Supplementary data for

Pd(IV) – Induced Nucleophile Delivery in a Cascade Double Heck Reaction

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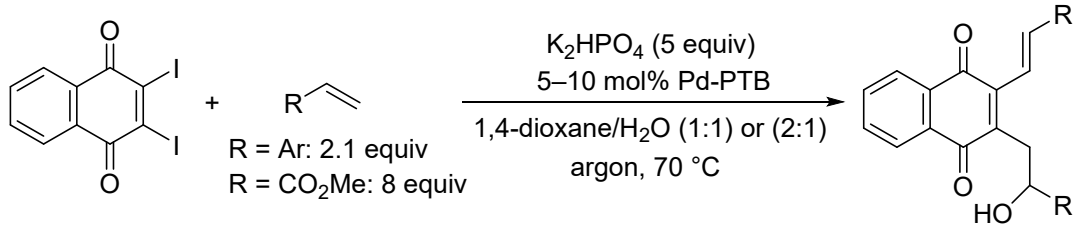
1. Materials and methods

Solvents were dried by the usual methods and then distilled prior to use. Commercially available styrenes, phenols, amines, and anilines were employed. Stock solutions of the catalyst were prepared by dissolving $Pd(OAc)_2$ (25 mg, 11.1 mmol) in 5 mL of either 1,4-dioxane or DMF at r.t. under argon atmosphere with a formation of the corresponding 22.3 mM solution. Palladacyclic catalysts were prepared from the stock 1,4-dioxane solution of $Pd(OAc)_2$ by addition of equimolar amount of the corresponding ligand. All catalysts solutions were stored for at least 24 h before the first employment. No difference in activity was observed for two commercial samples of $Pd(OAc)_2$ (from Sigma-Aldrich and Acros Organics). All inorganic bases were dissolved in water prior to addition to the reaction mixture. All catalytic reactions were carried out under argon atmosphere in pre-dried glassware without special care: either in closed round-bottom flasks or in the glass tubes with screw caps (sealed tubes). Vigorous stirring (1250 rpm) is necessary for the reactions to proceed to completion in the given time periods. Generally, excess of styrene significantly decreased the reaction rate under 1,4-dioxane–$KHCO_3$ conditions. 0.9 M aqueous stock solution of Me_2NH was prepared from equimolar amounts of $Me_2NH{\cdot}HCl$ and $KHCO_3$. Standard silica gel (0.060-0.200 mm, 60 Å), neutral and basic aluminum oxide (Brockmann I) for chromatography were used for the separation of the target material. NMR spectra were obtained on the Bruker Avance 300 or 600 equipment operating at 300 MHz for ^1H NMR and at either 75 MHz or 150 MHz for ^{13}C NMR with tetramethylsilane as internal standard. High resolution mass spectra (HRMS) were measured on the Bruker micrOTOF II instrument using electrospray ionization. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V); mass range from *m*/*z* 50 to *m*/*z* 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for CH_3CN solutions (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. IR spectra were recorded on Bruker Alpha-T spectrometer. Elemental analysis was performed on Perlin Elmer 2400 analyzer.

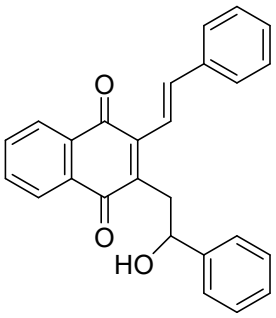
2. Experimental procedures

2.1 General procedure for cascade double Heck – hydroxide addition reaction of 2,3-diiodo-1,4-naphthoquinone (DINQ)



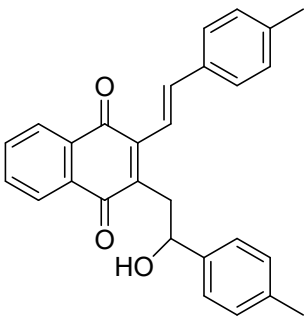
DINQ **1-6**

2,3-Diiodo-1,4-naphthoquinone[S1] (111 mg, 0.27 mmol) and either the corresponding styrene (0.57 mmol, 2.1 equiv) or methyl acrylate (186 mg, 1.16 mmol, 8 equiv) were dissolved in 1,4-dioxane (with a formation of homogeneous orange solution) followed by addition of K_2HPO_4 water solution and 22.3 mM 1,4-dioxane solution of Pd–PTB under argon atmosphere. (For 5 mol% Pd reactions 2.39 mL of 1,4-dioxane, 3 mL of 0.45 M aqueous K_2HPO_4 (5 equiv), and 0.61 mL of the Pd–PTB stock solution were used. For 10 mol% Pd reactions 2.78 mL of 1,4-dioxane, 2 mL of 0.675 M aqueous K_2HPO_4 (5 equiv), and 1.22 mL of the Pd–PTB stock solution were used.) The suspension was vigorously stirred in an aqueous bath at 70 °C (60 °C for methyl acrylate as a substrate) for the given amount of time until the full consumption of the starting diiodide. Solid NaCl was then added to the reaction mixture (until the saturation of the aqueous layer) followed by extractions with MTBE (3 × 4 ml). The combined organic layer was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and evaporated with 600 mg of silica gel. The powder residue was subjected to silica gel column chromatography.

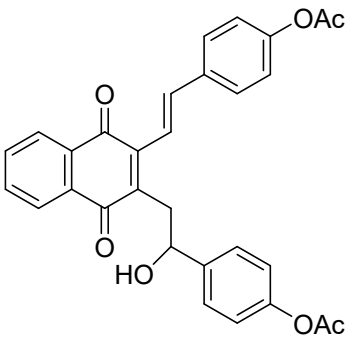


(E)-2-(2-hydroxy-2-phenylethyl)-3-styrylnaphthalene-1,4-dione (1). 5 mol% of Pd–PTB was used; reaction time – 3 h at 70 °C; eluent – hexane : ethyl acetate = 6 : 1; R_f 0.12. 55 mg (54 %) of pure target material was obtained after chromatography. Crystallization from the CH_2Cl_2/hexane solution by slow evaporation at 5 °C provided yellow puffy crystalline solid: mp 125–127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.69 (s, 1H), 3.26 (dd, 1H, J = 13.3 Hz, J = 4.5 Hz), 3.34 (dd, 1H, J = 13.3 Hz, J = 8.2 Hz), 5.10 (dd, 1H, J = 7.2 Hz, J = 4.5 Hz), 7.04 (d, 1H, J = 16.3 Hz), 7.24–7.55 (m, 10H), 7.66 (d, 1H, J = 16.3 Hz), 7.73–7.79 (m, 2H), 8.11–8.16 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.4, 74.0, 120.3, 125.5, 126.3, 126.6, 127.4, 127.8, 128.6, 128.8, 129.1, 132.0, 132.7, 133.6, 133.7, 137.1, 141.5, 141.8, 142.3, 144.1, 184.9, 186.2; IR (KBr, cm^{-1}) ν 3438, 3388, 3026, 1676, 1642, 1605,

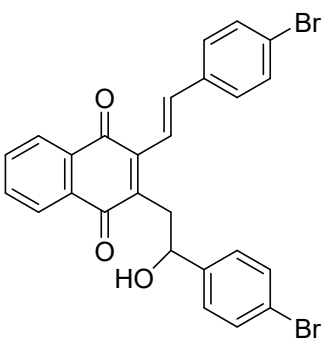
1449, 1295, 1037, 955, 752, 704, 542; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{26}H_{20}O_3$: 403.1305; found 403.1299.



(E)-2-(2-hydroxy-2-(p-tolyl)ethyl)-3-(4-methylstyryl)naphthalene-1,4-dione (2). 5 mol% of Pd–PTB was used; reaction time – 6 h at 70 °C; eluent – hexane : ethyl acetate = 6 : 1; R_f 0.13. 57 mg (52 %) of pure target material was obtained after chromatography. Crystallization from the CH_2Cl_2/hexane solution by slow evaporation at 5 °C provided dark red crystalline clusters: mp 112–113 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.36 (s, 3H), 2.68 (s, 1H), 3.16 (dd, 1H, J = 13.3 Hz, J = 4.4 Hz), 3.27 (dd, 1H, J = 13.3 Hz, J = 8.2 Hz), 5.00 (dd, 1H, J = 7.6 Hz, J = 4.2 Hz), 6.92 (d, 1H, J = 16.3 Hz), 7.10 (d, 2H, J = 7.7 Hz), 7.16 (d, 2H, J = 7.8 Hz), 7.29 (d, 2H, J = 7.7 Hz), 7.36 (d, 2H, J = 7.8 Hz), 7.59 (d, 1H, J = 16.3 Hz), 7.65–7.72 (m, 2H), 8.03–8.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 21.5, 37.4, 74.0, 119.5, 125.6, 126.3, 126.6, 127.4, 129.3, 129.6, 132.1, 132.9, 133.6, 133.7, 134.6, 137.5, 139.4, 141.3, 141.3, 141.6, 142.4, 185.0, 186.2; IR (KBr, cm^{-1}) ν 3511, 3023, 2921, 1644, 1594, 1513, 1351, 1291, 1179, 1049, 960, 815, 720, 533; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{28}H_{24}O_3$: 431.1618; found 431.1605.

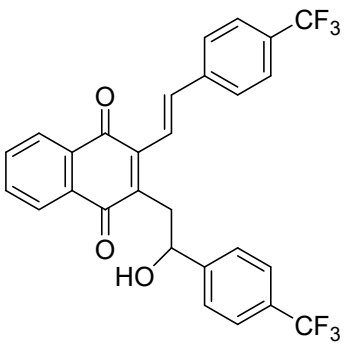


(E)-2-(2-hydroxy-2-(4-acetoxyphenyl)ethyl)-3-(4-acetoxystyryl)naphthalene-1,4-dione (3). 5 mol% of Pd–PTB was used; reaction time – 3 h at 70 °C; eluent – hexane : ethyl acetate = 2 : 1; R_f 0.16. 63 mg (47 %) of pure target material was obtained after chromatography. Crystallization from the CH_2Cl_2/hexane solution by slow evaporation at 5 °C provided dark red crystalline clusters: mp 131–134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.28 (s, 3H), 2.69 (s, 1H), 3.19 (dd, 1H, J = 13.5 Hz, J = 4.7 Hz), 3.27 (dd, 1H, J = 13.4 Hz, J = 8.6 Hz), 5.00 (dd, 1H, J = 7.2 Hz, J = 4.4 Hz), 6.97 (d, 1H, J = 16.4 Hz), 7.02 (d, 2H, J = 8.3 Hz), 7.09 (d, 2H, J = 8.3 Hz), 7.42 (d, 2H, J = 8.3 Hz), 7.48 (d, 2H, J = 8.3 Hz), 7.60 (d, 1H, J = 16.4 Hz), 7.66–7.71 (m, 2H), 8.02–8.08 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 21.2, 37.4, 73.5, 120.6, 121.8, 122.1, 126.3, 126.7, 126.7, 128.4, 132.1, 132.8, 133.7, 133.8, 134.9, 140.5, 141.8, 141.9, 142.4, 150.3, 151.3, 169.3, 169.4, 184.8, 186.1; IR (KBr, cm^{-1}) ν 3514, 3070, 2936, 1758, 1665, 1594, 1506, 1370, 1293, 1222, 1165, 1050, 1015, 961, 913, 841, 729, 645, 538; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{30}H_{24}O_7$: 519.1414; found 519.1409.

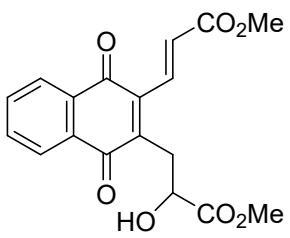


(E)-2-(2-(4-bromophenyl)-2-hydroxyethyl)-3-(4-bromostyryl)naphthalene-1,4-dione (4). 10 mol% of Pd–PTB was used; reaction time – 4 h at 70 °C; eluent – hexane : ethyl acetate = 6 : 1; R_f 0.10. 87 mg (60 %) of pure target material was obtained after

chromatography. Crystallization by slow diffusion of hexane into the $CHCl_3$ solution at 5 °C provided red-orange crystalline powder. High quality single crystals suitable for X-ray diffraction were grown from the $CDCl_3$ solution by slow evaporation at 5 °C: mp 175–178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.71 (s, 1H), 3.17 (d, 2H, J = 6.1 Hz), 5.00 (t, 1H, J = 5.9 Hz), 6.86 (d, 1H, J = 16.3 Hz), 7.24 (d, 2H, J = 8.3 Hz), 7.29 (d, 2H, J = 8.5 Hz), 7.39 (d, 2H, J = 8.3 Hz), 7.44–7.51 (m, 3H), 7.67–7.73 (m, 2H), 8.03–8.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.4, 73.4, 120.9, 121.8, 123.4, 126.4, 126.7, 127.4, 128.8, 131.8, 132.0, 132.1, 132.7, 133.8, 134.0, 136.0, 140.3, 141.7, 142.3, 143.1, 184.7, 186.1; IR (KBr, cm^{-1}) v 3469, 1663, 1608, 1484, 1352, 1295, 1067, 963, 815, 716, 518; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{26}H_{18}Br_2O_3$: 558.9515; found 558.9501.



(E)-2-(2-hydroxy-2-(4-(trifluoromethyl)phenyl)ethyl)-3-(4-(trifluoromethyl)styryl)naphthalene-1,4-dione (5). 10 mol% of Pd–PTB was used; reaction time – 2.5 h at 70 °C; eluent – hexane : ethyl acetate = 4 : 1; R_f 0.21. 74 mg (53 %) of pure target material was obtained after chromatography. Crystallization by slow diffusion of hexane into the $CHCl_3$ solution at 5 °C provided yellow crystalline powder: mp 178–179 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.66 (s, 1H), 3.16–3.27 (m, 2H), 5.13 (t, 1H, J = 5.9 Hz), 6.99 (d, 1H, J = 16.3 Hz), 7.49–7.57 (m, 6H), 7.59–7.64 (m, 3H), 7.71–7.76 (m, 2H), 8.07–8.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.5, 73.4, 122.6, 124.1 (q, J = 274 Hz), 124.1 (q, J = 274 Hz), 125.7, 125.7 (q, J = 4 Hz), 125.9 (q, J = 4 Hz), 126.5, 126.8, 127.4, 130.3 (q, J = 33 Hz), 130.8 (q, J = 33 Hz), 132.0, 132.7, 133.9, 134.1, 139.8, 140.4, 142.2, 142.2, 148.0, 184.6, 186.1; IR (KBr, cm^{-1}) v 3473, 1664, 1616, 1326, 1170, 1124, 1067, 966, 827, 716, 599; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{28}H_{18}F_6O_3$: 539.1052; found 539.1041.



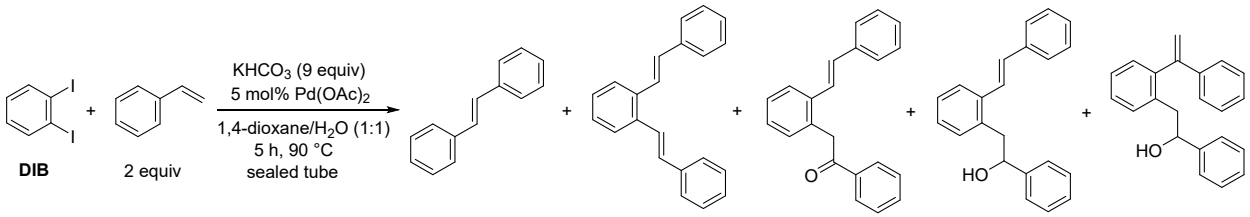
Methyl (E)-3-(3-(2-hydroxy-3-methoxy-3-oxopropyl)-1,4-dioxo-1,4-dihydronaphthalen-2-yl)acrylate (6). 10 mol% of Pd–PTB was used; reaction time – 3 h at 60 °C; eluent – hexane : ethyl acetate = 2 : 1; R_f 0.14. 32 mg (34 %) of pure target material was obtained after chromatography. Crystallization from the CH_2Cl_2/hexane solution by slow evaporation at 5 °C provided yellow X-ray quality crystals: mp 106–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.96 (br s, 1H), 3.09 (dd, 1H, J = 13.1 Hz, J = 8.4 Hz), 3.30 (dd, 1H, J = 13.1 Hz, J = 4.7 Hz), 3.78 (s, 3H), 3.79 (s, 3H), 4.43 (dd, 1H, J = 8.2 Hz, J = 4.9 Hz), 6.91 (d, 1H, J = 16.1 Hz), 7.65 (d, 1H, J = 16.1 Hz), 7.67–7.74 (m, 2H), 8.02–8.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.3, 52.1, 53.0, 69.7, 126.5, 126.8, 130.0, 131.8, 132.4, 133.9, 134.2, 135.4, 140.5, 144.4, 166.7, 174.2, 183.5, 184.8; IR (KBr, cm^{-1}) v 3446, 2953, 1741, 1717, 1661, 1591, 1441,

1284, 1246, 1206, 1097, 970, 716; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{18}H_{16}O_{27}$: 367.0788; found 367.0786.

*Gram-scale procedure for **1**:*

2,3-Diiodo-1,4-naphthoquinone (1.11 g, 2.7 mmol) and styrene (0.59 g, 5.7 mmol, 2.1 equiv) were dissolved in 24 mL of 1,4-dioxane. To the formed homogeneous orange solution 0.45 M K_2HPO_4 water solution (30 ml, 13.5 mmol, 5 equiv) was added followed by addition of 22.3 mM 1,4-dioxane solution of Pd–PTB (6 ml, 0.134 mmol, 5 mol%) under argon atmosphere. The suspension was vigorously stirred in an aqueous bath at 70 °C for 3 h until the full consumption of the starting diiodide. Solid NaCl was then added to the reaction mixture (until the saturation of the aqueous layer) followed by extractions with MTBE (3 × 30 ml). The combined organic layer was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and evaporated with 6 g of silica gel. The powder residue was subjected to silica gel column chromatography to afford 0.5 g (50 %) of pure target material as an orange solid.

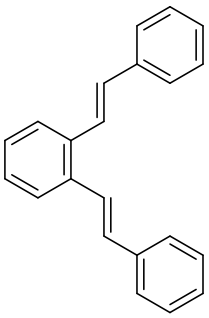
2.2 *Model reaction of 1,2-diiodobenzene (DIB) with styrene and water*



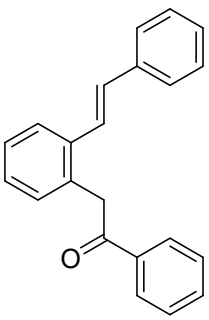
2%[b] **9**, 22%[b] **18**, 6%[b] **10**, 52%[c] **10'**, 3%[c]

1,2-Diiodobenzene (267 mg, 0.81 mmol) and styrene (168 mg, 1.62 mmol, 2 equiv) were dissolved in 7.18 mL of 1,4-dioxane. 0.8 M $KHCO_3$ aqueous solution (9 mL, 9 equiv) was added to the formed homogeneous solution in one portion followed by addition of 22.3 mM $Pd(OAc)_2$ 1,4-dioxane solution (1.82 mL, 5 mol%) under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed into a preheated to 90 °C oil bath for 5 h. After this time the solution became beige (loosing the deep brown color), while no starting material was detected by TLC. Solid NaCl was added to the reaction mixture (until the saturation of the aqueous layer) followed by extractions with MTBE (3 × 10 ml). The combined organic layer was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and evaporated with 1 g of silica gel. The powder residue was subjected to silica gel column chromatography.

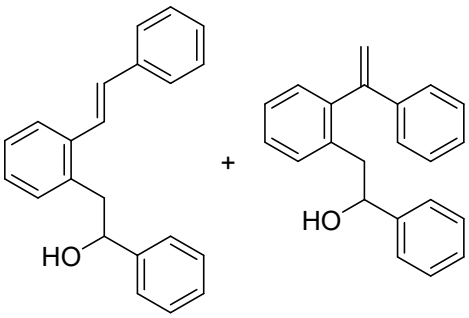
***trans*-Stilbene**. Eluent – hexane; R_f 0.29. 3 mg (2 %) of pure *trans*-stilbene was obtained after chromatography as white crystalline solid.



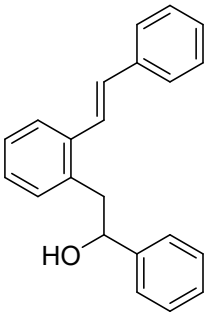
1,2-Di((E)-styryl)benzene (9). Eluent – hexane; R_f 0.16. 50 mg (22 %) of pure 1,2-di((E)-styryl)benzene was obtained after chromatography as light yellow solid. Crystallization from the hexane solution by slow evaporation at r.t. provided yellow needles: mp 116–117 °C (lit. 117–118 °C)[S2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, 2H, J = 16.1 Hz), 7.27–7.32 (m, 4H), 7.34–7.41 (m, 4H), 7.48 (d, 2H, J = 16.2 Hz), 7.49–7.56 (m, 4H), 7.59 (dd, 2H, J = 5.6 Hz, J = 3.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.7, 126.7, 126.8, 126.8, 127.8, 128.8, 131.5, 136.2, 137.6; Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.36; H, 6.35.



(E)-1-Phenyl-2-(2-styrylphenyl)ethan-1-one (18). Eluent – hexane : ethyl acetate = 20 : 1; R_f 0.18. 14 mg (6 %) of (E)-1-phenyl-2-(2-styrylphenyl)ethan-1-one was obtained after chromatography as light yellow oil which solidified on standing at r.t. to light yellow solid: mp 98–102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.47 (s, 2H), 7.00 (d, 1H, J = 16.0 Hz), 7.21–7.36 (m, 7H), 7.43 (d, 2H, J = 7.4 Hz), 7.49 (t, 2H, J = 7.7 Hz), 7.60 (t, 1H, J = 7.5 Hz), 7.67 (d, 1H, J = 7.7 Hz), 8.05 (d, 2H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6, 126.4, 126.5, 126.8, 127.7, 127.9, 128.0, 128.6, 128.8, 128.9, 131.0, 131.6; 133.0, 133.4, 136.9, 137.3, 137.5, 197.8; IR (KBr, cm^{-1}) v 3059, 3026, 2926, 1958, 1811, 1684, 1597, 1449, 1332, 1212, 961, 758, 691, 571, 538; HRMS (m/z) $[M + H]^+$ calcd for $C_{22}H_{18}O$: 299.1430; found 299.1430.



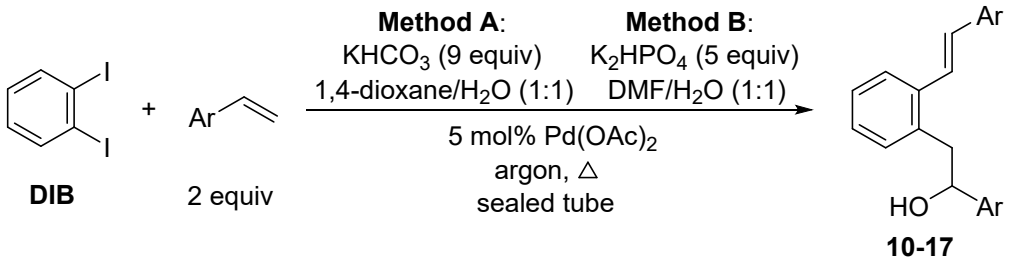
(E)-1-phenyl-2-(2-styrylphenyl)ethan-1-ol (10) and 1-Phenyl-2-(2-(1-phenylvinyl)phenyl)ethan-1-ol (10'). Eluent – hexane : ethyl acetate = 10 : 1; R_f 0.12. 134 mg (55 %) of the mixture of two inseparable isomers (1 to 18) was obtained after chromatography as light yellow oil. **10':** ^{1}H NMR (300 MHz, $CDCl_3$) (detectable signals) δ 2.79 (dd, 1H, J = 14.0 Hz, J = 9.1 Hz), 2.89 (dd, 1H, J = 14.0 Hz, J = 4.4 Hz), 4.74 (dd, 1H, J = 9.1 Hz, J = 4.4 Hz), 5.24 (d, 1H, J = 1.2 Hz), 5.85 (d, 1H, J = 1.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.6, 74.6, 116.0, 126.0, 126.8, 126.9, 127.6, 128.0, 128.2, 128.5, 128.8, 131.0, 131.2, 136.5, 141.0, 142.2, 144.5, 149.4.



Pure **10** was obtained by slow evaporation of the Et_2O/hexane solution of the mixture of the isomers at 5 °C as white crystalline fibers: mp 90–92 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97 (s, 1H), 3.11–3.23 (m, 2H), 4.91 (t, 1H, J = 6.5 Hz), 6.96 (d, 1H, J = 16.1 Hz), 7.13–7.41 (m, 12H), 7.49 (d, 2H, J = 7.6 Hz), 7.61 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6, 75.1, 125.9, 126.2, 126.3, 126.3, 126.7, 127.2, 127.7, 127.8, 128.5, 128.8, 130.8, 131.2,

135.9, 137.0, 137.6, 144.0; IR (KBr, cm^{-1}) *v* 3388, 3025, 2933, 1632, 1494, 1452, 1339, 1046, 956, 759, 690, 531; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{22}H_{20}O$: 323.1406; found 323.1408.

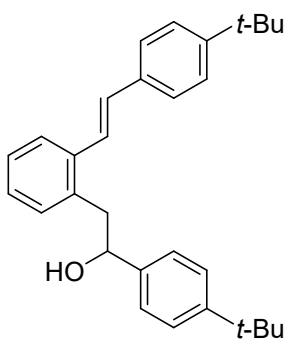
2.3 *General procedure for cascade double Heck – hydroxide addition reaction of 1,2-diiodobenzene (DIB)*



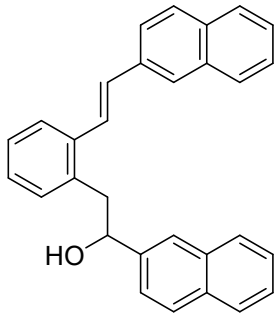
Method A: 1,2-Diiodobenzene (116 mg, 0.35 mmol) and the corresponding styrene (0.7 mmol, 2 equiv) were dissolved in 3.11 mL of 1,4-dioxane. 0.8 M $KHCO_3$ aqueous solution (3.9 mL, 9 equiv) was added to the formed homogeneous solution in one portion followed by addition of 22.3 mM $Pd(OAc)_2$ 1,4-dioxane solution (0.79 mL, 5 mol%) under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed into a preheated oil bath. The vigorous stirring was continued for the given amount of time until the full consumption of the starting diiodide. Solid NaCl was then added to the reaction mixture (until the saturation of the aqueous layer) followed by extractions with MTBE (3 × 5 ml). The combined organic layer was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and evaporated with 600 mg of silica gel. The powder residue was subjected to silica gel column chromatography.

Method B: 1,2-Diiodobenzene (116 mg, 0.35 mmol) and the corresponding styrene (1.05 mmol, 3 equiv) were dissolved in 3.11 mL of DMF. 0.45 M K_2HPO_4 water solution (3.9 mL, 5 equiv) was added to the formed homogeneous solution in one portion followed by addition of 22.3 mM $Pd(OAc)_2$ DMF solution (0.79 mL, 5 mol%) under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed into a preheated oil bath. The vigorous stirring was continued for the given amount of time until the full consumption of the starting diiodide. Solid NaCl was then added to the reaction mixture (until the saturation of the aqueous layer) followed by extractions with MTBE (4 × 5 ml). The combined organic layer was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and evaporated with 600 mg of silica gel. The powder residue was subjected to silica gel column chromatography.

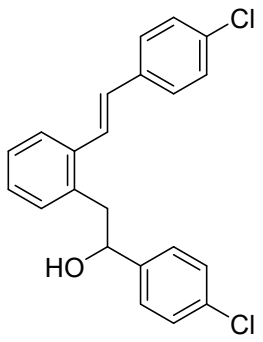
(E)-1-phenyl-2-(2-styrylphenyl)ethan-1-ol (10). **Method B**: reaction time – 1.5 h at 100 °C. 54 mg (51 %) of the mixture of two isomers was obtained after chromatography as white solid.



(E)-1-(4-(tert-butyl)phenyl)-2-(2-(4-(tert-butyl)styryl)phenyl)ethan-1-ol (11). **Method A**: reaction time – 5 h at 110 °C; eluent – hexane : ethyl acetate = 6 : 1; R_f 0.25. 79 mg (55 %) of pure target material was obtained after chromatography as an oil which solidified on standing at r.t. to a white solid: mp 97–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 1.35 (s, 9H), 1.91 (s, 1H), 3.12 (dd, 1H, J = 13.8 Hz, J = 8.4 Hz), 3.22 (dd, 1H, J = 13.8 Hz, J = 4.7 Hz), 4.43 (dd, 1H, J = 8.2 Hz, J = 4.7 Hz), 6.95 (d, 1H, J = 16.0 Hz), 7.19–7.45 (m, 12H), 7.61 (d, 1H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.4, 31.4, 34.6, 34.7, 43.5, 74.8, 125.5, 125.5, 125.6, 125.7, 126.1, 126.5, 127.2, 127.5, 130.5, 131.2, 134.9, 136.0, 137.2, 141.1, 150.7, 151.0; IR (KBr, cm^{-1}) ν 3543, 3448, 3057, 2960, 2866, 1905, 1610, 1513, 1457, 1361, 1267, 1108, 1048, 968, 817, 755, 560; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{30}H_{36}O$: 435.2658; found 435.2654.

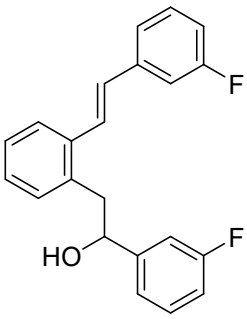


(E)-1-(naphthalen-2-yl)-2-(2-(2-(naphthalen-2-yl)vinyl)phenyl)ethan-1-ol (12). **Method B**: reaction time – 5 h at 105 °C; eluent – hexane : ethyl acetate = 6 : 1; R_f 0.14. 85 mg (61 %) of pure target material was obtained after chromatography. Crystallization from the Et_2O/hexane solution by slow evaporation at 5 °C provided colorless X-ray quality crystals: mp 121–122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 1H), 3.26 (dd, 1H, J = 13.8 Hz, J = 7.8 Hz), 3.33 (dd, 1H, J = 13.8 Hz, J = 5.2 Hz), 5.09 (dd, 1H, J = 7.2 Hz, J = 5.6 Hz), 7.06 (d, 1H, J = 16.0 Hz), 7.21–7.33 (m, 3H), 7.41–7.52 (m, 6H), 7.63–7.67 (m, 2H), 7.74–7.84 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6, 75.3, 123.6, 124.0, 124.6, 125.9, 126.0, 126.2, 126.2, 126.4, 126.6, 126.8, 127.3, 127.8, 127.8, 127.8, 127.8, 128.0, 128.1, 128.3, 128.4, 130.8, 131.2, 133.2, 133.4, 133.8, 135.1, 135.9, 137.1, 141.4; IR (KBr, cm^{-1}) ν 3549, 3474, 3049, 2936, 1627, 1596, 1505, 1453, 1362, 1272, 1160, 1034, 965, 863, 815, 743, 478; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{30}H_{24}O$: 423.1719; found 423.1709.

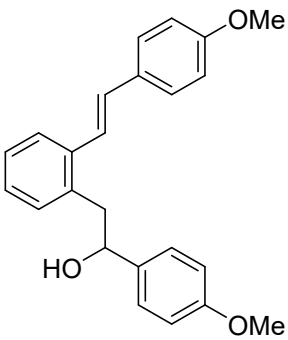


(E)-1-(4-chlorophenyl)-2-(2-(4-chlorostyryl)phenyl)ethan-1-ol (13). **Method B**: reaction time – 1.5 h at 100 °C; eluent – hexane : ethyl acetate = 6 : 1; R_f 0.14. 54 mg (42 %) of pure target material was obtained after chromatography as an oil which solidified on standing at r.t. to a white solid: mp 94–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97 (s, 1H), 3.12 (d, 2H, J = 6.7 Hz), 4.85 (t, 1H, J = 6.7 Hz), 6.83 (d, 1H, J = 16.1 Hz), 7.09–7.39 (m, 12H), 7.55 (d, 1H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.4, 74.5, 126.3, 126.7, 127.2, 127.4, 127.6, 127.8, 128.0, 128.6, 129.0, 130.0, 131.2, 133.5, 135.4, 136.0, 136.8, 142.2; IR (KBr, cm^{-1}) ν 3396, 3023, 2930, 1897, 1726, 1628, 1596, 1490,

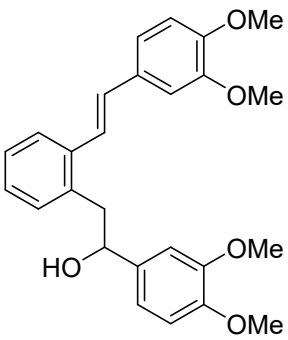
1405, 1325, 1091, 1010, 960, 810, 750, 535, 441; HRMS (*m/z*) [M + Na]$^+$ calcd for $C_{22}H_{18}Cl_2O$: 391.0627; found 391.0615.



(E)-1-(3-fluorophenyl)-2-(2-(3-fluorostyryl)phenyl)ethan-1-ol (14). **Method B**: reaction time – 3 h at 90 °C; eluent – hexane : ethyl acetate = 6 : 1; R_f 0.16. 47 mg (40 %) of pure target material was obtained after chromatography as an oil which solidified on standing at r.t. to a light grey solid: mp 71–72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.05 (s, 1H), 3.14 (d, 2H, J = 6.7 Hz), 4.88 (t, 1H, J = 6.7 Hz), 6.88 (d, 1H, J = 16.1 Hz), 6.88–7.05 (m, 4H), 7.12–7.36 (m, 8H), 7.58 (d, 1H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.4, 74.5 (d, J = 1.4 Hz), 112.7 (d, J = 14.9 Hz), 113.1 (d, J = 14.8 Hz), 114.5, 114.7, 121.4 (d, J = 2.8 Hz), 122.5 (d, J = 2.8 Hz), 126.3, 127.4, 127.4 (d, J = 2.5 Hz), 128.1, 129.7 (d, J = 2.7 Hz), 130.0 (d, J = 8.1 Hz), 130.2 (d, J = 8.4 Hz), 131.2, 135.6, 136.6, 139.9 (d, J = 7.7 Hz), 146.5 (d, J = 6.6 Hz), 162.7 (d, J = 246 Hz), 163.3 (d, J = 246 Hz); IR (KBr, cm^{-1}) ν 3391, 3028, 2927, 1922, 1722, 1581, 1489, 1448, 1262, 1145, 1051, 961, 864, 777, 678, 507, 461; HRMS (*m/z*) [M + Na]$^+$ calcd for $C_{22}H_{18}F_2O$: 359.1218; found 359.1211.

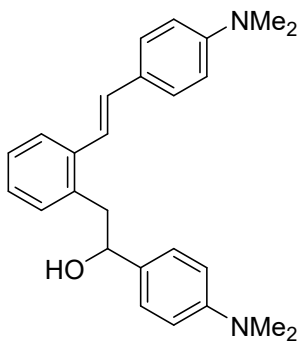


(E)-1-(4-methoxyphenyl)-2-(2-(4-methoxystyryl)phenyl)ethan-1-ol (15). **Method A**: reaction time – 4 h at 110 °C; eluent – hexane : ethyl acetate = 4 : 1; R_f 0.18. 84 mg (67 %) of pure target material was obtained after chromatography as a white solid: mp 100–103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (s, 1H), 3.14 (d, 2H, J = 6.6 Hz), 3.75 (s, 3H), 3.82 (s, 3H), 4.85 (t, 1H, J = 6.6 Hz), 6.81–6.96 (m, 5H), 7.11–7.26 (m, 6H), 7.41 (d, 2H, J = 8.5 Hz), 7.57 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6, 55.3, 55.4, 74.6, 113.9, 114.2, 124.2, 125.9, 127.1, 127.1, 127.3, 127.9, 130.2, 130.5, 131.1, 135.7, 136.2, 137.2, 159.2, 159.4; IR (KBr, cm^{-1}) ν 3396, 3003, 2933, 2834, 1604, 1512, 1459, 1300, 1249, 1176, 1033, 961, 823, 749, 539; HRMS (*m/z*) [M + Na]$^+$ calcd for $C_{24}H_{24}O_3$: 383.1618; found 383.1605.



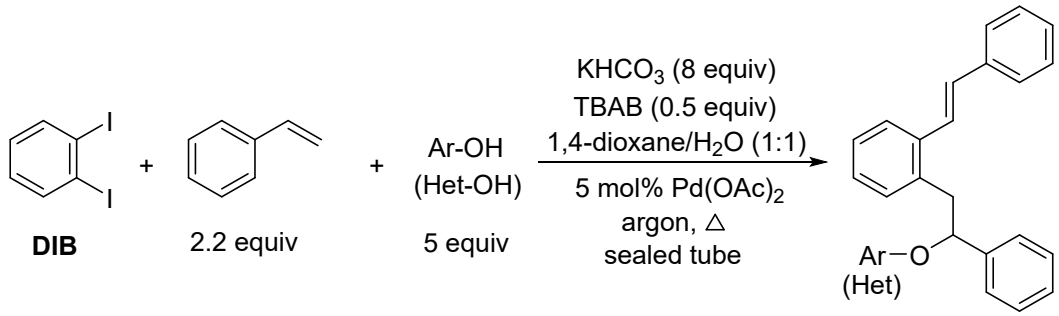
(E)-1-(3,4-dimethoxyphenyl)-2-(2-(3,4-dimethoxystyryl)phenyl)ethan-1-ol (16). **Method A**: reaction time – 9 h at 110 °C; eluent – hexane : ethyl acetate = 2 : 1 to 1 : 1; R_f (hexane : ethyl acetate = 1 : 1) 0.24. 103 mg (70 %) of pure target material was obtained after chromatography as a beige solid: mp 113–116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 1H), 3.14 (d, 2H, J = 6.4 Hz), 3.74 (s, 3H), 3.78 (s, 3H), 3.88 (s, 3H), 3.91 (s, 3H), 4.84 (t, 1H, J = 6.4 Hz), 6.71–6.86 (m, 5H), 6.98–7.03 (m, 2H), 7.08–7.25 (m, 4H), 7.54 (d, 1H, J = 7.4 Hz); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 43.5, 55.8, 56.0, 56.0, 56.1, 74.9, 109.2, 109.5, 111.1, 111.5, 117.9, 119.7, 124.5, 126.0, 127.1, 127.4, 130.4, 130.9, 131.1, 135.7, 136.7, 137.2, 148.6, 149.1, 149.1, 149.3; IR (KBr, cm^{-1}) ν 3404, 3005, 2930, 2834, 2042, 1596, 1514, 1462, 1418, 1267, 1139, 1025, 952, 797, 751, 617, 553; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{26}H_{28}O_5$: 443.1829; found 443.1828.



(E)-1-(4-(dimethylamino)phenyl)-2-(2-(4-(dimethylamino)styryl)phenyl)ethan-1-ol (17). **Method A**: TBAB (113 mg, 0.35 mmol, 1 equiv) was also added. Reaction time – 4 h at 115 °C; eluent – hexane : ethyl acetate = 3 : 1; R_f 0.10. 53 mg (39 %) of pure target material was obtained after chromatography as a brown oil; ^1H NMR (300 MHz, $CDCl_3$) δ 1.87 (s, 1H), 2.92 (s, 6H), 2.98 (s, 6H), 3.09–3.22 (m, 2H), 4.84 (dd, 1H, J = 7.5 Hz, J = 5.6 Hz), 6.70 (d, 2H, J = 8.5 Hz), 6.72 (d, 2H, J = 8.5 Hz), 6.91 (d, 1H, J = 16.0 Hz), 7.13–7.26 (m, 6H), 7.40 (d, 2H, J = 8.7 Hz), 7.60 (d, 1H, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.6, 40.8, 43.5, 74.7, 112.6, 112.7, 122.0, 125.7, 126.3, 126.8, 126.9, 127.7, 130.2, 130.6, 131.1, 132.2, 135.9, 137.6, 150.3, 150.3; IR (KBr, cm^{-1}) ν 3553, 3419, 2975, 2882, 2801, 1878, 1611, 1520, 1446, 1355, 1222, 1165, 1060, 947, 812, 754, 541; HRMS (*m/z*) $[M + H]^+$ calcd for $C_{26}H_{30}N_2O$: 387.2431; found 387.2423.

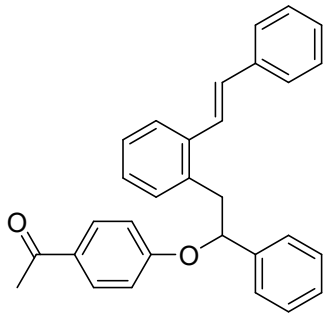
2.4 *General procedure for cascade double Heck – aryloxide addition reaction of 1,2-diiodobenzene (DIB)*



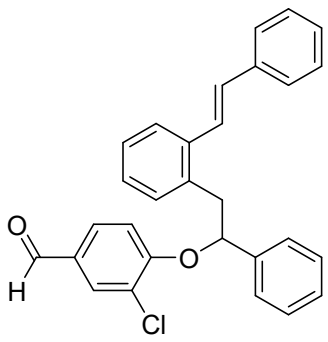
19-25

1,2-Diiodobenzene (71 mg, 0.215 mmol), styrene (49 mg, 0.47 mmol, 2.2 equiv), TBAB (35 mg, 0.108 mmol, 0.5 equiv), and the corresponding phenol (1.08 mmol, 5 equiv) were dissolved in 1.91 mL of 1,4-dioxane and 0.24 mL of H_2O. 0.8 M $KHCO_3$ aqueous solution (2.16 mL, 8 equiv) was added in one portion followed by addition of 22.3 mM $Pd(OAc)_2$ 1,4-dioxane solution (0.49 mL, 5 mol%) under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed into a preheated oil bath. The vigorous stirring was continued for the given amount of time until the full consumption of the starting diiodide. MTBE (3 mL) was then

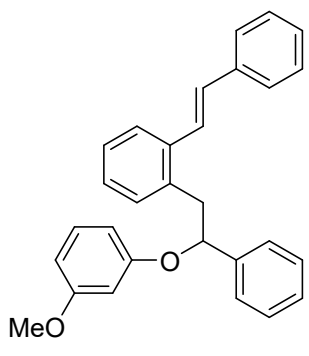
added to the cooled reaction mixture. The organic layer was combined with two additional MTBE extracts (2 × 3 mL) and evaporated to dryness. The residue was redissolved in MTBE and evaporated with 500 mg of either silica gel or neutral aluminum oxide. The powder residue was subjected to column chromatography.



(E)-1-(4-(1-phenyl-2-(2-styrylphenyl)ethoxy)phenyl)ethan-1-one (19). Reaction time – 2 h at 100 °C; chromatography on Al_2O_3; eluent – hexane : ethyl acetate = 15 : 1; R_f (SiO_2, hexane : ethyl acetate = 6 : 1) 0.20. 46 mg (51 %) of pure target material was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.49 (s, 3H), 3.36 (dd, 1H, J = 14.0 Hz, J = 5.6 Hz), 3.54 (dd, 1H, J = 14.0 Hz, J = 7.3 Hz), 5.44 (t, 1H, J = 6.4 Hz), 6.84 (d, 2H, J = 8.7 Hz), 6.98 (d, 1H, J = 16.0 Hz), 7.15–7.36 (m, 9H), 7.39–7.45 (m, 3H), 7.50–7.54 (m, 2H), 7.62 (d, 1H, J = 7.6 Hz), 7.78 (d, 2H, J = 8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 42.2, 81.2, 115.6, 126.0, 126.1, 126.5, 126.5, 126.7, 127.3, 127.6, 127.8, 128.1, 128.8, 128.8, 130.4, 130.8, 131.2, 135.1, 137.1, 137.6, 140.5, 162.0, 196.6; IR (KBr, cm^{-1}) v 3061, 3026, 2927, 1957, 1677, 1599, 1505, 1357, 1247, 1172, 1012, 960, 834, 760, 697, 594, 533; HRMS (m/z) $[M + H]^+$ calcd for $C_{30}H_{26}O_2$: 419.2006; found 419.2008.

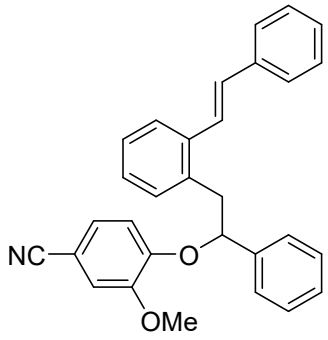


(E)-3-chloro-4-(1-phenyl-2-(2-styrylphenyl)ethoxy)benzaldehyde (20). 0.8 eq of TBAB (55 mg, 0.172 mmol) was used. Reaction time – 6 h at 110 °C; chromatography on SiO_2; eluent – hexane : ethyl acetate = 20 : 1 to 10 : 1; R_f (SiO_2, hexane : ethyl acetate = 10 : 1) 0.12. 53 mg (56 %) of pure target material was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.40 (dd, 1H, J = 14.0 Hz, J = 5.1 Hz), 3.60 (dd, 1H, J = 14.0 Hz, J = 7.5 Hz), 5.44 (t, 1H, J = 6.3 Hz), 6.77 (d, 1H, J = 8.5 Hz), 6.96 (d, 1H, J = 16.1 Hz), 7.21–7.38 (m, 9H), 7.39–7.45 (m, 4H), 7.47–7.54 (m, 2H), 7.60 (d, 1H, J = 7.3 Hz), 7.86 (s, 1H), 9.75 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.2, 82.4, 114.7, 124.7, 125.9, 126.2, 126.3, 126.7, 127.4, 127.6, 127.8, 128.4, 128.8, 128.9, 130.0, 130.3, 131.1, 131.3, 131.6, 134.7, 137.2, 137.5, 139.7, 158.3, 189.6; IR (KBr, cm^{-1}) v 3062, 3027, 2927, 2850, 2728, 1957, 1694, 1594, 1493, 1266, 1194, 1054, 1004, 963, 910, 760, 699, 529; HRMS (m/z) $[M + Na]^+$ calcd for $C_{29}H_{23}ClO_2$: 461.1279; found 461.1271.

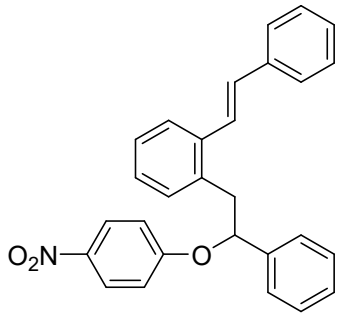


(E)-1-(2-(3-methoxyphenoxy)-2-phenylethyl)-2-styrylbenzene (21). Reaction time – 5 h at 110 °C; chromatography on Al_2O_3; eluent – hexane : ethyl acetate = 30 : 1; R_f (SiO_2, hexane : ethyl acetate = 20 : 1) 0.23. 27 mg (31 %) of pure target material was obtained as a colorless

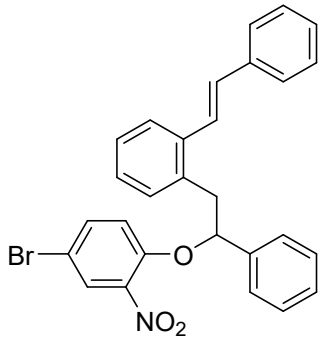
oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.28 (dd, 1H, J = 14.0 Hz, J = 5.5 Hz), 3.51 (dd, 1H, J = 14.0 Hz, J = 7.4 Hz), 3.67 (s, 3H), 5.34 (t, 1H, J = 6.4 Hz), 6.37–6.45 (m, 3H), 6.93–7.07 (m, 2H), 7.15–7.45 (m, 12H), 7.49–7.54 (m, 2H), 7.62 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.4, 55.2, 81.2, 102.6, 106.7, 108.3, 125.9, 126.1, 126.7, 127.1, 127.5, 127.7, 127.7, 127.8, 128.6, 128.8, 129.7, 130.5, 131.3, 135.6, 137.1, 137.7, 141.4, 159.4, 160.7; IR (KBr, cm^{-1}) ν 3061, 3026, 2929, 2411, 1599, 1491, 1451, 1284, 1199, 1150, 1045, 961, 836, 760, 697, 538; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{29}H_{26}O_2$: 429.1825; found 429.1819.



