One-Step Synthesis of 1-Halo-1,3-butadienes via Ruthenium-Catalysed Hydrohalogenative Dimerisation of Alkynes

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Supporting Information for Publication

Table of contents

General information

All catalytic reactions were carried out under inert atmosphere in Schlenk tubes. The complex $RuCl(C_5Me_5)(cod)$ was prepared according to the reported method.[1] ^1H, ^{19}F and ^{13}C NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers in deuterated chloroform or deuterated benzene solutions at 298 K. Mass spectra were obtained on Waters Q-Tof 2 high-resolution spectrometer in Centre Regional de Mesures de l'Ouest (CRMPO) of the University of Rennes 1. X-Ray crystallographic analysis was performed with an APEXII, Bruker-AXS diffractometer using Mo Kα radiation (λ= 0.71073 Å). The compounds were characterized by ^1H and ^{13}C NMR techniques including COSY, HMQC, HMBC and NOESY experiments.

[1] P. J. Fagan, W. S. Mahoney, J. C. Calabrese, I. D. Williams, *Organometallics*, 1990, **9**, 1843.

General procedure for the catalytic preparation of chlorinated dienes with HCl.

In a Schlenk tube under inert atmosphere, to a solution of 1,2-dichloroethane (0.5 mL) containing 0.05 mol of the precatalyst $RuCl(C_5Me_5)(cod)$ was added 1 mmol of the alkyne and 0.5 equiv of 2N HCl (in diethyl ether). The mixture was stirred at room temperature for 2 to 40 h. Reaction completion was monitored using GC or TLC techniques. The solvent was removed under vacuum and chlorinated dienes were separated as pure compounds using standard chromatography over silica gel.

General procedure for the catalytic preparation of halogenated dienes with CSA/$BnEt_3NX$.

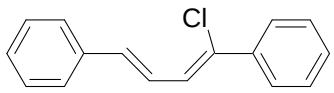
In a Schlenk tube under inert atmosphere, to a solution of 1,2-dichloroethane (0.5 mL) containing 0.05 mol of the precatalyst $RuCl(C_5Me_5)(cod)$, 0.5 mmol of CSA and 0.5 or 1.0 equiv of $BnEt_3NCl$ or $BnEt_3NBr$ was added 1 mmol of the alkyne. The mixture was stirred at room temperature for 2 to 19 h. Reaction completion was monitored using GC or TLC techniques. The solvent was removed under vacuum and halogenated dienes were separated as pure compounds using standard chromatography over silica gel.

General procedure for the synthesis of diene 4a via Suzuki-Miyaura reaction.

In a Schlenk tube under inert atmosphere containing the chlorodiene **1a** (77 mg, 0.32 mmol) and $Pd(OAc)_2$ (1.4 mg, 0.006 mmol) were added xylene (1.0 mL) and PCy_3 (20% in toluene, 23 µL, 0.015 mmol). The mixture was stirred at room temperature before to add phenylboronic acid (55 mg, 0.45 mmol) and K_2CO_3 (124 mg, 0.90 mmol). Then, the mixture was stirred at 80 °C for 18 h. After cooling, the solvent was removed under vacuum and the diene **4a** was purifying using standard chromatography over silica gel.

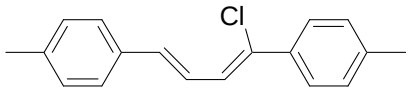
Spectroscopic data for compounds 2-4

(1*Z*, 3*E*)-1-chloro-1,4-diphenylbuta-1,3-diene **2a**[2]



