Supporting Information

Persulfate-mediated synthesis of polyfunctionalized benzenes in water via benzannulation of alkynes and α,β-unsaturated compounds

Gabriela F. P. de Souza[a] and Airton G. Salles, Jr[a]

[a] Department of Organic Chemistry, Institute of Chemistry, University of Campinas, P.O. Box 6154, Campinas, SP 13084-862, Brazil

Table of contents

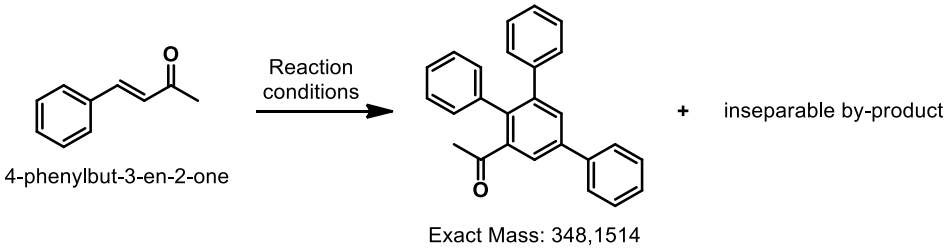
1. General Information

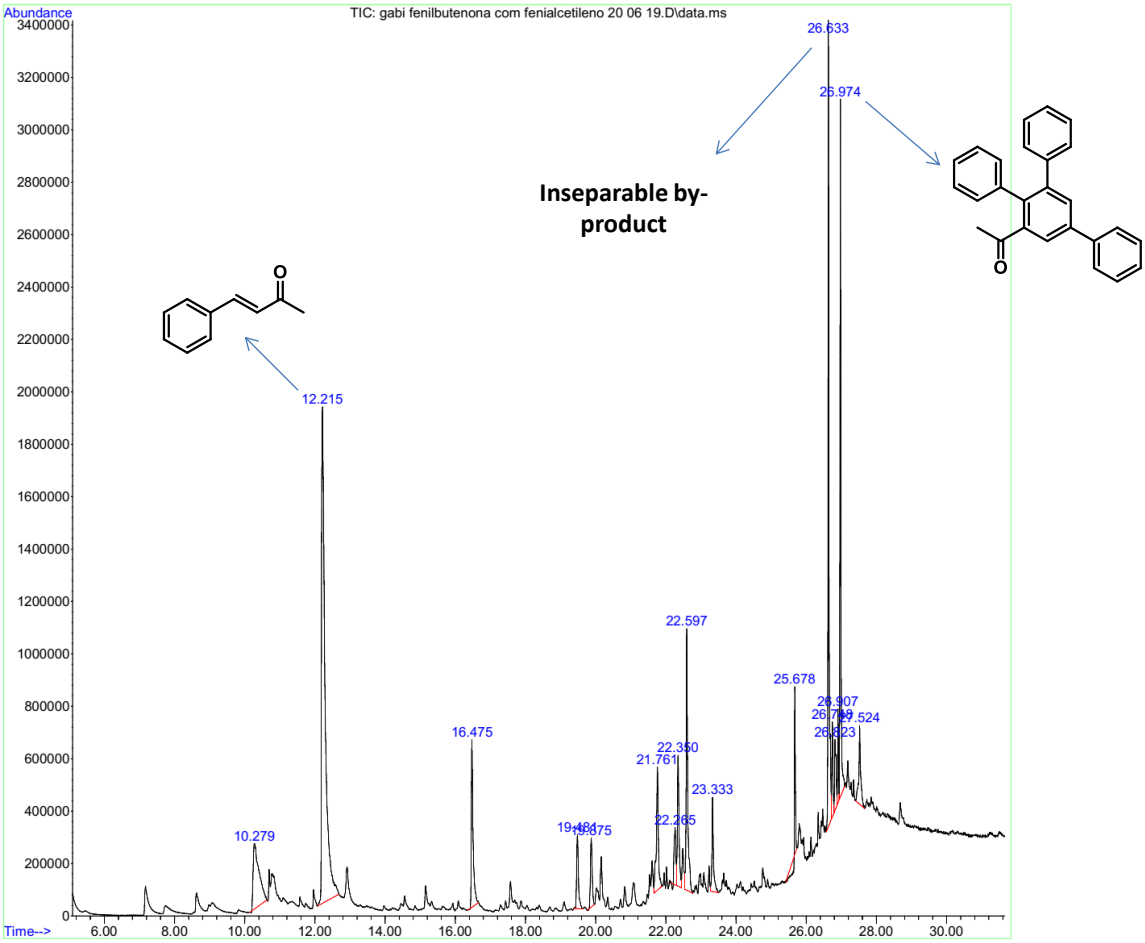
All reagents were purchased from commercial suppliers (Sigma-Aldrich, Oakwood and Combi-Blocks) and used without further purification, all solvents were analytical grade. Temperatures above room temperature were maintained by using an aluminum block heated on a hotplate, and reaction temperatures are reported as the temperature of the block surrounding the vessel. Thin layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness, visualization was accomplished with short wave UV light or $KMnO_4$ staining solution followed by heating. Melting points were measured on Buchi M-560 melting point apparatus and are uncorrected. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 400 MHz and 500 MHz in $CDCl_3$ solutions, at ambient temperature. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHZ and 125 MHz in $CDCl_3$ solutions, at ambient temperature. Chemicals shifts (δ) are given in ppm and the residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δH = 7.27 ppm, δC = 77.00 ppm). High resolution mass spectra were recorded on Thermo Scientific LTQ FT Ultra and Q Exactive Orbitrap spectrometers working with an electronspray ionization (ESI). The Gas Chromatography coupled to Mass Spectrometry (CG-MS) analyses were performed using a Network GC system 6890N (Agilent Technologies Inc., Palo Alto, CA, USA), equipped with a HP-5MS 5% Phenyl Methyl Silox (25.0 m × 250 µm × 0.25 µ nominal) capillary column. The GC analyses were carried out in split mode (ratio 150:1) using helium as carrier gas at a flow rate of 504 mL/min (7.65 psi). The injection port temperature was 250 °C; the oven was maintained at an initial temperature of 50 °C for 3 minutes, then programmed at 40 °C/min to a temperature of 280 °C, where it was held, post-run, for 2 minutes. The MS detector was at 250 °C, using H_2 flow at 40.00 mL/min, air at 400 mL/min and He makeup flow at 45.0 mL/min.

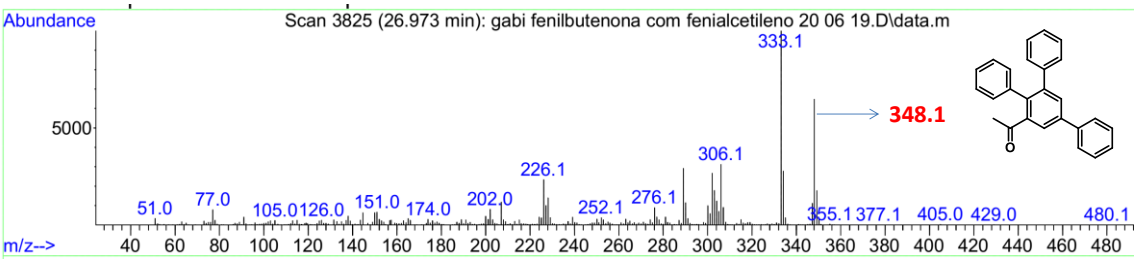
2. General Procedure for Benzannulation

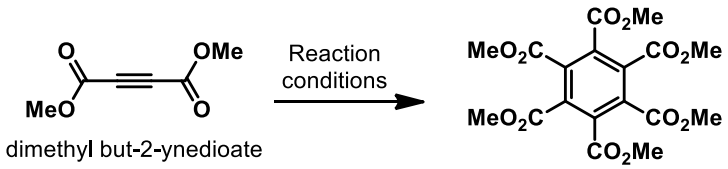
Phenylacetylenes (2.0 mmol, 2.0 equiv), α,β–unsaturated compound (1.0 mmol, 1.0 equiv), $(NH_4)_2S_2O_8$ (2.0 mmol, 2.0 equiv, using an aqueous solution 1.3 M) were added to 2 ml of water. The resulting suspension was capped with a rubber septum and stirred at 85 ^{o}C for 8 h. The stirring speed of the reaction mixture was kept at 1150 rpm to ensure a proper diffusion of reaction components. Then, the suspension was extracted with ethyl acetate (2 × 2 mL) and the combined organic layers were concentrated. The crude mixture was filtered through a plug of silica (40 mm internal diameter, 7.5 g of SiO_2) using 55 mL of a mixture of ethyl acetate / n-hexane (8:92) and followed by TLC to afford the desired pure product. For **3d** we have used a mixture of ethyl acetate / n-hexane (20:80) and for **3c** we have used a mixture of ethyl acetate / n-hexane (10:90).

3. GC-MS analysis of the reaction employing 4-phenylbut-3-en-2-one and internal alkynes



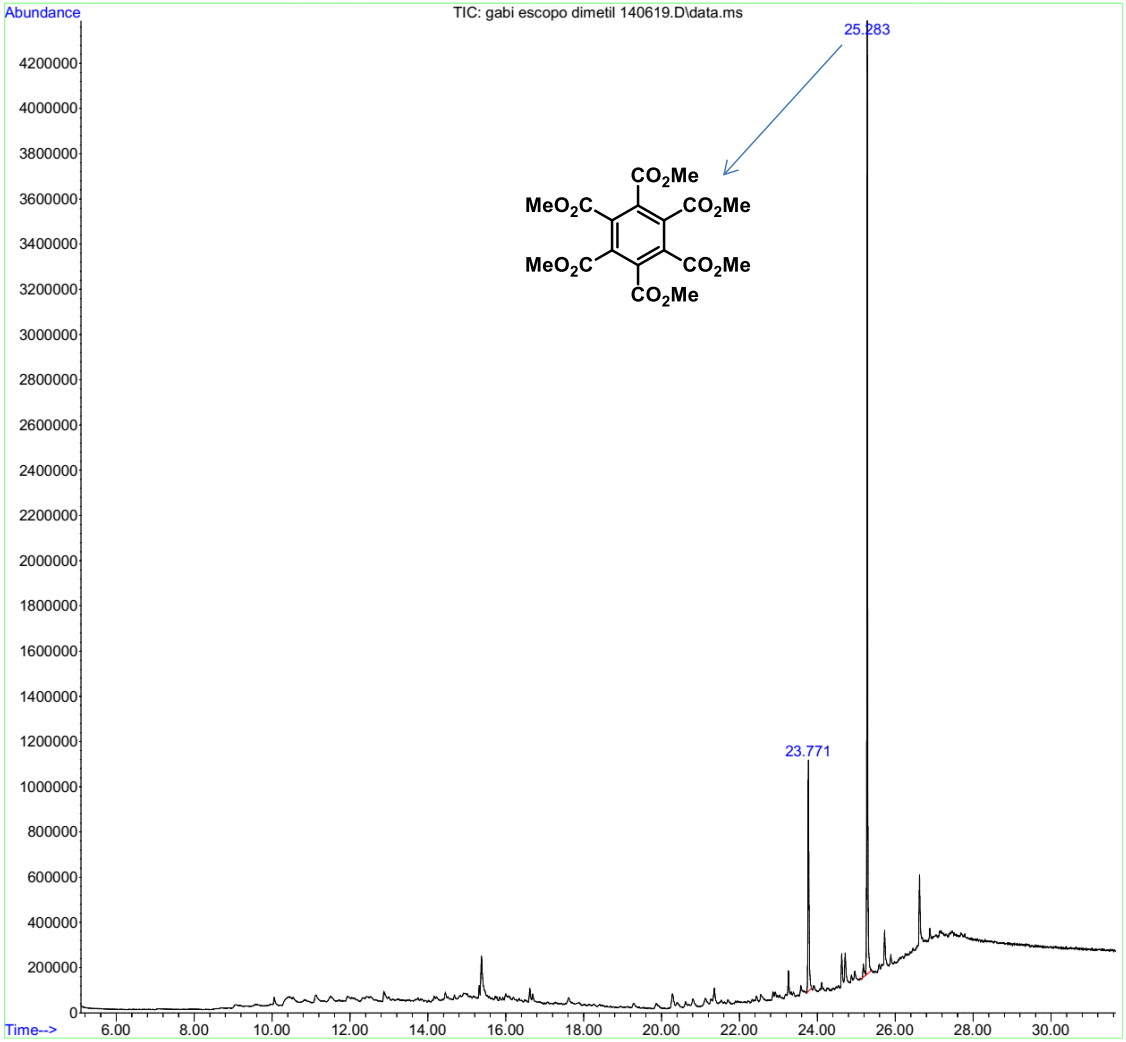


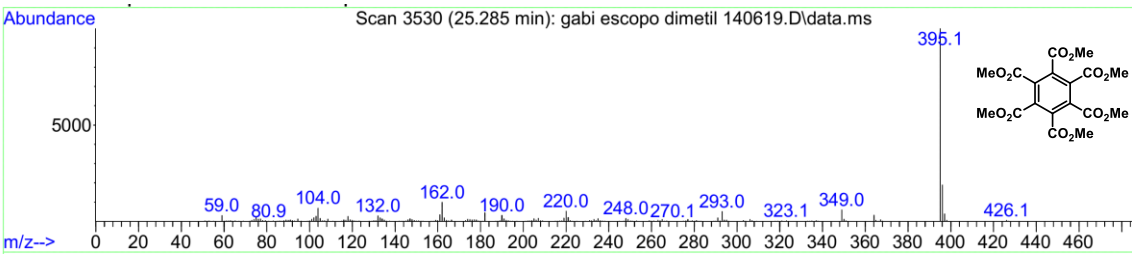


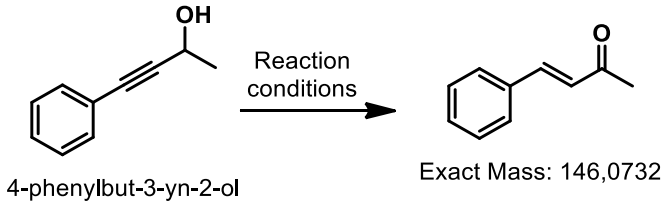


dimethyl but-2-ynedioate

Exact Mass: 426,0798







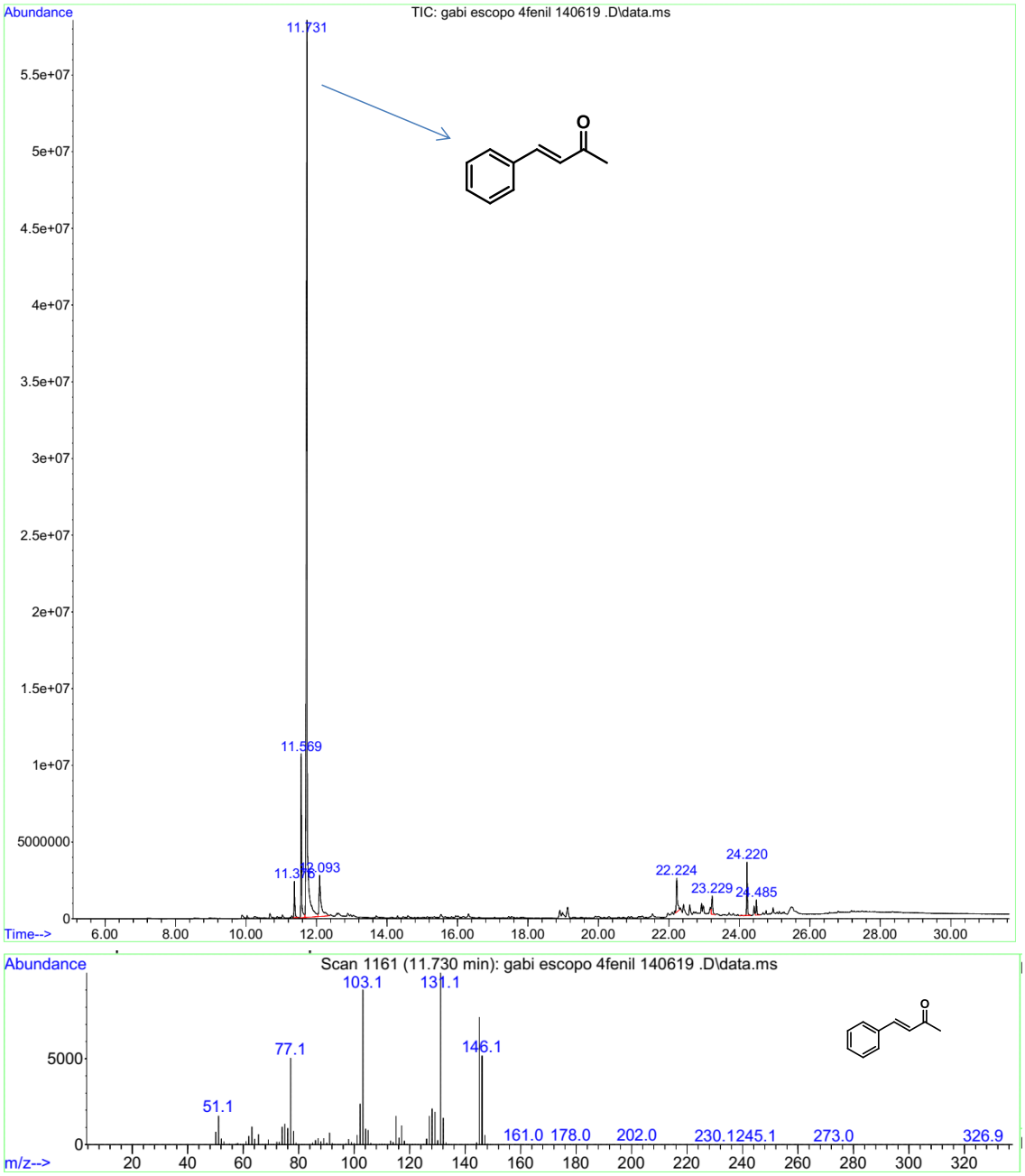


Figure S1. GC-MS analysis of the reaction employing 4-phenylbut-3-en-2-one and internal alkynes.