(E)-3-methoxy-4-(1-phenyl-2-(2-styrylphenyl)ethoxy)benzonitrile (22). Reaction time – 4 h at 110 °C; chromatography on Al_2O_3; eluent – hexane : ethyl acetate = 10 : 1; R_f (SiO_2, hexane : ethyl acetate = 10 : 1) 0.17. 58 mg (63 %) of pure target material was obtained as a light yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.34 (dd, 1H, J = 13.9 Hz, J = 5.9 Hz), 3.61 (dd, 1H, J = 13.9 Hz, J = 7.2 Hz), 3.83 (s, 3H), 5.41 (t, 1H, J = 6.4 Hz), 6.65 (d, 1H, J = 8.3 Hz), 6.90–7.04 (m, 3H), 7.14–7.36 (m, 9H), 7.37–7.45 (m, 3H), 7.49–7.54 (m, 2H), 7.60 (d, 1H, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.1, 56.2, 82.4, 104.1, 114.8, 115.3, 119.2, 126.0, 126.6, 127.3, 127.5, 127.5, 127.8, 127.8, 128.2, 128.6, 128.6, 128.8, 130.8, 131.3, 135.0, 137.3, 137.6, 140.0, 150.2, 151.5; IR (KBr, cm^{-1}) ν 3061, 3027, 2935, 2599, 2225, 1957, 1598, 1510, 1451, 1331, 1266, 1240, 1138, 1032, 964, 855, 810, 761, 701, 619, 532; HRMS (*m/z*) $[M + NH_4]^+$ calcd for $C_{30}H_{25}NO_2$: 449.2224; found 429.2221.

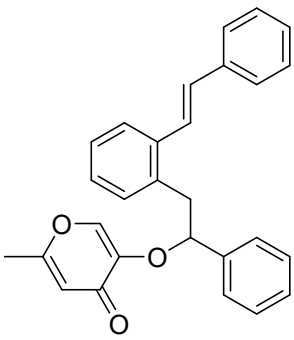


(E)-1-(2-(4-nitrophenoxy)-2-phenylethyl)-2-styrylbenzene (23). Reaction time – 2 h at 105 °C; chromatography on Al_2O_3; eluent – hexane : ethyl acetate = 40 : 1; R_f (SiO_2, hexane : ethyl acetate = 20 : 1) 0.14. 45 mg (50 %) of pure target material was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.36 (dd, 1H, J = 14.1 Hz, J = 5.5 Hz), 3.55 (dd, 1H, J = 14.1 Hz, J = 7.4 Hz), 5.44 (dd, 1H, J = 6.9 Hz, J = 5.9 Hz), 6.84 (d, 2H, J = 9.2 Hz), 6.99 (d, 1H, J = 16.1 Hz), 7.15–7.47 (m, 12H), 7.50–7.55 (m, 2H), 7.63 (d, 1H, J = 7.6 Hz), 8.03 (d, 2H, J = 9.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.2, 81.9, 115.8, 125.7, 125.9, 126.2, 126.3, 126.6, 127.4, 127.6, 127.9, 128.5, 128.9, 128.9, 131.0, 131.2, 134.8, 137.1, 137.5, 139.9, 141.5, 163.0; IR (KBr, cm^{-1}) ν 3061, 3027, 2931, 1957, 1591, 1513, 1342, 1259, 1172, 1112, 1007, 963, 845, 761, 699, 531; HRMS (*m/z*) $[M + NH_4]^+$ calcd for $C_{28}H_{23}NO_3$: 439.2016; found 439.2018.



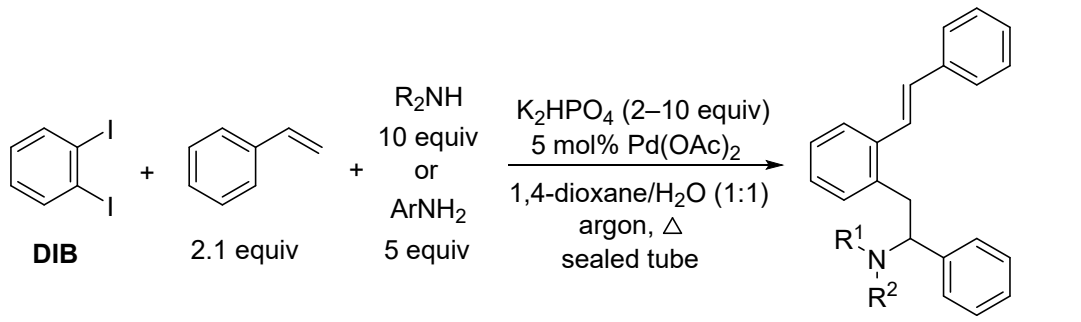
(E)-4-bromo-2-nitro-1-(1-phenyl-2-(2-styrylphenyl)ethoxy)benzene (24). Reaction time – 4 h at 105 °C; chromatography on Al_2O_3; eluent – hexane : ethyl acetate = 40 : 1; R_f

(SiO_2, hexane : ethyl acetate = 20 : 1) 0.16. 54 mg (50 %) of pure target material was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.34 (dd, 1H, J = 14.0 Hz, J = 5.5 Hz), 3.52 (dd, 1H, J = 14.0 Hz, J = 7.4 Hz), 5.39 (t, 1H, J = 6.4 Hz), 6.64 (d, 1H, J = 9.0 Hz), 6.93 (d, 1H, J = 16.1 Hz), 7.15–7.35 (m, 11H), 7.37–7.44 (m, 2H), 7.47–7.52 (m, 2H), 7.56 (d, 1H, J = 7.5 Hz), 7.86 (d, 1H, J = 2.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.1, 82.9, 111.9, 117.9, 126.0, 126.1, 126.7, 127.5, 127.7, 127.9, 128.0, 128.6, 128.6, 128.8, 129.0, 131.2, 131.7, 134.5, 136.3, 136.9, 137.4, 139.3, 141.0, 150.3; IR (KBr, cm^{-1}) v 3026, 2963, 1959, 1601, 1529, 1479, 1352, 1261, 1101, 1018, 802, 759, 698, 527; HRMS (m/z) $[M + NH_4]^+$ calcd for $C_{28}H_{22}BrNO_3$: 517.1121; found 517.1105.



(E)-2-methyl-5-(1-phenyl-2-(2-styrylphenyl)ethoxy)-4H-pyran-4-one (25). Reaction time – 2 h at 100 °C; chromatography on Al_2O_3; eluent – hexane : ethyl acetate = 5 : 1; R_f (SiO_2, hexane : ethyl acetate = 2 : 1) 0.17. 46 mg (52 %) of pure target material was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 3H), 3.33 (dd, 1H, J = 13.6 Hz, J = 7.7 Hz), 3.71 (dd, 1H, J = 13.7 Hz, J = 6.0 Hz), 5.33 (t, 1H, J = 6.8 Hz), 6.17 (s, 1H), 6.90 (d, 1H, J = 16.0 Hz), 7.09–7.34 (m, 11H), 7.36–7.43 (m, 2H), 7.50–7.59 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 41.7, 82.4, 114.5, 125.8, 126.3, 126.6, 126.7, 127.1, 127.5, 127.6, 128.2, 128.5, 128.7, 130.7, 131.4, 134.7, 137.1, 137.6, 139.5, 143.0, 146.0, 164.5, 174.8; IR (KBr, cm^{-1}) v 3061, 3028, 2928, 2242, 1957, 1648, 1595, 1495, 1451, 1409, 1209, 1162, 965, 910, 856, 762, 699, 538; HRMS (m/z) $[M + H]^+$ calcd for $C_{28}H_{24}O_3$: 409.1798; found 409.1788.

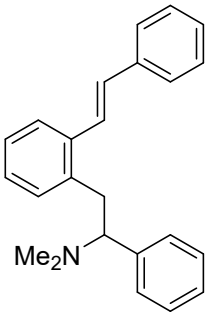
2.5 *General procedure for cascade double Heck – Secondary Amine or Aniline addition reaction of 1,2-diiodobenzene (DIB)*



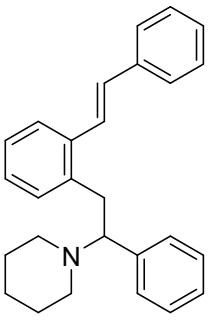
26-28, $R^1 = R^2$
29-31, R^1 = H, R^2 = Ar

For secondary amines:

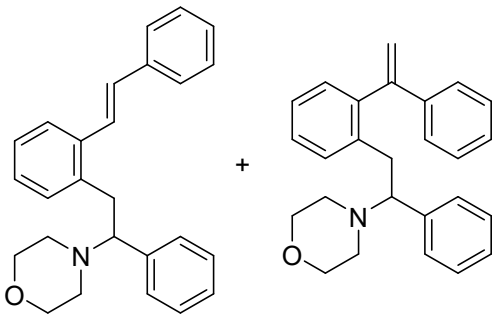
1,2-Diiodobenzene (116 mg, 0.35 mmol), styrene (77 mg, 0.74 mmol, 2.1 equiv), secondary amine (3.5 mmol, 10 equiv), and $K_2HPO_4 \cdot 3H_2O$ (160 mg, 0.7 mmol, 2 equiv) were dissolved in 3.11 mL of 1,4-dioxane and 3.9 mL of H_2O. 22.3 mM $Pd(OAc)_2$ 1,4-dioxane solution (0.79 mL, 5 mol%) was then added under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed into a preheated oil bath. The vigorous stirring was continued for the given amount of time until the full consumption of the starting diiodide. MTBE (5 mL) was added to the cooled reaction mixture. The organic layer was combined with two additional MTBE extracts (2 × 5 mL) and evaporated to dryness. The residue was dissolved in THF and evaporated with 600 mg of aluminum oxide. The powder residue was subjected to aluminum oxide column chromatography.



(E)-N,N-dimethyl-1-phenyl-2-(2-styrylphenyl)ethan-1-amine (26). 0.9 M aqueous stock solution of Me_2NH (3.9 mL, 10 equiv) was used. Reaction time – 6 h at 100 °C; basic Al_2O_3 was used for column chromatography; eluent – hexane : ethyl acetate = 2 : 1 to 1 : 1; R_f (SiO_2, ethyl acetate) 0.34. 85 mg (74 %) of pure target material as a white solid was obtained. Crystallization from the Et_2O/hexane solution by slow evaporation at 5 °C provided colorless X-ray quality needles: mp 110–111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 6H), 2.97 (dd, 1H, J = 13.2 Hz, J = 9.7 Hz), 3.38 (dd, 1H, J = 9.6 Hz, J = 4.6 Hz), 3.56 (dd, 1H, J = 13.2 Hz, J = 4.6 Hz), 6.77 (d, 1H, J = 7.6 Hz), 6.90 (d, 1H, J = 16.0 Hz), 6.98 (t, 1H, J = 7.5 Hz), 7.05–7.20 (m, 6H), 7.23–7.31 (m, 2H), 7.36 (t, 2H, J = 7.5 Hz), 7.45–7.51 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.1, 43.7, 72.7, 125.6, 126.4, 126.6, 126.6, 127.1, 127.2, 127.6, 127.9, 128.6, 128.8, 130.1, 131.1, 136.4, 137.3, 137.8, 140.5; IR (KBr, cm^{-1}) ν 3437, 3022, 2959, 2814, 2760, 2387, 1630, 1596, 1491, 1452, 1327, 1152, 1040, 958, 907, 764, 687, 539; HRMS (*m/z*) $[M + H]^+$ calcd for $C_{24}H_{25}N$: 328.2060; found 328.2059.



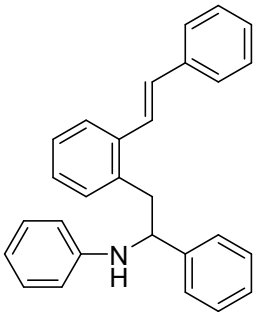
(E)-1-(1-phenyl-2-(2-styrylphenyl)ethyl)piperidine (27). Reaction time – 3 h at 105 °C; neutral $Al_2O_3$was used for column chromatography; eluent – hexane : ethyl acetate = 6 : 1 to 3 : 1; R_f (SiO_2, hexane : ethyl acetate = 2 : 1) 0.18. 54 mg (42 %) of pure target material as a white solid was obtained. Crystallization from the Et_2O/hexane solution by slow evaporation at 5 °C provided colorless needles: mp 108–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33–1.40 (m, 2H), 1.52–1.59 (m, 4H), 2.42–2.48 (m, 4H), 2.99 (dd, 1H, J = 14.5 Hz, J = 10.6 Hz), 3.48–3.57 (m, 2H), 6.83 (d, 1H, J = 7.6 Hz), 6.88 (d, 1H, J = 16.1 Hz), 6.99 (t, 1H, J = 7.4 Hz), 7.06–7.18 (m, 6H), 7.22–7.28 (m, 2H), 7.29–7.38 (m, 2H), 7.44–7.50 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.8, 26.5, 37.2, 52.1, 72.2, 125.6, 126.3, 126.6, 126.9, 126.9, 127.1, 127.6, 127.8, 128.8, 128.8, 130.0, 131.1, 136.5, 137.9, 138.0, 140.4; IR (KBr, cm^{-1}) ν 3023, 2931, 2851, 2784, 2743, 1595, 1492, 1450, 1325, 1159, 1112, 1070, 959, 763, 694, 533; HRMS (*m/z*) [M + H]$^+$ calcd for $C_{27}H_{29}N$: 368.2373; found 368.2374.



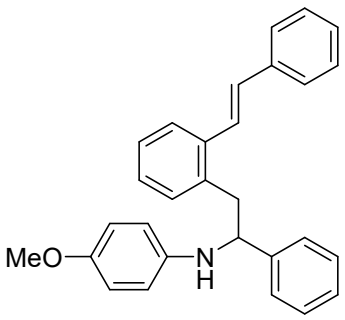
(E)-4-(1-phenyl-2-(2-styrylphenyl)ethyl)morpholine (28), 4-(1-phenyl-2-(2-(1-phenylvinyl)phenyl)ethyl)morpholine (28'). Reaction time – 5 h at 105 °C; neutral $Al_2O_3$was used for column chromatography; eluent – hexane : ethyl acetate = 6 : 1 to 3 : 1; R_f (SiO_2, hexane : ethyl acetate = 2 : 1) 0.37. 75 mg (58 %) of the mixture of two isomers as a light yellow solid was obtained: mp 109–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) **28 (H)** + **28' (H')** (3.5 to 1 mixture) δ 2.23–2.28 (m, 1H+1H'), 2.42–2.64 (m, 3H+3H'), 2.86–2.97 (m, 1H+1H'), 3.14 (dd, 1H', J = 13.4 Hz, J = 4.9 Hz), 3.30 (dd, 1H', J = 9.7 Hz, J = 4.9 Hz), 3.45 (dd, 1H, J = 9.3 Hz, J = 4.5 Hz), 3.52–3.61 (m, 2H+1H'), 3.67–3.75 (m, 3H+3H'), 5.10 (s, 1H'), 5.76 (s, 1H'), 6.69–6.78 (m, 1H+1H'), 6.88 (d, 1H, J = 16.1 Hz), 6.95–7.02 (m, 1H+3H'), 7.04–7.30 (m, 8H+8H'), 7.33–7.40 (m, 2H+2H'), 7.41–7.51 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) **28** δ 37.2, 51.8, 67.3, 72.2, 125.7, 126.5, 126.5, 126.6, 127.2, 127.2, 127.7, 128.0, 128.7, 128.8, 130.2, 131.1, 136.5, 137.1, 137.7, 140.2; **28'** δ 36.7, 51.4, 67.3, 71.0, 115.5, 125.9, 126.6, 127.0, 127.1, 127.9, 128.4, 128.6, 128.8, 130.4, 130.8, 137.0, 140.4, 140.8, 141.7, 149.3; IR (KBr, cm^{-1}) ν 3435, 3057, 3023, 2958, 2892, 2853, 2809, 1957, 1597, 1493, 1450, 1350, 1285, 1249, 1109, 965, 913, 863, 764, 702, 582, 533; HRMS (*m/z*) [M + H]$^+$ calcd for $C_{26}H_{27}NO$: 370.2165; found 370.2173.

For anilines:

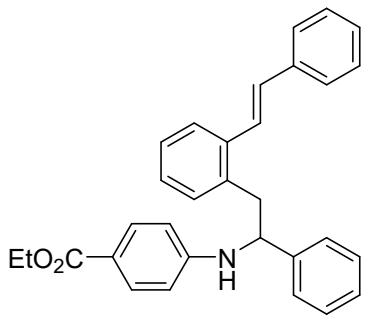
1,2-Diiodobenzene (116 mg, 0.35 mmol), styrene (77 mg, 0.74 mmol, 2.1 equiv), aniline (1.75 mmol, 5 equiv), and $K_2HPO_4 \cdot 3H_2O$ (0.8 g, 3.5 mmol, 10 equiv) were dissolved in 3.11 mL of 1,4-dioxane and 3.9 mL of H_2O. 22.3 mM $Pd(OAc)_2$ 1,4-dioxane solution (0.79 mL, 5 mol%) was then added under argon atmosphere. The mixture was vigorously stirred at r.t. 15 min and then placed into a preheated to 115 °C oil bath. The vigorous stirring was continued for the given amount of time until the full consumption of the starting diiodide. MTBE (5 mL) was added to the cooled reaction mixture. The organic layer was combined with two additional MTBE extracts (2 × 5 mL) and evaporated to dryness. The residue was dissolved in THF and evaporated with 600 mg of neutral aluminum oxide. The powder residue was subjected to neutral aluminum oxide column chromatography.



(E)-N-(1-phenyl-2-(2-styrylphenyl)ethyl)aniline (29). Reaction time – 4 h; eluent – hexane : ethyl acetate = 20 : 1 to 10 : 1; R_f (SiO_2, hexane : ethyl acetate = 20 : 1) 0.17. 96 mg (73 %) of pure target material as a white gum was obtained; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.19 (dd, 1H, J = 14.1 Hz, J = 8.0 Hz), 3.27 (dd, 1H, J = 14.1 Hz, J = 6.0 Hz), 4.25 (s, 1H), 4.61 (t, 1H, J = 6.9 Hz), 6.45 (d, 2H, J = 7.9 Hz), 6.62 (t, 1H, J = 7.3 Hz), 6.98 (d, 1H, J = 15.7 Hz), 7.01–7.06 (m, 2H), 7.12 (d, 1H, J = 7.3 Hz), 7.17–7.43 (m, 11H), 7.50 (d, 2H, J = 7.5 Hz), 7.60 (d, 1H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.6, 59.3, 113.8, 117.5, 126.2, 126.4, 126.4, 126.7, 127.3, 127.3, 127.7, 127.9, 128.7, 128.8, 129.1, 130.5, 131.3, 135.8, 137.1, 137.5, 143.6, 147.3; IR (KBr, cm^{-1}) v 3412, 3025, 2925, 2854, 1955, 1809, 1723, 1601, 1504, 1451, 1317, 1265, 1180, 1075, 1029, 963, 909, 759, 693, 538; HRMS (*m/z*) [M + H]$^+$ calcd for $C_{28}H_{25}N$: 376.2060; found 376.2053.

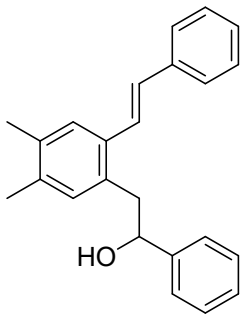


(E)-4-methoxy-N-(1-phenyl-2-(2-styrylphenyl)ethyl)aniline (30). Reaction time – 3 h; eluent – hexane : ethyl acetate = 10 : 1 to 6 : 1; R_f (SiO_2, hexane : ethyl acetate = 10 : 1) 0.19. 105 mg (74 %) of pure target material as a light yellow gum was obtained; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.15 (dd, 1H, J = 14.0 Hz, J = 8.0 Hz), 3.23 (dd, 1H, J = 14.0 Hz, J = 6.0 Hz), 3.64 (s, 3H), 3.95 (br s, 1H), 4.50 (t, 1H, J = 6.9 Hz), 6.38 (d, 2H, J = 8.6 Hz), 6.60 (d, 2H, J = 8.6 Hz), 6.95 (d, 1H, J = 16.1 Hz), 7.10 (d, 1H, J = 7.3 Hz), 7.15–7.41 (m, 11H), 7.48 (d, 2H, J = 7.6 Hz), 7.58 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.7, 55.8, 60.1, 114.8, 115.1, 126.2, 126.4, 126.5, 126.7, 127.2, 127.3, 127.7, 127.8, 128.7, 128.8, 130.5, 131.1, 135.9, 137.1, 137.5, 141.5, 143.8, 152.2; IR (KBr, cm^{-1}) v 3404, 3026, 2931, 2832, 1599, 1512, 1451, 1238, 1179, 1037, 963, 909, 820, 760, 699, 537; HRMS (*m/z*) [M + H]$^+$ calcd for $C_{29}H_{27}NO$: 406.2165; found 406.2171.



Ethyl (E)-4-((1-phenyl-2-(2-styrylphenyl)ethyl)amino)benzoate (31). Reaction time – 8 h; eluent – hexane : ethyl acetate = 6 : 1; R_f (SiO_2, hexane : ethyl acetate = 6 : 1) 0.13. 102 mg (65 %) of pure target material as a white gum was obtained; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 3H, J = 7.4 Hz), 3.19 (dd, 1H, J = 14.0 Hz, J = 7.7 Hz), 3.28 (dd, 1H, J = 14.1 Hz, J = 5.8 Hz), 4.25 (q, 2H, J = 7.4 Hz), 4.67 (t, 1H, J = 6.7 Hz), 4.68 (s, 1H), 6.37 (d, 2H, J = 8.4 Hz), 6.96 (d, 1H, J = 16.0 Hz), 7.07 (d, 1H, J = 7.4 Hz), 7.15–7.32 (m, 9H), 7.38 (t, 2H, J = 7.4 Hz), 7.48 (d, 2H, J = 7.6 Hz), 7.58 (d, 1H, J = 7.5 Hz), 7.71 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 42.2, 58.8, 60.2, 112.5, 119.1, 126.0, 126.3, 126.5, 126.7, 127.5, 127.5, 127.8, 128.0, 128.8, 128.9, 130.5, 131.3, 131.5, 135.2, 137.1, 137.3, 142.5, 150.8, 166.8; IR (KBr, cm^{-1}) ν 3370, 3026, 2927, 2855, 1959, 1694, 1607, 1523, 1453, 1276, 1175, 1108, 1027, 962, 910, 837, 760, 700, 539; HRMS (m/z) $[M + H]^+$ calcd for $C_{31}H_{29}NO_2$: 448.2271; found 448.2268.

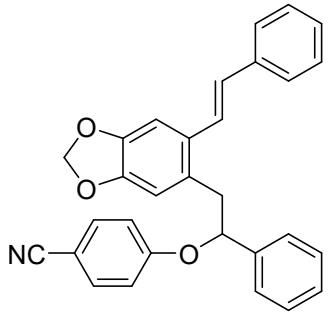
2.6 *General procedure for cascade double Heck – nucleophile addition reaction of selected unsaturated 1,2-diodides with styrene*



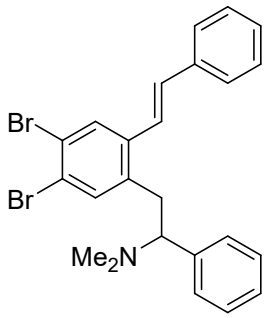
(E)-2-(4,5-dimethyl-2-styrylphenyl)-1-phenylethan-1-ol (32). **Method A**: 1,2-Diiodo-4,5-dimethylbenzene[S3] (125 mg, 0.35 mmol) and styrene (73 mg, 0.7 mmol, 2 equiv) were dissolved in 2.8 mL of 1,4-dioxane. 0.8 M $KHCO_3$ aqueous solution (3.9 mL, 9 equiv) was added to the formed homogeneous solution in one portion followed by addition of 22.3 mM $Pd(OAc)_2$ 1,4-dioxane solution (1.1 mL, 7 mol%) under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed into a preheated to 90 °C oil bath. The vigorous stirring was continued for 5 h at this temperature (additional 0.3 mL (2 mol%) of 22.3 mM $Pd(OAc)_2$ 1,4-dioxane solution should be added during this time in case the starting material could still be detected by the TLC after full decolorization of the reaction mixture). After completion of the reaction solid NaCl was added (until the saturation of the aqueous layer) followed by extractions with MTBE (3 × 5 ml). The combined organic layer was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and evaporated with 600 mg of silica gel. The powder residue was subjected to silica gel column chromatography; eluent – hexane : ethyl acetate = 10 : 1; R_f 0.11. 50 mg (44 %) of pure target material was obtained after chromatography as a white solid: mp 94–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (s, 1H), 2.25 (s, 3H), 2.28 (s, 3H), 3.03 (dd, 1H, J = 13.8 Hz, J = 8.9 Hz), 3.16 (dd, 1H, J = 13.8 Hz, J = 3.9 Hz), 4.88 (dd, 1H, J = 8.2 Hz, J = 3.9 Hz), 6.95 (d, 1H, J = 16.1 Hz), 6.98 (s, 1H), 7.22–7.42 (m, 10H), 7.49 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 19.5, 43.2, 75.1, 125.8,

126.1, 126.5, 127.3, 127.5, 127.7, 128.5, 128.8, 129.6, 132.4, 133.3, 134.3, 135.4, 136.4, 137.8, 144.2; IR (KBr, cm^{-1}) *v* 3371, 3022, 2920, 1939, 1791, 1595, 1496, 1450, 1201, 1057, 957, 758, 732, 691, 531; HRMS (*m/z*) $[M + NH_4]^+$ calcd for $C_{24}H_{24}O$: 346.2165; found 346.2167.

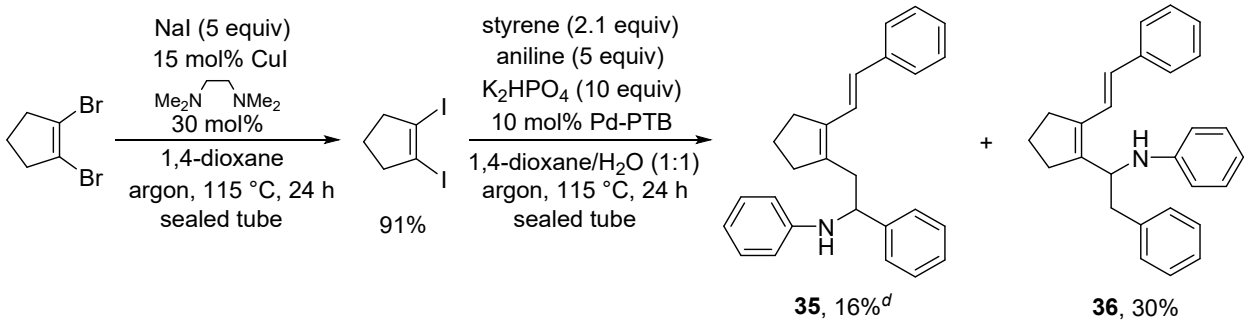
Method B: 1,2-Diiodo-4,5-dimethylbenzene (125 mg, 0.35 mmol) and styrene (109 mg, 1.05 mmol, 3 equv) were dissolved in 3.11 mL of DMF. 0.45 M K_2HPO_4 water solution (3.9 mL, 5 equiv) was added to the formed homogeneous solution in one portion followed by addition of 22.3 mM $Pd(OAc)_2$ DMF solution (0.79 mL, 5 mol%) under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed in a preheated to 105 °C oil bath for 2 h. Solid NaCl was then added to the reaction mixture (until the saturation of the aqueous layer) followed by extractions with MTBE (4 × 5 ml). The combined organic layer was evaporated to dryness; the residue was purified by silica gel column chromatography to provide 57 mg (50%) of the target material.

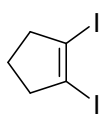


(E)-4-(1-phenyl-2-(6-styrylbenzo[d][1,3]dioxol-5-yl)ethoxy)benzonitrile (33). 5,6-Diiodobenzo[d][1,3]dioxole[S4] (101 mg, 0.27 mmol), styrene (59 mg, 0.57 mmol, 2.1 equiv), TBAB (70 mg, 0.22 mmol, 0.8 equiv), and 4-hydroxybenzonitrile (161 mg, 1.35 mmol, 5 equiv) were dissolved in 2.15 mL of 1,4-dioxane and 0.3 mL of H_2O. 0.8 M $KHCO_3$ aqueous solution (2.7 mL, 8 equiv) was added in one portion followed by addition of 22.3 mM $Pd(OAc)_2$ 1,4-dioxane solution (0.85 mL, 7 mol%) under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed into a preheated to 110 °C oil bath for 10 h. After this time no starting material was detected by TLC. MTBE (4 mL) was then added to the cooled reaction mixture. The organic layer was combined with two additional MTBE extracts (2 × 4 mL) and evaporated to dryness. The residue was dissolved in $CHCl_3$ and evaporated with 600 mg of neutral aluminum oxide. The powder residue was subjected to neutral aluminum oxide column chromatography; eluent – hexane : ethyl acetate = 6 : 1; R_f (SiO_2, hexane : ethyl acetate = 6 : 1) 0.18. 62 mg (52 %) of pure target material was obtained after chromatography as a light yellow gum; ^1H NMR (300 MHz, $CDCl_3$) δ 3.26 (dd, 1H, *J* = 14.3 Hz, *J* = 5.3 Hz), 3.42 (dd, 1H, *J* = 14.3 Hz, *J* = 7.5 Hz), 5.32 (dd, 1H, *J* = 6.7 Hz, *J* = 5.9 Hz), 5.98 (s, 2H), 6.67 (s, 1H), 6.81–6.89 (m, 3H), 7.11 (s, 1H), 7.23–7.45 (m, 11H), 7.49 (d, 2H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.1, 81.6, 101.2, 104.0, 105.6, 111.0, 116.6, 119.2, 125.9, 125.9, 126.4, 127.7, 128.3, 128.8, 128.9, 129.0, 129.2, 130.7, 133.8, 137.6, 139.9, 147.1, 147.2, 161.3; IR (KBr, cm^{-1}) *v* 3025, 2897, 2225, 1728, 1604, 1504, 1483, 1378, 1252, 1171, 1040, 835, 754, 698, 547; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{30}H_{23}NO_3$: 468.1570; found 468.1570.



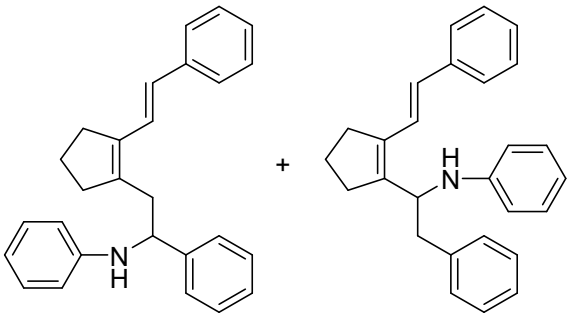
(E)-2-(4,5-dibromo-2-styrylphenyl)-N,N-dimethyl-1-phenylethan-1-amine (34). 1,2-Dibromo-4,5-diiodobenzene[S5] (171 mg, 0.35 mmol), styrene (77 mg, 0.74 mmol, 2.1 equiv), and $K_2HPO_4 \cdot 3H_2O$ (160 mg, 0.7 mmol, 2 equiv) were dissolved in 2.8 mL of 1,4-dioxane and 3.9 mL of 0.9 M aqueous Me_2NH stock solution. 22.3 mM $Pd(OAc)_2$ 1,4-dioxane solution (1.1 mL, 7 mol%) was then added under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed into a preheated to 110 °C oil bath for 18 h. After this time no starting material was detected by TLC. MTBE (5 mL) was then added to the cooled reaction mixture. The organic layer was combined with two additional MTBE extracts (2 × 5 mL) and evaporated to dryness. The residue was dissolved in THF and evaporated with 600 mg of basic aluminum oxide. The powder residue was subjected to basic aluminum oxide column chromatography; eluent – hexane : ethyl acetate = 10 : 1 to 4 : 1; R_f (SiO_2, ethyl acetate) 0.33. 109 mg (64 %) of pure target material was obtained after chromatography as a yellow solid. Crystallization from the Et_2O/hexane solution by slow evaporation at 5 °C provided yellow needles: mp 111–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71 (s, 1H), 2.26 (s, 6H), 2.86 (dd, 1H, J = 13.0 Hz, J = 9.4 Hz), 3.29 (dd, 1H, J = 9.1 Hz, J = 4.8 Hz), 3.41 (dd, 1H, J = 13.2 Hz, J = 4.7 Hz), 6.83 (d, 1H, J = 16.1 Hz), 6.98–7.06 (m, 4H), 7.13–7.25 (m, 3H), 7.28 (d, 1H, J = 7.0 Hz), 7.35 (t, 2H, J = 7.3 Hz), 7.42 (d, 1H, J = 7.3 Hz), 7.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.3, 43.6, 72.3, 122.4, 122.7, 124.2, 126.8, 127.5, 128.2, 128.2, 128.5, 128.9, 130.3, 131.8, 135.7, 137.0, 137.5, 138.2, 139.7; IR (KBr, cm^{-1}) ν 3026, 2956, 2811, 2755, 1598, 1492, 1454, 1329, 1205, 1121, 1041, 963, 886, 754, 688, 552; HRMS (*m/z*) $[M + H]^+$ calcd for $C_{24}H_{23}Br_2N$: 484.0270; found 484.0285.



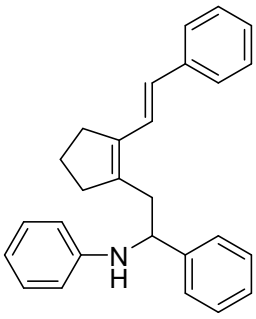


1,2-Diiodocyclopent-1-ene. 1,2-Dibromocyclopent-1-ene (2.26 g, 10 mmol), anhydrous sodium iodide (7.5 g, 50 mmol, 5 equiv), copper(I) iodide (0.29 g, 1.5 mmol, 15 mol%), and *N,N'*-dimethylethylenediamine (0.26 g, 3 mmol, 30 mol%) in 1,4-dioxane (15 mL) were vigorously stirred in a sealed tube under argon atmosphere at 115 °C for 24 h. After this time the suspension was filtered, the filtrate was combined with 4 additional CH_2Cl_2 washings and evaporated. The residue was dissolved in hexane and water forming two

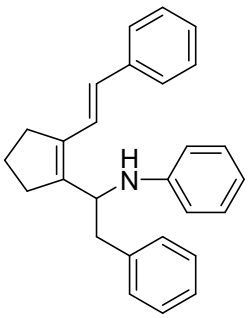
clear layers. The organic layer was washed with saturated $Na_2S_2O_3$ solution, dried with Na_2SO_4 and evaporated to give 3.1 g of yellow liquid. Purification by silica gel column chromatography with hexane as an eluent (R_f 0.55) followed by vacuum distillation provided 2.9 g (91 %) of colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (q, 2H, J = 7.5 Hz), 2.69 (t, 4H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.4, 44.4, 107.1; HRMS (*m/z*) $[M + H]^+$ calcd for $C_5H_6I_2$: 319.8553; found 319.8558.



(E)-N-(1-phenyl-2-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (35), (E)-N-(2-phenyl-1-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (36). 1,2-Diiodocyclopent-1-ene (156 mg, 0.49 mmol), styrene (107 mg, 1.03 mmol, 2.1 equiv), aniline (228 mg, 2.45 mmol, 5 equiv), and $K_2HPO_4 \cdot 3H_2O$ (1.12 g, 4.9 mmol, 10 equiv) were dissolved in 3.2 mL of 1,4-dioxane and 5.4 mL of H_2O. 22.3 mM Pd–PTB 1,4-dioxane solution (2.2 mL, 10 mol%) was added under argon atmosphere. The mixture was vigorously stirred at r.t. for 15 min and then placed into a preheated to 115 °C oil bath for 26 h. After this time no starting material was detected by TLC. MTBE (8 mL) was then added to the cooled reaction mixture. The organic layer was combined with two additional MTBE extracts (2 × 8 mL) and evaporated to dryness. The residue was dissolved in THF and evaporated with 1.2 g of neutral aluminum oxide. The powder residue was subjected to neutral aluminum oxide column chromatography.



(E)-N-(1-phenyl-2-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (35). Eluent – hexane : ethyl acetate = 50 : 1; R_f (SiO_2, hexane : ethyl acetate = 20 : 1) 0.27. 29 mg (16 %) of unstable **35** as a yellow oil was obtained: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84–1.92 (m, 2H), 2.41–2.48 (m, 2H), 2.62–2.67 (m, 2H), 2.70 (dd, 1H, J = 14.1, Hz, J = 5.0 Hz), 2.92 (dd, 1H, J = 14.1 Hz, J = 9.2 Hz), 4.07 (br s, 1H), 4.51 (dd, 1H, J = 9.0 Hz, J = 5.3 Hz), 6.44–6.54 (m, 3H), 6.67 (t, 1H, J = 7.4 Hz), 7.04–7.11 (m, 3H), 7.21–7.38 (m, 6H), 7.43–7.46 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9, 33.3, 37.3, 38.7, 57.0, 113.7, 117.6, 122.6, 126.3, 126.5, 127.2, 127.4, 128.8, 128.8, 129.2, 129.5, 138.0, 138.2, 139.4, 144.2, 147.6; IR (KBr, cm^{-1}) ν 3407, 3026, 2925, 2850, 1945, 1700, 1602, 1502, 1451, 1317, 1265, 1074, 956, 749, 694, 512; HRMS (*m/z*) $[M + H]^+$ calcd for $C_{27}H_{27}N$: 366.2216; found 366.2213.



(E)-N-(2-phenyl-1-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (36). Eluent – hexane : ethyl acetate = 20 : 1; R_f (SiO_2, hexane : ethyl acetate =

20 : 1) 0.21. 54 mg (30 %) of pure **36** as a white solid was obtained. Crystallization from the hexane solution by slow evaporation at 5 °C provided colorless X-ray quality crystals: mp 134–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76–1.88 (m, 2H), 2.38–2.48 (m, 2H), 2.55–2.64 (m, 2H), 2.91 (dd, 1H, J = 13.4 Hz, J = 7.1 Hz), 3.02 (dd, 1H, J = 13.4 Hz, J = 7.1 Hz), 3.83 (br s, 1H), 4.66 (t, 1H, J = 7.1 Hz), 6.37 (d, 1H, J = 15.8 Hz), 6.54 (d, 2H, J = 8.0 Hz), 6.65 (t, 1H, J = 7.3 Hz), 6.94 (d, 1H, J = 15.8 Hz), 7.10 (t, 2H, J = 7.9 Hz), 7.13–7.35 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 32.8, 33.5, 41.2, 53.5, 113.4, 117.6, 122.2, 126.4, 126.8, 127.3, 128.5, 128.6, 129.1, 129.3, 129.3, 129.3, 136.5, 138.0, 143.1, 147.7; IR (KBr, cm^{-1}) v 3390, 3027, 2919, 2836, 1729, 1603, 1505, 1318, 1249, 1072, 952, 753, 693, 509; HRMS (*m/z*) $[M + Na]^+$ calcd for $C_{27}H_{27}N$: 388.2036; found 388.2044.

3. ^{1}H and ^{13}C NMR spectra

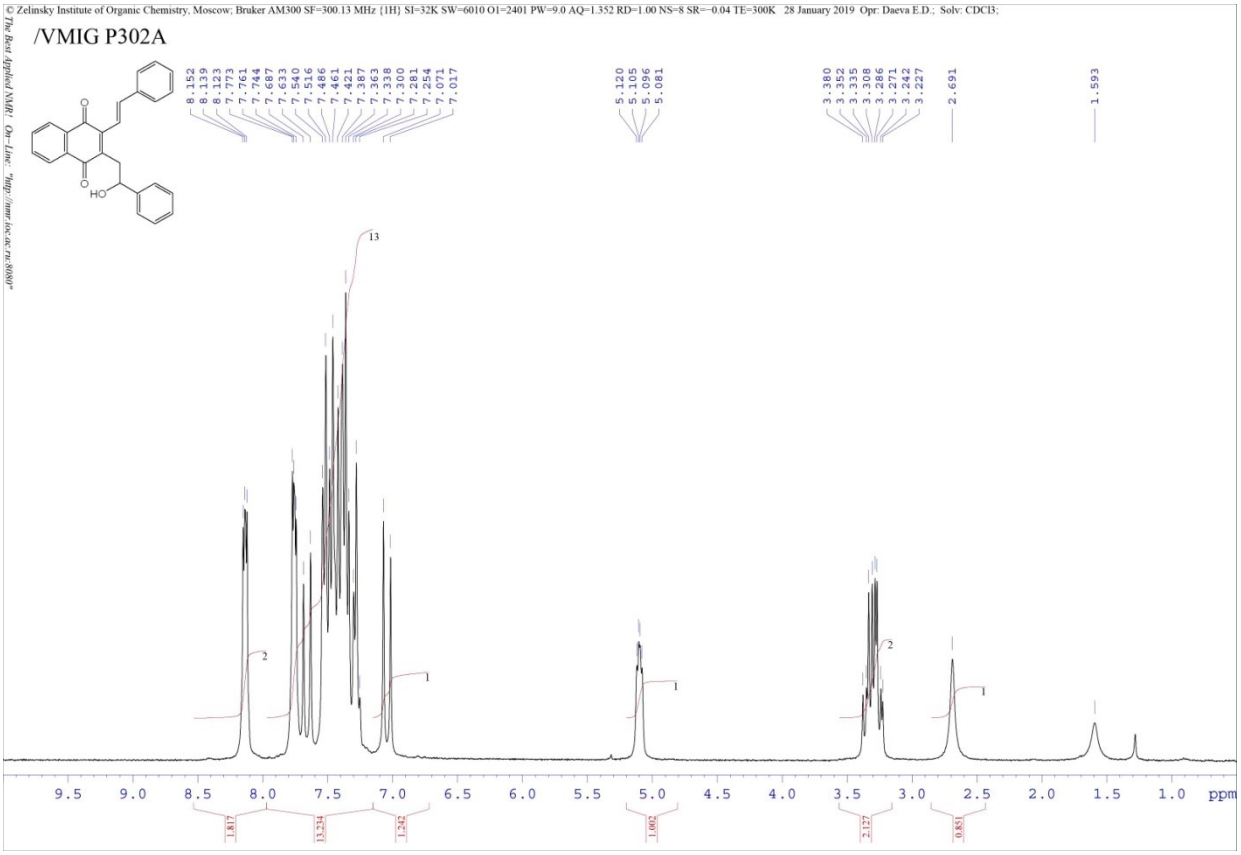


FIGURE S1. ^{1}H NMR spectrum of (E)-2-(2-hydroxy-2-phenylethyl)-3-styrylnaphthalene-1,4-dione (**1**) in $CDCl_3$.

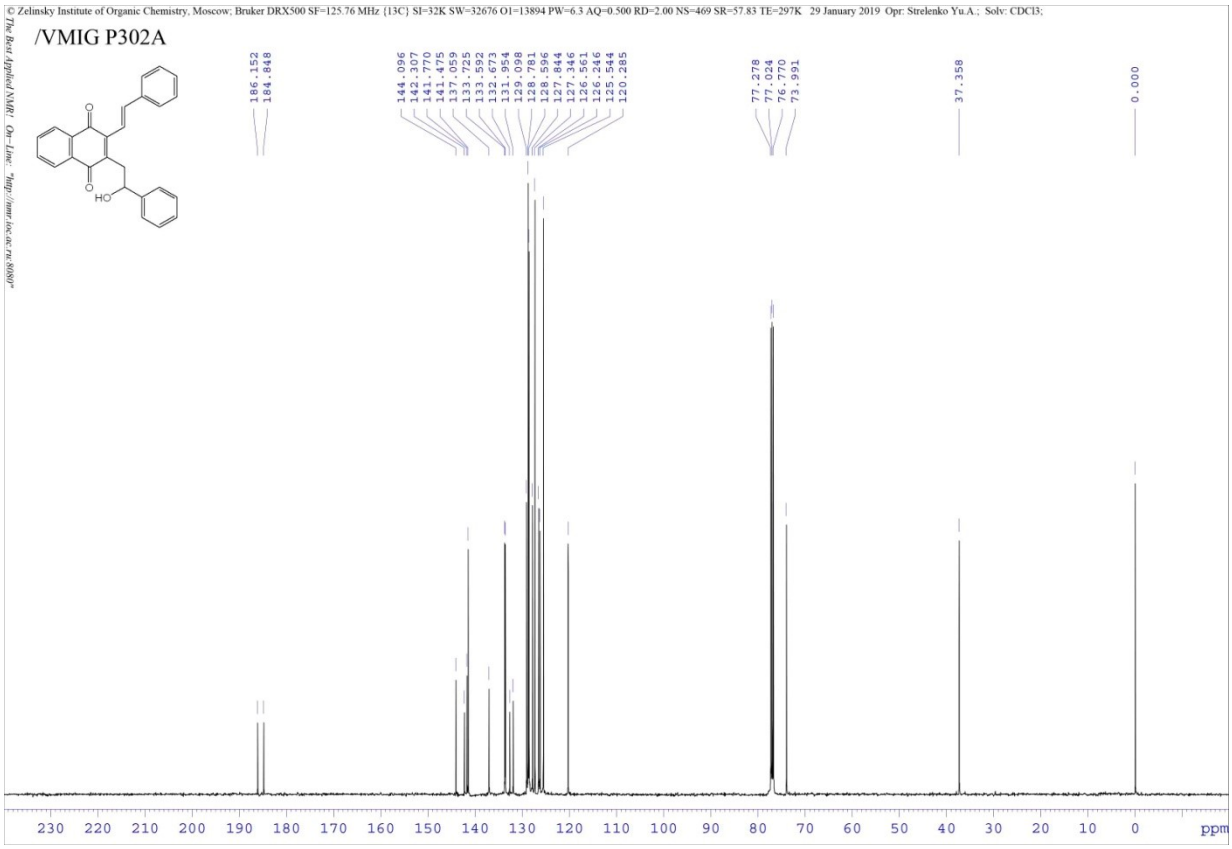


FIGURE S2. ^{13}C NMR spectrum of (E)-2-(2-hydroxy-2-phenylethyl)-3-styrylnaphthalene-1,4-dione (**1**) in $CDCl_3$.

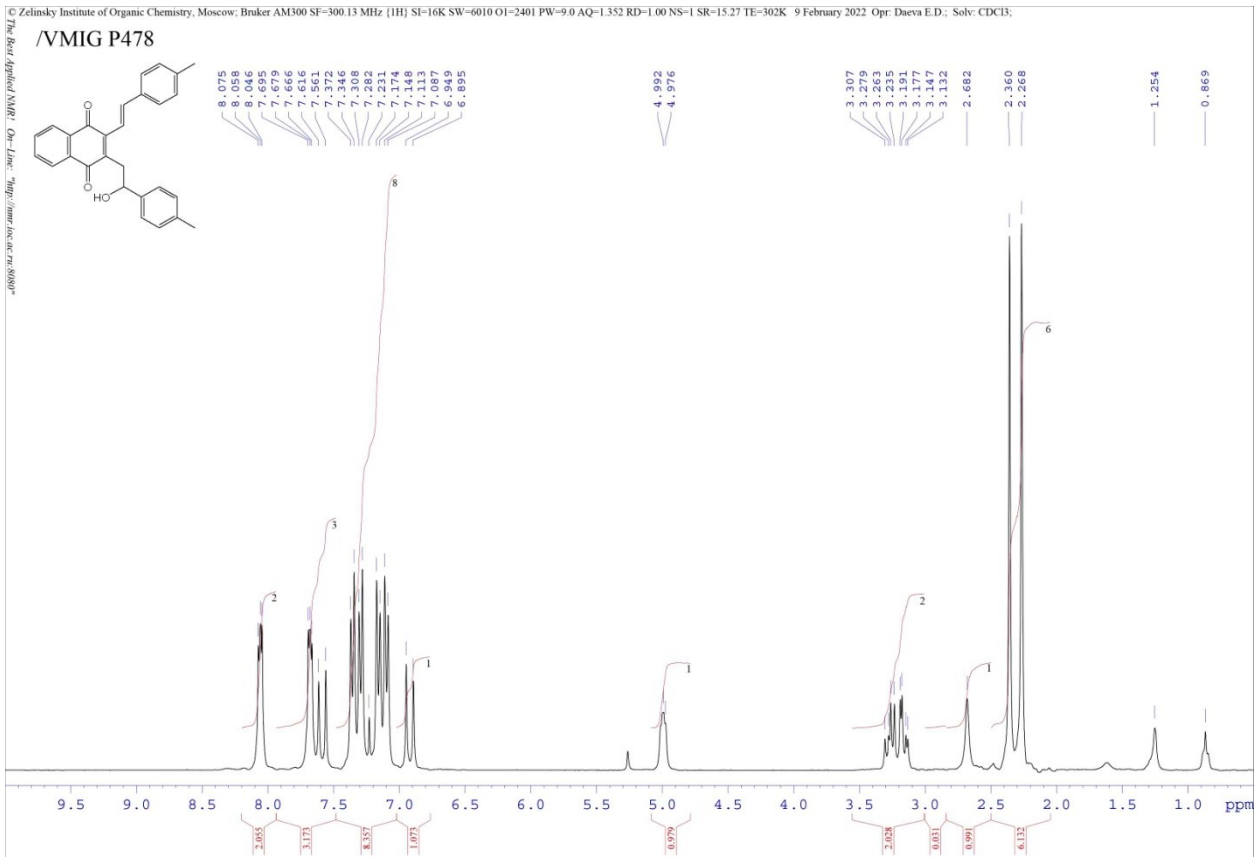


FIGURE S3. ^{1}H NMR spectrum of (E)-2-(2-hydroxy-2-(p-tolyl)ethyl)-3-(4-methylstyryl)naphthalene-1,4-dione (**2**) in $CDCl_3$.

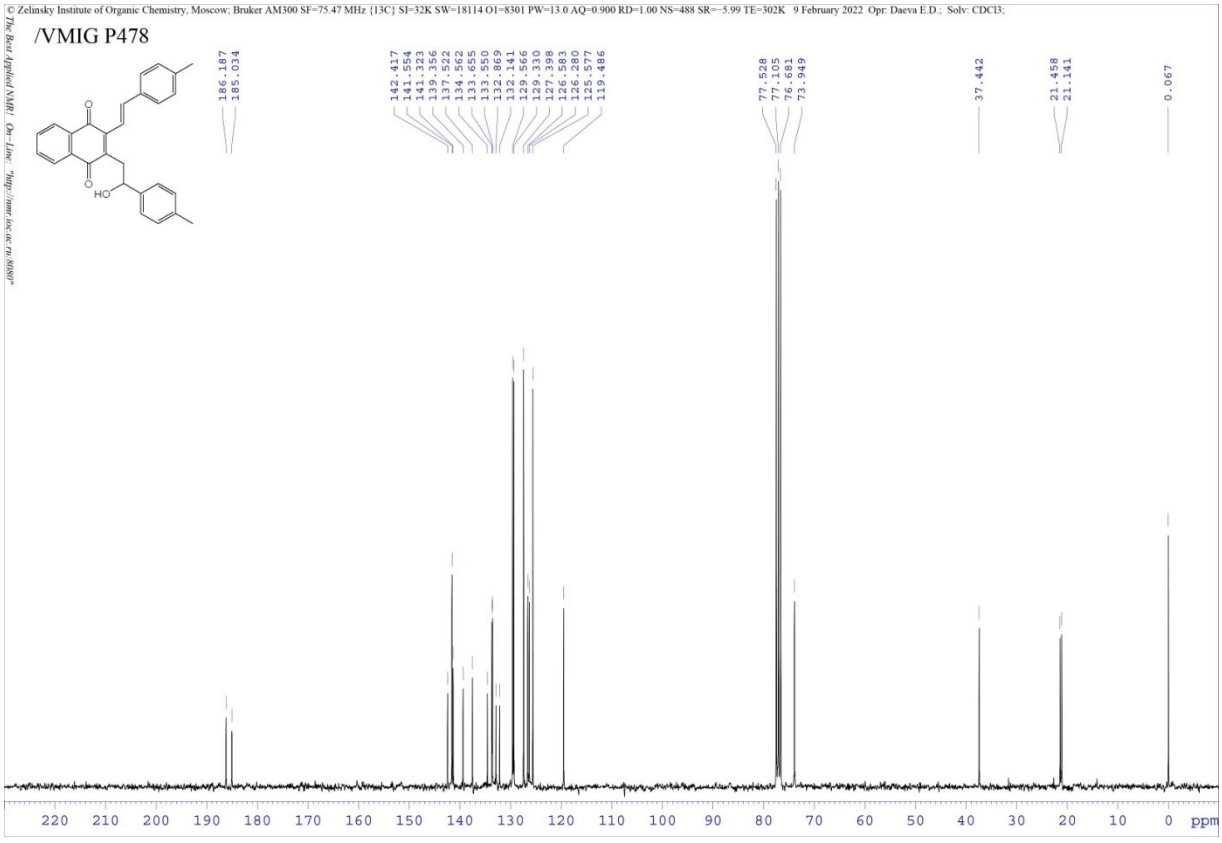


FIGURE S4. ^{13}C NMR spectrum of (E)-2-(2-hydroxy-2-(p-tolyl)ethyl)-3-(4-methylstyryl)naphthalene-1,4-dione (**2**) in $CDCl_3$.

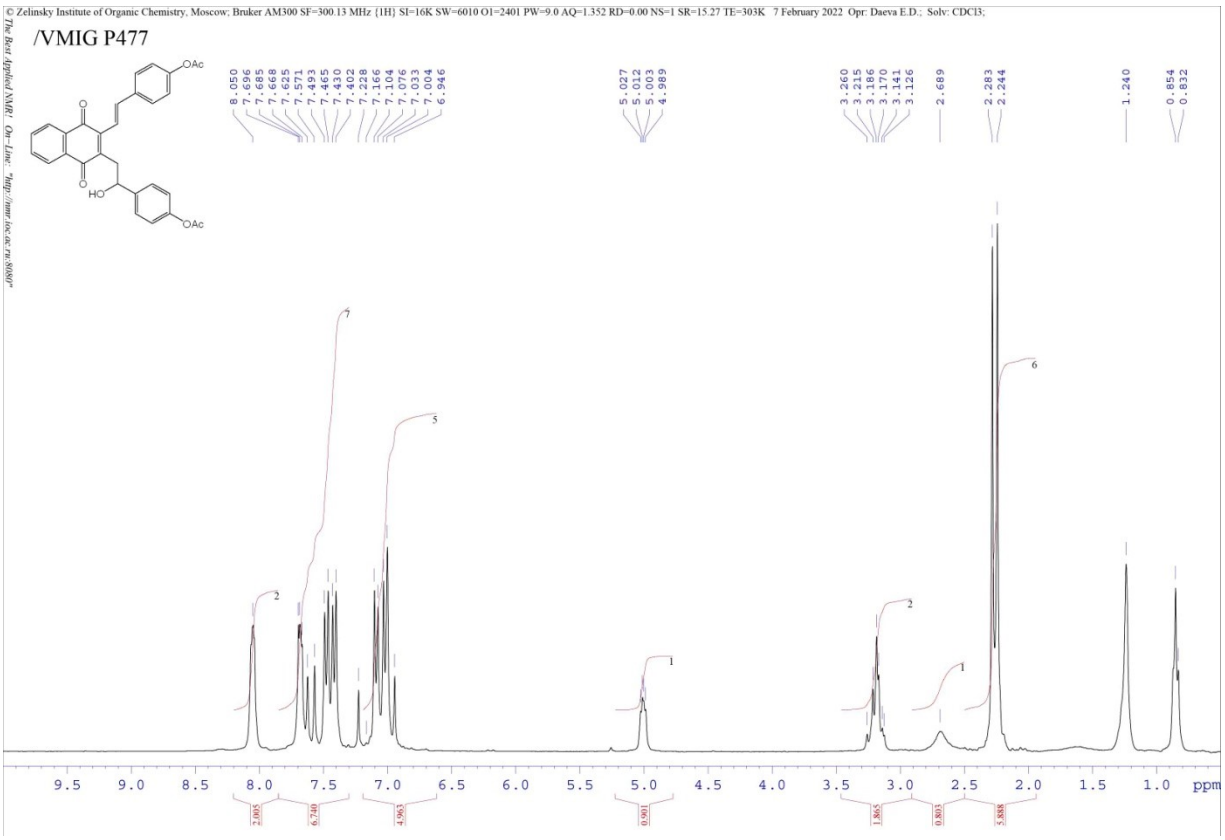


FIGURE S5. ^{1}H NMR spectrum of (E)-2-(2-hydroxy-2-(4-acetoxyphenyl)ethyl)-3-(4-acetoxystyryl)naphthalene-1,4-dione (**3**) in $CDCl_3$.

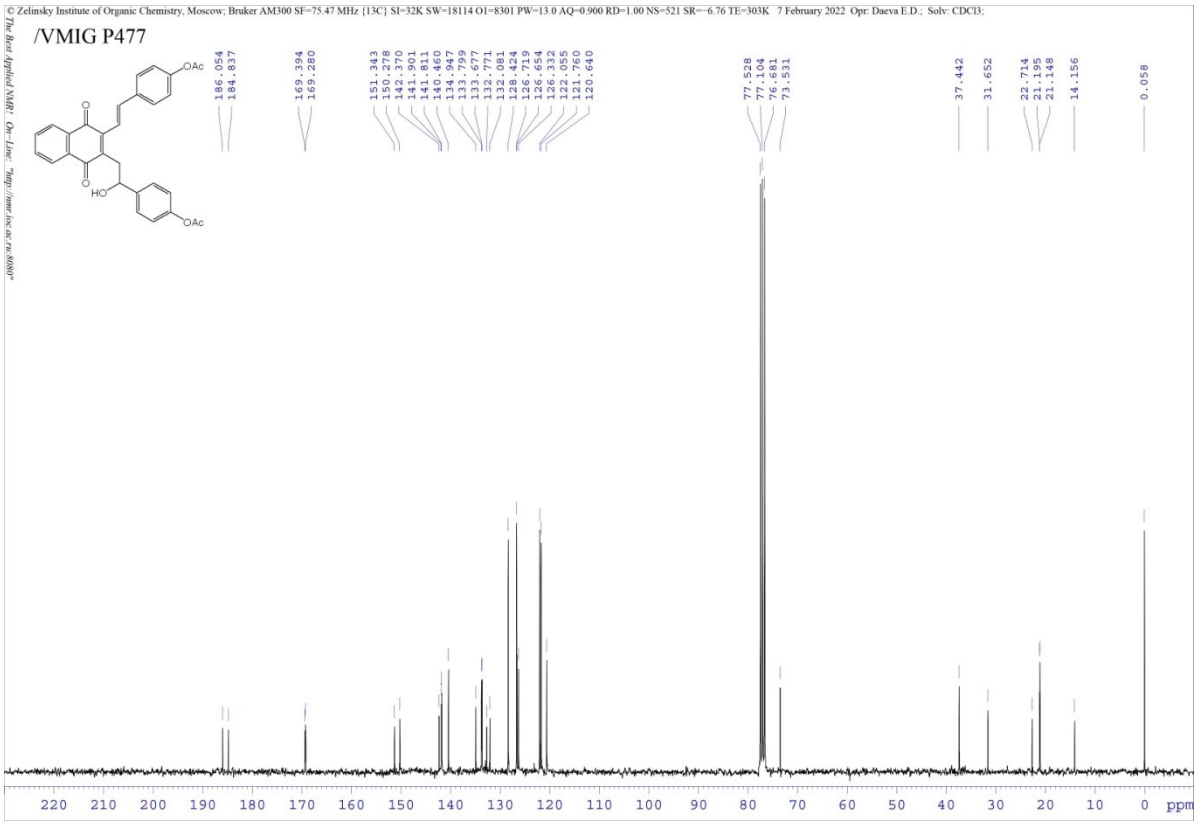


FIGURE S6. ^{13}C NMR spectrum of (E)-2-(2-hydroxy-2-(4-acetoxyphenyl)ethyl)-3-(4-acetoxystyryl)naphthalene-1,4-dione (**3**) in $CDCl_3$.

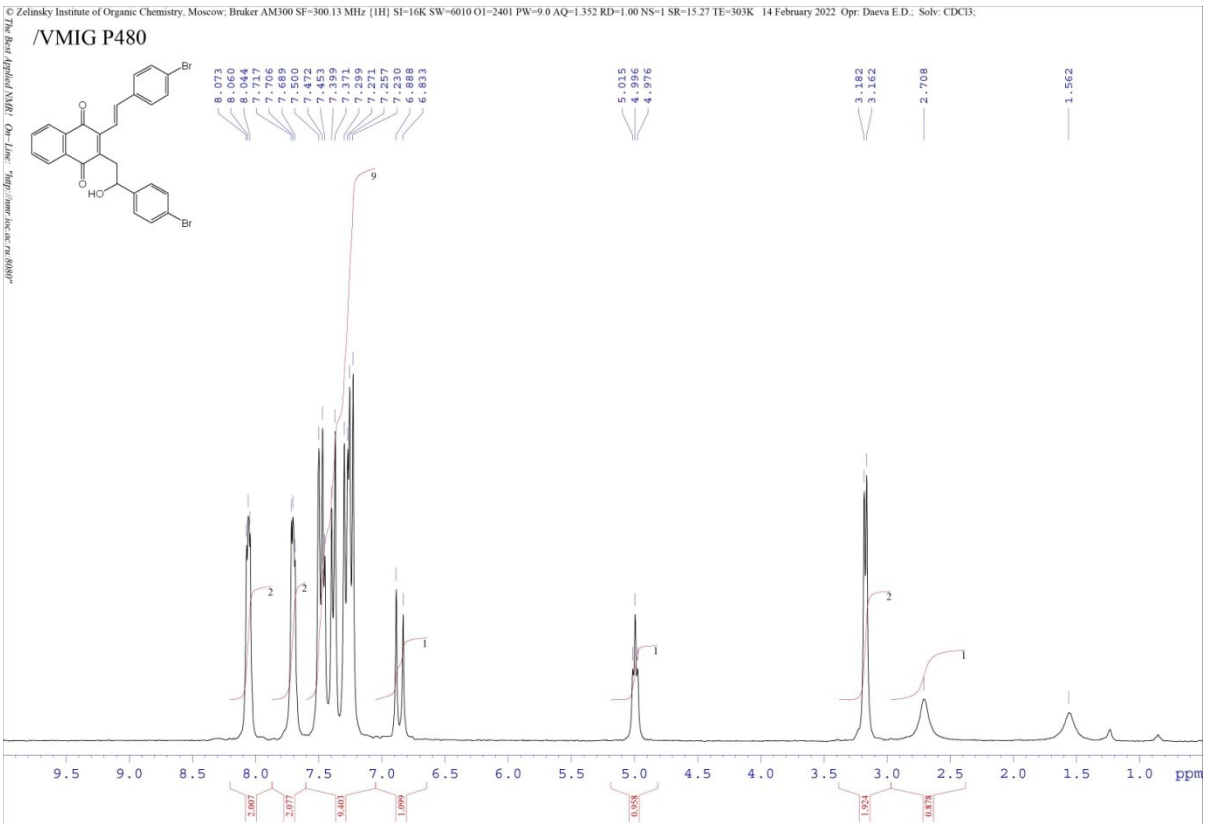


FIGURE S7. ^{1}H NMR spectrum of (E)-2-(2-(4-bromophenyl)-2-hydroxyethyl)-3-(4-bromostyryl)naphthalene-1,4-dione (**4**) in $CDCl_3$.

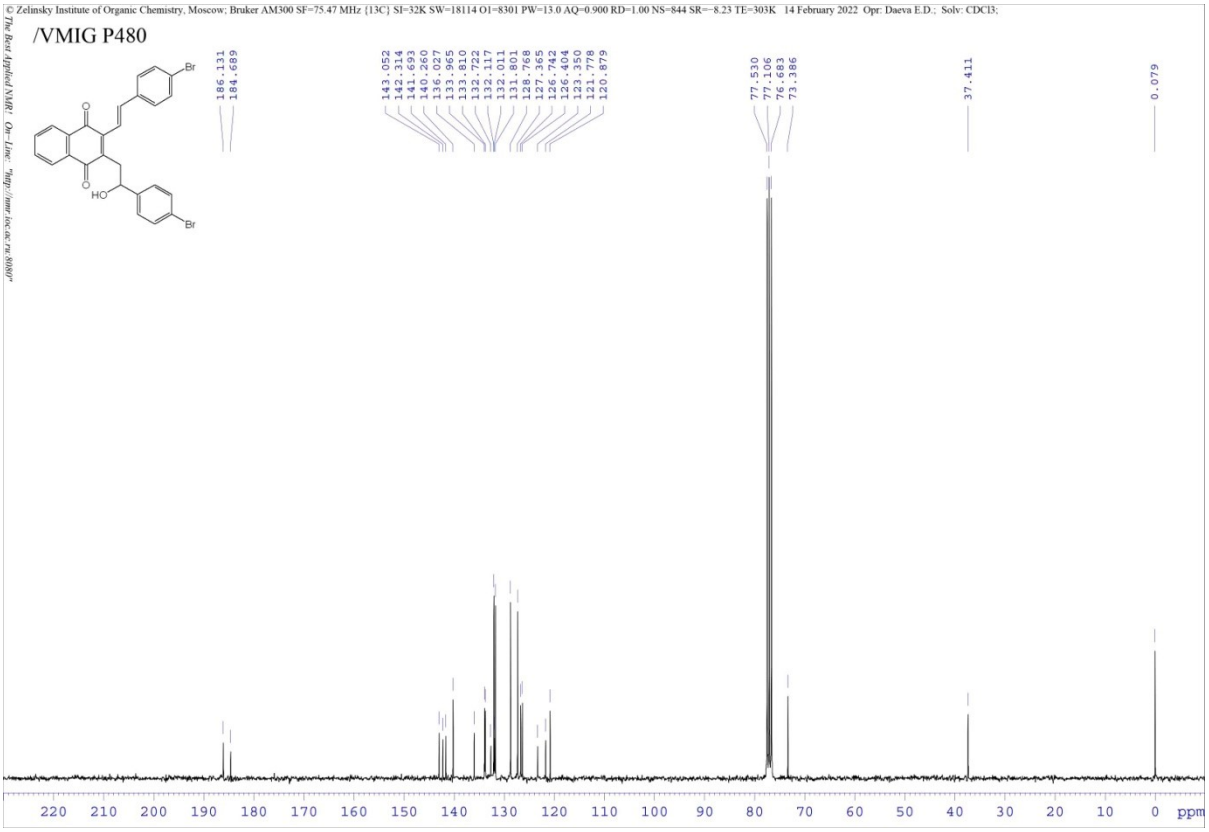


FIGURE S8. ^{13}C NMR spectrum of (E)-2-(2-(4-bromophenyl)-2-hydroxyethyl)-3-(4-bromostyryl)naphthalene-1,4-dione (**4**) in $CDCl_3$.

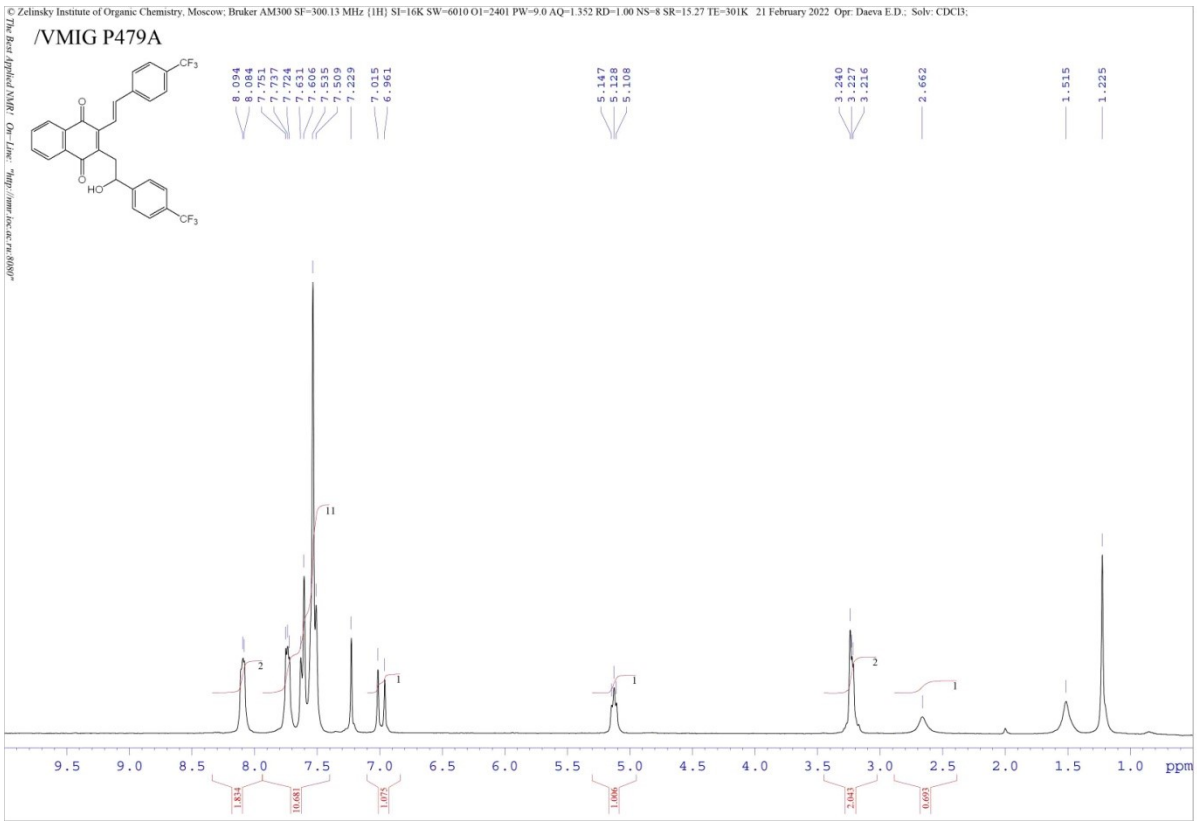


FIGURE S9. ^{1}H NMR spectrum of (E)-2-(2-hydroxy-2-(4-(trifluoromethyl)phenyl)ethyl)-3-(4-(trifluoromethyl)styryl)naphthalene-1,4-dione (**5**) in $CDCl_3$.

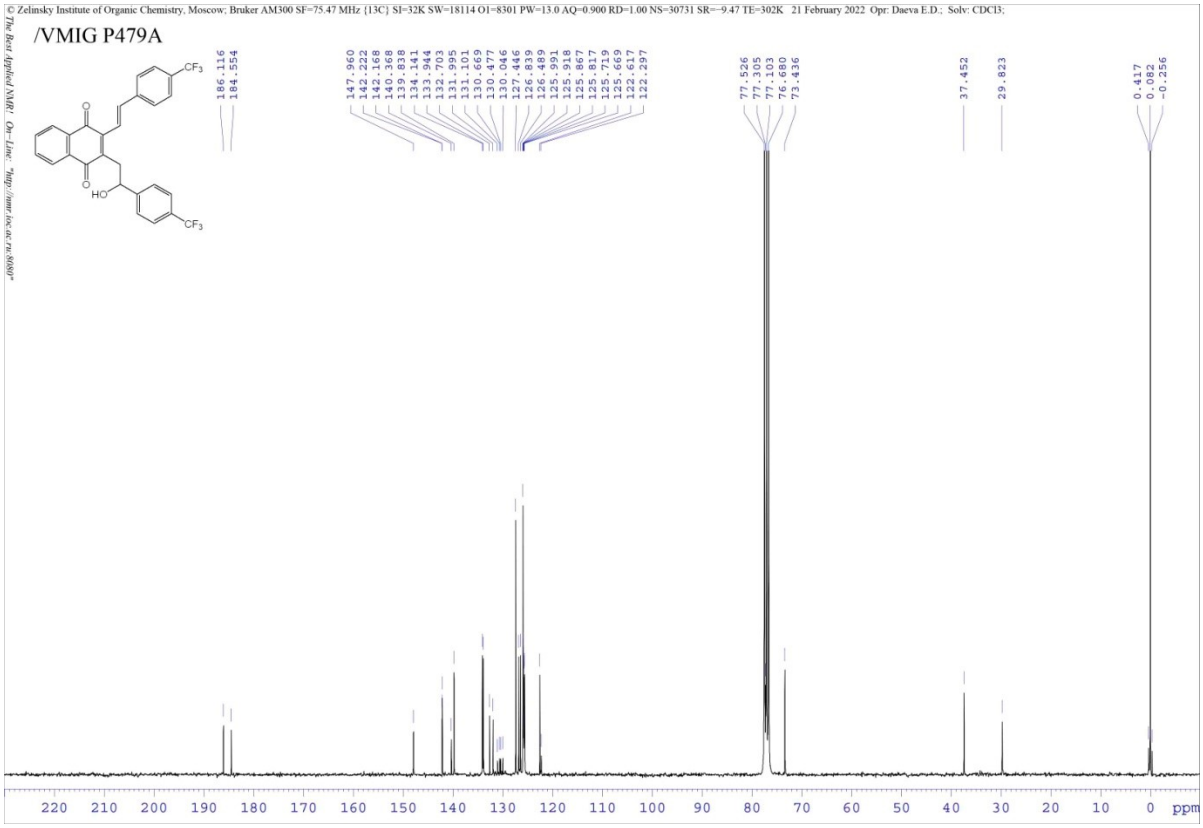


FIGURE S10. ^{13}C NMR spectrum of (E)-2-(2-hydroxy-2-(4-(trifluoromethyl)phenyl)ethyl)-3-(4-(trifluoromethyl)styryl)naphthalene-1,4-dione (**5**) in $CDCl_3$.

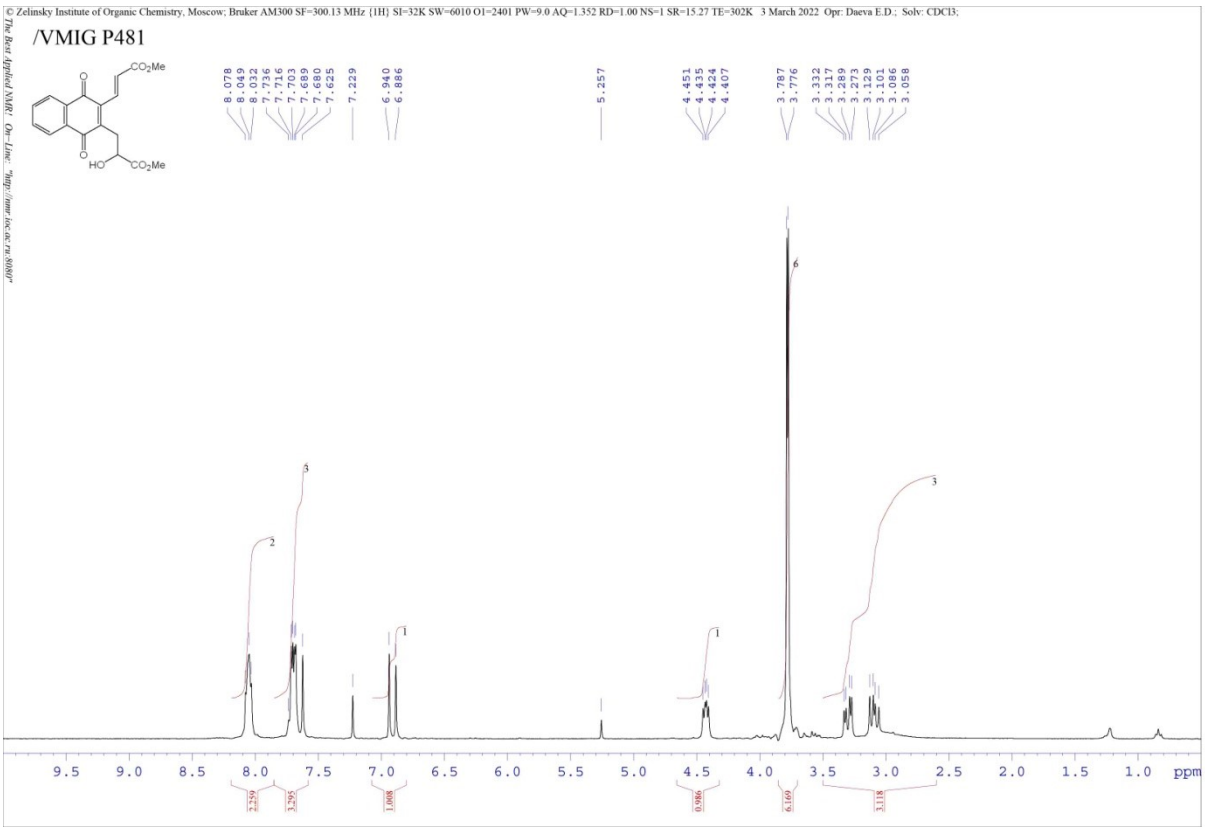


FIGURE S11. ^{1}H NMR spectrum of (E)-3-(3-(2-hydroxy-3-methoxy-3-oxopropyl)-1,4-dioxo-1,4-dihydronaphthalen-2-yl)acrylate (**6**) in $CDCl_3$.

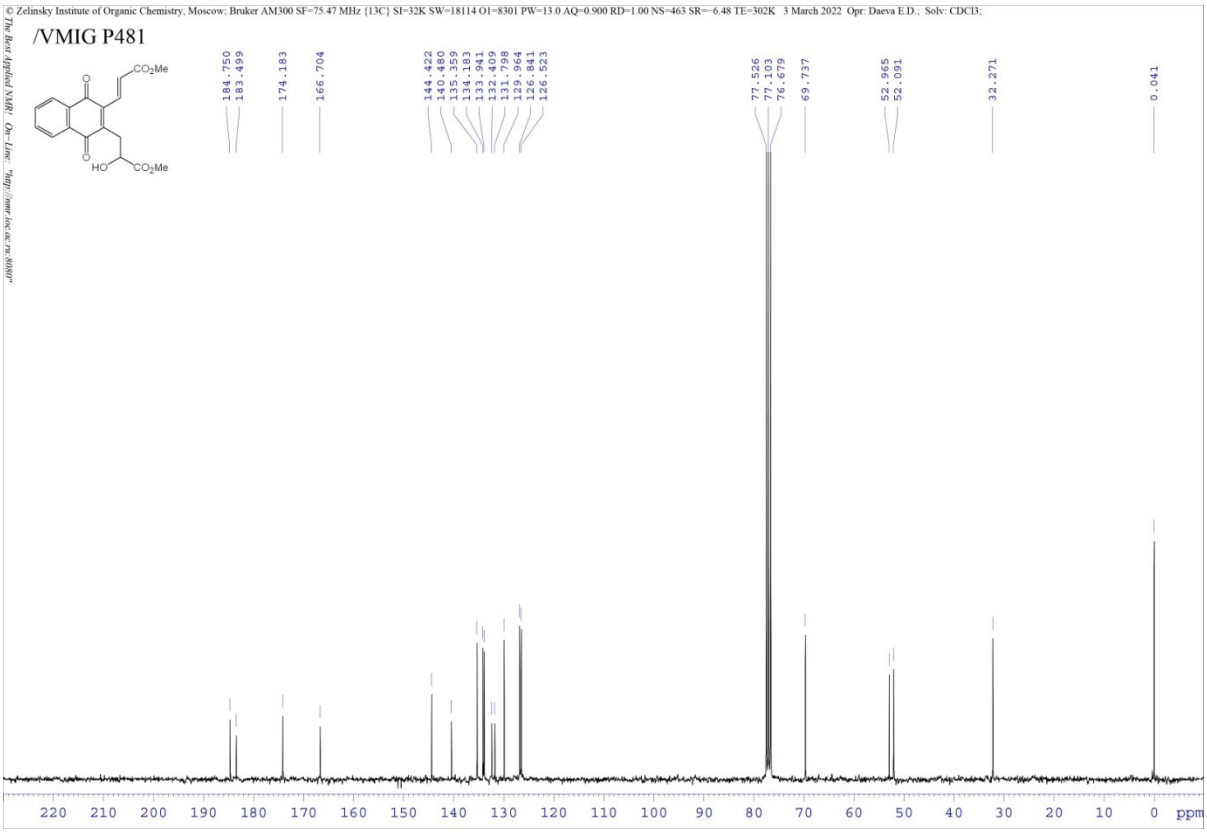


FIGURE S12. ^{13}C NMR spectrum of (E)-3-(3-(2-hydroxy-3-methoxy-3-oxopropyl)-1,4-dioxo-1,4-dihydronaphthalen-2-yl)acrylate (**6**) in $CDCl_3$.

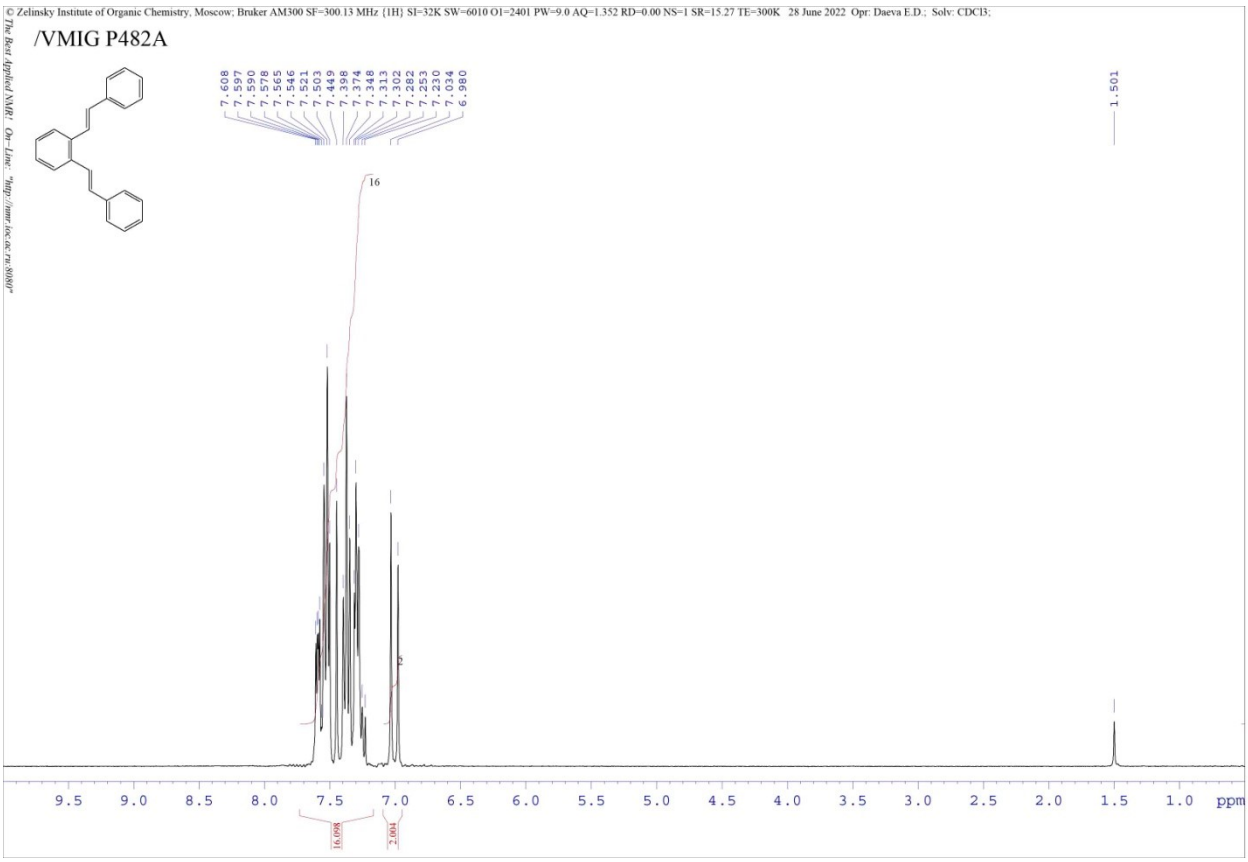


FIGURE S13. ^{1}H NMR spectrum of 1,2-di((E)-styryl)benzene (**9**) in $CDCl_3$.

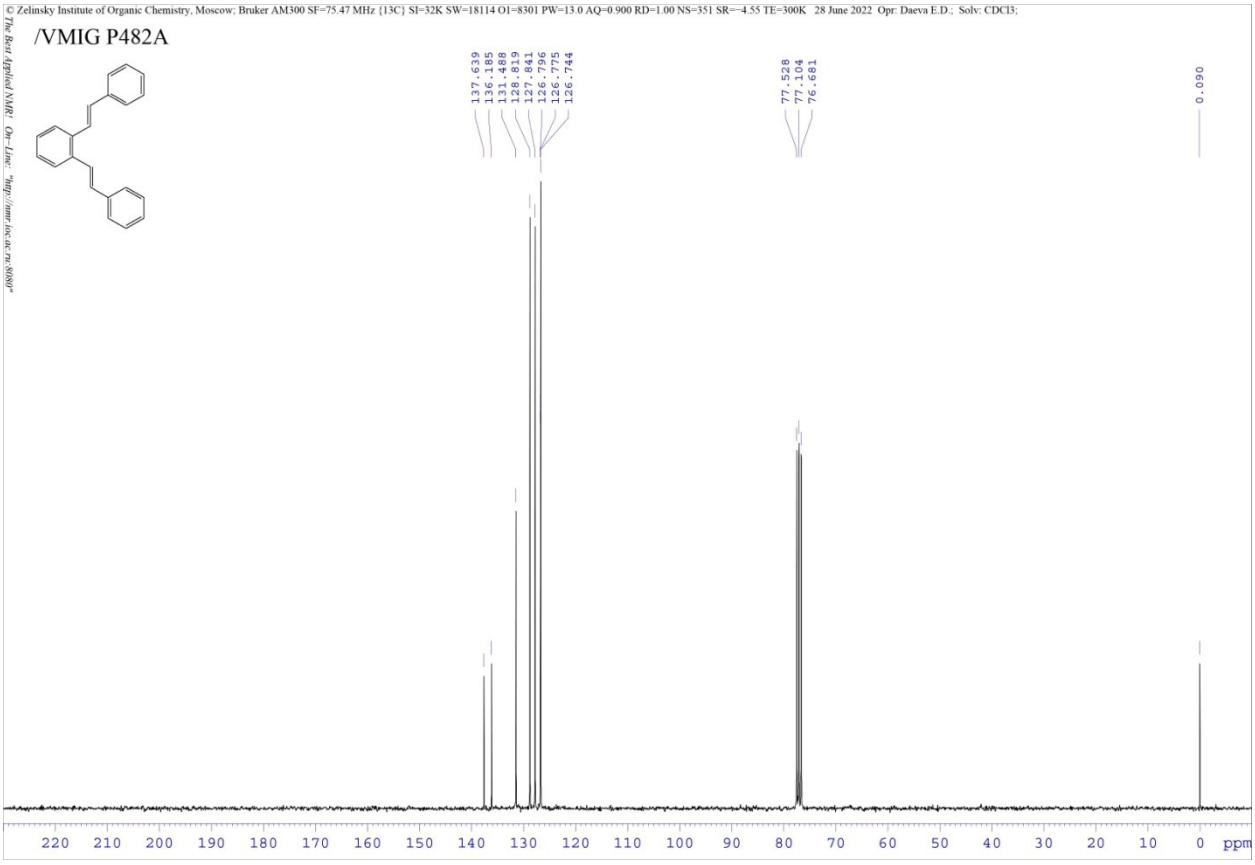


FIGURE S14. ^{13}C NMR spectrum of 1,2-di((E)-styryl)benzene (**9**) in $CDCl_3$.

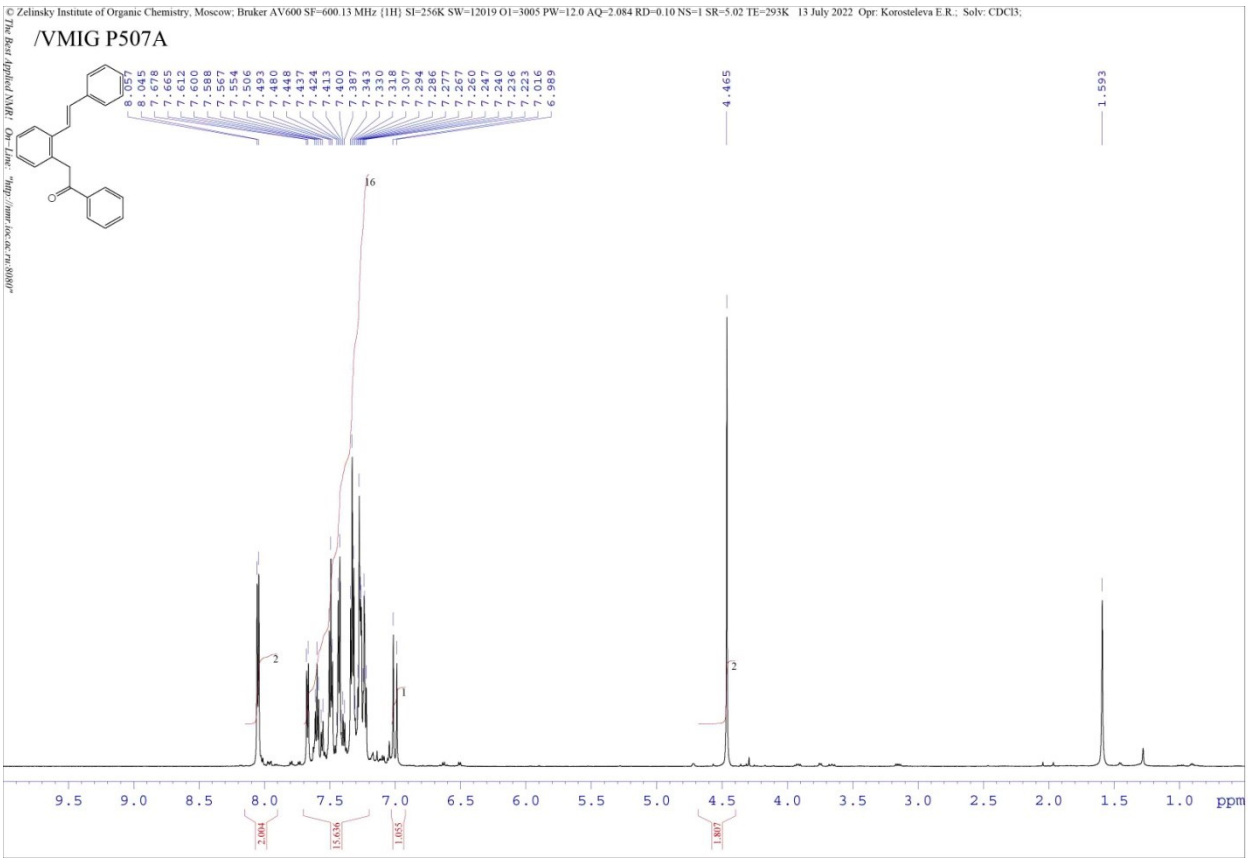


FIGURE S15. ^{1}H NMR spectrum of (E)-1-phenyl-2-(2-styrylphenyl)ethan-1-one (**18**) in $CDCl_3$.

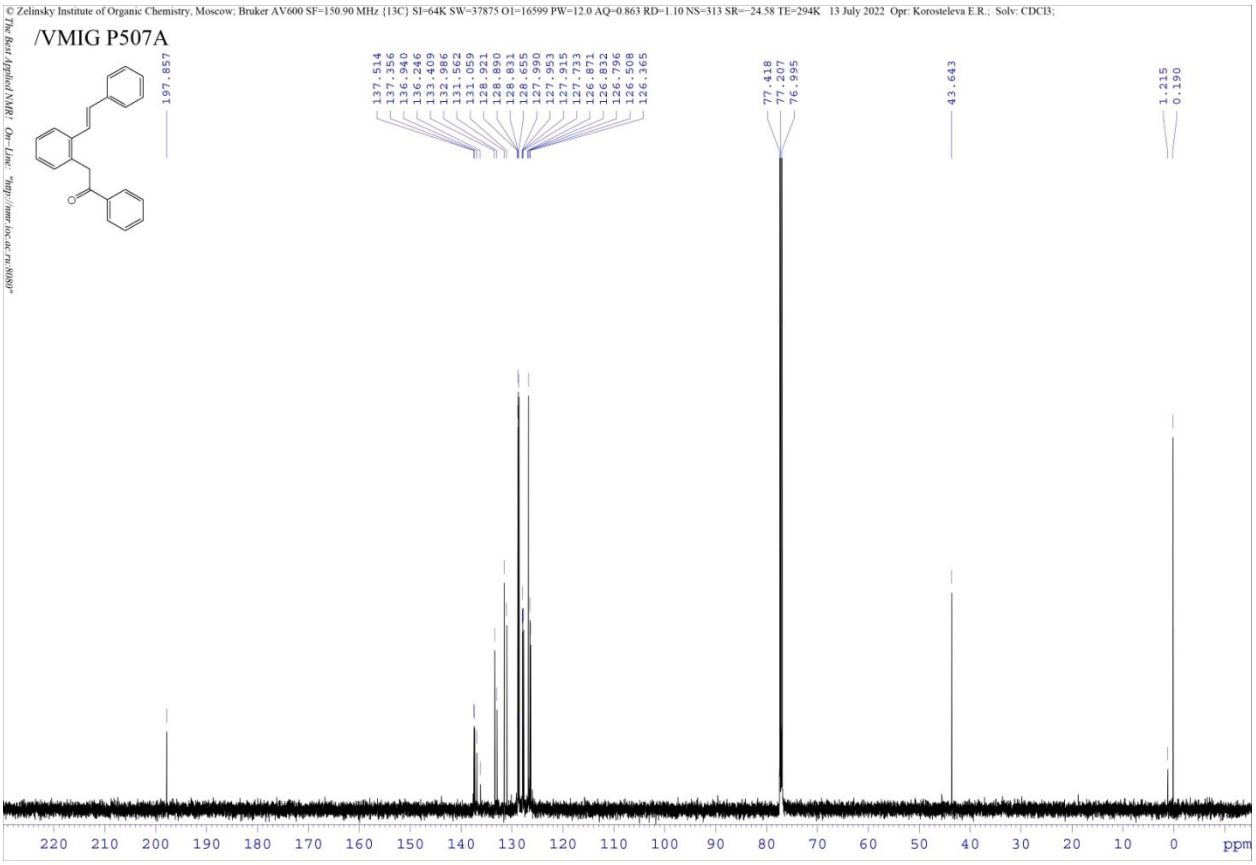


FIGURE S16. ^{13}C NMR spectrum of (E)-1-phenyl-2-(2-styrylphenyl)ethan-1-one (**18**) in $CDCl_3$.

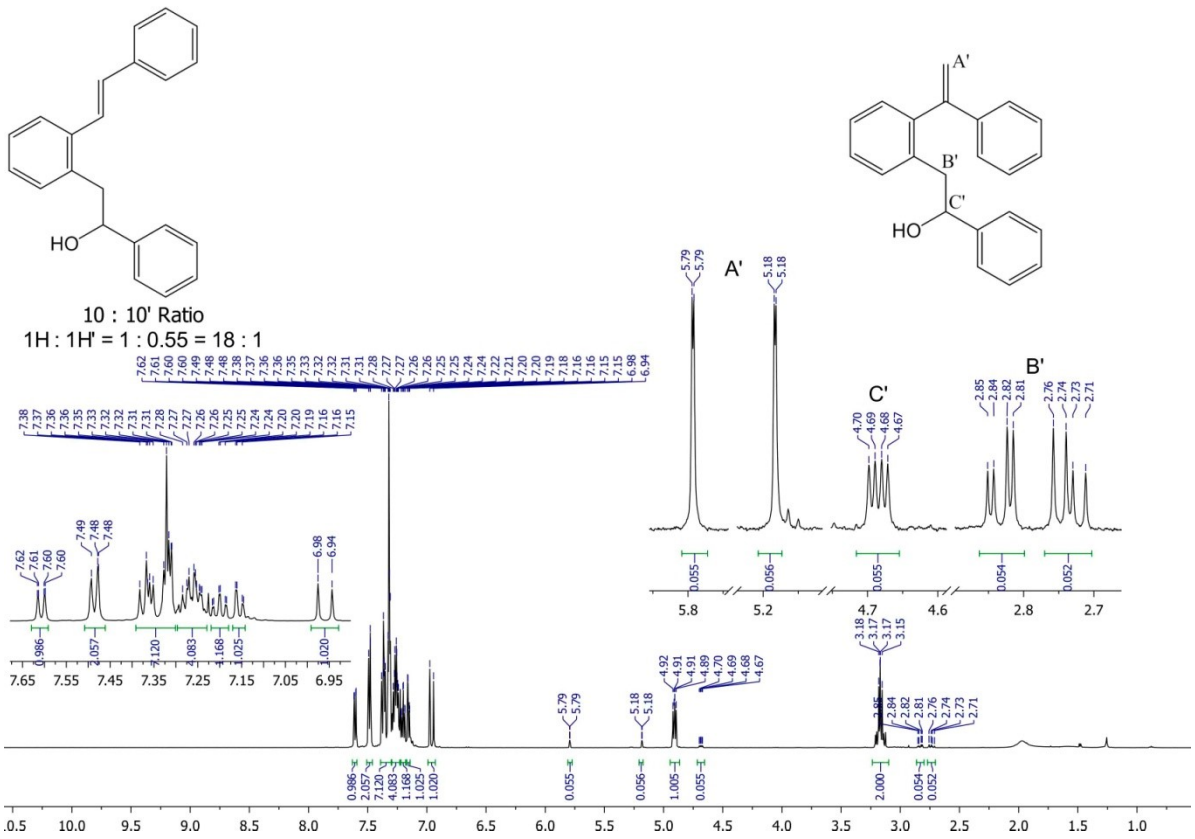


FIGURE S17. ^{1}H NMR spectrum of the mixture of (E)-1-phenyl-2-(2-styrylphenyl)ethan-1-ol (**10**) and 1-phenyl-2-(2-(1-phenylvinyl)phenyl)ethan-1-ol (**10'**) in $CDCl_3$.

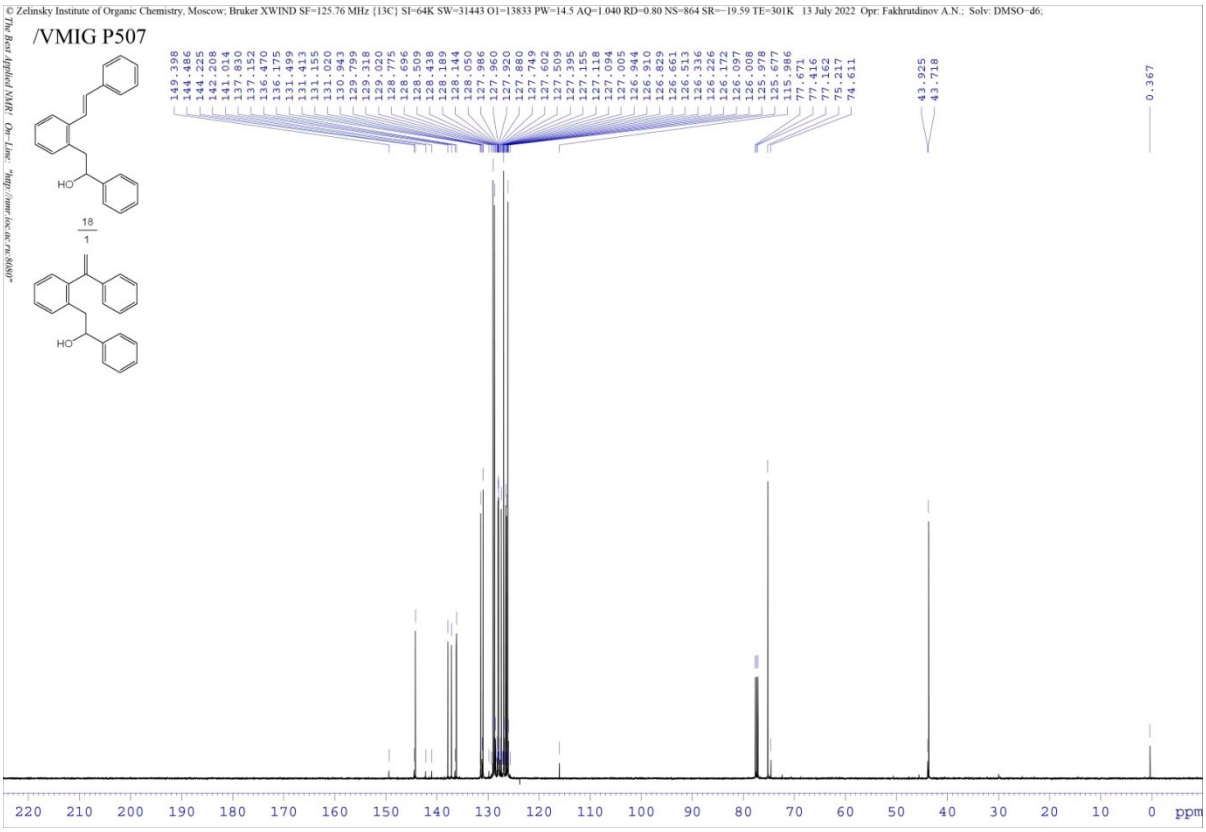


FIGURE S18. ^{13}C NMR spectrum of the mixture of (E)-1-phenyl-2-(2-styrylphenyl)ethan-1-ol (**10**) and 1-phenyl-2-(2-(1-phenylvinyl)phenyl)ethan-1-ol (**10'**) in $CDCl_3$.

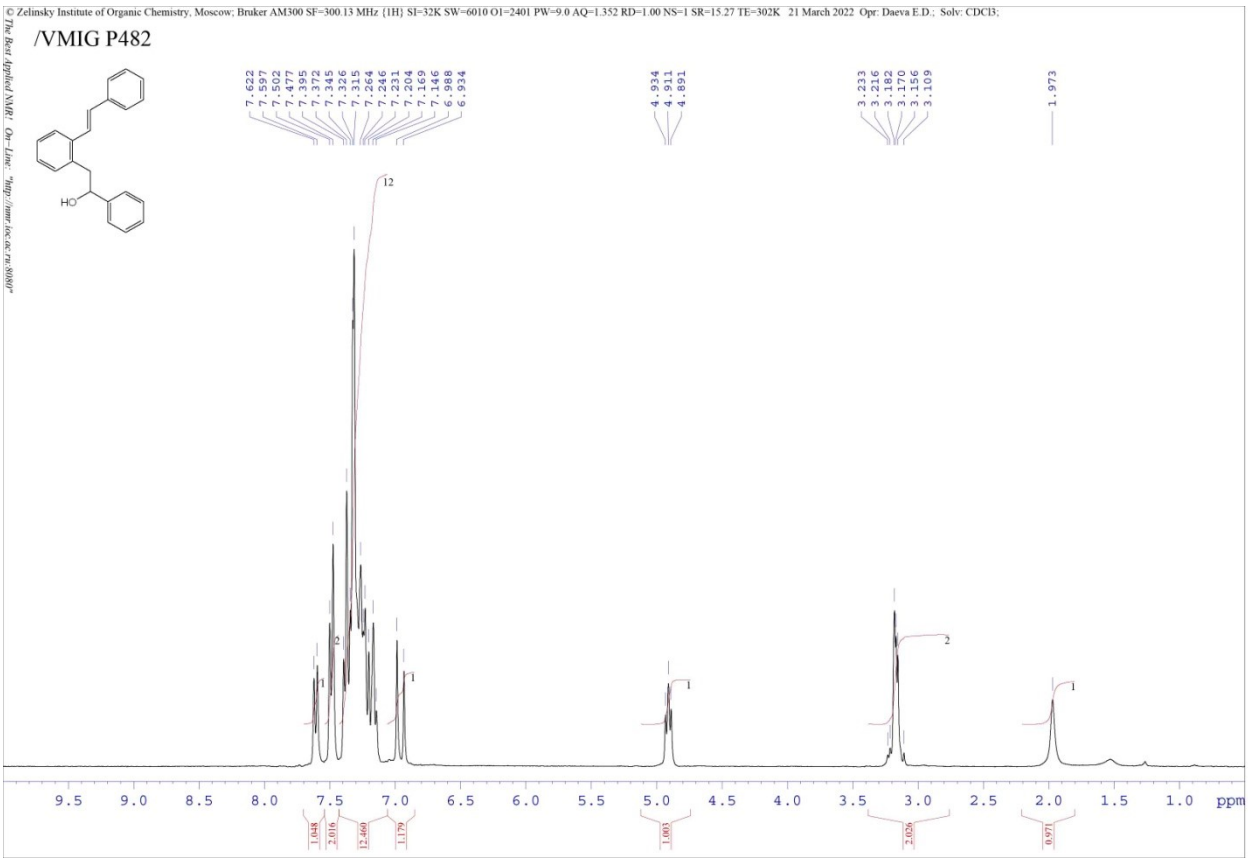


FIGURE S19. ^{1}H NMR spectrum of (E)-1-phenyl-2-(2-styrylphenyl)ethan-1-ol (**10**) in $CDCl_3$.

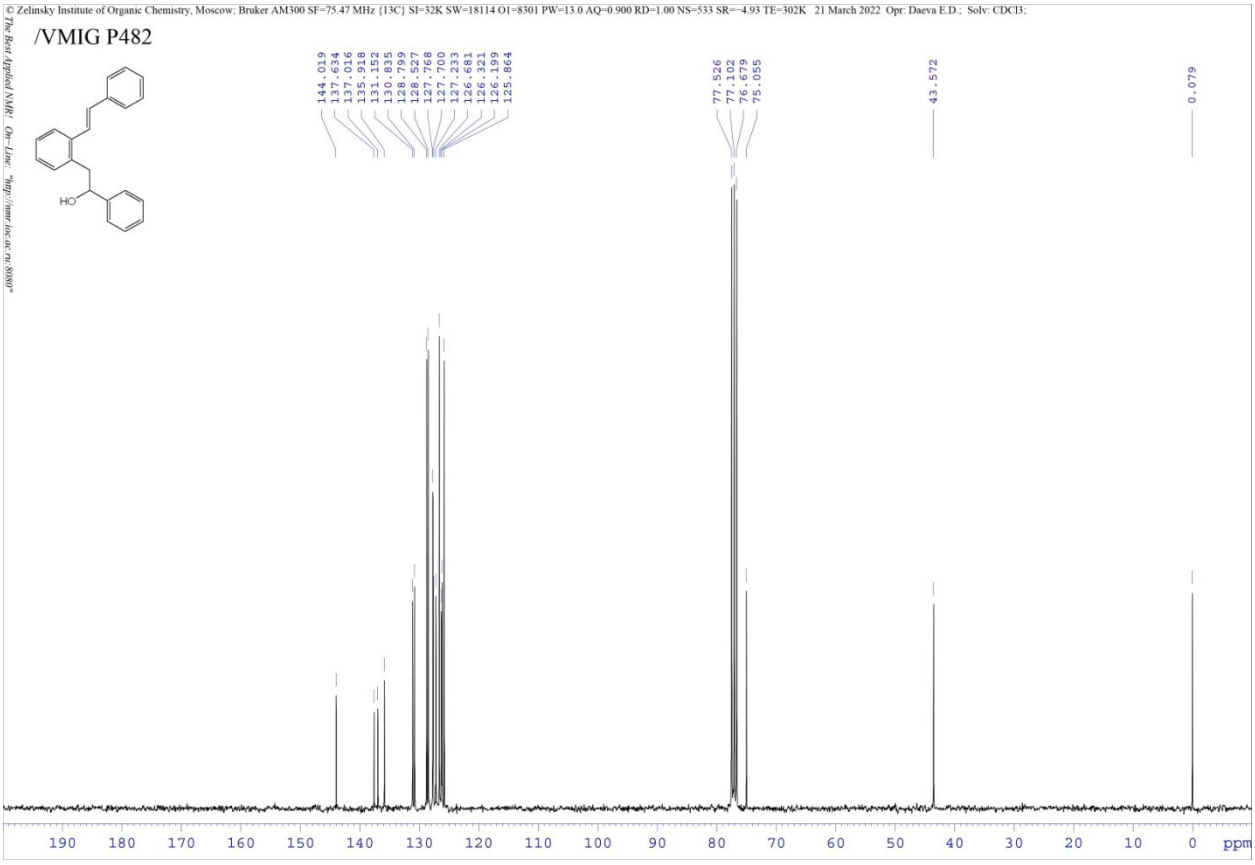


FIGURE S20. ^{13}C NMR spectrum of (E)-1-phenyl-2-(2-styrylphenyl)ethan-1-ol (**10**) in $CDCl_3$.

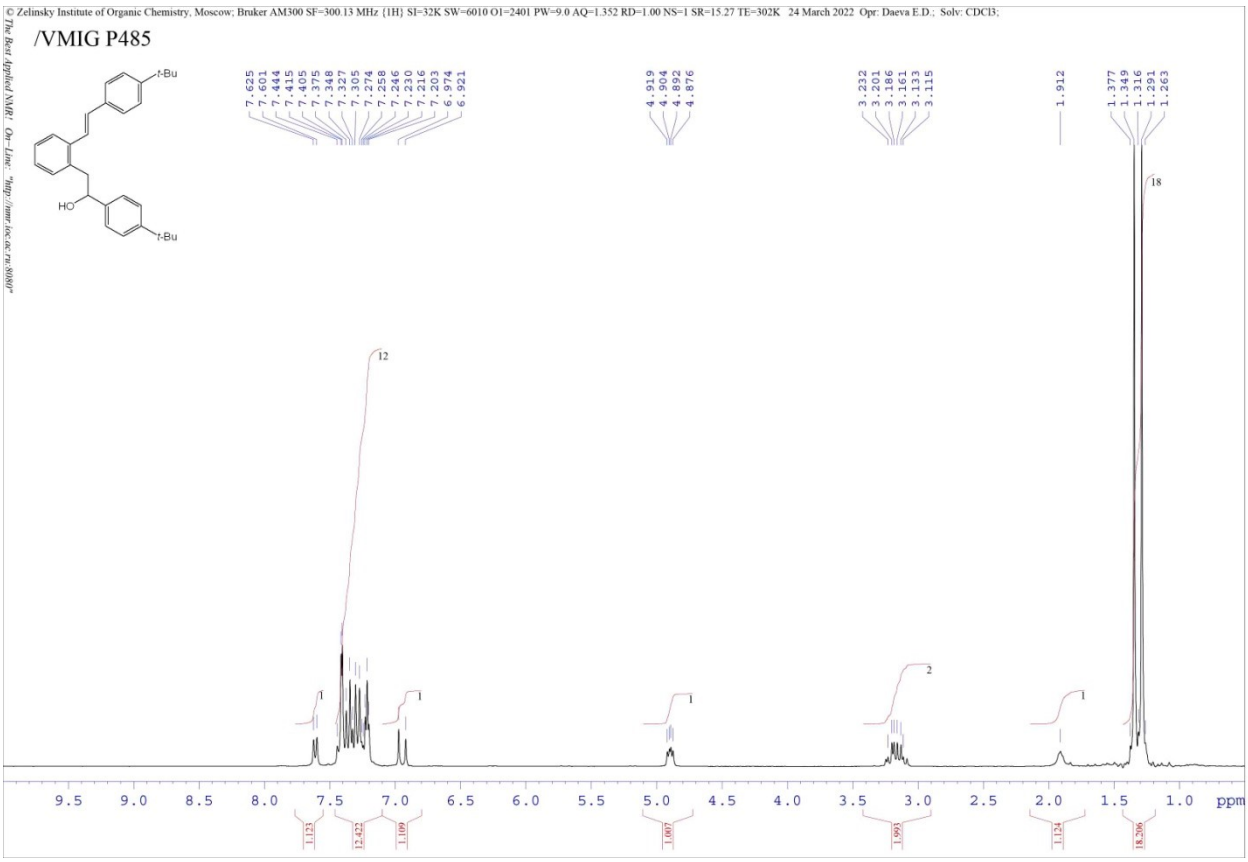


FIGURE S21. ^{1}H NMR spectrum of (E)-1-(4-(tert-butyl)phenyl)-2-(2-(4-(tert-butyl)styryl)phenyl)ethan-1-ol (**11**) in $CDCl_3$.

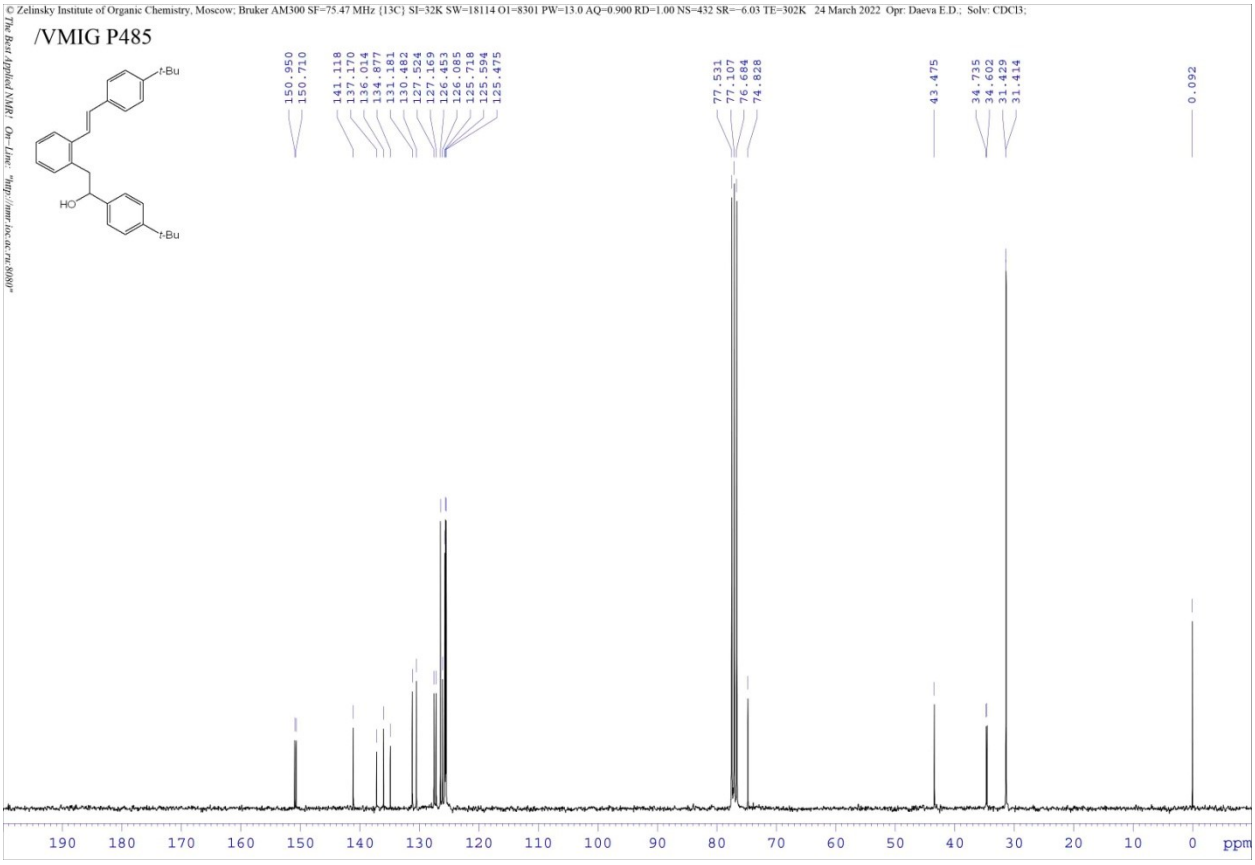


FIGURE S22. ^{13}C NMR spectrum of (E)-1-(4-(tert-butyl)phenyl)-2-(2-(4-(tert-butyl)styryl)phenyl)ethan-1-ol (**11**) in $CDCl_3$.

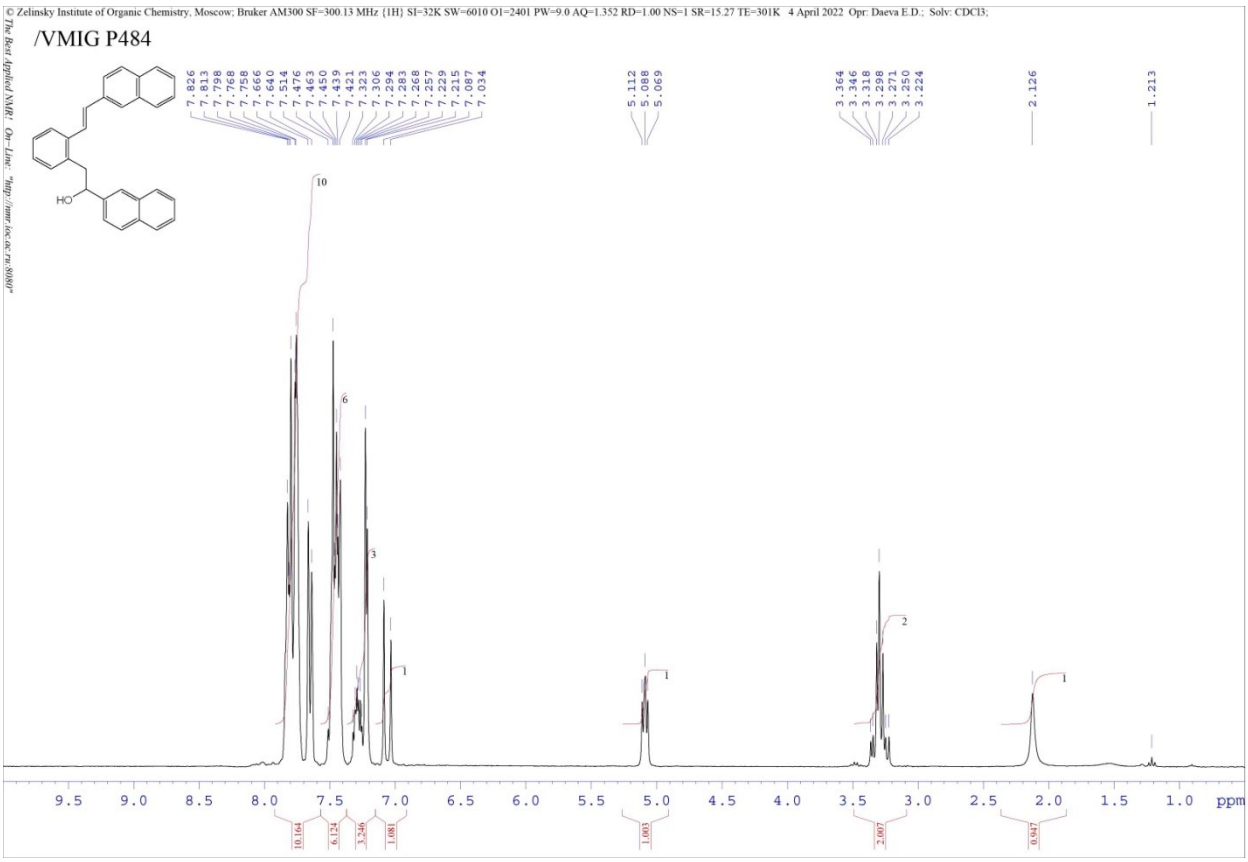


FIGURE S23. ^{1}H NMR spectrum of (E)-1-(naphthalen-2-yl)-2-(2-(2-(naphthalen-2-yl)vinyl)phenyl)ethan-1-ol (**12**) in $CDCl_3$.

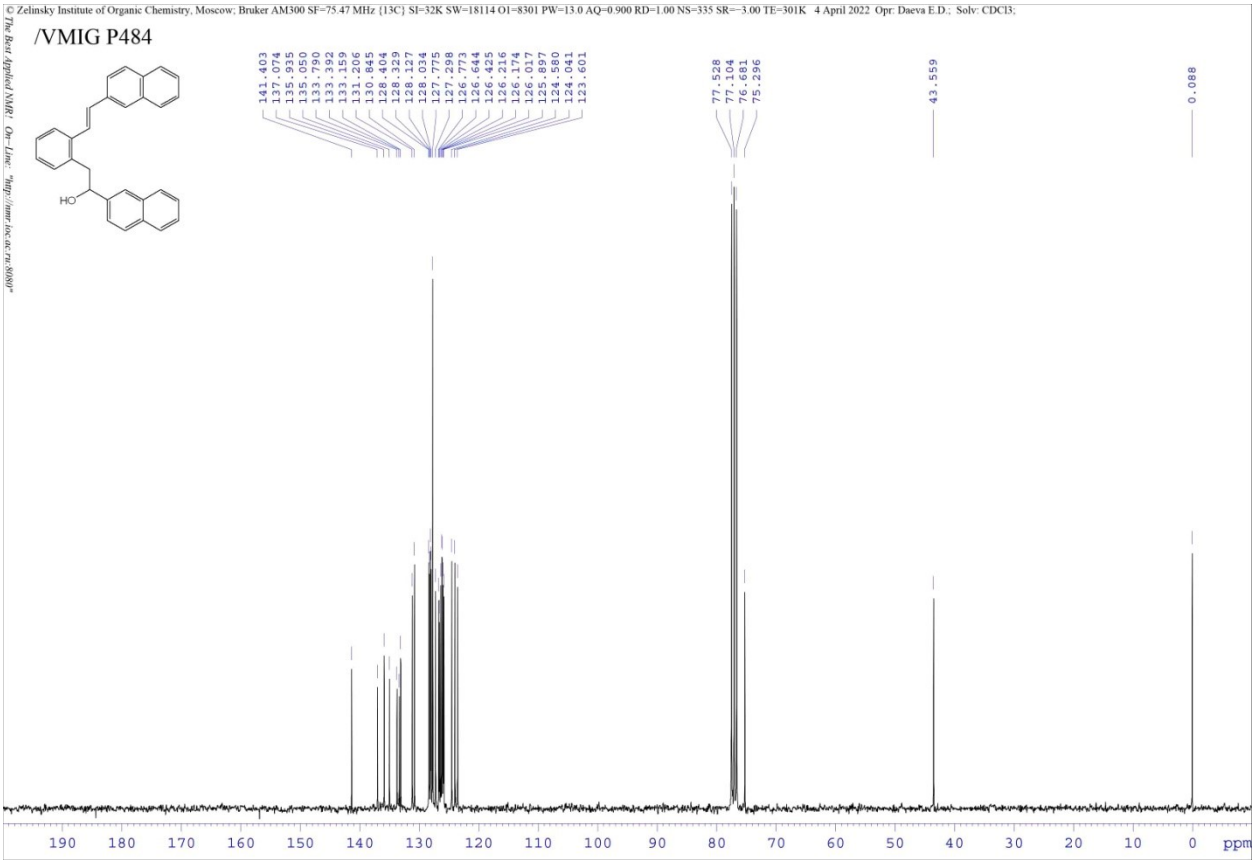


FIGURE S24. ^{13}C NMR spectrum of (E)-1-(naphthalen-2-yl)-2-(2-(2-(naphthalen-2-yl)vinyl)phenyl)ethan-1-ol (**12**) in $CDCl_3$.

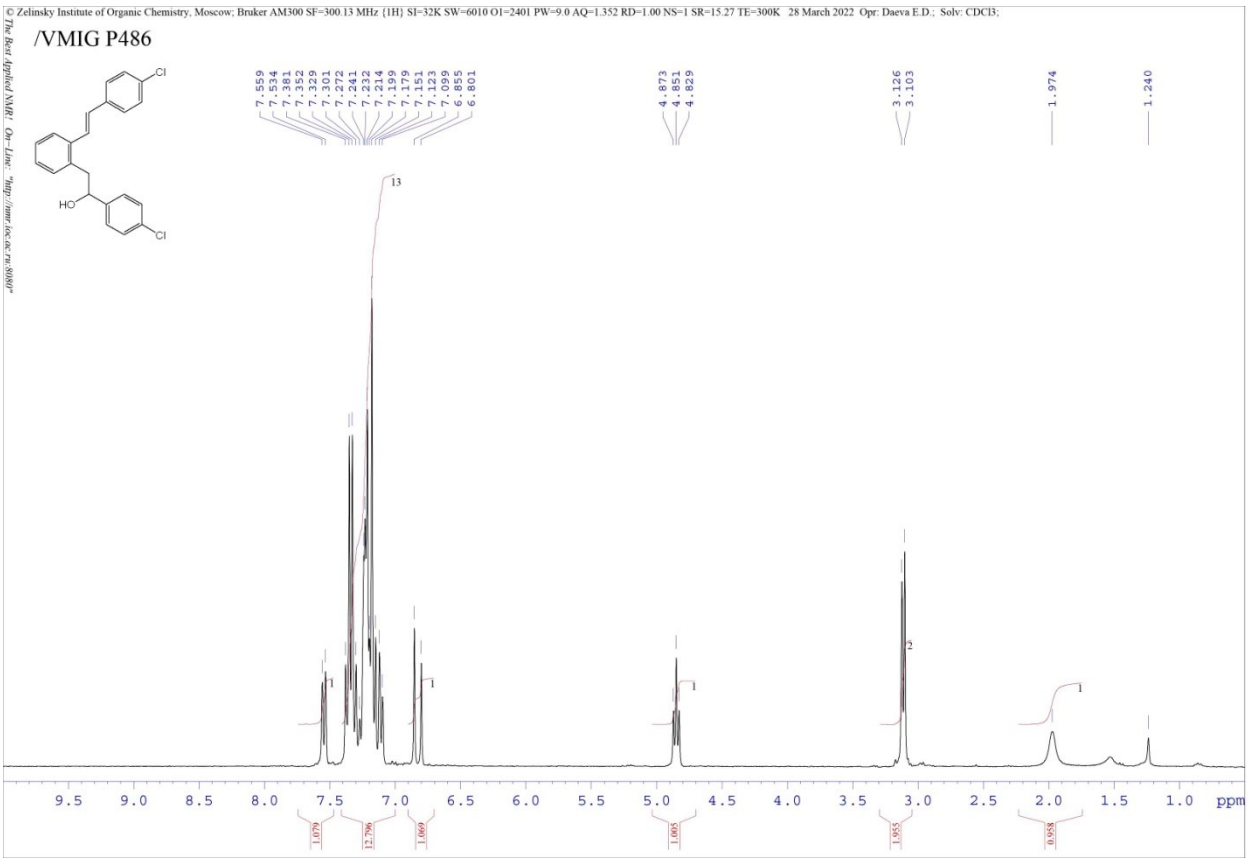


FIGURE S25. ^{1}H NMR spectrum of (E)-1-(4-chlorophenyl)-2-(2-(4-chlorostyryl)phenyl)ethan-1-ol (**13**) in $CDCl_3$.

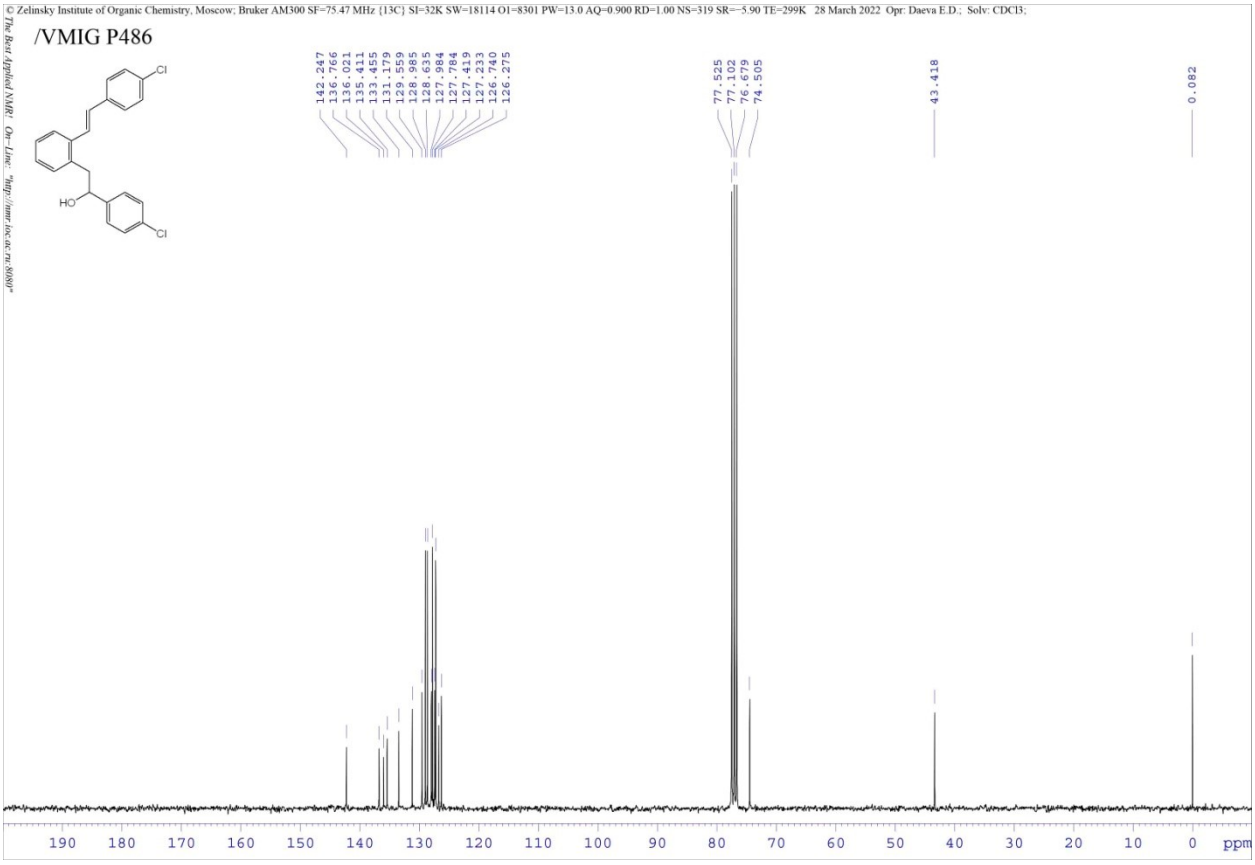


FIGURE S26. ^{13}C NMR spectrum of (E)-1-(4-chlorophenyl)-2-(2-(4-chlorostyryl)phenyl)ethan-1-ol (**13**) in $CDCl_3$.

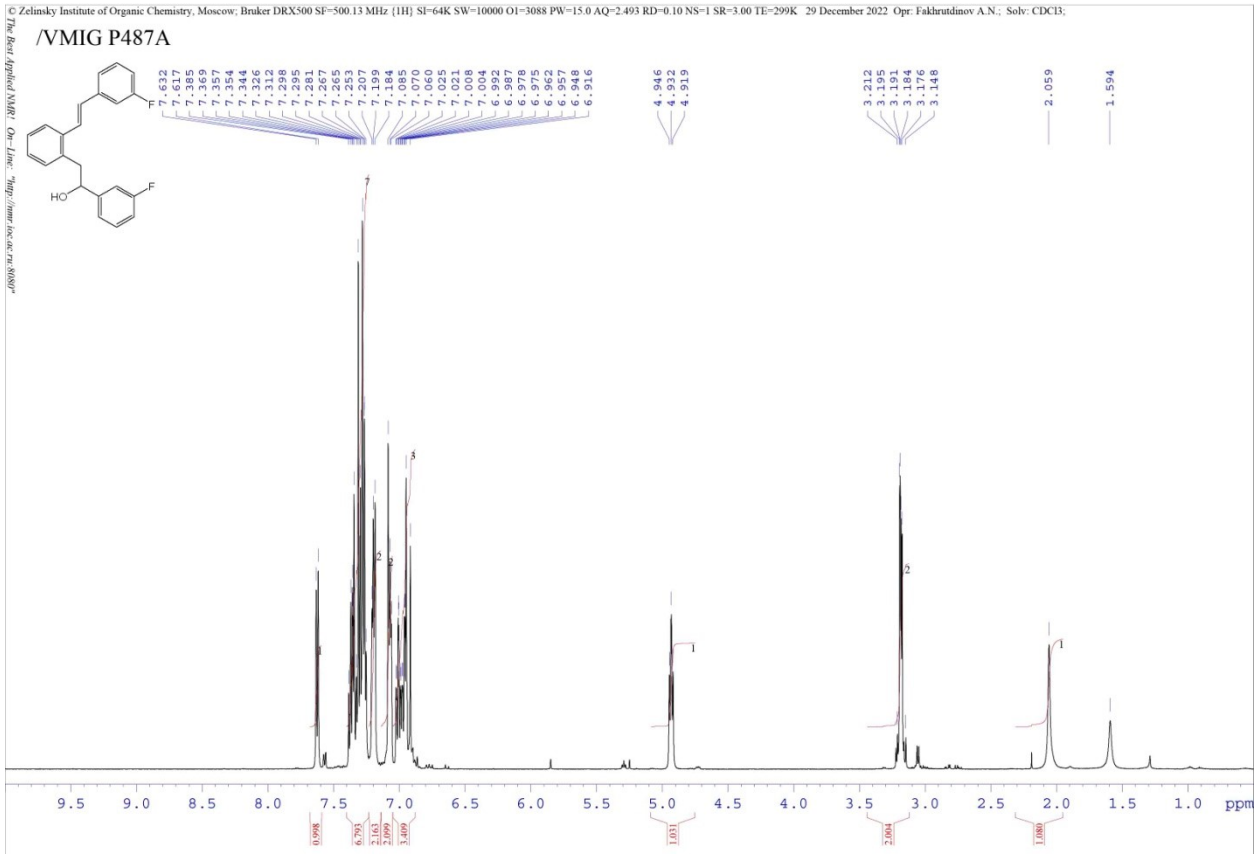


FIGURE S27. ^{1}H NMR spectrum of (E)-1-(3-fluorophenyl)-2-(2-(3-fluorostyryl)phenyl)ethan-1-ol (**14**) in $CDCl_3$.

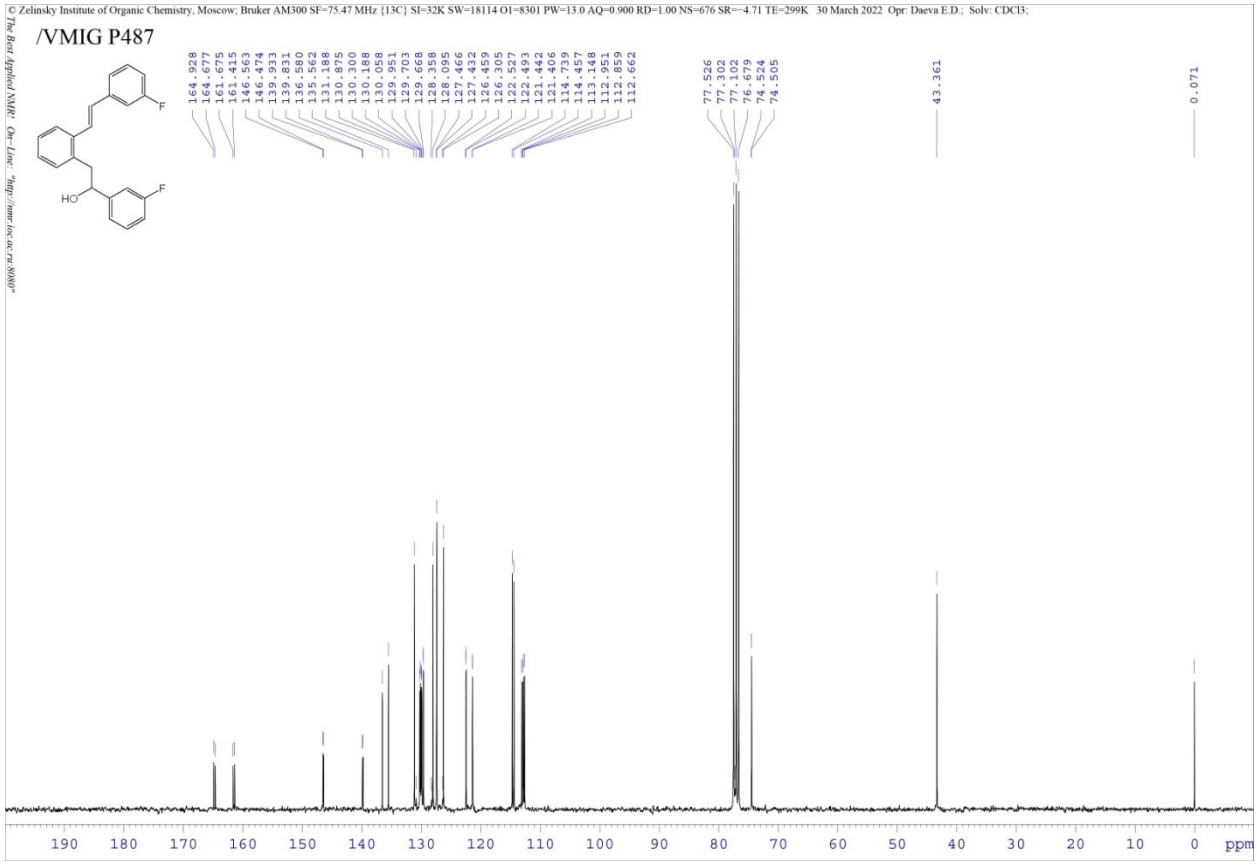


FIGURE S28. ^{13}C NMR spectrum of (E)-1-(3-fluorophenyl)-2-(2-(3-fluorostyryl)phenyl)ethan-1-ol (**14**) in $CDCl_3$.

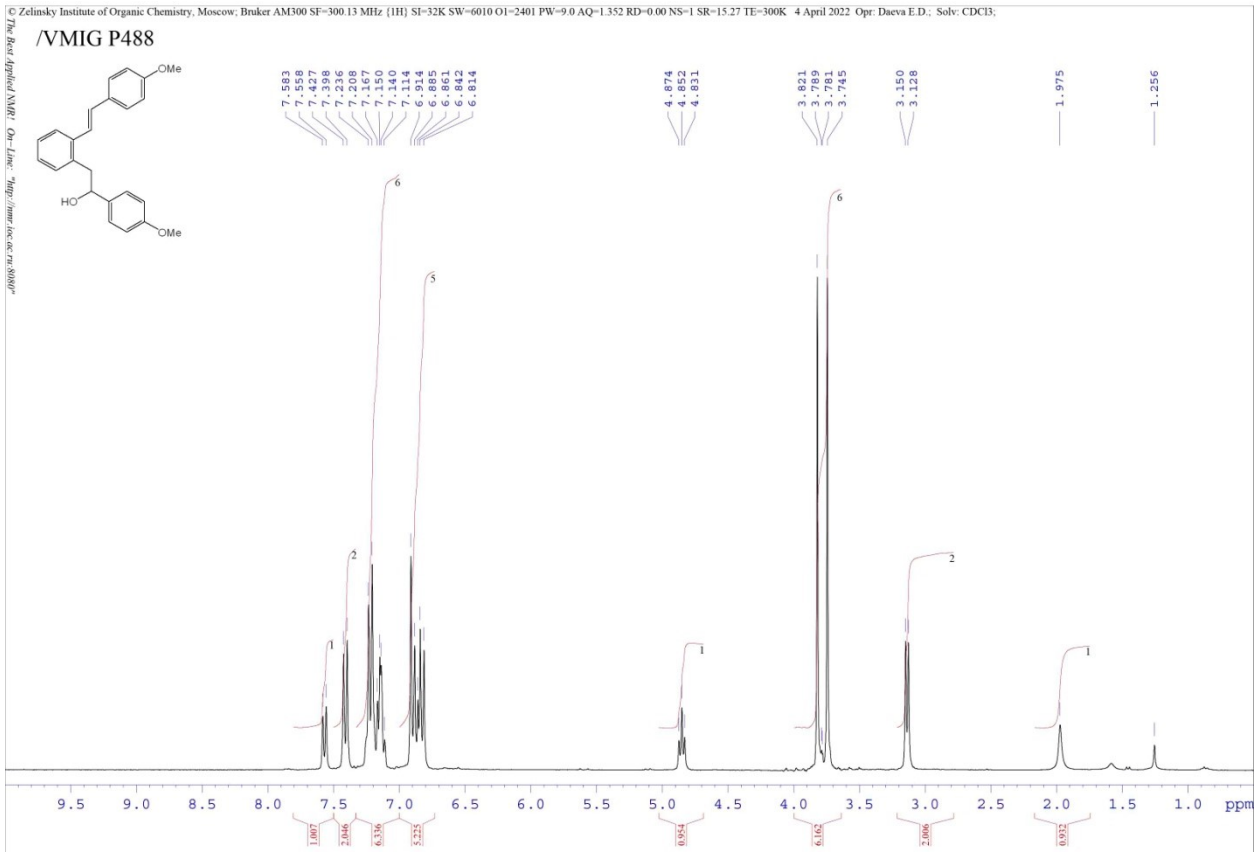


FIGURE S29. ^{1}H NMR spectrum of (E)-1-(4-methoxyphenyl)-2-(2-(4-methoxystyryl)phenyl)ethan-1-ol (**15**) in $CDCl_3$.

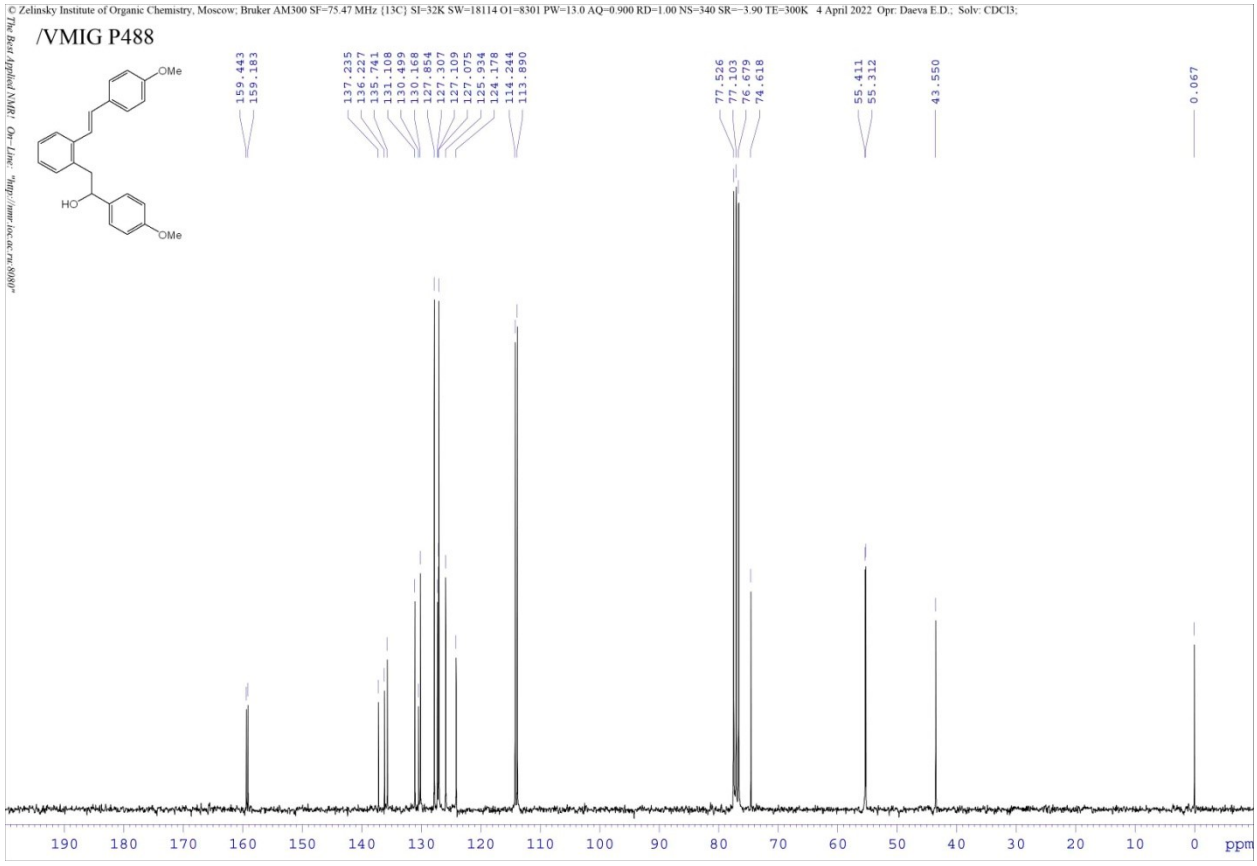


FIGURE S30. ^{13}C NMR spectrum of (E)-1-(4-methoxyphenyl)-2-(2-(4-methoxystyryl)phenyl)ethan-1-ol (**15**) in $CDCl_3$.

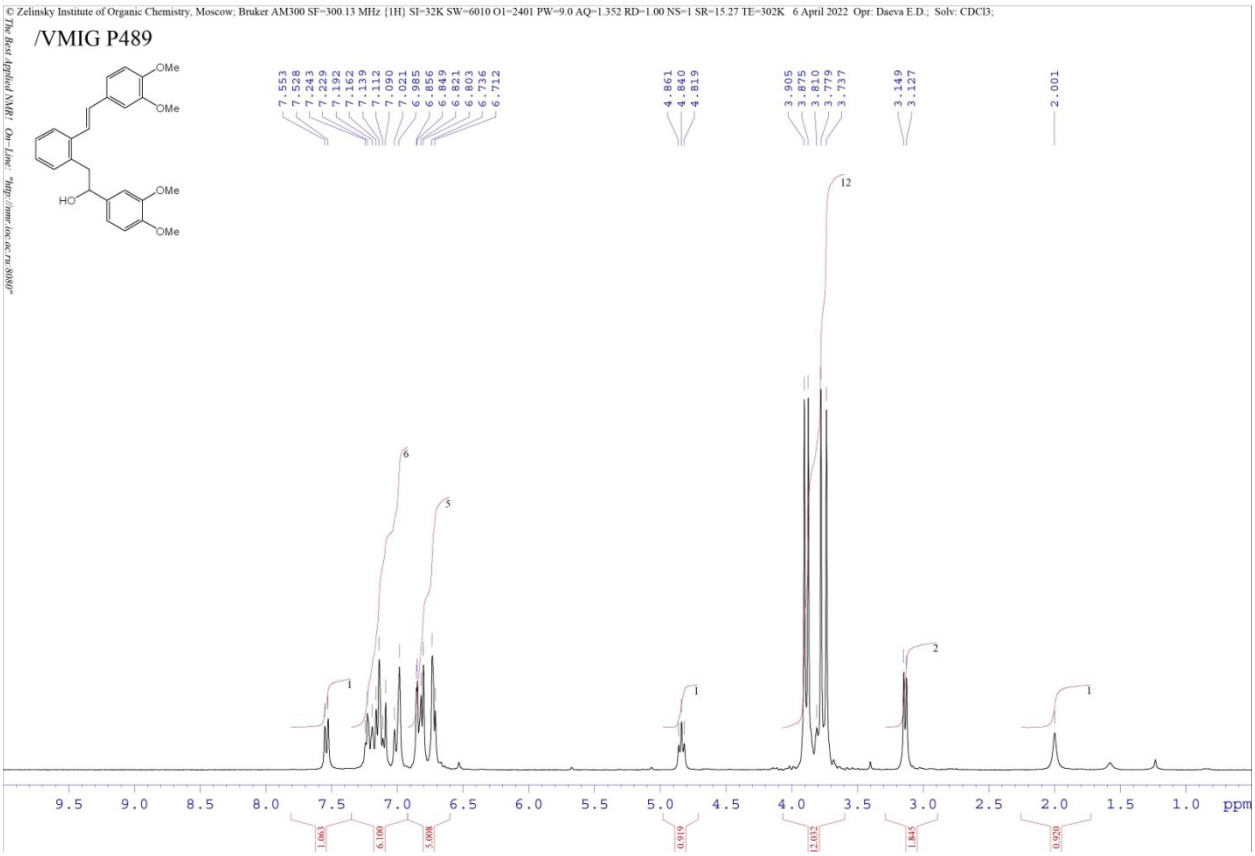


FIGURE S31. ^{1}H NMR spectrum of (E)-1-(3,4-dimethoxyphenyl)-2-(2-(3,4-dimethoxystyryl)phenyl)ethan-1-ol (**16**) in $CDCl_3$.

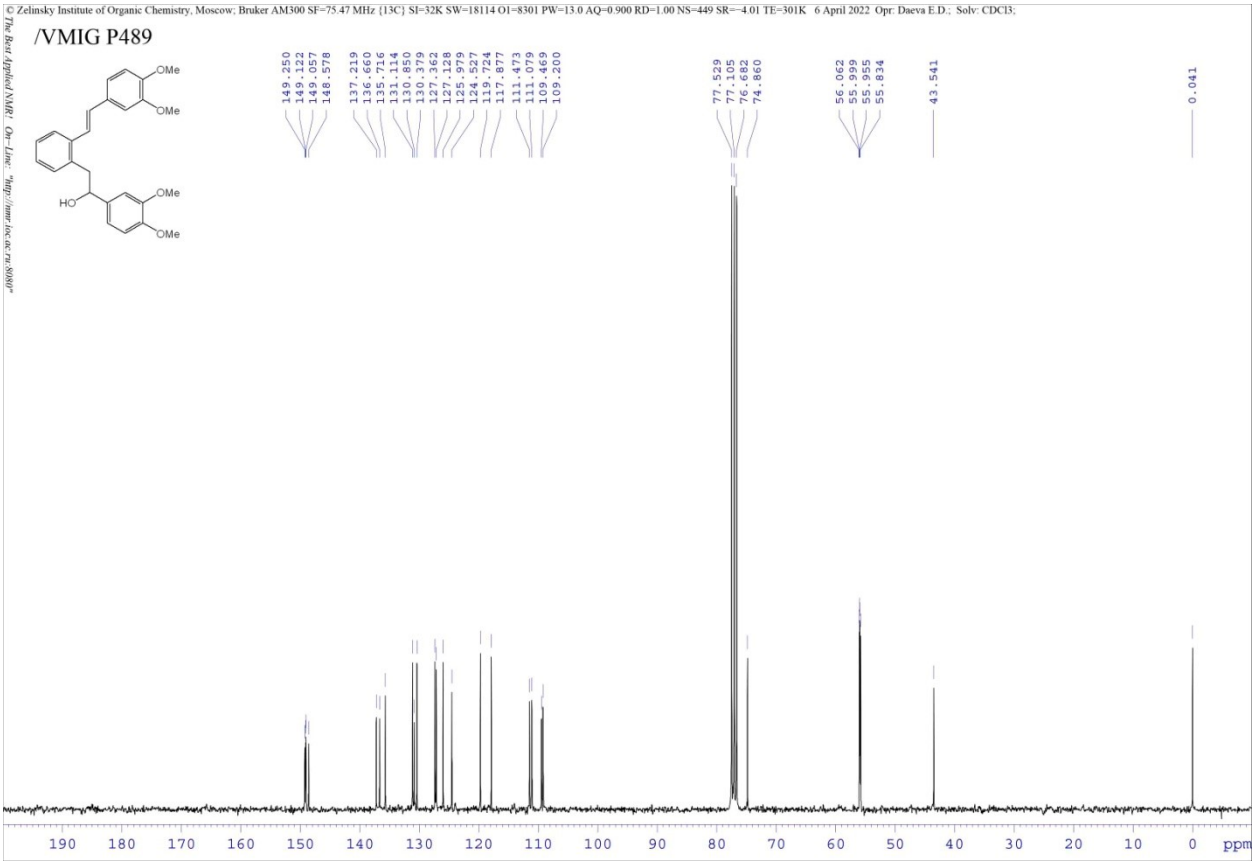


FIGURE S32. ^{13}C NMR spectrum of (E)-1-(3,4-dimethoxyphenyl)-2-(2-(3,4-dimethoxystyryl)phenyl)ethan-1-ol (**16**) in $CDCl_3$.

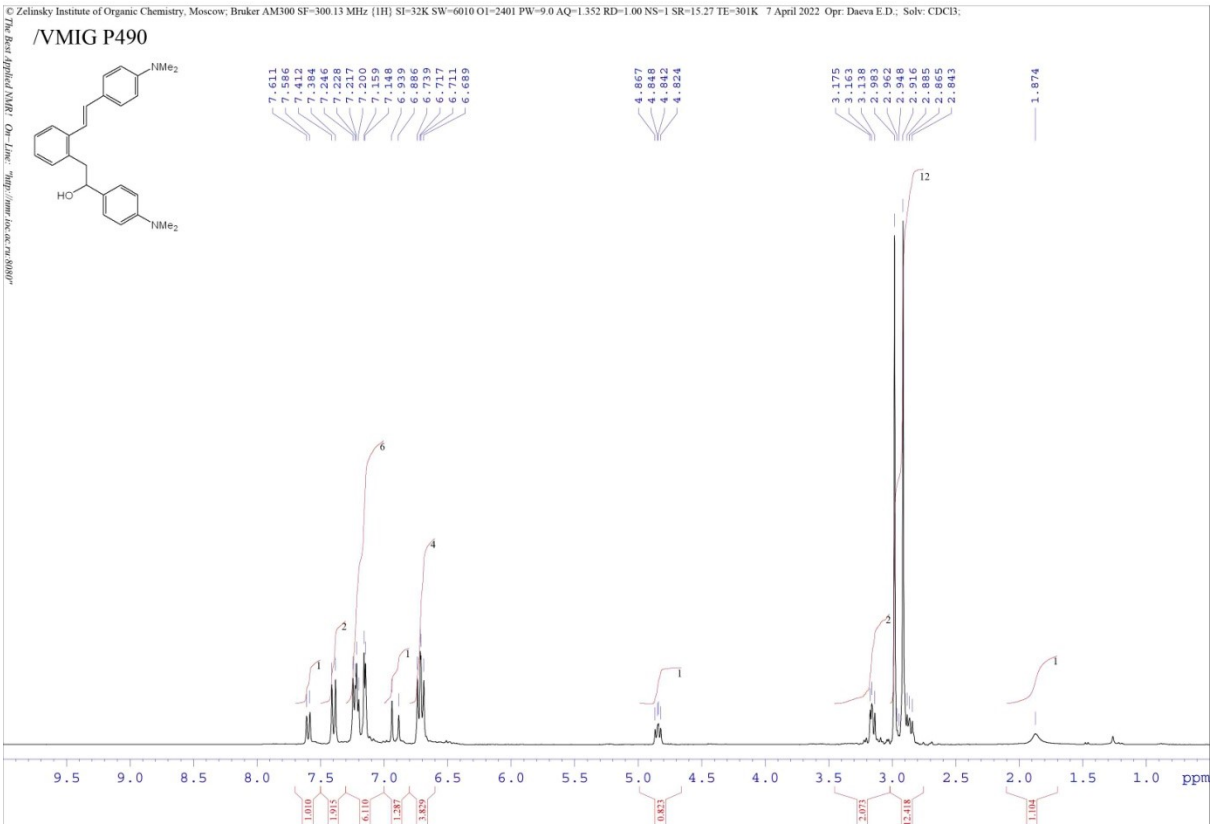


FIGURE S33. ^{1}H NMR spectrum of (E)-1-(4-(dimethylamino)phenyl)-2-(2-(4-(dimethylamino)styryl)phenyl)ethan-1-ol (**17**) in $CDCl_3$.

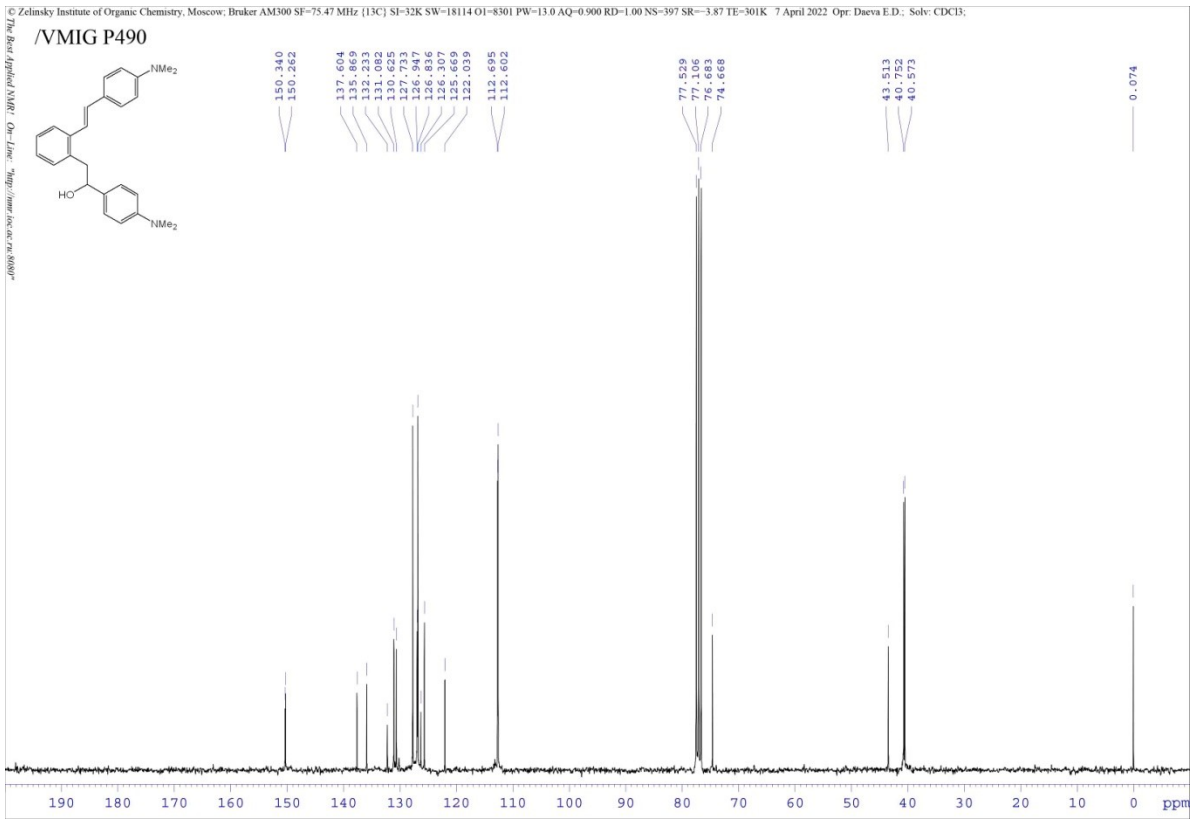


FIGURE S34. ^{13}C NMR spectrum of (E)-1-(4-(dimethylamino)phenyl)-2-(2-(4-(dimethylamino)styryl)phenyl)ethan-1-ol (**17**) in $CDCl_3$.

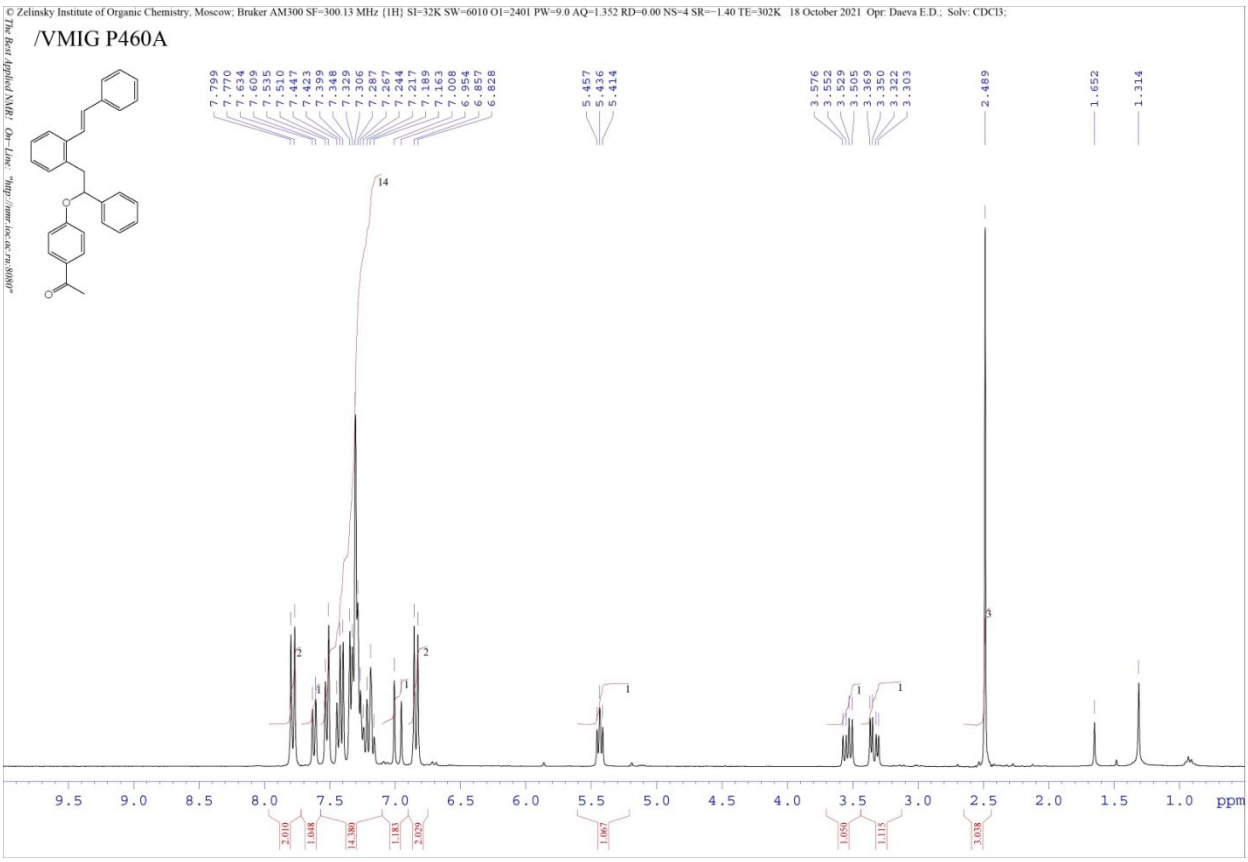


FIGURE S35. ^{1}H NMR spectrum of (E)-1-(4-(1-phenyl-2-(2-styrylphenyl)ethoxy)phenyl)ethan-1-one (**19**) in $CDCl_3$.

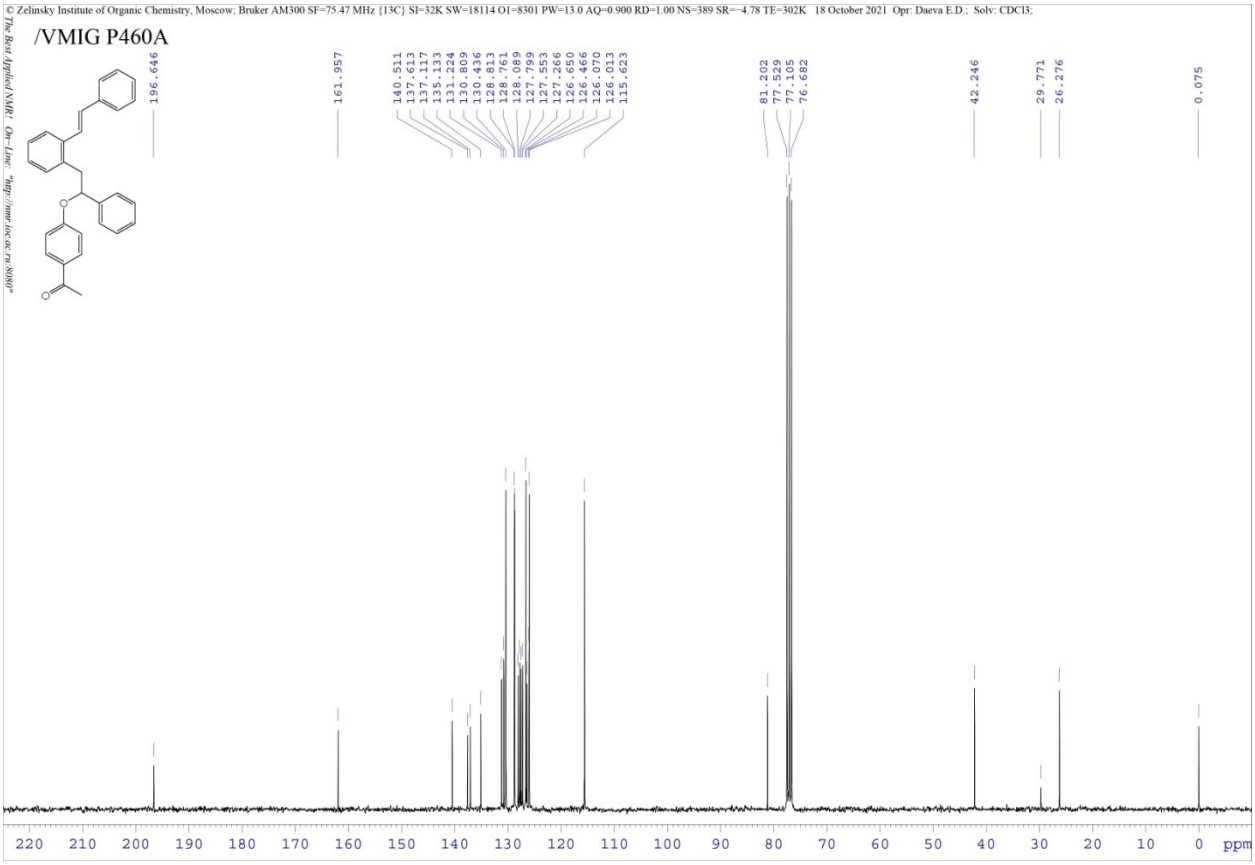


FIGURE S36. ^{13}C NMR spectrum of (E)-1-(4-(1-phenyl-2-(2-styrylphenyl)ethoxy)phenyl)ethan-1-one (**19**) in $CDCl_3$.

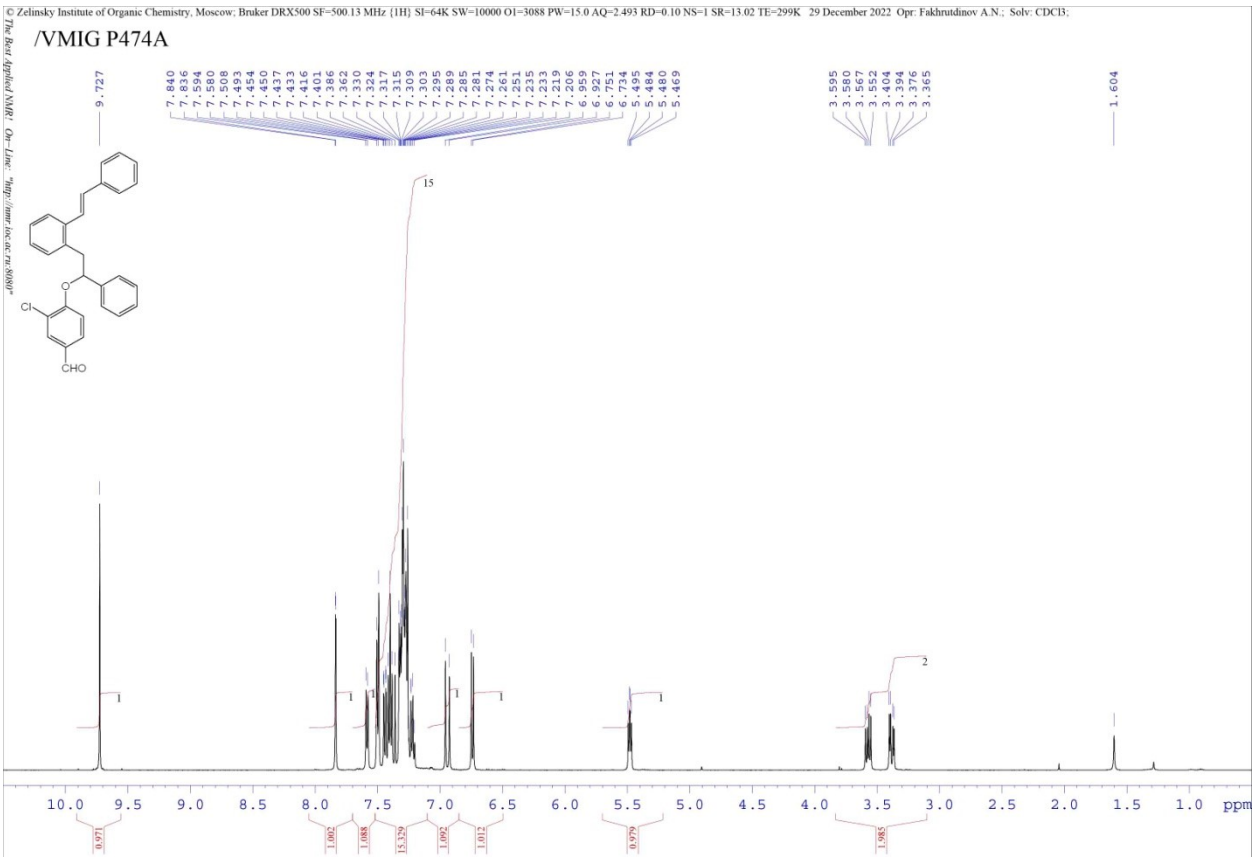


FIGURE S37. ^{1}H NMR spectrum of (E)-3-chloro-4-(1-phenyl-2-(2-styrylphenyl)ethoxy)benzaldehyde (**20**) in $CDCl_3$.

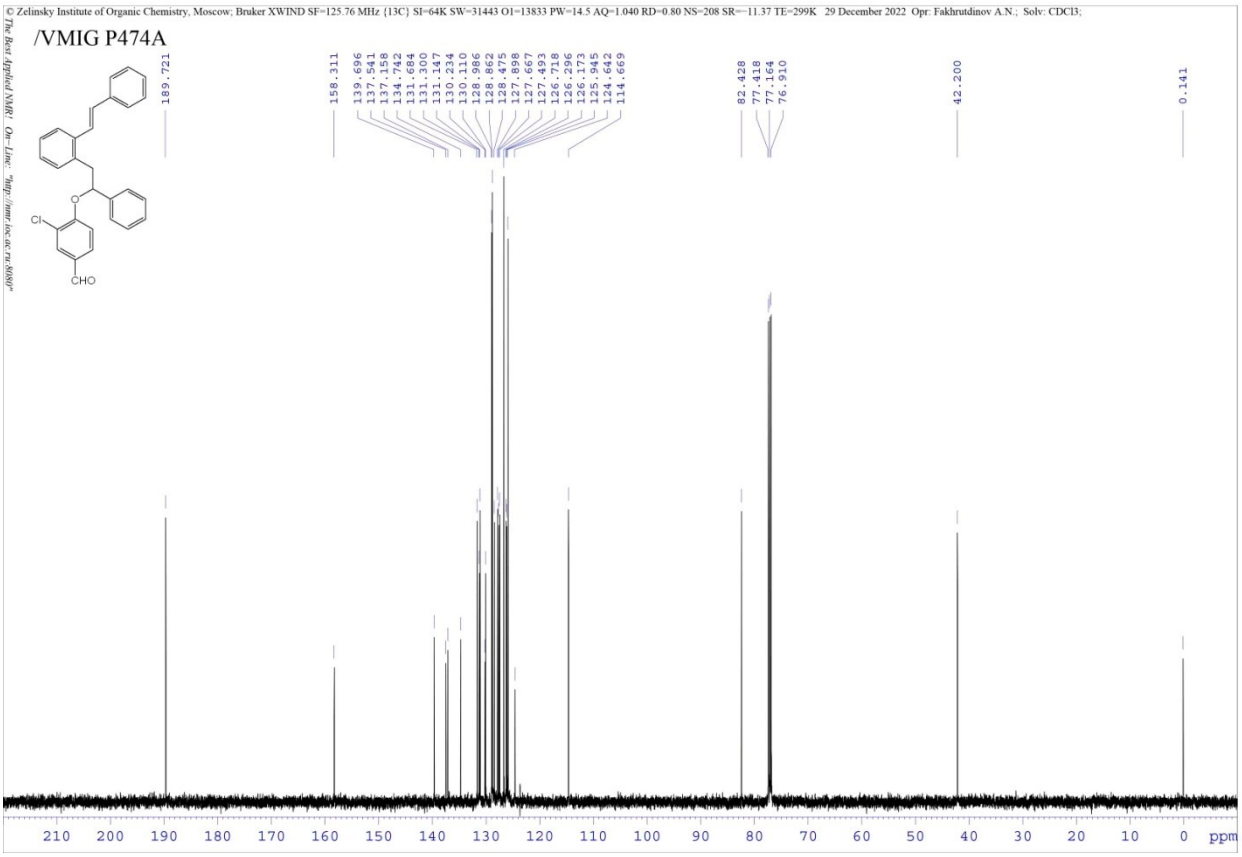


FIGURE S38. ^{13}C NMR spectrum of (E)-3-chloro-4-(1-phenyl-2-(2-styrylphenyl)ethoxy)benzaldehyde (**20**) in $CDCl_3$.

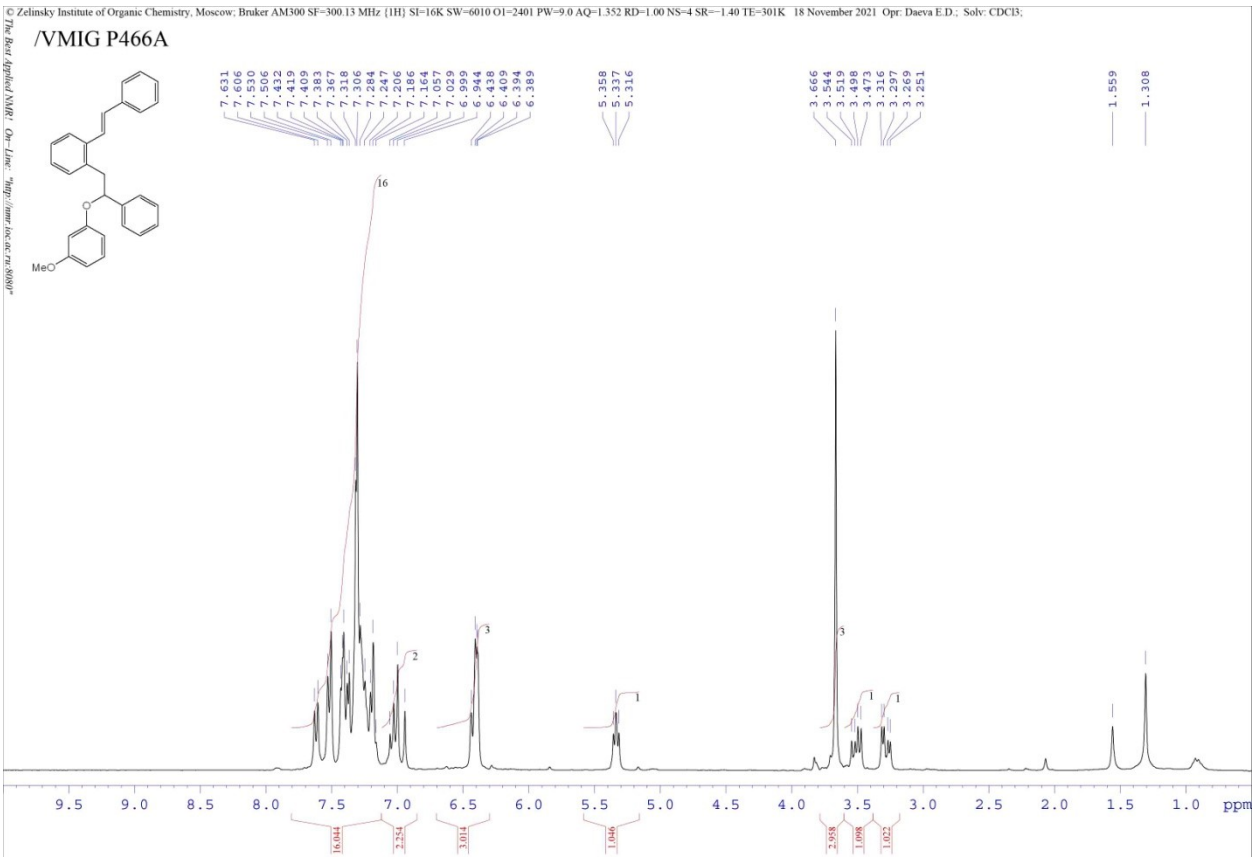


FIGURE S39. ^{1}H NMR spectrum of (E)-1-(2-(3-methoxyphenoxy)-2-phenylethyl)-2-styrylbenzene (**21**) in $CDCl_3$.

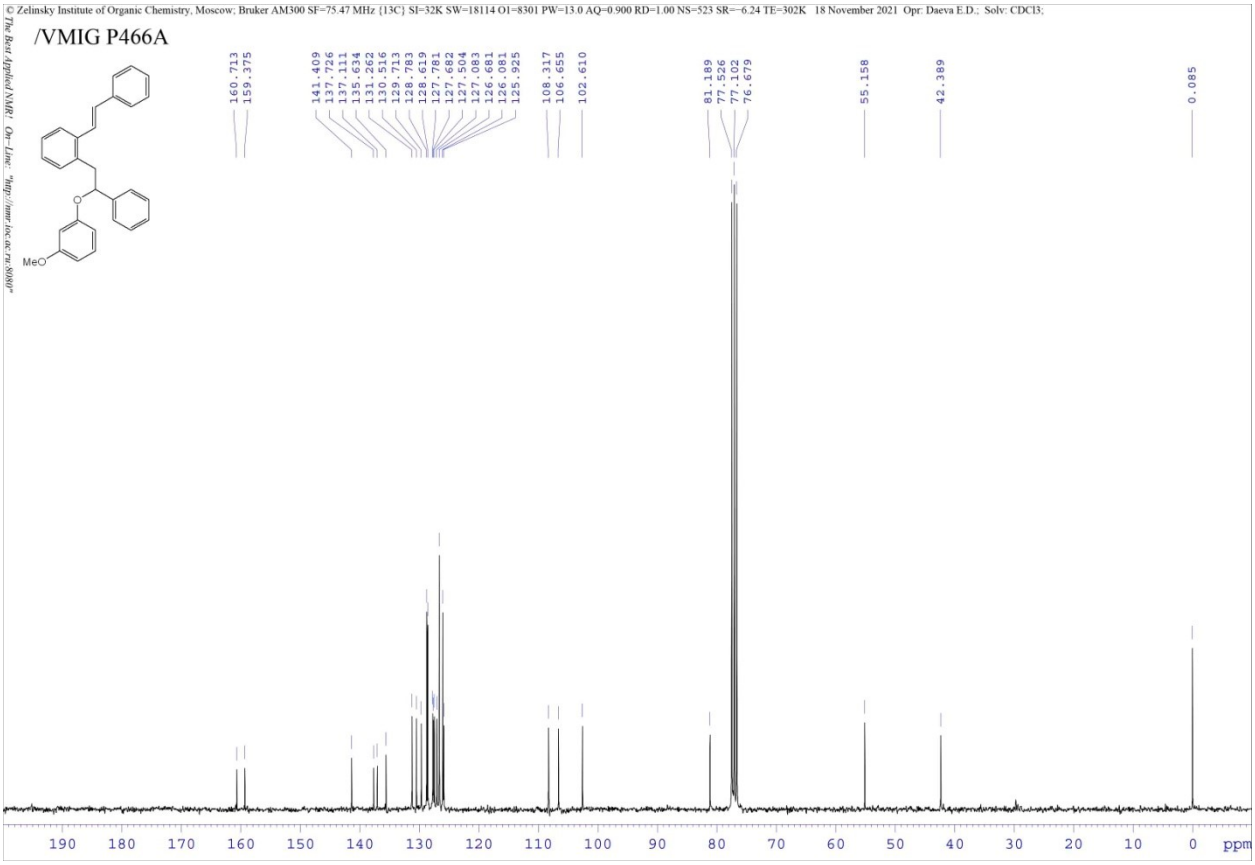


FIGURE S40. ^{13}C NMR spectrum of (E)-1-(2-(3-methoxyphenoxy)-2-phenylethyl)-2-styrylbenzene (**21**) in $CDCl_3$.

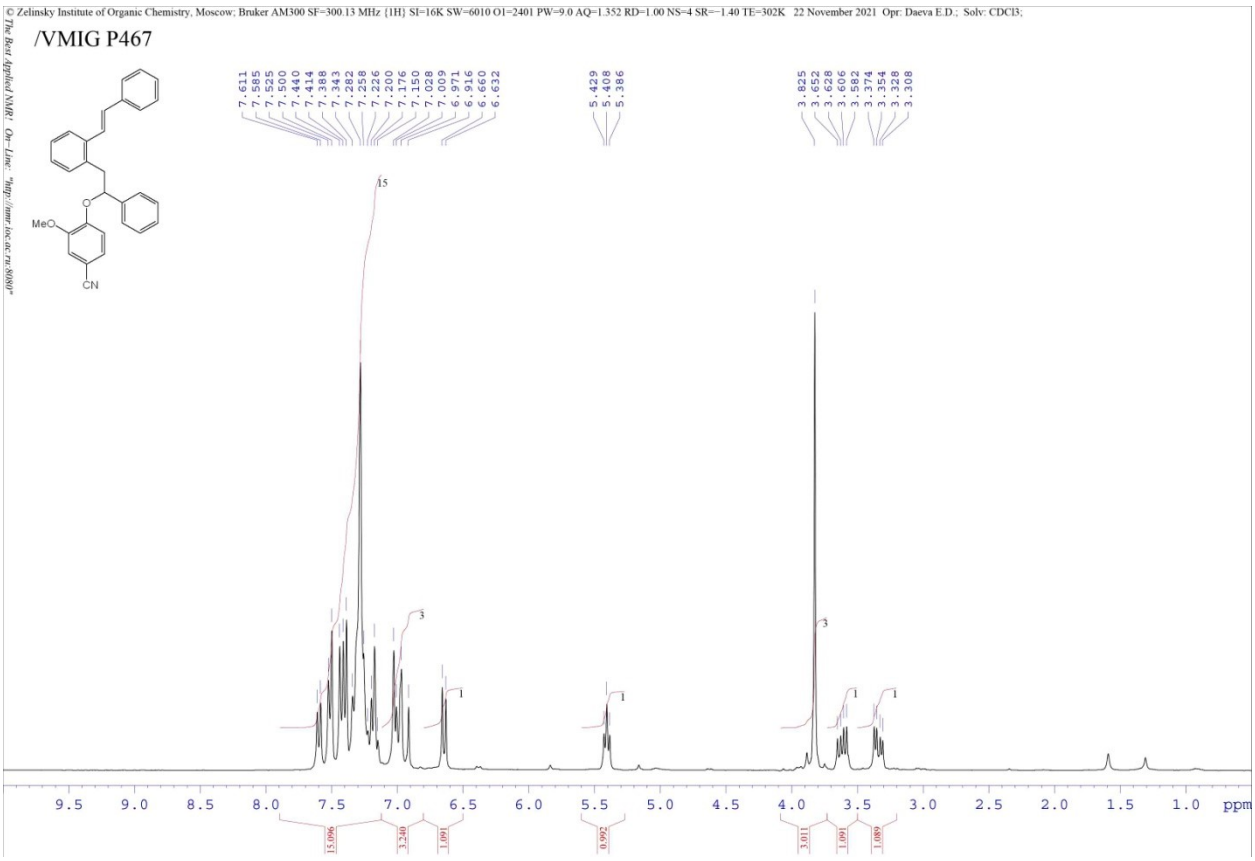


FIGURE S41. ^{1}H NMR spectrum of (E)-3-methoxy-4-(1-phenyl-2-(2-styrylphenyl)ethoxy)benzonitrile (**22**) in $CDCl_3$.

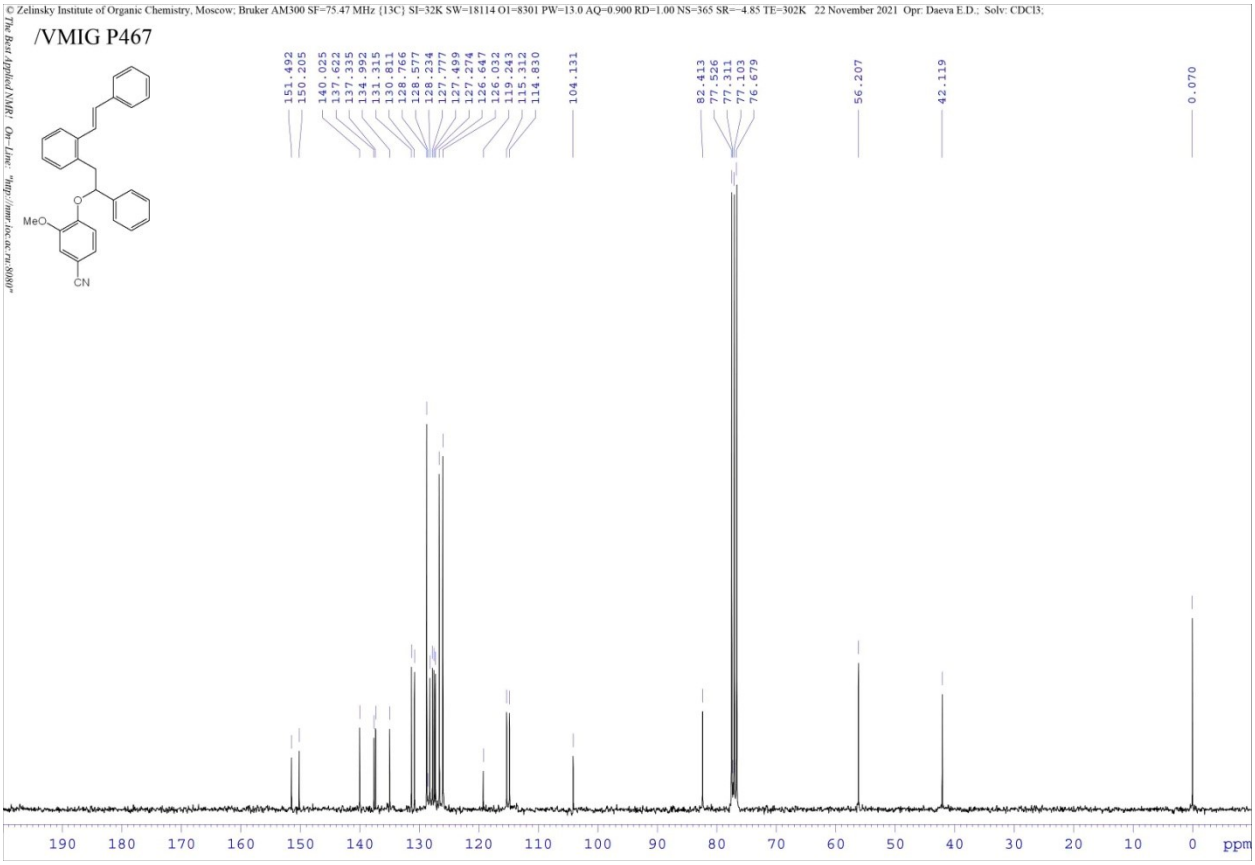


FIGURE S42. ^{13}C NMR spectrum of (E)-3-methoxy-4-(1-phenyl-2-(2-styrylphenyl)ethoxy)benzonitrile (**22**) in $CDCl_3$.

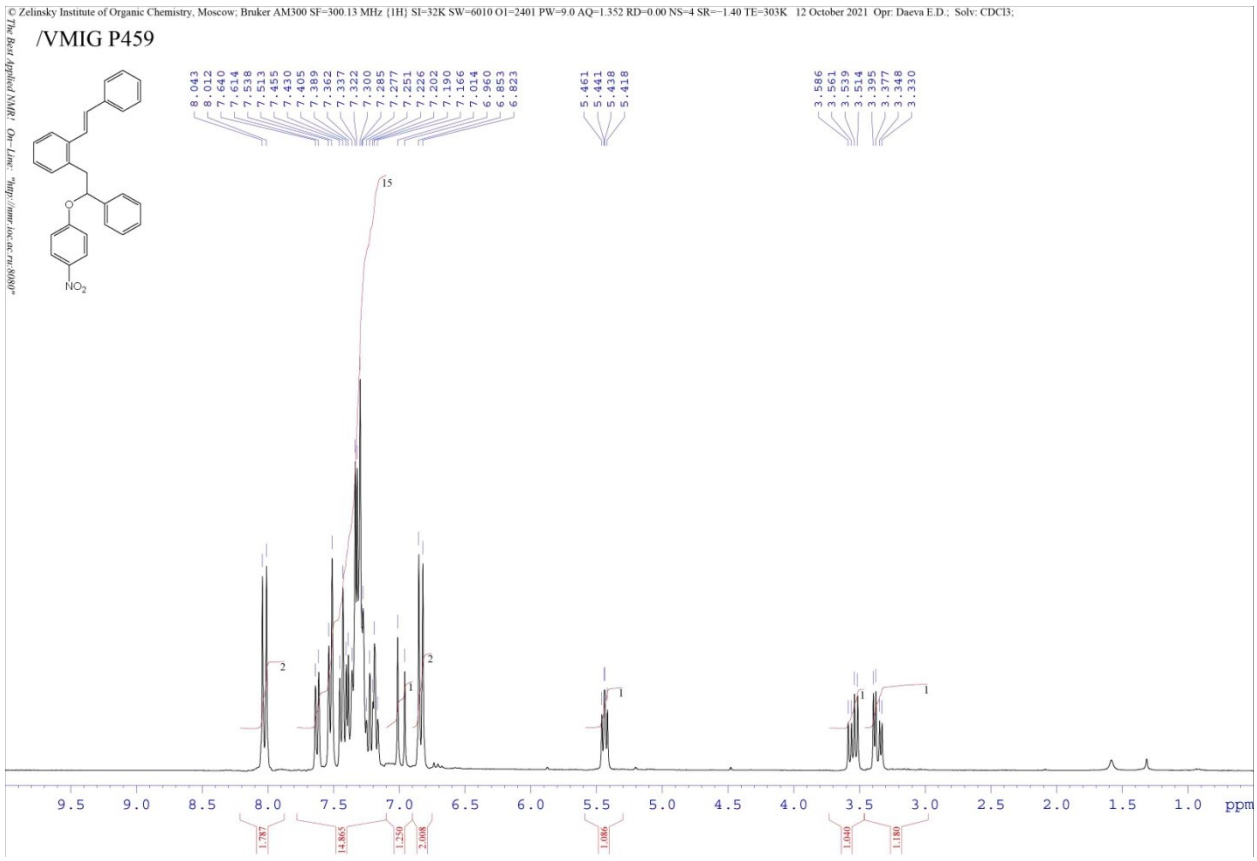


FIGURE S43. ^{1}H NMR spectrum of (E)-1-(2-(4-nitrophenoxy)-2-phenylethyl)-2-styrylbenzene (**23**) in $CDCl_3$.

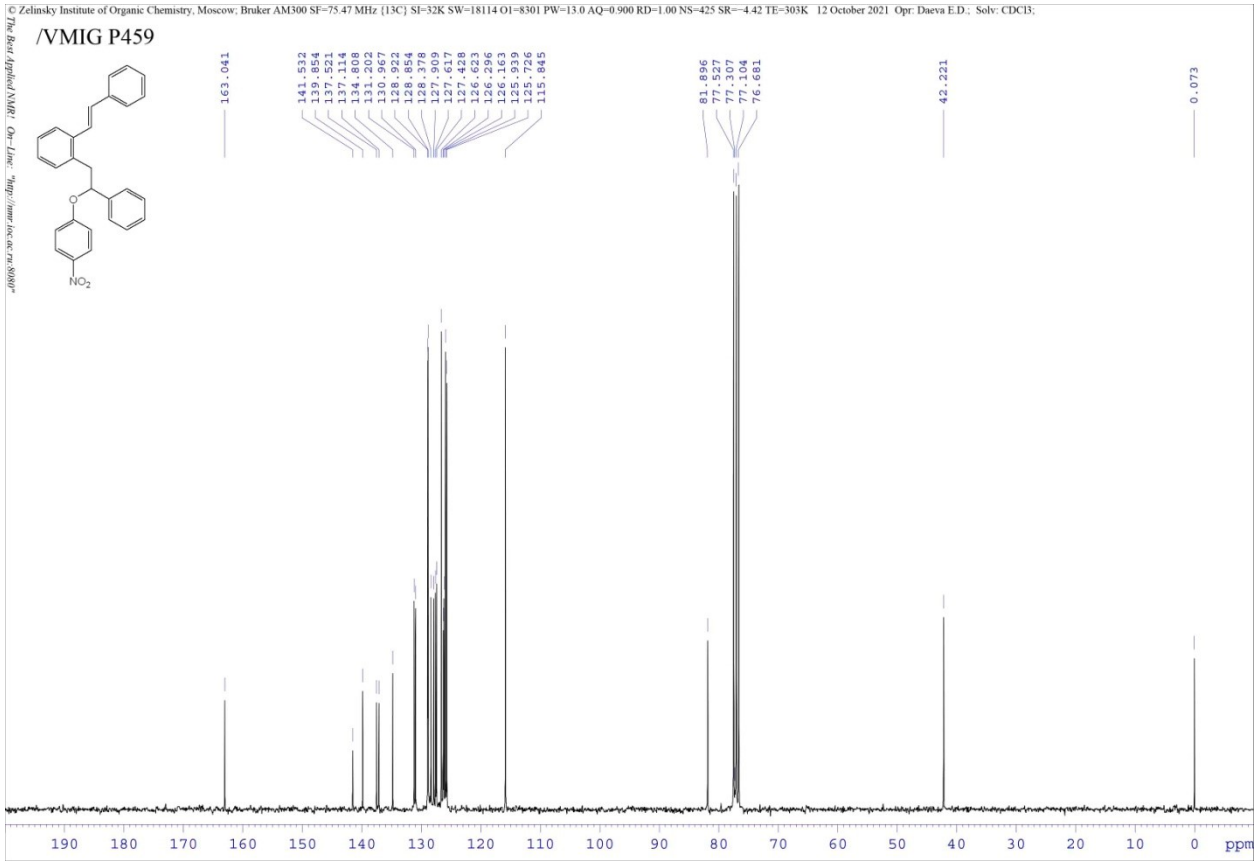


FIGURE S44. ^{13}C NMR spectrum of (E)-1-(2-(4-nitrophenoxy)-2-phenylethyl)-2-styrylbenzene (**23**) in $CDCl_3$.

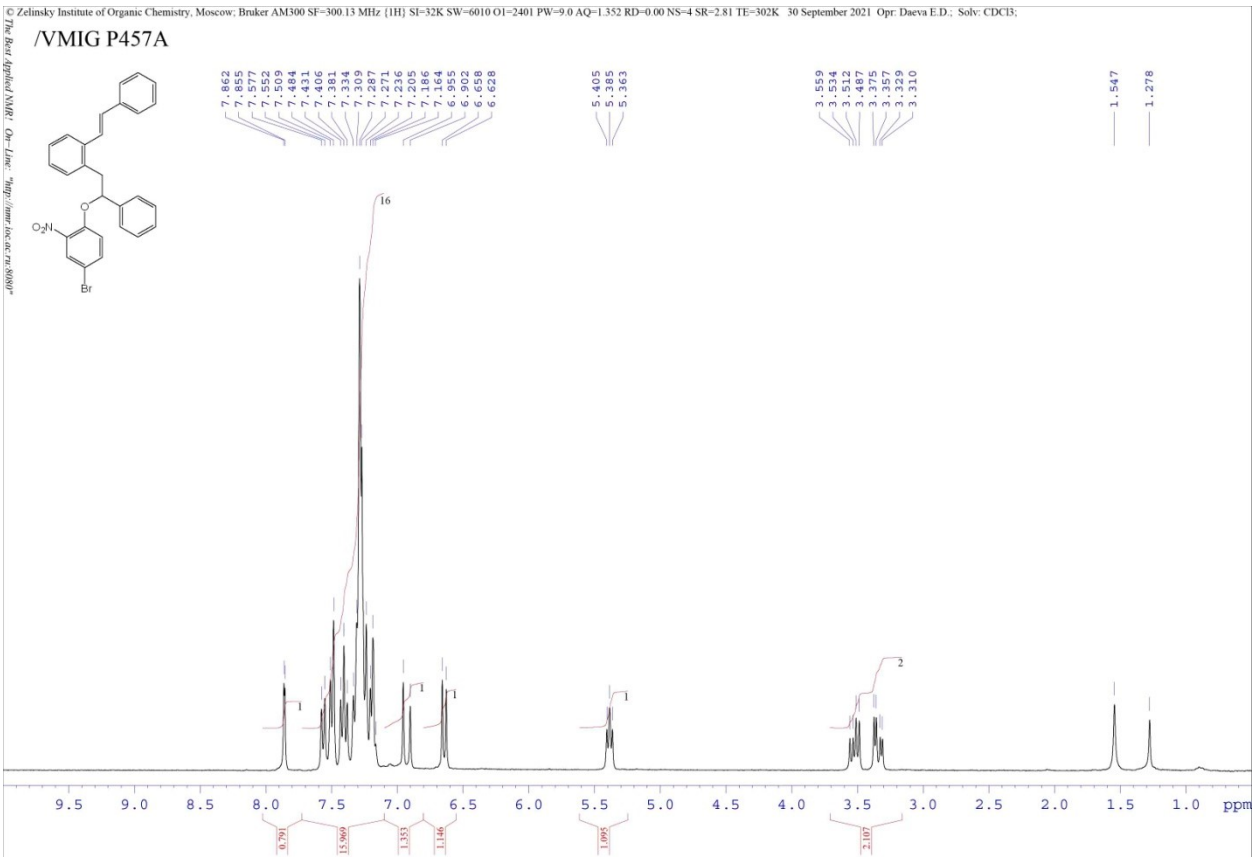


FIGURE S45. ^{1}H NMR spectrum of (E)-4-bromo-2-nitro-1-(1-phenyl-2-(2-styrylphenyl)ethoxy)benzene (**24**) in $CDCl_3$.

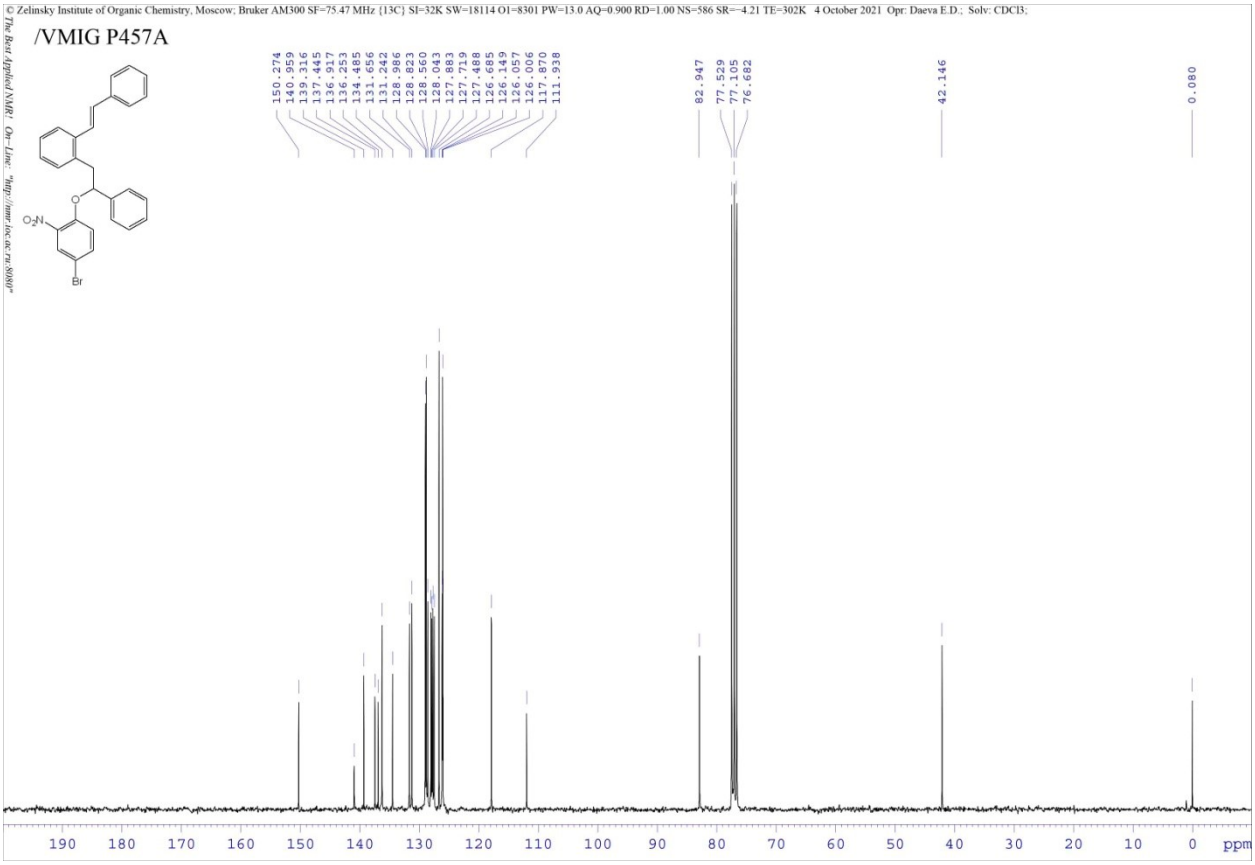


FIGURE S46. ^{13}C NMR spectrum of (E)-4-bromo-2-nitro-1-(1-phenyl-2-(2-styrylphenyl)ethoxy)benzene (**24**) in $CDCl_3$.

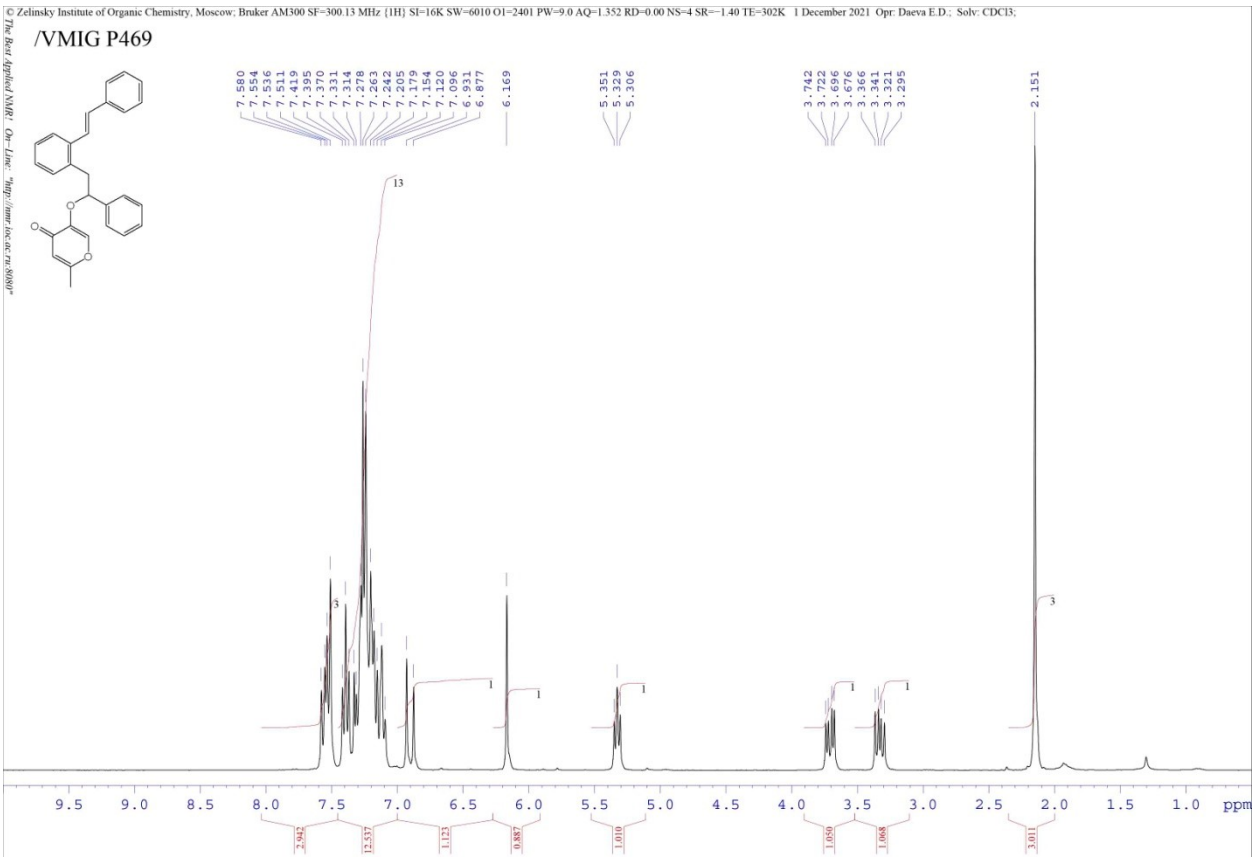


FIGURE S47. ^{1}H NMR spectrum of (E)-2-methyl-5-(1-phenyl-2-(2-styrylphenyl)ethoxy)-4H-pyran-4-one (**25**) in $CDCl_3$.

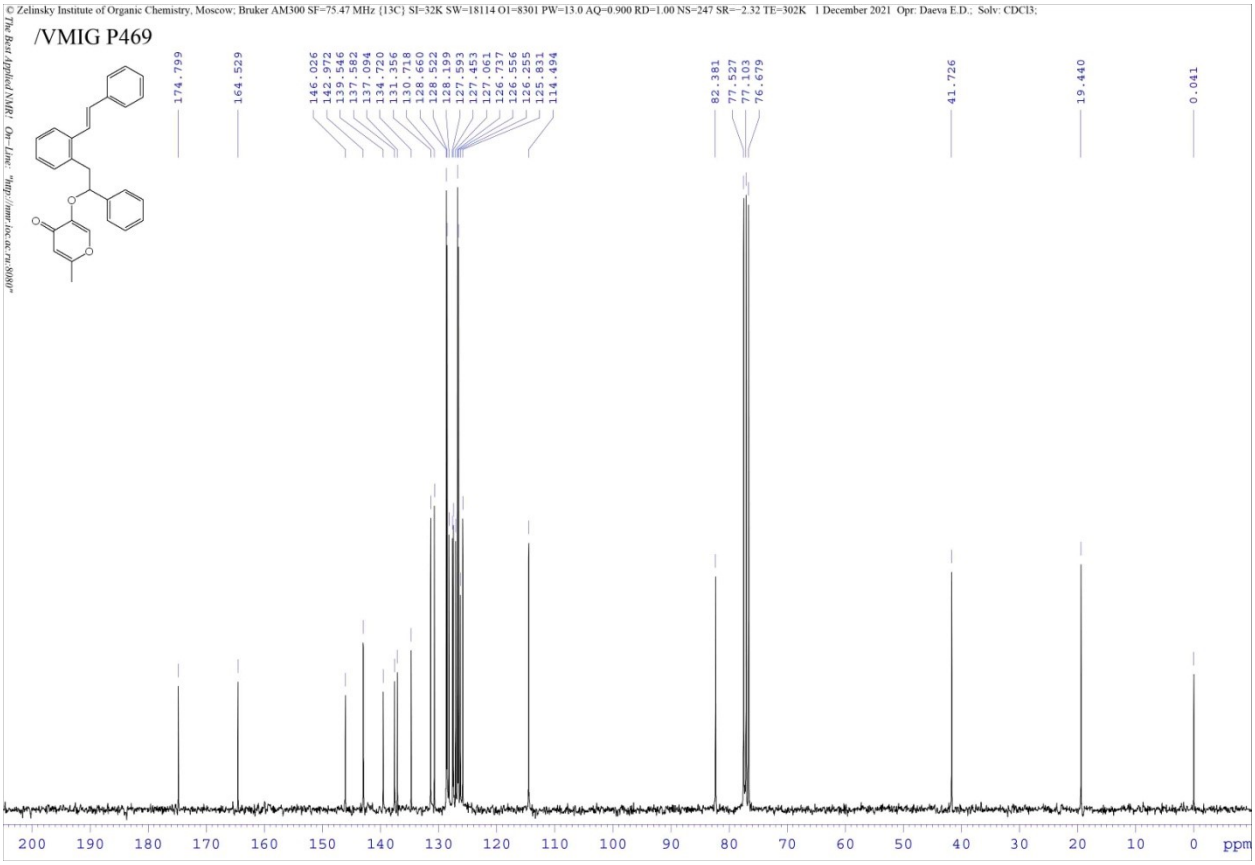


FIGURE S48. ^{13}C NMR spectrum of (E)-2-methyl-5-(1-phenyl-2-(2-styrylphenyl)ethoxy)-4H-pyran-4-one (**25**) in $CDCl_3$.

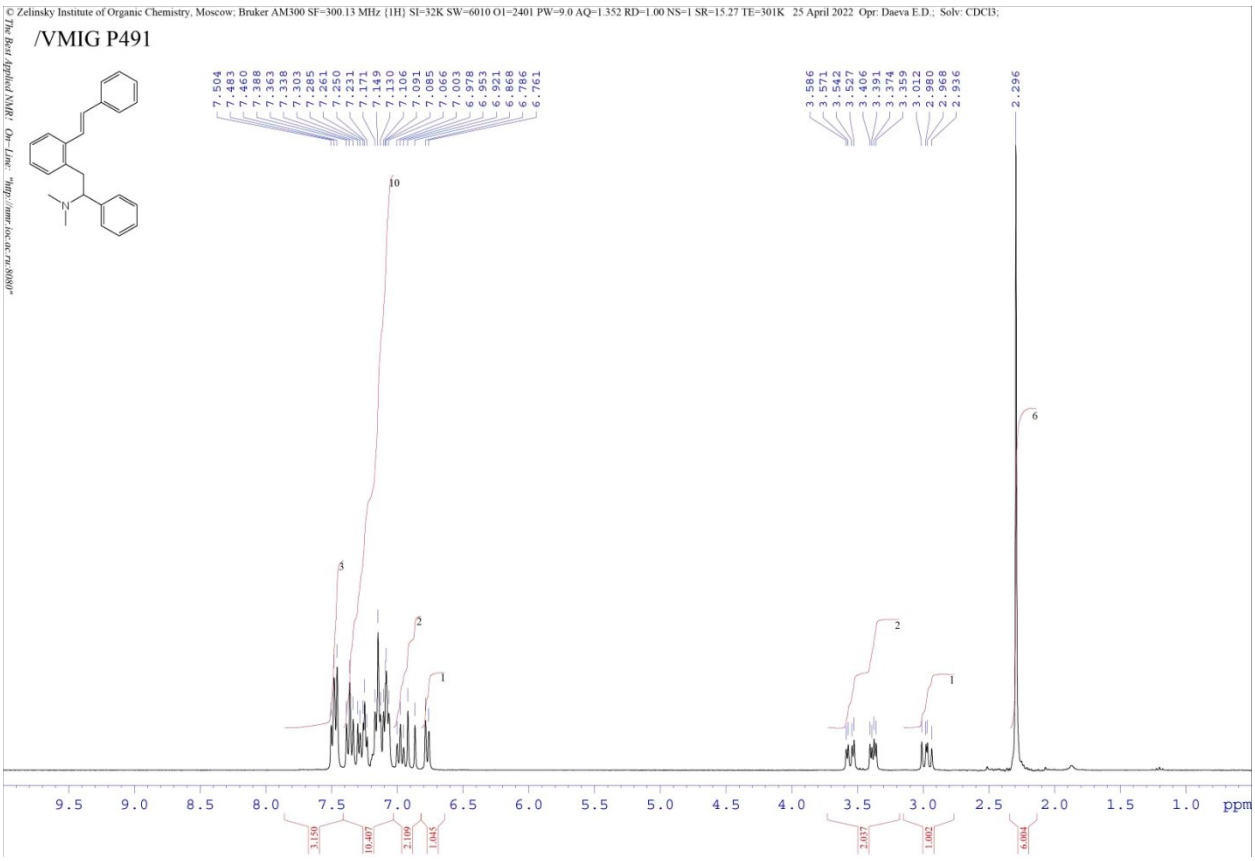


FIGURE S49. ^{1}H NMR spectrum of (E)-N,N-dimethyl-1-phenyl-2-(2-styrylphenyl)ethan-1-amine (**26**) in $CDCl_3$.

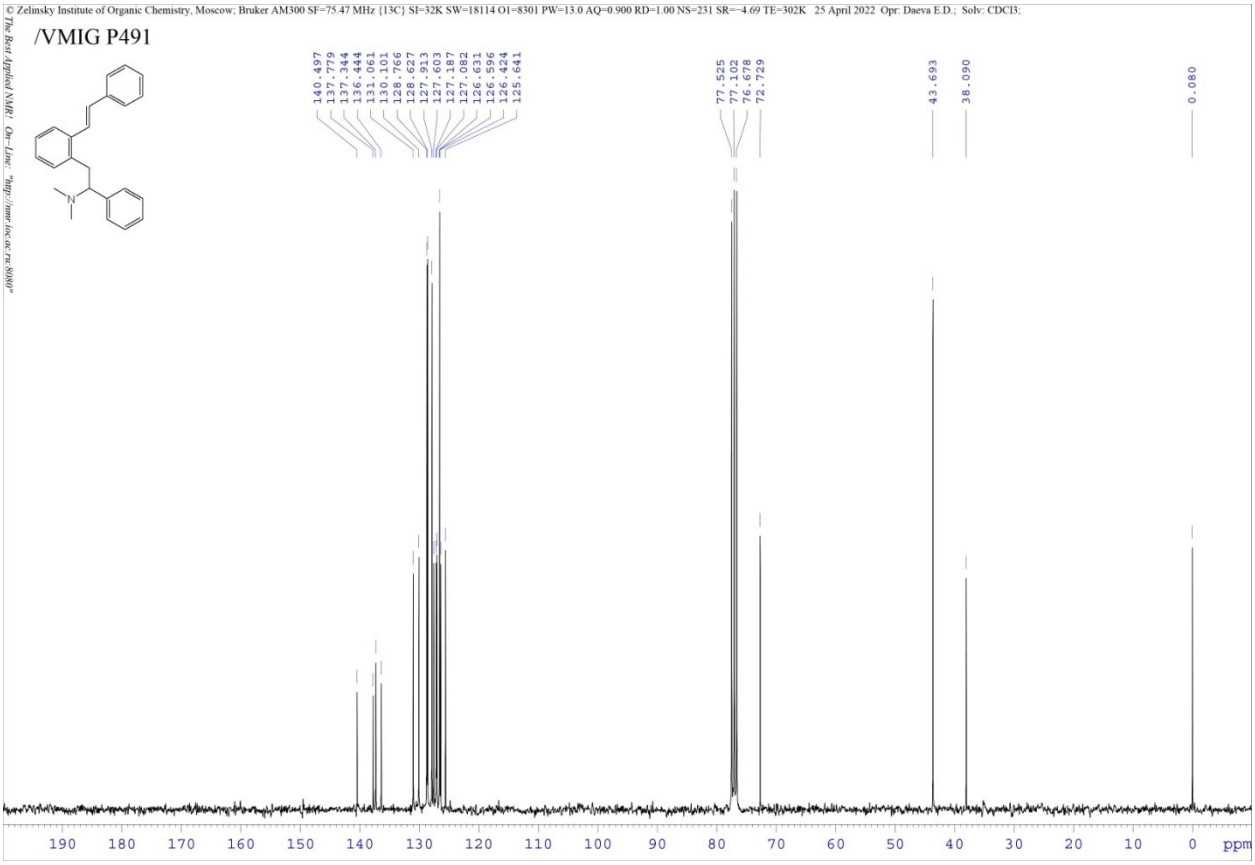


FIGURE S50. ^{13}C NMR spectrum of (E)-N,N-dimethyl-1-phenyl-2-(2-styrylphenyl)ethan-1-amine (**26**) in $CDCl_3$.

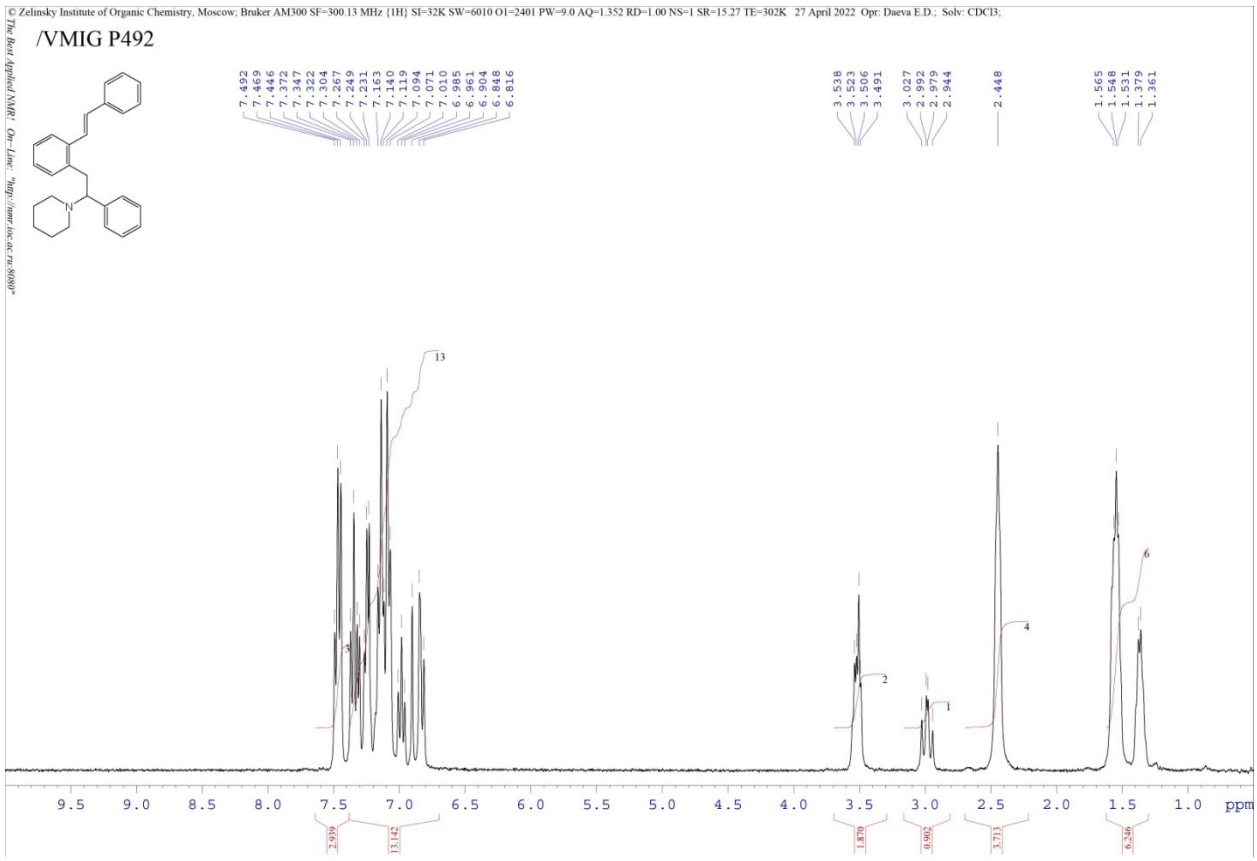


FIGURE S51. ^{1}H NMR spectrum of (E)-1-(1-phenyl-2-(2-styrylphenyl)ethyl)piperidine (**27**) in $CDCl_3$.

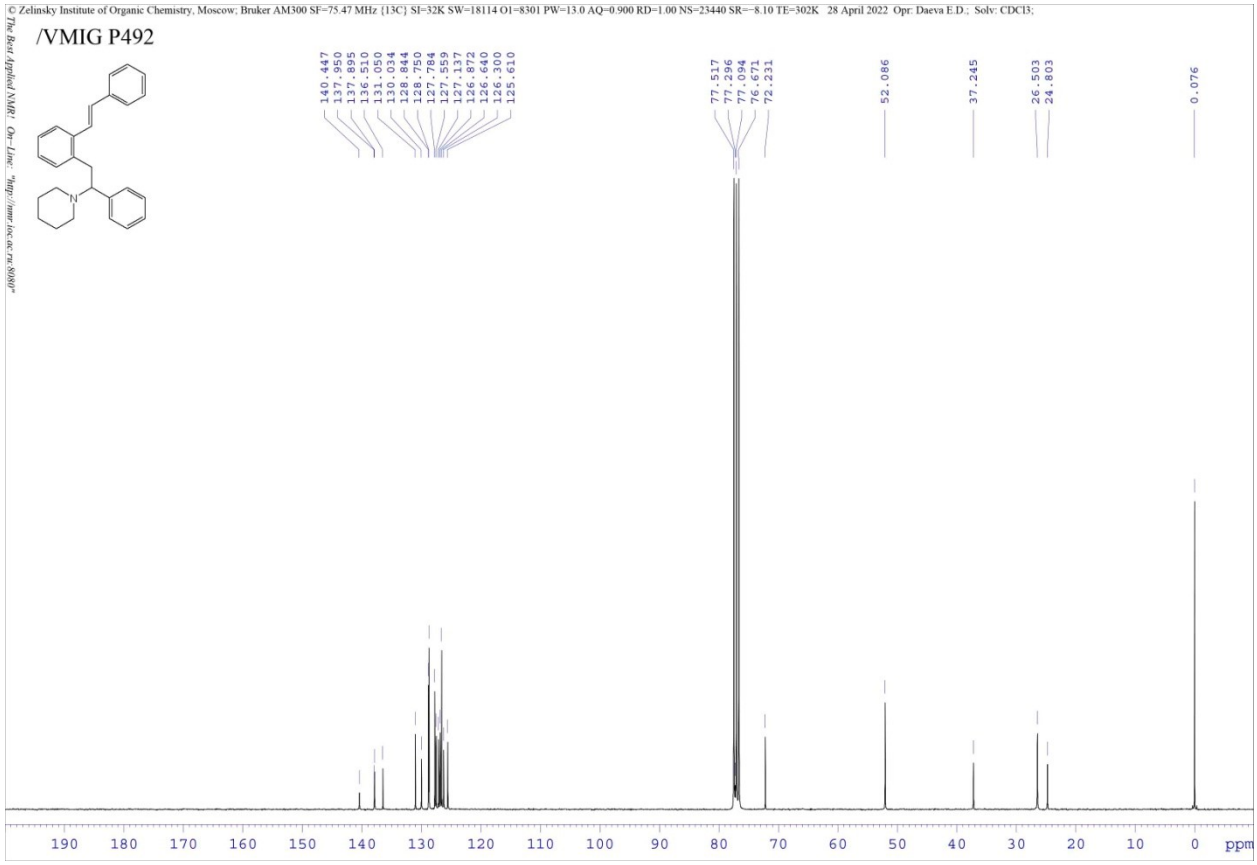


FIGURE S52. ^{13}C NMR spectrum of (E)-1-(1-phenyl-2-(2-styrylphenyl)ethyl)piperidine (**27**) in $CDCl_3$.

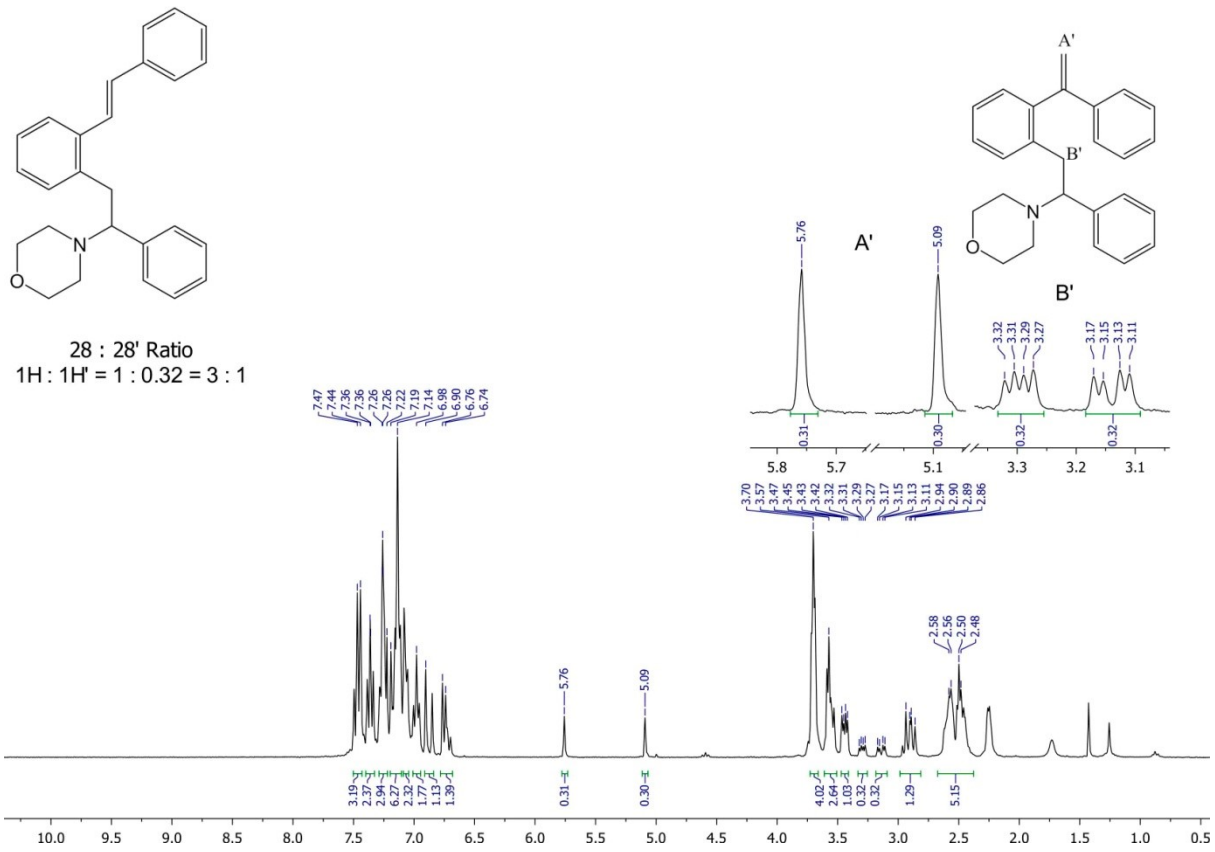


FIGURE S53. ^{1}H NMR spectrum of (E)-4-(1-phenyl-2-(2-styrylphenyl)ethyl)morpholine (**28**) and 4-(1-phenyl-2-(2-(1-phenylvinyl)phenyl)ethyl)morpholine (**28'**) in $CDCl_3$.

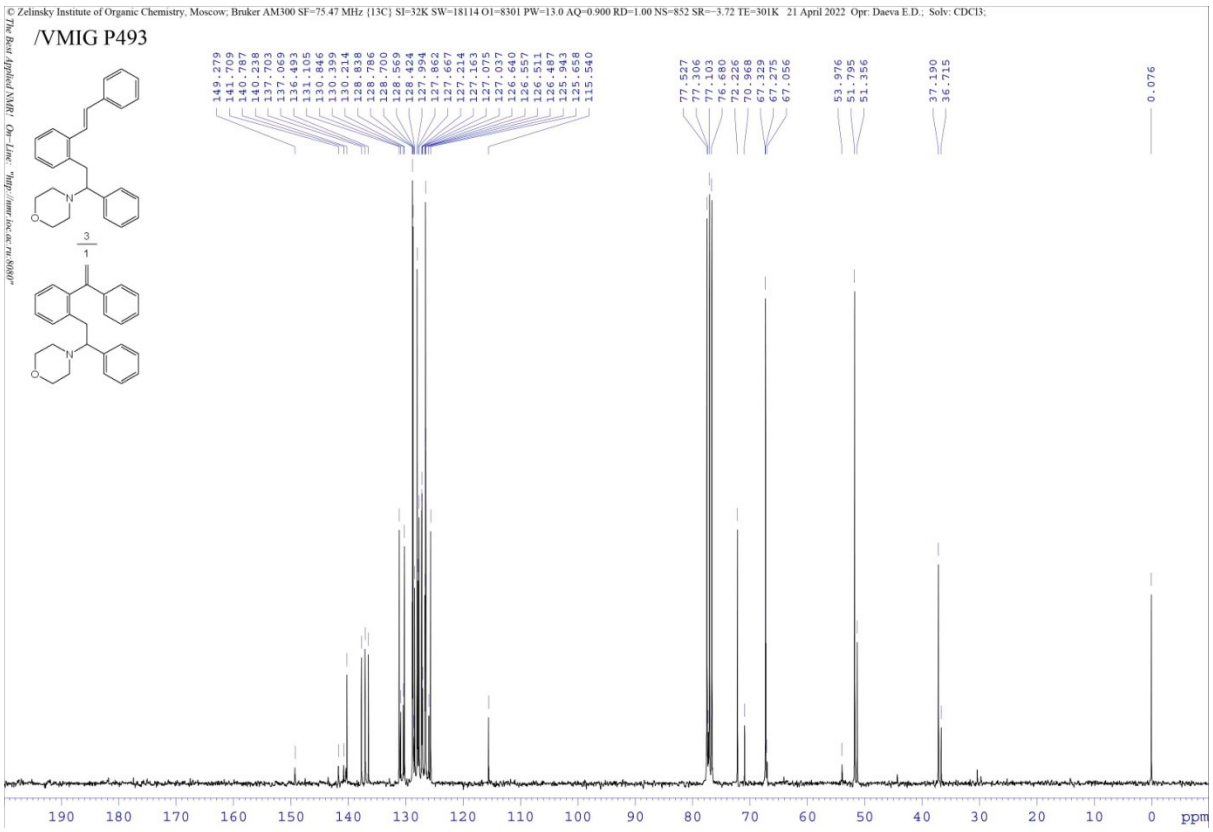


FIGURE S54. ^{13}C NMR spectrum of (E)-4-(1-phenyl-2-(2-styrylphenyl)ethyl)morpholine (**28**) and 4-(1-phenyl-2-(2-(1-phenylvinyl)phenyl)ethyl)morpholine (**28'**) in $CDCl_3$.

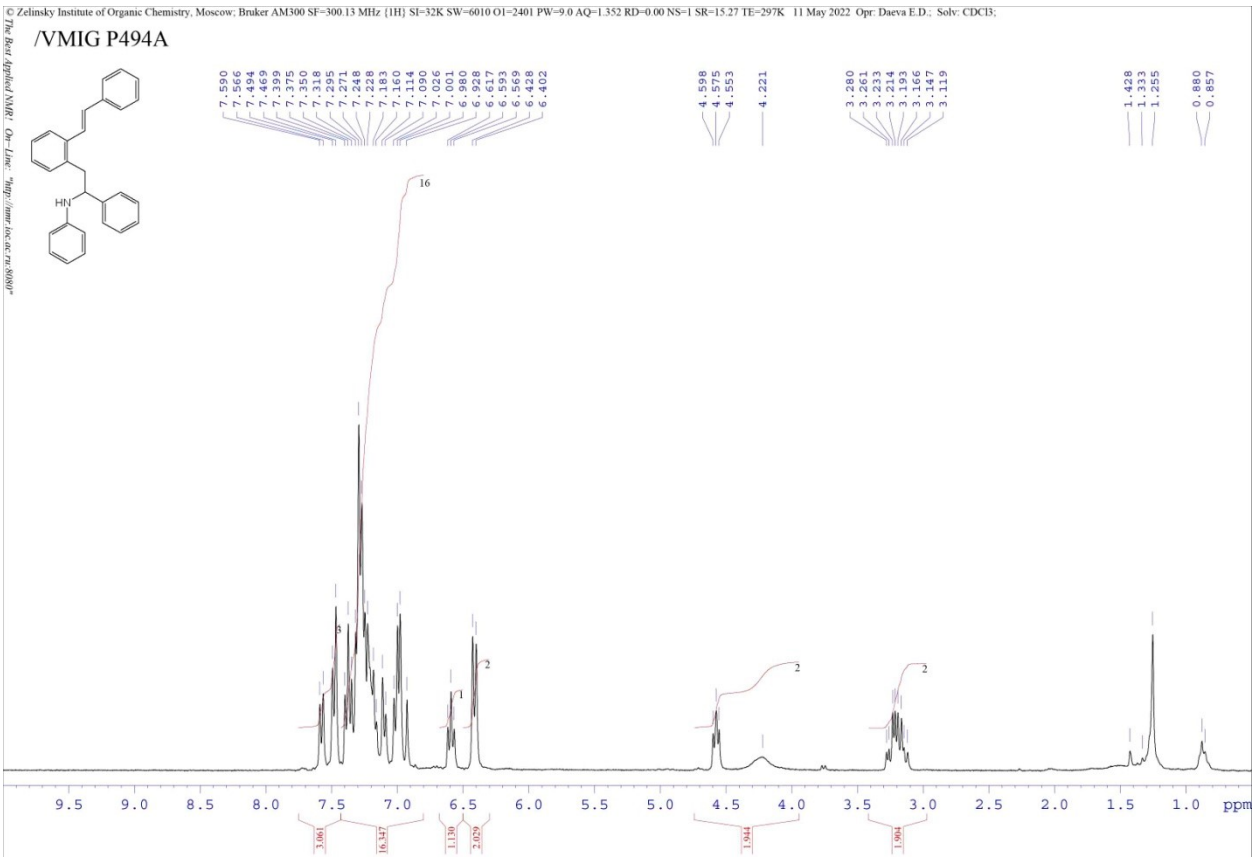


FIGURE S55. ^{1}H NMR spectrum of (E)-N-(1-phenyl-2-(2-styrylphenyl)ethyl)aniline (**29**) in $CDCl_3$.

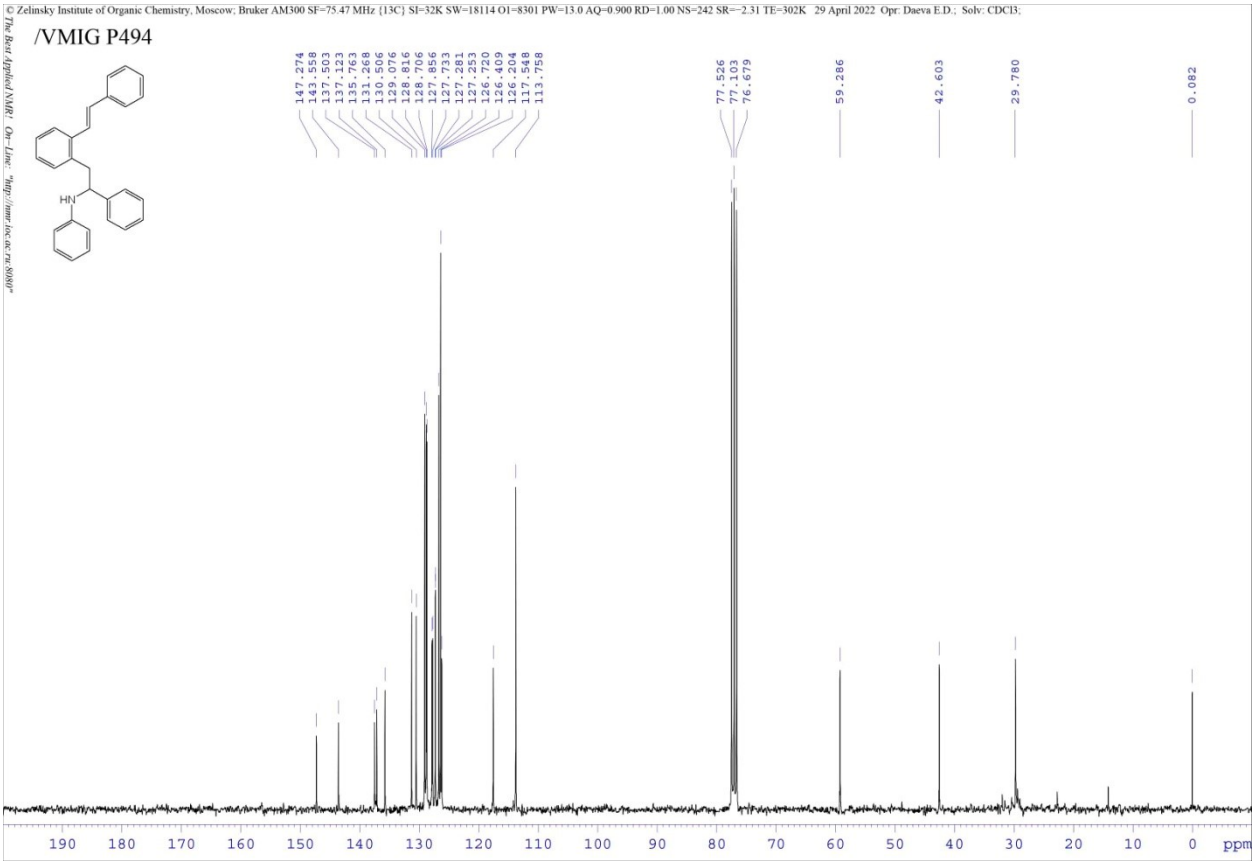


FIGURE S56. ^{13}C NMR spectrum of (E)-N-(1-phenyl-2-(2-styrylphenyl)ethyl)aniline (**29**) in $CDCl_3$.

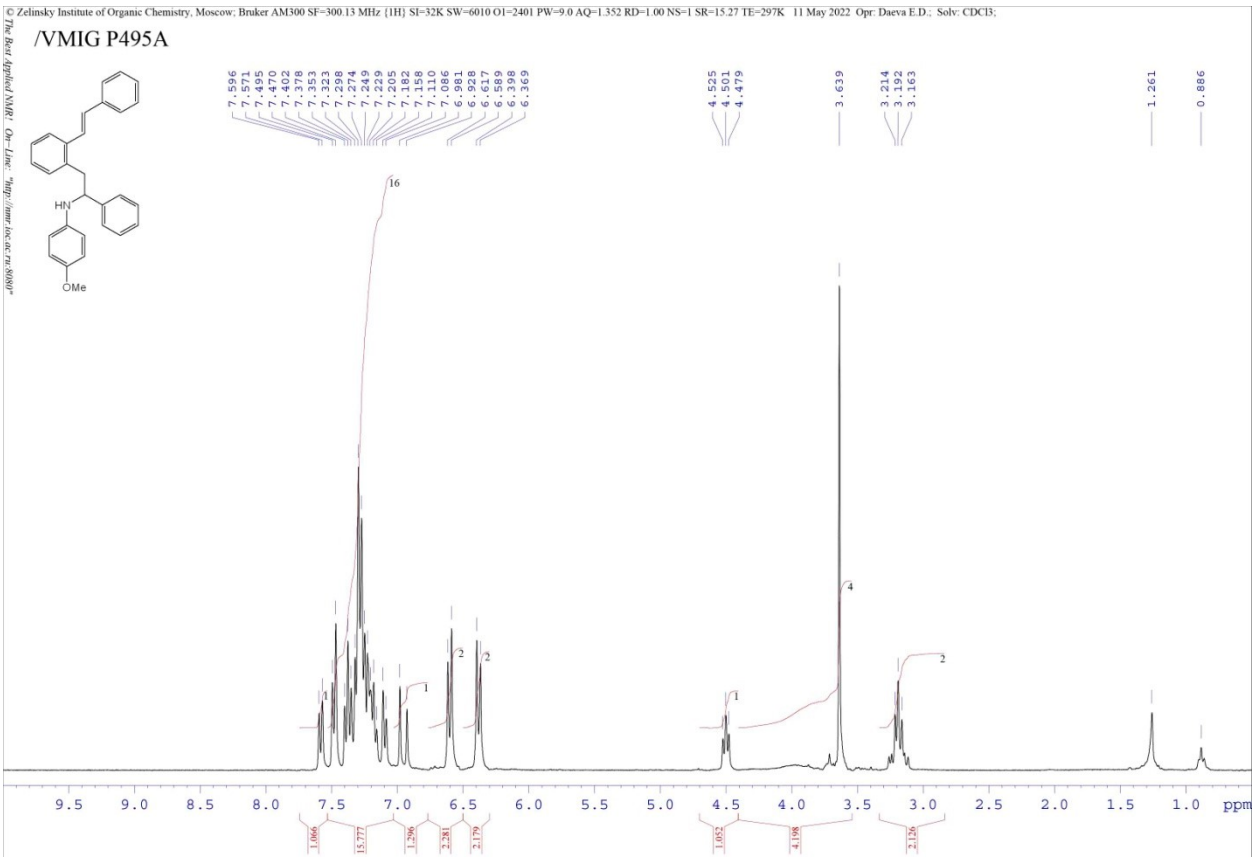


FIGURE S57. ^{1}H NMR spectrum of (E)-4-methoxy-N-(1-phenyl-2-(2-styrylphenyl)ethyl)aniline (**30**) in $CDCl_3$.

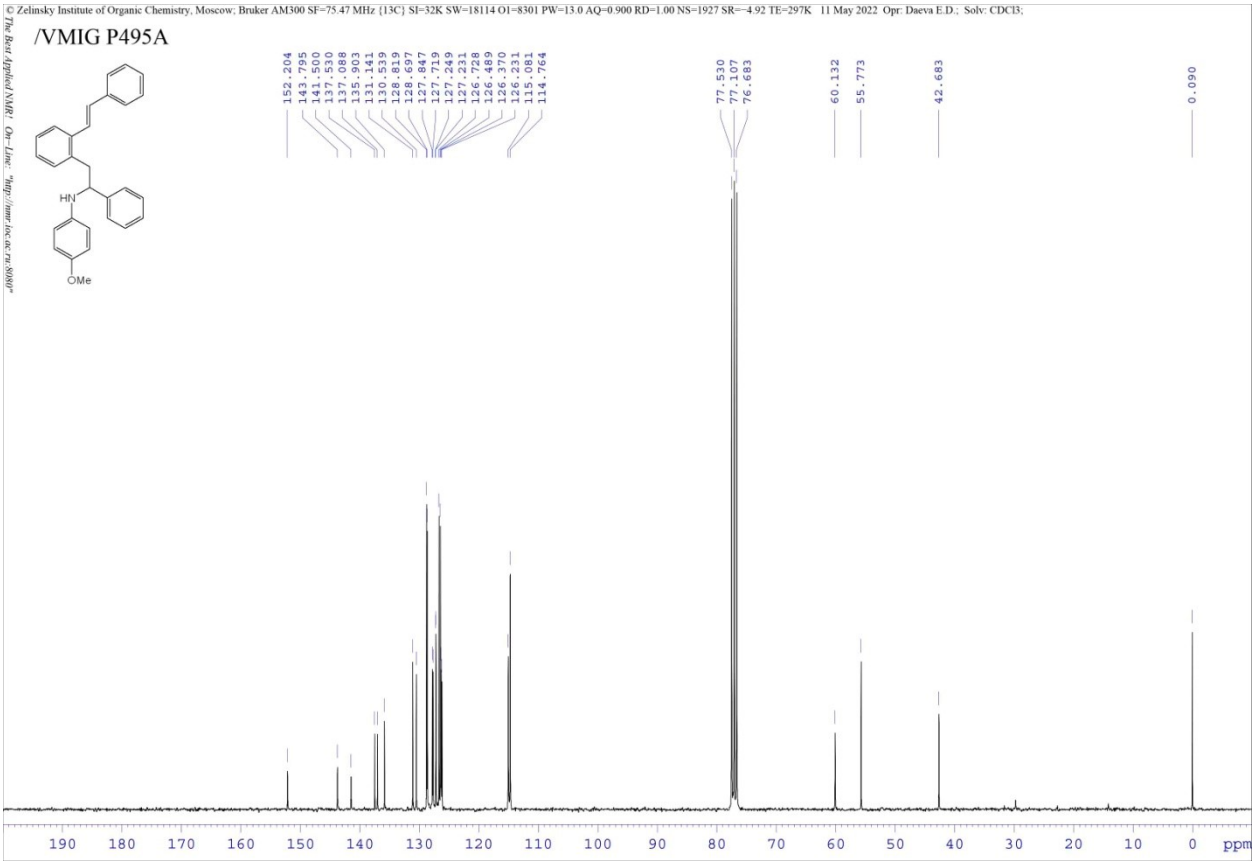


FIGURE S58. ^{13}C NMR spectrum of (E)-4-methoxy-N-(1-phenyl-2-(2-styrylphenyl)ethyl)aniline (**30**) in $CDCl_3$.

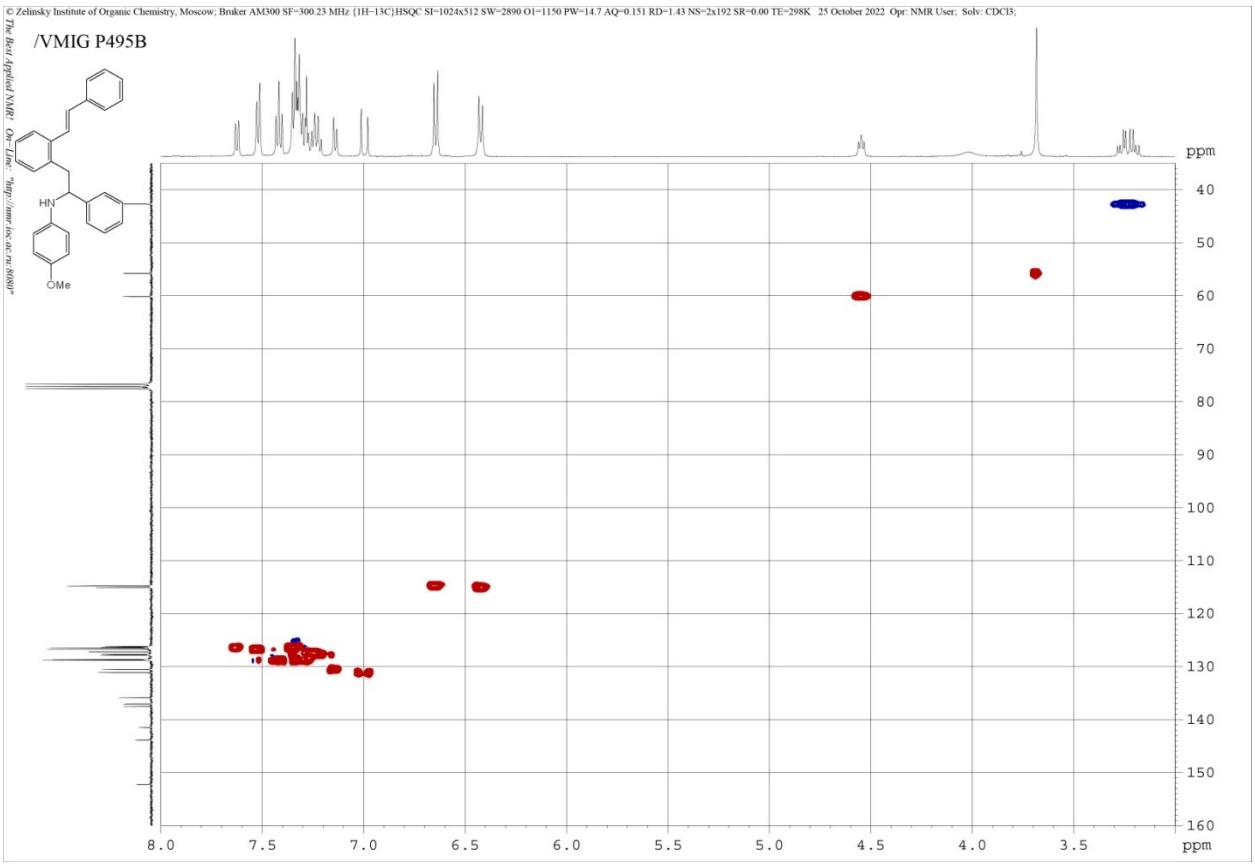


FIGURE S59. ^{1}H – ^{13}C HSQC NMR spectrum of (E)-4-methoxy-N-(1-phenyl-2-(2-styrylphenyl)ethyl)aniline (**30**) in $CDCl_3$.

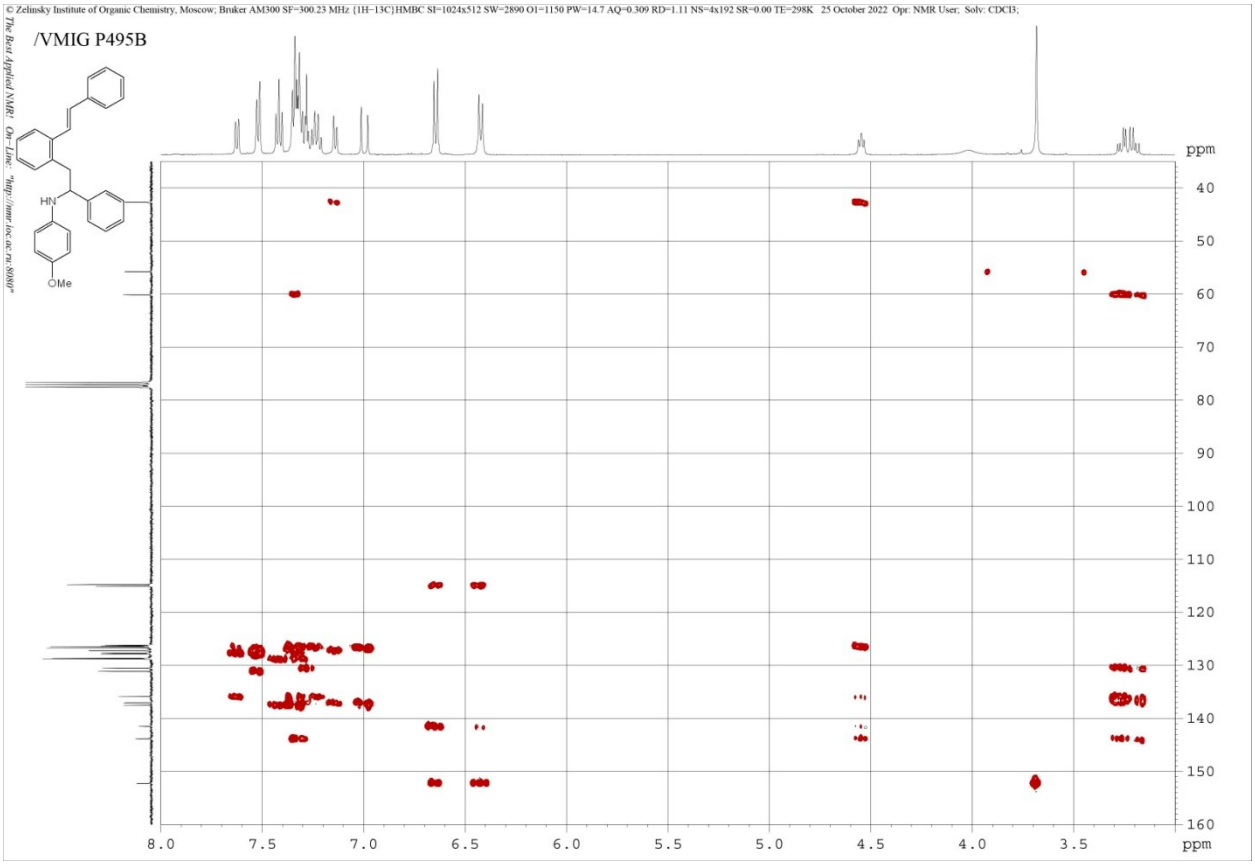


FIGURE S60. ^{1}H – ^{13}C HMBC NMR spectrum of (E)-4-methoxy-N-(1-phenyl-2-(2-styrylphenyl)ethyl)aniline (**30**) in $CDCl_3$.

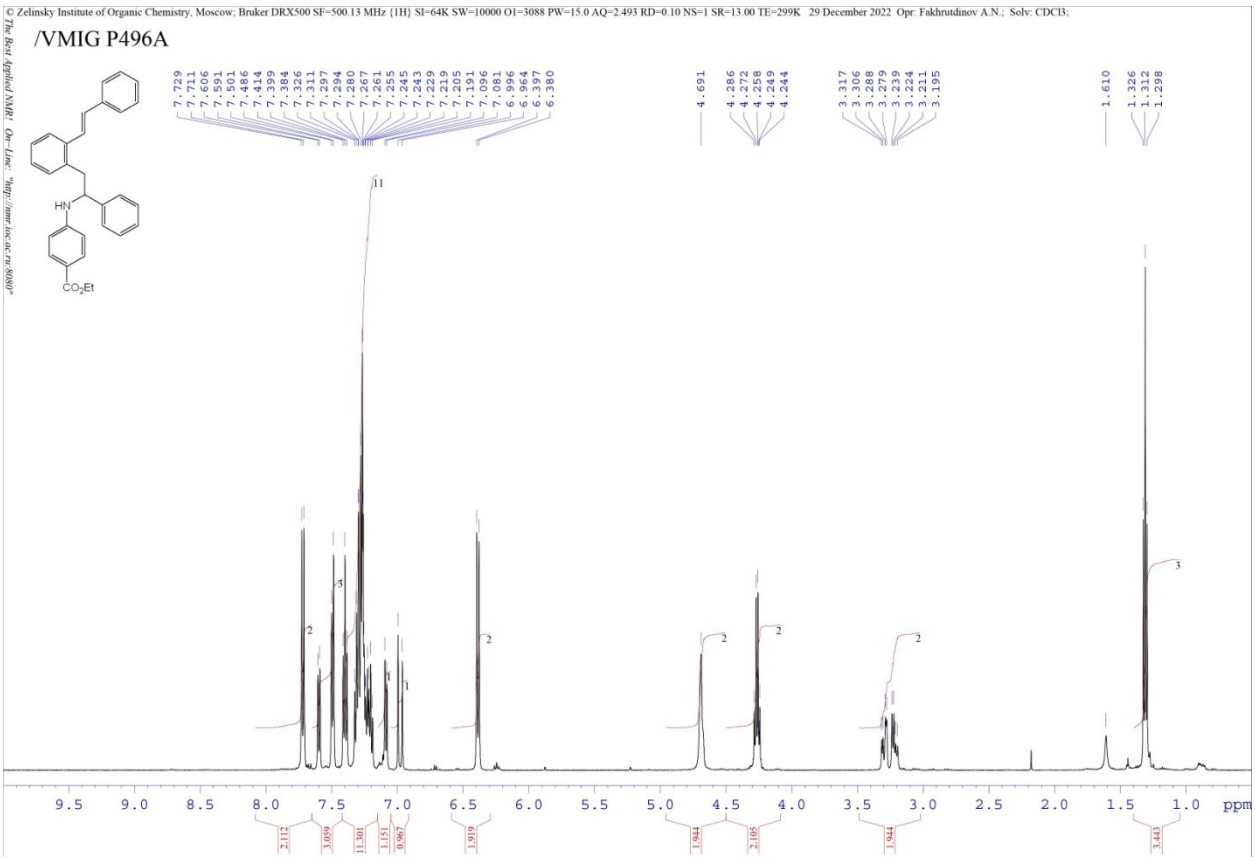


FIGURE S61. ^{1}H NMR spectrum of ethyl (E)-4-((1-phenyl-2-(2-styrylphenyl)ethyl)amino)benzoate (**31**) in $CDCl_3$.

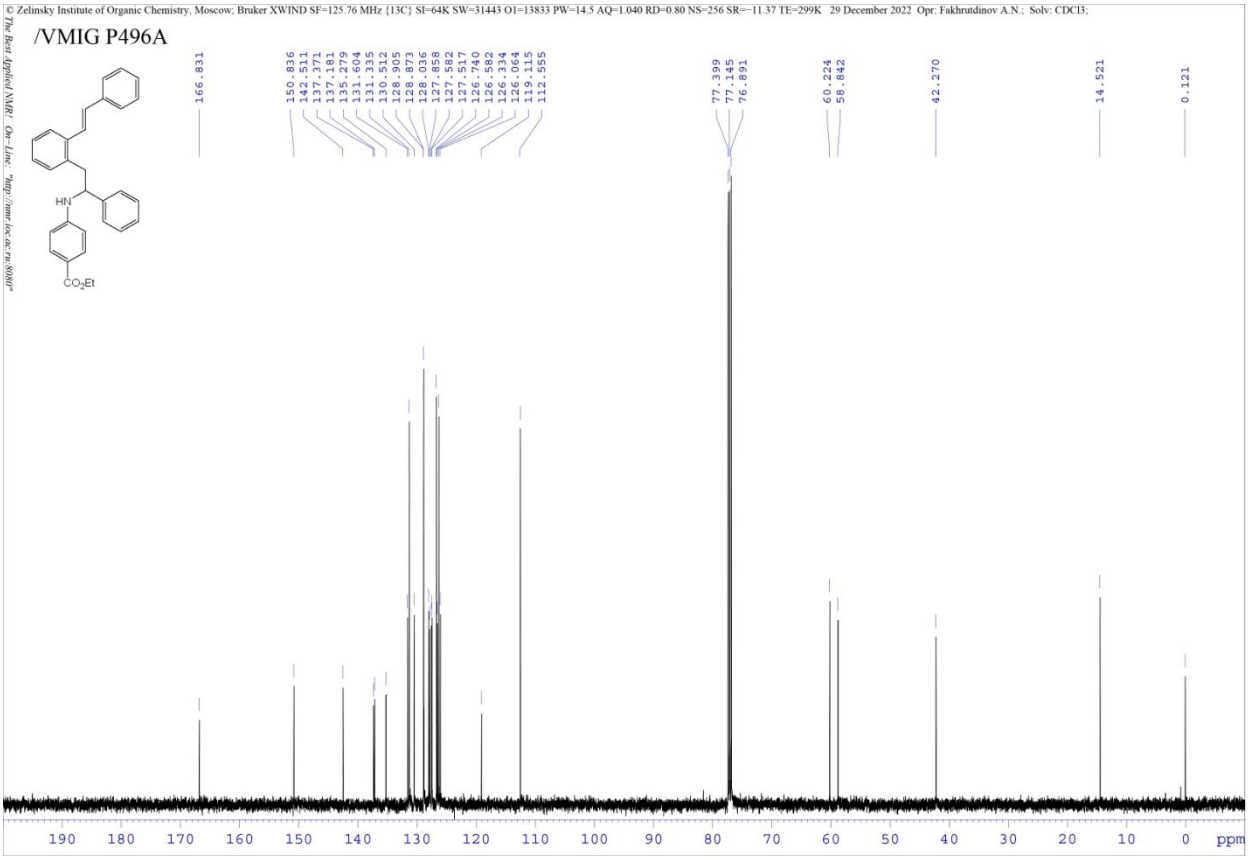


FIGURE S62. ^{13}C NMR spectrum of ethyl (E)-4-((1-phenyl-2-(2-styrylphenyl)ethyl)amino)benzoate (**31**) in $CDCl_3$.

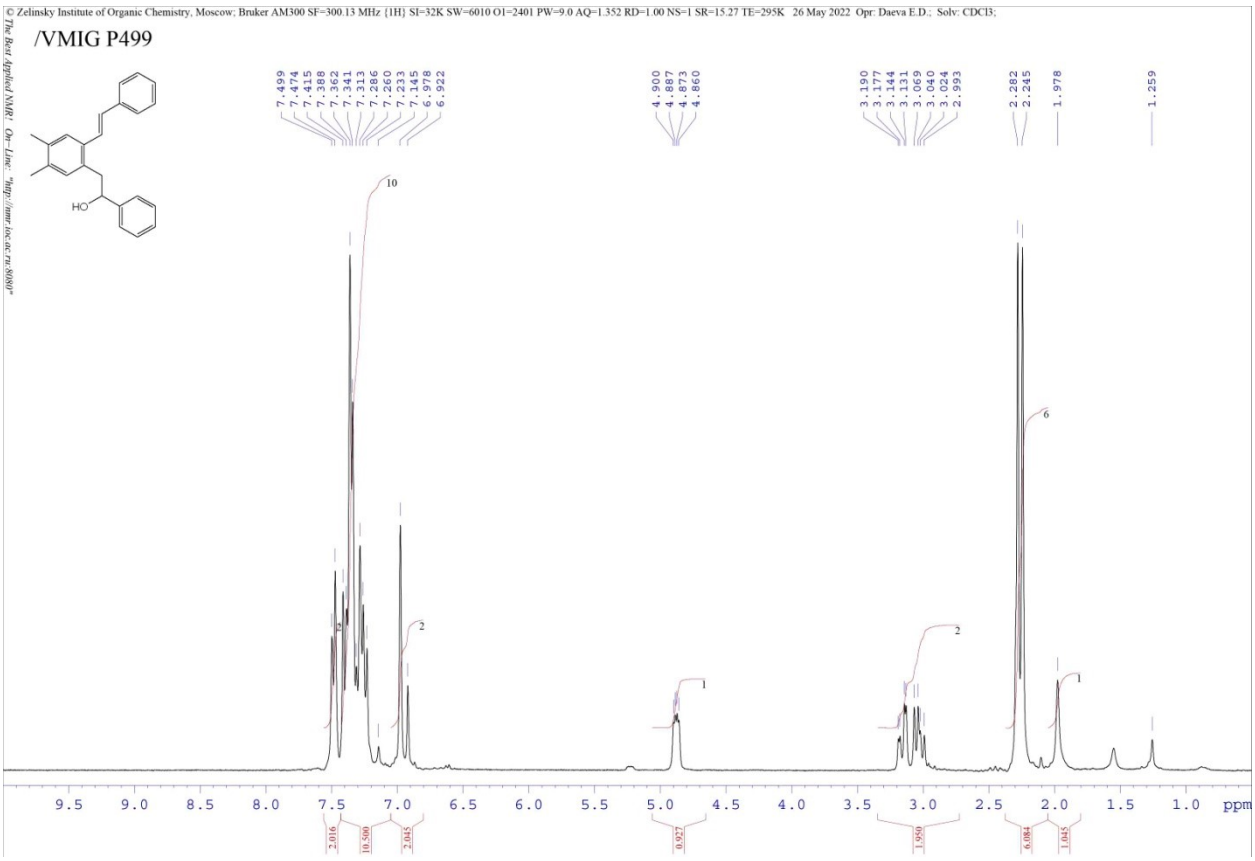


FIGURE S63. ^{1}H NMR spectrum of (E)-2-(4,5-dimethyl-2-styrylphenyl)-1-phenylethan-1-ol (**32**) in $CDCl_3$.

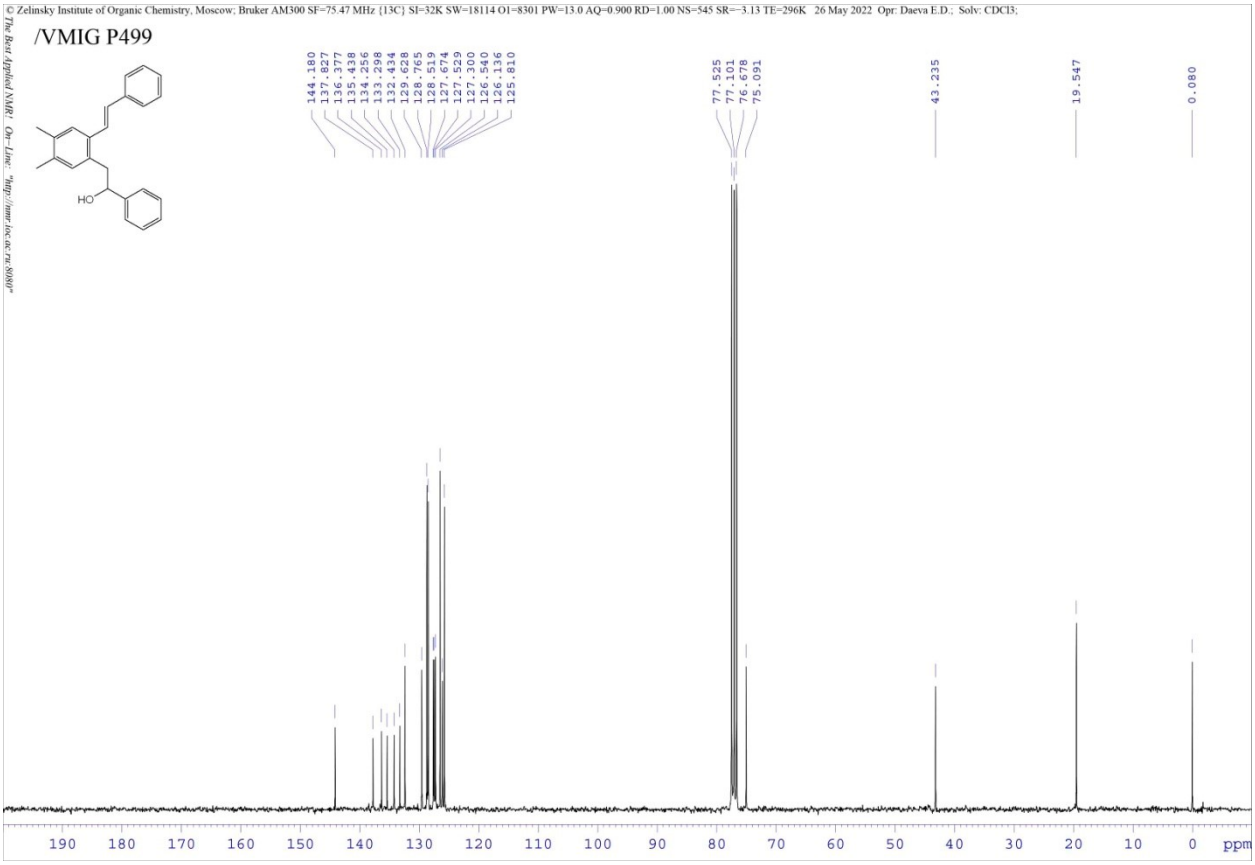


FIGURE S64. ^{13}C NMR spectrum of (E)-2-(4,5-dimethyl-2-styrylphenyl)-1-phenylethan-1-ol (**32**) in $CDCl_3$.

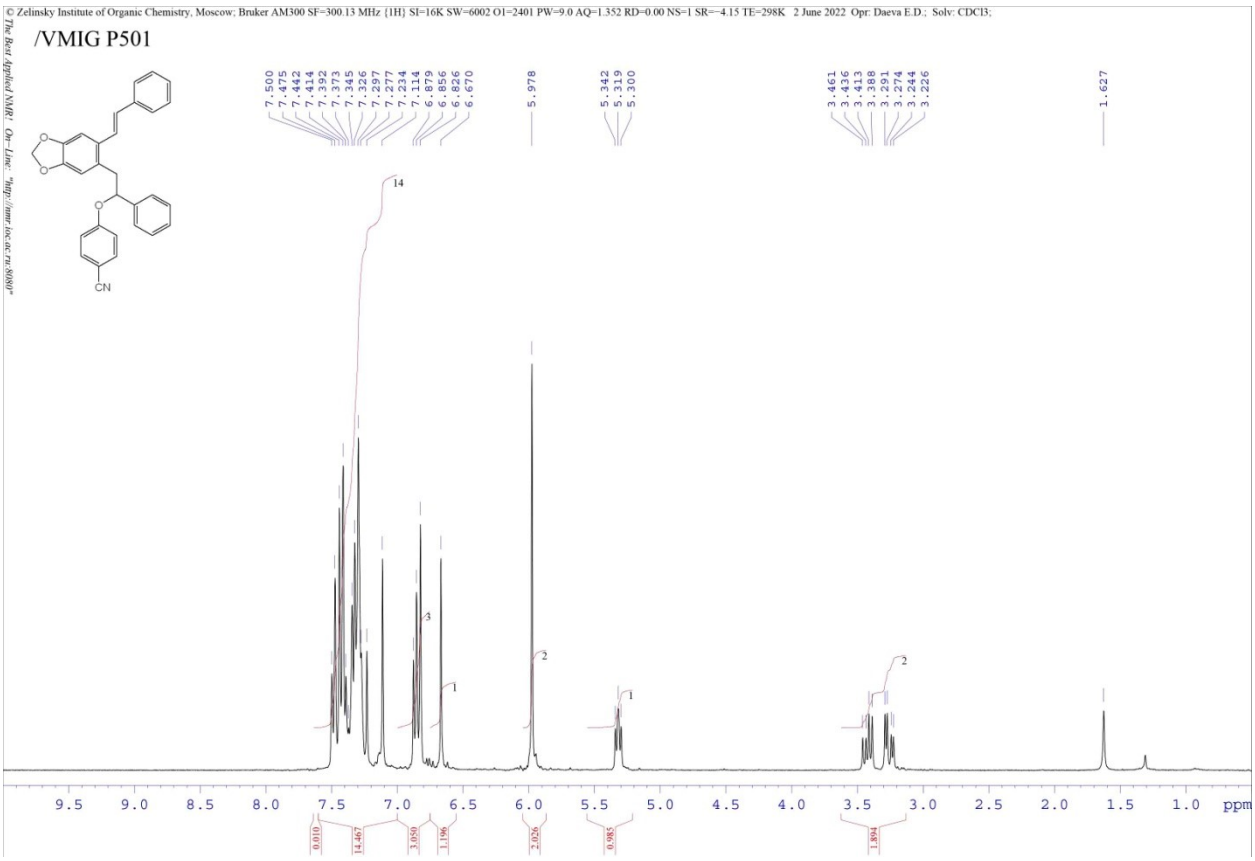


FIGURE S65. ^{1}H NMR spectrum of (E)-4-(1-phenyl-2-(6-styrylbenzo[d][1,3]dioxol-5-yl)ethoxy)benzonitrile (**33**) in $CDCl_3$.

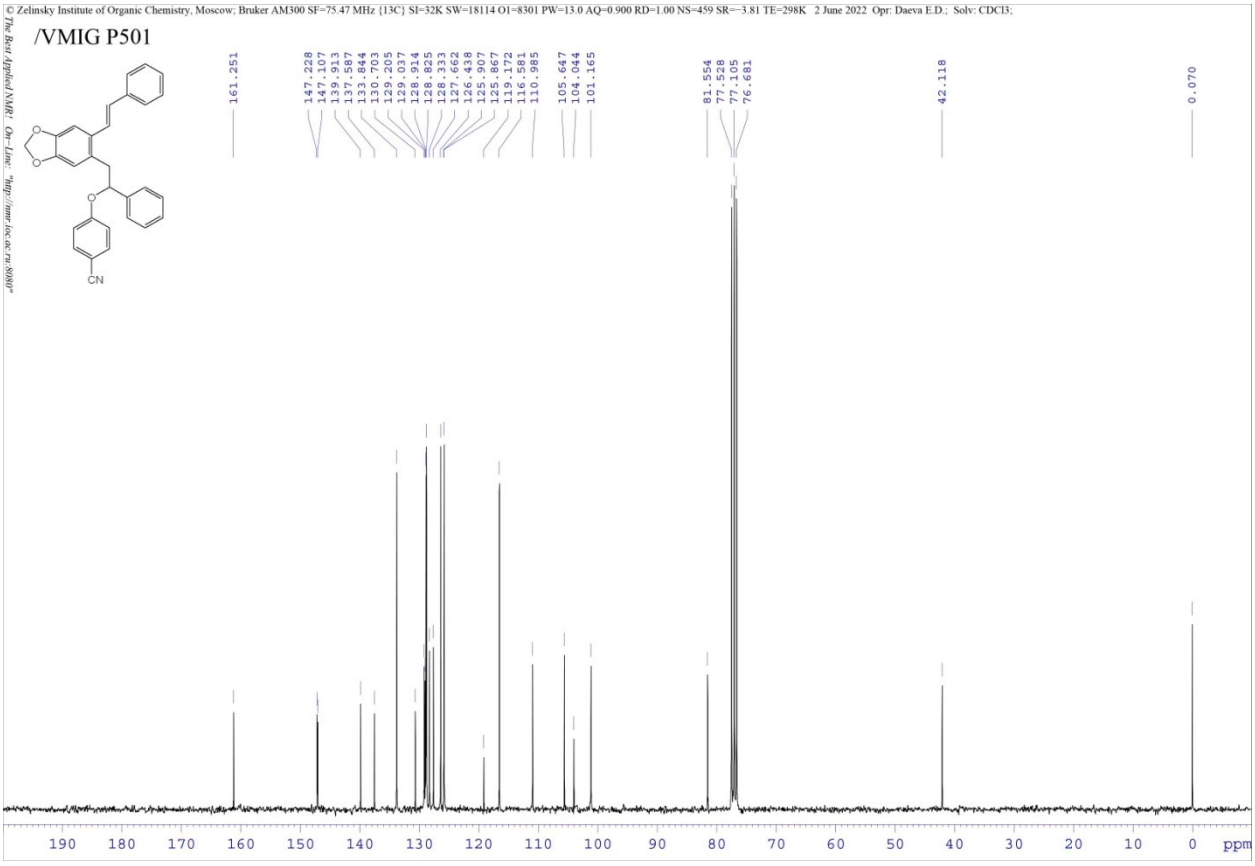


FIGURE S66. ^{13}C NMR spectrum of (E)-4-(1-phenyl-2-(6-styrylbenzo[d][1,3]dioxol-5-yl)ethoxy)benzonitrile (**33**) in $CDCl_3$.

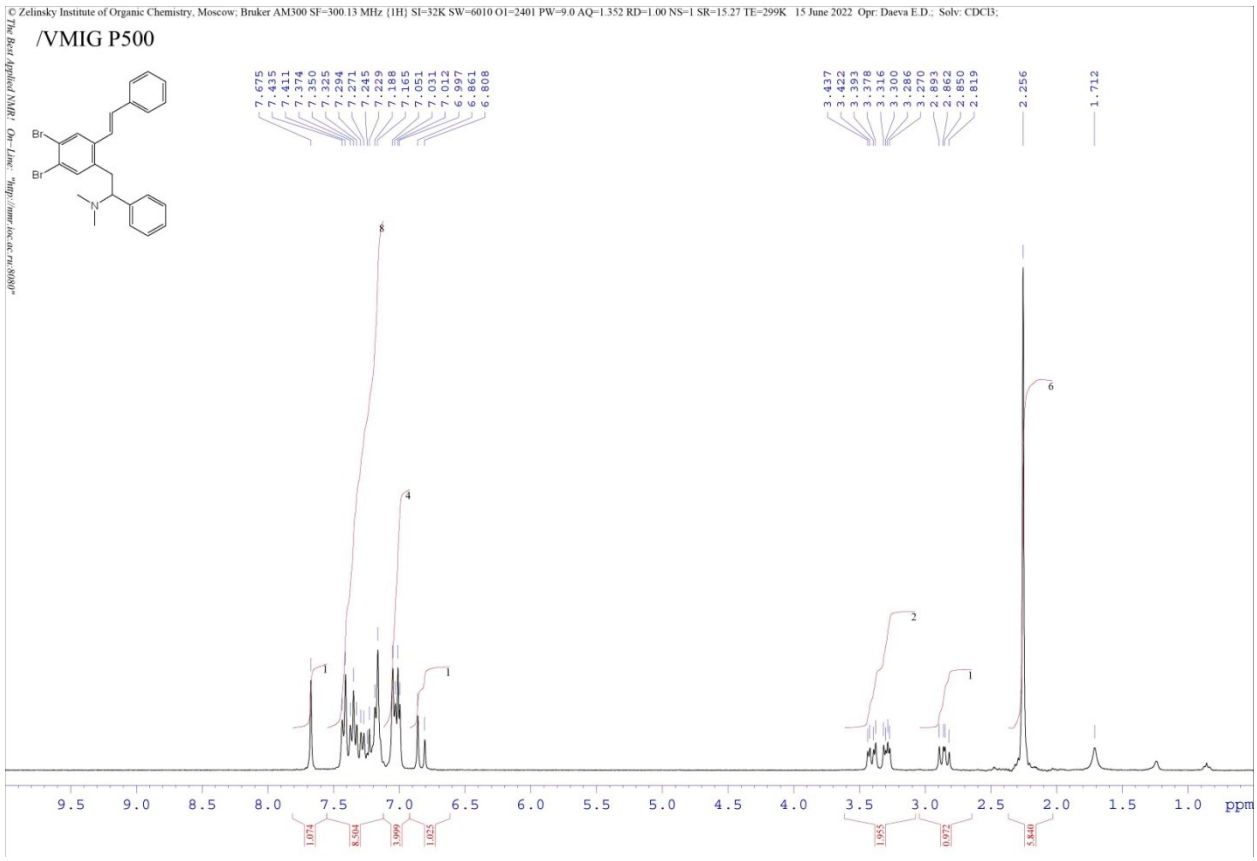


FIGURE S67. ^{1}H NMR spectrum of (E)-2-(4,5-dibromo-2-styrylphenyl)-N,N-dimethyl-1-phenylethan-1-amine (**34**) in $CDCl_3$.

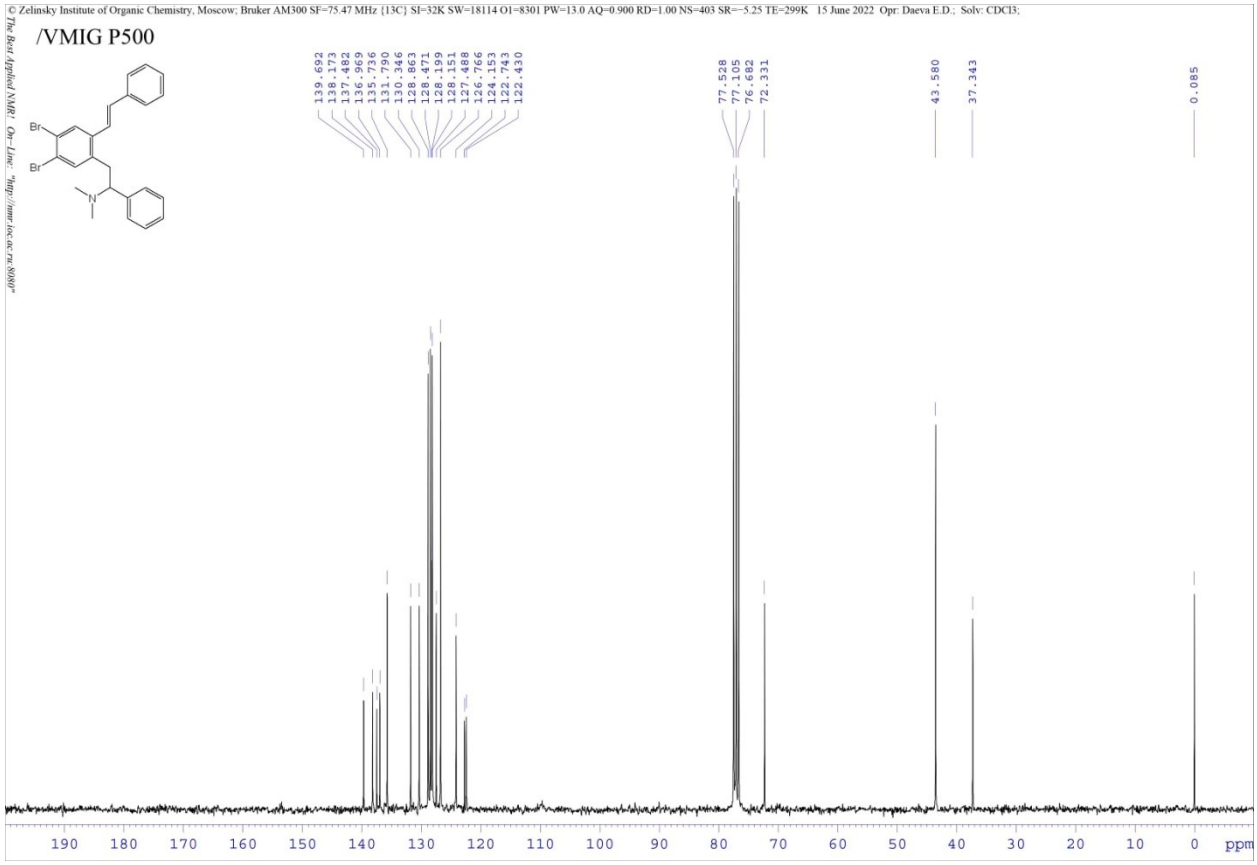


FIGURE S68. ^{13}C NMR spectrum of (E)-2-(4,5-dibromo-2-styrylphenyl)-N,N-dimethyl-1-phenylethan-1-amine (**34**) in $CDCl_3$.

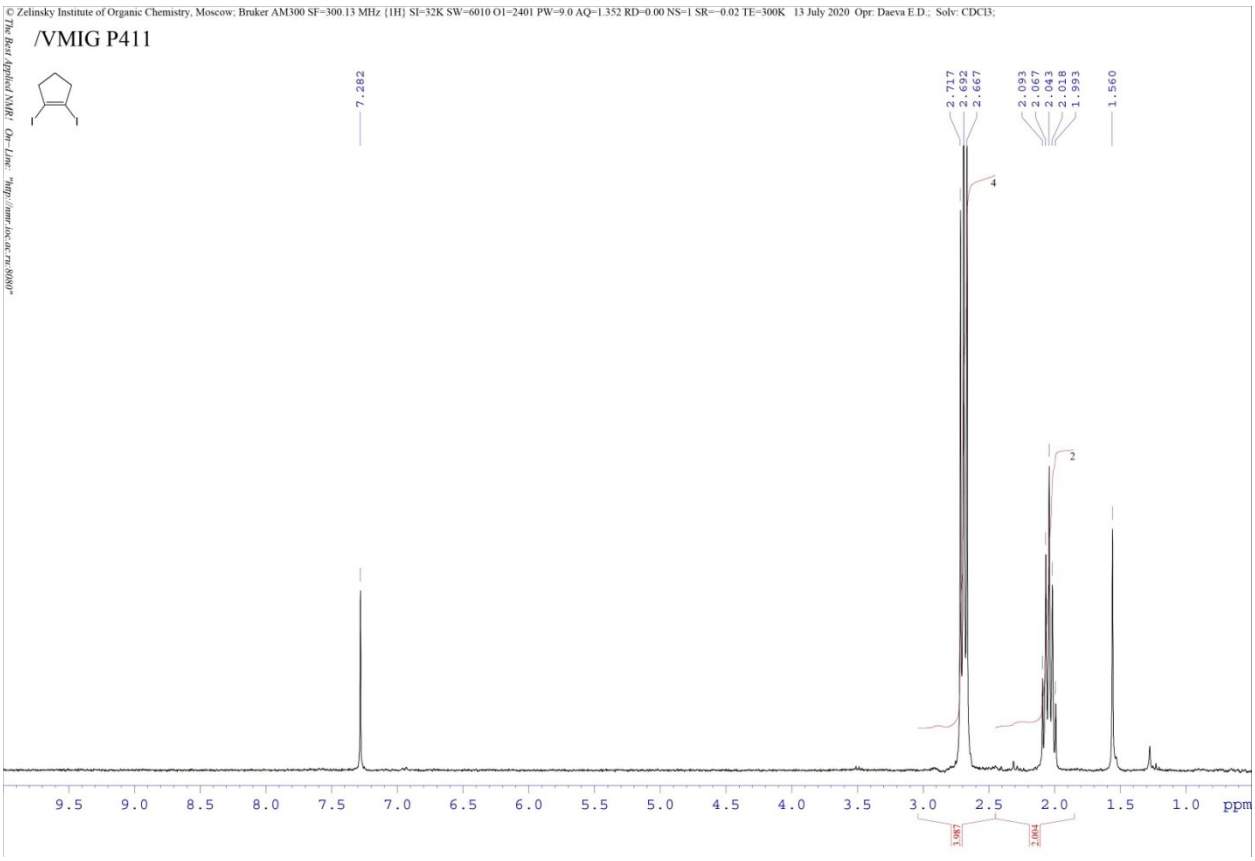


FIGURE S69. ^{1}H NMR spectrum of 1,2-diiodocyclopent-1-ene in $CDCl_3$.

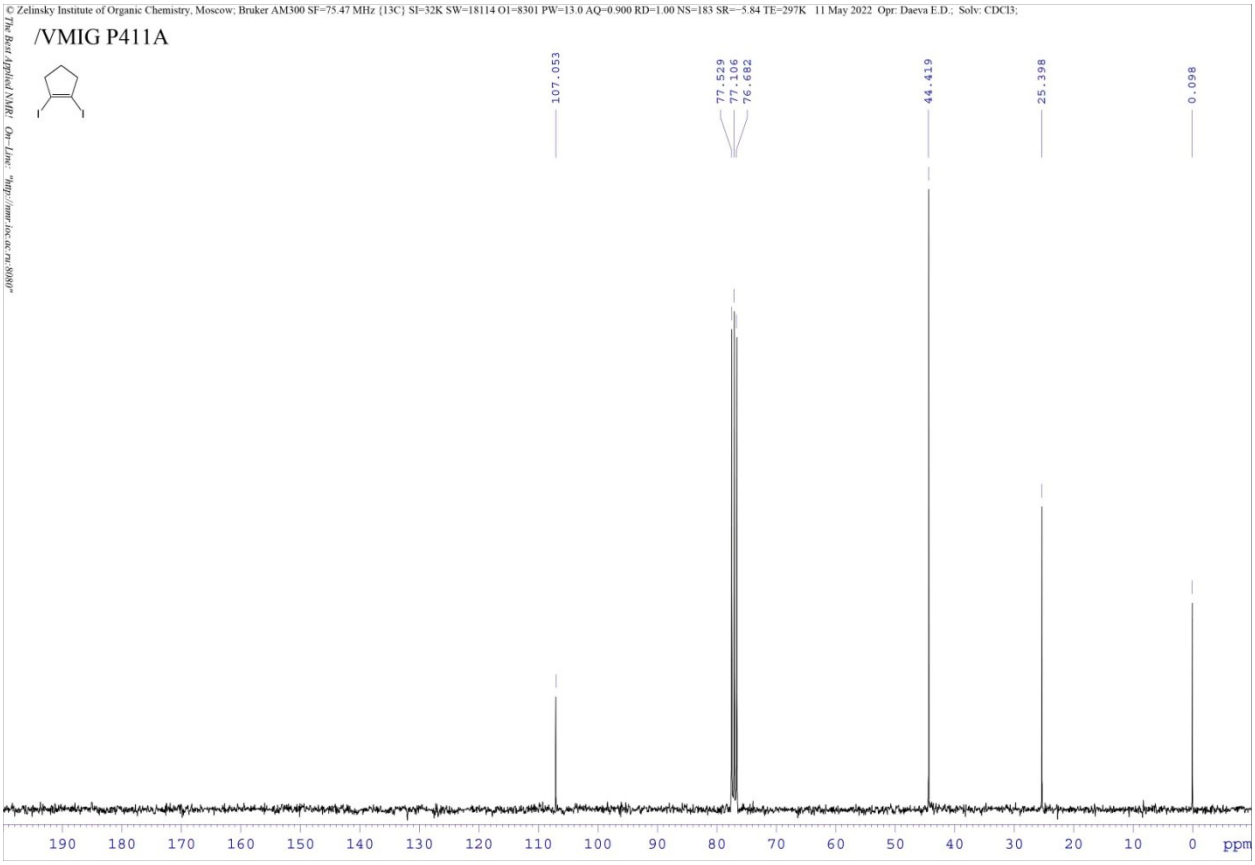


FIGURE S70. ^{13}C NMR spectrum of 1,2-diiodocyclopent-1-ene in $CDCl_3$.

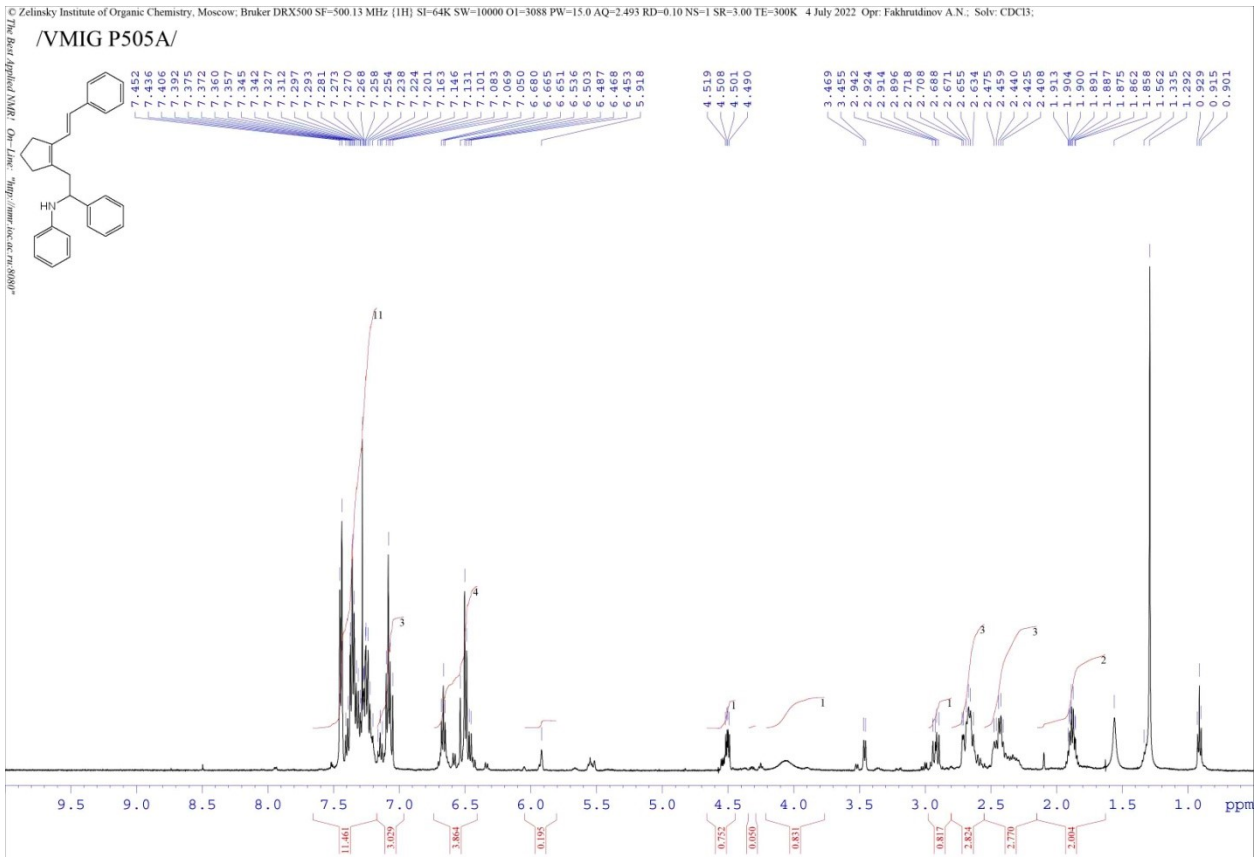


FIGURE S71. ^{1}H NMR spectrum of (E)-N-(1-phenyl-2-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (**35**) in $CDCl_3$.

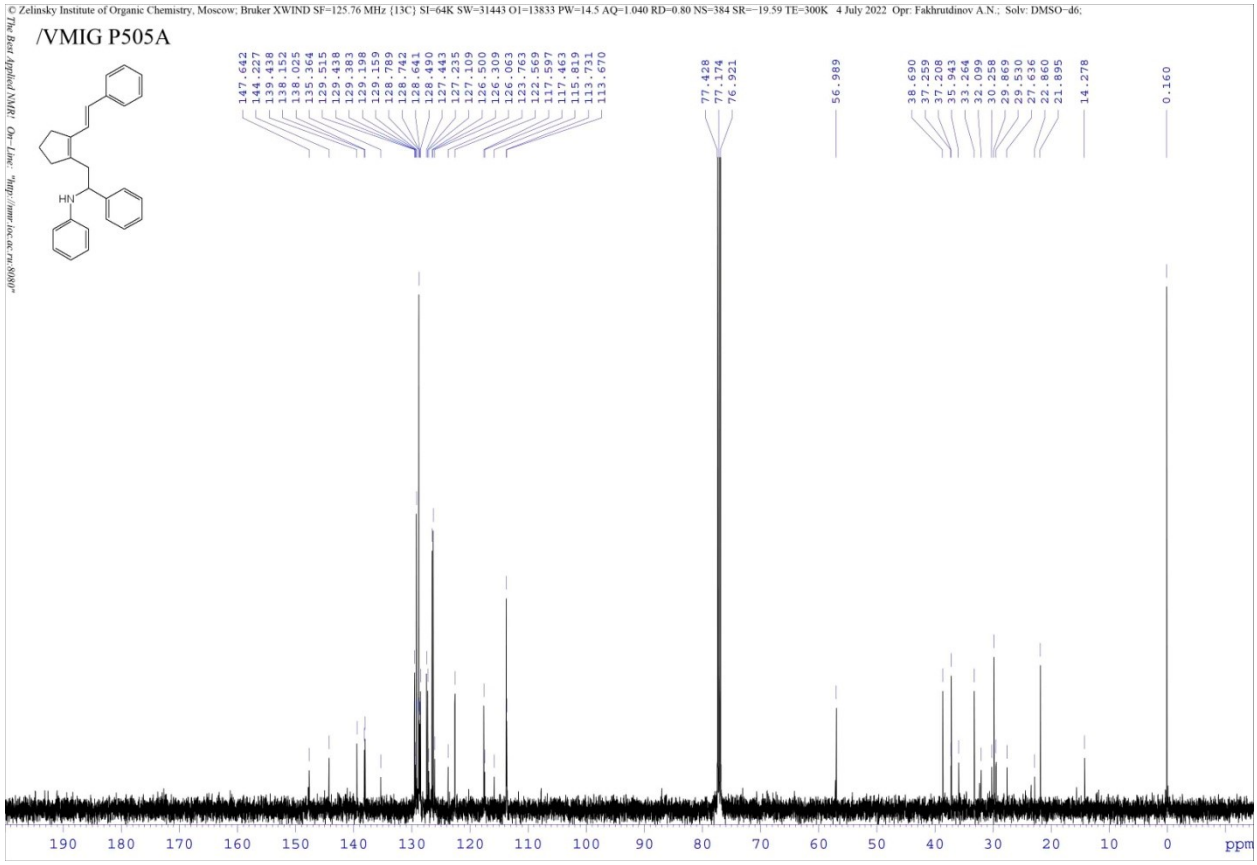


FIGURE S72. ^{13}C NMR spectrum of (E)-N-(1-phenyl-2-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (**35**) in $CDCl_3$.

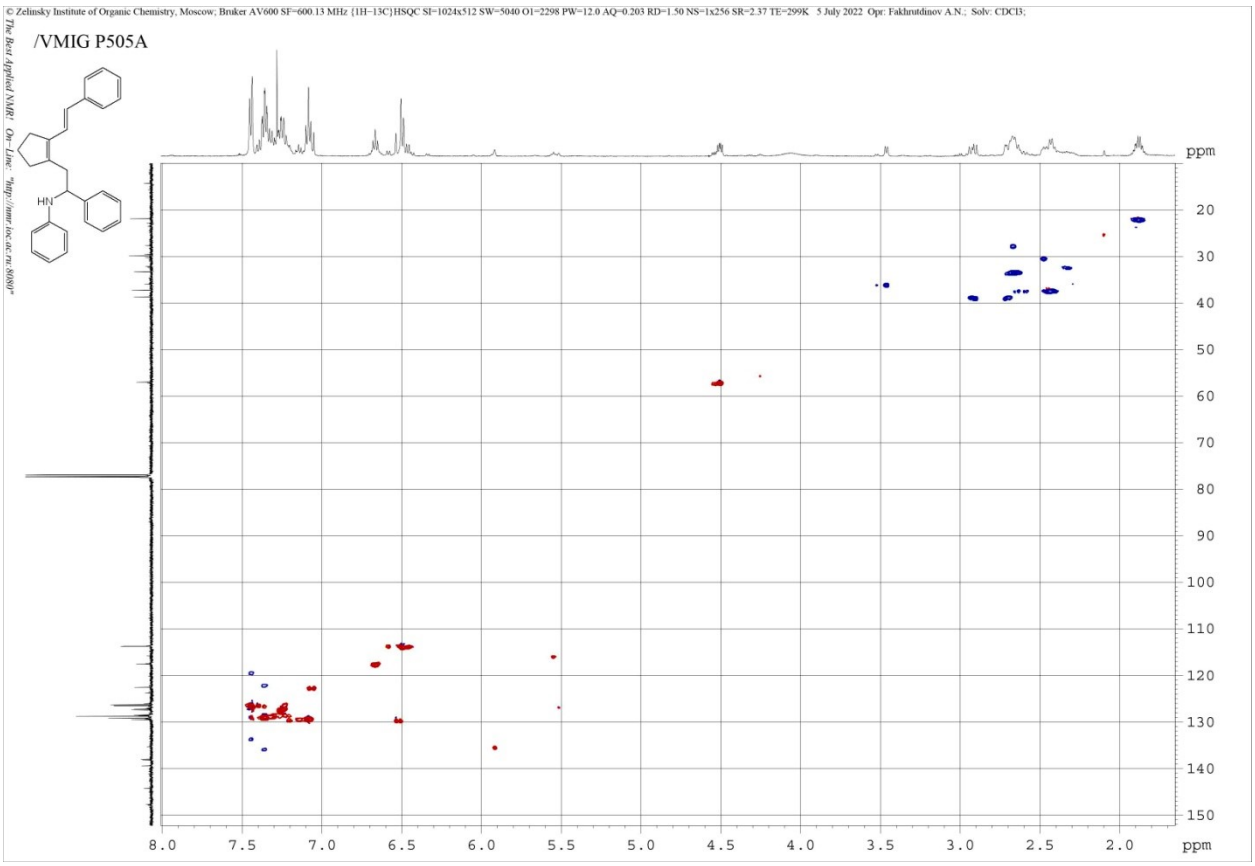


FIGURE S73. ^{1}H – ^{13}C HSQC NMR spectrum of (E)-N-(1-phenyl-2-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (**35**) in $CDCl_3$.

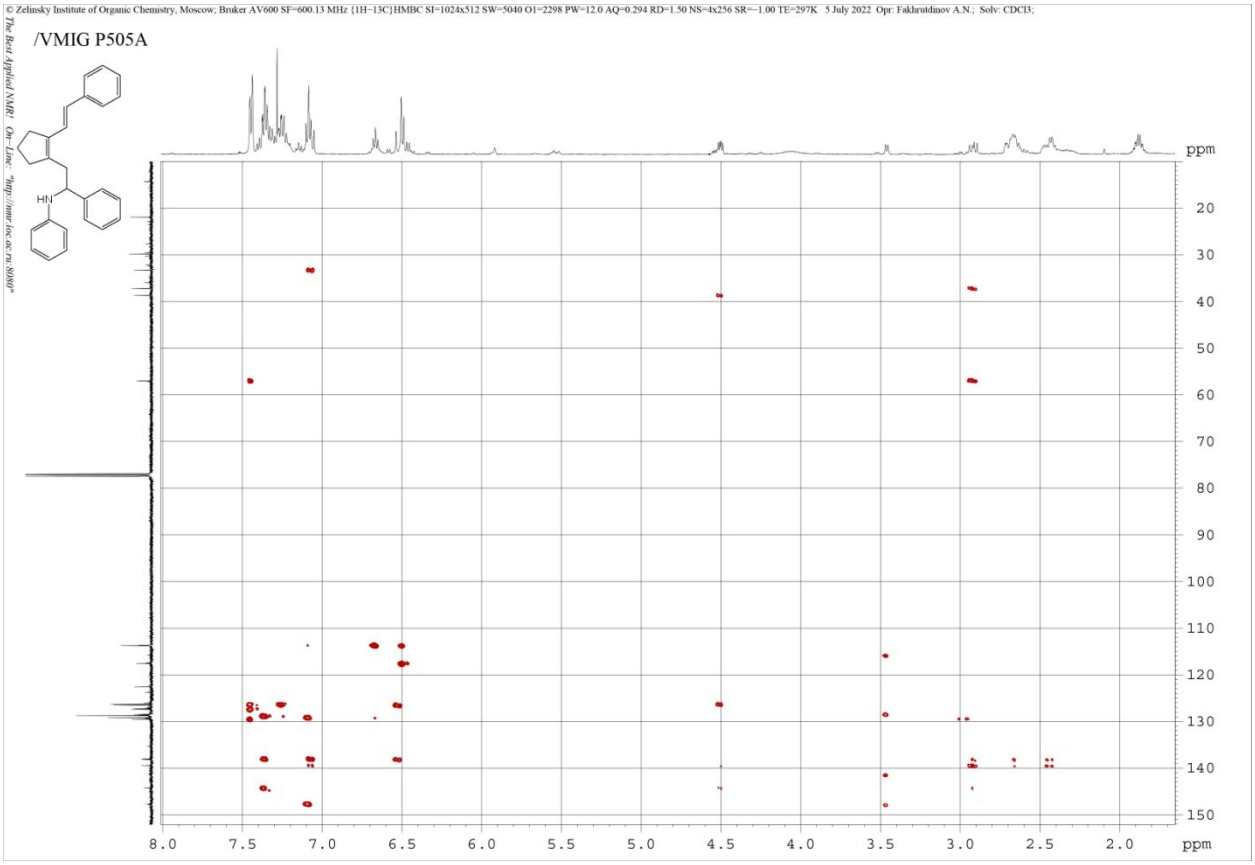


FIGURE S74. ^{1}H – ^{13}C HMBC NMR spectrum of (E)-N-(1-phenyl-2-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (**35**) in $CDCl_3$.

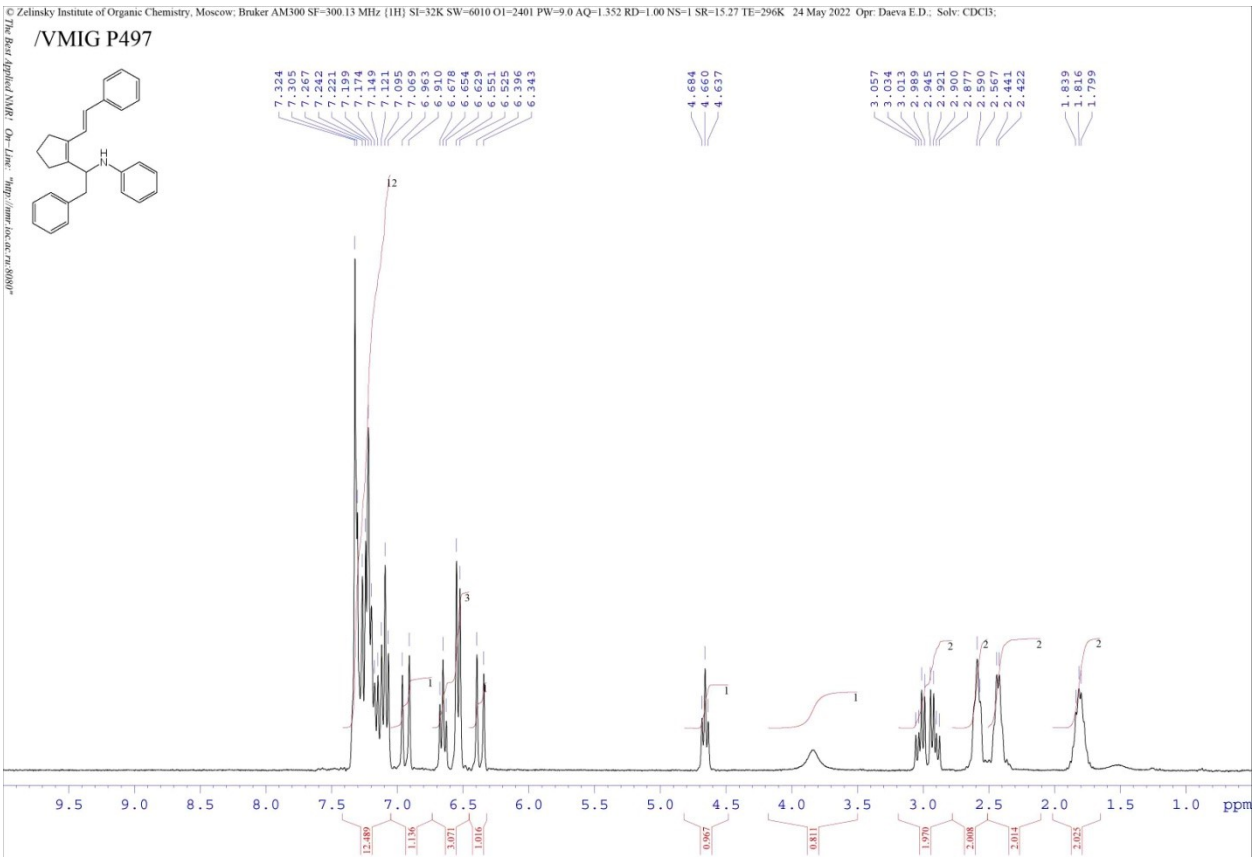


FIGURE S75. ^{1}H NMR spectrum of (E)-N-(2-phenyl-1-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (**36**) in $CDCl_3$.

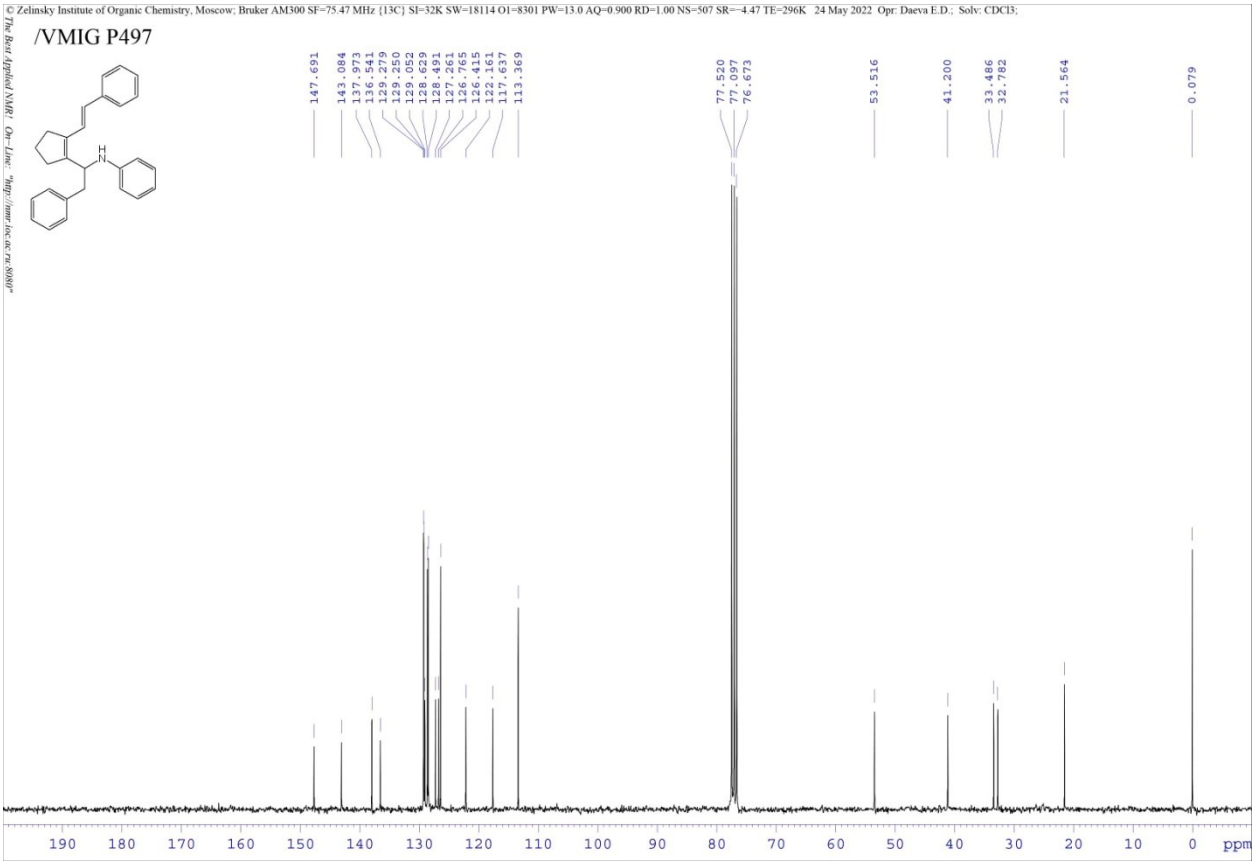


FIGURE S76. ^{13}C NMR spectrum of (E)-N-(2-phenyl-1-(2-styrylcyclopent-1-en-1-yl)ethyl)aniline (**36**) in $CDCl_3$.

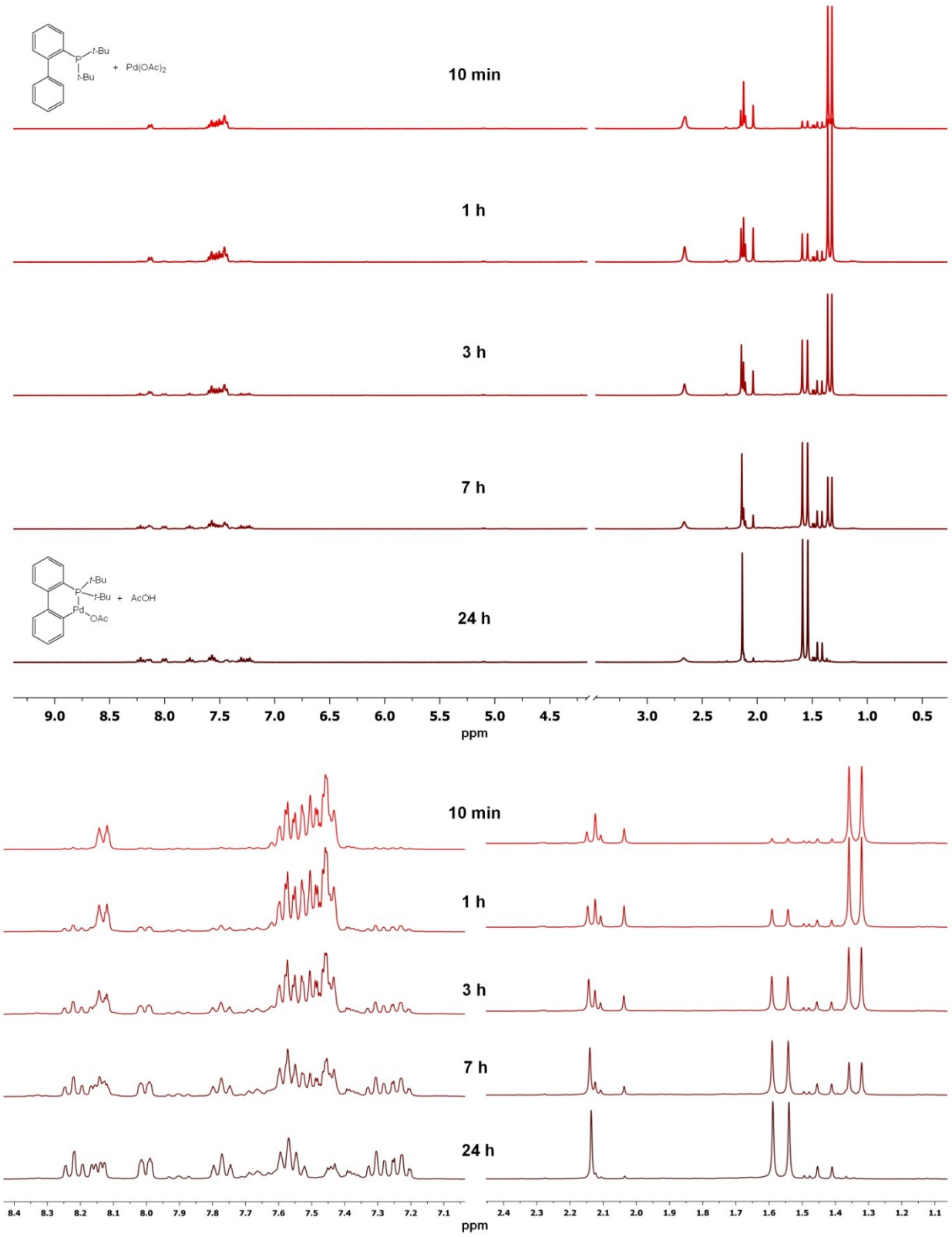


FIGURE S77. ^{1}H NMR spectra monitoring of the formation of palladacycle Pd–PTB in 1,4-dioxane.

4. Single-crystal X-ray structure determination

X-ray diffraction data for **4** and **12** were collected at 100 K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (shutterless φ- and ω-scan technique), using graphite monochromatized Mo K_α-radiation. The intensity data were integrated by the SAINT program[S6] and were semi-empirically corrected for absorption and decay from equivalent reflections using SADABS.[S7] X-ray diffraction data for **6**, **26**, **27**, and **36** were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K_α-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[S8] All structures were solved by direct methods using SHELXT[S9] and refined by the full-matrix least-squares method on F^2 using SHELXL-2018[S10] in the SHELXTL program suite[S6] (**4** and **12**) or in the OLEX2 program[S11] (**6**, **26**, **27**, and **36**). All non-hydrogen atoms were refined with anisotropic displacement parameters. Locations of hydroxy H-atoms in **4**, **6**, **12**, and of amino H-atom in **36** were found from the electron density-difference map; they were refined with individual isotropic displacement parameters. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A disorder of the >CH–OH fragment in **4** was regularly modeled by *SADI* and *EADP* SHELXL restrains. **6** was processed as a regular non-merohedral twin: equivalent reflections were merged by a conventional way, the number of collected reflection was set to the number of independent reflections, R_{int}=0. The SHELXTL program suite[S6] was used for molecular graphics.

Crystal data, data collection and structure refinement details are summarized in Table S1. The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2222212–2222217 for **4**, **6**, **12**, **26**, **27**, **36**, correspondingly; they also contain the supplementary crystallographic data. These data can be obtained free of charge from the CCDC *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data, data collection and structure refinement details for **4**, **6**, and **12**

Identification code	**4**	**6**	**12**
Empirical formula	$C_{26}H_{18}Br_2O_3$	$C_{18}H_{16}O_7$	$C_{30}H_{24}O$
Formula weight	538.22	344.31	400.49
Temperature (K)	100(2)	100.00(10)	100(2)
Wavelength (Å)	0.71073	1.54184	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a (Å)	37.4948(7)	4.94730(10)	11.1904(2)
b (Å)	5.55660(10)	13.4572(2)	8.1110(2)
c (Å)	27.3597(5)	23.6162(3)	46.9573(9)
β (°)	130.3290(10)	92.7680(10)	93.9210(10)
Volume ($Å^3$)	4345.51(15)	1570.46(4)	4252.12(15)
Z	8	4	8
Calcd density (g/cm^3)	1.645	1.456	1.251
μ (mm^{-1})	3.757	0.957	0.074
F(000)	2144	720	1696
Crystal size (mm)	0.5×0.3×0.2	0.05×0.03×0.02	0.68×0.15×0.12
θ range (°)	2.175–33.137	3.748–77.779	2.433–33.139
Index ranges	-57≤h≤57, -8≤k≤8, -42≤l≤42	-5≤h≤6, -17≤k≤17, -29≤l≤29	-17≤h≤16, -12≤k≤12, -72≤l≤71
Reflections			
Collected	101028	5674	136595
Independent [R_{int}]	8288 [0.0690]	5674 [-]	15999 [0.0995]
Observed (I>2σ(I))	5602	5497	10996
Completeness to $\theta_{full}/\theta_{max}$	0.999 / 0.999	1.000 / 0.995	0.999 / 0.986
T_{max} / T_{min}	0.7465 / 0.5443	1.00000 / 0.79757	0.7465 / 0.6983
Data / restraints / parameters	8288 / 3 / 289	5674 / 0 / 233	15999 / 0 / 567
Goodness-of-fit on F^2	1.027	1.054	1.032
R1 / wR2 [I>2σ(I)]	0.0403 / 0.0802	0.0370 / 0.1029	0.0606 / 0.1257
R1 / wR2 (all data)	0.0739 / 0.0917	0.0378 / 0.1038	0.1022 / 0.1459
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ ($\bar{e}\cdot Å^{-3}$)	0.574 / -0.790	0.244 / -0.200	0.368 / -0.263
CCDC number			

Table S1. Crystal data, data collection and structure refinement details for **26**, **27**, and **36** (*cont.*)

Identification code	**26**	**27**	**36**
Empirical formula	$C_{24}H_{25}N$	$C_{27}H_{29}N$	$C_{27}H_{27}N$
Formula weight	327.45	367.51	365.49
Temperature (K)	100.01(10)	100.01(10)	100.00(10)
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pbca	Pbcn	$P2_1/c$
Unit cell dimensions			
a (Å)	5.58245(2)	38.6981(3)	12.22731(8)
b (Å)	19.16935(9)	5.37771(3)	21.32536(13)
c (Å)	34.33220(14)	19.93774(12)	8.10901(4)
β (°)	90	90	105.5065(7)
Volume ($Å^3$)	3673.95(3)	4149.18(4)	2037.47(2)
Z	8	8	4
Calcd density (g/cm^3)	1.184	1.177	1.192
μ (mm^{-1})	0.511	0.505	0.514
F(000)	1408	1584	784
Crystal size (mm)	0.05×0.03×0.02	0.05×0.03×0.02	0.55×0.43×0.05
θ range (°)	2.574–77.701	2.283–77.782	3.752 –77.742
Index ranges	-6≤h≤6, -24≤k≤23, -43≤l≤43	-49≤h≤48, -6≤k≤4, -24≤l≤25	-15≤h≤15, -27≤k≤26, -7≤l≤10
Reflections			
Collected	47670	30001	25819
Independent [R_{int}]	3877 [0.0270]	4389 [0.0240]	4338 [0.0220]
Observed (I>2σ(I))	3665	4144	4145
Completeness to $\theta_{full}/\theta_{max}$	1.000 / 0.993	0.999 / 0.992	1.000 / 0.999
T_{max} / T_{min}	1.00000 / 0.82739	1.00000 / 0.87783	1.000 / 0.372
Data / restraints / parameters	3877 / 0 / 228	4389 / 0 / 253	4338 / 0 / 257
Goodness-of-fit on F^2	1.032	1.033	1.026
R1 / wR2 [I>2σ(I)]	0.0359 / 0.0934	0.0362 / 0.0929	0.0374 / 0.0908
R1 / wR2 (all data)	0.0373 / 0.0946	0.0379 / 0.0944	0.0388 / 0.0919
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ ($\bar{e}\cdot Å^{-3}$)	0.199 / -0.177	0.210 / -0.164	0.222 / -0.219
CCDC number			

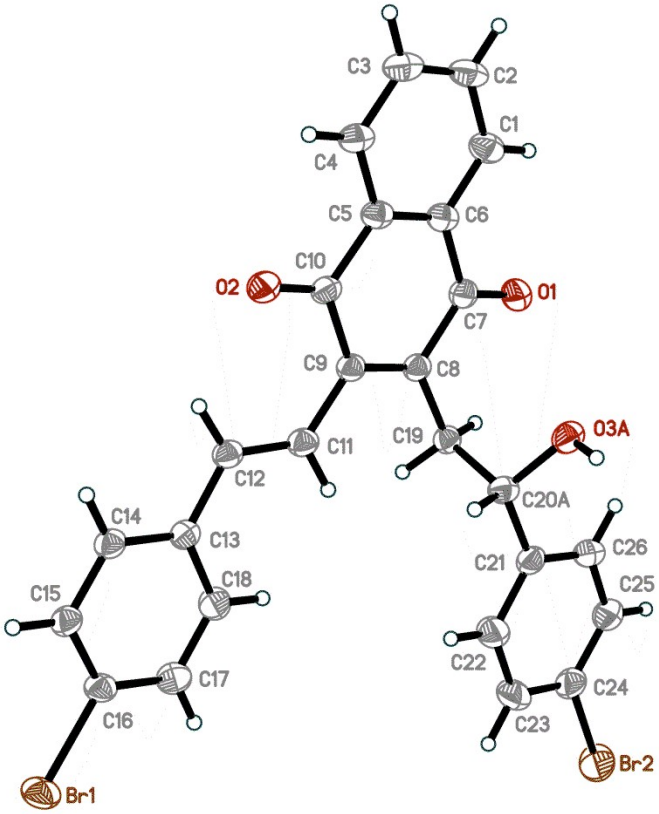


Fig. S78. The structure of **4** (p=50%). Disorder of the >CH–OH fragment is omitted.

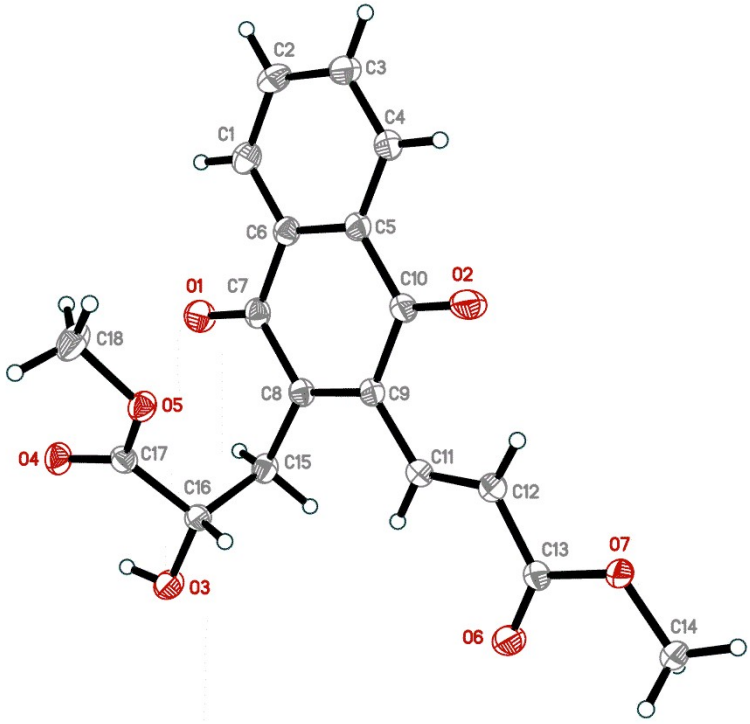


Fig. S79. The structure of **6** (p=50%).

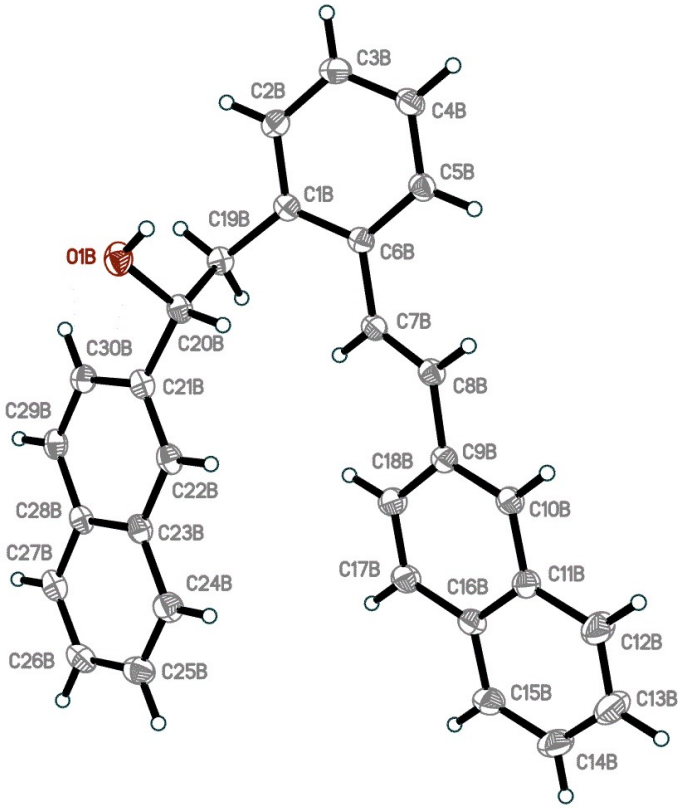


Fig. S80. The structure of **12** (p=50%). One of two crystallographically non-equivalent molecules is shown.

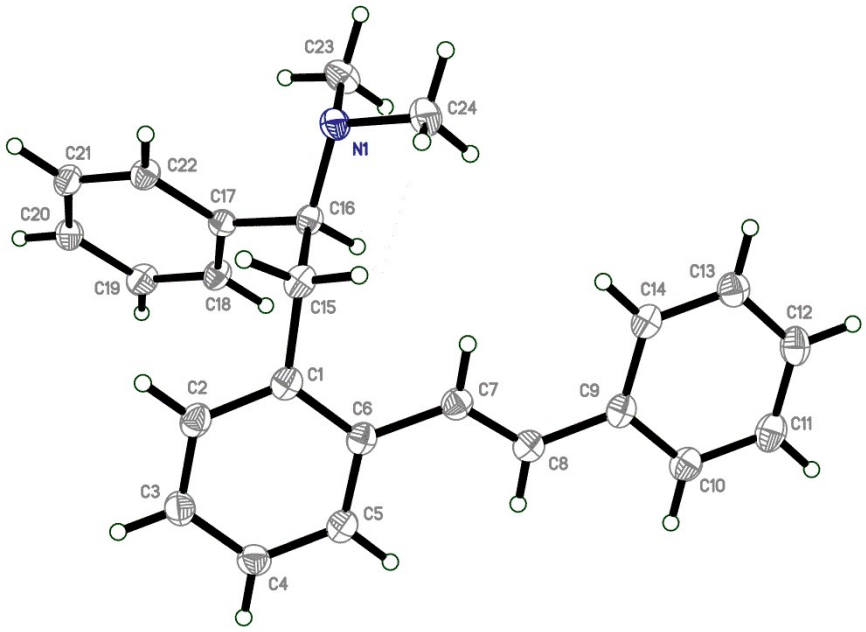


Fig. S81. The structure of **26** (p=50%).

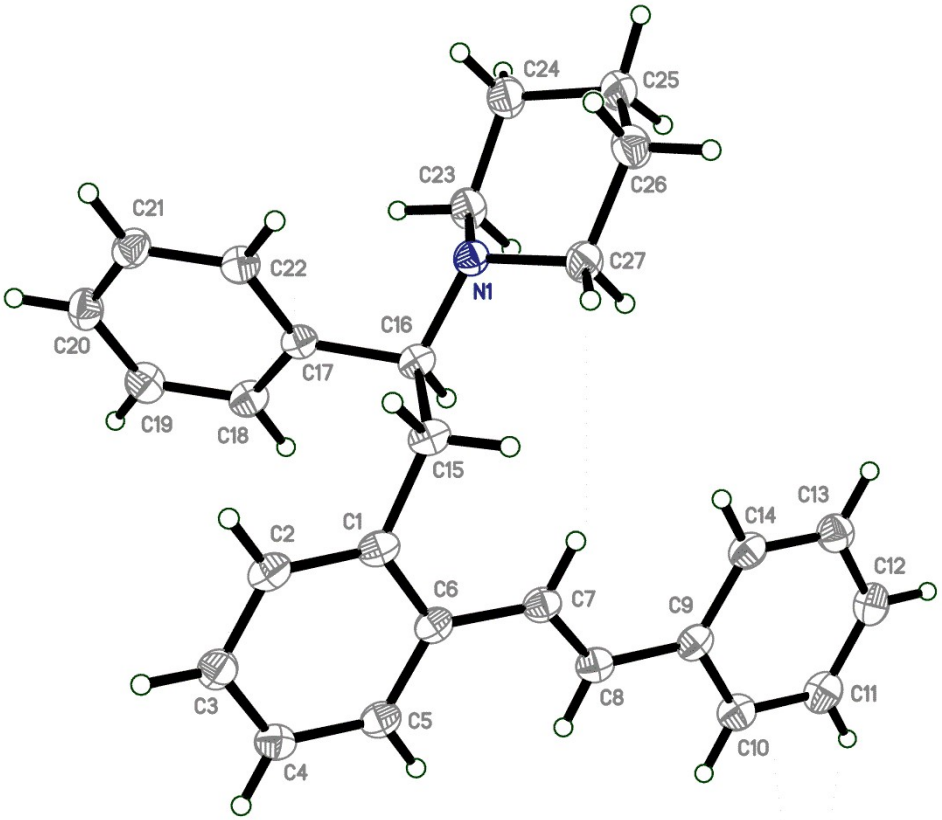


Fig. S82. The structure of **27** (p=50%).

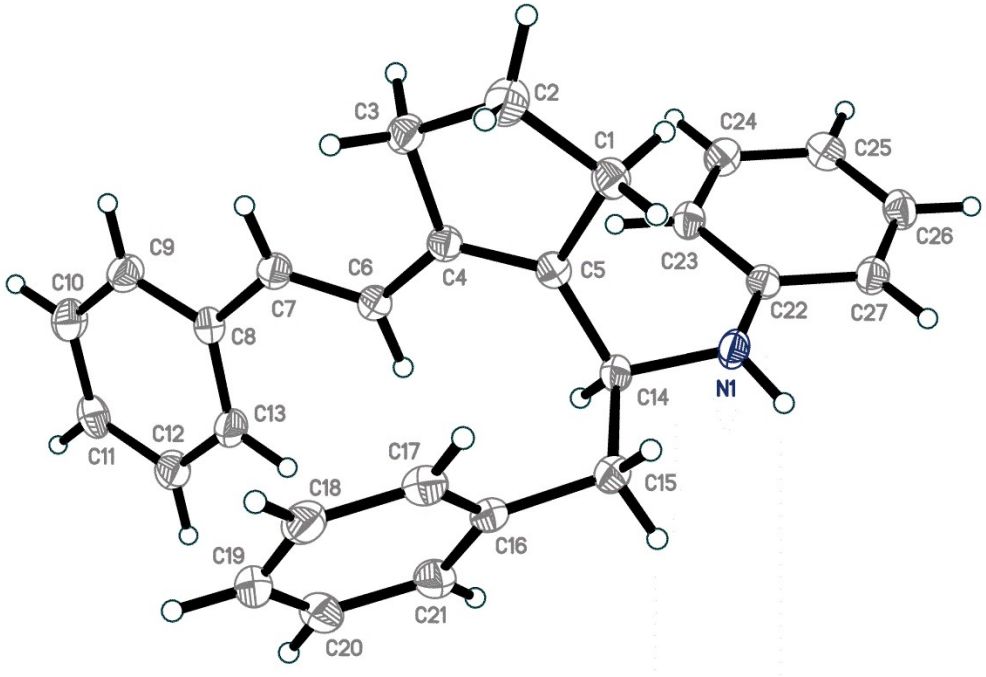


Fig. S83. The structure of **36** (p=50%).

5. References.

S1. Migulin, V. A. *Synthesis,* 2020, **52**, 60–68.

S2. Heck, R. F.; Nolley J. P., Jr. *J. Org. Chem.,* 1972, **37**, 2320–2322.

S3. Liedtke, R.; Harhausen, M.; Fröhlich, R.; Kehr, G.; Erker, G. *Org. Lett.,* 2012*,* **14***,* 1448–1451.

S4. Imamoto, T.; Tamura, K.; Zhang, Z.; Horiuchi, Y.; Sugiya, M.; Yoshida, K.; Yanagisawa, A.; Gridnev, I. D. *J. Am. Chem. Soc.,* 2012*,* **134***,* 1754–1769.

S5. Juríček, M.; Kouwer, P. H. J.; Rehák, J.; Sly, J.; Rowan, A. E. *J. Org. Chem.,* 2009*,* **74***,* 21–25.

S6. Bruker. APEX-III. *Bruker AXS Inc.*, Madison, Wisconsin, USA, 2019.

S7. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *J. Appl. Cryst.,* 2015, **48**, 3–10.

S8. CrysAlisPro. Version 1.171.42. *Rigaku Oxford Diffraction*, 2021.

S9. Sheldrick, G. M. *Acta Cryst.,* 2015, A**71**, 3–8.

S10. Sheldrick, G. M. *Acta Cryst.* 2015, C**71**, 3–8.

S11. Dolomanov O. V.; Bourhis L. J.; Gildea R. J.; Howard J. A. K.; Puschmann H. *J. Appl. Cryst.* 2009, **42**, 339–341.