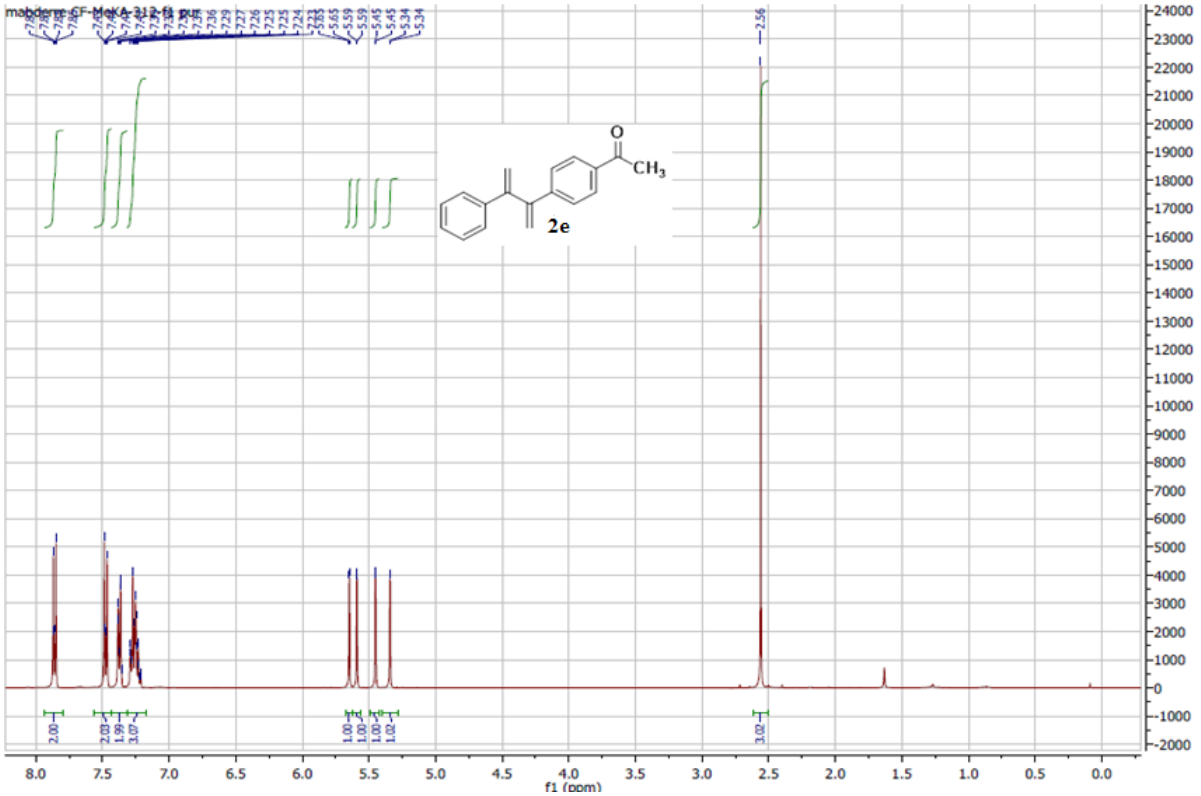


Figure S9: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 1-(4-(3-phenylbuta-1,3-dien-2-yl)phenyle)ethanone **(2e)**

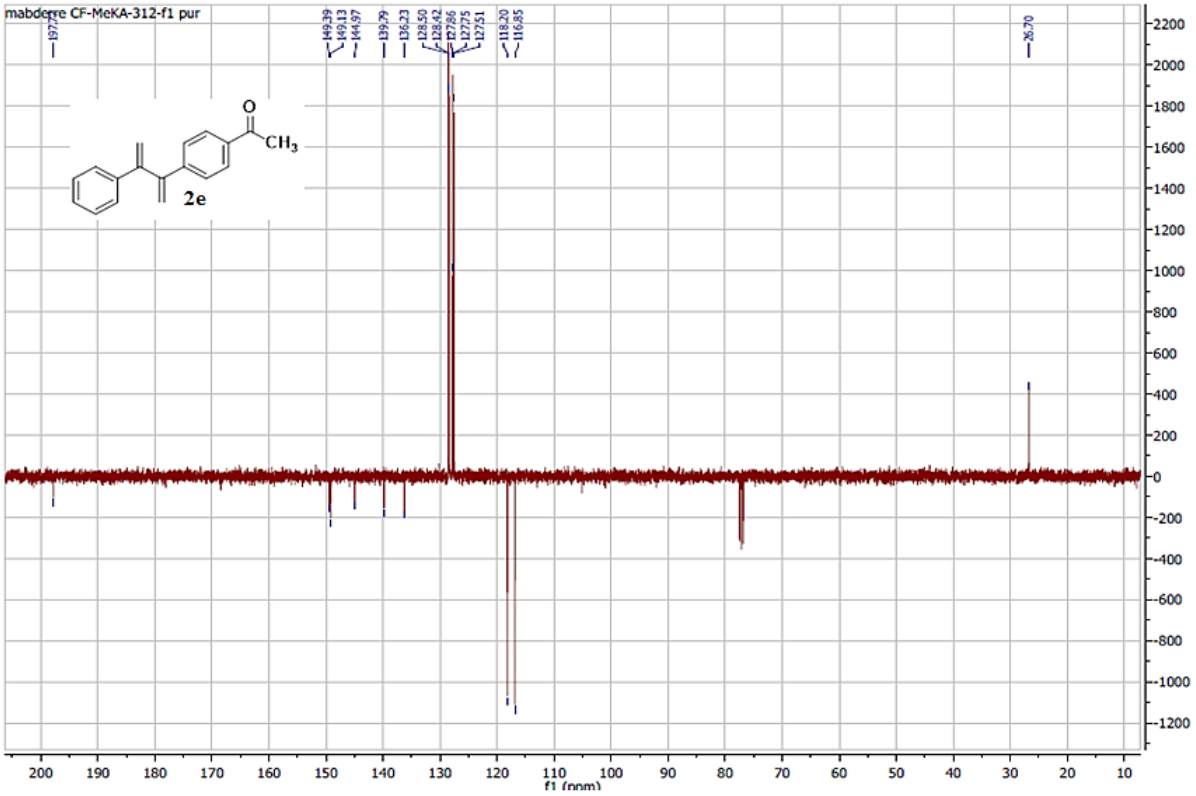


Figure S10 : ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 1-(4-(3-phenylbuta-1,3-dien-2-yl)phenyle)ethanone **(2e)**

