BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

$AlBr_3$-Promoted stereoselective *anti*-hydroarylation of the acetylene bond in 3-arylpropynenitriles by electron-rich arenes: synthesis of 3,3-diarylpropenenitriles

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Experimental procedures, compound characterization, and ^1H and ^{13}C NMR spectra of compounds

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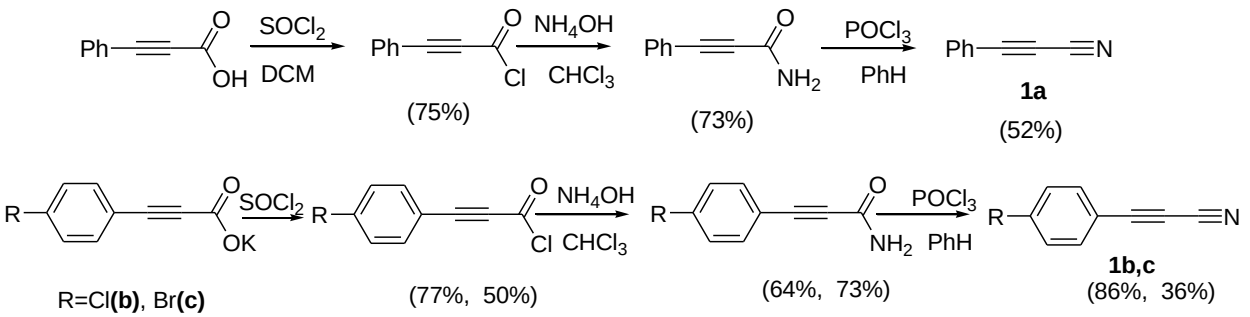
1. General remarks. NMR spectra of solutions of compounds in $CDCl_3$ were recorded on a Bruker AVANCE III 400 spectrometer at 25 °C (at 400 and 100 MHz for ^{1}H and ^{13}C NMR spectra, respectively). The residual proton solvent peak $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR spectra and the carbon signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra were used as references. HRMS was carried out using a Bruker maXis HRMS-ESI-QTOF instruments. Chromato-mass-spectrometry was performed with a Shimadzu QP-2010 Ultra with a SPB-1 SULFUR capillary column (30 m × 0.32 mm), thickness of the stationary phase 1.25 μm. The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates (Alugram SIL G/UV-254), using UV light for detection. Preparative TLC was performed on silica gel Chemapol L 5/40 with petroleum ether eluation. IR spectra were registered for solutions of compounds in $CHCl_3$ or for KBr disks on a Bruker IR spectrometer.

2. Synthesis and characterization of starting compounds 3-arylpropynenitriles 1a–c.

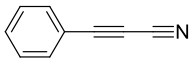
Synthesis of 3-arylpropynenitriles **1a–c** was carried out from the corresponding 3-arylpropynoic acids or their potassium salts, which were converted into acyl chlorides and then to amides; dehydration of the latter gave the target compounds (Scheme S1).



Scheme S1. Synthesis of 3-arylpropynenitriles **1a–c**.

General procedure for dehydration of 3-arylpropynamides. Synthesis of nitriles 1a–c. Phosphorus oxychloride ($POCl_3$, 4 mL) was added to a solution of 3-arylpropynamide (6 mol) in 60 mL of benzene. The reaction mixture was refluxed for 4 h. Then, it was diluted with 100 mL of dichloromethane, 100 mL of an aqueous saturated aqueous solution of $NaHCO_3$ were added, and this heterogeneous mixture was magnetically stirred at room temperature for 3–5 hours. The organic layer was separated, washed with water (100 mL), and dried with Na_2SO_4. The solvent was removed under reduced pressure. The nitriles **1b**, **c** were isolated by flash chromatography on silica gel, using a mixture of hexane/ethyl acetate 10:1 (v/v). Nitrile **1a** was used without additional purification.

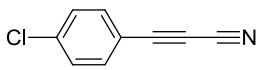
3-Phenylpropynenitrile 1a [1], yield of 52%, orange oil:



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.43 (m, Har, 2H,), 7.52-7.56 (m, Har, 1H), 7.60-7.62 (m, Har, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 63.2(C), 83.1(C), 105.6(C≡N), 117.7 (Car), 129.0(CarH), 132.0(CarH), 133.6(CarH).

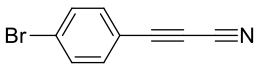
3-(4-Chlorophenyl)propynenitrile 1b[1], yield of 86%, yellow solid, m.p. 88-91ºC:



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.41(m, Har, 2H,), 7.53-7.56 (m, Har, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 64.1(C), 81.8(C), 105.4(C≡N), 116.1(Car), 129.5(CarH), 134.8(CarH), 138.7(Car).

3-(4-Bromophenyl)propynenitrile 1c [1], yield of 36%, orange oil:



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.44 (m, Har 2H), 7.51-7.53 (m, Har. 2H,);

^{13}C NMR (100 MHz, $CDCl_3$): δ 64.0(C), 81.8(C), 105.2(C≡N), 116.2(Car), 126.9(Car), 132.2(CarH), 134.6(CarH).

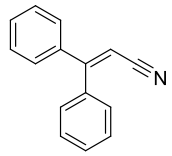
3. Synthesis and characterization of *E,Z*-3,3-diarylpropenenitriles 2a–o and 3-arylindenones 3a, b.

General procedure for the reaction of 3-arylpropynenitriles 1 with arenes under the action of $AlBr_3$. Synthesis of 3,3-diarylpropenenitriles 2. 3-Arylpropynenitrile **1** (0.64 mmol) was added to a mixture of $AlBr_3$ (1.07 g, 4 mmol, 6 equiv) with arene (2.5 mL). The reaction mixture was magnetically stirred at room temperature for 2 h. Then, the reaction was quenched with water (100 mL). The reaction products were extracted into EtOAc (3 × 100 mL), the combined extracts were washed with water (2 × 60 mL), saturated aqueous solution of $NaHCO_3$ (100 mL), water again (2 × 60 mL), and dried with Na_2SO_4. After evaporation of the solvent under reduced pressure, the obtained residue was subjected to thin-layer chromatography on silica gel using mixture of petroleum ether/ethyl acetate 10:1 (v/v) or a mixture of petroleum ether/dichloromethane/diethyl ether 20:5:1 (v/v/v). Yields of the products were determined after chromatographic isolation.

General procedure for the reaction of 3-arylpropynenitrile 1 with benzene in TfOH. Synthesis of 3,3-diarylpropenenitriles 2. 3-Arylpropynenitrile **1** (0.78 mmol) was added to a mixture of benzene (1 mL) in TfOH (2 mL). The reaction mixture was magnetically stirred at 0 °C or at room temperature for 1 h. Then, the reaction was quenched with water (100 mL). The reaction products were extracted into EtOAc (3 × 100 mL), the combined extracts were washed with water (2 × 60 mL), saturated aqueous solution of $NaHCO_3$ (100 mL), water again (2 × 60 mL), and dried with Na_2SO_4. After evaporation of the solvent under reduced pressure, the obtained residue was subjected to thin-layer chromatography on silica gel using a mixture of petroleum ether/ethyl acetate 10:1 (v/vol). Yields of the products were determined after chromatographic isolation.

General procedure for the cyclization of 3,3-diarylpropenenitriles 3 in TfOH. Synthesis of 3-arylindenones 3a, b. Solution of 3,3-diarylpropenenitrile **2** (0.4 mmol) in TfOH (2 mL) was magnetically stirred at room temperature for 1 h. Then the reaction was quenched with water (100 mL) and the reaction products were extracted into EtOAc (3 × 100 mL), the combined extracts were washed with water (2 × 60 mL), saturated aqueous solution of $NaHCO_3$ (100 mL), water again (2 × 60 mL), and dried with Na_2SO_4. After evaporation of the solvent under reduced pressure, the obtained residue was subjected to thin-layer chromatography on silica gel using a mixture of petroleum ether/ethyl acetate 10:1 (v/v). Yields of the products were determined after chromatographic isolation.

3,3-Diphenylprop-2-enenitrile 2a [2], obtained from nitrile **1a** and benzene with $AlBr_3$ in yield of 34%, or from nitrile **1a** and benzene in TfOH in yield of 31%, slightly yellow oil:



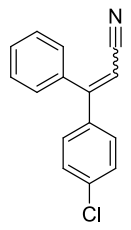
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74 (s, 1H, -CH=), 7.29-7.31 (m, 2H, Har), 7.38 (t, 2H, Har, *J = 8.0* Hz), 7.43-7.47 (m, 6H, Har);

^{13}C NMR (100 MHz, $CDCl_3$): δ 95.0(-CH=), 118.0(C≡N), 128.6(CarH), 128.7(CarH), 128.8(CarH), 129.7(CarH), 130.1(CarH), 130.5(CarH), 137.2(Car), 139.0(Car), 163.3 (C);

IR (KBr), ν, cm $^{-1}$: 2213 (C≡N);

HRMS, *m/z*: calcd. $C_{15}H_{11}N^+$ $[M+Na]^+$ 228.0784, found 228.0789.

(*E*-) and (*Z*)-3-(4-Chlorophenyl)-3-(phenyl)- prop-2-enenitrile 2b [2] obtained from nitrile **1b** and benzene with $AlBr_3$ in yield of 25%, or from nitrile **1b** and benzene in TfOH in yield of 55%, slightly yellow oil:

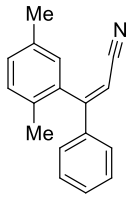


^{1}H NMR (400 MHz, $CDCl_3$): mixture of (E-) and (Z)-isomers, δ 5.72 (s, 1H, -CH=), 5.74 (s, 1H, -CH=), 7.24 (d, 2H, Har, *J =8.8* Hz), 7.28 (d, 2H, Har, *J = 7.2* Hz), 7.34-7.47 (m, 14H, Har);

^{13}C NMR (100 MHz, $CDCl_3$): mixture of (E-) and (Z)-isomers, δ 95.4 (2-CH=), 117.7(2 C≡N), 128.5(CarH), 128.8(CarH), 128.9(CarH), 129.0(CarH), 129.1(CarH), 129.6(CarH), 129.9(CarH), 130.4(CarH), 130.8(CarH), 131.1(CarH), 135.6(Car), 136.4(Car), 136.7(Car), 136.8(Car), 137.5(Car), 138.6(Car), 162.0 (2C);

HRMS, *m/z*: calcd. $C_{15}H_{10}ClNNa^+$ $[M+Na]^+$ 262.0394, found 262.0394.

(*Z*)-3-(2,5-Dimethylphenyl)-3-phenylprop-2-enenitrile 2c obtained from nitrile **1a** and 1,4-dimethylbenzene with $AlBr_3$ in yield of 30%, slightly yellow oil:



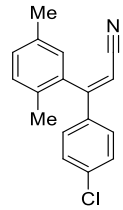
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 5.96 (s, 1H, -CH=), 7.04 (s, 1H, Har), 7.17 (s, 2H, Har), 7.29 (d, 2H, Har, *J = 6.8* Hz), 7.36 (t, 2H, Har, *J = 6.8* Hz), 7.39-7.43 (m, 1H, Har);

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2(CH_3), 21.0(CH_3), 96.2(-CH=), 117.2(C≡N), 127.3(CarH), 129.0(CarH), 129.7(CarH), 130.2(CarH), 130.6(CarH), 130.7(CarH), 132.7(Car), 135.7(Car), 136.6(Car), 137.6(Car), 136.8(Car), 163.3(C);

IR (KBr), ν, cm $^{-1}$: 2215 (C≡N);

HRMS, *m/z*: calcd. $C_{17}H_{15}NNa^+$ $[M+Na]^+$ 256.1097, found 256.1102

(*Z*)-3-(2,5-Dimethylphenyl)-3-(4-chlorophenyl)prop-2-enenitrile 2d obtained from nitrile **1b** and 1,4-dimethylbenzene with $AlBr_3$ in yield of 35%, slightly yellow oil:



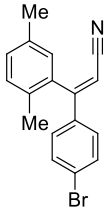
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 5.94 (s, 1H, -CH=), 7.01 (s, 1H, Har), 7.17 (s, 2H, Har), 7.21 (d, 2H, Har, *J = 8.6* Hz), 7.32 (d, 2H, Har, *J = 8.6* Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ: 19.2(CH_3), 21.0(CH_3), 96.6(-CH=), 117.2(C≡N), 128.5(CarH), 129.3(CarH), 129.7(CarH), 130.4(CarH), 130.9(CarH), 132.7(Car), 135.9(Car), 136.1(Car), 136.2(Car), 136.8(Car), 162.0(C);

IR (KBr), ν, cm $^{-1}$: 2216 (C≡N);

HRMS, *m/z*: calcd. $C_{17}H_{14}ClNNa^+$ $[M+Na]^+$ 290.0707, found 290.0704.

(*Z*)-3-(4-Bromophenyl)-3-(2,5-dimethylphenyl)prop-2-enenitrile 2e obtained from nitrile **1c** and 1,4-dimethylbenzene with $AlBr_3$ in yield of 40%, slightly yellow oil:



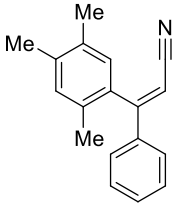
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 5.94 (s, 1H, -CH=), 7.00 (s, 1H, Har), 7.14 (d, 2H, Har, *J = 8.6* Hz), 7.16 (s, 2H, Har), 7.48 (d, 2H, Har, *J = 8.6* Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2(CH_3), 21.0(CH_3), 96.7(-CH=), 117.2(C≡N), 125.2(Car), 128.8(CarH), 129.7(CarH), 130.5(CarH), 130.9(CarH), 132.3(CarH), 132.7(Car), 135.9(Car), 136.1(Car), 136.5(Car), 162.1(C);

IR (KBr), ν, cm $^{-1}$: 2216 (C≡N);

HRMS, *m/z*: calcd. $C_{17}H_{14}BrNNa^+$ $[M+Na]^+$ 334.0202, found 334.0192.

(*Z*)-3-(2,4,5-Trimethylphenyl)-3-phenylprop-2-enenitrile 2f obtained from nitrile **1a** and 1,2,4-trimethylbenzene with $AlBr_3$ in yield of 26%, slightly yellow oil:



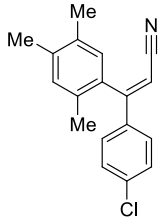
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 5.93 (s, 1H, -CH=), 6.98 (s, 1H, Har), 7.05 (s, 1H, Har), 7.28-7.40 (m, 5H, Har);

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2(CH_3), 19.3(CH_3), 19.7(CH_3), 96.1(-CH=), 117.8(C≡N), 127.3(CarH), 128.9(CarH), 130.3(CarH), 130.5(CarH), 132.2(CarH), 133.1(Car), 134.2(Car), 134.3(Car), 137.9(Car), 138.0(Car), 163.4(C);

IR (KBr), ν, cm $^{-1}$: 2214 (C≡N);

HRMS, *m/z*: calcd. $C_{18}H_{17}NNa^+$ $[M+Na]^+$ 270.1253, found 270.1256.

(*Z*)-3-(4-Chlorophenyl)-3-(2,4,5-trimethylphenyl)prop-2-enenitrile 2g obtained from nitrile **1b** and 1,2,4-trimethylbenzene with $AlBr_3$ in yield of 38%, slightly yellow oil:

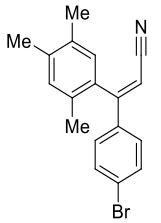


^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 5.90 (s, 1H, -CH=), 6.96 (s, 1H, Har), 7.05,(s, 1H, Har), 7.22 (d, 2H, Har, *J = 8.4* Hz), 7.32 (d, 2H, Har, *J = 8.8* Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2(CH_3), 19.3(CH_3), 19.7(CH_3), 96.5(-CH=), 117.4(C≡N), 128.6(CarH), 129.2(CarH), 130.3(CarH), 132.3(CarH), 133.0(Car), 133.7(Car), 134.4(Car), 136.4(Car), 136.7(Car), 138.2(Car), 162.1(C);

HRMS, *m/z*: calcd. $C_{18}H_{16}ClNNa^+$ $[M+Na]^+$ 304.0863, found 304.0864.

(*Z*)-3-(4-Bromophenyl)-3-(2,4,5-trimethylphenyl)prop-2-enenitrile 2h obtained from nitrile **1c** and 1,2,4-trimethylbenzene with $AlBr_3$ in yield of 25%, slightly yellow oil:



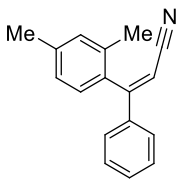
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 5.91 (s, 1H, -CH=), 6.95 (s, 1H, Har), 7.04 (s, 1H, Har), 7.15 (d, 2H, Har, *J = 8.4* Hz), 7.47 (d, 2H, Har, *J = 8.4* Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2(CH_3), 19.4(CH_3), 19.7(CH_3), 96.6(-CH=), 117.4(C≡N), 125.1(Car), 128.8(CarH), 130.3(CarH), 132.2(CarH), 132.3(CarH), 133.1(Car), 133.6(Car), 134.5(Car), 136.9(Car), 138.2(Car), 162.2(C);

IR (KBr), ν, cm $^{-1}$: 2215 (C≡N);

HRMS, *m/z*: calcd. $C_{18}H_{16}BrNNa^+$ $[M+Na]^+$ 348.0358, found 348.0359.

(*Z*)-3-(2,4-Dimethylphenyl)-3-phenylprop-2-enenitrile 2i obtained from nitrile **1a** and 1,3-dimethylbenzene with $AlBr_3$ in yield of 42%; slightly yellow oil:



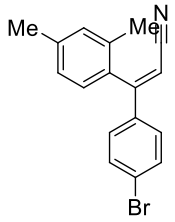
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 5.94 (s, 1H, -CH=), 7.09-7.12 (m, 3H, Har), 7.28d (d, 2H, Har, *J=7.2* Hz), 7.32-7.36 (m, 2H, Har), 7.38-7.42 (m, 1H, Har);

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7(CH_3), 21.4(CH_3), 96.3(-CH=), 117.7(C≡N), 126.9 (CarH), 127.3(CarH), 128.9(CarH), 129.3(CarH), 130.6(CarH), 131.7(CarH), 133.9(Car), 135.8(Car), 137.9(Car), 139.4(Car), 163.4(C);

IR (KBr), ν, cm $^{-1}$: 2215 (C≡N);

HRMS, *m/z*: calcd. $C_{17}H_{15}NNa^+$ $[M+Na]^+$ 256.1097, found 256.1099.

(*Z*)-3-(4-Bromophenyl)-3-(2,4-dimethylphenyl)prop-2-enenitrile 2j obtained from nitrile **1c** and 1,3-dimethylbenzene with $AlBr_3$ in yield of 33%, slightly yellow oil:

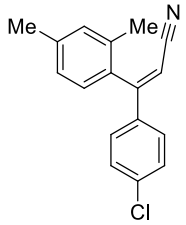


^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 5.93 (s, 1H, -CH=), 7.09-7.12 (m, 3H, Har), 7.14 (d, 2H, Har, *J = 8.8* Hz), 7.48 (d, 2H, Har, *J = 8.4* Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7(CH_3), 21.4(CH_3), 96.8(-CH=), 117.4(C≡N), 125.2(Car), 127.1(CarH), 128.7(CarH), 129.3(CarH), 131.8(CarH), 132.2(Car), 133.4(Car), 135.8(Car), 136.8(Car), 139.7(Car), 162.2(C);

HRMS, *m/z*: calcd. $C_{17}H_{14}BrNNa^+$ $[M+Na]^+$ 334.0202, found 334.0200.

(*Z*)-3-(4-Chlorophenyl)-3-(2,4-dimethylphenyl)prop-2-enenitrile 2k obtained from nitrile **1b** and 1,3-dimethylbenzene with $AlBr_3$ in yield of 64%, slightly yellow oil:



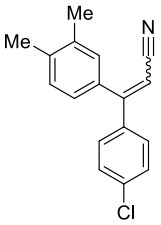
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 5.92 (s, 1H, -CH=), 7.01-7.09 (m, 3H, Har), 7.21 (d, 2H, Har, *J = 8.6* Hz), 7.32 (m, 2H, Har, *J = 8.6* Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7(CH_3), 21.4(CH_3), 96.7(-CH=), 117.4(C≡N), 127.1 (CarH), 128.6(CarH), 129.2(CarH), 129.3(CarH), 131.8(CarH), 133.4(Car), 135.8(Car), 136.3(Car), 136.8(Car), 139.7(Car), 162.1(C);

IR (KBr), ν, cm $^{-1}$: 2216 (C≡N);

HRMS, *m/z*: calcd. $C_{17}H_{14}ClNNa^+$ $[M+Na]^+$ 290.0707, found 290.0735.

(*E*)- and (*Z*)-3-(4-Chlorophenyl)-3-(3,4-dimethylphenyl)prop-2-enenitrile 2l obtained from nitrile **1b** and 1,2-dimethylbenzene with $AlBr_3$ in yield of 20%, slightly yellow oil:

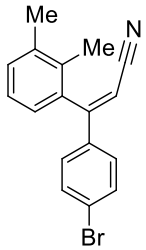


^{1}H NMR (400 MHz, $CDCl_3$): mixture of (E-) and (Z)-isomers, δ 2.25 (s, 3H, CH_3), 2.28 (c 3H, CH_3), 2.29 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 5.63 (s, 1H, -CH=), 5.70 (c 1H, -CH=), 6.98-7.00 (m, 1H, Har), 7.03 (s, 1H, Har), 7.12-7.17 (m, 3H, Har), 7.20-7.22 (m, 1H, Har), 7.24 (d, 2H, Har, *J = 7.2* Hz), 7.34 (d, 2H, Har, *J =7.2* Hz), 7.37 (d, 2H, Har, *J = 6.8* Hz), 7.42 (d, 2H, Har, *J = 7.2* Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8(CH_3), 19.9(CH_3), 94.3(-CH=), 94.6(-CH=), 118.0(2C≡N), 126.1(CarH), 127.2(CarH), 128.9(CarH), 129.0(CarH), 129.6(CarH), 129.9(CarH), 130.0(CarH), 130.1(CarH), 130.6(CarH), 131.0(CarH), 134.3(Car), 135.8(Car), 136.1(Car), 136.2(Car), 136.6(Car), 137.1(Car), 137.3(Car), 137.9(Car), 139.4(Car), 140.0(Car), 162.2(2C);

HRMS, *m/z*: calcd. $C_{17}H_{14}ClNNa^+$ $[M+Na]^+$ 290.0707, found 290.0704.

(*Z*)-3-(4-Bromophenyl)-3-(2,3-dimethylphenyl)prop-2-enenitrile 2m obtained from nitrile **1c** and 1,2-dimethylbenzene with $AlBr_3$ in yield of 20%, slightly yellow oil:

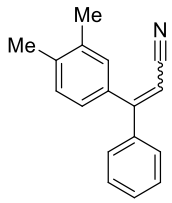


^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 5.97 (s, 1H, -CH=), 7.04 (d, 1H, Har, *J = 6.0* Hz), 7.14 (m, 2H, Har, *7.2* Hz), 7.20 (t, 1H, Har, *J = 6.4* Hz), 7.25 (d, 1H, Har, *J = 6.0* Hz), 7.48 (d, 2H, Har, *J = 6.8* Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ 16.7(CH_3), 20.5(CH_3), 96.8(-CH=), 117.3(C≡N), 125.2(Car), 126.1(CarH), 127.0(CarH), 128.7(CarH), 131.2(CarH), 132.3(CarH), 134.4(Car), 136.4(Car), 136.7(Car), 138.0(Car), 162.6(C);

HRMS, *m/z*: calcd. $C_{17}H_{14}BrNNa^+$ $[M+Na]^+$ 334.0202, found 334.0199.

(*E*)- and (*Z*)-3-(3,4-Dimethylphenyl)-3-phenylprop-2-enenitrile 2n [3] obtained from nitrile **1a** and 1,2-dimethylbenzene with $AlBr_3$ in yield of 25%, slightly yellow oil:



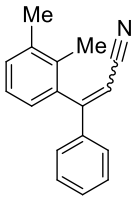
^{1}H NMR (400 MHz, $CDCl_3$): mixture of (E-) and (Z)-isomers, δ 2.25 (c 3H, CH_3), 2.28 (c 3H, CH_3), 2.29 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 5.66 (c 1H, -CH=), 5.70 (s, 1H, -CH=), 7.01 (m, 1H, Har), 7.07(s, 1H, Har), 7.13 (d, 1H, Har, *J = 8.0* Hz), 7.17-7.21 (m, 3H, Har), 7.29-7.31 (m, 2H, Har), 7.35-7.38 (m, 2H, Har), 7.42-7.46 (m, 5H, Har);

^{13}C NMR (100 MHz, $CDCl_3$): mixture of (E-) and (Z)-isomers, δ 19.8(CH_3), 19.9(3CH_3), 93.9(-CH=), 94.2(-CH=), 118.3(2C≡N), 126.2(CarH), 127.3(CarH), 128.6(CarH), 128.7(CarH), 129.6(CarH), 129.7(CarH), 129.9(CarH), 130.0(2CarH), 130.4(CarH), 130.7(CarH), 134.7(Car), 136.7(Car), 136.9(Car), 137.1(Car), 137.4(Car), 139.1(Car), 139.5(Car), 139.7(Car), 163.4(C), 163.5(C);

IR (KBr), ν, cm^{-1}: 2212 (C≡N);

HRMS, *m/z*: calcd. $C_{17}H_{15}NNa^+$$[M+Na]^+$ 256.1097, found 256.1097.

3-(2,3-Dimethylphenyl)-3-phenylprop-2-enenitrile 2o (E- or Z-configuration was unclear) obtained from nitrile **1a** and 1,2-dimethylbenzene with $AlBr_3$ in yield of 20%, slightly yellow oil:



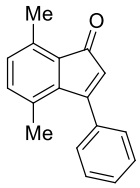
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 5.98 (s, 1H, -CH=), 7.06d (d, 1H, Har, *J = 6.0* Hz), 7.19 (t, 1H, Har, *J = 6.0* Hz), 7.24 (d, 1H, Har, *J = 6.4* Hz), 7.28 (d, 2H, Har, *J = 6.0* Hz), 7.35 (t, 2H, Har, *J = 6.0* Hz), 7.38-7.41 (m, 1H, Har);

^{13}C NMR (100 MHz, $CDCl_3$): δ 16.7(CH_3), 20.5(CH_3), 96.3(-CH=), 117.6(C≡N), 125.9(CarH), 127.1(CarH), 127.3(CarH), 129.0(CarH), 130.6(CarH), 130.9(CarH), 134.4(Car), 136.9(Car), 137.8(2Car), 163.8(C);

IR (KBr), ν, cm $^{-1}$: 2215 (C≡N);

HRMS, *m/z*: calcd. $C_{17}H_{15}NNa^+$[M+Na]$^+$ 256.1097, found 256.1096.

4,7-Dimethyl-3-phenyl-1*H*-inden-1-one 3a obtained from nitrile **2c** в TfOH in yield of 70%, slightly yellow oil:



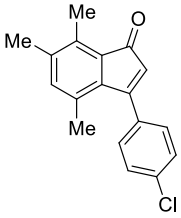
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87 s, 3H, CH_3), 2.53 (s, 3H, CH_3), 5.73 (s, 1H, -CH=), 6.92-6.96 (m, 2H, Har), 7.37-7.46 (m, 5H, Har);

^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2(CH_3), 19.7(CH_3), 126.2(CarH), 127.0(CarH), 128.6(CarH), 129.0(CarH), 130.8(Car), 132.8(CarH), 135.6(Car), 136.5(Car), 136.7(CarH), 141.9(Car), 164.8(C), 198.8(C=O);

IR (KBr), ν, cm $^{-1}$: 1699 (C=O);

HRMS, *m/z*: calcd. $C_{17}H_{15}O^+$ [M+H]$^+$ 235.1117, found 235.1117.

3-(4-Chlorophenyl)-4,6,7-trimethyl-1*H*- inden-1-one 3b obtained from nitrile **2g** в TfOH in yield of 55%, slightly yellow oil:



^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 5.66 (s, 1H, -CH=), 6.83 (s, 1H, Har), 7.32 (m, 2H, Har, *J = 8.0* Hz), 7.41 (m, 2H, Har, *J = 6.8* Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ 12.9(CH_3), 19.2(CH_3), 19.7(CH_3), 126.2(CarH), 128.5(CarH), 128.7(Car), 128.9(CarH), 130.2(Car), 130.0(Car), 135.1(Car), 135.7(Car), 137.2(CarH), 139.5(Car), 140.5(Car), 163.3(C), 198.9(C=O);

IR (KBr), ν, cm^{-1}: 1694 (C=O);

HRMS, *m/z*: calcd. $C_{18}H_{15}ClNaO^+$ [M+Na]$^+$ 305.0704, found 305.0701.

4. References

[1] T. Wang, H. Yin, N. Jiao, *Adv. Synth. Catal*., **2013**, *355*, 1207– 1210.

[2] J. Masllorens, M. Moreno-Mañas, A. Pla-Quintana, R.Pleixats, A. Roglans, *Synthesis*, **2002**, 1903-1911.

[3] L. Hao, F. Wu, Z.-C. Ding, S.-X. Xu, Y.-L. Ma, L. Chen, Z.-P. Zhan, *Chem.Eur.J*., **2012**, *18*, 6453-6456.

5. ^{1}H and ^{13}C NMR spectra, DEPT-135, COSY, NOESY spectra of compounds 1a-c, 2a-o, 3a,b

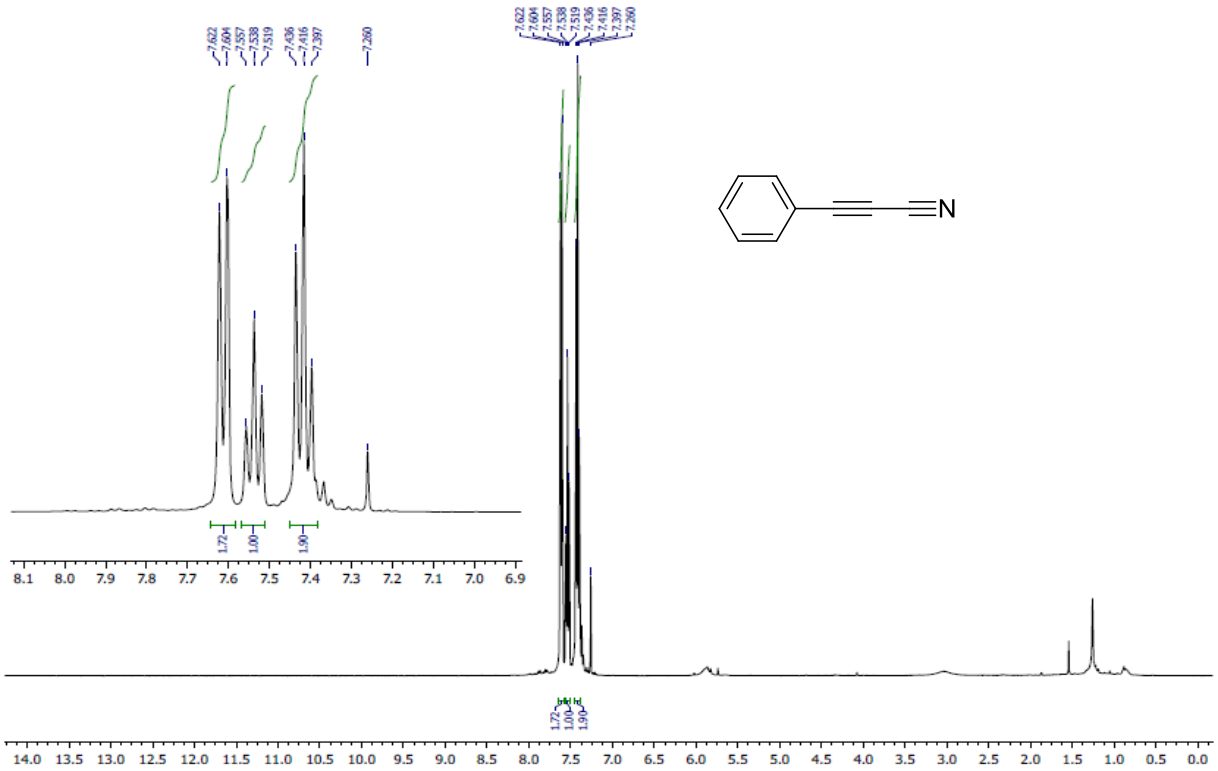


Figure S1. ^{1}H NMR spectrum of compound **1a** ($CDCl_3$, 400 MHz).

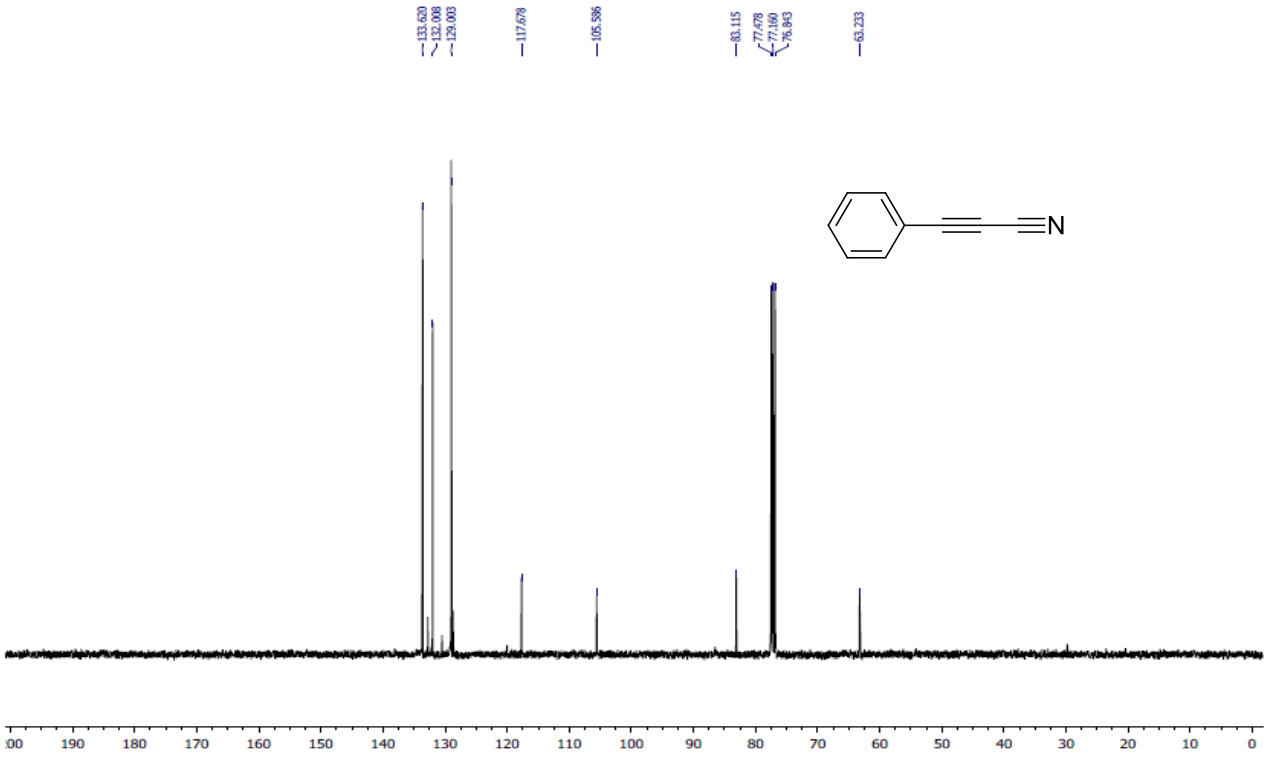


Figure S2. ^{13}C NMR spectrum of compound **1a** ($CDCl_3$, 100 MHz).

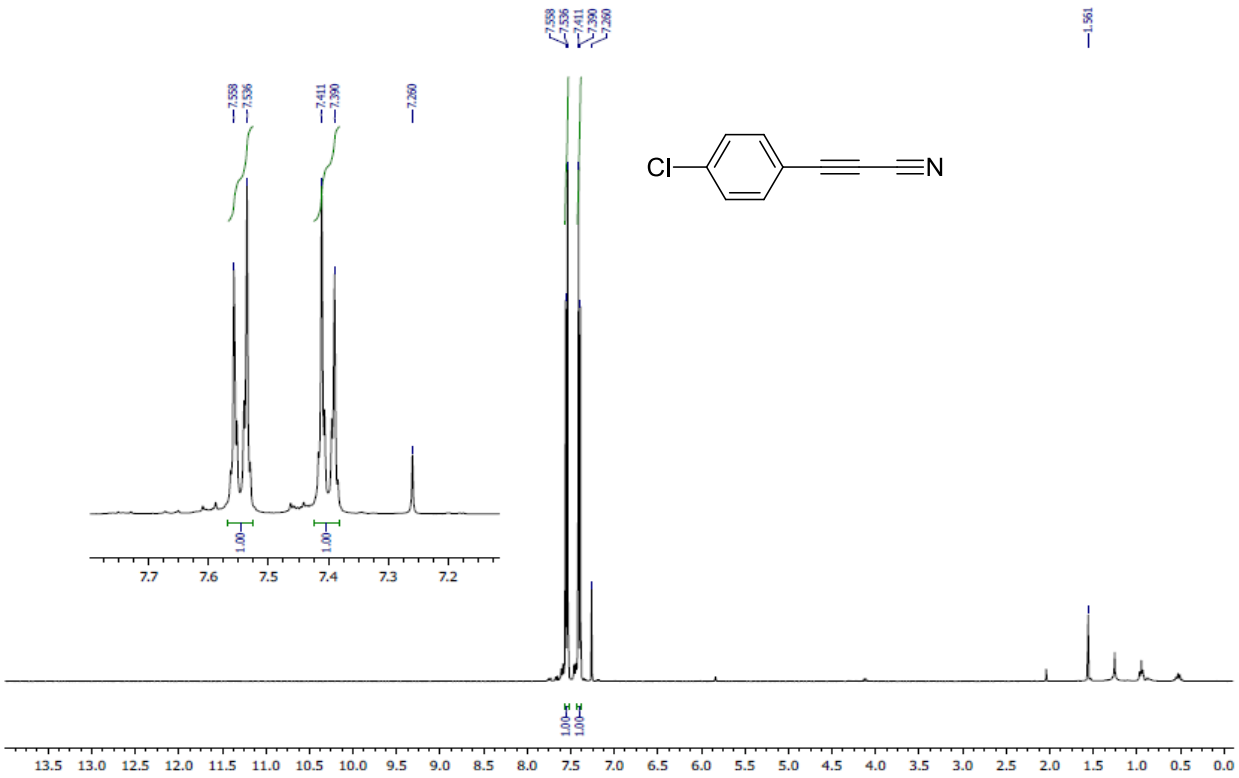


Figure S3. ^{1}H NMR spectrum of compound **1b** ($CDCl_3$, 400 MHz).

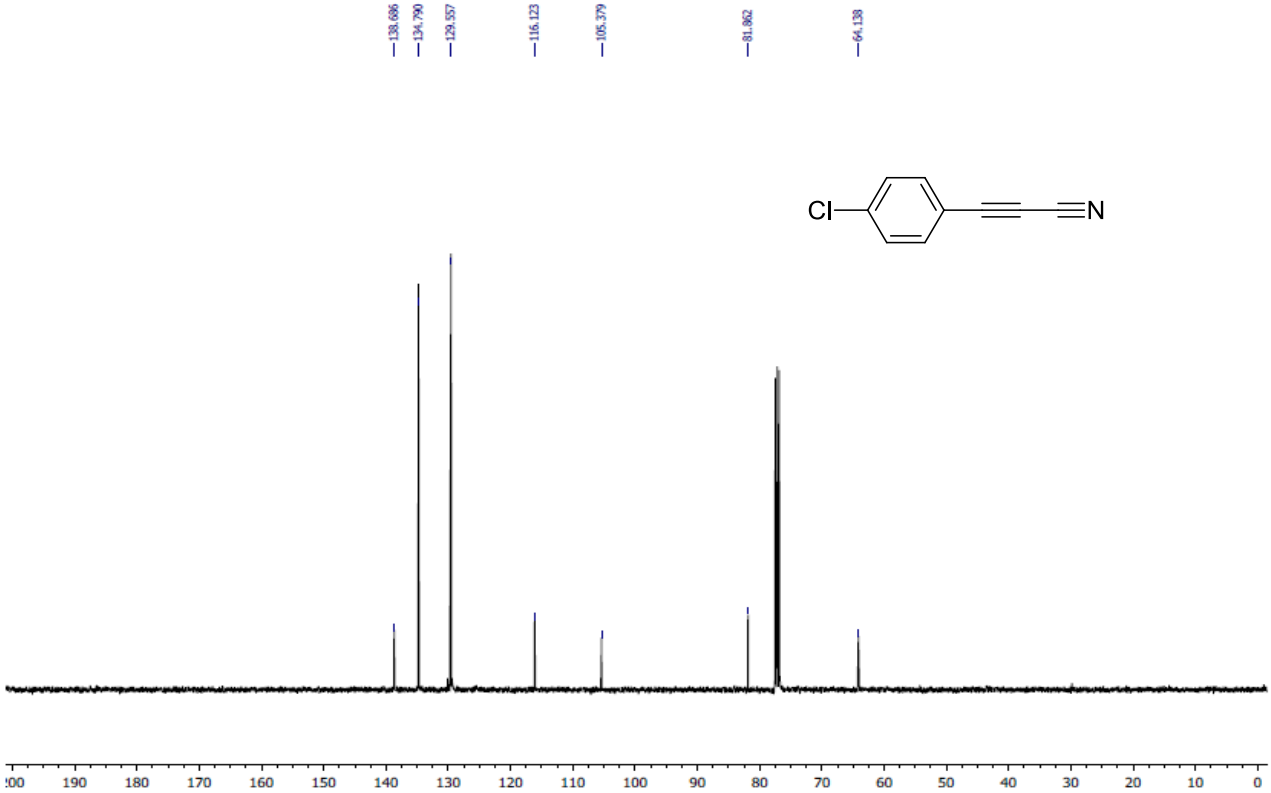


Figure S4. ^{13}C NMR spectrum of compound **1b** ($CDCl_3$, 100 MHz).

