Supporting information

Transition Metal Free Domino Sequential Synthesis of (*E*)-Stilbenes, Biarylmethanes and Biarylethers using Et_2AlCl as a Lewis Acid†

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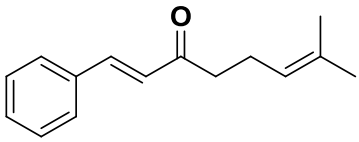
General information

All reagents were purchased from commercial suppliers and used without further purification. IR spectra of the compounds were recorded on Perkin-Elmer AC-1 spectrometer. ^{1}H NMR spectra were run on Bruker Advance DPX 300 MHz spectrometer in $CDCl_3$ and TMS was used as internal standard. ESI mass spectra were recorded on JEOL SX 102/DA-6000. Silica gel 230-400 mesh was used as stationary phase to isolate the compounds.

General procedure (I) for monoalkenylation of ketones

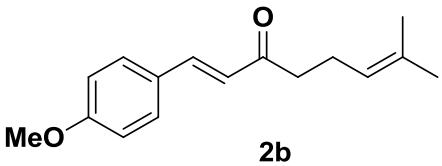
Ketone (1.0 eqv) was added drop wise by syringe to a stirred solution of sodium hydride (2.0 eqv) in DMF (10 mL for 500 mg ketone) at -20°C. The resulting pale yellow solution was stirred for 20 min at -20°C then prenylbromide (2.0 eqv) was added drop wise by syringe. The reaction mixture was stirred for 20 min at this temperature, then the reaction flask was removed from the cooling bath and was allowed to reach to room temperature. The reaction mixture was stirred for 2-5 h at room temperature. Then reaction was quenched by adding ice cold water and extracted three times with ether. Ether part was concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane) as eluent to provide the desired product.

Spectroscopic data of monoalkenylated ketones



2a

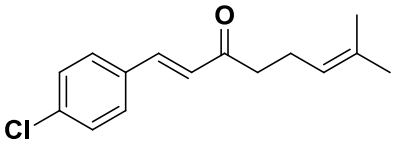
(*E*)-7-methyl-1-phenylocta-1,6-dien-3-one (**2a**) Following the general procedure **I**, **2a** was prepared using *(E)*-4-phenylbut-3-en-2-one (500 mg, 3.4 mmol), sodium hydride (200 mg, 6.8 mmol), 3,3-dimethylallyl bromide (1.0 ml, 6.8 mmol), and DMF (10 ml). The product R_f 0.78 (10% ethylacetate: hexane) was isolated as yellow oil 670 mg (71% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 1.:99). IR (Neat) 3397, 2973, 2365, 1715, 1611, 1449, 1375, 1225, 1165, 979, 749, 704 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.59-7.54 (m, 4H), 7.39-7.37 (m, 2H), 6.81 (d, *J* = 16.0 Hz, 1H), 5.11 (t, *J* = 7.1 Hz, 1H), 2.97-2.76 (m, 2H), 2.53-2.33 (m, 1H), 2.27-2.12 (m, 1H), 1.67 (s, 3H), 1.62 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 203.2 (C=O), 142.1 (CH), 134.9 (C), 133.4 (C), 130.3 (CH), 128.9 (2CH), 128.3 (2CH), 125.7 (CH), 121.7 (CH), 51.0 (CH_2), 30.0 (CH_2), 25.8 (CH_3), 17.8 (CH_3). MS (ESI) *m/z* 215.1 $(M+H)^+$.



2b

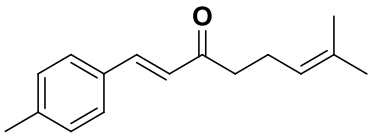
(E)-1-(4-methoxyphenyl)-7-methylocta-1,6-dien-3-one (**2b**) Following the general procedure **I**, **2b** was prepared using *(E)*-4-(4-methoxyphenyl)but-3-en-2-one (500 mg, 2.8 mmol), sodium hydride (136 mg, 5.6 mmol), 3,3-dimethylallyl bromide (0.7 ml, 5.6 mmol), and DMF (10 ml). The product R_f 0.66 (10% ethylacetate: hexane) was isolated as yellow oil 463 mg (67% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 2:98). IR (Neat) 3958, 3679, 3554, 2916, 2835, 2360, 2039, 1600, 1510, 1426, 1364, 1245, 1170, 972, 807, 543, 505 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.52-7.47 (m, 3H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 16.3 Hz, 1H), 5.11 (t, *J* = 8.5 Hz, 1H), 3.82 (s, 3H), 2.92-2.81 (m, 2H), 2.43-2.33 (m, 1H), 2.28-2.18 (m, 1H), 1.68 (s, 3H), 1.62 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 198.2 (C=O), 161.6 (C), 142.8 (CH), 133.1 (C), 129.9 (2CH), 127.0 (C),

124.8 (CH), 123.9 (CH), 114.5 (2CH), 56.5 (CH_3), 48.0 (CH_2), 31.0 (CH_2), 25.3 (CH_3), 18.6 (CH_3). MS (ESI) *m/z* 245.1 $(M+H)^+$.



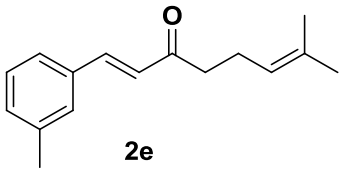
2c

(E)-1-(4-chlorophenyl)-7-methylocta-1,6-dien-3-one (**2c**) Following the general procedure **I**, **2c** was prepared using *(E)*-4-(4-chlorophenyl)but-3-en-2-one (500 mg, 2.77 mmol), sodium hydride (133 mg, 5.54 mmol), 3,3-dimethylallyl bromide (0.7 ml, 5.54 mmol), and DMF (10 ml). The product R_f 0.72 (10% ethylacetate: hexane) was isolated as yellow oil 455 mg (66% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 1.5:98.5). IR (Neat) 3971, 3725, 3472, 3275, 3016, 2281, 1911, 1659, 1483, 1408, 1361, 1254, 1197, 1086, 978, 811, 681, 568, 489 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.47-7.41 (m, 3H), 7.35-7.32 (m, 2H), 6.66 (d, *J* = 16.3 Hz, 1H), 5.13 (t, *J* = 7.1 Hz, 1H), 2.92-2.83 (m, 2H), 2.45-2.35 (m, 1H), 2.29-2.20 (m, 1H), 1.69 (s, 3H), 1.64 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 198.1 (C=O), 142.7 (CH), 135.3 (C), 134.7 (C), 132.1 (C), 129.5 (2CH), 129.1 (2CH), 126.3 (CH), 122.6 (CH), 46.2 (CH_2), 31.5 (CH_2), 25.9 (CH_3), 18.6 (CH_3). MS (ESI) *m/z* 249.1 $(M+H)^+$.



2d

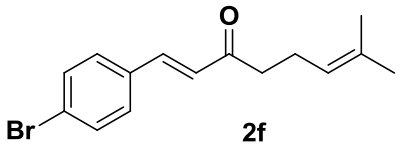
(E)-7-methyl-1-p-tolylocta-1,6-dien-3-one (**2d**) Following the general procedure **I**, **2d** was prepared using *(E)*-4-p-tolylbut-3-en-2-one (500 mg, 3.1 mmol), sodium hydride (150 mg, 6.2 mmol), 3,3-dimethylallyl bromide (0.7 ml, 6.2 mmol), and DMF (10 ml). The product R_f 0.80 (10% ethylacetate: hexane) was isolated as yellow oil 412 mg (58% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 1.5:98.5). IR (Neat) 3841, 3469, 3020, 2924, 2856, 2737, 2370, 1682, 1607, 1512, 1417, 1361, 1258, 1177, 980, 803, 757, 490 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) 7.48-7.37 (m, 3H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 15.9 Hz, 1H), 5.10 (t, *J* = 6.9 Hz, 1H), 2.96-2.88 (m, 2H), 2.44 (s, 3H), 2.39-2.18 (m, 2H), 1.67 (s, 3H), 1.61 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 198.6 (C=O), 143.4 (CH), 140.9 (C), 133.2 (C), 131.6 (C), 129.7 (2CH), 128.6 (2CH), 126.5 (CH), 124.3 (CH), 46.3 (CH_2), 30.3 (CH_2), 25.2 (CH_3), 20.9 (CH_3), 18.3 (CH_3). MS (ESI) *m/z* 229.1 $(M+H)^+$.



2e

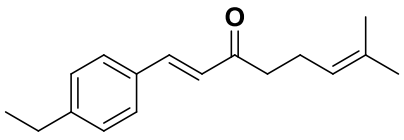
(E)-7-methyl-1-m-tolylocta-1,6-dien-3-one (**2e**) Following the general procedure **I**, **2e** was prepared using *(E)*-4-m-tolylbut-3-en-2-one (500 mg, 3 mmol), Sodium hydride (150 mg, 6 mmol), 3,3-dimethylallyl bromide (0.7 ml, 6 mmol), and DMF (10 ml). The product R_f 0.80 (10% ethylacetate: hexane) was isolated as yellow oil 405 mg (57% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 1.5:98.5). IR (Neat) 3840, 3469, 3020, 2924, 2856, 2737, 2370, 1702, 1607, 1512, 1417, 1361, 1258, 1177, 980, 803, 757, 490 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.67-7.31 (m, 5H), 6.86 (d, *J* = 16.6 Hz,

1H), 5.18 (t, *J* = 7.5 Hz, 1H) 2.97-2.88 (m, 2H), 2.40 (s, 3H), 2.35-2.26 (m, 1H), 2.11-2.03 (m, 1H), 1.68 (s, 3H), 1.64 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 198.2 (C=O), 143.6 (CH), 138.5 (C), 134.1 (C), 131.4 (CH), 130.9 (C), 128.9 (CH), 128.6 (CH), 126.9 (CH), 125.4 (CH), 120.9 (CH), 50.3 (CH), 30.8 (CH_2), 24.8 (CH_3), 21.1 (CH_3), 17.9 (CH_3). MS (ESI) *m/z* 229.1 $(M+H)^+$.



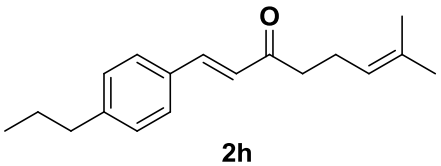
2f

(E)-1-(4-bromophenyl)-7-methylocta-1,6-dien-3-one (**2f**) Following the general procedure **I**, **2f** was prepared using *(E)*-4-(4-bromophenyl)but-3-en-2-one (500 mg, 2.2 mmol), sodium hydride (107 mg, 4.4 mmol), 3,3-dimethylallyl bromide (0.5 ml, 4.4 mmol), and DMF (10 ml). The product R_f 0.82 (10% ethylacetate: hexane) as yellow oil 451 mg (69% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 1:99). IR (Neat) 3377, 3016, 2972, 2360, 1700, 1611, 1520, 1448, 1380, 1220, 1175, 980, 749, 708 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.43-7.38 (m, 3H), 7.32-7.28 (m, 2H), 6.60 (d, *J* = 16.3 Hz, 1H), 5.24 (t, *J* = 6.5 Hz, 1H), 3.03-2.94 (m, 2H), 2.56-2.46 (m, 1H), 2.41-2.32 (m, 1H), 1.81 (s, 3H), 1.75 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 198.6 (C=O), 142.9 (CH), 135.1 (C), 132.3 (2CH), 131.9 (C), 129.7 (2CH), 126.3 (CH), 124.1 (C), 123.5 (CH), 47.1 (CH_2), 30.3 (CH_2), 24.8 (CH_3), 17.7 (CH_3). MS (ESI) *m/z* 293.1 $(M+H)^+$.



2g

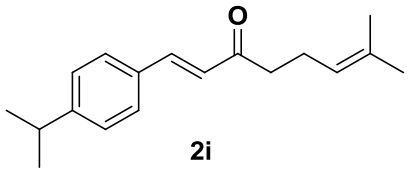
(E)-1-(4-ethylphenyl)-7-methylocta-1,6-dien-3-one (**2g**) Following the general procedure **I**, **2g** was prepared using *(E)*-4-(4-ethylphenyl)but-3-en-2-one (500 mg, 2.9 mmol), sodium hydride (138 mg, 5.8 mmol), 3,3-dimethylallyl bromide (0.7 ml, 5.8 mmol), and DMF (10 ml). The product R_f 0.82 (10% ethylacetate: hexane) was isolated as yellow oil 440 mg (63% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 1:99). IR (Neat) 3369, 3020, 2922, 2856, 2737, 2370, 1680, 1607, 1512, 1418, 1362, 1260, 1177, 980, 920, 910, 803, 757 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.57-7.51 (m, 3H), 7.36-7.34 (m, 2H), 6.78 (d, *J* = 16.1 Hz, 1H), 5.08 (t, *J* = 7.9 Hz, 1H), 2.87-2.78 (m, 2H), 2.64-2.54 (m, 2H), 2.39-2.30 (m, 1H), 2.25-2.16 (m, 1H), 1.65 (s, 3H), 1.59 (s, 3H), 1.16-1.12 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 198.7 (C=O), 146.7 (C), 143.0 (CH), 133.9 (C), 131.1 (C), 129.1 (2CH), 127.2 (2CH), 126.3 (CH), 124.4 (CH), 51.2 (CH_2), 31.4 (CH_2), 28.3 (CH_2), 24.8 (CH_3), 18.5 (CH_3), 13.3 (CH_3). MS (ESI) *m/z* 243.1 $(M+H)^+$.



2h

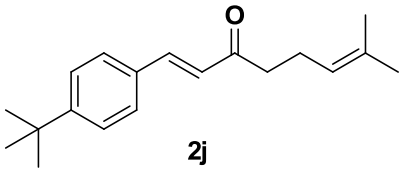
(E)-7-methyl-1-(4-propylphenyl)octa-1,6-dien-3-one (**2h**) Following the general procedure **I**, **2h** was prepared using *(E)*-4-(4-propylphenyl)but-3-en-2-one (500 mg, 2.6 mmol), sodium hydride (127 mg, 5.2 mmol), 3,3-dimethylallyl bromide (0.6 ml, 5.2 mmol), and DMF (10

ml). The product R_f 0.86 (10% ethylacetate: hexane) was isolated as yellow oil 440 mg (65% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.5:99.5). IR (Neat) 3360, 3012, 2920, 2866, 2740, 2380, 1680, 1610, 1511, 1420, 1360, 1262, 1170, 981, 940, 920, 912, 805, 755 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.61-7.55 (m, 3H), 7.40-7.38 (m, 2H), 6.82 (d, *J* = 15.9 Hz, 1H), 5.12 (t, *J* = 8.0 Hz, 1H), 2.91-2.81 (m, 2H), 2.74-2.65 (m, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.44-2.34 (m, 1H), 2.28-2.19 (m, 1H), 1.79 (s, 3H), 1.74 (s, 3H), 1.67-1.53 (m, 3H), 0.91 (t, *J* = 7.3 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ 203.0 (C=O), 144.4 (C), 142.1 (CH), 134.7 (C), 131.4 (C), 128.8 (2CH), 128.2 (2CH), 126.4 (CH), 124.2 (CH), 47.8 (CH_2), 38.1 (CH_2), 31.0 (CH_2), 26.2 (CH_2), 24.8 (CH_3), 18.3 (CH_3), 13.5 (CH_3). MS (ESI) *m/z* 257.2 $(M+H)^+$.



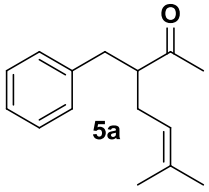
2i

(E)-1-(4-isopropylphenyl)-7-methylocta-1,6-dien-3-one (**2i**) Following the general procedure **I**, **2i** was prepared using *(E)*-4-(4-isopropylphenyl)but-3-en-2-one (500 mg, 2.6 mmol), sodium hydride (127 mg, 5.2 mmol), 3,3-dimethylallyl bromide (0.6 ml, 5.2 mmol), and DMF (10 ml). The product R_f 0.84 (10% ethylacetate: hexane) was isolated as yellow oil 452 mg (66% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 1:99). IR (Neat) 3160, 2940, 2880, 2744, 2390, 1675, 1625, 1490, 1420, 1370, 1362, 1226, 971, 930, 820, 805, 715 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.50-7.42 (m, 3H), 7.21-7.17 (m, 2H), 6.66 (d, *J* = 16.2 Hz, 1H), 4.96 (t, *J* = 7.2 Hz, 1H), 2.93-2.81 (m, 1H), 2.74-2.65 (m, 2H), 2.28-2.13 (m, 1H), 2.10-2.04 (m, 1H), 1.66 (s, 3H), 1.63 (s, 3H), 1.26 (d, *J* = 6.4 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ 198.7 (C=O), 151.8 (C), 143.7 (CH), 132.0 (C), 130.9 (C), 128.4 (2CH), 127.0 (2CH), 126.2 (CH), 121.4 (CH), 51.9 (CH_2), 34.1 (CH), 30.7 (CH_2), 25.7 (CH_3), 23.7 ($2CH_3$), 17.9 (CH_3). MS (ESI) *m/z* 257.1 $(M+H)^+$.



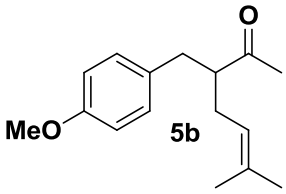
2j

(E)-1-(4-tert-butylphenyl)-7-methylocta-1,6-dien-3-one (**2j**) Following the general procedure **I**, **2j** was prepared using *(E)*-4-(4-tert-butylphenyl)but-3-en-2-one (500 mg, 2.47 mmol), sodium hydride (118 mg, 4.94 mmol), 3,3-dimethylallyl bromide (0.6 ml, 4.94 mmol), and DMF (10 ml). The product R_f 0.90 (10% ethylacetate: hexane) was isolated as yellow oil 468 mg (70% yield) by column chromatography on silica gel (230-400 mesh) using (hexane). IR (Neat) 3130, 2980, 2860, 2790, 1665, 1620, 1510, 1470, 1375, 1370, 1220, 970, 930, 840, 710 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.75-7.72 (m, 3H), 7.47-7.44 (m, 2H), 6.78 (d, *J* = 15.4 Hz, 1H), 5.08 (t, *J* = 7.3 Hz, 1H), 2.87-2.78 (m, 2H), 2.40-2.30 (m, 1H), 2.25-2.15 (m, 1H), 1.65 (s, 3H), 1.59 (s, 3H), 1.39 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ 201.7 (C=O), 152.8 (C), 143.2 (CH), 132.4 (C), 131.9 (C), 128.2 (2CH), 126.3 (2CH), 126.0 (CH), 124.2 (CH), 44.1 (CH_2), 34.3 (C), 31.4 ($3CH_3$), 30.7 (CH_2), 24.6 (CH_3), 17.9 (CH_3). MS (ESI) *m/z* 271.2 $(M+H)^+$.

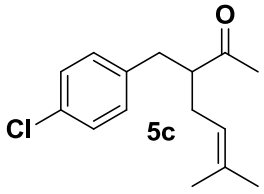


5a

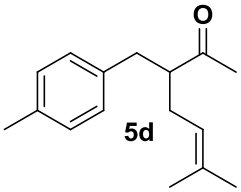
3-benzyl-6-methylhept-5-en-2-one (**5a**) Following the general procedure **I**, **5a** was prepared using benzyl acetone (**4a**) (500 mg, 3.3 mmol), Sodium hydride (200 mg, 6.6 mmol) ,3,3-dimethylallyl bromide (1.0 ml, 6.6 mmol), and DMF (10 ml). The product R_f 0.70 (10% ethylacetate: hexane) was isolated as yellow oil 450 mg (70% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 3:97). IR (Neat) 3914, 3752, 3414, 3022, 2926, 2366, 2336, 1708, 1653, 1495, 1451, 1370, 1219, 1161, 764, 701, 699 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.28-7.14 (m, 5H), 5.08 (t, *J* = 6.1 Hz, 1H), 2.94-2.65 (m, 3H), 2.36-2.19 (m, 2H), 2.00 (s, 3H), 1.71 (s, 3H), 1.59 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 212.1(C=O), 139.8(C), 134.0(C), 128.8(2CH), 128.4(2CH), 126.2(CH), 120.9(CH), 54.8(CH), 37.3(CH_2), 30.5(CH_2), 30.2(CH_3), 25.8(CH_3), 17.8(CH_3). MS (ESI) *m/z* 217.3 $(M+H)^+$.



3-(4-methoxybenzyl)-6-methylhept-5-en-2-one (**5b**) Following the general procedure **I**, **5b** was prepared using 4-methoxybenzyl acetone (**4b**) (500 mg, 2.8 mmol), sodium hydride (134 mg, 5.6 mmol), 3,3-dimethylallyl bromide (0.7 ml, 5.6 mmol), and DMF (10 ml). The product R_f 0.64 (10% ethylacetate: hexane) was isolated as yellow oil 422 mg (61% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 4:96). IR (Neat) 3903, 3852, 3682, 3441, 2925, 2820, 2367, 2336, 1702, 1650, 1490, 1450, 1370, 1229, 1170, 768, 710, 682 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.18 (t, *J* = 8.3 Hz, 1H), 3.83 (s, 3H), 3.04-2.75 (m, 3H), 2.47-2.25 (m, 2H), 2.09 (s, 3H), 1.81 (s, 3H), 1.69 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 209.5 (C=O), 158.5 (C), 133.1 (C), 130.8 (C), 128.9 (2CH), 122.9 (CH), 114.2 (2CH), 55.7 (CH_3), 49.5 (CH), 36.7 (CH_2), 30.4 (CH_2), 29.2 (CH_3), 24.5 (CH_3), 17.6 (CH_3). MS (ESI) *m/z* 247.1 $(M+H)^+$.

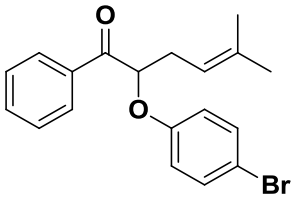


3-(4-chlorobenzyl)-6-methylhept-5-en-2-one (**5c**) Following the general procedure **I**, **5c** was prepared using 4-chloro benzyl acetone (4c) (500 mg, 2.7 mmol), sodium hydride (130 mg, 5.4 mmol) 3,3-dimethylallyl bromide (0.6 ml, 5.4 mmol), and DMF (10 ml). The product R_f 0.66 (10% ethylacetate: hexane) was isolated as yellow oil 444 mg (65% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 4:96). IR (Neat) 3122, 2930, 2866, 1710, 1643, 1485, 1471, 1380, 1225, 961, 777, 760, 711, 690 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2H), 7.29-7.23 (m, 2H), 5.16 (t, *J* = 7.6 Hz, 1H), 3.03-2.73 (m, 3H), 2.44-2.24 (m, 2H), 2.08 (s, 3H), 1.78 (s, 3H), 1.68 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ 209.8 (C=O), 137.5 (C), 133.5 (C), 132.3 (C), 130.3 (2CH), 129.1 (2CH), 123.3 (CH), 49.9 (CH), 37.0 (CH_2), 30.7 (CH_2), 29.6 (CH_3), 24.8 (CH_3), 17.9 (CH_3). MS (ESI) *m/z* 251.1 $(M+H)^+$.