Chromatography on silica gel using pentane/dichloromethane (90/10) as eluting mixture afforded compound **2a** as white solid, identified by NMR spectra according to the reported data. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.71 (d, 2H, *J* = 8.4 Hz, Ar); 7.53 (d, 2H, *J* = 8.0 Hz, Ar); 7.42-7.34 (m, 6H, Ar + =CH); 7.32-7.294 (m, 1H, Ar); 6.96 (d, 1H, *J* = 10.4 Hz, =CH); 6.82 (d, 1H, *J* = 15.7 Hz, =CH). ^{1}H NMR (400 MHz, C_6D_6) δ ppm: 7.57 (d, 2H, *J* = 7.8 Hz, Ar); 7.47 (dd, 1H, *J* = 15.7 Hz, *J* = 10.4 Hz, =CH); 7.29 (d, 2H, *J* = 7.2 Hz, Ar); 7.10-7.01 (m, 6H, Ar); 6.68 (d, 1H, *J* = 10.4 Hz, =CH); 6.50 (d, 1H, *J* = 15.7 Hz, =CH). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 137.7, 137.0, 135.7, 132.8, 128.7, 128.6, 128.4, 128.2, 126.8, 126.2, 125.9, 125.0. HRMS calcd for $[M+H]^+$ $C_{16}H_{14}{}^{35}Cl$ 241.0784, found: 241.0785.

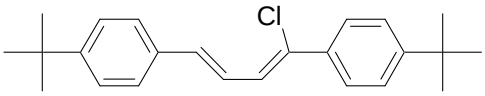
(1*Z*, 3*E*)-1-chloro-1,4-di(4-methylphenyl)buta-1,3-diene **2b**



Chromatography on silica gel using pentane/diethyl ether (90/10) as eluting mixture afforded compound **2b** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.60 (d, 2H, *J* = 8.2 Hz, Ar); 7.42 (d, 2H, *J* = 8.0 Hz, Ar); 7.33 (dd, 1H, *J* = 15.7 Hz, *J* = 10.4 Hz, =CH); 7.21 (d, 2H, *J* = 8.5 Hz, Ar); 7.19 (d, 2H, *J* = 8.3 Hz, Ar); 6.92 (d, 1H, *J* = 10.4 Hz, =CH); 6.77 (d, 1H, *J* = 15.7 Hz, =CH); 2.40 (s, 3H, CH_3); 2.39 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 138.6, 138.1, 135.2, 135.0, 134.4, 132.4, 129.4, 129.1, 126.7, 126.1, 125.2, 124.2, 21.3, 21.1. HRMS calcd for $[M+H]^+$ $C_{18}H_{18}{}^{35}Cl$ 269.1097, found: 269.1095.

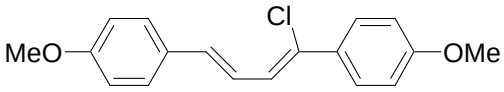
[2] T. Iwai, T. Fujihara, J. Terao, Y. Tsuji, *J. Am. Chem. Soc.*, 2009, **131**, 6668.

(1*Z*, 3*E*)-1-chloro-1,4-di(4-tert-butylphenyl)buta-1,3-diene **2c**



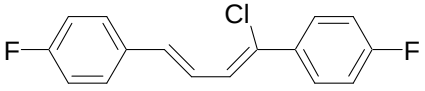
Chromatography on silica gel using pentane as eluent afforded compound **2c** as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.65 (d, 2H, *J* = 8.7 Hz, Ar); 7.47 (d, 2H, *J* = 8.4 Hz, Ar); 7.43 (d, 2H, *J* = 8.9 Hz, Ar); 7.41 (d, 2H, *J* = 8.8 Hz, Ar); 7.35 (dd, 1H, *J* = 15.7 Hz, *J* = 10.4 Hz, =CH); 6.95 (d, 1H, *J* = 10.4 Hz, =CH); 6.80 (d, 1H, *J* = 15.7 Hz, =CH); 1.39 (s, 9H, *t*-Bu); 1.37 (s, 9H, *t*-Bu). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 151.8, 151.3, 135.1, 135.0, 134.4, 132.4, 126.5, 125.9, 125.6, 125.4, 125.3, 124.5, 34.7, 34.6, 31.2, 31.2. HRMS calcd for $[M]^+$ $C_{24}H_{29}{}^{35}Cl$ 352.1958, found: 352.1962.