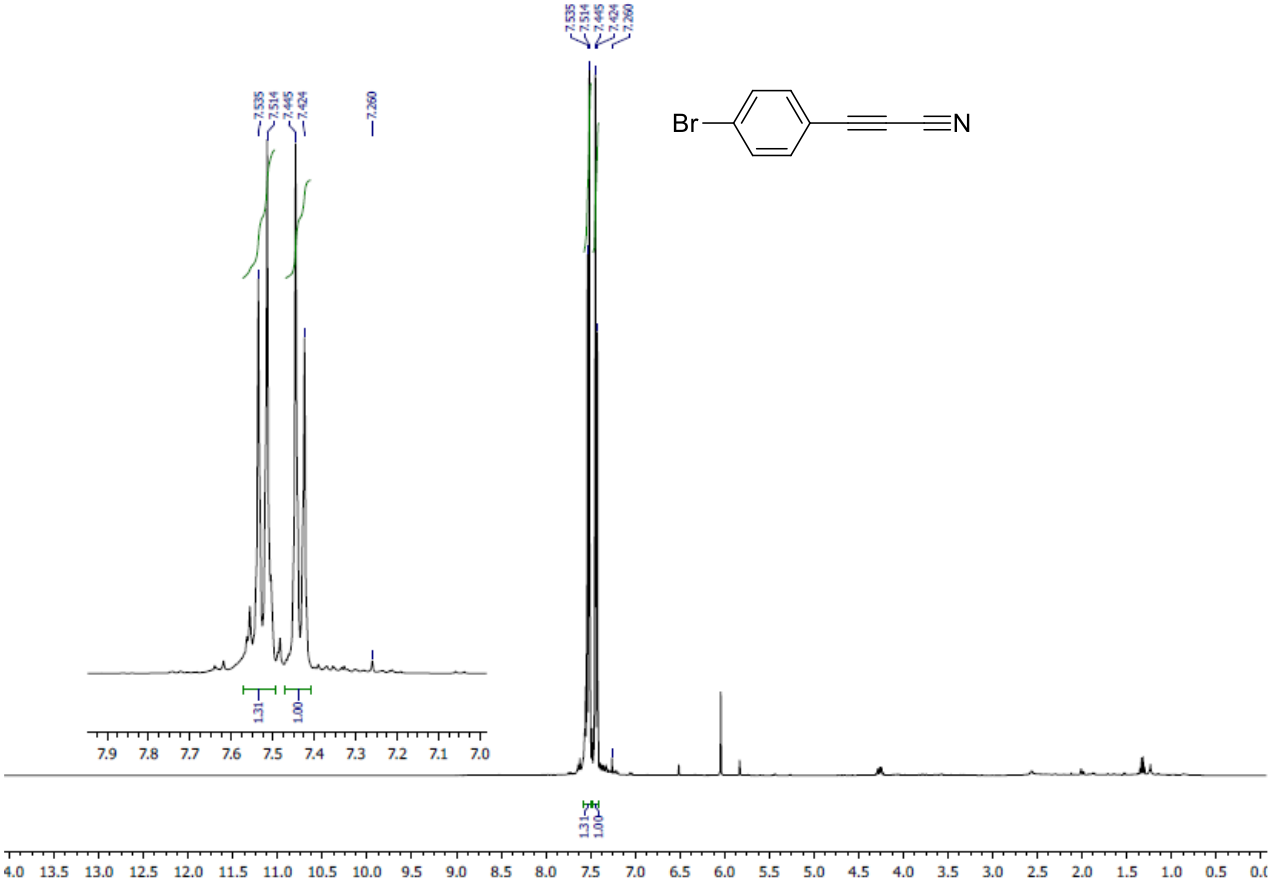


Figure S5. ^{1}H NMR spectrum of compound **1c** ($CDCl_3$, 400 MHz).

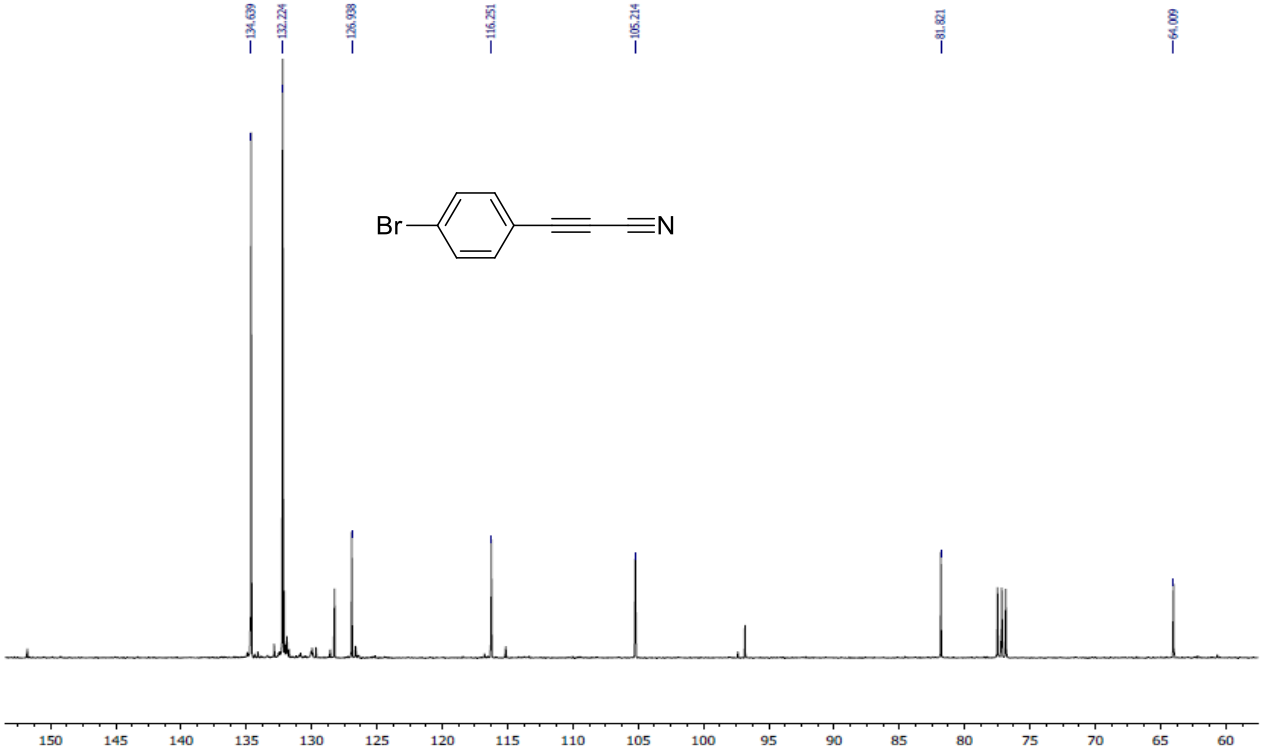


Figure S6. ^{13}C NMR spectrum of compound **1c** ($CDCl_3$, 100 MHz).

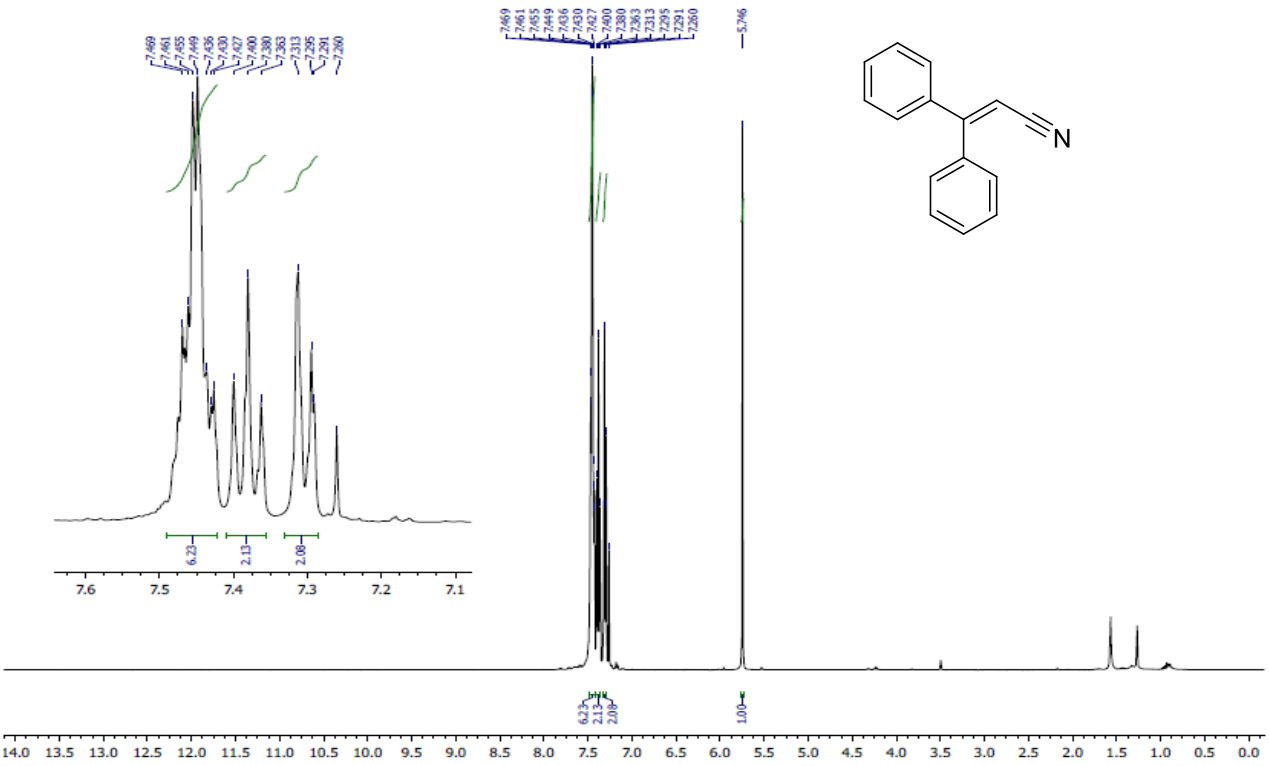


Figure S7. ^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 400 MHz).

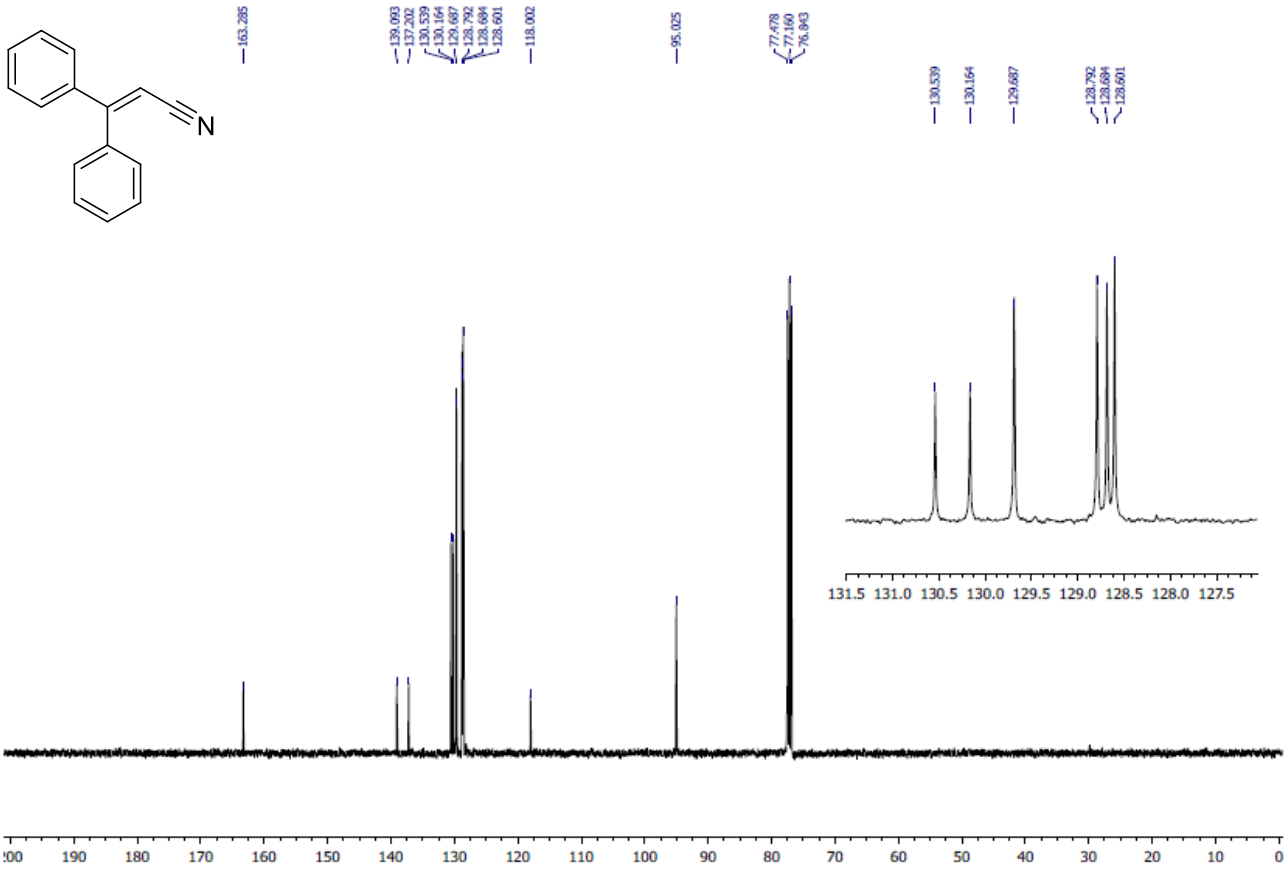


Figure S8. ^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 100 MHz).

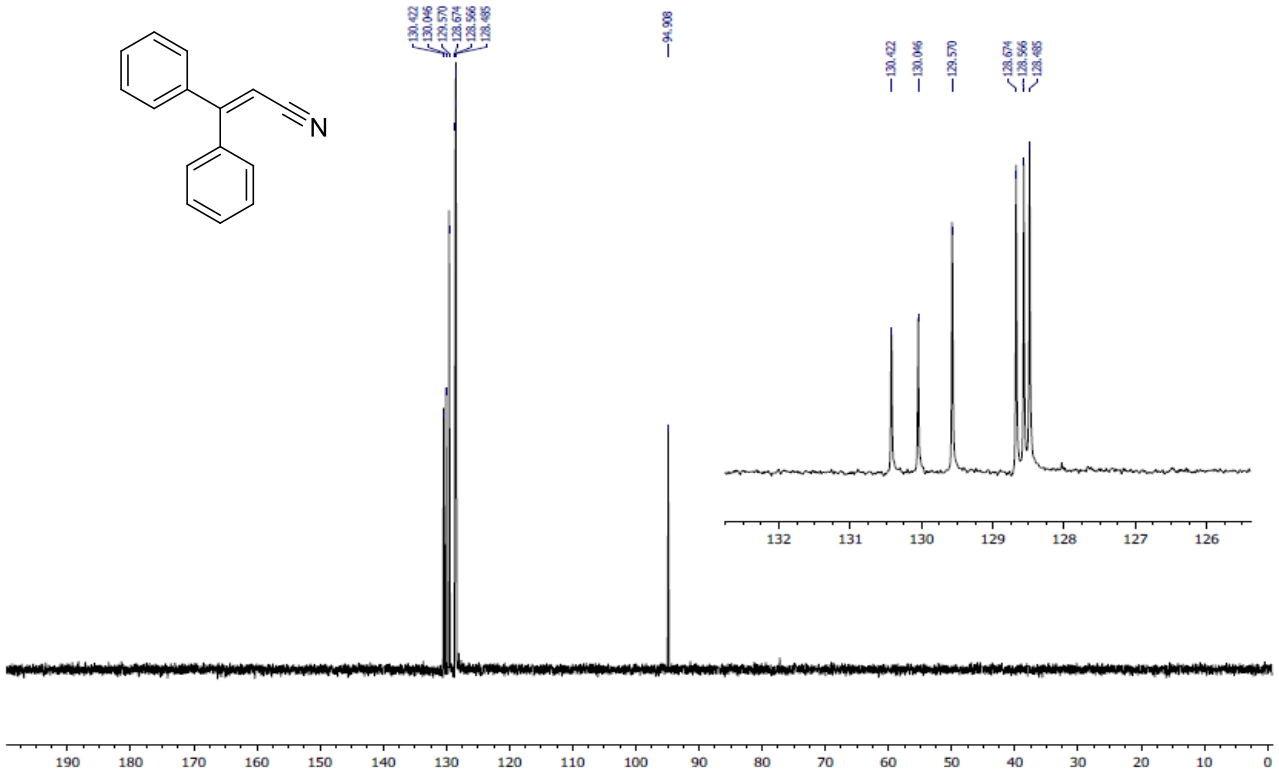


Figure S9. DEPT^{135} NMR spectrum of compound **2a** ($CDCl_3$, 400 MHz).

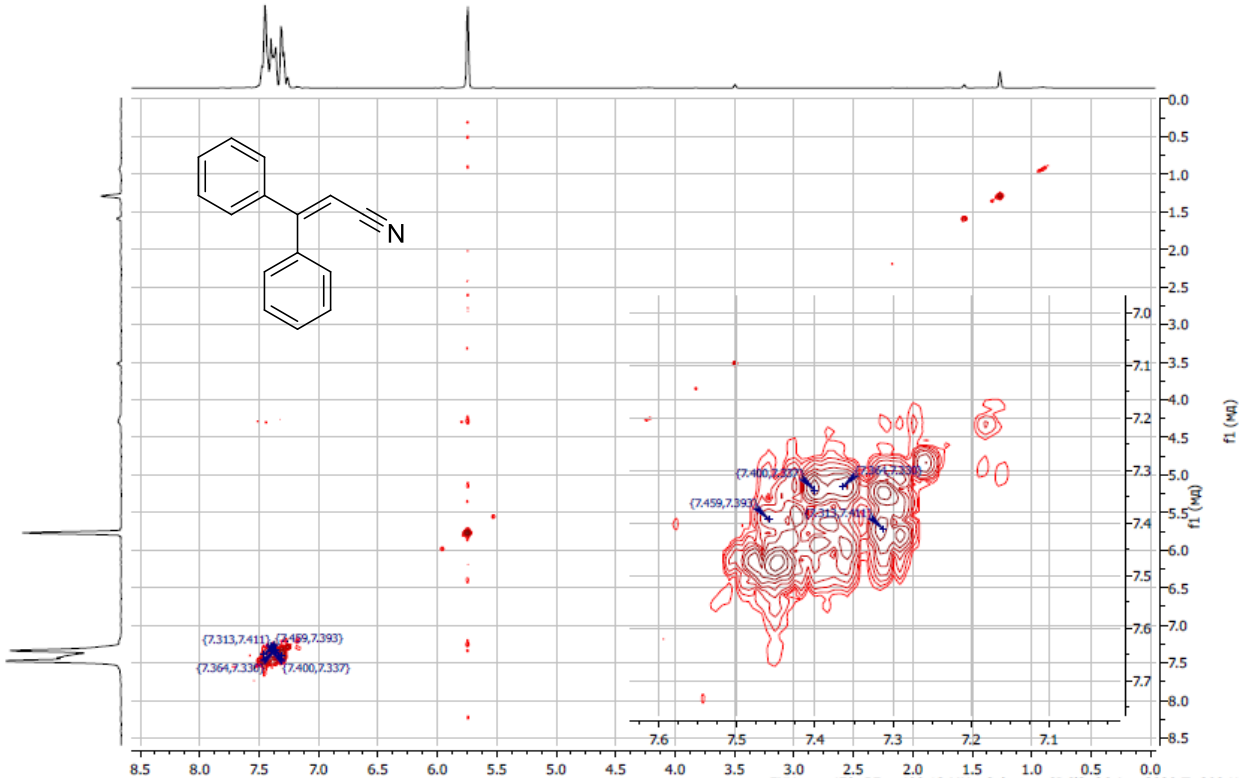


Figure S10. COSY NMR spectrum of compound **2a** ($CDCl_3$, 400 MHz).

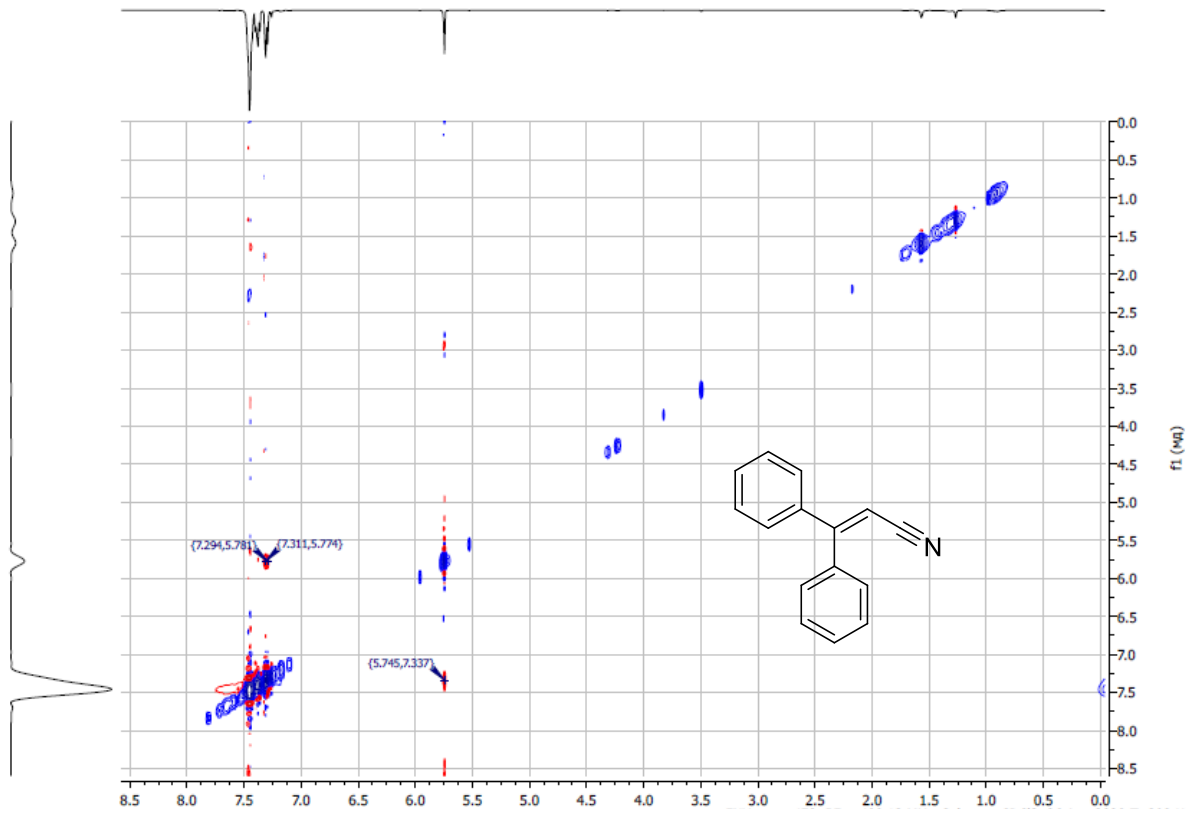


Figure S11. NOESY NMR spectrum of compound **2a** ($CDCl_3$, 400 MHz).

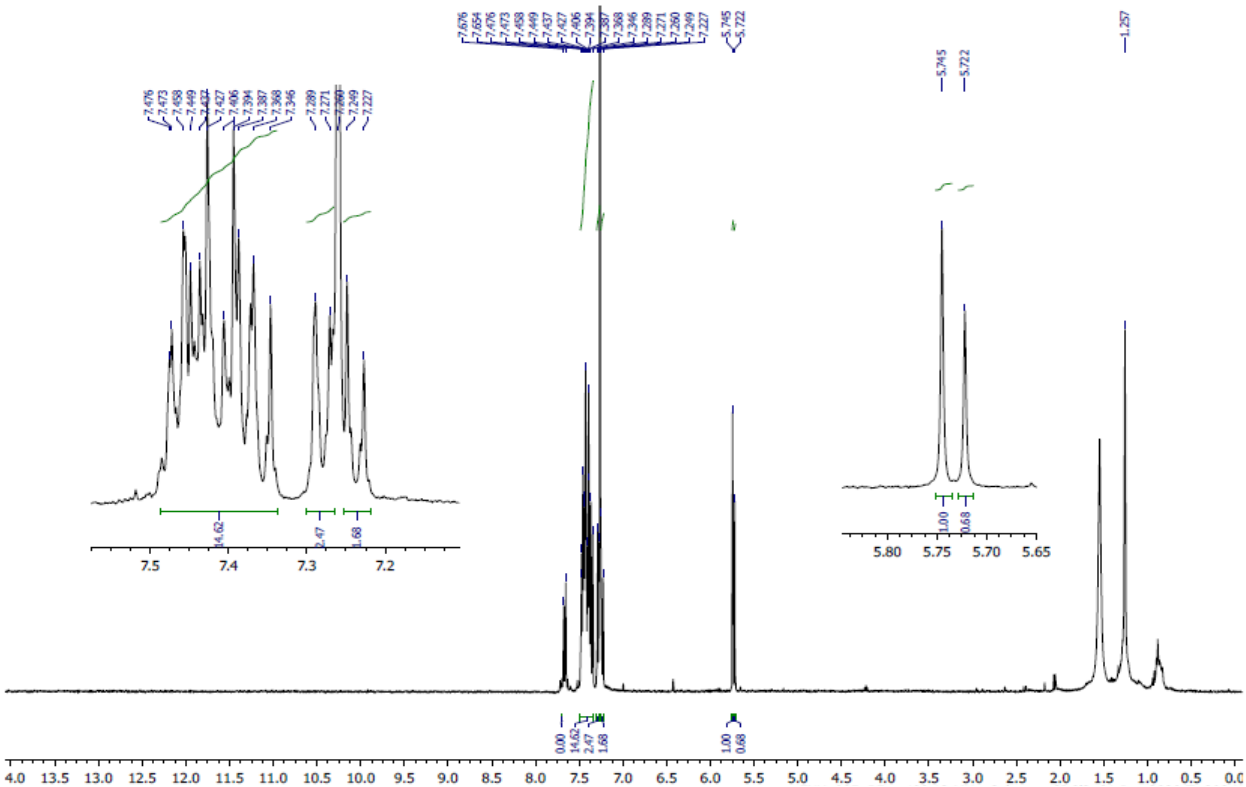


Figure S12. ^1H NMR spectrum of mixture of compounds *E*-,*Z*-**2b** ($CDCl_3$, 400 MHz).

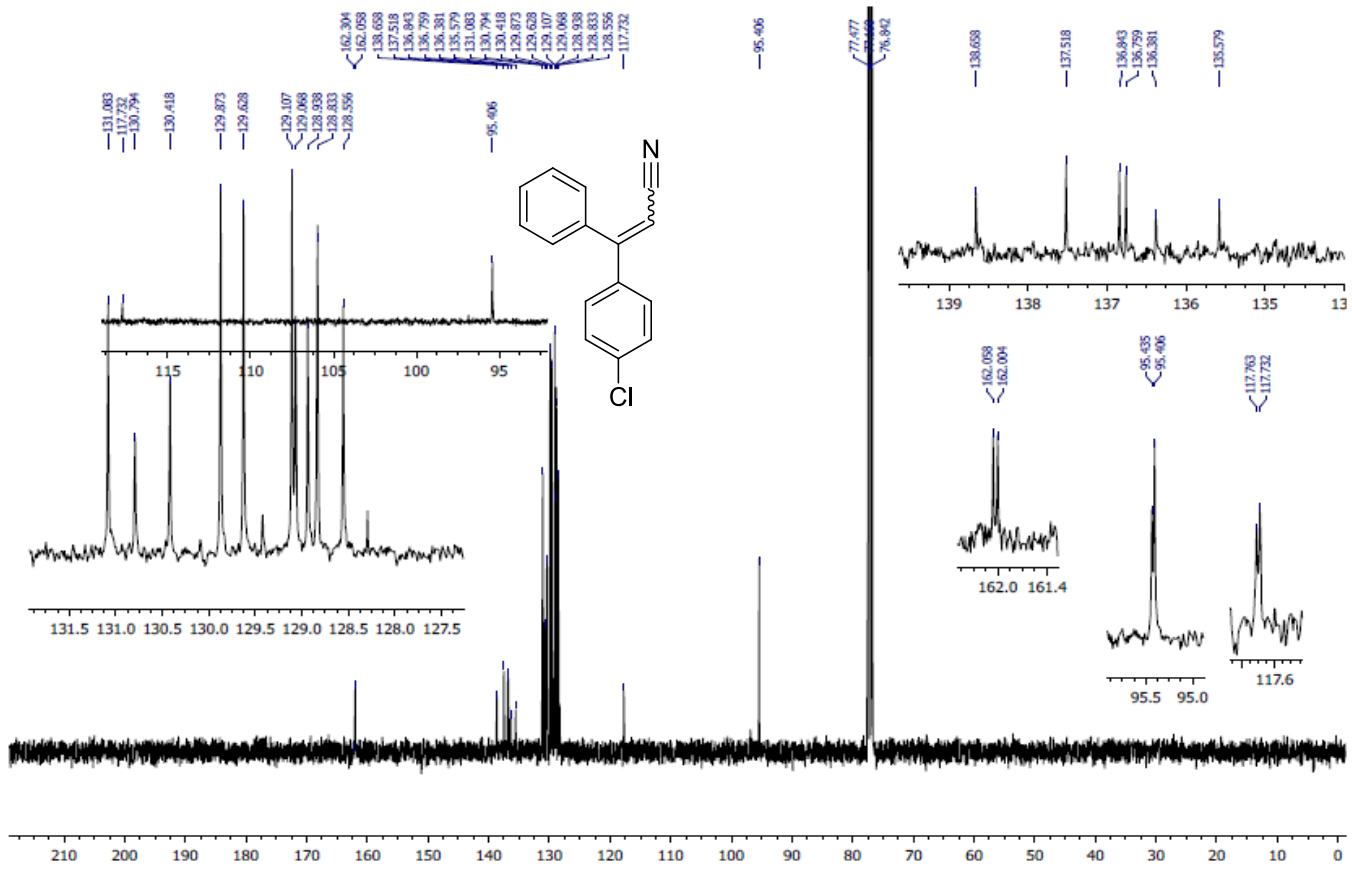


Figure S13. ^{13}C NMR spectrum of mixture of compounds *E*,*Z*-**2b** ($CDCl_3$, 100 MHz).

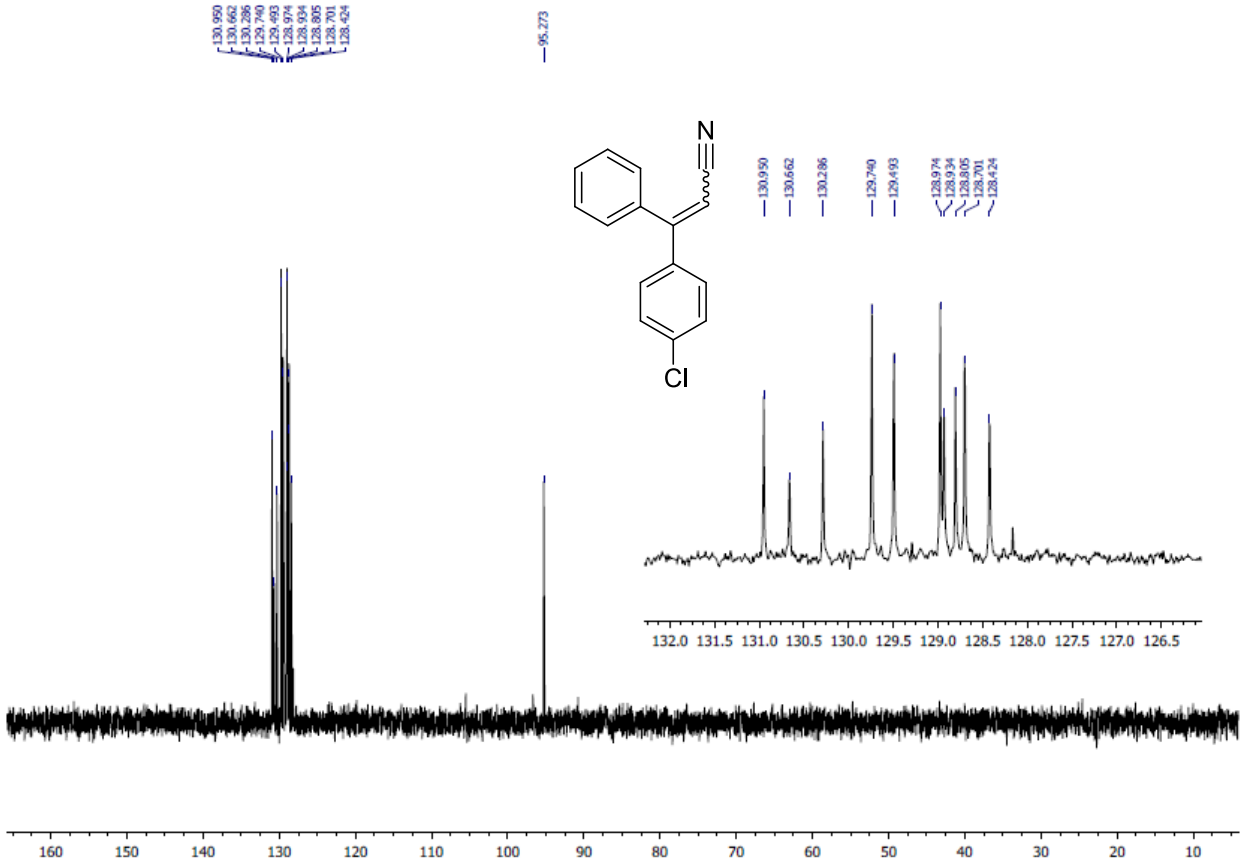


Figure S14. DEPT^{135} NMR spectrum of mixture of compounds *E*,*Z*-**2b** ($CDCl_3$, 400 MHz).

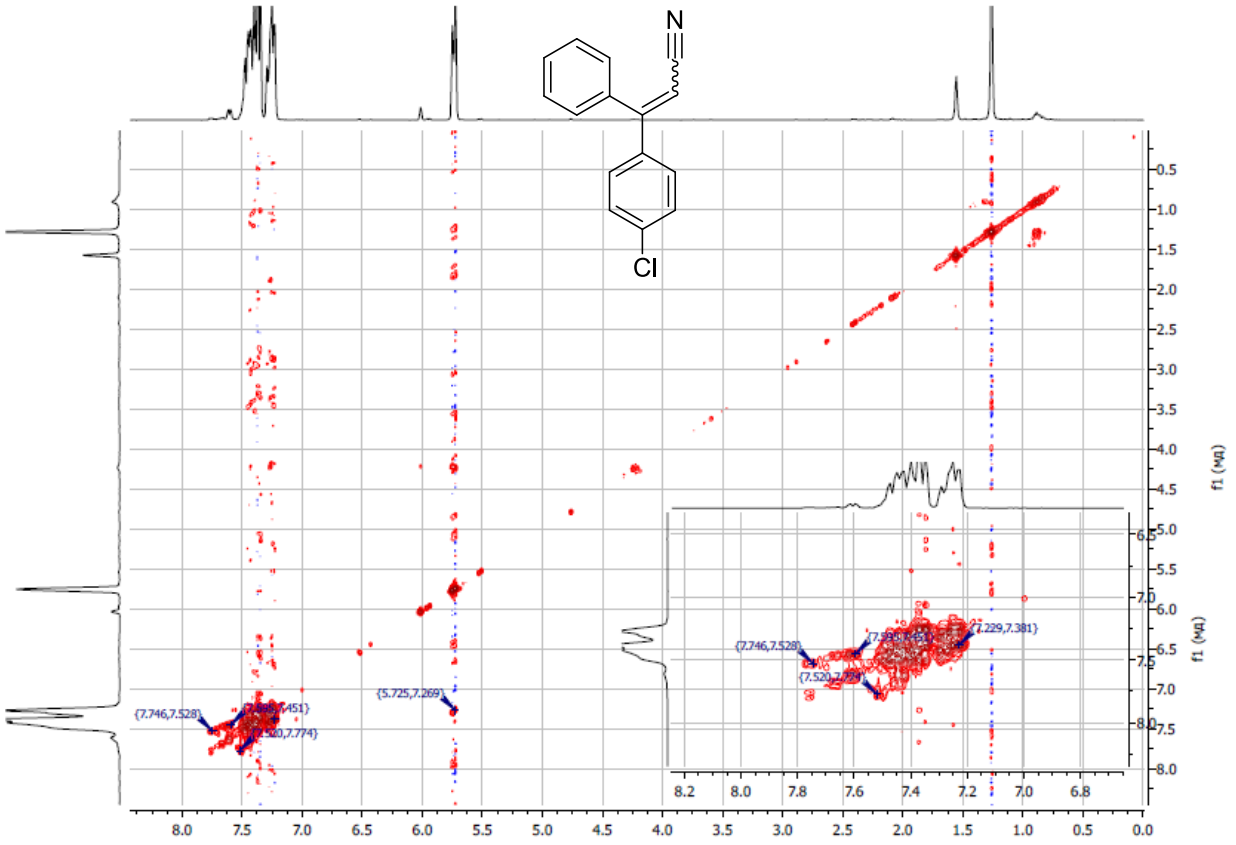


Figure S15. COSY NMR spectrum of mixture of compounds *E*,*Z*-**2b** ($CDCl_3$, 400 MHz).

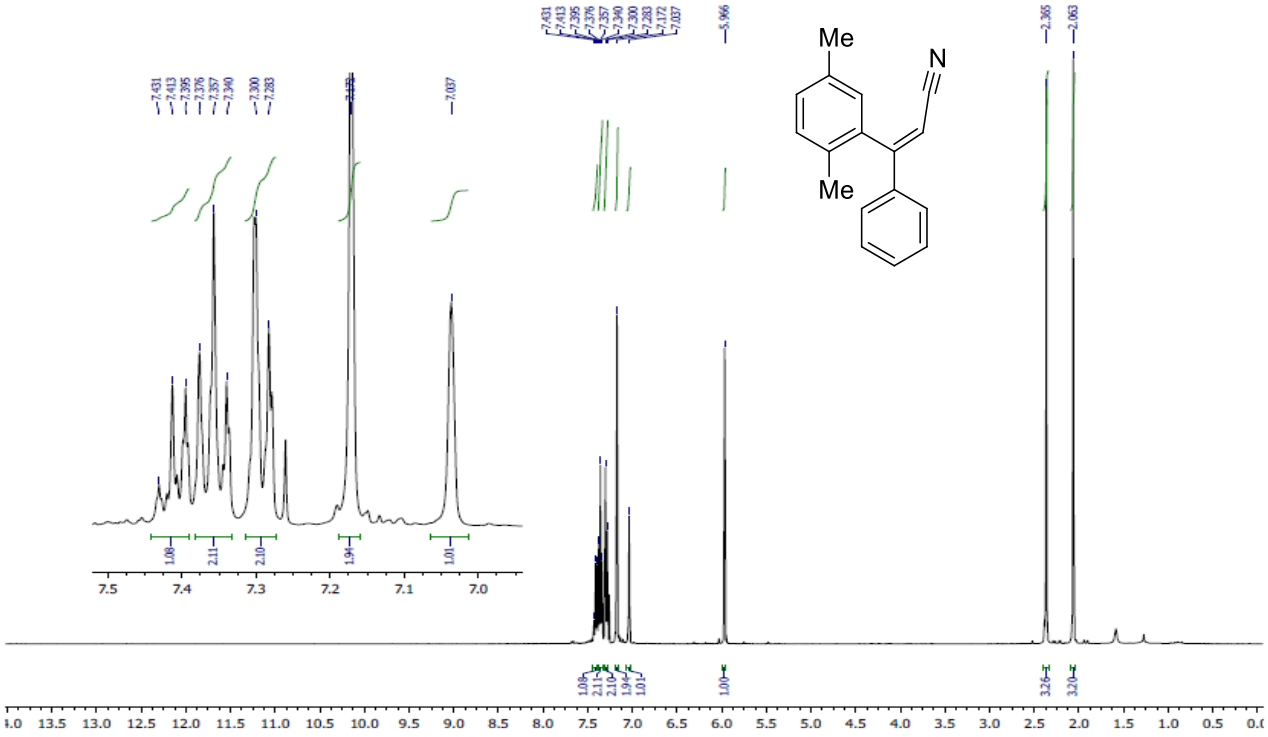


Figure S16. ^1H NMR spectrum of compound **2c** ($CDCl_3$, 400 MHz).