The targeted product obtained using 4-phenylbut-3-en-2-one was not separable employing only a plug of silica. As the aim of the whole process is to avoid the use of regular amount of silica and solvents and consequently reduce the E-factor, we decided to rank it as an unsuccessful substrate and not to employ a complete flash chromatography which would impair the sustainability of the transformation.

In the reaction employing 4-phenylbut-3-yn-2-ol, it is interesting to observe that a formal reduction of the triple bond occurred during the transformation. It lends support to the same formal reduction proposed for the generation of styrene from phenylacetylene presented in item 10 of this Supporting Information.

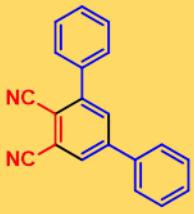
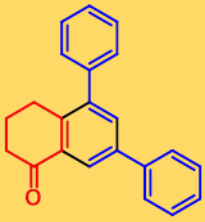
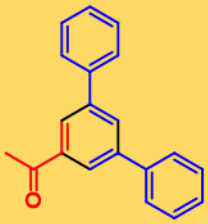
4. Green metrics

The following formulae were used for calculating Atom Economy (AE) and E factor, according to literature.[1]

$$Atom\ Economy\ (AE) = \frac{Molecular\ weight\ of\ product}{\sum Molecular\ weight\ of\ reactants}\ x\ 100$$

$$E\ factor = \frac{Mass\ of\ waste}{Mass\ of\ product}$$

Table S1. Green metrics for three representative products.

Green-metrics			
AE	99.3%	99.3%	99.3%
E-factor	187	171	196

5. Experiment to check water purity after the reaction

Following the **General Procedure for Benzannulation** employing phenylacetylene, methyl vinyl ketone and D_2O as reaction solvent we could check how clean from organic residues D_2O was. After the reaction time, usual workup using ethyl

[1] (a) R. A. Sheldon, *Green Chem.*, 2017, **19**, 18. (b) R. A. Sheldon, *ACS Sustain. Chem. Eng.*, 2018, **6**, 32.

acetate was performed. The organic phase was evaporated and redissolved in $CDCl_3$ for ^1H NMR analysis (Figure S2).

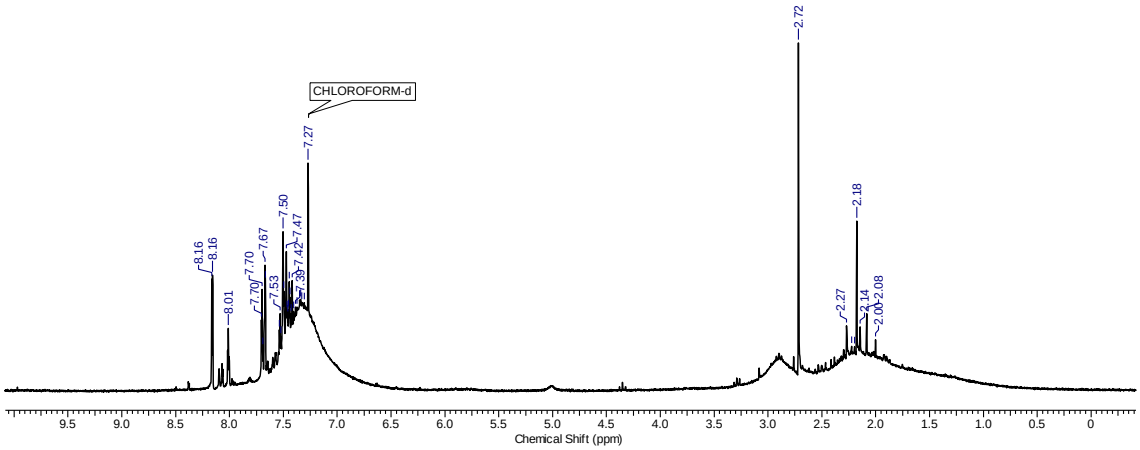


Figure S2. ^1H NMR spectrum of the crude mixture. Peaks relative to product **3i** can be seen.

The D_2O phase was then checked by ^1H NMR (Figure S3).

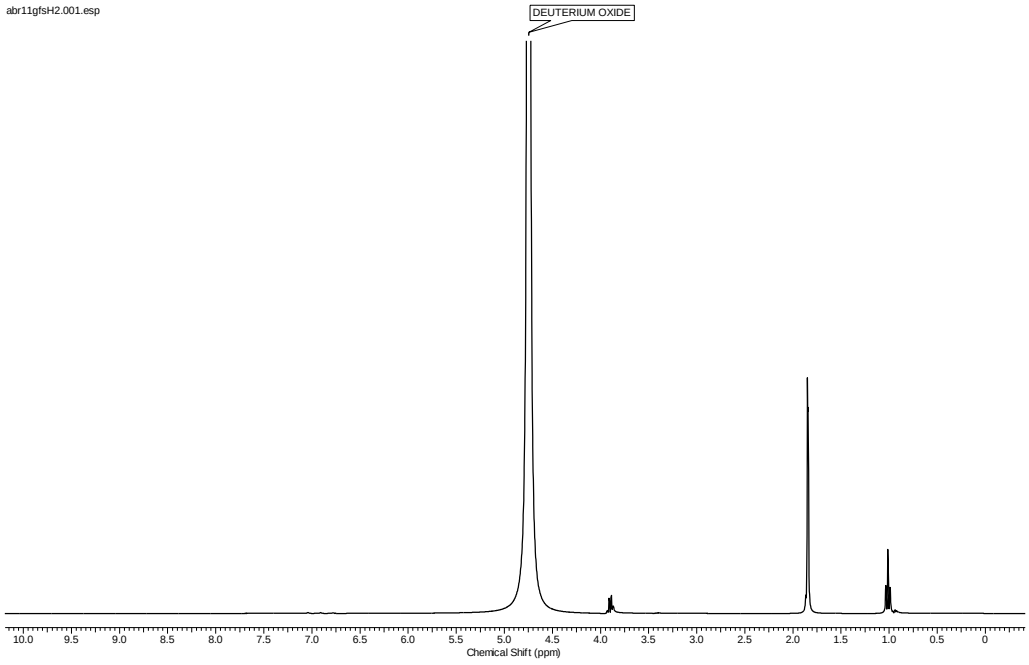


Figure S3. ^1H NMR spectrum of D_2O employed as a reaction solvent after the extraction using ethyl acetate.

As pointed in the main text, residual peaks of ethyl acetate can be seen but no other organic residue is observable.

6. Radical trapping experiment

The optimized reaction was carried out following the sequence: 1.0 mL of water, TEMPO (1.0 mmol, 2 equiv.), phenylacetylene (1.0 mmol, 2 equiv.), methyl vinyl ketone (0.50 mmol, 1 equiv.) and $(NH_4)_2S_2O_8$ (1.0 mmol). The resulting suspension was stirred at 85 ^oC for 4 h. The stirring speed of the reaction mixture was kept at 1150 rpm to ensure a proper diffusion of reaction components. The suspension was extracted with ethyl acetate (2 × 2 mL) and the combined organic layers were concentrated. The resulting crude mixture was taken for GC-MS analysis.

7. Intermediate determination

Phenylacetylene (1.0 mmol), methyl vinyl ketone (0.5 mmol), $(NH_4)_2S_2O_8$ (1.0 mmol) and 2 mL of water were employed following the **General Procedure for Benzannulation**. Aliquots of the reaction mixture were taken (5 min, 10 min and 30 min) and analyzed by GC-MS (Figure S4) and ^1H NMR (Figure S5).

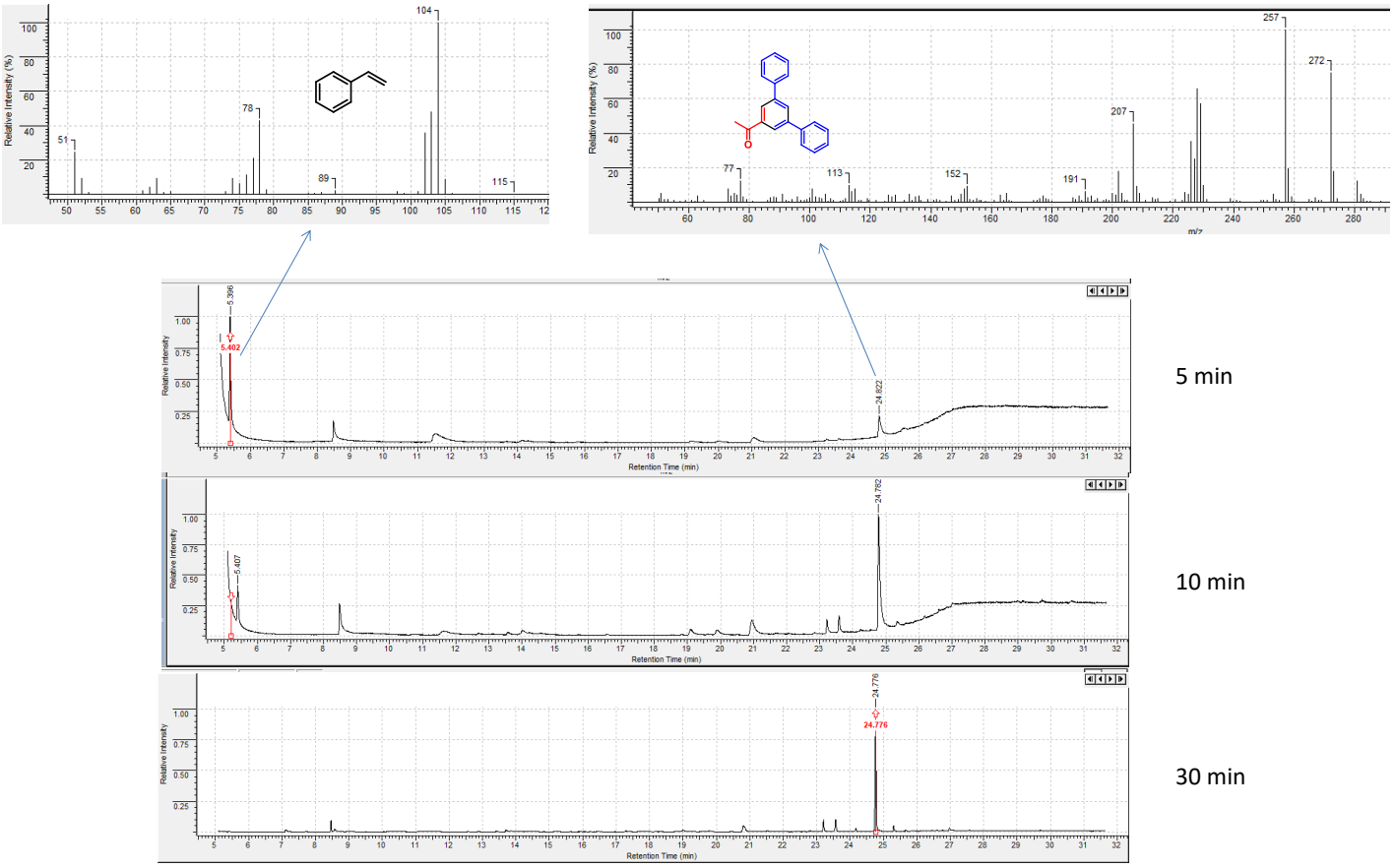
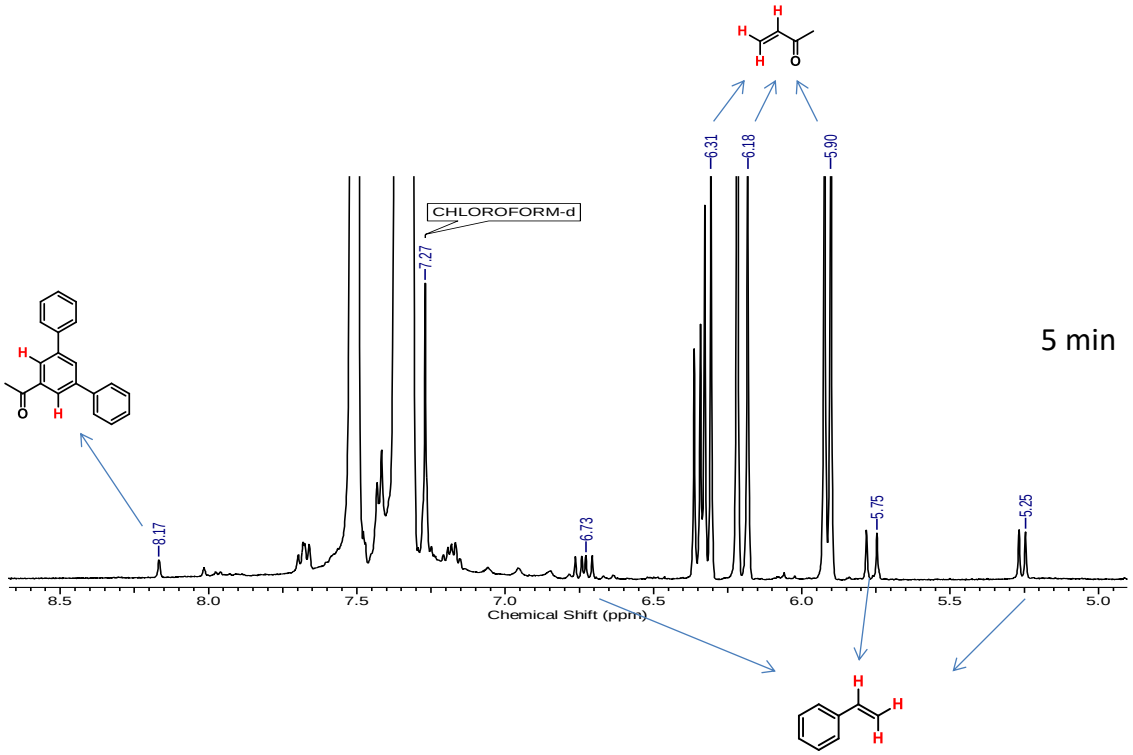
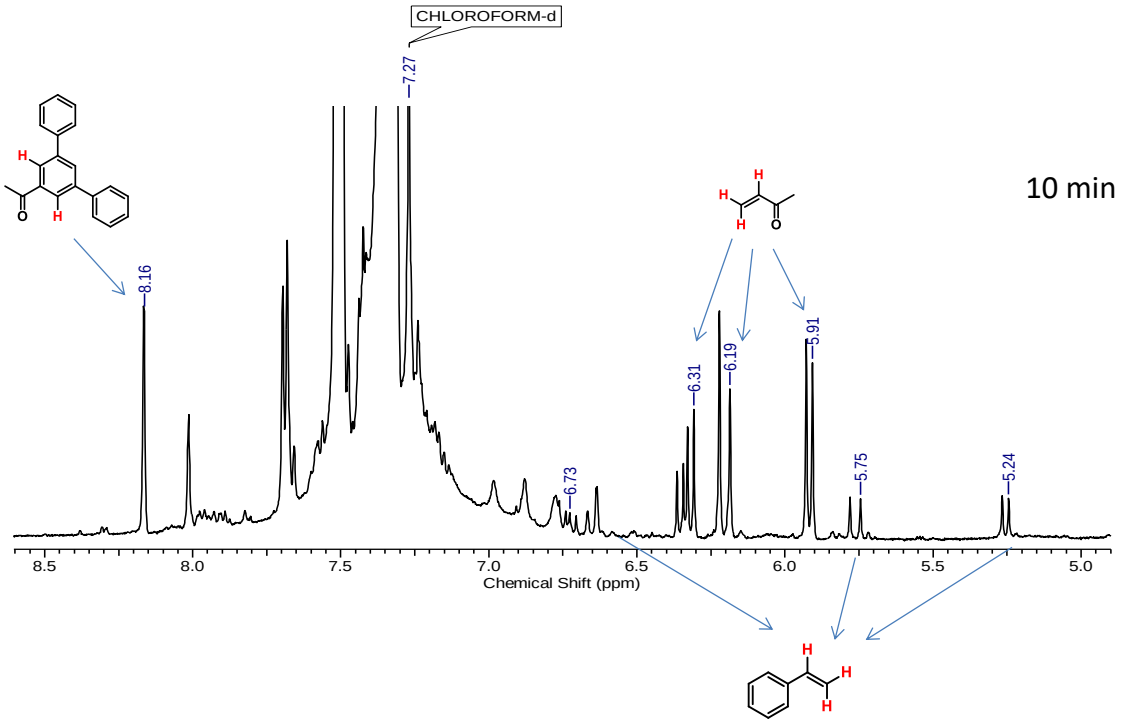


Figure S4. Qualitative kinetics for intermediate determination (GC-MS).


CHLOROFORM-d
7.27
6.31
6.18
5.90
8.17
6.73
5.75
5.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
Chemical Shift (ppm)
5 min


CHLOROFORM-d
7.27
8.16
6.31
6.19
5.91
6.73
5.75
5.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
Chemical Shift (ppm)
10 min

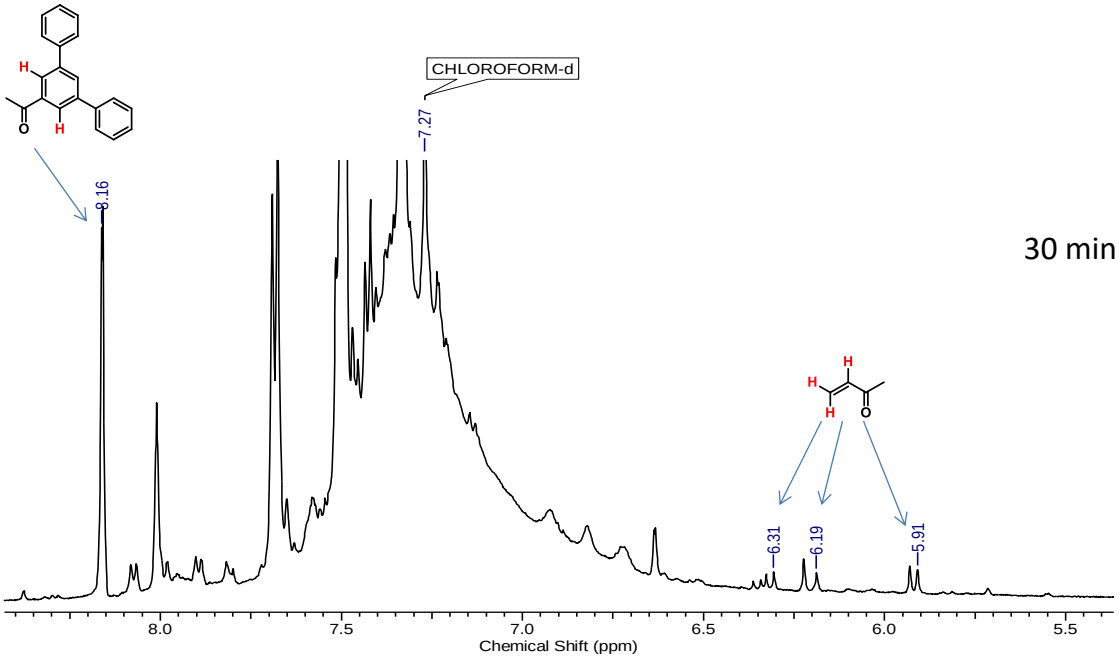


Figure S5. Qualitative kinetics for intermediate determination (^{1}H NMR).