(1*Z*, 3*E*)-1-chloro-1,4-di(4-methoxyphenyl)buta-1,3-diene **2d**



Chromatography on silica gel using pentane/diethyl ether (85/15) as eluting mixture afforded compound **2d** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.61 (d, 2H, *J* = 8.9 Hz, Ar); 7.44 (d, 2H, *J* = 8.7 Hz, Ar); 7.19 (dd, 1H, *J* = 15.6 Hz, *J* = 10.3 Hz, =CH); 6.90 (d, 2H, *J* = 8.9 Hz, Ar); 6.891 (d, 2H, *J* = 8.8 Hz, Ar); 6.81 (d, 1H, *J* = 10.3 Hz, =CH); 6.71 (d, 1H, *J* = 15.6 Hz, =CH); 3.84 (s, 3H, OCH_3); 3.83 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 159.9, 159.6, 134.3, 131.5, 130.6, 130.1, 128.0, 127.5, 124.5, 123.2, 114.2, 113.8, 55.4, 55.3. HRMS calcd for $[M]^+$ $C_{18}H_{17}O_2{}^{35}Cl$ 300.0917, found: 300.0905.

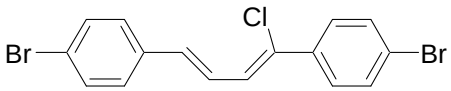
(1*Z*, 3*E*)-1-chloro-1,4-di(4-fluorophenyl)buta-1,3-diene **2e**



Chromatography on silica gel using pentane/diethyl ether (95/5) as eluting mixture afforded compound **2e** as pale yellow solid. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: - 112.6 (m); - 113.0 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.65 (dd, 2H, *J* = 9.0 Hz, *J* = 5.2 Hz, Ar); 7.47 (dd, 2H, *J* = 8.7 Hz, *J* = 5.4 Hz, Ar); 7.22 (dd, 1H, *J* = 15.7 Hz, *J* = 10.3 Hz, =CH); 7.09-7.03 (m,

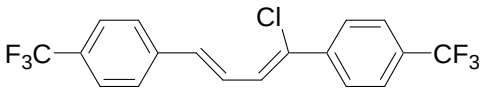
4H, Ar); 6.84 (d, 1H, *J* = 10.3 Hz, =CH); 6.75 (d, 1H, *J* = 15.7 Hz, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 162.9 (d, *J* = 249.5 Hz), 162.7 (d, *J* = 248.5 Hz), 134.4, 133.9 (d, *J* = 3.5 Hz), 133.2 (d, *J* = 3.2 Hz), 131.7, 128.3 (d, *J* = 8.1 Hz), 128.1 (d, *J* = 8.2 Hz), 125.6 (m), 124.6 (d, *J* = 2.4 Hz), 115.8 (d, *J* = 21.8 Hz), 115.4 (d, *J* = 21.9 Hz). HRMS calcd for $[M]^+$ $C_{16}H_{11}F_2{}^{35}Cl$ 276.0517, found: 276.0518.

(1*Z*, 3*E*)-1-chloro-1,4-di(4-bromophenyl)buta-1,3-diene **2f**



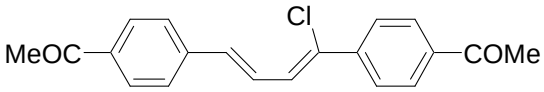
Chromatography on silica gel using pentane/diethyl ether (90/10) as eluting mixture afforded compound **2f** as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.54 (d, 2H, *J* = 9.0 Hz, Ar); 7.50 (d, 2H, *J* = 9.0 Hz, Ar); 7.47 (d, 2H, *J* = 8.5 Hz, Ar); 7.36 (d, 2H, *J* = 8.5 Hz, Ar); 7.29 (dd, 1H, *J* = 15.7 Hz, *J* = 10.4 Hz, =CH); 6.90 (d, 1H, *J* = 10.4 Hz, =CH); 6.73 (d, 1H, *J* = 15.7 Hz, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 136.5, 135.8, 134.8, 132.3, 131.9, 131.6, 128.2, 127.7, 126.0, 125.4, 122.9, 122.2. HRMS calcd for $[M]^+$ $C_{16}H_{11}{}^{35}Cl^{79}Br_2$ 395.8916, found: 395.8911.