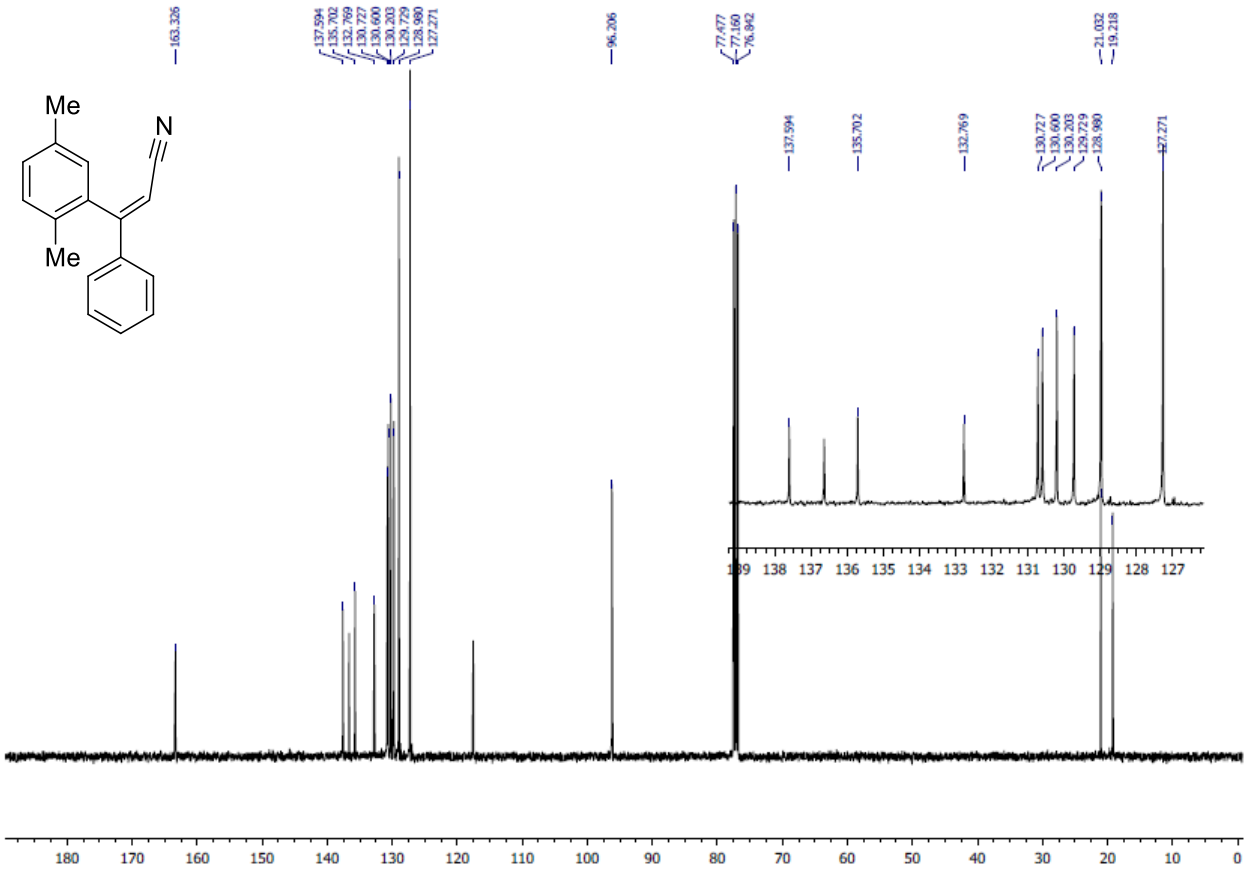


Figure S17. ^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 100 MHz).

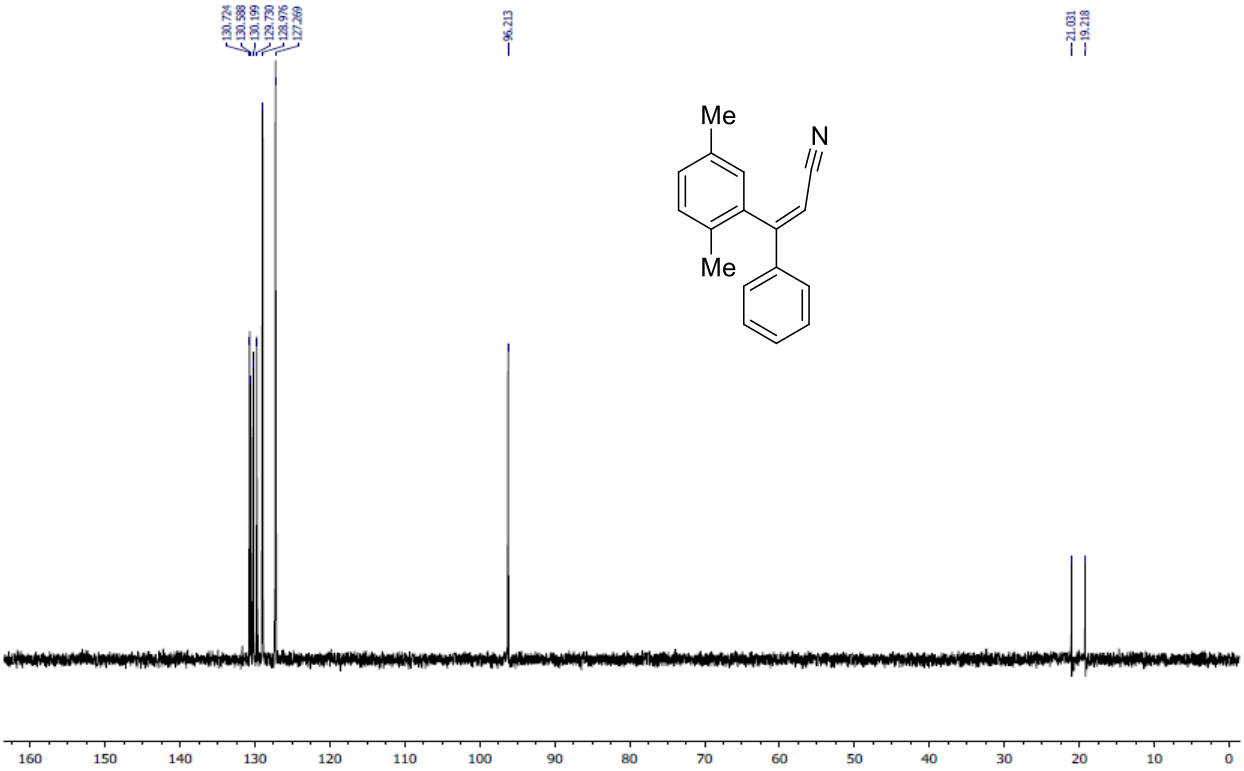


Figure S18. DEPT^{135} NMR spectrum of compound **2c** ($CDCl_3$, 400 MHz).

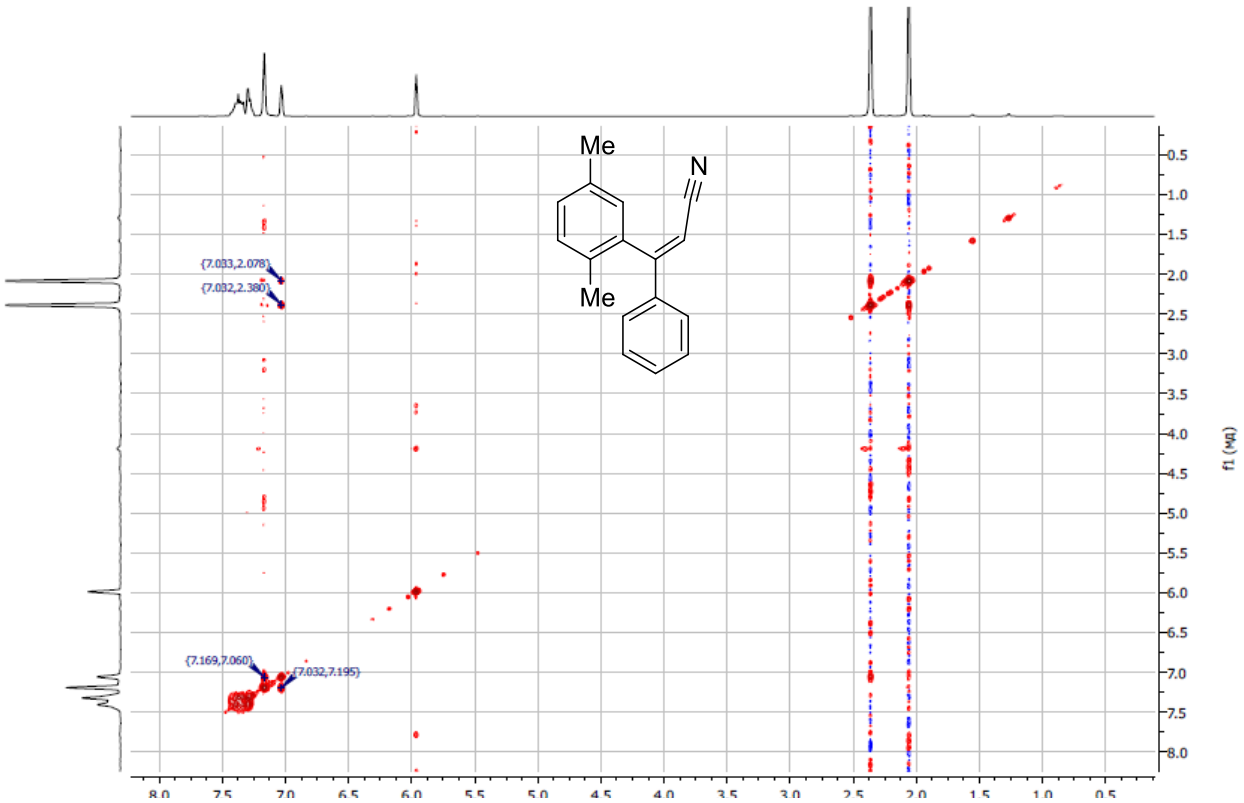


Figure S19. COSY NMR spectrum of compound **2c** ($CDCl_3$, 400 MHz).

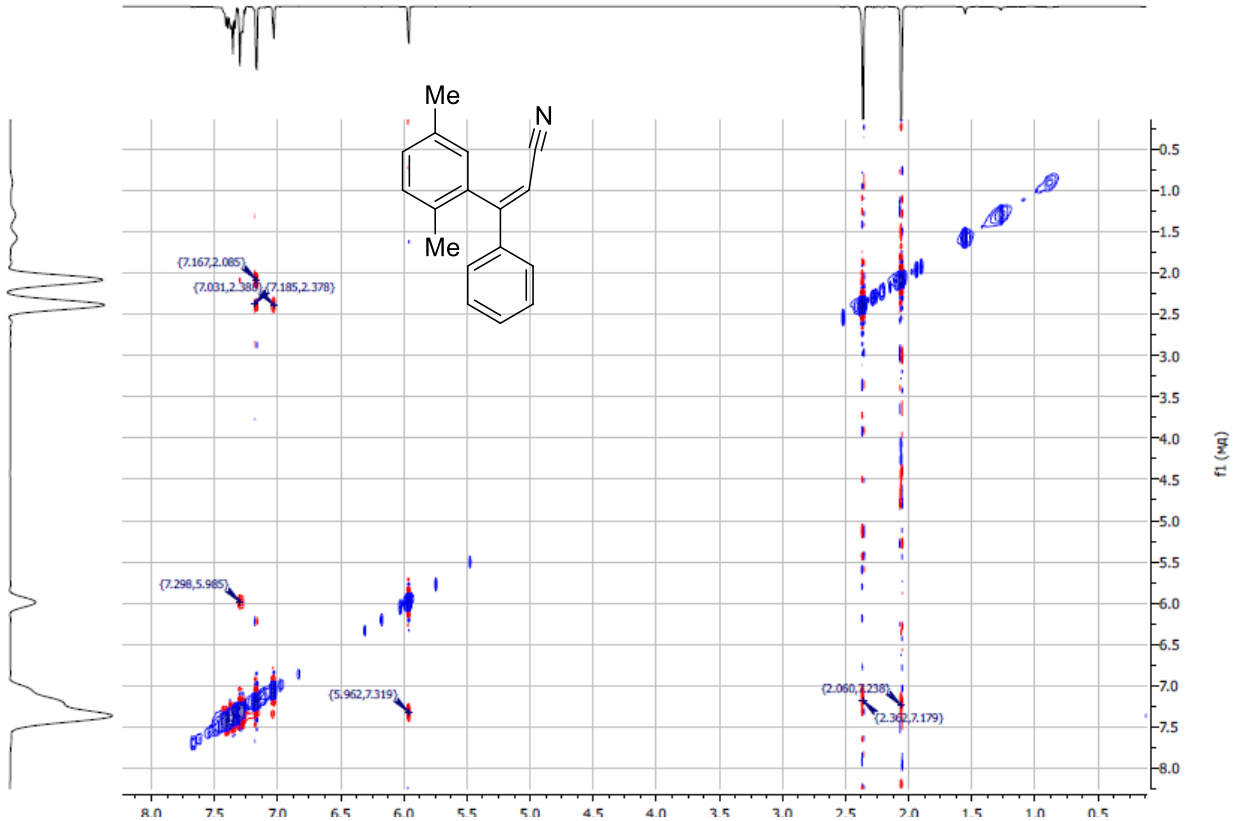


Figure S20. NOESY NMR spectrum of compound **2c** ($CDCl_3$, 400 MHz).

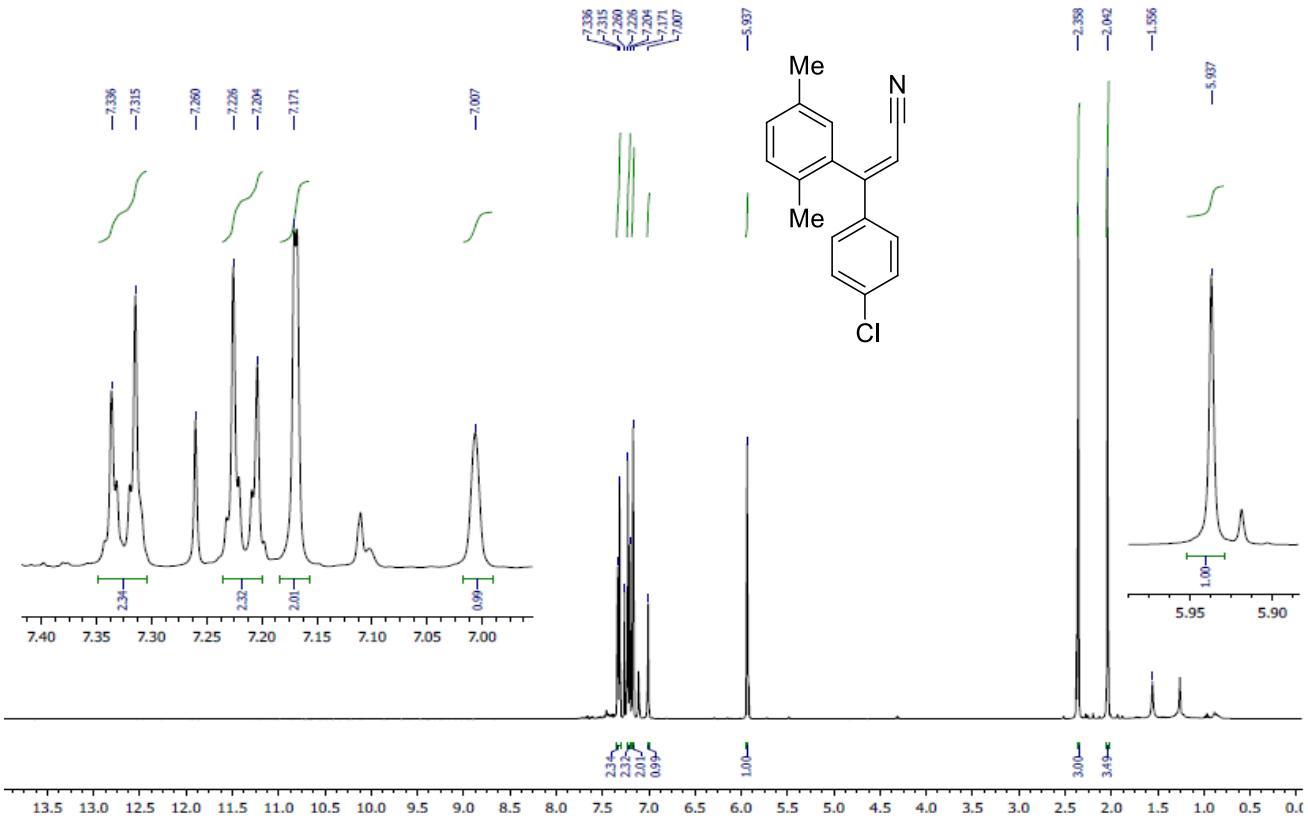


Figure S21. ^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz).

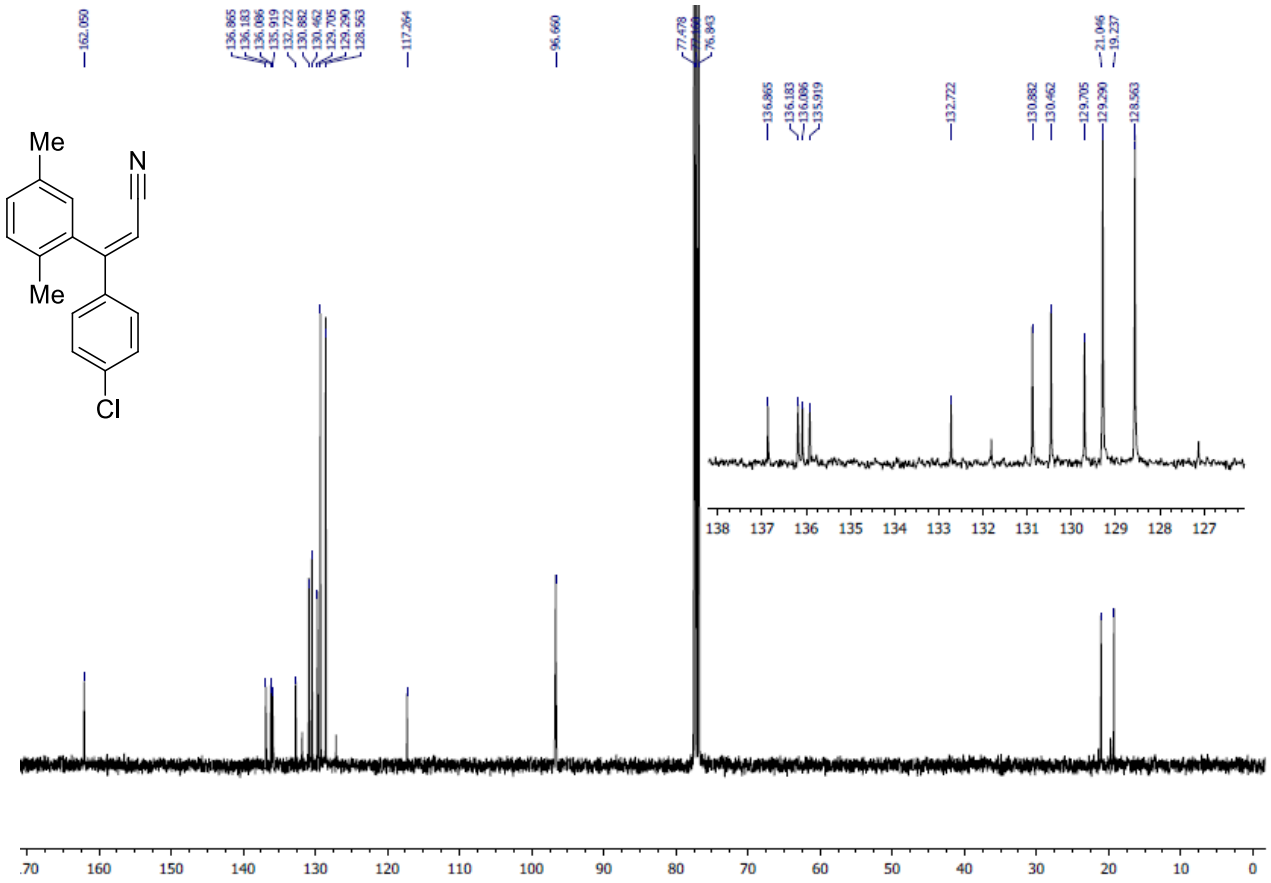


Figure S22. ^{13}C NMR spectrum of compound **2d** ($CDCl_3$, 100 MHz).

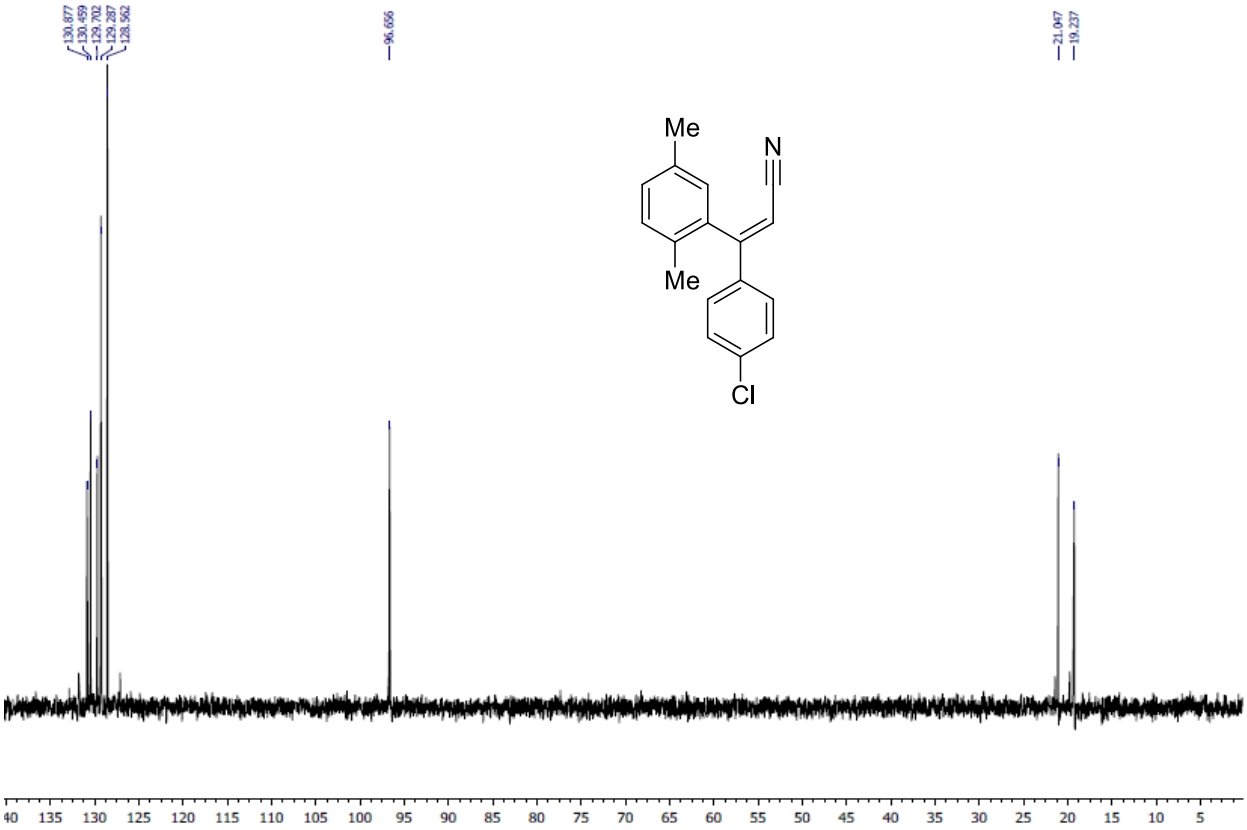


Figure S23. DEPT^{135} NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz).

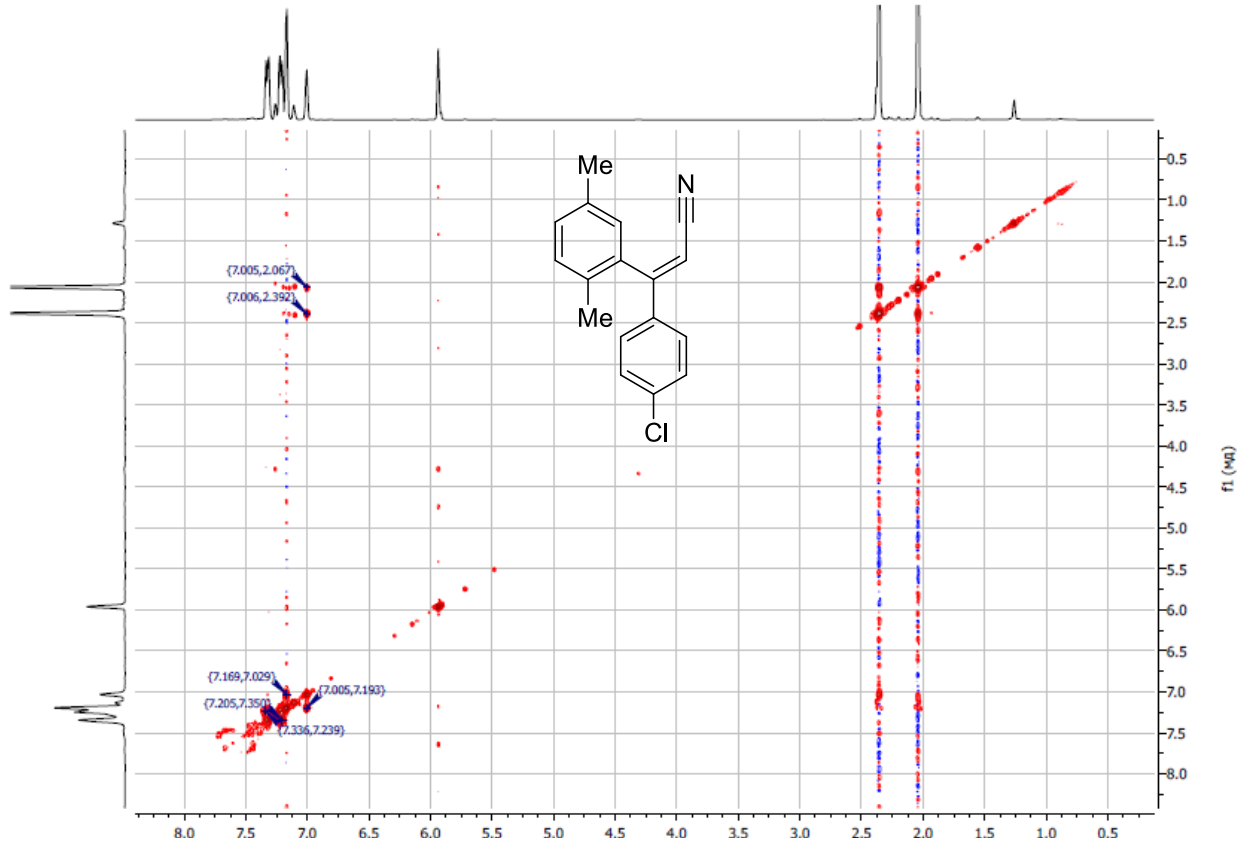


Figure S24. COSY NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz).

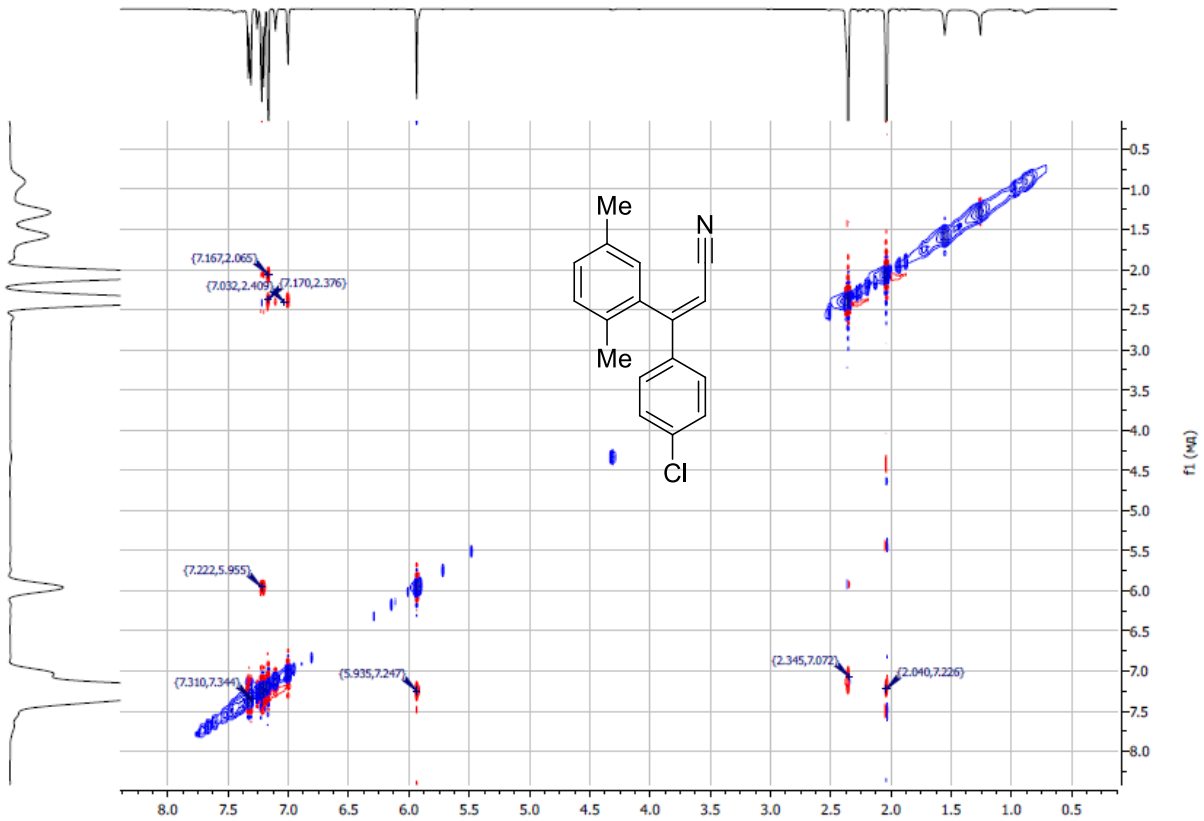


Figure S25. NOESY NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz).

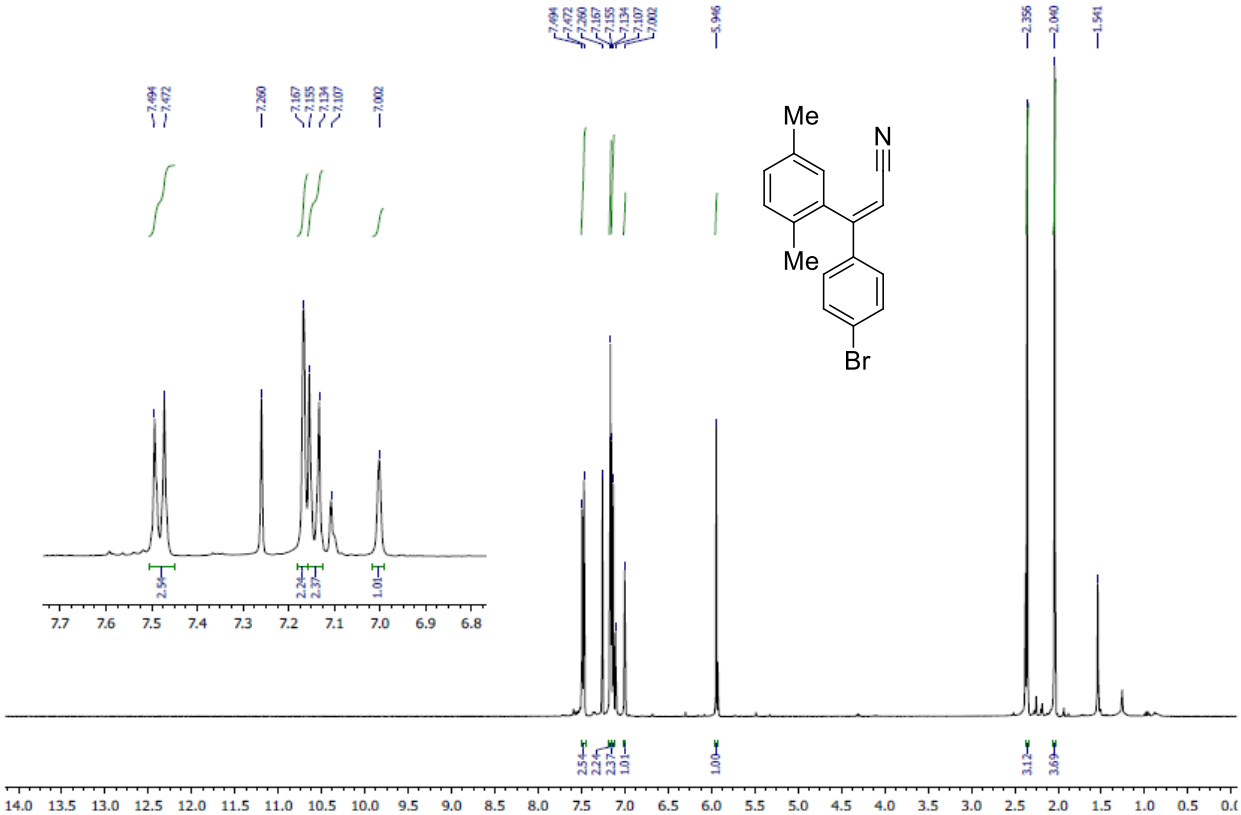


Figure S26. ^1H NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz).

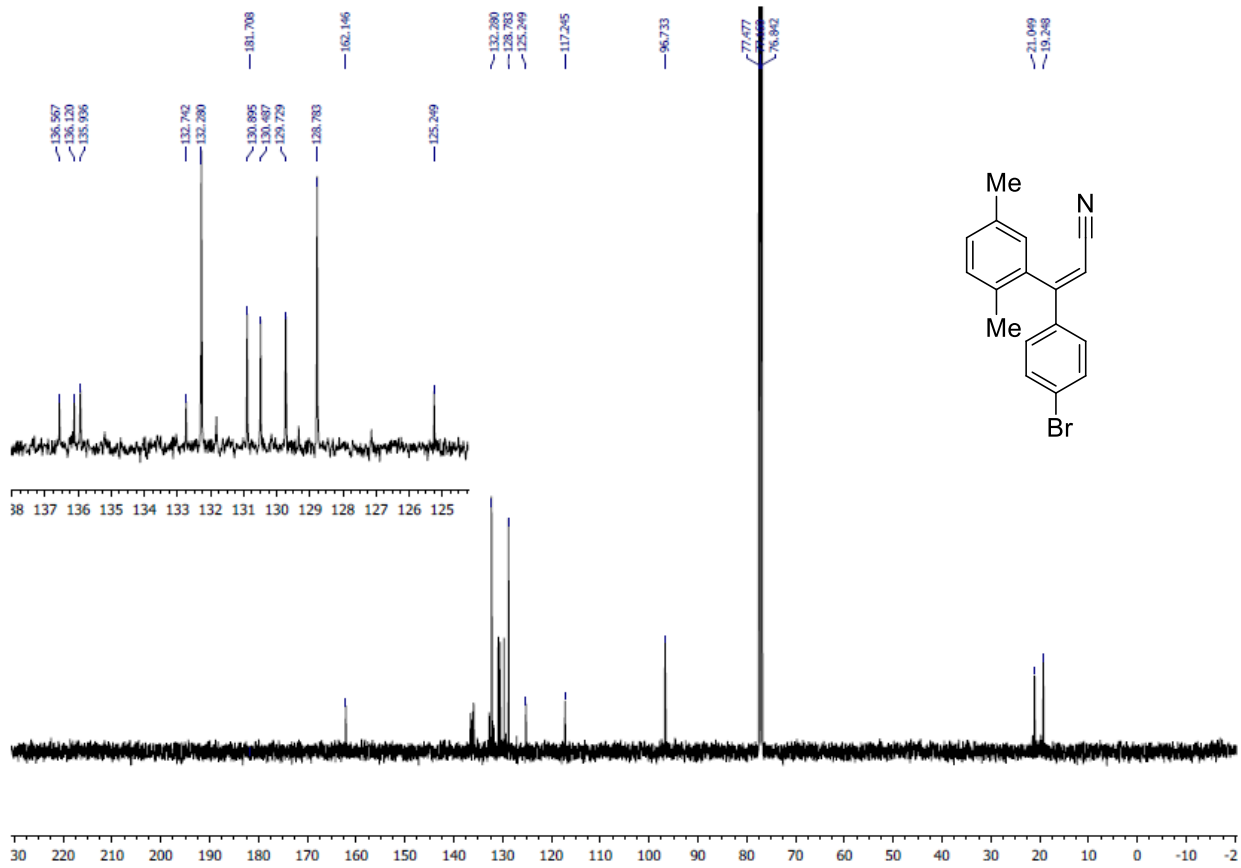


Figure S27. ^{13}C NMR spectrum of compound **2e** ($CDCl_3$, 100 MHz).

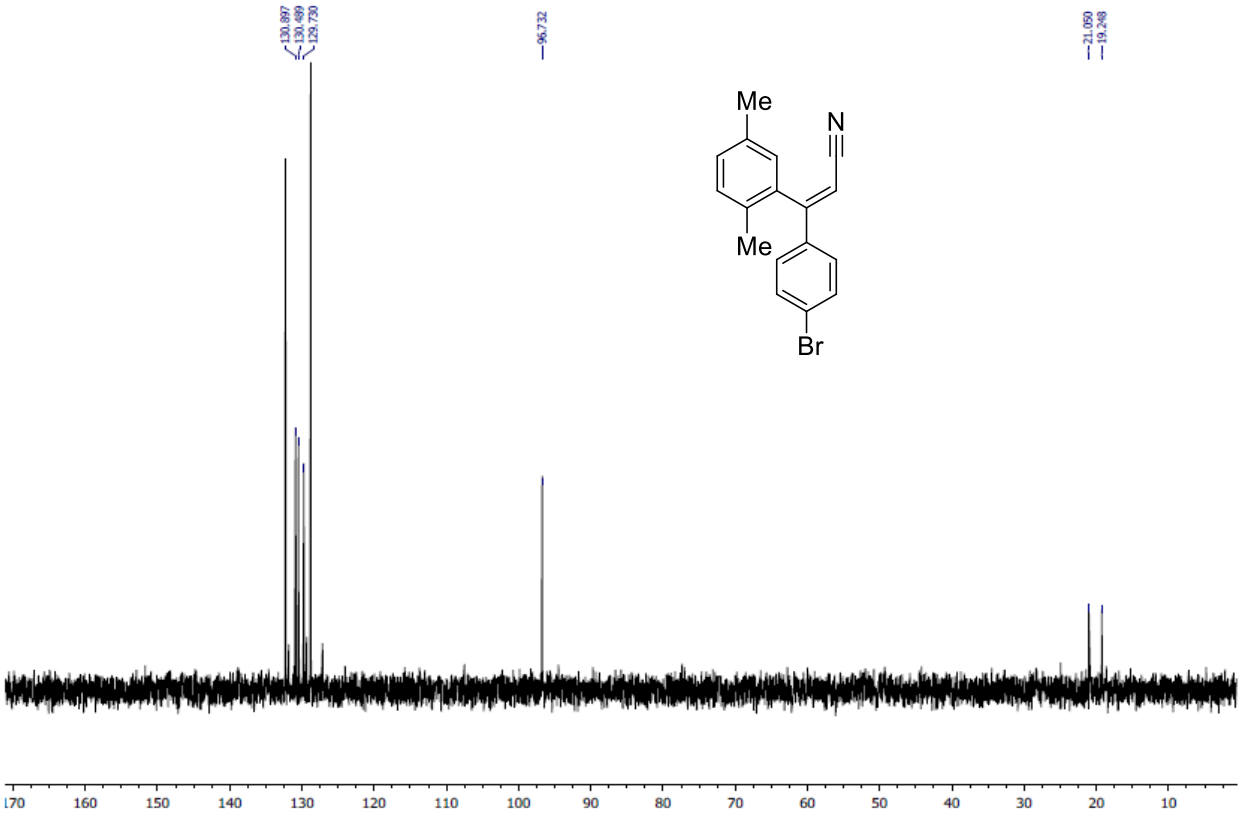


Figure S28. DEPT^{135} NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz).