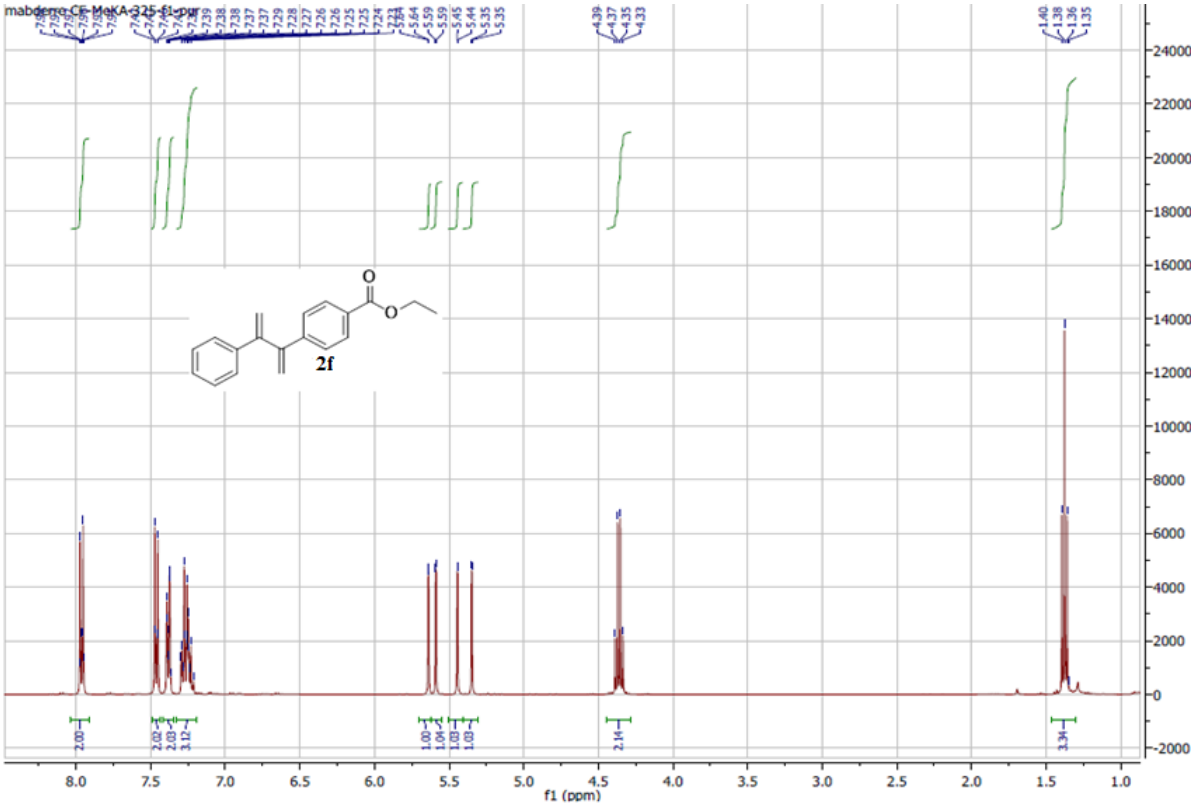


Figure S11 : ^{1}H NMR spectra (400 MHz, $CDCl_3$) of ethyl-4-(3-phenylebuta-1,3-dien-2-yl)benzoate **(2f)**

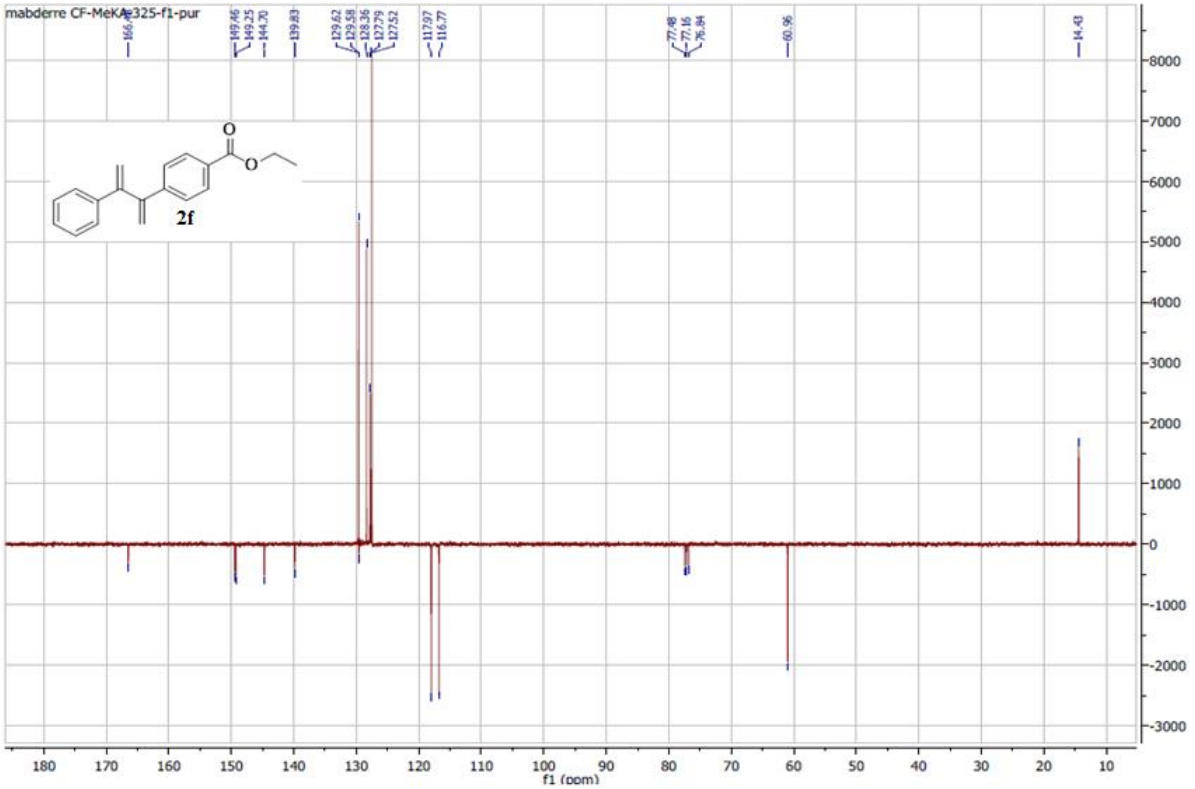


Figure S12 : ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of ethyl-4-(3-phenylebuta-1,3-dien-2-yl)benzoate **(2f)**

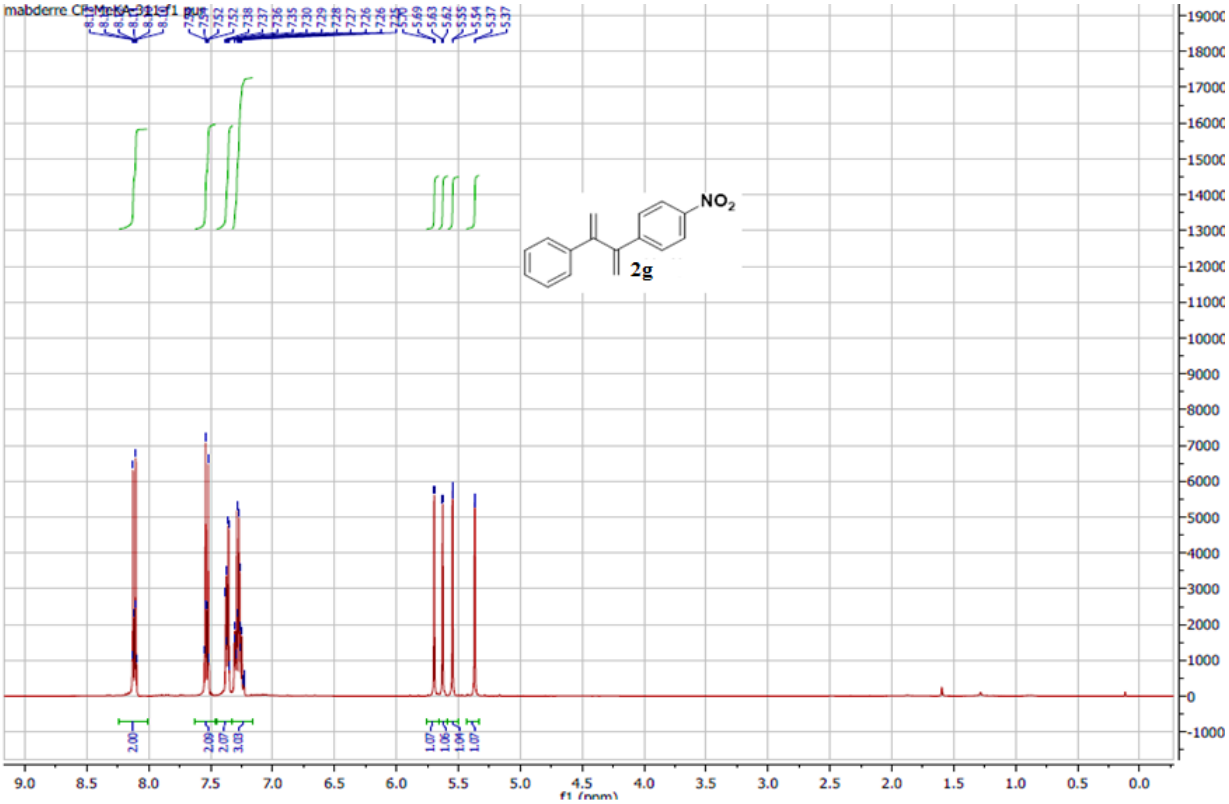


Figure S13. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 2-(4-nitrophenyl)-3-phenyl-1,3-butadiene **(2g)**