One can observe a gradual disappearance of the peak relative to styrene over time with concomitant increase in the intensity of the peak relative to the product. It suggests that styrene is a potential intermediate in this transformation.

8. Three-component reaction

1-ethynyl-4-methylbenzene (0.5 mmol), methyl vinyl ketone (0.5 mmol), styrene (0.5 mmol), $(NH_4)_2S_2O_8$ (1.0 mmol) and 2 mL of water were employed following the **General Procedure for Benzannulation**. An aliquot of the reaction mixture was taken after 2 h and analyzed by GC-MS (Figure S6).

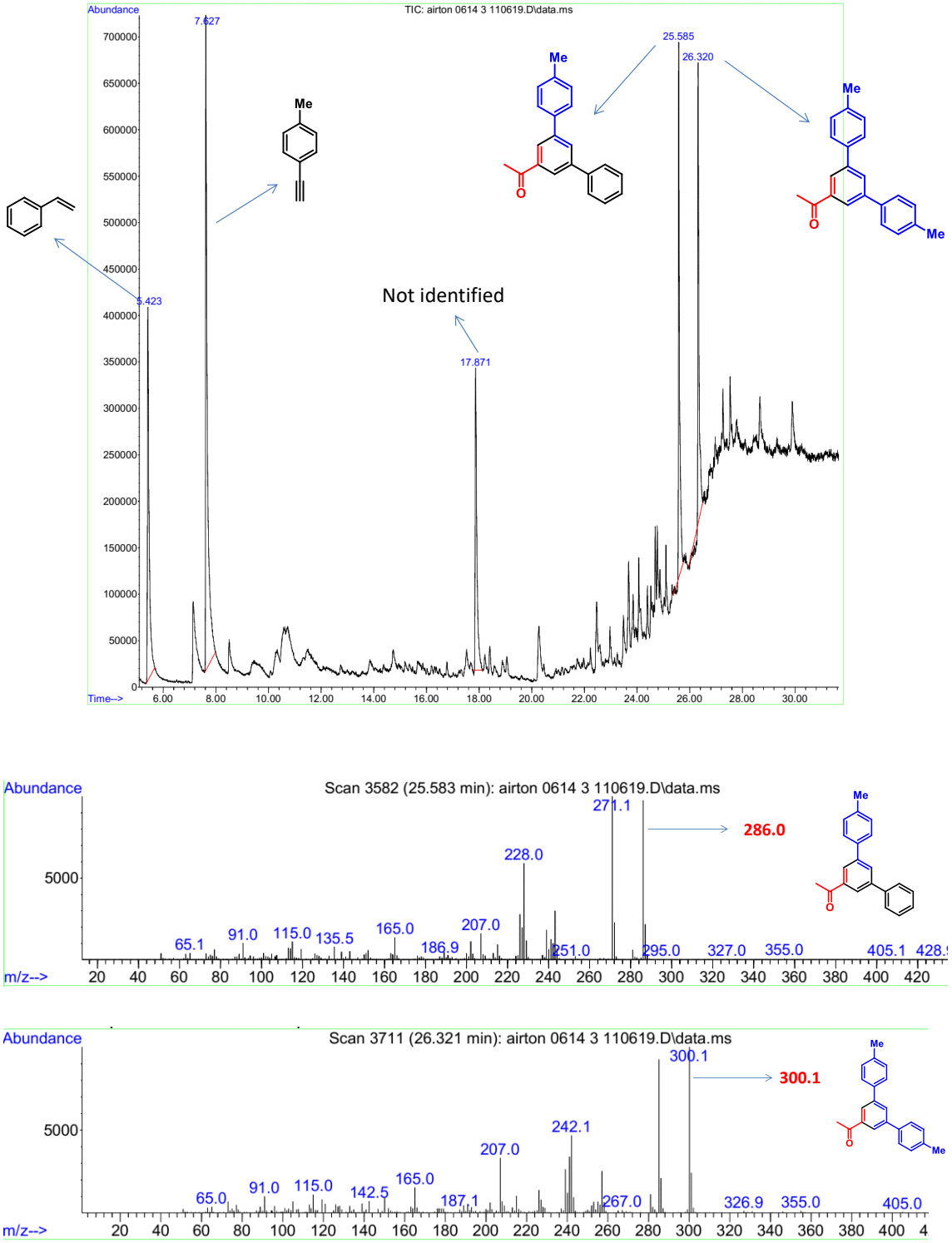


Figure S6. GC-MS analysis of the three-component reaction.

This experiment was designed to furnish a product with different substituents on the phenyl rings. In this way, we could be confident that one phenyl ring comes from the styrene and the other comes from the 1-ethynyl-4-methylbenzene. The outcome observed here strongly indicates the participation of styrene in the reaction mechanism.

9. Only phenylacetylene under the reaction conditions

Phenylacetylene (1.0 mmol), $(NH_4)_2S_2O_8$ (1.0 mmol) and 2 mL of water were employed following the **General Procedure for Benzannulation**. After 5 min, the suspension was extracted with ethyl acetate (2 × 2 mL), the combined organic layers were concentrated and analyzed by ^{1}H NMR and GC-MS (Figure S7).

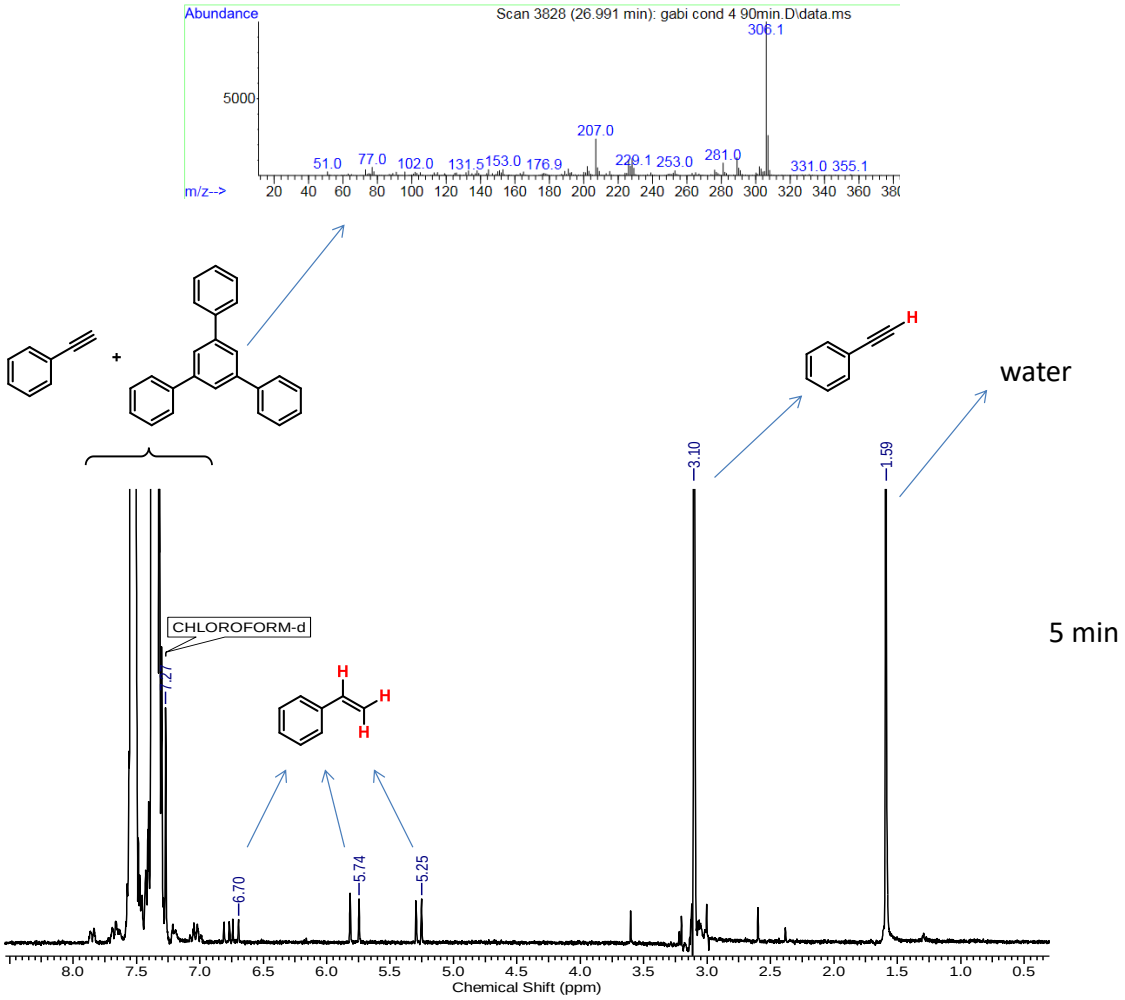
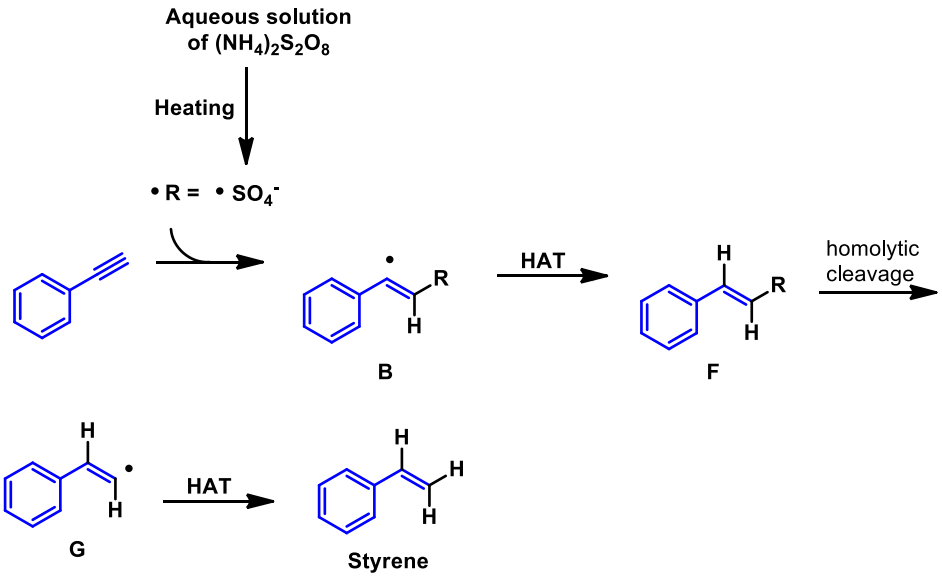


Figure S7. ^{1}H NMR spectrum of the reaction after 5 min.

It is possible to observe in the ^{1}H NMR peaks relative to styrene after only 5 min. As the reaction progresses, 1,3,5-triarylbenzene is formed (detected by GC-MS at 26.991 min, m/z = 306.1) and styrene disappears. It shows that the generation of styrene from phenylacetylene is possible under our reaction conditions and the formation of triarylbenzene probably follows a mechanism similar to the one presented in Scheme 4 in the manuscript.

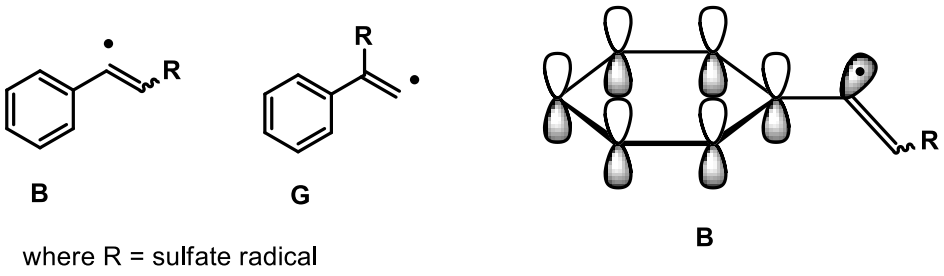
10. Mechanistic hypothesis to explain styrene generation from phenylacetylene



Under the reaction conditions, we hypothesize sulfate radical (generated from an aqueous solution of ammonium persulfate) adds to phenylacetylene furnishing radical **B**. Hydrogen atom transfer to **B** gives intermediate **F** which cleaves to form radical **G**. Another hydrogen atom transfer leads to styrene.

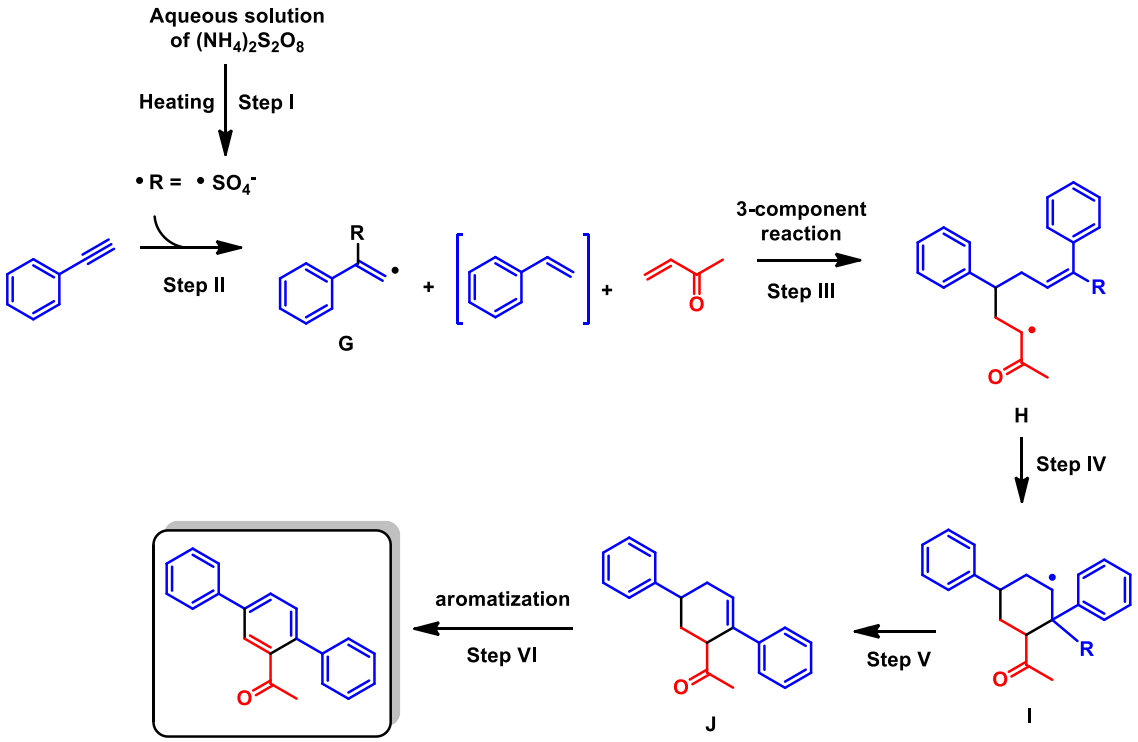
11. Proposed rationalization to explain the observed regioselectivy in the transformation

Our hypothesis relies upon the stability of the radical **B** over the radical **G**. We believe radical **B,** which gives the observed regioisomer, might be stabilized by delocalization to the phenyl ring π–orbitals despite the disruption of the conjugation between the double bond and the phenyl ring whereas radical **G** doesn't benefit from such interaction (see H. Yan, G. Rong, D. Liu, Y. Zheng, J. Chen and J. Mao, *Org. Lett.*, 2014, **16**, 6306–6309 as an evidence of this interaction):



where R = sulfate radical

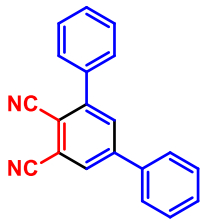
Employing radical **G** would lead to another regioisomer not observed in our approach:



Radical **B** would follow the mechanism presented in the Scheme 4 of the manuscript.

12. Characterization of the products

[1,1':3',1''-terphenyl]-4',5'-dicarbonitrile (3a)



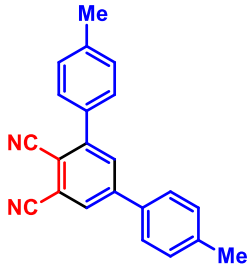
Prepared from phenylacetylene and fumaronitrile following the general procedure to give the product as colourless oil (90% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.00 (d, 1H, *J* = 1.47 Hz), 7.95 (d, 1H, *J* = 1.47 Hz), 7.65–7.60 (m, 4H),7.57–7.52 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 112.61, 115.36, 115.80, 117.81, 127.26, 128.69, 129.10, 129.49, 129.74, 129.80, 130.51, 132.48, 136.59, 137.01, 146.23, 147.75.

HRMS m/z (ESI): calcd. for $C_{20}H_{13}N_2$ $[M+H]^+$ 281.1079, found 281.1078.