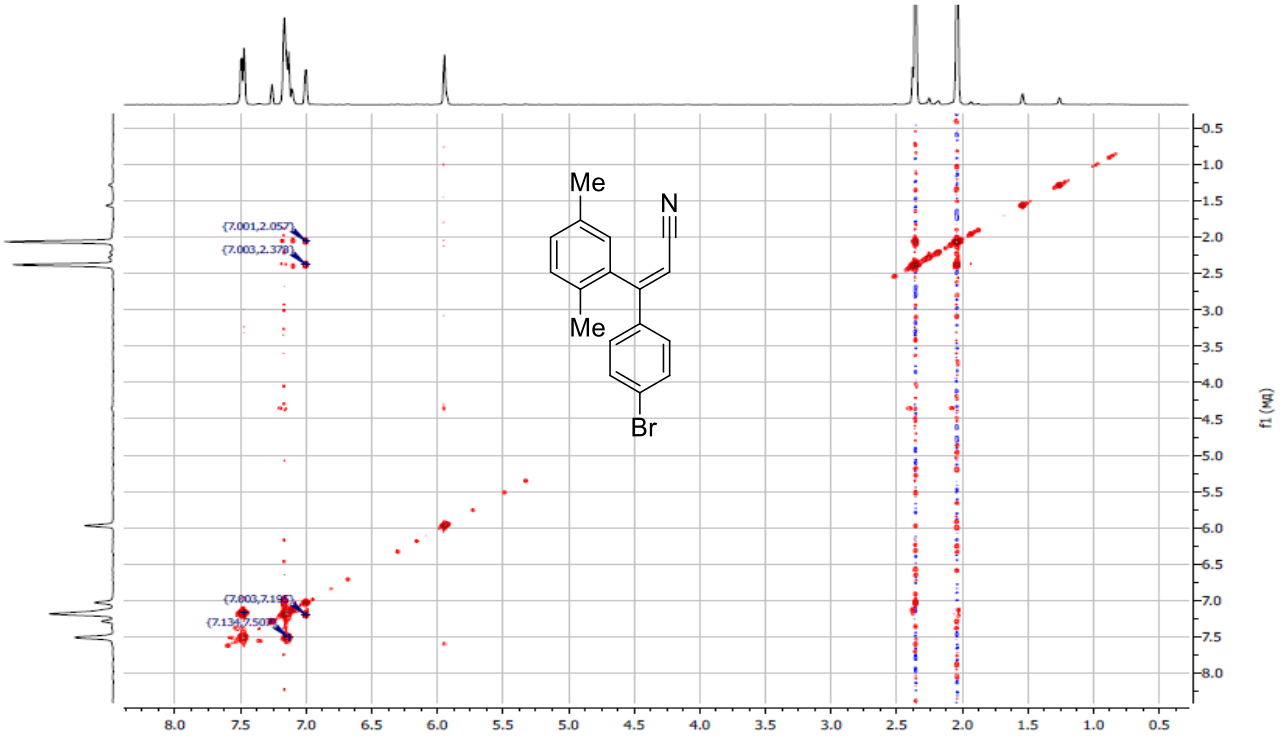


Figure S29. COSY NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz).

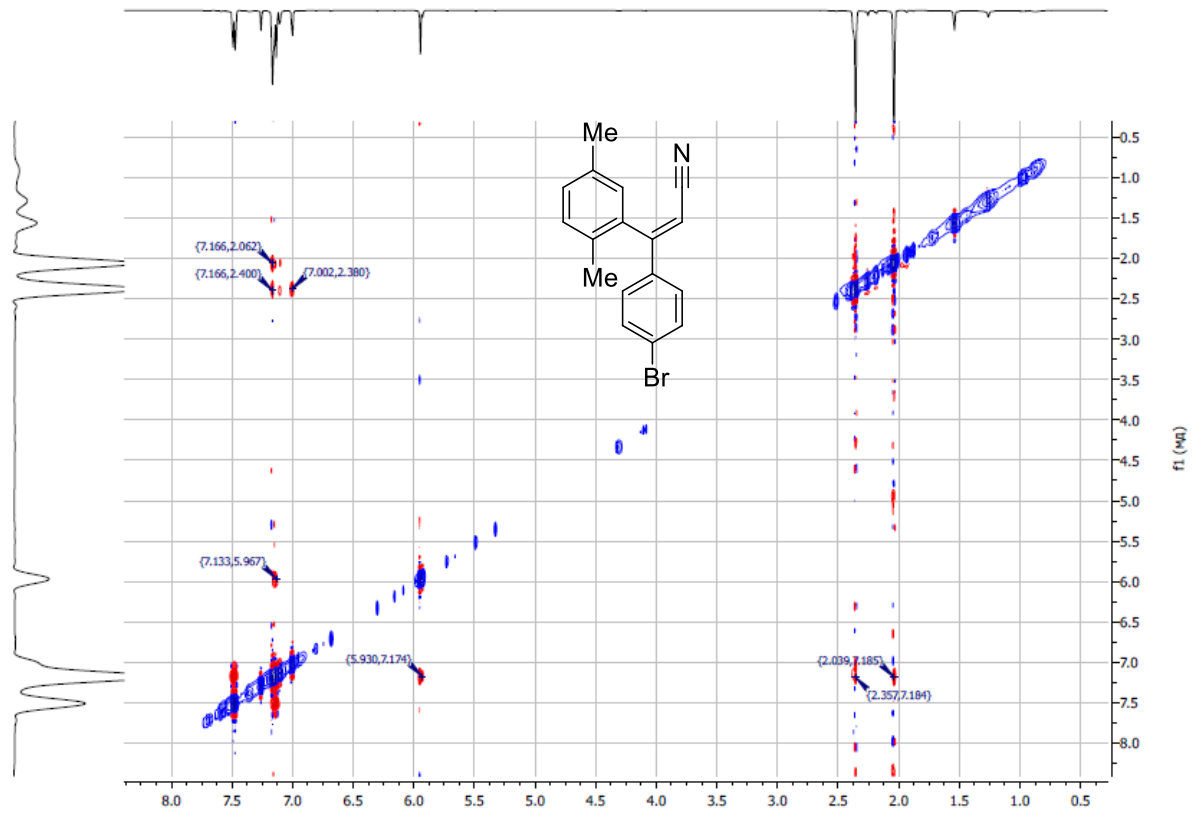


Figure S30. NOESY NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz).

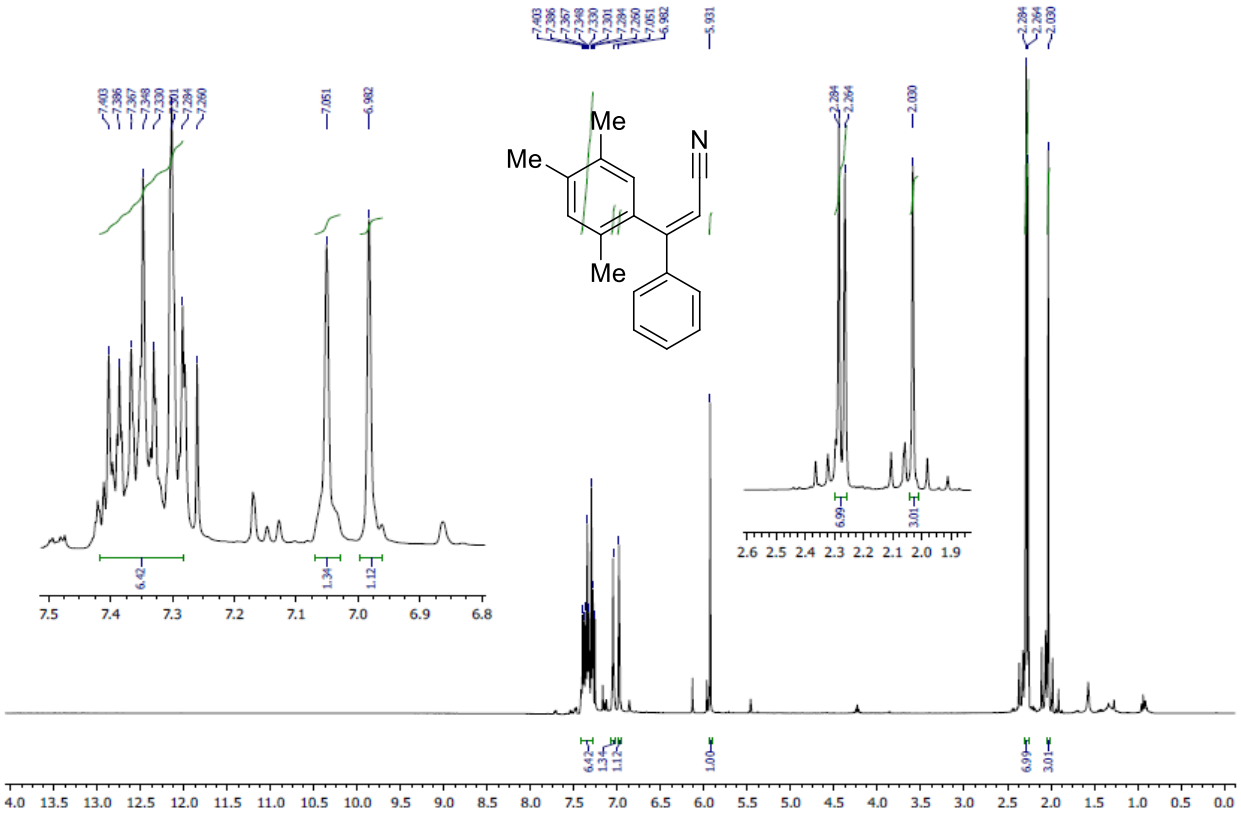


Figure S31. ^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz).

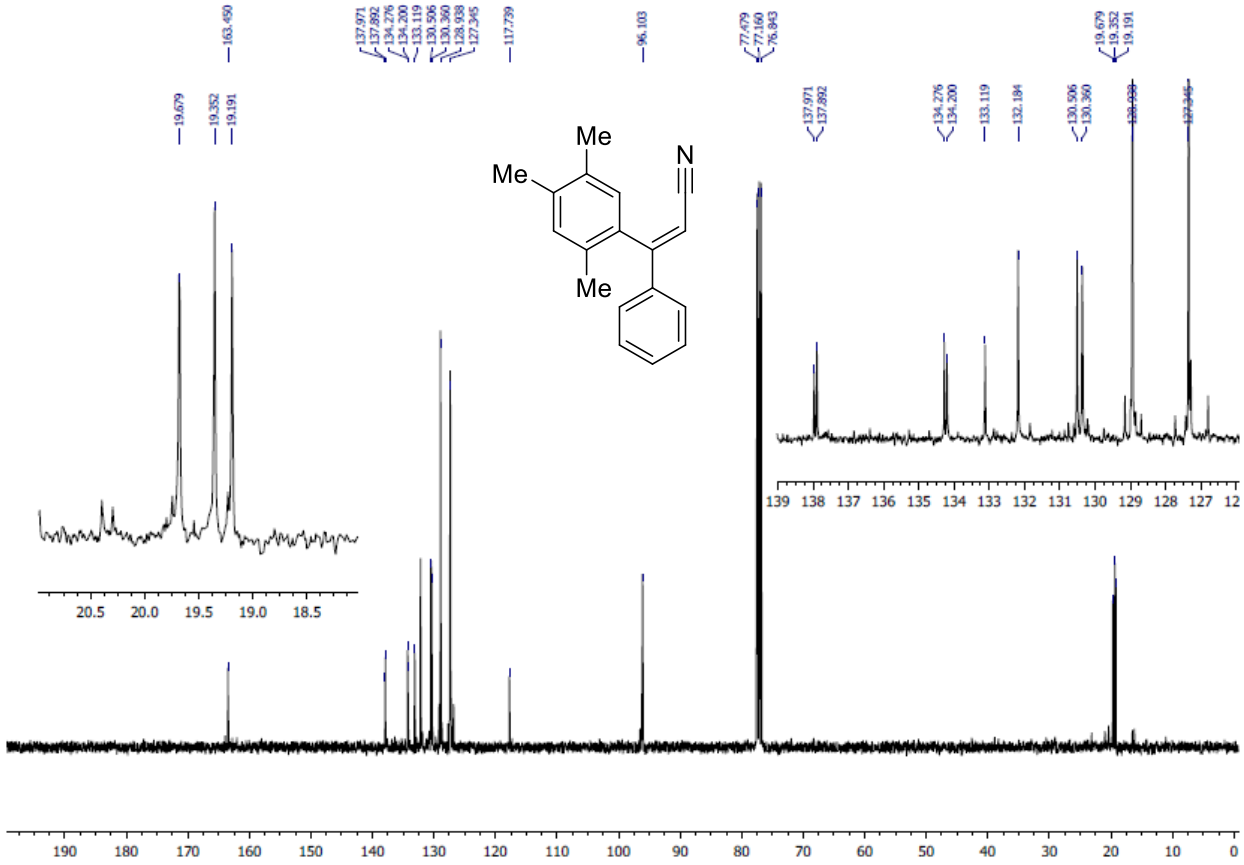


Figure S32. ^{13}C NMR spectrum of compound **2f** ($CDCl_3$, 100 MHz).

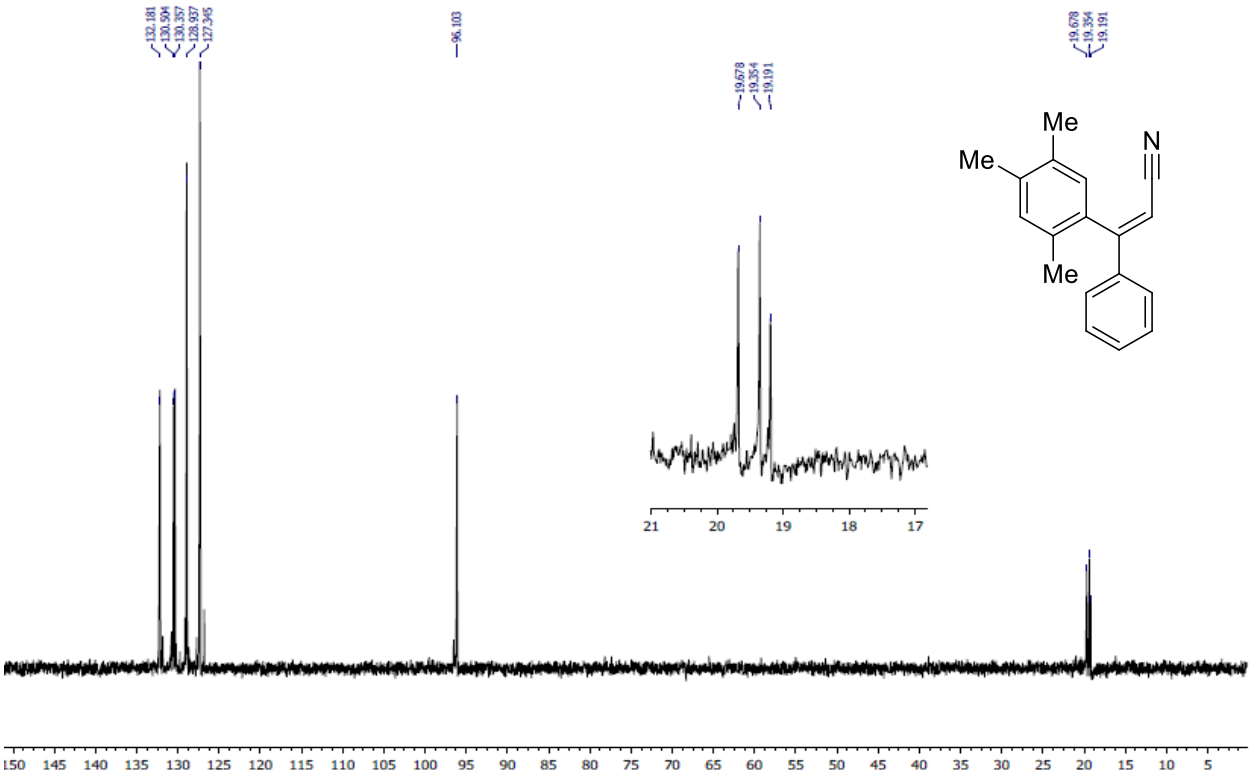


Figure S33. DEPT[135] NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz)

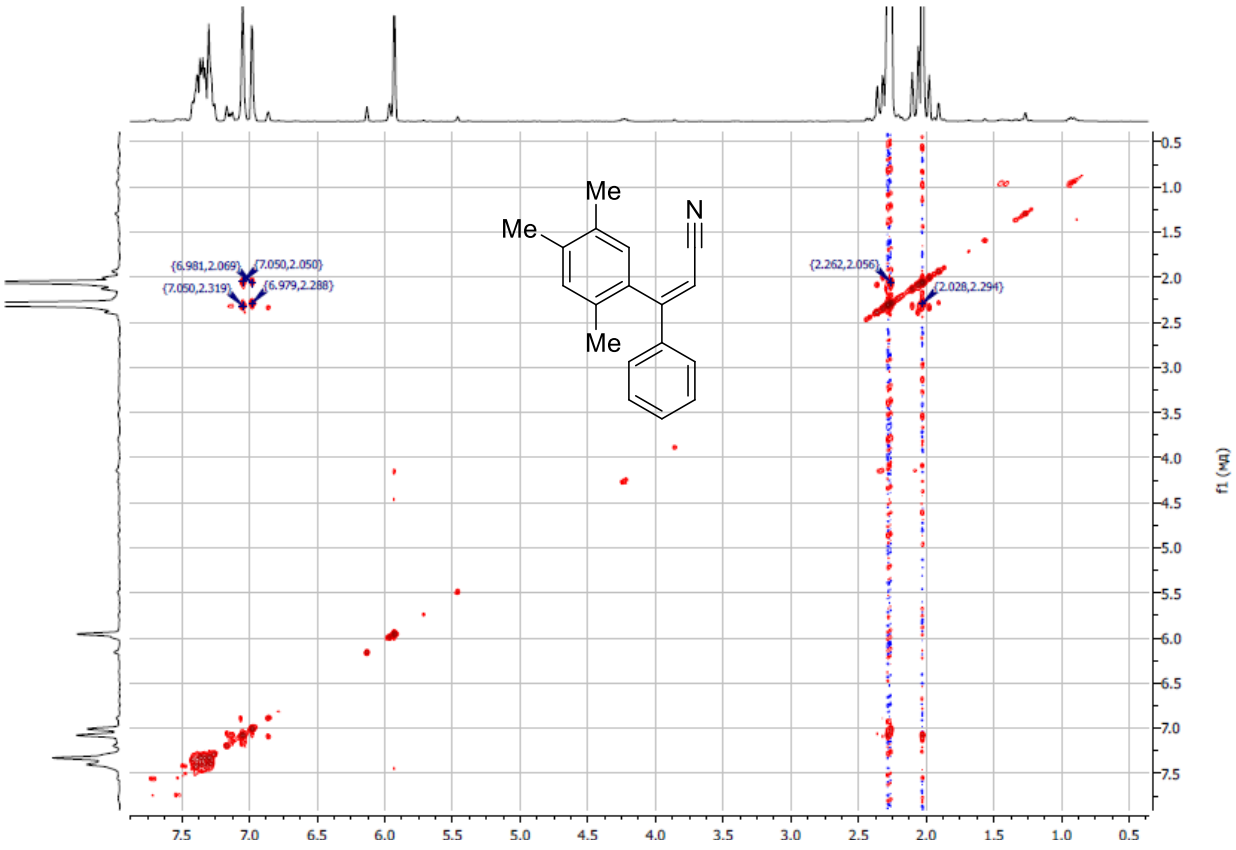


Figure S34. COSY NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz).

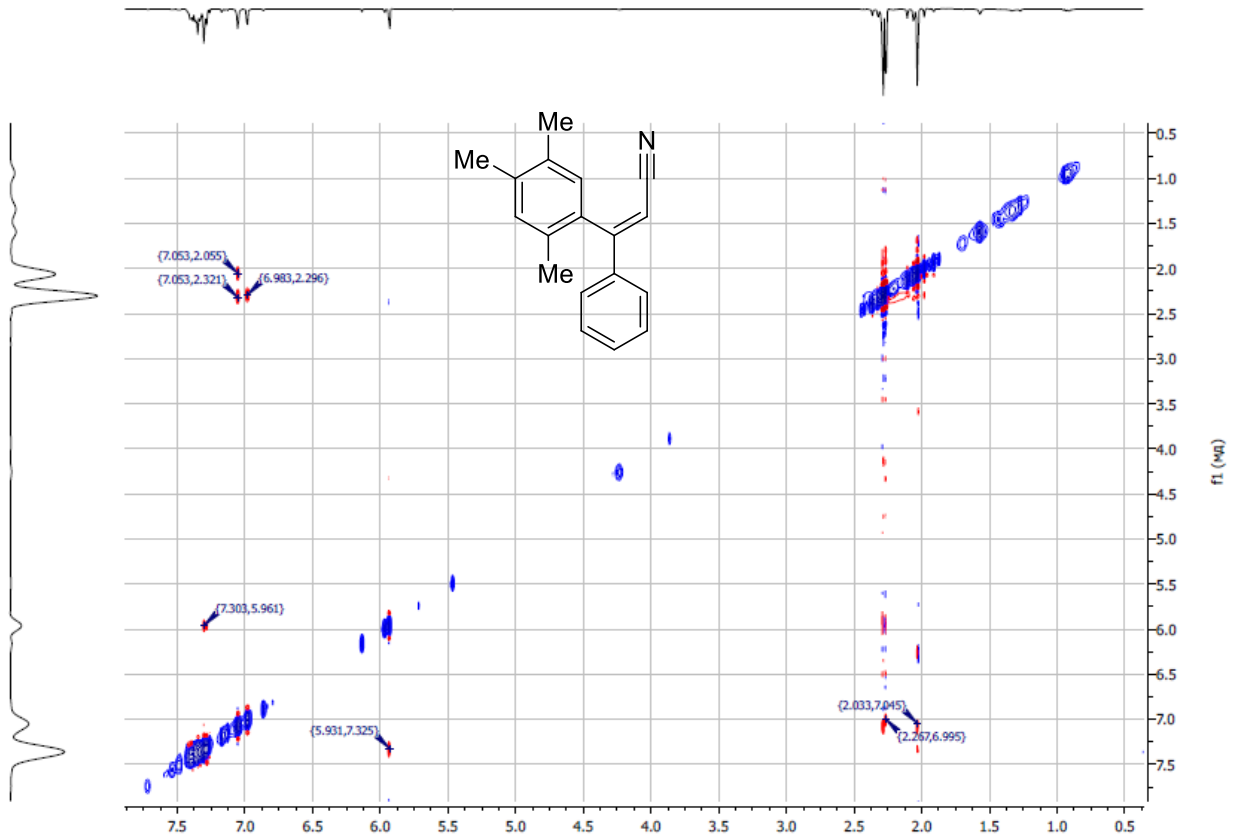


Figure S35. NOESY NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz).

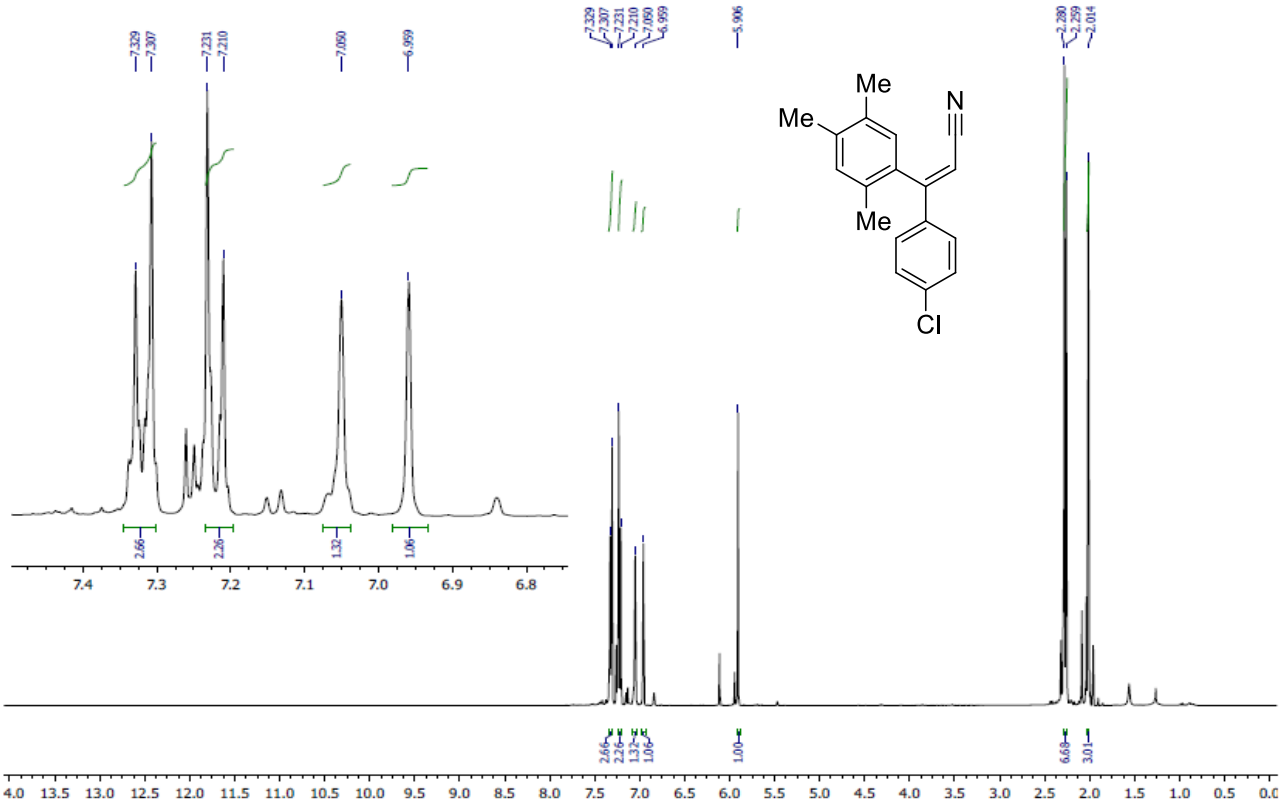


Figure S36. ^1H NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz).

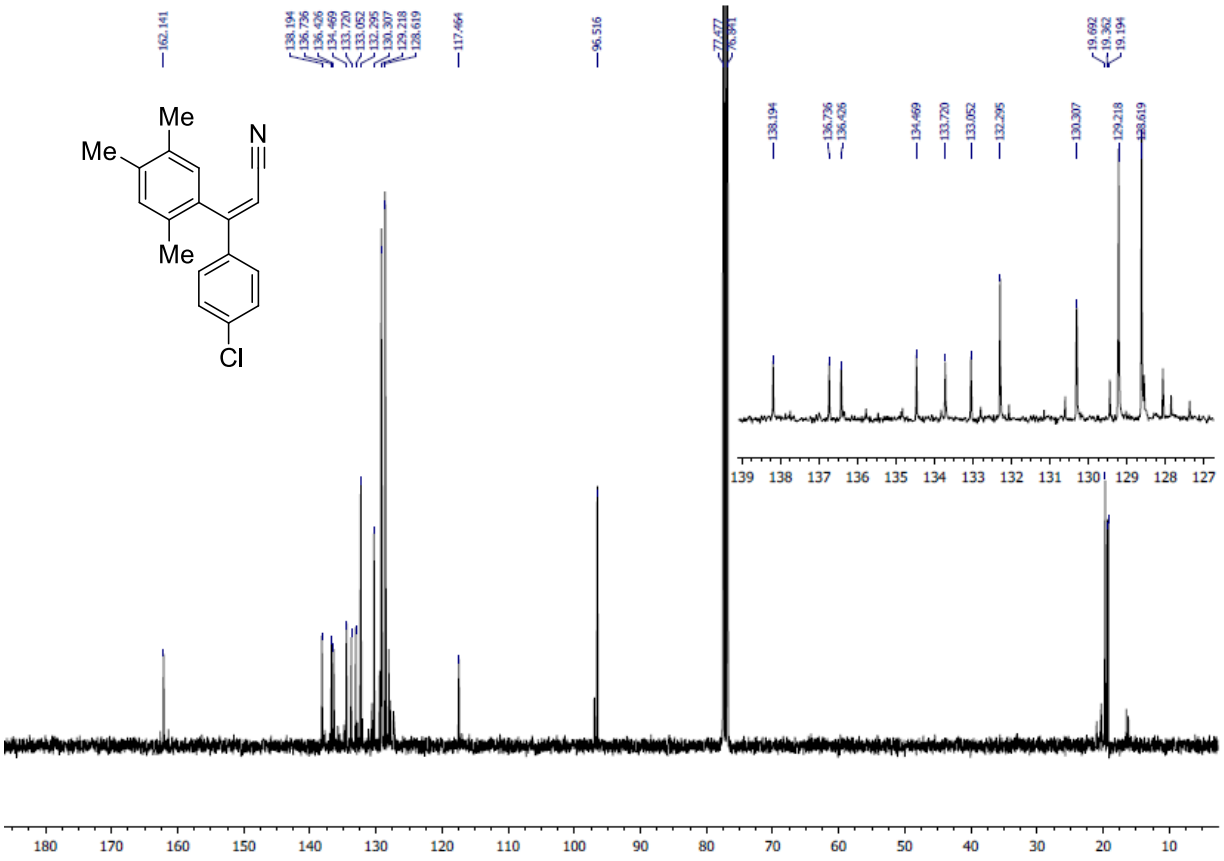


Figure S37. ^{13}C NMR spectrum of compound **2g** ($CDCl_3$, 100 MHz).

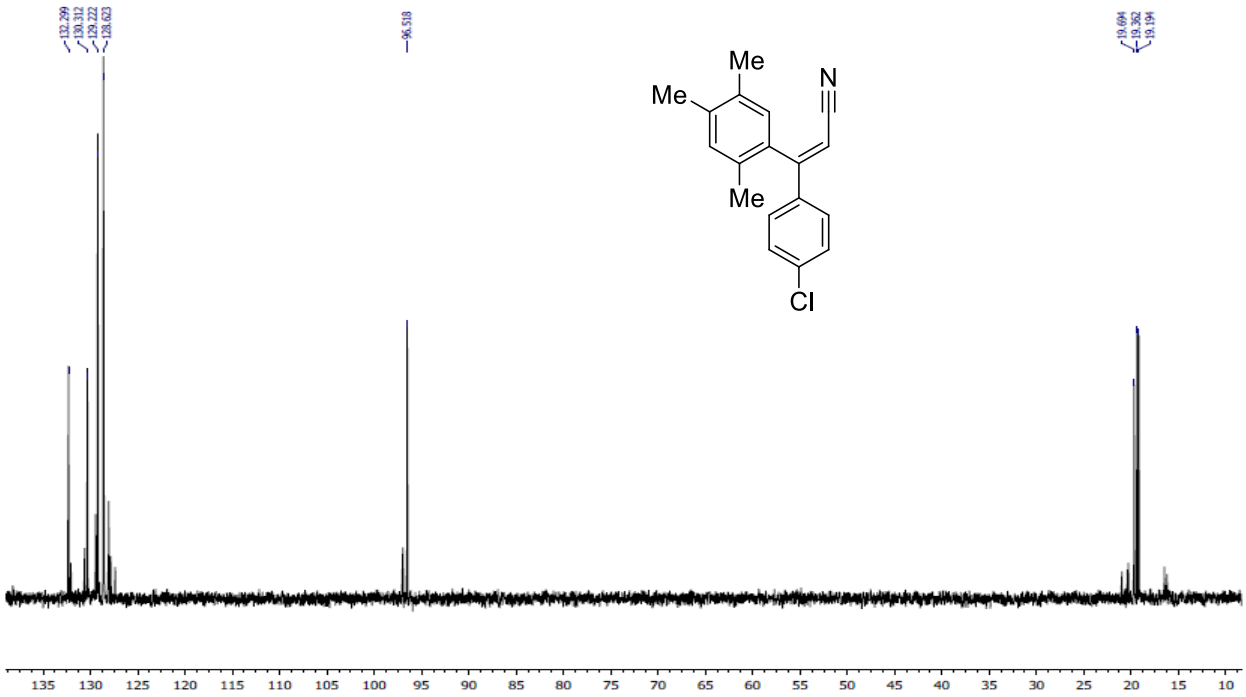


Figure S38. DEPT^{135} NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz).

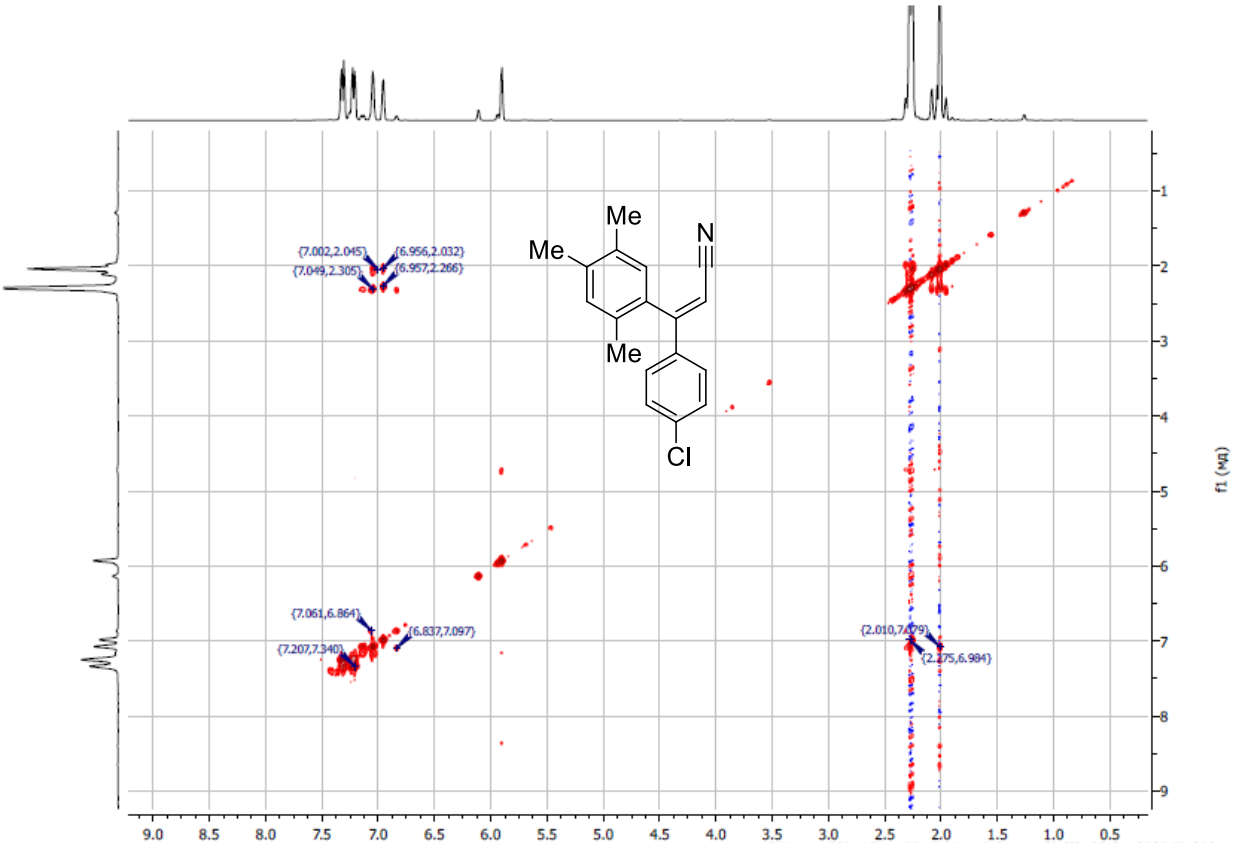


Figure S39. COSY NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz).

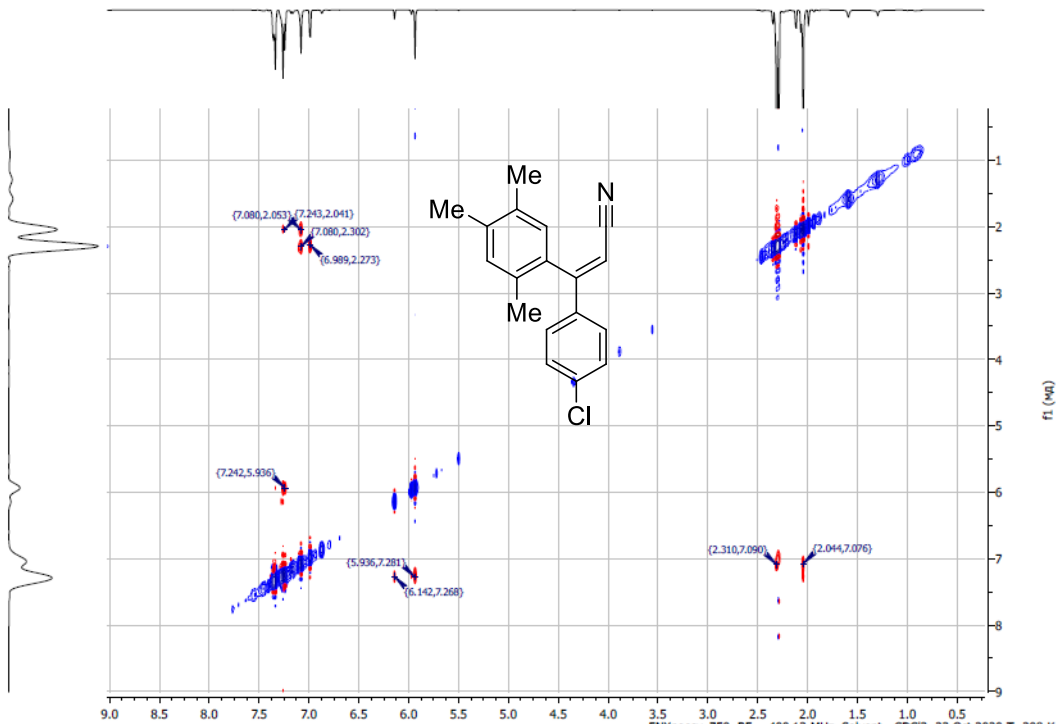


Figure S40. NOESY NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz).

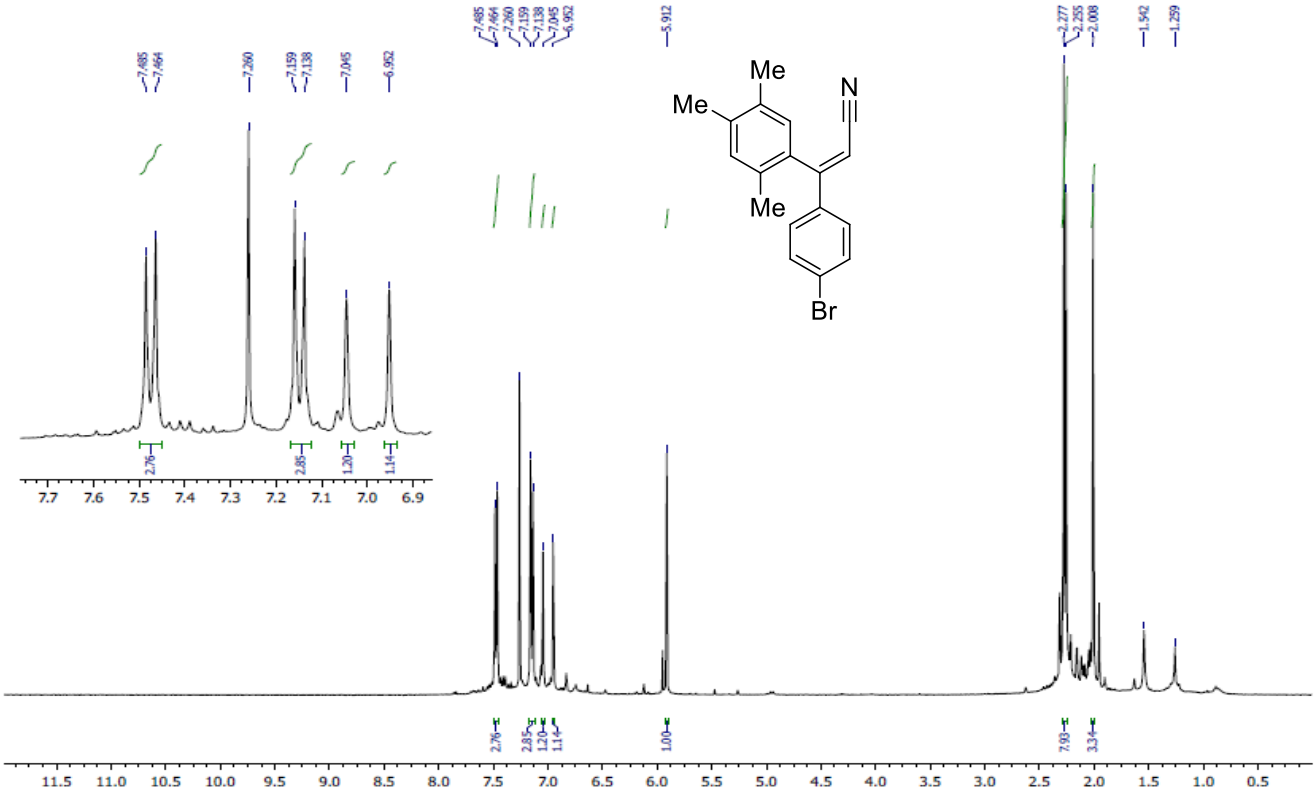


Figure S41. ^{1}H NMR spectrum of compound **2h** ($CDCl_3$, 400 MHz).