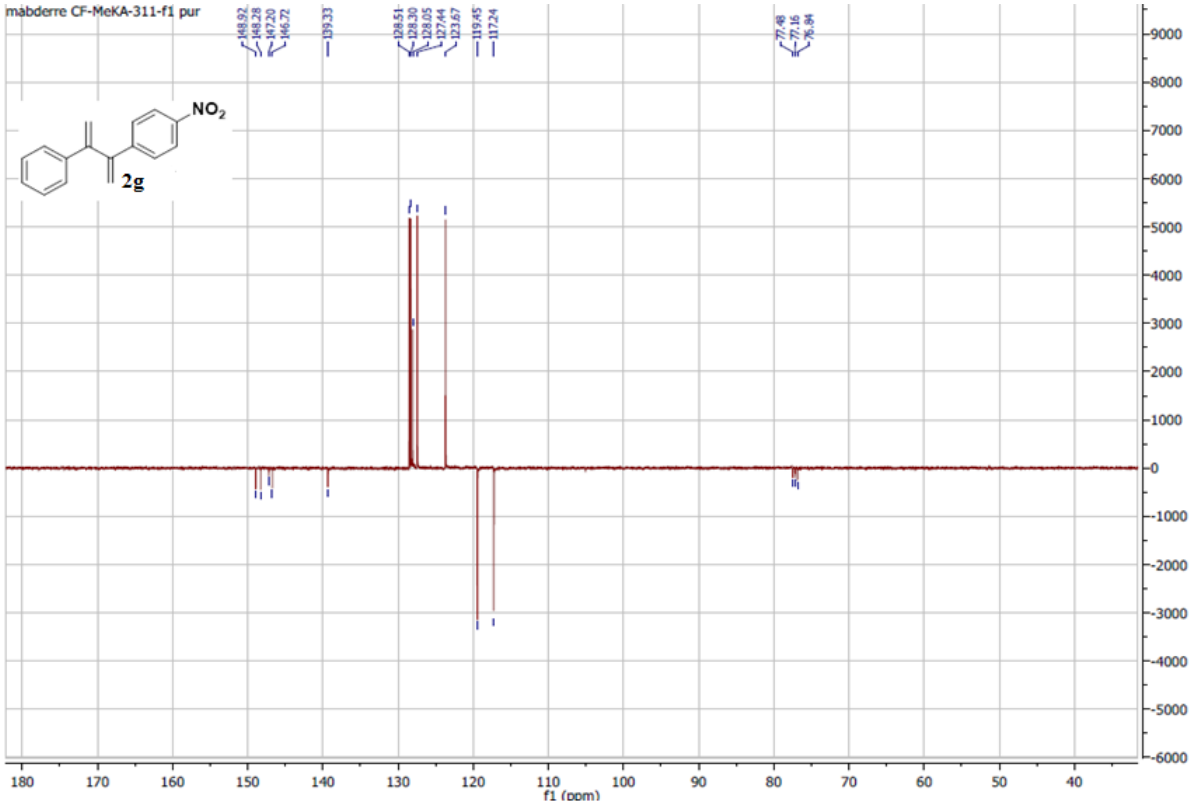


Figure S14. ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 2-(4-nitrophenyl)-3-phenyl-1,3-butadiene **(2g)**

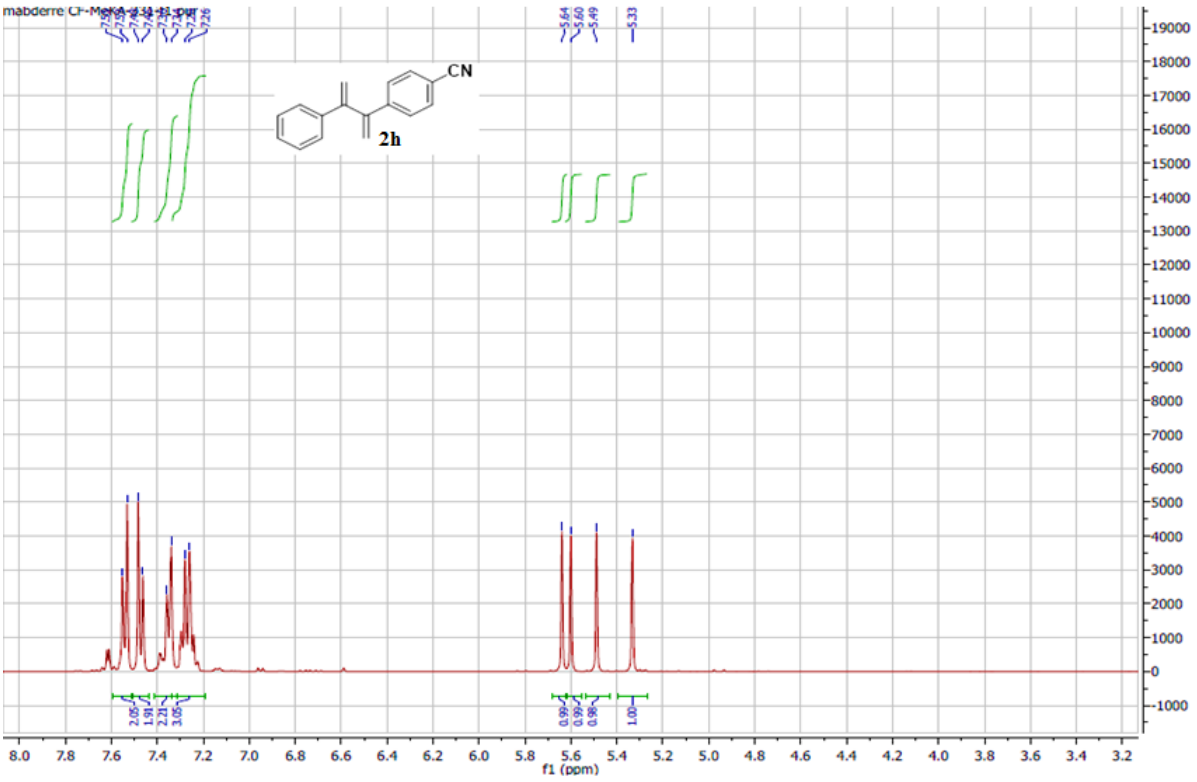


Figure S15. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 4-(3-phenylbutadien-2-yl)benzonitril **(2h)**

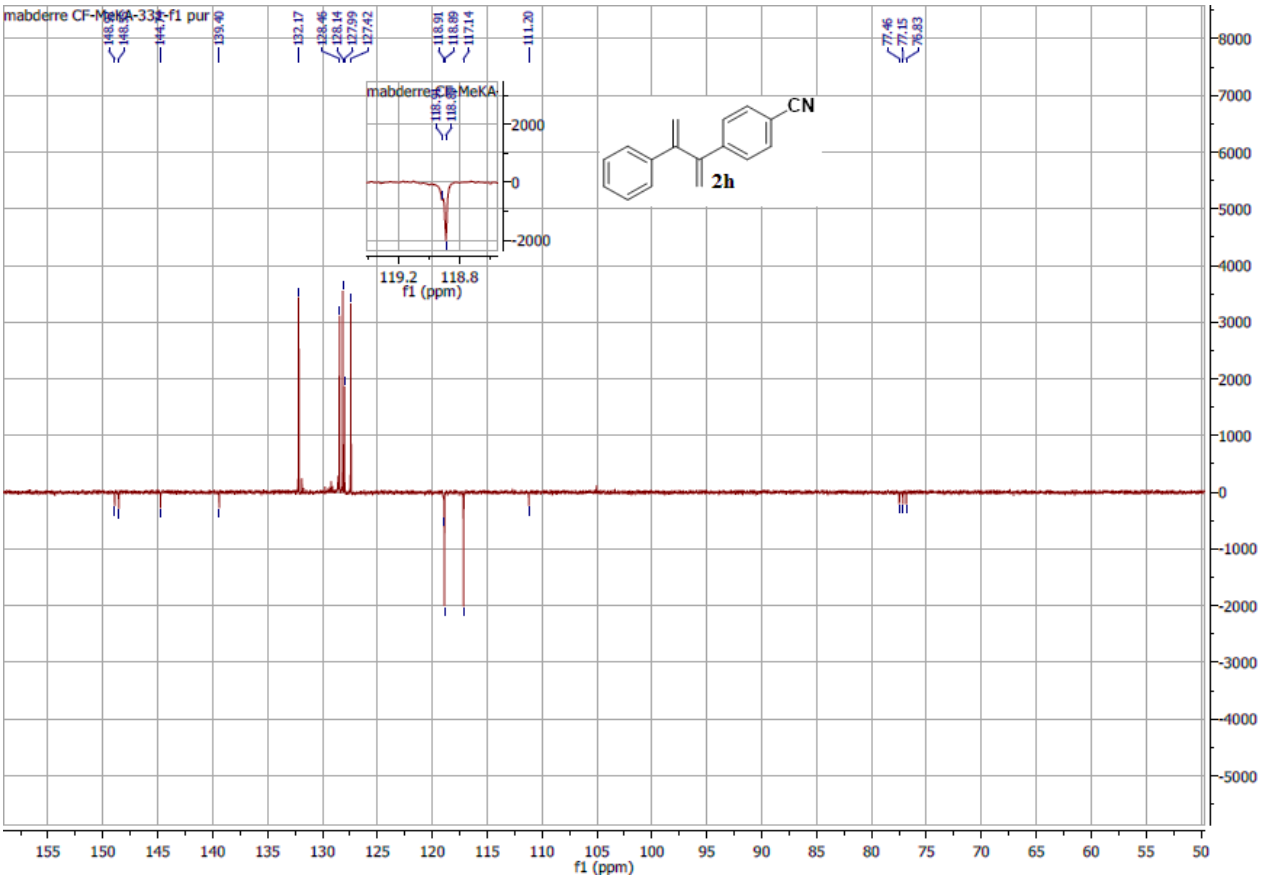


Figure S16. ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 4-(3-phenylbutadien-2-yl)benzonitril **(2h)**