(1*Z*, 3*E*)-1-chloro-1,4-di(4-trifluoromethylphenyl)buta-1,3-diene **2g**



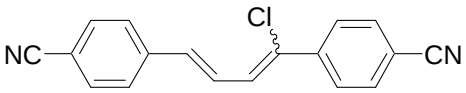
Chromatography on silica gel using pentane/diethyl ether (90/10) as eluting mixture afforded compound **2g** as pale yellow solid. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: - 62.6; - 62.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.79 (d, 2H, *J* = 8.3 Hz, Ar); 7.65 (d, 2H, *J* = 8.4 Hz, Ar); 7.64-7.58 (m, 4H, Ar); 7.41 (dd, 1H, *J* = 15.7 Hz, *J* = 10.4 Hz, =CH); 7.02 (d, 1H, *J* = 10.4 Hz, =CH); 6.87 (d, 1H, *J* = 15.7 Hz, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 140.8, 140.1, 135.2, 132.8, 130.7 (q, *J* = 32.7 Hz), 130.1 (q, *J* = 32.7 Hz), 127.2, 127.0, 126.8, 126.6, 125.7 (q, *J* = 3.8 Hz), 125.5 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.0 Hz), 123.9 (q, *J* = 272.0 Hz). HRMS calcd for $[M]^+$ $C_{18}H_{11}F_6{}^{35}Cl$ 376.0454, found: 376.0450.

(1*Z*, 3*E*)-1-chloro-1,4-di(4-acylphenyl)buta-1,3-diene **2h**



Chromatography on silica gel using pentane/dichloromethane/ethylacetate (50/40/10) as eluting mixture afforded compound **2h** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.97 (d, 2H, *J* = 8.6 Hz, Ar); 7.94 (d, 2H, *J* = 8.3 Hz, Ar); 7.78 (d, 2H, *J* = 8.6 Hz, Ar); 7.58 (d, 2H, *J* = 8.4 Hz, Ar); 7.45 (dd, 1H, *J* = 15.7 Hz, *J* = 10.4 Hz, =CH); 7.06 (d, 1H, *J* = 10.4 Hz, =CH); 6.88 (d, 1H, *J* = 15.7 Hz, =CH); 2.62 (s, 3H, CH_3); 2.60 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 197.3, 197.2, 141.5, 141.2, 137.0, 136.6, 135.7, 133.3, 128.9, 128.5, 127.4, 127.2, 126.9, 126.4, 26.6, 26.5. HRMS calcd for $[M+H]^+$ $C_{20}H_{18}O_2{}^{35}Cl$ 325.0995, found: 325.0995.

(1*Z*, 3*E*) and (1*E*, 3*E*) -1-chloro-1,4-di(4-cyanophenyl)buta-1,3-diene **2i**



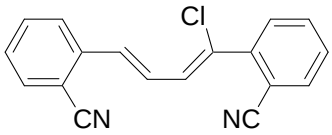
Chromatography on silica gel using pentane/dichloromethane/ethylacetate (65/30/5) as eluting mixture afforded compound (1*E*,3*E*)-**2i** as pale yellow solid and pentane/dichloromethane/ethylacetate (60/30/10) as eluting mixture afforded compound (1*Z*, 3*E*)-**2i** as yellow solid.

(1*Z*, 3*E*) -1-chloro-1,4-di(4-cyanophenyl)buta-1,3-diene : ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.79 (d, 2H, *J* = 8.5 Hz, Ar); 7.68 (d, 2H, *J* = 8.5 Hz, Ar); 7.65 (d, 2H, *J* = 8.4 Hz, Ar); 7.59 (d, 2H, *J* = 8.4 Hz, Ar); 7.43 (dd, 1H, *J* = 15.7 Hz, *J* = 10.4 Hz, =CH); 7.05 (d, 1H, *J* = 10.4 Hz, =CH); 6.86 (d, 1H, *J* = 15.7 Hz, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 141.3, 140.9, 135.4, 133.1, 132.6, 132.3, 127.8, 127.7, 127.3, 126.8, 118.7, 118.3, 112.4, 111.7. HRMS calcd for $[M+H]^+$ $C_{18}H_{12}N_2{}^{35}Cl$ 291.0689, found: 291.0684.