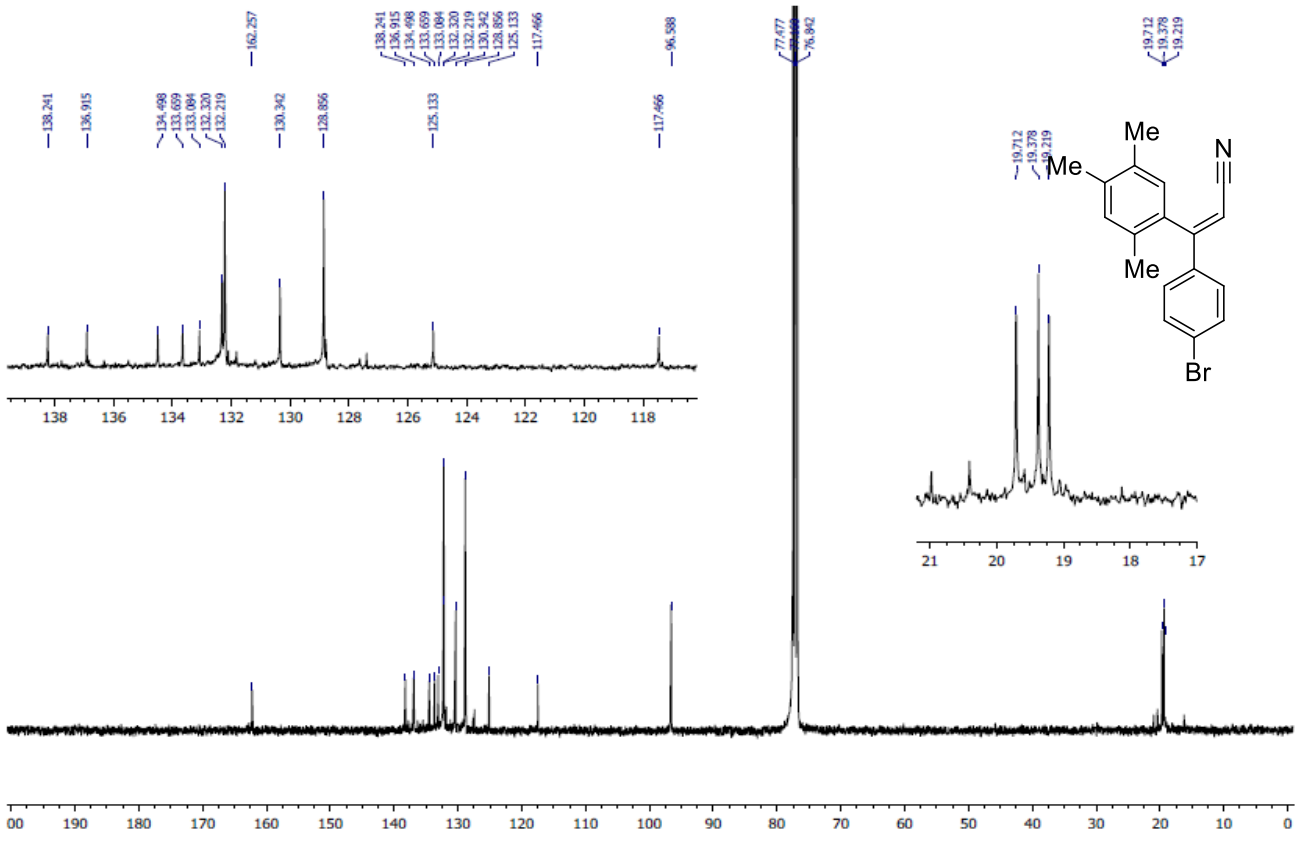


Figure S42. ^{13}C NMR spectrum of compound **2h** ($CDCl_3$, 100 MHz).

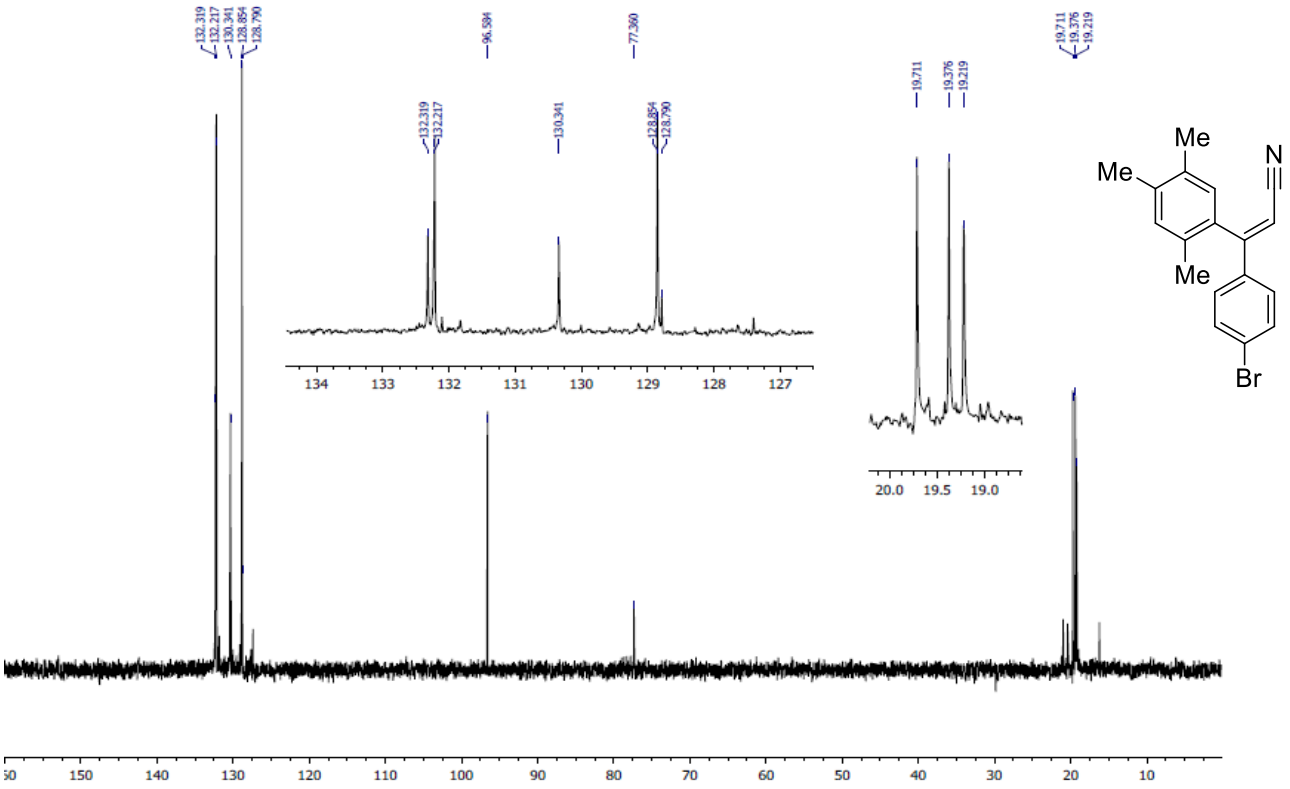


Figure S43. DEPT[135] NMR spectrum of compound **2h** ($CDCl_3$, 400 MHz).

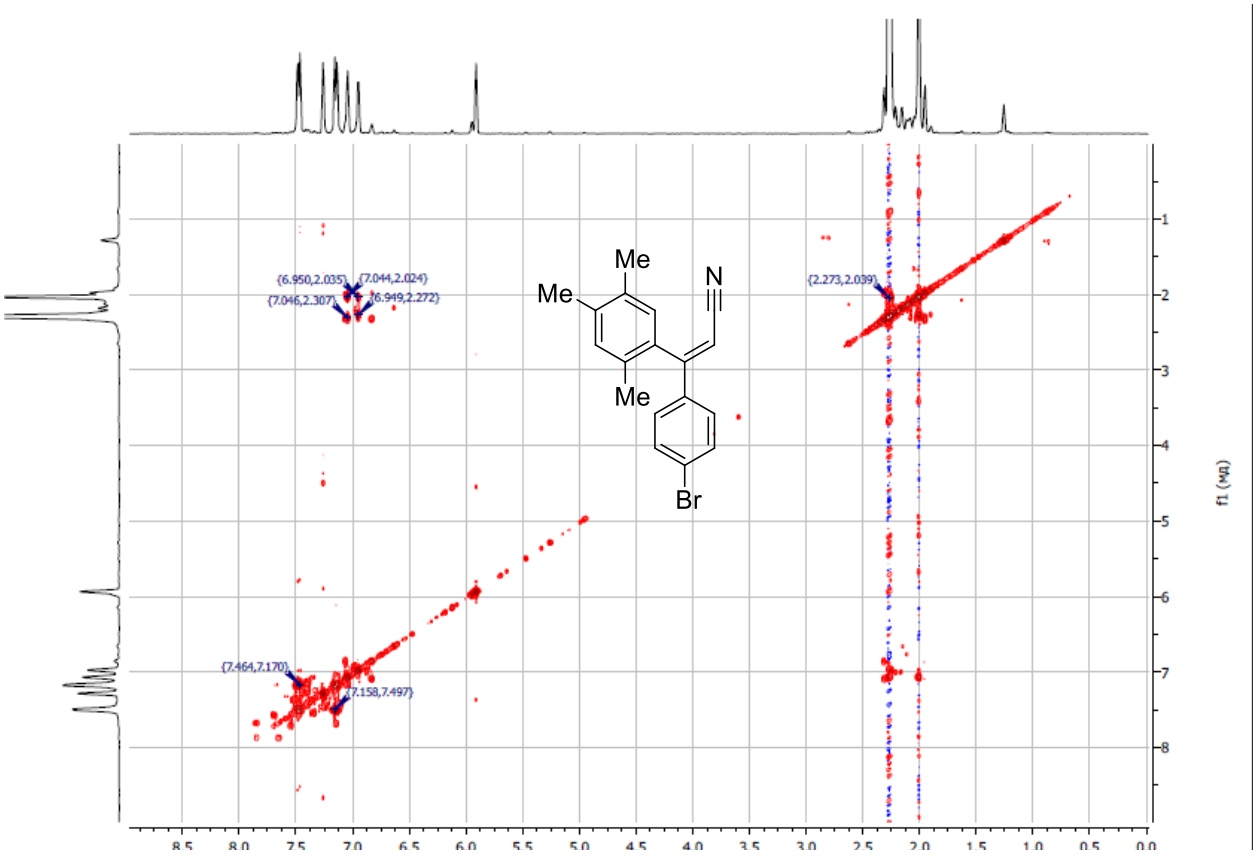


Figure S44. COSY NMR spectrum of compound **2h** ($CDCl_3$, 400 MHz).

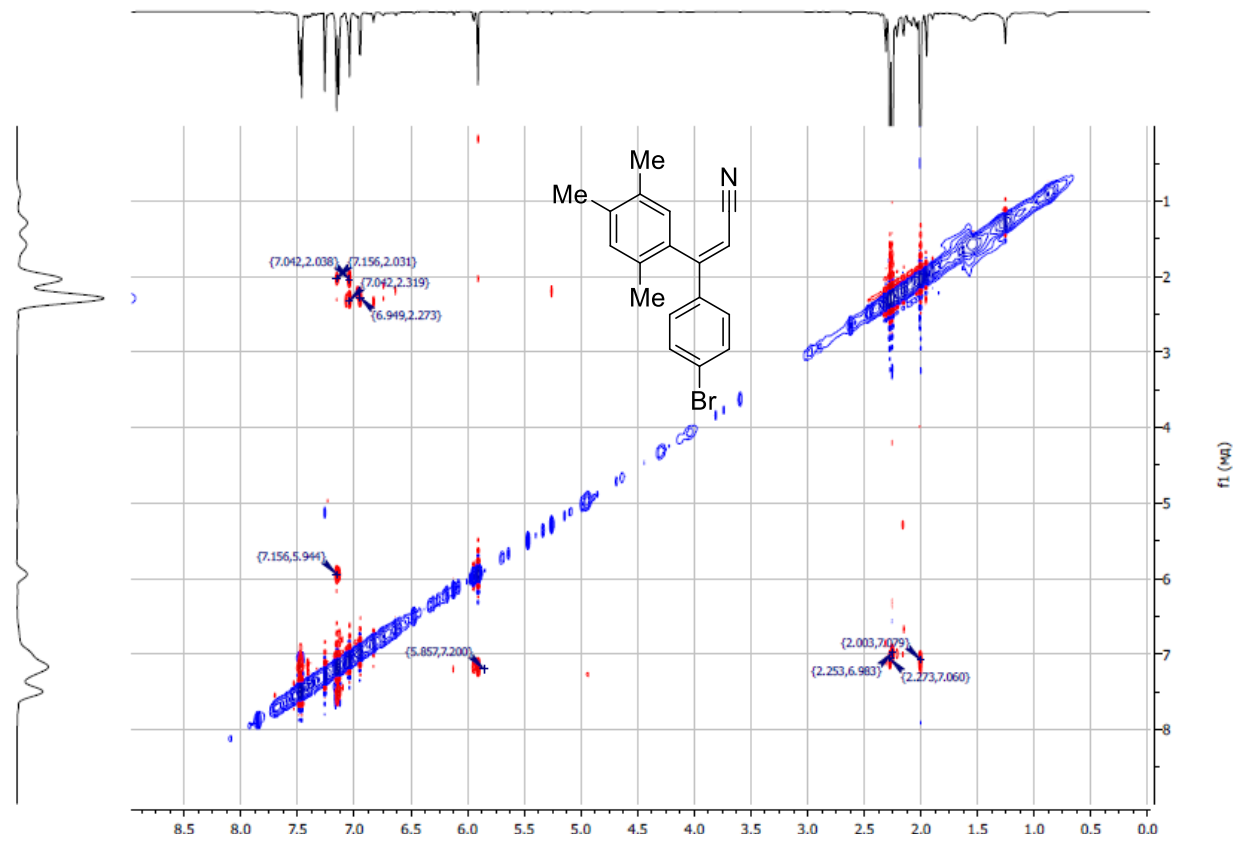


Figure S45. NOESY NMR spectrum of compound **2h** ($CDCl_3$, 400 MHz).

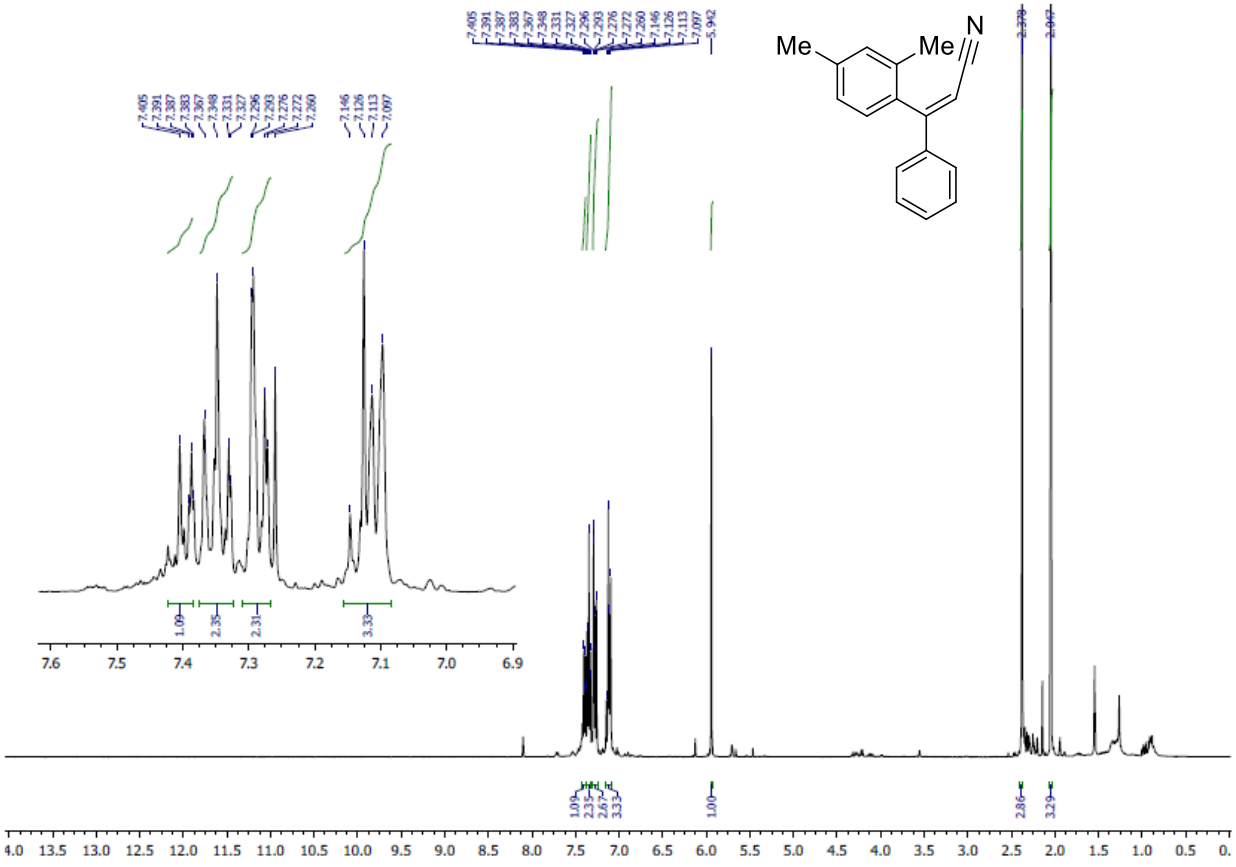


Figure S46. ^1H NMR spectrum of compound **2i** ($CDCl_3$, 400 MHz).

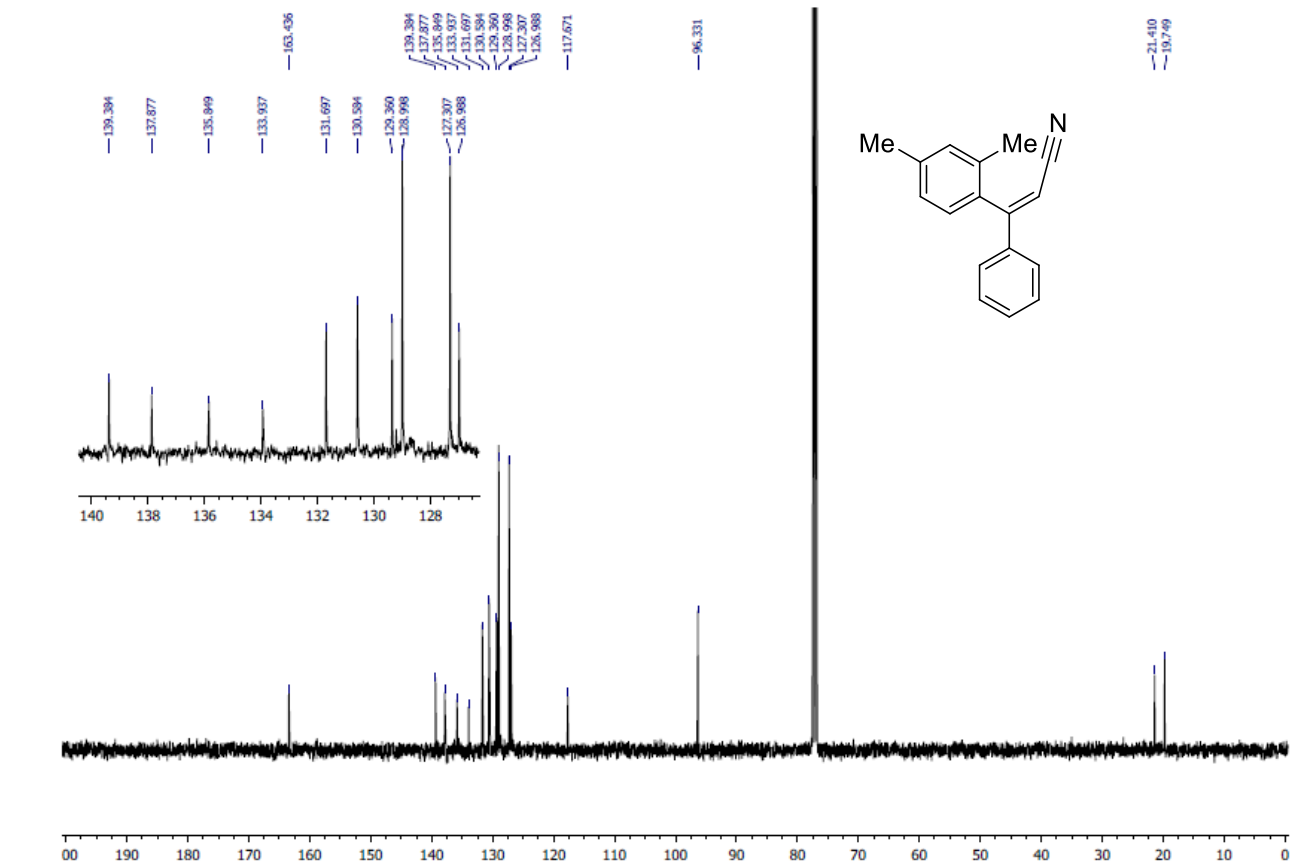


Figure S47. ^{13}C NMR spectrum of compound **2i** ($CDCl_3$, 100 MHz).

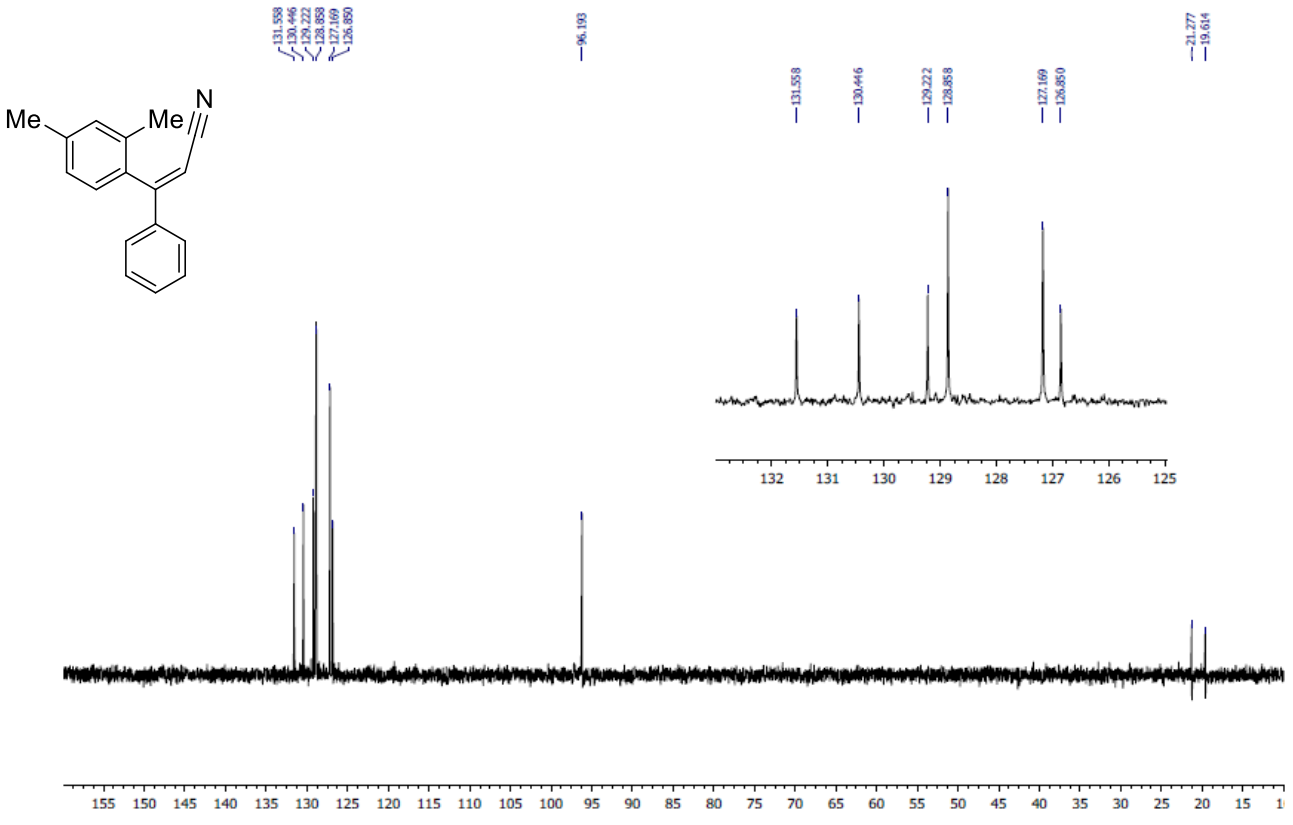


Figure S48. DEPT^{135} NMR spectrum of compound **2i** ($CDCl_3$, 400 MHz).

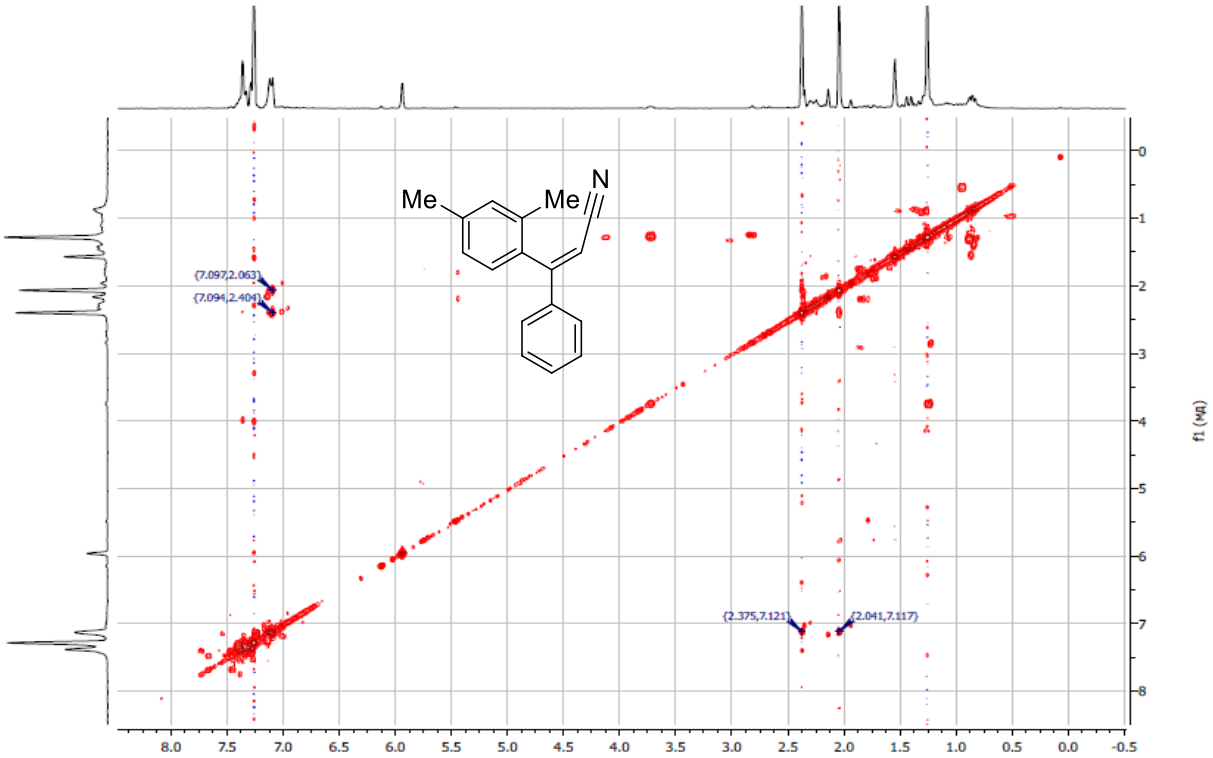


Figure S49. COSY NMR spectrum of compound **2i** ($CDCl_3$, 400 MHz).

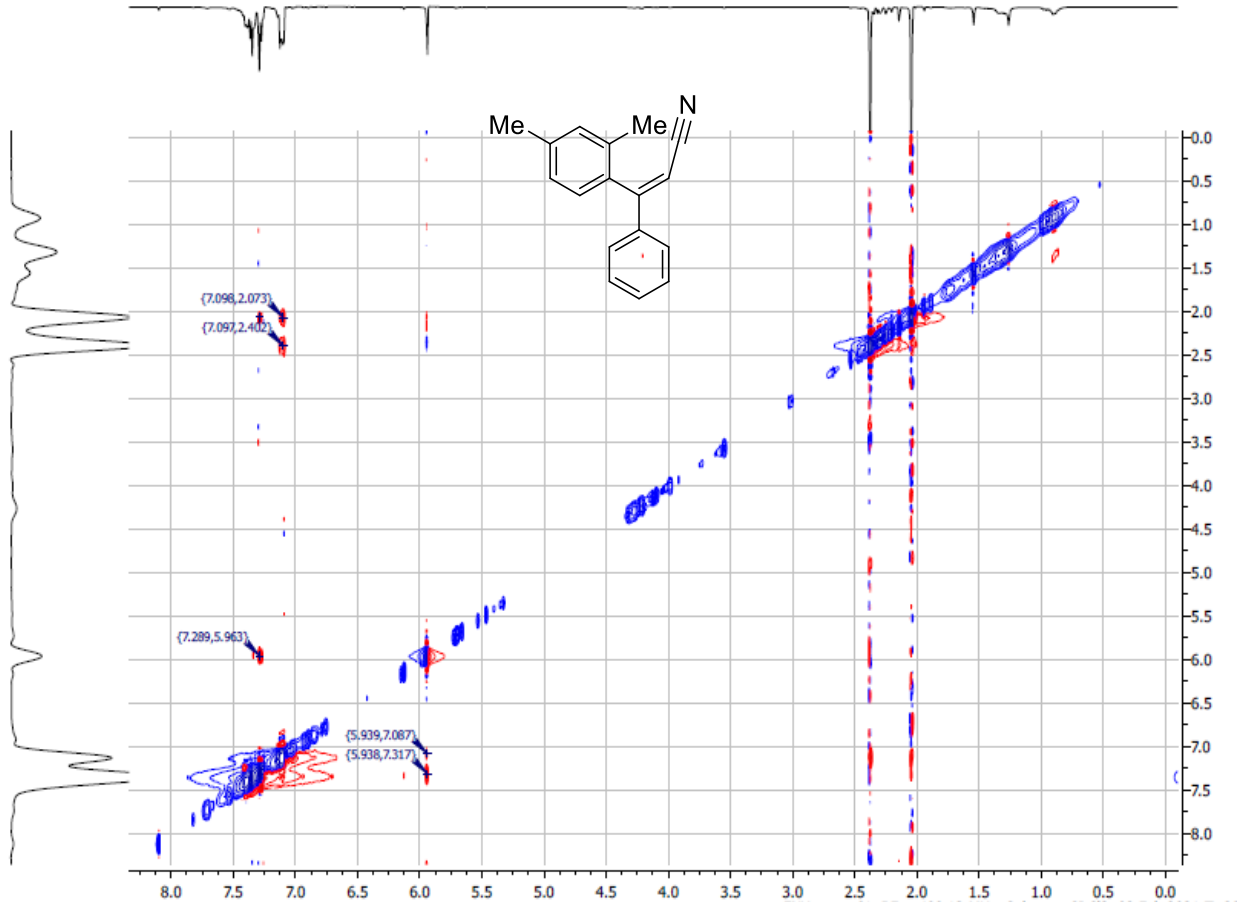


Figure S50. NOESY NMR spectrum of compound **2i** ($CDCl_3$, 400 MHz).

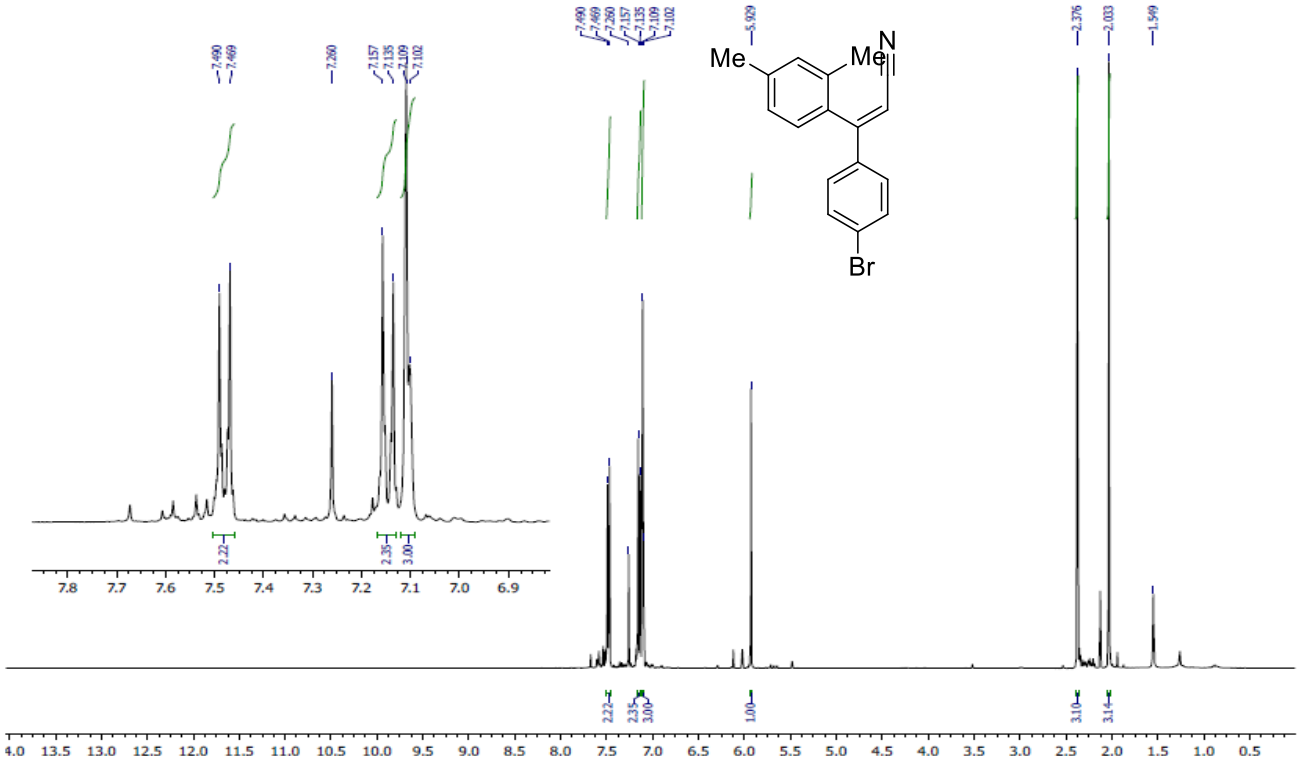


Figure S51. ^{1}H NMR spectrum of compound **2j** ($CDCl_3$, 400 MHz).

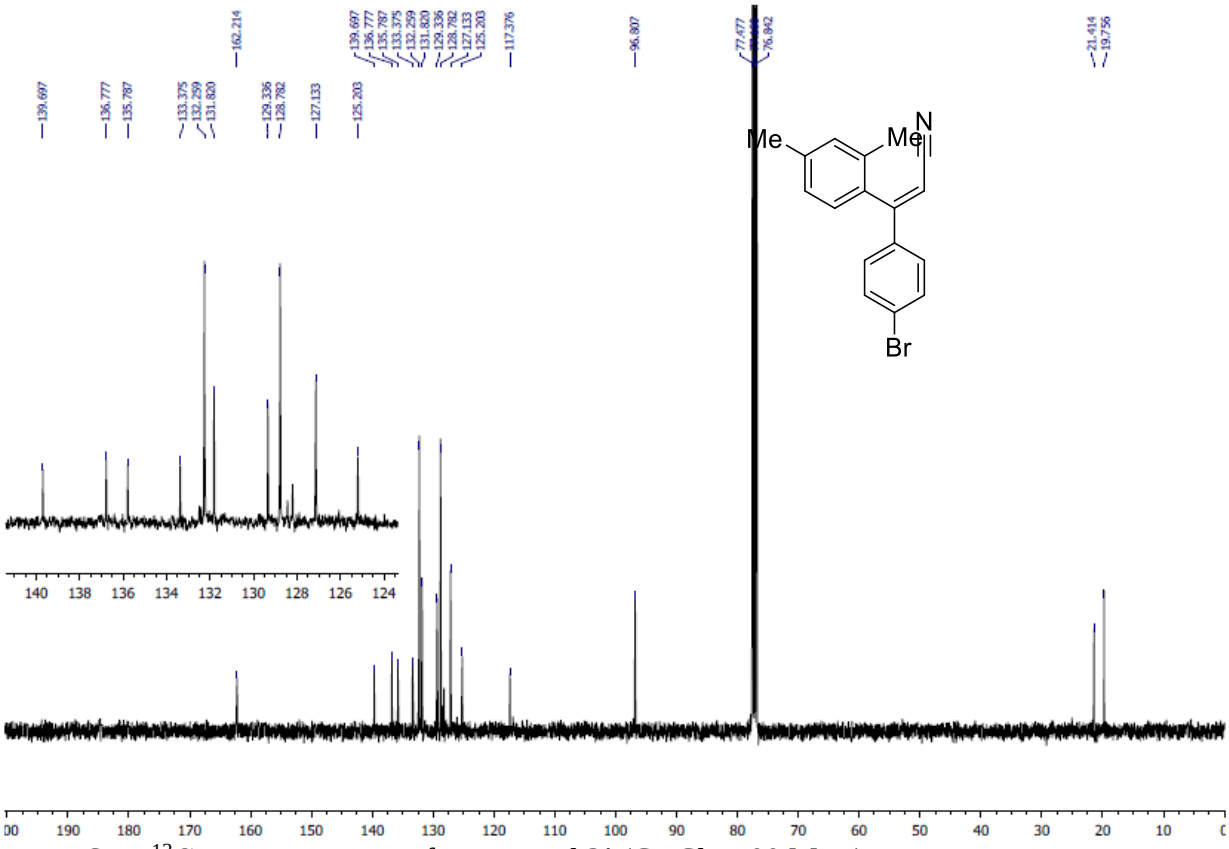


Figure S52. ^{13}C NMR spectrum of compound **2j** ($CDCl_3$, 100 MHz).