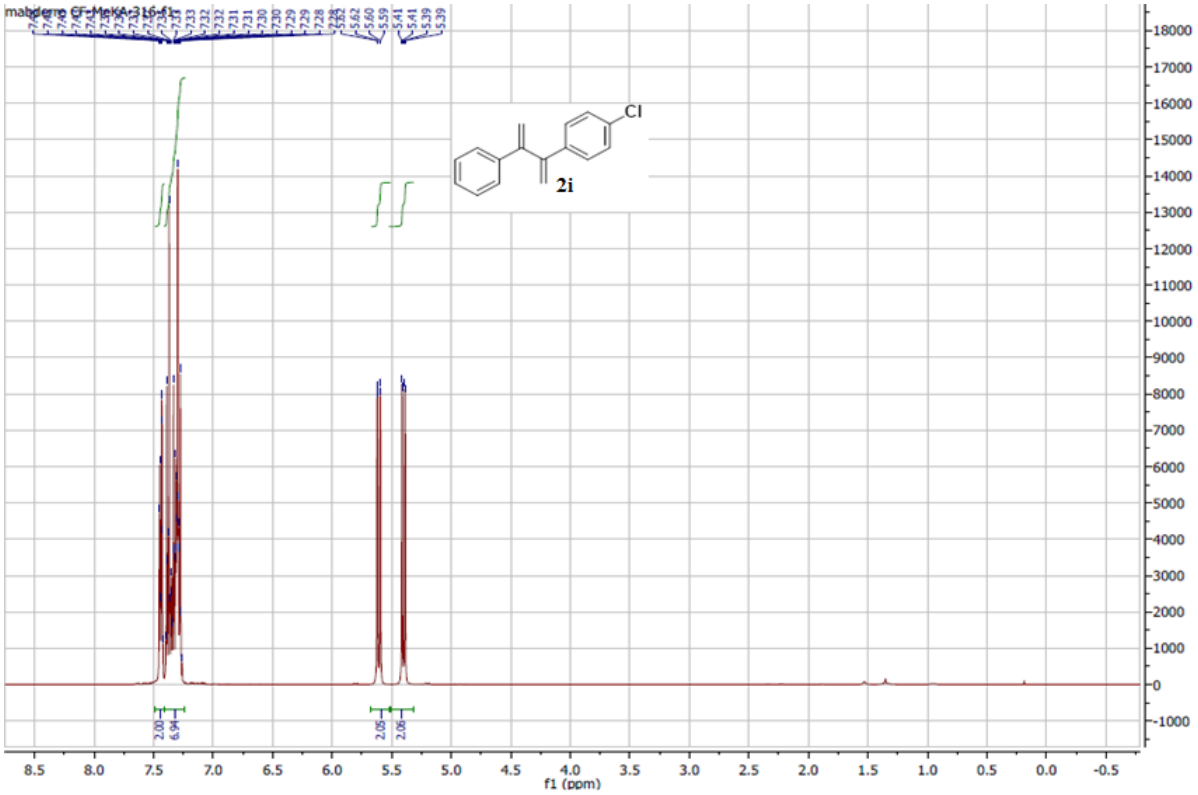


Figure S17. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 1-Chloro-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2i)**

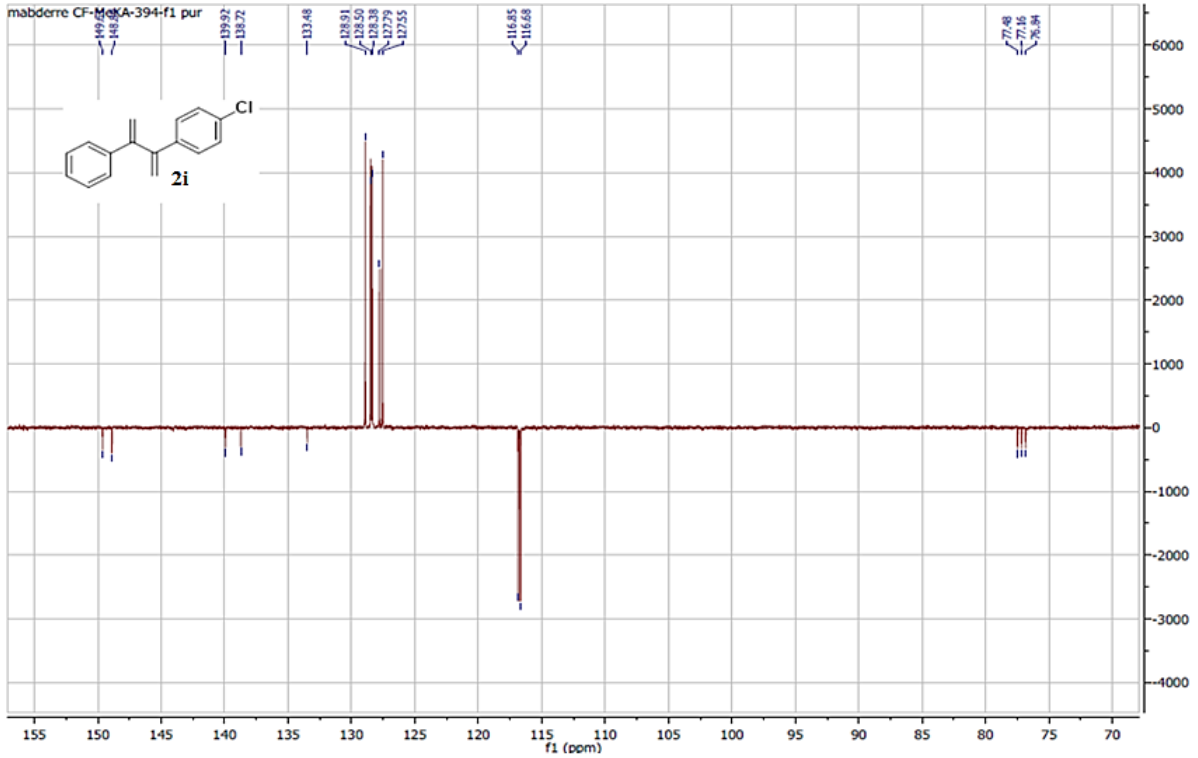


Figure S18. ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 1-Chloro-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2i)**