(1*E*, 3*E*) -1-chloro-1,4-di(4-cyanophenyl)buta-1,3-diene : ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.74 (d, 2H, *J* = 8.4 Hz, Ar); 7.60 (d, 2H, *J* = 8.4 Hz, Ar); 7.57 (d, 2H, *J* = 8.4 Hz, Ar); 7.39 (d, 2H, *J* = 8.4 Hz, Ar); 6.84-6.68 (m, 3H, =CH). ^{1}H NMR (400 MHz, C_6D_6) δ ppm: 7.39-7.36 (m, 2H, Ar); 7.20 (d, 2H, *J* = 8.3 Hz, Ar); 7.16-7.12 (m, 2H, Ar); 6.88 (d, 2H, *J* = 8.3 Hz, Ar); 6.67 (d, 1H, *J* = 11.3 Hz, =CH); 6.60 (dd, 1H, *J* = 14.9 Hz, *J* = 11.3 Hz, =CH); 6.22 (d, 1H, *J* = 14.9 Hz, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 141.2, 140.7, 133.8, 133.1,

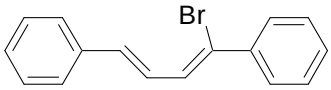
132.5, 132.3, 130.7, 129.9, 127.0, 126.4, 118.6, 118.1, 113.0, 111.4. HRMS calcd for $[M+Na]^+$ $C_{18}H_{11}N_2{}^{35}ClNa$ 313.0509, found: 313.0511.

(1*Z*, 3*E*)-1-chloro-1,4-di(2-cyanophenyl)buta-1,3-diene **2j**



Chromatography on silica gel using pentane/diethyl ether/dichloromethane (65/5/30) as eluting mixture afforded compound **2j** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.83 (d, 1H, *J* = 8.1 Hz, Ar); 7.73 (d, 1H, *J* = 7.8 Hz, Ar); 7.67-7.58 (m, 4H, Ar); 7.49-7.47 (m, 1H, Ar); 7.45-7.44 (m, 1H, =CH); 7.38-7.36 (m, 1H, Ar); 7.19 (d, 1H, *J* = 15.7 Hz, =CH); 6.94 (d, 1H, *J* = 10.3 Hz, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 141.8, 139.5, 133.8, 133.2, 132.8, 132.7, 132.5, 130.9, 130.6, 129.7, 129.2, 128.5, 128.0, 125.7, 117.6, 111.5, 110.9. HRMS calcd for $[M+H]^+$ $C_{18}H_{12}N_2{}^{35}Cl$ 291.0689, found: 291.0680.

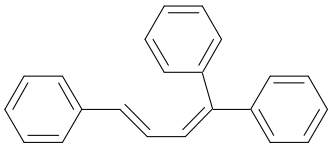
(1*Z*, 3*E*)-1-bromo-1,4-diphenylbuta-1,3-diene **3a**[3]



Chromatography on silica gel using pentane/dichloromethane (90/10) as eluting mixture afforded compound **3a** as white solid, identified by NMR spectra according to the reported data. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.66 (d, 2H, *J* = 7.3 Hz, Ar); 7.53 (d, 2H, *J* = 7.4 Hz, Ar); 7.40-7.29 (m, 7H, Ar + =CH); 7.02 (d, 1H, *J* = 10.2 Hz, =CH); 6.86 (d, 1H, *J* = 15.6 Hz, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 139.4, 136.9, 136.3, 129.4, 128.7, 128.7, 128.4, 128.3, 127.5, 126.8, 125.8. HRMS calcd for $[M]^+$ $C_{16}H_{13}{}^{79}Br$ 284.0201, found: 284.0211.

[3] H. J. Reich, I. L. Reich, *J. Org. Chem.*, 1975, **40**, 2248.

(3*E*)-1,1,4-triphenylbuta-1,3-diene **4a**[4]