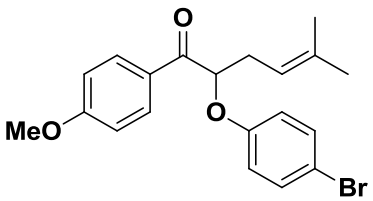
5d

6-methyl-3-(4-methylbenzyl)hept-5-en-2-one (**5d**) Following the general procedure **I**, **5d** was prepared using 4-methylbenzyl acetone (**4d**) (500 mg, 3 mmol), sodium hydride (144 mg, 6 mmol), 3,3-dimethyl allylbromide (0.7 ml, 6 mmol), and DMF (10 ml). The product R_f 0.74 (10% ethylacetate: hexane) was isolated as yellow oil 462 mg (74% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 2:98). IR (Neat) 3070, 2920, 2860, 1705, 1623, 1485, 1461, 1375, 1225, 1180, 864, 700 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.27-7.21 (m, 4H), 5.18 (t, *J* = 7.9 Hz, 1H), 3.04-2.74 (m, 3H), 2.50-2.41 (m, 1H), 2.34 (s, 3H), 2.31-2.25 (m, 1H), 2.09 (s, 3H), 1.80 (s, 3H), 1.69 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ 209.5 (C=O), 136.9 (C), 136.2 (C), 133.1 (C), 129.2 (2CH), 128.5 (2CH), 122.9 (CH), 49.6 (CH), 36.7 (CH_2), 30.4 (CH_2), 29.2 (CH_3), 24.5 (CH_3), 20.8 (CH_3), 17.6 (CH_3). MS (ESI) *m/z* 231.1 $(M+H)^+$.



8a

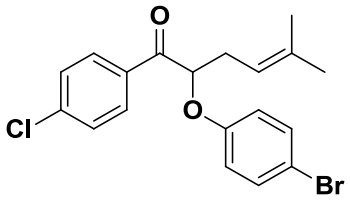
2-(4-bromophenoxy)-5-methyl-1-phenylhex-4-en-1-one (**8a**) Following the general procedure **I**, **8a** was prepared using 2-(4-bromophenoxy)-1-phenylethanone (**7a**) (500 mg, 1.7 mmol), sodium hydride (82 mg, 3.4 mmol), 3,3-dimethylallyl bromide (0.4 ml, 3.4 mmol), and DMF (10 ml).The product R_f 0.46 (10% ethylacetate: hexane) was isolated as yellow oil 412 mg (67% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 5:95). IR (Neat) 3118, 2932, 2843, 2812, 2360, 1688, 1600, 1510, 1466, 1374, 1170, 1155, 1047, 957, 843, 760, 669, 656 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.52-7.35 (m, 3H), 7.32 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 5.29-5.20 (m, 2H), 2.52 (t, *J* = 6.1 Hz, 2H), 1.71 (s, 3H), 1.61 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 201.5 (C=O), 156.3 (C), 134.4 (C), 133.4 (C), 132.7 (CH), 132.0 (2CH), 128.9 (2CH), 128.3 (2CH), 119.9 (CH), 117.4 (2CH), 114.5 (C), 79.0 (C), 31.4 (CH_2), 24.5 (CH_3), 17.6 (CH_3). MS (ESI) *m/z* 359.1 $(M+H)^+$.



8b

2-(4-bromophenoxy)-1-(4-methoxyphenyl)-5-methylhex-4-en-1-one (**8**) Following the general procedure **I**, **8b** was prepared using 2-(4-bromophenoxy)-1-(4-methoxyphenyl) ethanone (**7b**) (500 mg, 1.5 mmol), sodium hydride (70 mg, 3 mmol), 3,3-dimethylallyl

bromide (0.5 ml, 3 mmol), and DMF (10 ml).The product R_f 0.42 (10% ethylacetate: hexane) was isolated as yellow oil 420 mg (69% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 6:94). IR (Neat) 3117, 2930, 2840, 2810, 2365, 1698, 1601, 1512, 1468, 1375, 1300, 1274, 1220, 1173, 1150, 1043, 950, 840, 760, 669, 655 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.30-5.19 (m, 2H), 3.86 (s, 3H), 2.75 (t, *J* = 6.6 Hz, 2H), 1.70 (s, 3H), 1.60 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ 196.6 (C=O), 164.0 (C), 157.0 (C), 135.5 (C), 132.3 (2C), 132.2 (2CH), 127.3 (C), 118.3 (C), 117.0 (2CH), 113.9 (2CH), 113.5 (C), 81.5 (C), 55.5 (CH_3), 32.3 (CH_2), 25.7 (CH_3), 18.0 (CH_3). MS (ESI) *m/z* 389.1 $(M+H)^+$.



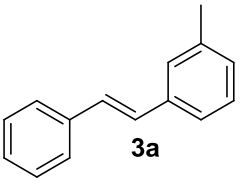
8c

2-(4-bromophenoxy)-1-(4-chlorophenyl)-5-methylhex-4-en-1-one (**8c**) Following the general procedure **I**, **8c** was prepared using 2-(4-bromophenoxy)-1-(4-methoxyphenyl) ethanone (**7c**) (500 mg, 1.53 mmol), sodium hydride (74 mg, 3.06 mmol), 3,3-dimethylallyl bromide (0.4 ml, 3.06 mmol), and DMF (10 ml). The product R_f 0.44 (10% ethylacetate: hexane) was isolated as yellow oil 402 mg (66% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 5:95). IR (Neat) 3110, 2940, 2830, 2815, 2367, 1695, 1602, 1514, 1462, 1376, 1170, 1160, 1044, 952, 847, 760, 679, 650 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 5.28-5.17 (m, 2H), 2.75 (t, *J* = 6.8 Hz, 2H), 1.70 (s, 3H), 1.67 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 201.5 (C=O), 156.4 (C), 141.9 (C), 134.5 (C), 132.7 (C), 132.0 (2CH), 129.4 (2CH), 128.7 (2CH), 120.0 (CH), 117.5 (2CH), 114.5 (C), 79.0 (C), 31.4 (CH_2), 24.5 (CH_3), 17.6 (CH_3). MS (ESI) *m/z* 393.0 $(M+H)^+$.

General procedure (II) for synthesis of (*E*)-Stilbenes, Biaryl methanes and Biaryl ethers

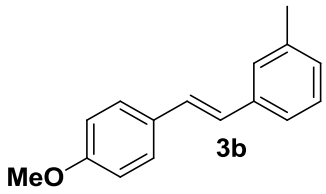
To a stirred solution of monoalkenylated ketone (0.46 mmol) in dry dioxane (2 ml) was added 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane) at room temperature under nitrogen and stirred for 2.5-10 hours. The formation of products was monitored by TLC and long range UV lamp (365 nm wave length). Ice-cold water (10 mL) was added to quench the reaction. The aqueous phase was then extracted with diethyl ether (4 x 10 mL) and the combined organic phases washed with brine (10 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to leave a yellowish crude oil, that was purified by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane) to provide the desired product.

Spectroscopic data of (*E*)-Stilbenes, Biaryl methanes and Biaryl ethers

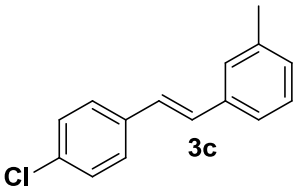


3a

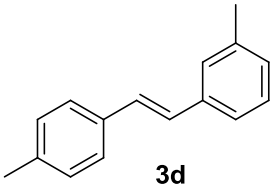
(E)-1-methyl-3-styrylbenzene (**3a**) Following the general procedure **II**, **3a** was prepared using **2a** (89 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.44 (5% ethylacetate: hexane) was isolated as yellow oil 50 mg (61% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.5:99.5) as eluant. IR (Neat): ν_{max} 3021, 2921, 1600, 1495, 966, 785, 695 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.35 (t, *J* = 1.3 Hz, 1H), 7.30-7.25 (m, 3H), 7.22-7.12 (m, 4H), 7.04-7.00 (m, 1H), 2.35 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 137.9 (C), 137.8 (C), 136.1 (C), 131.7 (CH), 130.4 (CH), 129.6 (CH), 129.2 (2CH), 128.3 (C), 128.3 (3CH), 127.8 (CH), 127.0 (CH), 21.4 (CH_3). MS (ESI) *m/z* 195.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{15}H_{14}$: 194.1096; found:195.1099 $(M+H)^+$. IR and ^{1}H-NMR data was identical with that previously reported (L. Wang, H. Li and P. Li, *Tetrahedron*, 2009, **65**, 364).



(E)-1-(4-methoxystyryl)-3-methylbenzene (**3b**). Following the general procedure **II**, **3b** was prepared using **2b** (112 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.40 (5% ethylacetate: hexane) was isolated as yellow oil 53 mg (52% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 1.5:98.5) as eluant. IR (Neat) 3020, 2831, 1605, 1510, 1460, 1365, 1290, 1180, 1030, 968, 830, 690 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 1.2 Hz, 1H), 7.24-7.14 (m, 2H), 7.15 (d, *J* = 16.3 Hz, 1H), 7.04 (d, *J* = 16.3 Hz, 1H), 6.98-6.95 (m, 1H), 6.85 (d, *J* = 7.5 Hz, 2H), 3.77 (s, 3H), 2.31 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 161.7 (C), 138.5 (C), 138.5 (C), 132.4 (CH), 131.1 (CH), 130.2 (2CH), 129.6 (C), 129.0 (CH), 128.9 (CH), 128.4 (CH), 127.6 (CH), 115.4 (2CH), 56.9 (CH_3), 22.1 (CH_3). MS (ESI) *m/z* 225.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{16}H_{16}O$: 224.1201; found: 225.1503 $(M+H)^+$.

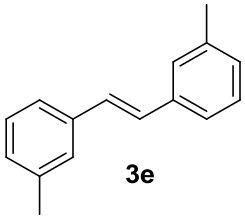


(E)-1-(4-chlorostyryl)-3-methylbenzene (**3c**). Following the general procedure **II**, **3c** was prepared using **2c** (114 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.41 (5% ethylacetate: hexane) was isolated as yellow oil 61 mg (58% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 1:99) as eluant. IR (Neat) 3030, 2861, 1610, 1500, 1460, 978, 840, 680 755. cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39-7.33 (m, 4H), 7.31-7.23 (m, 3H), 7.22 (d, *J* = 16.3 Hz, 1H), 7.17 (d, *J* = 16.3 Hz, 1H), 7.06-7.02 (m, 1H), 2.37 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ 137.5 (C), 137.4 (C), 135.2 (C), 134.9 (C), 131.3 (CH), 130.0 (CH), 129.1 (2CH), 128.9 (2CH), 127.9 (CH), 127.8 (CH), 127.4 (CH), 126.5 (CH), 20.9 (CH_3). MS (ESI) *m/z* 229.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{15}H_{13}Cl$: 228.0706; found: 229.0876 $(M+H)^+$.



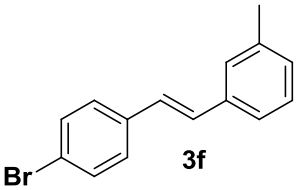
3d

(E)-1-methyl-3-(4-methylstyryl)benzene (**3d**) Following the general procedure **II**, **3d** was prepared using **2d** (105 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.45 (5% ethylacetate: hexane) was isolated as yellow oil 60 mg (62% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.3:99.7) as eluant. IR (Neat) 3080, 2963, 2880, 1615, 1488, 970, 850 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.26-7.17 (m, 4H), 7.07 (d, *J* = 16.2 Hz, 1H), 6.98 (d, *J* = 16.1 Hz, 1H), 2.39 (s, 3H), 2.38 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 139.4 (C), 137.7 (2C), 134.0 (C), 131.5 (CH), 130.3 (CH), 129.2 (2CH), 128.2 (3CH), 128.1 (CH), 127.6 (CH), 126.8 (CH), 21.2 (CH_3), 21.1 (CH_3). MS (ESI) *m/z* 209.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{16}H_{16}$: 208.1252; found: 209.1262 $(M+H)^+$.



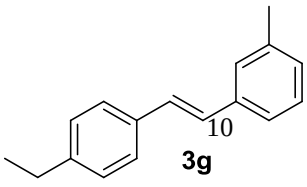
3e

(E)-1,2-dim-tolylethene (**3e**) Following the general procedure **II**, **3e** was prepared using **2e** (105 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.45 (5% ethyl-acetate: hexane) was isolated as yellow oil 63 mg (63% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.3:99.7) as eluant. IR (Neat) 3080, 2963, 2880, 1625, 1488, 970, 850 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.49-7.43 (m, 4H), 7.36-7.28 (m, 4H), 7.03 (s, 3H), 2.37 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 137.7 (2C), 137.6 (2C), 131.5 (2CH), 130.2 (2CH), 128.2 (2CH), 128.1 (2CH), 126.7 (2CH), 21.2 ($2CH_3$). MS (ESI) *m/z* 209.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{16}H_{16}$: 208.1252; found: 209.1252 $(M+H)^+$.



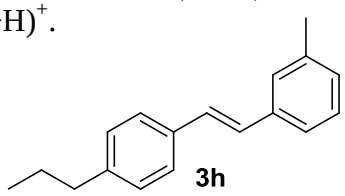
3f

(E)-1-(4-bromostyryl)-3-methylbenzene (**3f**). Following the general procedure **II**, **3f** was prepared using **2f** (134 mg, 0.46 mmmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.46 (5% ethylacetate: hexane) was isolated as yellow oil 72 mg (57% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.3:99.7) as eluant. IR (Neat) 2955, 2870, 1620, 1585, 1450, 1375, 1262, 690 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 1.4 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.27-7.22 (m, 2H), 7.21 (d, *J* = 16.1 Hz, 1H), 7.15 (d, *J* = 16.1 Hz, 1H), 7.04-7.00 (m, 1H), 2.35(s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 137.7 (C), 137.6 (C), 135.7 (C), 132.2 (2CH), 131.5 (CH), 130.2 (CH), 129.5 (2CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 126.7 (CH), 124.1 (C), 21.2 (CH_3). MS (ESI) *m/z* 273.0 $(M+H)^+$. HRMS (ESI) calculated for $C_{15}H_{13}Br$: 272.0201; found 273.0222 $(M+H)^+$.



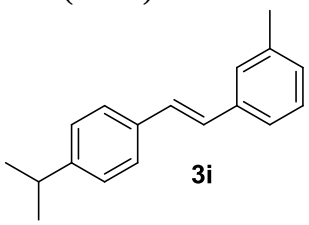
3g

(E)-1-(4-ethylstyryl)-3-methylbenzene (**3g**). Following the general procedure **II**, **3g** was prepared using **2g** (150 mg, 0.46 mmmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.45 (5% ethylacetate: hexane) was isolated as yellow oil 88 mg (65% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.3:99.7) as eluant. IR (Neat) 3030, 2960, 2872, 2850, 1620, 1590, 1466, 1380, 1420, 1375, 1262, 830, 722 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 1.3 Hz, 1H), 7.31-7.27 (m, 2H), 7.24-7.22 (m, 1H), 7.19-7.16 (m, 1H), 7.06-7.02 (m, 1H), 2.65 (q, *J* = 6.5 Hz, 2H), 2.37 (s, 3H), 1.33 (t, *J* = 6.6 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ 146.5 (C), 137.7 (C), 137.6 (C), 133.9 (C), 131.5 (CH), 130.2 (CH), 129.1 (2CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 127.2 (2CH), 126.7 (CH), 28.2 (CH_2), 21.2 (CH_3), 13.2 (CH_3). MS (ESI) *m/z* 223.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{17}H_{18}$: 222.1409; found: 223.1510 $(M+H)^+$.



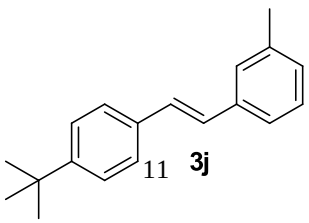
3h

(E)-1-methyl-3-(4-propylstyryl)benzene (**3h**). Following the general procedure **II**, **3h** was prepared using **2h** (118 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.47 (5% ethylacetate: hexane) was isolated as yellow oil 75 mg (69% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.2:99.8) as eluant. IR (Neat) 3000, 2950, 2930, 2875, 2855, 1625, 1595, 1456, 1422, 1390, 1376, 1265, 820, 725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 1.3 Hz, 1H), 7.32-7.25 (m, 2H), 7.24-7.22 (m, 3H), 7.20-7.17 (m, 1H), 7.06-7.03 (m, 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.78 (s, 3H), 1.80-1.69 (m, 2H), 1.07 (t, *J* = 6.6 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.2 (C), 137.7 (2C), 134.3 (C), 131.6 (CH), 130.3 (CH), 128.2 (CH), 128.1 (CH), 127.8 (2CH), 127.7 (2CH), 126.8 (CH), 38.2 (CH_2), 24.5 (CH_2), 21.2 (CH_3), 13.0 (CH_3). MS (ESI) *m/z* 237.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{18}H_{20}$: 236.1565; found: 237.1585 $(M+H)^+$.



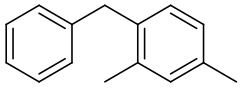
3i

(E)-1-(4-isopropylstyryl)-3-methylbenzene (**3i**). Following the general procedure **II**, **3i** was prepared using **2i** (118 mg) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.47 (5% ethylacetate: hexane) was isolated as yellow oil 72 mg (67% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.2:99.8) as eluant. IR (Neat) 3000, 2955, 2900, 2866, 1621, 1585, 1452, 1422, 1377, 1330, 1255, 825, 725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.47-7.39 (m, 4H), 7.30-7.21 (m, 4H), 7.12-7.08 (m, 1H), 6.94 (d, *J* = 15.2 Hz, 1H), 3.13-3.01 (m, 1H), 2.36 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 148.4 (C), 138.1 (C), 137.5 (C), 135.1 (C), 128.6 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.1 (CH), 126.7 (2CH), 126.5 (2CH), 123.6 (CH), 33.9 (CH), 23.9 ($2CH_3$), 21.5 (CH_3). MS (ESI) *m/z* 237.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{18}H_{20}$: 236.1565; found: 237.1565 $(M+H)^+$.



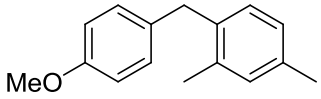
11 **3j**

(E)-1-(4-tert-butylstyryl)-3-methylbenzene (**3j**). Following the general procedure **II**, **3j** was prepared using **2j** (115 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.48 (5% ethylacetate: hexane) was isolated as yellow oil 62 mg (58% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.2:99.8) as eluant. IR (Neat) 3100, 2965, 2861, 1626, 1585, 1500, 1380, 830 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34-7.32 (m, 3H), 7.25-7.23 (m, 4H), 7.21 (d, *J* = 16.2 Hz, 1H), 7.13 (d, *J* = 16.2 Hz, 1H), 7.02-6.98 (m, 1H), 2.33 (s, 3H), 1.37 (m, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 152.5 (C), 137.6 (C), 137.5 (C), 132.2 (C), 131.4 (CH), 130.1 (CH), 128.0 (CH), 127.9 (3CH), 127.5 (CH), 126.7 (CH), 125.9 (2CH), 34.2 (C), 31.3 ($3CH_3$), 21.1 (CH_3). MS (ESI) *m/z* 251.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{19}H_{22}$: 250.1722; found: 251.1832 $(M+H)^+$.



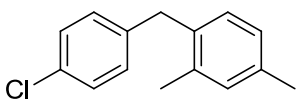
6a

1-benzyl-2,4-dimethylbenzene (**6a**) Following the general procedure **6a** was prepared using **5a** (99 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.44 (5% ethylacetate: hexane) was isolated as pale yellow oil 78 mg (72% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.3:99.7) as eluant. IR (Neat) 2924, 2864, 1662, 1496, 1451, 1217 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39-7.24 (m, 7H), 7.13 (brs, 1H), 4.08 (s, 2H), 2.45 (s, 3H), 2.34 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 140.8 (C), 136.5 (C), 136.0 (C), 135.9 (C), 131.2 (CH), 130.0 (CH), 128.8 (2CH), 128.5 (2CH), 126.7 (CH), 125.9 (CH), 39.2 (CH_2), 21.1 (CH_3), 19.7 (CH_3). MS (ESI) *m/z* 197.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{15}H_{16}$: 196.1252; found: 197.14300 $(M+H)^+$.



6b

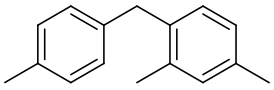
1-(4-methoxybenzyl)-2,4-dimethylbenzene (**6b**) Following the general procedure **II**, **6b** was prepared using **5b** (113 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.40 (5% ethylacetate: hexane) was isolated as yellow oil 81 mg (78% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.5:99.5) as eluant. IR (Neat) 2930, 2860, 2820, 1660, 1495, 1452, 1260, 1220 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.3 Hz, 2H), 7.09-7.01 (m, 3H), 6.96 (d, *J* = 7.5 Hz, 2H), 3.78 (s, 5H), 3.73 (s, 2H), 2.33 (s, 3H), 2.30 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 159.1 (C), 137.6 (C), 135.7 (C), 135.5 (C), 132.8 (C), 130.6 (CH), 130.1 (2CH), 129.9 (CH), 128.1 (CH), 114.5 (2CH), 56.0 (CH_3), 37.9 (CH_2), 21.2 (CH_3), 20.4 (CH_3). MS (ESI) *m/z* 227.3 $(M+H)^+$. HRMS (ESI) calculated for $C_{16}H_{18}O$: 226.1358 $(M+H)^+$; found: 227.1355 $(M+H)^+$.



6c

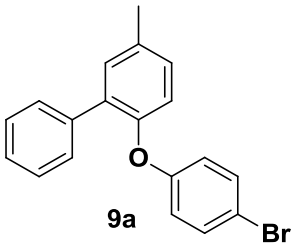
1-(4-chlorobenzyl)-2,4-dimethylbenzene (**6c**) Following the general procedure **II**, **6c** was prepared using **5c** (115 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.42 (5% ethylacetate: hexane) was isolated as yellow oil 77 mg (72% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.5:99.5) as eluant. IR (Neat) 2920, 2862, 1661, 1490, 1450, 1222, 800 cm^{-1}.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.5 Hz, 2H), 7.16-7.13 (m, 3H), 7.06-7.01 (m, 2H), 3.71 (s, 2H), 2.34 (s, 3H), 2.32 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 140.5 (C), 138.4 (C), 136.5 (C), 136.3 (C), 133.3 (C), 131.4 (CH), 130.8 (2CH), 130.1 (2CH), 128.9 (CH), 38.7 (CH_2), 21.9 (CH_3), 21.2 (CH_3). MS (ESI) *m/z* 231.1 $(M+H)^+$. HRMS (ESI) calculated for $C_{15}H_{15}Cl$: 230.0862; found: 231.0964 $(M+H)^+$.



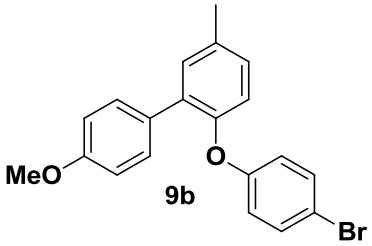
6d

2,4-dimethyl-1-(4-methylbenzyl)benzene (**6d**) Following the general procedure **II**, **6d** was prepared using **5d** (106 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.46 (5% ethylacetate: hexane) was isolated as yellow oil 67 mg (74% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 0.2:99.8) as eluant. IR (Neat) 2922, 2866, 1655, 1498, 1455, 1218 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.19-7.13 (m, 5H), 7.07-7.03 (m, 2H), 3.72 (s, 2H), 2.36 (s, 6H), 2.34 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 139.3 (C), 137.6 (C), 137.5 (C), 135.7 (C), 135.5 (C), 130.6 (CH), 129.9 (CH), 129.7 (2CH), 129.1 (2CH), 128.1 (CH), 37.9 (CH_2), 21.2 (CH_3), 21.1 (CH_3), 20.4 (CH_3). MS (ESI) *m/z* 197.2 $(M+H)^+$. HRMS (ESI) calculated for $C_{15}H_{16}$: 196.1252; found: 197.2270 $(M+H)^+$.