4,4''-dimethyl-[1,1':3',1''-terphenyl]-4',5'-dicarbonitrile (3b)



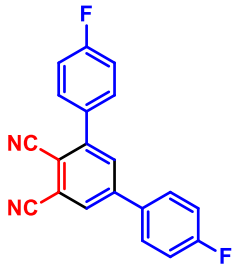
Prepared from 1-ethynyl-4-methylbenzene and fumaronitrile following the general procedure to give the product as a colourless oil (82% yield).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.95 (s, 1H), 7.98 (s, 1H), 7.53–7.49 (dd, *J* = 11.95, 8.17 Hz, 4H), 7.35 (t, *J* = 9.43 Hz, 4H), 2.46 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (100MHz, Chloroform-*d*): δ 21.25, 21.32, 112.08, 115.61, 115.94, 117.68, 127.08, 128.56, 129.78, 130.19, 132.06, 133.82, 134.17, 139.90, 140.09, 146.05, 147.75.

HRMS m/z (ESI): calcd. for $C_{20}H_{13}N_2$ $[M+H]^+$ 309.1392, found 309.1398.

4,4''-difluoro-[1,1':3',1''-terphenyl]-4',5'-dicarbonitrile (3c)



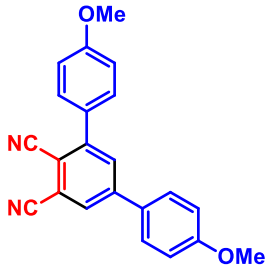
Prepared from 1-ethynyl-4-fluorobenzene and fumaronitrile following the general procedure to give the product as a pale yellow oil (85% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.96 (d, *J* = 1.96 Hz, 1H), 7.87 (d, *J* = 1.96 Hz, 1H), 7.63–7.58 (m, 4H), 7.28–7.22 (m, 4H).

^{13}C NMR (125MHz, Chloroform-*d*): δ 115.57, 116.24, 116.46, 116.60, 116.81, 117.99, 129.13, 129.21, 130.41, 130.63, 130.72, 132.16, 133.08, 145.30, 146.78, 162.60.

HRMS m/z (ESI): calcd. for $C_{20}H_{11}F_2N_2$ $[M+H]^+$ 317.0890, found 317.0901.

4,4''-dimethoxy-[1,1':3',1''-terphenyl]-4',5'-dicarbonitrile (3d)



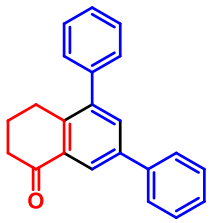
Prepared from 1-ethynyl-4-methoxybenzene and fumaronitrile following the general procedure using 4.0 equiv of $(NH_4)_2S_2O_8$ and 24 h reaction time to give the product as a pale yellow oil (65% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.91 (d, *J* = 1.89 Hz, 1H), 7.87 (d, *J* = 1.89 Hz, 1H), 7.57 (dd, *J* = 11.32, 8.80 Hz, 4H), 7.05 (dd, *J* = 10.69, 8.80 Hz, 4H), 3.90 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (125MHz, Chloroform-*d*): δ 55.48, 114.52, 114.92, 115.80, 116.01, 128.50, 129.01, 129.46, 130.05, 131.53, 147.39, 160.78.

HRMS m/z (ESI): calcd. for $C_{22}H_{17}N_2O_2$ $[M+H]^+$ 341.1290, found 341.1273.

6,8-diphenyl-3,4-dihydronaphthalen-1(2H)-one (3e)



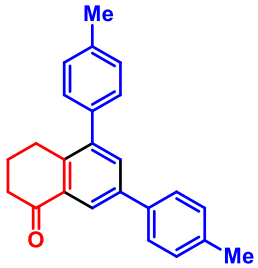
Prepared from phenylacetylene and cyclohexenone following the general procedure to give the product as a pale yellow oil (92% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.37 (d, *J* = 2.26 Hz, 1H), 7.72 (d, *J* = 2.26 Hz, 1H), 7.67 (dd, *J* = 8.28, 1.51 Hz, 2H), 7.49–7.37 (m, 8H), 2.89 (t, *J* = 6.02 Hz, 2H), 2.72 (ap t, *J* = 6.02 Hz, 2H), 2.09 (quint, *J* = 6.02 Hz, 2H).

^{13}C NMR (125MHz, Chloroform-*d*): δ 23.19, 28.01, 39.02, 124.86, 127.00, 127.46, 127.64, 128.35, 128.85, 129.19, 133.17, 133.41, 139.13, 139.78, 140.81, 142.51, 198.60.

HRMS m/z (ESI): calcd. for $C_{22}H_{19}O$ $[M+H]^+$ 299.1436, found 299.1420.

1-(4,4''-dimethyl-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3f)



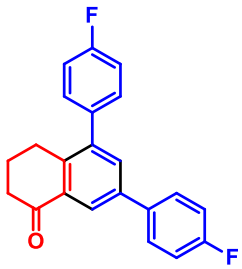
Prepared from 1-ethynyl-4-methylbenzene and cyclohexenone following the general procedure to give the product as a pale yellow oil (80% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.33(d, *J* = 1.96 Hz, 1H), 7.69 (d, *J* = 1.96 Hz, 1H), 7.55 (d, *J* = 8.31, 2H), 7.24–7.27 (m, 6H), 2.88 (t, *J* = 5.87 Hz, 2H), 2.70 (ap t, *J* = 6.85 Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H), 2.07 (quint, *J* = 6.36 Hz, 2H).

^{13}C NMR (125MHz, Chloroform-*d*): δ 21.08, 21.18, 23.21, 28.04, 39.03, 124.43, 126.81, 128.43, 129.01, 129.08, 129.55, 133.05, 133.35, 136.93, 137.17, 137.45, 137.66, 139.01, 140.60, 142.41, 198.72.

HRMS m/z (ESI): calcd. for $C_{24}H_{23}O$ $[M+H]^+$ 327.1749, found 327.1750.

6,8-bis(4-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one (3g)



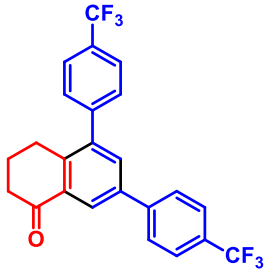
Prepared from 1-ethynyl-4-fluorobenzene and cyclohexenone following the general procedure to give the product as a pale yellow oil (78% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.31(d, J = 2.45 Hz, 1H), 7.63–7.60 (m, 3H), 7.33 (dd, J = 8.80, 5.38, 2H), 7.19–7.11 (m, 4H), 2.85 (t, J = 6.36 Hz, 2H), 2.72 (ap t, J = 6.85 Hz, 2H), 2.09 (quint, J = 6.36 Hz, 2H).

^{13}C NMR (125MHz, Chloroform-*d*): δ 23.12, 27.95, 38.92, 115.25, 115.46, 115.67, 115.89, 124.85, 128.56, 128.64, 130.73, 130.82, 132.95, 133.50, 135.77, 136.27, 136.31, 140.81, 141.59, 161.07, 161.47, 163.52, 163.92, 198.37.

HRMS m/z (ESI): calcd. for $C_{22}H_{17}F_2O$ $[M+H]^+$ 335.1247, found 335.1235.

6,8-bis(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalen-1(2H)-one (3h)



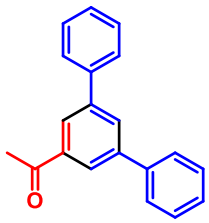
Prepared from 1-ethynyl-4-(trifluoromethyl)benzene and cyclohexenone following the general procedure to give the product as a pale yellow oil (82% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.41(d, J = 2.45 Hz, 1H), 7.78–7.69 (m, 7H), 7.50 (d, J = 8.31, 2H), 2.87 (t, J = 5.87 Hz, 2H), 2.75 (ap t, J = 6.85 Hz, 2H), 2.11 (quint, J = 6.36 Hz, 2H).

^{13}C NMR (125MHz, Chloroform-*d*): δ 23.04, 29.69, 38.86, 125.45, 125.50, 125.74, 125.92, 127.30, 129.56, 132.79, 141.45, 197.93.

HRMS m/z (ESI): calcd. for $C_{24}H_{17}F_6O$ $[M+H]^+$ 435.1184, found 435.1180.

3-phenyloxiran-2-yl)(2-(trifluoromethyl)phenyl)methanone (3i)

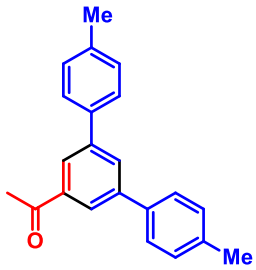


Prepared from phenylacetylene and methyl vinyl ketone following the general procedure to give the product as a white solid (m.p. = 100–102 ^{o}C, 88% yield). All data was consistent with that previously reported.[2]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.16 (d, 2H, *J* = 1.51 Hz), 8.01 (ap t, *J* = 1.51 Hz, 1H), 7.70–7.68 (m, 4H),7.51 (t, *J* = 7.53 Hz, 4H), 7.43 (t, *J* = 7.53 Hz, 2H), 2.72 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 26.89, 125.93, 127.30, 127.94, 128.96, 130.56, 138.18, 140.22, 142.33, 198.03.

1-(4,4''-dimethyl-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3j)



Prepared from 1-ethynyl-4-methylbenzene and methyl vinyl ketone following the general procedure to give the product as colourless oil (93% yield).

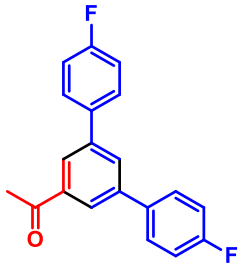
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.12 (d, *J* = 1.47 Hz, 2H), 7.98 (t, *J* = 1.47 Hz, 1H), 7.57 (d, *J* = 8.31, 4H), 7.30 (d, *J* = 7.83, 4H), 2.71 (s, 3H), 2.44 (s, 6H).

^{13}C NMR (125MHz, Chloroform-*d*): δ 21.14, 26.89, 125.47, 127.11, 129.67, 130.18, 137.39, 137.79, 138.14, 142.19, 198.17.

HRMS m/z (ESI): calcd. for $C_{22}H_{21}O$ $[M+H]^{+}$ 301.1592, found 301.1600.

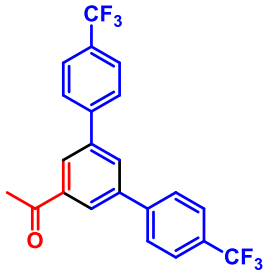
[2] J. D. Kehlbeck, E. J. Dimise, S. M. Sparks, S. Ferrara, J. M. Tanski and C. M. Anderson, *Synthesis (Stuttg).*, 2007, 1979–1983.

1-(4,4''-difluoro-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3k)



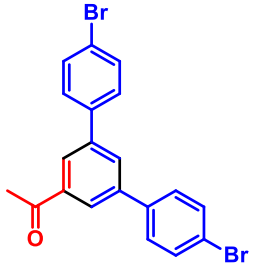
Prepared from 1-ethynyl-4-fluorobenzene and methyl vinyl ketone following the general procedure to give the product as a pale yellow oil (80% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.09 (d, J = 1.47 Hz, 2H), 7.89 (t, J = 1.96 Hz, 1H), 7.65–7.61 (m, 4H), 7.19 (t, J = 8.80, 4H), 2.71 (s, 3H).
^{13}C NMR (125MHz, Chloroform-*d*): δ 26.84, 115.80, 116.02, 125.71, 128.86, 128.95, 130.18, 136.18, 138.27, 141.43, 161.61, 164.08, 197.82.
HRMS m/z (ESI): calcd. for $C_{20}H_{15}F_2O$ $[M+H]^+$ 309.1091, found 309.1084.

1-(4,4''-bis(trifluoromethyl)-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3l)



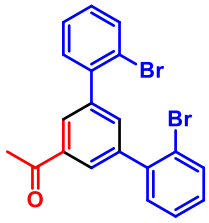
Prepared from 1-ethynyl-4-(trifluoromethyl)benzene and methyl vinyl ketone following the general procedure to give the product as pale yellow oil (87% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.21 (d, J = 1.26 Hz, 2H), 8.00 (t, J = 1.26 Hz, 1H), 7.80–7.76 (m, 8H), 2.74 (s, 3H).
^{13}C NMR (125MHz, Chloroform-*d*): δ 26.88, 123.19, 126.00 (q, ^{3}J = 3.73 Hz), 126.79, 127.66, 130.17, 130.38, 130.58, 138.54, 141.24, 143.39, 197.39.
HRMS m/z (ESI): calcd. for $C_{22}H_{15}F_6O$ $[M+H]^+$ 409.1027, found 409.1045.

1-(4,4''-dibromo-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3m)



Prepared from 1-bromo-4-ethynylbenzene and methyl vinyl ketone following the general procedure to give the product as pale yellow oil (95% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.12 (d, J = 1.89 Hz, 2H), 7.91 (t, J = 1.89 Hz, 1H), 7.62 (d, J = 8.80 Hz, 4H), 7.53 (d, J = 8.17, 4H), 2.71 (s, 3H).
^{13}C NMR (125MHz, Chloroform-*d*): δ 26.88, 122.46, 125.99, 128.87, 129.98, 132.16, 138.91, 141.36, 197.66.
HRMS m/z (ESI): calcd. for $C_{20}H_{15}Br_2O$ $[M+H]^+$ 428.9490, found 428.9472.

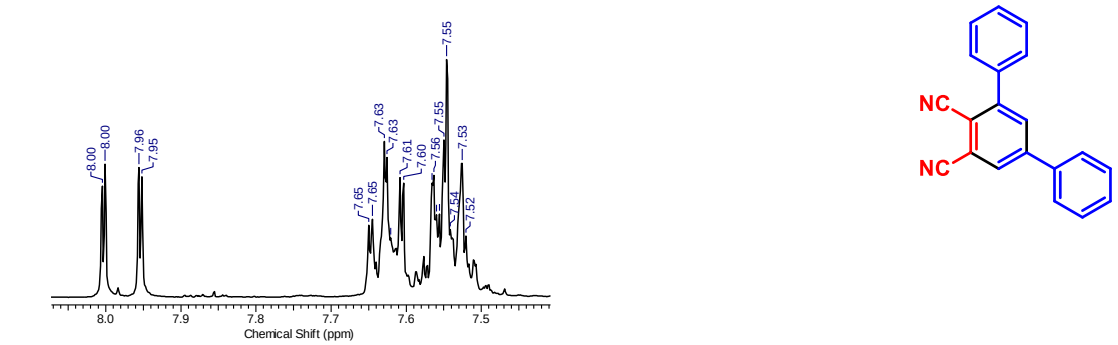
1-(2,2''-dibromo-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3n)

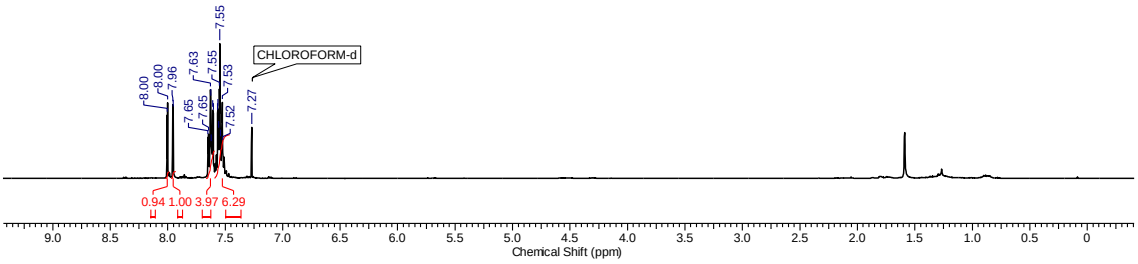


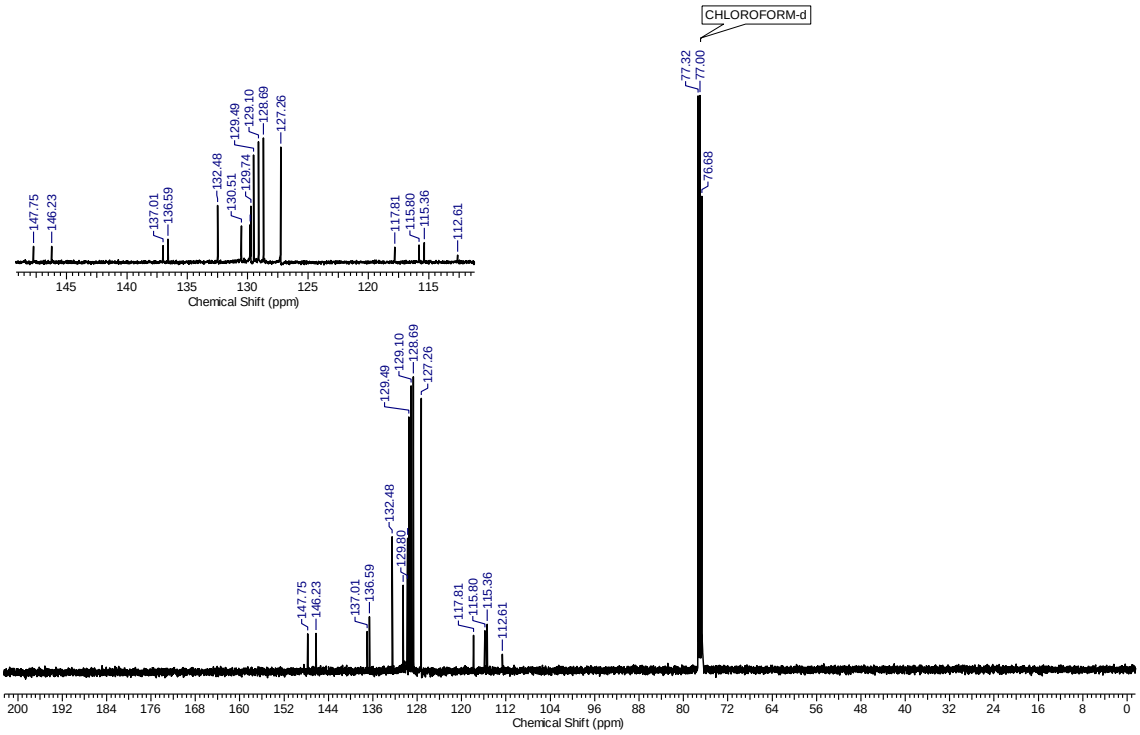
Prepared from 1-bromo-2-ethynylbenzene and methyl vinyl ketone following the general procedure to give the product as pale yellow oil (92% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.04 (d, J = 1.89 Hz, 2H), 7.72–7.70 (m, 3H), 7.43–7.39 (m, 4H), 7.28–7.24 (m, 2H), 2.68 (s, 3H).
^{13}C NMR (125MHz, Chloroform-*d*): δ 26.83, 122.54, 127.60, 128.51, 129.33, 131.28, 133.27, 135.06, 136.80, 141.21, 141.25, 197.63.
HRMS m/z (ESI): calcd. for $C_{20}H_{15}Br_2O$ $[M+H]^+$ 428.9490, found 428.9476.