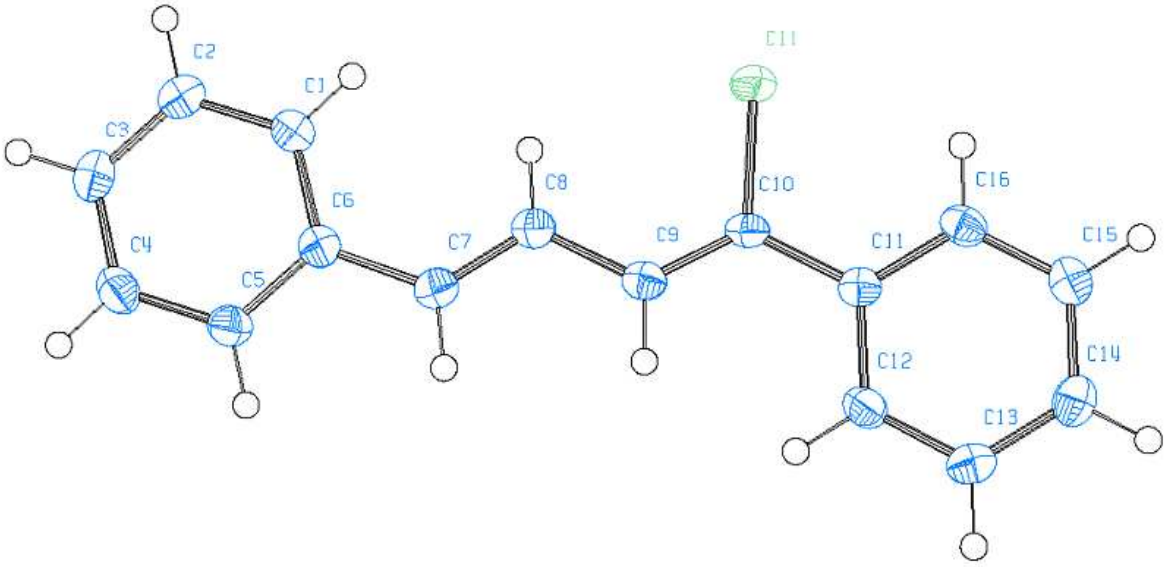
Chromatography on silica gel using pentane/dichloromethane (90/10) as eluting mixture afforded compound **4a** as white solid, identified by NMR spectra according to the reported data. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.47-7.37 (m, 3H, Ar); 7.34-7.25 (m, 11H, Ar); 7.22-7.19 (m, 1H, Ar); 6.95-6.88 (m, 2H, =CH); 6.80-6.72 (m, 1H, =CH). ^{1}H NMR (400 MHz, C_6D_6) δ ppm: 7.34-7.32 (m, 2H, Ar); 7.26-7.24 (m, 2H, Ar); 7.18-7.07 (m, 8H, Ar + =CH); 7.05-6.94 (m, 4H, Ar); 6.86 (d, 1H, J = 11.1 Hz, =CH); 6.62 (d, 1H, J = 15.5 Hz, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 143.2, 142.3, 139.8, 137.5, 134.0, 130.6, 128.6, 128.3, 128.3, 128.2, 128.2, 127.6, 127.5, 127.4, 127.1, 126.5.

Structural data for (1*Z*, 3*E*)-2a and (1*E*, 3*E*)-2i

Crystal structure analysis of **(**1*Z*, 3*E***)-2a**: (C_{16} H_{13} Cl_1); M = 240.71. APEXII, Bruker-AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 150(2) K; orthorhombic $P2_12_12_1$ (I.T.#19), a = 5.6950(3), b = 7.5345(5), c = 28.7029(17) Å, V = 1231.61(13) Å^3, Z = 4, d = 1.298 g.cm^{-3}, μ = 0.283 mm^{-1}. The structure was solved by direct methods using the *SIR97* program,[5] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*)[6] with the aid of the *WINGX*[7] program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except linked hydrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. A final refinement on F^2 with 2831 unique intensities and 154 parameters converged at $\omega R(F^2)$ = 0.0738 ($R(F)$ = 0.0326) for 2540 observed reflections with $I > 2\sigma(I)$.