9a

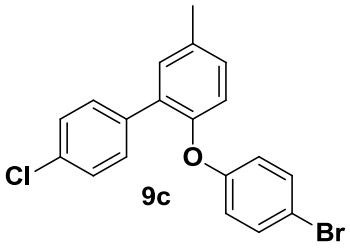
2-(4-bromophenoxy)-5-methylbiphenyl (**9a**) Following the general procedure **II**, **9a** was prepared using **8a** (167 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.48 (10% ethylacetate: hexane) was isolated as brown oil 95 mg (59% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 4:96) as eluant. IR (Neat) 2963, 1615, 1270, 700 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2H), 7.52 (d, *J* = 1.4 Hz, 1H), 7.44-7.30 (m, 5H), 7.19-7.17 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 2H), 2.33 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.8 (C), 147.6 (C), 136.3 (C), 134.9 (C), 133.3 (C), 132.2 (2CH), 129.7 (CH), 129.4 (2CH), 128.6 (2CH), 127.6 (CH), 126.9 (CH), 120.4 (2CH), 118.3 (CH), 116.9 (C), 21.0 (CH_3). MS (ESI) *m/z* 339.0 $(M+H)^+$. HRMS (ESI) calculated for $C_{19}H_{15}BrO$: 338.0306; found: 339.0308 $(M+H)^+$.



9b

2-(4-bromophenoxy)-4'-methoxy-5-methylbiphenyl (**9b**) Following the general procedure **II**, **9b** was prepared using **8b** (179 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.44 (10% ethylacetate: hexane) was isolated as yellow oil 102 mg

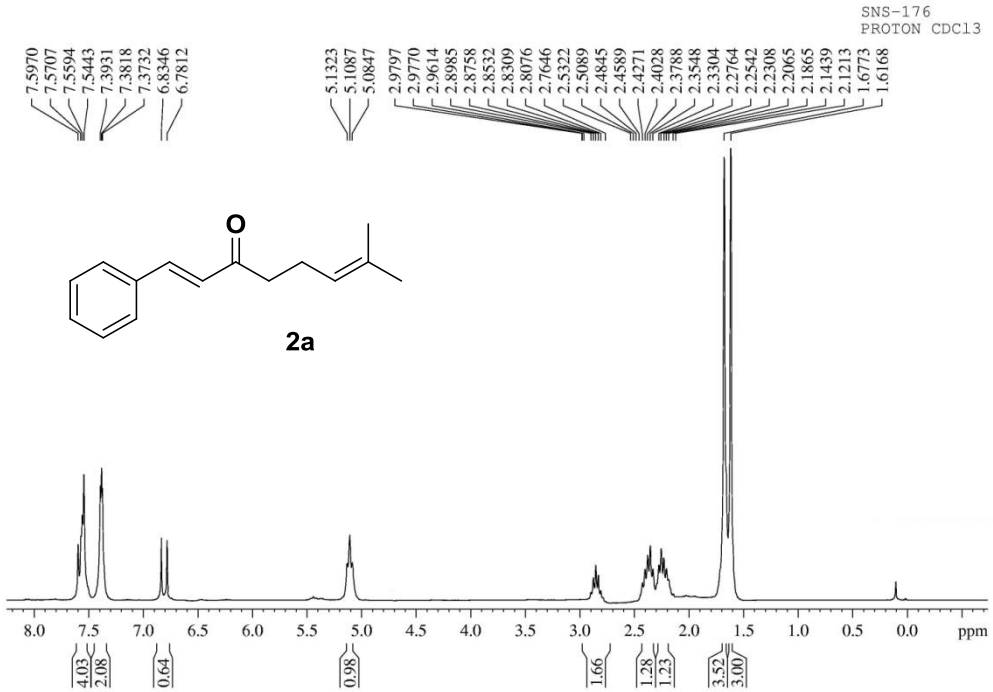
(54% yield) by column chromatography on silica (230-400 mesh) gel using (ethyl acetate/hexane, 6:94) as eluant. IR (Neat) 2960, 2874, 2815, 1606, 1458, 1285, 1270, 700 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 1.5 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.27-7.18 (m, 2H), 7.05 (d, *J* = 7.3 Hz, 2H), 6.81 (d, *J* = 7.7 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 159.2 (C), 154.9 (C), 147.7 (C), 134.9 (C), 133.4 (C), 132.3 (2CH), 131.8 (2CH), 129.8 (CH), 127.9 (C), 127.7 (CH), 120.5 (2CH), 118.4 (CH), 117.1 (C), 114.7 (2CH), 56.0 (CH_3), 21.2 (CH_3). MS (ESI) *m/z* 369.0 $(M+H)^+$. HRMS (ESI) calculated for $C_{20}H_{17}BrO_2$: 368.0412; found: 369.0614 $(M+H)^+$.



9c

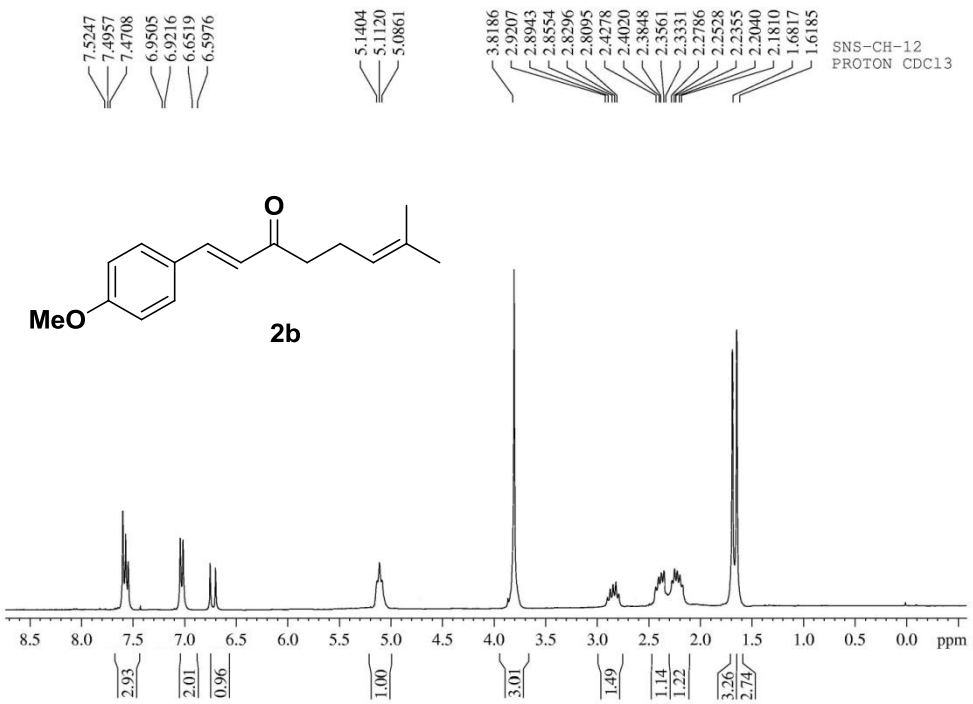
2-(4-bromophenoxy)-4'-chloro-5-methylbiphenyl (**9c**) Following the general procedure **II**, **9c** was prepared using **8c** (180 mg, 0.46 mmol) and 0.70 ml (0.70 mmol) of Et_2AlCl (1.0 M in hexane). The product R_f 0.46 (10% ethylacetate: hexane) was isolated as yellow oil 92 mg (57% yield) by column chromatography on silica gel (230-400 mesh) using (ethyl acetate/hexane, 5:95) as eluant. IR (Neat) 2875, 2820, 1603, 1456, 1290, 1270, 715 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 1.5 Hz, 1H), 7.49-7.43 (m, 4H), 7.23-7.20 (m, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 2H), 2.37 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.8 (C), 147.6 (C), 134.8 (C), 133.7 (C), 133.6 (C), 133.3 (C), 132.2 (2CH), 130.6 (2CH), 129.7 (CH), 128.8 (2CH), 127.6 (CH), 120.4 (2CH), 118.2 (CH), 116.9 (C), 21.0 (CH_3). MS (ESI) *m/z* 373.0 $(M+H)^+$. HRMS (ESI) calculated for $C_{19}H_{14}BrClO$: 372.0463 $(M+H)^+$; found: 373.0453 $(M+H)^+$.

Copies of ^{1}H-NMR and ^{13}C-NMR



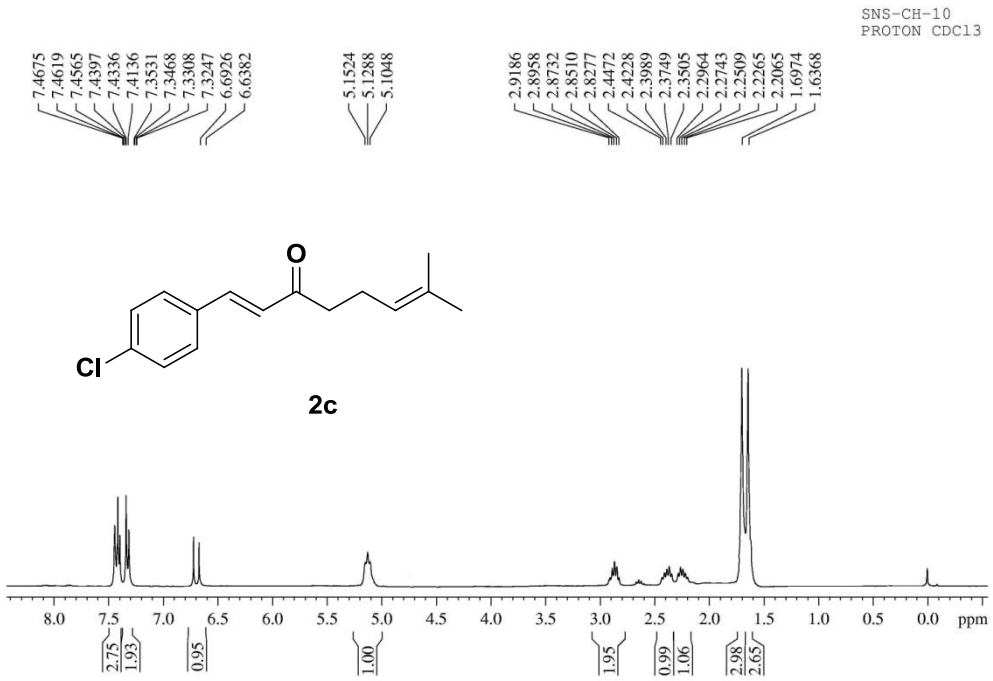
^{1}H NMR spectrum of 2a (300 MHz, $CDCl_3$)

^{13}C NMR spectrum of 2a (75 MHz, $CDCl_3$)

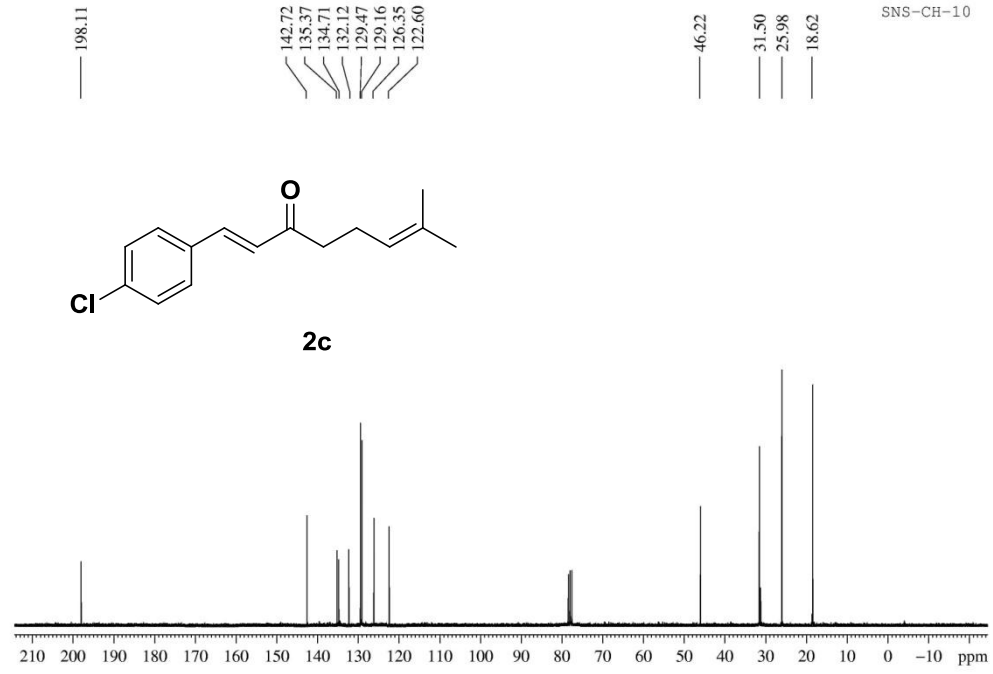


^{1}H NMR spectrum of 2b (300 MHz, $CDCl_3$)

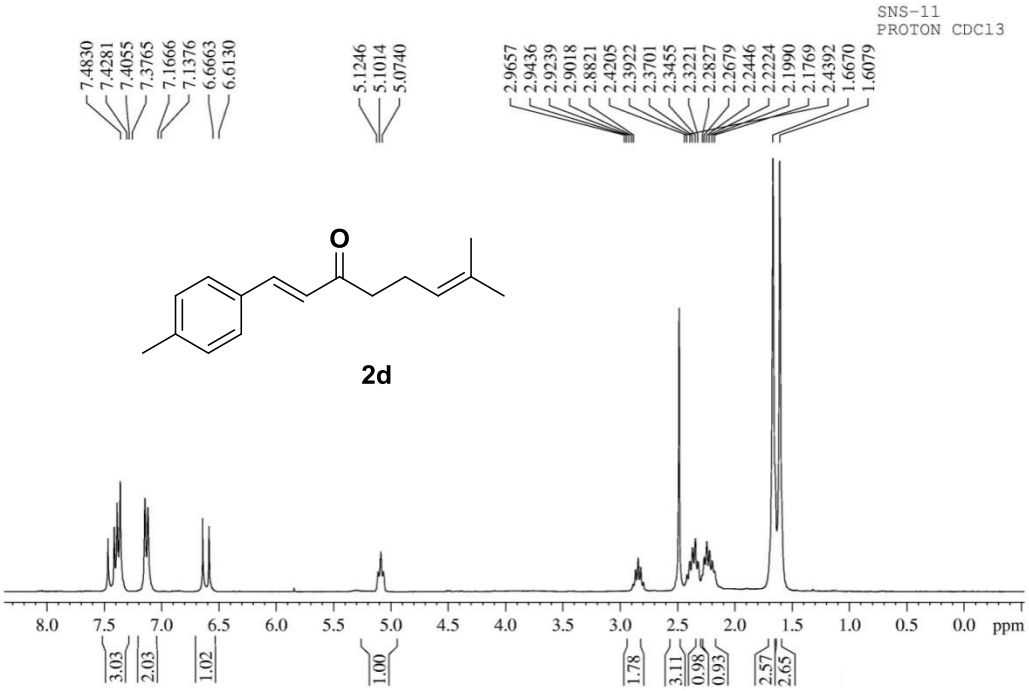
^{13}C NMR spectrum of 2b (75 MHz, $CDCl_3$)



^{1}H NMR spectrum of 2c (300 MHz, $CDCl_3$)

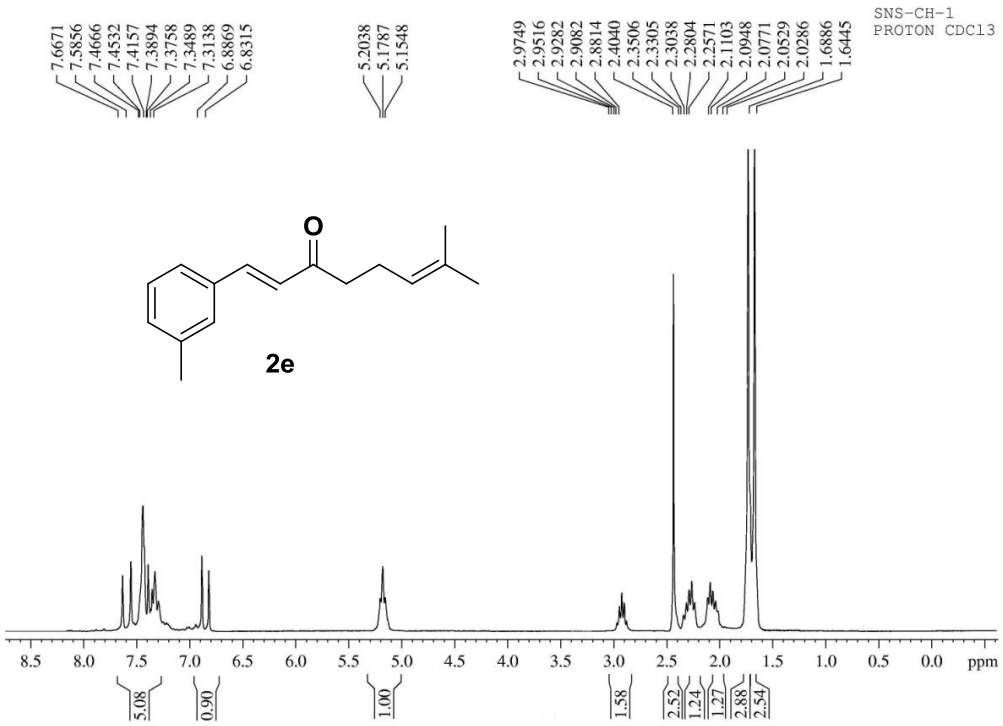


^{13}C NMR spectrum of 2c (75 MHz, $CDCl_3$)

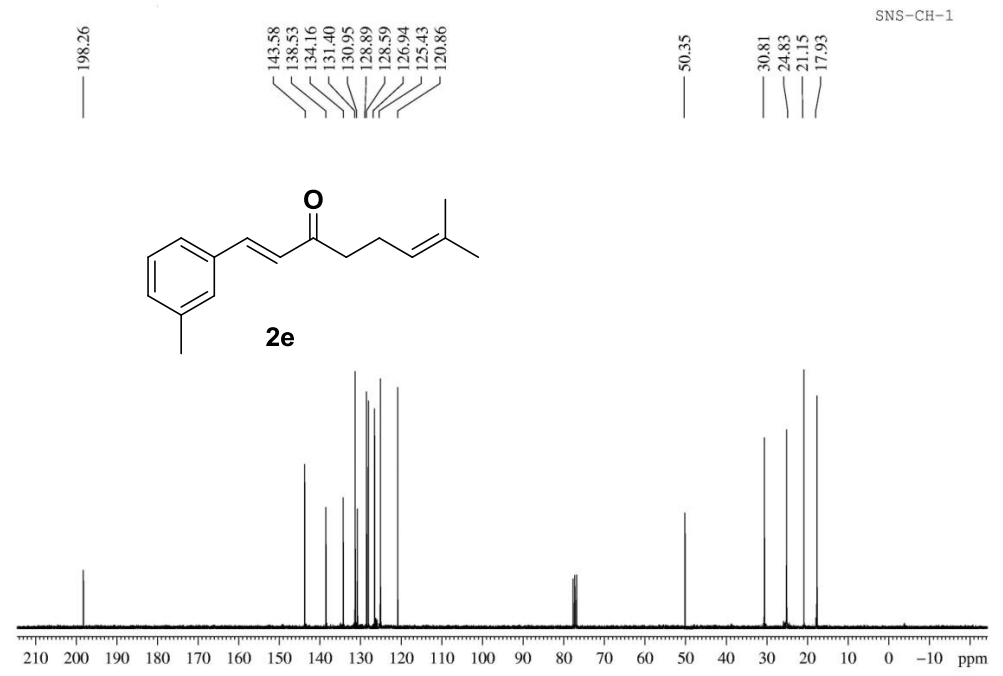


^{1}H NMR spectrum of 2d (300 MHz, $CDCl_3$)

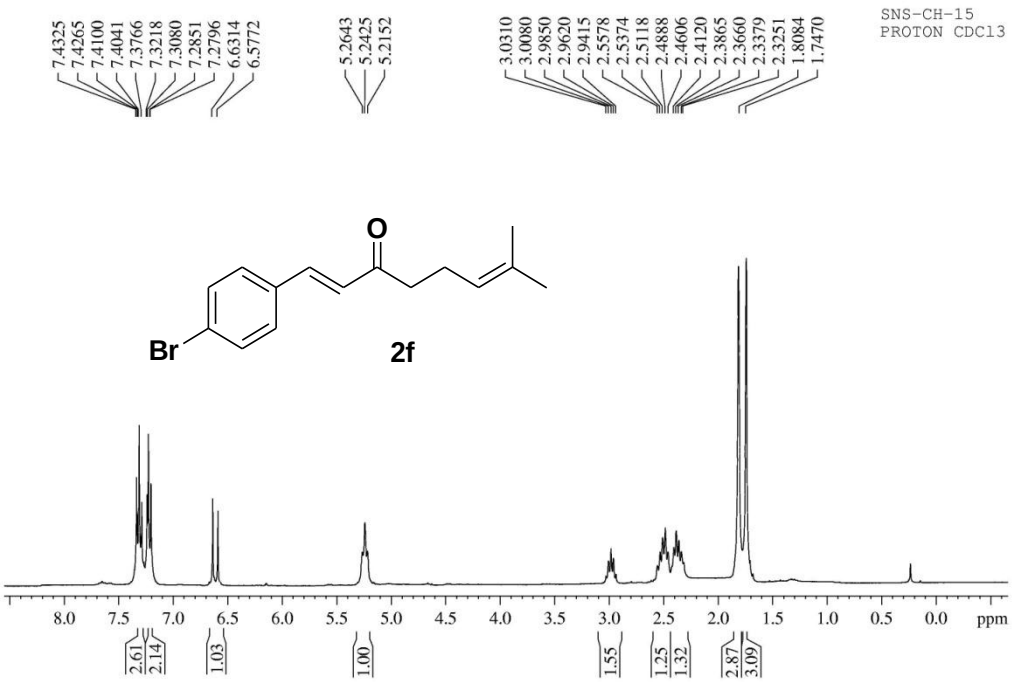
^{13}C NMR spectrum of 2d (75 MHz, $CDCl_3$)



^{1}H NMR spectrum of 2e (300 MHz, $CDCl_3$)

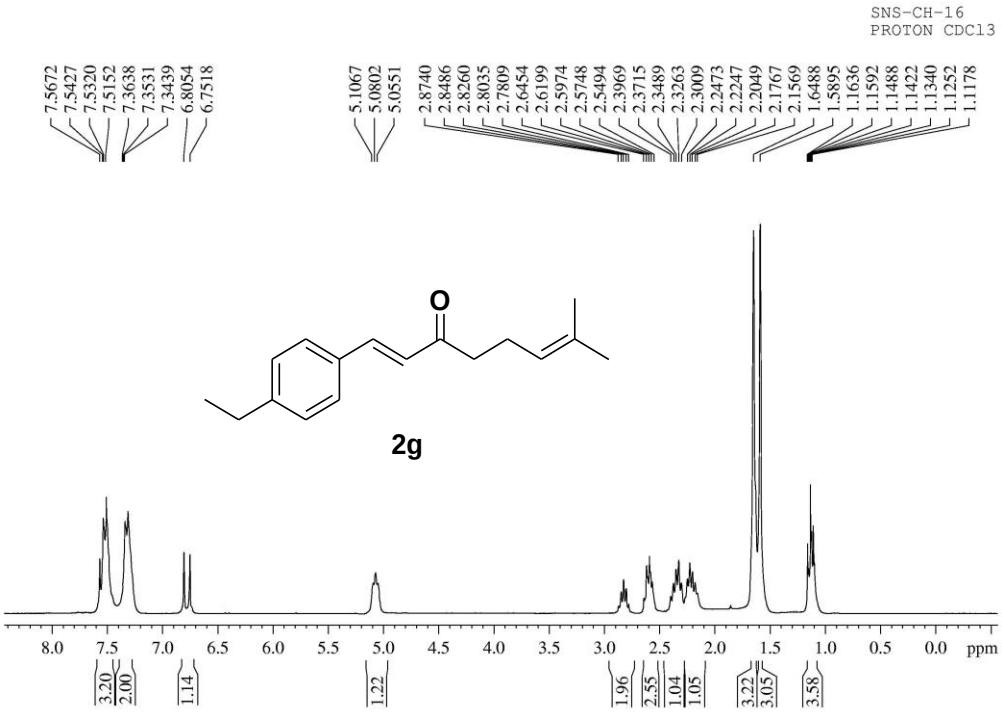


^{13}C NMR spectrum of 2e (75 MHz, $CDCl_3$)

