N-Heterocyclic carbene-catalyzed umpolung of styrenes: mechanistic elucidation and selective tail-to-tail dimerization

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Supporting Information

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1. General considerations

General Procedures: All reactions were performed in oven-dried or flame-dried reaction vessels, modified Schlenk flasks, or round-bottom flasks. The flasks were fitted with glass stoppers or septa, the modified Schlenk flask were fitted with Teflon screw caps, and reactions were conducted under an atmosphere of argon. Gas-tight syringes with stainless steel needles or cannulae were used to transfer air- and moisture-sensitive liquids. All moisture- and/or air sensitive solid compounds were manipulated inside an argon-filled glovebox. Flash column chromatography was performed using silica gel (40–63 µm, 230–400 mesh, Merck).

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates (Merck) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and to a solution of $KMnO_4$ (1 g of $KMnO_4$, 6 g of K_2CO_3, and 0.1 g of KOH in 100 mL of H_2O) followed by heating.

Organic solutions were concentrated at 40 °C on Heidolph 4000 rotary evaporators at ~10 mbar followed by drying on vacuum pump at <1 mbar.

Materials. Commercial reagents and solvents were used as received with the following exceptions: K_3PO_4 and KO^tBu were dried by heating at 110 °C under vacuum for 12 h, left to cool under argon and stored inside an argon-filled glovebox. NaH (60% in mineral oil) was washed free of mineral oil with dry pentane, dried *in vacuo*, and stored inside an argon-filled glovebox. DBU was distilled and stored under argon. CH_2Cl_2 was dried by refluxing on CaH_2 followed by distillation under argon. Dry 1,4-dioxane was stored over activated MS 4Å under argon in a Schlenk bottle. Dry d_8-THF was obtained by refluxing d_8-THF over Na/benzophenone followed by distillation under argon. For individual substrates, see the section on the preparation of starting materials.

Instrumentation.

- Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with Bruker AV 300, AV 400, Varian VNMRS 500 or Agilent DD2 600 spectrometers. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$), CD_2Cl_2: δ 5.32 ($CHDCl_2$), d_8-THF δ 3.58 (d_7-THF)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant(s) (Hz), integration].
- Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with Bruker AV 300, AV 400, Varian VNMRS 500 or Agilent DD2 600 spectrometers. Carbon chemical shifts are reported in parts per million (δ scale) and are referenced using the carbon resonances of the solvent (δ 77.16 ($CDCl_3$), δ 54.00 (CD_2Cl_2), δ 67.57 (d_8-

THF)). Data are reported as follows: chemical shift [multiplicity (if not singlet), assignment (C_q = fully substituted carbon)].

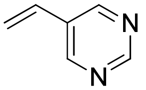
- Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were recorded with with Bruker AV 300, Varian VNMRS 500 or Agilent DD2 600 spectrometers. Fluorine chemical shifts are reported in parts per million (*δ* scale) and are referenced using an external reference ($CFCl_3$). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), integration].
- Infrared data (IR) were obtained on Varian 3100 FT-IR (Excalibur Series) with an ATR unit and are reported in frequency of absorption (cm^{-1}).
- GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with Agilent 5975C VL MSD or 5975 inert Mass Selective Detector (EI) on an HP-5MS column (0.25 mm x 30 m, Film: 0.25 µm). The measurment begins with injection at temperature T_0 (50 °C), which is held for 3 min. The column is then heated to temperature T_1 (290 °C, ramp = 40 °C), which is held for 3 min.
- High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics MicroTof using an electrospray (ESI) ionization source or on a Thermo Scientific Orbitrap LTQ XL using an electrospray (ESI) ionization source.

2. Preparation of starting materials

p-Cyanostyrene **2a**, 4-vinylpyridine **2d**, 2-vinylpyridine **2e**, 3,5-bis-(trifluoromethyl)-styrene **2g**, *p*-trifluoromethylstyrene **2h**, and butyl methacrylate **8** were purchased and used without further purification. Styrene **2b** was purchased and distilled before use. Phenyl-(4-vinylphenyl)-methanone **2c** and methyl-4-vinylbenzoate **2i** were synthesized according to our previously published procedure.(1)

5-Vinylpyrimidine **2f**, *N,N-d*iisopropyl-4-vinylbenzamide **2j** and 1-(4-vinylphenyl)ethanone **2k** were synthesized following known procedures.

2.1 5-Vinylpyrimidine



2f

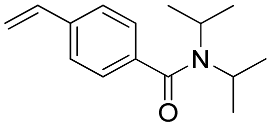
5-Vinylpyrimidine was prepared following a literature procedure.(2)
In an argon-filled glovebox, a Schlenk tube was charged with 10.6 mg $PdCl_2$ (0.06 mmol, 0.02 equiv), 47.0 mg triphenylphosphine (0.18 mmol, 0.06 equiv), and 2.932 g Cs_2CO_3 (9.0 mmol, 3 equiv). 477 mg (3.0 mmol, 1 equiv) 5-bromopyrimidine and 402 mg (3.0 mmol, 1 equiv) potassium vinyltrifluoroborate were added. After the addition of 6 mL of THF/H_2O (9:1), the flask was sealed and stirred at 85 °C for 22 h. After this time, the reaction mixture was cooled to room temperature, and 9 mL of H_2O were added. The mixture was extracted three times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and all volatiles were removed *in vacuo*. The residue was purified by flash column chromatography (*n*-pentane/Et_2O 1:1 → 1:1.5), yielding 249 mg (2.35 mmol, 78%) **2f** as a yellowish liquid.
Analytical data were in accordance with those reported in the literature.(2)

TLC (*n*-pentane/Et_2O 1:1) $R_f = 0.22$ (UV, $KMnO_4$).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.10 (s, 1H), 8.77 (s, 2H), 6.65 (dd, J = 17.8, 11.1 Hz, 1H), 5.93 (d, J = 17.7 Hz, 1H), 5.52 (d, J = 11.1 Hz).

GC/MS: 5.33 min (107, 106, 105, 79, 53, 52, 51, 50, 49).

2.1 *N,N*-Diisopropyl-4-vinylbenzamide



2j

N,N-Diisopropyl-4-vinylbenzamide was prepared following a similar literature procedure.(3) Methyl-4-vinylbenzoate **2i**(1) (324 mg, 2 mmol, 1 equiv) was dissolved in 6.67 mL of methanol, and 6.67 mL of an aqueous solution of NaOH (6 M, 40 mmol, 20 equiv) was added, and the reaction mixture was stirred at room temperature for 2 h. When TLC indicated that no starting material was left, the reaction mixture was acidified with HCl until pH = 1. The mixture was extracted with ethyl acetate (3 x 50 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4. After filtration, all volatiles were removed *in vacuo*, and the resulting colorless solid was used in the next step without further purification. The residue was dissolved in 20 mL of dry CH_2Cl_2, and oxalyl chloride (0.34 mL, 4 mmol, 2 equiv) was added at room temperature. After a few drops of DMF had been added, the reaction was stirred at room temperature for 2 h. All volatiles were removed *in vacuo*, and the resulting yellow oil was used without further purification.

The residue was dissolved in in 20 mL of dry CH_2Cl_2 and distilled diisopropylamine (703 µL, 5 mmol, 2.5 equiv) was added at room temperature. After stirring for 3 h at room temperature, the reaction was stopped by adding 20 mL of brine. The mixture was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organic phases were dried over Na_2SO_4. After filtration, all volatiles were removed *in vacuo* yielding a yellow solid, which was purified by flash column chromatography (*n*-pentane/ethyl acetate 9:1 → 8:2) yielding **2j** as a colorless solid (407.1 mg, 1.76 mmol, 88% over 3 steps).

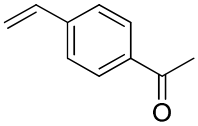
Analytical data were in accordance with those reported in the literature.(4)

TLC (*n*-pentane/ethyl acetate 80:20) R_f = 0.36 (UV, $KMnO_4$).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.43–7.40 (m, 2H), 7.29–7.26 (m, 2H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.78 (dd, J = 17.6, 0.9 Hz, 1H), 5.29 (dd, J = 10.9, 0.8 Hz, 1H), 3.69 (br s, 2H), 1.33 (br s, 12H).

GC/MS: 8.66 min (231, 188, 131, 103, 77).

2.2 1-(4-Vinylphenyl)ethanone



2k

1-(4-Vinylphenyl)ethanone was prepared following a literature procedure.(2)

In an argon-filled glovebox, a Schlenk tube was charged with 17.7 mg $PdCl_2$ (0.1 mmol, 0.02 equiv), 78.7 mg triphenylphosphine (0.3 mmol, 0.06 equiv), and 4.887 g Cs_2CO_3 (15.0 mmol, 3 equiv). 995 mg (5.0 mmol, 1 equiv) 4'-bromoacetophenone and 670 mg (5.0 mmol, 1 equiv) potassium vinyltrifluoroborate were added. After the addition of 10 mL of THF/H_2O (9:1), the flask was sealed and stirred at 85 °C for 22 h. After this time, the reaction mixture was cooled to room temperature, and 15 mL of H_2O were added. The mixture was extracted three times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and all volatiles were removed *in vacuo*. The residue was purified by flash column chromatography (*n*-pentane/Et_2O 10:1), yielding 554 mg (3.79 mmol, 76%) **2k** as a yellowish liquid.

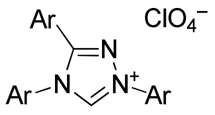
TLC (*n*-pentane/Et_2O 10:1) R_f = 0.27 (UV).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.96–7.89 (m, 2H), 7.53–7.45 (m, 2H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 5.88 (dd, J = 17.6, 0.8 Hz, 1H), 5.40 (dd, J = 10.9, 0.8 Hz, 1H), 2.60 (s, 3H).

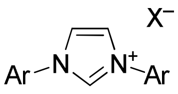
GC/MS: 7.05 min (146, 132, 131, 104, 103, 102, 77, 76, 63, 51, 50, 43).

3. Preparation of catalysts

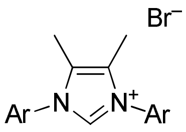
NHC-precursors **1a**,(5) **1b**,(6) **1c**,(7) **1d**,(8) **1e**,(9) **1f**(10),**1g**(11), and **1h**(11) were prepared according to literature procedures.



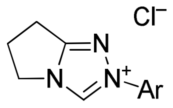
1a: Ar = Ph
1g: Ar = 4-MeO(C_6H_4)



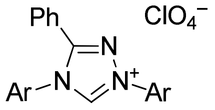
1b: Ar = Mes, X = Cl
1c: Ar = 2,6-(MeO)$_2$(C_6H_4), X = I



1d: Ar = Ph



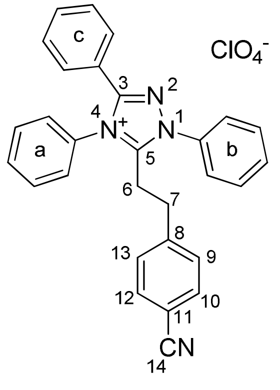
1e: Ar = Ph
1f: Ar = Mes



1h: Ar = 4-MeO(C_6H_4)

4. Stoichiometric reactions of NHCs with styrenes

5-(4-Cyanophenylethyl)-1,3,4-triphenyl-1*H*-1,2,4-triazol-4-ium perchlorate



3a

A flame-dried Schlenk flask was charged with 795.6 mg (2.0 mmol, 1 equiv) of the triazolium salt **1a** in an argon-filled glovebox. Using an overpressure of argon, 8 mL (0.25 M) of dry 1,4-dioxane were added. Afterwards, 299 µL (2.0 mmol, 1 equiv) DBU and 258.3 mg (2.0 mmol, 1 equiv) *p*-cyanostyrene **2a** were added. The flask was sealed and placed in a preheated oilbath at 80 °C for 24 h. After cooling the now biphasic reaction mixture to room temperature, it was diluted with CH_2Cl_2 and filtered through a short pad of silica. All volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with CH_2Cl_2/MeOH (99:1 → 97.5:2.5) as the eluents, yielding **3a** (824.9 mg; 1.57 mmol; 79%) as a colorless solid.

TLC (CH_2Cl_2/MeOH 90:10) $R_f = 0.28$ (UV, $KMnO_4$).

^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm) = 7.85–7.82 (m, 2H, *o*-Ph^b), 7.71–7.68 (m, 2H, *o*-Ph^a), 7.66–7.63 (m, 2H, *p*-Ph^a & *p*-Ph^b), 7.59–7.54 (m, 4H, *m*-Ph^a & *m*-Ph^b), 7.47–7.43 (m, 3H, *o*-Ph^c & *p*-Ph^c), 7.42–7.41 (m, 2H, C10-H, C12-H), 7.30–7.27 (m, 2H, *m*-Ph^c), 6.84–6.82 (m, 2H, C9-H, C13-H), 3.28–3.24 (m, 2H, C6-H), 2.74–2.70 (m, 2H, C7-H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ (ppm) = 154.5 (C5 & C3), 143.7 (C8), 135.3 (*i*-Ph^b), 133.1 (C10 & C12), 132.5 (*p*-Ph^b), 132.5 (*p*-Ph^c), 132.3 (*p*-Ph^a), 131.9 (*i*-Ph^a), 131.3 (*m*-Ph^a), 130.7 (*m*-Ph^b), 130.1 (*o*-Ph^c), 129.4 (C9 & C13), 129.3 (*m*-Ph^c), 128.2 (*o*-Ph^a), 126.6 (*o*-Ph^b), 123.1 (*i*-Ph^c), 118.9 (C14), 111.5 (C11), 31.9 (C7), 26.5 (C6).

^{1}H, ^{1}H GCOSY (400 MHz, CD_2Cl_2) δ ^{1}H (ppm) / δ ^{1}H (ppm) = 7.85–7.82 / 7.66–7.63, 7.59–7.54; 7.71–7.68 / 7.66–7.63, 7.59–7.54; 7.47–7.43 / 7.30–7.27; 7.42–7.41 / 6.84–6.82; 3.28–3.24 / 2.74–2.70.

^{1}H{^{1}H} NOE (600 MHz, CD_2Cl_2) δ ^{1}H (ppm) / δ ^{1}H (ppm) = 7.85–7.82 / 7.59–7.54, 3.28–3.24, 2.74–2.70; 7.71–7.68 / 7.85–7.82, 7.59–7.54, 7.47–7.43, 7.30–7.27, 3.28–3.24, 2.74–2.70; 7.66–7.63 / 7.85–7.82, 7.71–7.68, 7.59–7.54; 7.59–7.54 / 7.85–7.82, 7.66–7.63, 7.71–7.68; 7.47–7.43 / 7.30–7.27; 7.42–7.41 / 6.84–6.82; 7.30–7.27 / 7.47–7.43; 3.28–3.24 / 7.85–

7.82, 7.71–7.68, 6.84–6.82, 2.74–2.70; 2.74–2.70 / 7.85–7.82, 7.71–7.68, 6.84–6.82, 3.28–3.24 [selected signals].

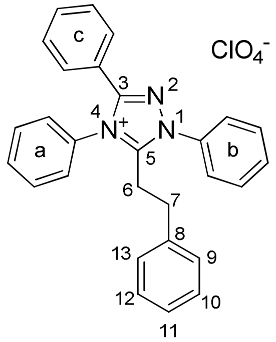
^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, CD$_2$Cl$_2$) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 7.85–7.82 / 126.6; 7.71–7.68 / 128.2; 7.66–7.63 / 132.5, 132.3; 7.59–7.54 /131.1, 130.7; 7.47–7.43 / 132.5, 130.1; 7.42–7.41 / 133.1; 7.30–7.27 / 129.3; 6.84–6.82 / 129.4; 3.28–3.24 / 26.5; 2.74–2.70 / 31.9.

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, CD$_2$Cl$_2$) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 7.85–7.82 / 135.3, 132.5, 126.6; 7.71–7.68 / 132.3; 7.66–7.63 / 128.2, 126.6; 7.59–7.54 / 135.3, 131.9, 131.3, 130.7; 7.47–7.43 / 154.5, 132.5, 129.3; 7.42–7.41 / 143.7, 133.1, 118.9 ; 7.30–7.27 / 130.1, 129.3, 123.1; 6.84–6.82 / 129.4, 111.5, 31.9 ; 3.28–3.24 / 154.5, 143.7, 31.9; 2.74–2.70 / 154.5, 143.7, 129.4, 26.5 [selected signals].

ATR-FTIR (cm^{-1}) 3068, 2227, 1552, 1503, 1453, 1085, 1082, 826, 765, 692, 622.

HRMS (ESI) calculated for $C_{29}H_{23}N_4^+$: 427.1917, found: 427.1924.

5-(Phenylethyl)-1,3,4-triphenyl-1*H*-1,2,4-triazol-4-ium perchlorate



3b

A flame-dried Schlenk flask was charged with 795.6 mg (2.0 mmol, 1 equiv) of the triazolium salt **1a** in an argon-filled glovebox. Using an overpressure of argon, 8 mL (0.25 M) of dry 1,4-dioxane were added. Afterwards, 299 µL (2.0 mmol, 1 equiv) DBU and 343 µL (312.5 mg, 3 mmol, 1.5 equiv) of styrene **2b** were added. The flask was sealed and placed in a preheated oilbath at 160 °C for 16 h. After cooling the now biphasic reaction mixture to room temperature, it was diluted with CH$_2$Cl$_2$ and filtered through a short pad of silica gel. All volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with CH$_2$Cl$_2$/MeOH (99:1 → 95:5) as eluents yielding a yellow solid. This solid was further purified by recrystallization from CH$_2$Cl$_2$/*n*-pentane, yielding **3b** (447.9 mg; 0.89 mmol; 45%) as a colorless solid.

TLC (CH$_2$Cl$_2$/MeOH 90:10) R_f = 0.45 (UV, KMnO$_4$).

^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ (ppm) = 7.80–7.79 (m, 2H, *o*-Ph^b), 7.65–7.61 (m, 2H, *p*-Ph^a & *p*-Ph^b), 7.60–7.57 (m, 4H, *o*-Ph^a & *m*-Ph^b), 7.55–7.52 (m, 2H, *m*-Ph^a), 7.47–7.44 (m, 3H, *o*-Ph^c & *p*-Ph^c), 7.31–7.29 (m, 2H, *m*-Ph^c), 7.21–7.15 (m, 3H, C10-H, C11-H, C12-H), 6.72–6.71 (m, 2H, C9-H, C13-H), 3.30 (t, *J* = 7.9 Hz, 2H, C6-H), 2.64 (t, *J* = 7.9 Hz, 2H, C7-H).

^{13}C NMR (151 MHz, CD$_2$Cl$_2$) δ (ppm) = 155.2 (C5), 154.3 (C3), 138.2 (C8), 135.4 (*i*-Ph^b), 132.5 (*p*-Ph^c), 132.4 (*p*-Ph^a), 132.2 (*p*-Ph^b), 131.9 (*i*-Ph^a), 131.2 (*m*-Ph^a), 130.7 (*o*-Ph^a), 130.1 (*o*-Ph^c), 129.5 (C10 & C12), 129.4 (*m*-Ph^c), 128.5 (C9 & C13), 128.2 (*m*-Ph^b), 127.8 (C11), 126.6 (*o*-Ph^b), 123.2 (*i*-Ph^c), 32.0 (C7), 27.3 (C6).

^{1}H, ^{1}H GCOSY (600 MHz, CD$_2$Cl$_2$) δ ^{1}H (ppm) / δ ^{1}H (ppm) = 7.80–7.79 / 7.65–7.61, 7.60–7.57; 7.65–7.61 / 7.80–7.79, 7.60–7.57, 7.55–7.52; 7.60–7.57 / 7.80–7.79, 7.65–7.61, 7.55–7.52; 7.55–7.52 / 7.65–7.61, 7.60–7.57; 7.47–7.44 / 7.31–7.29; 7.31–7.29 / 7.47–7.44; 7.21–7.15 / 6.72–6.71; 6.72–6.71 / 7.21–7.15; 3.30 / 2.64; 2.64 / 3.30.

^{1}H{^{1}H} NOE (500 MHz, CD$_2$Cl$_2$) δ ^{1}H (ppm) / δ ^{1}H (ppm) = 7.80–7.79 / 7.60–7.57, 3.30, 2.64; 7.65–7.61 / 7.80–7.79; 7.60–7.57 / 7.80–7.79; 7.47–7.44 / 7.60–7.57, 7.31–7.29; 7.31–7.29 / 7.47–7.44 / 6.72–6.71; 6.72–6.71 / 7.21–7.15, 3.30, 2.64; 3.30 / 7.80–7.79, 7.60–7.57, 6.72–6.71; 2.64 / 7.80–7.79, 7.60–7.57, 6.72–6.71, 3.30 [selected signals].

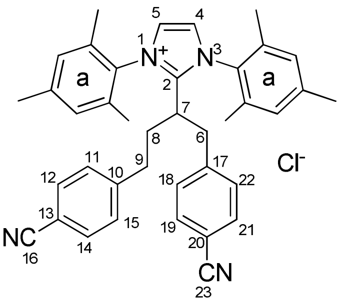
^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, CD$_2$Cl$_2$) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 7.80–7.79 / 126.6; 7.65–7.61 / 132.4, 132.2; 7.60–7.57 / 130.7, 128.2; 7.55–7.52 / 131.2; 7.47–7.44 / 132.5, 130.1; 7.31–7.29 / 129.4; 7.21–7.15 / 129.5, 127.8; 6.72–6.71 / 128.5; 3.30 / 27.3, 2.64 / 32.0.

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, CD$_2$Cl$_2$) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 7.80–7.79 / 135.4, 132.2, 126.6; 7.65–7.61 / 128.2, 126.6; 7.60–7.57 / 135.4, 132.4, 131.2; 7.55–7.52 / 132.4, 131.2; 7.47–7.44 / 154.3, 132.5, 130.1; 7.31–7.29 / 130.7, 129.5, 123.2; 7.21–7.15 / 138.2, 129.5, 128.5; 6.72–6.71 / 127.8, 32.0; 3.30 / 155.2, 138.2, 32.0; 2.64 / 155.2, 138.2, 128.5, 27.3 [selected signals].

ATR-FTIR (cm^{-1}) 3065, 1595, 1554, 1503, 1457, 1377, 1178, 1087, 987, 928, 759, 691, 622.

HRMS (ESI) calculated for $C_{28}H_{24}N_3^+$: 402.1965, found: 402.1967.

2-(1,2-Bis(4-cyanophenyl)ethyl)-1,3-dimesityl-1*H*-imidazol-3-ium chloride



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A flame-dried Schlenk flask was charged with 170.5 mg IMes·HCl **1b** (0.5 mmol, 1 equiv) in an argon-filled glovebox. Using standard Schlenk techniques, 2mL dry 1,4-dioxane were added. 75 µL of distilled DBU (0.5 mmol, 1equiv) and 193.7 mg (1.5 mmol, 3 equiv) of *p*-cyanostyrene **2a** were added via syringe, and the flask was sealed. The reaction was stirred in a preheated oilbath at 80 °C for 24 h. After this time, the reaction mixture was cooled to room temperature, transferred to a round-bottom flask, and all volatiles were removed *in vacuo*. The resulting orange oil was first purified by flash column chromatography (CH_2Cl_2/MeOH 95:5 → 90:10) and afterwards recrystallized from a toluene/chlorobenzene mixture yielding 245.7 mg (0.41 mmol, 82%) of a slightly yellow solid.

TLC (CH_2Cl_2/MeOH 90:10) R_f = 0.20 (UV, $KMnO_4$).

^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm) = 8.19 (s, 2H, C4-H & C5-H), 7.54–7.52(m, 2H, C19-H & C21-H), 7.43–7.42(m, 2H, C12-H & C14-H), 7.18 (s, 2H, *m*-Ph^a), 7.15 (s, 2H, *m*-Ph^a), 6.85–6.83 (m, 2H, C18-H & C22-H), 6.70–6.69 (m, 2H, C11-H & C15-H), 3.05 (dd, *J* = 14.0, 3.0 Hz, 1H, C6-H), 3.00 (ddt, *J* = 10.4, 4.8, 2.9 Hz, 1H, C7-H), 2.56 (dd, *J* = 13.8, 10.5 Hz, 1H, C6-H), 2.44 (s, 6H, Ph^a-CH_3), 2.24–2.14 (m, 1H, C9-H), 2.13 (s, 6H, Ph^a-CH_3), 2.11 (s, 6H, Ph^a-CH_3),2.07–2.04 (m, 1H, C9-H), 1.85–1.79 (m, 1H, C8-H), 1.65–1.59 (m, 1H, C8-H).

^{13}C NMR (151 MHz, CD_2Cl_2) δ (ppm) = 148.6 (C2), 144.8 (C10), 143.0 (Ph^a-C$_q$), 142.6 (C17), 135.0 (Ph^a-C$_q$), 134.9 (Ph^a-C$_q$), 133.3 (C19 & C21), 132.8 (C12 & C14), 131.0 (*m*-Ph^a), 130.9 (*m*-Ph^a), 130.5 (Ph^a-C$_q$), 129.9 (C18 & C22), 129.2 (C11 & C15), 126.9 (C4 & C5), 118.9 (C16), 118.5 (C23), 112.2 (C20), 111.1 (C13), 38.8 (C6), 37.6 (C7), 34.4 (C9), 32.9 (C8), 21.5 (Ph^a-CH_3), 18.5 (Ph^a-CH_3), 18.4 (Ph^a-CH_3).

^{1}H, ^{1}H GCOSY (600 MHz, CD_2Cl_2) δ ^{1}H (ppm) / δ ^{1}H (ppm) = 7.54–7.52 / 6.85–6.83; 7.43–7.42 / 6.70–6.69; 7.18 / 2.44, 2.13, 2.11; 7.15 / 2.44, 2.13, 2.11; 6.85–6.83 / 7.54–7.52; 6.70–6.69 / 7.43–7.42; 3.05 / 3.00; 3.00 / 3.05, 1.85–1.79, 1.65–1.59; 2.56 / 3.05, 3.00; 2.44 / 7.18, 7.15; 2.24–2.14 / 2.07–2.04, 1.85–1.79, 1.65–1.59; 2.13 / 7.18, 7.15; 2.11 / 7.18, 7.15; 2.07–2.04 / 2.24–2.14, 1.85–1.79, 1.65–1.59; 1.85–1.79 / 3.00, 2.24–2.14, 2.07–2.04, 1.65–1.59; 1.65–1.59 / 3.00, 2.24–2.14, 2.07–2.04, 1.85–1.79.

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, CD_2Cl_2) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 8.19 / 126.9; 7.54–7.52 / 133.3; 7.43–7.42 / 132.8; 7.18 / 130.9; 7.15 / 131.0; 6.85–6.83 / 129.9; 6.70–6.69 / 129.2; 3.05 / 38.8; 3.00 / 37.6; 2.56 / 38.8; 2.44 / 21.5; 2.24–2.14 / 34.4; 2.13 / 18.5; 2.11 / 18.4 ;2.07–2.04 / 34.4; 1.85–1.79 / 32.9; 1.65–1.59 / 32.9.

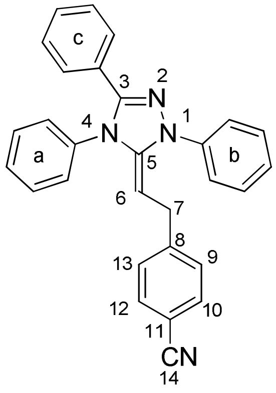
^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, CD_2Cl_2) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 8.19 / 148.6, 130.5; 7.54–7.52 / 142.6, 133.3, 118.5; 7.43–7.42 / 144.8, 132.8, 118.9; 7.18 / 131.0, 130.5, 21.5, 18.4; 7.15 / 130.9, 130.5, 21.5, 18.5; 6.85–6.83 / 129.9, 112.2, 38.8; 6.70–6.69 / 129.2, 111.1, 34.4; 3.05 / 148.6, 142.6, 129.9, 37.6, 32.9; 3.00 / 148.6, 142.6, 32.9; 2.56 / 148.6, 142.6, 129.9, 37.6, 32.9; 2.44 / 143.0, 131.0, 130.9; 2.24–2.14 / 144.8, 129.2, 37.6, 32.9; 2.13 / 134.9, 130.9, 130.5; 2.11 / 135.0, 131.0, 130.5; 2.07–2.04 / 144.8, 129.2, 37.6, 32.9; 1.85–1.79 / 148.6, 144.8, 38.8, 37.6, 34.4; 1.65–1.59 / 148.6, 144.8, 38.8, 37.6, 34.4 [selected signals].

ATR-FTIR (cm^{-1}) 3388, 2955, 2227, 1630, 1607, 1498, 1347, 1277, 1237, 1149, 1080, 1035, 858, 823, 700.

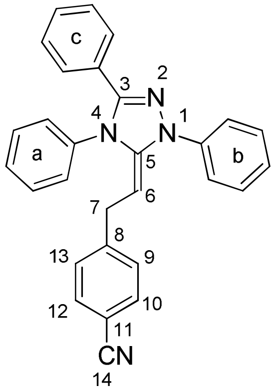
HRMS (ESI) calculated for $C_{39}H_{39}N_4^{+}$: 563.3169, found: 563.3163.

5. Formation of the deoxy Breslow intermediates

4-(2-(1,3,4-Triphenyl-1*H*-1,2,4-triazol-5(4*H*)-ylidene)ethyl)benzonitrile



(*Z*)-5a



(*E*)-5a

30.0 mg (0.06 mmol, 1equiv) of **3a** and 2.1 mg (0.09 mmol, 1.5 equiv) of NaH, which was washed free of paraffin oil, were dissolved in dry d$_8$-THF in an argon-filled glovebox. The solution was transferred to an NMR tube, and the tube was sealed and immediately submitted for measuring. The NMR spectra showed full conversion to an *E*/*Z*-mixture (1:3.2) of **5a**.

^{1}H NMR (400 MHz, d$_8$-THF)
(*Z*)-Isomer: δ (ppm) = 7.47–7.17(m, 15H, Ph^a, Ph^b, Ph^c), 7.13–7.09 (m, 4H, C9-H, C10-H, C12-H, C13-H), 3.44 (t, J = 7.4 Hz, 1H, C6-H), 3.06 (d, J = 7.4 Hz, 2H, C7-H). **(*E*)-Isomer:** δ (ppm) = 7.65–7.62 (m, 2H, *o*-Ph^b), 7.47–7.17 (m, 13H, Ph^a, *m*-Ph^b & *p*-Ph^b, Ph^c), 7.13–7.09 (m, 4H, C9-H, C10-H, C12-H, C13-H), 4.18 (t, J = 8.0 Hz, 1H, C6-H), 2.90 (d, J = 8.0 Hz, 2H, C7-H).