13. ^{1}H NMR and ^{13}C NMR spectral data

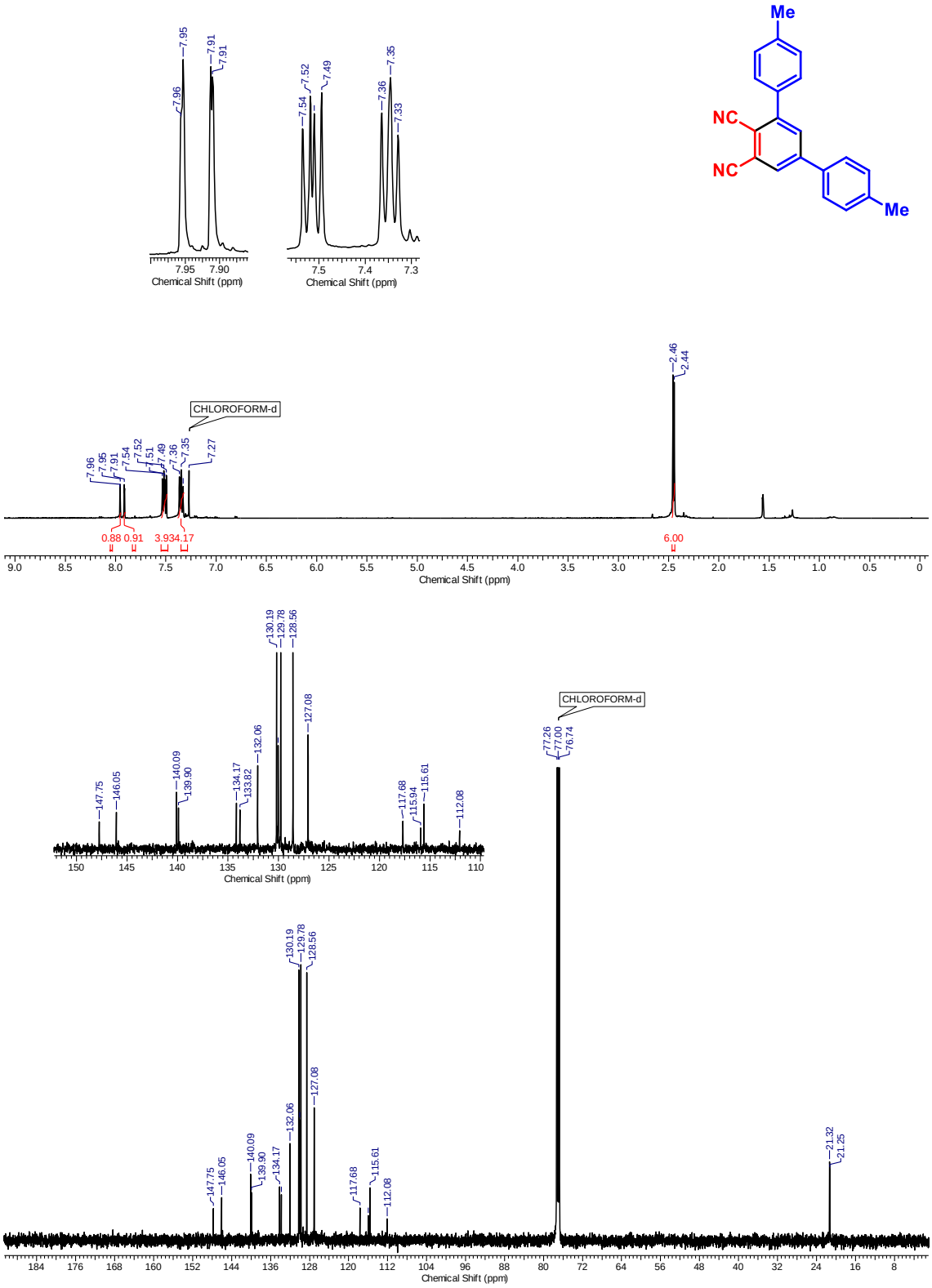
[1,1':3',1''-terphenyl]-4',5'-dicarbonitrile (3a)



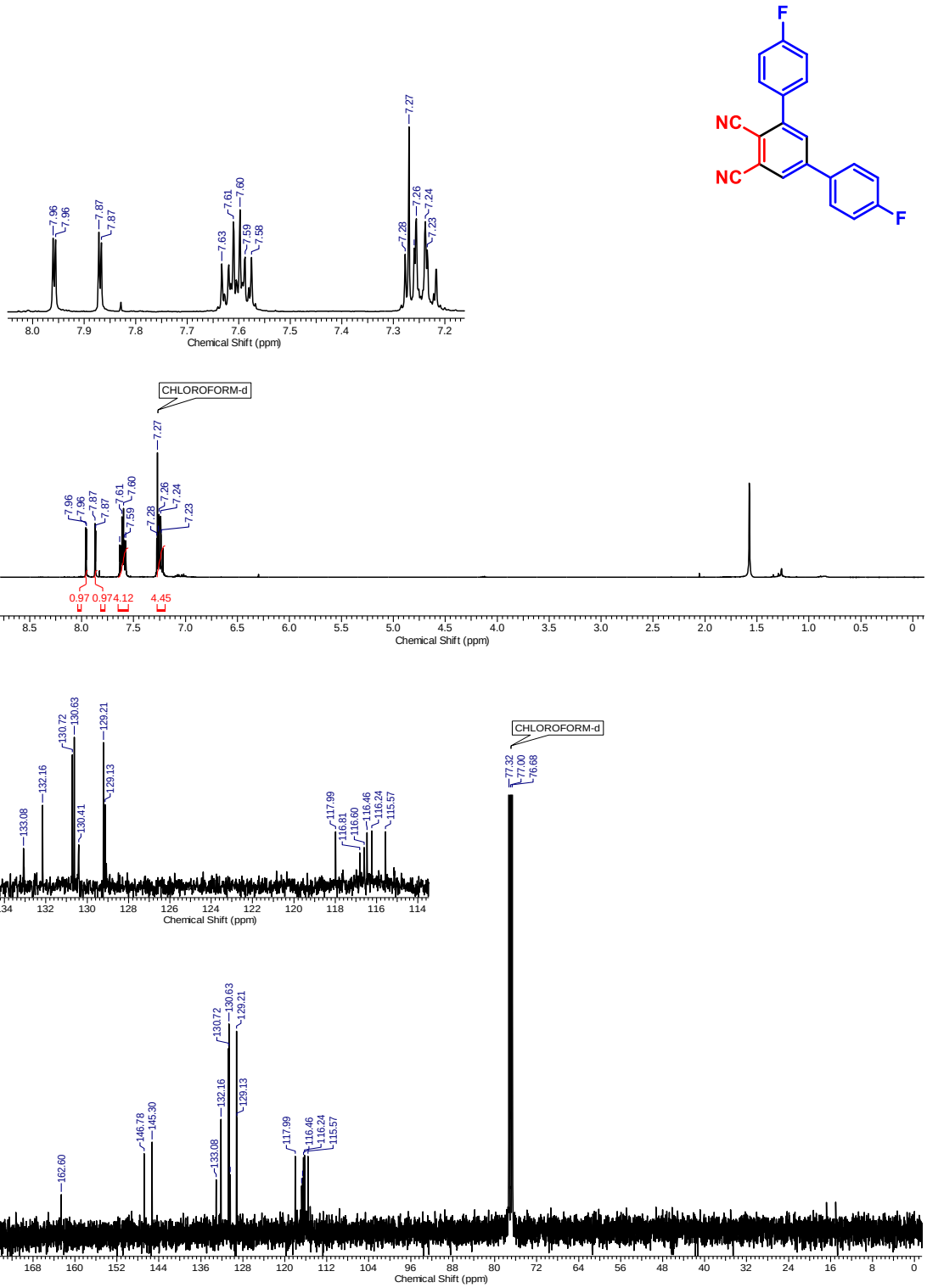




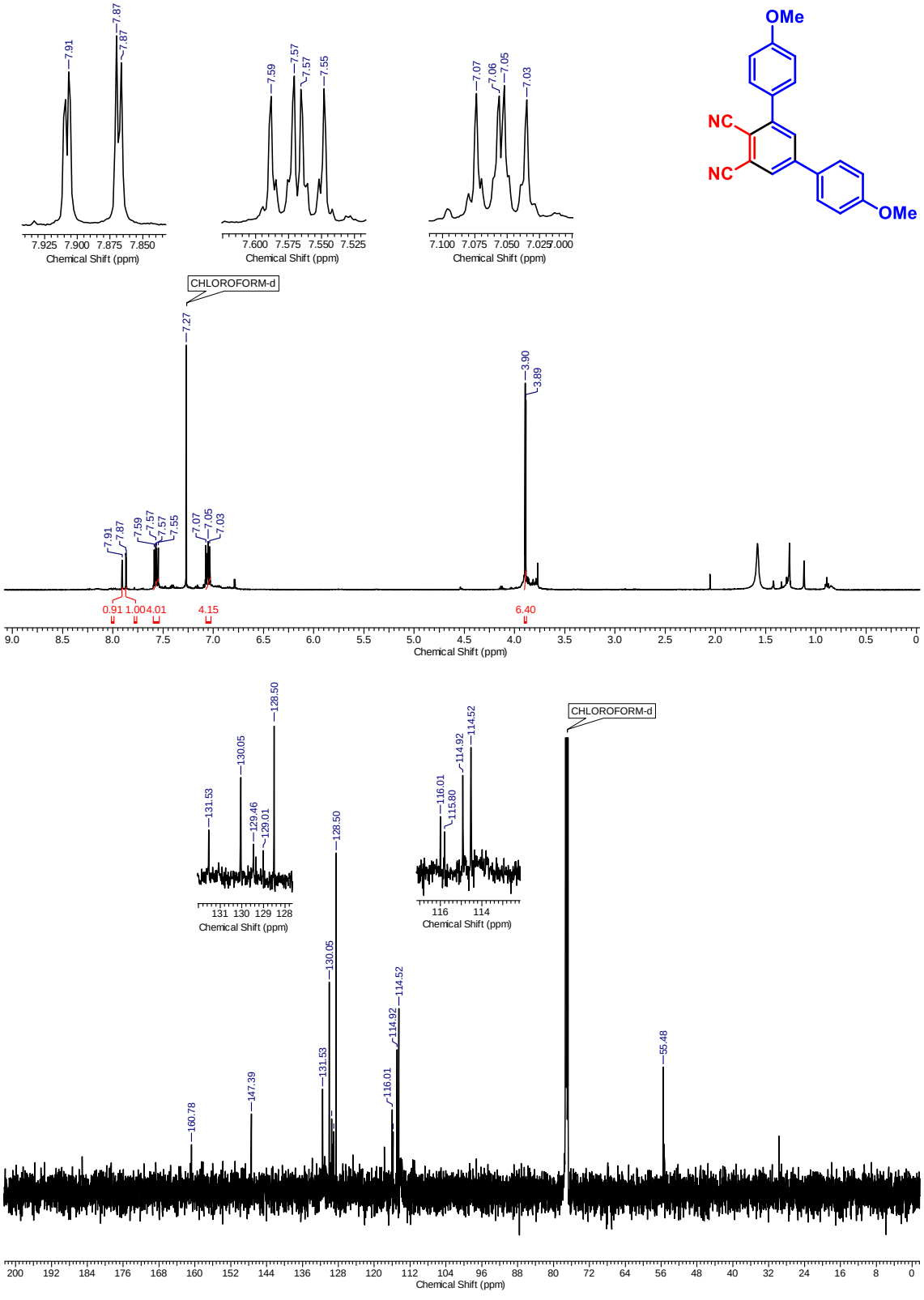
4,4''-dimethyl-[1,1':3',1''-terphenyl]-4',5'-dicarbonitrile (3b)



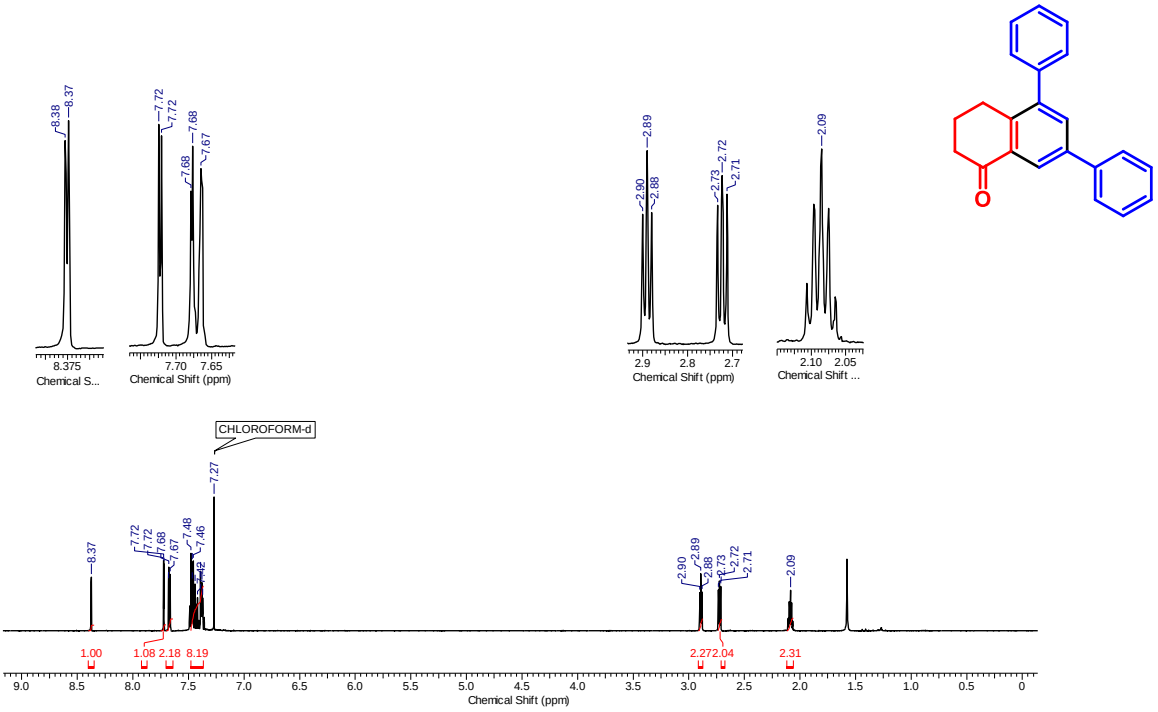
4,4''-difluoro-[1,1':3',1''-terphenyl]-4',5'-dicarbonitrile (3c)

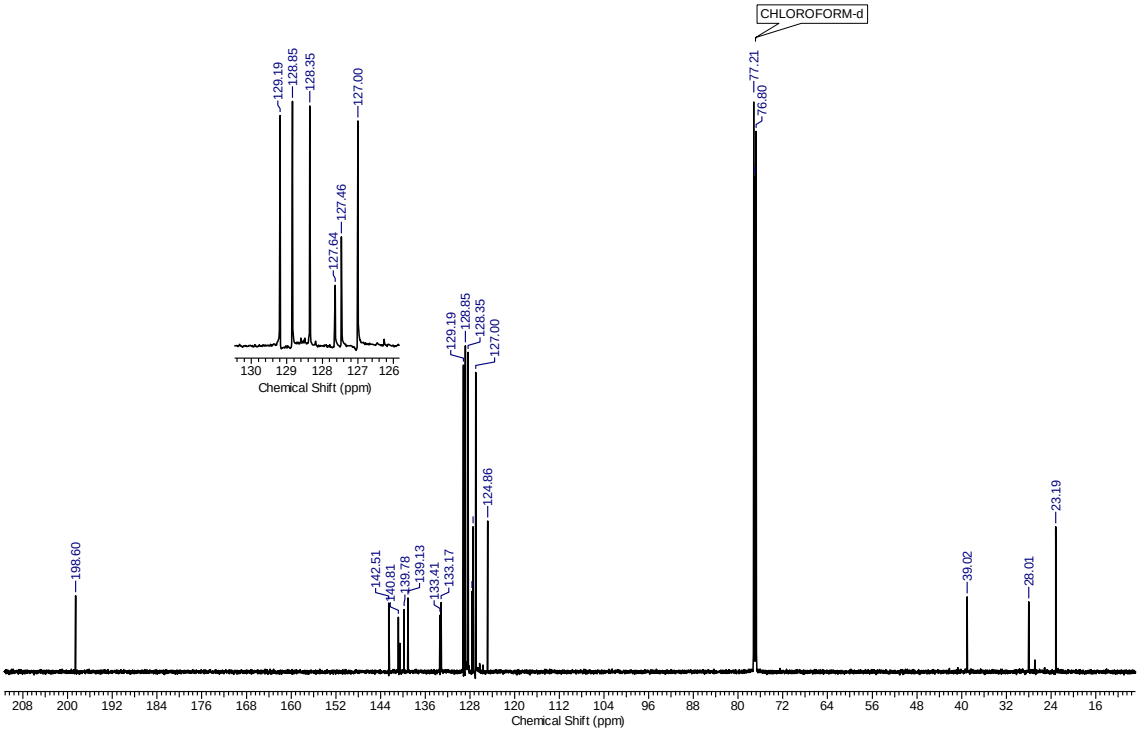


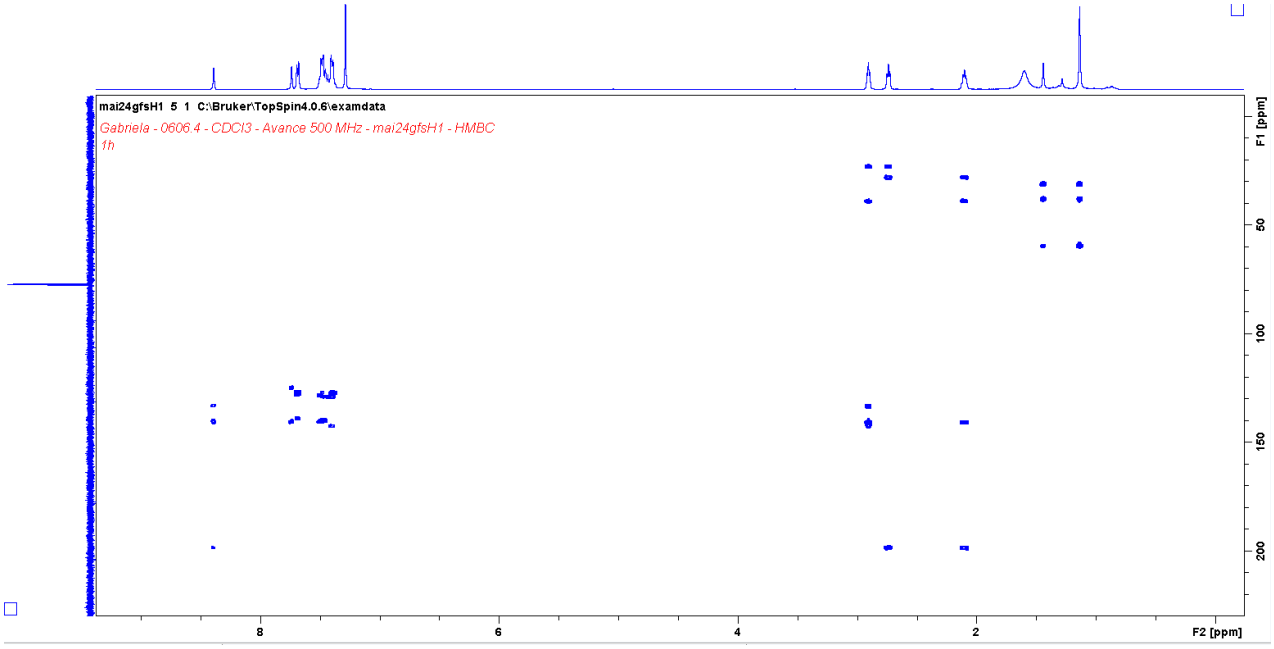
4,4''-dimethoxy-[1,1':3',1''-terphenyl]-4',5'-dicarbonitrile (3d)