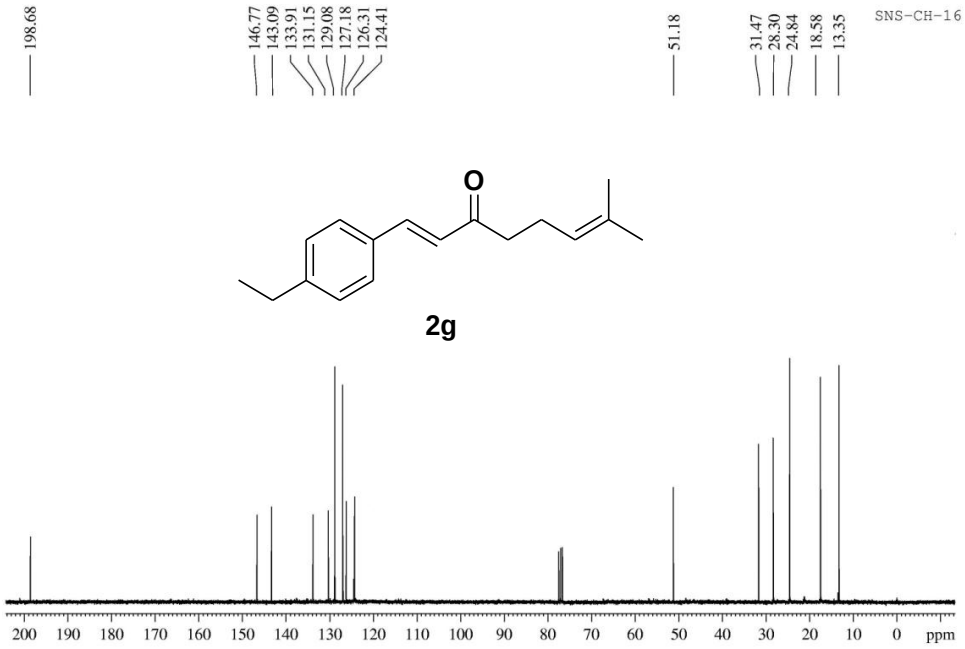


^{1}H NMR spectrum of 2f (300 MHz, $CDCl_3$)

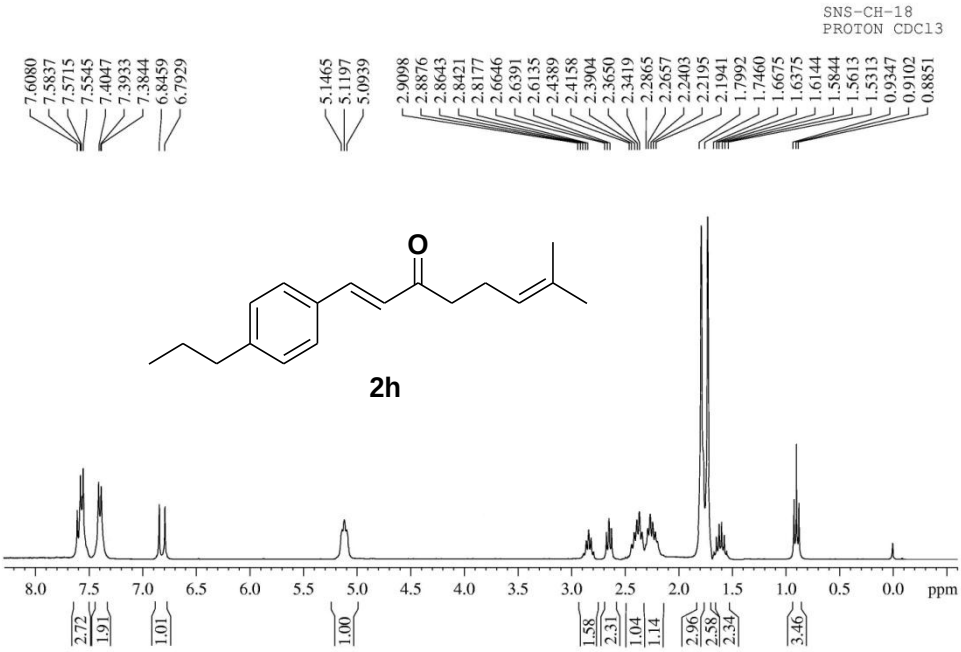
^{13}C NMR spectrum of 2f (75 MHz, $CDCl_3$)



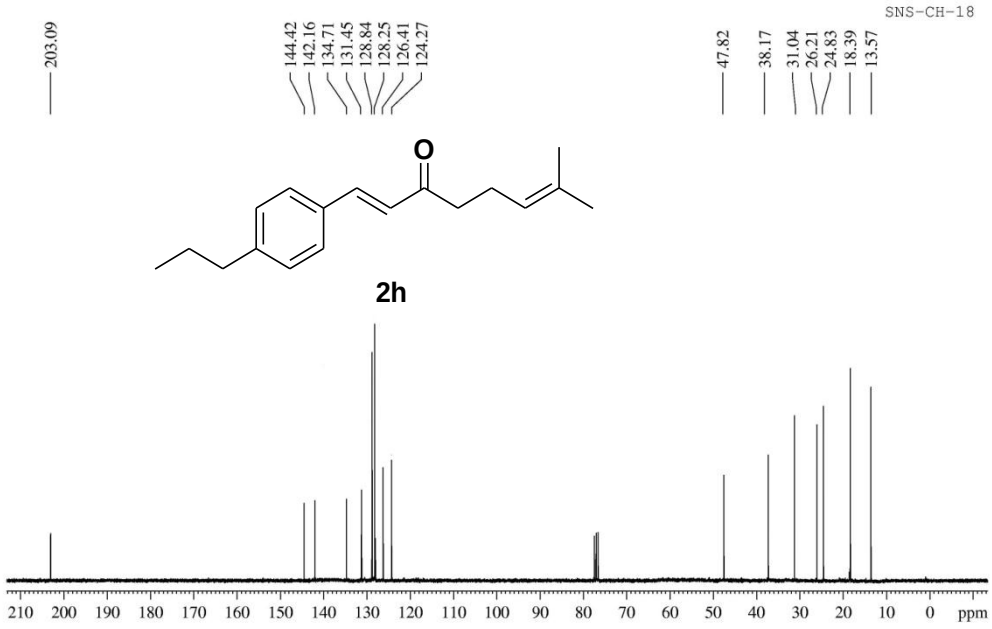
^{1}H NMR spectrum of 2g (300 MHz, $CDCl_3$)



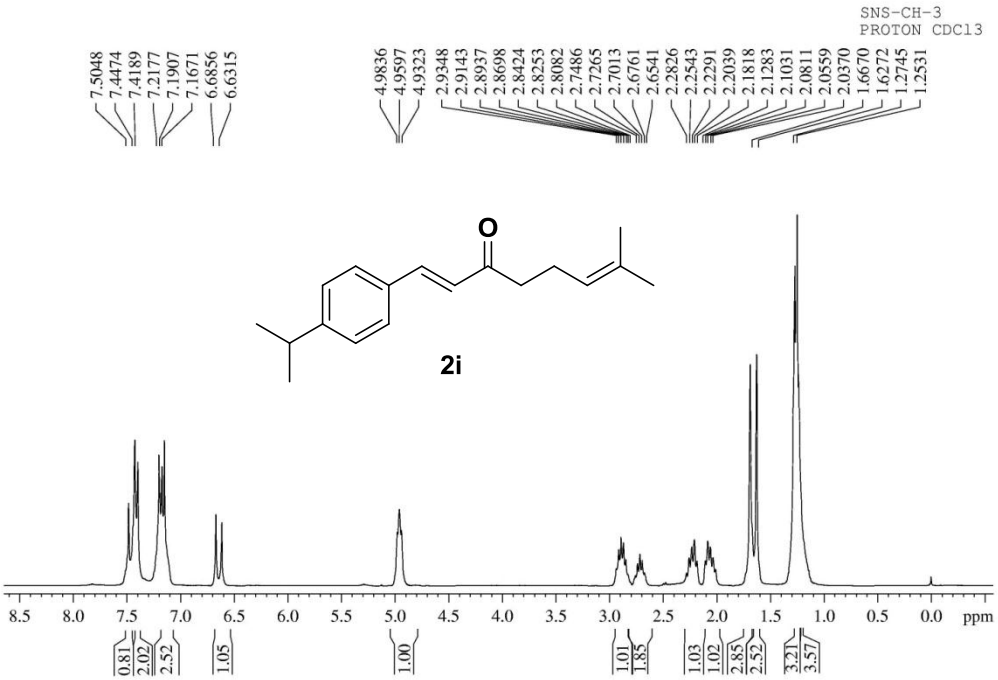
^{13}C NMR spectrum of 2g (75 MHz, $CDCl_3$)



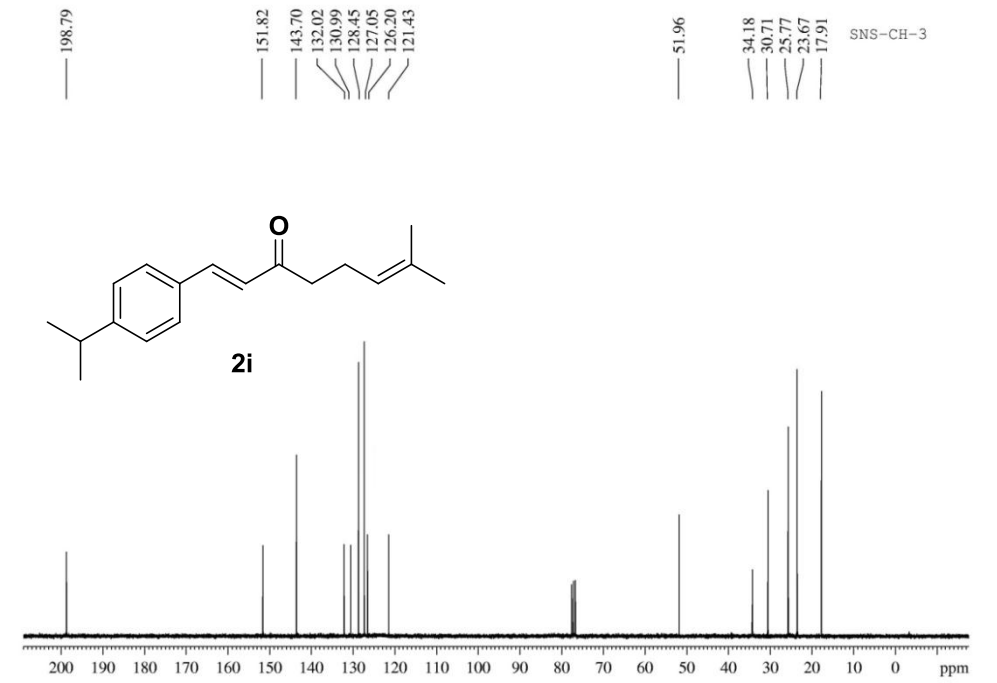
^{1}H NMR spectrum of 2h (300 MHz, $CDCl_3$)



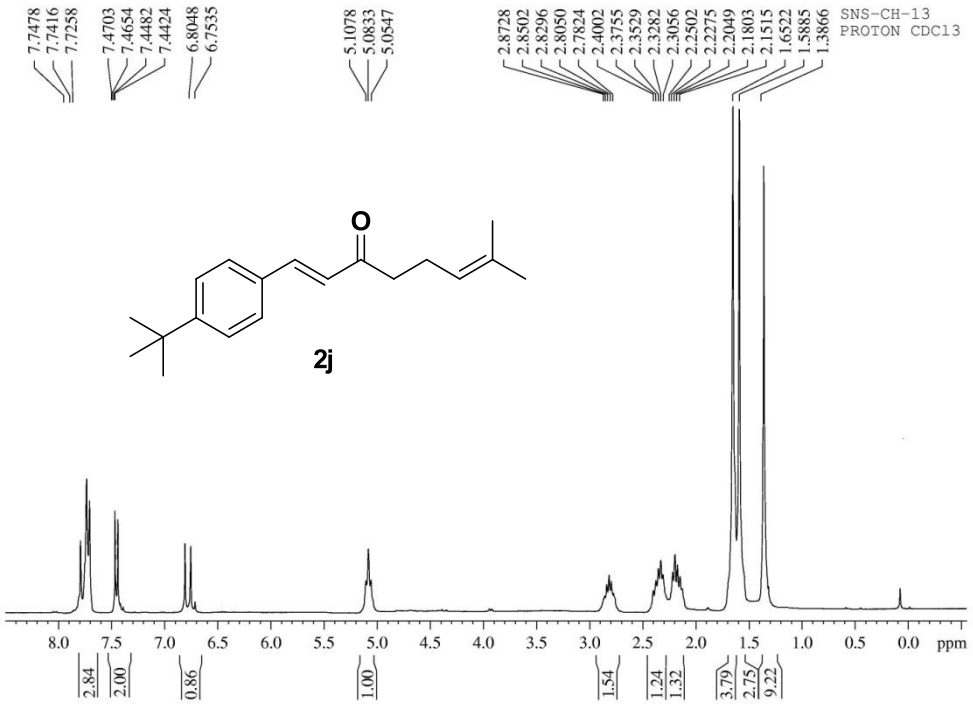
^{13}C NMR spectrum of 2h (75 MHz, $CDCl_3$)



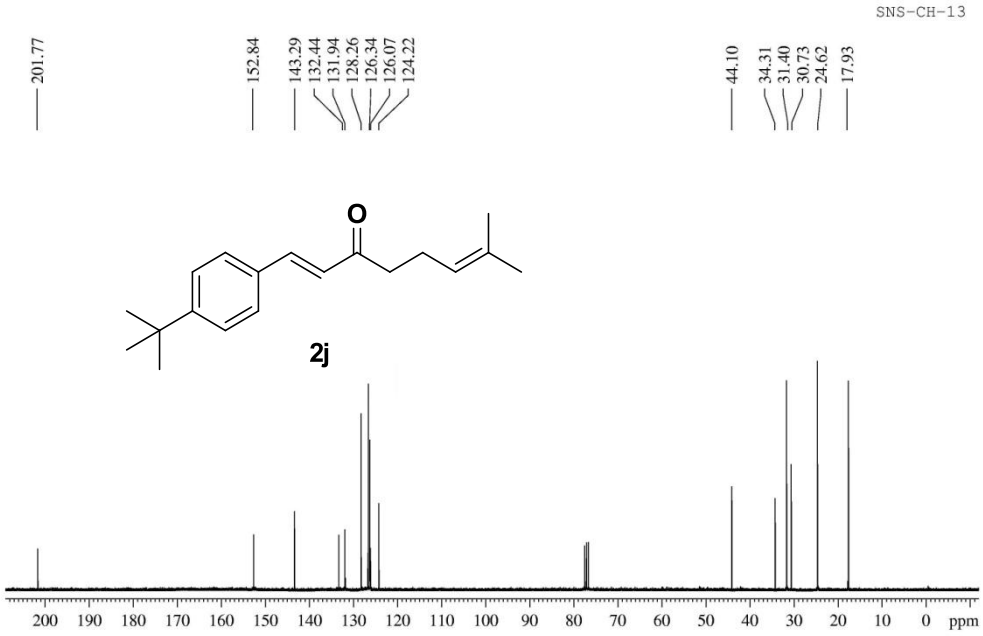
^{1}H NMR spectrum of 2i (300 MHz, $CDCl_3$)



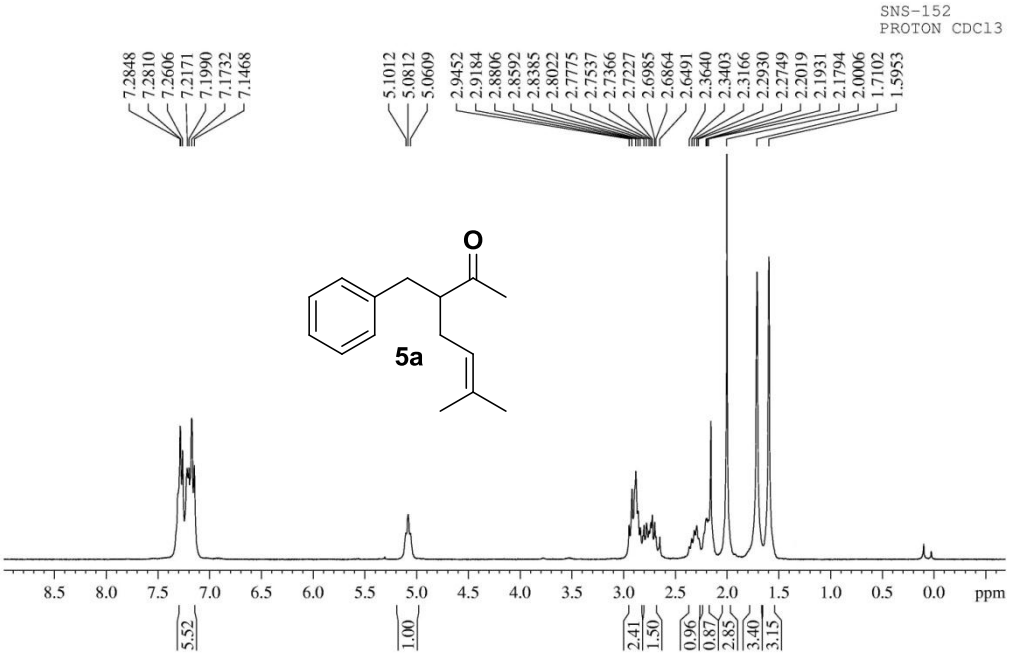
^{13}C NMR spectrum of 2i (75 MHz, $CDCl_3$)



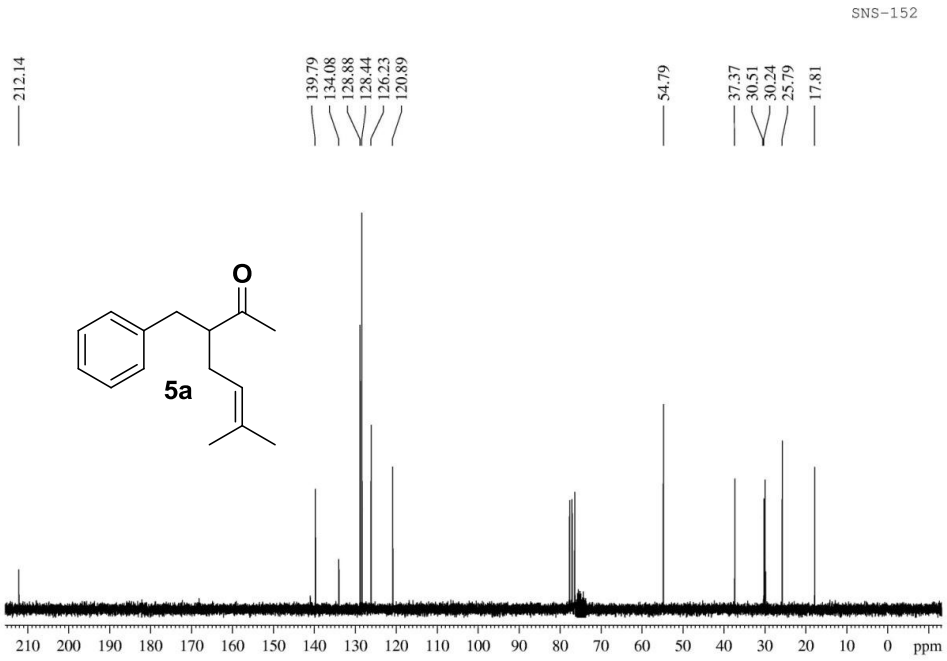
^{1}H NMR spectrum of 2j (300 MHz, $CDCl_3$)



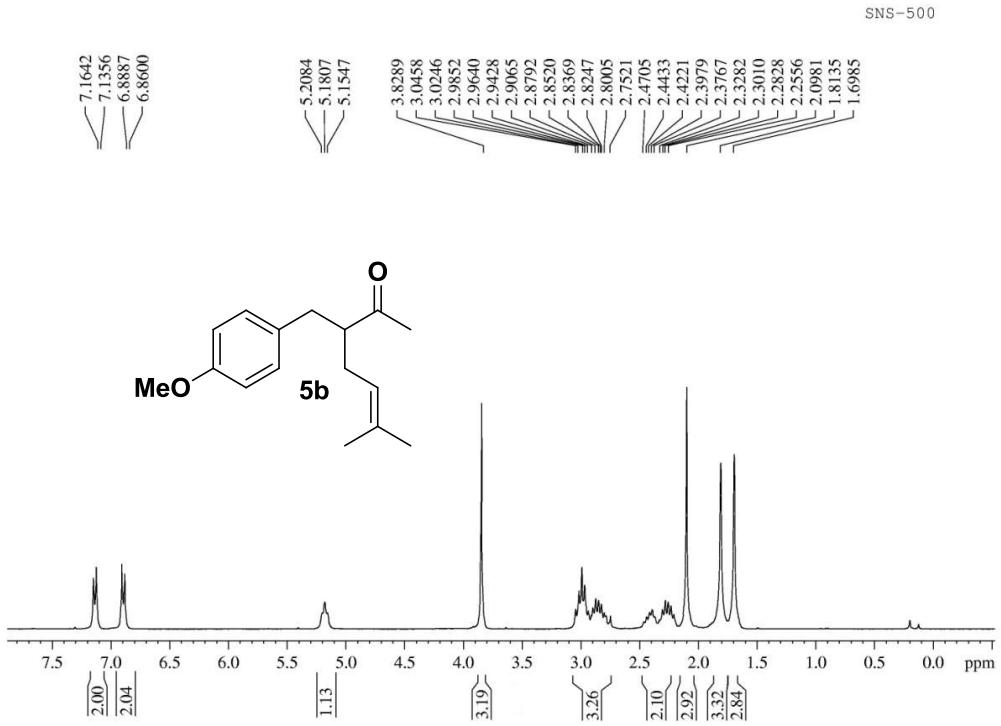
^{13}C NMR spectrum of 2j (75 MHz, $CDCl_3$)



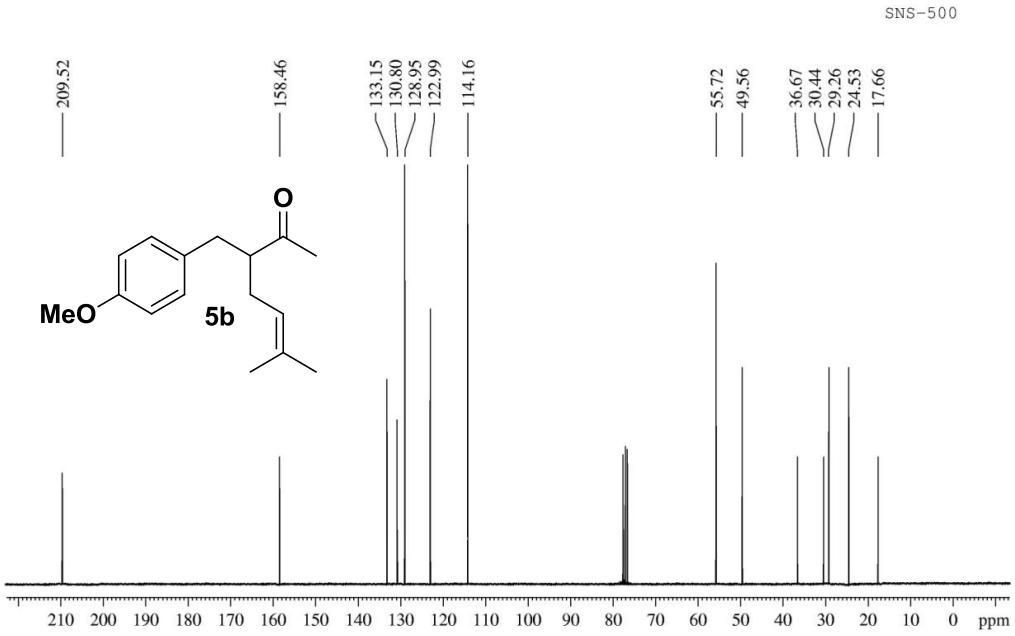
^{1}H NMR spectrum of 5a (300 MHz, $CDCl_3$)



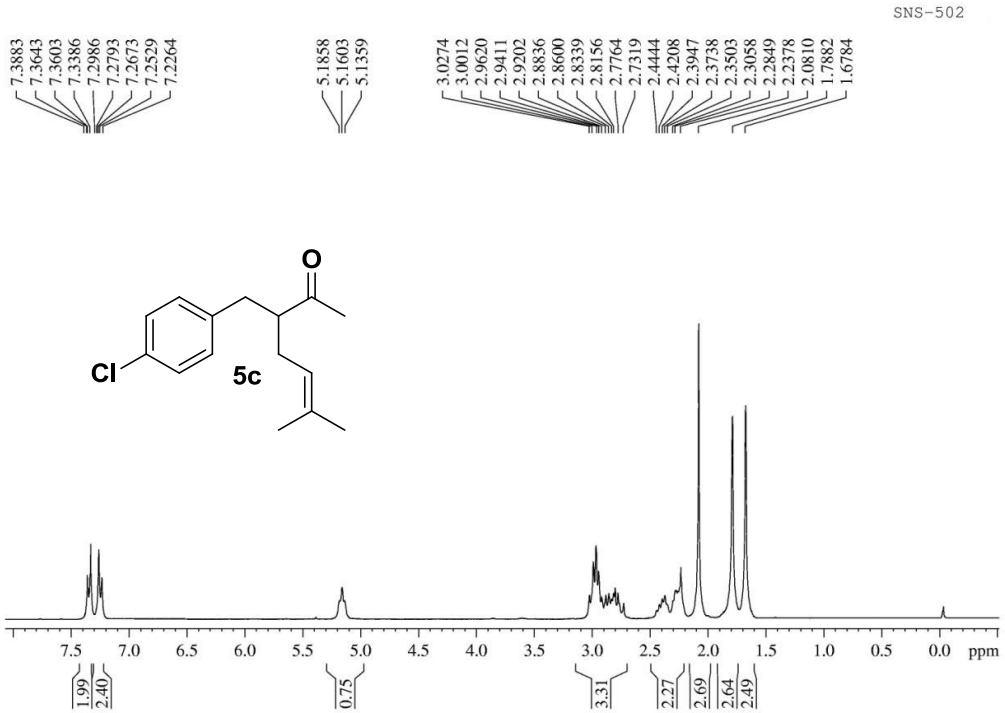
^{13}C NMR spectrum of 5a (75 MHz, $CDCl_3$)



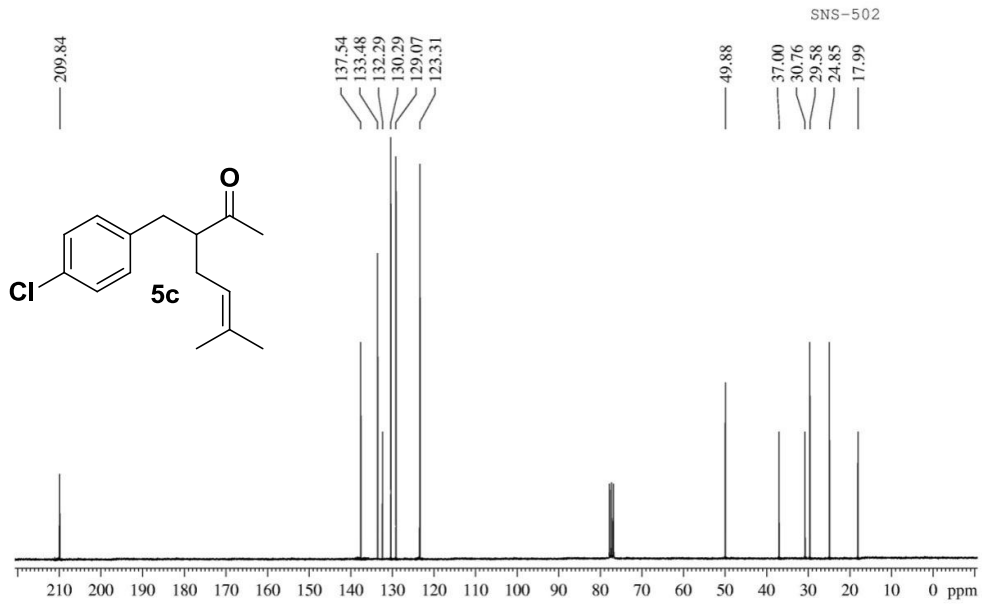
^{1}H NMR spectrum of 5b (300 MHz, $CDCl_3$)



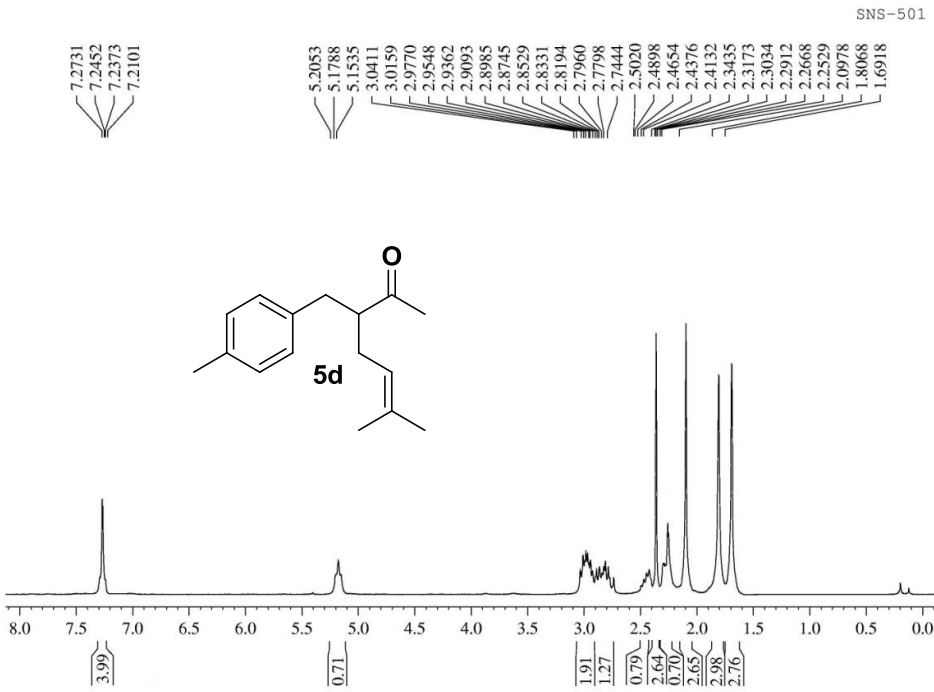
^{13}C NMR spectrum of 5b (75 MHz, $CDCl_3$)



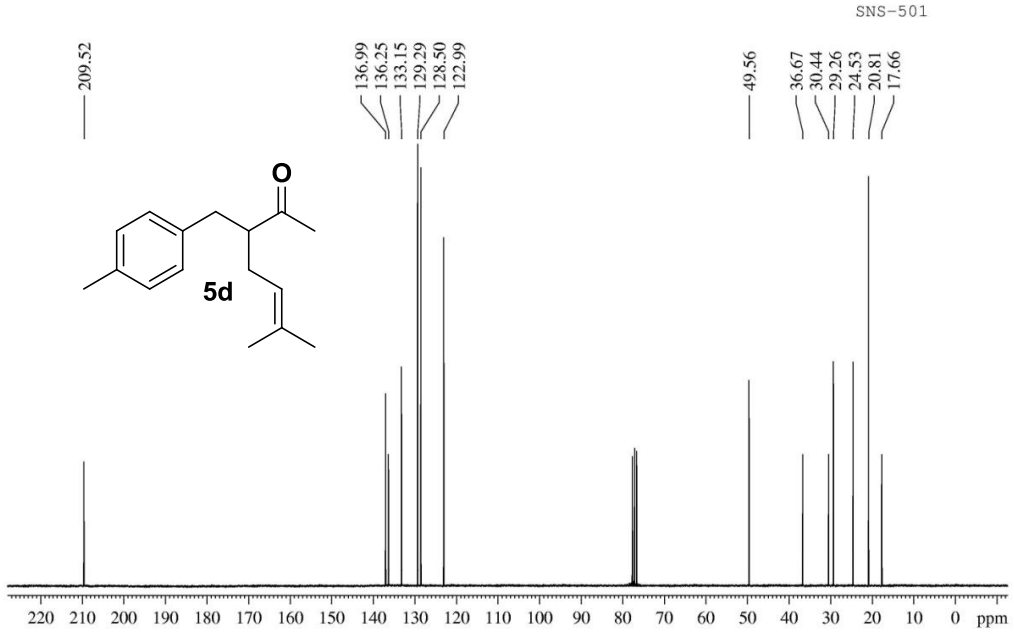
^{1}H NMR spectrum of 5c (300 MHz, $CDCl_3$)



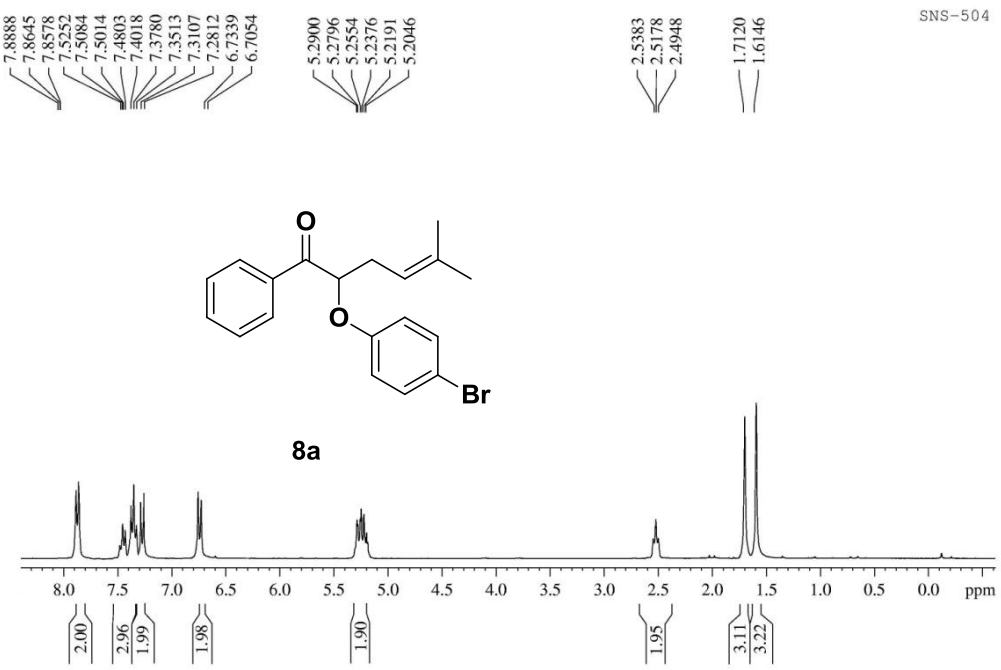
^{13}C NMR spectrum of 5c (75 MHz, $CDCl_3$)



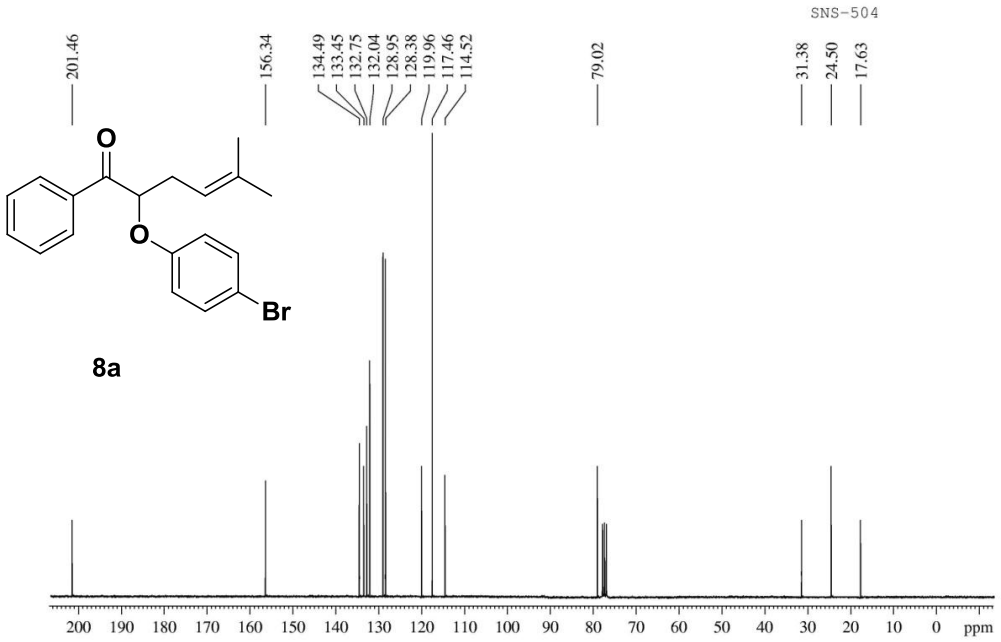
^{1}H NMR spectrum of 5d (300 MHz, $CDCl_3$)



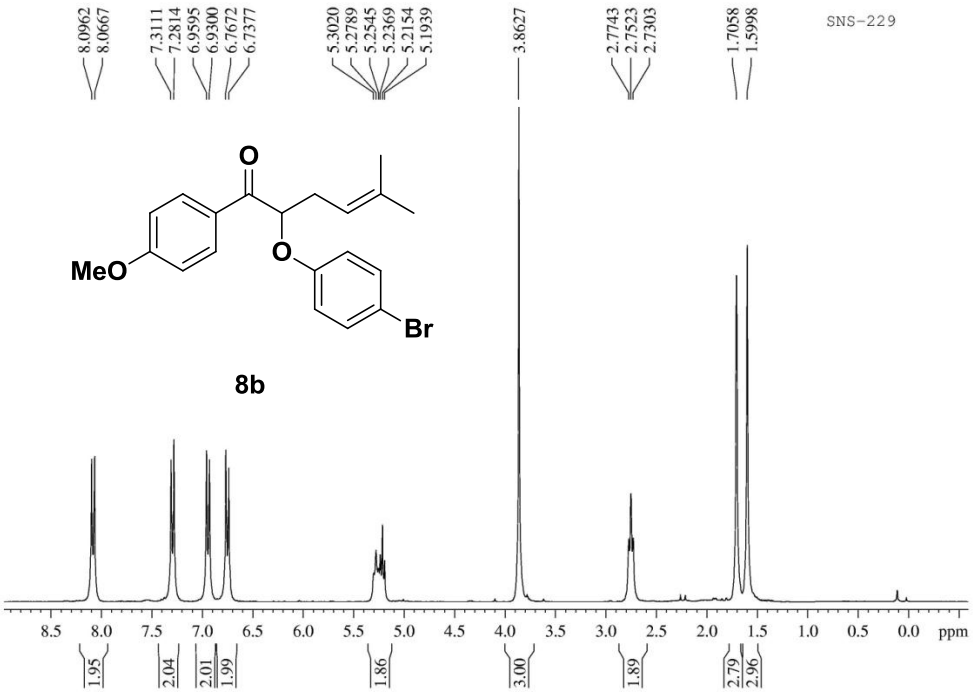
^{13}C NMR spectrum of 5d (75 MHz, $CDCl_3$)



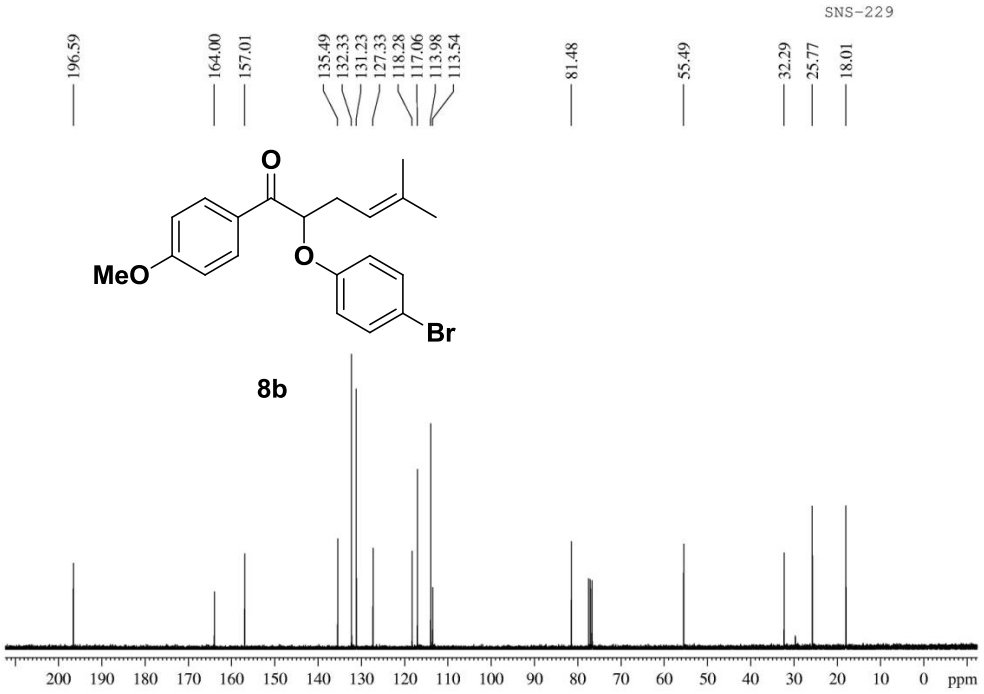
^{1}H NMR spectrum of 8a (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of 8a (75 MHz, $CDCl_3$)



^{1}H NMR spectrum of 8b (300 MHz, $CDCl_3$)



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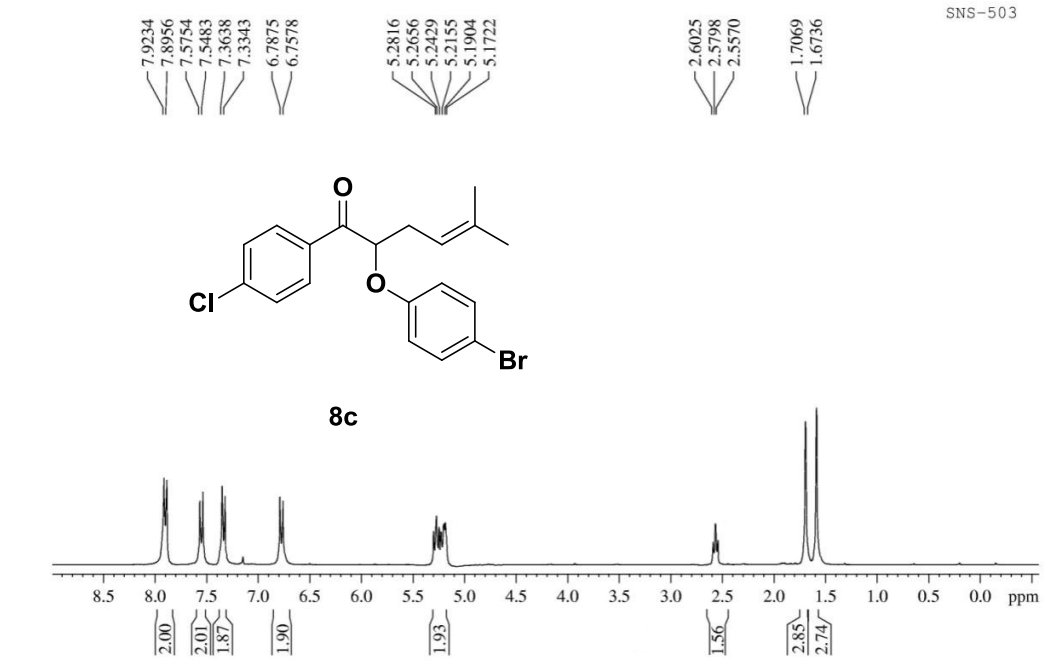

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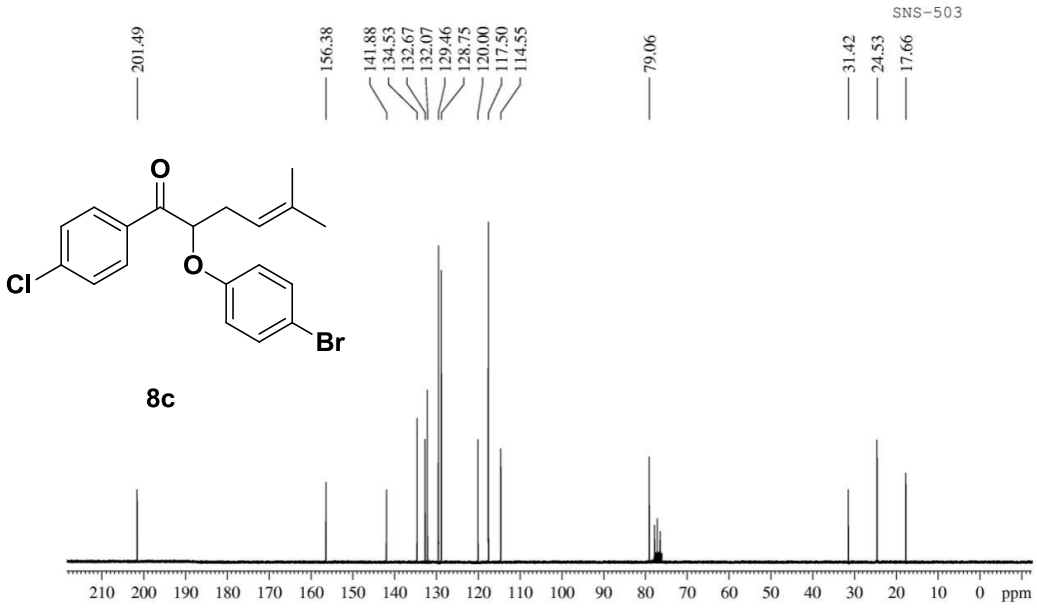

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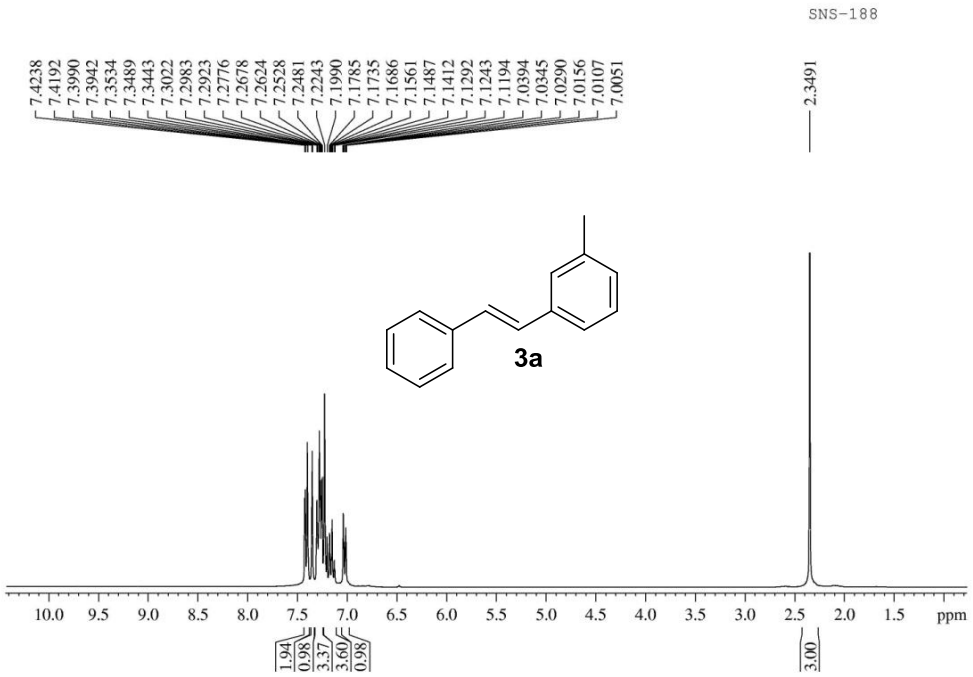
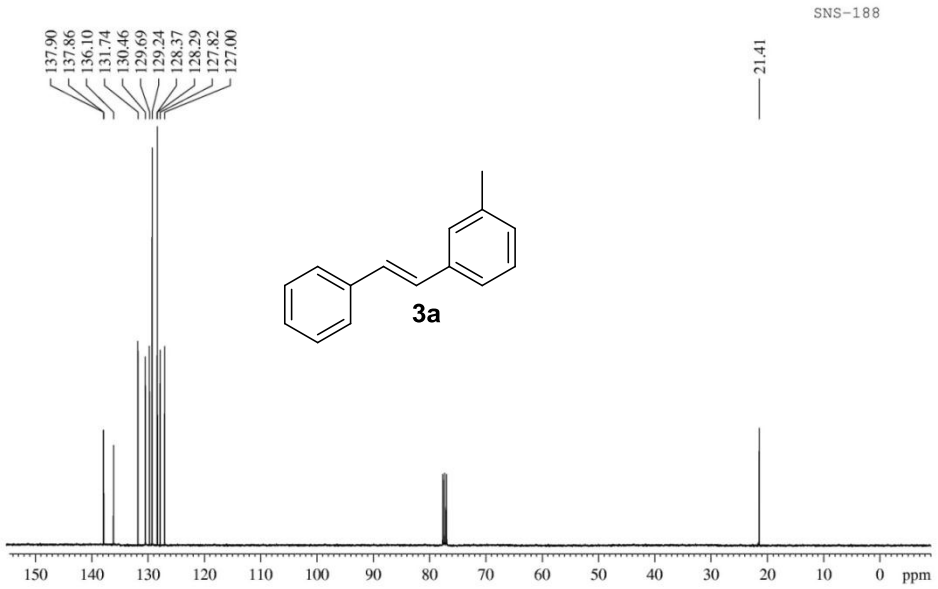
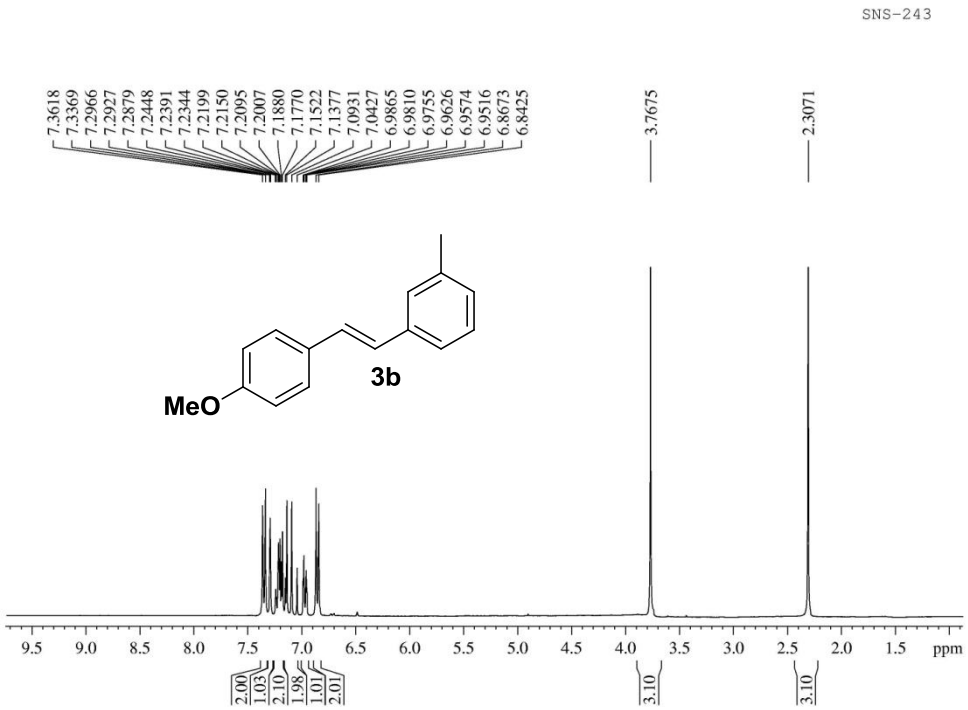


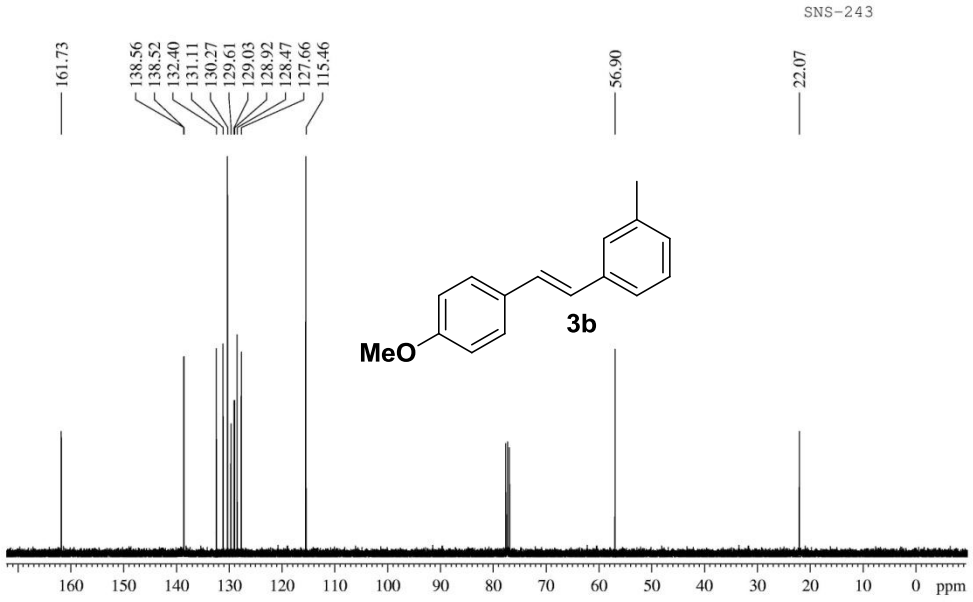
^{1}H NMR spectrum of 3a (300 MHz, $CDCl_3$)



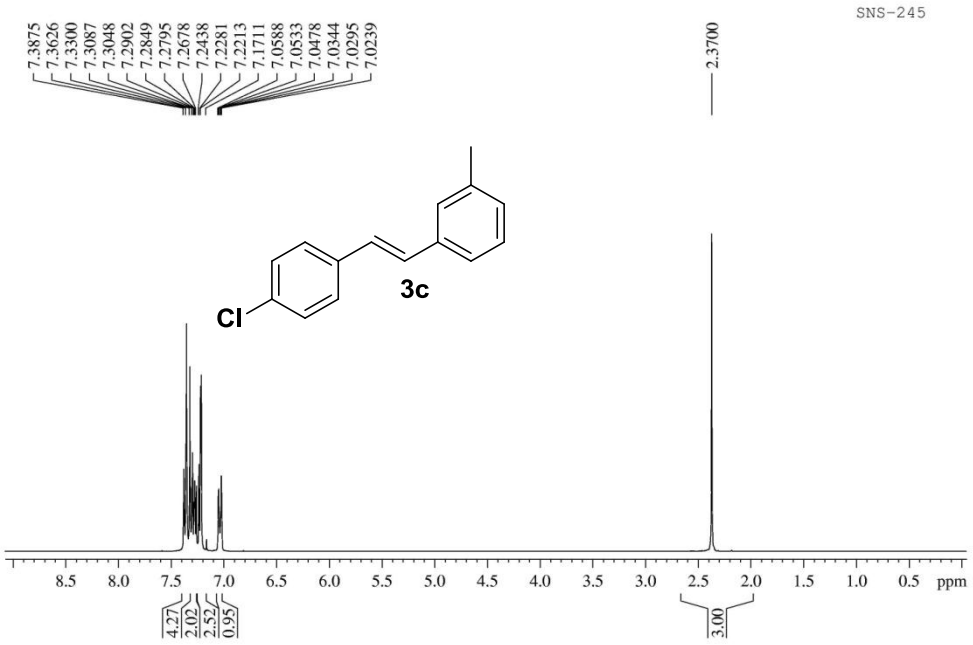
^{13}C NMR spectrum of 3a (75 MHz, $CDCl_3$)



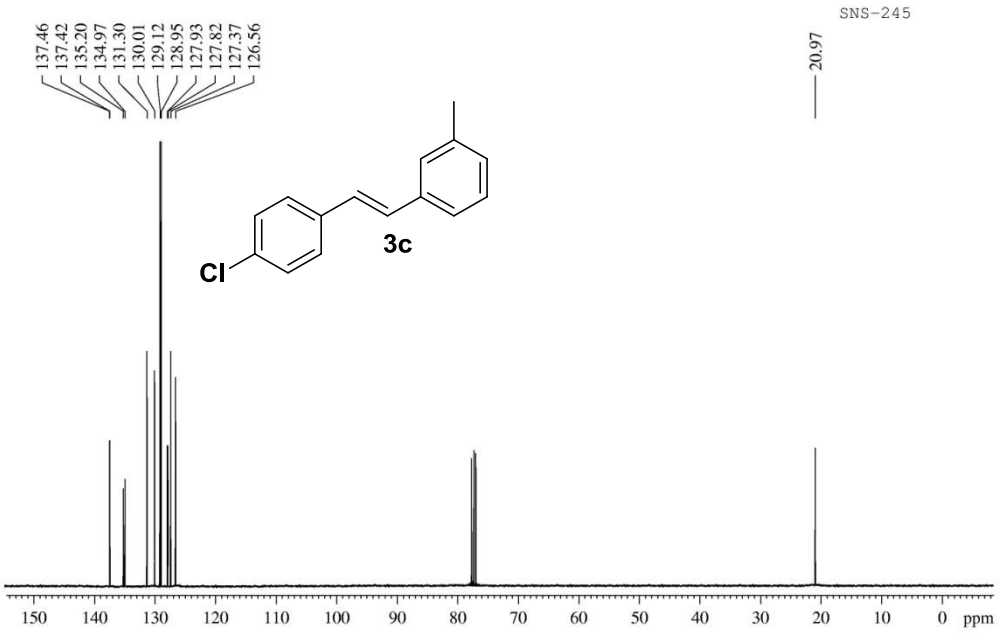
^{1}H NMR spectrum of 3b (300 MHz, $CDCl_3$)



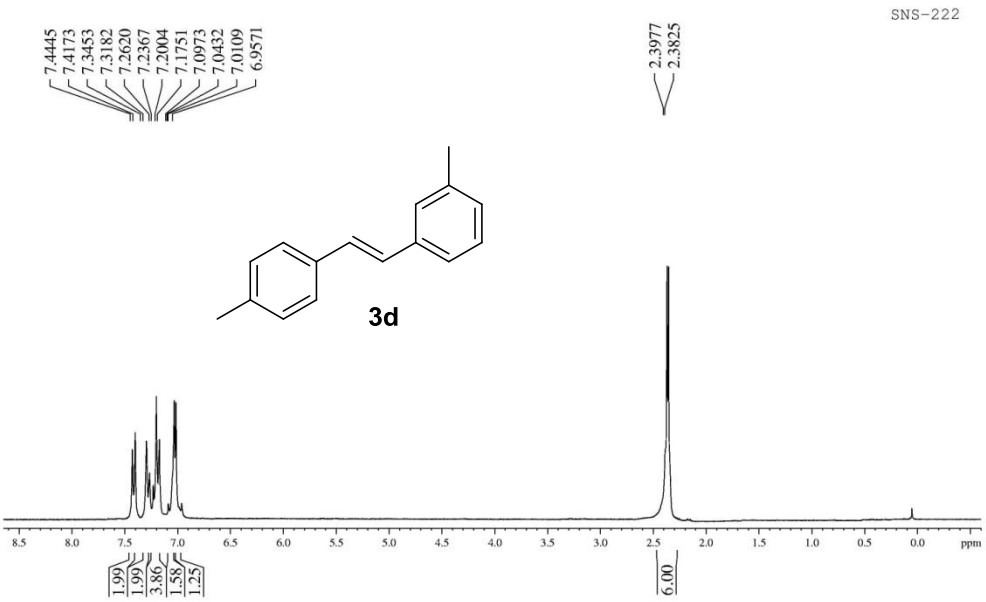
^{13}C NMR spectrum of 3b (75 MHz, $CDCl_3$)



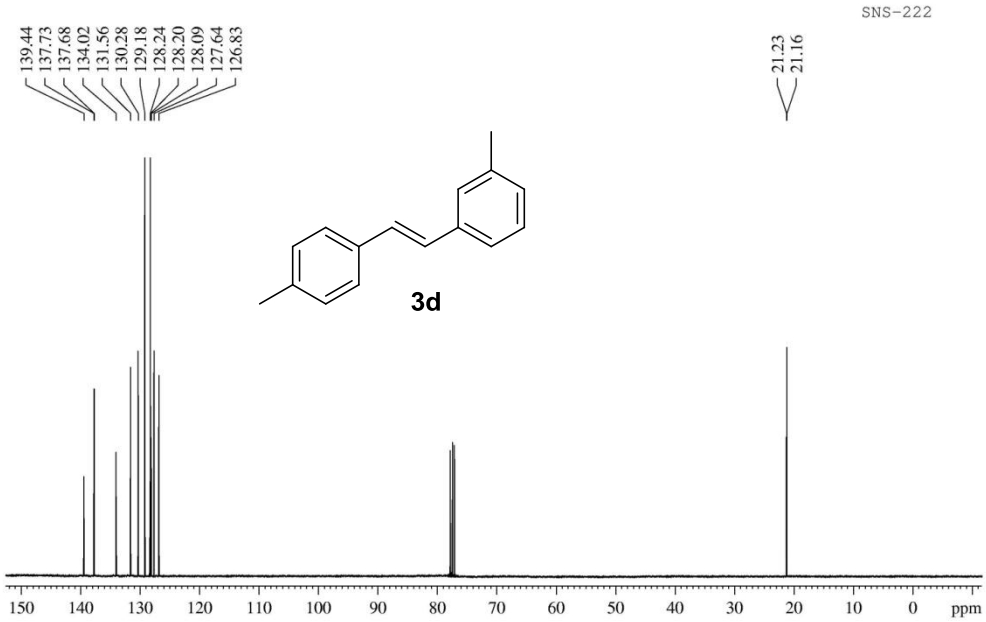
^{1}H NMR spectrum of 3c (300 MHz, $CDCl_3$)



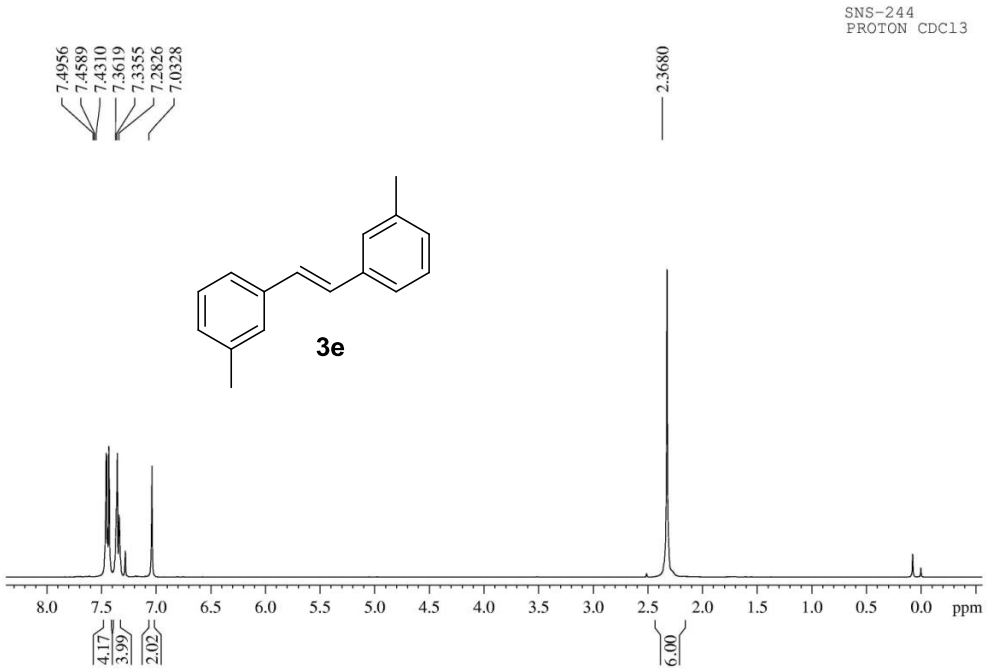
^{13}C NMR spectrum of 3c (75 MHz, $CDCl_3$)



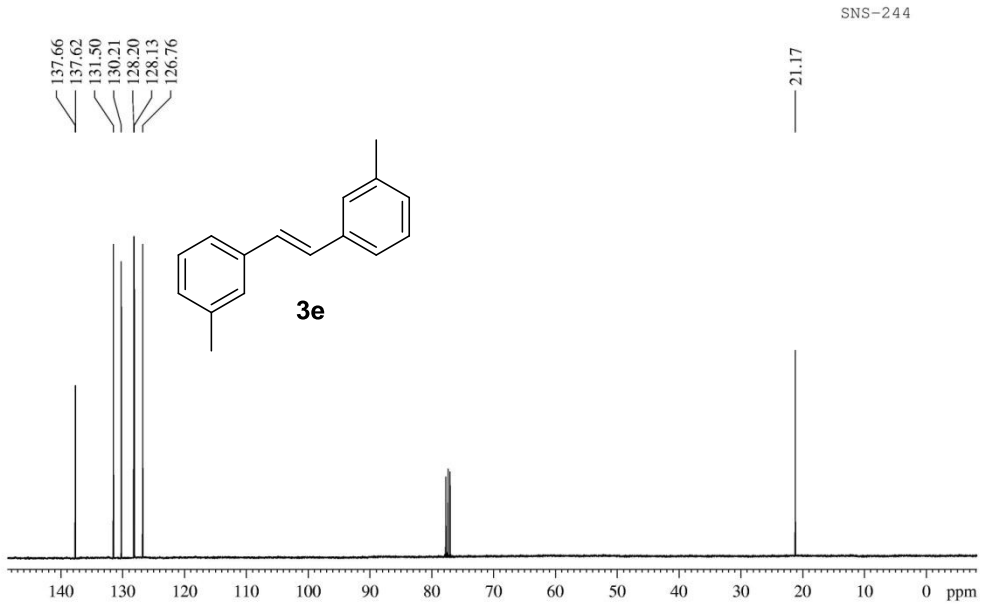
^{1}H NMR spectrum of 3d (300 MHz, $CDCl_3$)



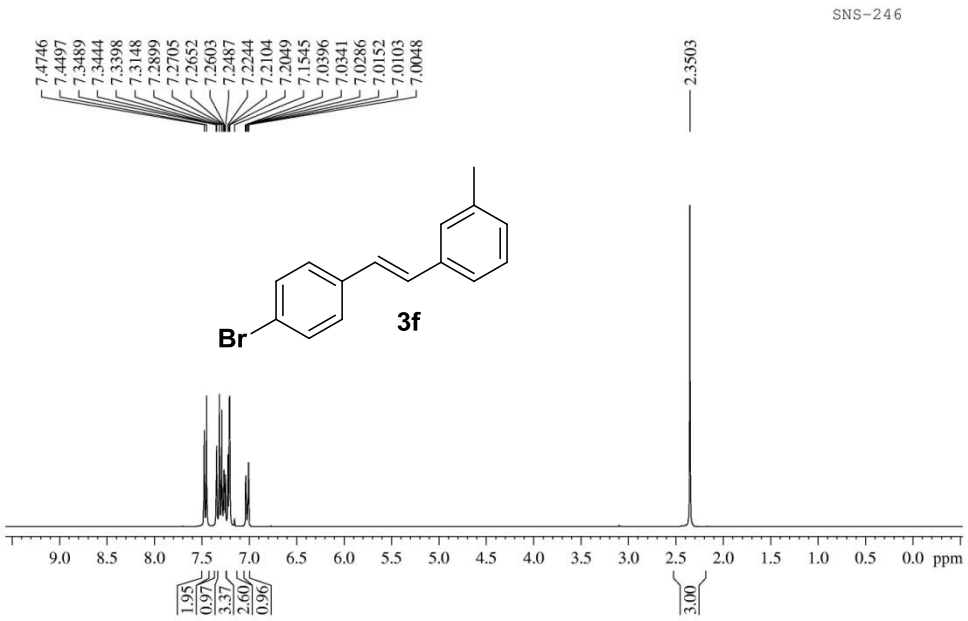
^{13}C NMR spectrum of 3d (75 MHz, $CDCl_3$)



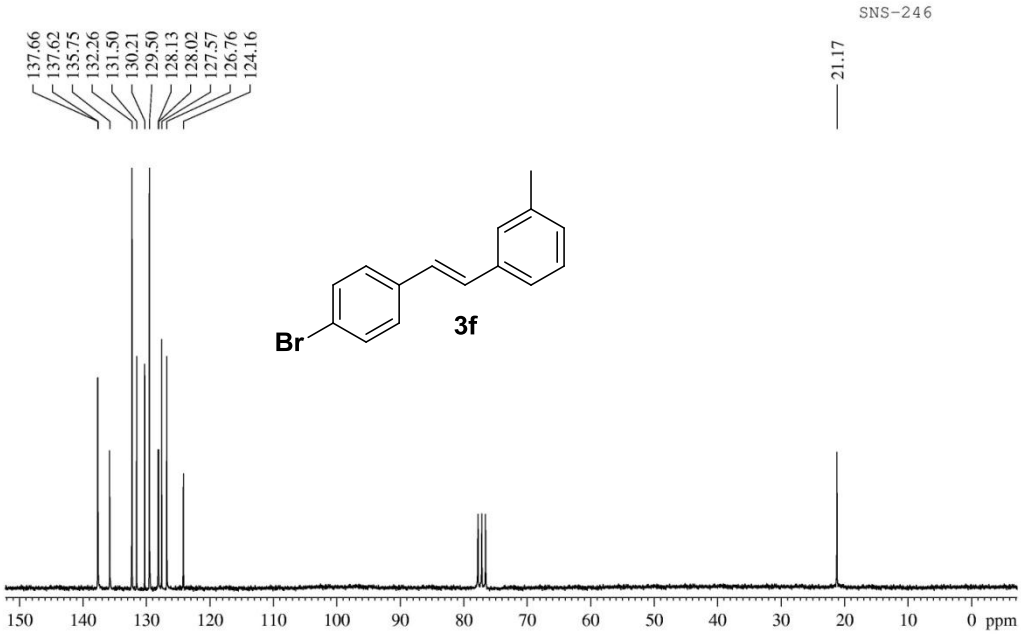
^{1}H NMR spectrum of 3e (300 MHz, $CDCl_3$)



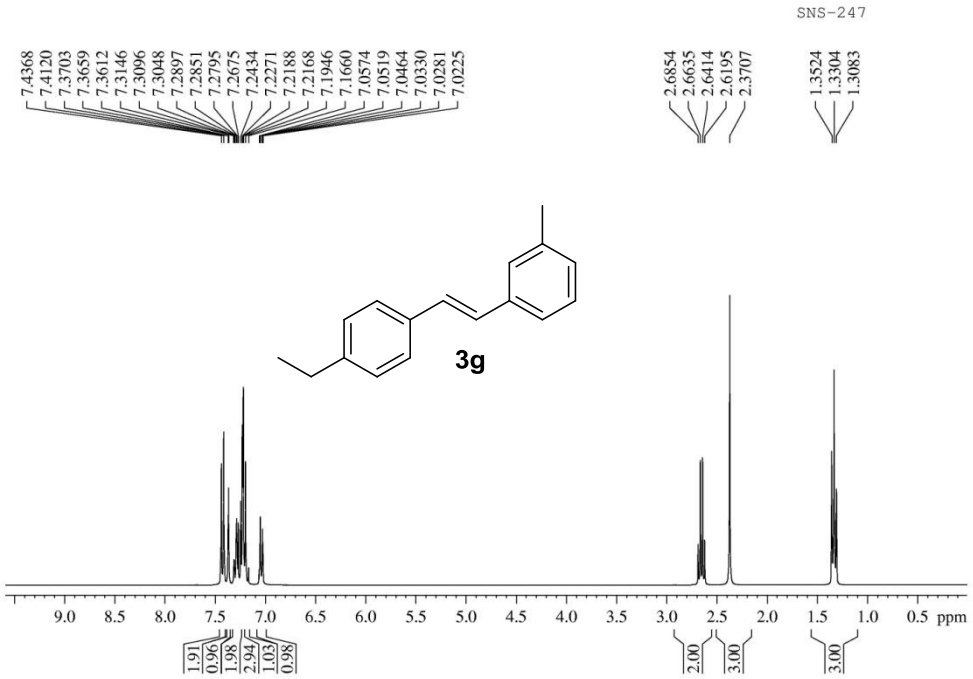
^{13}C NMR spectrum of 3e (75 MHz, $CDCl_3$)



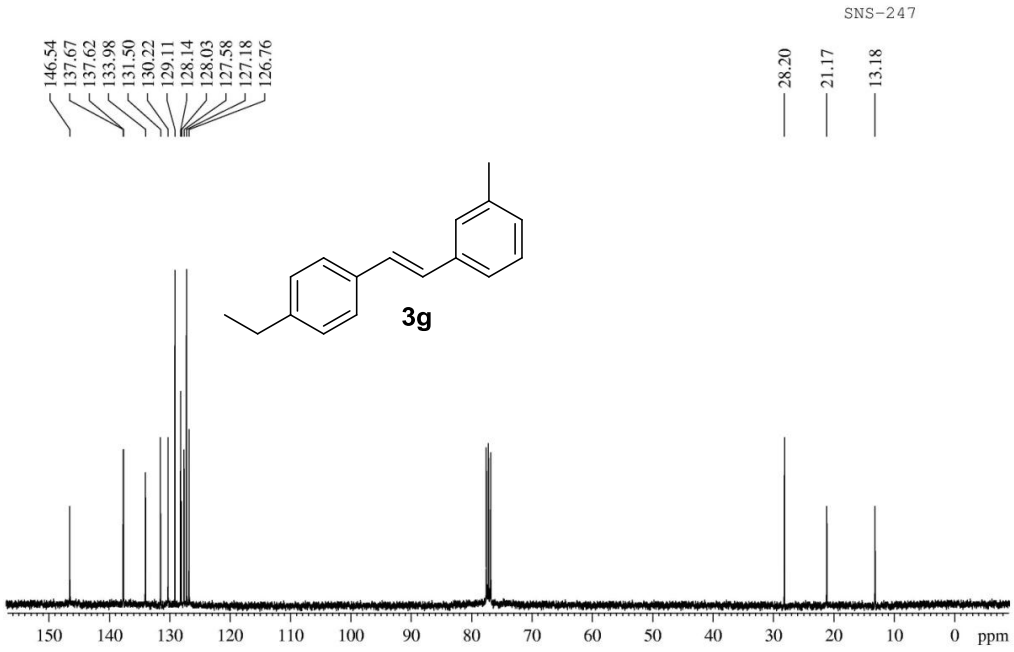
^{1}H NMR spectrum of 3f (300 MHz, $CDCl_3$)



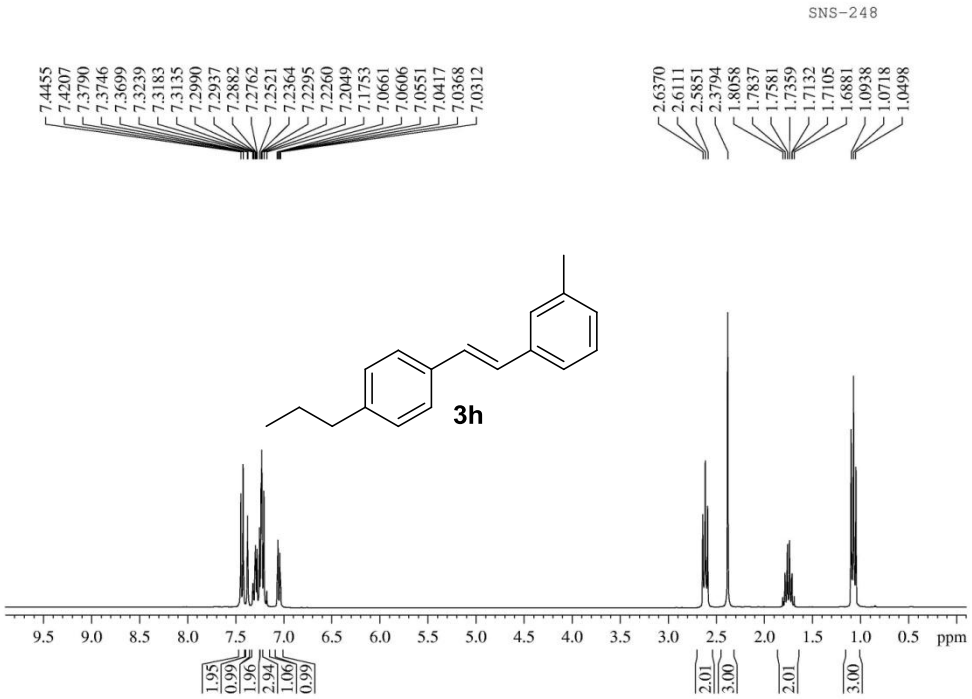
^{13}C NMR spectrum of 3f (75 MHz, $CDCl_3$)



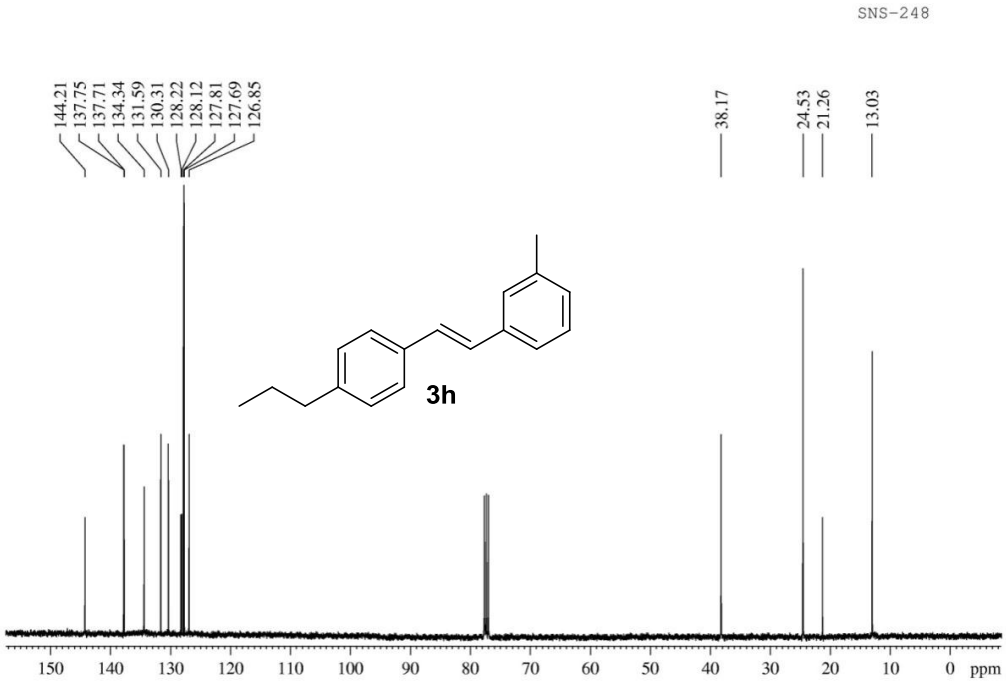
^{1}H NMR spectrum of 3g (300 MHz, $CDCl_3$)



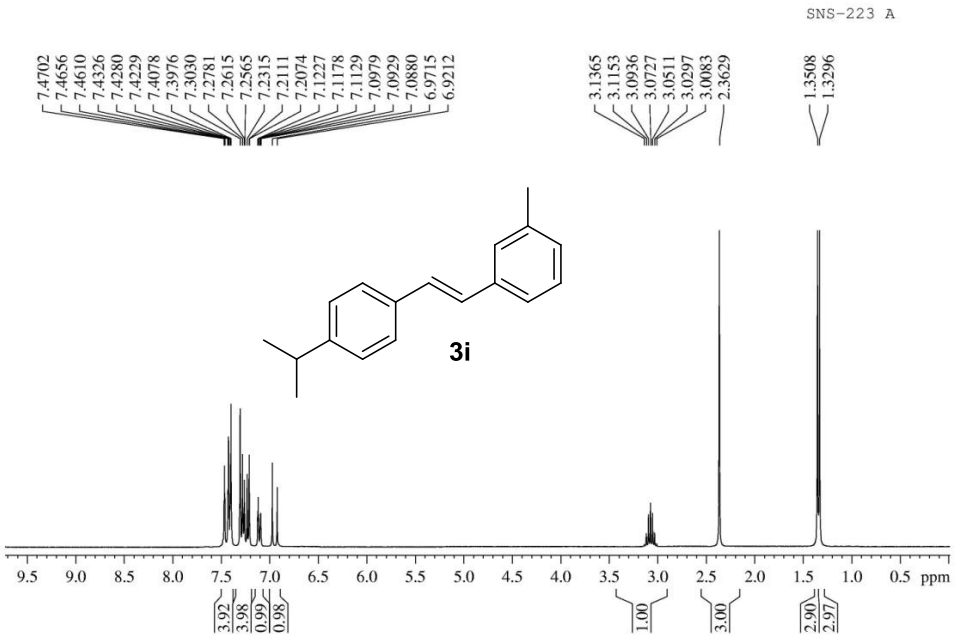
^{13}C NMR spectrum of 3g (75 MHz, $CDCl_3$)



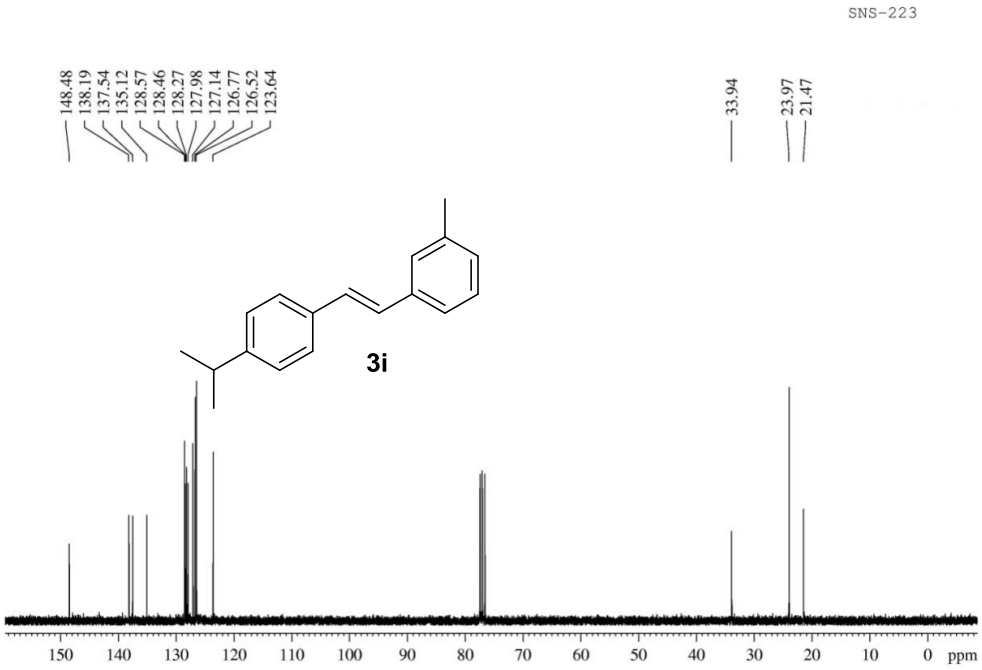
^{1}H NMR spectrum of 3h (300 MHz, $CDCl_3$)



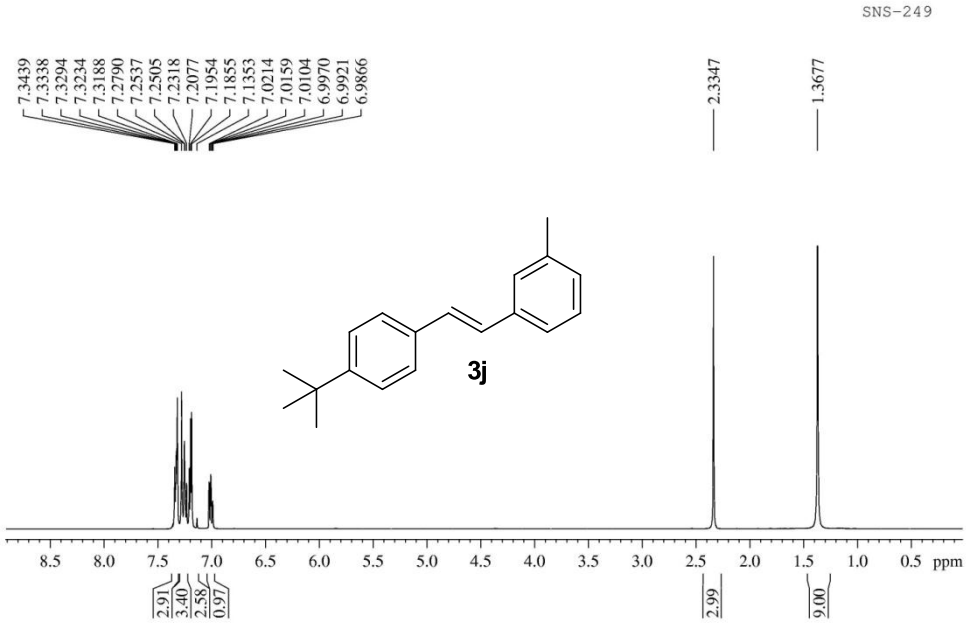
^{13}C NMR spectrum of 3h (75 MHz, $CDCl_3$)



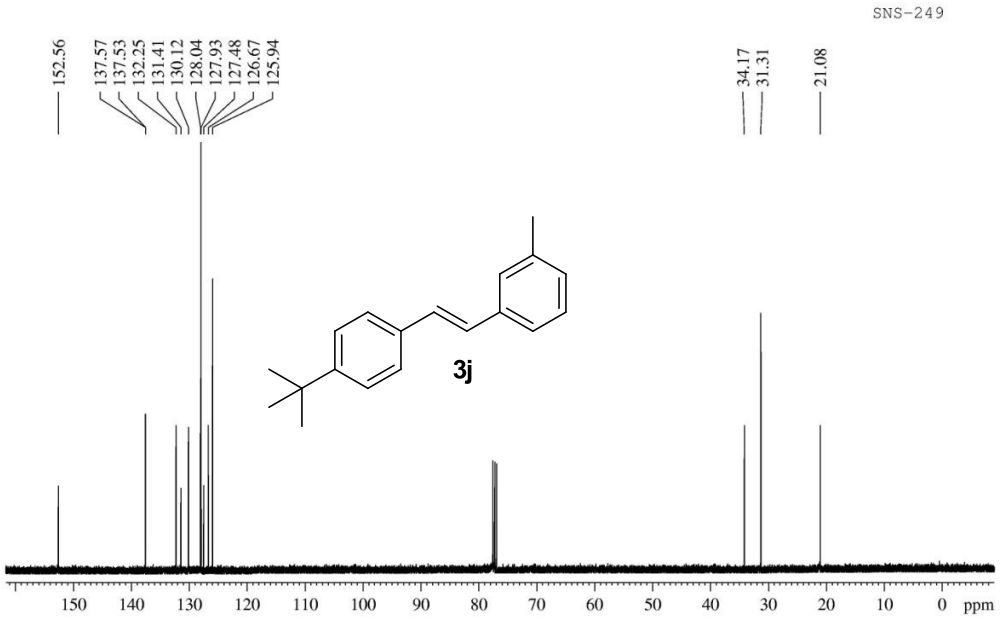
^{1}H NMR spectrum of 3i (300 MHz, $CDCl_3$)



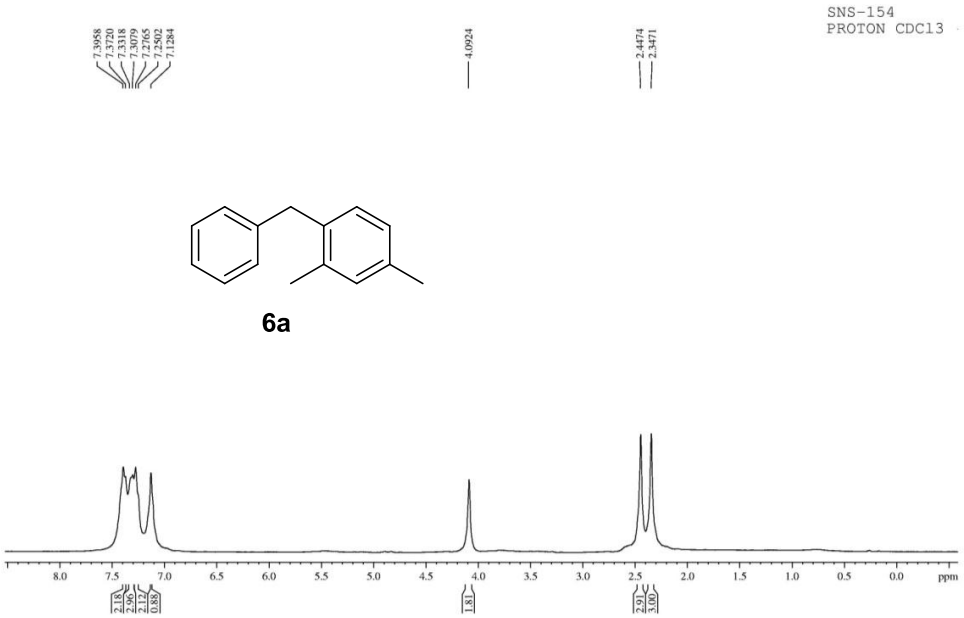
^{13}C NMR spectrum of 3i (75 MHz, $CDCl_3$)



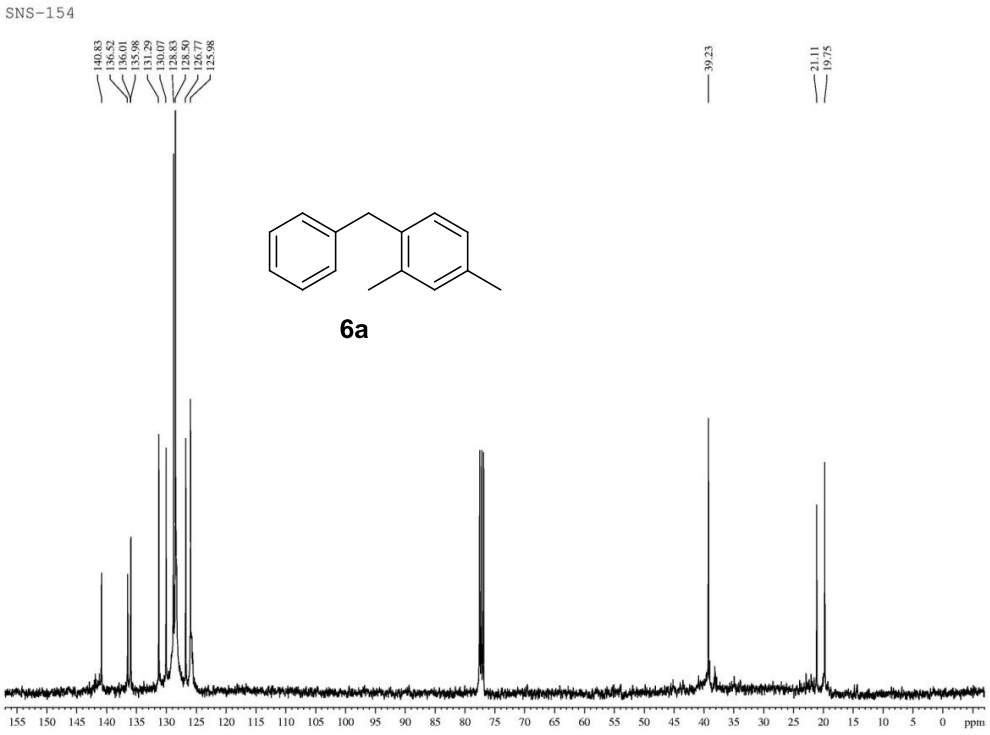
^{1}H NMR spectrum of 3j (300 MHz, $CDCl_3$)



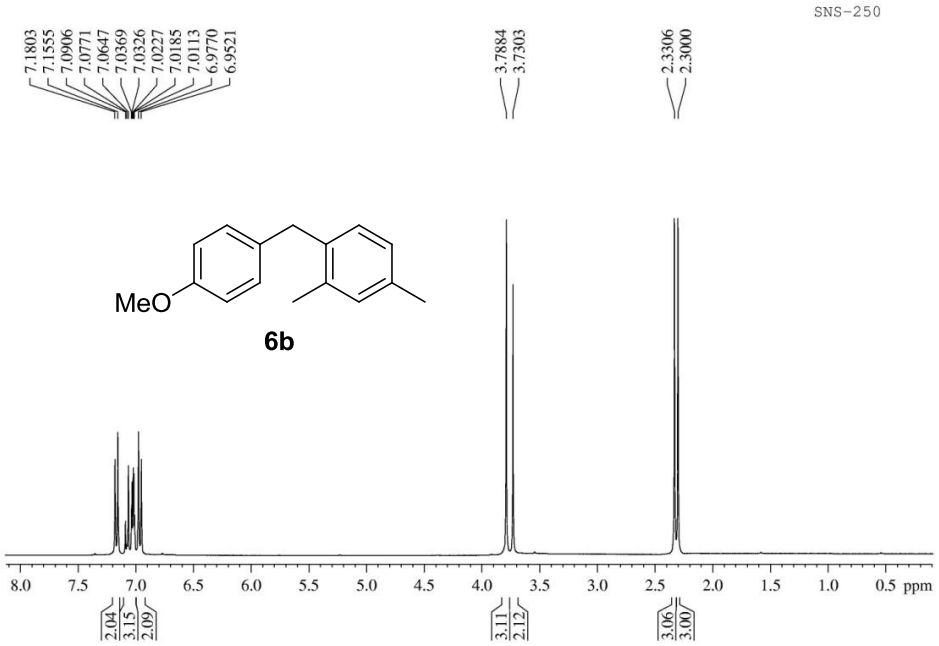
^{13}C NMR spectrum of 3j (75 MHz, $CDCl_3$)



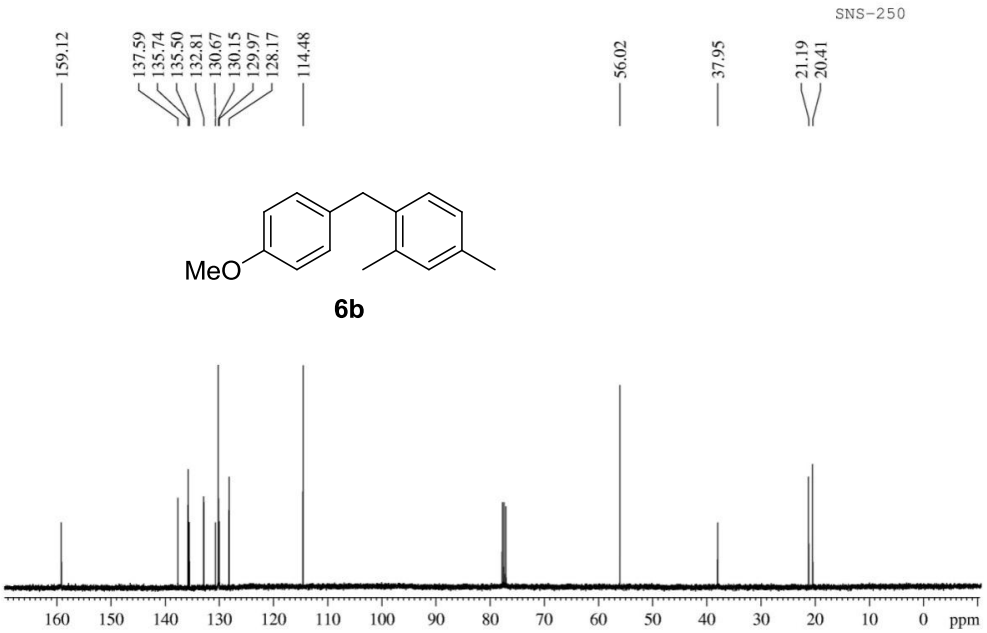
^{1}H NMR spectrum of 6a (300 MHz, $CDCl_3$)



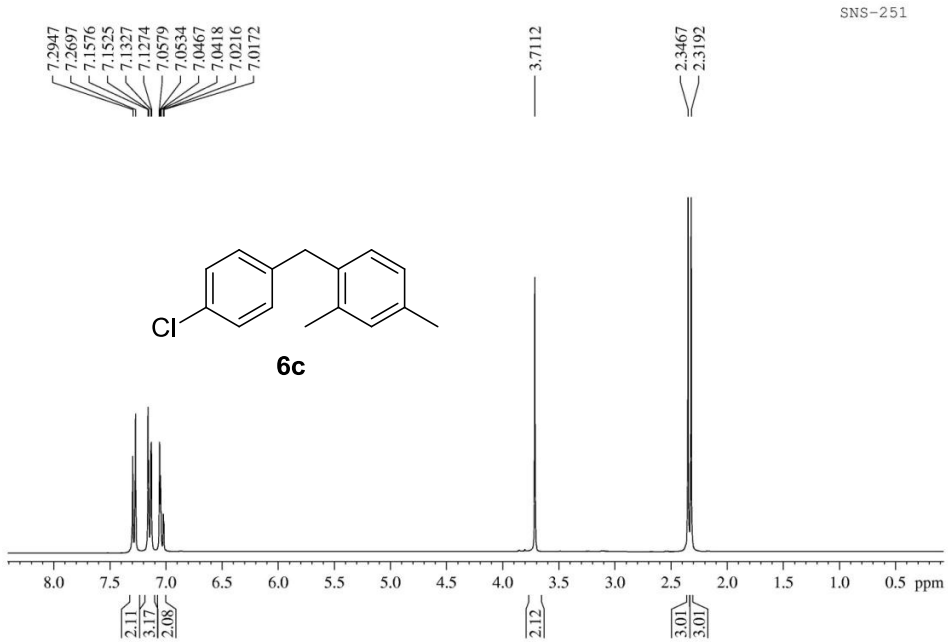
^{13}C NMR spectrum of 6a (75 MHz, $CDCl_3$)



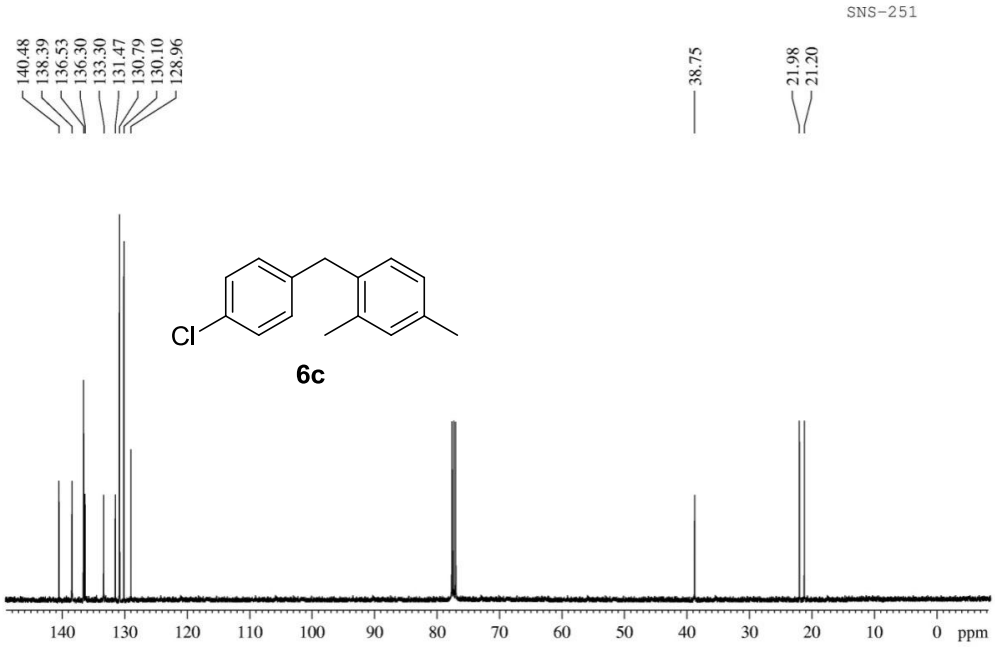
^{1}H NMR spectrum of 6b (300 MHz, $CDCl_3$)



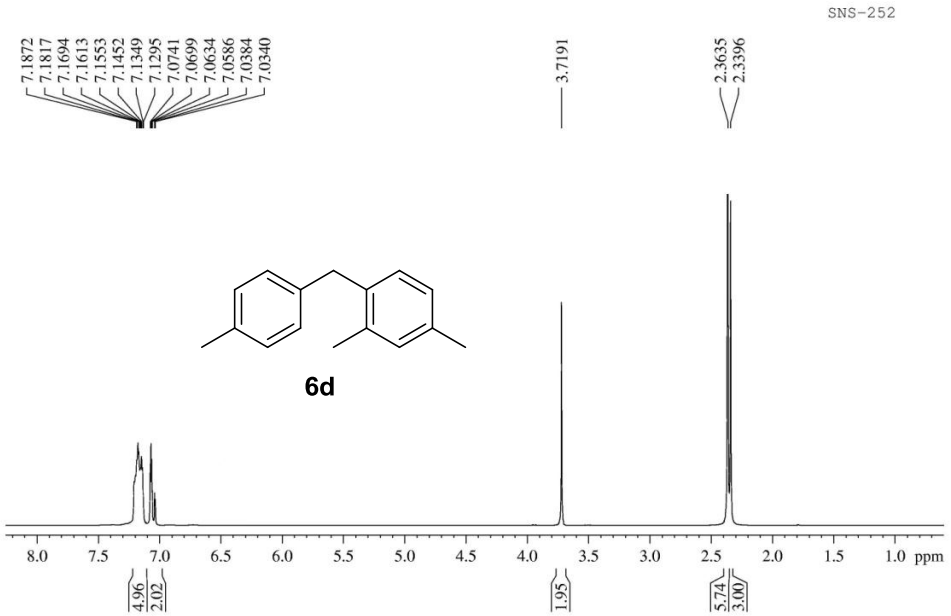
^{13}C NMR spectrum of 6b (75 MHz, $CDCl_3$)



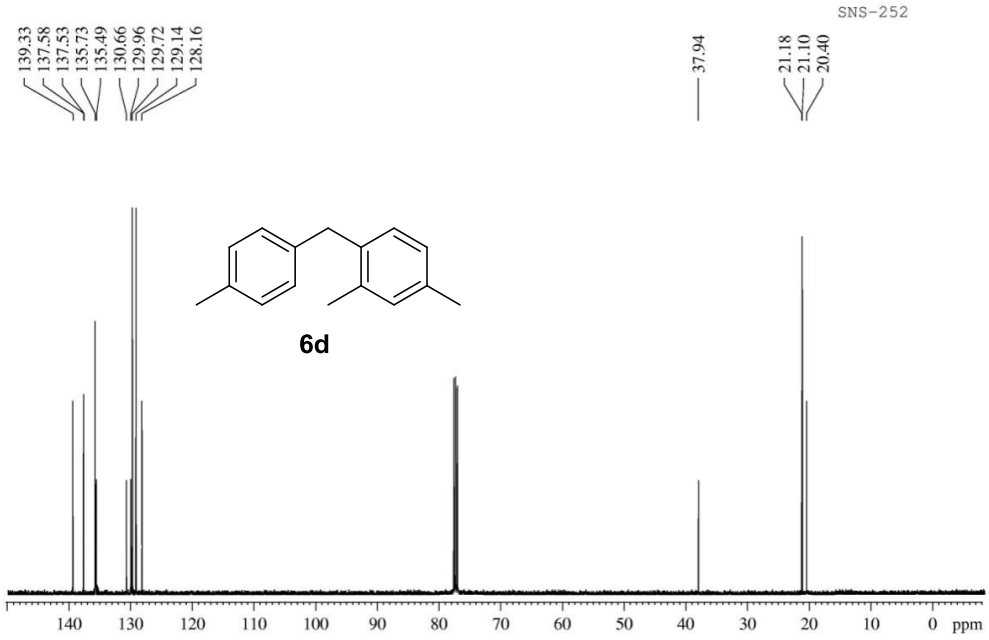
^{1}H NMR spectrum of 6c (300 MHz, $CDCl_3$)



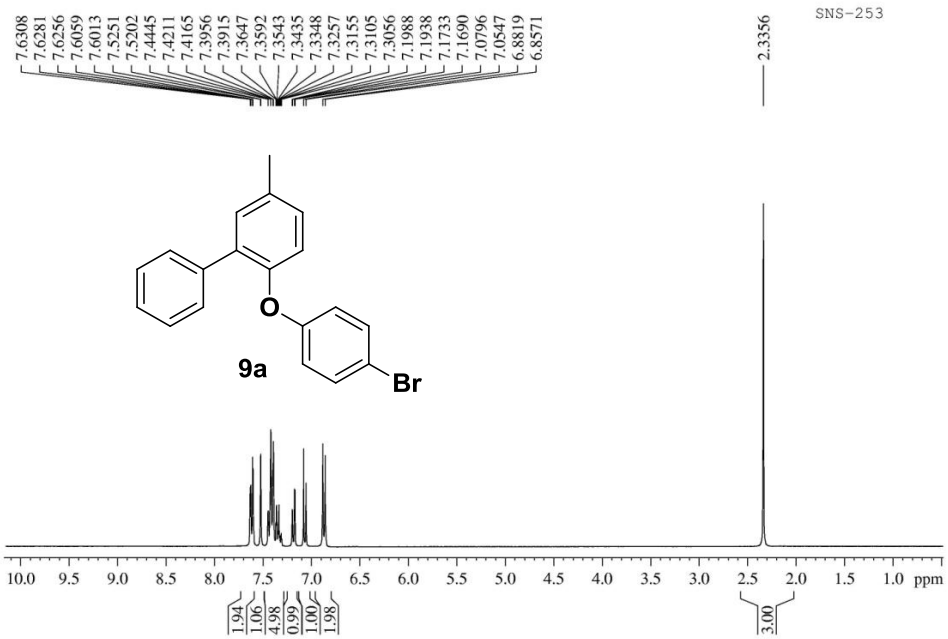
^{13}C NMR spectrum of 6c (75 MHz, $CDCl_3$)



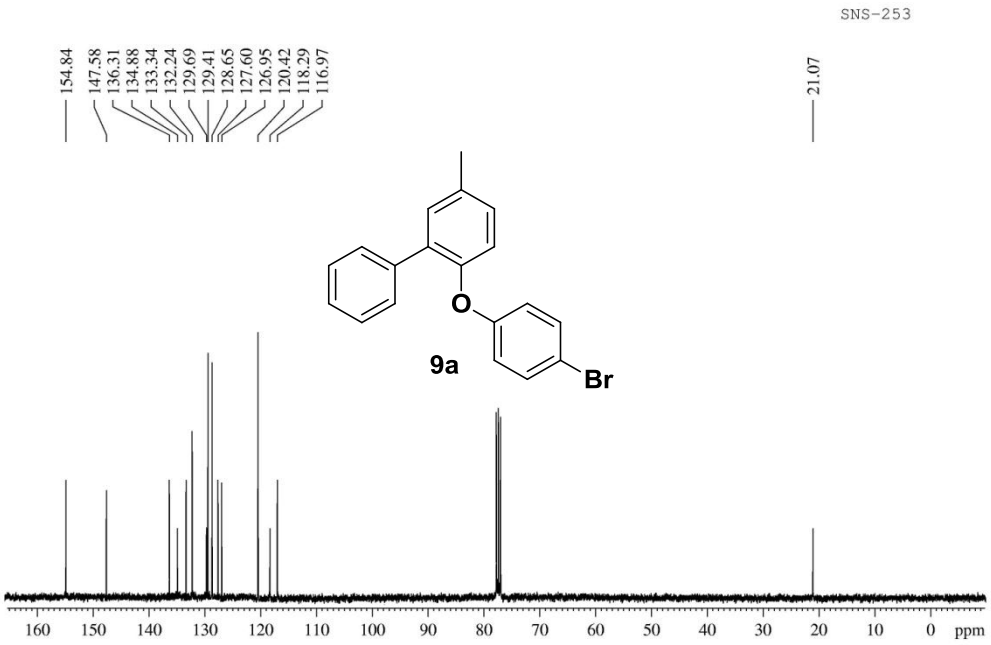
^{1}H NMR spectrum of 6d (300 MHz, $CDCl_3$)



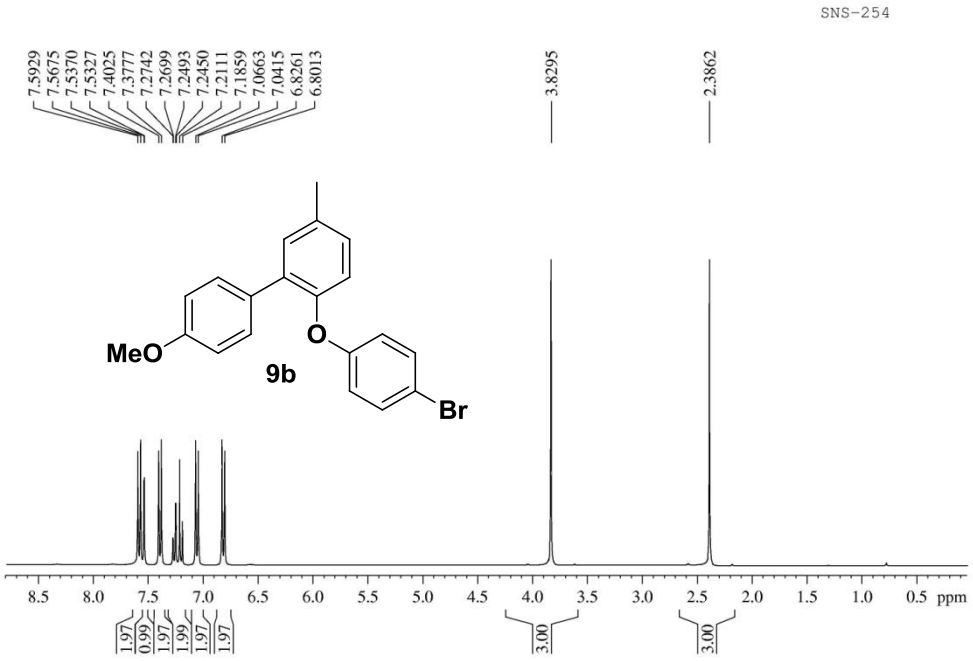
^{13}C NMR spectrum of 6d (75 MHz, $CDCl_3$)



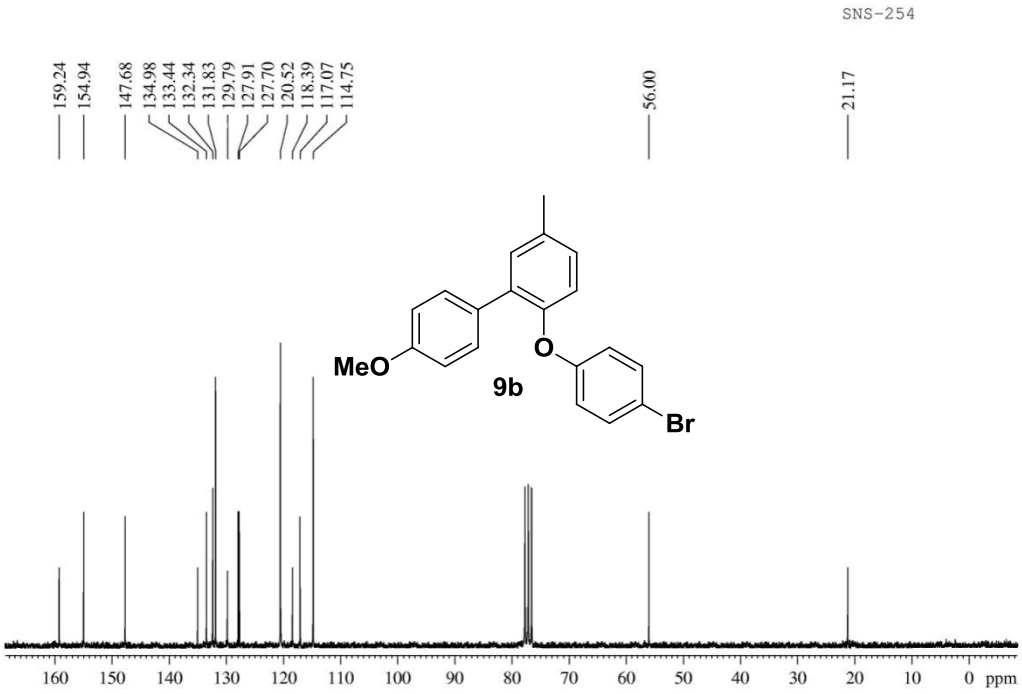
^{1}H NMR spectrum of 9a (300 MHz, $CDCl_3$)



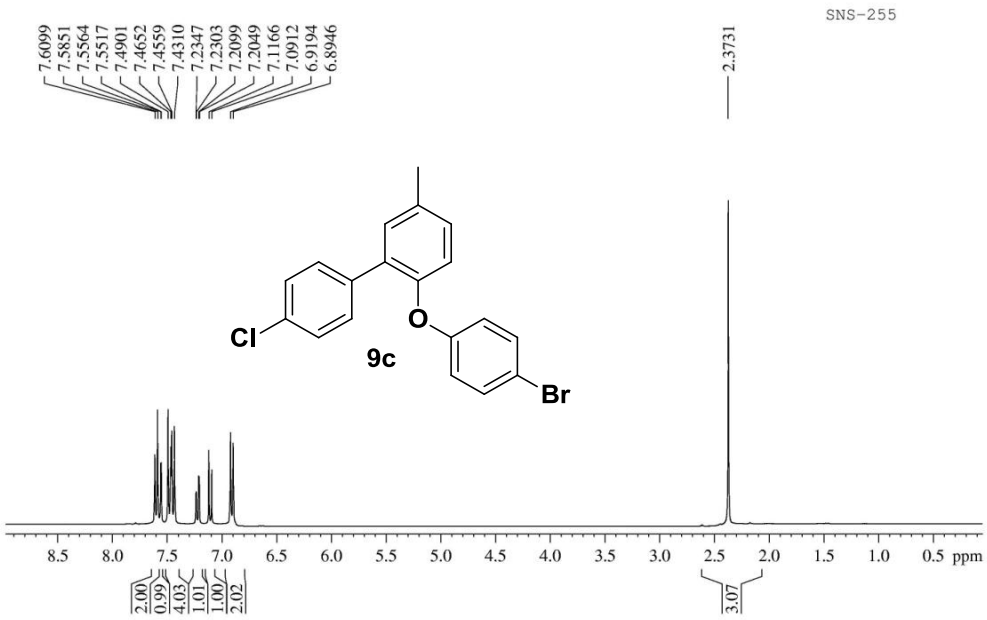
^{13}C NMR spectrum of 9a (75 MHz, $CDCl_3$)



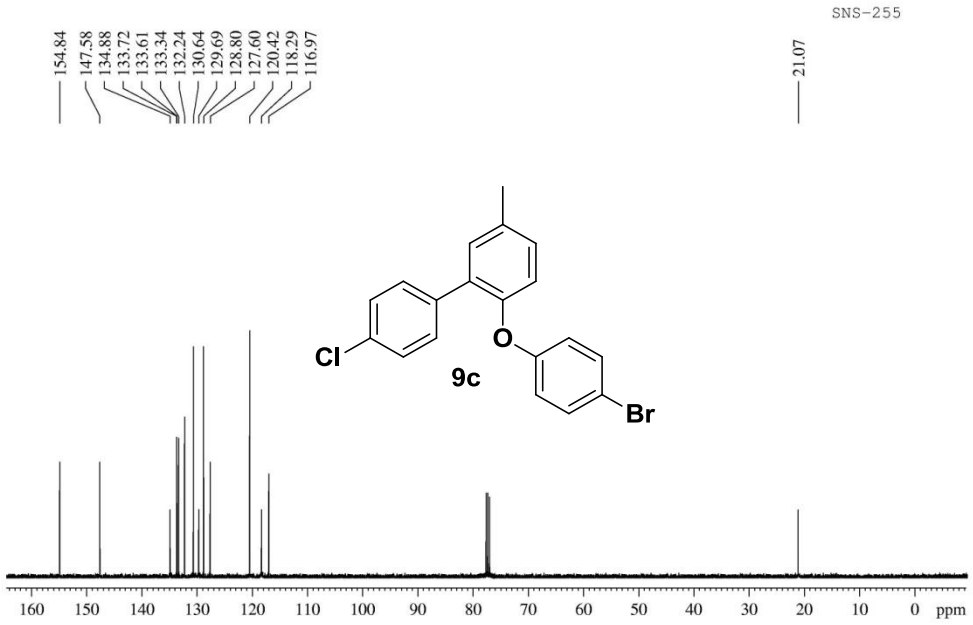
^{1}H NMR spectrum of 9b (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of 9b (75 MHz, $CDCl_3$)



^{1}H NMR spectrum of 9c (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of 9c (75 MHz, $CDCl_3$)