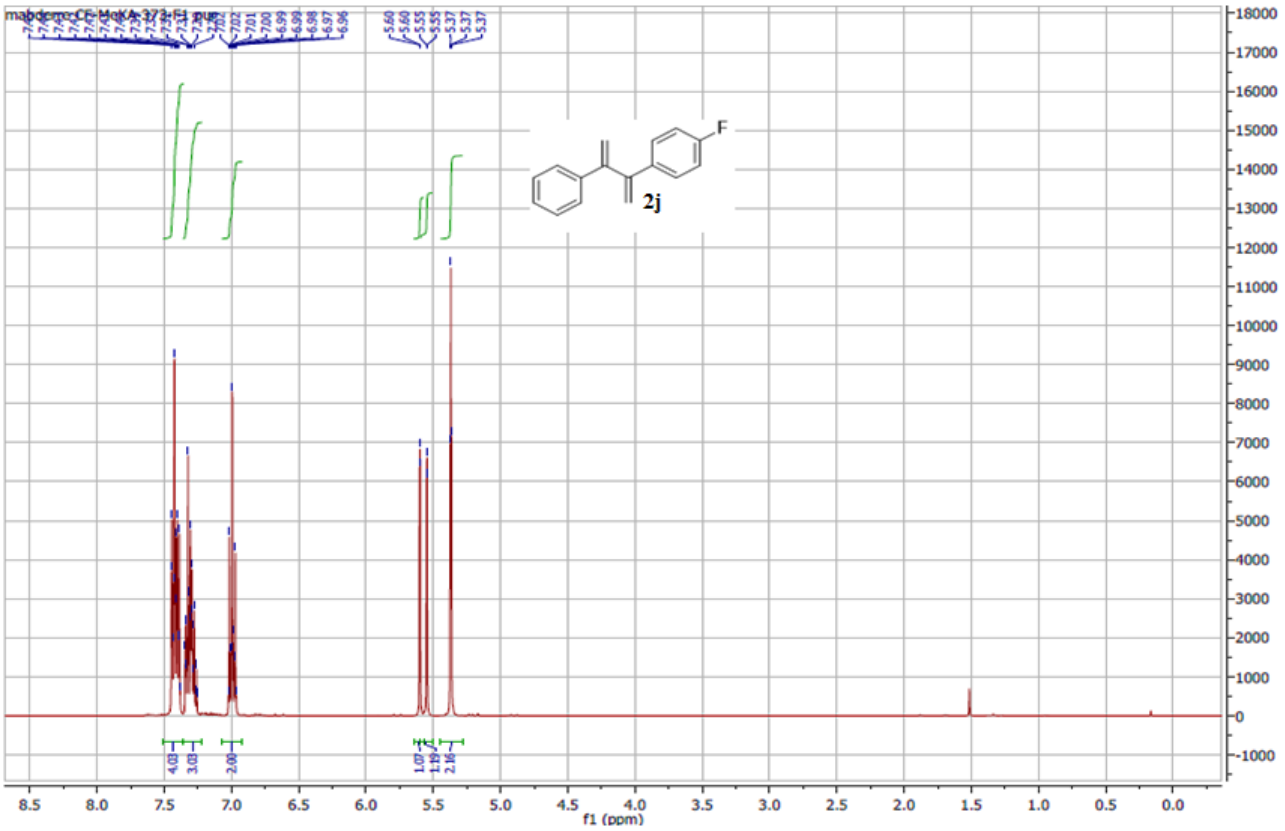


Figure S19. : ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 1-Fluoro-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2j)**

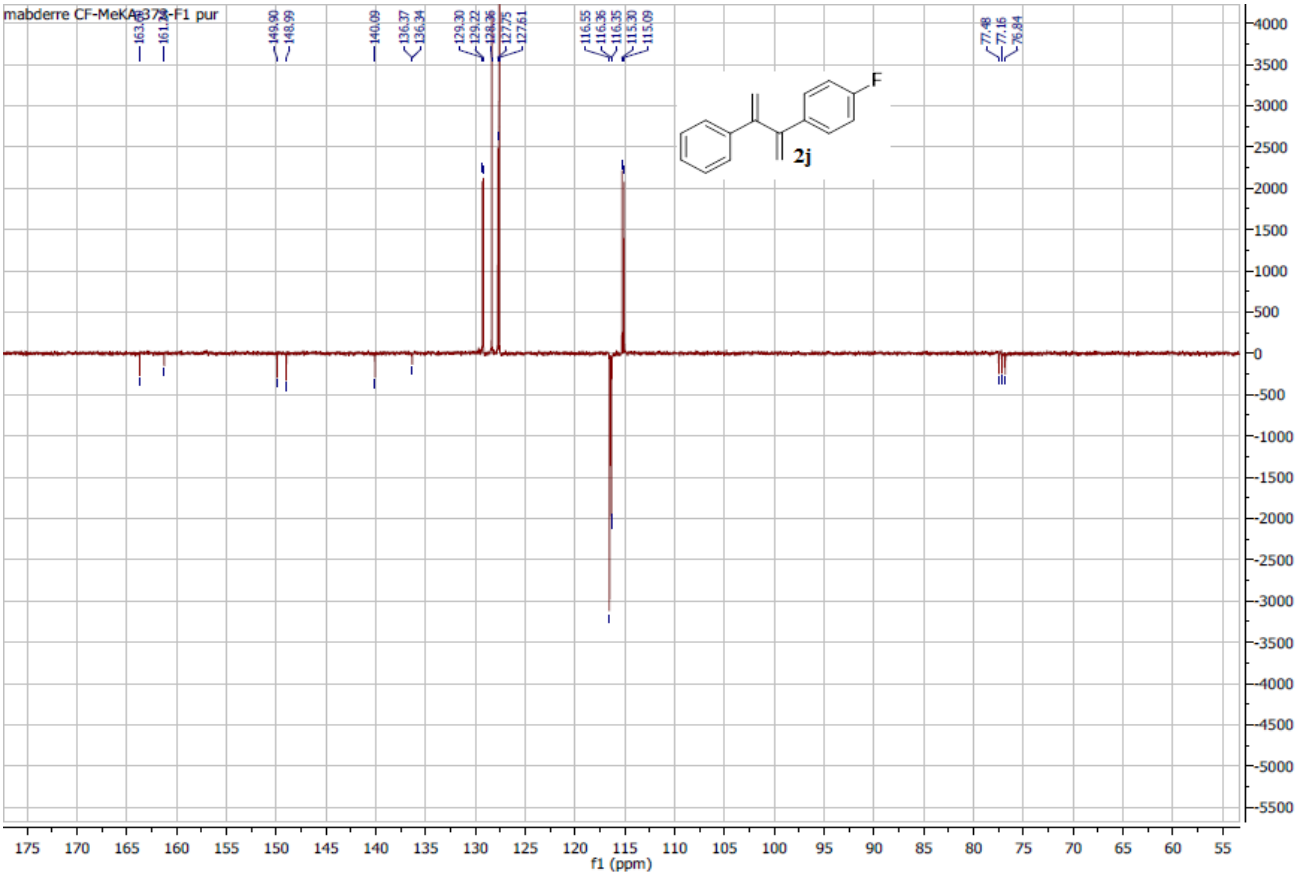


Figure S20. ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 1-Fluoro-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2j)**

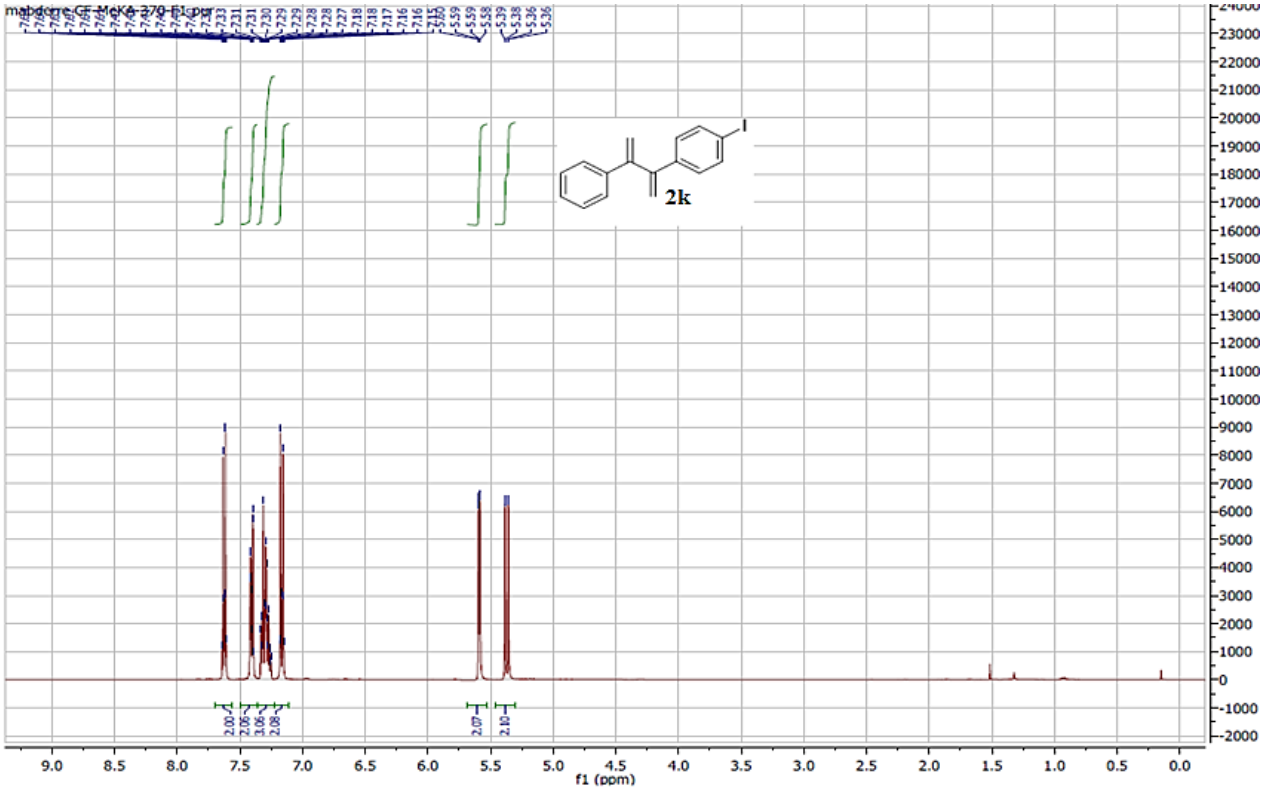


Figure S21. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 1-Iodo-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2k)**