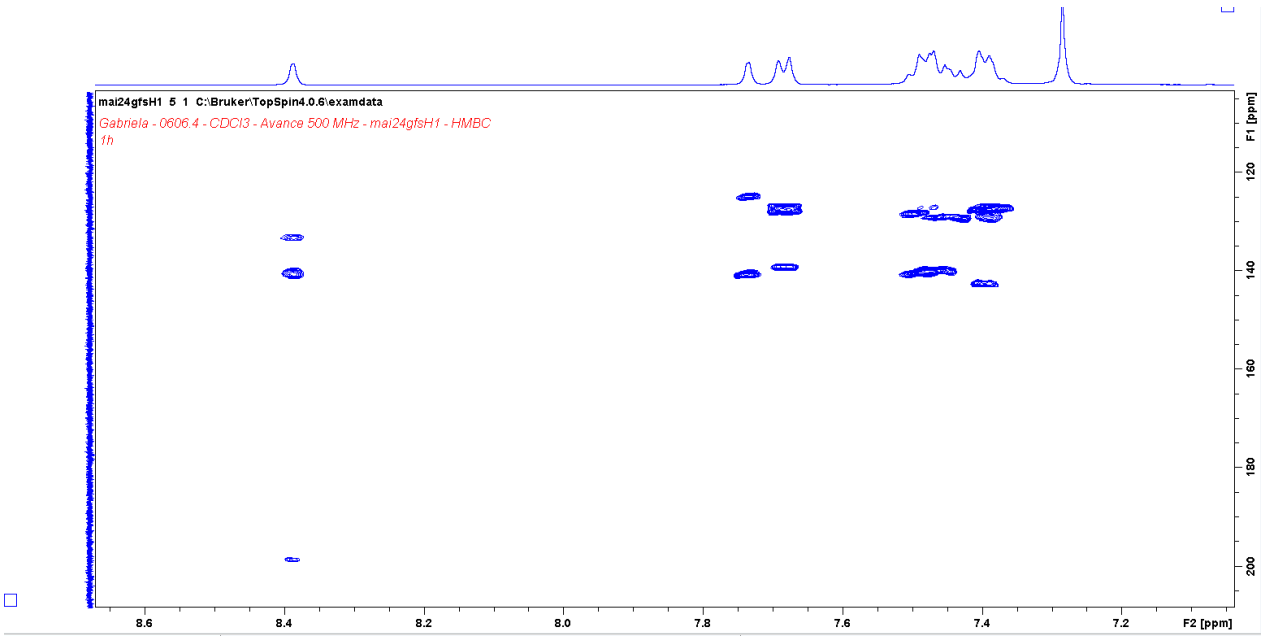
]6,8-diphenyl-3,4-dihydronaphthalen-1(2H)-one (3e)



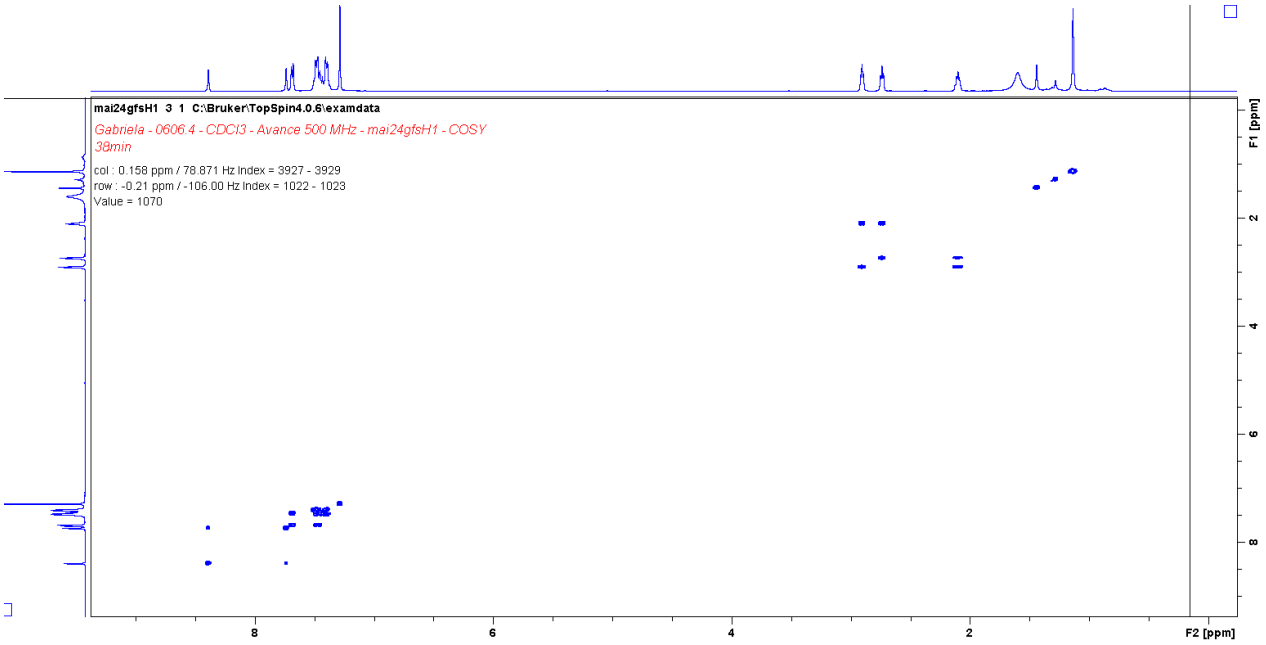




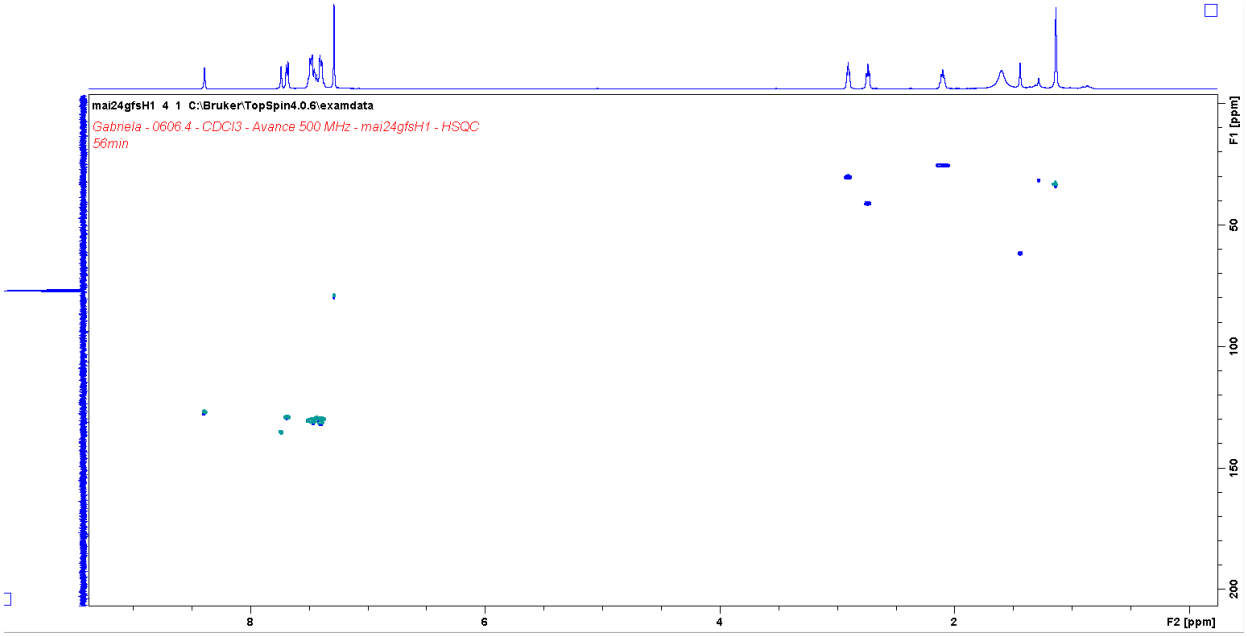
HMBC spectrum of 3e



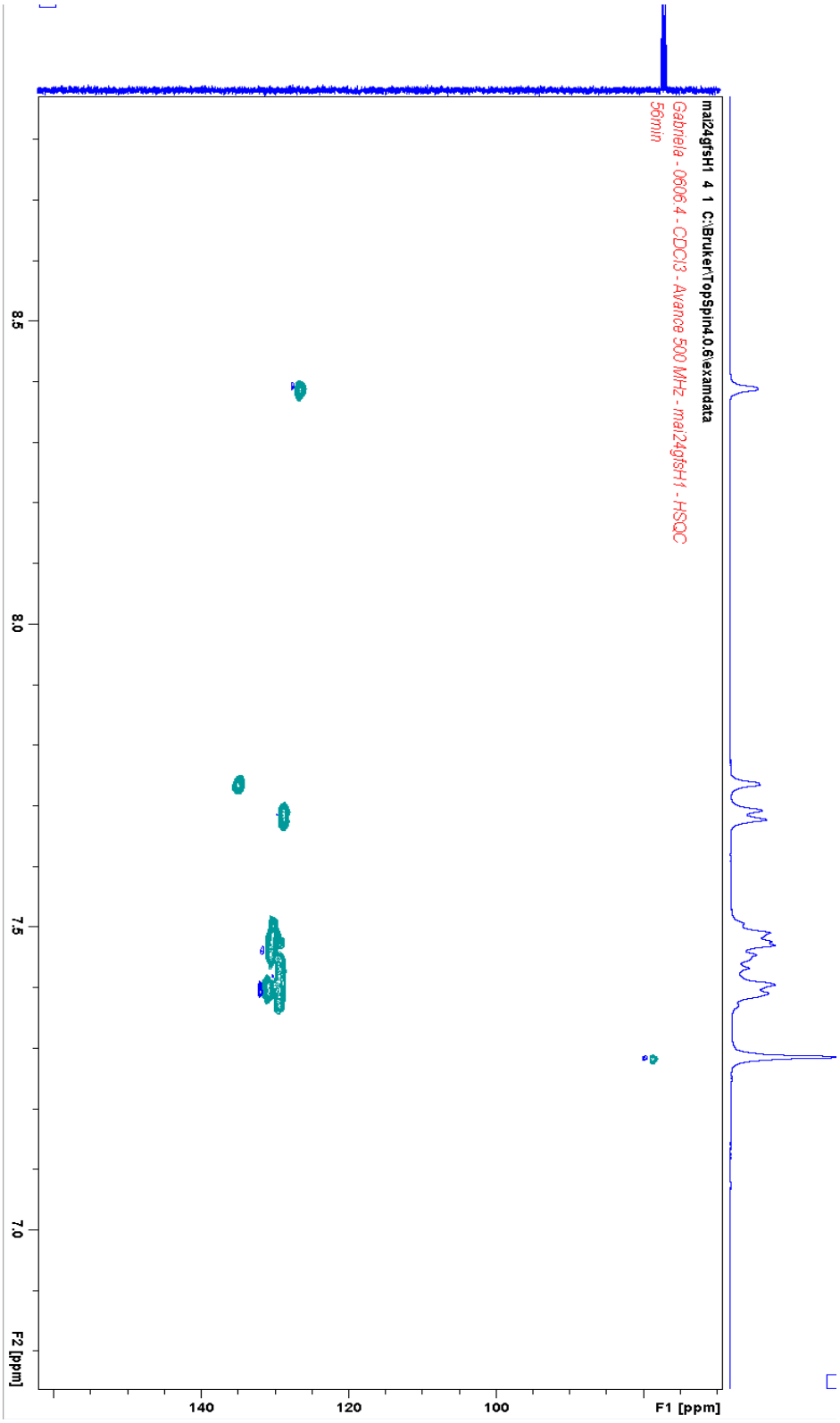
HMBC spectrum of 3e



Cosy spectrum of 3e

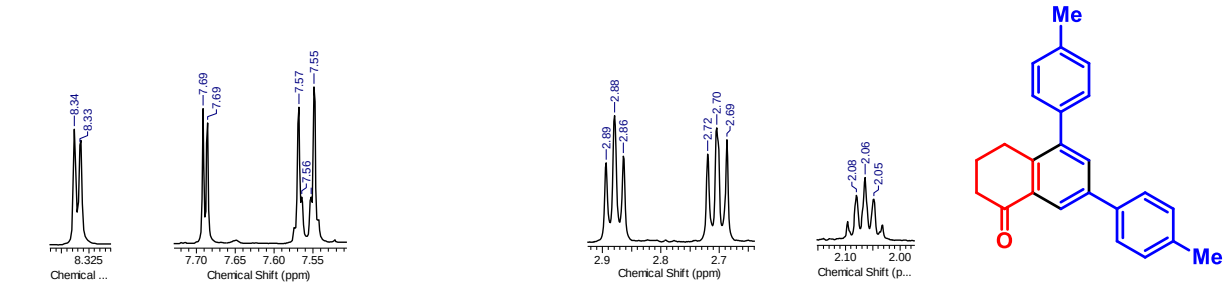


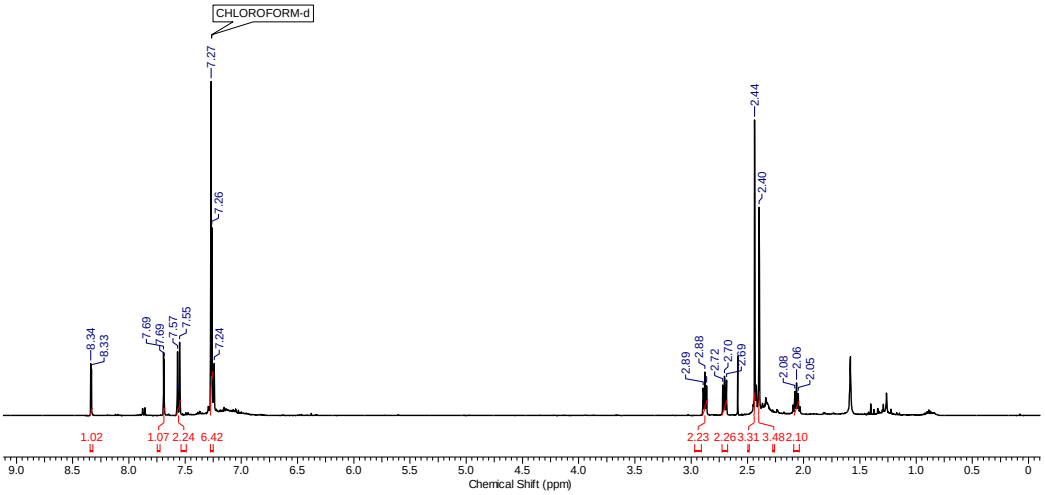
HSQC spectrum of 3e

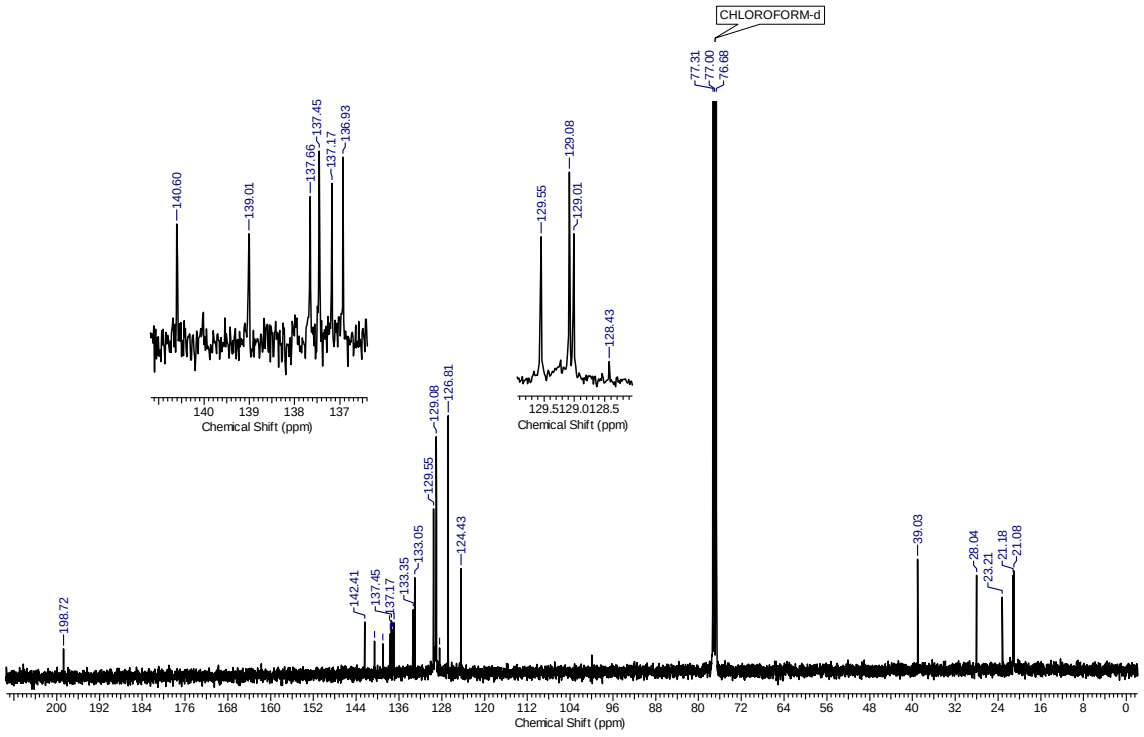


HSQC spectrum of 3e

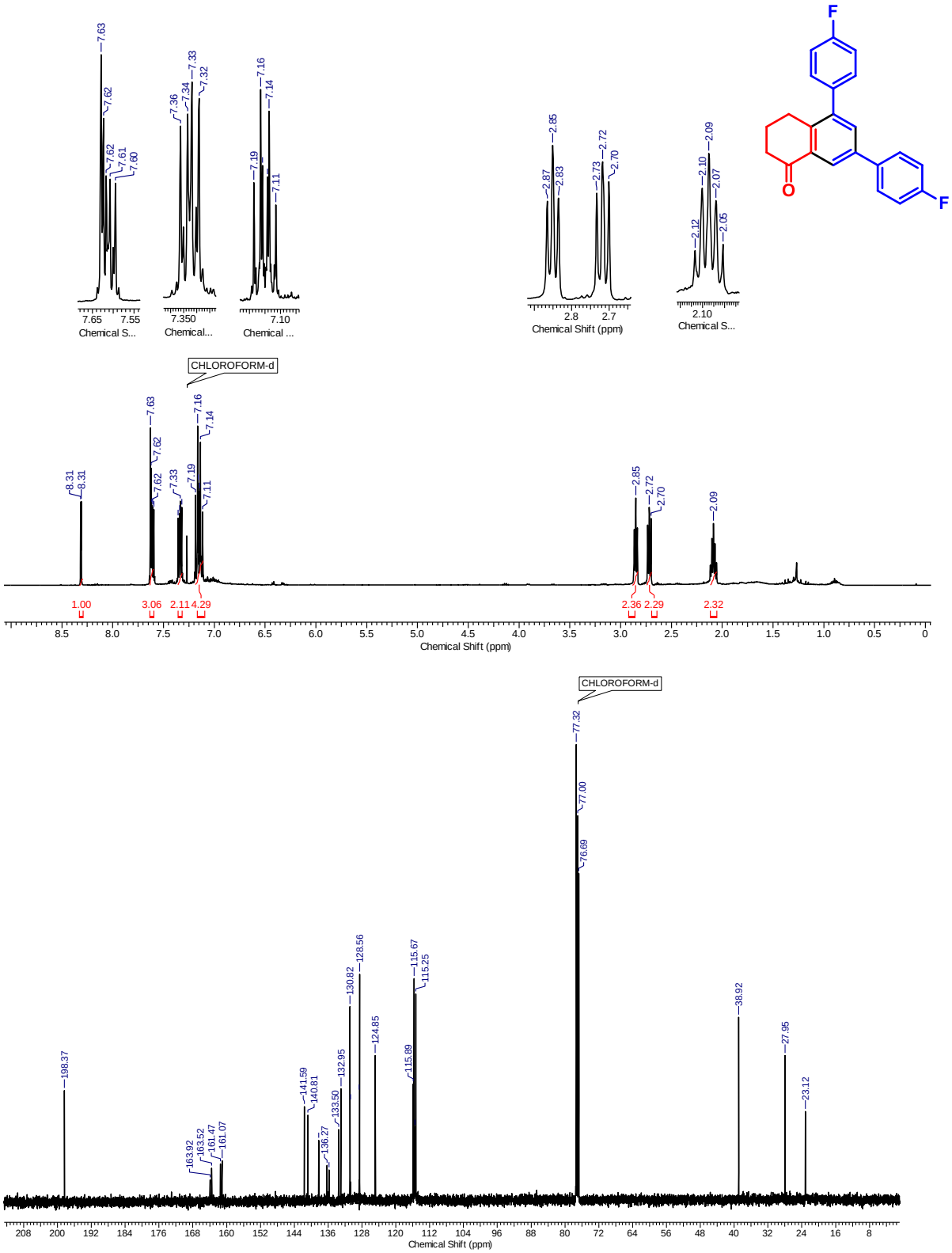
1-(4,4''-dimethyl-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3f)



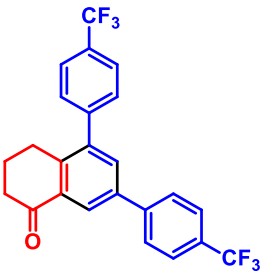


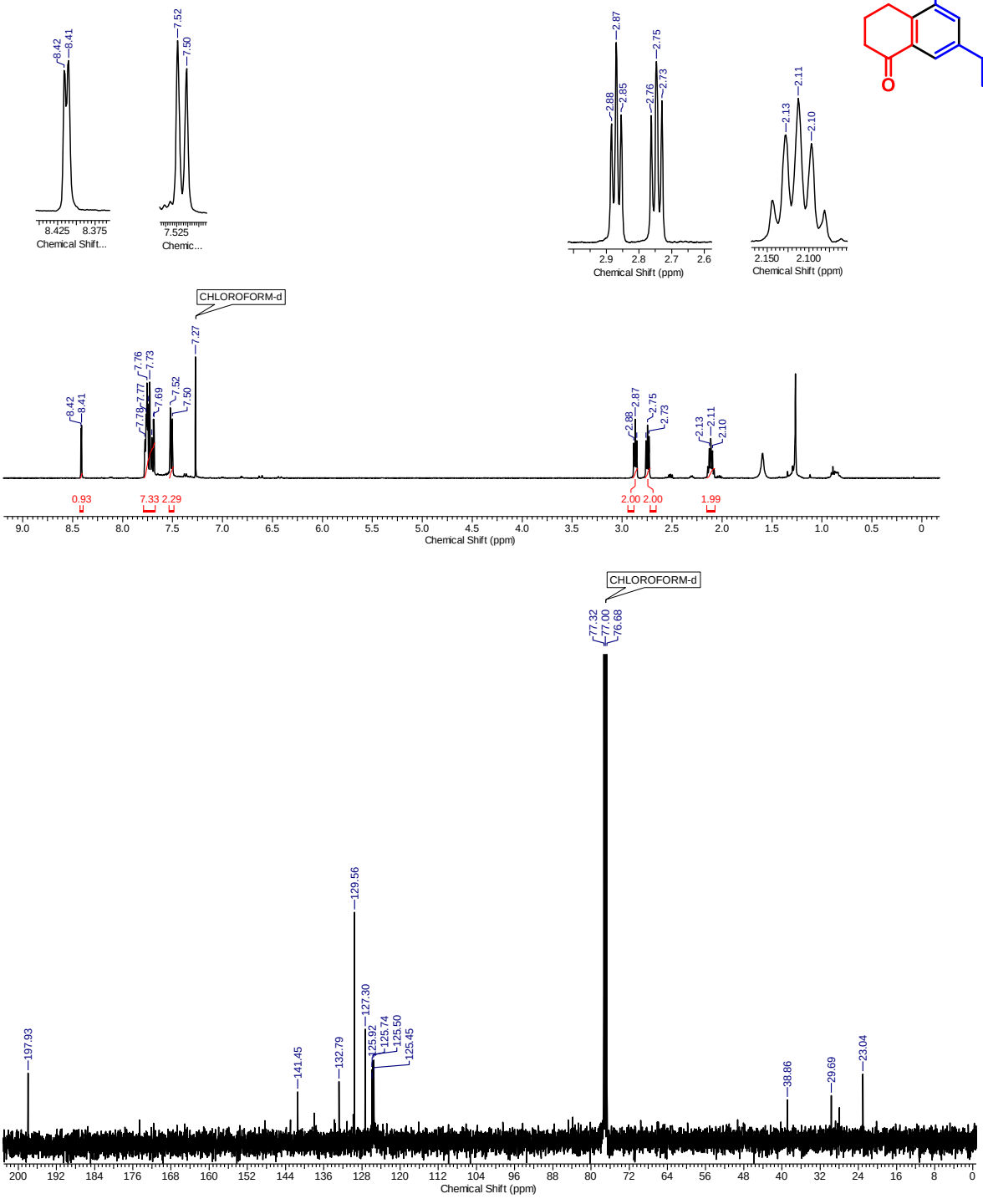


6,8-bis(4-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one (3g)

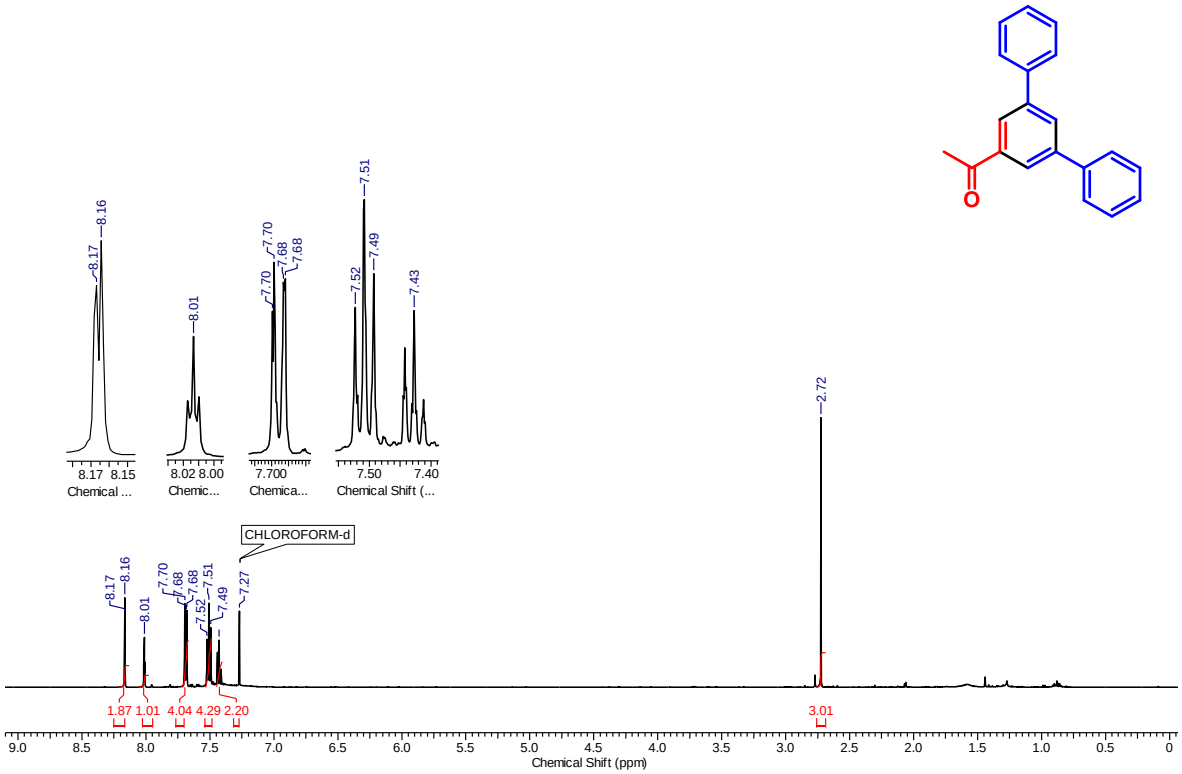


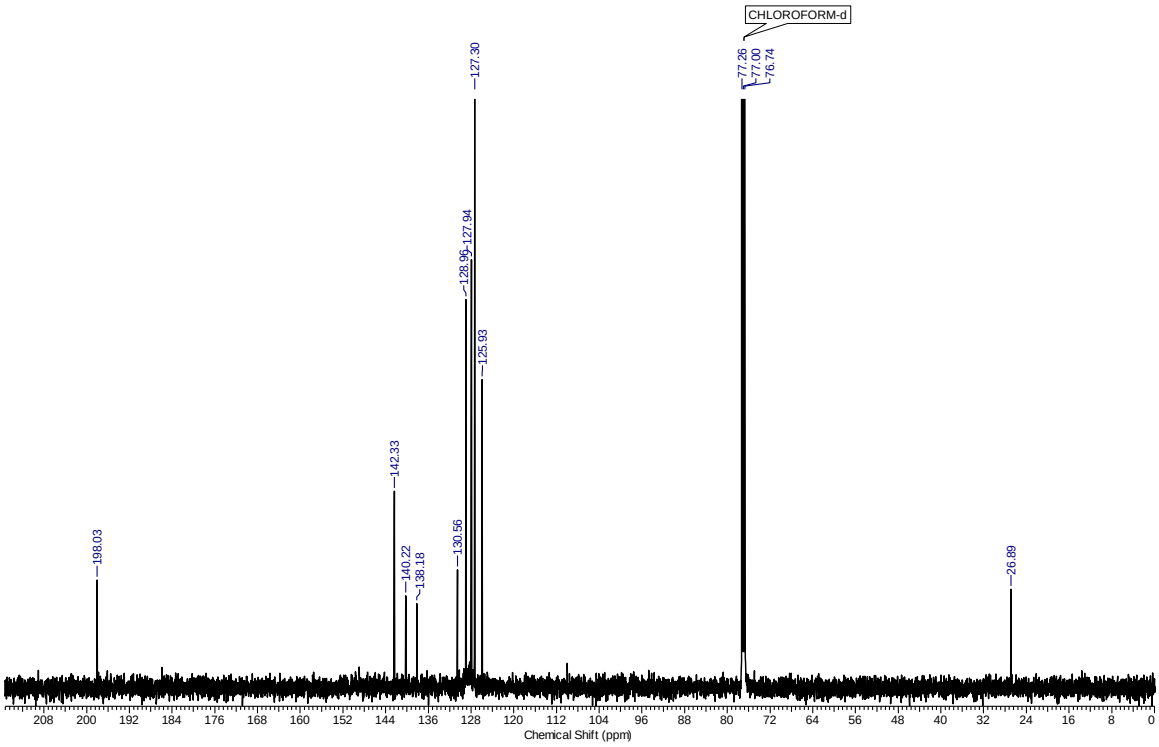
6,8-bis(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalen-1(2H)-one (3h)



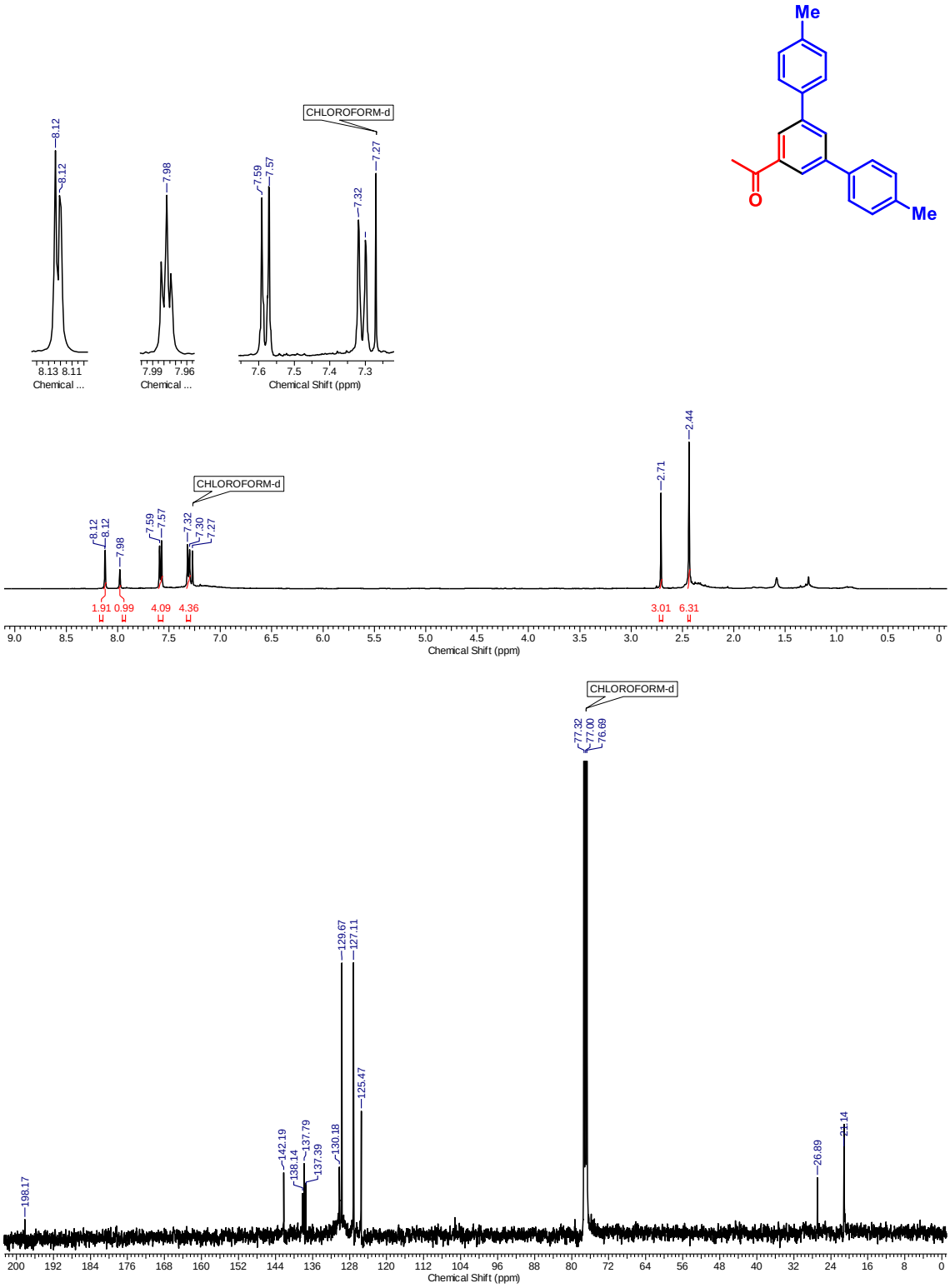


3-phenyloxiran-2-yl)(2-(trifluoromethyl)phenyl)methanone (3i)

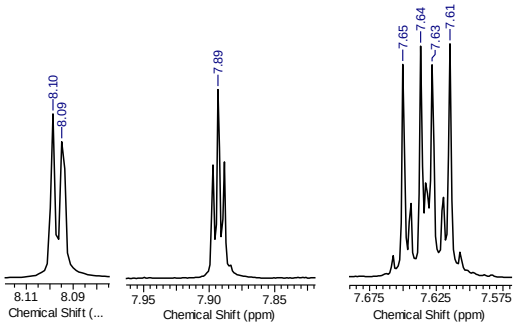


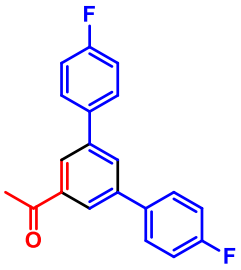


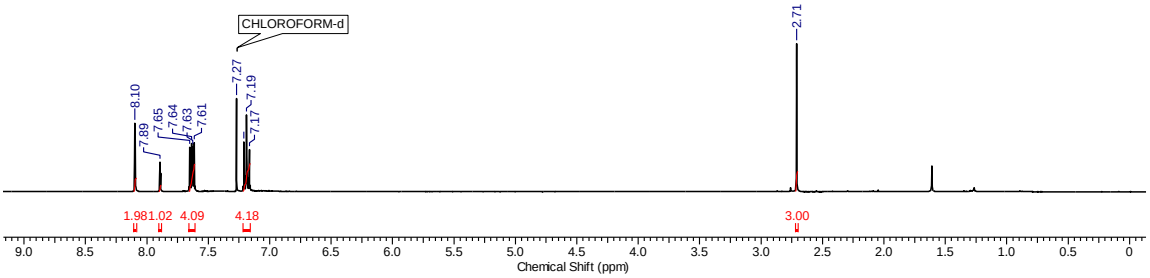
1-(4,4''-dimethyl-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3j)

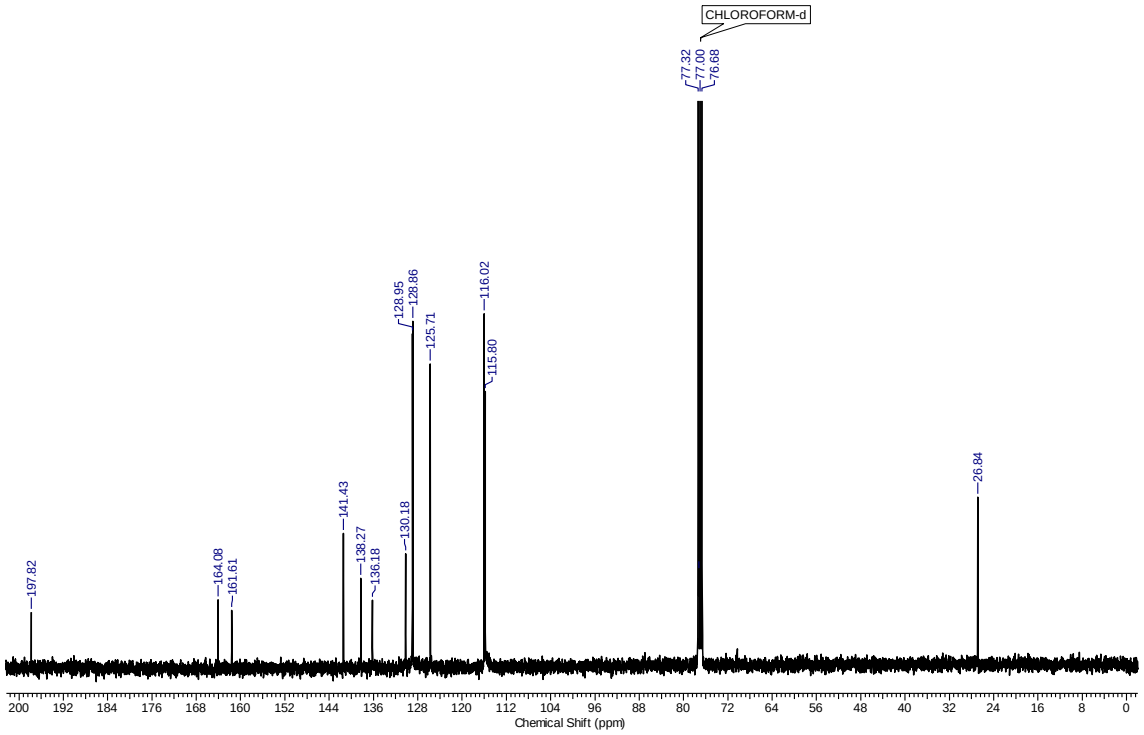


1-(4,4''-difluoro-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3k)

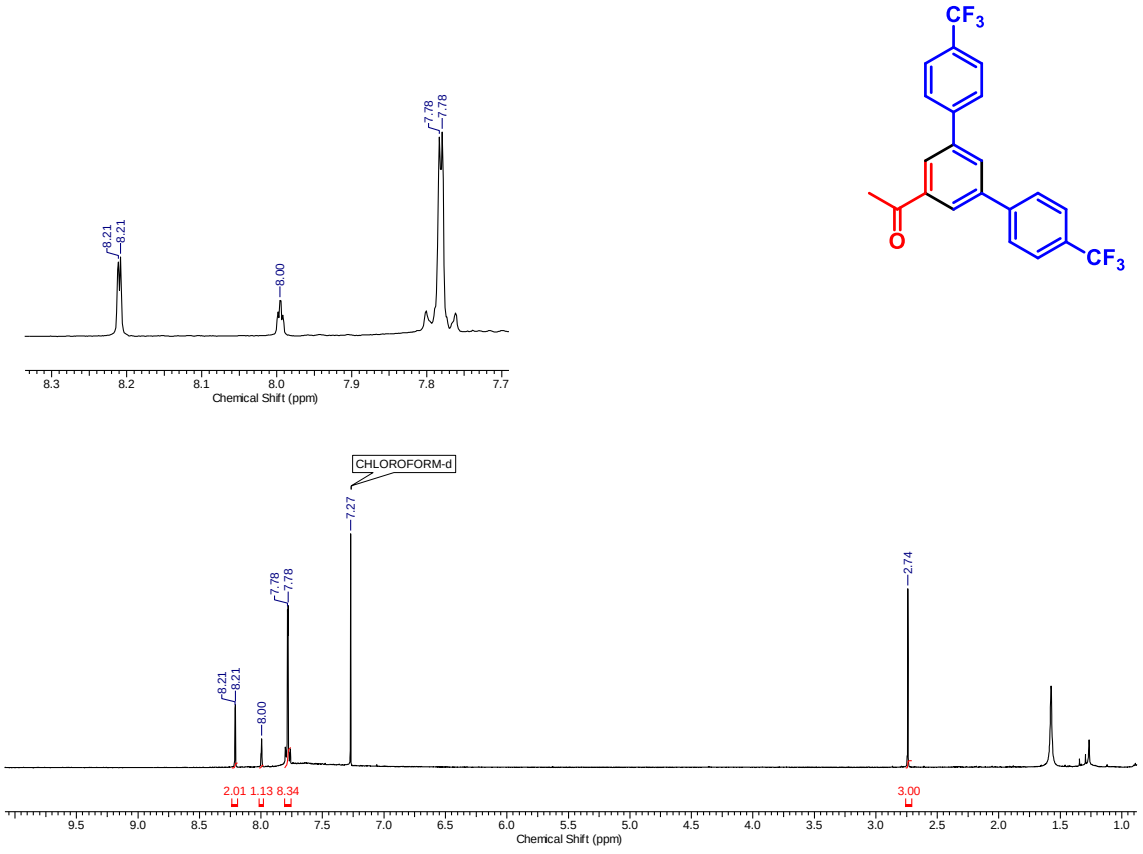


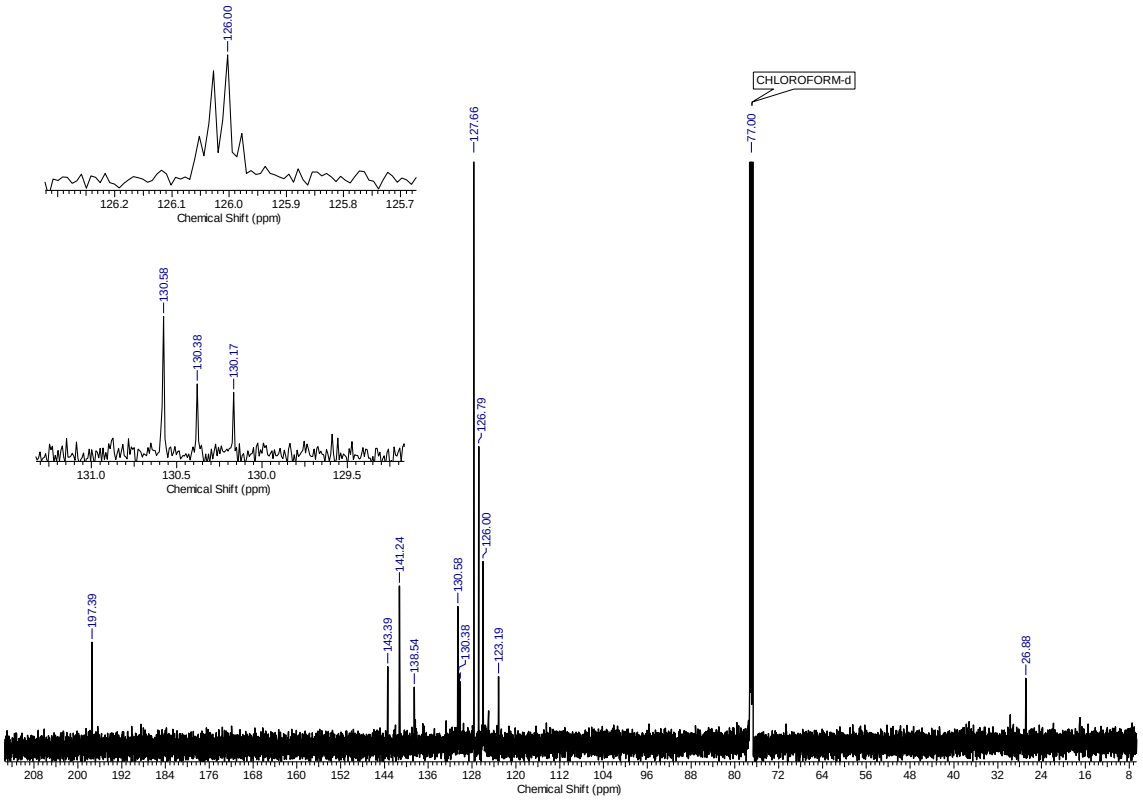




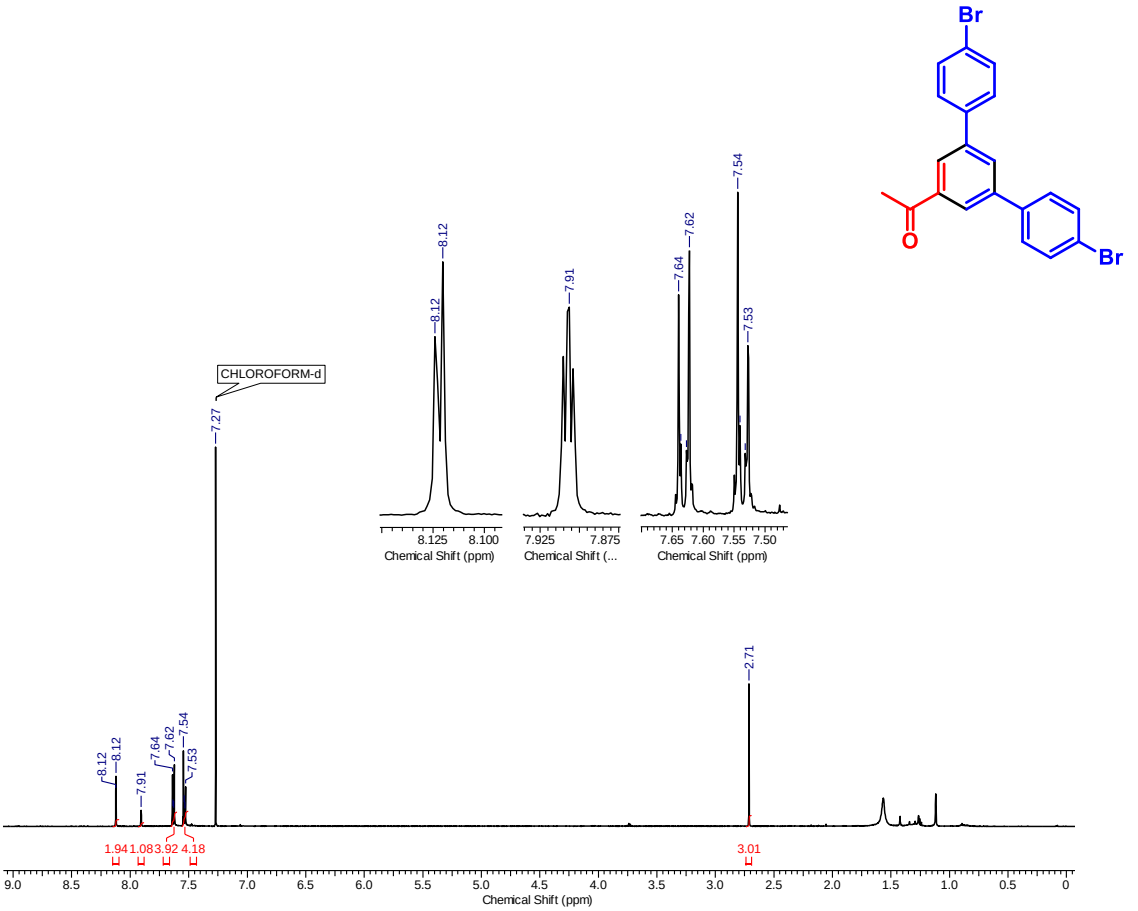


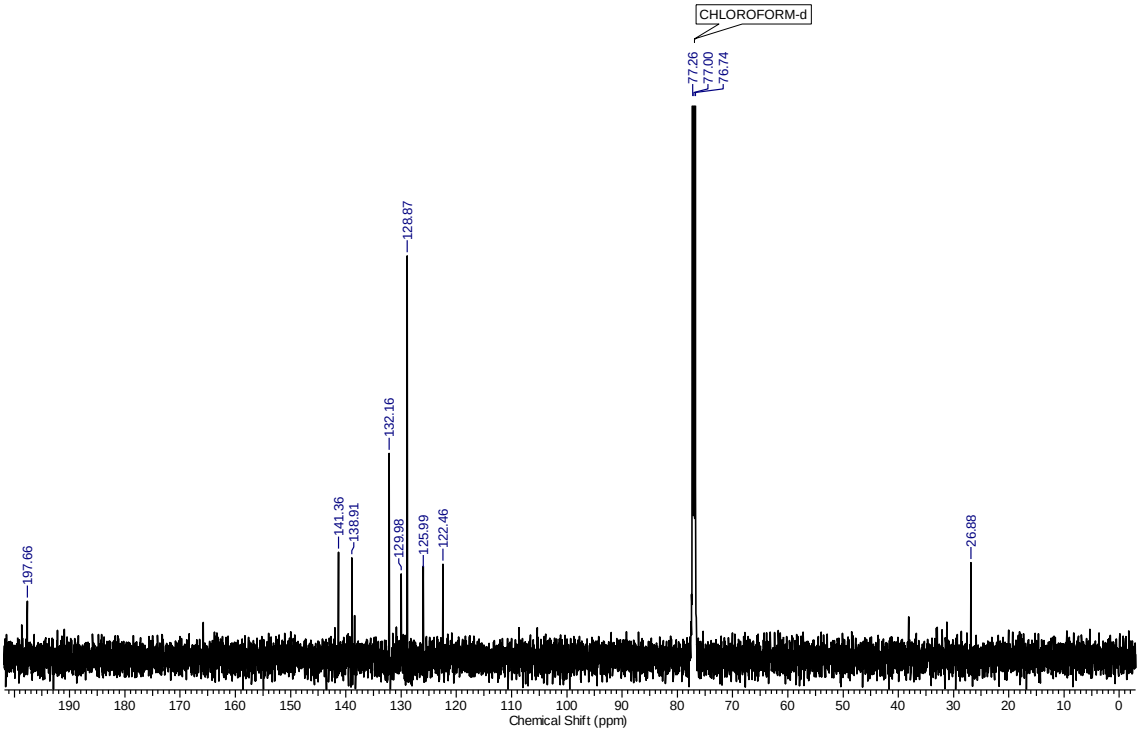
1-(4,4''-bis(trifluoromethyl)-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3l)





1-(4,4''-dibromo-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3m)





1-(2,2''-dibromo-[1,1':3',1''-terphenyl]-4'-yl)ethanone (3n)