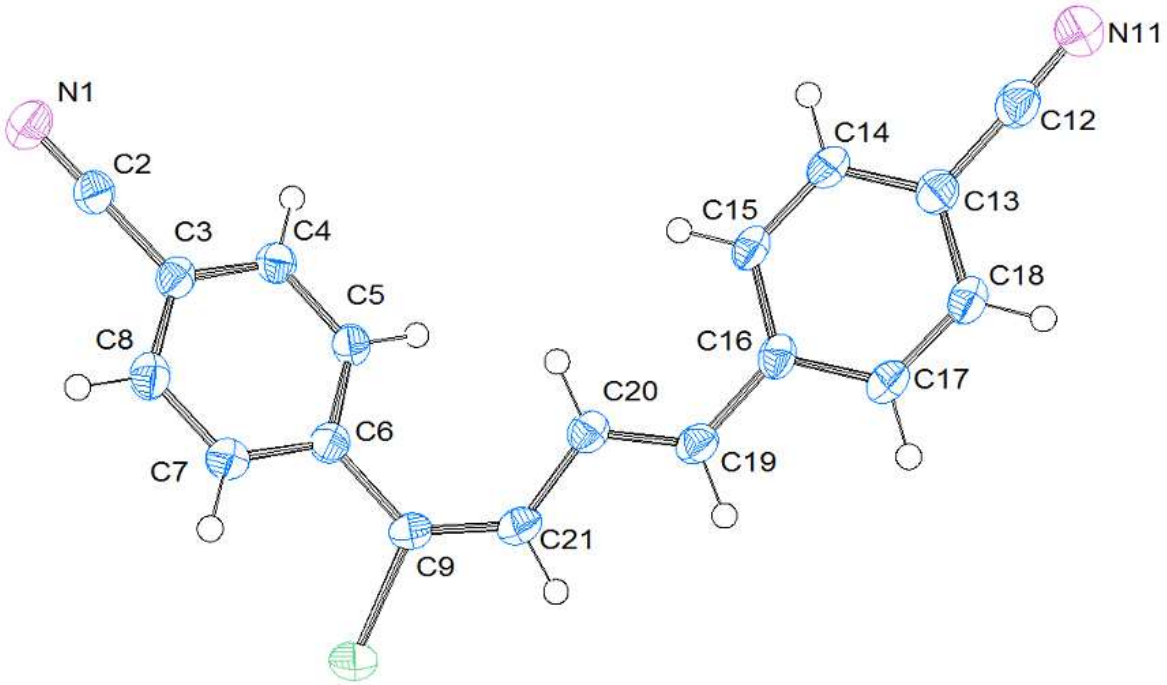
[4] C. C. Yu, D. K. P. Ng, B.-L. Chen, T.-Y. Luh, *Organometallics*, 1994, **13**, 1487.
[5] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115.
[6] G.M. Sheldrick, *Acta Cryst.* A64, 2008, 112.
[7] L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837.

Selected interatomic distances (Å) and angles (°): C6 - C7 = 1.466(2), C7 - C8 = 1.343(2), C8 - C9 = 1.447(2), C9 - C10 = 1.343(2), C10 - C11 = 1.480(2), C5 - C6 - C7 - C8 = 173.96(16), C7 - C8 - C9 - C10 = -175.57(17), C9 - C10 - C11 - C12 = 3.7(2).



Crystal structure analysis of **(1*E*, 3*E*)-2i**: (C_{18} H_{11} Cl N_2); *M* = 290.74. APEXII, Bruker-AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), *T* = 150(2) K; monoclinic $P2_1/c$ (I.T.#14), a = 11.0766(6), b = 10.0123(6), c = 13.7838(7) Å, β = 108.455(2) °, *V* = 1450.04(14) $Å^3$, *Z* = 4, *d* = 1.332 $g.cm^{-3}$, μ = 0.257 mm^{-1}. The structure was solved by direct methods using the *SIR97* program,[5] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*)[6] with the aid of the *WINGX*[7] program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 3304 unique intensities and 190 parameters converged at $\omega R(F^2)$ = 0.1036 ($R(F)$ = 0.0473) for 2346 observed reflections with $I > 2\sigma(I)$.

Selected interatomic distances (Å) and angles (°): C6 - C9 = 1.479(2), C9 - C21 = 1.347(2), C20 - C21 = 1.445(2), C19 - C20 = 1.346(2), C16 - C19 = 1.458(3), C5 - C6 - C9 - C21 = 36.6(3), C19 - C20 - C21 - C9 = 175.15(18), C15 - C16 - C19 - C20 = -17.8(3).


N11
N1
C12
C14
C2
C13
C15
C3
C4
C18
C5
C8
C16
C20
C17
C6
C19
C7
C21
C9