Supporting Information

for

Stereoselective synthesis of triarylethylenes via a copper-palladium catalyzed decarboxylative cross-coupling. Synthesis of (Z)-tamoxifen

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I/ General

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware.

1-Methyl-2-pyrrolidone (NMP) and 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone (DMPU) were dried by distillation over calcium hydride.

Potassium and caesium carboxylates were dried under vacuum at room temperature for 6 h.

All other starting materials were purchased from commercial sources and used without any further purification.

Yields refer to isolated yields of compounds estimated to be ≥ 97% pure as determined by ^{1}H-NMR, ^{13}C-NMR and GC analysis. All compounds give satisfactory HRMS analyses.

^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance III 400 spectrometer with chemical shifts reported relative to residual solvent peaks ($CDCl_3$: 7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C). The peak patterns are indicated as follows: s = singlet; d = doublet; t = triplet; m = multiplet; q = quartet. The coupling constants, *J*, are reported in Hertz (Hz).

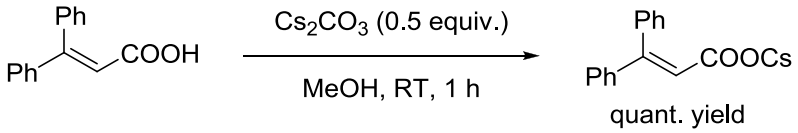
GC analyses were recorded on a Hewlett-Packard HP 6890 chromatograph equipped with a capillary column HP-5MS (50m x 0.25mm x 0.25µm).

Mass Spectra (MS) were recorded on a Hewlett-Packard HP 5973 (electronic impact).

The analytical data for the known compounds were found to match with the literature data.

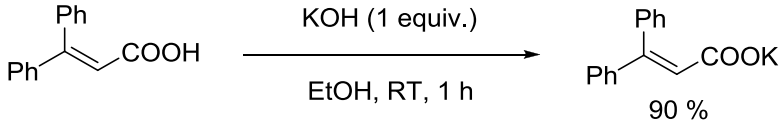
II/ Typical Procedures

a) Typical procedure for the preparation of caesium carboxylates: synthesis of caesium 3,3-diphenyl acrylate.



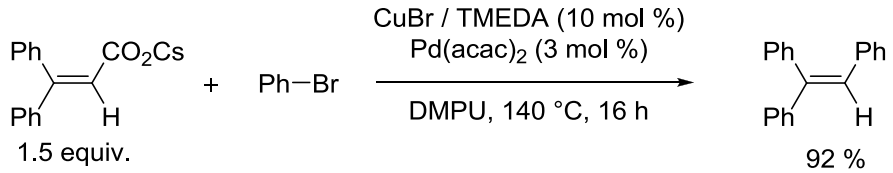
An oven-dried and nitrogen flushed 500 mL four-necked flask equipped with a mechanical stirrer was charged with 3,3-diphenylacrylic acid (22.43 g, 100 mmol, 1 equiv.) and methanol (100 mL). After stirring for 5 min, Cs_2CO_3 (16.3 g, 50 mmol, 0.5 equiv) was added to the solution in about 1 h. The reaction mixture was then stirred for 1 h at room temperature. Methanol was removed *in vacuo* and the resulting solid was dried under vacuum (0.1 Torr) for 6 h to provide caesium 3,3-diphenylacrylate in quantitative yield (35.5 g).

b) Typical procedure for the preparation of potassium carboxylates: synthesis of potassium 3,3-diphenyl acrylate.



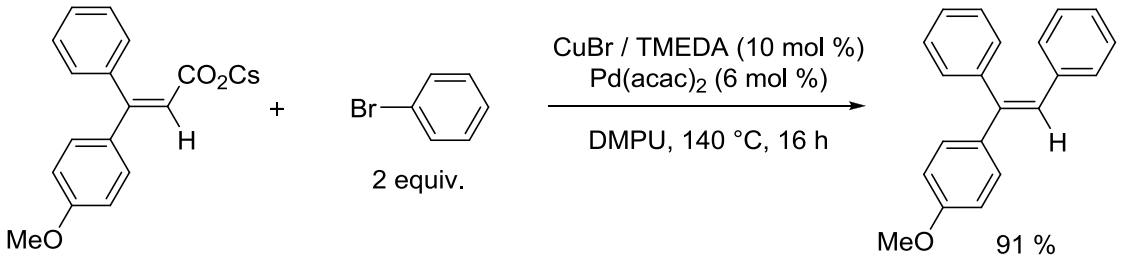
An oven dried and nitrogen flushed 500 mL four-necked round-bottomed flask equipped with a mechanical stirrer was charged with 3,3-diphenylacrylic acid (22.43 g, 100 mmol, 1 equiv.) and ethanol (100 mL). Then, a solution of potassium hydroxide (100.00 mmol, 1 equiv.) in ethanol (100 mL) was added dropwise in 1 h. After completion of the addition, the reaction mixture was stirred for 1 h at room temperature. The white precipitate which is formed was collected by filtration through a 7-cm Büchner funnel. If no precipitation occurred, ethanol was removed *in vacuo* (4 Torr) until obtaining a white solid. In both cases, the resulting solid was washed sequentially with cold (0 °C) ethanol (2 x 30 mL) and cold (0 °C) diethyl ether (2 x 30 mL), then dried *in vacuo* (0.1 Torr) to provide potassium 3,3-diphenyl acrylate (23.6 g, 90 %).

c) Typical procedure for the cross coupling of 3,3-diphenylacrylate with aryl bromides: synthesis of 1,1,2-triphenylethylene.



An oven-dried, nitrogen flushed 25 mL two-necked round-bottomed flask equipped with a magnetic stirrer and a condenser was charged with caesium 3,3-diphenylacrylate (1.07 mg, 3.00 mmol, 1.5 equiv.), bromobenzene (314 mg, 2.00 mmol, 1 equiv.), copper(I) bromide (28.5 mg, 0.20 mmol, 0.1 equiv.), palladium(II) acetylacetonate (18 mg, 0.06 mmol, 0.03 equiv.), TMEDA (23.3 mg, 0.20 mmol, 0.1 equiv.), and DMPU (3 mL). The resulting mixture was stirred at 140 °C for 16 h. The reaction mixture was then cooled to room temperature, quenched with aqueous HCl (1N, 20 mL) and filtered through celite. The aqueous phase was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with water (2 x 50 mL) and brine, dried over Na_2SO_4, filtered, and solvents were removed *in vacuo*. The residue was purified by flash chromatography on silicagel (eluent: diethyl ether/petroleum ether = 99:1) yielding 1,1,2-triphenylethylene as a white solid (471 mg, 92 %).

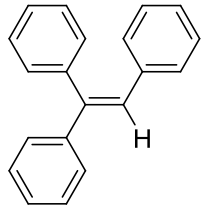
d) Typical procedure for the stereoselective cross coupling of 3,3-diarylacrylates with aryl bromides: example of the synthesis of 1-(4-methoxyphenyl)-1,2-diphenylethylene.



An oven-dried and nitrogen flushed 25 mL two-necked round-bottomed flask equipped with a magnetic stirrer and a condenser was charged with caesium 3-(4-methoxyphenyl),3-phenylacrylate (356 mg, 1.00 mmol, 1 equiv.), bromobenzene (314 mg, 2.00 mmol, 2 equiv.), copper(I) bromide (14.5 mg, 0.10 mmol, 0.1 equiv.), palladium(II) acetylacetonate (18 mg, 0.06 mmol, 0.06 equiv.), TMEDA (12 mg, 0.10 mmol, 0.1 equiv.), and DMPU (2 mL). The resulting mixture was stirred at 140 °C for 16 h. The reaction mixture was then cooled to room temperature, quenched with aqueous HCl (1N, 20 mL) and filtered through celite. The aqueous phase was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with water (2 x 50 mL) and brine, dried over Na_2SO_4, filtered, and solvents were removed *in vacuo*. The residue was purified by flash chromatography on silicagel (eluent: diethyl ether/petroleum ether = 97:3) yielding 1-(4-methoxyphenyl)-1,2-diphenylethylene as a white solid (260 mg, 91 %).

III/ Analytical data

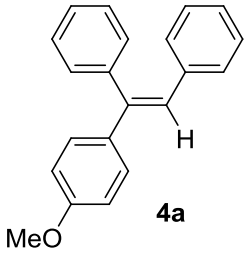
1,1,2-triphenylethylene[1]



2

1,1,2-triphenylethylene was prepared from caesium 3,3-diphenylacrylate (1.07 g, 3.00 mmol) and bromobenzene (314 mg, 2 mmol). It was isolated as a white solid (471 mg, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.26 (m, 8H), 7.21 – 7.19 (m, 2H), 7.12 – 7.09 (m, 3H), 7.02 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.96 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.58, 142.74, 140.51, 137.53, 130.53, 129.69, 128.77, 128.34, 128.31, 128.10, 127.75, 127.64, 127.54, 126.88 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 256.1252, found: *m/z* = 256.1260.

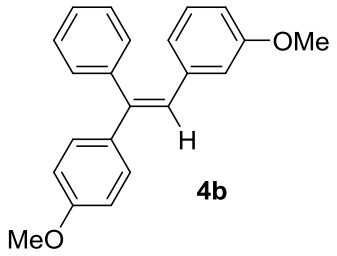
(*E*)-1-(4-methoxyphenyl)-1,2-diphenylethylene[2]



4a

(*E*)-1-(4-methoxyphenyl)-1,2-diphenyl ethylene was prepared from caesium (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate (386 mg, 1.00 mmol) and bromobenzene (316 mg, 2.00 mmol). It was isolated as a white solid (260 mg, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.29 (m, 3H), 7.24 (d, *J* = 8.9 Hz, 2H), 7.20 – 7.18 (m, 2H), 7.12 – 7.05 (m, 3H), 7.02 – 6.97 (m, 2H), 6.88 (s, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.52, 142.37, 140.80, 137.84, 136.29, 130.57, 129.60, 128.92, 128.73, 128.07, 127.48, 126.74, 126.61, 113.85, 55.47 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 286.1358, found: *m/z* = 286.1365.

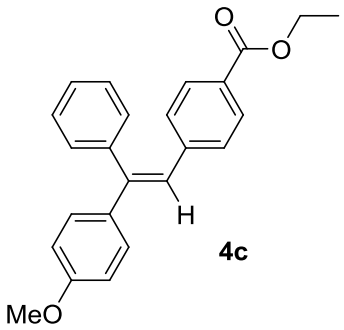
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(3-methoxyphenyl)ethylene



4b

(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(3-methoxyphenyl)ethylene was prepared from caesium (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate (386 mg, 1.00 mmol) and 3-bromoanisole (374 mg, 2.00 mmol). It was isolated as a white solid (285 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.29 (m, 3H), 7.25 (d, *J* = 9.0 Hz, 2H), 7.22 – 7.20 (m, 2H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.88 (s, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.67 – 6.62 (m, 2H), 6.51 – 6.48 (m, 1H), 3.80 (s, 3H), 3.50 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.56, 159.33, 142.54, 140.92, 139.09, 136.11, 130.55, 129.02, 128.88, 128.81, 127.51, 126.58, 122.62, 113.95, 113.87, 113.48, 55.49, 54.97 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 316.1463, found: *m/z* = 316.1462.

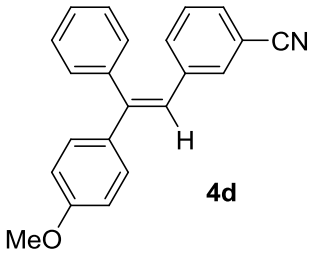
Ethyl (*E*)-4-[(2-methoxyphenyl)-2-phenylvinyl]benzoate



4c

(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(ethyl 4-benzoate)ethylene was prepared from caesium (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate (386 mg, 1.00 mmol) and ethyl 4-bromobenzoate (458 mg, 2.00 mmol). It was isolated as a yellow solid (322 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.31 (m, 3H), 7.26 (d, *J* = 8.9 Hz, 2H), 7.18 – 7.16 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.91 (s, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.60, 159.88, 144.74, 142.49, 140.31, 135.76, 130.46, 129.39, 129.36, 129.12, 128.88, 128.35, 127.88, 125.66, 113.93, 60.88, 55.50, 14.47 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 358.1569, found: *m/z* = 358.1572.

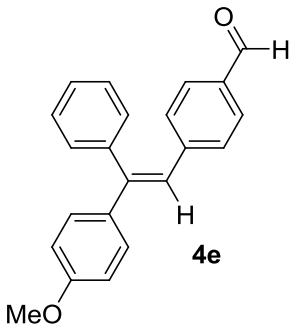
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(3-cyanophenyl)ethylene



4d

(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(3-benzonitrile)ethylene was prepared from caesium (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate (386 mg, 1.00 mmol) and 3-bromobenzonitrile (362 mg, 2.00 mmol). It was isolated as a white solid (267 mg, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.34 (m, 4H), 7.27 – 7.24 (m, 3H), 7.19 – 7.18 (m, 2H), 7.17 – 7.14 (m, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 6.83 (s, 1H), 3.83 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.87, 145.03, 139.59, 139.07, 135.15, 133.63, 132.97, 130.25, 129.80, 129.06, 129.04, 128.80, 128.18, 123.89, 118.99, 113.86, 112.22, 55.49 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 311.1310, found: *m/z* = 311.1314.

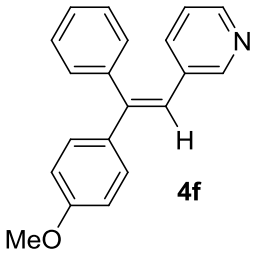
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(4-formylphenyl)ethylene



4e

(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(4-formylphenyl)ethylene was prepared from caesium (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate (386 mg, 1.00 mmol) and 4-bromobenzaldehyde (368 mg, 2.00 mmol). It was isolated as a yellow solid (226 mg, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.88 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.33 (m, 3H), 7.28 (d, *J* = 8.9 Hz, 2H), 7.20 – 7.17 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.93 (s, 1H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 191.86, 159.90, 145.66, 144.25, 140.00, 135.42, 134.25, 130.38, 129.98, 129.58, 129.20, 128.94, 128.08, 125.28, 113.85, 55.49 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 314.1307, found: *m/z* = 314.1314.

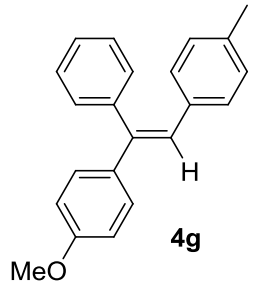
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(3-pyridyl)ethylene



4f

(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(3-pyridyl)ethylene was prepared from caesium (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate (386 mg, 1.00 mmol) and 3-bromopyridine (314 mg, 2.00 mmol). It was isolated as a yellow oil (241 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.33 (d, *J* = 1.9 Hz, 1H), 8.29 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.36 – 7.32 (m, 3H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.19 – 7.17 (m, 2H), 7.15 – 7.12 (m, 1H), 6.98 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.88 – 6.85 (m, 3H), 3.82 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.73, 151.01, 147.29, 144.74, 139.88, 135.78, 135.33, 133.62, 130.25, 129.02, 128.94, 127.98, 122.87, 122.48, 113.81, 55.46 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 287.1310, found: *m/z* = 287.1315.

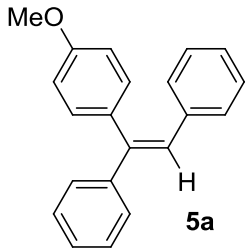
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(4-methylphenyl)ethylene[3]



4g

(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(4-methylphenyl)ethylene was prepared from caesium (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate (386 mg, 1.00 mmol) and 4-bromotoluene (342 mg, 2.00 mmol). It was isolated as a white solid (261 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 7.21 – 7.19 (m, 2H), 6.90 – 6.82 (m, 7H), 3.80 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.40, 141.48, 141.02, 136.45, 136.40, 134.98, 130.57, 129.51, 128.83, 128.75, 127.39, 126.70, 113.83, 55.48, 21.24 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 300.1514, found: *m/z* = 300.1519.

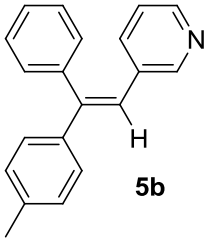
(*Z*)-1-(4-methoxyphenyl)-1,2-diphenylethylene[4]



5a

(*Z*)-1-(4-methoxyphenyl)-1,2-diphenyl ethylene was prepared from caesium (*Z*)-3-(4-methoxyphenyl)-3-phenylacrylate (386 mg, 1.00 mmol) and bromobenzene (316 mg, 2.00 mmol). It was isolated as a white solid (237 mg, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.27 (m, 5H), 7.16 – 7.10 (m, 5H), 7.07 – 7.05 (m, 2H), 6.90 (s, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.12, 144.00, 142.42, 137.83, 132.70, 131.78, 129.66, 128.30, 128.12, 127.97, 127.87, 127.61, 126.75, 114.16, 55.35 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 286.1358, found: *m/z* = 286.1353.

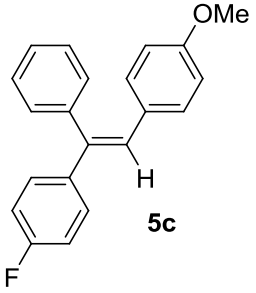
(*E*)-1-(4-methylphenyl)-1-phenyl-2-(3-pyridyl)ethylene



5b

(*E*)-1-(4-methylphenyl)-1-phenyl-2-(3-pyridyl)ethylene was prepared from caesium (*E*)-3-(4-methylphenyl)-3-phenylacrylate (370 mg, 1.00 mmol) and 3-bromopyridine (314 mg, 2.00 mmol). It was isolated as a yellow (216 mg, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (d, *J* = 2.2 Hz, 1H), 8.30 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.35 – 7.33 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.17 (m, 2H), 7.15 – 7.13 (m, 3H), 6.99 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.90 (s, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.12, 147.49, 145.08, 139.95, 139.85, 138.10, 135.81, 133.48, 130.24, 129.15, 129.00, 127.95, 127.61, 123.39, 122.85, 21.30 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 271.1361, found: *m/z* = 271.1366.

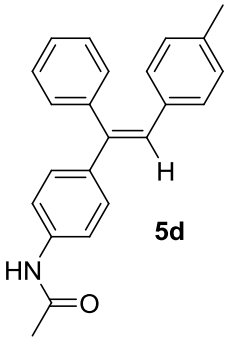
(*E*)-1-(4-fluorophenyl)-1-phenyl-2-(4-methoxyphenyl)ethylene



5c

(*E*)-1-(4-fluorophenyl)-1-phenyl-2-(4-methoxyphenyl)ethylene was prepared from caesium (*E*)-3-(4-fluorophenyl)-3-phenylacrylate (374 mg, 1.00 mmol) and 4-bromoanisole (374 mg, 2.00 mmol). It was isolated as a white solid (240 mg, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.33 (m, 3H), 7.28 – 7.24 (m, 2H), 7.21 – 7.18 (m, 2H), 7.00 – 6.93 (m, 4H), 6.85 (s, 1H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.20 (d), 158.38, 140.43, 139.73 (d), 139.55, 130.73, 130.32, 129.87, 128.96 (d), 128.77, 127.46, 127.40, 114.98 (d), 113.41, 55.14 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 304.1263, found: *m/z* = 304.1260.

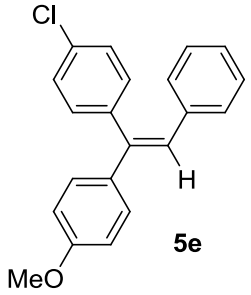
(*E*)-1-(4-acetamidophenyl)-1-phenyl-2-(4-methylphenyl)ethylene



5d

(*E*)-1-(4-acetamidophenyl)-1-phenyl-2-(4-methylphenyl)ethylene was prepared from caesium (*E*)-3-(4-acetamidophenyl)-3-phenylacrylate (413 mg, 1.00 mmol) and 4-bromotoluene (342 mg, 2.00 mmol). It was isolated as an orange solid (252 mg, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 – 7.42 (m, 3H), 7.33 – 7.31 (m, 3H), 7.26 – 7.24 (m, 2H), 7.20 – 7.17 (m, 2H), 6.94 – 6.88 (m, 5H), 2.25 (s, 3H), 2.16 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.46, 141.08, 140.55, 139.66, 137.23, 136.64, 134.60, 130.47, 129.54, 128.82, 128.79, 128.19, 127.57, 127.48, 119.67, 24.73, 21.29 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 327.1623, found: *m/z* = 327.1628.

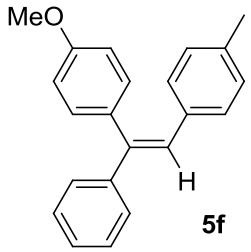
(*Z*)-1-(4-chlorophenyl)-1-(4-methoxyphenyl)-2-phenylethylene



5e

(*Z*)-1-(4-chlorophenyl)-1-(4-methoxyphenyl)-2-phenylethylene was prepared from caesium (*Z*)-3-(4-chlorophenyl)-3-(4-methoxyphenyl)acrylate (374 mg, 1.00 mmol) and 4-bromobenzene (314 mg, 2.00 mmol). It was isolated as a white solid (266 mg, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.9 Hz, 2H), 7.15 – 7.11 (m, 5H), 7.03 – 6.98 (m, 2H), 6.88 (s, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.50, 141.01, 139.13, 137.40, 135.76, 133.35, 132.02, 129.55, 128.97, 128.94, 128.21, 127.24, 126.82, 113.80, 55.45 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 320.0968, found: *m/z* = 320.0961.

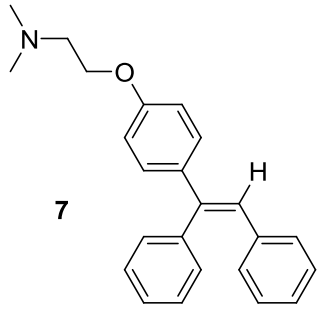
(*Z*)-1-(4-methoxyphenyl)-1-phenyl-2-(4-methylphenyl)ethylene[3]



5f

(*Z*)-1-(4-methoxyphenyl)-1-phenyl-2-(4-methylphenyl)ethylene was prepared from caesium (*Z*)-3-(4-methoxyphenyl)-3-phenylacrylate (386 mg, 1.00 mmol) and 4-bromotoluene (342 mg, 2.00 mmol). It was isolated as a white solid (261 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 – 7.20 (m, 5H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.88 (s, 4H), 6.81 – 6.78 (m, 3H), 3.77 (s, 3H), 2.20 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.01, 144.08, 141.47, 136.57, 134.90, 132.89, 131.73, 129.55, 128.87, 128.27, 127.93, 127.76, 127.45, 114.15, 55.35, 21.33 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 300.1514, found: *m/z* = 300.1516.

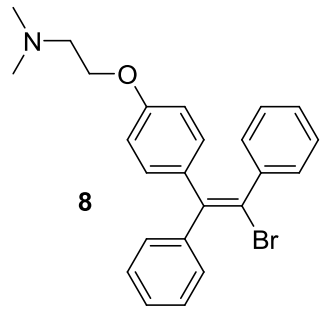
(*E*)-1-(4-phenoxy-*N*,*N*-dimethylethylamine)-1,2-diphenylethylene[5]



7

(*E*)-1-(4-phenoxy-*N*,*N*-dimethylethylamine)-1,2-diphenylethylene was prepared from caesium (*E*)-3-(4-phenoxy-*N*,*N*-dimethylethylamine)-3-phenylacrylate (17.72 g, 40.00 mmol) and 4-bromobenzene (15.72 g, 80.00 mmol). It was isolated as a yellow solid (11.54 g, 84 %, *E* / *Z* = 97:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.30 (m, 3H), 7.24 (d, *J* = 8.9 Hz, 2H), 7.21 – 7.18 (m, 2H), 7.14 – 7.07 (m, 3H), 7.01 – 6.98 (m, 2H), 6.89 (s, 1H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.07 (t, *J* = 5.8 Hz, 2H), 2.73 (t, *J* = 5.8 Hz, 2H), 2.33 (s, 6H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.65, 142.22, 140.67, 137.72, 136.19, 130.51, 129.56, 128.84, 128.73, 128.05, 127.47, 126.63, 114.35, 66.13, 58.43, 46.06 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 343.1936, found: *m/z* = 343.1928.

(*E*)-1-Bromo-2-{4-[2-(*N*,*N*-dimethylamino)ethoxy]phenyl}-1,2-diphenylethylene

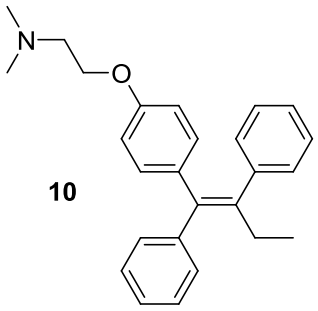


8

According to the procedure described by Nunes,[5] a solution of bromine (575 mg, 3.6 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of (*E*)-1-(4-phenoxy-*N*,*N*-dimethylethylamine)-1,2-diphenylethylene (1.03 g, 3 mmol) and Et_3N (1.20 g, 12 mmol) in CH_2Cl_2 (10 mL) at r.t. Then, the reaction mixture was kept overnight in the dark and washed with a saturated aqueous solution of $NaHSO_3$ to destroy the excess of bromine (until disappearance of the color). The organic layer was washed with a 10% aqueous KOH solution (20 mL) and dried over Na_2SO_4. CH_2Cl_2 was evaporated to give 1.11 g (86 %) of an *E*/*Z* mixture (75:25) of (*E*)-1-bromo-2-{4-[[2-(*N*,*N*-dimethylamino)ethoxy]phenyl}-1,2-diphenylethylene as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.35 (m, 2H), 7.34 – 7.31 (m, 3H), 7.20 – 7.14 (m, 5H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 3.94 (t, *J* = 5.7 Hz, 2H), 2.66 (t, *J* = 5.7 Hz, 2H), 2.29 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.75, 144.07, 143.09, 141.34, 133.47, 131.65, 130.36, 129.62, 128.18, 128.09, 127.98,

127.83, 121.05, 113.86, 65.76, 58.24, 45.93 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 421.1041, found: *m/z* = 421.1047.

(*Z*)-Tamoxifen[6]

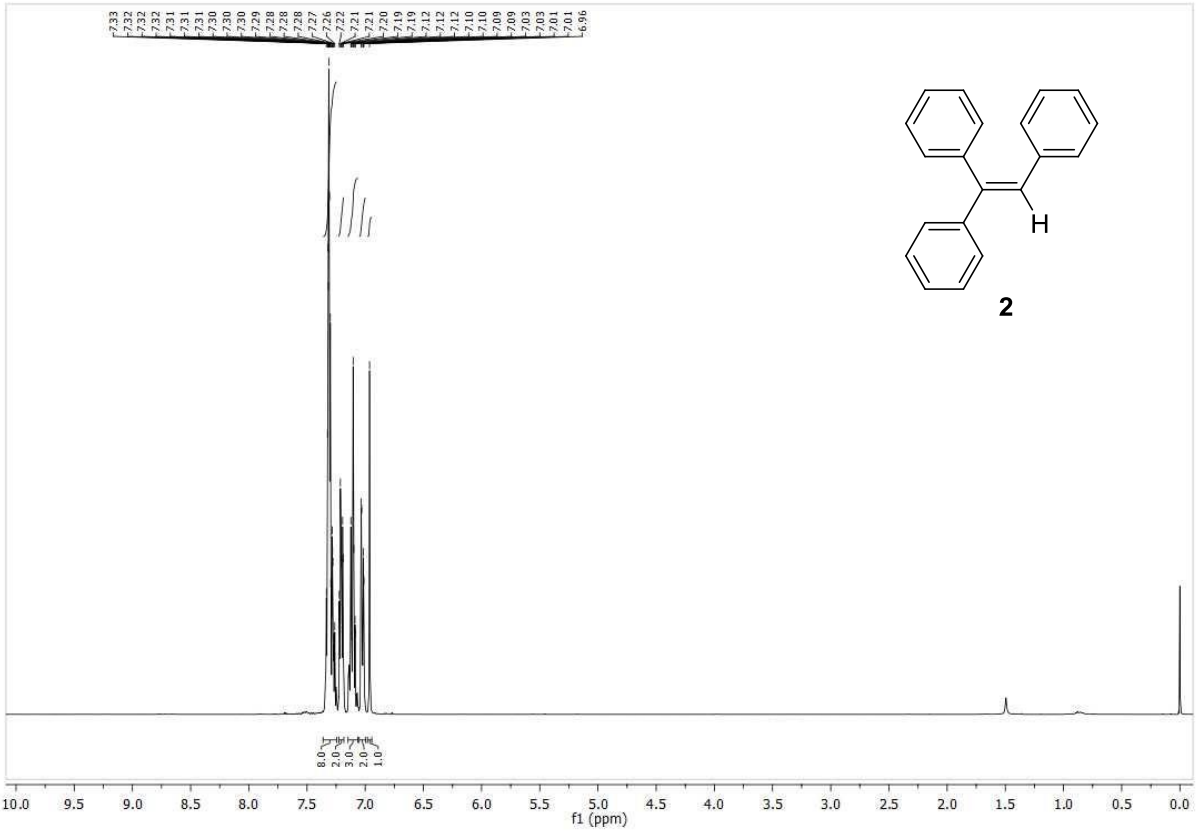


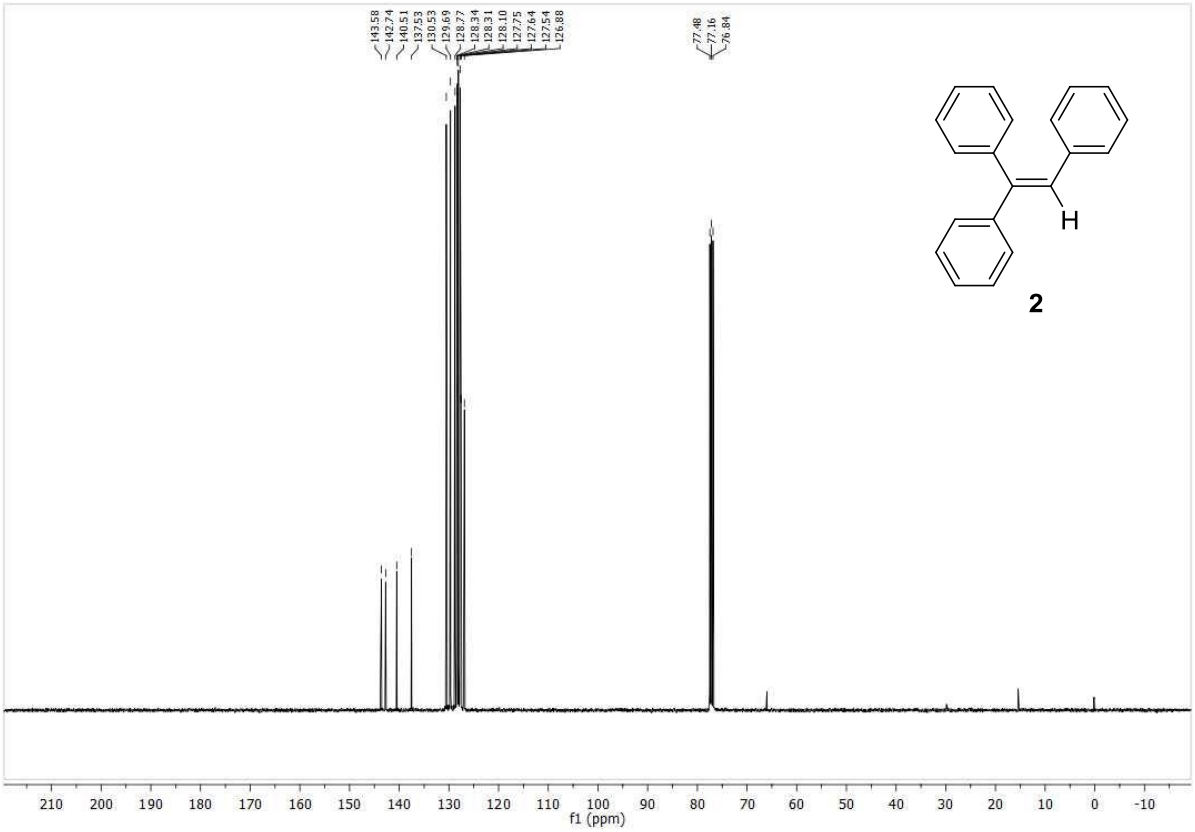
10

A 50 mL, four-necked, round-bottomed flask equipped with a mechanical stirrer was charged with (*E*)-1-bromo-2-{4-[[2-(dimethylamino)ethoxy]phenyl}-1,2-diphenylethylene (3 mmol, 1.26 g, 1 eq.) and THF (10 mL). Then, a solution of ethyllithium in ether (1M, 3.15 mmol, 3.15 mL, 1.05 eq.) was added dropwise at -78 °C in 1 h. After completion of the addition, the reaction mixture was stirred for 1 h at -78 °C then warmed to room temperature and stirred for 4 h. Solvents were removed *in vacuo*. The crude product was purified by chromatography on a silicagel column (eluent: petroleum ether / acetone / triethylamine (10:1:1)) yielding (*Z*)-tamoxifen as a white solid (780 mg, 72 %, *E* / *Z* = 93:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.37 (m, 2H), 7.33 – 7.27 (m, 3H), 7.22 – 7.15 (m, 5H), 6.81 (d, J = 8.9 Hz, 2H), 6.59 (d, J = 8.9 Hz, 2H), 3.98 (t, J = 5.7 Hz, 2H), 2.73 (t, J = 5.7 Hz, 2H), 2.48 (q, J = 7.4 Hz, 2H), 2.33 (s, 6H), 0.96 (t, J = 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.95, 144.02, 142.70, 141.26, 138.49, 135.71, 131.94, 129.72, 129.63, 128.04, 127.96, 126.49, 126.09, 113.55, 65.75, 58.23, 45.96, 29.04, 13.59 ppm. HR-MS (EI, 70 eV) calc: *m/z* = 371.2249, found: *m/z* = 371.2251.

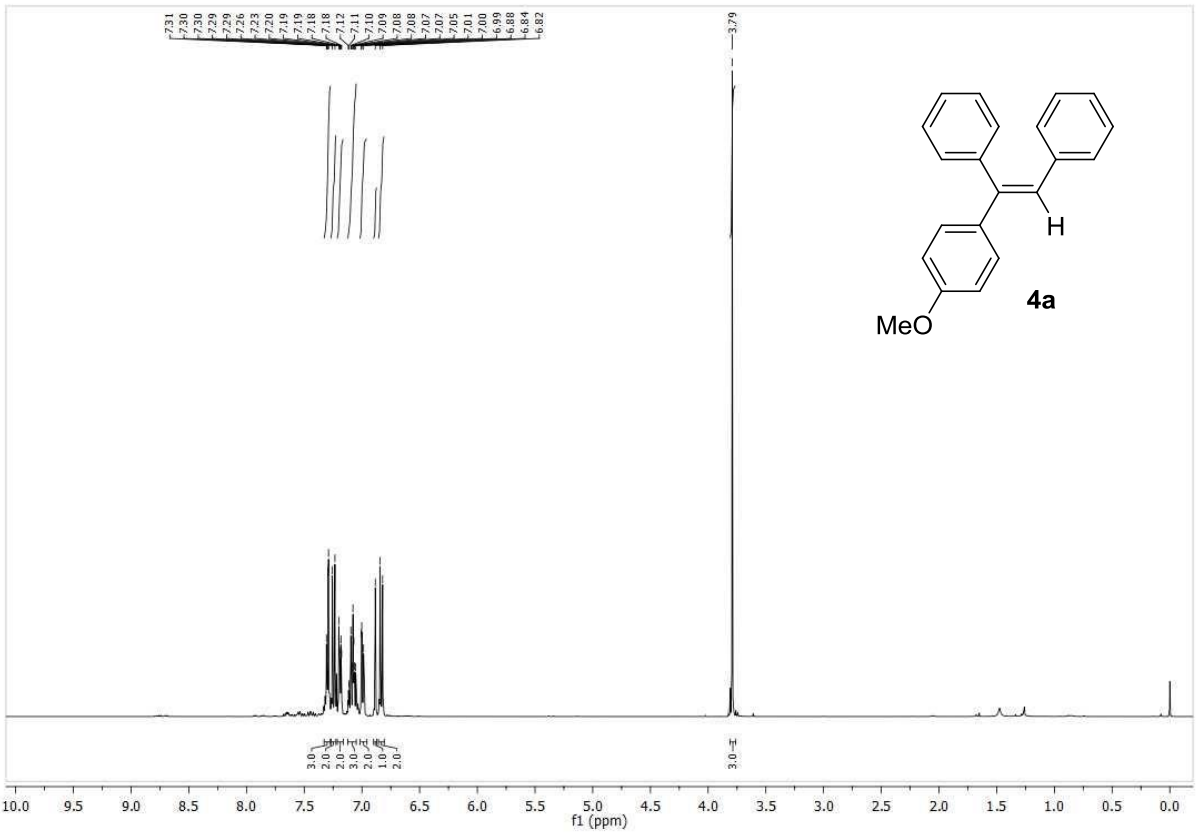
IV/ ^{1}H and ^{13}C spectra

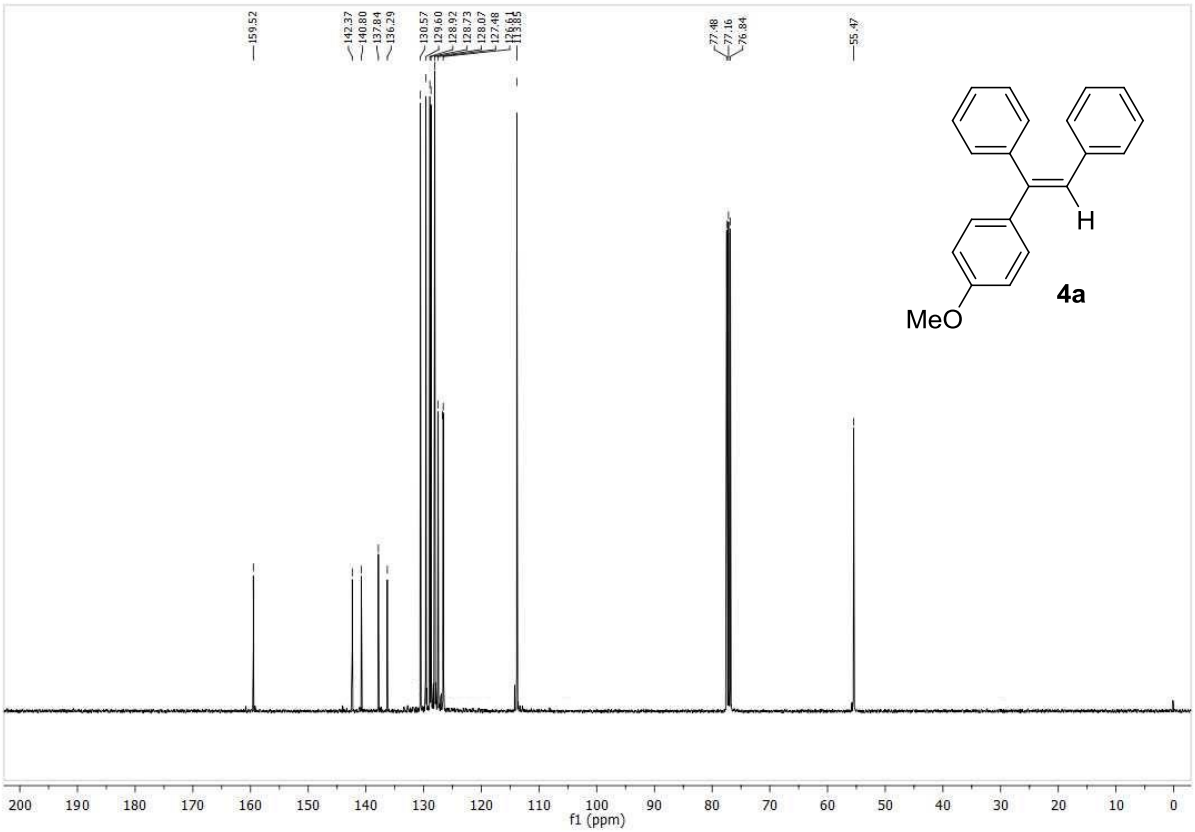
1,1,2-triphenylethylene



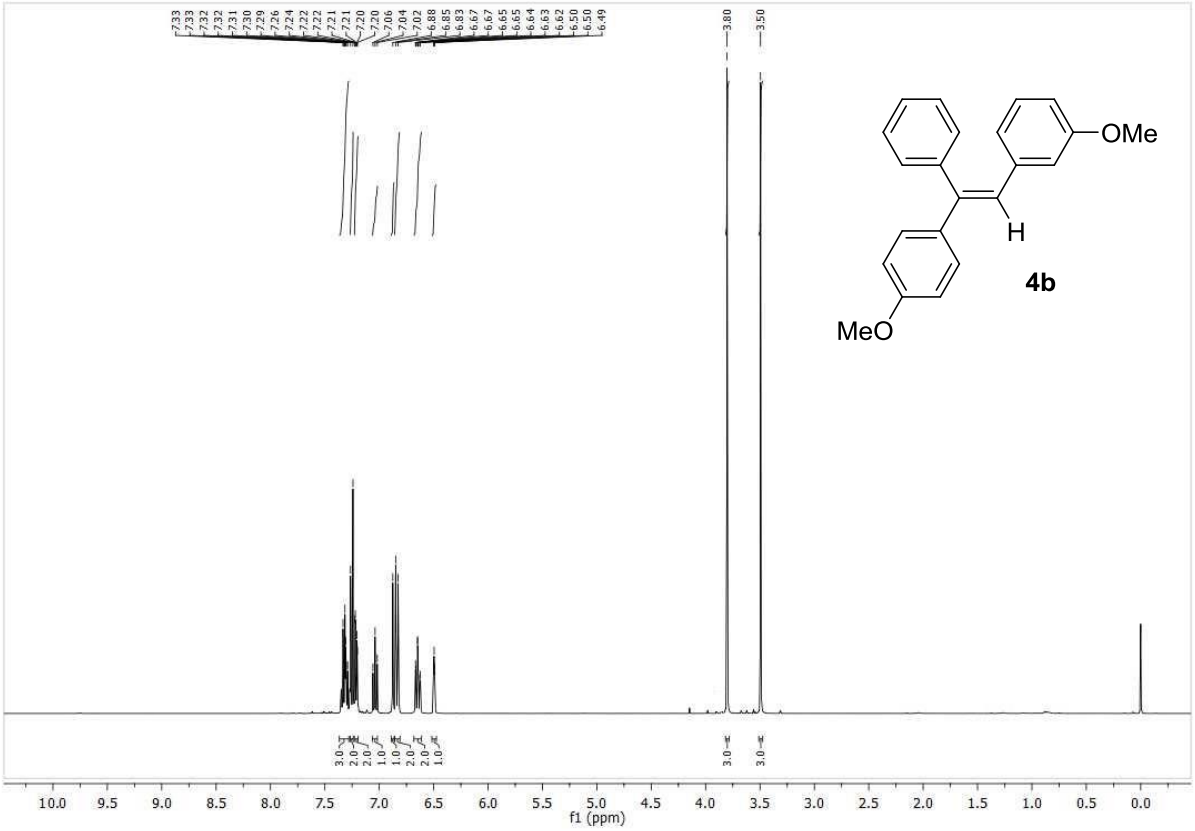


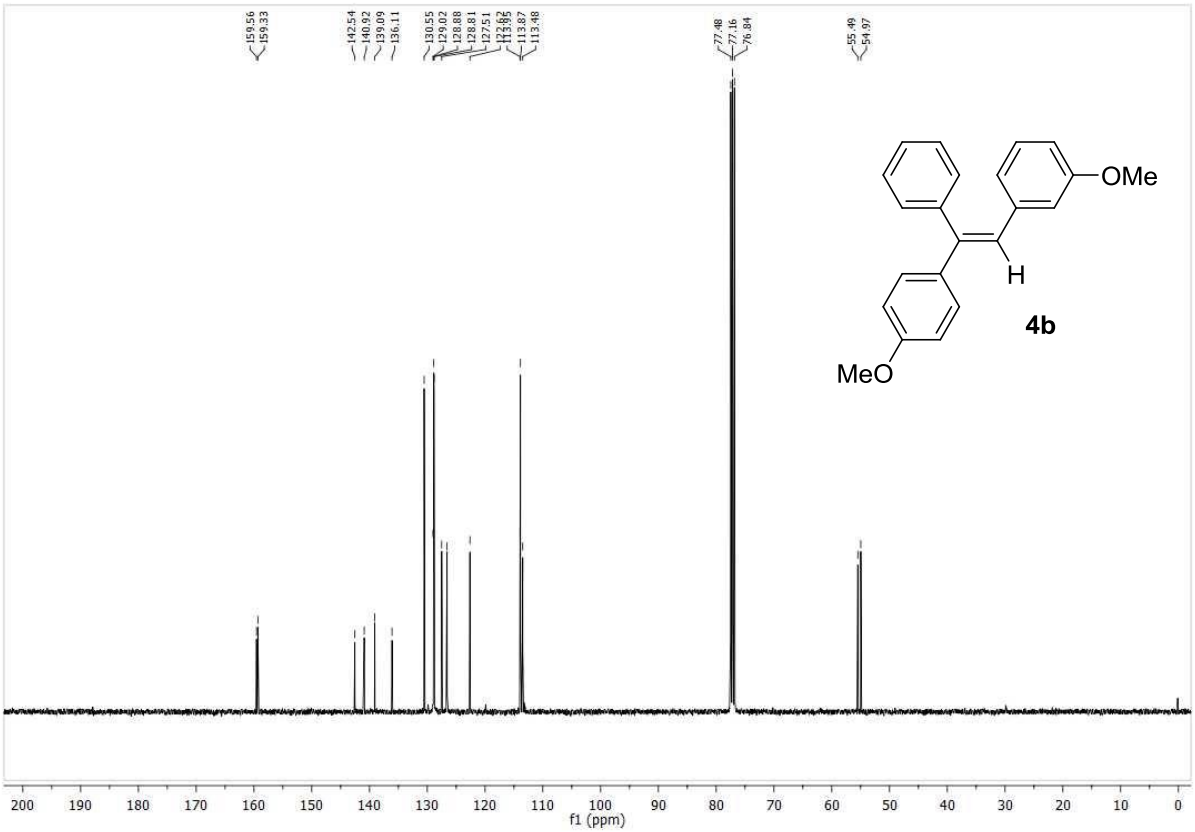
(*E*)-1-(4-methoxyphenyl)-1,2-diphenylethylene



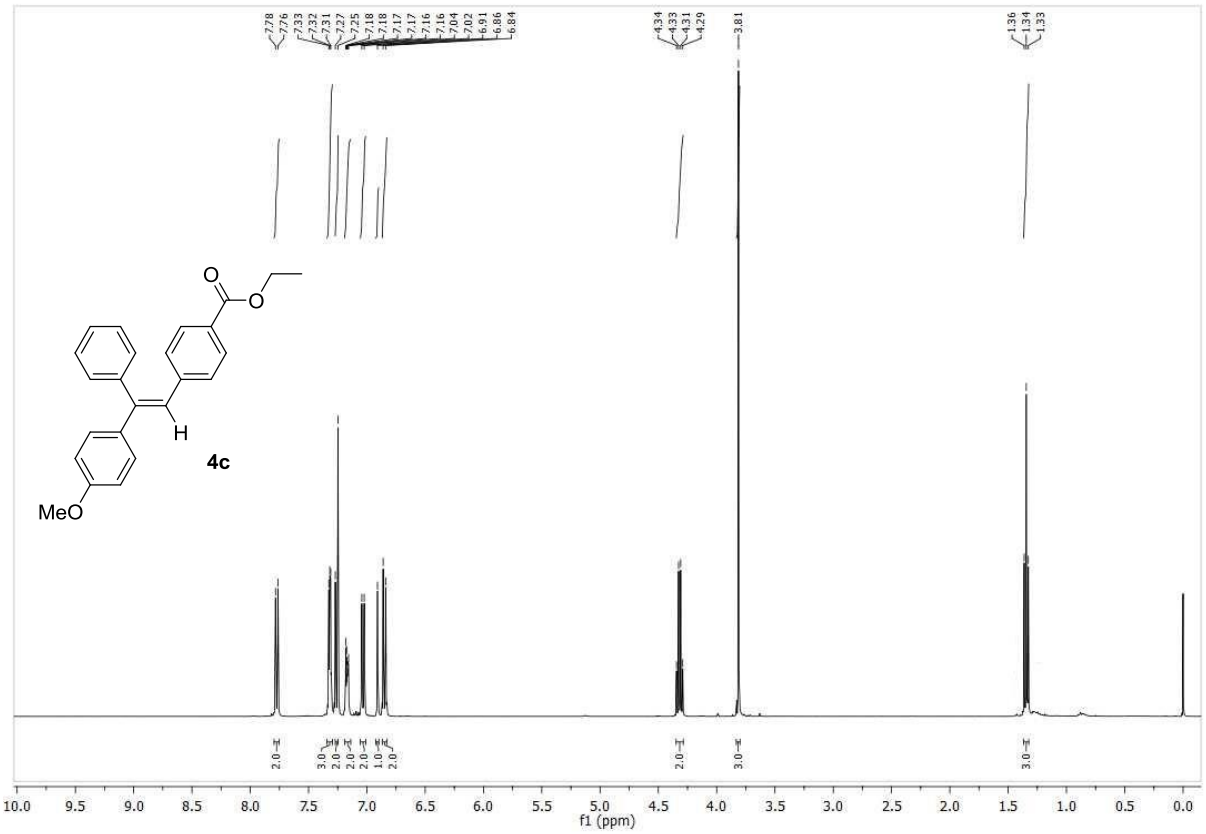


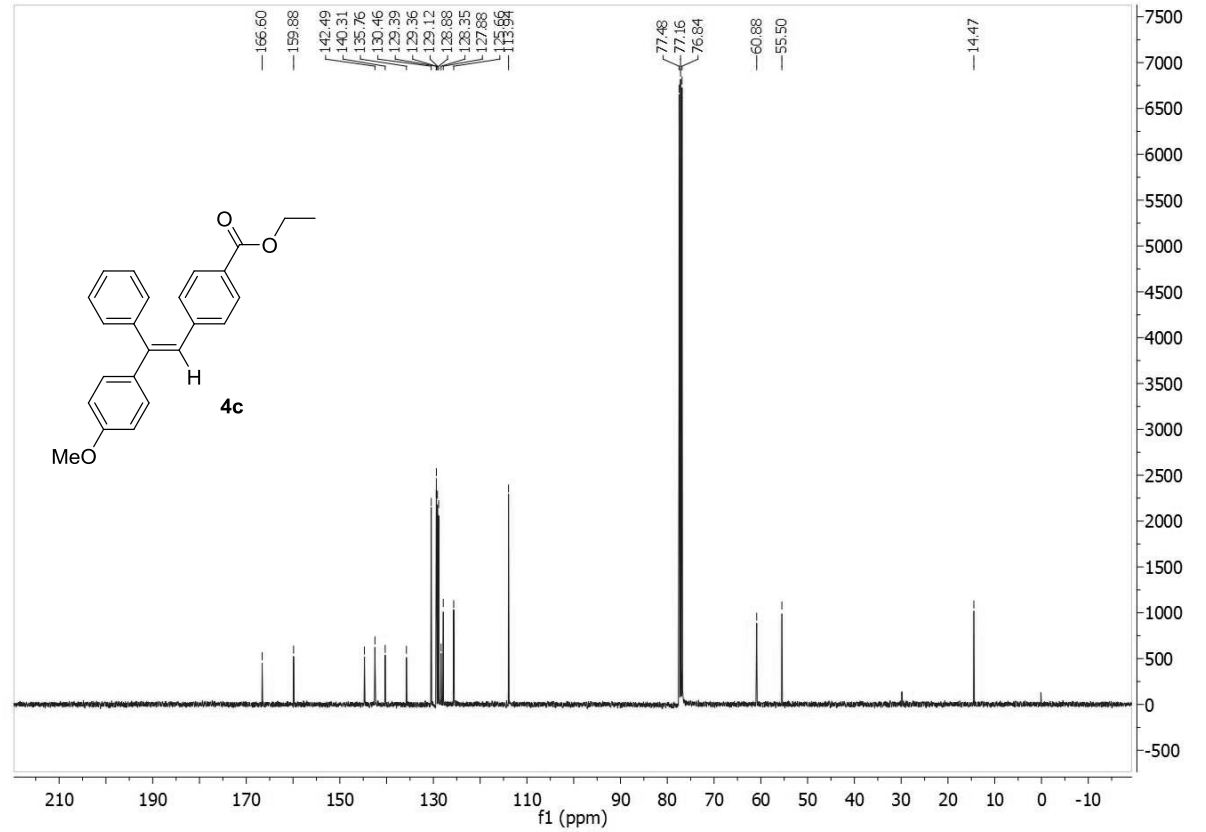
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(3-methoxyphenyl)ethylene



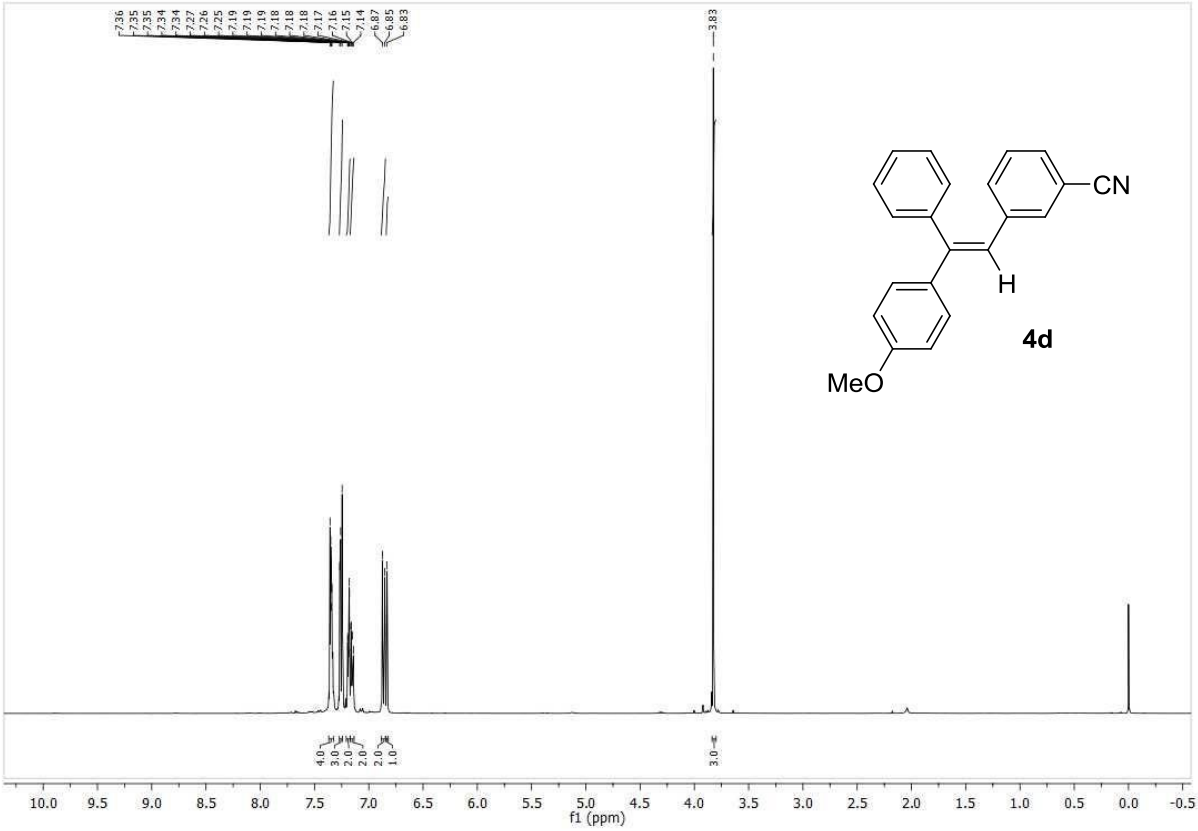


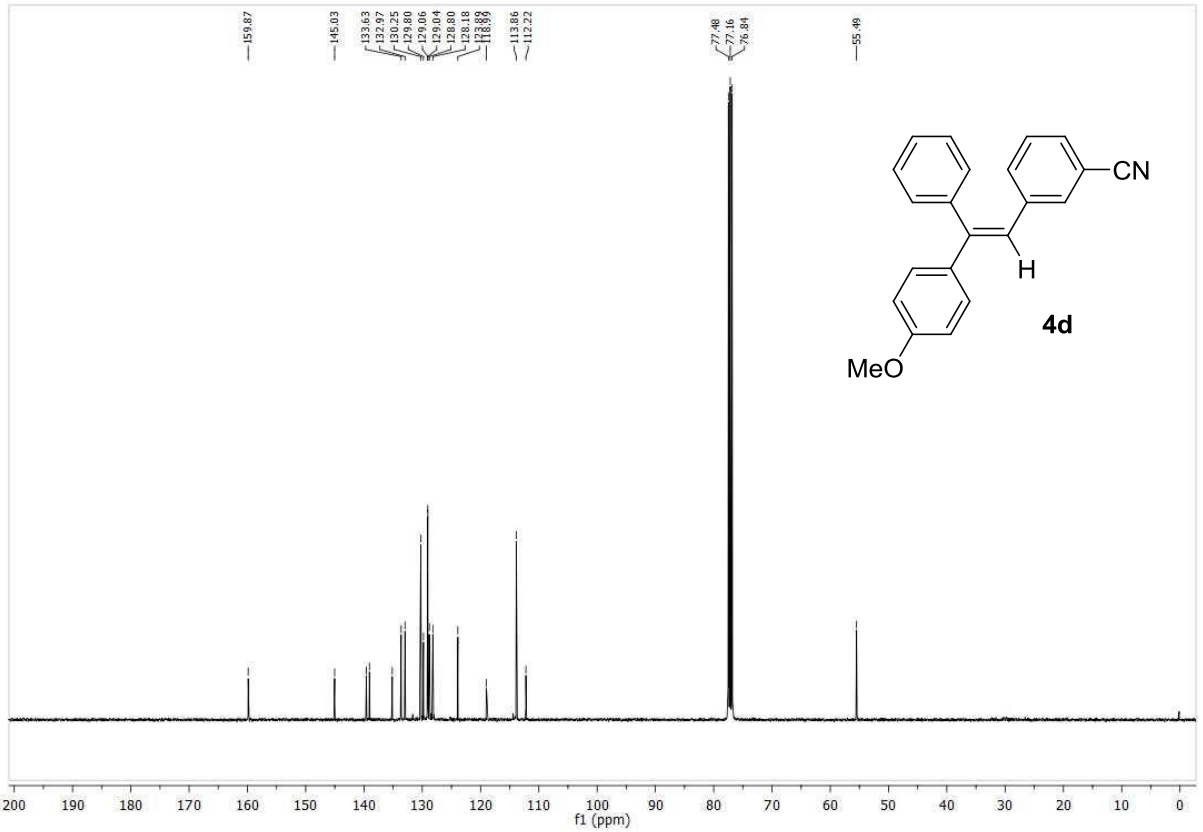
Ethyl (*E*)-4-[(2-methoxyphenyl)-2-phenylvinyl]benzoate



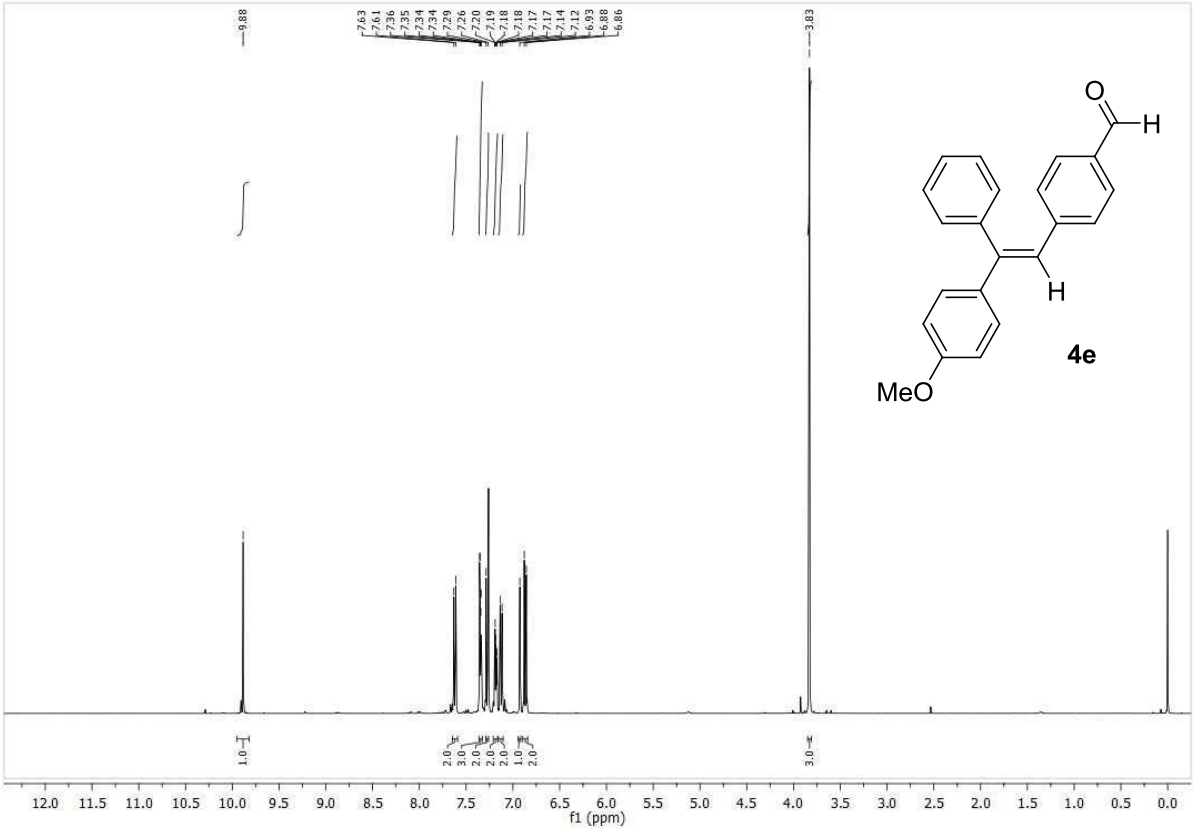


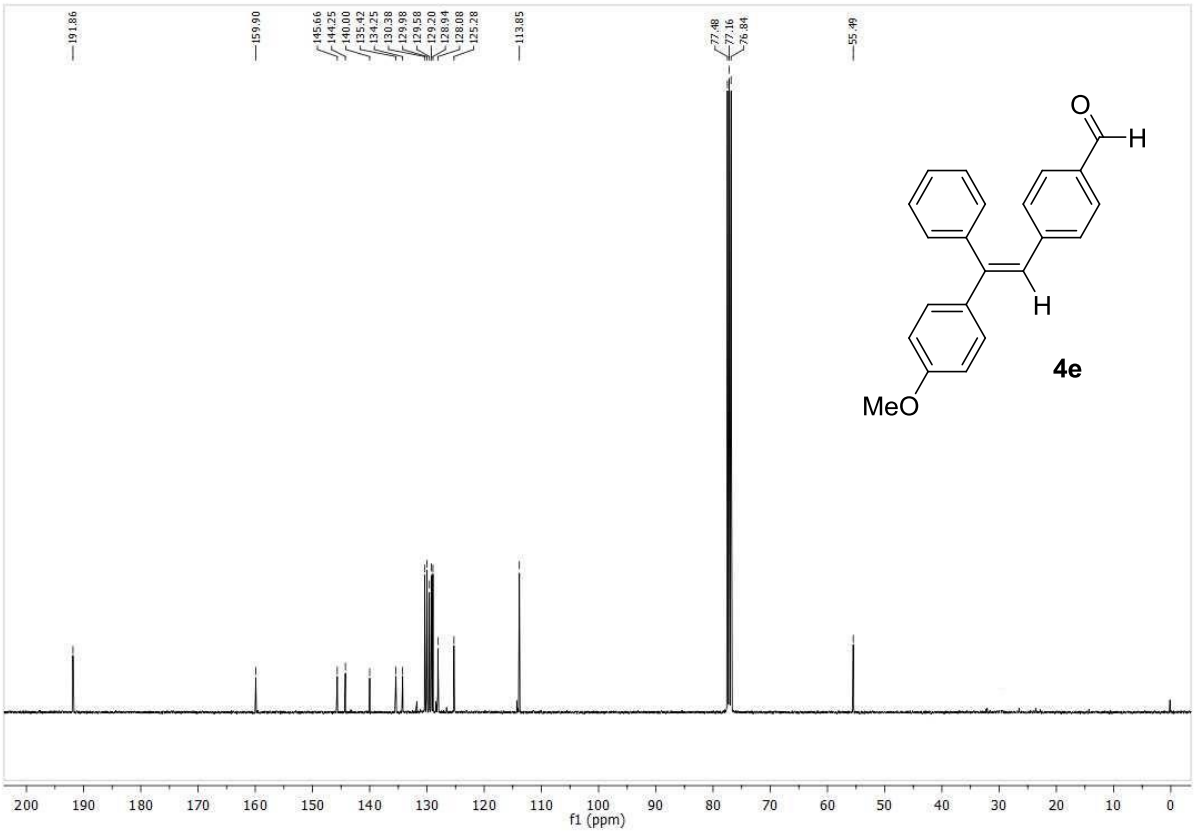
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(3-cyanophenyl)ethylene



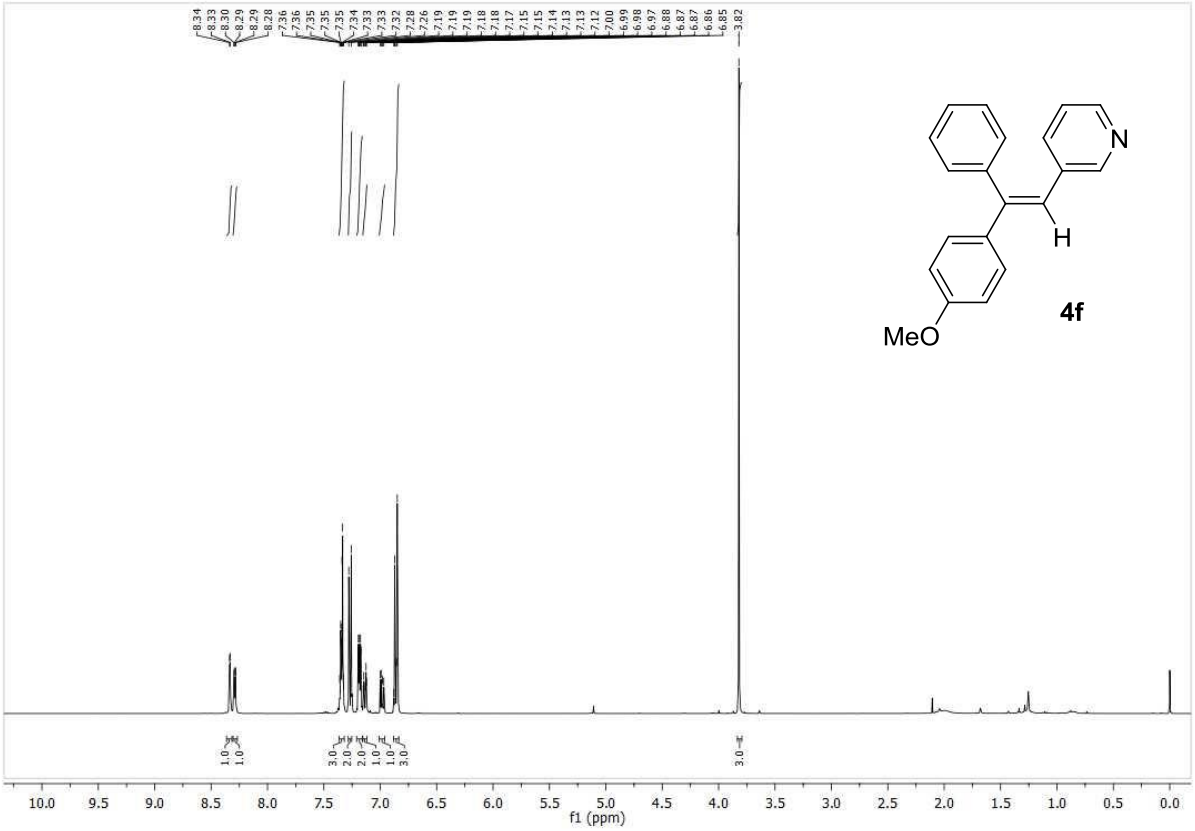


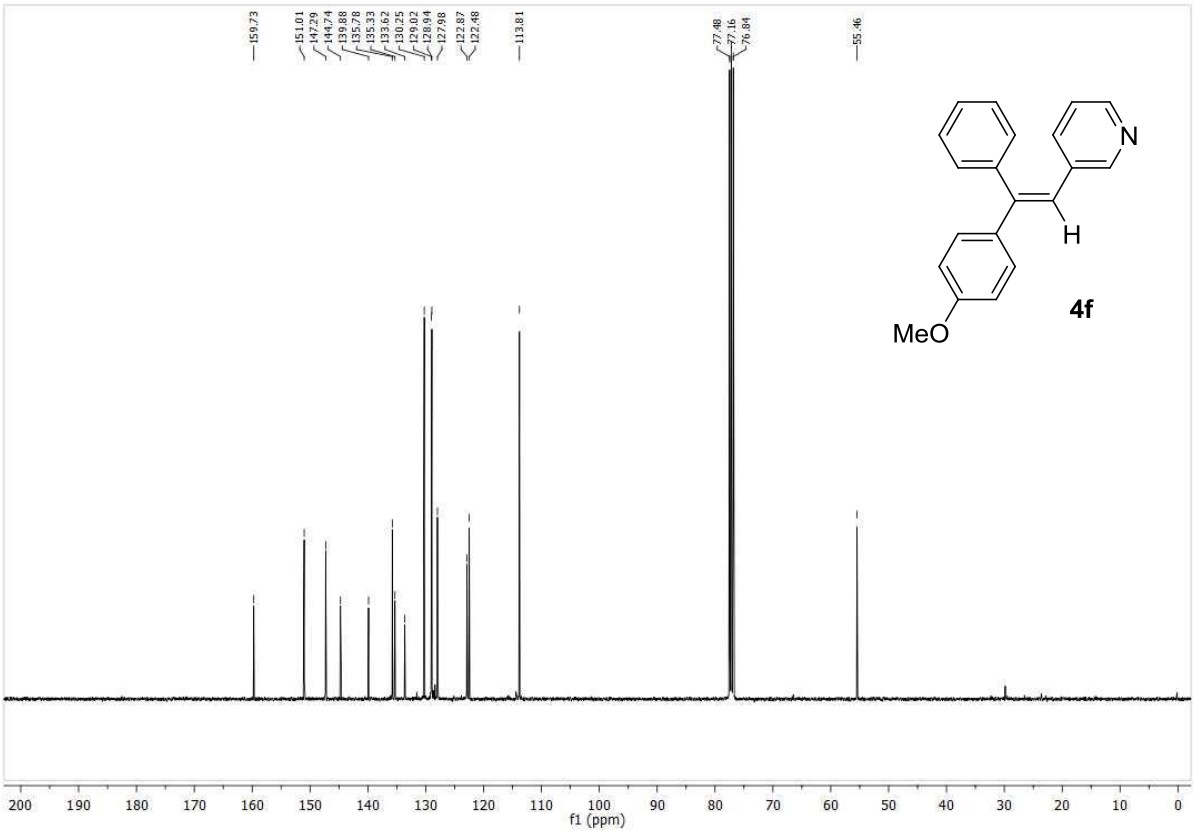
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(4-formylphenyl)ethylene



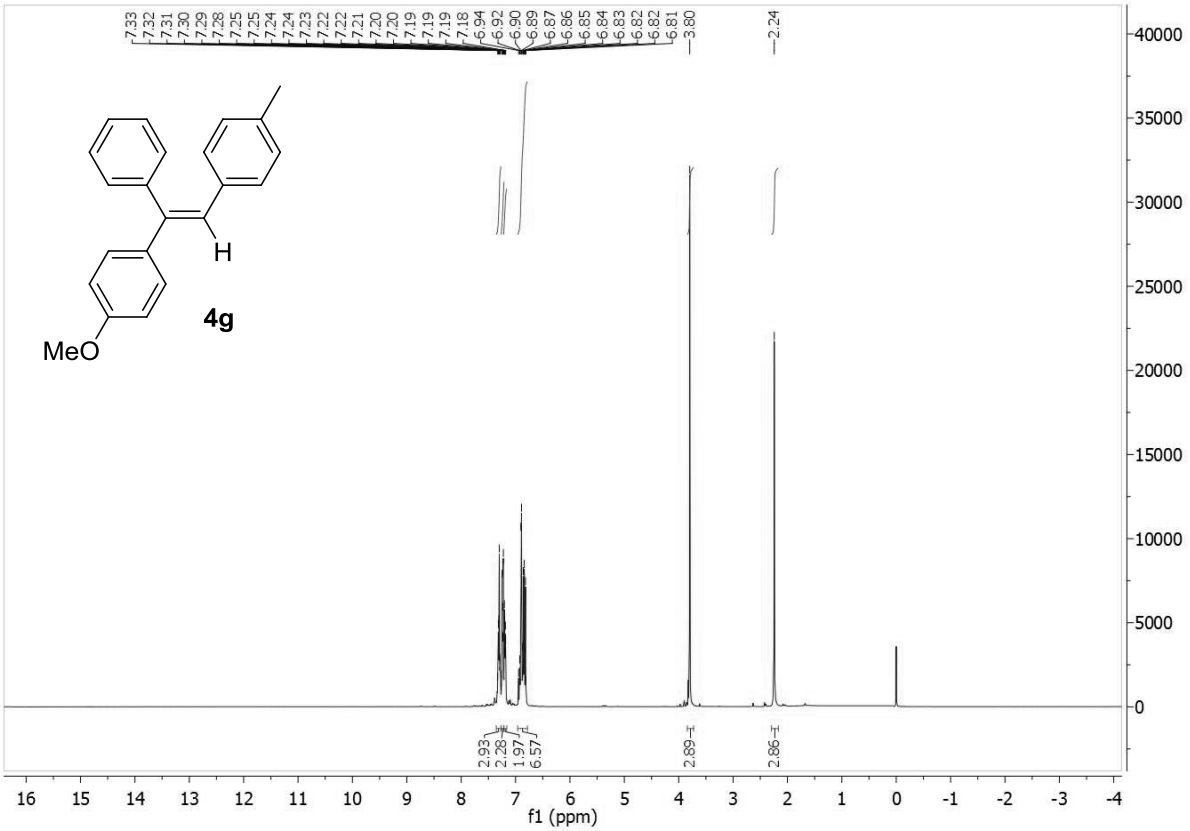


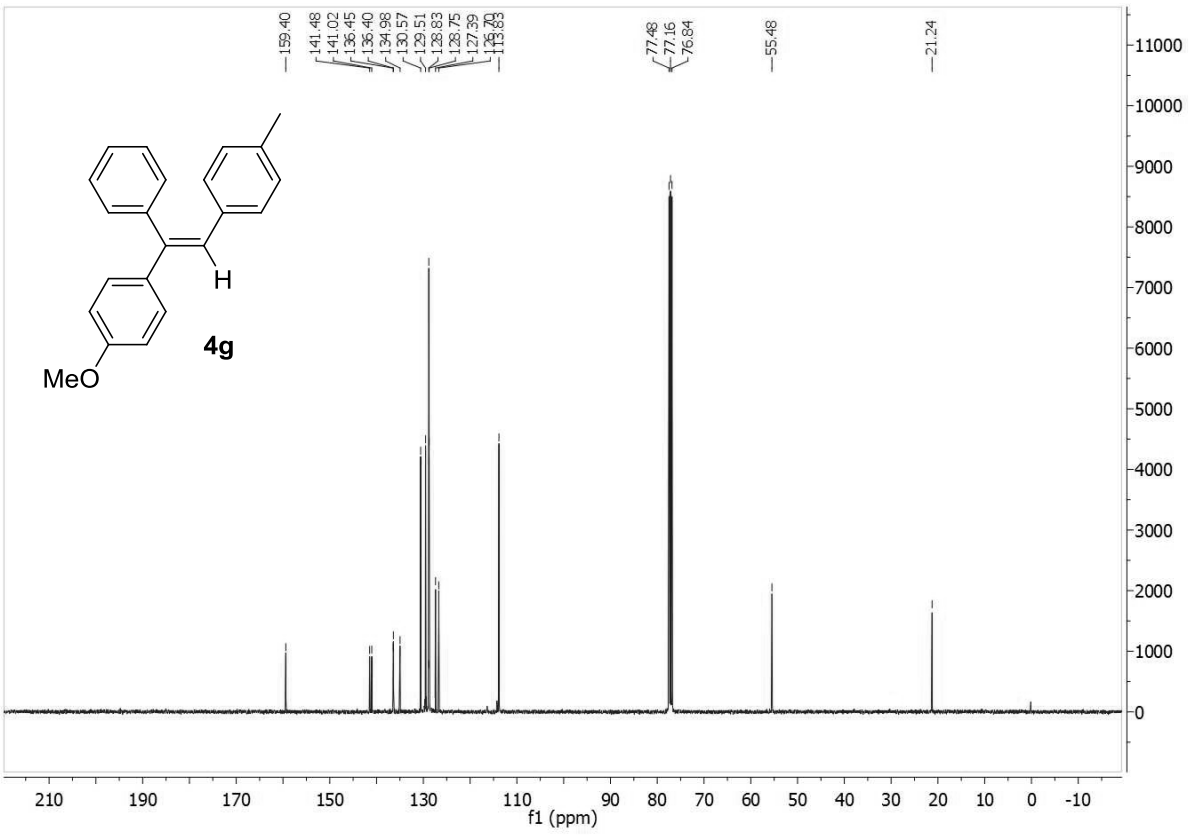
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(3-pyridyl)ethylene



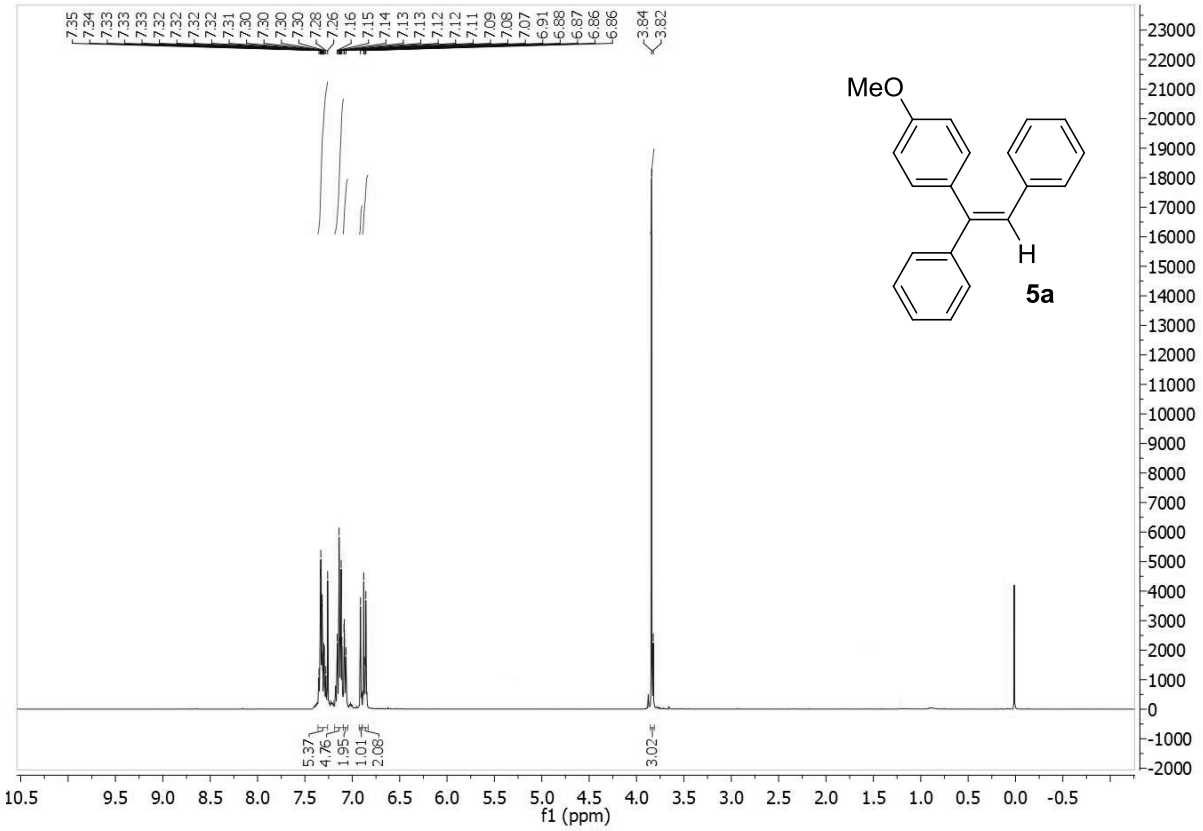


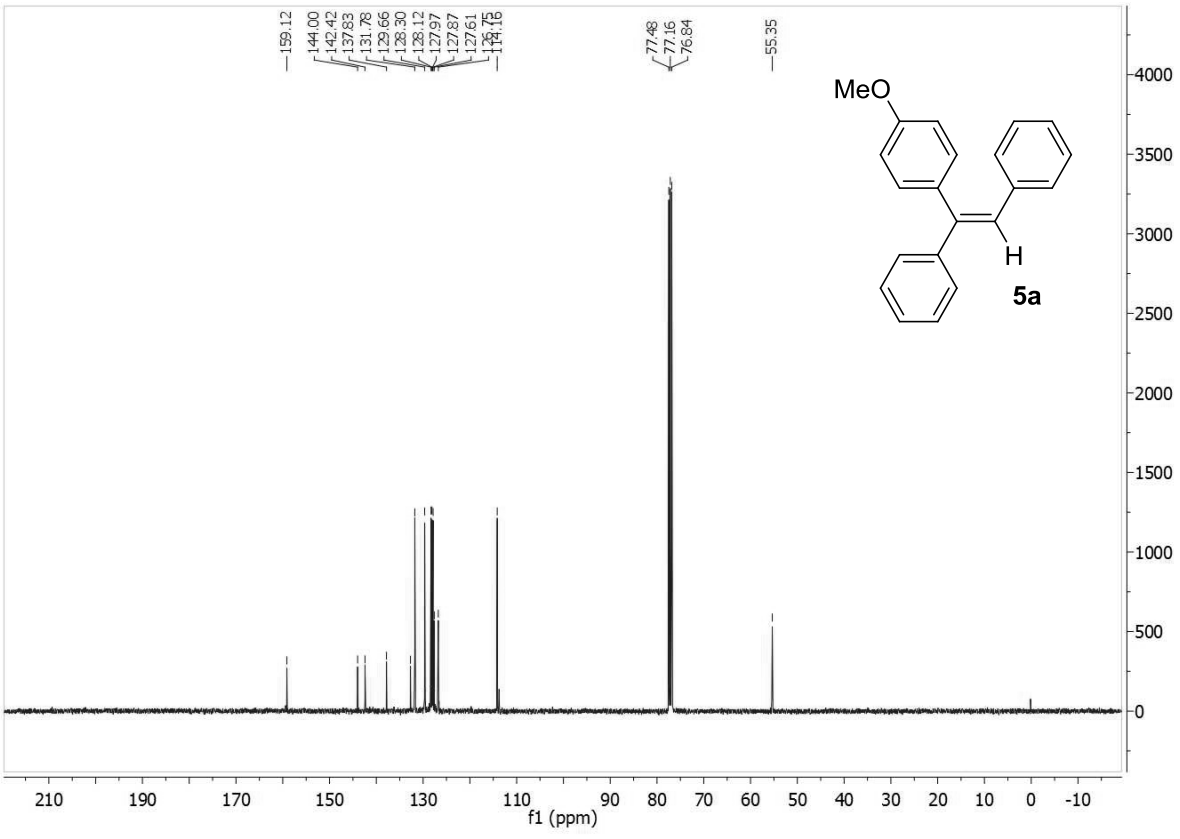
(*E*)-1-(4-methoxyphenyl)-1-phenyl-2-(4-methylphenyl)ethylene



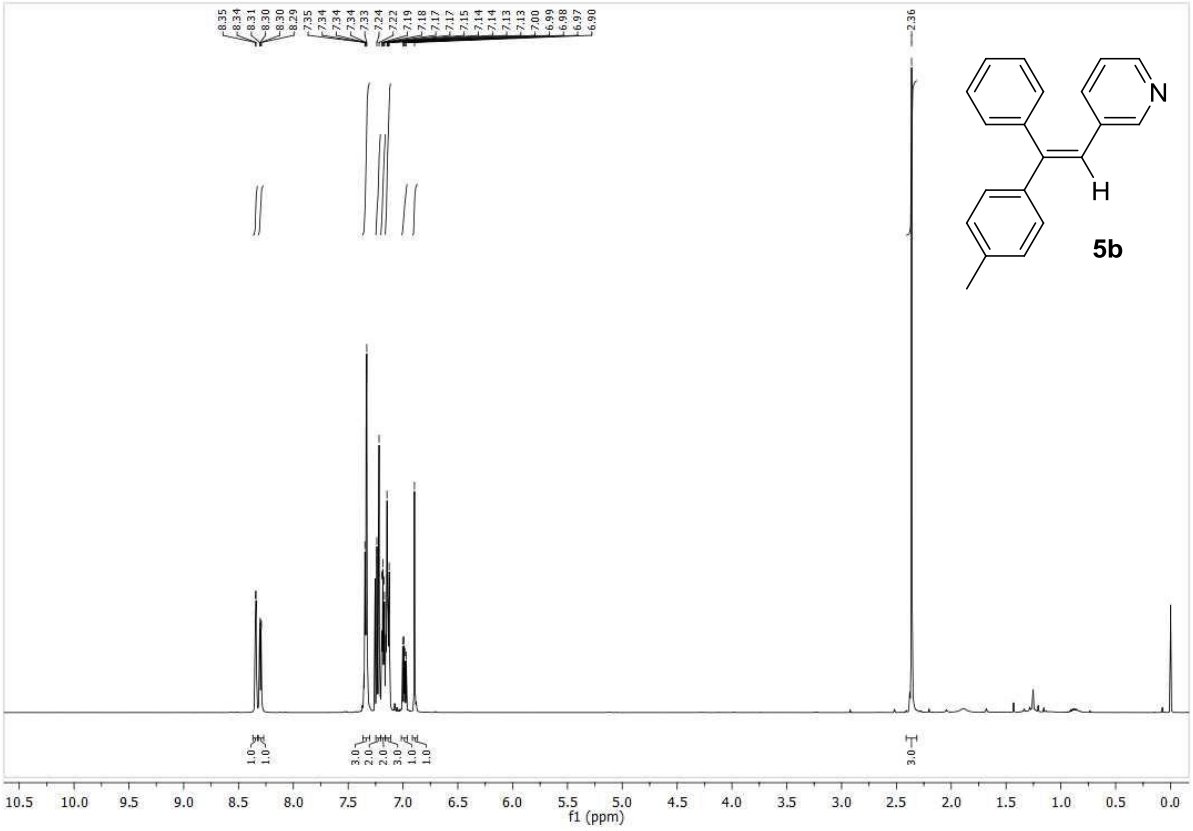


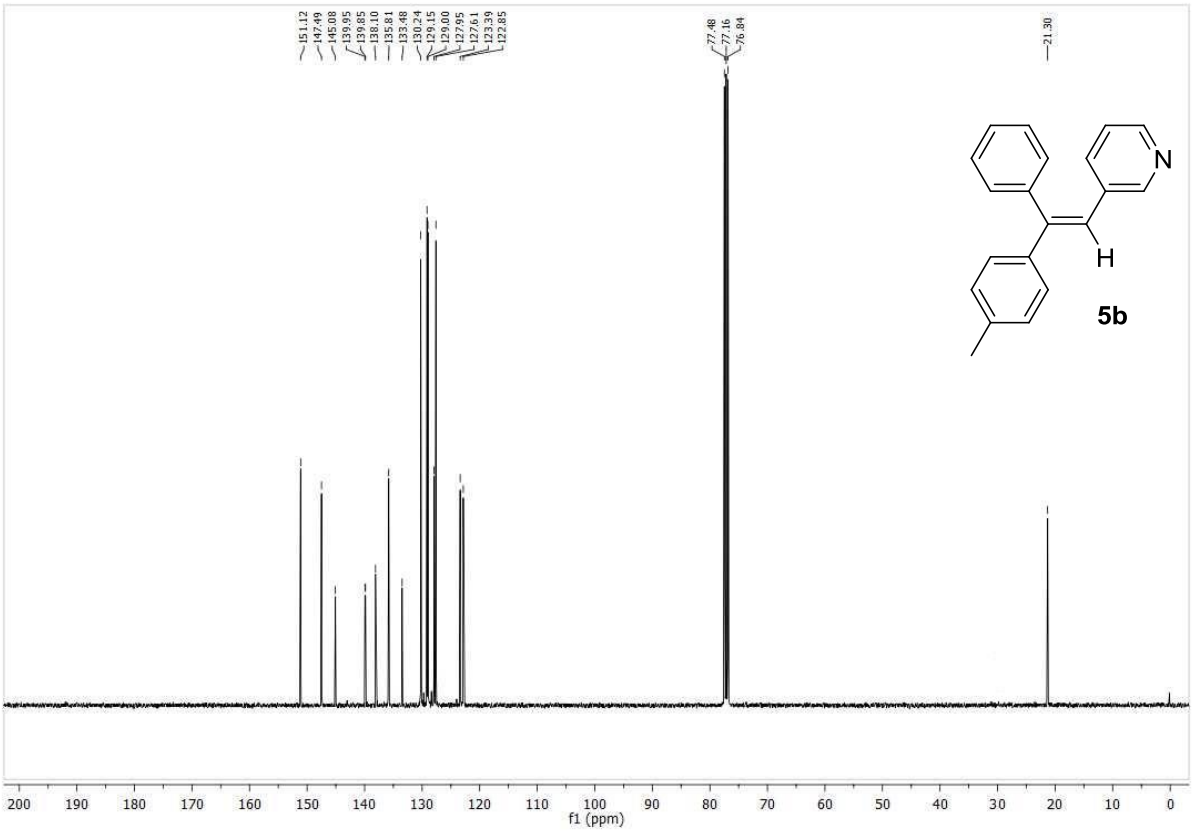
(*Z*)-1-(4-methoxyphenyl)-1,2-diphenylethylene



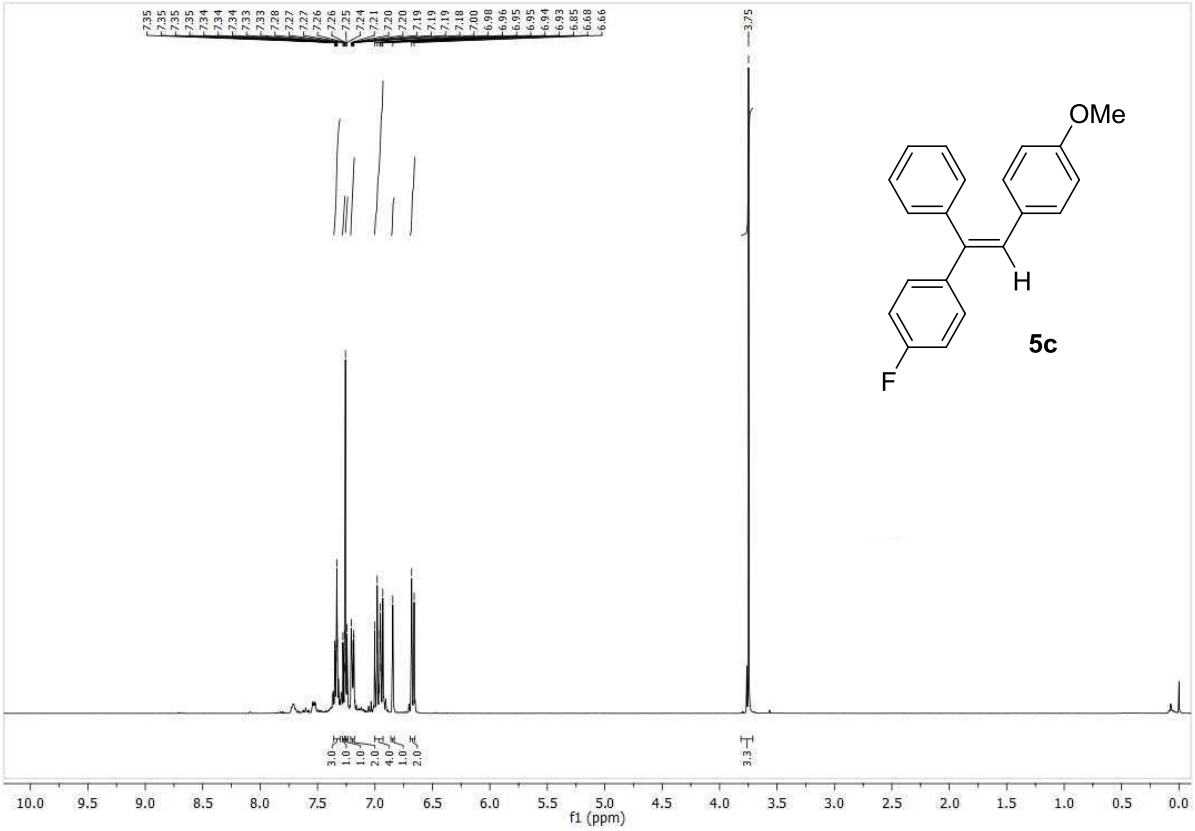


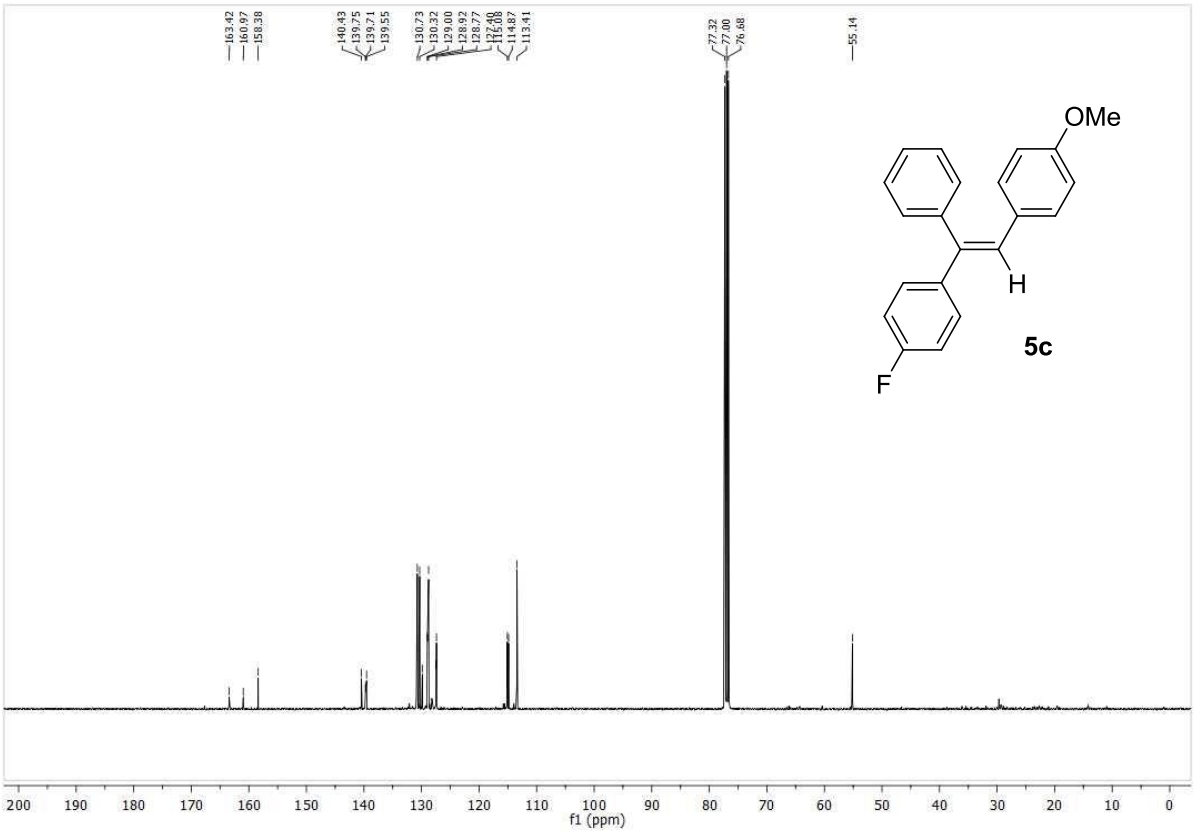
(*E*)-1-(4-methylphenyl)-1-phenyl-2-(3-pyridyl)ethylene



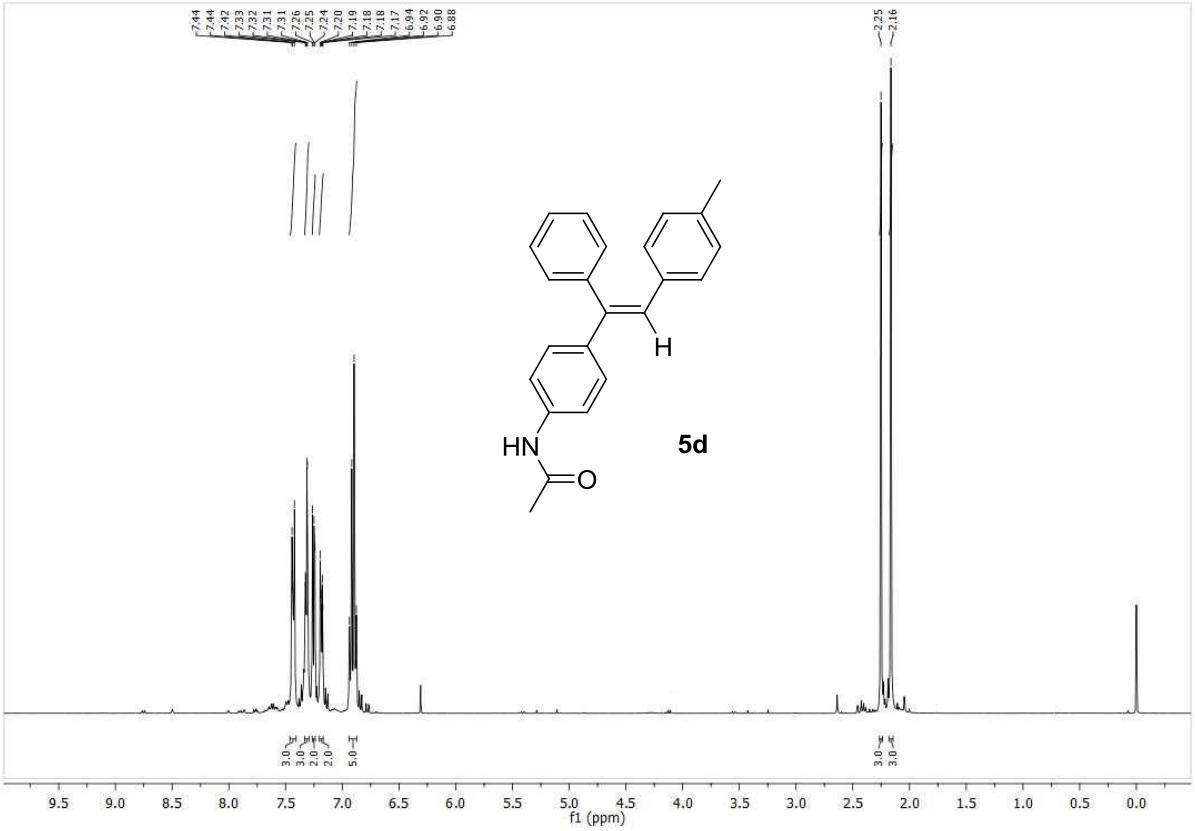


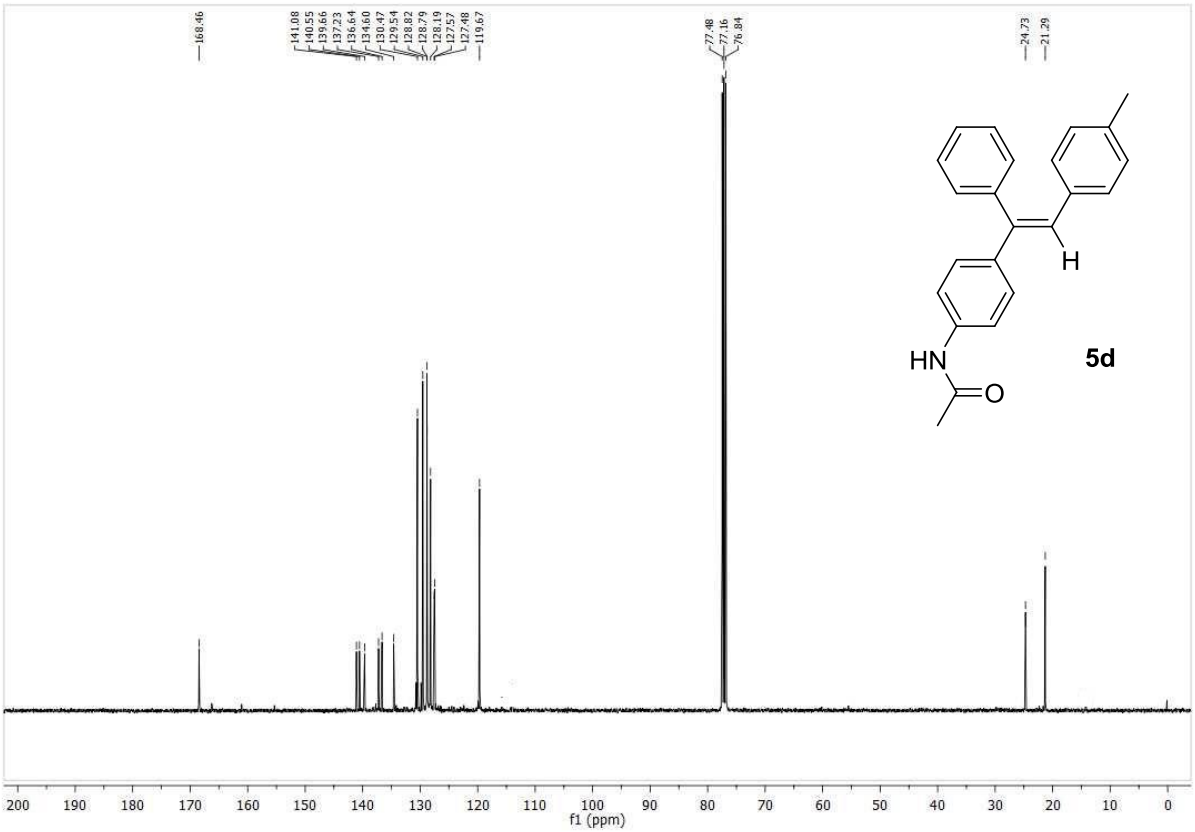
(*E*)-1-(4-fluorophenyl)-1-phenyl-2-(4-methoxyphenyl)ethylene



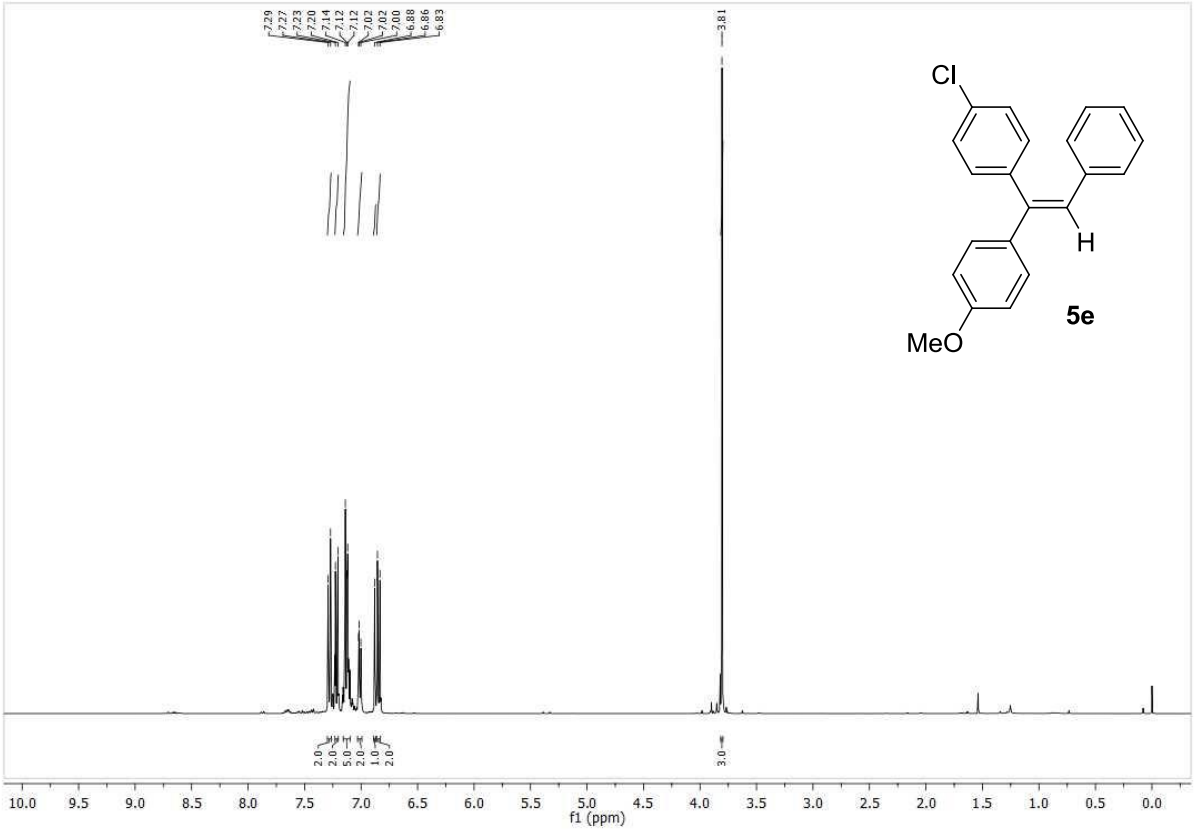


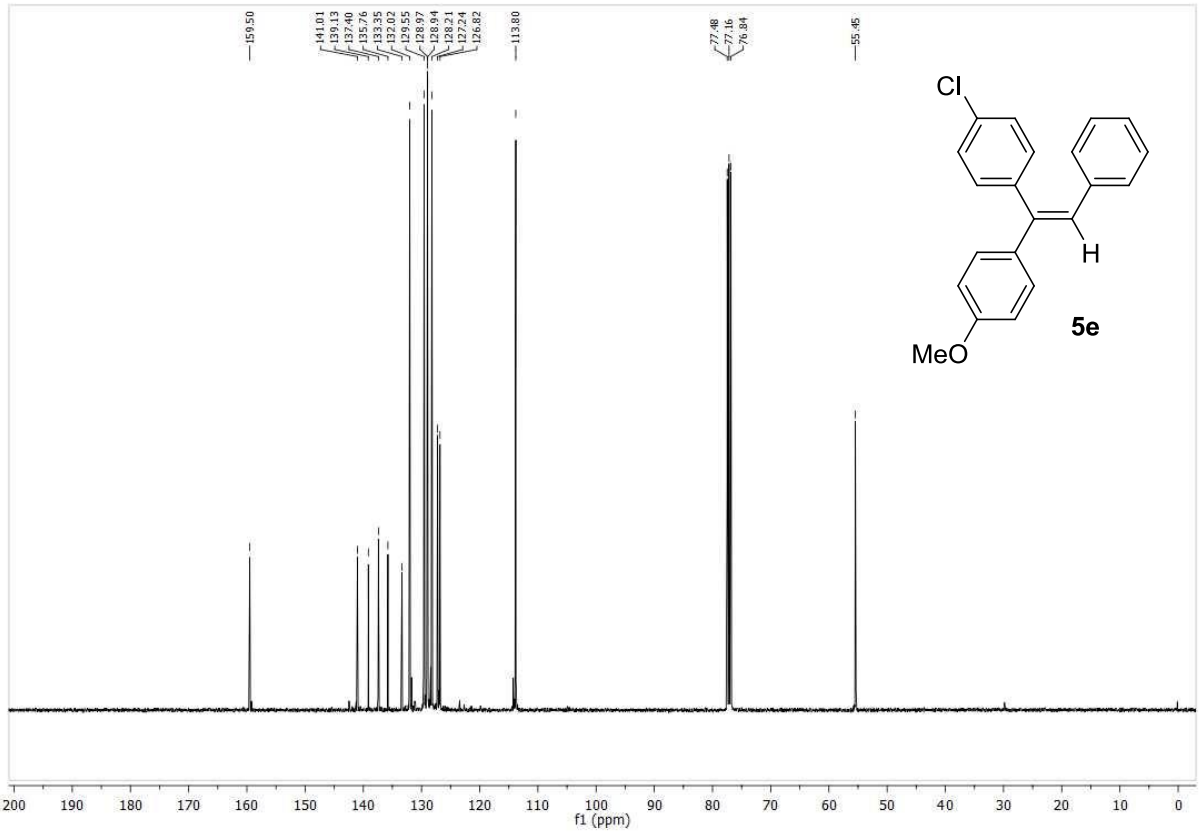
(*E*)-1-(4-acetamidophenyl)-1-phenyl-2-(4-methylphenyl)ethylene



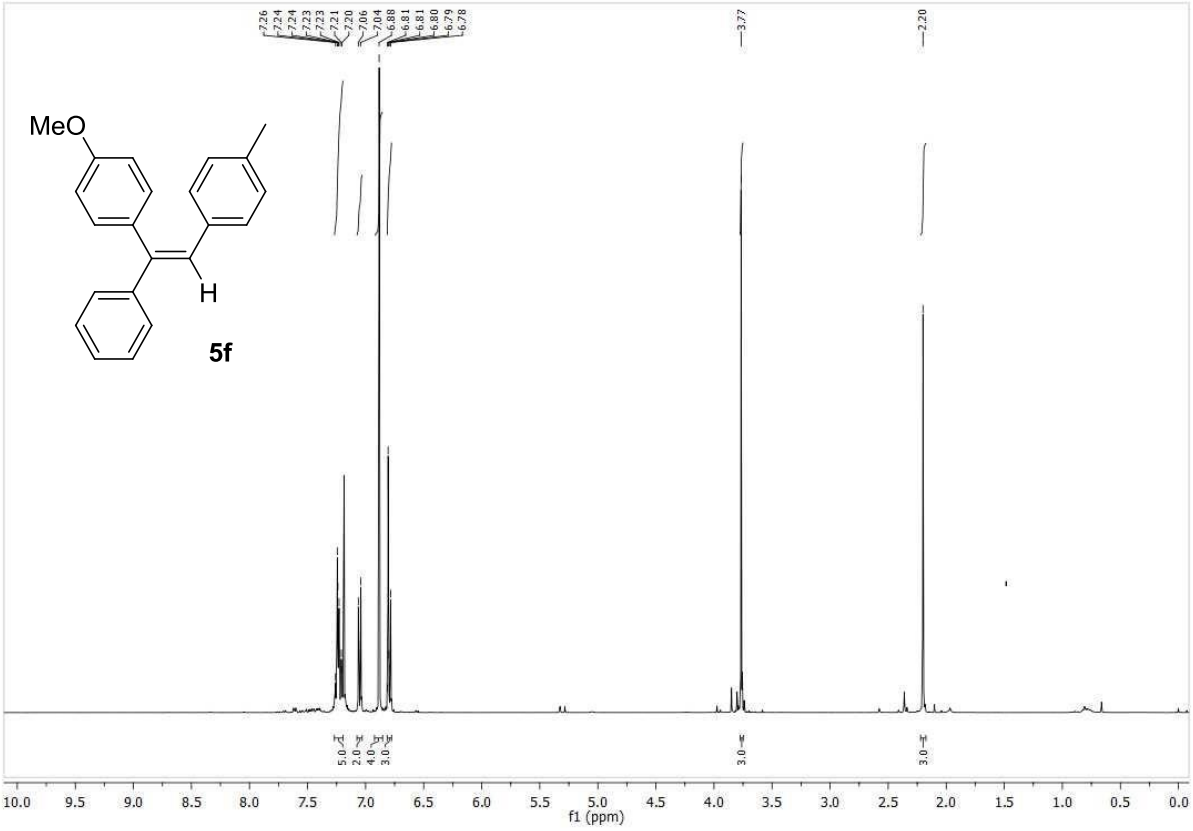


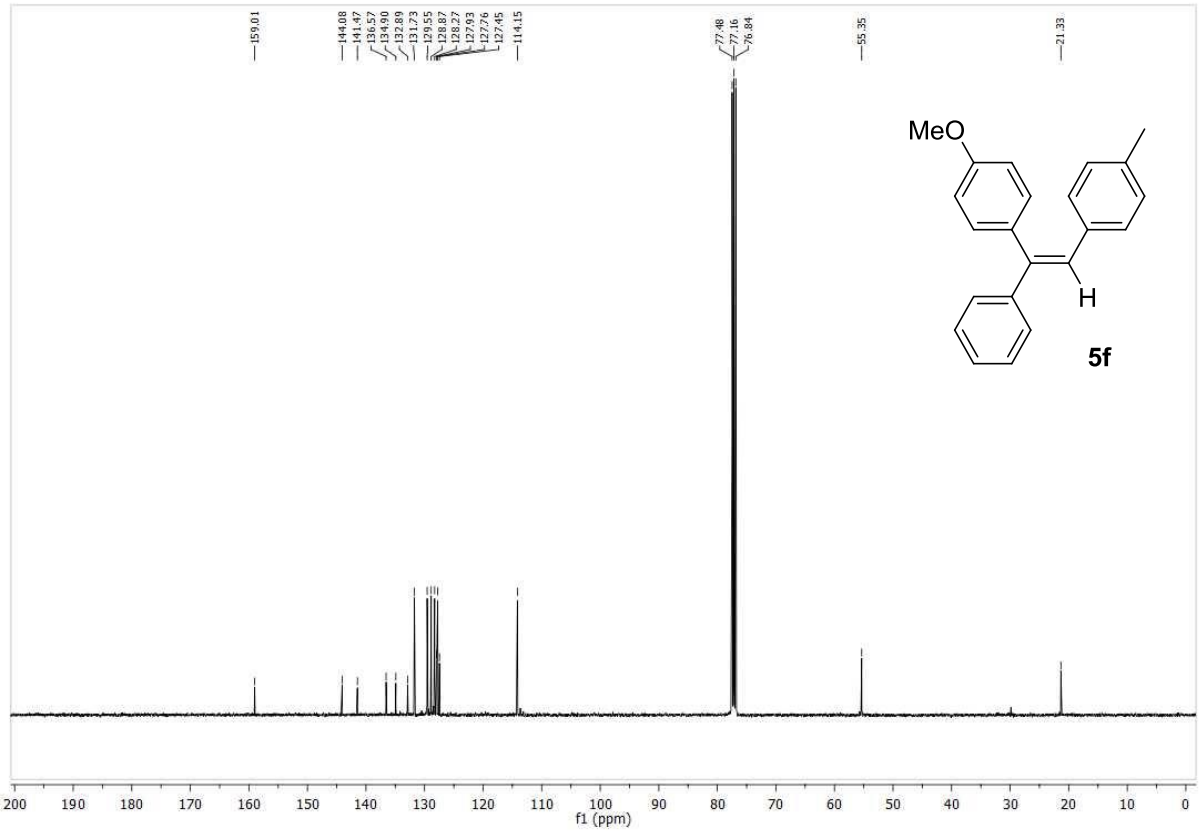
(*Z*)-1-(4-chlorophenyl)-1-(4-methoxyphenyl)-2-phenylethylene



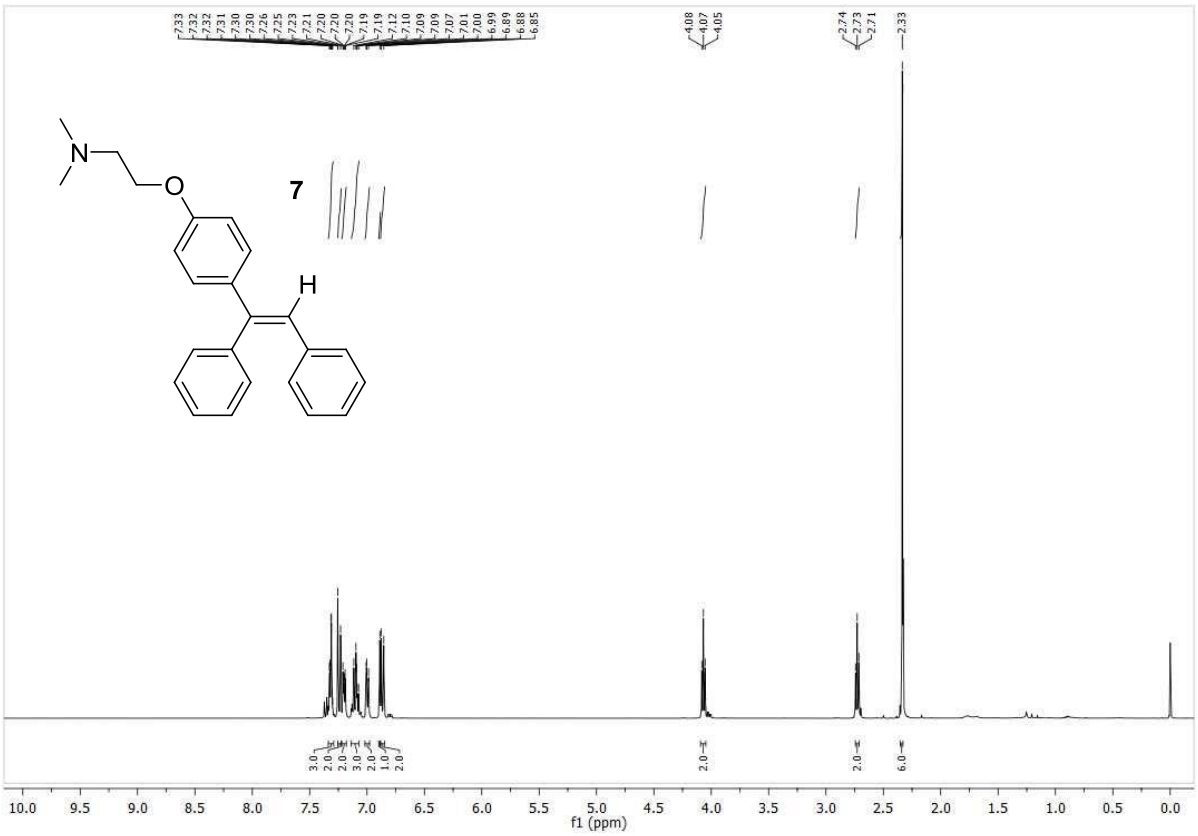


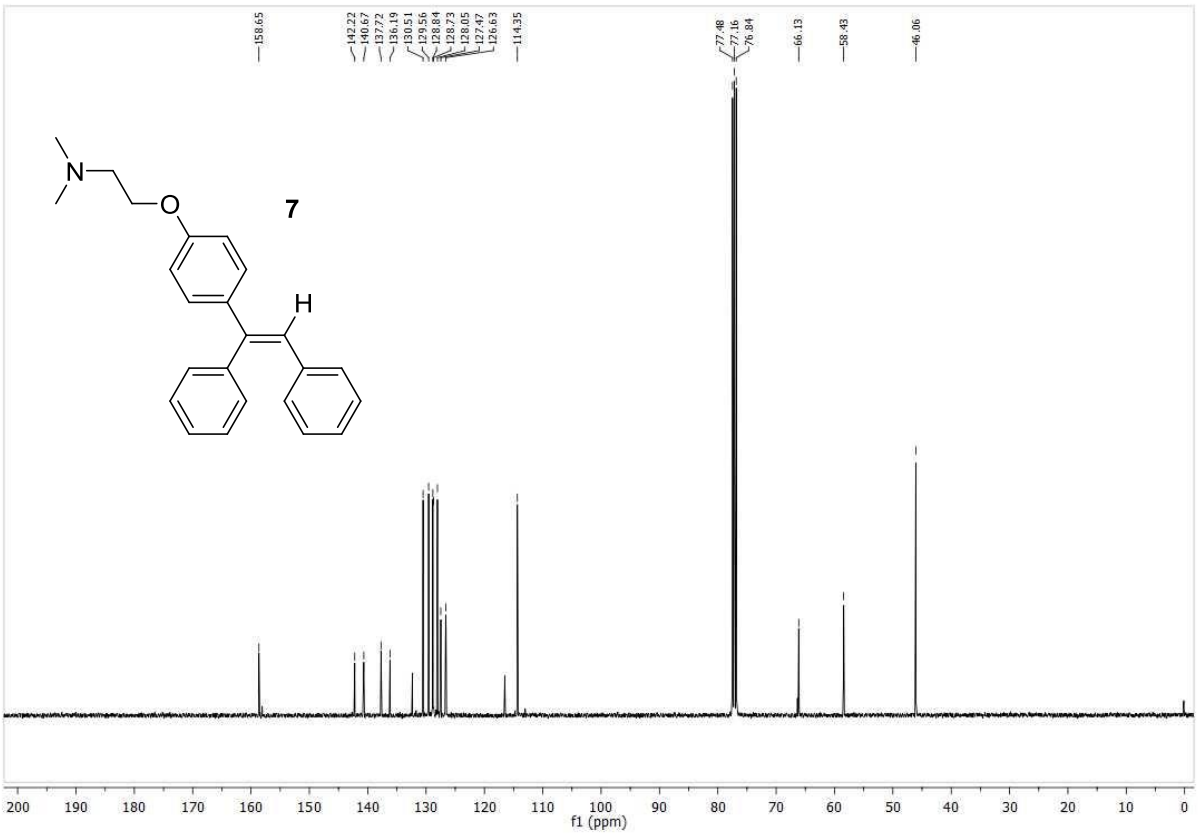
(*Z*)-1-(4-methoxyphenyl)-1-phenyl-2-(4-methylphenyl)ethylene



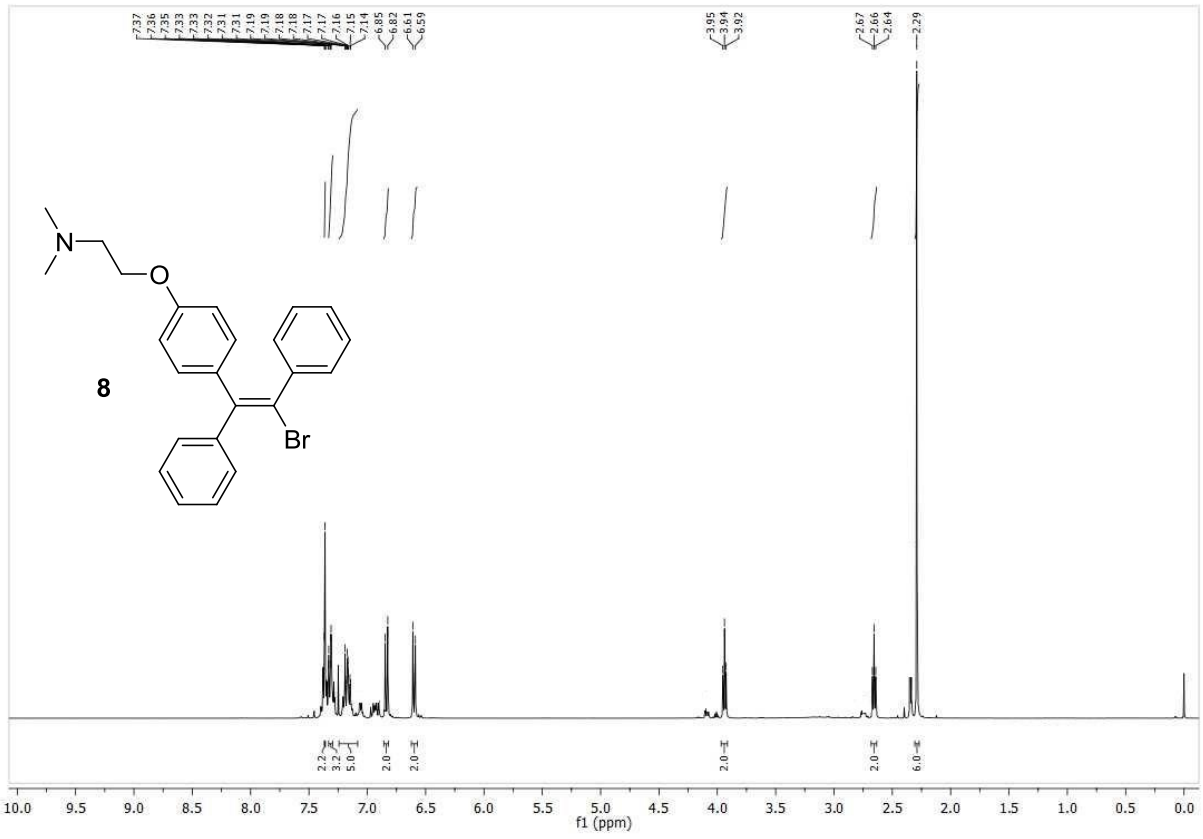


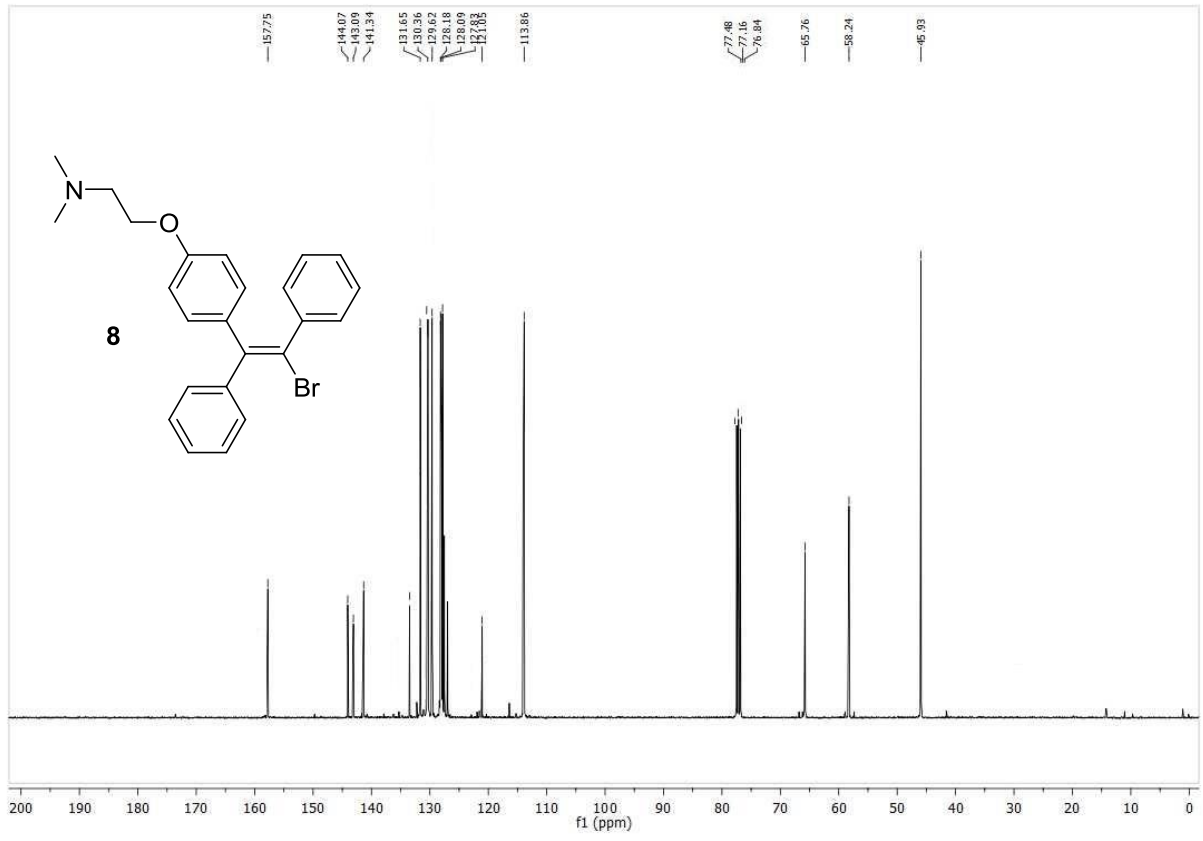
(*E*)-1-(4-phenoxy-*N*,*N*-dimethylethylamine)-1,2-diphenylethylene



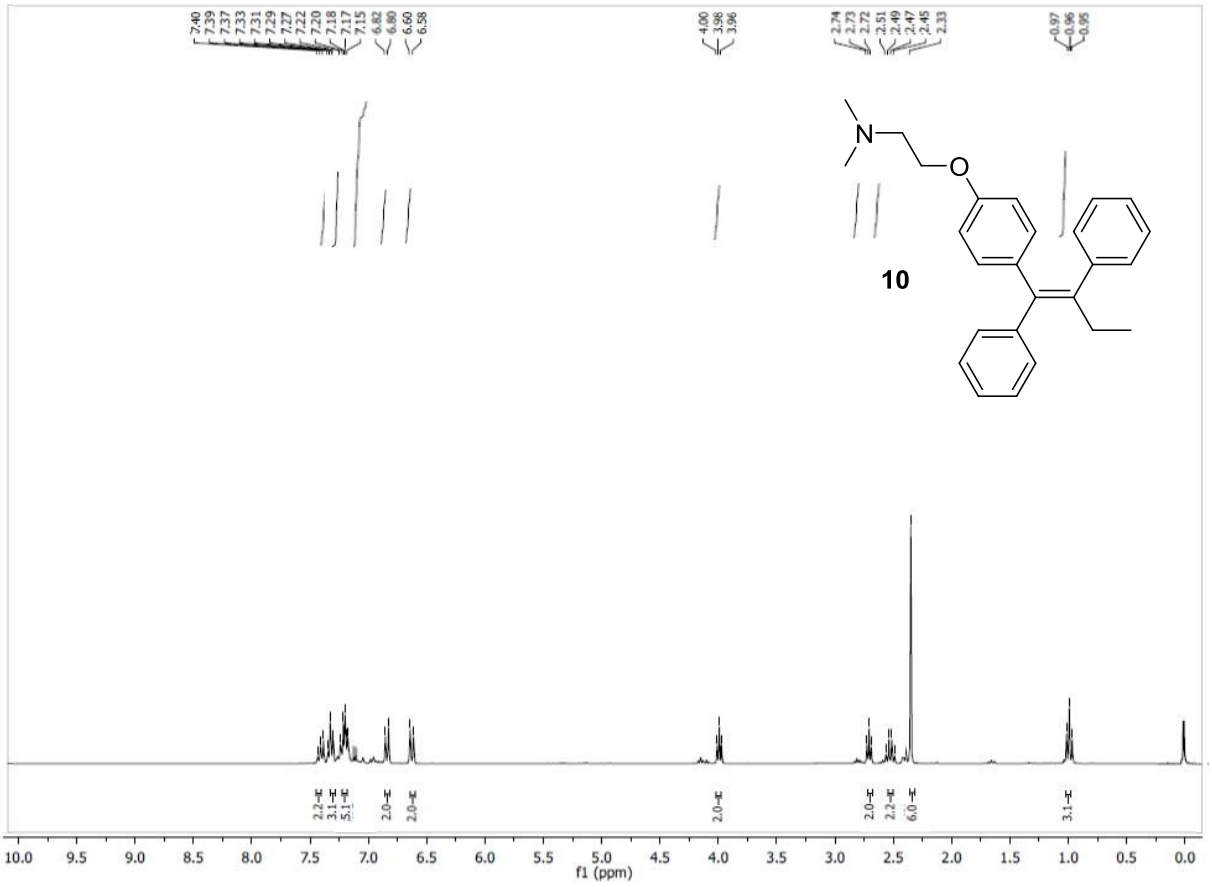


(*E*)-1-Bromo-2-{4-[2-(*N*,*N*-dimethylamino)ethoxy]phenyl}-1,2-diphenylethylene





(*Z*)-Tamoxifen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6.60
6.58
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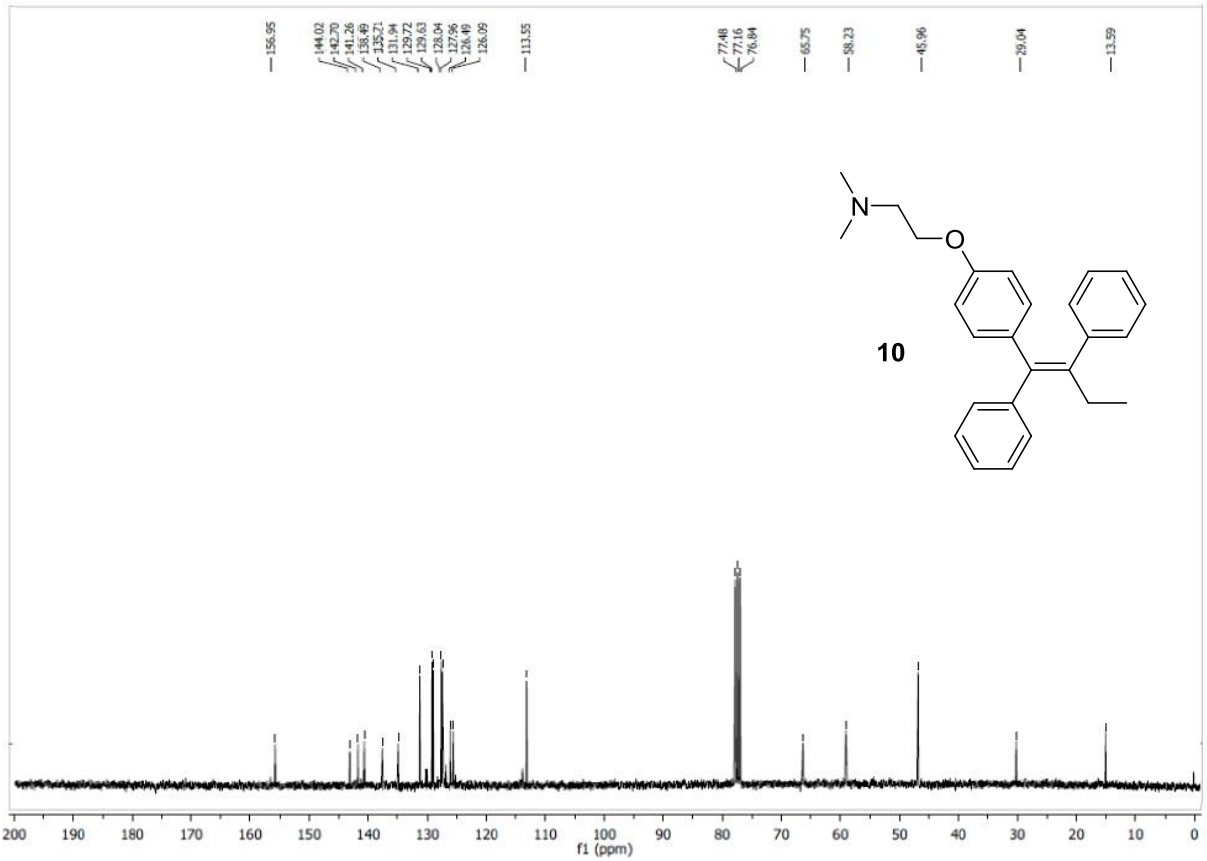
2.73
2.72
2.51
2.49
2.47
2.45
2.33
0.97
0.96
0.95
N
O
10
2.2
3.1
5.1
2.0
2.0
2.0
2.0
2.2
6.0
3.1
f1 (ppm)


156.95
144.02
142.70
141.26
138.49
135.21
131.94
129.72
129.63
128.04
127.96
126.49
126.09
113.55
77.48
77.16
76.84
65.75
58.23
45.96
29.04
13.59
N
O
10
f1 (ppm)

V/ References

[1] Compared to commercial product.

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