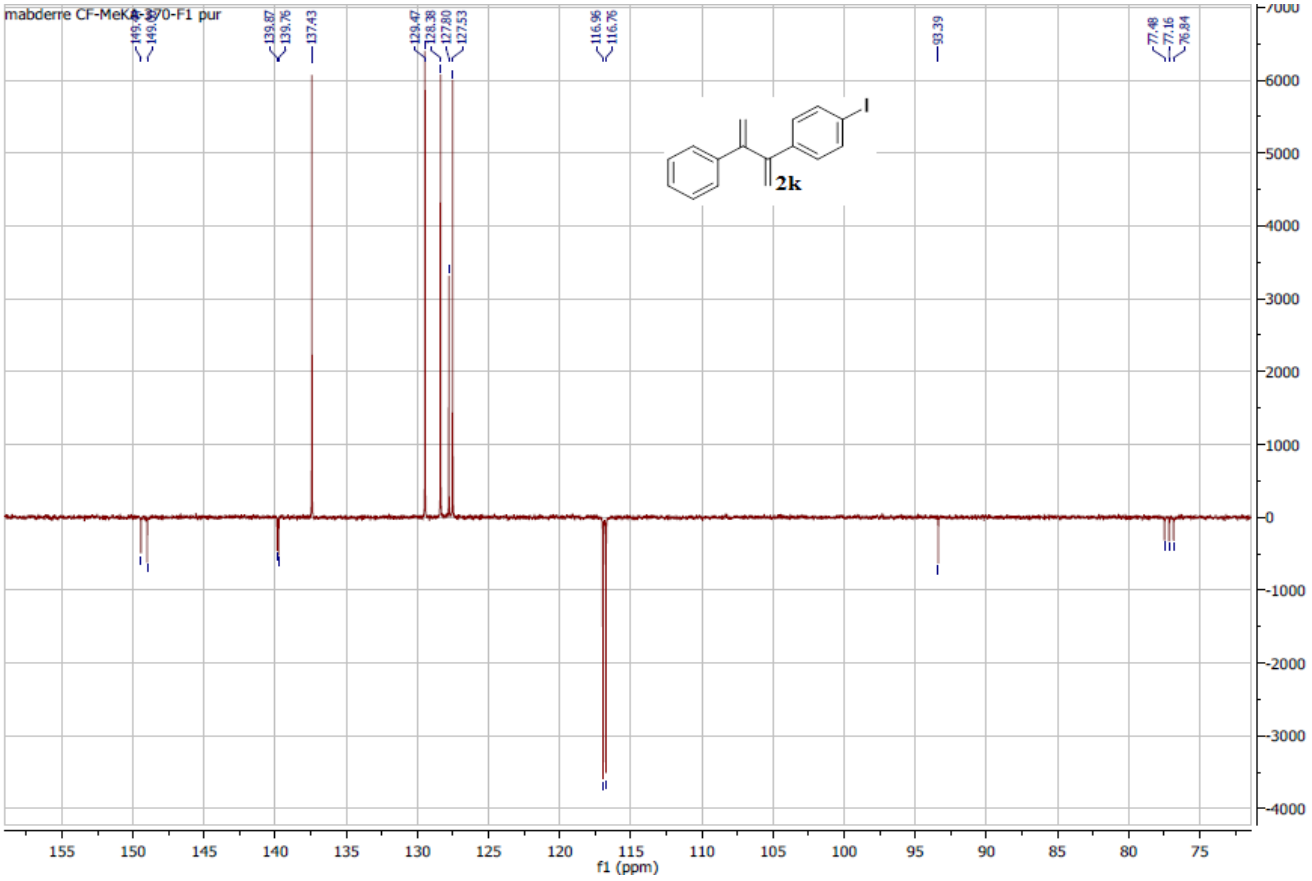


Figure S22. ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 1-Iodo-4-(3-phenylbuta-1,3-dien-2-yl)benzene **(2k)**

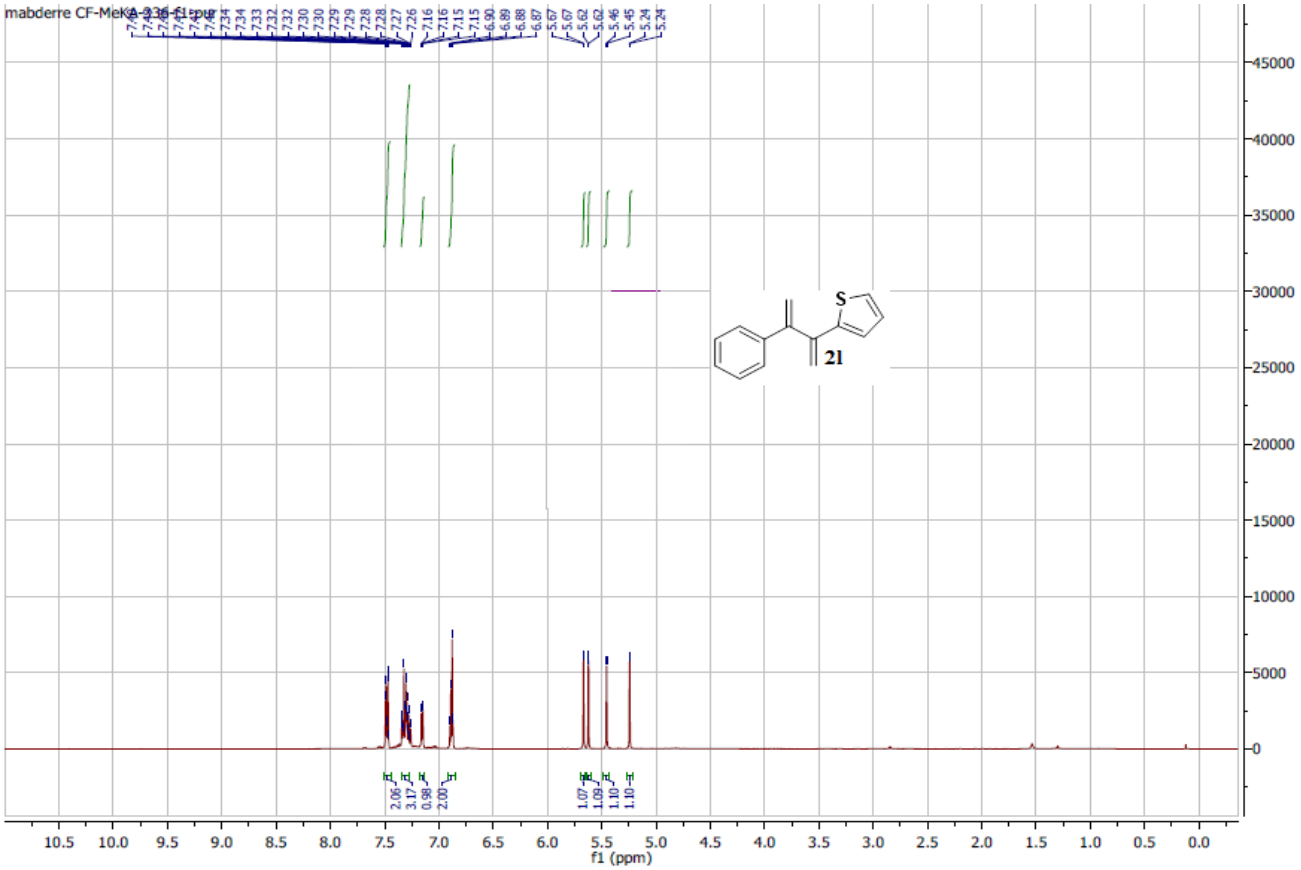


Figure S23. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 2-(3-phenylbuta-1,3-dien-2-yl) thiophene **(2l)**