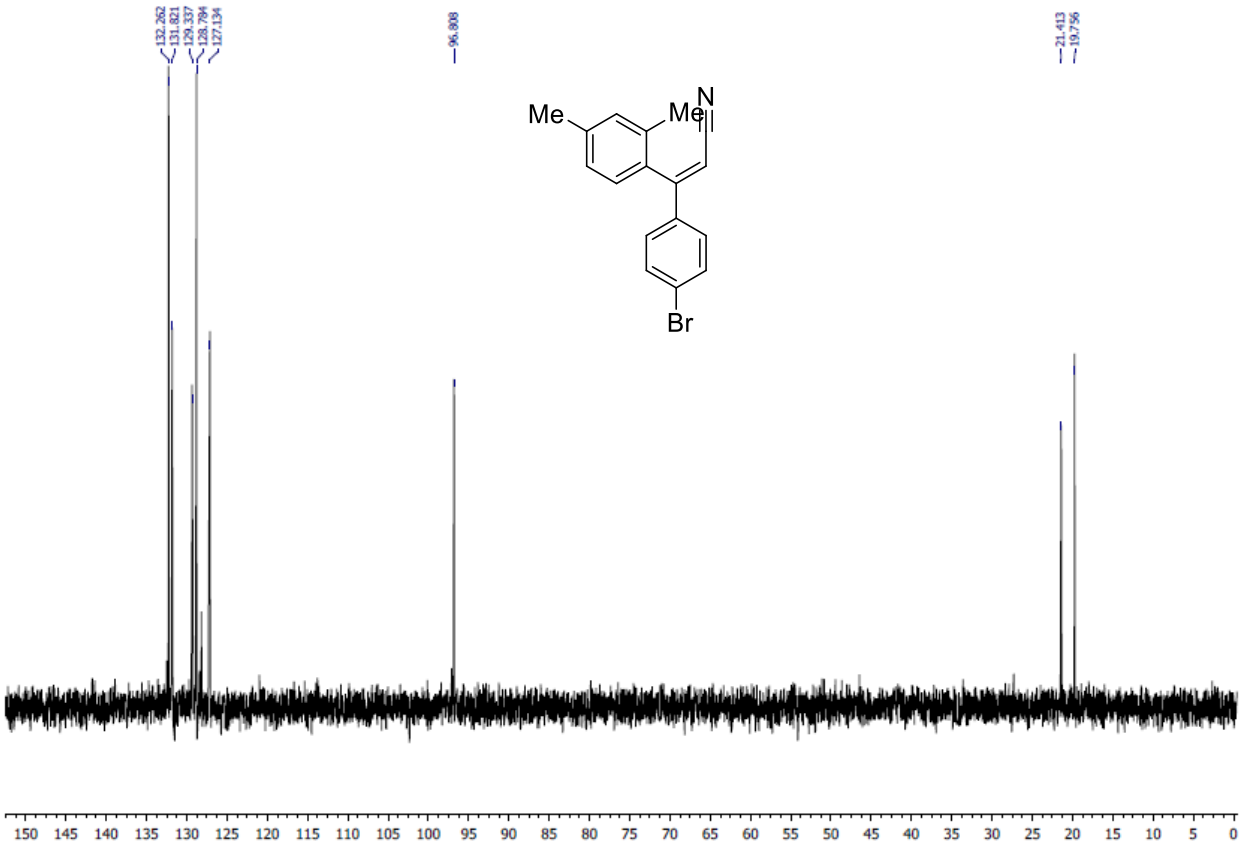


Figure S53. DEPT^{135} NMR spectrum of compound **2j** ($CDCl_3$, 400 MHz).

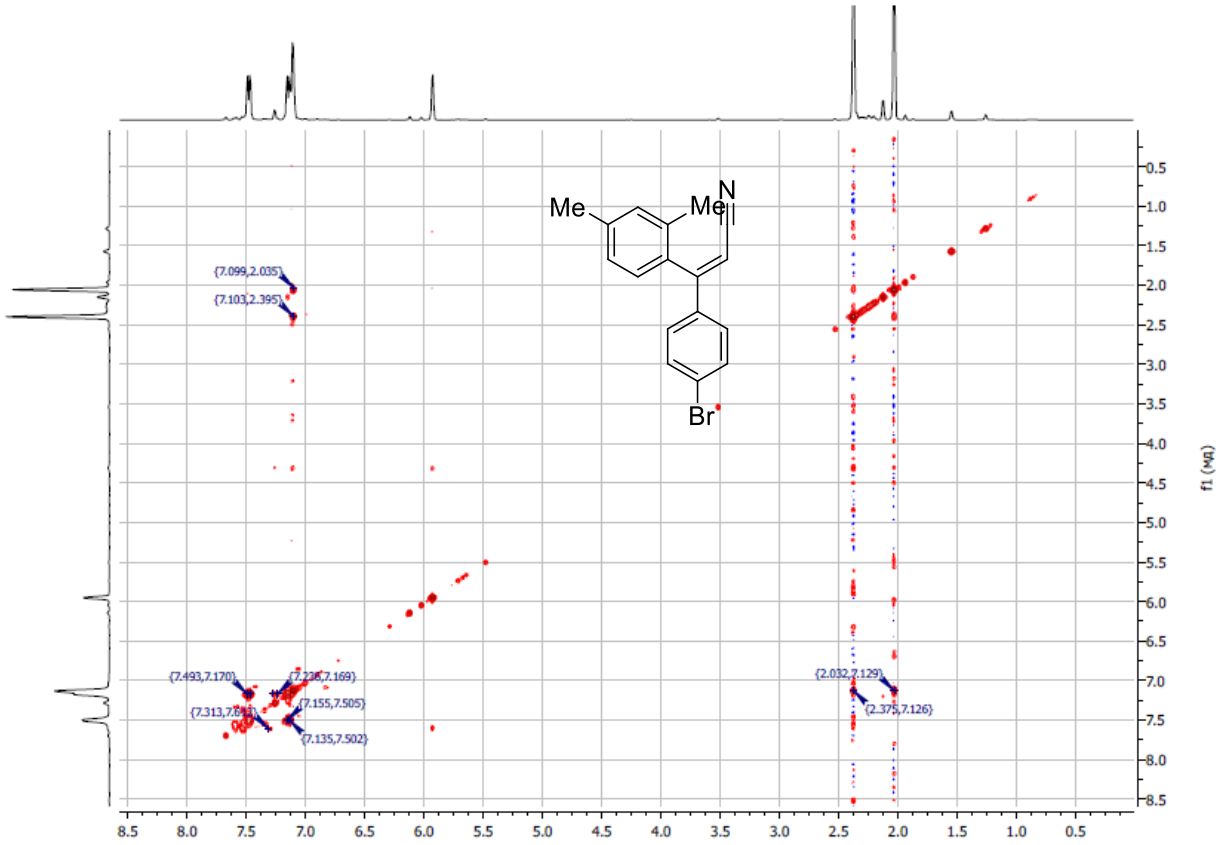


Figure S54. COSY NMR spectrum of compound **2j** ($CDCl_3$, 400 MHz).

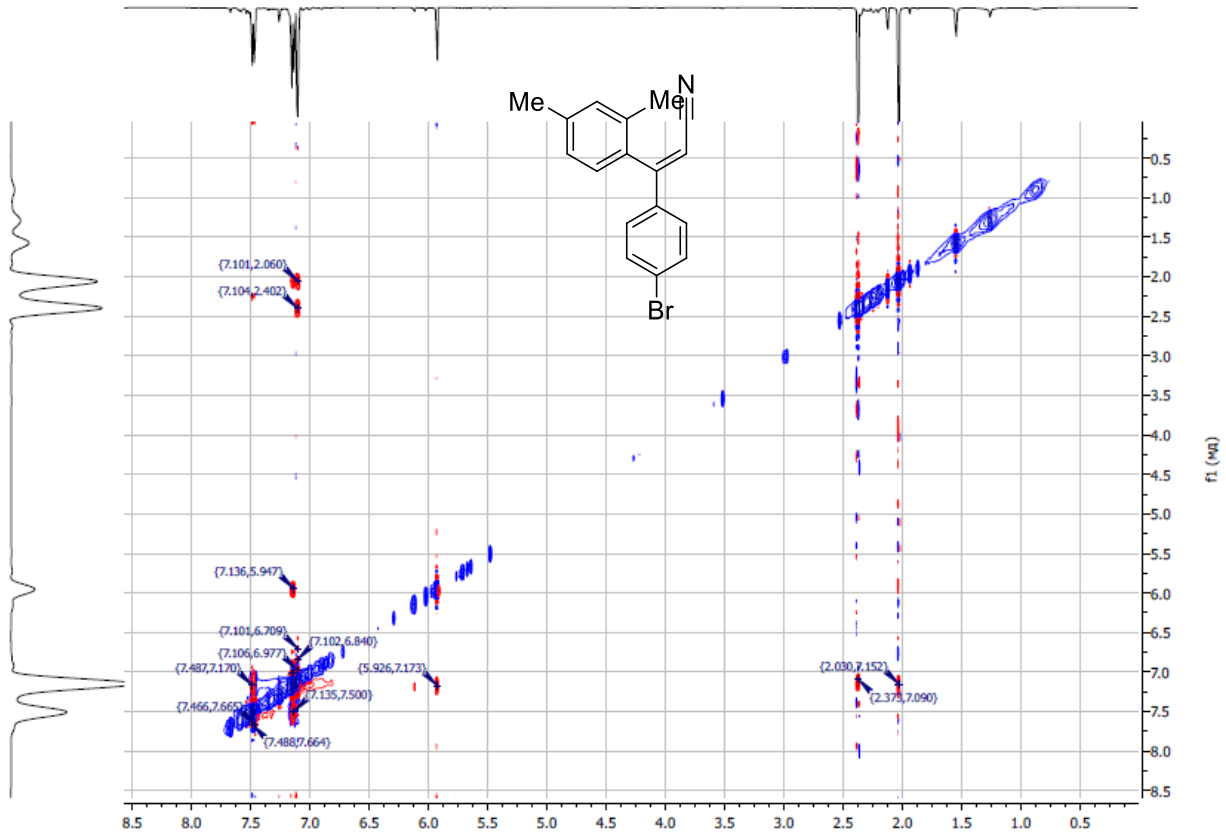


Figure S55. NOESY NMR spectrum of compound **2j** ($CDCl_3$, 400 MHz).

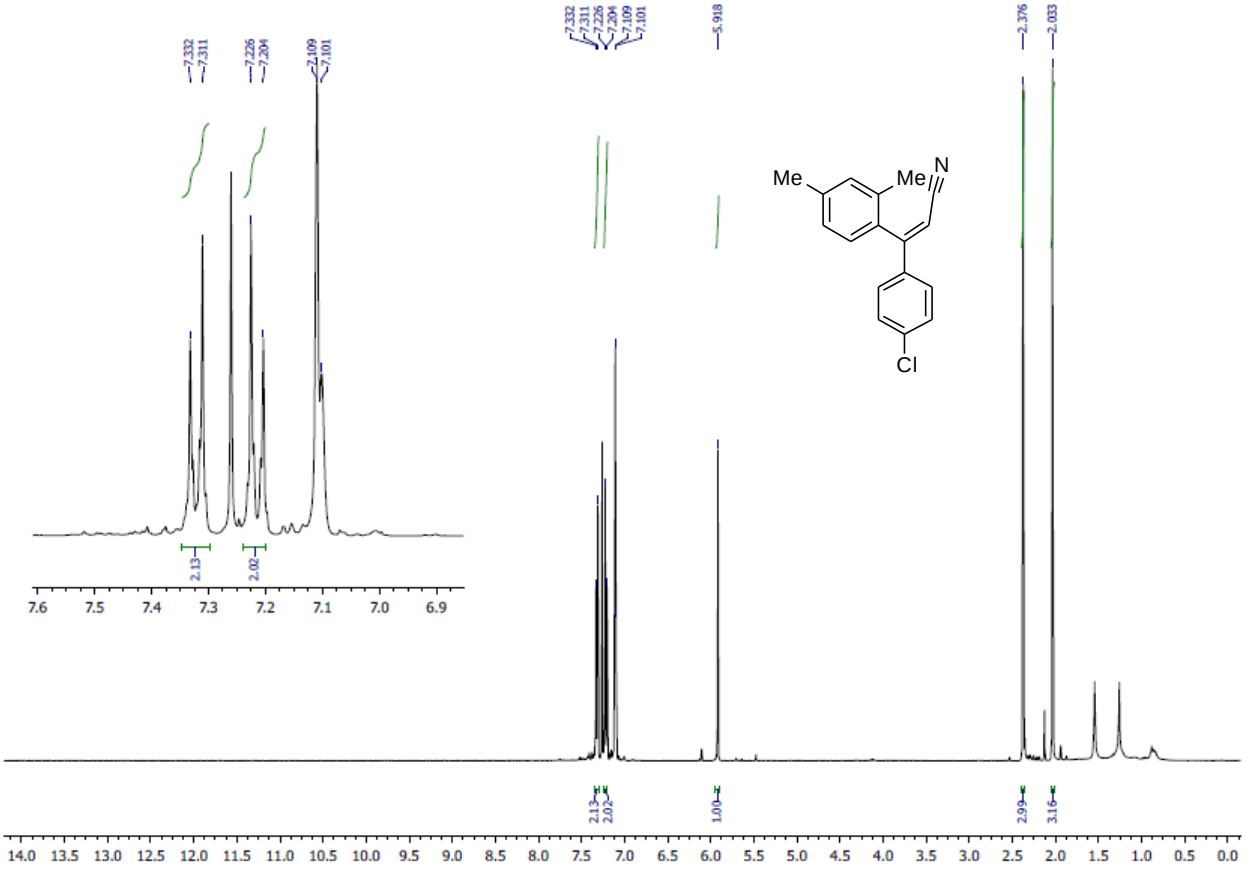


Figure S56. ^1H NMR spectrum of compound **2k** ($CDCl_3$, 400 MHz).

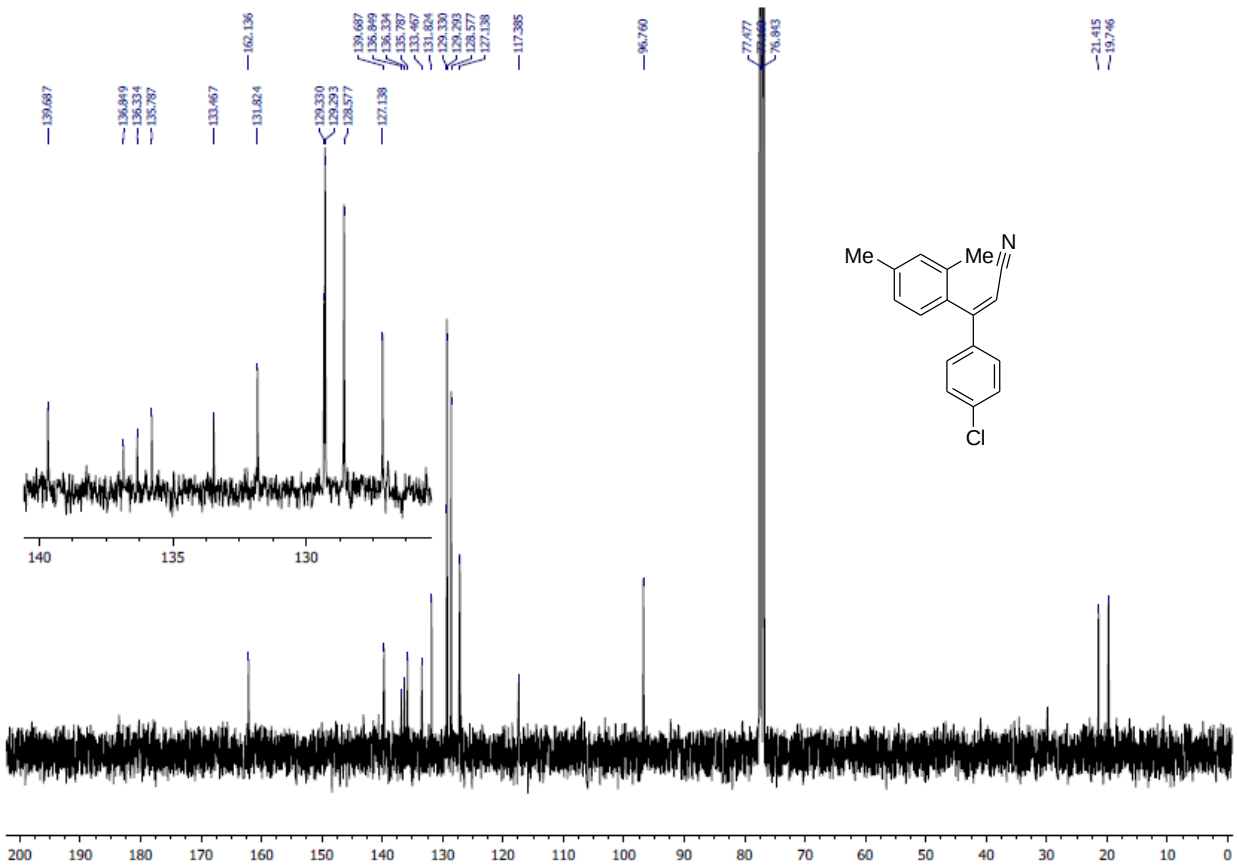


Figure S57. ^{13}C NMR spectrum of compound **2k** ($CDCl_3$, 100 MHz).

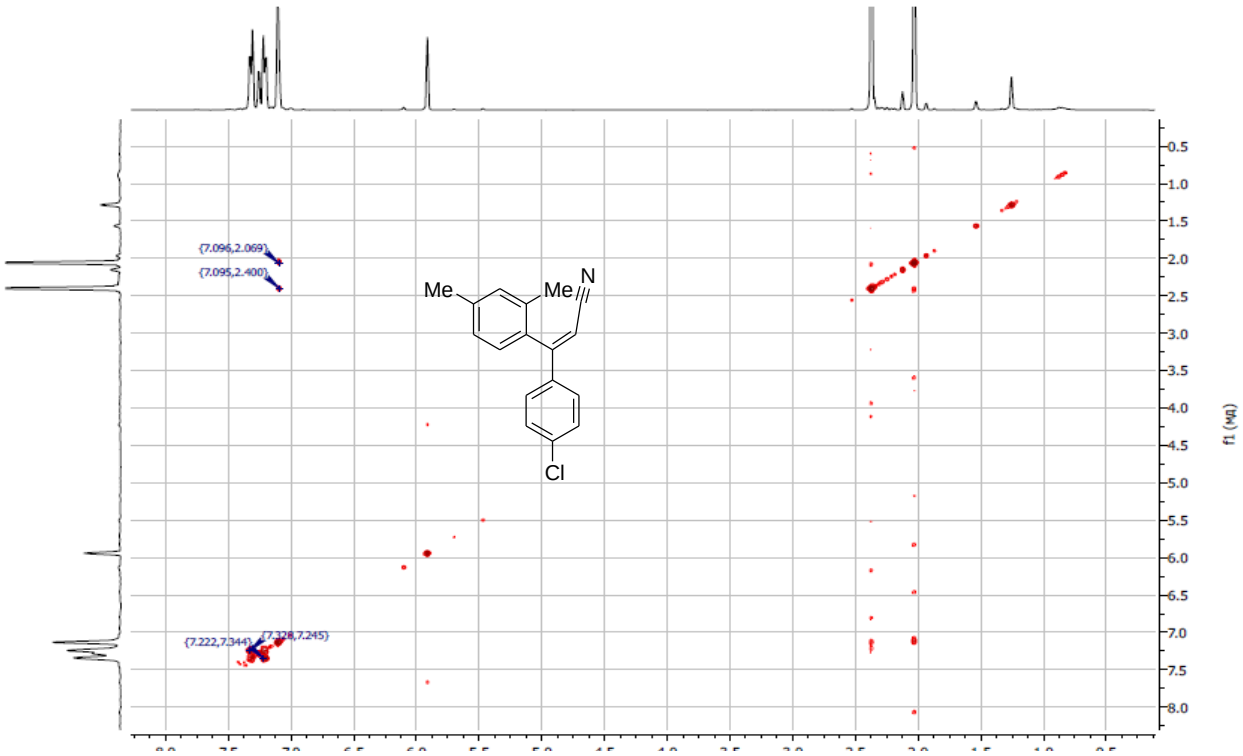


Figure S58. COSY NMR spectrum of compound **2k** ($CDCl_3$, 400 MHz).

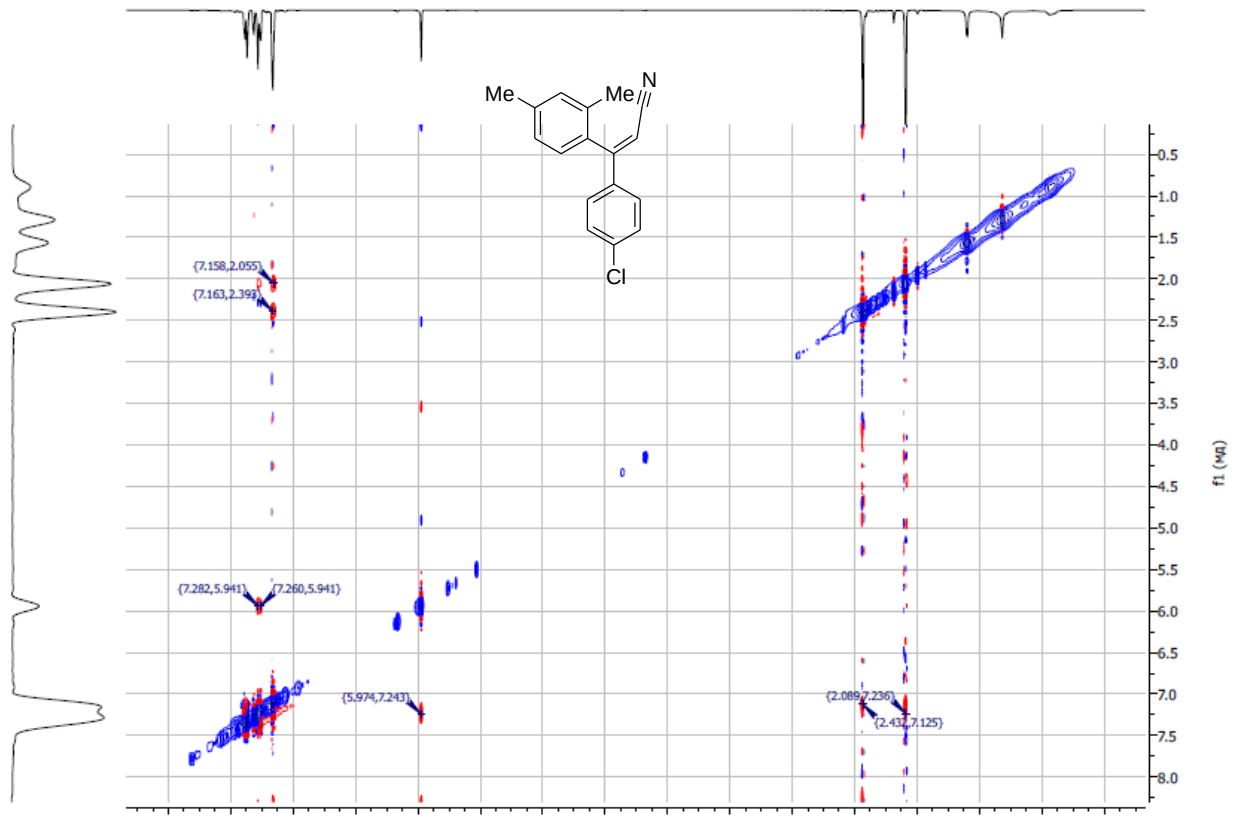


Figure S59. NOESY NMR spectrum of compound **2k** ($CDCl_3$, 400 MHz).

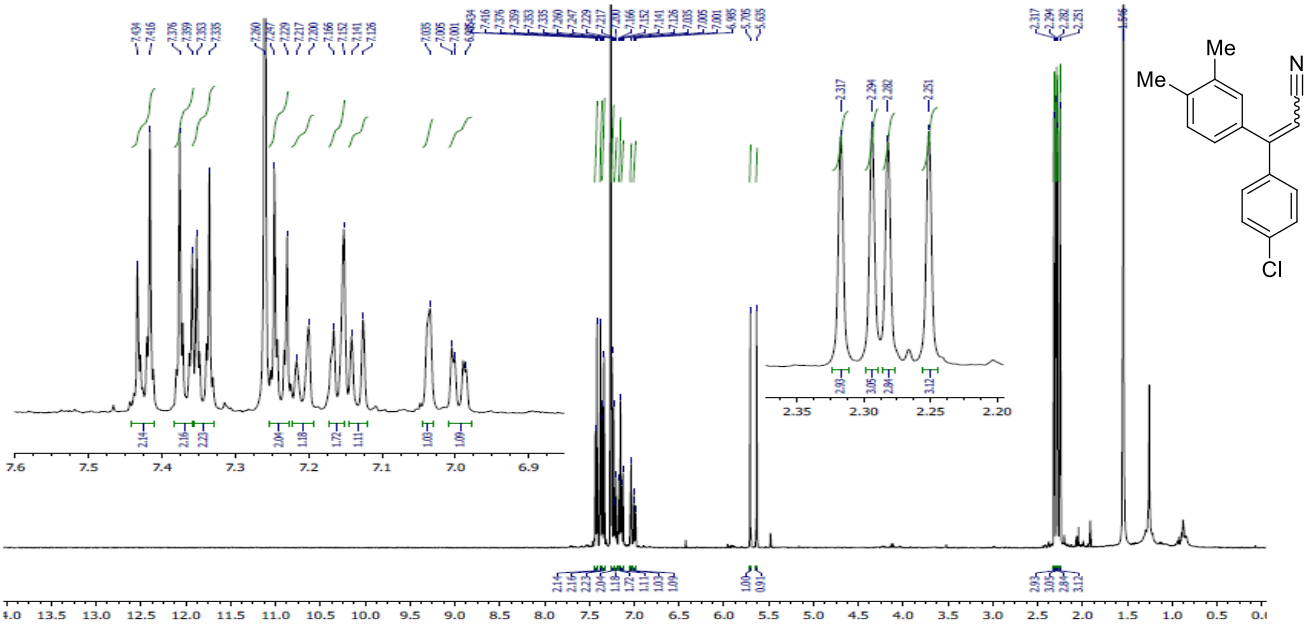


Figure S60. ^1H NMR spectrum of mixture of compounds *E,Z*-**2l** ($CDCl_3$, 400 MHz).

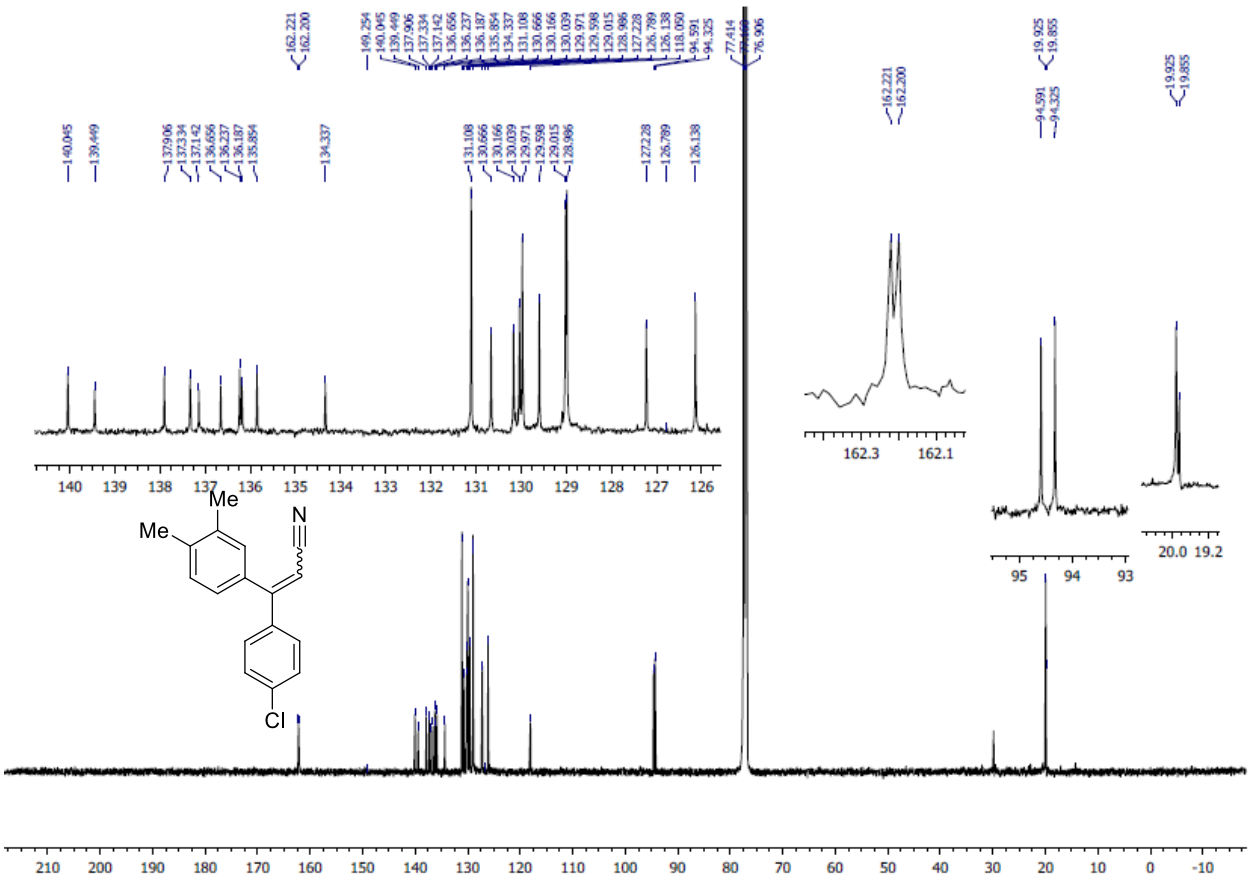


Figure S61. ^{13}C NMR spectrum of mixture of compounds *E,Z*-**2l** ($CDCl_3$, 100 MHz).

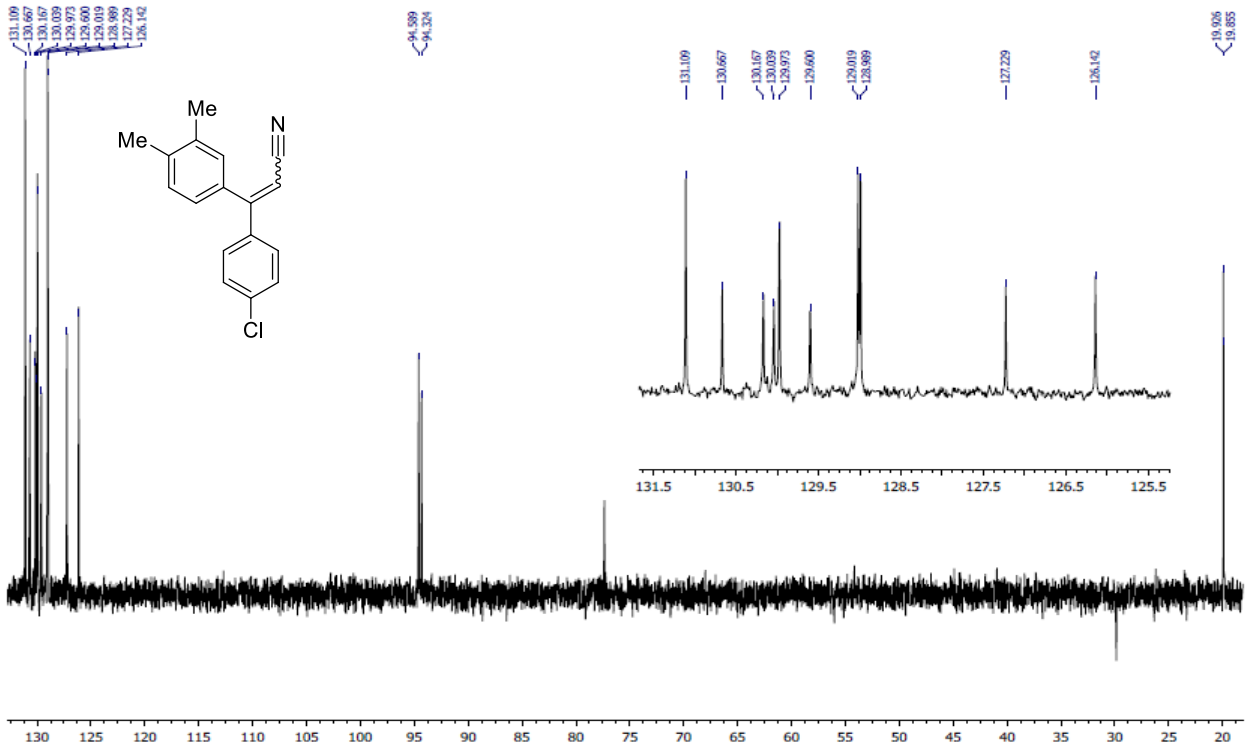


Figure S62. DEPT^{135} NMR spectrum of mixture of compounds *E,Z*-**2l** ($CDCl_3$, 400 MHz).

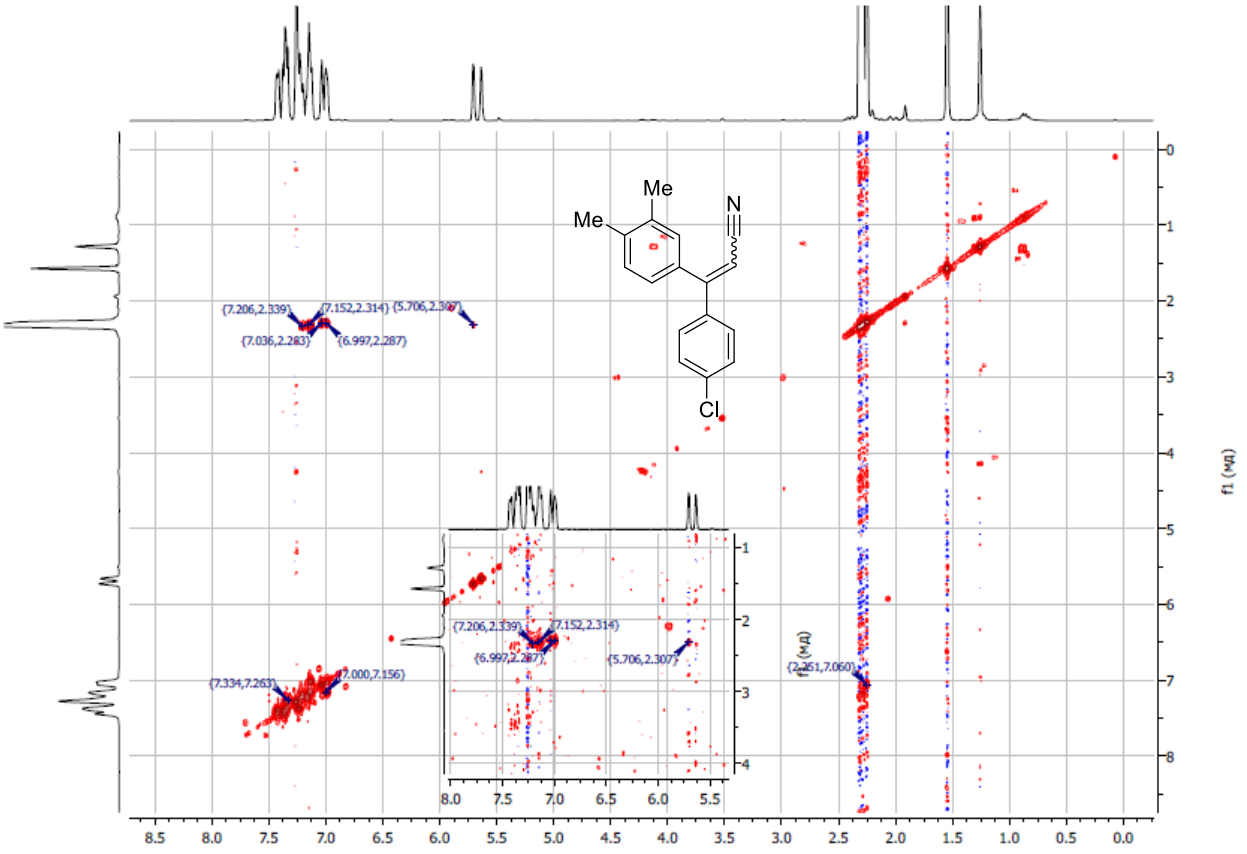


Figure S63. COSY NMR spectrum of mixture of compounds *E*,*Z*-**2l** ($CDCl_3$, 400 MHz).

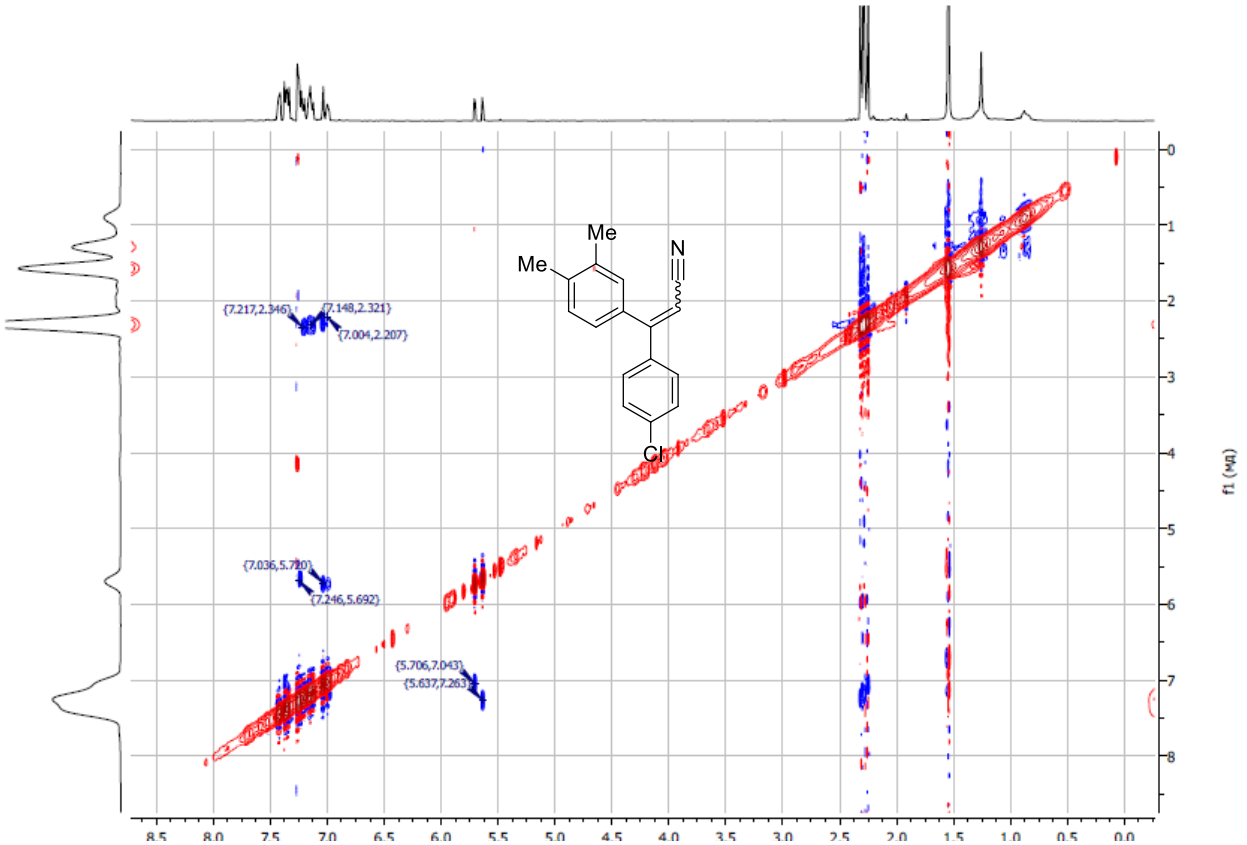


Figure S64. NOESY NMR spectrum of mixture of compounds *E*,*Z*-**2l** ($CDCl_3$, 400 MHz).

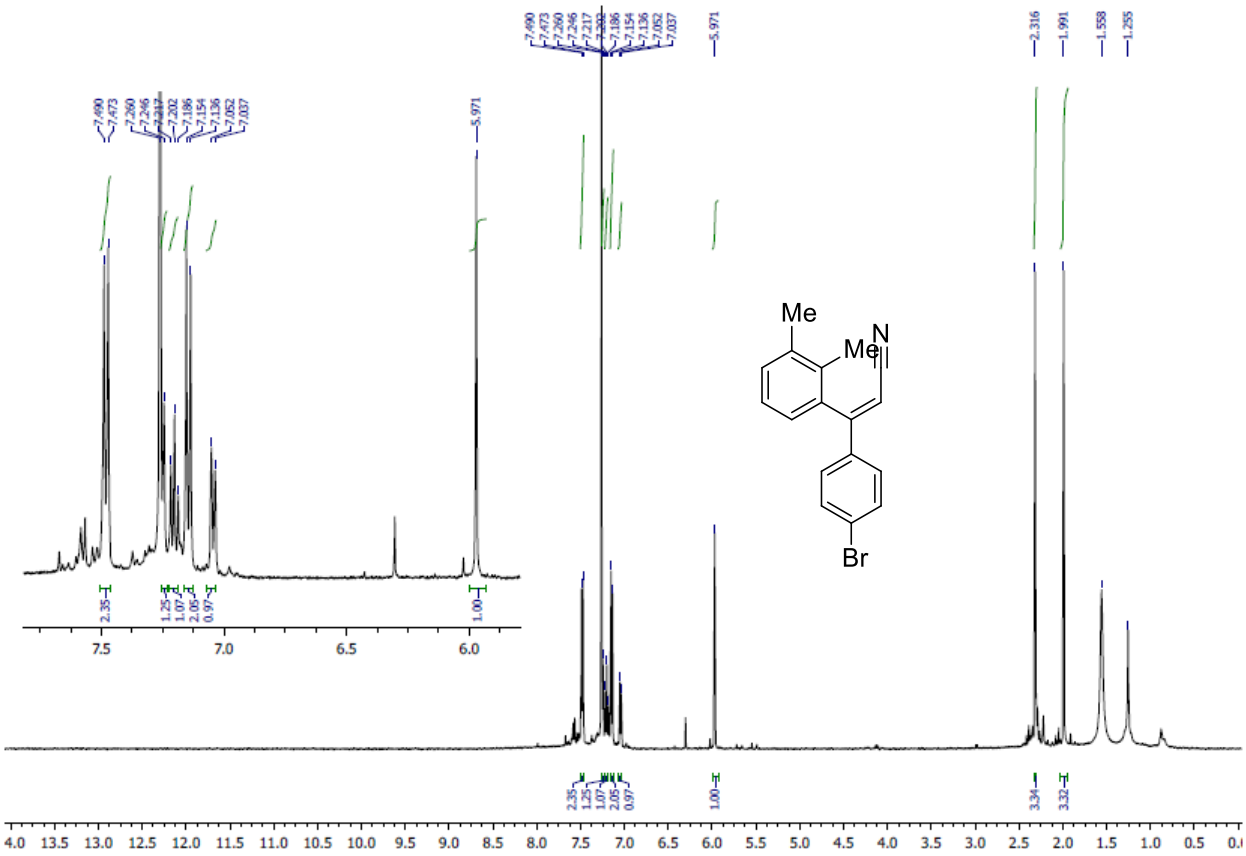


Figure S65. ^{1}H NMR spectrum of compound **2m** ($CDCl_3$, 400 MHz).