^{13}C NMR (101MHz, d$_8$-THF) δ (ppm) = 150.5 ($C_{q,}$ (*E*)-C5), 150.0 (C_q, (*Z*)-C5), 149.6 (C_q, (*E*)-C3), 149.3 (C_q, (*Z*)-C3), 147.6 (C_q, (*Z*)-C8), 146.2 (C_q, (*E*)-C8), 143.1 (C_q), 142.1 (C_q), 139.4 (C_q), 138.4 (C_q), 132.6 (CH), 132.6 (CH), 131.1 (CH), 131.0 (CH), 130.4 (CH), 130.4 (CH), 130.2 (CH), 130.1 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.5 (CH), 129.4 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.7 (CH), 128.3 (C_q), 128.2 (C_q),125.6 (CH), 124.9 (CH), 124.0 (CH), 122.8 (CH), 122.5 (CH), 119.6 (C_q, (*Z*)-C14), 119.5 (C_q, (*E*)-C14), 110.6 (C_q,(*Z*)-C11), 110.4 (C_q, (*E*)-C11), 67.1 (CH, (*Z*)-C6), 64.7 (CH, (*E*)-C6), 34.1 ($CH_{2,}$ (*Z*)-C7), 31.4 (CH_2, (*E*)-C7).

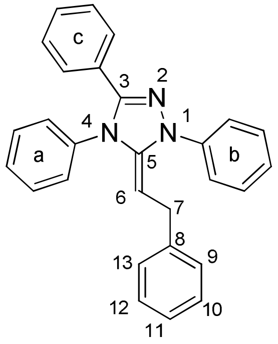
^{1}H, ^{1}H GCOSY (400 MHz, d$_8$-THF) δ ^{1}H (ppm) / δ ^{1}H (ppm) = 7.65–7.62 / 7.47–7.17; 7.47–7.17 / 7.65–7.62, 7.13–7.09; 7.13–7.09 / 7.47–7.17; 4.18 / 2.90; 3.44 / 3.06; 3.06 / 3.44; 2.90 / 4.18.

^{1}H{^{1}H} NOE (600 MHz, d$_8$-THF) δ ^{1}H (ppm) / δ ^{1}H (ppm) = 7.65–7.62 / 7.47–7.17; 7.47–7.17 / 7.13–7.09; 7.13–7.09 / 7.47–7.17; 4.18 / 7.65–7.62; 3.44 / 7.47–7.17, 7.13–7.09; 3.06 / 7.47–7.17, 7.13–7.09, 3.44; 2.90 / 4.18 [selected signals].

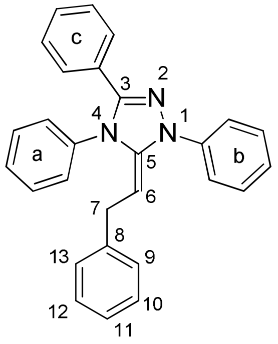
^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, d$_8$-THF) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 7.65–7.62 / 122.5; 7.47–7.17 / 132.6, 131.1, 131.0, 130.4, 130.4, 130.2, 130.1, 129.8, 129.7, 129.5, 129.4, 129.2, 129.1, 129.0, 128.7, 124.0, 122.8; 7.13–7.09 / 132.6, 129.8, 125.6, 124.9; 4.18 / 64.7; 3.44 / 67.1; 3.06 / 34.1; 2.90 / 31.4.

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, d$_8$-THF) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 7.65–7.62 / 132.6, 131.0, 129.9; 7.13–7.09 / 129.8, 124.0, 110.6, 110.4; 4.18 / 150.5; 3.44 / 150.0, 149.3; 3.06 / 150.0, 147.6, 129.7, 67.1; 2.90 / 150.5, 146.2, 129.5, 64.7 [selected signals].

1,3,4-Triphenyl-5-(2-phenylethylidene)-4,5-dihydro-1*H*-1,2,4-triaziole



(*Z*)-5b



(*E*)-5b

30.0 mg (0.06 mmol, 1 equiv) of **3b** and 2.2 mg (0.09 mmol, 1.5 equiv) of NaH, which was washed free of paraffin oil, were dissolved in dry d$_8$-THF in an argon-filled glovebox. The solution was transferred to an NMR tube, and the tube was sealed and immediately submitted for measuring. The NMR spectra showed full conversion to an *E*/*Z*-mixture (1:2.5) of **5b**.

^{1}H NMR (600 MHz, d$_8$-THF)
(*Z*)-Isomer: δ (ppm) = 7.45–6.94 (m, 20H, Ph^a, Ph^b, Ph^c, C9-H, C10-H, C11-H, C12-H, C13-H), 3.52 (t, *J* = 7.2 Hz, 1H, C6-H), 2.98 (d, *J* = 7.2 Hz, 2H, C7-H). **(*E*)-Isomer:** δ (ppm) = 7.64–7.61 (m, 2H, *o*-Ph^b), 7.45–6.94 (m, 18H, Ph^a, *m*-Ph^b & *p*-Ph^b, Ph^c, C9-H,C10-H, C11-H, C12-H, C13-H), 4.22 (t, *J* = 7.6 Hz, 1H, C6-H), 2.81 (d, *J* = 7.6 Hz, 2H, C7-H).

^{13}C NMR (75 MHz, d$_8$-THF) δ (ppm) = 149.7 (C$_q$), 149.3 (C$_q$), 146.7 (C$_q$), 145.4 (C$_q$), 144.6 (C$_q$, (*E*)-C5), 144.1 (C$_q$, (*Z*)-C5), 143.5 (C$_q$), 142.3 (C$_q$), 139.8 (C$_q$), 138.6 (C$_q$), 131.1 (CH), 130.9 (CH), 130.3 (CH), 130.3 (CH), 130.1 (CH), 129.7 (CH), 129.5 (CH), 129.3 (CH), 129.2 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.8 (CH), 128.8 (CH), 128.7 (CH), 128.7 (CH), 128.4 (C$_q$), 128.3 (C$_q$), 126.2 (CH), 125.0 (CH), 124.5 (CH), 123.4 (CH), 122.1 (CH), 69.9 (CH, (*Z*)-C6), 67.5 (CH, (*E*)-C6), 34.4 (CH$_2$, (*Z*)-C7), 31.4 (CH$_2$, (*E*)-C7).

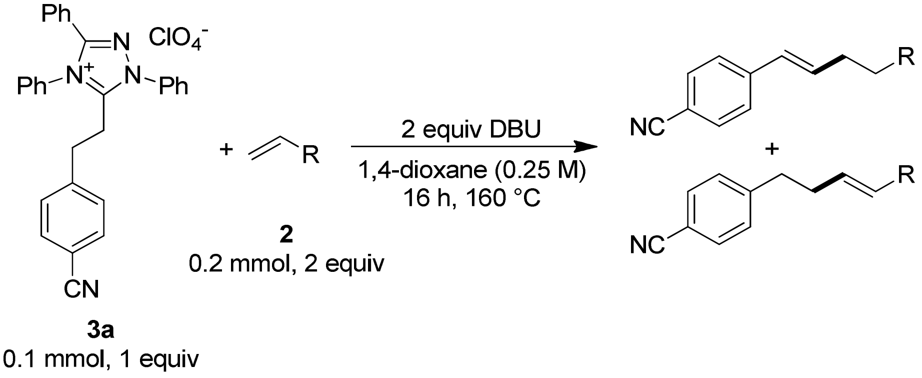
^{1}H, ^{1}H GCOSY (600 MHz, d$_8$-THF) δ ^{1}H (ppm) / δ ^{1}H (ppm) = 7.64–7.61 / 7.45–6.94; 7.45–6.94 / 7.64–7.61; 4.22 / 2.81; 3.52 / 2.98; 2.98 / 3.52; 2.81/ 4.22.

^{1}H{^{1}H} NOE (600 MHz, d$_8$-THF) δ ^{1}H (ppm) / δ ^{1}H (ppm) = 7.64–7.61 / 7.45–6.94, 4.22; 7.45–6.94 / 3.52, 2.98; 4.22 / 7.64–7.61, 2.81; 3.52 / 2.98; 2.98 / 7.45–6.94, 3.52; 2.81 / 4.22 [selected signals].

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, d$_8$-THF) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 7.64–7.61 / 122.1; 7.45–6.94 / 131.1, 130.9, 130.3, 130.3, 130.1, 129.7, 129.5, 129.3, 129.2, 129.2, 129.1, 129.0, 129.0, 128.9, 128.8, 128.8, 128.8, 128.7, 128.7, 126.2, 125.0, 124.5, 123.4; 4.22 / 67.6; 3.52 / 69.9; 2.98 / 34.3; 2.81/ 31.4.

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, d$_8$-THF) δ ^{1}H (ppm) / δ ^{13}C (ppm) = 7.64–7.61 / 124.5, 122.1; 4.22 / 144.6; 3.52 / 144.1; 2.98 / 146, 7, 144.1, 128.9, 69.9; 2.81/ 144.6, 128.8, 67.5 [selected signals].

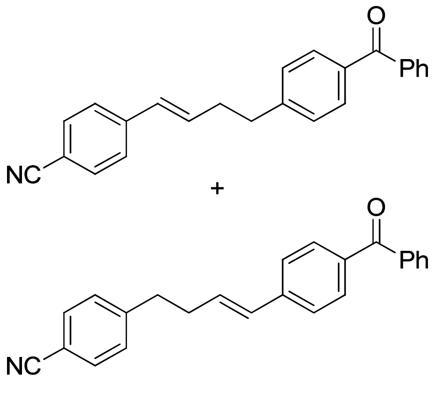
6. Reactions of deoxy Breslow intermediate **3a**



General procedure for the reaction of the NHC-styrene-adduct **3a** with other styrenes:

52.7 mg (0.10 mmol, 1 equiv) **3a** was added to a flame-dried Schlenk tube inside an argon-filled glovebox. Using standard Schlenk techniques, 0.4 mL of dry 1,4-dioxane (0.25 M) and 30 µL (0.20 mmol, 2 equiv) of distilled DBU were added to the flask. The styrene **2** (0.20 mmol, 2 equiv) was added with a syringe to the reaction, and the flask was sealed. The sealed flask was heated to 160 °C for 16 h. After this time, the reaction mixture was transferred to a round-bottom flask, and all volatiles were removed *in vacuo*. The residue was then purified by flash column chromatography.

(*E*)-4-(4-(4-Benzoylphenyl)but-1-en-1-yl)benzonitrile and (*E*)-4-(4-(4-benzoylphenyl)but-3-en-1-yl)benzonitrile



6a

Prepared following the general procedure starting from phenyl-(4-vinylphenyl)-methanone **2c** (41.7 mg, 0.2 mmol). Purification by flash column chromatography (*n*-pentane/ethyl acetate

90:10) yielded **6a** (17.4 mg, 0.05 mmol, 52%, 1:1 mix of the two double-bond regioisomers) as a colorless solid.

TLC (*n*-pentane/ethyl acetate 80:20) R_f = 0.40 (UV, $KMnO_4$).

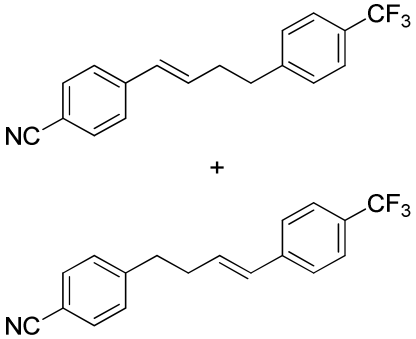
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.80–7.75 (m, 4H), 7.61–7.56 (m, 3H), 7.51–7.45 (m, 2H), 7.42–7.38 (m, 2H), 7.34–7.31 (m, 2H), 6.48–6.30 (m, 2H), 2.92–2.86 (m, 2H), 2.65–2.55 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 196.6 (C_q), 196.3 (C_q), 147.1 (C_q), 146.4 (C_q), 142.1 (C_q), 141.5 (C_q), 137.9 (C_q), 137.9 (C_q), 136.2 (C_q), 135.7 (C_q), 133.6 (CH), 132.5 (CH), 132.4 (CH), 132.4 (CH), 132.4 (CH), 131.8 (CH), 130.8 (CH), 130.6 (CH), 130.5 (CH), 130.1 (CH), 130.1 (CH), 129.6 (CH), 129.4 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 126.6 (CH), 125.9 (CH), 119.2 (C_q), 119.2 (C_q), 110.4 (C_q), 110.1 (C_q), 35.8 (CH_2), 35.6 (CH_2), 34.6 (CH_2), 34.5 (CH_2).

ATR-FTIR (cm^{-1}) 3033, 2942, 2227, 1646, 1599, 1503, 1449, 1412, 1317, 1276, 1175, 969, 923, 740, 702.

HRMS (ESI) calculated for $C_{24}H_{19}NOH^+$: 338.1539, found: 338.1534,
calculated for $C_{24}H_{19}NONa^+$: 360.1359, found: 360.1352.

(*E*)-4-(4-(4-(Trifluoromethyl)phenyl)but-1-en-1-yl)benzonitrile and (*E*)-4-(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)benzonitrile



6b

Prepared following the general procedure starting from *p*-trifluoromethylstyrene **2h** (30 µL, 0.20 mmol). Purification by flash column chromatography (*n*-pentane/ethyl acetate 95:5) yielded **6b** (13.1 mg, 0.04 mmol, 43%, 1:1 mix of the two double-bond regioisomers) as a brown solid, which still contains traces of a third isomer of **6b** (about 5%).

TLC (*n*-pentane/ethyl acetate 90:10) R_f = 0.32 (UV, $KMnO_4$).

^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm) = 7.60–7.54 (m, 4H), 7.40–7.38 (m, 2H), 7.32–7.31 (m, 2H), 6.43–6.27 (m, 2H), 2.89–2.86 (m, 2H), 2.61–2.55 (m, 2H).

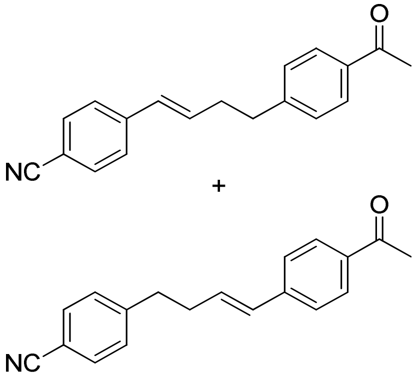
^{19}F NMR (564 MHz, CDCl$_3$) δ (ppm) = –62.39 (s, 3F, isomer A), –63.51 (s, 3F, isomer B).

^{13}C NMR (151 MHz, CDCl$_3$) δ (ppm) = 147.1 (C$_q$), 145.4–145.3 (m, C$_q$), 142.0 (C$_q$), 140.9–140.8 (m, C$_q$), 133.4 (CH), 132.5 (CH),132.4 (CH), 131.6 (CH), 130.1 (CH), 129.7 (CH), 129.4 (CH), 128.9 (CH), 126.6 (CH), 126.3 (CH), 110.5 (C$_q$), 110.1 (C$_q$), 125.6 (q, J = 3.8 Hz, CH), 125.5 (q, J = 3.8 Hz, CH), 119.1 (C$_q$), 119.1 (C$_q$), 35.8 (CH$_2$), 35.4 (CH$_2$), 34.6 (CH$_2$), 34.3 (CH$_2$).(12)

ATR-FTIR (cm^{-1}) 3043, 2936, 2220, 1650, 1604, 1502, 1453, 1414, 1322, 1166, 1108, 1065, 1017, 968, 847, 804, 597.

HRMS (Orbitrap) calculated for $C_{18}H_{14}F_3Na^+$: 324.09706, found: 324.09685.

(*E*)-4-(4-(4-Acetylphenyl)but-1-en-1-yl)benzonitrile and (*E*)-4-(4-(4-acetylphenyl)but-3-en-1-yl)benzonitrile



6c

Prepared following the general procedure starting from 1-(4-vinylphenyl)ethanone **2k** (29.2 mg, 0.2 mmol). Purification by flash column chromatography (*n*-pentane/ethyl acetate 90:10) yielded **6c** (15.6 mg, 0.06 mmol, 56%, 1:1 mix of the two double-bond regioisomers) as a yellow solid.

TLC (*n*-pentane/ethyl acetate 80:20) R_f = 0.29 (UV, KMnO$_4$).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.91–7.88 (m, 2H), 7.60–7.56 (m, 2H), 7.39–7.37 (m, 2H), 7.32–7.29 (m, 2H), 6.45–6.30 (m, 2H), 2.89–2.85 (m, 2H), 2.62–2.55 (m, 5H).

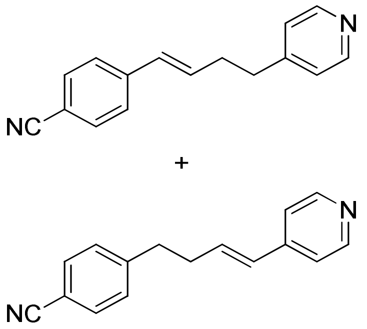
^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 197.9 (C$_q$), 197.7 (C$_q$), 147.1 (C$_q$), 147.1 (C$_q$), 142.1 (C$_q$), 142.0 (C$_q$), 135.9 (C$_q$), 135.4 (C$_q$), 133.6 (CH), 132.5 (CH), 132.4 (CH), 132.0 (CH), 130.5 (CH), 129.7 (CH), 129.4 (CH), 128.9 (CH), 128.8 (CH), 128.8 (CH), 126.6 (CH), 126.1

(CH), 119.2 (C_q), 119.2 (C_q), 110.4 (C_q), 110.1 (C_q), 35.8 (CH_2), 35.6 (CH_2), 34.5 (CH_2), 34.4 (CH_2), 26.7 (CH_3), 26.7 (CH_3).

ATR-FTIR (cm^{-1}) 3038, 2921, 2226, 1676, 1600, 1411, 1360, 1267, 1175, 1015, 966, 798, 601, 552.

HRMS (ESI) calculated for $C_{19}H_{17}NONa^+$: 298.1202, found: 298.1203.

(*E*)-4-(4-(Pyridin-4-yl)but-1-en-1-yl)benzonitrile and (*E*)-4-(4-(pyridin-4-yl)but-3-en-1-yl)benzonitrile



6d

Prepared following the general procedure starting from 4-vinylpyridine **2d** (22 µL, 0.20 mmol). Purification by flash column chromatography (CH_2Cl_2/MeOH 99:1) yielded **6d** (14.7 mg, 0.06 mmol, 63%, 1:1 mix of the two double-bond regioisomers) as a colorless solid.

TLC (CH_2Cl_2/MeOH 9:1) $R_f = 0.42$ (UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.52–8.51 (m, 2H, both isomers), 7.60–7.56 (m, 2H, both isomers), 7.39–7.37 (m, 2H, isomer A), 7.32–7.30 (m, 2H, isomer B), 7.19–7.17 (m, 2H, isomer B), 7.15–7.14 (m, 2H, isomer A), 6.48–6.30 (m, 2H, both isomers), 2.89–2.85 (m, 2H, isomer B), 2.83–2.79 (m, 2H, isomer A), 2.62–2.55 (m, 2H, both isomers).

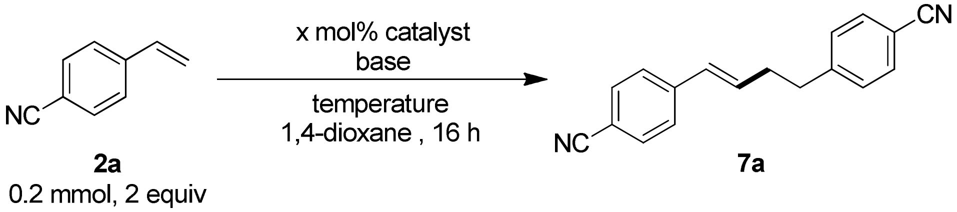
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 150.3 (C_q), 150.0 (CH), 149.9 (CH), 146.9 (C_q), 144.9 (C_q), 141.9 (C_q), 134.1 (CH), 133.0 (CH), 132.5 (CH), 132.4 (CH), 129.9 (CH), 129.4 (CH), 129.2 (CH), 126.6 (CH), 124.0 (CH), 120.8 (CH), 119.1 (C_q), 119.1 (C_q), 110.6 (C_q), 110.2 (C_q), 35.6 (CH_2), 34.8 (CH_2), 34.3 (CH_2), 33.7 (CH_2).

ATR-FTIR (cm^{-1}) 3033, 2220, 1595, 1503, 1416, 1176, 962, 852, 806, 696, 551.

HRMS (ESI) calculated for $C_{16}H_{14}N_2H^+$: 235.1230, found: 235.1232.

7. Optimization of the reaction conditions for the catalytic dimerization

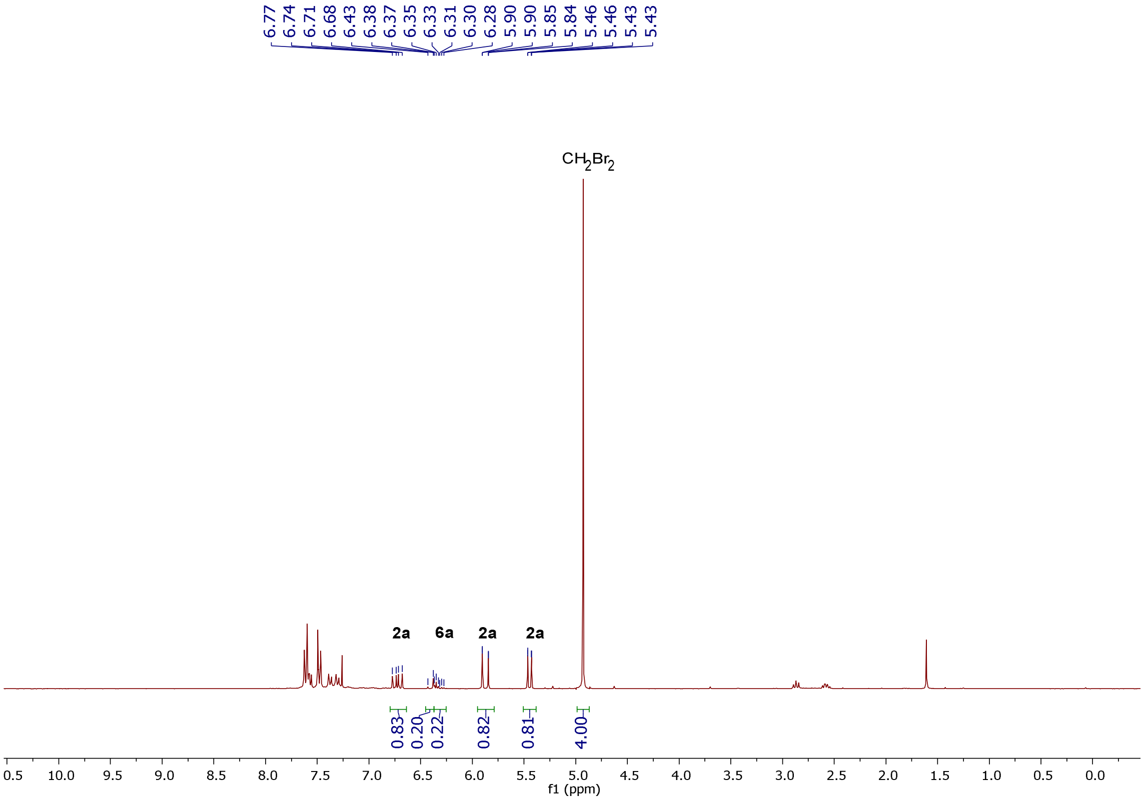
The optimization of the dimerization of *p*-cyanostyrene **2a** was performed following the general reaction:



A flame-dried Schlenk tube was charged with the azolium salt **1** (5, 10, or 20 mol%) in an argon-filled glovebox. Solid bases were also stored in the glovebox and added to the azolium salt. Dry 1,4-dioxane (0.4 mL, 0.5 M) was added via a syringe outside of the glovebox using a positive pressure of argon. Styrene **2a** (2 equiv, 25.8 mg, 0.20 mmol) was added with a syringe. Liquid bases were also added with a syringe. The reaction was sealed and stirred for 16 h at the indicated temperature in a preheated oilbath. After the reaction time, the flask was cooled to room temperature and the reaction mixture was diluted with CH_2Cl_2 and filtered over a short pad of silica gel. The filtered solution was concentrated under reduced pressure. The residue was dissolved in $CDCl_3$, and 14 µL (0.20 mmol, 2 equiv) of CH_2Br_2 were added as internal standard.

The yield was determined by ^{1}H NMR spectroscopy using the following characteristic peaks:

Compound	Characteristic peaks
2a	6.72 (dd, *J* = 17.6 Hz, 10.9 Hz, 1H), 5.87 (dd, *J* = 17.6 Hz, 0.6 Hz, 1H), 5.45 (dd, *J* = 10.9 Hz, 0.6 Hz, 1H)
7a	6.40 (d, *J* = 16.0 Hz, 1H), 6.33 (dt, *J* = 15.9, 5.8 Hz, 1H)



Using the conditions of the acrylate umpolung,(13) no yield was observed (Entry 1), but a simple increase in the temperature to 120 °C (Entry 2) or 140 °C (Entry 3) gave the desired product **7a**. As two equivalents of the starting material are added to the reaction, as this reaction is a dimerization, the percentages of product and starting material add up to more than 100%.

Entry	**Catalyst**	**Base**	**Temperature**	**2a** (%)	**7a** (%)
1	10 mol% **1a**	1 equiv DBU	80 °C	148	0
2	10 mol% **1a**	1 equiv DBU	120 °C	82	21
3	10 mol% **1a**	1 equiv DBU	140 °C	13	77

Following these encouraging results, we investigated the influence of the amount of base. At 120 °C, doubling the amount of base led to a substantial increase in yield (Entry 4), but at 140 °C not much difference was observed (Entry 5).

Entry	**Catalyst**	**Base**	**Temperature**	**2a** (%)	**7a** (%)
4	10 mol% **1a**	2 equiv DBU	120 °C	0	81
5	10 mol% **1a**	2 equiv DBU	140 °C	11	78

Furthermore, we hoped to increase the yield by screening different NHC precursors. The two NHCs that were successful in the stoichiometric reaction were also able to catalyze the homodimerization of *p*-cyanostyrene **2a** (Entry 6 and 7). IMes·HCl **1b** gave a yield of 61%, which could not be increased by changing the aryl substituents to the more electron-rich 2,6-dimethoxyphenyl-group in **1c** (Entry 8, 0%) or to unsubstituted phenyl groups in **1d** (Entry 9, 5%). Hence, we tried variations of the triazolium-derived NHCs, but again no improvement could be observed, as the salts **1e** and **1f** (Entry 10 and 11, both 0%) both failed as catalysts. Therefore, in line with the results of the acrylate umpolung,(13) NHC **1a** is unique in catalyzing the Michael umpolung. The more electron-rich variations of **1a**, which were introduced by Fu et al. for the intramolecular Michael umpolung,(11) gave higher conversion than **1a**. The variation with two electron-rich methoxy groups **1h** gave an improved yield of 83% (Entry 12), while the variation with three of these groups (**1g**) gave full conversion to the desired product **7a** (Entry 13).

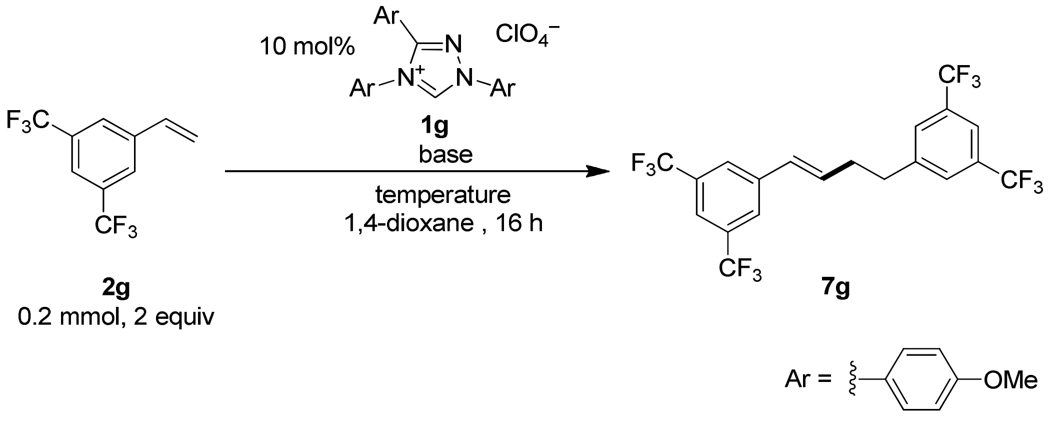
Entry	Catalyst	Base	Temperature	**2a** (%)	**7a** (%)
6	10 mol% **1a**	2 equiv DBU	140 °C	11	78
7	10 mol% **1b**	2 equiv DBU	140 °C	87	61
8	10 mol% **1c**	2 equiv DBU	140 °C	128	0
9	10 mol% **1d**	2 equiv DBU	140 °C	153	5
10	10 mol% **1e**	2 equiv DBU	140 °C	84	0
11	10 mol% **1f**	2 equiv DBU	140 °C	60	0
12	10 mol% **1h**	2 equiv DBU	140 °C	0	83
13	10 mol% **1g**	2 equiv DBU	140 °C	0	99

Lowering the catalyst loading to 5 mol% was not possible, even with a longer reaction time of 65 h, as only a reduced yield of 87% was obtained (Entry 14). Furthermore, the reaction time of 16 h could not been reduced, as the product was only obtained in 88% yield after 8 h with 10 mol% of catalyst (Entry 15). Hence, the conditions of Entry 13 were kept for the investigation of the scope of the dimerization.

Entry	Catalyst	Base	Temperature	**2a** (%)	**7a** (%)
14 65 h reaction time	5 mol% **1g**	2 equiv DBU	140 °C	0	87
15 8 h reaction time	10 mol% **1g**	2 equiv DBU	140 °C	11	88

When using these optimized conditions for other styrenes, we realized that these conditions were not optimal for less electron-poor styrenes, such as 3,5-bis-(trifluoromethyl)-styrene **2g**.

Using the optimized conditions, only 41% of the product **7g** was obtained (Entry 16). Hence, a further optimization of the reaction conditions was carried out with **1g** as catalyst.



The following characteristic peaks were used for the optimization of the dimerization of **7g**:

Compound	Characteristic peaks
2g	6.78 (dd, *J* = 17.6 Hz, 10.9 Hz, 1H), 5.92 (d, *J* = 17.6 Hz, 1H), 5.50 (d, *J* = 10.9, 1H)
7g	6.47 (d, *J* = 16.0 Hz, 1H), 6.37 (dt, *J* = 15.8, 6.3 Hz, 1H)

Using strong bases, such as KO^{t}Bu (Entry 17) or KHMDS (Entry 20) did not yield any product, and the use of other amine bases, such as Hünig's base (Entry 19), also gave no conversion to the product. Using weak inorganic bases such as K_3PO_4 gave a low yield of 10% (Entry 18), therefore, DBU was found to be the most suitable base.

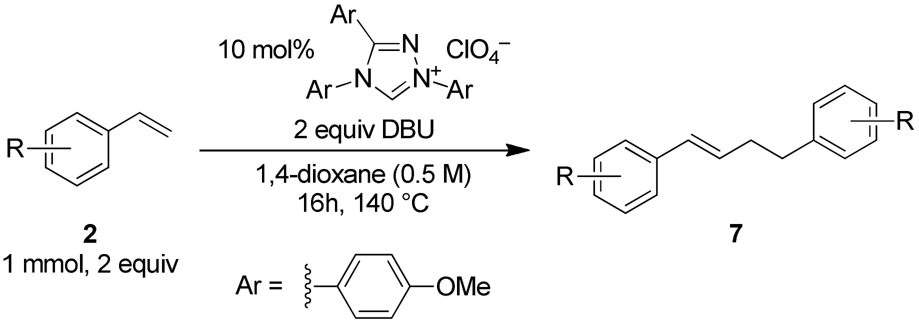
Entry	**Base**	**Temperature**	**Concentration of 2f**	**2g** (%)	**7g** (%)
16	2 equiv DBU	140 °C	0.5 M	7	41
17	2 equiv KO^{t}Bu	140 °C	0.5 M	10	0
18	2 equiv K_3PO_4	140 °C	0.5 M	13	10
19	2 equiv NEt(^{i}Pr)$_2$	140 °C	0.5 M	15	0
20	2 equiv KHMDS	140 °C	0.5 M	0	0

A further increase in the reaction temperature to 160 °C was beneficial, and the yield increased to 66% (Entry 21). This yield could further be increased by using less solvent, and running the reaction at a higher concentration (Entry 21). These harsher conditions (160 °C and 2 M instead of 0.5 M) were then used for the more challenging substrates (cf. Table 3 in the paper).

Entry	**Base**	**Temperature**	**Concentration of 2f**	**2g** (%)	**7g**(%)
21	2 equiv DBU	160 °C	0.5 M	0	66
22	2 equiv DBU	160 °C	2 M	0	77

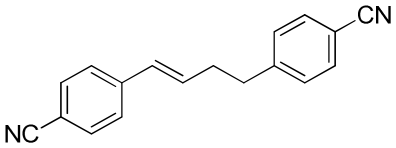
8. Synthesis and characterization of the products

General procedure for the homocoupling of styrenes



The triazolium salt **1g** (24.4 mg, 0.05 mmol, 0.1 equiv) was added to a flame dried Schlenk flask in an argon-filled glovebox. Using standard Schenk techniques, dry 1,4-dioxane (2 mL, 0.5 M), DBU (149 µL, 1.0 mmol, 2.0 equiv) and the styrene **2** (1.0 mmol, 2.0 equiv) were added to the flask. The flask was sealed, and the reaction mixture was stirred for 16 h at 140 °C in a preheated oil bath. Afterwards, the reaction was cooled to room temperature, diluted with CH_2Cl_2 and filtered through a short pad of silica gel. Removal of all volatiles at reduced pressure yielded the crude product, which was purified by flash column chromatography on silica gel to obtain the desires products.

(*E*)-4,4`-(But-1-ene-1,4-diyl)dibenzonitrile



7a

Prepared following the general procedure starting from *p*-cyanostyrene **2a** (129.2 mg, 1.0 mmol). Purification by flash column chromatography (*n*-pentane/ethyl acetate 80:20) yielded **7a** (113.0 mg, 0.44 mmol, 87%) as a colorless solid.

TLC (*n*-pentane/ethyl acetate 80:20) $R_f = 0.25$ (UV, $KMnO_4$).

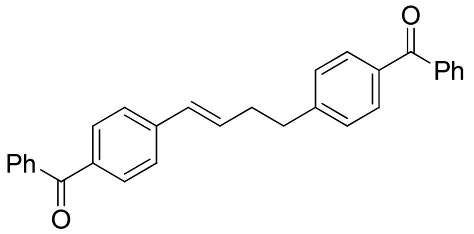
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.60–7.54 (m, 4H), 7.39–7.35 (m, 2H), 7.33–7.28 (m, 2H), 6.40 (d, J = 16.0 Hz, 1H), 6.33 (dt, J = 15.9, 5.8 Hz, 1H), 2.89–2.84 (m, 2H), 2.61–2.54 (m, 2H).

^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) = 144.9 (C$_q$), 141.8 (C$_q$), 133.0 (CH), 132.5 (CH), 132.5 (CH), 129.9 (CH), 129.3 (CH), 126.6 (CH), 119.1 (C$_q$), 119.1 (C$_q$), 110.4 (C$_q$), 110.1 (C$_q$), 35.6 (CH$_2$), 34.3 (CH$_2$).

ATR-FTIR (cm^{-1}) 2933, 2219, 1650, 1604, 1506, 1413, 1177, 1082, 967, 854, 824, 806, 697, 622.

HRMS (ESI) calculated for $C_{18}H_{14}N_2Na^+$: 281.1049, found: 281.1052.

(*E*)-4,4`-(But-1-ene-1,4-diyl)dibenzophenone



7c

Prepared following the general procedure starting from phenyl-(4-vinylphenyl)-methanone **2c** (208.3 mg, 1.0 mmol). Purification by flash column chromatography (*n*-pentane/ethyl acetate 95:5 → 80:20) yielded **7c** (175.9 mg, 0.42 mmol, 84%) as a colorless solid.

TLC (*n*-pentane/ethyl acetate 90:10) R_f= 0.19 (UV, KMnO$_4$).

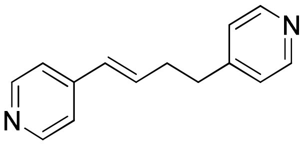
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.81–7.76 (m, 8H), 7.61–7.56 (m, 2H), 7.50–7.41 (m, 6H), 7.35–7.32 (m, 2H), 6.49 (d, J = 16.0 Hz, 1H), 6.41 (dt, J = 15.8, 6.4 Hz, 1H), 2.93–2.89 (m, 2H), 2.65–2.60 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 196.6 (C$_q$), 196.3 (C$_q$), 146.7 (C$_q$), 141.8 (C$_q$), 137.9 (C$_q$), 137.9 (C$_q$), 136,1 (C$_q$), 135.6 (C$_q$), 132.5 (CH), 132.4 (CH), 132.4 (CH), 130.8 (CH), 130.6 (CH), 130.2 (CH),130.1 (CH), 130.0 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 125.9 (CH), 35.7 (CH$_2$), 34.7 (CH$_2$).

ATR-FTIR (cm^{-1}) 3051, 2909, 1644, 1596, 1443, 1410, 1278, 1178, 1147, 1074, 967, 937, 921, 850, 735, 691, 623.

HRMS (ESI) calculated for $C_{30}H_{24}O_2Na^+$: 439.1669, found: 439.1670.

(*E*)-4,4`-(But-1-ene-1,4-diyl)dipyridine



7d

Prepared following a modified procedure starting from 4-vinylpyridine **2d** (108 µL, 1.0 mmol). The reaction was stirred at 160 °C for 16 h instead of at 140 °C and with only 0.5 mL of 1,4-dioxane (2 M). Purification by flash column chromatography (CH_2Cl_2 /methanol 99:1 → 96:4) yielded **7d** (95.3 mg, 0.45 mmol, 91%) as a colorless solid.

TLC (CH_2Cl_2/methanol 90:10) R_f = 0.30 (UV, $KMnO_4$).

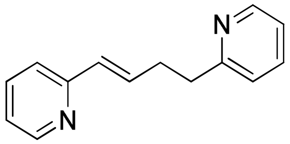
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.51–8.48 (m, 4H), 7.16–7.10 (m, 4H), 6.42 (dt, J = 15.8, 6.40 Hz, 1H), 6.31 (d, J = 16.0 Hz, 1H), 2.81–2.76 (m, 2H), 2.60–2.52 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 150.2 (CH), 150.1 (C_q), 149.9 (CH), 144.7 (C_q), 133.9 (CH), 129.1 (CH), 123.9 (CH), 120.7 (CH), 34.6 (CH_2), 33.5 (CH_2).

ATR-FTIR (cm^{-1}) 1590, 1552, 1499, 1455, 1379, 2085, 1079, 758, 691.

HRMS (ESI) calculated for $C_{14}H_{14}N_2H^+$: 211.1230, found: 211.1234.

(*E*)-2,2`-(But-1-ene-1,4-diyl)dipyridine



7e

Prepared following a modified procedure starting from 2-vinylpyridine **2e** (108 µL, 1.0 mmol). The reaction was stirred at 160 °C for 16 h instead of at 140 °C and with only 0.5 mL of 1,4-dioxane (2 M). Purification by flash column chromatography (CH_2Cl_2/ methanol 97.5:2.5) yielded **7e** (68.0 mg, 0.32 mmol, 65%) as a brown oil, which still contained an inseparable isomer of **7e** (about 5%).

TLC (CH_2Cl_2/methanol 90:10) R_f = 0.40 (UV, $KMnO_4$).

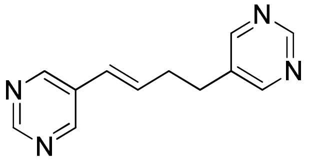
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.53–8.48 (m, 2H), 7.59–7.53 (m, 2H), 7.20–7.14 (m, 2H), 7.10–7.03 (m, 2H), 6.77 (dt, J = 15.7, 6.9 Hz, 1H), 6.50 (dt, J = 15.7, 1.5 Hz, 1H), 2.97 (dd, J = 9.0, 6.6 Hz, 2H), 2.70 (dtd, J = 8.8, 6.9, 1.5 Hz, 2H).

^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) = 161.2 (C$_q$), 155.9 (C$_q$), 149.5 (CH), 149.4 (CH), 136.5 (CH), 136.4 (CH), 134.6 (CH), 130.7 (CH), 123.0 (CH), 121.7 (CH), 121.2 (CH), 121.2 (CH), 37.8 (CH$_2$), 32.9 (CH$_2$).

ATR-FTIR (cm^{-1}) 3053, 3005, 2925, 2851, 1653, 1585, 1564, 1470, 1432, 1300, 1148, 1090, 1051, 992, 970, 831, 751, 694, 621.

HRMS (ESI) calculated for $C_{14}H_{14}N_2H^+$: 211.1230, found: 211.1238,
calculated for $C_{14}H_{14}N_2Na^+$: 233.1049, found: 233.1059.

(*E*)-5,5'-(But-1-ene-1,4-diyl)dipyrimidine



7f

Prepared following a modified procedure starting from 5-vinylpyrimidine **2f** (106.1 mg, 1.0 mmol). The reaction was stirred at 160 °C for 16 h instead of at 140 °C and with only 0.5 mL of 1,4-dioxane (2 M). Purification by flash column chromatography (CH$_2$Cl$_2$/methanol 99:1 → 95:5) yielded **7f** (35.8 mg, 0.17 mmol, 34%) as a brown solid, which still contained an inseparable isomer of **7f** (about 5%).

TLC (CH$_2$Cl$_2$/methanol 90:10) $R_f = 0.33$ (UV, KMnO$_4$).

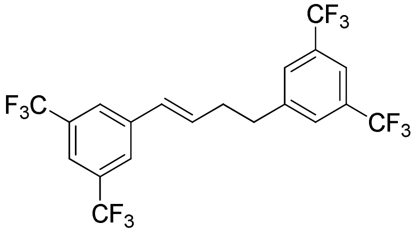
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 9.07–9.03 (m, 2H), 8.65–8.54 (m, 4H), 6.39–6.29 (m, 2H), 2.84–2.80 (m, 2H), 2.63–2.58 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 157.4 (CH), 157.2 (CH), 156.8 (CH), 154.1 (CH), 134.0 (C$_q$), 132.9 (CH), 130.6 (C$_q$), 125.0 (CH), 34.1 (CH$_2$), 29.9 (CH$_2$).

ATR-FTIR (cm^{-1}) 3023, 2927, 2854, 1655, 1556, 1511, 1442, 1406, 1107, 965, 914, 843, 722, 634..

HRMS (ESI) calculated for $C_{12}H_{12}N_4H^+$: 213.1135, found: 213.1150.

(*E*)-5,5`-(But-1-ene-1,4-diyl)bis(1,3-bis(trifluoromethyl)benzene)



7g

Prepared following a modified procedure starting from 3,5-bis(trifluoromethyl)-styrene **2g** (180 µL, 1.0 mmol). The reaction was stirred at 160 °C for 16 h instead of at 140 °C and with only 0.5 mL of 1,4-dioxane (2 M). Purification by flash column chromatography (*n*-pentane/ethyl acetate 99.5:0.5 → 99:1) yielded **7g** (203.0 mg, 0.42 mmol, 85%) as a colorless, crystalline solid.

TLC (*n*-pentane/ethyl acetate 90:10) $R_f = 0.49$ (UV, $KMnO_4$).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.75 (br s, 1H), 7.72 (br s, 3H), 7.67 (br s, 2H), 6.48 (d, $J = 16.0$ Hz, 1H), 6.38 (dt, $J = 15.8, 6.3$ Hz, 1H), 3.00–2.94 (m, 2H), 2.67–2.60 (m, 2H).

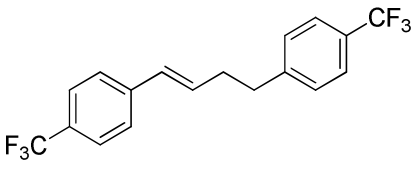
^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = –62.94 (s, 6F), –63.12 (s, 6F).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 143.6 (C_q), 139.4 (C_q), 132.8 (CH), 132.1 (q, $J = 33.3$ Hz, C_q), 131.9 (q, $J = 33.2$ Hz, C_q), 129.2 (CH), 128.9–128.7 (m, CH), 126.1–125.9 (m, CH), 123.5 (q, $J = 272.6$ Hz, C_q), 123.5 (q, $J = 272.5$ Hz, C_q), 120.9 (septet, $J = 3.9$ Hz, CH), 120.5 (septet, $J = 3.9$ Hz, CH), 35.2 (CH_2), 34.4 (CH_2).

ATR-FTIR (cm^{-1}) 1379, 1278, 1157, 1105, 968, 897, 844, 732, 700, 683, 624.

HRMS (Orbitrap) calculated for $C_{20}H_{12}F_{12}CF_3CO_2^-$: 593.06033, found: 593.06004.

(*E*)-4,4`-(But-1-ene-1,4-diyl)bis((trifluoromethyl)benzene)



7h

Prepared following a modified procedure starting from 4-(trifluoromethyl)-styrene **2h** (148 µL, 172.1 mg, 1.0 mmol). The reaction was stirred at 160 °C for 16 h instead of at 140 °C and with only 0.5 mL of 1,4-dioxane (2 M). Purification by flash column chromatography (*n*-pentane/ethyl acetate 99.5:0.5) yielded **7h** (80.3 mg, 0.23 mmol, 47%) as a colorless solid, that still contained an inseparable isomer of **7h** (about 5%).

TLC (*n*-pentane/ethyl acetate 95:5) R_f = 0.57 (UV, $KMnO_4$).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.56 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.32 (dt, *J* = 15.8 Hz, 6.5 Hz, 1H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.62–2.54 (m, 2H).

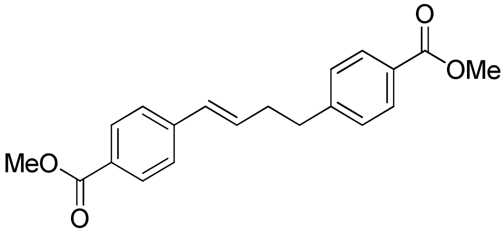
^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = –62.3 (s, 3F), –62.5 (s, 3F).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 145.6–145.5 (m, C_q), 141.1–141.0 (m, C_q), 132.5 (CH), 129.9 (CH), 129.1 (q, *J* = 28.9 Hz, C_q), 128.9 (CH), 128.6 (q, *J* = 32.2 Hz, C_q), 126.3 (CH), 125.6 (q, *J* = 3.6 Hz, CH), 125.5 (q, *J* = 3.7 Hz, CH), 124.5 (q, *J* = 272.0 Hz, C_q), 124.4 (q, *J* = 271.7 Hz, C_q), 35.5 (CH_2), 34.6 (CH_2).

ATR-FTIR (cm^{-1}) 2931, 1614, 1416, 1320, 1164, 1104, 1065, 1015, 968, 956, 847, 804, 652, 633, 594.

HRMS (Orbitrap) calculated for $C_{18}H_{14}F_6Ag^+$: 451.00451, found: 451.00438.

(*E*)-Dimethyl-4,4`-(but-1-ene-1,4-diyl)dibenzoate



7i

7i was prepared following the general procedure, but with 20 mol% of **1g** (48.8 mg, 0.1 mmol, 0.2 equiv) starting from methyl 4-vinylbenzoate **2i** (162.2 mg, 1.0 mmol). Purification by flash column chromatography (*n*-pentane/ethyl acetate 95:5 → 90:10) yielded **7i** (57.7 mg, 0.18 mmol, 36%) as a colorless solid.

TLC (*n*-pentane/ethyl acetate 95:5) R_f = 0.25 (UV, $KMnO_4$).

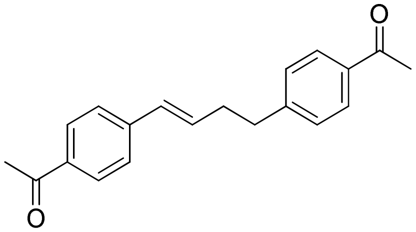
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.98–7.92 (m, 4H), 7.36–7.25 (m, 4H), 6.42 (q, *J* = 16.0 Hz, 1H), 6.32 (dt, *J* = 15.8 Hz, 6.1 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.86–2.81 (m, 2H), 2.59–2.52 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 167.2 (C_q), 167.0 (C_q), 147.0 (C_q), 142.1 (C_q), 132.3 (CH), 130.2 (CH), 130.0 (CH), 129.9 (CH), 128.6 (C_q), 128.6 (CH), 128.1 (C_q), 126.0 (CH), 52.1 (CH_3), 52.1 (CH_3), 35.7 (CH_2), 34.6 (CH_2).

ATR-FTIR (cm^{-1}) 2947, 2844, 1709, 1604, 1566, 1508, 1434, 1414, 1276, 1180, 1103, 1018, 962, 760, 735, 698.

HRMS (ESI) calculated for $C_{20}H_{20}O_4Na^+$: 347.1254, found: 347.1261.

(*E*)-4,4`-(But-1-ene-1,4-diyl)diacetophenone



7k

Prepared following a modified procedure starting from 1-(4-vinylphenyl)-ethanone **2k** (146.2 mg, 1.0 mmol). The reaction was stirred at 160 °C for 16 h instead of at 140 °C and with only 0.5 mL of 1,4-dioxane (2 M). Purification by flash column chromatography (*n*-pentane/ethyl acetate 80:20) yielded **7k** (116.1 mg, 0.40 mmol, 79%) as a colorless solid.

TLC (*n*-pentane/ethyl acetate 80:20) $R_f = 0.19$ (UV, $KMnO_4$).

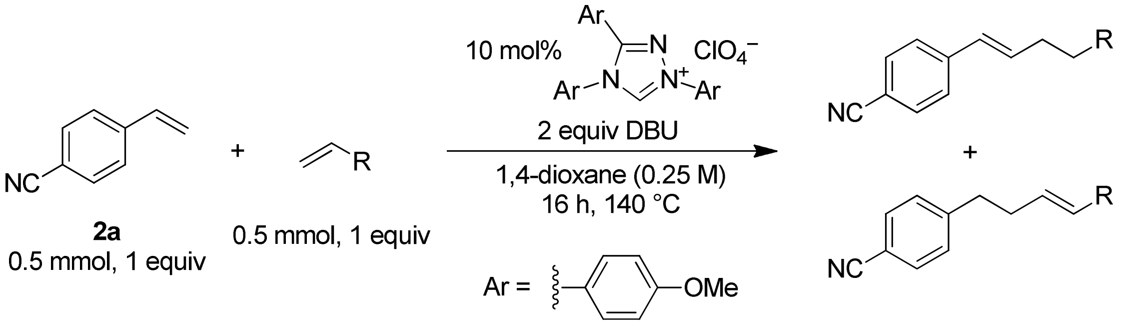
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90–7.86 (m, 4H), 7.38–7.36 (m, 2H), 7.30–7.28 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.35 (dt, *J* = 15.8, 6.3 Hz, 1H), 2.88–2.84 (m, 2H), 2.66–2.55 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 197.9 (C_q), 197.6 (C_q), 147.2 (C_q), 142.2 (C_q), 135.7 (C_q), 135.3 (C_q), 132.5 (CH), 130.1 (CH), 128.8 (CH), 128.8 (CH), 128.7 (CH), 126.1 (CH), 35.6 (CH_2), 34.5 (CH_2), 26.7 (CH_3), 26.6 (CH_3).

ATR-FTIR (cm^{-1}) 3333, 2918, 2850, 1672, 1599, 1561, 1411, 1360, 1305, 1267, 1183, 1111, 1076, 1016, 962, 859, 830, 795, 690, 591.

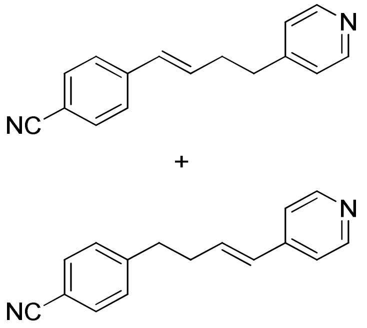
HRMS (ESI) calculated for $C_{20}H_{20}O_2Na^+$: 315.1356, found: 315.1353.

General procedure for the cross-coupling of styrenes



The triazolium salt **1g** (24.4 mg, 0.05 mmol, 0.1 equiv) was added to a flame-dried Schlenk flask in an argon-filled glovebox. Using standard Schenk techniques, dry 1,4-dioxane (2 mL, 0.25 M), DBU (149 µL, 1.0 mmol, 2 equiv), and *p*-cyanostyrene **2a** (0.5 mmol, 1 equiv) were added to the flask. The coupling partner (0.5 mmol, 1 equiv) was added to the mixture, the flask was sealed, and the reaction mixture was stirred for 16 h at 140 °C in a preheated oil bath. Afterwards, the reaction was cooled to room temperature, and all volatiles were removed at reduced pressure. The resulting residue was purified by flash column chromatography to obtain the desired product.

(*E*)-4-(4-(pyridin-4-yl)but-1-en-1-yl)benzonitrile and (*E*)-4-(4-(pyridin-4-yl)but-3-en-1-yl)benzonitrile



6d

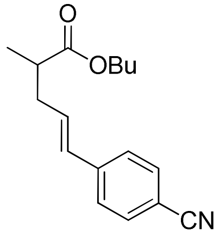
Prepared following the general procedure using 4-vinylpyridine **2d** (54 µL, 0.5 mmol, 1 equiv) as the coupling partner. Purification by flash column chromatography (CH_2Cl_2 /methanol 99:1 → 98:2) yielded **6d** (41.9 mg, 0.18 mmol, 36%, 1:1 mix of the two double-bond regioisomers) as a brown solid.

The analytic data was in accordance with the previously reported data for **6d** (see chapter 6).

(*E*)-Butyl 5-(4-cyanophenyl)-2-methylpent-2/4-enoate

Prepared following the general procedure using butyl methacrylate **8** (80 µL, 0.5 mmol, 1 equiv) as the coupling partner. Purification by flash column chromatography (*n*-pentane/ethyl acetate 95:5 → 90:10) yielded **9a** (34.5 mg, 0.13 mmol, 25%) and **9b** (14.2 mg, 0.05 mmol, 10%) as colorless oils.

(*E*)-Butyl 5-(4-cyanophenyl)-2-methylpent-4-enoate



9a

TLC (*n*-pentane/ethyl acetate 95:5) $R_f = 0.29$ (UV, $KMnO_4$).

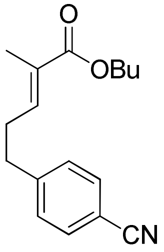
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.58–7.55 (m, 2H), 7.41–7.38 (m, 2H), 6.45–6.25 (m, 2H), 4.07 (t, J = 6.5 Hz, 2H), 2.67–2.53 (m, 2H), 2.43–2.34 (m, 1H), 1.63–1.54 (m, 2H), 1.41–1.29 (m, 2H), 1.20 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 175.9 (C_q), 141.9 (C_q), 132.5 (CH), 131.8 (CH), 130.7 (CH), 126.7 (CH), 119.2 (C_q), 110.5 (C_q), 64.5 (CH_2), 39.6 (CH), 37.2 (CH_2), 30.8 (CH_2), 19.3 (CH_2), 17.0 (CH_3), 13.8 (CH_3).

ATR-FTIR (cm^{-1}) 2961, 1729, 1605, 1504, 1460, 1353, 1272, 1174, 1121, 1065, 970, 852.

HRMS (ESI) calculated for $C_{17}H_{21}NO_2Na^+$: 294.1465, found: 294.1463.

(*E*)-Butyl 5-(4-cyanophenyl)-2-methylpent-2-enoate



9b

TLC (*n*-pentane/ethyl acetate 95:5) $R_f = 0.25$ (UV, $KMnO_4$).

^{1}H NMR (300 MHz, CDCl$_3$) *δ* (ppm) = 7.59–7.57 (m, 2H), 7.30–7.27 (m, 2H), 6.75–6.70 (m, 1H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.84–2.79 (m, 2H), 2.53–2.46 (m, 2H), 1.76 (d, *J* = 0.9 Hz, 3H), 1.69–1.59 (m, 2H), 1.45–1.33 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) *δ* (ppm) = 168.1 (C$_q$), 146.9 (C$_q$), 139.7 (CH), 132.4 (CH), 129.3 (CH), 129.3 (C$_q$), 119.1 (C$_q$), 110.2 (C$_q$), 64.6 (CH$_2$), 35.0 (CH$_2$), 30.8 (CH$_2$), 30.0 (CH$_2$), 19.4 (CH$_2$), 13.9 (CH$_3$), 12.5 (CH$_3$).

ATR-FTIR (cm^{-1}): 2959, 1709, 1650, 1608, 1458, 1264, 1176, 1122, 1078, 1021, 890.

HRMS (ESI) calculated for $C_{17}H_{21}NO_2Na^+$: 294.1465, found: 294.1463.

9. References

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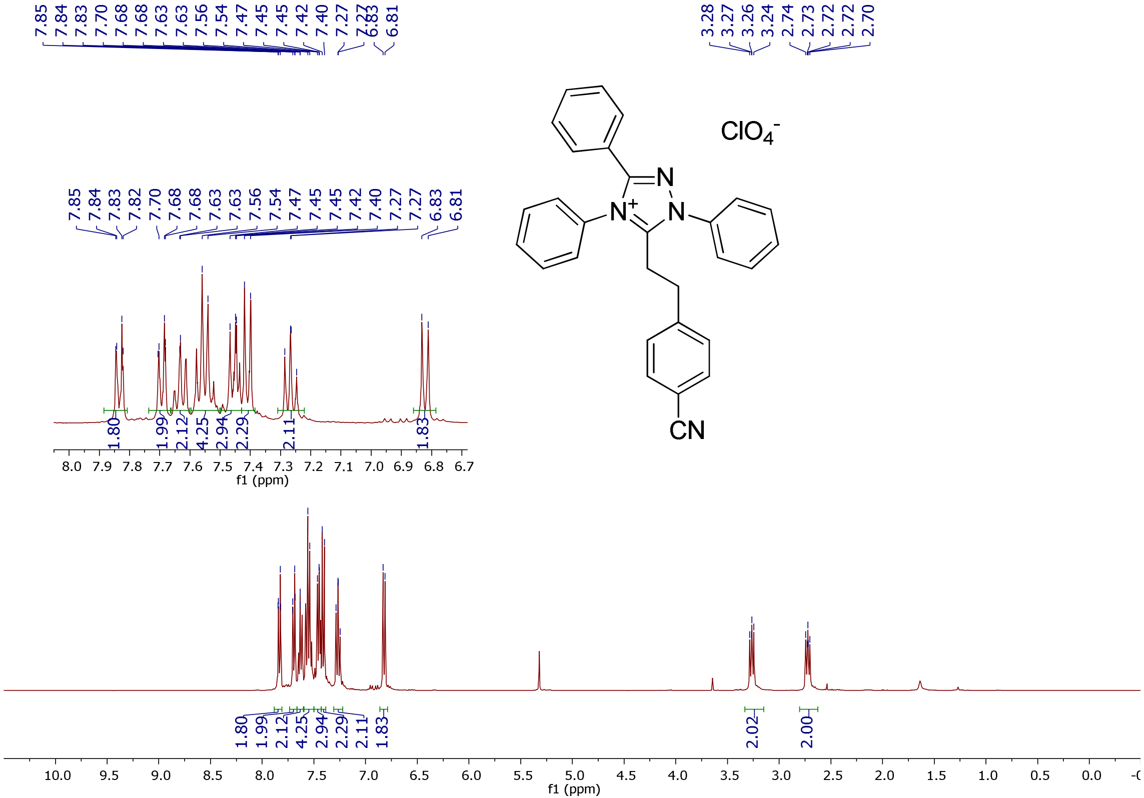
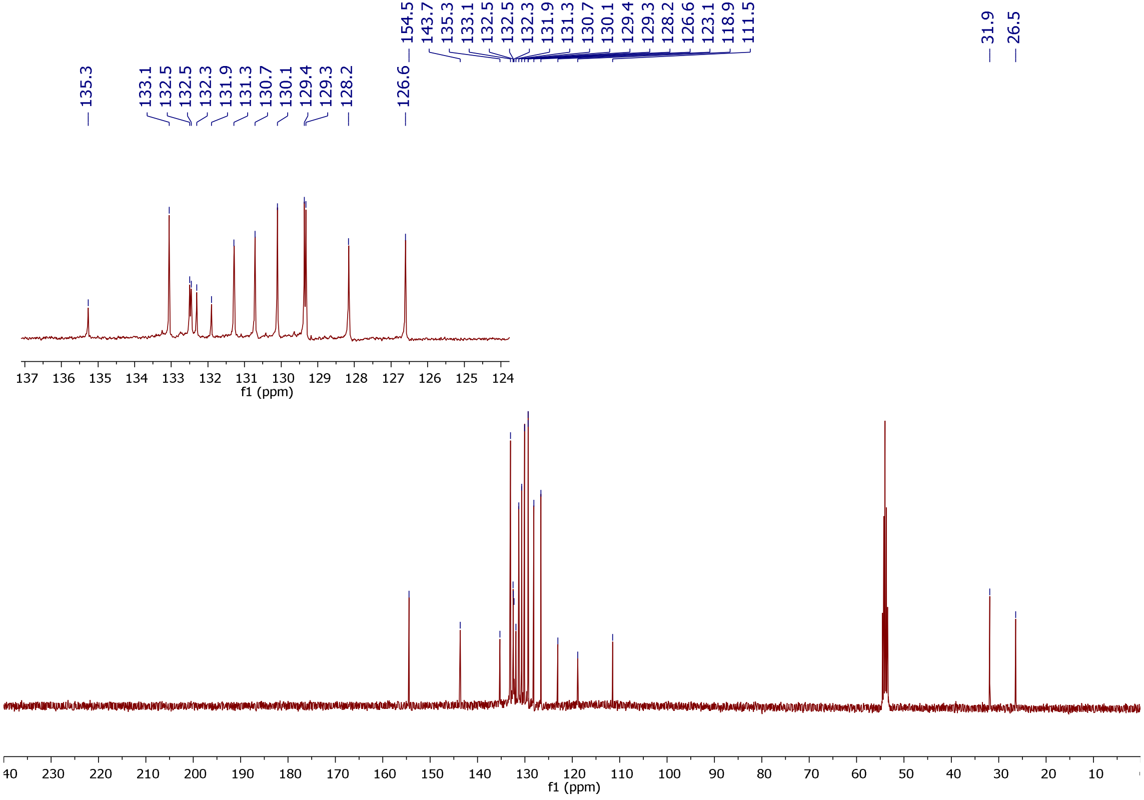
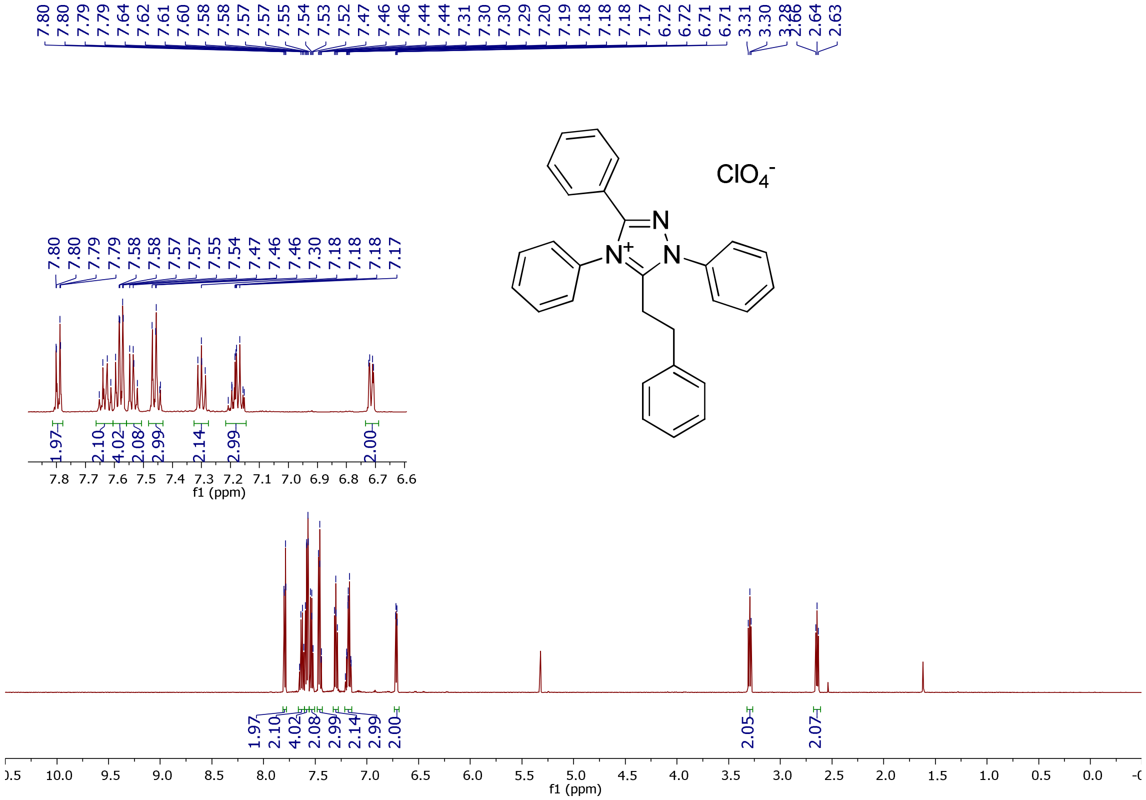
10. NMR-spectra of **3**, **4**, **5**, **6**, **7**, **8**, **9**

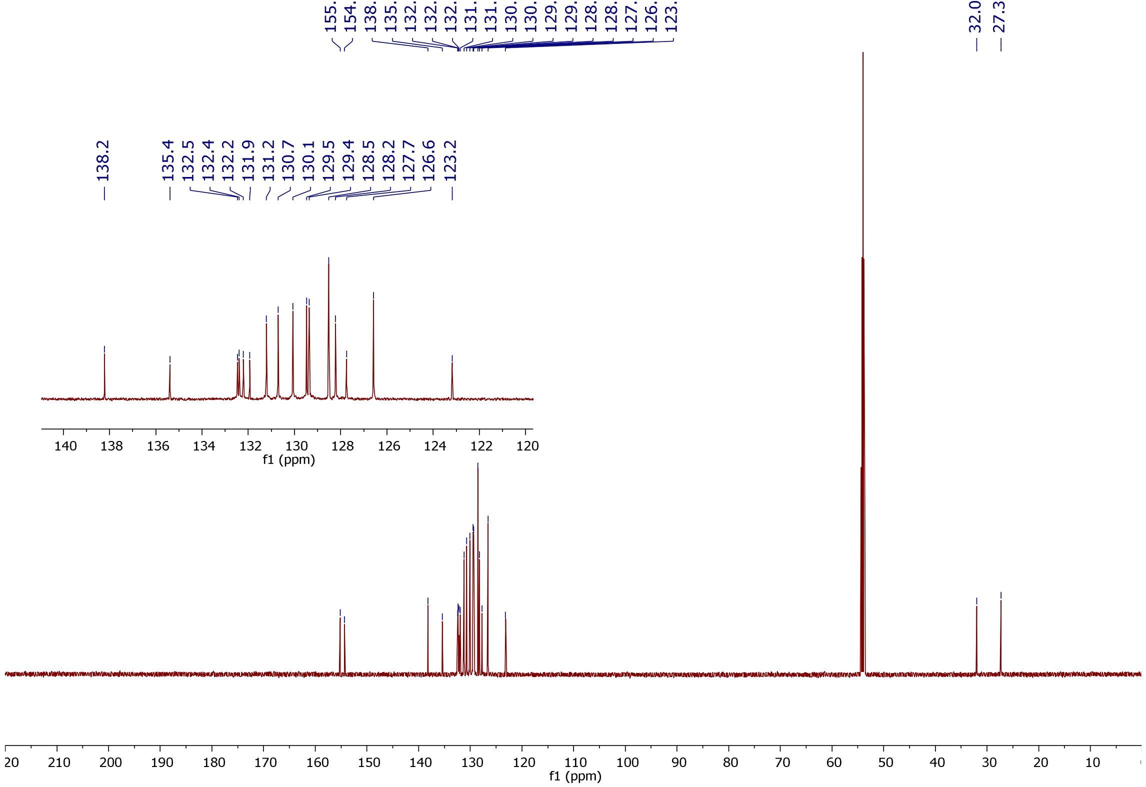
5-(4-Cyanophenylethyl)-1,3,4-triphenyl-1*H*-1,2,4-triazol-4-ium perchlorate **3a**



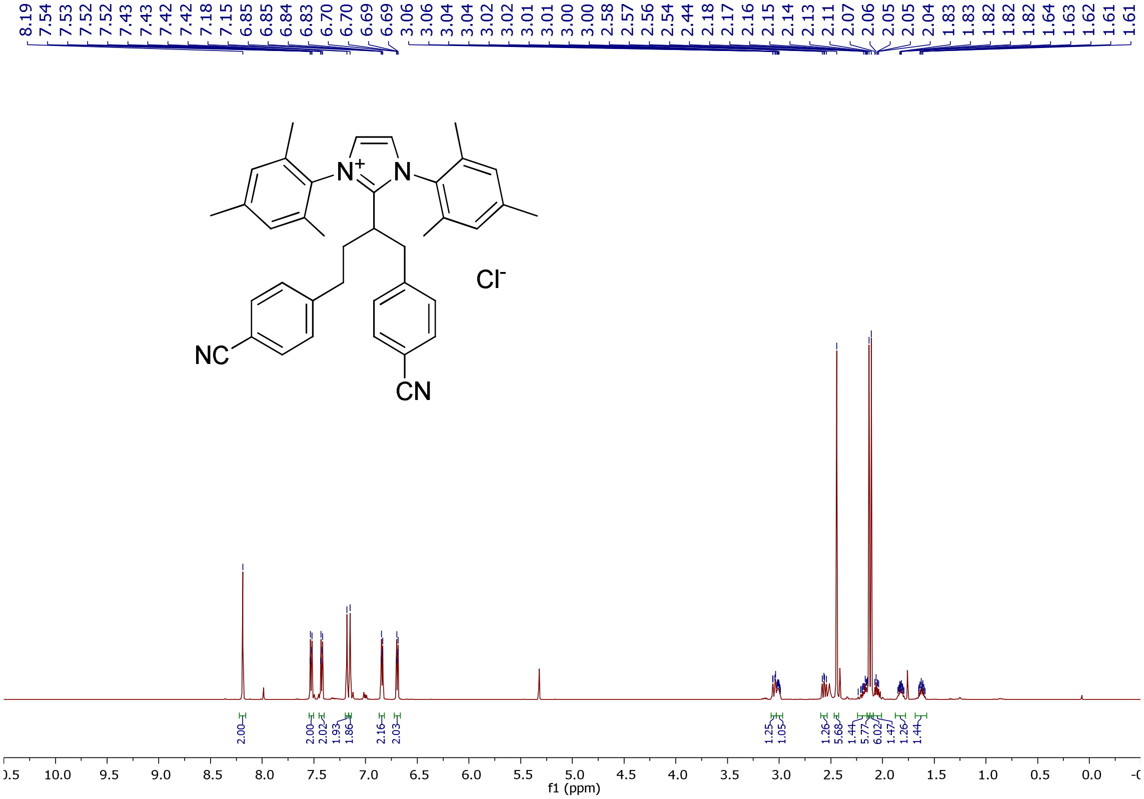


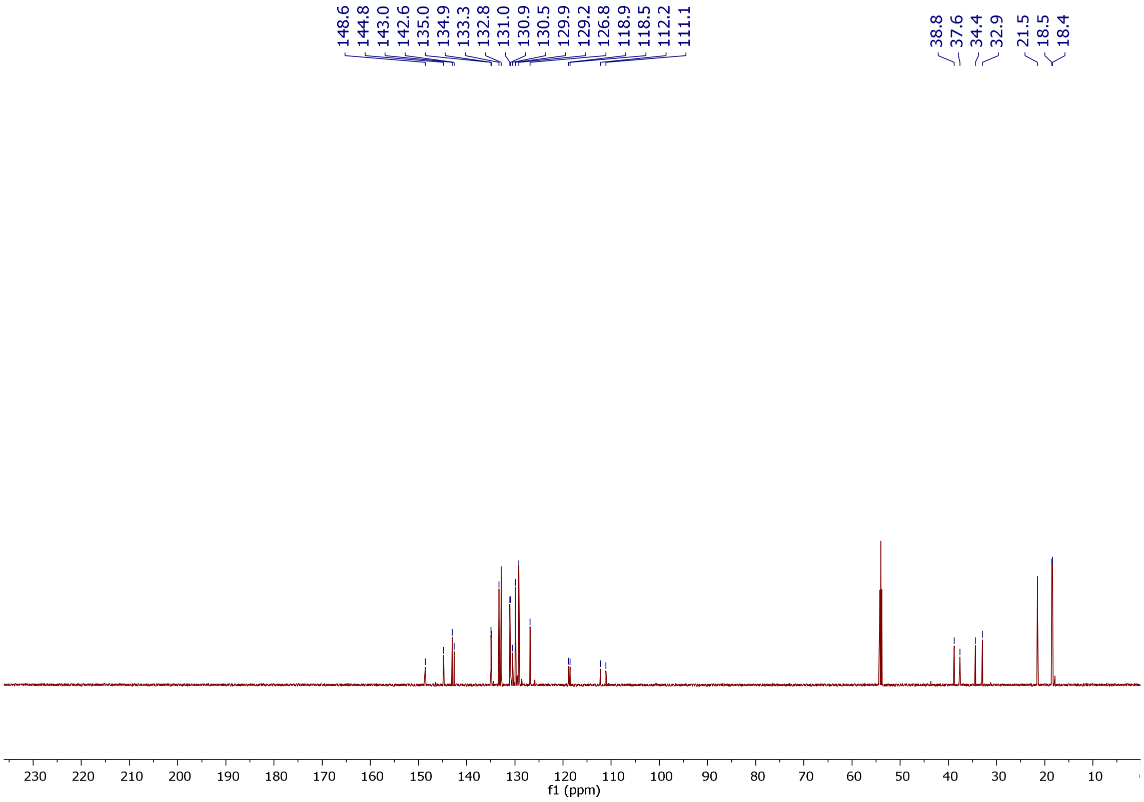
5-(Phenylethyl)-1,3,4-triphenyl-1*H*-1,2,4-triazol-4-ium perchlorate **3b**



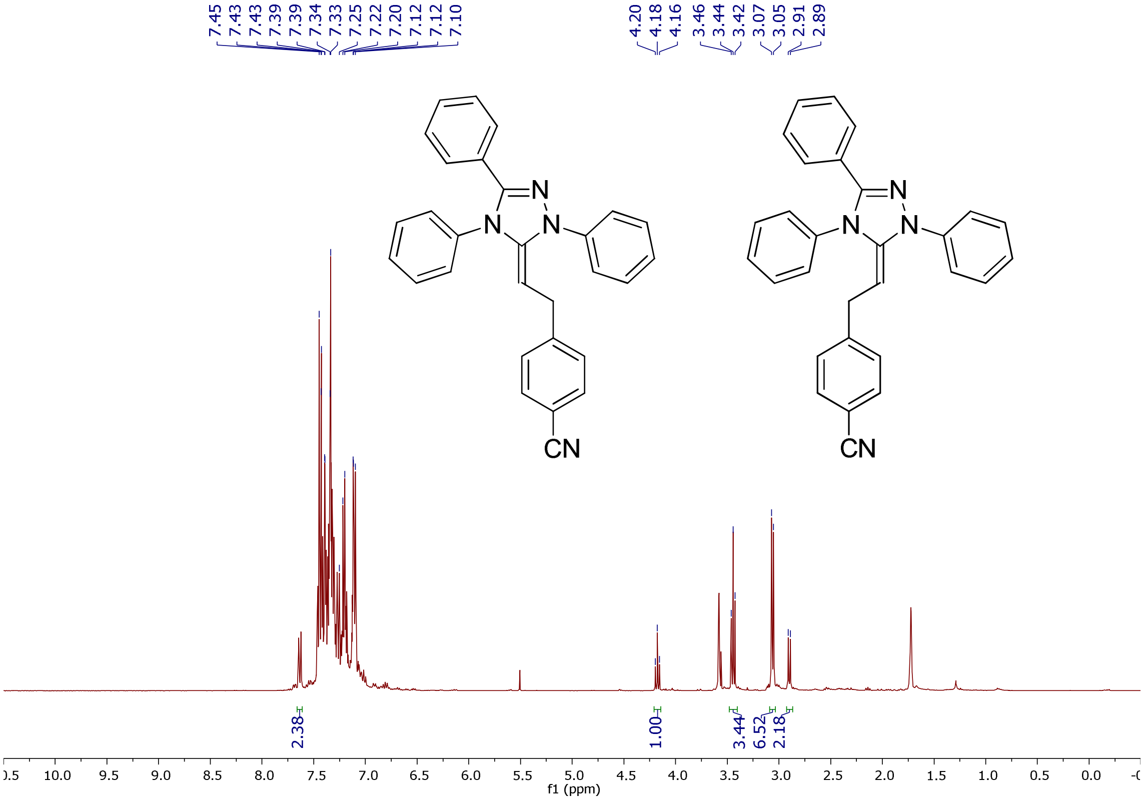


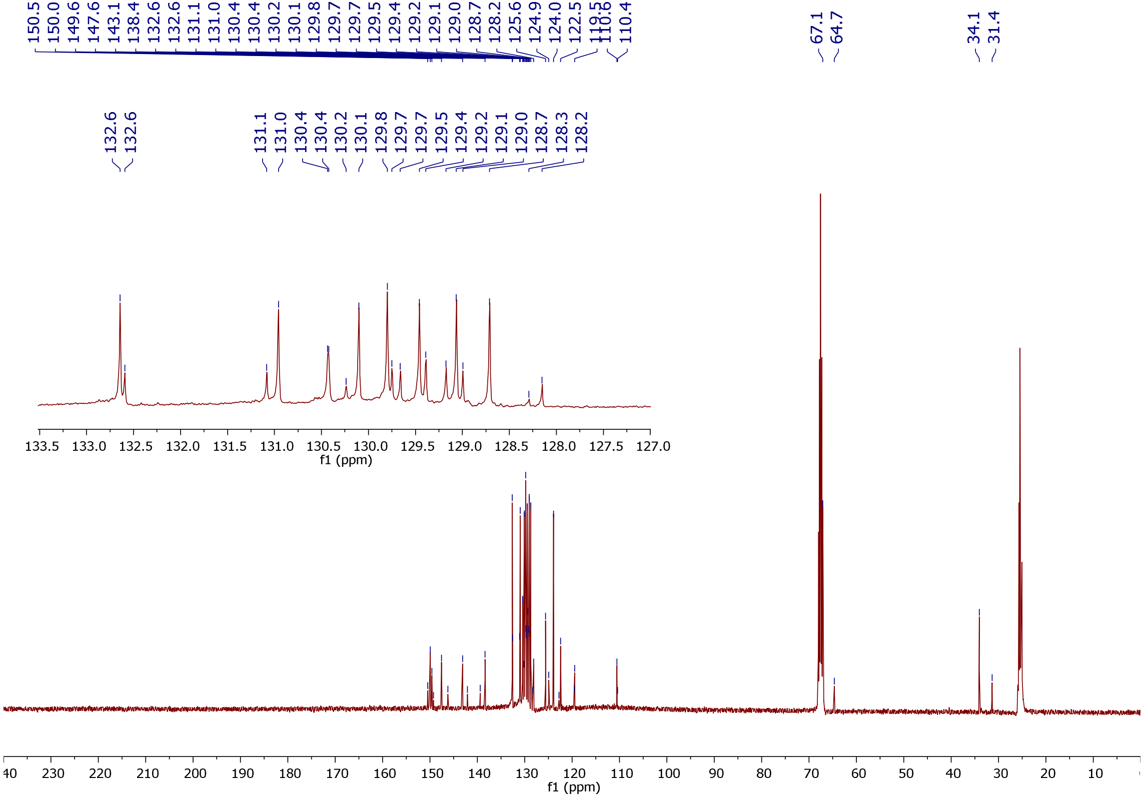
2-(1,2-Bis(4-cyanophenyl)ethyl)-1,3-dimesityl-1H-imidazol-3-ium chloride **4**

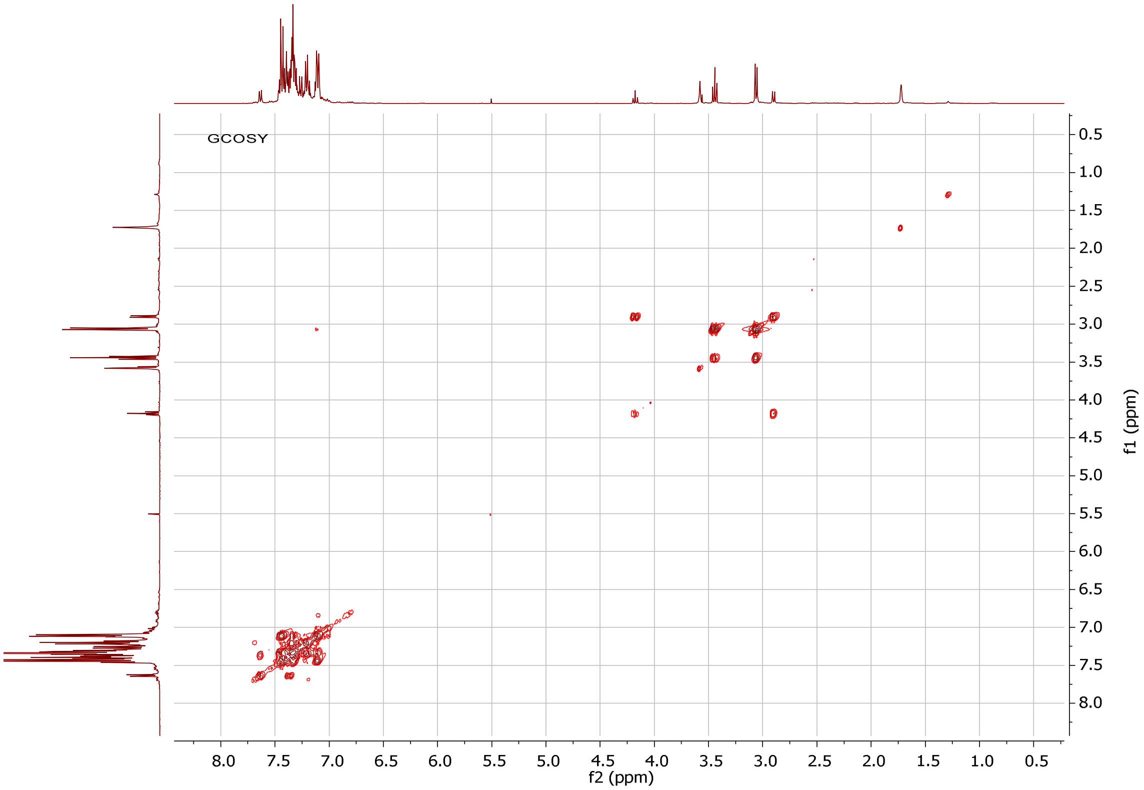


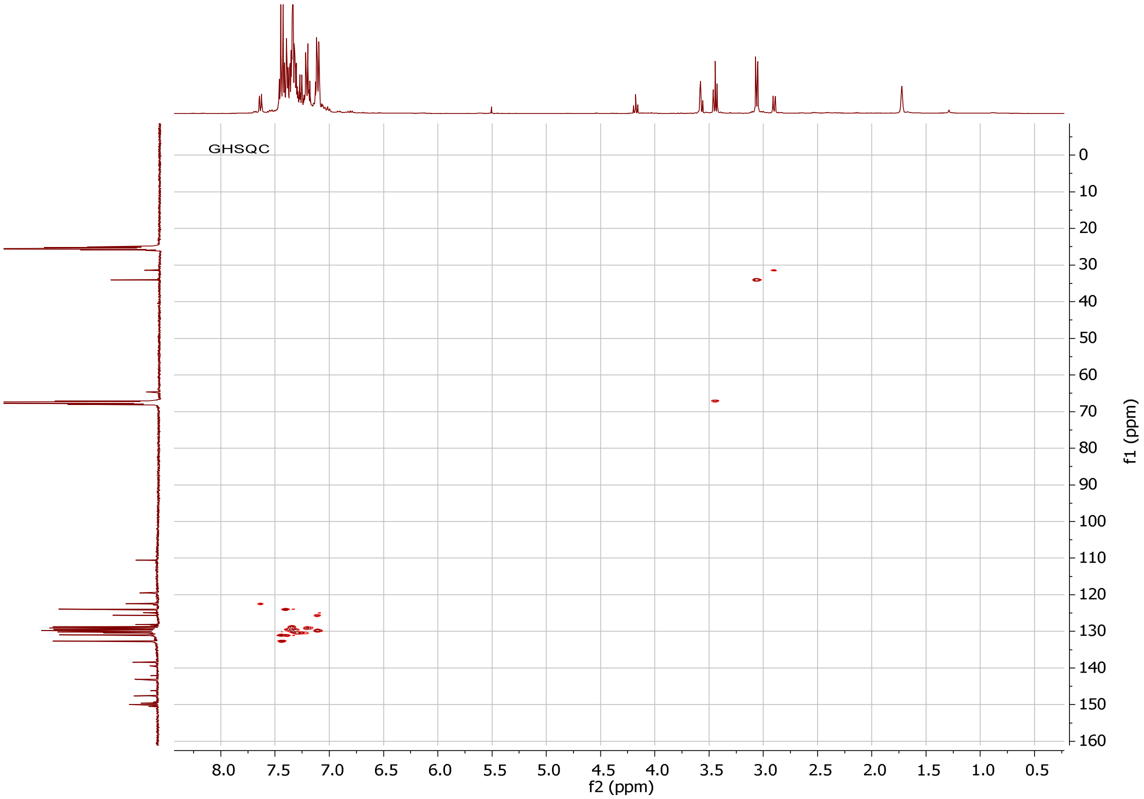


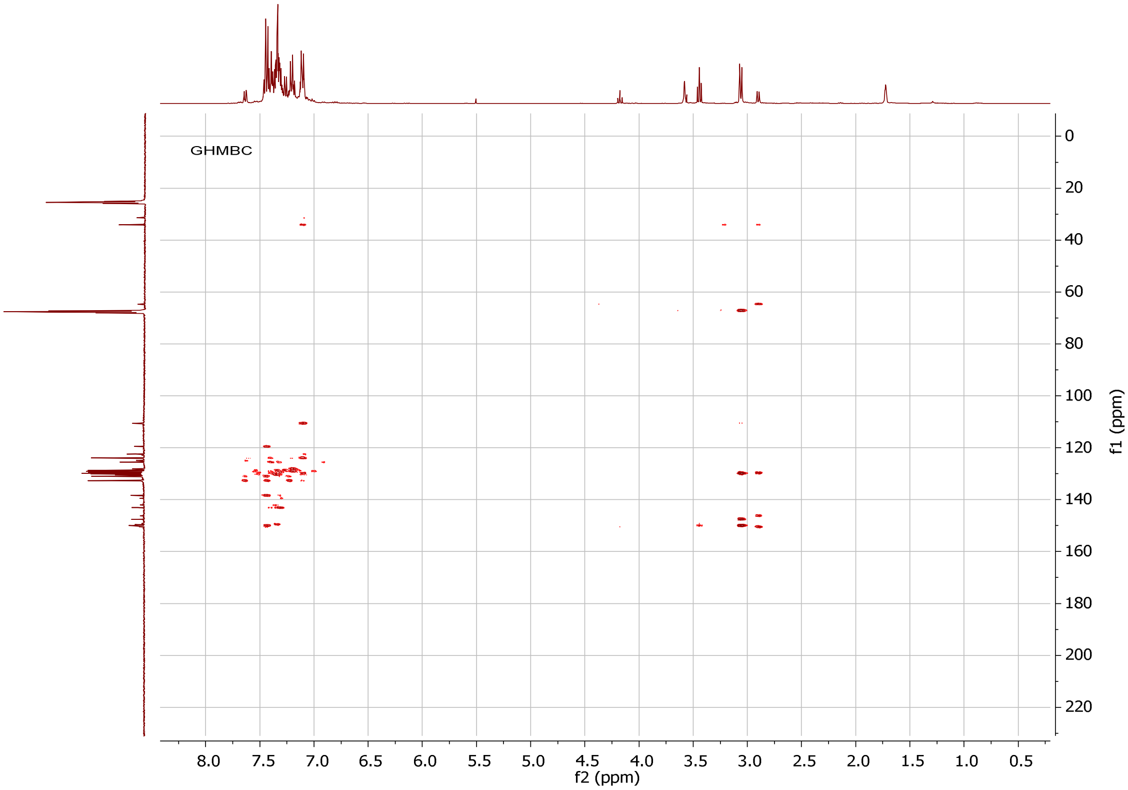
4-(2-(1,3,4-Triphenyl-1H-1,2,4-triazol-5(4H)-ylidene)ethyl)benzonitrile **5a**