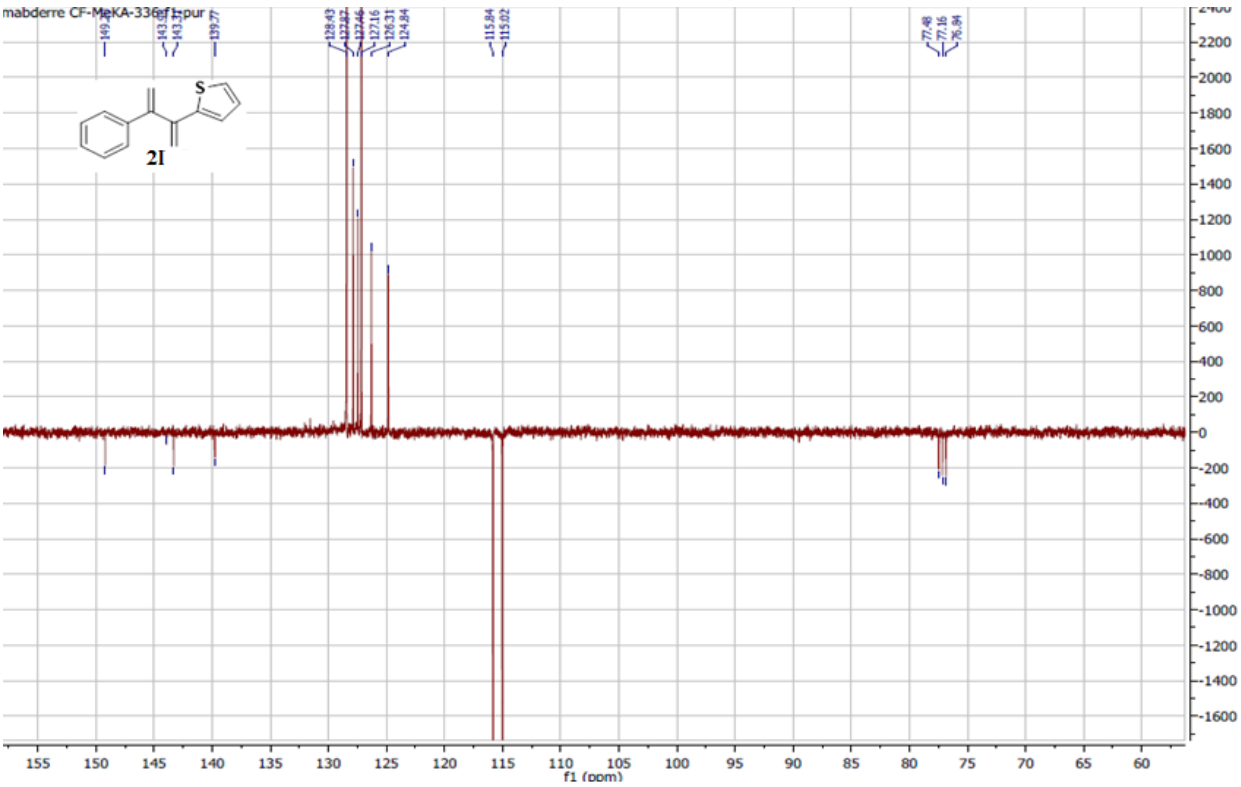


Figure S24. ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 2-(3-phenylbuta-1,3-dien-2-yl) thiophene **(2l)**

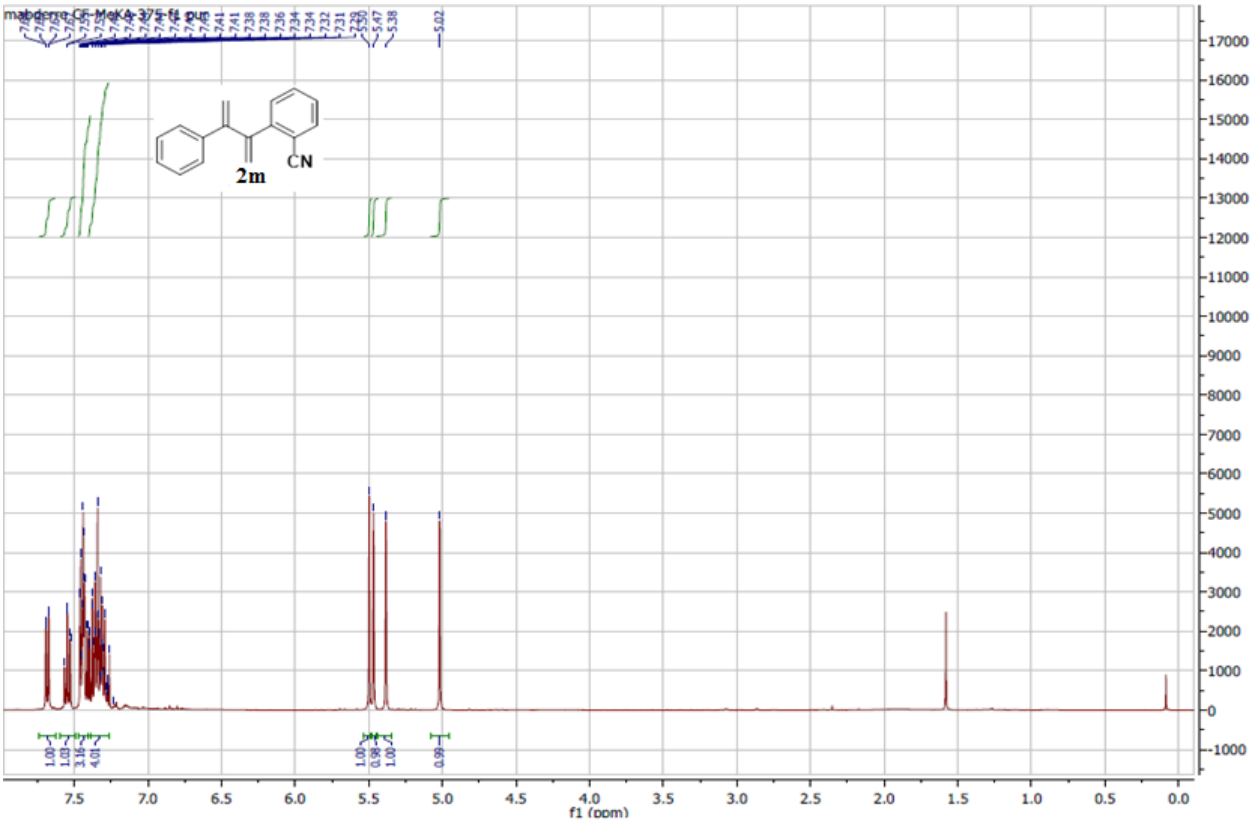


Figure S25 : ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 2-(3-phenylbutadien-2-yl)benzonitril **(2m)**

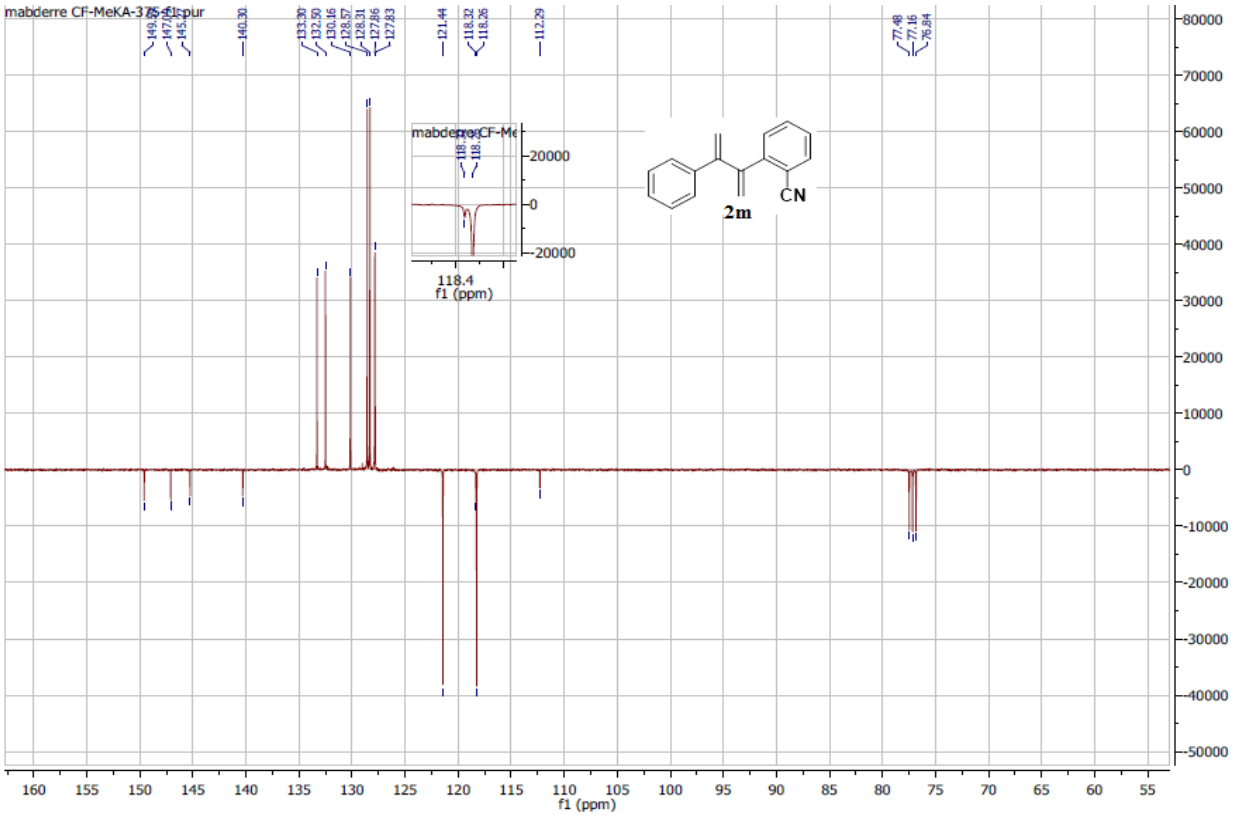


Figure S26. ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of 2-(3-phenylbutadien-2-yl)benzonitril **(2m)**

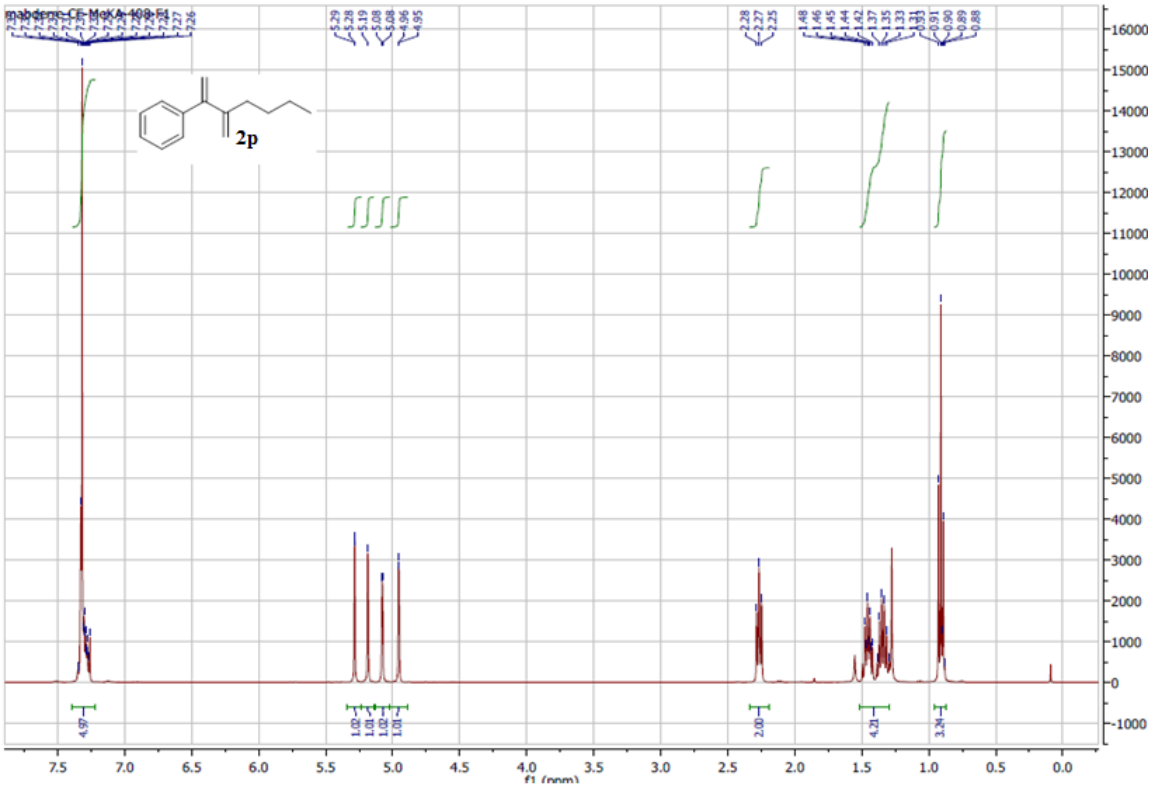


Figure S27. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of (3-methylenhept-1-en-2-yl)benzene **(2p)**

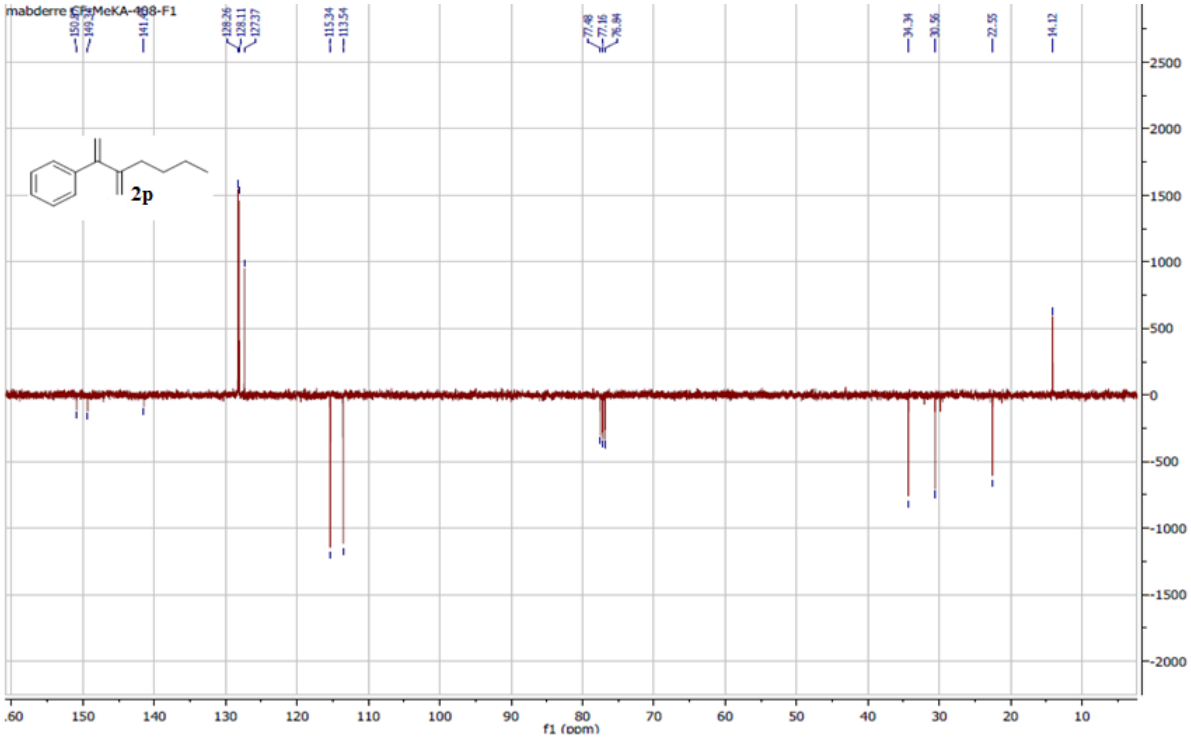


Figure S28. ^{13}C NMR (Jmod) spectra (100 MHz, $CDCl_3$) of (3-methylenhept-1-en-2-yl)benzene **(2p)**