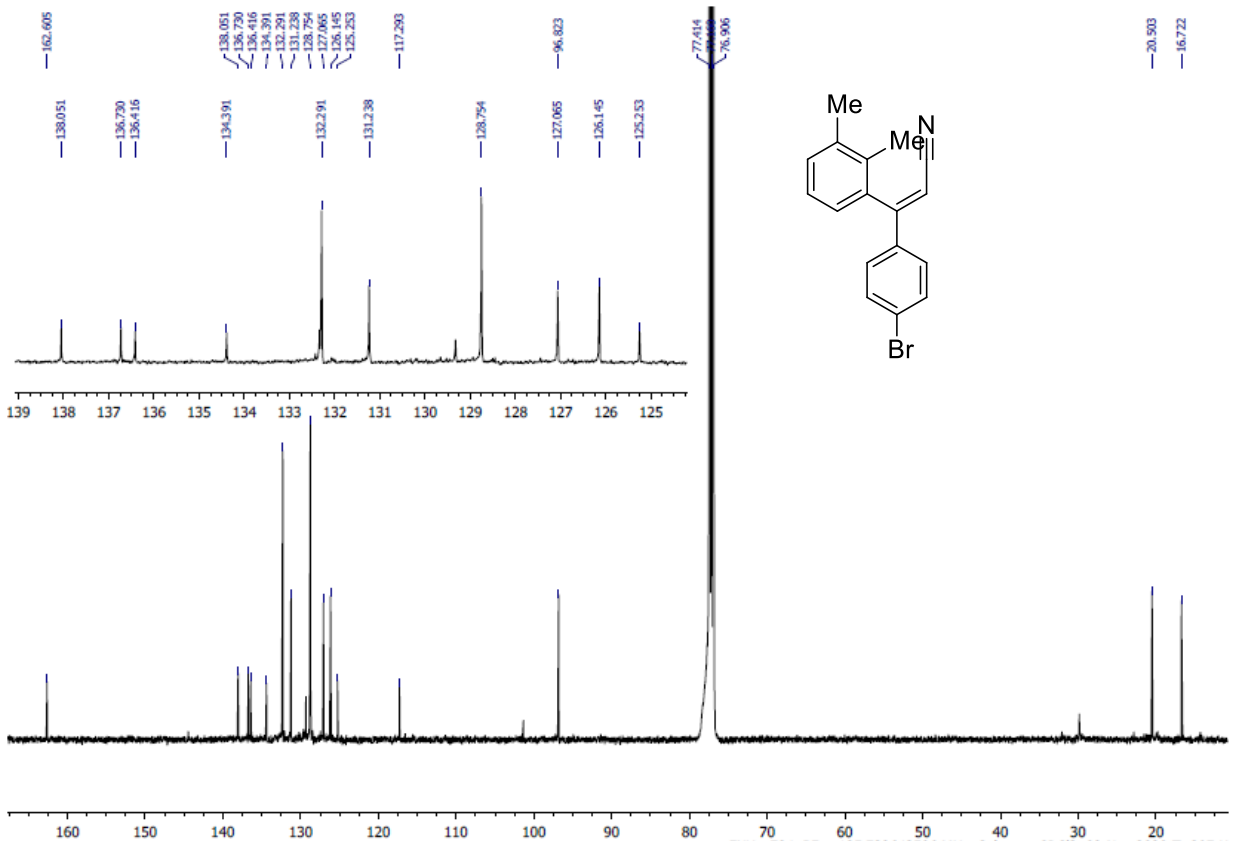


Figure S66. ^{13}C NMR spectrum of compound **2m** ($CDCl_3$, 100 MHz).

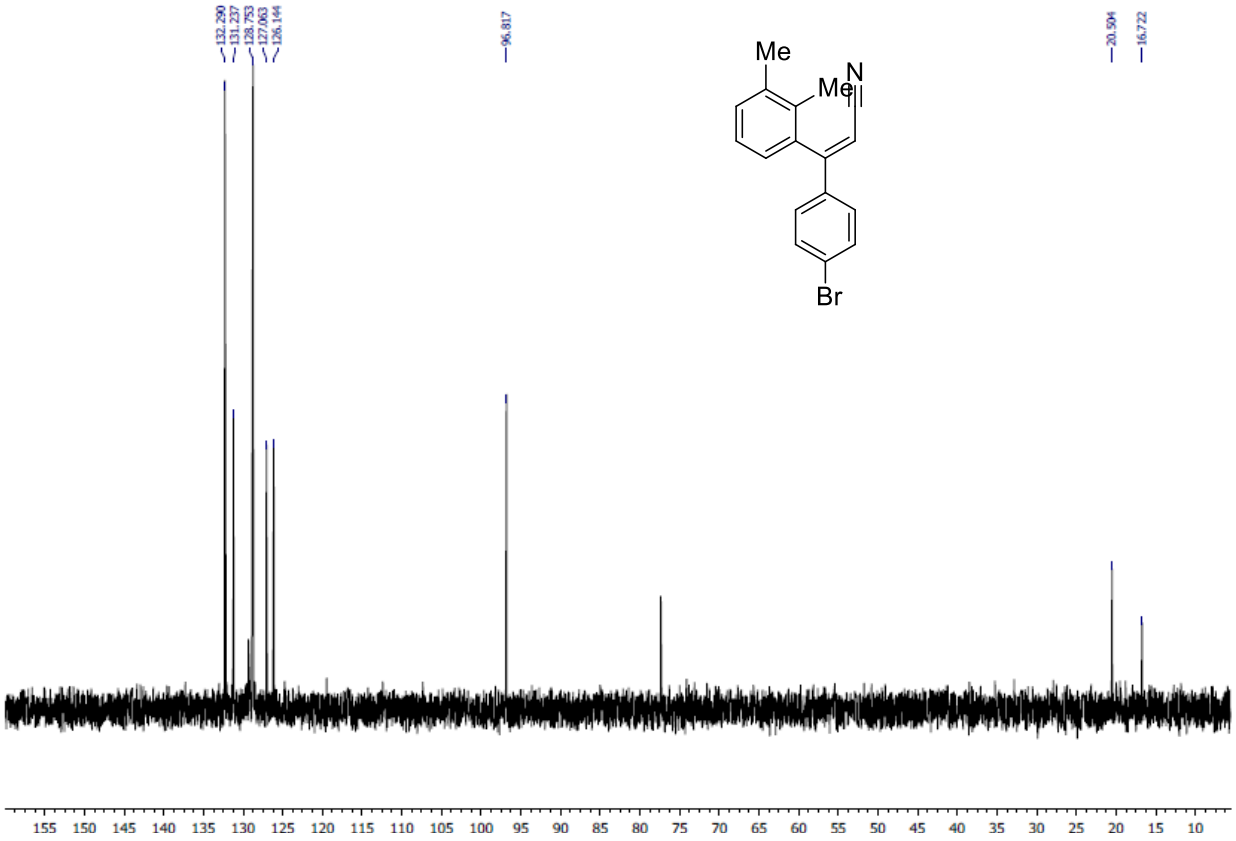


Figure S67. DEPT^{135} NMR spectrum of compound **2m** ($CDCl_3$, 400 MHz).

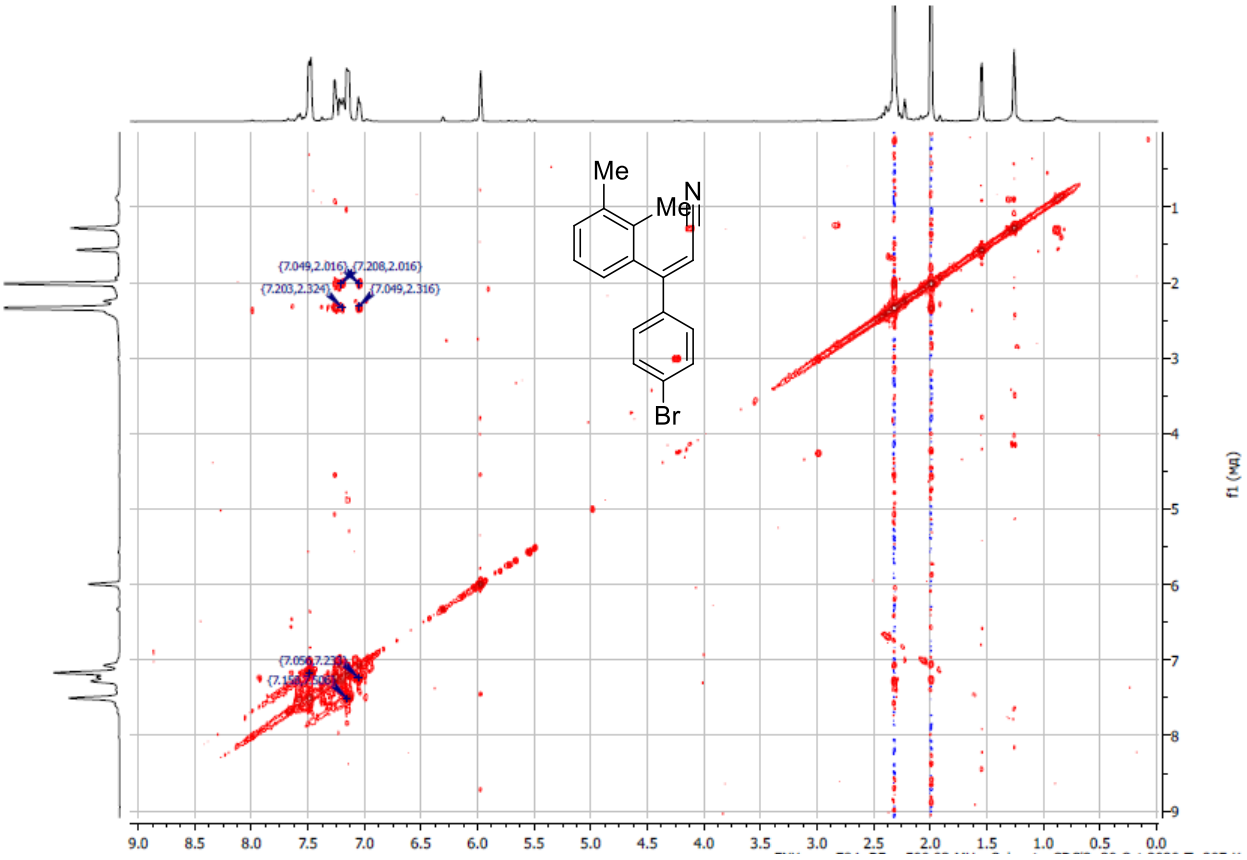


Figure S68. COSY NMR spectrum of compound **2m** ($CDCl_3$, 400 MHz).

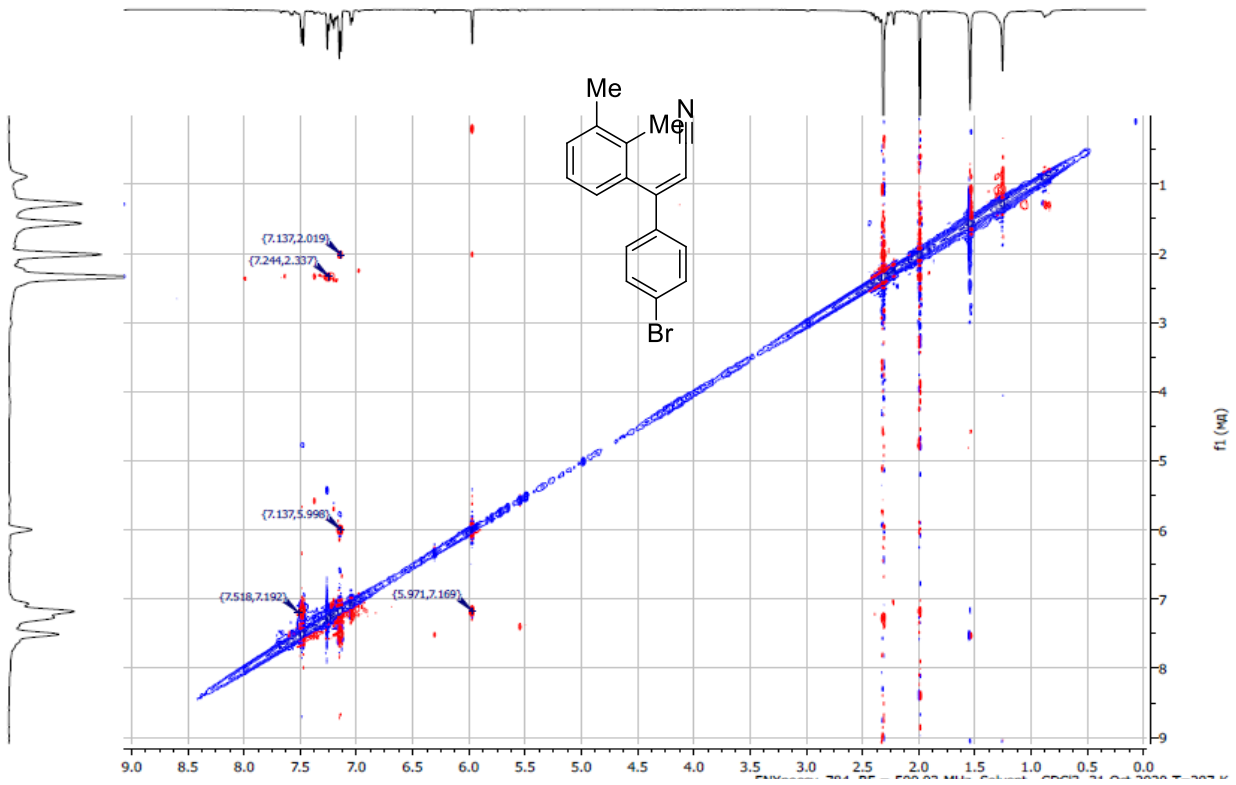


Figure S69. NOESY NMR spectrum of compound **2m** ($CDCl_3$, 400 MHz).

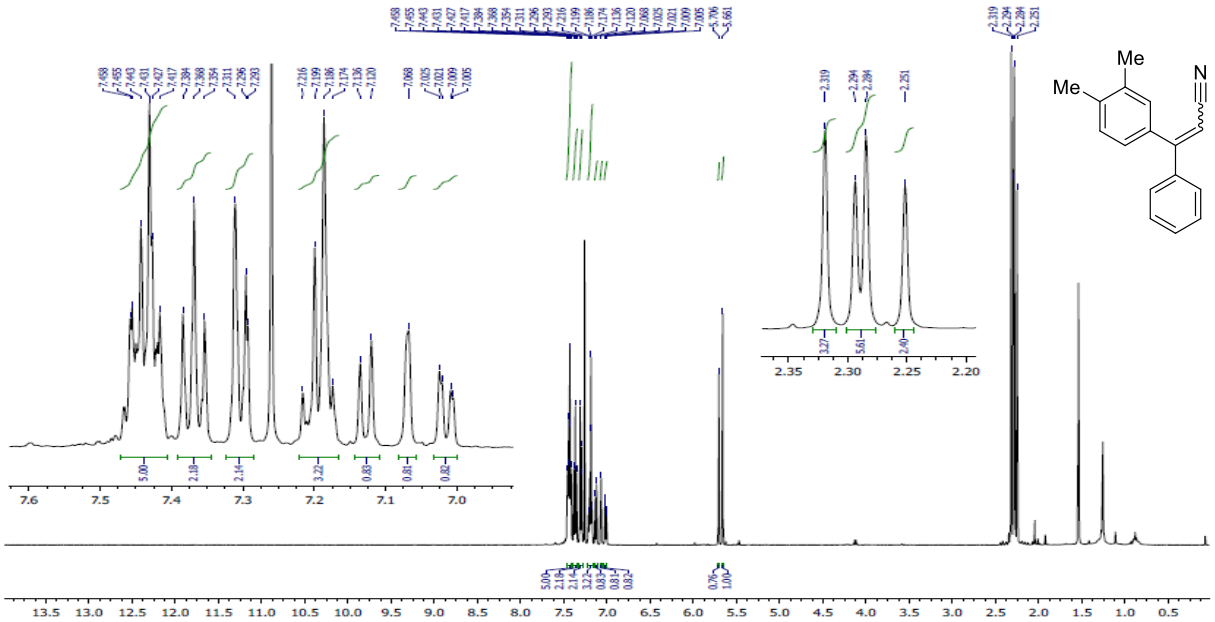


Figure S70. ^1H NMR spectrum of mixture of compounds *E*,*Z*-**2n** ($CDCl_3$, 400 MHz).

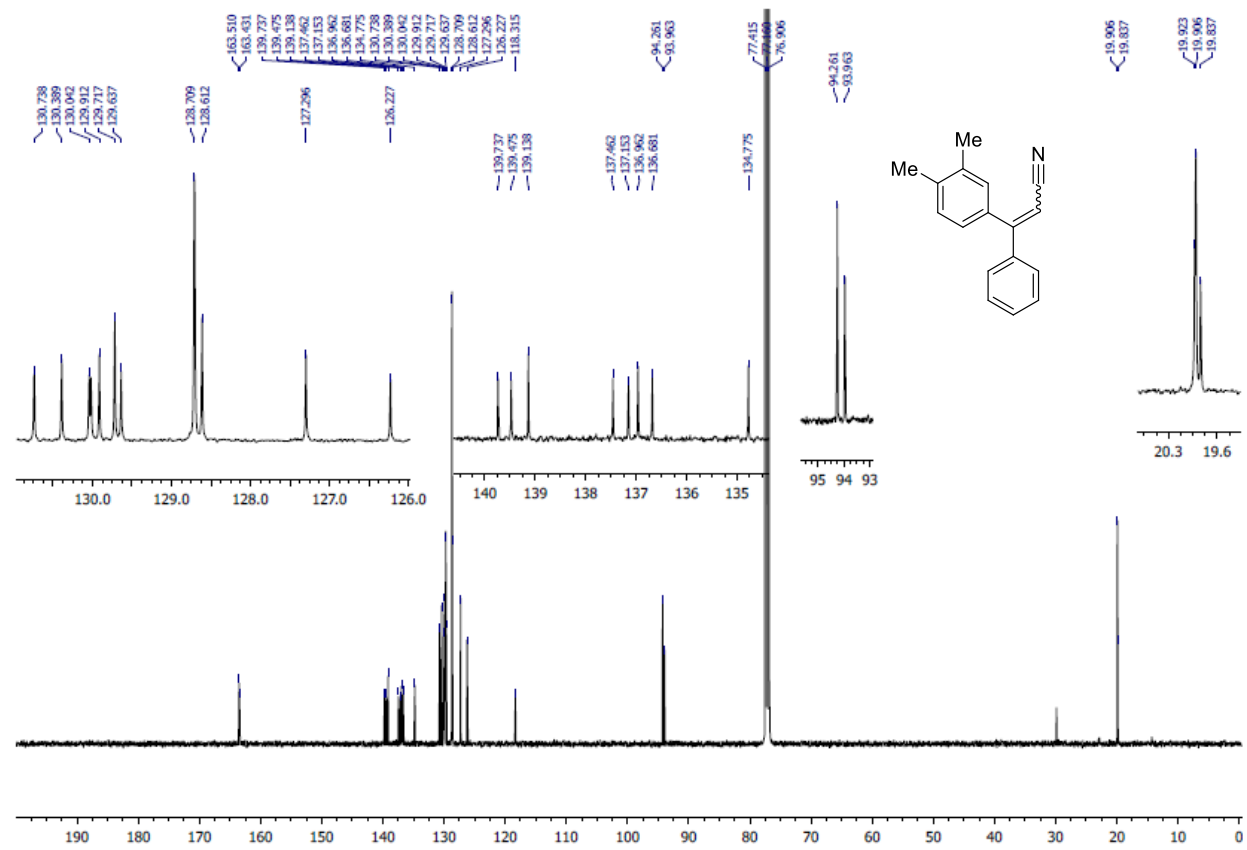


Figure S71. ^{13}C NMR spectrum of mixture of compounds *E*,*Z*-**2n** ($CDCl_3$, 100 MHz).

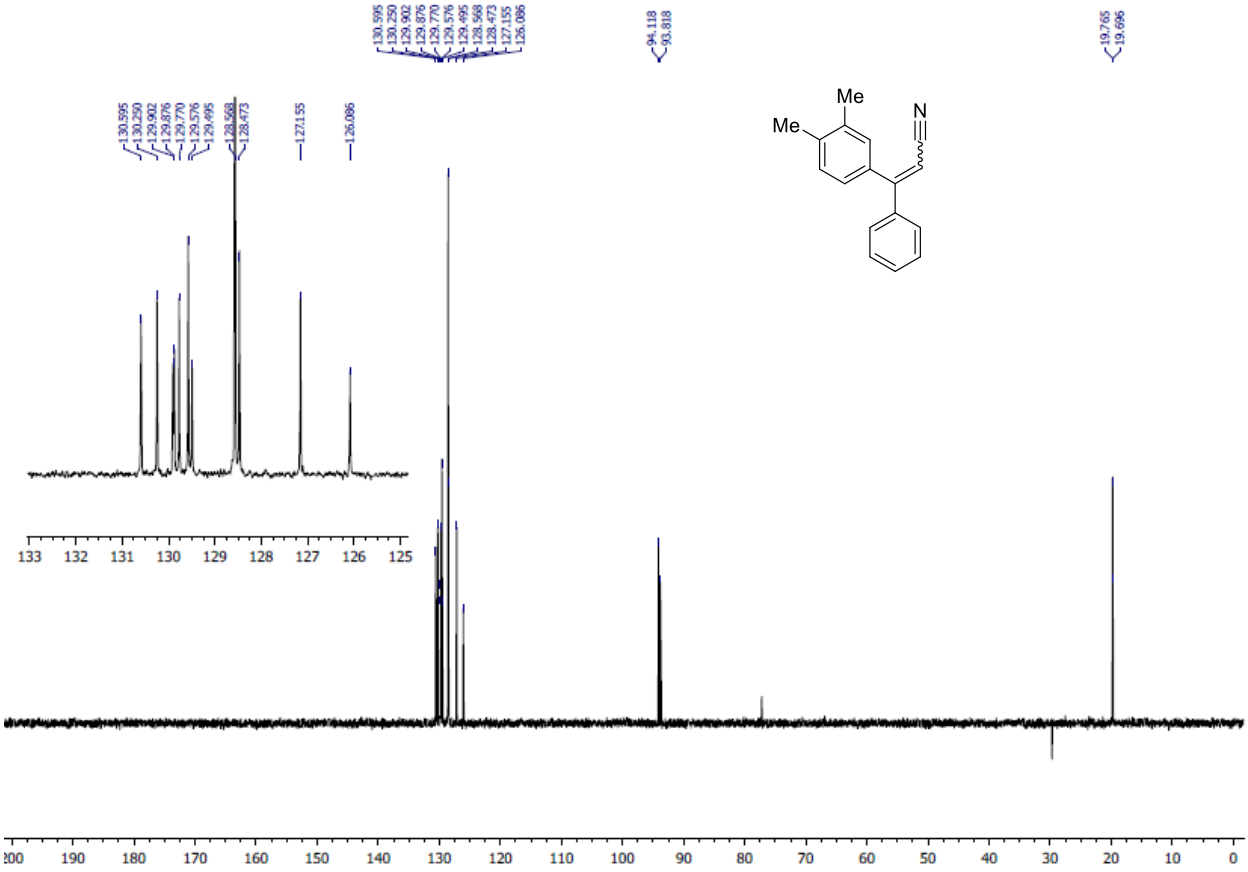


Figure S72. DEPT^{135} NMR spectrum of mixture of compounds *E*,*Z*-**2n** ($CDCl_3$, 400 MHz).

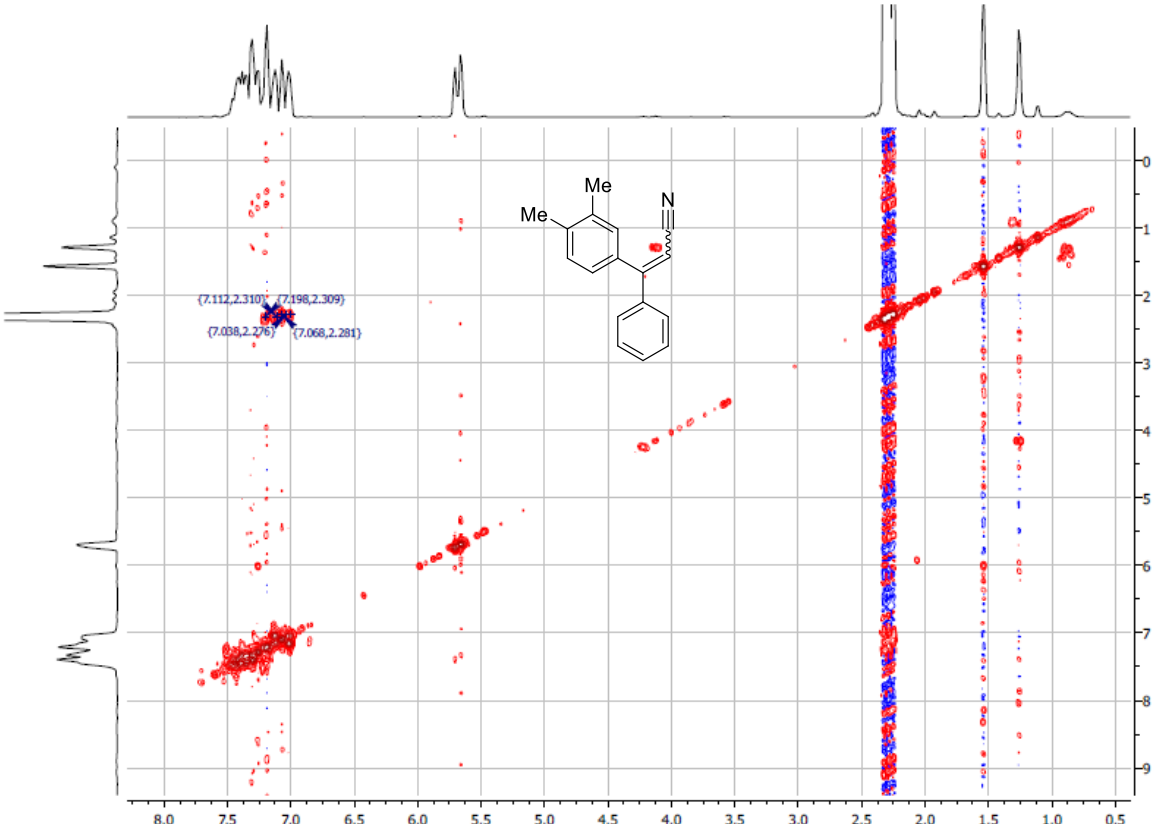


Figure S73. COSY NMR spectrum of mixture of compounds *E*,*Z*-**2n** ($CDCl_3$, 400 MHz).

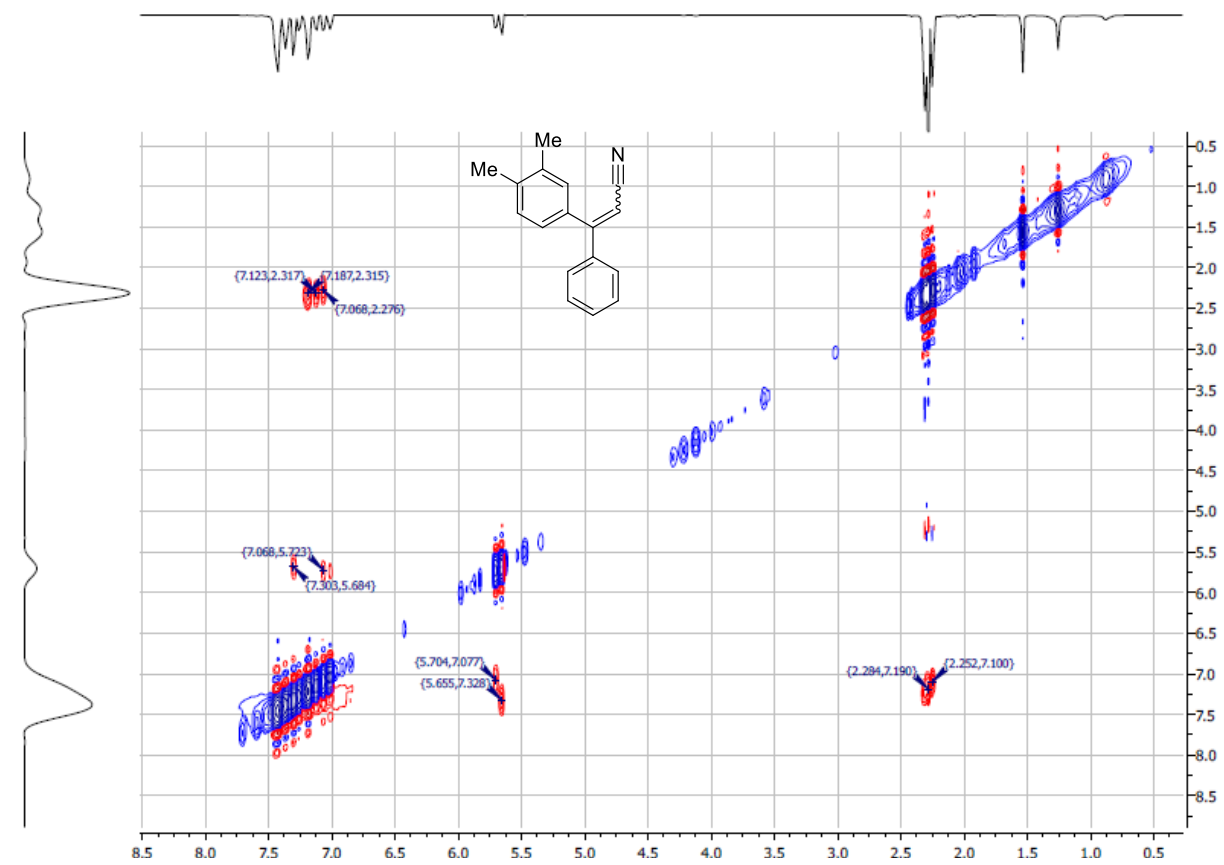


Figure S74. NOESY NMR spectrum of mixture of compounds *E*,*Z*-**2n** ($CDCl_3$, 400 MHz).

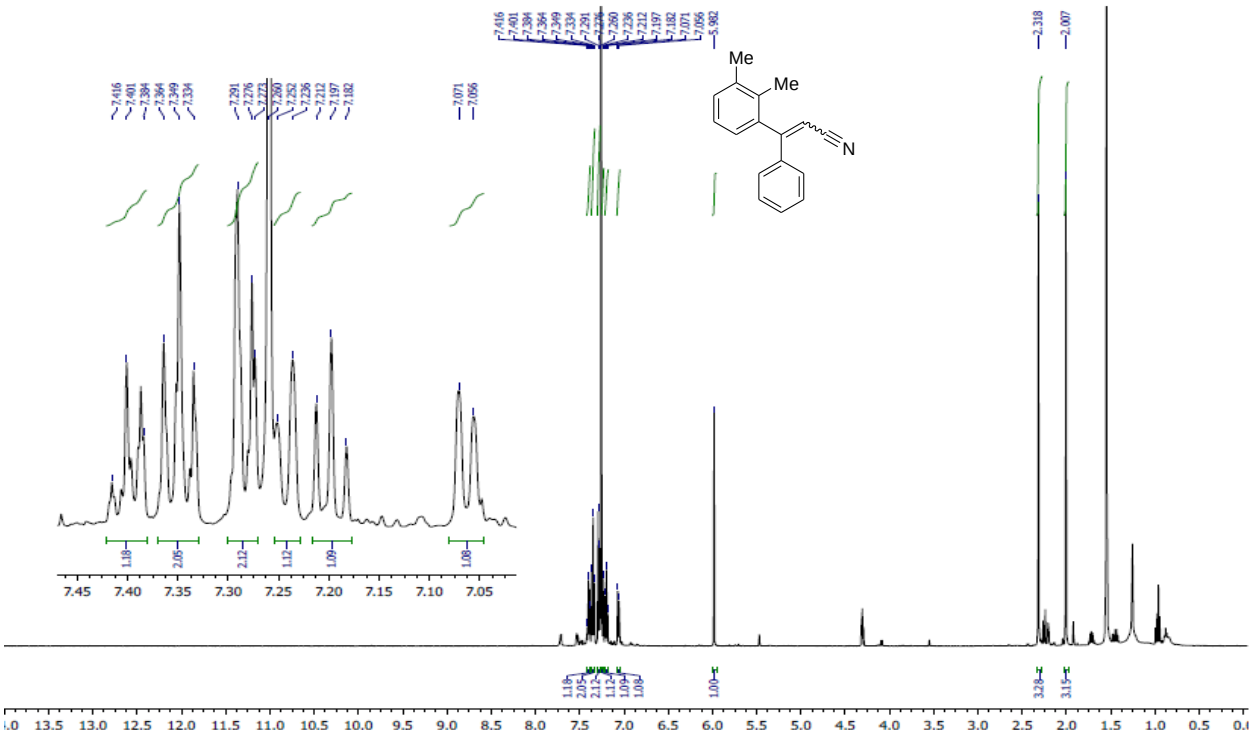


Figure S75. ^{1}H NMR spectrum of compound **2o** ($CDCl_3$, 400 MHz).

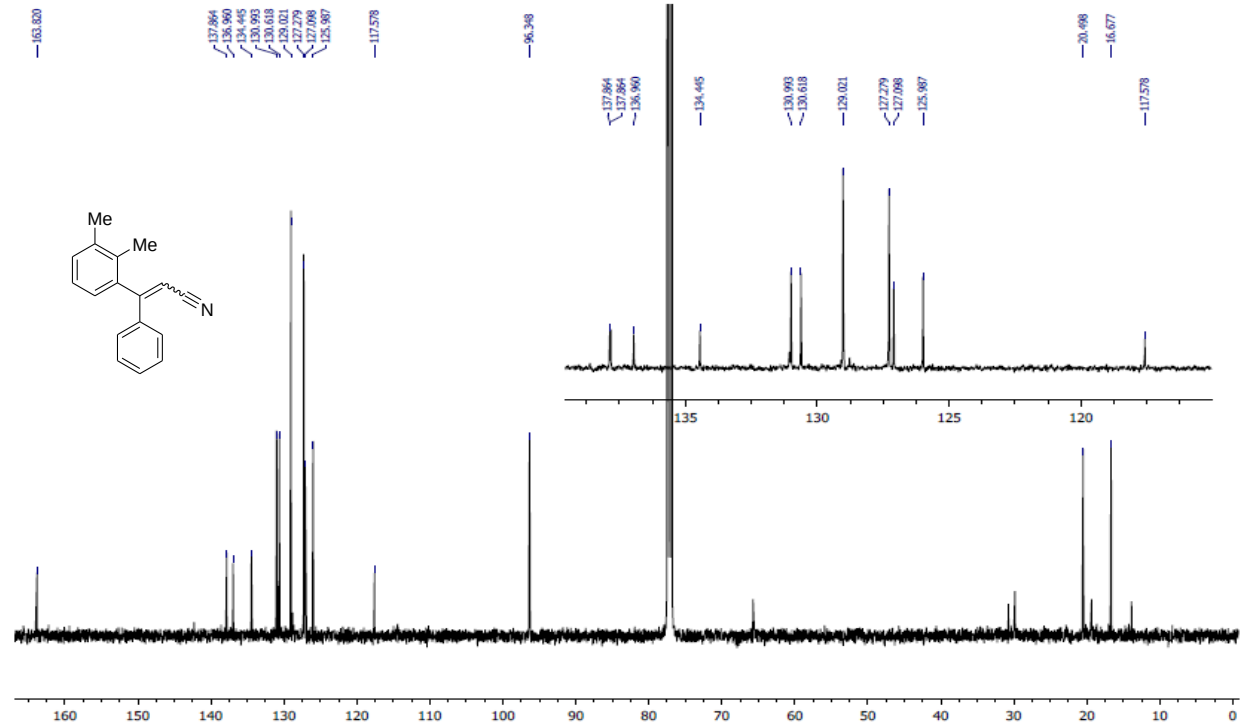


Figure S76. ^{13}C NMR spectrum of compound **2o** ($CDCl_3$, 100 MHz).

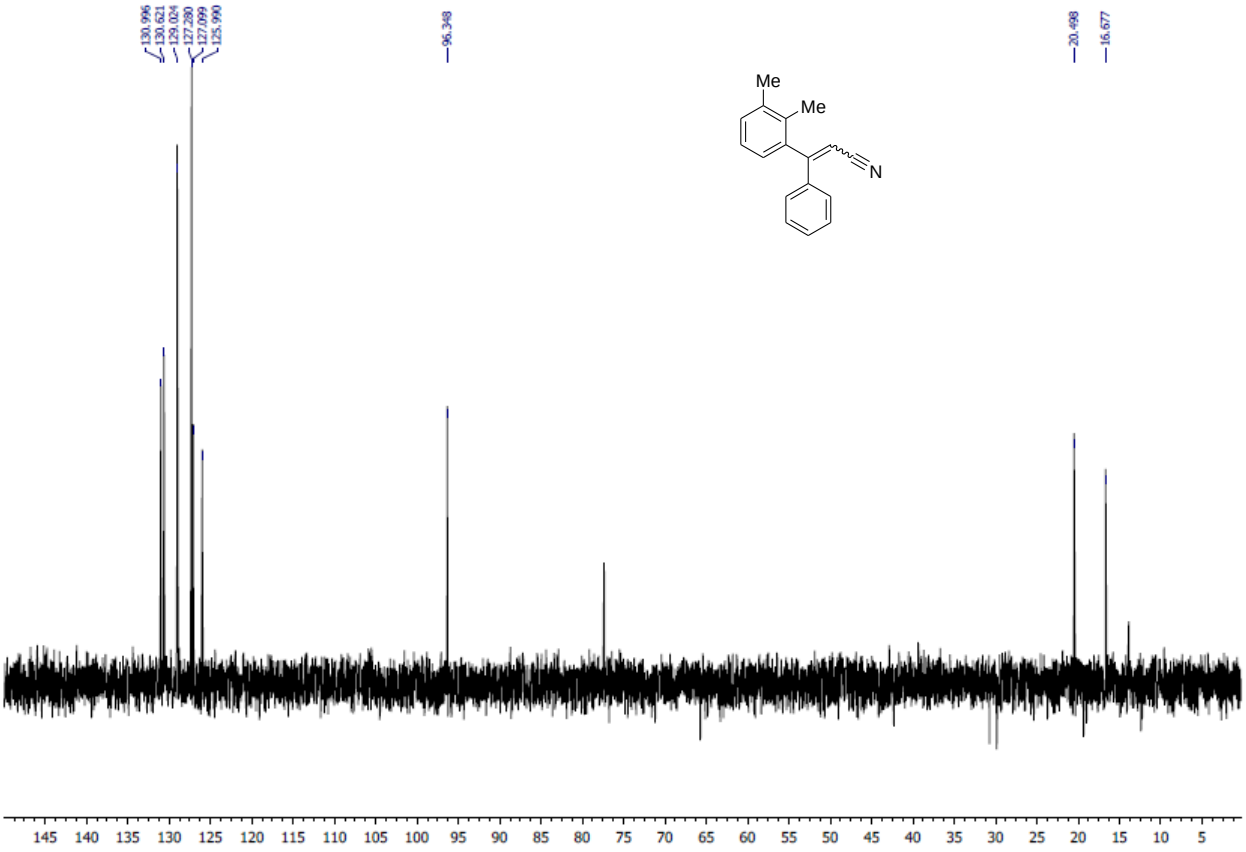


Figure S77. DEPT[135] NMR spectrum of compound **2o** ($CDCl_3$, 400 MHz).