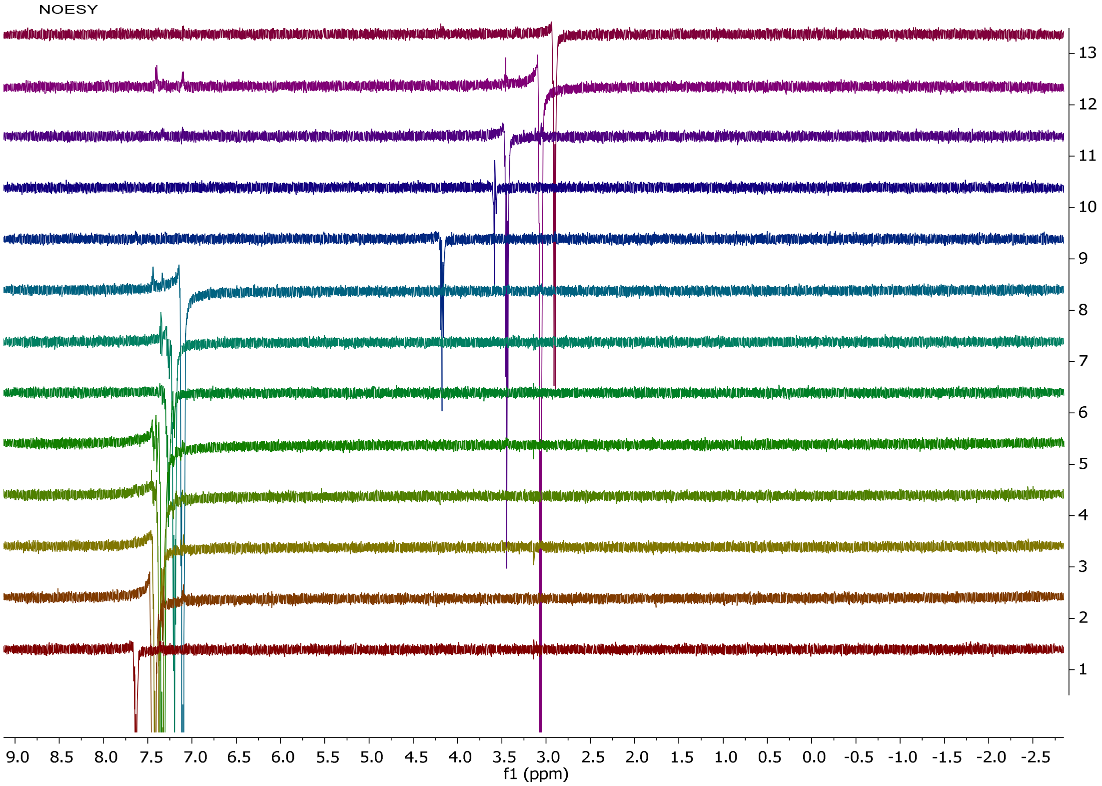




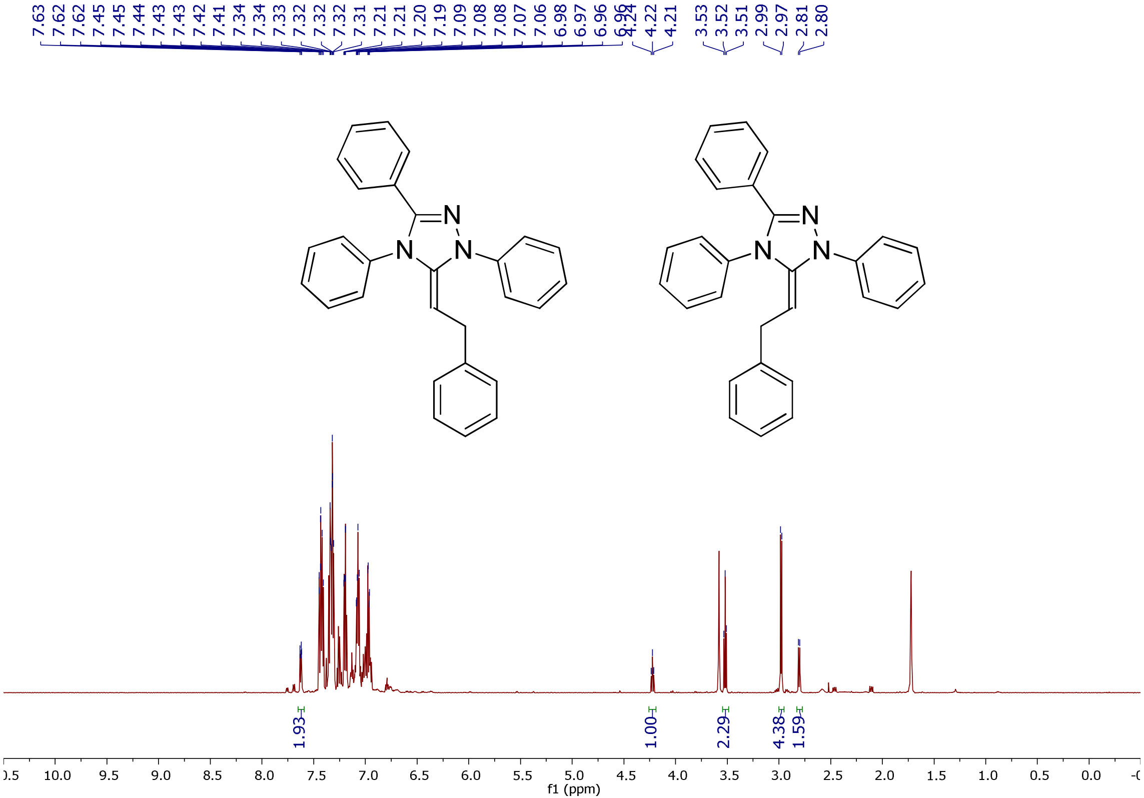

GCOSY
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

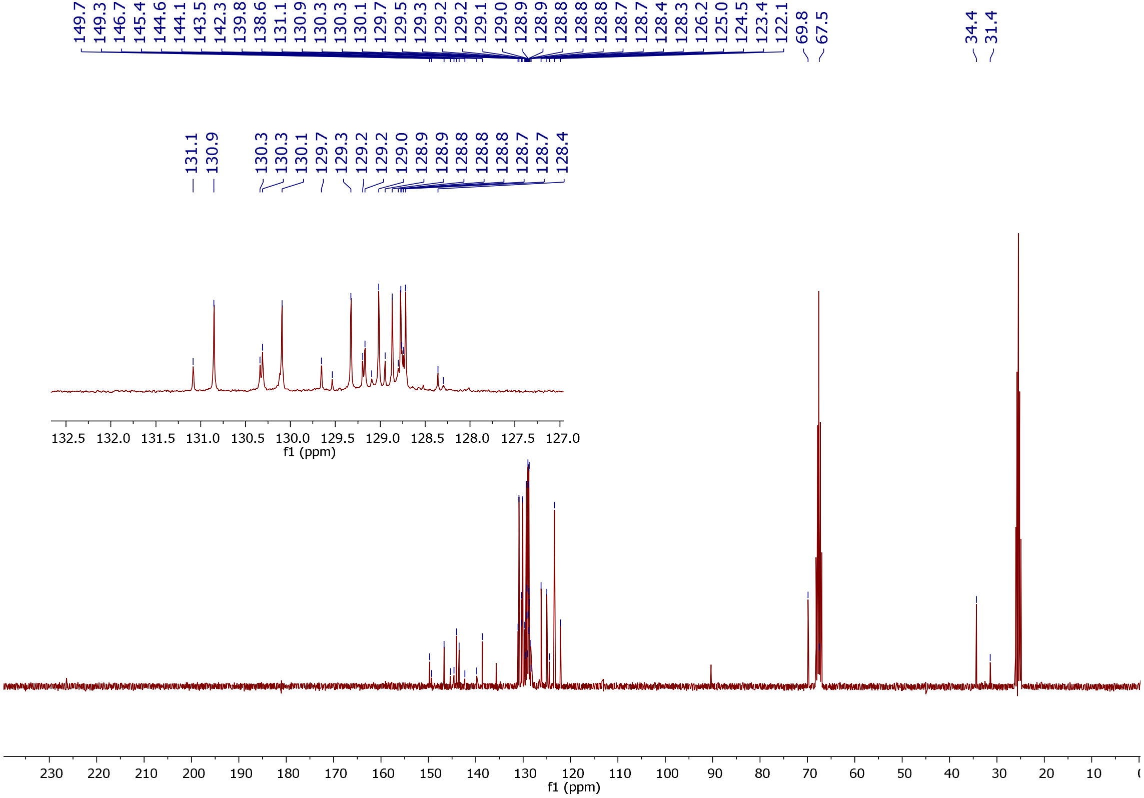

GHSQC
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

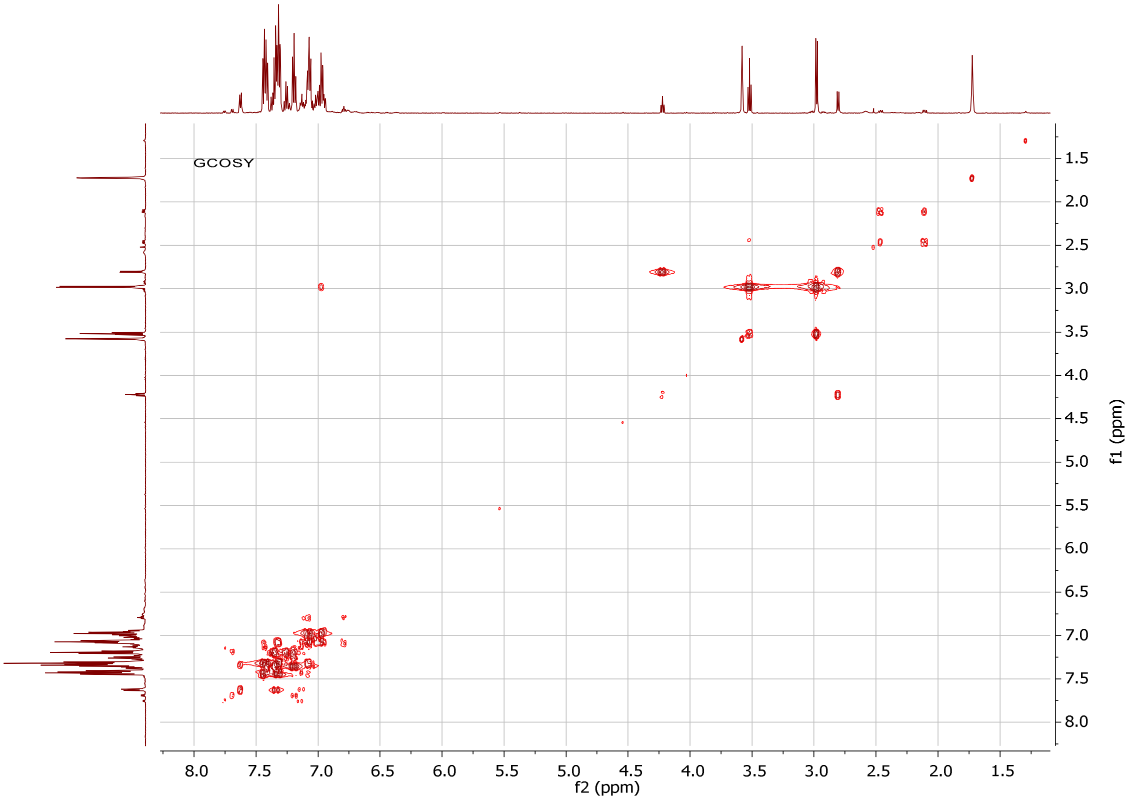

GHMBC
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
0 20 40 60 80 100 120 140 160 180 200 220

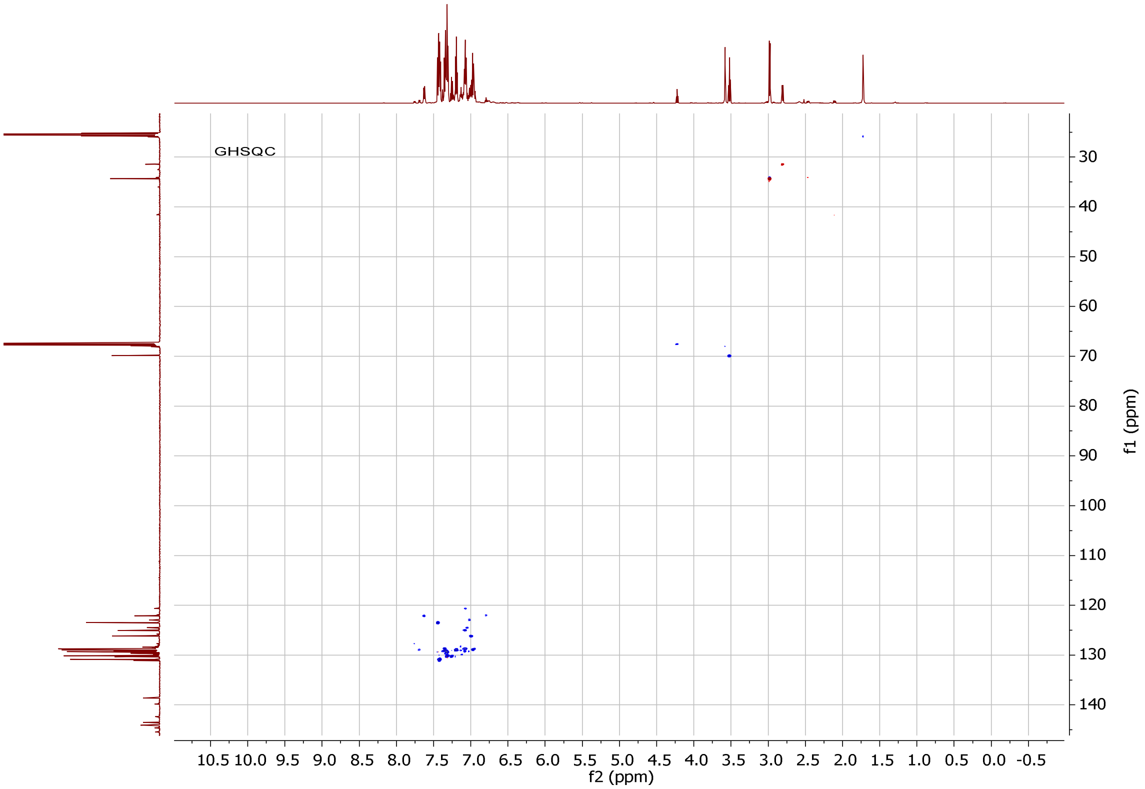

NOESY
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
1 2 3 4 5 6 7 8 9 10 11 12 13

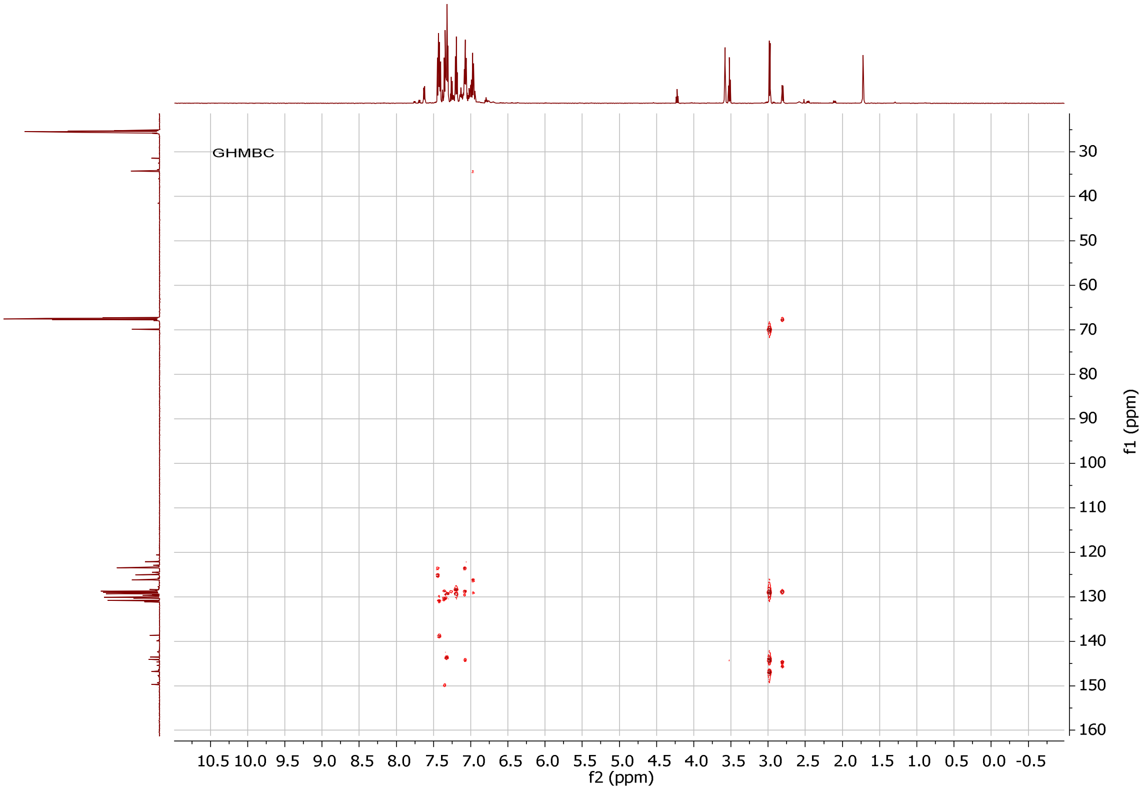
1,3,4-Triphenyl-5-(2-phenylethylidene)-4,5-dihydro-1*H*-1,2,4-triaziole **5b**



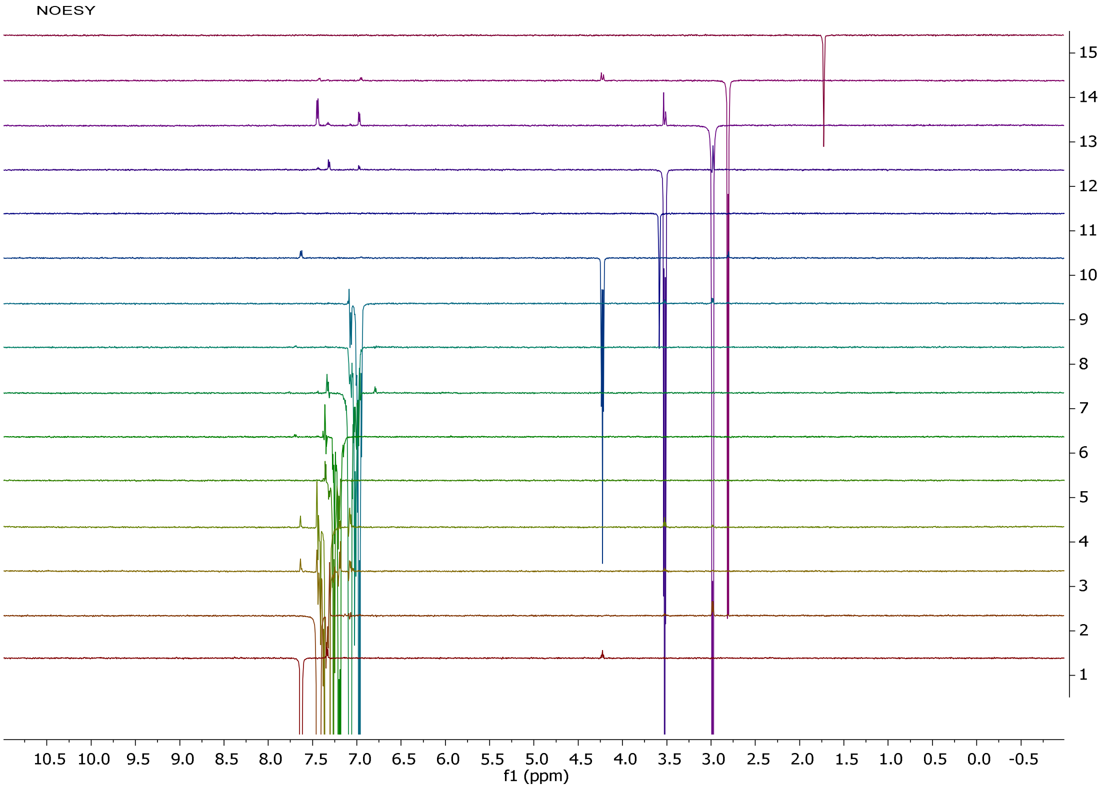



GCOSY
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f2 (ppm)


GHSQC
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)

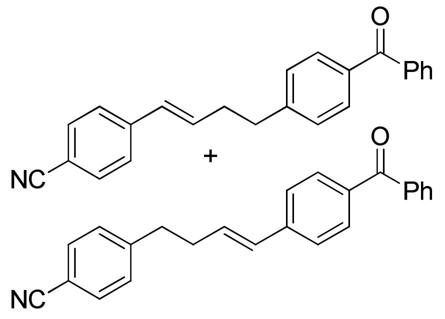


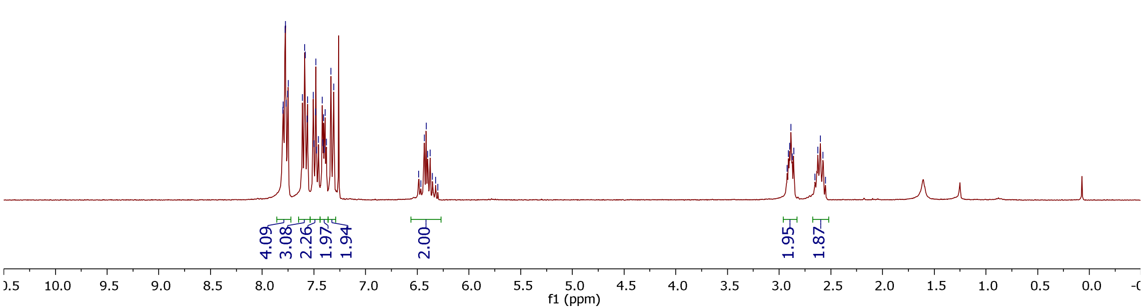
GHMBC
f2 (ppm)
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
30 40 50 60 70 80 90 100 110 120 130 140 150 160

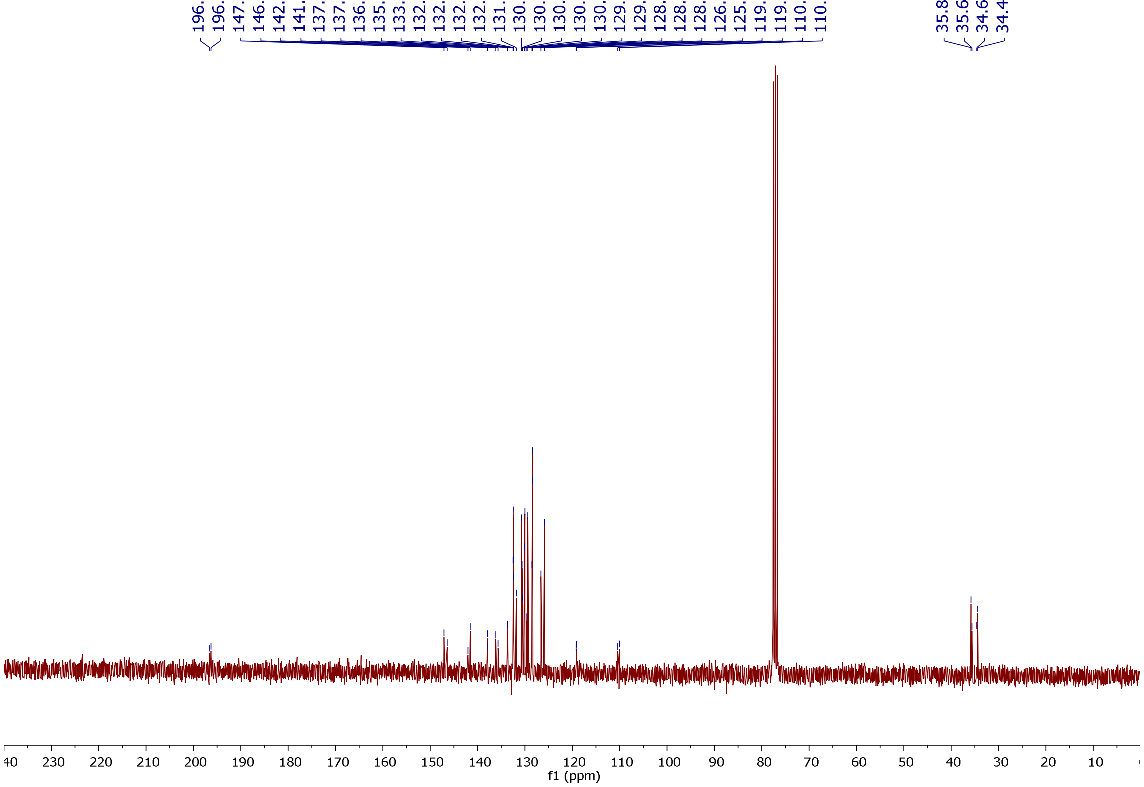


NOESY
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

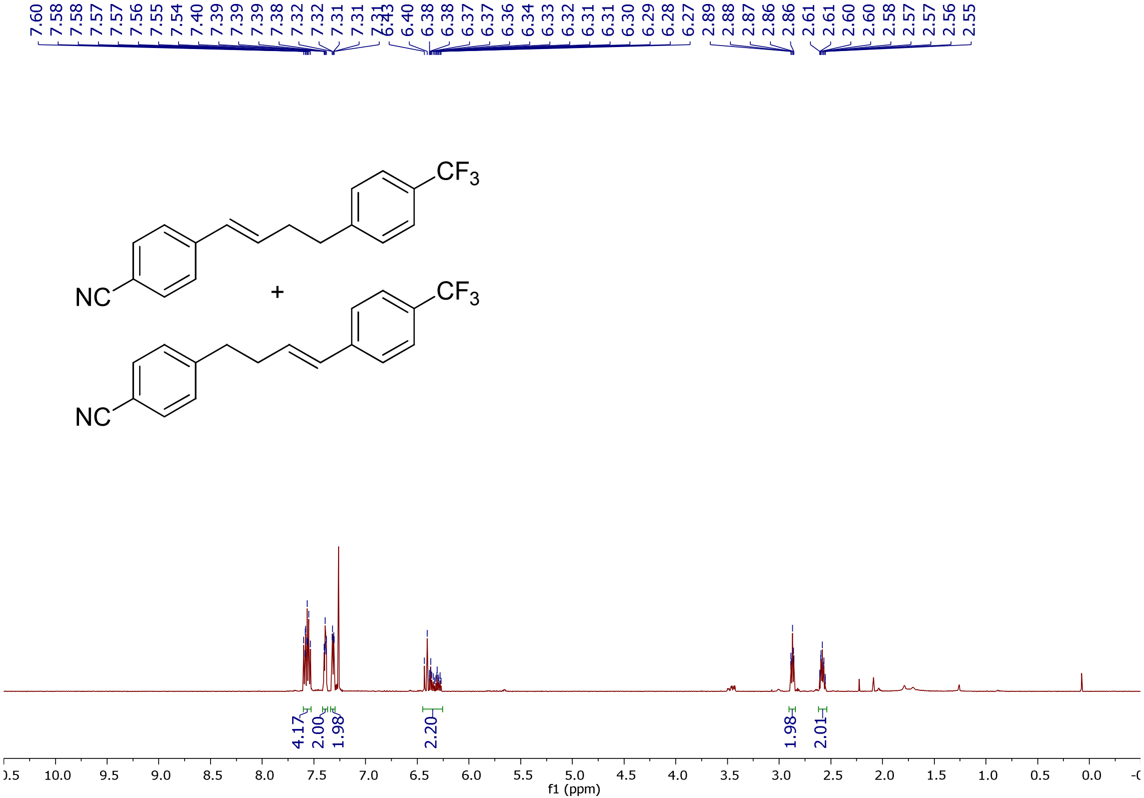
(*E*)-4-(4-(4-benzoylphenyl)but-1-en-1-yl)benzonitrile + (*E*)-4-(4-(4-benzoylphenyl)but-3-en-1-yl)benzonitrile **6a**

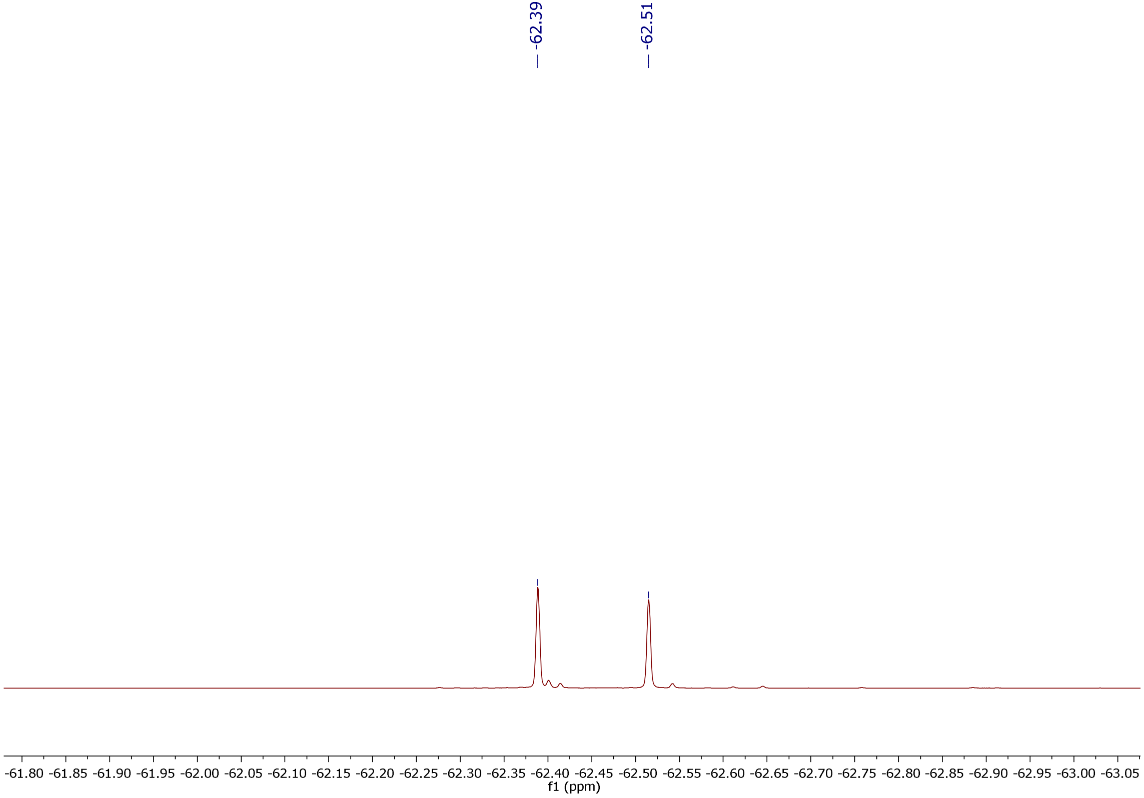


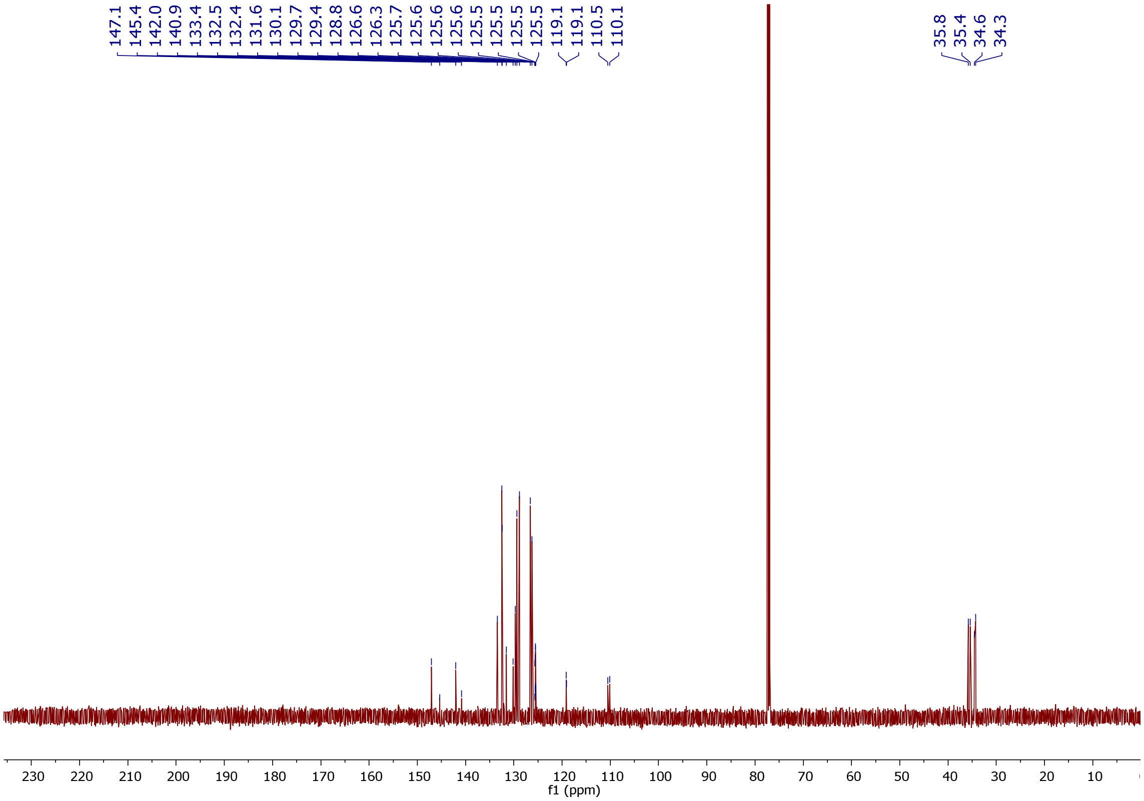




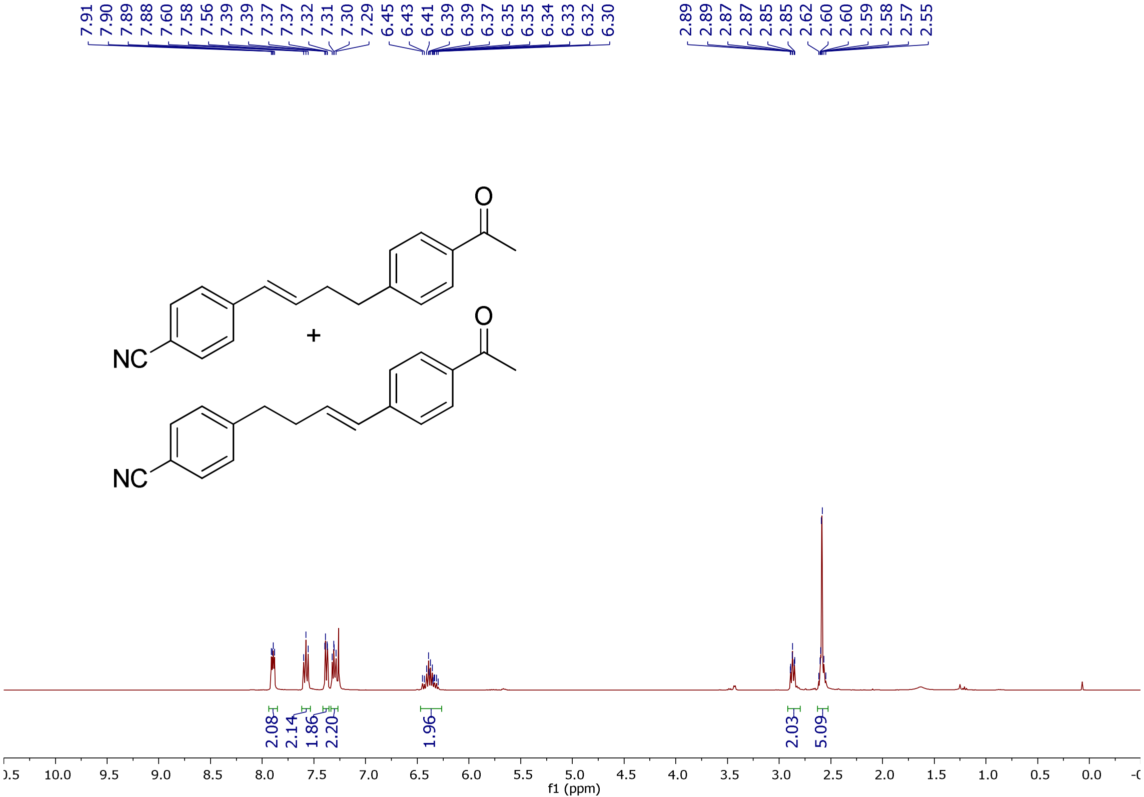
(*E*)-4-(4-(4-(trifluoromethyl)phenyl)but-1-en-1-yl)benzonitrile + (*E*)-4-(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)benzonitrile **6b**

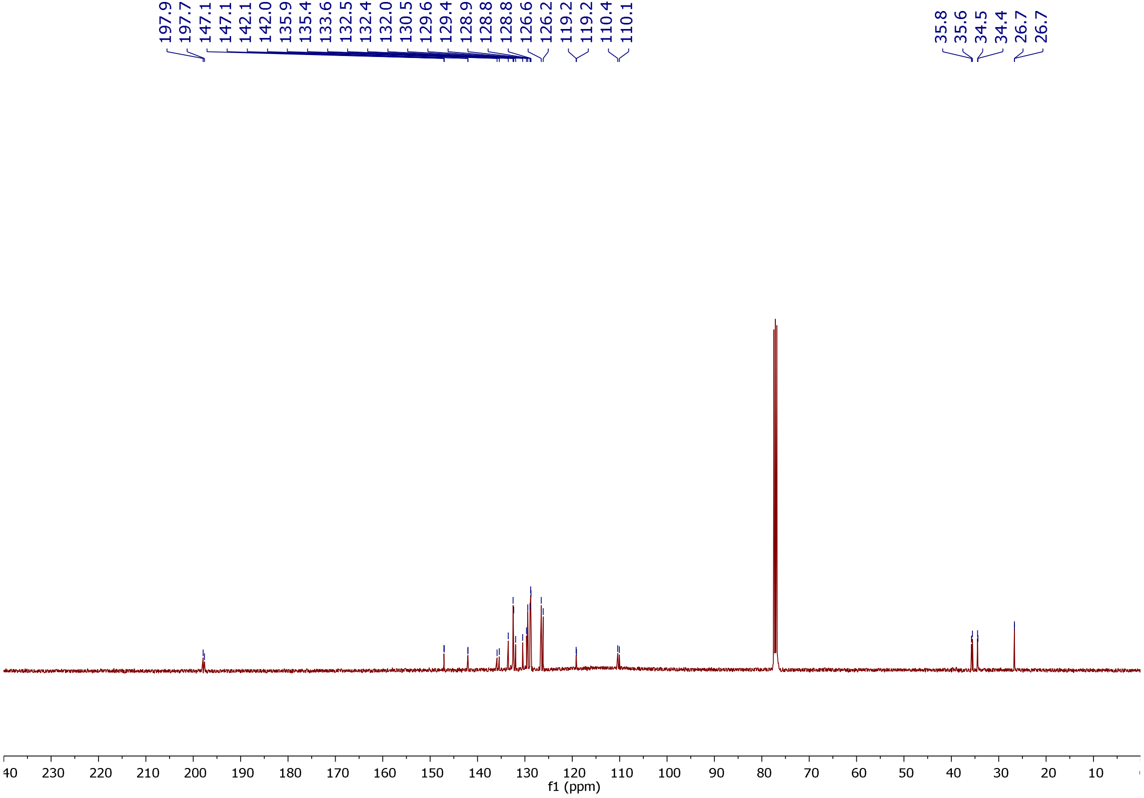




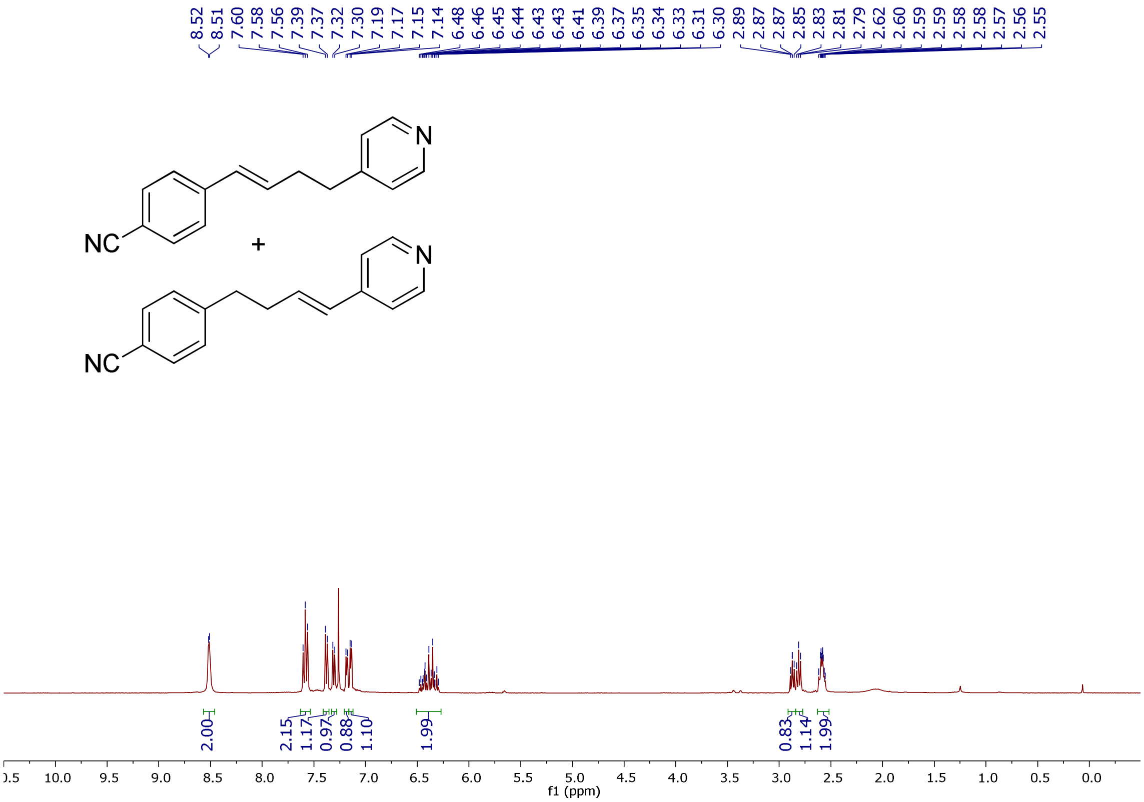

147.1
145.4
142.0
140.9
133.4
132.5
132.4
131.6
130.1
129.7
129.4
128.8
126.6
126.3
125.7
125.6
125.6
125.6
125.5
125.5
125.5
125.5
119.1
119.1
110.5
110.1
35.8
35.4
34.6
34.3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

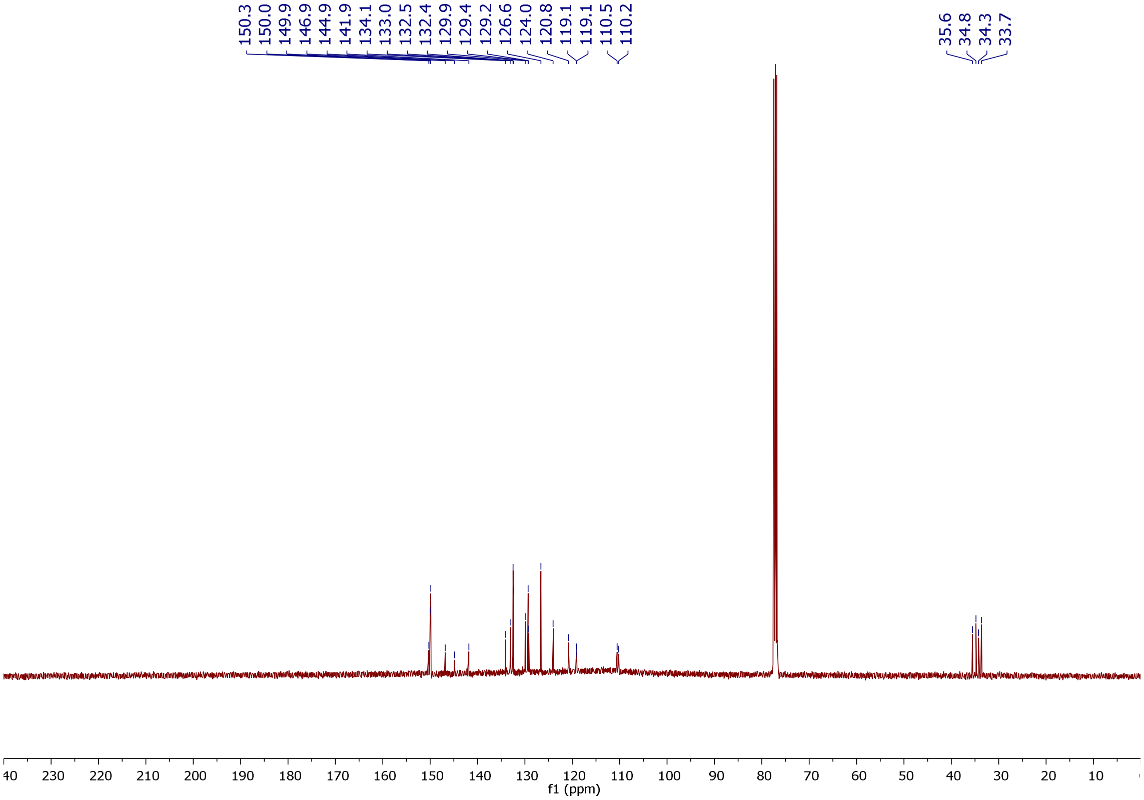
(*E*)-4-(4-(4-acetylphenyl)but-1-en-1-yl)benzonitrile + (*E*)-4-(4-(4-acetylphenyl)but-3-en-1-yl)benzonitrile **6c**



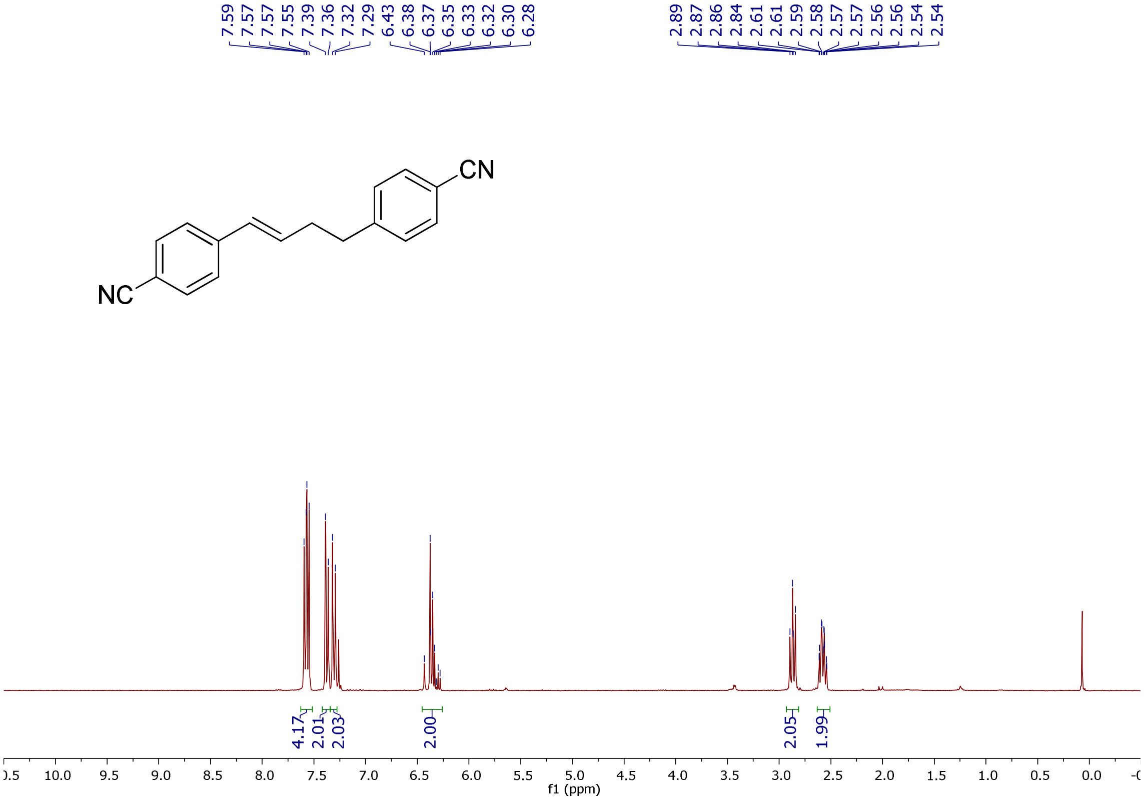


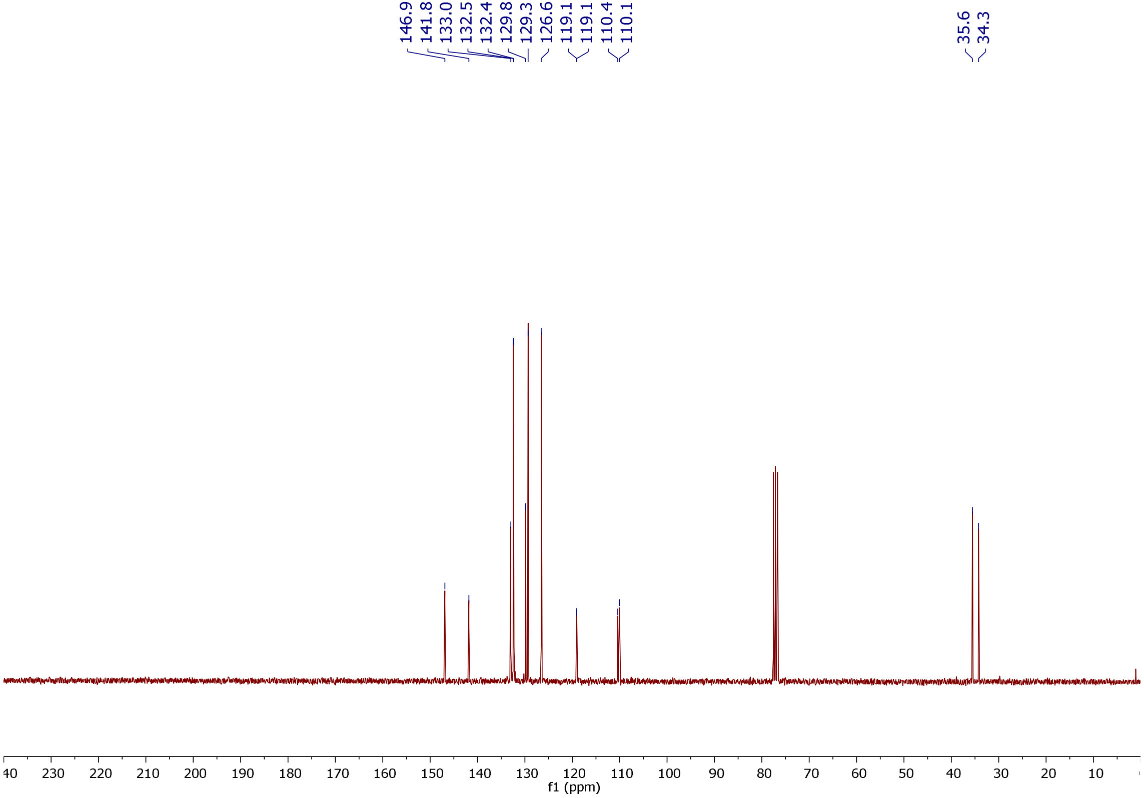
(*E*)-4-(4-(pyridin-4-yl)but-1-en-1-yl)benzonitrile + (*E*)-4-(4-(pyridin-4-yl)but-3-en-1-yl)benzonitrile **6d**



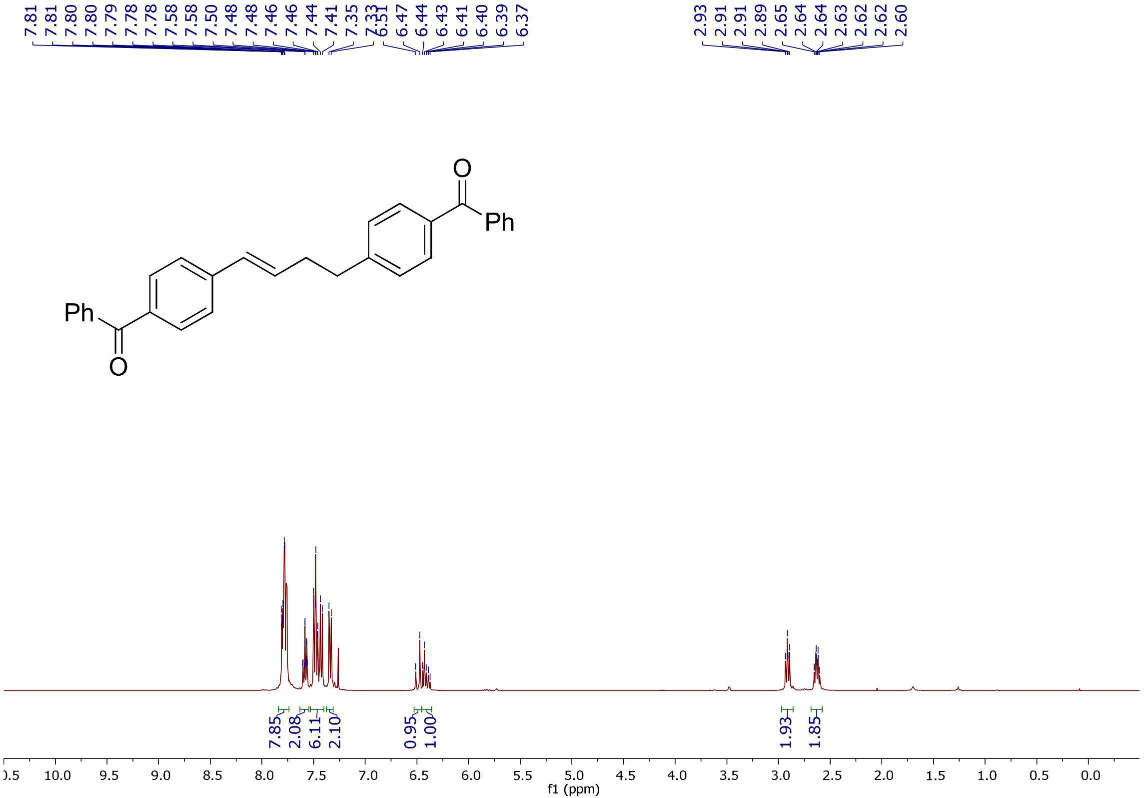


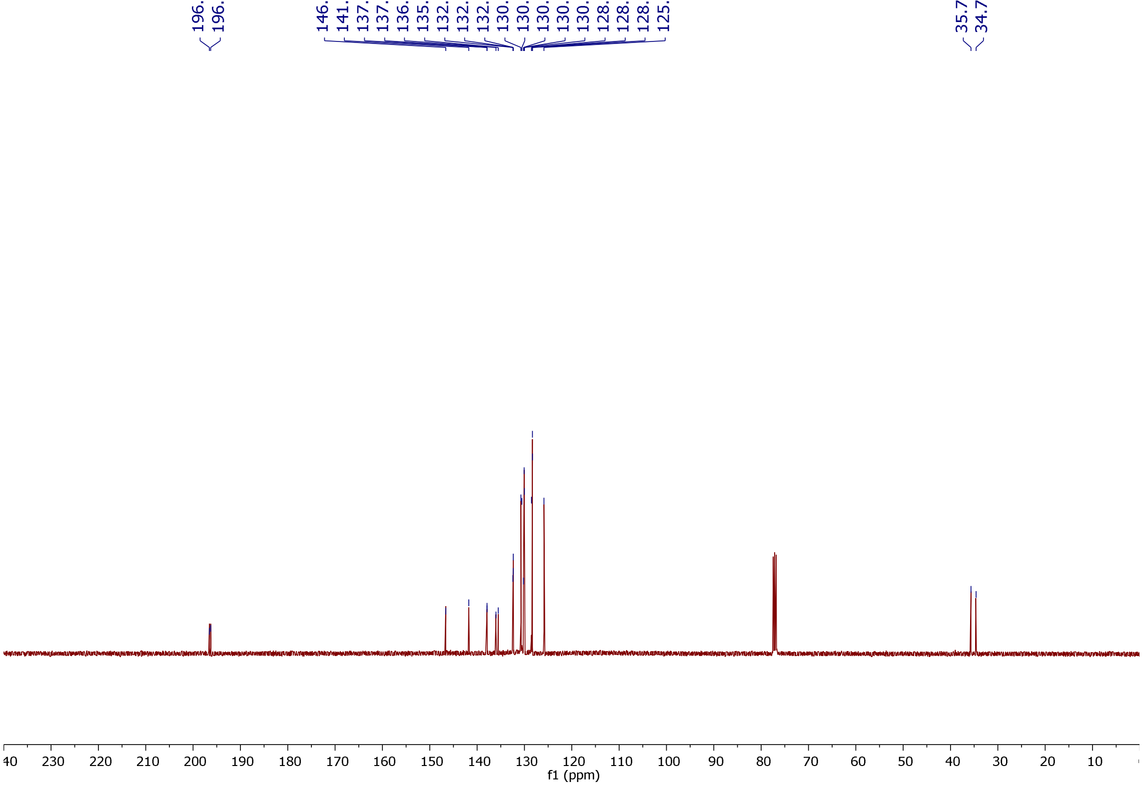
(*E*)-4,4`-(But-1-ene-1,4-diyl)dibenzonitrile **7a**



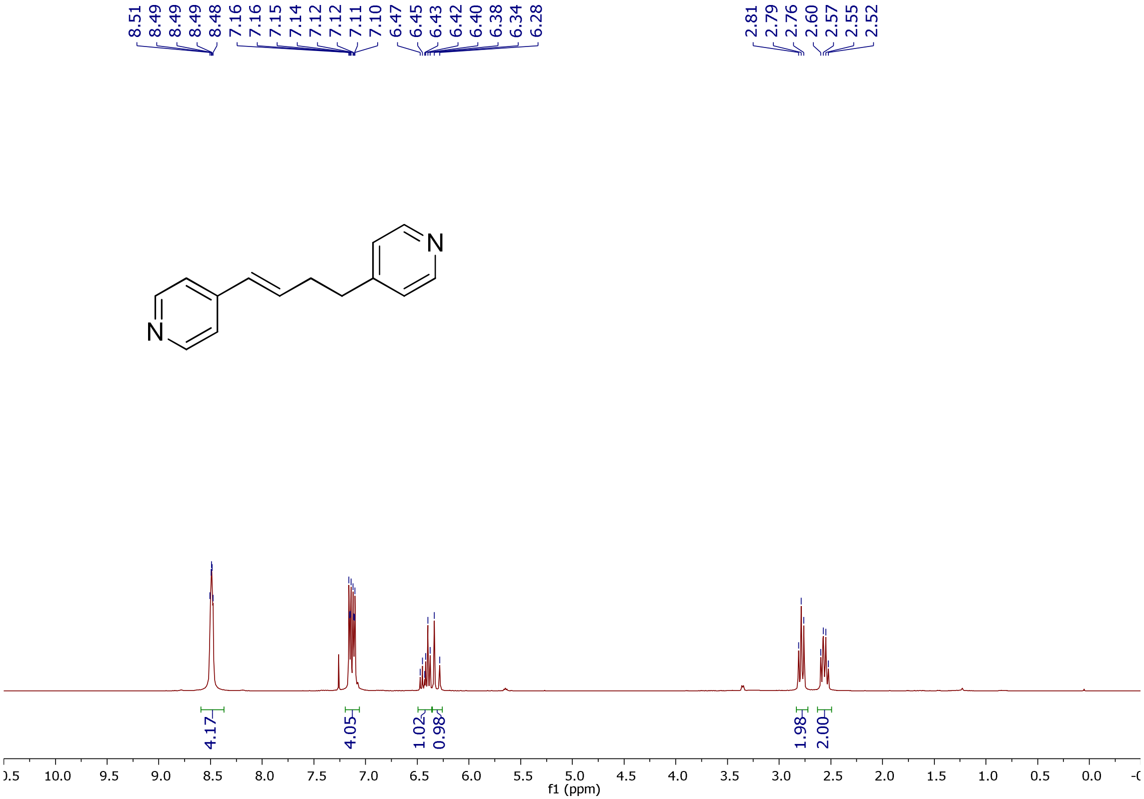


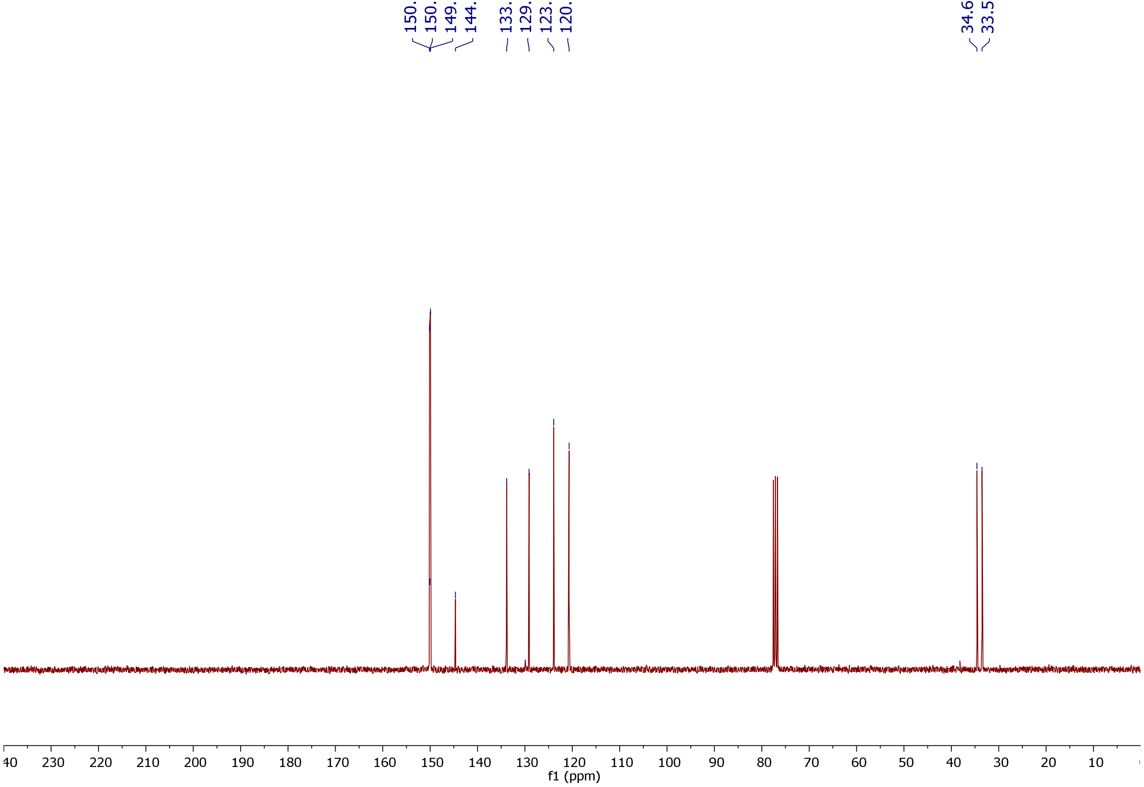
(*E*)-4,4`-(But-1-ene-1,4-diyl)dibenzophenone **7c**



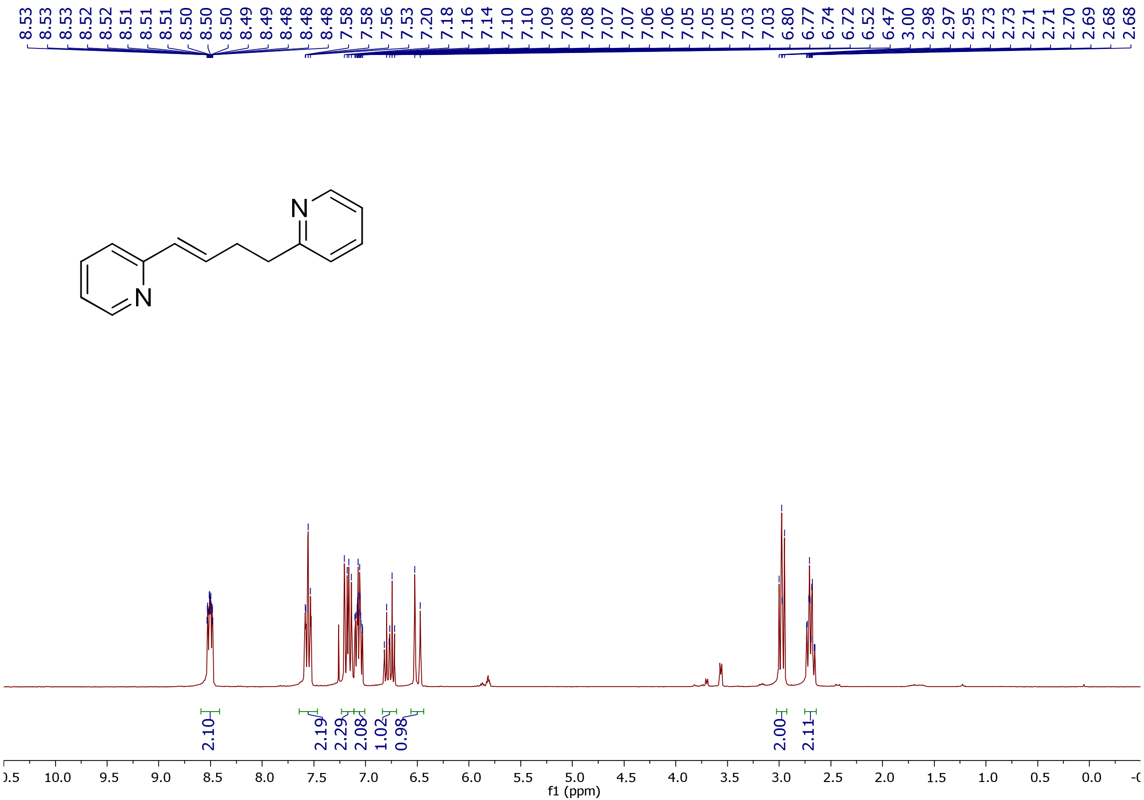


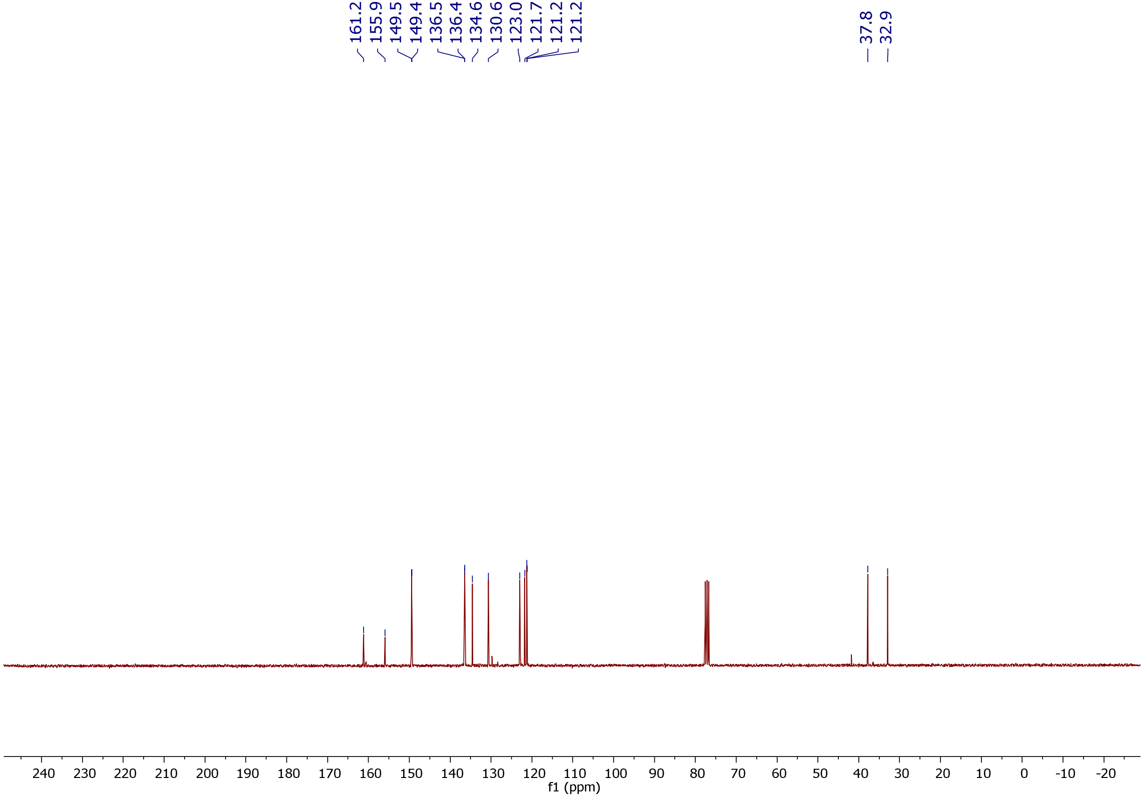
(*E*)-4,4`-(But-1-ene-1,4-diyl)dipyridine **7d**



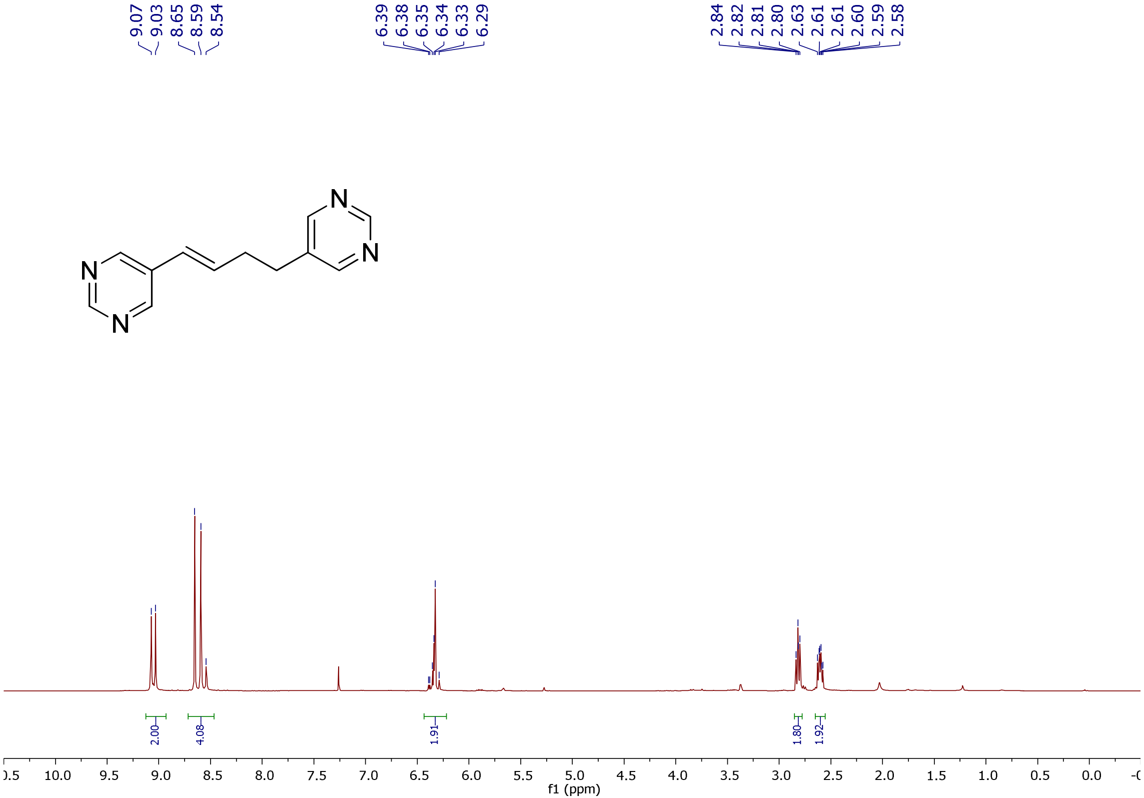


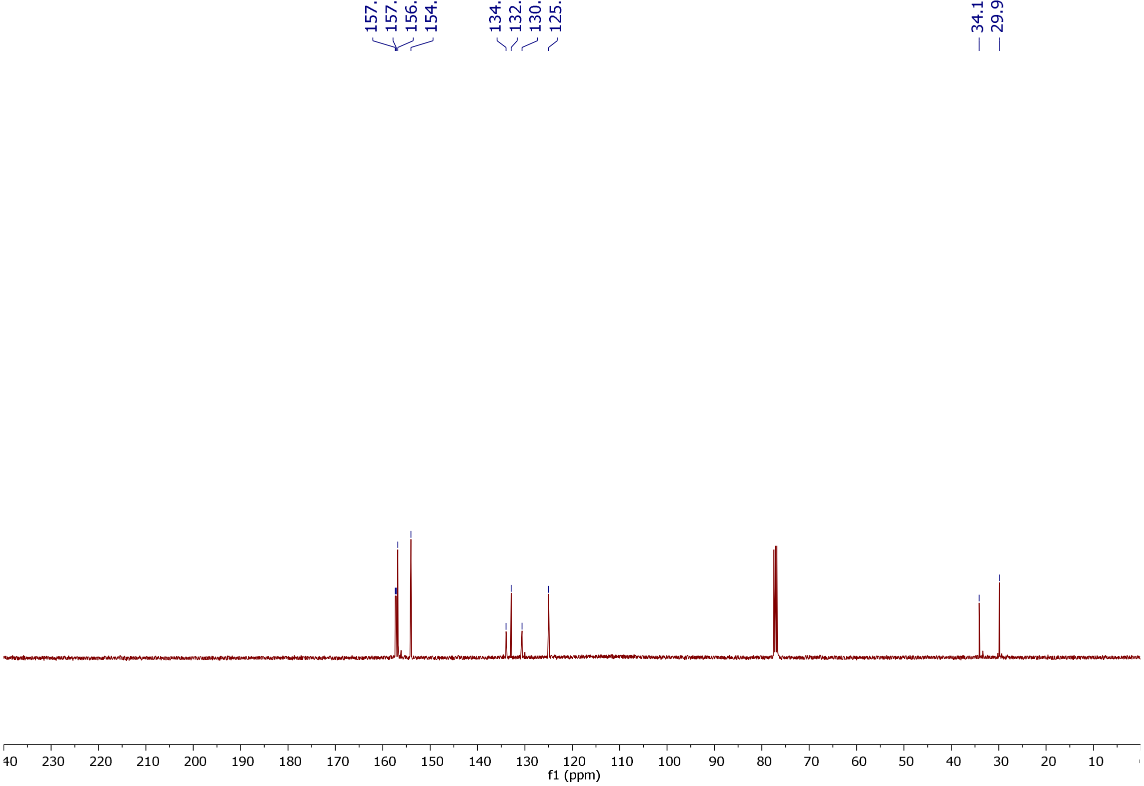
(*E*)-2,2`-(But-1-ene-1,4-diyl)dipyridine **7e**



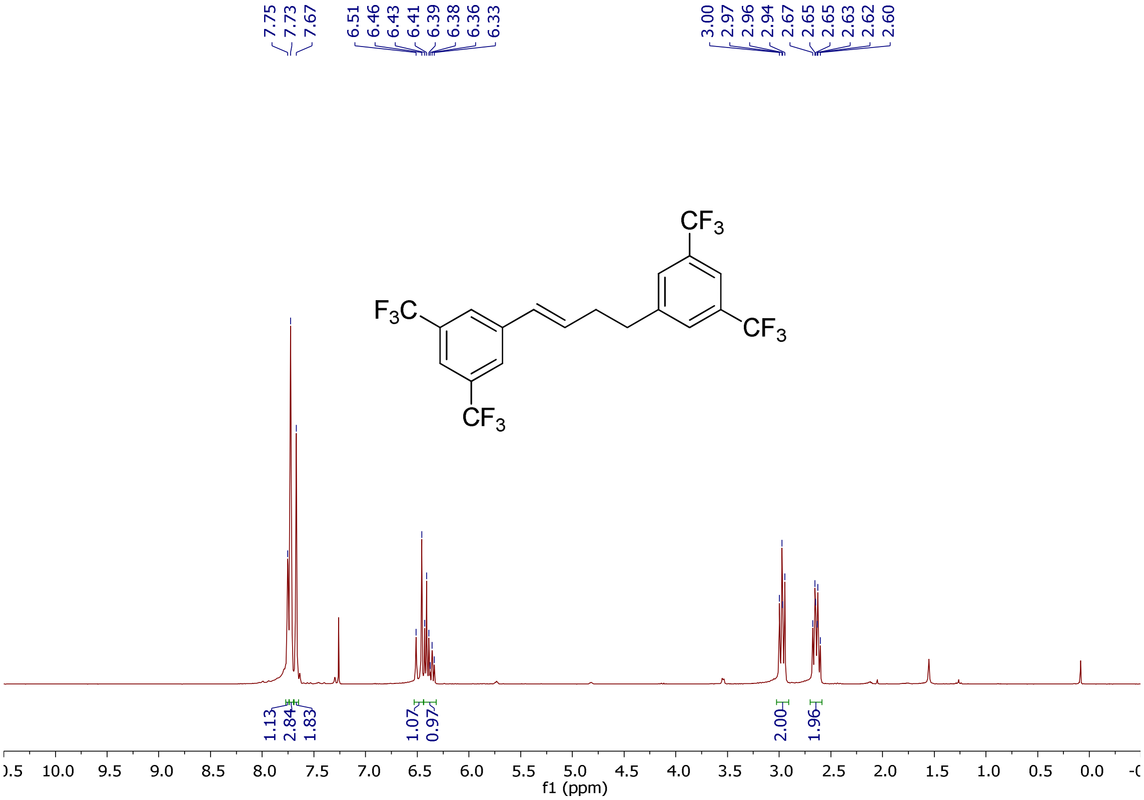


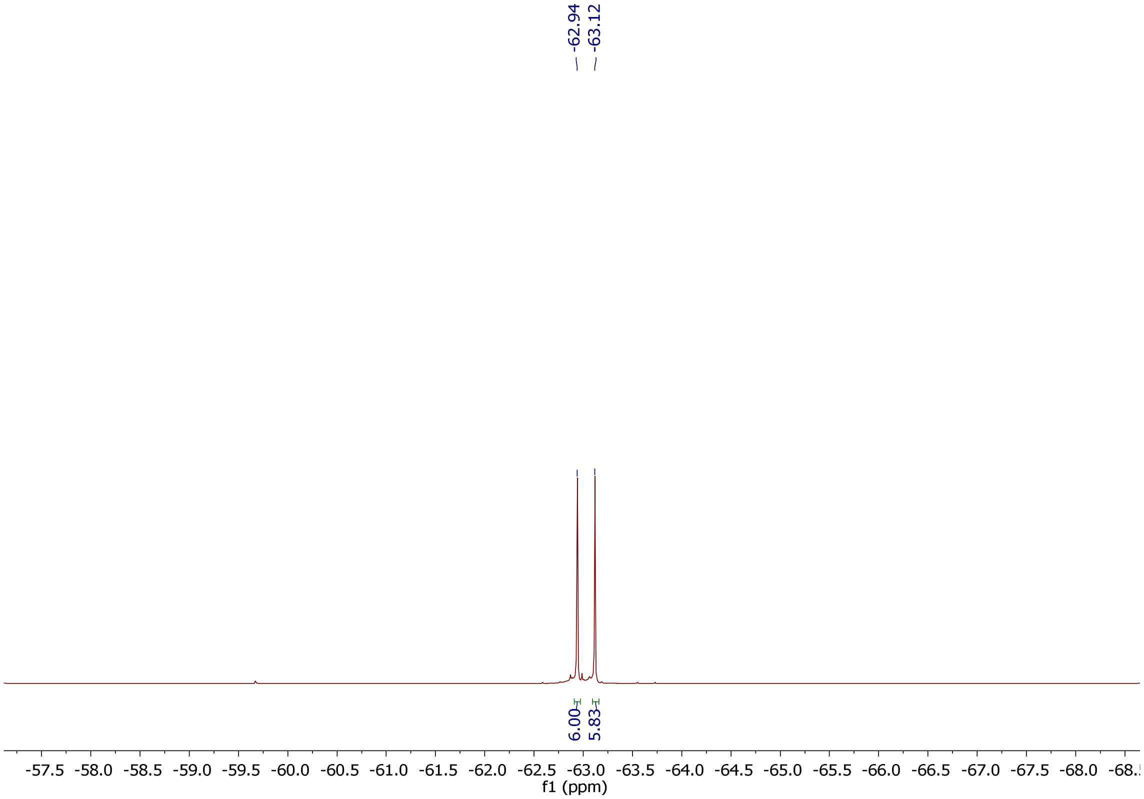
(*E*)-5,5'-(But-1-ene-1,4-diyl)dipyrimidine**7f**

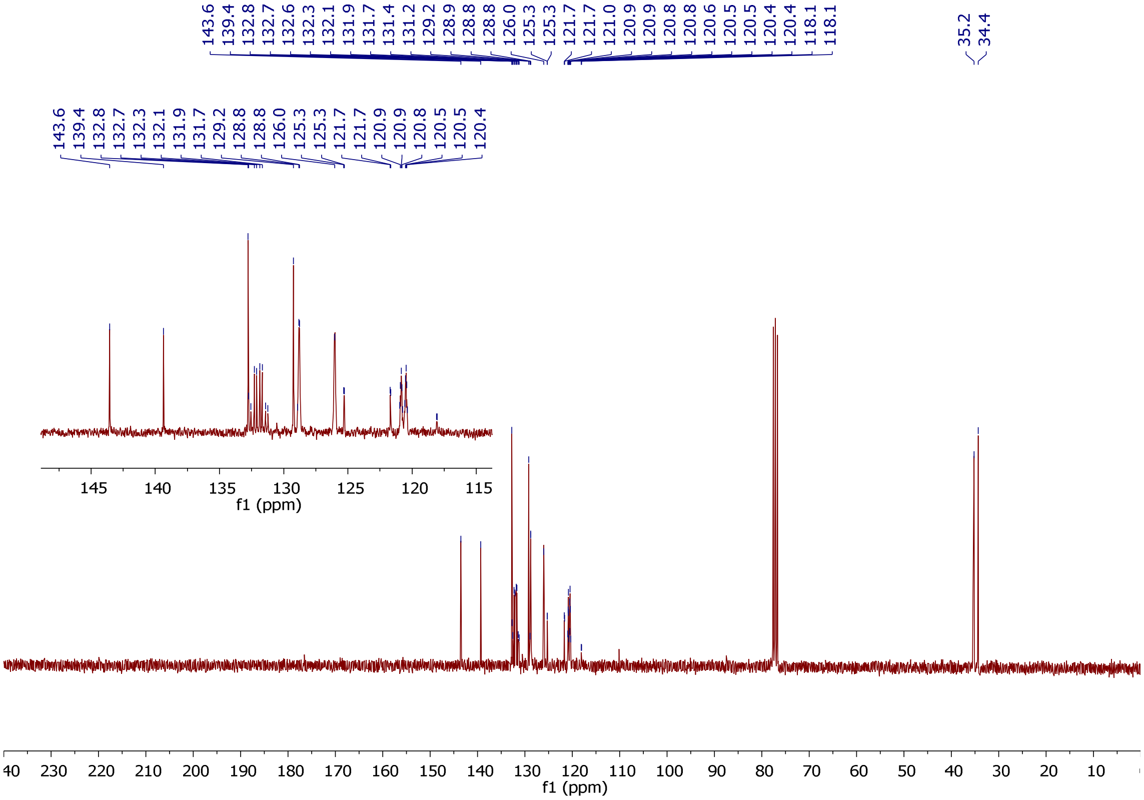




(*E*)-5,5`-(But-1-ene-1,4-diyl)bis(1,3-bis(trifluoromethyl)benzene) **7g**



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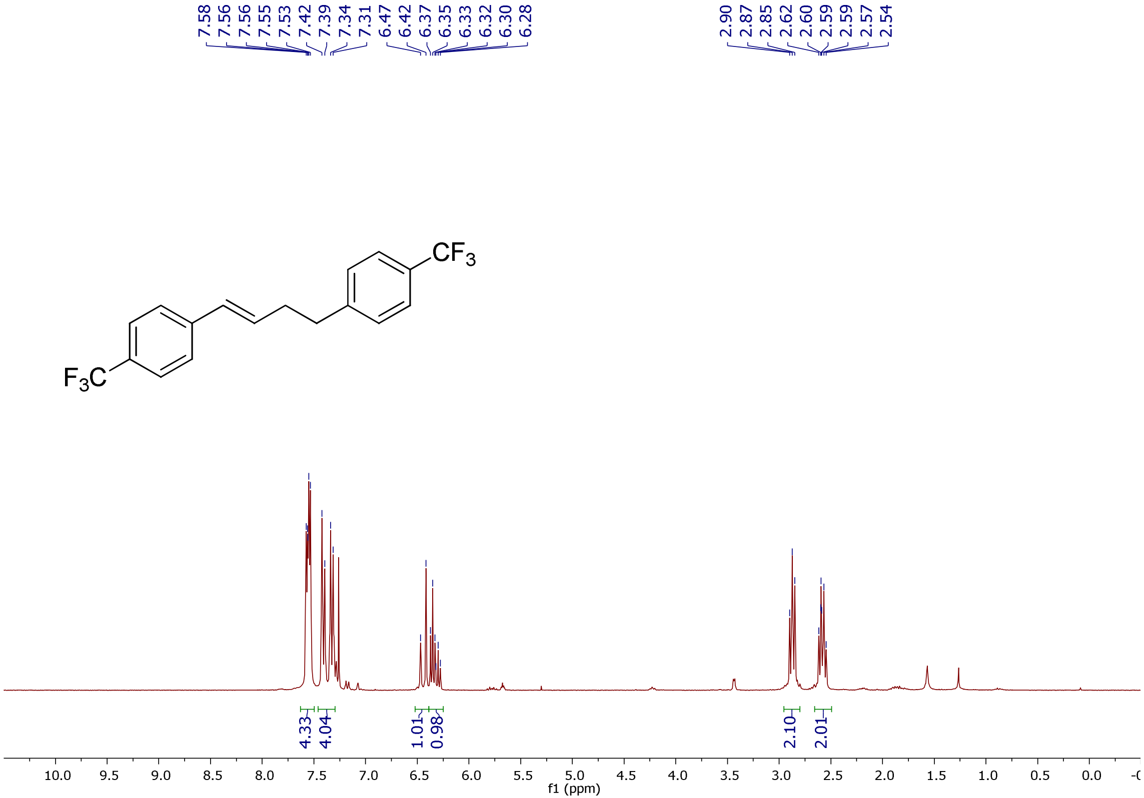
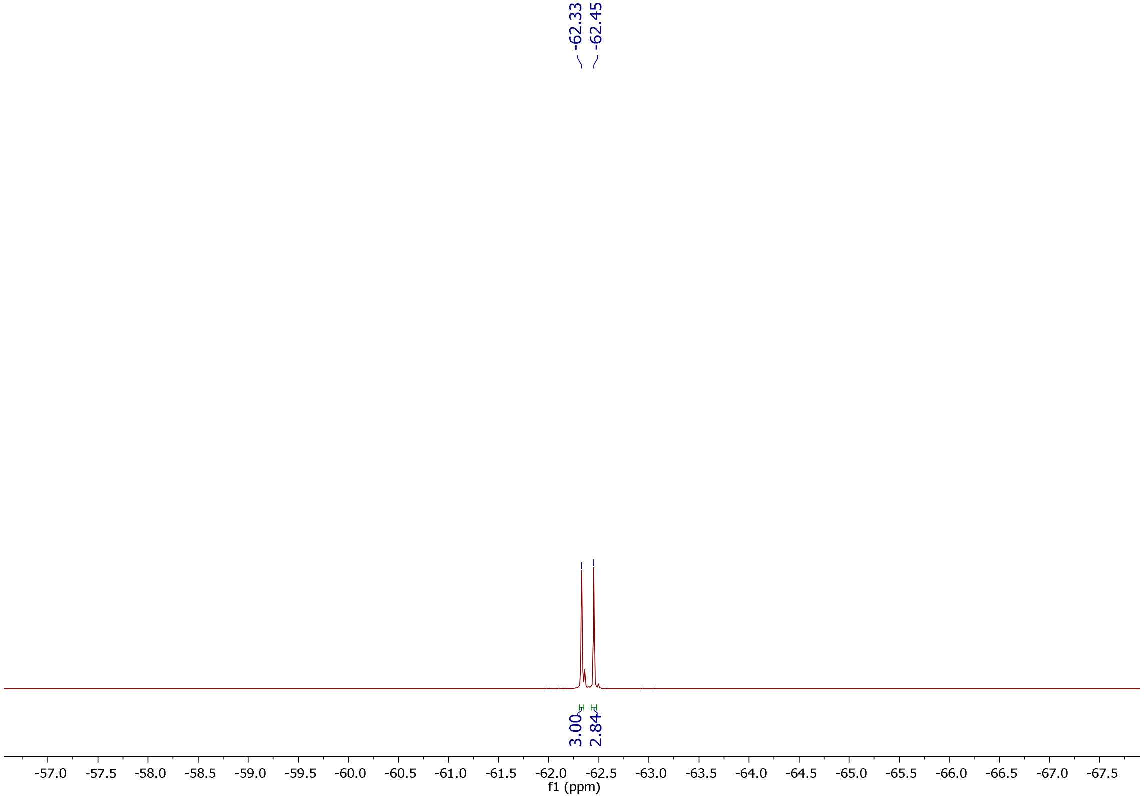
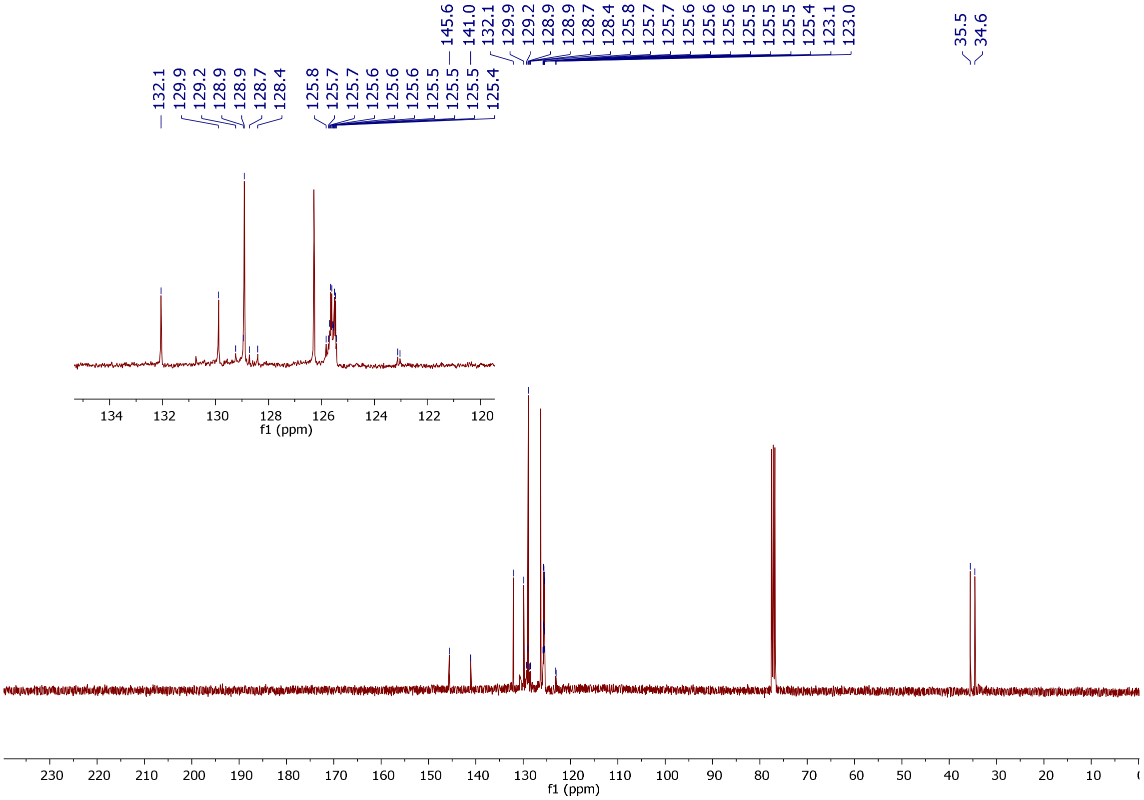
139.4
132.8
132.7
132.6
132.3
132.1
131.9
131.7
131.4
131.2
129.2
128.9
128.8
128.8
126.0
125.3
125.3
121.7
121.7
121.0
120.9
120.9
120.8
120.8
120.6
120.5
120.5
120.4
120.4
118.1
118.1
35.2
34.4
143.6
139.4
132.8
132.7
132.3
132.1
131.9
131.7
129.2
128.8
128.8
126.0
125.3
125.3
121.7
121.7
120.9
120.9
120.8
120.5
120.5
120.4
145
140
135
130
125
120
115
f1 (ppm)
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

(*E*)-4,4`-(But-1-ene-1,4-diyl)bis((trifluoromethyl)benzene) **7h**



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128.9
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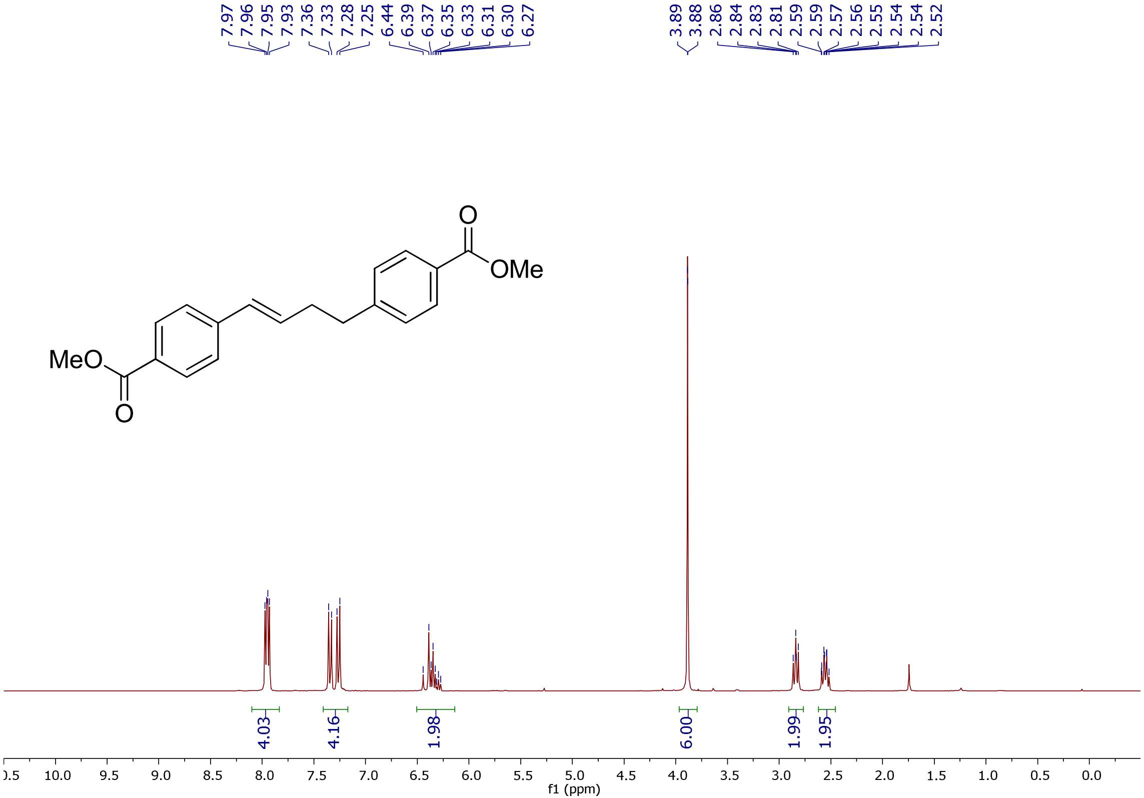
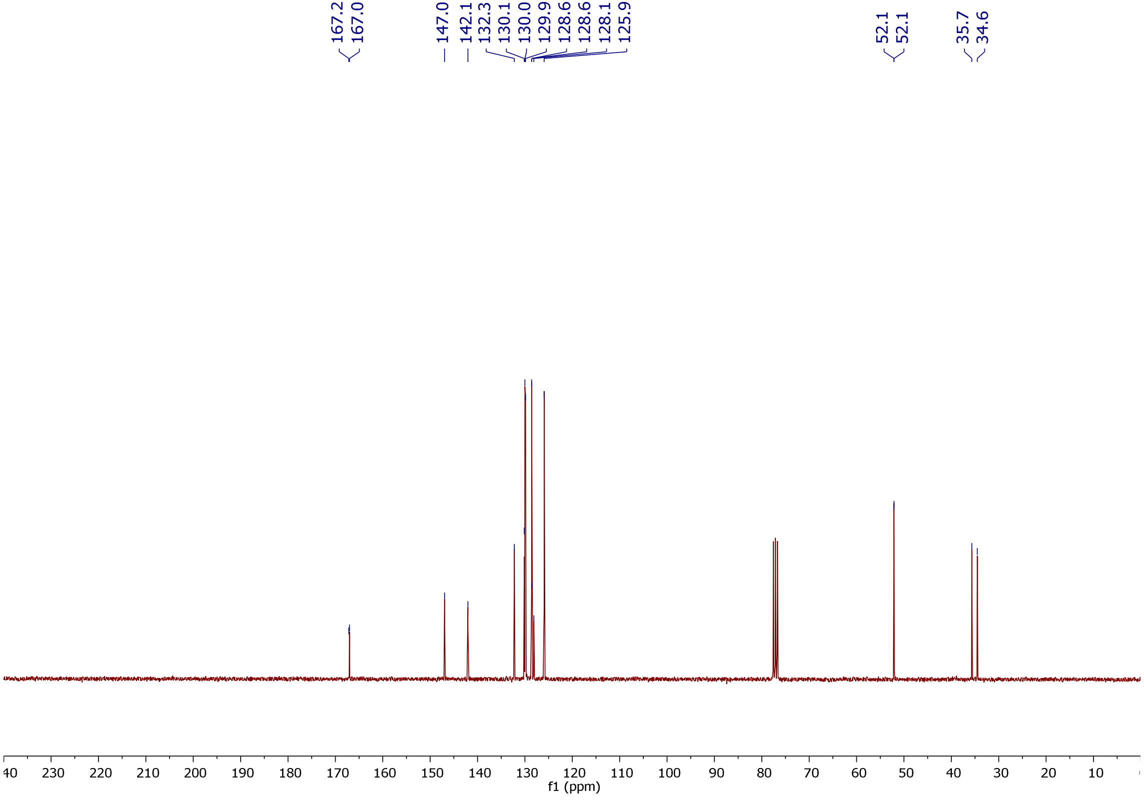
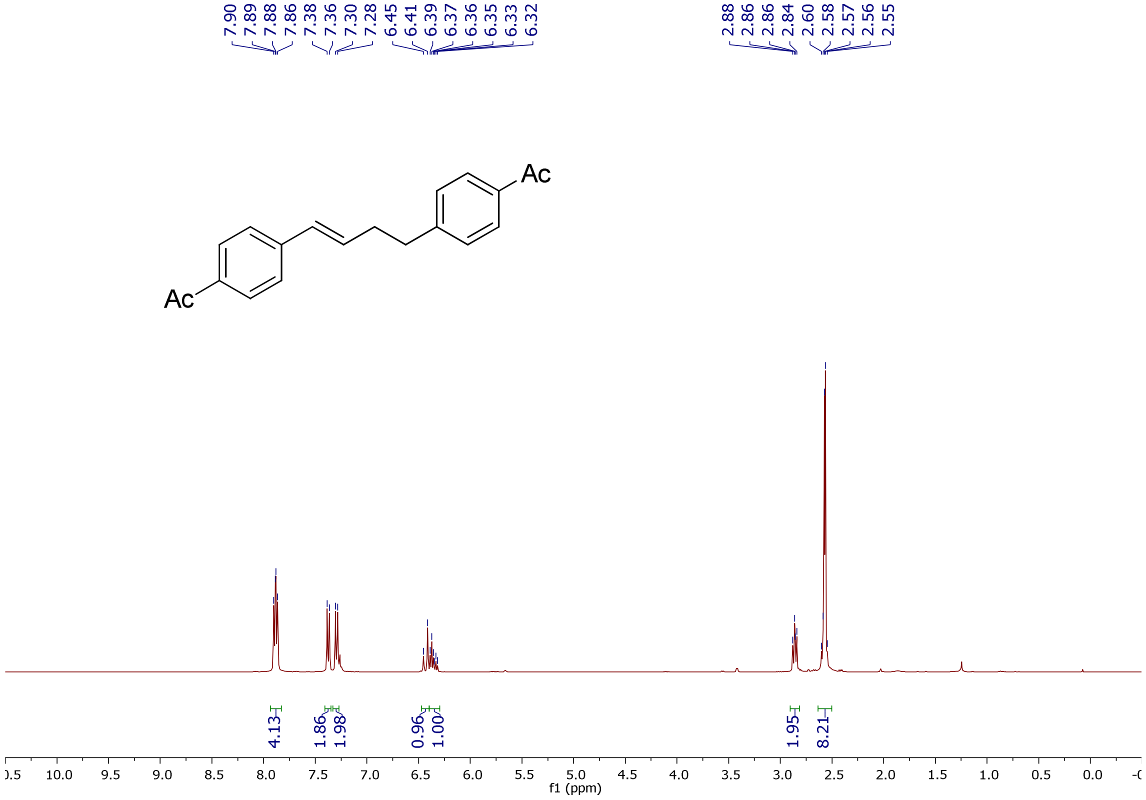
125.8
125.7
125.7
125.6
125.6
125.5
125.5
125.5
125.4
123.1
123.0
35.5
34.6
132.1
129.9
129.2
128.9
128.9
128.7
128.4
125.8
125.7
125.7
125.6
125.6
125.5
125.5
125.5
125.4
134
132
130
128
126
124
122
120
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

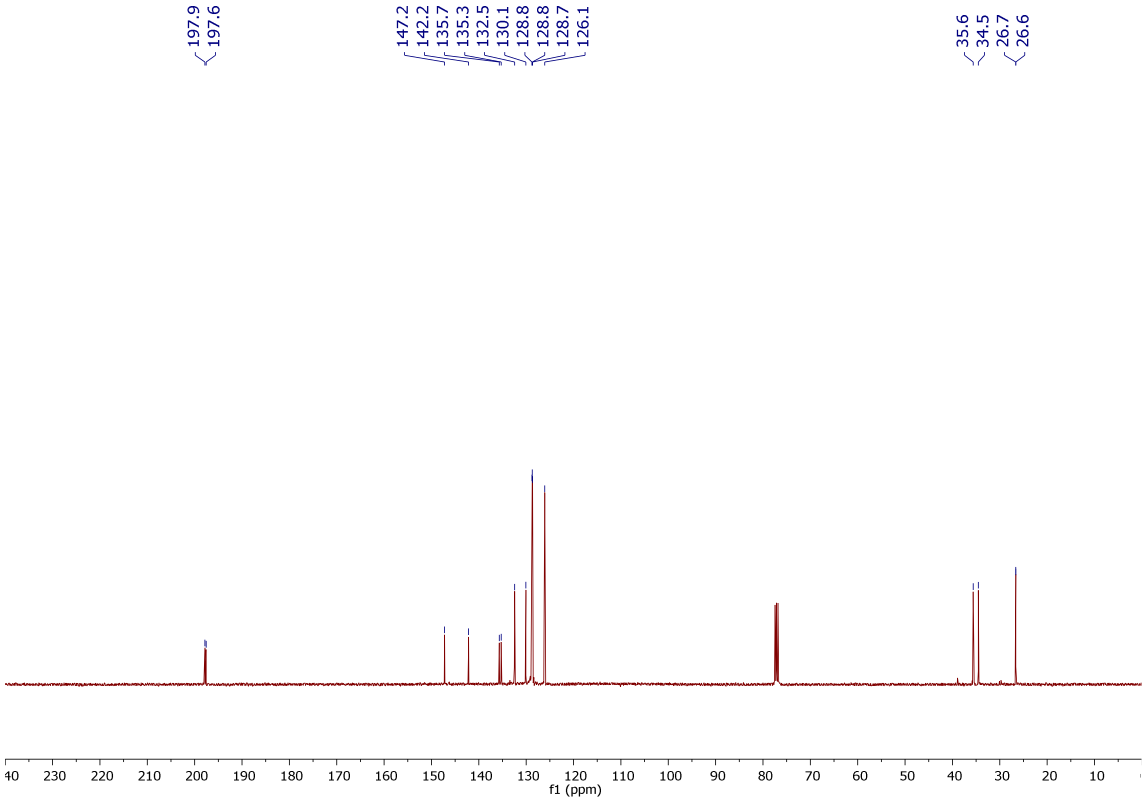
(*E*)-Dimethyl-4,4`-(but-1-ene-1,4-diyl)dibenzoate **7i**



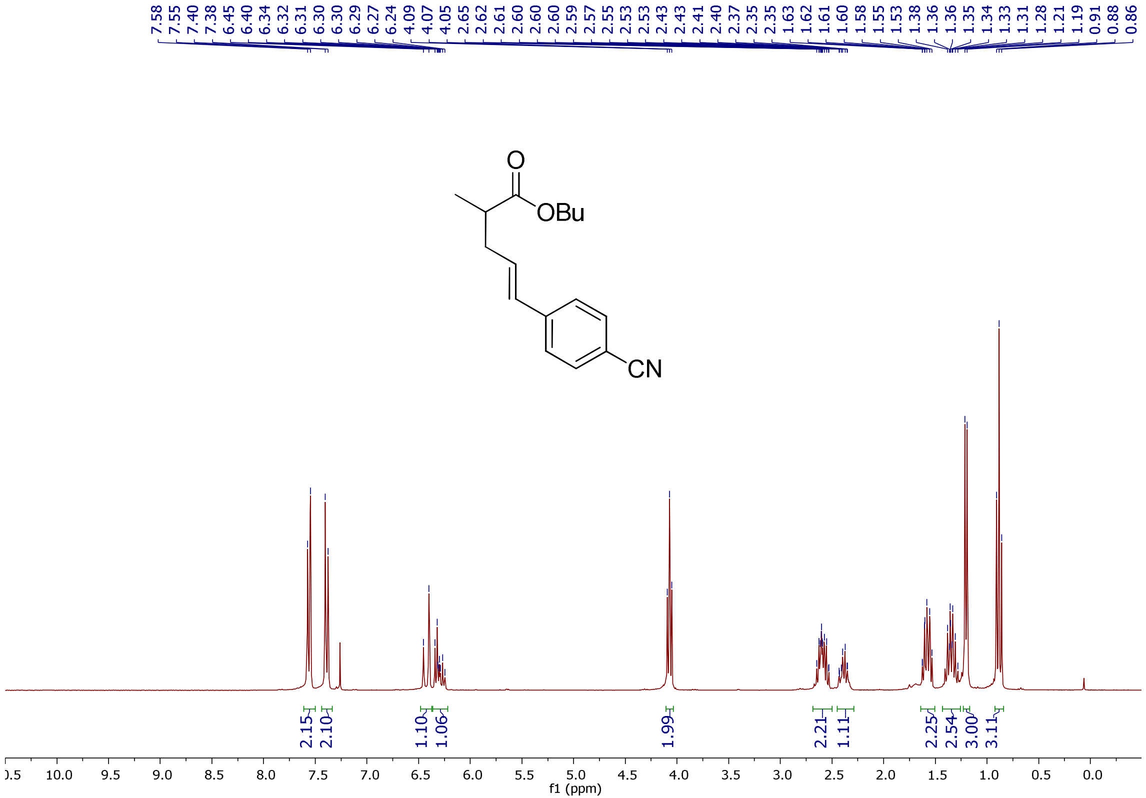


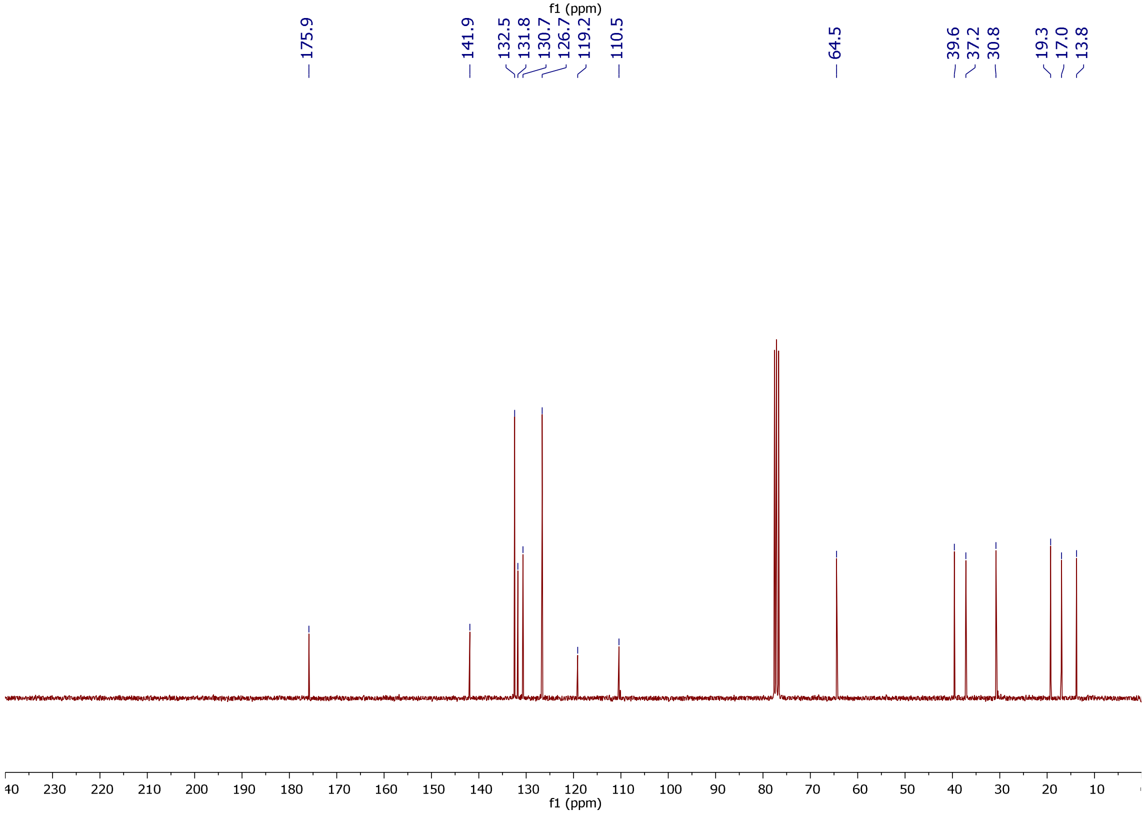
(*E*)-4,4`-(But-1-ene-1,4-diyl)diacetophenone **7k**



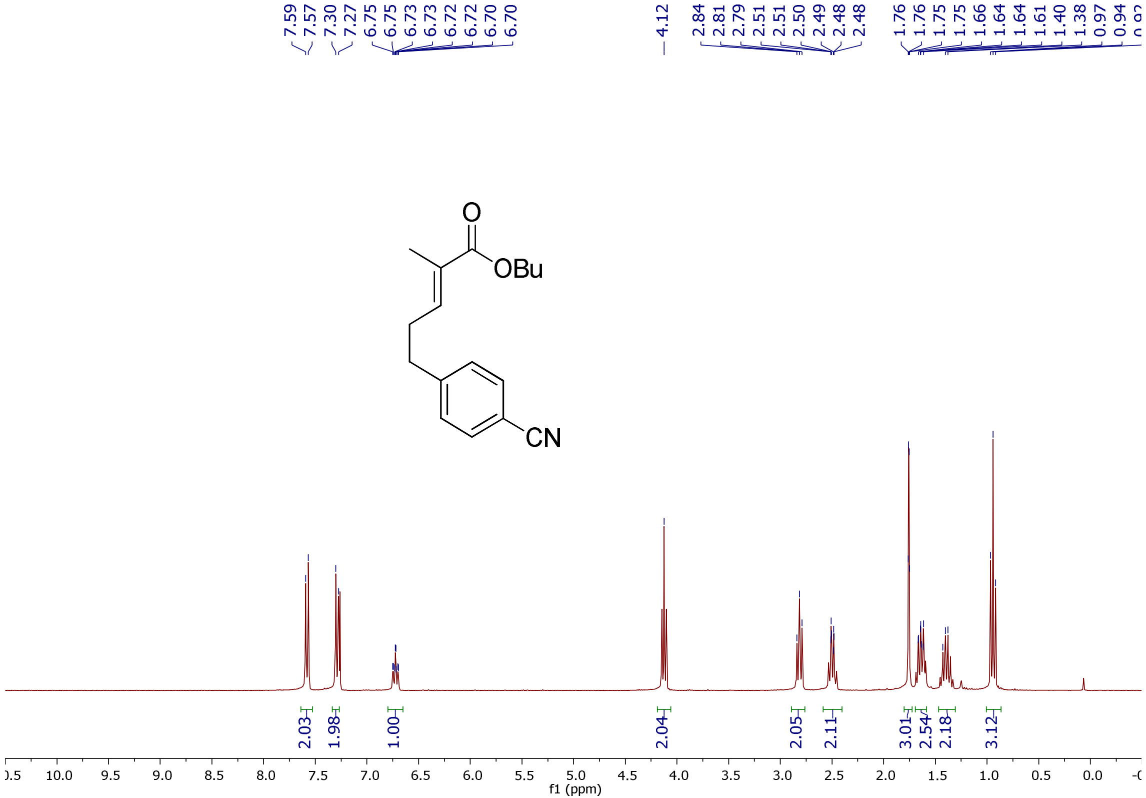


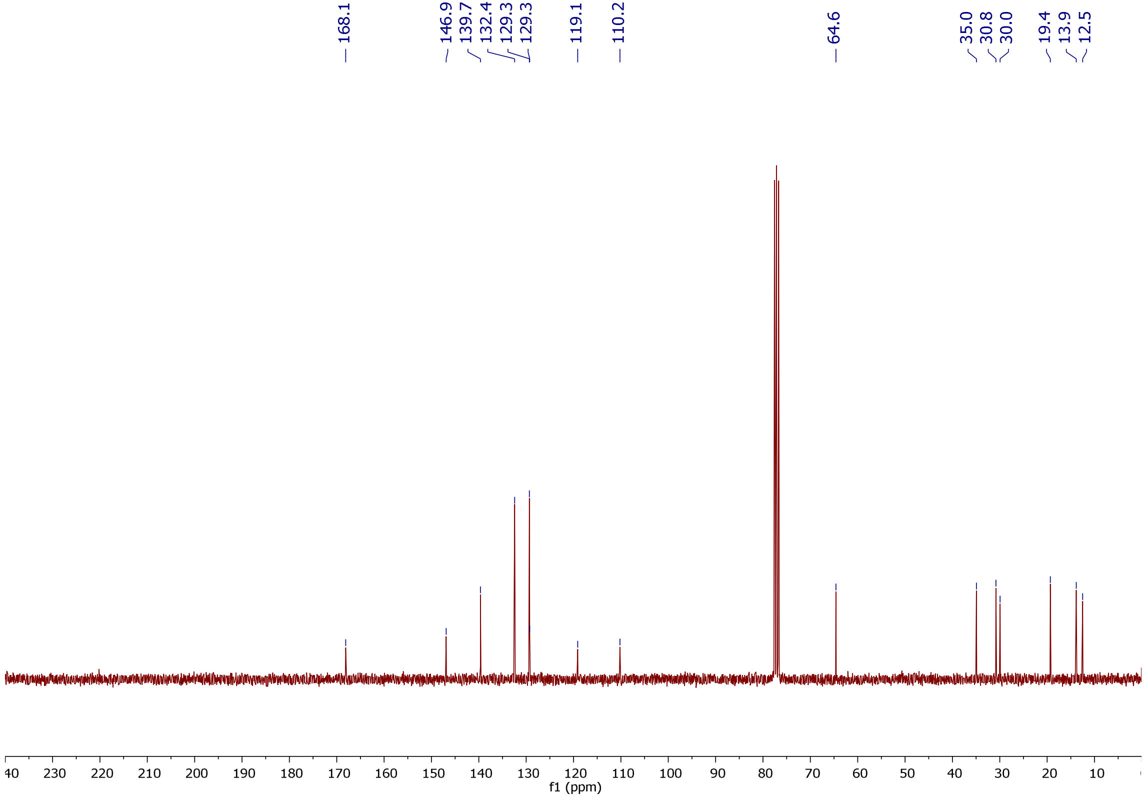
(*E*)-Butyl 5-(4-cyanophenyl)-2-methylpent-4-enoate **9a**





<u>(*E*)-Butyl 5-(4-cyanophenyl)-2-methylpent-2-enoate **9b**</u>



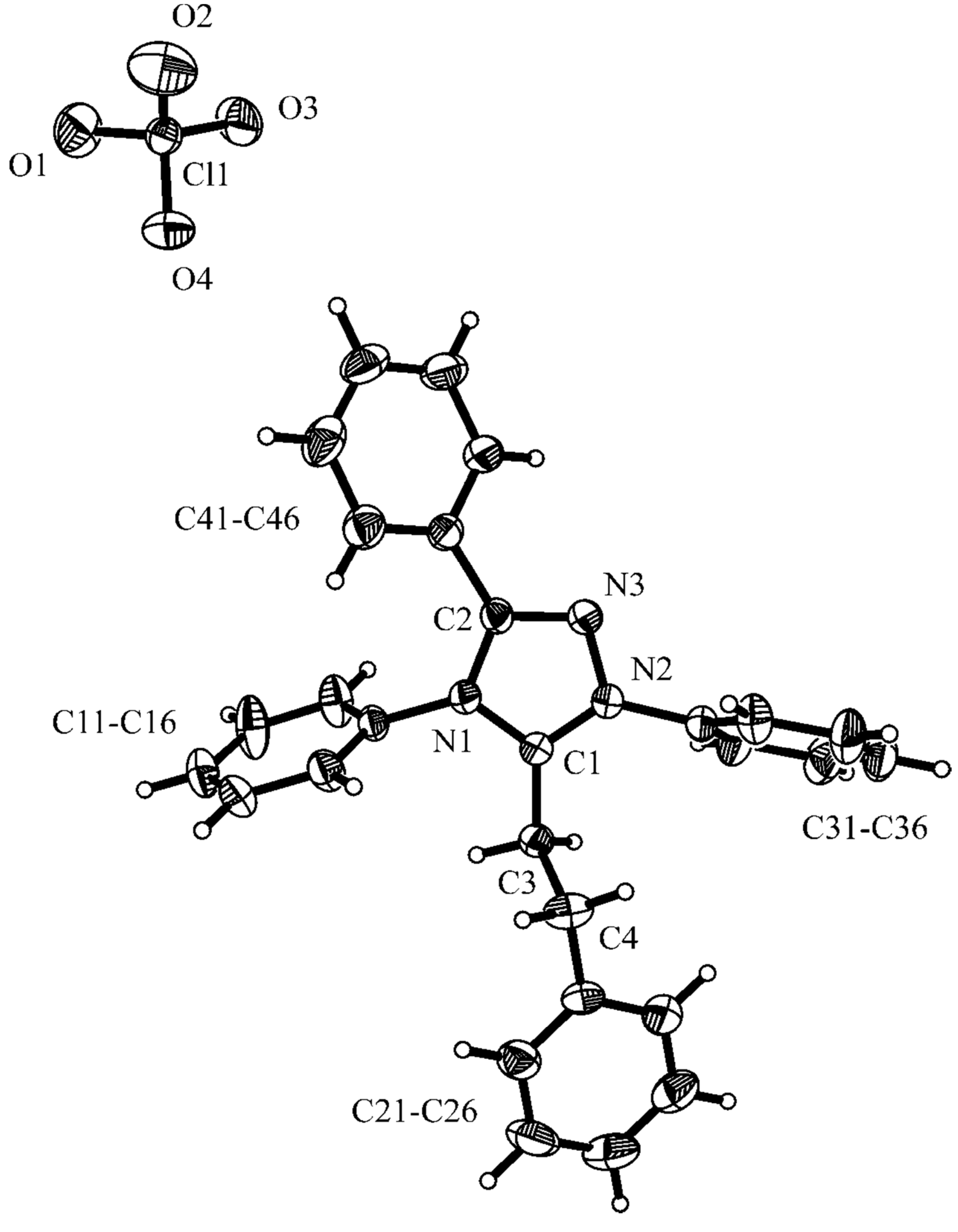


11. Single crystal X-ray structures of **3b** and **7g**

X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: For the compound **3b** a disordered over two positions ClO_4 anion was found in the asymmetric unit. Several restraints (SADI, SIMU, ISOR and SAME) were used in order to improve refinement stability. Compound **7g** present two CF_3 groups and the unit C1-C2-C3-C4 disordered over two positions. Several restraints (SADI, SIMU, ISOR, SAME, EADP and EXYZ) were used in order to improve refinement stability.

X-ray crystal structure analysis of 3b (glo7415): formula $C_{28}H_{24}ClN_3O_4$, M = 501.95, pale yellow crystal, 0.28 x 0.22 x 0.12 mm, a = 10.8692(2), b = 18.4448(5), c = 13.7073(3) Å, β = 112.226(2)°, V = 2543.9(1) Å^3, ρ_{calc} = 1.311 gcm^{-3}, μ = 0.189 mm^{-1}, empirical absorption correction (0.948 ≤ T ≤ 0.977), Z = 4, monoclinic, space group Cc (No. 9), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 8954 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 4567 independent (R_{int} = 0.032) and 4416 observed reflections [I>2σ(I)], 363 refined parameters, R = 0.041, wR^2 = 0.112, max. (min.) residual electron density 0.17 (-0.12) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



X-ray crystal structure analysis of 7g (glo7490): formula $C_{20}H_{12}F_{12}$, *M* = 480.30, colourless crystal, 0.18 x 0.14 x 0.10 mm, *a* = 4.9161(1), *b* = 23.9350(1), *c* = 8.1723(1) Å, *β* = 95.541(1)°, *V* = 957.12(2) Å^3, ρ_{calc} = 1.667 gcm^{-3}, μ = 1.626 mm^{-1}, empirical absorption correction (0.758 ≤ T ≤ 0.854), *Z* = 4, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 5920 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 1694 independent (R_{int} = 0.039) and 1554 observed reflections [$I>2\sigma(I)$], 364 refined parameters, *R* = 0.059, wR^2 = 0.175, max. (min.) residual electron density 0.34 (-0.23) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms. Flack parameter: 0.3(4).