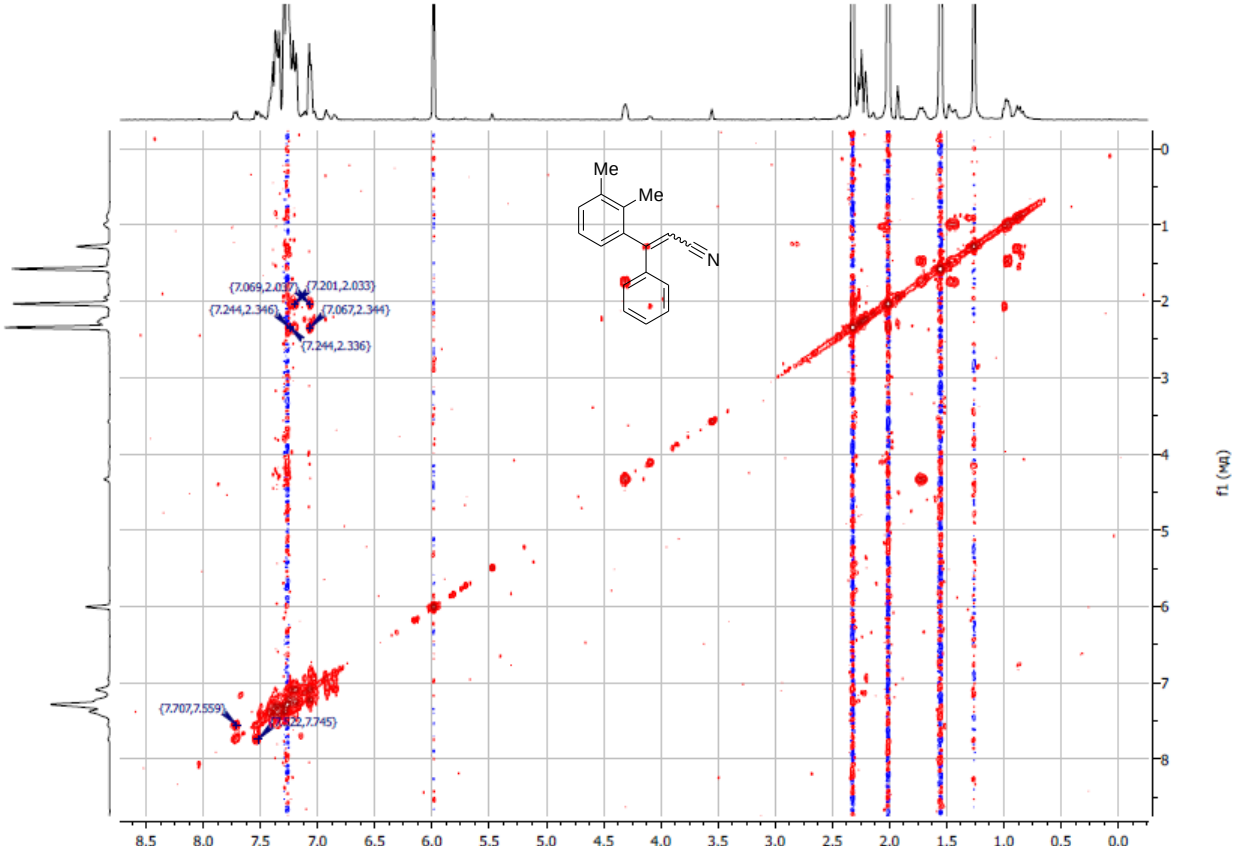


Figure S78. COSY NMR spectrum of compound **2o** ($CDCl_3$, 400 MHz).

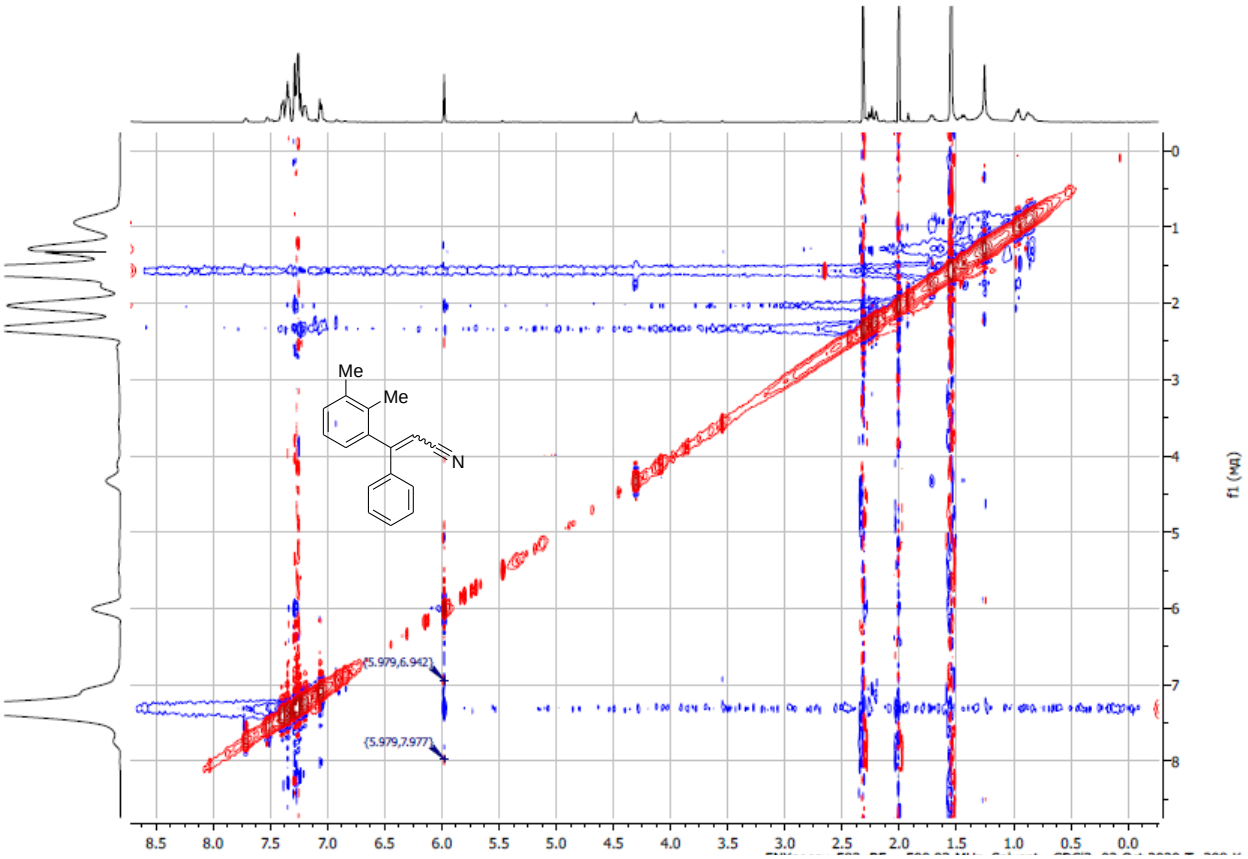


Figure S79. NOESY NMR spectrum of compound **2o** ($CDCl_3$, 400 MHz).

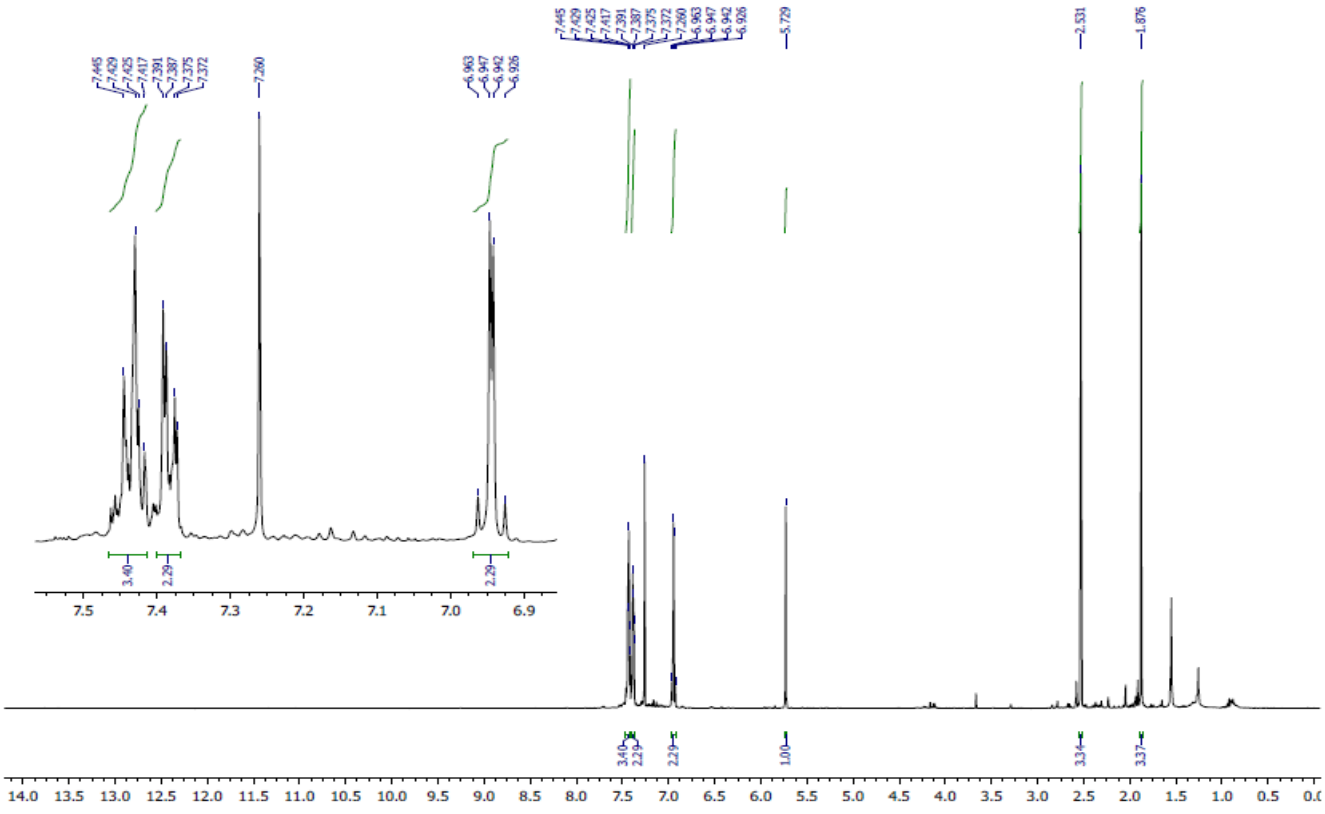


Figure S80. ^1H NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz).

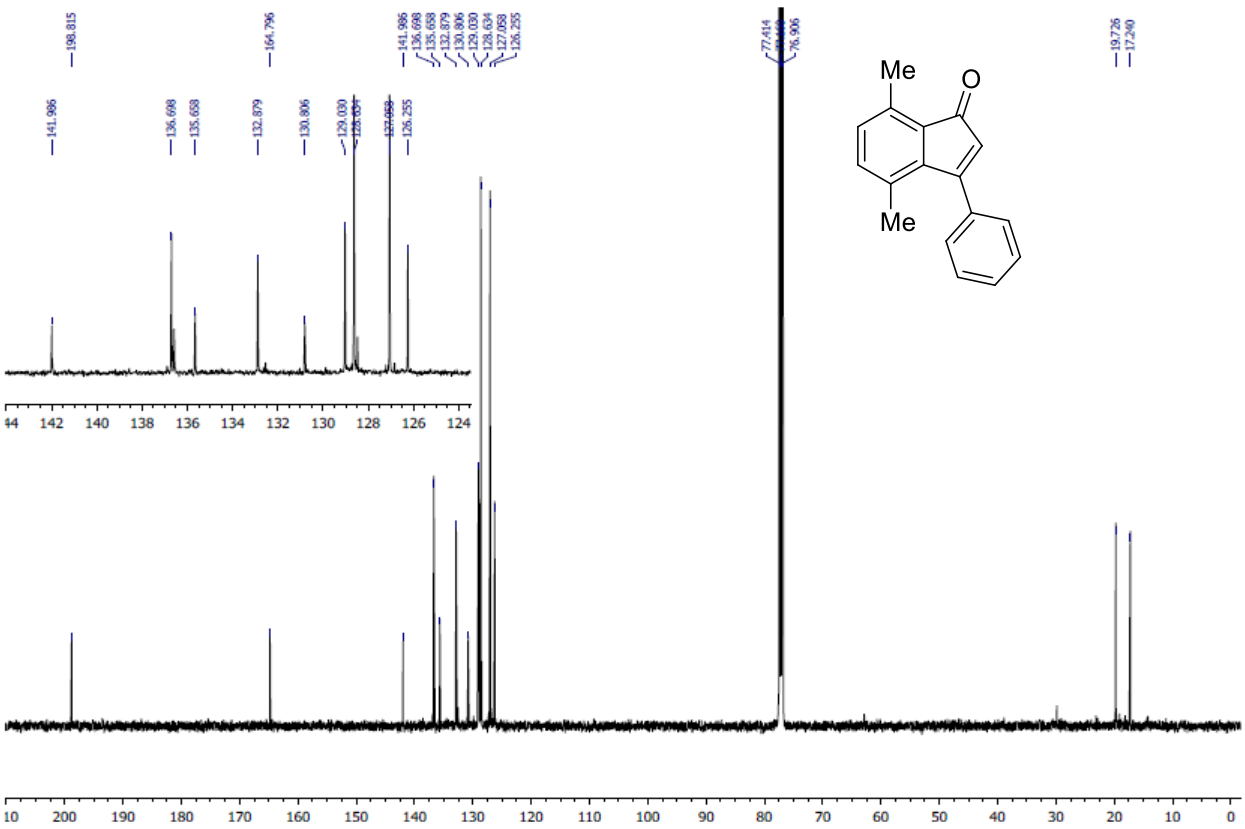


Figure S81. ^{13}C NMR spectrum of compound **3a** ($CDCl_3$, 100 MHz).

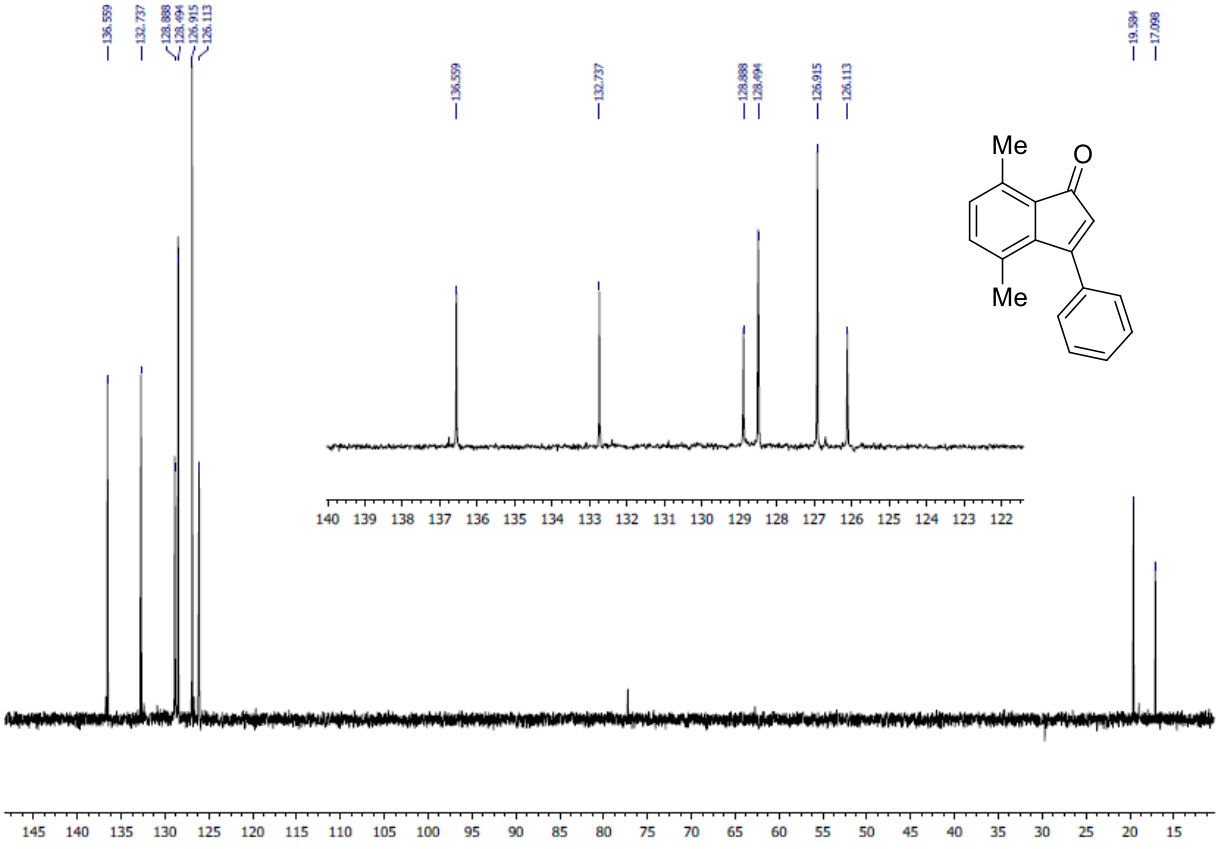


Figure S82. DEPT^{135} NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz).

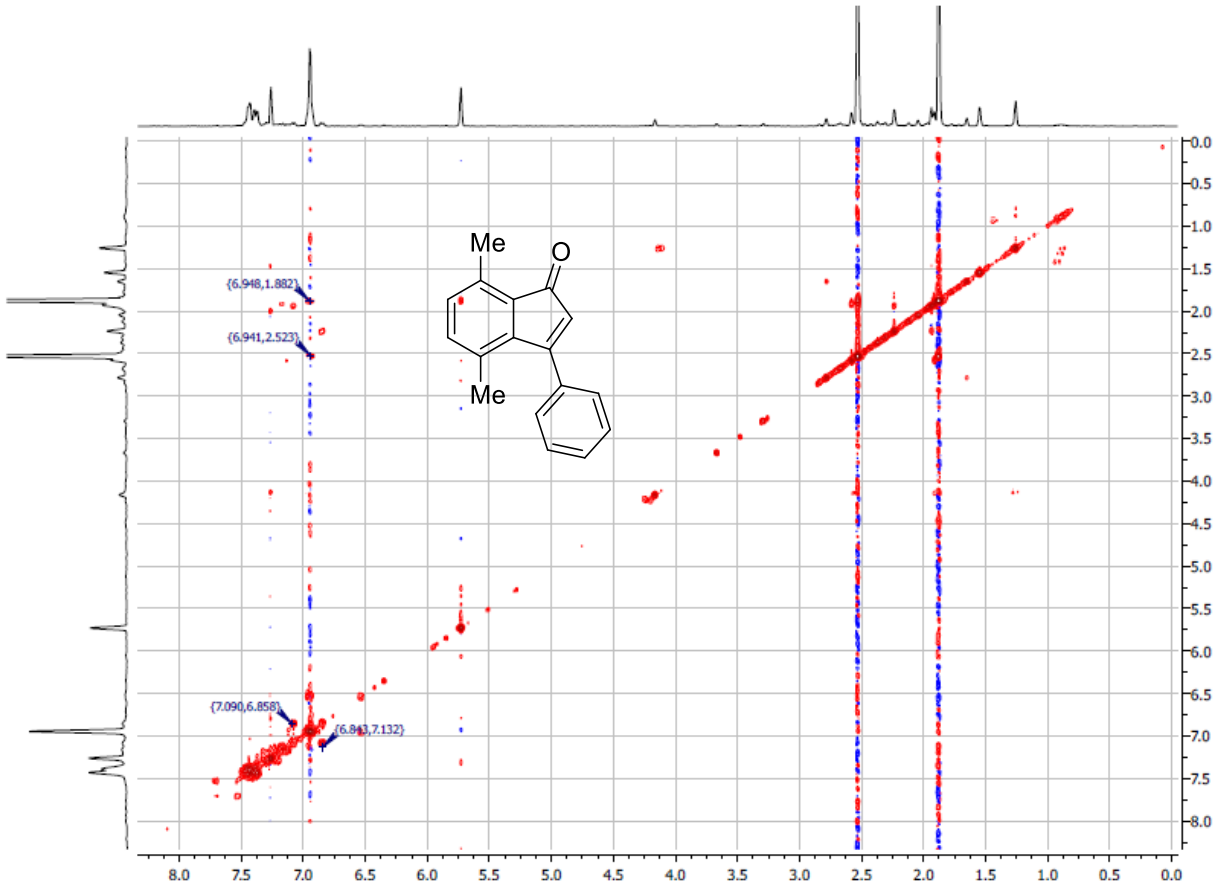


Figure S83. COSY NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz).

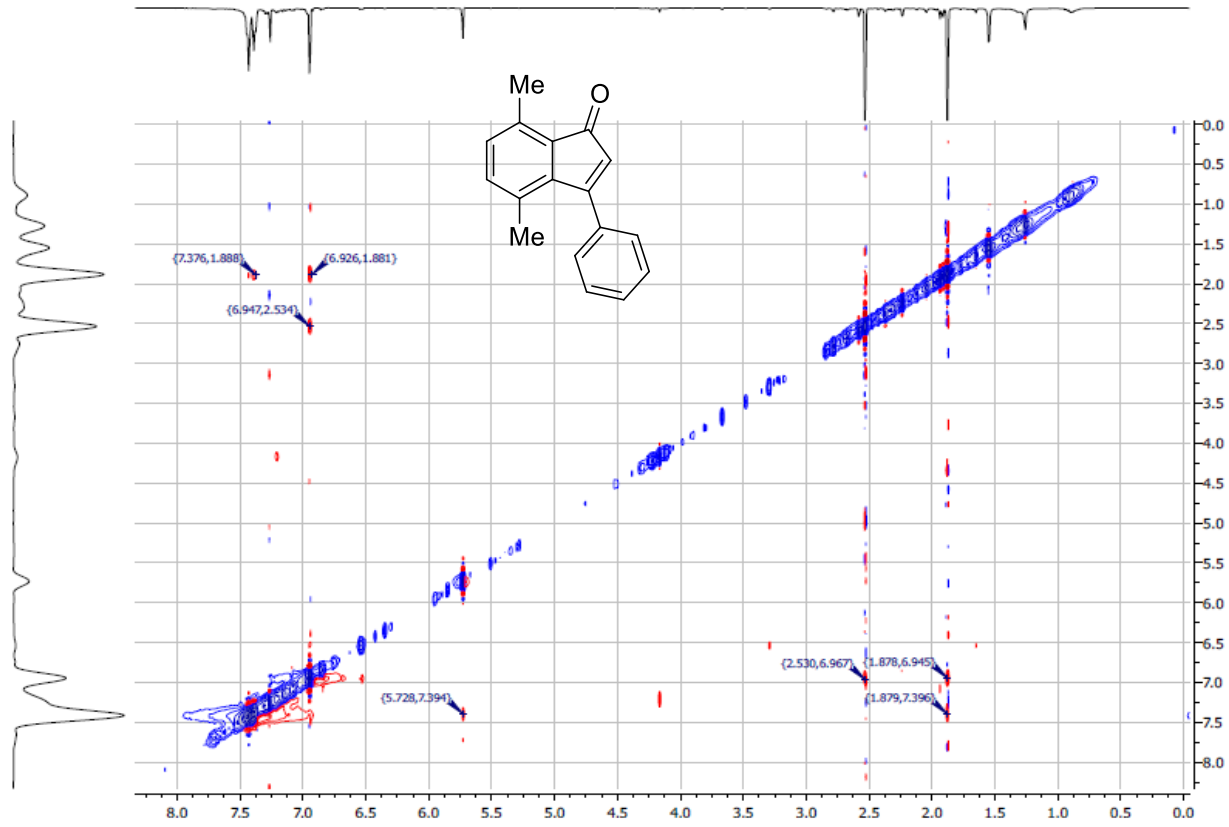


Figure S84. NOESY NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz).

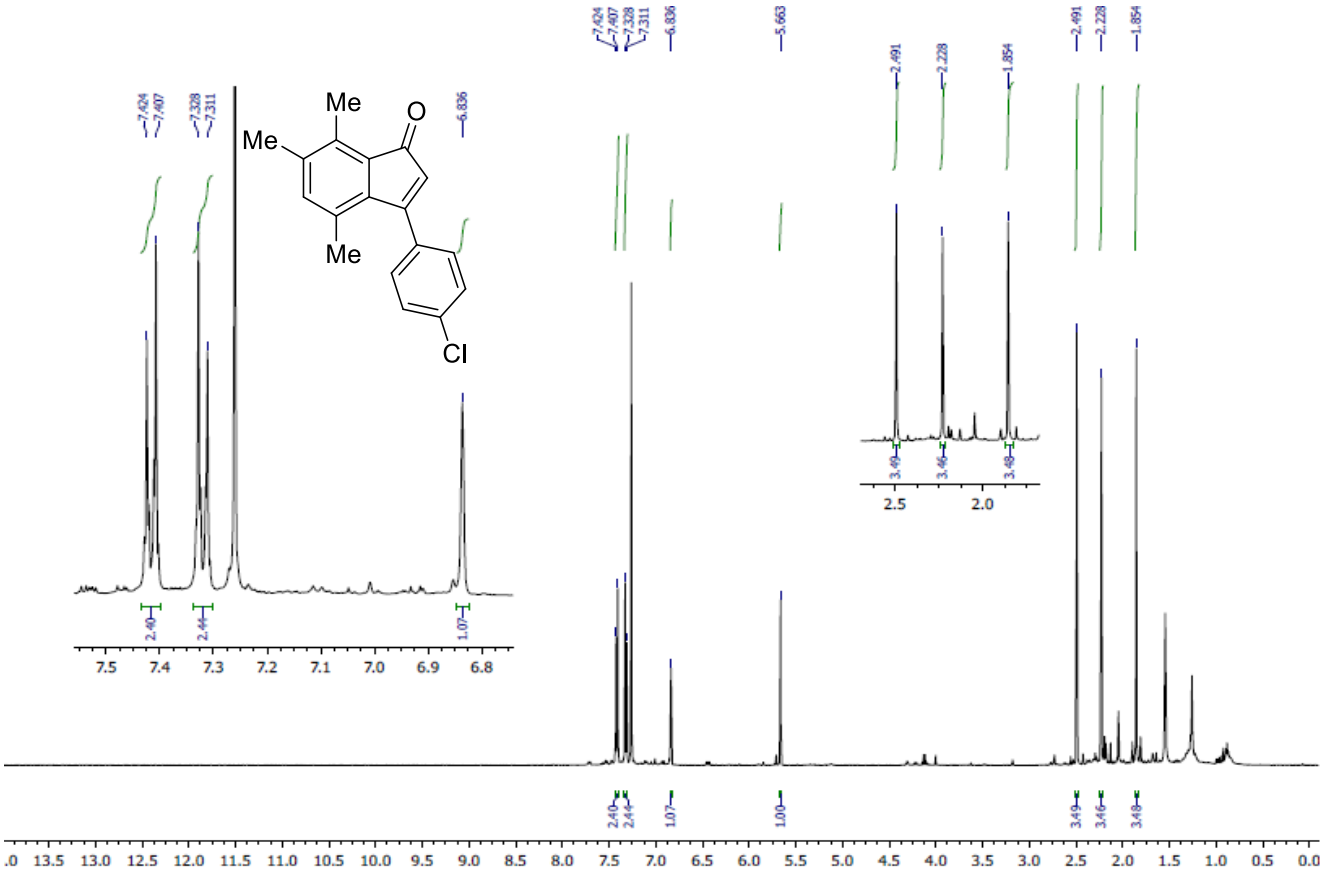


Figure S85. ^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz).

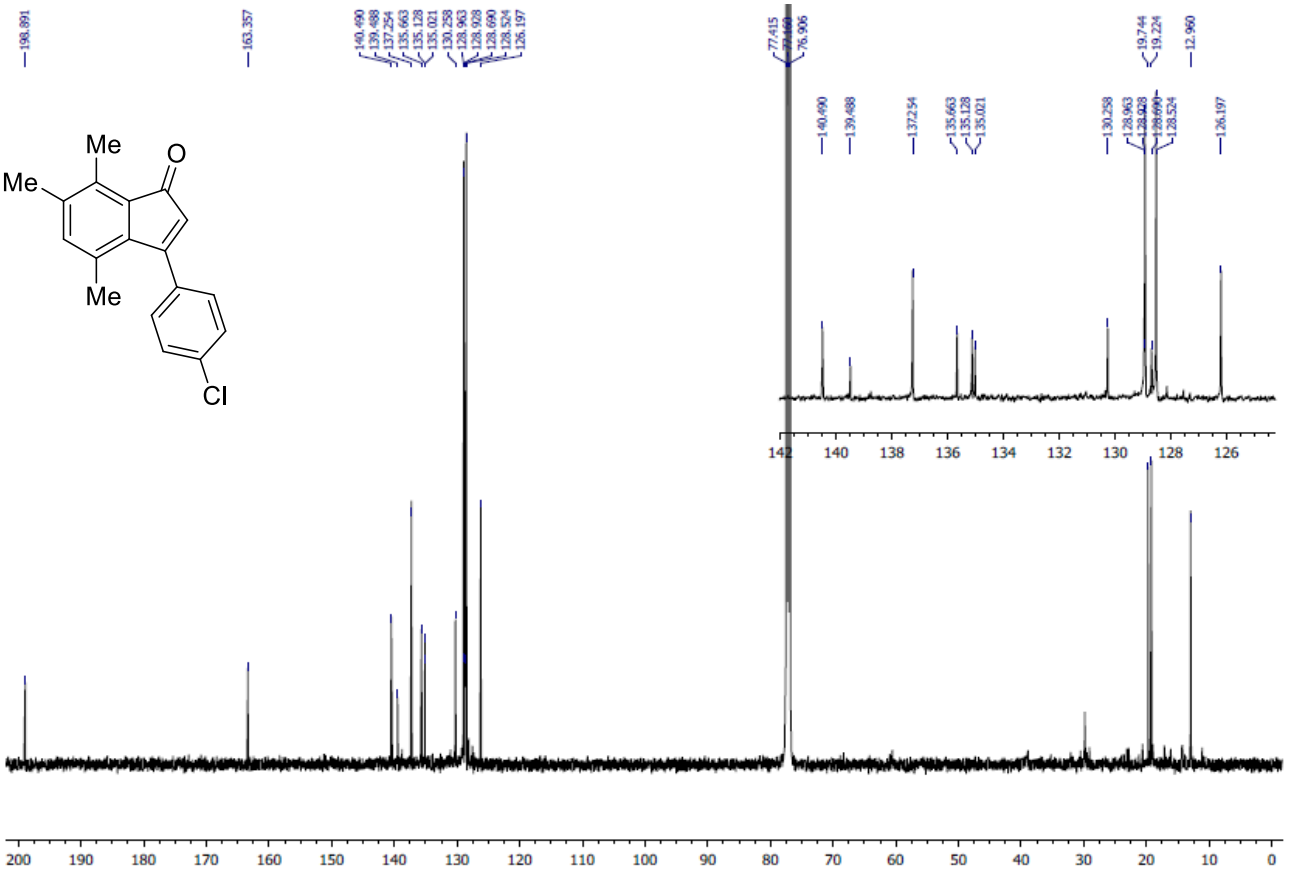


Figure S86. ^{13}C NMR spectrum of compound **3b** ($CDCl_3$, 100 MHz).

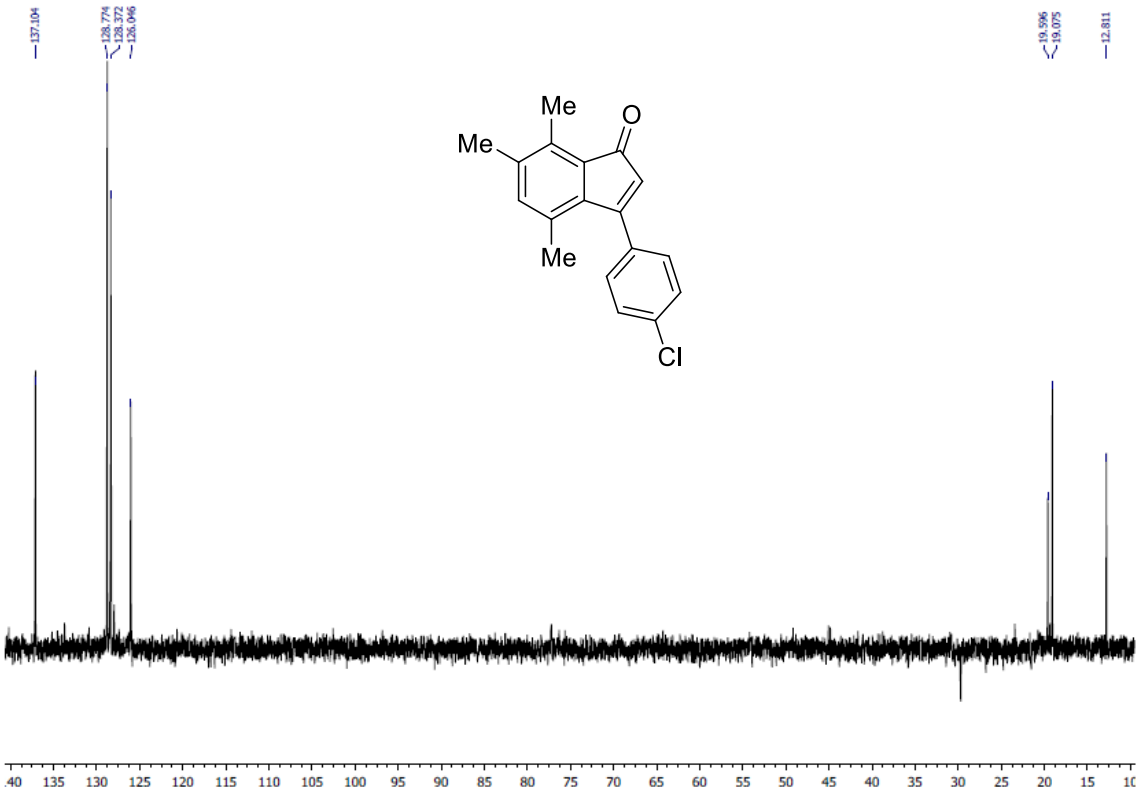


Figure S87. DEPT^{135} NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz).

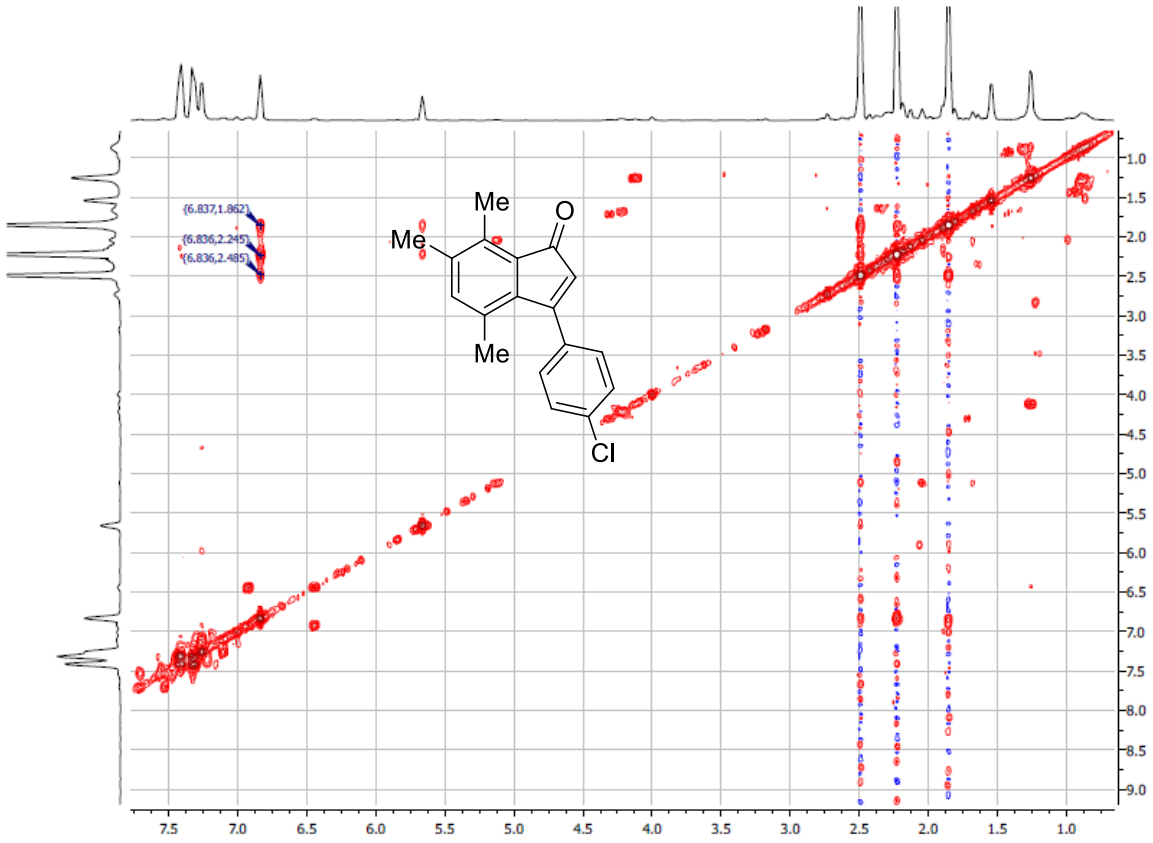


Figure S88. COSY NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz).

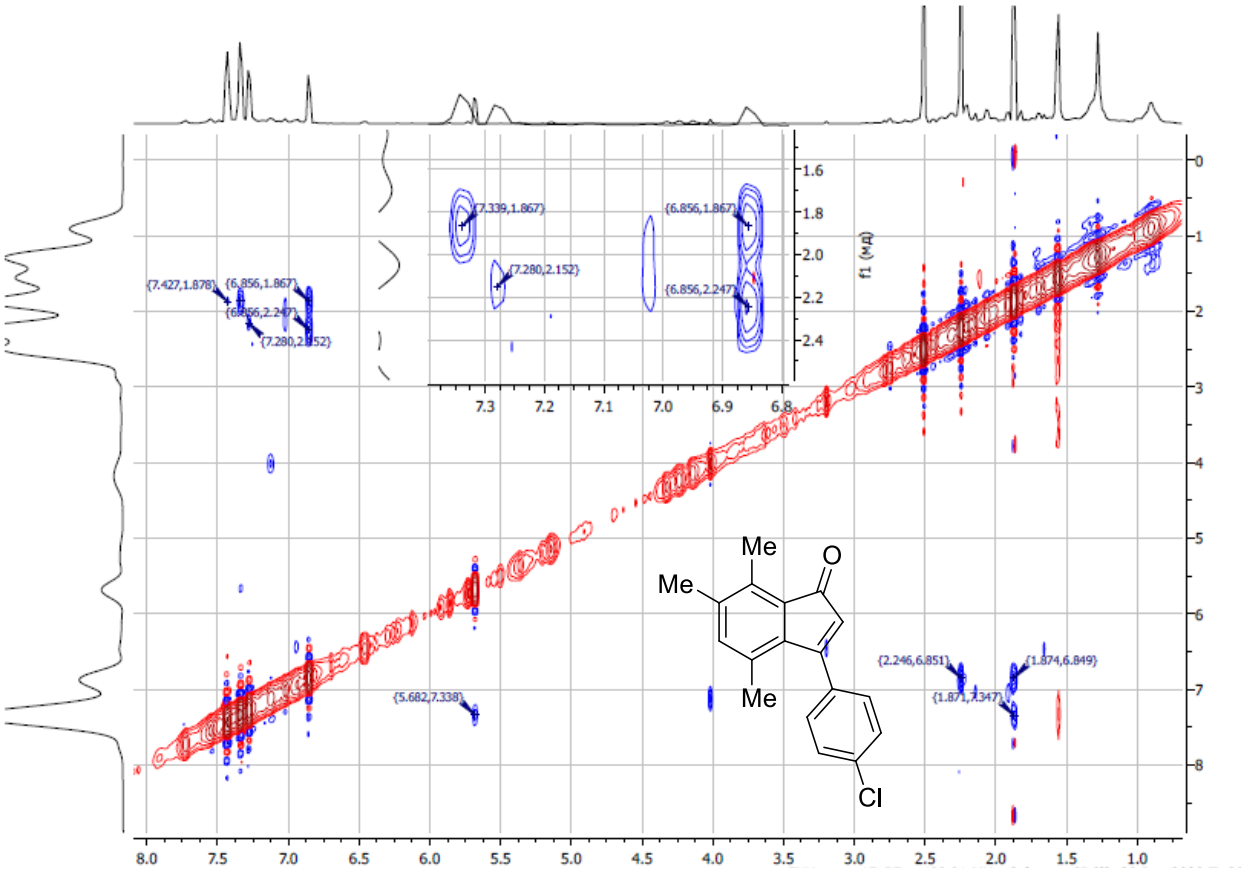


Figure S89. NOESY NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz).