Electronic Supplementary Materials

TfOH-Promoted Synthesis of Indoles and Benzofurans Involving Cyclative Transposition of Vinyl Ketone

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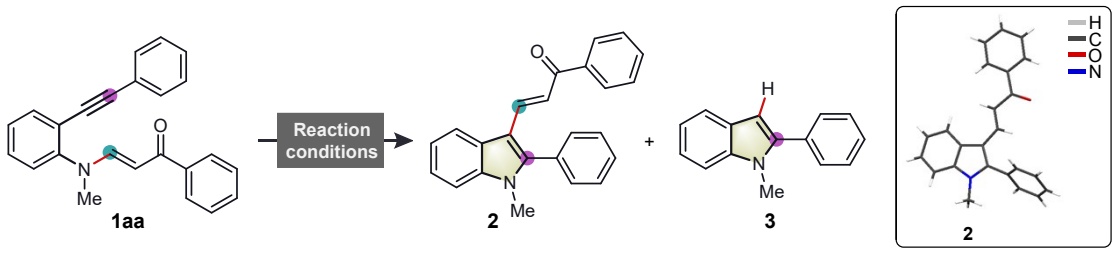
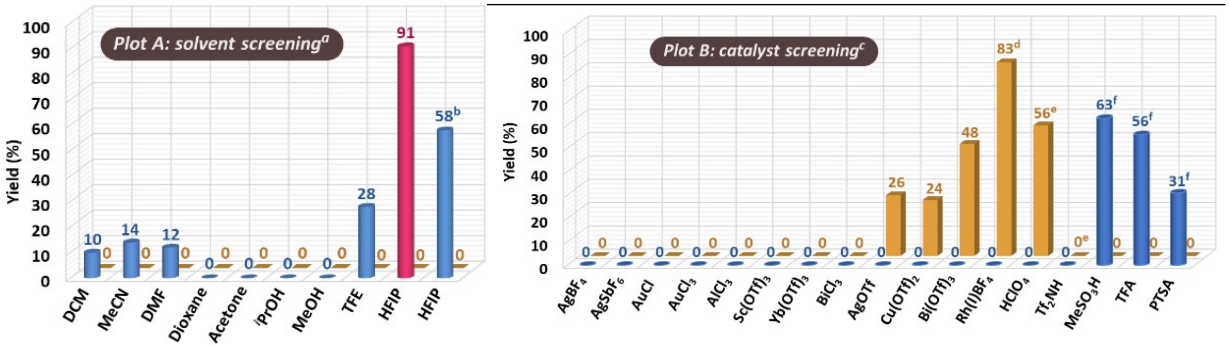
ESI-1 General information:

All the reactions dealing with air and/or moisture-sensitive compounds were performed under an atmosphere of nitrogen with oven-dried glasswares and standard syringe/septa techniques. The abbreviation "rt" refers to reactions carried out approximately at 25 ºC. Silica gel plates 60 F_{254} were used for thin layer chromatography (TLC) purpose and compounds were visualized by using UV light and/or by treatment with Seebach solution (phosphomolibdic acid (2.5 g), $Ce(SO_4)_2$ (1 g), Conc. H_2SO_4 (6 mL), H_2O (94 mL) followed by heating. Column chromatography was performed on silica gel (100-200 mesh) using ethyl acetate and hexanes mixture as eluent. ^1H, ^{13}C and ^{19}F spectra were recorded on a 400 MHz or 500 MHz spectrometers. Chemical shifts are reported in ppm relative to $CDCl_3$ (for ^1H, δ 7.26), and $CDCl_3$ (for ^{13}C, δ 77.06). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, pent = pentate, sext = sextet, sept = septet and m = multiplet. IR spectra were recorded on a FT/IR spectrometer and are reported in cm^{-1}. High-resolution mass spectra (HRMS) were recorded using an ESI-TOF machine. Melting points were determined by using MR-VIS visual melting range apparatus and are uncorrected. X-ray data were collected at 293 K on a diffractometer with dual source. Mo-Kα (λ = 0.71073 Å) radiation as used to collect the X-ray reflections of the crystal. The UV-vis absorption spectrum was recorded on a UV-Vis spectrophotometer and emission spectrum was recorded on a fluorescence spectrometer. UV-Vis spectrum was recorded with a slit width of 1 nm. Slit widths of 3 and 5 nm were used on the excitation and emission monochromators respectively for fluorescence.

Materials: Unless otherwise noted, all commercial reagents and solvents were obtained from commercial supplier and used without further purification. Dichloromethane (DCM), 1,2-dichloroethane (DCE) and chloroform were distilled over CaH_2. THF was dried over sodium and freshly distilled before use. Gold and silver catalysts were purchased from Sigma-Aldrich.

ESI-2 Optimization of reaction conditions for the synthesis of indole derivative 2:





Reaction conditions. All the reactions were carried out using **1aa** (0.02 mmol) for 12 h and optimized reaction for 4 h. [a]TfOH (50 mol%). [b]20 mol% of TfOH was used. [c]10 mol% of metal lewis acid catalyst was used for catalyst screening. [d]$Rh(I)BF_4$ means $Rh(cod)(MeCN)BF_4$ and used in 5 mol%. [e]20 mol% catalyst was used. [f]50 mol% of catalyst was used. Front and back row correspond to the yields of **2** and **3** respectively.

Experiments were carried out to get the best reaction conditions for the synthesis of indole derivative **2** using vinylogous amide derivative **1aa** and TfOH (ESI-2). Reactions conducted in solvents such as CH_2Cl_2, CH_3CN, DMF and TFE, although resulted in poor yields of the expected indole derivative **2**, motivated us to try other conditions. Solvents such as dioxane and acetone did not facilitate any reaction and the unreacted starting material was isolated. To our delight, the target product was isolated in 91% yield with an exclusive *E* geometry of the olefin when the reaction was performed using 50 mol% of TfOH in HFIP at room temperature (entry 9, plot A, ESI-2). Reducing the amount of TfOH reduced the yield further. Importantly, the reaction did not proceed in the presence of other Lewis/Brønsted acid catalysts (entries 1-14, plot B, ESI-2). In the presence of catalysts such as AgOTf, $Cu(OTf)_2$, $Bi(OTf)_3$, Rh(I), and $HClO_4$, the reaction resulted in *N*-methyl-2-phenylindole **3** with the extrusion of alkenyl ketone moiety (entries 9-13, plot B). Other Brønsted acids such as TFA, $MeSO_3H$ and PTSA, though promoted the reaction, resulted in moderate to low yields (entries 15-17, plot B). The superiority of HFIP as the solvent is overwhelming as it known to polarize the substrates and stabilize the polar intermediates.

ESI-3 Synthesis of vinylogous amides derived from *o*-alkynylanilines 1 and vinylogous esters derived from *o*-alkynylphenols 35:

General Procedure 1 (GP-1):

Step 1. NaH (1.2 equiv.) was added to an oven-dried RB flask containing dry DMF (3 mL/mmol) under N_2 atmosphere. Then 2-iodo aniline (1.0 equiv.) in dry DMF (1 mL/mmol) was added dropwise to it at 0 °C and the mixture was stirred for 30 minutes. Then MeI (1.1 equiv.) in dry DMF (1 mL/mmol) was added slowly and the reaction mixture was warmed to rt and stirred overnight. After that, water was added and the resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with saturate brine solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get the crude product which was purified by column chromatography (silica gel, hexanes/EtOAc) to afford 2-iodo-N-methylaniline derivative (**48**).[1]

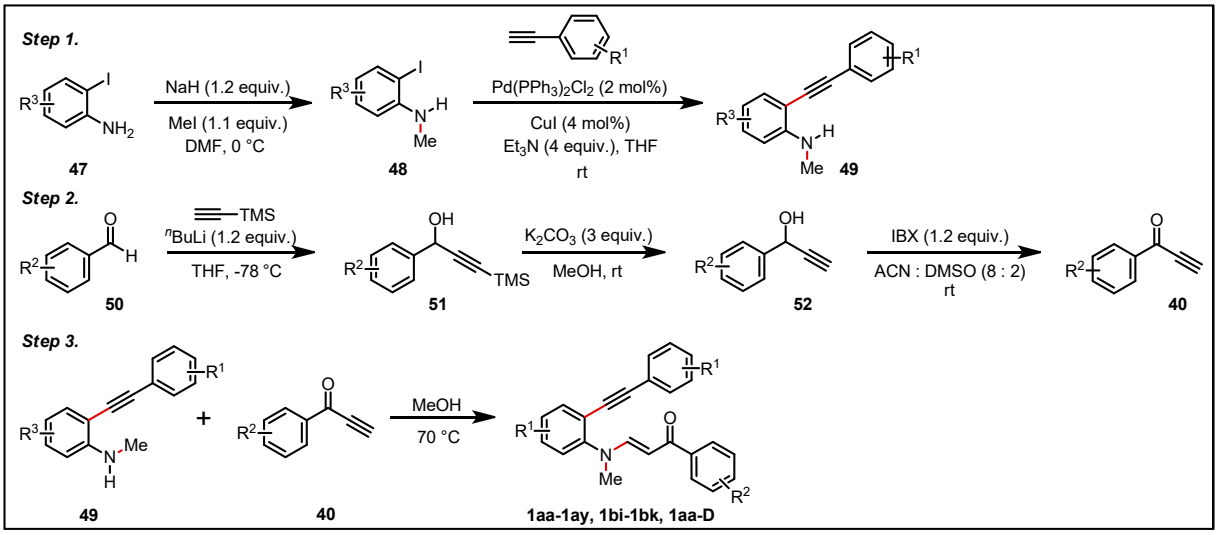
2-Iodo-N-methylaniline (**48**) (1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (0.02 equiv.) and CuI (0.04 equiv.) were dissolved in dry THF (3 mL/mmol) in a round bottom flask under nitrogen atmosphere at rt. Then triethylamine (4 equiv.) was added to the reaction mixture. After 5 minutes of stirring, the corresponding alkyne (1.1 equiv.) in dry THF (1 mL/mmol) was added

and the reaction mixture was allowed to stir overnight at rt. After completion of the reaction as indicated by TLC, the reaction mixture was filtered through a pad of celite and the solvent was evaporated under reduced pressure to get the crude product which was purified by column chromatography (silica gel, hexanes/EtOAc) to get the desired 2-alkynyl-N-methyl aniline (**49**).[2]

Step 2. To a solution of trimethylsilyl acetylene (1.1 equiv.) in dry THF (3 mL per mmol) at -78 °C under N_2 atmosphere was added ^{n}BuLi (1.2 equiv., 2.5 M solution in hexane). Then it was allowed to stir at -78 °C for 20 minutes. It was brought to rt and the stirring was continued. After 1h, corresponding aldehyde (1 equiv.) in dry THF (1 mL/mmol) was added to the reaction mixture at -78 °C. After 15 minutes, it was warmed up to rt and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction was quenched with saturated aqueous NH_4Cl solution. Then it was extracted using ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to get crude TMS protected alkynol (**51**).[3]

K_2CO_3 (3 equiv.) was added to the crude 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ol (**51**) (1 equiv.) in MeOH (3 mL/mmol). The reaction mixture was allowed to stir for 2 h at rt. The reaction mixture was filtered through a pad of celite and washed with DCM. The residue was washed with saturated aqueous NH_4Cl solution followed by saturated brine solution and dried over anhydrous Na_2SO_4.The solvent was evaporated under reduced pressure to get crude product alkynol (**52**).[3] The crude alkynol **52** was dissolved in DMSO/CH_3CN (2:8) solvent system (3 mL/mmol) and treated with IBX (1.2 equiv.). It was stirred at rt overnight. The reaction mixture was filtered through a pad of celite and the filtrate was washed with water followed by saturated brine solution and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford the crude product which was purified by column chromatography (silica gel, hexanes/EtOAc) to get the desired alkynone derivative (**40**).[4]

Step 3. 2-Iodo-N-methylaniline (**49**) (1.0 equiv.) and alkynone (**40**) (1.0 equiv.) were dissolved in MeOH (3 mL/mmol) and the reaction mixture was stirred overnight at 70 °C. After completion of the reaction (as monitored by TLC), the reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, hexanes/EtOAc) to get the desired product vinylogous amides derived from *o*-alkynylanilines (**1**).



Scheme S1. Preparation of vinylogous amides derived from *o*-alkynylanilines **1aa-1ay, 1bi-1bk, 1aa-D**.

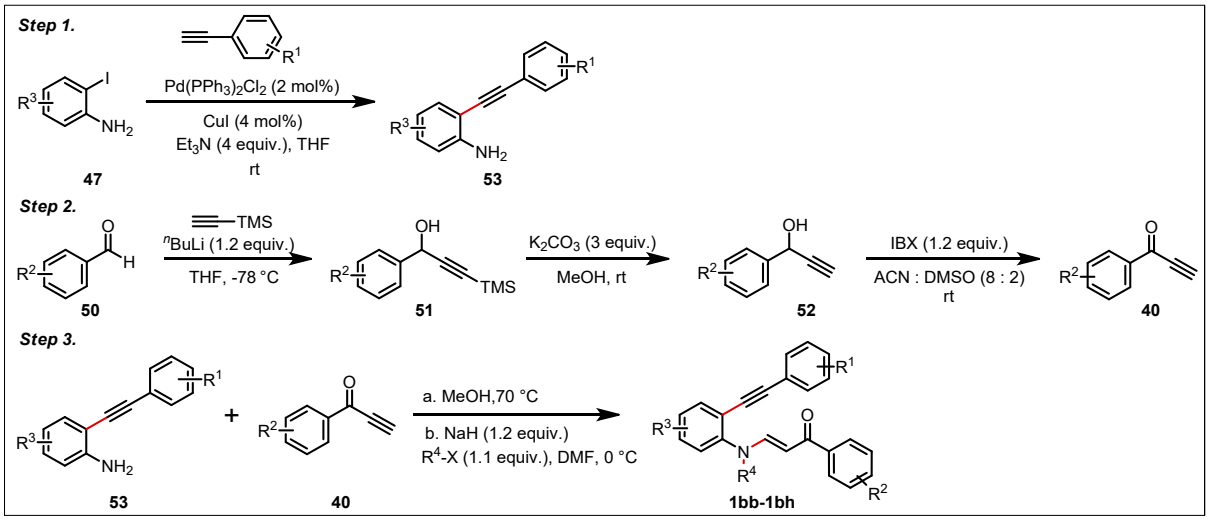
General procedure 2 (GP-2):

Step 1. 2-Iodo-aniline (**47**) (1.0 equiv.) and $Pd(PPh_3)_2Cl_2$ (0.02 equiv.) and CuI (0.04 equiv.) were dissolved in dry THF (3 mL/mmol) in a RB flask under nitrogen atmosphere at rt. Then triethylamine (4 equiv.) was added to the reaction mixture. After 5 minutes of stirring, a solution of the corresponding alkyne (1.1 equiv.) in dry THF (1 mL/mmol) was added and the reaction mixture was allowed to stir overnight at rt. After completion of the reaction as indicated by TLC, the reaction mixture was filtered through a pad of celite and the solvent was evaporated under reduced pressure to get the crude product which was purified by column chromatography (silica gel, hexanes/EtOAc) to get the desired 2-alkynyl aniline (**53**).[2]

Step 2. Same as the step 2 of **GP-1**.

Step 3. 2-Alkynylaniline (**58**) (1.0 equiv.) and alkynone (**40**) (1.0 equiv.) were dissolved in MeOH (3 mL/mmol) and the reaction mixture was stirred overnight at 70 °C. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, hexanes/EtOAc) to get the desired product.

NaH (1.2 equiv.) was added to an oven-dried RB flask containing dry DMF (3 mL/mmol) under N_2 atmosphere. Then compound obtained from previous step (1.0 equiv.) dissolved in dry DMF (1 mL/mmol) was added drop wise to it at 0 °C and the mixture was stirred for 30 minutes. Then R^4X (1.1 equiv.) in dry DMF (1 mL/mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After that, water was added and the resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with saturated brine solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford vinylogous amides derived from *o*-alkynylanilines (**1**).[1]



Scheme S2. Preparation of vinylogous amides derived from *o*-alkynylanilines derivatives **1bb-1bh**.

General procedure 3 (GP-3):

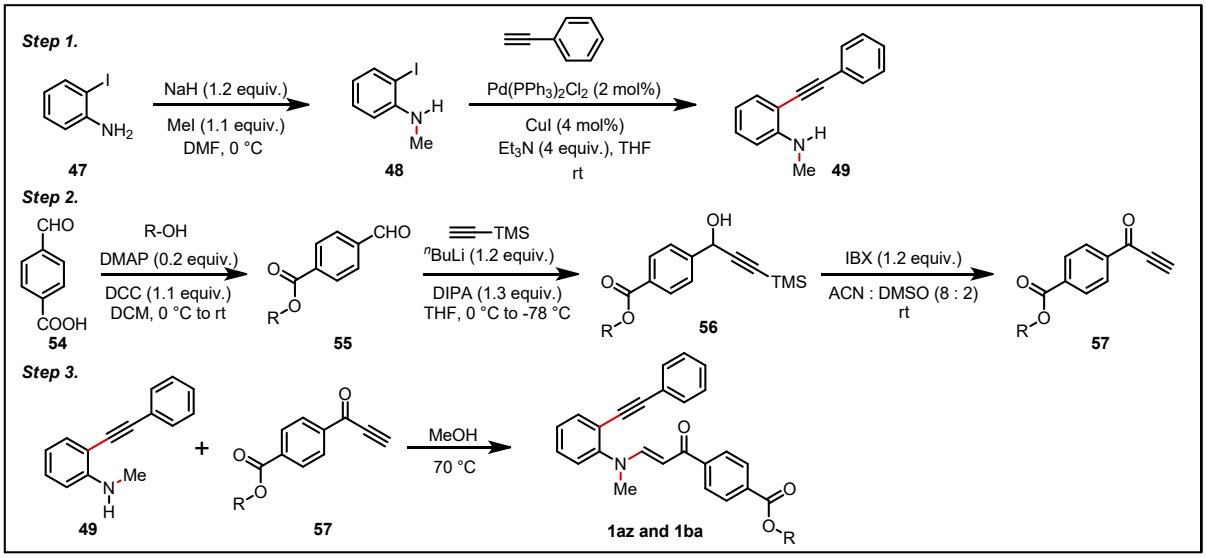
Step 1. Same as the step 1 of **GP-1**.

Step 2. To a solution of R^3OH (1.2 equiv.) in dry DCM (3 mL/mmol), DMAP (20 mol%) was added followed by 4-carboxybenzaldehyde **54** (1 equiv.). Then DCC (1.1 equiv.) was added to the reaction mixture at 0 °C. The mixture was stirred at rt for 24 h. The dicyclohexyl urea formed in the reaction was removed by filtration through silica gel. The organic layer was washed three times with 10% aqueous HCl solution followed by 5% aqueous $NaHCO_3$ solution. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the crude product **55**.

To a solution of DIPA (1.3 equiv.) in dry THF (3 mL/mmol), ^{n}BuLi (2.5M solution in hexane, 1.2 equiv.) was added at 0 °C under N_2 atmosphere. The solution was stirred at the same temperature for 1 h. Then the reaction mixture was cooled to -78 °C and trimethylsilyl acetylene (1.1 equiv.) in dry THF (1 mL/mmol) was added. After 1h, the corresponding aldehyde **55** (1 equiv.) in dry THF (1 mL/mmol) was added to the reaction mixture and stirred for 3 h at -78 °C strictly. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. Then it was extracted using ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to get crude product **56**.

The crude **56** (1 equiv.) was dissolved in DMSO/CH_3CN (2:8) solvent system (3 mL/mmol) and treated with IBX (1.2 equiv.). After overnight stirring at room temperature the crude was filtered through a pad of celite and the filtrate was washed with water followed by saturated brine solution and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford the crude propargylic ketone which was purified by column chromatography (silica gel, hexanes/EtOAc) to get the pure alkynone **57**.[4]

Step 3. Same as the step 3 of **GP-1**.



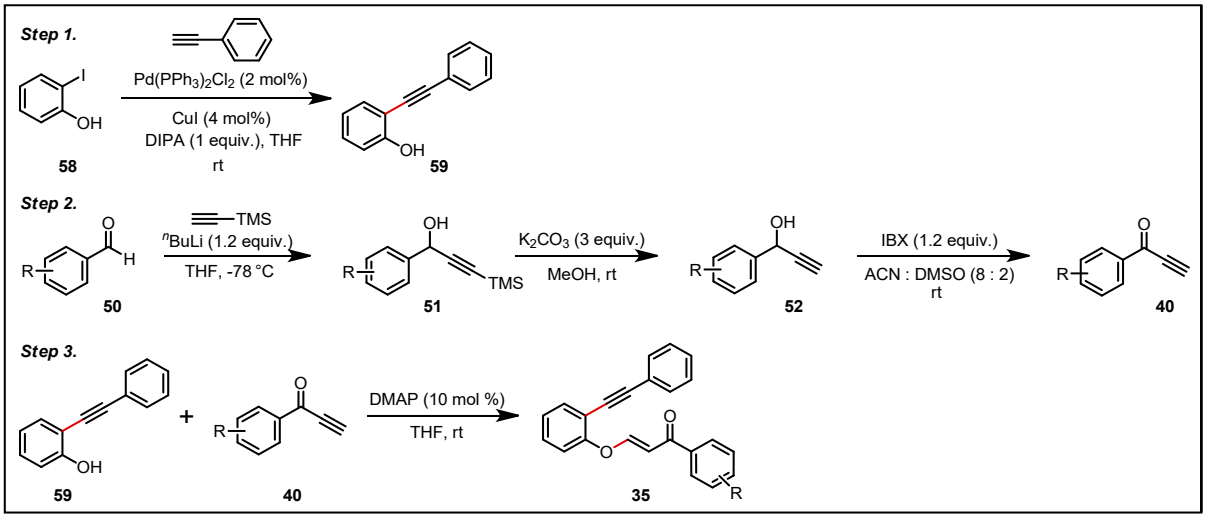
Scheme S3. Preparation of vinylogous amides derived from *o*-alkynylanilines **1az** and **1ba**.

General procedure 4 (GP-4):

Step 1. 2-Iodophenol **58** (1.0 equiv.) and $Pd(PPh_3)_2Cl_2$ (0.02 equiv.) and CuI (0.04 equiv.) were dissolved in dry THF (3 mL/mmol) in an oven-dried RB flask under nitrogen atmosphere at rt. Then DIPA (1 equiv.) was added to the reaction mixture. After 5 minutes of stirring, the corresponding alkyne (1.1 equiv.) in dry THF (3 mL/mmol) was added and the reaction mixture was allowed to stir overnight at rt. The reaction mixture was filtered through a pad of celite and the solvent was evaporated under reduced pressure to get the crude product which was purified by column chromatography (silica gel, hexanes/EtOAc) to get the desired 2-alkynyl phenol **59**.[5]

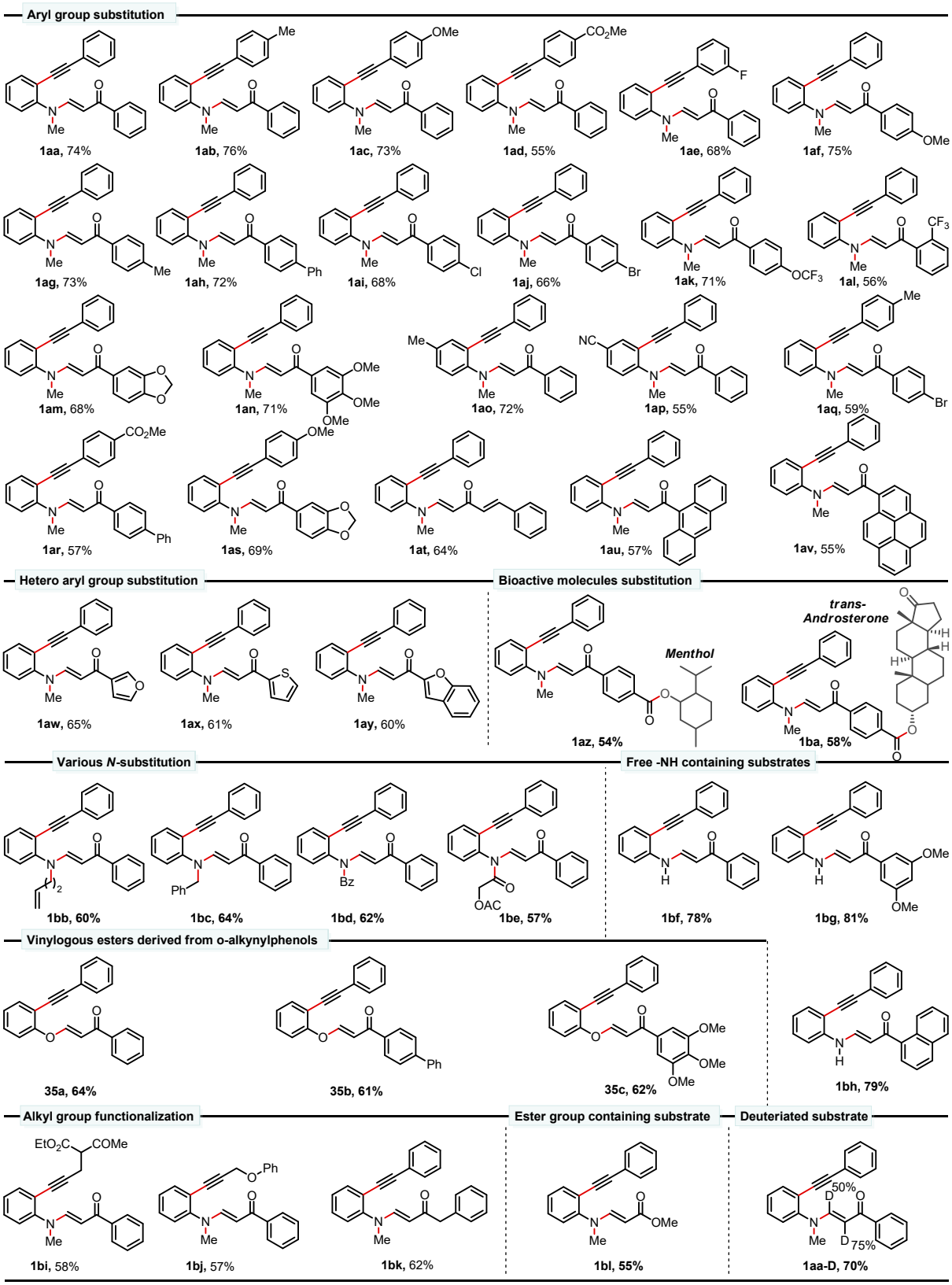
Step 2. Same as the step 2 of **GP-1**.

Step 3. 2-Alkynyl phenol **59** (1.0 equiv.) and alkynone **40** (1.0 equiv.) were dissolved in THF (3 mL/mmol). DMAP (10 mol%) was added to the reaction mixture and allowed to stir at rt. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, hexanes/EtOAc) to get the desired vinylogous esters derived from *o*-alkynylphenols **35**.[6]



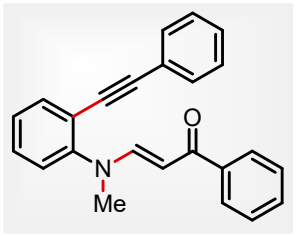
Scheme S4. Preparation of vinylogous esters derived from o-alkynylphenols **35**.

ESI-4 List of synthesized substrates:



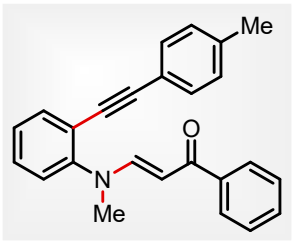
ESI-5 Analytical data of vinylogous amides derived from *o*-alkynylanilines 1 and vinylogous esters derived from *o*-alkynylphenols 35:

(*E*)-3-(Methyl(2-(phenylethynyl)phenyl)amino)-1-phenylprop-2-en-1-one (1aa):



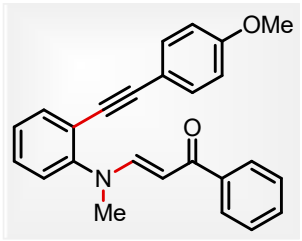
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as dark yellow gummy liquid (376.5 mg, 74%). R_f value = 0.16 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.13 (d, J = 12.7 Hz, 1H), 7.93 (s, 2H), 7.59 (d, J = 7.4 Hz, 1H), 7.51 – 7.34 (m, 7H), 7.33 – 7.29 (m, 3H), 7.23 (d, J = 7.8 Hz, 1H), 6.09 (s, 1H), 3.46 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.6, 152.5, 140.3, 133.7, 131.6, 131.2, 129.5, 128.7, 128.4, 128.2, 127.7, 127.4, 126.5, 125.0, 122.7, 109.1, 96.2, 95.3, 85.8, 38.8. IR (neat): ν/ cm^{-1} = 3061, 1626, 1519, 1446, 1272, 1211, 1052, 921, 751. HRMS: *m/z* [M+H]$^+$ calcd for $C_{24}H_{20}NO$: 338.1539, found: 338.1540.

(*E*)-3-(Methyl(2-(p-tolylethynyl)phenyl)amino)-1-phenylprop-2-en-1-one (1ab):



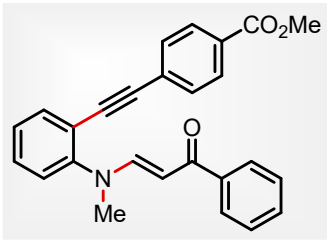
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (398.4 mg, 76%). R_f value = 0.23 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.14 (d, J = 12.4 Hz, 1H), 7.95 (s, 2H), 7.57 (d, J = 6.9 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.39 (d, J = 8.1 Hz, 2H), 7.34 (t, J = 6.9 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.11 (d, J = 7.9 Hz, 2H), 6.10 (s, 1H), 3.44 (s, 3H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.5, 152.5, 140.2, 138.8, 133.5, 131.4, 131.1, 129.2, 129.1, 128.1, 127.6, 126.4, 124.9, 119.6, 116.1, 108.9, 96.1, 95.5, 85.1, 38.7, 21.4. IR (neat): ν/ cm^{-1} = 2919, 1640, 1525, 1484, 1336, 1274, 1174, 759. HRMS: *m/z* [M+H]$^+$ calcd for $C_{25}H_{22}NO$: 352.1696, found: 352.1699.

(*E*)-3-((2-((4-Methoxyphenyl)ethynyl)phenyl)(methyl)amino)-1-phenylprop-2-en-1-one (1ac):



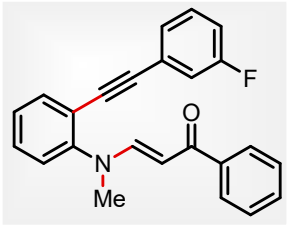
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (404.6 mg, 73%). R_f value = 0.47 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.16 (d, J = 12.5 Hz, 1H), 7.95 (s, 2H), 7.51 (d, J = 5.1 Hz, 1H), 7.41 (d, J = 7.3 Hz, 5H), 7.26 (s, 1H), 7.16 (d, J = 10.8 Hz, 2H), 6.78 (d, J = 7.2 Hz, 2H), 6.08 (s, 1H), 3.70 (s, 3H), 3.38 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 189.1, 159.6, 152.2, 139.9, 133.1, 132.8, 130.9, 128.8, 128.0, 127.4, 126.1, 124.5, 119.0, 115.9, 114.4, 113.8, 108.7, 98.0, 97.7, 95.2, 84.4, 54.9, 38.4. IR (neat): ν/ cm^{-1} = 2931, 1642, 1536, 1335, 1244, 1024, 830, 700. HRMS: *m/z* [M+Na]$^+$ calcd for $C_{25}H_{21}NO_2Na$: 390.1465, found: 390.1461.

(*E*)-Methyl 4-((2-(methyl(3-oxo-3-phenylprop-1-en-1-yl)amino)phenyl)ethynyl)benzoate (1ad):



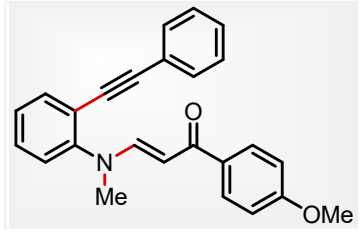
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (324.7 mg, 55%). M.P. = 54 - 55°C. R_f value = 0.18 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.15 (d, J = 12.4 Hz, 1H), 7.95 (d, J = 8.3 Hz, 4H), 7.58 (d, J = 7.4 Hz, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.47 – 7.36 (m, 4H), 7.25 – 7.20 (m, 2H), 6.09 (s, 1H), 3.88 (s, 3H), 3.43 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.4, 166.3, 152.3, 140.0, 133.8, 132.3, 131.4, 131.2, 129.9, 129.8, 129.5, 128.6, 128.2, 127.6, 127.3, 126.4, 124.9, 116.2, 109.1, 96.2, 94.3, 88.6, 52.1, 38.7. IR (neat): ν/ cm^{-1} = 2951, 1720, 1542, 1433, 1272, 1105, 700. HRMS: *m/z* [M+Na]$^+$ calcd for $C_{26}H_{21}NO_3Na$: 418.1414, found: 418.1414.

(*E*)-3-((2-((3-Fluorophenyl)ethynyl)phenyl)(methyl)amino)-1-phenylprop-2-en-1-one (1ac):



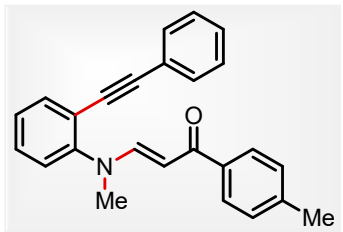
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (362.2 mg, 68%). R_f value = 0.45 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.21 (d, J = 12.2 Hz, 1H), 8.00 (s, 2H), 7.60 (d, J = 7.2 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.38 (t, J = 7.1 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.22 (d, J = 9.6 Hz, 2H), 7.02 (t, J = 8.0 Hz, 1H), 6.14 (s, 1H), 3.45 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.5, 162.3 (d, J = 247.2 Hz), 161.4, 152.4, 148.6, 140.2, 133.8, 131.3, 130.1 (d, J = 8.5 Hz), 129.9, 128.3, 127.7, 127.5 (d, J = 2.9 Hz), 126.5, 124.9, 124.5 (d, J = 9.6 Hz), 118.3 (d, J = 22.9 Hz), 116.0 (d, J = 21.1 Hz), 96.2, 93.9, 86.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ/ ppm = -112.60. IR (neat): ν/ cm^{-1} = 3057, 1643, 1535, 1492, 1276, 1047, 759. HRMS: *m/z* [M+Na]$^+$ calcd for $C_{24}H_{18}NOFNa$: 378.1265, found: 378.1257.

(*E*)-1-(4-Methoxyphenyl)-3-(methyl(2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1af):



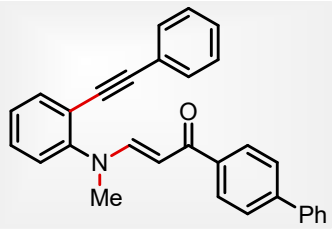
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (411.5 mg, 75%). R_f value = 0.17 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.14 (d, J = 12.7 Hz, 1H), 7.95 (s, 2H), 7.61 – 7.42 (m, 3H), 7.37 – 7.28 (m, 5H), 7.23 (d, J = 11.6 Hz, 1H), 6.92 (d, J = 8.1 Hz, 2H), 6.06 (s, 1H), 3.85 (s, 3H), 3.46 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 188.5, 162.3, 141.5, 133.7, 132.8, 131.6, 129.8, 129.5, 128.7, 128.4, 127.9, 122.8, 116.3, 114.1, 113.4, 109.1, 95.8, 95.3, 85.9, 55.4, 30.4. IR (neat): ν/ cm^{-1} = 2924, 1721, 1645, 1573, 1247, 1166, 1024, 752. HRMS: *m/z* [M+H]$^+$ calcd for $C_{25}H_{22}NO_2$: 368.1645, found: 368.1644.

(*E*)-3-(Methyl(2-(phenylethynyl)phenyl)amino)-1-(p-tolyl)prop-2-en-1-one (1ag):



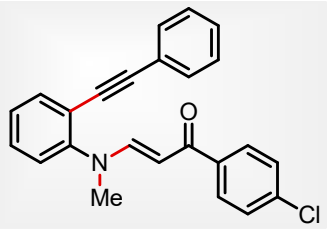
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (386.4 mg, 73%). R_f value = 0.27 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.16 (d, J = 12.8 Hz, 1H), 7.89 (s, 2H), 7.56 (d, J = 7.7 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.30 – 7.26 (m, 3H), 7.24 – 7.16 (m, 5H), 6.10 (s, 1H), 3.41 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 188.9, 151.9, 148.4, 141.4, 137.3, 133.4, 131.3, 129.3, 128.7, 128.5, 128.2, 127.6, 126.2, 124.7, 122.5, 118.8, 95.9, 95.1, 85.7, 38.6, 21.3. IR (neat): ν/ cm^{-1} = 2926, 1737, 1640, 1562, 1278, 1054, 878, 690. HRMS: *m/z* [M+H]$^+$ calcd for $C_{25}H_{22}NO$: 352.1696, found: 352.1696.

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(methyl(2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1ah):



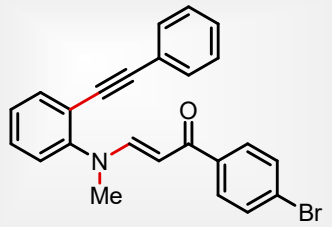
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (449.6 mg, 72%). R_f value = 0.12 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.24 (d, J = 12.2 Hz, 1H), 8.09 (s, 2H), 7.71 – 7.64 (m, 4H), 7.61 (d, J = 7.0 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.34 – 7.31 (m, 4H), 7.22 (d, J = 6.0 Hz, 1H), 6.18 (s, 1H), 3.46 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 188.7, 152.2, 148.4, 143.7, 140.1, 138.8, 133.5, 131.4, 129.4, 128.7, 128.6, 128.3, 128.2, 127.7, 127.0, 126.8, 124.7, 122.5, 118.7, 116.1, 108.9, 107.1, 95.9, 95.2, 85.8, 38.7. IR (neat): ν/ cm^{-1} = 3055, 1641, 1532, 1275, 1203, 1007, 752. HRMS: *m/z* [M+H]$^+$ calcd for $C_{30}H_{24}NO$: 414.1852, found: 414.1863.

(*E*)-1-(4-Chlorophenyl)-3-(methyl(2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1ai):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (378.6 mg, 68%). R_f value = 0.13 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.14 (d, J = 12.4 Hz, 1H), 7.88 (s, 2H), 7.60 (d, J = 6.1 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.39 (d, J = 6.5 Hz, 3H), 7.32 (s, 3H), 7.27 (d, J = 1.0 Hz, 1H), 7.22 (d, J = 6.8 Hz, 1H), 6.03 (s, 1H), 3.46 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 188.0, 152.9, 138.6, 137.3, 133.7, 132.1, 131.6, 129.5, 129.1, 128.8, 128.4, 126.7, 125.1, 122.7, 119.2, 116.3, 109.0, 95.6, 95.4, 85.7, 38.8. IR (neat): ν/ cm^{-1} = 3057, 1640, 1527, 1340, 1277, 1091, 750. HRMS: *m/z* [M+H]$^+$ calcd for $C_{24}H_{19}NOCl$: 372.1150, found: 372.1156.

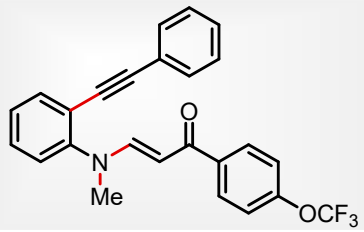
(*E*)-1-(4-Bromophenyl)-3-(methyl(2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1aj):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid

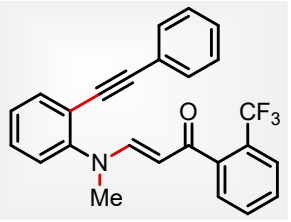
(412.5 mg, 66%). R_f value = 0.18 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.15 (d, J = 12.0 Hz, 1H), 7.81 (s, 2H), 7.53 (s, 3H), 7.47 (d, J = 7.0 Hz, 2H), 7.28 (s, 4H), 7.22 (s, 1H), 7.16 (s, 1H), 6.02 (s, 1H), 3.41 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 188.9, 152.6, 148.2, 138.8, 133.5, 131.4, 131.2, 129.4, 129.2, 128.6, 128.3, 126.4, 125.7, 124.7, 122.5, 118.8, 95.4, 95.2, 85.6, 38.7. IR (neat): ν/ cm^{-1} = 3054, 1641, 1533, 1334, 1275, 1007, 752. HRMS: *m/z* [M+H]$^+$ calcd for $C_{24}H_{19}NOBr$: 416.0645, found: 416.0649.

(E)-3-(Methyl(2-(phenylethynyl)phenyl)amino)-1-(4-(trifluoromethoxy)phenyl)prop-2-en-1-one (1ak):



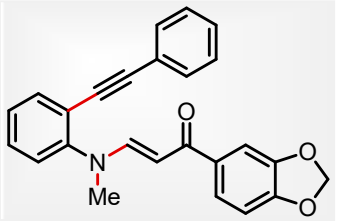
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (446.6 mg, 71%). R_f value = 0.42 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.16 (d, J = 12.4 Hz, 1H), 7.98 (s, 2H), 7.59 (d, J = 6.2 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.37 – 7.23 (m, 8H), 6.05 (d, J = 10.9 Hz, 1H), 3.45 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 187.7, 152.9, 151.2, 148.4, 138.6, 133.6, 131.5, 129.4, 128.7, 128.4, 125.4 (q, J = 161.1 Hz), 122.6, 120.5, 120.4 (q, J = 258.4 Hz), 120.2, 116.2, 109.0, 95.5, 95.3, 85.7, 38.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ/ ppm = -57.57. IR (neat): ν/ cm^{-1} = 3054, 1635, 1527, 1292, 1166, 1128, 744. HRMS: *m/z* [M+H]$^+$ calcd for $C_{25}H_{19}NO_2F_3$: 422.1362, found: 422.1369.

(*E*)-3-(Methyl(2-(phenylethynyl)phenyl)amino)-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one (1al):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (343.5 mg, 56%). R_f value = 0.27 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 7.65 (t, J = 7.4 Hz, 1H), 7.56 – 7.50 (m, 4H), 7.42 (s, 2H), 7.36 (t, J = 3.0 Hz, 4H), 7.32 (t, J = 6.5 Hz, 1H), 7.23 (s, 1H), 7.14 (s, 1H), 5.70 (d, J = 12.7 Hz, 1H), 3.37 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 192.7, 153.9, 148.1, 141.0, 133.6, 131.5, 131.4, 129.4, 128.8, 128.7, 128.4, 128.3, 127.6, 127.2 (d, J = 31.7 Hz),, 126.7, 126.2 (q, J = 4.7 Hz), 124.9, 123.9 (q, J = 274.1 Hz), 122.5, 119.2, 101.2, 95.3, 85.4, 38.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ/ ppm = -58.01. IR (neat): ν/ cm^{-1} = 2921, 1651, 1542, 1311, 1273, 1115, 1031, 753. HRMS: *m/z* [M+H]$^+$ calcd for $C_{25}H_{19}NOF_3$: 406.1413, found: 406.1415.

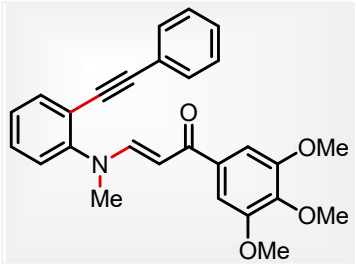
(*E*)-1-(Benzo[*d*][1,3]dioxol-5-yl)-3-(methyl(2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1am):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (391.4 mg, 68%). R_f value = 0.26 (30% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.18 (d, J = 12.3 Hz, 1H), 7.60

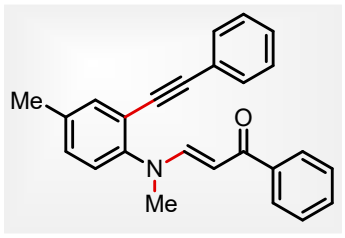
(s, 2H), 7.52 (d, J = 3.5 Hz, 3H), 7.38 – 7.32 (m, 4H), 7.23 (s, 2H), 6.85 (d, J = 6.8 Hz, 1H), 6.07 (s, 1H), 6.00 (s, 2H), 3.46 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 187.4, 151.9, 150.1, 147.6, 134.6, 133.4, 131.6, 131.3, 129.3, 128.5, 128.2, 126.2, 124.8, 122.8, 122.5, 118.7, 107.8, 107.4, 101.3, 95.4, 95.1, 85.7, 38.5. IR (neat): ν/ cm^{-1} = 2898, 1639, 1538, 1437, 1238, 1032, 752. HRMS: m/z $[M+H]^+$ calcd for $C_{25}H_{20}NO_3$: 382.1438, found: 382.1440.

(*E*)-3-(Methyl(2-(phenylethynyl)phenyl)amino)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (1an):



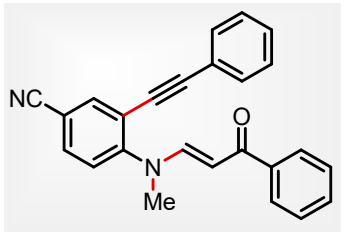
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (452.0 mg, 71%). R_f value = 0.19 (40% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.11 (d, J = 12.7 Hz, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.34 (t, J = 7.0 Hz, 1H), 7.28 (s, 3H), 7.24 – 7.17 (m, 4H), 6.01 (s, 1H), 3.88 (s, 9H), 3.44 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 188.4, 152.8, 141.0, 135.7, 133.5, 131.4, 129.4, 128.6, 128.3, 126.5, 125.0, 122.6, 119.0, 116.1, 108.9, 105.2, 95.7, 95.1, 85.7, 60.7, 56.2, 38.7. IR (neat): ν/ cm^{-1} = 2940, 1632, 1531, 1450, 1296, 1120, 982, 755. HRMS: m/z $[M+H]^+$ calcd for $C_{27}H_{26}NO_4$: 428.1856, found: 428.1864.

(*E*)-3-(Methyl(4-methyl-2-(phenylethynyl)phenyl)amino)-1-phenylprop-2-en-1-one (1ao):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (382.6 mg, 72%). R_f value = 0.28 (20% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.12 (d, J = 12.7 Hz, 1H), 7.94 (s, 2H), 7.50 – 7.46 (m, 3H), 7.45 – 7.39 (m, 3H), 7.32 – 7.28 (m, 3H), 7.13 (d, J = 15.8 Hz, 2H), 6.09 (s, 1H), 3.43 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ/ ppm = 189.6, 152.7, 146.2, 140.3, 136.4, 133.9, 131.5, 131.1, 130.2, 128.6, 128.4, 128.2, 127.6, 124.9, 122.7, 118.8, 95.8, 94.8, 85.9, 38.9, 20.7. IR (neat): ν/ cm^{-1} = 3054, 1642, 1526, 1484, 1336, 1274, 1207, 1174, 982, 817, 759. HRMS: m/z $[M+H]^+$ calcd for $C_{25}H_{22}NO$: 352.1696, found: 352.1699.

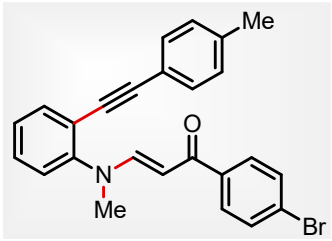
(*E*)-4-(Methyl(3-oxo-3-phenylprop-1-en-1-yl)amino)-3-(phenylethynyl)benzonitrile (1ap):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (301.5 mg, 55%). R_f value = 0.14 (30% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.17 (d, J = 12.8 Hz, 1H), 7.94

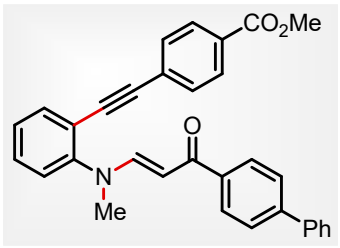
(d, J = 7.1 Hz, 2H), 7.84 (s, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.48 (d, J = 6.9 Hz, 3H), 7.44 (d, J = 7.3 Hz, 2H), 7.33 – 7.27 (m, 4H), 6.18 (d, J = 12.8 Hz, 1H), 3.46 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.3, 151.2, 150.4, 139.6, 137.6, 132.4, 131.6, 129.2, 128.4, 128.3, 127.9, 127.7, 124.9, 121.8, 119.5, 117.5, 109.6, 98.3, 97.6, 83.9, 38.8. IR (neat): ν/ cm^{-1} = 2919, 1582, 1539, 1333, 1220, 1092, 734. HRMS: m/z $[M+H]^+$ calcd for $C_{25}H_{19}N_2O$: 363.1492, found: 363.1494.

(*E*)-1-(4-bromophenyl)-3-(methyl(2-(p-tolylethynyl)phenyl)amino)prop-2-en-1-one (1aq):



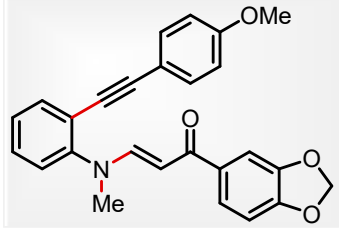
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (380.1 mg, 59%). R_f value = 0.12 (15% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.14 (d, J = 12.5 Hz, 1H), 7.81 (s, 2H), 7.54 (s, 3H), 7.37 (d, J = 8.1 Hz, 2H), 7.32 (s, 1H), 7.22 (s, 1H), 7.18 (s, 1H), 7.09 (d, J = 7.7 Hz, 2H), 6.03 (d, J = 11.3 Hz, 1H), 3.42 (s, 3H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ/ ppm = 187.9, 152.7, 148.2, 138.9, 133.5, 131.3, 131.27, 129.2, 129.1, 126.4, 125.7, 124.8, 119.4, 119.1, 116.1, 108.8, 98.1, 95.5, 95.4, 85.0, 38.7, 21.4. IR (neat): ν/ cm^{-1} = 2920, 1639, 1521, 1337, 1266, 1057, 759. HRMS: m/z $[M+Na]^+$ calcd for $C_{25}H_{20}NOBrNa$: 452.0620, found: 452.0619.

(*E*)-Methyl 4-((2-((3-([1,1'-biphenyl]-4-yl)-3-oxoprop-1-en-1-yl)(methyl)amino)phenyl)-ethynyl)benzoate (1ar):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (402.9 mg, 57%). R_f value = 0.15 (20% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.21 (d, J = 12.5 Hz, 1H), 8.04 (s, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.69 – 7.59 (m, 6H), 7.55 (d, J = 8.5 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.24 (d, J = 7.8 Hz, 1H), 6.17 (s, 1H), 3.89 (s, 3H), 3.47 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ/ ppm = 188.7, 166.3, 152.2, 143.9, 140.2, 138.7, 133.8, 131.4, 131.2, 130.4, 129.9, 129.8, 129.5, 128.8, 128.2, 127.7, 127.3, 127.1, 126.8, 126.5, 125.0, 96.1, 94.3, 88.6, 52.1, 39.0. IR (neat): ν/ cm^{-1} = 3026, 1720, 1643, 1537, 1273, 1105, 984, 735. HRMS: m/z $[M+H]^+$ calcd for $C_{32}H_{26}NO_3$: 472.1907, found: 472.1897.

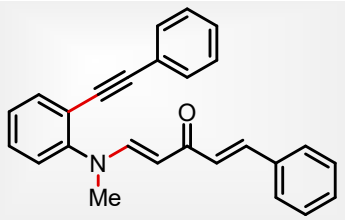
(*E*)-1-(Benzo[d][1,3]dioxol-5-yl)-3-((2-((4-methoxyphenyl)ethynyl)phenyl)(methyl) amino)prop-2-en-1-one (1as):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (423.1 mg, 69%). R_f value = 0.13 (20% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.12 (d, J = 12.4 Hz, 1H), 7.52 (d, J = 4.7 Hz, 2H), 7.46 (s, 1H), 7.39 (d, J = 6.8 Hz, 2H), 7.28 (s, 1H), 7.18 (d, J = 12.5 Hz, 2H), 6.79 (d, J = 5.3 Hz, 3H), 6.00 (s, 1H), 5.94 (s, 2H), 3.72 (s, 3H), 3.39 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm =

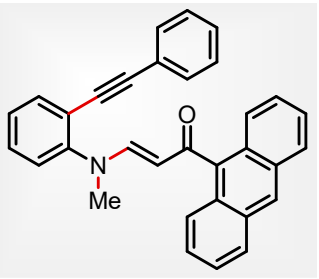
187.3, 175.8, 159.7, 152.0, 150.1, 147.6, 134.6, 133.2, 132.8, 128.9, 126.2, 124.7, 122.8, 119.0, 114.5, 113.9, 107.8, 107.4, 101.3, 97.7, 95.2, 84.5, 55.0, 38.5. IR (neat): ν/ cm^{-1} = 2898, 1639, 1539, 1437, 1240, 1090, 1031, 745. HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{22}NO_4$: 412.1543, found: 412.1541.

(1*E*,4*E*)-1-(Methyl(2-(phenylethynyl)phenyl)amino)-5-phenylpenta-1,4-dien-3-one (1at):



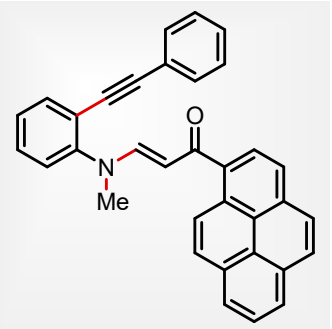
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (350.6 mg, 64%). R_f value = 0.23 (25% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) *δ*/ ppm = 8.11 (d, *J* = 12.8 Hz, 1H), 7.65 (d, *J* = 15.8 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.53 – 7.46 (m, 4H), 7.31 – 7.25 (m, 7H), 7.20 (s, 1H), 7.14 (d, *J* = 6.0 Hz, 1H), 6.92 (d, *J* = 14.1 Hz, 1H), 5.65 (s, 1H), 3.36 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ*/ ppm = 186.7, 151.0, 148.0, 139.1, 135.2, 133.3, 131.2, 129.2, 129.16, 128.4, 128.1, 127.6, 127.1, 126.0, 124.4, 122.3, 118.5, 108.7, 100.1, 95.0, 85.6, 38.3. IR (neat): ν/ cm^{-1} = 3054, 1606, 1531, 1443, 1328, 1083, 976, 734. HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{22}NO$: 364.1696, found: 364.1696.

(*E*)-1-(Anthracen-9-yl)-3-(methyl(2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1au):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (337.0 mg, 57%). R_f value = 0.34 (25% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) *δ*/ ppm = 8.40 (s, 1H), 8.11 (s, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.55 (s, 3H), 7.41 (s, 6H), 7.33 (s, 3H), 7.15 (s, 2H), 6.03 (s, 1H), 3.38 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) *δ*/ ppm = 183.1, 149.8, 148.1, 143.7, 134.1, 133.5, 131.6, 131.2, 129.3, 128.8, 128.5, 128.3, 127.2, 126.8, 26.0, 125.9, 125.2, 122.7, 119.5, 116.2, 109.0, 95.3, 94.9, 85.4, 38.8. IR (neat): ν/ cm^{-1} = 2921, 1640, 1536, 1332, 1220, 1090, 735. HRMS: *m/z* $[M+H]^+$ calcd for $C_{32}H_{24}NO$: 438.1852, found: 438.1853.

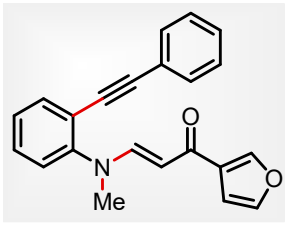
(*E*)-3-(Methyl(2-(phenylethynyl)phenyl)amino)-1-(pyren-2-yl)prop-2-en-1-one (1av):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (384.1 mg, 55%). R_f value = 0.15 (20% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) *δ*/ ppm = 8.68 (d, *J* = 8.1 Hz, 1H), 8.16 (t, *J* = 7.2 Hz, 3H), 8.12 – 7.96 (m, 6H), 7.63 – 7.59 (m, 2H), 7.50 (s, 1H), 7.40 – 7.37 (m, 3H), 7.22 – 7.08 (m, 3H), 6.13 (d, *J* = 10.9 Hz, 1H), 3.40 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) *δ*/ ppm = 194.6, 153.6, 148.1, 136.6, 133.4, 131.9, 131.4, 131.0, 130.6, 129.3, 128.7, 128.4, 128.0, 127.1, 125.9, 125.3, 125.27, 125.2, 125.1, 124.7, 124.4, 124.0, 122.6, 118.9, 102.4, 95.1, 85.6, 38.6. IR (neat): ν/ cm^{-1} = 2921,

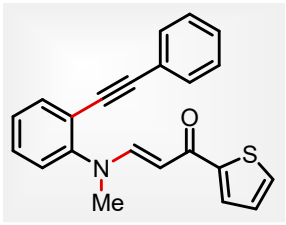
1643, 1538, 1337, 1273, 1041, 746. HRMS: *m/z* $[M+H]^+$ calcd for $C_{34}H_{24}NO$: 462.852, found: 462.859.

(*E*)-1-(Furan-3-yl)-3-(methyl(2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1aw):



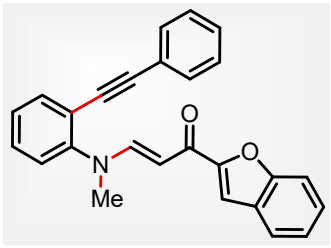
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (321.1 mg, 65%). R_f value = 0.24 (20% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.15 (d, J = 12.5 Hz, 1H), 7.56 (d, J = 6.1 Hz, 1H), 7.51 (s, 1H), 7.49 – 7.45 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.27 (m, 3H), 7.24 – 7.13 (m, 3H), 6.48 (s, 1H), 6.05 (s, 1H), 3.42 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 177.9, 154.5, 151.6, 144.5, 133.6, 131.5, 129.4, 128.6, 128.3, 126.4, 124.9, 122.6, 119.0, 116.1, 114.1, 111.9, 108.9, 95.2, 85.7, 38.7. IR (neat): ν/ cm^{-1} = 2910, 1639, 1538, 1462, 1278, 1059, 749. HRMS: *m/z* $[M+H]^+$ calcd for $C_{22}H_{18}NO_2$: 328.1332, found: 328.1320.

(*E*)-3-(Methyl(2-(phenylethynyl)phenyl)amino)-1-(thiophen-2-yl)prop-2-en-1-one (1ax):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (316.8 mg, 61%). R_f value = 0.23 (25% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.11 (d, J = 12.1 Hz, 1H), 7.68 (s, 1H), 7.55 (d, J = 6.7 Hz, 1H), 7.47 – 7.43 (m, 3H), 7.31 (d, J = 7.0 Hz, 1H), 7.28 – 7.24 (m, 3H), 7.23 (s, 1H), 7.17 (d, J = 5.6 Hz, 1H), 7.06 (s, 1H), 5.97 (s, 1H), 3.41 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ/ ppm = 181.4, 151.7, 148.3, 147.1, 133.6, 131.5, 130.9, 129.4, 129.0, 128.6, 128.4, 127.6, 126.5, 125.0, 122.6, 119.1, 95.6, 95.3, 85.7, 38.8. IR (neat): ν/ cm^{-1} = 2920, 1627, 1534, 1413, 1276, 1054, 759. HRMS: *m/z* $[M+H]^+$ calcd for $C_{22}H_{18}NOS$: 344.1104, found: 344.1107.

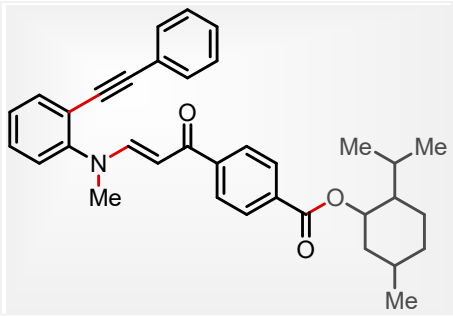
(*E*)-1-(Benzofuran-2-yl)-3-(methyl(2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1ay):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (342.5 mg, 60%). R_f value = 0.22 (20% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.25 (d, J = 12.0 Hz, 1H), 7.60 (s, 1H), 7.47 (s, 5H), 7.34 (s, 1H), 7.22 (s, 5H), 7.09 (s, 2H), 6.23 (d, J = 10.9 Hz, 1H), 3.38 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 178.6, 154.9, 151.8, 147.9, 133.3, 131.2, 129.2,

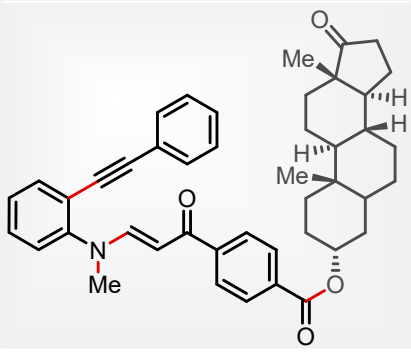
128.4, 128.1, 127.5, 126.5, 126.3, 124.5, 123.1, 122.3, 122.26, 118.5, 111.7, 109.5, 95.4, 95.1, 85.4, 38.5. IR (neat): ν/ cm^{-1} = 3085, 1631, 1535, 1452, 1339, 1278, 1071, 743. HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{20}NO_2$: 378.1489, found: 378.1496.

(*E*)-2-Isopropyl-5-methylcyclohexyl 4-(3-(methyl(2-(phenylethynyl)phenyl)amino)-acryloyl)benzoate (1az):



The title compound was prepared following **GP-3** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as reddish yellow gummy liquid (278.9 mg, 54%). R_f value = 0.09 (10% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) *δ*/ ppm = 8.14 (d, *J* = 12.3 Hz, 1H), 8.09 (d, *J* = 5.7 Hz, 2H), 7.97 (s, 2H), 7.58 (d, *J* = 5.6 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.36 (s, 1H), 7.31 – 7.28 (m, 4H), 7.21 (d, *J* = 5.9 Hz, 1H), 6.07 (d, *J* = 10.9 Hz, 1H), 4.98 – 4.92 (m, 1H), 3.45 (s, 3H), 2.13 (d, *J* = 11.8 Hz, 1H), 1.96 (s, 1H), 1.73 (d, *J* = 11.8 Hz, 2H), 1.56 (s, 2H), 1.25 (s, 1H), 1.16 – 1.09 (m, 2H), 0.92 (t, *J* = 4.7 Hz, 6H), 0.80 (d, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) *δ*/ ppm = 188.7, 165.6, 153.1, 148.4, 143.9, 133.7, 132.8, 131.5, 129.4, 128.7, 128.4, 127.5, 126.6, 124.9, 122.6, 119.2, 96.2, 95.3, 85.6, 75.1, 47.2, 40.9, 38.9, 34.3, 31.4, 26.5, 23.7, 22.0, 20.7, 16.6. IR (neat): ν/ cm^{-1} = 2919, 1656, 1501, 1440, 1255, 1033, 751. HRMS: *m/z* $[M+Na]^+$ calcd for $C_{35}H_{37}NO_3Na$: 542.2666, found: 542.2666.

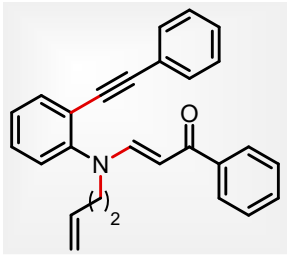
(3*R*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*E*)-3-(methyl(2-(phenylethynyl)phenyl)amino)-acryloyl)benzoate (1ba):



The title compound was prepared following **GP-3** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as reddish yellow gummy liquid (379.4 mg, 58%). R_f value = 0.31 (20% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) *δ*/ ppm = 8.12 (d, *J* = 12.1 Hz, 1H), 8.06 (d, *J* = 5.8 Hz, 2H), 7.94 (s, 2H), 7.59 (d, *J* = 5.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 6.2 Hz, 4H), 7.22 (s, 1H), 6.06 (d, *J* = 10.1 Hz, 1H), 4.98 – 4.92 (m, 1H), 3.46 (s, 3H), 2.43 (dd, *J* = 19.2, 8.7 Hz, 1H), 2.11 – 2.02 (m, 1H),

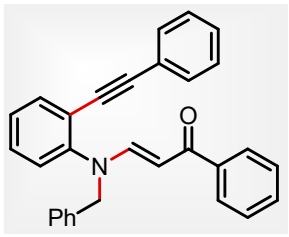
1.99 – 1.91 (m, 2H), 1.80 (d, J = 14.6 Hz, 4H), 1.67 (d, J = 12.0 Hz, 2H), 1.58 – 1.48 (m, 3H), 1.36 (s, 1H), 1.28 (d, J = 5.9 Hz, 2H), 1.25 (s, 3H), 1.11 (t, J = 12.3 Hz, 1H), 1.04 – 0.95 (m, 1H), 0.90 (s, 3H), 0.86 (s, 3H), 0.75 (t, J = 10.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 188.8, 165.7, 153.1, 143.9, 133.7, 132.9, 131.6, 132.9, 131.6, 129.5, 128.8, 128.4, 127.5, 126.8, 125.0, 122.7, 96.2, 95.4, 74.4, 54.4, 51.4, 47.8, 44.8, 36.8, 35.9, 35.7, 35.1, 34.1, 31.6, 30.9, 28.3, 27.5, 21.8, 20.5, 13.8, 12.3, 1.02. IR (neat): ν/ cm^{-1} = 2920, 1717, 1540, 1498, 1262, 1012, 753. HRMS: m/z $[M+H]^+$ calcd for $C_{44}H_{48}NO_4$: 654.3578, found: 654.3582.

(*E*)-3-(But-3-en-1-yl(2-(phenylethynyl)phenyl)amino)-1-phenylprop-2-en-1-one (1bb):



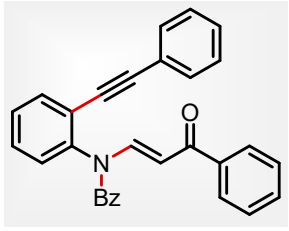
The title compound was prepared following **GP-2** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (340.3 mg, 60%). R_f value = 0.35 (20% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.05 (d, J = 12.4 Hz, 1H), 7.92 – 7.79 (m, 2H), 7.63 (s, 1H), 7.53 – 7.46 (m, 3H), 7.44 – 7.34 (m, 4H), 7.32 – 7.26 (m, 5H), 5.84 – 5.74 (m, 1H), 5.11 (d, J = 17.2 Hz, 1H), 5.07 (d, J = 10.2 Hz, 1H), 3.89 (s, 2H), 2.45 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.1, 152.4, 139.9, 135.2, 134.0, 133.3, 131.2, 131.0, 130.8, 129.2, 128.4, 128.1, 127.8, 127.3, 122.2, 117.1, 95.2, 95.0, 85.4, 56.6, 50.5, 42.0, 33.1. IR (neat): ν/ cm^{-1} = 3025, 1719, 1537, 1273, 1187, 1105, 1055, 763. HRMS: m/z $[M+H]^+$ calcd for $C_{27}H_{24}NO$: 378.1852, found: 378.1860.

(*E*)-3-(But-3-en-1-yl(2-(phenylethynyl)phenyl)amino)-1-phenylprop-2-en-1-one (1bc):



The title compound was prepared following **GP-2** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (398.9 mg, 64%). R_f value = 0.54 (20% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.26 (d, J = 12.8 Hz, 1H), 7.81 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 6.3 Hz, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.0 Hz, 1H), 7.37 (t, J = 7.4 Hz, 4H), 7.34 – 7.26 (m, 8H), 7.20 (s, 1H), 6.12 (s, 1H), 5.05 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.6, 152.4, 147.4, 140.0, 135.7, 133.7, 131.5, 131.1, 129.3, 128.6, 128.3, 128.1, 127.6, 127.2, 126.8, 125.3, 122.5, 97.0, 95.4, 85.8, 55.0. IR (neat): ν/ cm^{-1} = 3056, 1643, 1535, 1446, 1281, 1200, 1043, 753. HRMS: m/z $[M+H]^+$ calcd for $C_{30}H_{24}NO$: 414.1852, found: 414.1858.

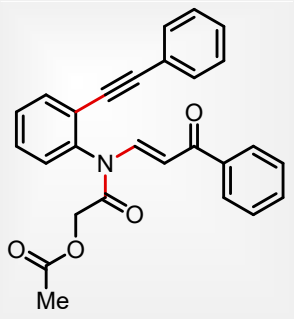
(*E*)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)-*N*-(2-(phenylethynyl)phenyl)benzamide (1bd):



The title compound was prepared following **GP-2** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as reddish yellow gummy liquid (395.4 mg, 62%). R_f value = 0.16 (20% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.86 (d, J = 13.7 Hz, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.1 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.50 - 7.44 (m, 2H), 7.42 (s, 1H), 7.40 (d, J = 7.7 Hz, 3H), 7.38 – 7.34 (m, 4H), 7.28 (t, J = 7.5 Hz, 2H), 6.09 (d, J = 13.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ/ ppm = 190.4, 170.1, 144.1, 139.9, 138.4, 133.9, 133.3, 132.2, 131.6, 131.1, 129.5, 129.1, 129.0, 128.9, 128.7, 128.4, 128.3, 128.0, 127.9, 122.9, 122.1, 107.4, 95.5,

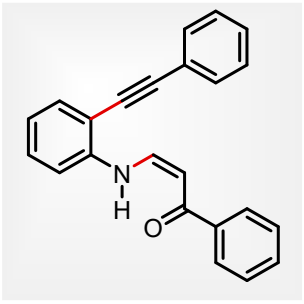
84.8. IR (neat): ν/ cm^{-1} = 3067, 1680, 1560, 1448, 1263, 1160, 1017, 753. HRMS: *m/z* $[M+Na]^+$ calcd for $C_{30}H_{21}NO_2Na$: 450.1465, found: 450.1467.

(*E*)-2-Oxo-2-((3-oxo-3-phenylprop-1-en-1-yl)(2-(phenylethynyl)phenyl)amino)ethyl acetate (1be):



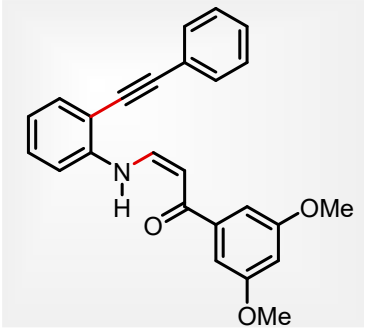
The title compound was prepared following **GP-2** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as reddish yellow gummy liquid (362.8 mg, 57%). R_f value = 0.21 (20% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) *δ*/ ppm = 8.77 (d, *J* = 14.0 Hz, 1H), 7.79 – 7.75 (m, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.49 – 7.43 (m, 3H), 7.44 – 7.40 (m, 1H), 7.37 – 7.31 (m, 5H), 5.81 (d, *J* = 14.0 Hz, 1H), 4.52 (dd, *J* = 34.5, 15.7 Hz, 2H), 2.13 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ*/ ppm = 190.8, 170.1, 166.2, 141.7, 138.4, 137.3, 133.7, 132.3, 131.9, 130.33, 130.3, 129.2, 129.0, 128.5, 128.4, 128.2, 123.4, 121.7, 108.1, 96.4, 83.3, 61.9, 20.4. IR (neat): ν/ cm^{-1} = 3074, 1631, 1535, 1339, 1278, 1138, 1071, 742. HRMS: *m/z* $[M+Na]^+$ calcd for $C_{27}H_{21}NO_4Na$: 446.1363, found: 446.1364.

(*E*)-1-Phenyl-3-((2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1bf):



The title compound was prepared following **GP-2** without protection of nitrogen, using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow solid (378.6 mg, 78%). M.P. = 121 - 122°C. R_f value = 0.84 (25% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) *δ*/ ppm = 12.74 (d, *J* = 12.1 Hz, 1H), 7.99 (t, *J* = 6.7 Hz, 4H), 7.62 – 7.53 (m, 2H), 7.53 – 7.44 (m, 3H), 7.44 – 7.35 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.03 (td, *J* = 7.5, 0.9 Hz, 1H), 6.13 (d, *J* = 8.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) *δ*/ ppm = 190.7, 142.8, 141.7, 139.3, 132.7, 132.3, 131.6, 129.5, 128.5, 128.4, 128.37, 127.5, 123.1, 122.7, 112.6, 112.5, 97.0, 94.9, 84.6. IR (neat): ν/ cm^{-1} = 3050, 1631, 1583, 1456, 1236, 1016, 750. HRMS: *m/z* $[M+Na]^+$ calcd for $C_{23}H_{17}NONa$: 346.1202, found: 346.1200.

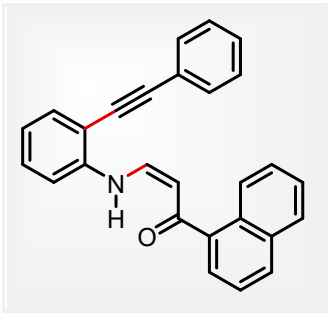
(*E*)-1-(3,5-dimethoxyphenyl)-3-((2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1bg):



The title compound was prepared following **GP-2** without protection of nitrogen, using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow solid (465.9 mg, 81%). M.P. = 124 - 125°C. R_f value = 0.72 (25% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) *δ*/ ppm = 12.82 (d, *J* = 12.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.54 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.50 (dd, *J* = 12.2, 8.0 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 2.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.64 (t, *J* = 2.2 Hz, 1H), 6.04 (d, *J* = 7.9 Hz, 1H), 3.86 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ*/ ppm = 189.7, 160.5, 142.7, 141.4, 141.0, 132.3, 132.1, 129.4, 128.3, 128.1, 122.9, 122.4, 112.3, 112.0, 105.1, 103.6, 96.8, 94.6, 84.6, 55.2. IR

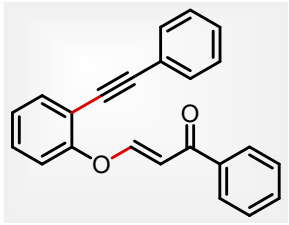
(neat): ν/ cm^{-1} = 1640, 1502, 1326, 1194, 1009, 766. HRMS: *m/z* $[M+H]^+$ calcd for $C_{25}H_{22}NO_3$: 384.1594, found: 384.1597.

(*E*)- 1-(naphthalen-1-yl)-3-((2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (1bh):



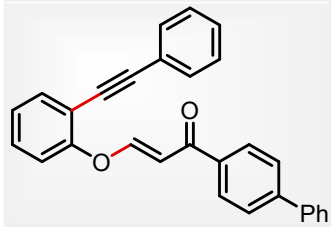
The title compound was prepared following **GP-2** without protection of nitrogen, using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow solid (442.4 mg, 79%). M.P. = 119 - 120°C. R_f value = 0.77 (25% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) *δ*/ ppm = 12.81 (d, *J* = 12.1 Hz, 1H), 8.49 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.90 (dd, *J* = 17.4, 8.5 Hz, 2H), 7.62 (dd, *J* = 12.2, 8.1 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.36 – 7.30 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.76 – 6.71 (m, 1H), 6.28 (d, *J* = 7.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) *δ*/ ppm = 190.5, 147.8, 142.8, 141.7, 136.6, 135.0, 132.7, 132.3, 131.5, 129.8, 129.6, 129.4, 128.5, 128.4, 128.3, 127.8, 126.4, 124.2, 123.1, 122.7, 118.0, 114.4, 112.6, 108.0, 97.0, 95.1, 85.9, 84.7. IR (neat): ν/ cm^{-1} = 1589, 1468, 1262, 1196, 1069, 730, 698. HRMS: *m/z* $[M+H]^+$ calcd for $C_{27}H_{20}NO$: 374.1539, found: 374.1542.

(*E*)-1-Phenyl-3-(2-(phenylethynyl)phenoxy)prop-2-en-1-one (35a):



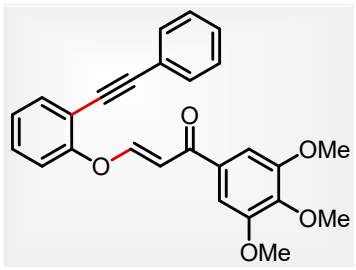
The title compound was prepared following **GP-4** using 2-iodo phenol (330 mg, 1.5 mmol); obtained as yellow gummy liquid (312.8 mg, 64%). R_f value = 0.59 (15% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) *δ*/ ppm = 8.01 (d, *J* = 11.8 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 5.1 Hz, 3H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 11.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) *δ*/ ppm = 190.5, 161.1, 156.3, 138.5, 133.8, 132.6, 131.7, 129.9, 128.7, 128.6, 128.2, 125.4, 122.9, 118.9, 115.6, 106.9, 95.3, 84.0. IR (neat): ν/ cm^{-1} = 3070, 1664, 1561, 1442, 1213, 1014, 746. HRMS: *m/z* $[M+H]^+$ calcd for $C_{23}H_{17}O_2$: 325.1223, found: 325.1222.

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(2-(phenylethynyl)phenoxy)prop-2-en-1-one (35b):



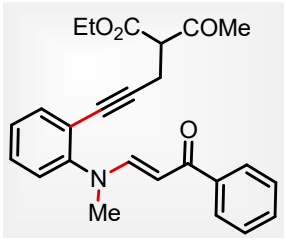
The title compound was prepared following **GP-4** using 2-iodo phenol (330 mg, 1.5 mmol); obtained as yellow gummy liquid (367.3 mg, 61%). R_f value = 0.50 (10% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) *δ*/ ppm = 8.07 (d, *J* = 11.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.66 – 7.60 (m, 3H), 7.58 – 7.53 (m, 2H), 7.48 (t, *J* = 7.1 Hz, 2H), 7.45 – 7.35 (m, 3H), 7.35 – 7.32 (m, 2H), 7.26 – 7.20 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 11.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ*/ ppm = 189.9, 160.8, 156.2, 145.3, 139.9, 137.0, 133.7, 131.6, 129.9, 128.9, 128.7, 128.6, 128.4, 128.1, 127.2, 127.1, 125.3, 122.8, 120.3, 118.7, 115.4, 114.8, 106.7, 95.2, 84.0. IR (neat): ν/ cm^{-1} = 3057, 1661, 1564, 1478, 1194, 1029, 749. HRMS: *m/z* $[M+Na]^+$ calcd for $C_{29}H_{20}O_2Na$: 423.1356, found: 423.1355.

(*E*)-3-(2-(Phenylethynyl)phenoxy)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (35c):



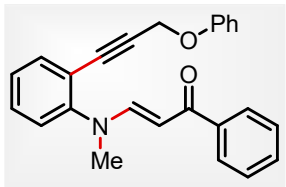
The title compound was prepared following **GP-4** using 2-iodo phenol (330 mg, 1.5 mmol); obtained as yellow gummy liquid (385.0 mg, 62%). R_f value = 0.22 (15% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 7.98 (d, J = 11.8 Hz, 1H), 7.59 (dd, J = 7.7, 1.6 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.41 – 7.35 (m, 1H), 7.34 – 7.28 (m, 3H), 7.25 – 7.20 (m, 2H), 7.17 (s, 2H), 6.74 (d, J = 11.8 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.2, 160.7, 156.3, 153.0, 142.2, 133.7, 133.6, 131.6, 129.9, 128.7, 128.3, 125.3, 122.7, 118.7, 115.4, 106.6, 105.6, 95.2, 83.9, 60.9, 56.3. IR (neat): ν/ cm^{-1} = 3056, 1662, 1564, 1477, 1205, 1030, 745. HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{26}H_{22}O_5Na$: 437.1359, found: 437.1362.

(*E*)-Ethyl 2-acetyl-5-(2-(methyl(3-oxo-3-phenylprop-1-en-1-yl)amino)phenyl)pent-4-ynoate (1bi):



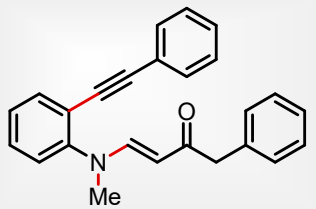
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); with a modification like the alkyne used in step 1 was prepared from propargyl bromide and ethylacetoacetate. **1bi** was obtained as yellow gummy liquid (351.5 mg, 58%). R_f value = 0.29 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.01 (d, J = 11.8 Hz, 1H), 7.92 (s, 2H), 7.38 (s, 4H), 7.25 (s, 1H), 7.13 (s, 1H), 7.09 (s, 1H), 6.03 (s, 1H), 4.16 – 4.08 (m, 2H), 3.76 (s, 1H), 3.29 (s, 3H), 2.88 (t, J = 6.5 Hz, 2H), 2.22 (s, 3H), 1.16 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 200.9, 188.8, 167.8, 152.1, 139.8, 133.5, 131.0, 129.0, 128.0, 127.4, 126.1, 124.6, 118.6, 115.5, 108.5, 98.1, 95.3, 92.1, 61.5, 57.7, 38.4, 29.3, 18.2, 13.8. IR (neat): ν/ cm^{-1} = 2973, 1737, 1642, 1537, 1489, 1335, 1276, 1042, 163. HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{25}H_{25}NO_4Na$: 426.1676, found: 426.1674.

(*E*)-3-(Methyl(2-(3-phenoxyprop-1-yn-1-yl)phenyl)amino)-1-phenylprop-2-en-1-one (1bj):



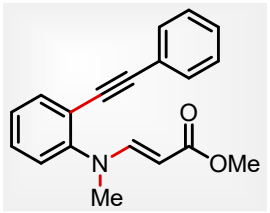
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); with a modification like the alkyne used in step 1 was prepared from propargyl bromide and phenol. **1bj** was obtained as yellow gummy liquid (312.4 mg, 57%). R_f value = 0.16 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 7.97 (s, 5H), 7.47 (s, 5H), 7.29 (d, J = 7.0 Hz, 2H), 7.02 – 6.93 (m, 3H), 6.00 (s, 1H), 4.92 (s, 2H), 3.22 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.1, 157.4, 152.5, 140.2, 140.0, 139.9, 133.8, 131.1, 129.8, 129.4, 128.1, 127.6, 127.2, 121.4, 114.9, 98.2, 95.7, 90.0, 83.4, 56.2, 38.5. IR (neat): ν/ cm^{-1} = 3055, 1642, 1536, 1489, 1333, 1273, 1018, 753. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{25}H_{22}NO_2$: 368.1645, found: 368.1649.

(*E*)-4-(Methyl(2-(phenylethynyl)phenyl)amino)-1-phenylbut-3-en-2-one (1bk):



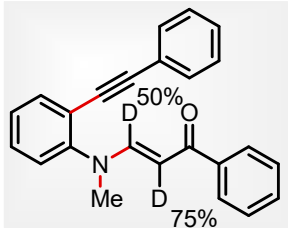
The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as yellow gummy liquid (328.5 mg, 62%). R_f value = 0.27 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 7.95 (d, J = 12.4 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 7.8 Hz, 2H), 7.35 – 7.31 (m, 5H), 7.28 (s, 3H), 7.24 (s, 2H), 7.12 (d, J = 7.9 Hz, 1H), 5.41 (d, J = 7.5 Hz, 1H), 3.74 (s, 2H), 3.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ ppm = 195.8, 151.2, 140.7, 136.5, 133.7, 131.5, 129.4, 129.3, 128.7, 128.5, 128.4, 126.4, 124.8, 122.7, 99.2, 95.2, 85.8, 48.7, 38.5. IR (neat): ν/ cm^{-1} = 3025, 1656, 1545, 1493, 1331, 1275, 1088, 752. HRMS: *m/z* $[M+Na]^+$ calcd for $C_{25}H_{21}NONa$: 374.1515, found: 374.1511.

(*E*)-Methyl 3-(methyl(2-(phenylethynyl)phenyl)amino)acrylate (1bl):



The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); obtained as gummy liquid (257.8 mg, 59%). R_f value = 0.72 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 7.90 (d, J = 13.2 Hz, 1H), 7.55 (dd, J = 7.7, 1.5 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.35 – 7.30 (m, 4H), 7.20 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 8.00 Hz, 1H), 4.90 (d, J = 11.5 Hz, 1H), 3.68 (s, 3H), 3.30 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 169.4, 151.0, 133.6, 131.4, 129.3, 128.6, 128.3, 125.9, 124.8, 122.8, 116.2, 108.9, 95.1, 88.7, 86.0, 50.6, 38.6. IR (neat): ν/ cm^{-1} = 1734, 1562, 1515, 1368, 1218, 1010, 743. HRMS: *m/z* $[M+Na]^+$ calcd for $C_{19}H_{17}NO_2Na$: 314.1151, found: 314.1155.

Deuterated (*E*)-3-(methyl(2-(phenylethynyl)phenyl)amino)-1-phenylprop-2-en-1-one (1aa-D):

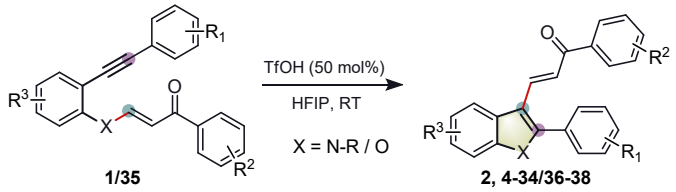


The title compound was prepared following **GP-1** using 2-iodo aniline (330 mg, 1.5 mmol); using methanol-D_4 as solvent in step-3. **1aa-D** was obtained as yellow solid (238.5 mg, 70%). M.P. = 118 - 119°C. R_f value = 0.35 (25% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.13 (s, 0.5H), 7.94 (s, 2H), 7.59 (d, J = 5.3 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.43 (s, 2H), 7.37 (s, 1H), 7.32 – 7.26 (m, 4H), 7.23 (s, 1H), 6.09 (s, 0.25H), 3.46 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.6, 152.5, 140.3, 133.7, 131.6, 131.2, 129.5, 128.7, 128.4, 128.2, 127.7, 126.5, 125.2, 122.7, 96.3, 95.3, 85.8, 39.1. IR (neat): ν/ cm^{-1} = 3060, 1626, 1519, 1446, 1272, 1052, 921, 751. HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}NOD_2$: 339.1592, found: 339.1595.

ESI-6 Synthesis of functionalized indoles and benzofurans promoted by TfOH:

General Procedure 5 (GP-5):

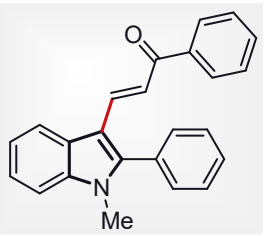
To a mixture of **1**/**35** (1 equiv.) in HFIP (0.1 M), 50 mol% TfOH was added under nitrogen atmosphere. Then the reaction mixture was stirred for 3-5 hrs. After the completion of the reaction as mentioned by the TLC, the reaction mixture was quenched with a saturated $NaHCO_3$ solution. Then it was extracted using ethyl acetate and water. The combined organic layers was washed with saturated brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (using silica gel, EtOAc/hexanes eluent) to get the corresponding functionalized indole/benzofurans derivative in an analytically pure form.



Scheme S5. Preparation of functionalized indoles/benzofurans **2, 4-34**/**36-38**.

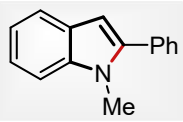
ESI-7 Analytical data of the synthesized multifunctionalized indoles and benzofurans:

(*E*)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)-1-phenylprop-2-en-1-one (2, Scheme 2):



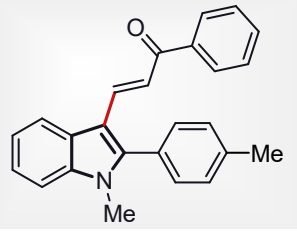
The title compound was prepared following **GP-5** using **1aa** (67.5 mg, 0.2 mmol); obtained as yellow solid (61.4 mg, 91%). M.P. = 179 - 180°C. R_f value = 0.44 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.15-8.10 (m, 1H), 8.02 (d, J = 8.1 Hz, 2H), 7.97 (dd, J = 15.2, 2.1 Hz, 1H), 7.62 (d, J = 15.5 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.42 – 7.38 (m, 2H), 3.66 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 190.5, 146.9, 139.4, 139.2, 138.1, 132.0, 130.9, 129.9, 129.4, 128.7, 128.4, 128.2, 125.7, 123.2, 122.0, 120.9, 117.3, 111.4, 110.3, 31.3. IR (neat): ν/ cm^{-1} = 1580, 1560, 1365, 1152, 1128, 1011, 698, 671. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{24}H_{20}NO$: 338.1539, found: 338.1537.

1-Methyl-2-phenyl-1*H*-indole (3):



^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.45 – 8.41 (m, 1H), 7.84 – 7.80 (m, 2H), 7.57 – 7.52 (m, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.39 – 7.33 (m, 3H), 3.85 (s, 3H).

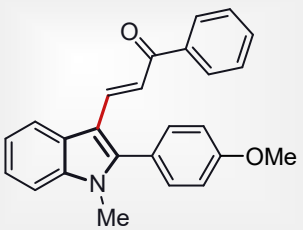
(*E*)-3-(1-Methyl-2-(*p*-tolyl)-1*H*-indol-3-yl)-1-phenylprop-2-en-1-one (4, Scheme 2):



The title compound was prepared following **GP-5** using **1ab** (70.3 mg, 0.2 mmol); obtained as yellow solid (62.6 mg, 89%). M.P. = 182 - 183°C. R_f value = 0.31 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.14 – 8.10 (m, 1H), 8.03 (d, J = 7.0 Hz, 2H), 7.98 (d, J = 15.5 Hz, 1H), 7.62 (d, J = 15.5 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H),7.49 (t, J = 7.0 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.40 (d,

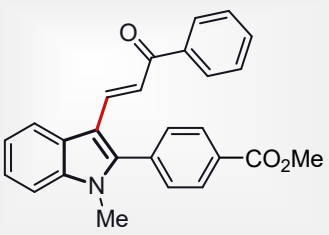
J = 2.9 Hz, 1H), 7.39 – 7.30 (m, 5H), 3.66 (s, 3H), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ/ ppm = 190.4, 147.3, 139.6, 139.4, 139.3, 139.1, 132.0, 130.8, 129.5, 128.4, 128.2, 126.9, 125.7, 123.1, 121.9, 120.8, 117.0, 111.3, 110.3, 31.2, 21.4. IR (neat): ν/ cm^{-1} = 1652, 1558, 1222, 1176, 1012, 805, 701. HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}NO$: 352.1696, found: 352.1696.

(*E*)-3-(2-(4-Methoxyphenyl)-1-methyl-1*H*-indol-3-yl)-1-phenylprop-2-en-1-one (5, Scheme 2):



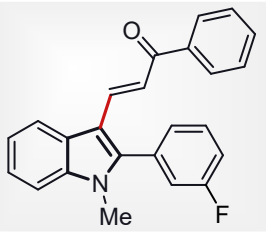
The title compound was prepared following **GP-5** using **1ac** (73.5 mg, 0.2 mmol); obtained as yellow solid (67.6 mg, 92%). M.P. = 171 - 172°C. R_f value = 0.59 (20% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.12 – 8.08 (m, 1H), 8.02 (d, J = 7.0 Hz, 2H), 7.96 (d, J = 15.5 Hz, 1H), 7.60 (d, J = 15.5 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.39 – 7.34 (m,4H), 7.08 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H), 3.66 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 190.5, 160.5, 147.2, 139.7, 139.4, 138.1, 132.3, 132.0, 128.4, 128.3, 125.8, 123.1, 122.0, 121.97, 120.8, 117.0, 114.3, 111.4, 110.3, 55.5, 31.3. IR (neat): ν/ cm^{-1} = 1712, 1557, 1468, 1270, 1115, 1011, 745. HRMS: *m/z* $[M+H]^+$ calcd for $C_{25}H_{22}NO_2$: 368.1645, found: 368.1643.

(*E*)-Methyl 4-(1-methyl-3-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-2-yl)benzoate (6, Scheme 2):



The title compound was prepared following **GP-5** using **1ad** (79.1 mg, 0.2 mmol); obtained as yellow solid (64.9 mg, 82%). M.P. = 184 - 185°C. R_f value = 0.34 (20% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.23 (d, J = 8.1 Hz, 2H), 8.12 (d, J = 7.3 Hz, 1H), 8.00 (d, J = 7.5 Hz, 2H), 7.89 (d, J = 15.5 Hz, 1H), 7.63 (d, J = 15.5 Hz, 1H), 7.53 (d, J = 8.0 Hz, 3H), 7.51 – 7.44 (m, 3H), 7.44 – 7.36 (m, 2H), 3.99 (s, 3H), 3.68 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 190.4, 166.5, 145.2, 139.1, 138.7, 138.4, 134.6, 132.2, 131.1, 130.9, 130.0, 128.5, 128.3, 125.7, 123.7, 122.2, 121.1, 118.2, 111.9, 110.4, 52.5, 31.5. IR (neat): ν/ cm^{-1} = 1735, 1562, 1515, 1342, 1219, 1010, 743. HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{22}NO_3$: 396.1594, found: 396.1598.

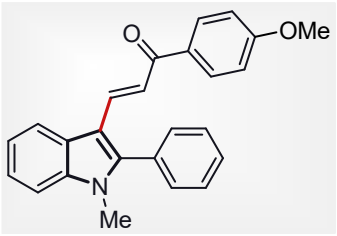
(*E*)-3-(2-(3-Fluorophenyl)-1-methyl-1*H*-indol-3-yl)-1-phenylprop-2-en-1-one (7, Scheme 2):



The title compound was prepared following **GP-5** using **1ae** (71.1 mg, 0.2 mmol); obtained as yellow solid (61.8 mg, 87%). M.P. = 163 - 164°C. R_f value = 0.48 (10% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.11 (d, J = 6.9 Hz, 1H), 8.01 (d, J = 7.0 Hz, 2H), 7.90 (d, J = 15.6 Hz, 1H), 7.62 (d, J = 15.6 Hz, 1H), 7.57 - 7.52 (m, 2H), 7.51 – 7.46 (m, 2H), 7.46 – 7.44 (m, 1H), 7.42 – 7.36 (m, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.16 (dt, J = 9.1, 2.0 Hz, 1H), 3.67 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz,

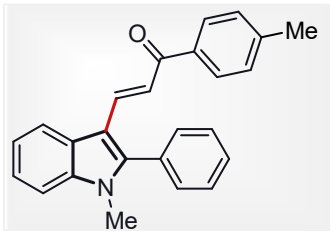
$CDCl_3$) δ/ ppm = 190.6, 162.7 (d, J = 248.2 Hz), 145.0, 138.8, 138.7 (d, J = 96.3 Hz), 132.2, 132.0, 130.5 (d, J = 8.5 Hz), 128.7, 128.4 (d, J = 21.1 Hz), 128.1, 127.0, 125.6, 123.6, 122.2, 121.0, 118.0, 118.0 (d, J = 21.8 Hz), 116.6 (d, J = 20.8 Hz), 111.7, 110.4, 31.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ/ ppm = -111.6. IR (neat): ν/ cm^{-1} = 1738, 1555, 1444, 1177, 1215, 1012, 741. HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}FNO$: 356.1445, found: 356.1446.

(*E*)-1-(4-Methoxyphenyl)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (8, Scheme 2):



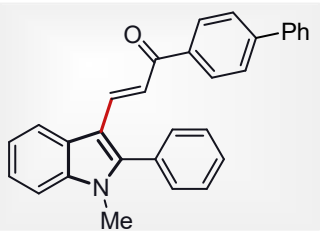
The title compound was prepared following **GP-5** using **1af** (73.5 mg, 0.2 mmol); obtained as yellow solid (66.9 mg, 91%). M.P. = 181 - 182°C. R_f value = 0.68 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.14 – 8.10 (m, 1H), 8.03 (d, J = 8.6 Hz, 2H), 7.94 (d, J = 15.5 Hz, 1H), 7.62 (d, J = 15.5 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.44 (d, J = 8.0 Hz, 3H), 7.42 - 7.37 (m, 2H), 6.98 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H), 3.66 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 188.8, 162.9, 146.5, 138.5, 138.1, 132.1, 131.0, 130.4, 130.1, 129.3, 128.8, 125.8, 123.2, 121.9, 120.8, 117.3, 113.7, 111.4, 110.3, 55.4, 31.2. IR (neat): ν/ cm^{-1} = 1646, 1598, 1461, 1369, 1282, 1160, 787, 696. HRMS: *m/z* $[M+H]^+$ calcd for $C_{25}H_{22}NO_2$: 368.1645, found: 368.1645.

(*E*)-3-(1-Methyl-2-phenyl-1*H*-indol-3-yl)-1-(*p*-tolyl)prop-2-en-1-one (9, Scheme 2):



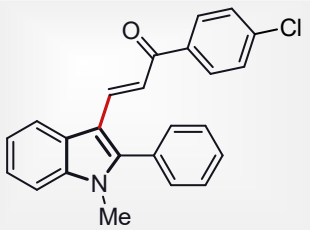
The title compound was prepared following **GP-5** using **1ag** (70.3 mg, 0.2 mmol); obtained as yellow solid (64.7 mg, 92%). M.P. = 178 - 179°C. R_f value = 0.61 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.15 – 8.10 (m, 1H), 8.00 – 7.92(m, 3H), 7.62 (d, J = 15.5 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.46 – 7.42 (m, 3H), 7.42 – 7.37 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.65 (s, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 189.9, 146.6, 142.7, 138.9, 138.1, 136.6, 130.9, 130.0, 129.3, 129.1, 128.7, 128.3, 125.7, 123.2, 121.9, 120.8, 117.3, 111.4, 110.3, 31.2, 21.6. IR (neat): ν/ cm^{-1} = 1649, 1558, 1362, 1277, 1176, 805, 701. HRMS: *m/z* $[M+H]^+$ calcd for $C_{25}H_{22}NO$: 352.1696, found: 352.1696.

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (10, Scheme 2):



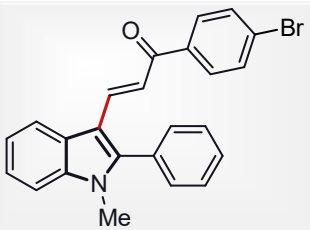
The title compound was prepared following **GP-5** using **1aj** (82.7 mg, 0.2 mmol); obtained as yellow solid (74.4 mg, 90%). M.P. = 188 - 189°C. R_f value = 0.39 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.19 – 8.15 (m, 1H), 8.12 (d, J = 8.2 Hz, 2H), 8.03 (d, J = 15.5 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.71 – 7.66 (m, 3H), 7.60 – 7.54 (m, 3H), 7.53 – 7.41 (m, 8H), 3.66 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 189.8, 146.9, 144.7, 140.1, 139.3, 138.1, 137.9, 130.9, 129.9, 129.3, 128.9, 128.8, 128.7, 128.0, 127.2, 127.1, 125.7, 123.2, 122.0, 120.9, 117.1, 111.4, 110.3, 31.2. IR (neat): ν/ cm^{-1} = 1652, 1562, 1367, 1283, 1221, 1005, 730, 696. HRMS: *m/z* $[M+H]^+$ calcd for $C_{30}H_{24}NO$: 414.1852, found: 414.1852.

(*E*)-1-(4-Chlorophenyl)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (11, Scheme 2):



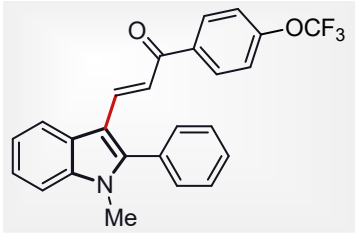
The title compound was prepared following **GP-5** using **1ak** (74.3 mg, 0.2 mmol); obtained as yellow solid (66.1 mg, 89%). M.P. = 169 - 170°C. R_f value = 0.28 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.11 – 8.07 (m, 1H), 7.99 – 7.91 (m, 3H), 7.56 – 7.50 (m, 4H), 7.46 – 7.37 (m, 7H), 3.64 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 188.9, 147.1, 139.8, 138.2, 138.1, 137.5, 130.9, 129.8, 129.6, 129.4, 128.7, 128.6, 125.6, 123.3, 122.0, 120.8, 116.4, 111.3, 110.3, 31.2. IR (neat): ν/ cm^{-1} = 1642, 1553, 1363, 1275, 1007, 809, 724, 652. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{19}ClNO$: 372.1150, found: 372.1151.

(*E*)-1-(4-Bromophenyl)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (12, Scheme 2):



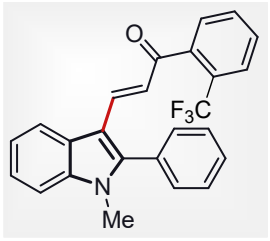
The title compound was prepared following **GP-5** using **1aj** (83.3 mg, 0.2 mmol); obtained as yellow solid (72.4 mg, 87%). M.P. = 173 - 174°C. R_f value = 0.23 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.10 – 8.07 (m, 1H), 7.96 (d, *J* = 15.4 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.51 (d, *J* = 15.5 Hz, 1H), 7.44 – 7.37 (m, 5H), 3.65 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 189.1, 147.1, 139.9, 138.1, 138.0, 131.6, 130.9, 129.9, 129.8, 129.4, 128.8, 126.9, 125.7, 123.3, 122.1, 120.8, 116.6, 111.4, 110.3, 31.3. IR (neat): ν/ cm^{-1} = 1649, 1550, 1283, 1068, 1005, 805, 724, 668. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{19}BrNO$: 416.0645, found: 416.0645.

(*E*)-3-(1-Methyl-2-phenyl-1*H*-indol-3-yl)-1-(4-(trifluoromethoxy)phenyl)prop-2-en-1-one (13, Scheme 2):



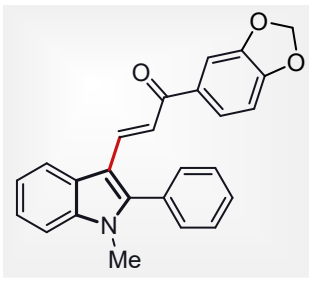
The title compound was prepared following **GP-5** using **1ak** (84.3 mg, 0.2 mmol); obtained as yellow solid (70.8 mg, 84%). M.P. = 173 - 174°C. R_f value = 0.58 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.09 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 15.5 Hz, 1H), 7.58 – 7.51 (m, 4H), 7.47- 7.42 (m, 3H), 7.42 – 7.36 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.68 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 189.0, 151.8, 147.3, 140.2, 138.2, 137.6, 131.0, 130.1, 129.9, 129.5, 128.8, 125.7, 123.4, 122.2, 120.9, 120.4, 120.4 (q, *J* = 259.7 Hz), 116.7, 111.4, 110.4, 31.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ/ ppm = -57.6. IR (neat): ν/ cm^{-1} = 1646, 1556, 1255, 1153, 1012, 802, 697. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{19}F_3NO_2$: 422.1362, found: 422.138.

(*E*)-3-(1-Methyl-2-phenyl-1*H*-indol-3-yl)-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one (14, Scheme 2):



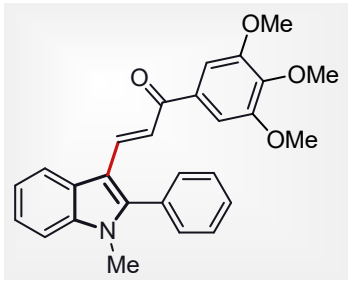
The title compound was prepared following **GP-5** using **1al** (81.1 mg, 0.2 mmol); obtained as yellow solid (66.5 mg, 82%). M.P. = 169 - 170°C. R_f value = 0.49 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.00 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 6.8 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.47 – 7.44 (m, 3H), 7.43 - 7.39 (m, 3H), 7.38 – 7.29 (m, 4H), 7.10 (d, J = 16.0 Hz, 1H), 3.66 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 195.2, 147.3, 142.6, 140.1, 138.2, 131.4, 130.8, 129.4, 129.38, 129.1, 128.6, 128.2, 127.5 (q, J = 32.8 Hz), 126.4, 125.4, 125.1, 123.5, 122.3, 121.8, 120.9, 110.9, 110.3, 31.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ/ ppm = -61.3. IR (neat): ν/ cm^{-1} = 1599, 1467, 1368, 1259, 1122, 1031, 699. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{25}H_{19}F_3NO$: 406.1413, found: 406.1413.

(*E*)-1-(Benzo[*d*][1,3]dioxol-5-yl)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (15, Scheme 2):



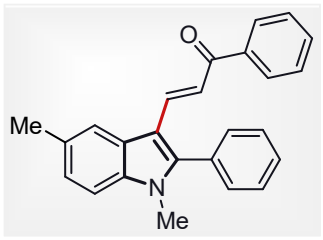
The title compound was prepared following **GP-5** using **1am** (76.3 mg, 0.2 mmol); obtained as yellow solid (67.9 mg, 89%). M.P. = 161 - 162°C. R_f value = 0.51 (30% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.11 – 8.08 (m, 1H), 7.92 (d, J = 15.5 Hz, 1H), 7.63 (dd, J = 8.1, 1.7 Hz, 1H), 7.57 – 7.50 (m, 5H), 7.46 – 7.42 (m, 3H), 7.41 - 7.35 (m, 2H), 6.88 (d, J = 8.1 Hz, 1H), 6.05 (s, 2H), 3.67 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 188.5, 151.1, 148.1, 146.7, 138.9, 138.2, 134.1, 131.0, 130.1, 129.4, 128.8, 125.8, 124.1, 123.3, 122.0, 120.9, 117.1, 111.5, 110.3, 108.4, 107.9, 101.7, 31.3. IR (neat): ν/ cm^{-1} = 1738, 1553, 1437, 1237, 1109, 840, 751. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{25}H_{20}NO_3$: 382.1438, found: 382.1437.

(*E*)-3-(1-Methyl-2-phenyl-1*H*-indol-3-yl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (16, Scheme 2):



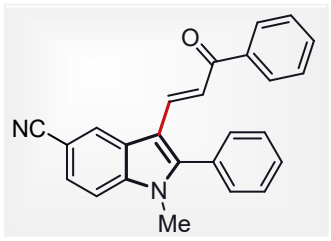
The title compound was prepared following **GP-5** using **1an** (85.5 mg, 0.2 mmol); obtained as yellow solid (76.9 mg, 90%). M.P. = 178 - 179°C. R_f value = 0.35 (40% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.07 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 15.5 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.48 - 7.43 (m, 4H), 7.42 – 7.34 (m, 2H), 7.21 (s, 2H), 3.92 (s, 9H), 3.67 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.6, 153.0, 146.4, 141.8, 139.2, 138.1, 134.7, 130.9, 130.3, 129.4, 128.9, 126.0, 123.3, 122.0, 120.6, 117.4, 111.3, 110.3, 105.9, 61.0, 56.4, 31.3. IR (neat): ν/ cm^{-1} = 1640, 1551, 1326, 1122, 1009, 812, 699. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{27}H_{26}NO_4$: 428.1856, found: 428.1856.

(*E*)-3-(1,5-Dimethyl-2-phenyl-1*H*-indol-3-yl)-1-phenylprop-2-en-1-one (17, Scheme 2):



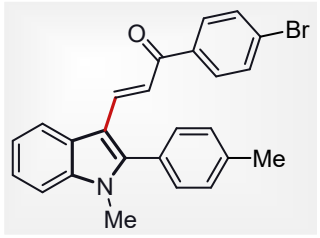
The title compound was prepared following **GP-5** using **1ao** (70.3 mg, 0.2 mmol); obtained as yellow solid (66.1 mg, 94%). M.P. = 162- 163°C. R_f value = 0.43 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.00 – 7.96 (m, 2H), 7.92 (d, J = 15.5 Hz, 1H), 7.88 (s, 1H), 7.57-7.51 (m, 5H), 7.50 – 7.45 (m, 2H), 7.43 (dd, J = 7.5, 1.9 Hz, 2H), 7.33 (d, J = 8.3 Hz, 1H), 7.21 (dd, J = 8.3, 1.0 Hz, 1H), 3.64 (s, 3H), 2.58 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 190.9, 147.0, 139.8, 139.4, 136.6, 132.0, 131.6, 131.0, 130.1, 129.4, 128.8, 128.4, 128.3, 126.0, 124.8, 120.8, 117.3, 111.0, 110.0, 31.4, 21.9. IR (neat): ν/ cm^{-1} = 1552, 1530, 1281, 1218, 1013, 736, 699. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{25}H_{22}NO$: 352.1696, found: 352.1700.

(*E*)-1-Methyl-3-(3-oxo-3-phenylprop-1-en-1-yl)-2-phenyl-1*H*-indole-5-carbonitrile (18, Scheme 2):



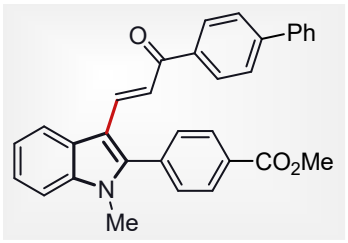
The title compound was prepared following **GP-5** using **1ap** (72.5 mg, 0.2 mmol); obtained as yellow solid (58 mg, 80%). M.P. = 163 - 164°C. R_f value = 0.33 (30% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.41 (d, J = 0.9 Hz, 1H), 8.02 – 7.99 (m, 2H), 7.88 (d, J = 15.7 Hz, 1H), 7.63 (dd, J = 8.5, 1.5 Hz, 1H), 7.60-7.56 (m, 4H), 7.55 – 7.48 (m, 4H), 7.46 – 7.42 (m, 2H), 3.70 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 19.1, 148.2, 139.6, 138.7, 137.6, 134.6, 132.6, 130.9, 130.0, 129.1, 128.7, 128.3, 126.2, 126.0, 125.6, 125.4, 120.4, 118.9, 111.7, 111.1, 104.9, 31.6. IR (neat): ν/ cm^{-1} = 1642, 1556, 1255, 1153, 1012, 696. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{25}H_{19}N_2O$: 363.1492, found: 363.1494.

(*E*)-1-(4-Bromophenyl)-3-(1-methyl-2-(p-tolyl)-1*H*-indol-3-yl)prop-2-en-1-one (19, Scheme 2):



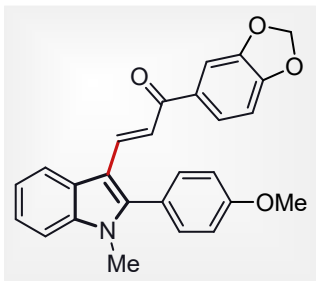
The title compound was prepared following **GP-5** using **1aq** (86.1 mg, 0.2 mmol); obtained as yellow solid (80.1 mg, 93%). M.P. = 176 - 177°C. R_f value = 0.29 (15% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.09 – 8.06 (m, 1H), 7.96 (d, J = 15.4 Hz, 1H), 7.86 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 15.5 Hz, 1H), 7.42 – 7.34 (m, 5H), 7.31 (d, J = 7.9 Hz, 2H), 3.65 (s, 3H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 189.1, 147.6, 140.2, 139.5, 138.1, 138.0, 131.6, 130.8, 129.8, 129.5, 126.8, 126.75, 125.7, 123.2, 122.0, 120.8, 116.2, 111.3, 110.3, 31.3, 21.4. IR (neat): ν/ cm^{-1} = 1642, 1550, 1463, 1282, 1068, 1005, 805, 724. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{25}H_{21}BrNO$: 430.0801, found: 430.0801.

(*E*)-Methyl 4-(3-(3-([1,1'-biphenyl]-4-yl)-3-oxoprop-1-en-1-yl)-1-methyl-1*H*-indol-2-yl)benzoate (20, Scheme 2):



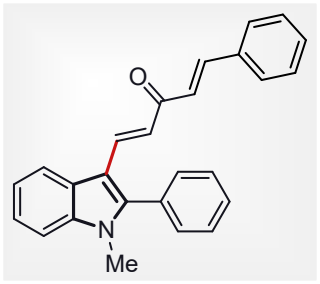
The title compound was prepared following **GP-5** using **1ar** (94.3 mg, 0.2 mmol); obtained as yellow solid (80.2 mg, 85%). M.P. = 181 - 182°C. R_f value = 0.41 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.24 (d, J = 8.1 Hz, 2H), 8.14 (dd, J = 6.1, 2.0 Hz, 1H), 8.08 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 15.5 Hz, 1H), 7.70 (t, J = 8.1 Hz, 2H), 6.67 – 6.63 (m, 3H), 7.55 (d, J = 8.1 Hz, 2H), 7.51 – 7.44 (m, 3H), 7.42 – 7.38 (m, 3H), 3.99 (s, 3H), 3.68 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.9, 166.5, 145.2, 144.9, 140.2, 138.6, 138.4, 137.8, 134.6, 131.1, 131.0, 130.0, 129.0, 128.9, 128.1, 127.3, 127.2, 125.7, 123.7, 122.2, 121.1, 118.1, 112.0, 110.4, 52.4, 31.4. IR (neat): ν/ cm^{-1} = 1716, 1563, 1466, 1274, 1105, 1012,732. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{32}H_{26}NO_3$: 472.1907, found: 472.1908.

(*E*)-1-(Benzo[*d*][1,3]dioxol-5-yl)-3-(2-(4-methoxyphenyl)-1-methyl-1*H*-indol-3-yl)prop-2-en-1-one (21, Scheme 2):



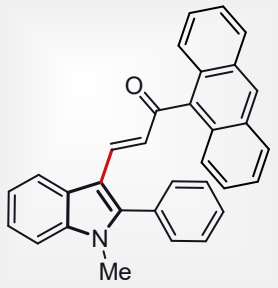
The title compound was prepared following **GP-5** using **1as** (82.3 mg, 0.2 mmol); obtained as yellow solid (74.5 mg, 91%). M.P. = 163 - 164°C. R_f value = 0.46 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.10 – 8.06 (m, 1H), 7.92 (d, J = 15.4 Hz, 1H), 7.64 (dd, J = 8.1, 1.7 Hz, 1H), 7.54 (d, J = 15.4 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.39 – 7.34 (m, 4H), 7.07 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.1 Hz, 1H), 6.05 (s, 2H), 3.91 (s, 3H), 3.66 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 188.5, 160.5, 151.0, 148.0, 146.9, 139.2, 138.1, 134.1, 132.3, 125.8, 124.0, 123.1, 122.0, 121.9, 120.8, 116.6, 114.3, 111.3, 110.2, 108.4, 107.8, 101.7, 55.5, 31.2. IR (neat): ν/ cm^{-1} = 1744, 1552, 1437, 1278,1236, 1030, 840, 735. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{22}NO_4$: 412.1543, found: 412.1548.

(1*E*,4*E*)-1-(1-Methyl-2-phenyl-1*H*-indol-3-yl)-5-phenylpenta-1,4-dien-3-one (22, Scheme 2):



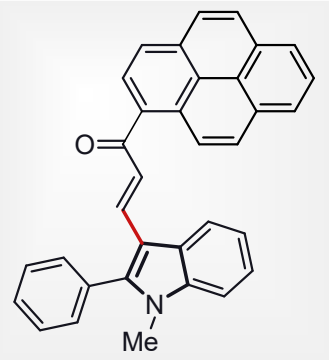
The title compound was prepared following **GP-5** using **1at** (72.7 mg, 0.2 mmol); obtained as yellow solid (62.5 mg, 86%). M.P. = 168 - 169°C. R_f value = 0.31 (25% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.11(d, J = 8.6 Hz, 1H), 7.85 (d, J = 15.8 Hz, 1H), 7.66 (d, J = 15.9 Hz, 1H), 7.60 – 7.53 (m, 5H), 7.46 – 7.43 (m,3H), 7.42 – 7.34 (m, 5H), 7.14 (d, J = 15.7 Hz, 1H), 7.01 (d, J = 15.9 Hz, 1H), 3.67 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.0, 146.7, 141.6, 138.2, 138.16, 135.4, 131.0, 130.1, 130.0, 129.5, 128.9, 128.8, 128.3, 126.6, 125.8, 123.3, 122.0, 121.4, 121.0, 111.3, 110.3, 31.3. IR (neat): ν/ cm^{-1} = 1610,1559, 1368, 1269, 1098, 984, 818, 733. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{22}NO$: 364.1696, found: 364.1697.

(*E*)-1-(Anthracen-9-yl)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (23, Scheme 2):



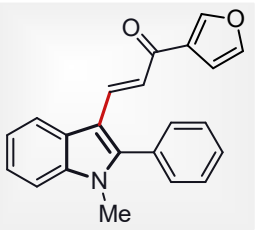
The title compound was prepared following **GP-5** using **1au** (87.5 mg, 0.2 mmol); obtained as yellow solid (74.4 mg, 85%). M.P. = 171 - 172°C. R_f value = 0.53 (25% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.41(s, 1H), 8.05 (d, J = 7.4 Hz, 1H), 8.04 - 7.98 (m, 4H), 7.49 – 7.42 (m, 4H), 7.41 – 7.30 (m, 5H), 7.23 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 7.2 Hz, 2H), 3.60 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 200.1, 147.0, 143.9, 138.3, 135.5, 131.1, 130.6, 129.0, 128.8, 128.5, 128.4, 128.2, 127.7, 127.3, 126.1, 125.9, 125.3, 124.8, 123.5, 122.3, 121.0, 110.9, 110.3, 31.4. IR (neat): ν/ cm^{-1} = 1673, 1589, 1468, 1196, 1069, 821,731, 699. HRMS: *m*/*z* [M]$^+$ calcd for $C_{32}H_{24}NO$: 438.1852, found: 438.1852.

(*E*)-3-(1-Methyl-2-phenyl-1*H*-indol-3-yl)-1-(pyren-2-yl)prop-2-en-1-one (24, Scheme 2):



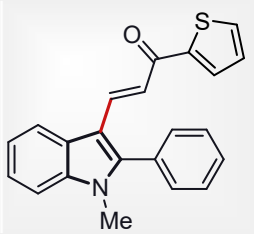
The title compound was prepared following **GP-5** using **1av** (92.3 mg, 0.2 mmol); obtained as yellow solid (75.7 mg, 82%). M.P. = 175 - 176°C. R_f value = 0.38 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.61 (d, J = 9.3 Hz, 1H), 8.20 – 8.14 (m, 2H), 8.12 (d, J = 9.3 Hz, 1H), 8.10 – 8.07 (m, 2H), 8.05 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 15.9 Hz, 1H), 7.52 (d, J = 15.9 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.40 – 7.25 (m, 7H), 3.65 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 196.4, 147.1, 141.2, 138.2, 135.6, 132.7, 131.3, 130.8, 130.77, 129.6, 129.2, 129.1, 129.6, 128.5, 128.4, 127.3, 126.2, 126.0, 125.8, 125.7, 125.3, 124.9, 124.6, 124.3, 123.4, 123.0, 122.8, 122.2, 121.0, 111.3, 110.3, 31.4. IR (neat): ν/ cm^{-1} = 1738, 1649, 1563, 1365, 1365, 1253, 1014, 742, 697. HRMS: *m*/*z* [M]$^+$ calcd for $C_{34}H_{24}NO$: 462.1852, found: 462.1850.

(*E*)-1-(Furan-3-yl)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (25, Scheme 2):



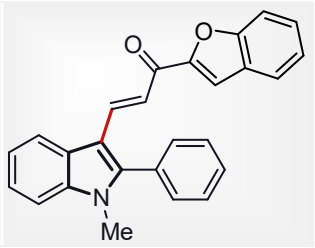
The title compound was prepared following **GP-5** using **1aw** (65.5 mg, 0.2 mmol); obtained as yellow solid (56.3 mg, 86%). M.P. = 166 - 167°C. R_f value = 0.57 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.15 – 8.11 (m, 1H), 7.95 (d, J = 15.7 Hz, 1H), 7.61 (d, J = 1.6 Hz, 1H), 7.55 (d, J = 7.0 Hz, 3H), 7.50 (d, J = 15.7 Hz, 1H), 7.44 – 7.41 (m, 3H), 7.40 – 7.36 (m, 2H), 7.22 (d, J = 3.5 Hz, 1H), 6.55 (dd, J = 3.5, 1.7 Hz, 1H), 3.65 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 178.6, 154.4, 147.0, 145.7, 138.5, 138.1, 130.9, 129.9, 129.4, 128.7, 125.7, 123.2, 122.0, 120.9, 116.7, 116.0, 112.2, 111.3, 110.3, 31.3. IR (neat): ν/ cm^{-1} = 1615, 1565, 1462, 1364, 1229, 1067, 872, 711. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{22}H_{18}NO_2$: 328.1332, found: 328.1333.

(*E*)-3-(1-Methyl-2-phenyl-1*H*-indol-3-yl)-1-(thiophen-2-yl)prop-2-en-1-one (26, Scheme 2):



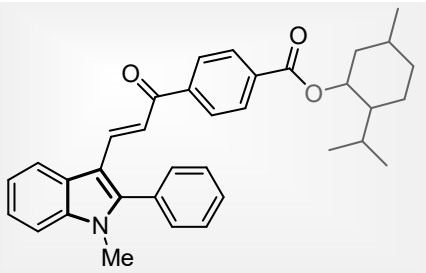
The title compound was prepared following **GP-5** using **1ax** (68.7 mg, 0.2 mmol); obtained as yellow solid (57 mg, 83%). M.P. = 162 - 163°C. R_f value = 0.51 (25% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.11 – 8.09 (m, 1H), 7.94 (d, J = 15.4 Hz, 1H), 7.79 (d, J = 3.6 Hz, 1H), 7.60 (d, J = 7.4 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.48 (s, 1H), 7.46 – 7.42 (m, 3H), 7.41 – 7.36 (m, 2H), 7.16 (t, J = 4.2 Hz, 1H), 3.63 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 182.4, 146.9, 146.6, 138.6, 138.2, 132.6, 131.0, 130.6, 130.0, 129.5, 128.8, 128.0, 125.9, 123.3, 122.1, 120.8, 117.2, 111.3, 110.3, 31.3. IR (neat): ν/ cm^{-1} = 1639, 1365, 1278, 1061, 735, 703, 640. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{22}H_{18}NOS$: 344.1104, found: 344.1104.

(*E*)-1-(Benzofuran-2-yl)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (27, Scheme 2):



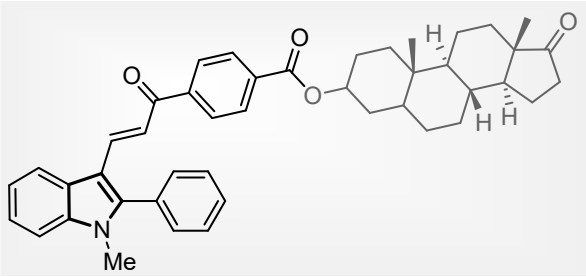
The title compound was prepared following **GP-5** using **1ay** (75.5 mg, 0.2 mmol); obtained as yellow solid (67.2 mg, 89%). M.P. = 166 - 167°C. R_f value = 0.47 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.21 – 8.18 (m, 1H), 8.03 (d, J = 15.6 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.59 – 7.53 (m, 4H), 7.49 – 7.40 (m, 6H), 7.31 (t, J = 7.2 Hz, 1H), 3.67 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 180.1, 155.6, 154.7, 147.6, 139.3, 138.2, 131.0, 129.8, 129.5, 128.8, 127.6, 127.5, 125.8, 123.6, 123.4, 123.0, 122.2, 121.1, 116.7, 112.4, 111.7, 111.5, 110.4, 31.4. IR (neat): ν/ cm^{-1} = 1738, 1568, 1368, 1287, 1050, 737. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{26}H_{20}NO_2$: 378.1489, found: 378.1486.

(*E*)-2-Isopropyl-5-methylcyclohexyl 4-(3-(1-methyl-2-phenyl-1*H*-indol-3-yl)acryloyl)benzoate (28, Scheme 2):



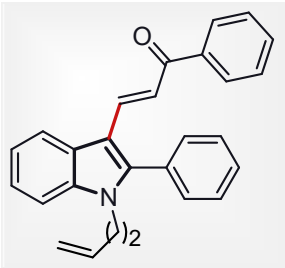
The title compound was prepared following **GP-5** using **1az** (103.9 mg, 0.2 mmol); obtained as yellow solid (76.9 mg, 74%). M.P. = 158 - 159°C. R_f value = 0.34 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.15 (d, J = 8.2 Hz, 2H), 8.10 (dd, J = 5.8, 3.1 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 15.5 Hz, 1H), 7.58 – 7.53 (m, 4H), 7.45 – 7.37 (m, 5H), 4.98 (td, J = 10.9, 4.4 Hz, 1H), 3.65 (s, 3H), 2.17 (d, J = 11.8 Hz, 1H), 2.02 – 1.96 (, 1H), 1.75 (d, J = 10.7 Hz, 2H), 1.60 (t, J = 11.7 Hz, 2H), 1.29 – 1.10 (m, 3H), 0.96 (d, J = 6.7 Hz, 6H), 0.83 (d, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 189.8, 165.5, 147.3, 142.7, 140.2, 138.1, 133.5, 130.5, 129.8, 129.6, 129.4, 128.8, 128.0, 125.7, 123.4, 122.1, 120.8, 116.9, 114.4, 110.4, 45.2, 47.2, 40.9, 34.3, 31.4, 31.3, 26.5, 23.6, 22.0, 20.8, 16.5. IR (neat): ν/ cm^{-1} = 1714, 1581, 1367, 1270, 1215, 1113, 710. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{35}H_{38}NO_3$: 520.2846, found: 520.2849.

(8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*E*)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)acryloyl)benzoate (29, Scheme 2):



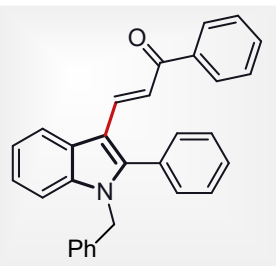
The title compound was prepared following **GP-5** using **1ba** (130.7 mg, 0.2 mmol); obtained as yellow solid (91.5 mg, 70%). M.P. = 162 - 163°C. R_f value = 0.62 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.14 – 8.07 (m, 3H), 8.01 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 15.5 Hz, 1H), 7.57 – 7.52 (m, 4H), 7.47 – 7.37 (m, 5H), 5.01 – 4.92 (m, 1H), 3.67(s, 3H), 2.44 (dd, J = 19.2, 8.7 Hz, 1H), 2.12 – 2.03 (m, 1H), 2.00 – 1.90 (m, 2H), 1.81 (d, J = 12.4 Hz, 3H), 1.69(d, J = 12.9 Hz, 3H), 1.59 – 1.47 (m, 3H), 1.24 (d, J = 15.1 Hz, 1H), 1.40 – 1.31 (m, 2H), 1.29 (d, J = 10.8 Hz, 2H), 1.26 (s, 1H), 1.17 – 1.08 (m, 1H), 1.05 – 0.99 (m, 1H), 0.91 (s, 3H), 0.87 (s, 3H), 0.76 (td, J = 11.9, 4.1 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 221.3, 189.9, 165.5, 147.4, 142.7, 140.3, 138.1, 133.6, 130.9, 129.8, 129.6, 129.5, 128.8, 128.0, 125.7, 123.4, 122.2, 120.9, 117.0, 111.4, 110.4, 74.6, 54.3, 51.4, 47.8, 44.7, 36.8, 35.9, 35.7, 35.1, 34.0, 31.5, 31.4, 30.8, 28.3, 27.5, 21.8, 20.5, 13.8, 12.3. IR (neat): ν/ cm^{-1} = 1712, 1557, 1217, 1011, 745, 701. HRMS: m/z [M+H]$^+$ calcd for $C_{44}H_{48}NO_4$: 654.3578, found: 654.3581.

(*E*)-3-(1-(But-3-en-1-yl)-2-phenyl-1*H*-indol-3-yl)-1-phenylprop-2-en-1-one (30, Scheme 3):



The title compound was prepared following **GP-5** using **1bb** (75.5 mg, 0.2 mmol); obtained as yellow solid (61.2 mg, 81%). M.P. = 177 - 178°C. R_f value = 0.59 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.13 – 8.09 (m, 1H), 7.99 (d, J = 7.1 Hz, 2H), 7.88 (d, J = 15.6 Hz, 1H), 7.59 – 7.51 (m, 5H), 7.47 (t, J = 7.7 Hz, 3H), 7.45 – 7.41 (m, 2H), 7.40 – 7.35 (m, 2H), 5.58 (ddt, J = 13.8, 10.2, 6.8 Hz, 1H), 4.99 – 4.91 (m, 2H), 4.13 (t, J = 7.5 Hz, 2H), 2.42 (q, J = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ/ ppm = 190.5, 146.6, 139.3, 137.2, 133.9, 132.1, 130.9, 130.3, 129.5, 128.8,128.4, 128.3, 126.0, 123.2, 122.0, 121.0, 117.7, 117.4, 111.8, 110.7, 49.0, 46.6, 43.8, 34.0. IR (neat): ν/ cm^{-1} = 1649, 1563, 1364, 1281, 1219, 1014, 742. HRMS: m/z [M+H]$^+$ calcd for $C_{27}H_{24}NO$: 378.1852, found: 378.1852.

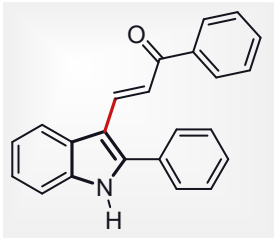
(*E*)-3-(1-Benzyl-2-phenyl-1*H*-indol-3-yl)-1-phenylprop-2-en-1-one (31, Scheme 3):



The title compound was prepared following **GP-5** using **1bc** (82.7 mg, 0.2 mmol); obtained as yellow solid (72.8 mg, 88%). M.P. = 186 - 187°C. R_f value = 0.71 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.14 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 7.1 Hz, 2H), 7.96 (d, J = 15.6 Hz, 1H), 7.63 (d, J = 15.6 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.51 – 7.44 (m, 5H), 7.40 – 7.33 (m, 3H), 7.30 – 7.27 (m, 2H), 7.26 (s, 1H), 7.25 – 7.23 (m, 2H), 7.97 (d, J = 6.3 Hz, 2H), 5.29 (s,

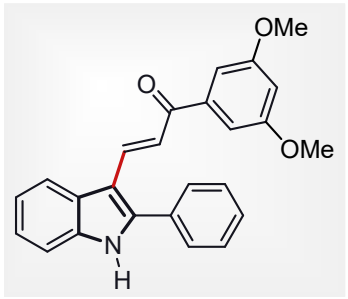
2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ/ ppm = 190.5, 147.0, 139.3, 139.2, 137.7, 137.0, 132.1, 130.9, 129.9, 129.5, 128.9, 128.8, 128.5, 128.3, 127.6, 126.1, 126.0, 123.5, 122.2, 121.0, 117.9, 111.9, 111.3, 48.0. IR (neat): ν/ cm^{-1} = 1739, 1652, 1565, 1363, 1219, 1012, 697. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{30}H_{24}NO$: 414.1852, found: 414.1857.

(*E*)-1-Phenyl-3-(2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (32, Scheme 3):



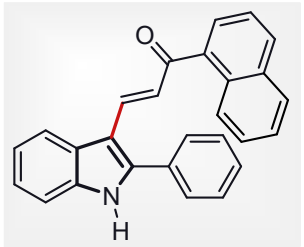
The title compound was prepared following **GP-5** using **1bf** (64.7 mg, 0.2 mmol); obtained as yellow solid (53.0 mg, 82%). M.P. = 160 - 161°C. R_f value = 0.93 (25% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.98 (s, 1H), 8.21 (d, *J* = 15.5 Hz, 1H), 8.09 (d, *J* = 7.3 Hz, 1H), 8.05 (d, *J* = 7.1 Hz, 2H), 7.73 (d, *J* = 15.5 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.47 – 7.43 (m, 4H), 7.36 – 7.29 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ/ ppm = 191.0, 144.2, 139.5, 136.6, 132.3, 131.2, 129.3, 129.27, 129.1, 128.6, 128.4, 126.6, 123.6, 122.0, 121.1, 118.5, 111.8, 110.9. IR (neat): ν/ cm^{-1} = 1738, 1366, 1258, 1228, 1016, 795. HRMS: *m*/*z* $[M]^+$ calcd for $C_{23}H_{18}NO$: 324.1383, found: 324.1384.

(*E*)-1-(3,5-Dimethoxyphenyl)-3-(2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (33, Scheme 3):



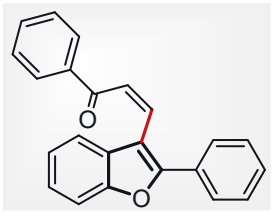
The title compound was prepared following **GP-5** using **1bg** (76.7 mg, 0.2 mmol); obtained as yellow solid (65.2 mg, 85%). M.P. = 166 - 167°C. R_f value = 0.85 (25% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 9.60 (s, 1H), 8.23 (d, *J* = 15.5 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 15.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.30 (m, 4H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 2.2 Hz, 2H), 6.66 (t, *J* = 2.2 Hz, 1H), 3.82 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 190.9, 160.8, 144.6, 141.2, 140.1, 136.7, 131.0, 129.2, 129.1, 128.9, 126.5, 123.5, 121.9, 120.9, 118.1, 111.9, 110.6, 106.3, 104.4, 55.5. IR (neat): ν/ cm^{-1} = 1741, 1552, 1451, 1292, 1189, 1037, 742. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{22}NO_3$: 384.1594, found: 384.1599.

(*E*)-1-(Naphthalen-1-yl)-3-(2-phenyl-1*H*-indol-3-yl)prop-2-en-1-one (34, Scheme 3):



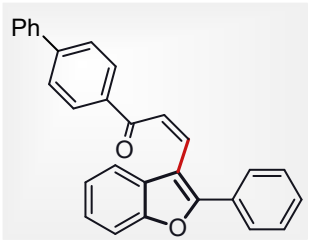
The title compound was prepared following **GP-5** using **1bh** (74.7 mg, 0.2 mmol); obtained as yellow solid (60.5 mg, 81%). M.P. = 167 - 168°C. R_f value = 0.88 (25% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ/ ppm = 9.53 (s, 1H), 8.56 (s, 1H), 8.30 (d, *J* = 15.4 Hz, 1H), 8.13 (t, *J* = 7.1 Hz, 2H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 15.4 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.54 – 7.51 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.28 (m, 5H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm = 191.1, 144.5, 139.8, 139.79, 136.7, 136.4, 135.3, 132.6, 131.1, 129.5, 129.3, 129.1, 128.9, 128.4, 128.1, 127.8, 126.6, 124.6, 123.6, 121.9, 121.0, 118.3, 112.0, 110.8. IR (neat): ν/ cm^{-1} = 1739, 1546, 1372, 1214, 1121, 740. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{27}H_{20}NO$: 374.1539, found: 374.1541.

(*Z*)-1-Phenyl-3-(2-phenylbenzofuran-3-yl)prop-2-en-1-one (36, Scheme 3):



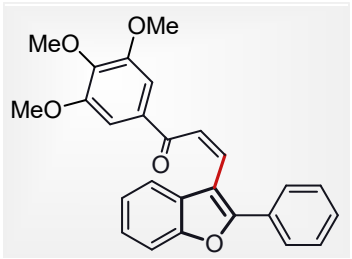
The title compound was prepared following **GP-5** using **35a** (64.9 mg, 0.2 mmol); obtained as yellow solid (58.4 mg, 90%). M.P. = 158 - 159°C. R_f value = 0.72 (15% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 7.93 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.51 – 7.46 (m, 4H), 7.44 – 7.36 (m, 3H), 7.26 – 7.22 (m, 1H), 7.21 (d, J = 12.0 Hz, 1H), 7.14 – 7.11 (m, 2H), 7.10 (d, J = 12.0 Hz, 1H). Prominent peaks for minor product, 8.20 (d, J = 15.6 Hz, 1H), 8.07 (d, J = 8.1 Hz, 2H), 8.00 – 7.96 (m, 1H), 7.79 (d, J = 5.1 Hz, 2H), 7.59 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 7.4 Hz, 3H), 7.51 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ/ ppm = 191.9, 154.1, 137.9, 132.9, 132.8, 130.3, 129.1, 128.7, 128.6, 128.5, 127.8, 127.1, 127.0, 124.7, 122.8, 121.6, 113.7, 111.2. IR (neat): ν/ cm^{-1} = 1710, 1656, 1604, 1446, 1258, 1220, 1004, 734. HRMS: m/z [M+H]$^+$ calcd for $C_{23}H_{17}O_2$: 325.1223, found: 325.1221.

(*Z*)-1-([1,1'-Biphenyl]-4-yl)-3-(2-phenylbenzofuran-3-yl)prop-2-en-1-one (37, Scheme 3):



The title compound was prepared following **GP-5** using **35b** (80.1 mg, 0.2 mmol); obtained as yellow solid (69.7 mg, 87%). M.P. = 162 - 163°C. R_f value = 0.69 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.03 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 7.7 Hz, 2H), 7.63 (t, J = 8.3 Hz, 4H), 7.54 – 7.40 (m, 8H), 7.30 – 7.26 (m, 1H), 7.25 (d, J = 12.8 Hz, 1H), 7.18 – 7.14 (m, 2H). Prominent peaks for minor product, 8.25 (d, J = 15.6 Hz, 1H), 8.18 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 7.5 Hz, 3H), 7.56 (t, J = 7.1 Hz, 5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 191.4, 154.2, 145.6, 140.0, 136.7, 132.7, 130.4, 129.3, 129.1, 129.0, 128.95, 128.8, 128.2, 127.8, 127.4, 127.3, 127.1, 125.5, 124.7, 123.9, 122.8, 121.6, 121.1, 113.8, 111.3. IR (neat): ν/ cm^{-1} = 1656, 1578, 1451, 1273, 1070, 744. HRMS: m/z [M+H]$^+$ calcd for $C_{29}H_{21}O_2$: 401.1536, found: 401.1538.

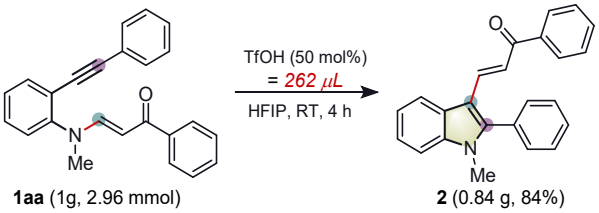
(*Z*)-3-(2-Phenylbenzofuran-3-yl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (38, Scheme 3):



The title compound was prepared following **GP-5** using **35c** (82.9 mg, 0.2 mmol); obtained as yellow solid (72.9 mg, 88%). M.P. = 163 - 164°C. R_f value = 0.43 (15% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ ppm = 8.18 (d, J = 15.6 Hz, 1H), 7.95 (d, J = 8.7 Hz, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 15.6 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.45 – 7.38 (m, 2H), 7.32 (s, 2H), 3.96 (s, 6H), 3.95 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 191.5, 154.0, 153.9, 152.8, 142.4, 133.0, 132.0, 130.3, 129.1, 128.7, 127.6, 127.5, 127.4, 124.8, 122.8, 121.3, 113.6, 111.2, 106.1, 60.9, 56.1. IR (neat): ν/ cm^{-1} = 1740, 1574, 1333, 1217, 1123, 1002, 740, 694. HRMS: m/z [M+H]$^+$ calcd for $C_{26}H_{23}O_5$: 415.1540, found: 415.1539.

ESI-8 Gram scale synthesis of functionalized indole derivative 2

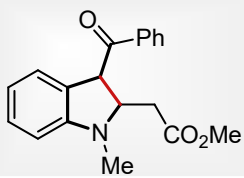
To a mixture of **1aa** (1g, 1 equiv.) in HFIP (0.05 M, 15 mL), 50 mol% TfOH (262 µL) was added under nitrogen atmosphere. Then the reaction mixture was stirred for 4 hrs. After the completion of the reaction, the reaction mixture was quenched with a saturated $NaHCO_3$ solution. Then it was extracted using ethyl acetate and water. The combined organic layers was washed with saturated brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (using silica gel, EtOAc/hexanes eluent) to get the functionalized indole **2** in 0.84 g (84%).



Scheme S6. Gram scale synthesis of functionalized indole derivative **2**

ESI-9 Control Experiments:

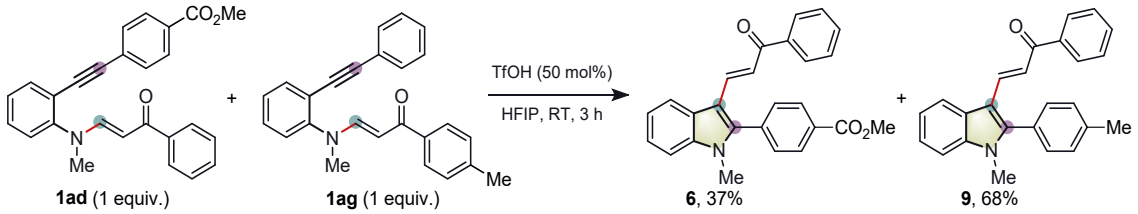
Methyl 2-(3-benzoyl-1-methylindolin-2-yl)acetate (39, eq. 3, Scheme 5):



The title compound was prepared following **GP-5** using **1bk** (61.9 mg, 0.2 mmol); obtained as yellow solid (35.3 mg, 57%). M.P. = 168 - 169°C. R_f value = 0.81 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.09 (d, J = 7.1 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.55 (t, J = 7.9 Hz, 2H), 7.10 (t, J = 7.7 Hz, 1H), 6.70 (d, J = 7.4 Hz, 1H), 6.55 (td, J = 7.5, 0.9 Hz, 1H), 6.52 (d, J = 7.9 Hz, 1H), 5.12 (d, J = 8.7 Hz, 1H), 4.41 (td, J = 8.7, 3.9 Hz, 1H), 3.53 (s, 3H), 2.86 (dd, J = 14.6, 3.9 Hz, 1H), 2.86 (s, 3H), 2.66 (dd, J = 14.6, 8.7 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 197.3, 171.4, 152.2, 137.3, 133.4, 129.2, 128.9, 128.7, 126.9, 124.0, 118.1, 107.9, 65.1, 54.4, 51.7, 37.9, 34.4. IR (neat): ν/ cm^{-1} = 1716, 1562, 1466, 1274, 1105, 1012, 769. HRMS: m/z [M+H]$^+$ calcd for $C_{19}H_{18}NO_3$: 308.1292, found: 308.1302.

Cross-over Experiment (eq. 4, Scheme 5):

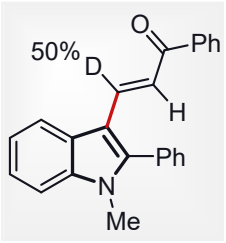
A equimolar mixture of substrates **1ad** (15.8 mg, 1 equiv.) and **1ag** (14.0 mg, 1 equiv.) were dissolved in HFIP (1 mL, 0.1 M)and TfOH (2µL, 50 mol%) was added to it. Then the reaction mixture was continuous stirring for 3 hrs. After that, the reaction mixture was concentrated under reduced pressure and the mixture of product **6** and **9** was separated by column chromatography (silica gel, hexanes/EtOAc) and analyzed by ^{1}H NMR spectra to find out that indoles **6** and **9** were formed in almost 1:1.8 ratio.



Scheme S7. Cross-over experiment for the synthesis of indoles **6** and **9**.

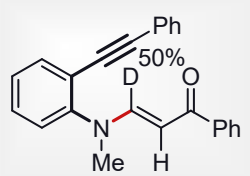
Deuterium Scrambling Experiments (eq. 6-7, Scheme 5):

Deuterated (*E*)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)-1-phenylprop-2-en-1-one (2-D, eq. 6, Scheme 5):



The title compound was prepared following **GP-5** using **1aa-D** (67.9 mg, 0.2 mmol); obtained as yellow solid (61.8 mg, 91% using TfOH; 63.1 mg, 93% using TfOD). M.P. = 176 - 177°C. R_f value = 0.44 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.14 – 8.10 (m, 1H), 8.01 (d, J = 7.1 Hz, 2H), 7.95 (d, J = 15.5 Hz, 0.5 H), 7.61 (d, J = 15.5 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.48 (t, J = 7.6 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.42 – 7.36 (m, 2H), 3.67 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 190.5, 146.9, 139.4, 139.3, 138.2, 132.0, 131.0, 130.0, 129.4, 128.4, 128.5, 128.3, 125.8, 123.3, 122.0, 120.9, 117.4, 111.5, 110.3, 31.3. IR (neat): ν/ cm^{-1} = 1581, 1560, 1462, 1365, 1285, 1219, 1011, 732. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{24}H_{19}DNO$: 339.1602, found: 339.1603.

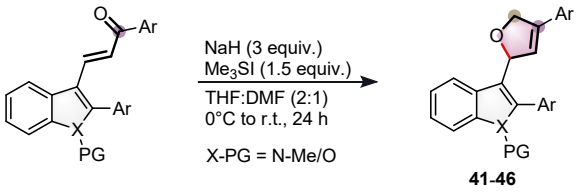
Deuterated (*E*)-3-(methyl(2-(phenylethynyl)phenyl)amino)-1-phenylprop-2-en-1-one (1aa-D', eq. 7, Scheme 4):



^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 8.13 (d, J = 12.2 Hz, 0.5 H), 7.93 (s, 2H), 7.59 (d, J = 6.4 Hz, 1H), 6.50 – 6.35 (m, 7H), 7.31 (d, J = 5.3 Hz, 3H), 7.23 (d, J = 6.8 Hz, 1H), 6.08 (s, 1H), 3.46 (s, 3H). IR (neat): ν/ cm^{-1} = 1640, 1578, 1526, 1277, 1208, 1044, 753. HRMS: *m*/*z* [M-H]$^+$ calcd for $C_{24}H_{19}NOD$: 339.1602, found: 339.1602.

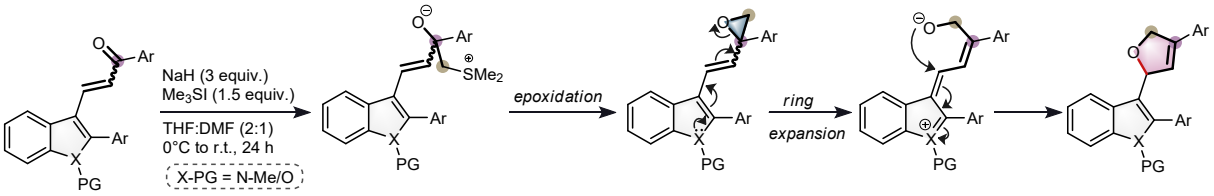
ESI-10 Late-stage transformation of synthesized indole and benzofurans leading to 2,5-dihydrofuran derivatives (GP-6):

NaH (1.5 equiv.) and Me_3SI (1.5 equiv.) were taken in a 2:1 mixture of dry THF:DMF (0.1 M) and stirred at 0 °C under nitrogen atmosphere for 30 mins. Then the reaction mixture is allowed to bring to room temperature and a solution of the synthesized indole/benzofuran derivatives in THF was added dropwise to it. Then the reaction mixture was continuous stirred for 24 hrs. After the completion of the reaction, it was poured into ice-cooled saturated NH_4Cl solution, extracted with ethyl acetate and washed with saturated brine solution. The combined organic layers were then concentrated under reduced pressure and crude was purified and separated by column chromatography (silica gel, hexanes/EtOAc) to get 2,5-dihydrofuran derivatives (**41**-**46**) in an analytically pure form.

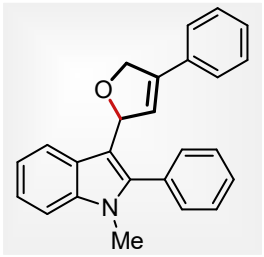


Scheme S8. Preparation of 2,5-dihydrofuran derivatives **41-46**.

Mechanism:

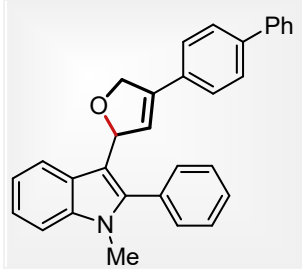


1-Methyl-2-phenyl-3-(4-phenyl-2,5-dihydrofuran-2-yl)-1*H*-indole (41, Scheme 5):



The title compound was prepared following **GP-6** using **2** (50.6 mg, 0.15 mmol), obtained as off-white gummy (50.1 mg, 95%). R_f value = 0.61 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm = 7.68 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 5.3 Hz, 3H), 7.50 – 7.46 (m, 1H), 7.44 – 7.33 (m, 7H), 7.29 – 7.24 (m, 1H), 7.10 (t, J = 7.2 Hz, 1H), 6.33 (d, J = 0.74 Hz, 1H), 6.11 (t, J = 4.5 Hz, 1H), 5.30 (dd, J = 11.9, 5.8 Hz, 1H), 5.15(d, J = 11.8 Hz, 1H), 3.64 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm = 139.9, 138.6, 137.7, 132.7, 131.1, 131.0, 128.7, 128.5, 128.4, 128.1, 126.4, 126.0, 124.4, 122.1, 120.1, 120.0, 112.3, 109.6, 82.8, 75.1, 30.8. IR (neat): ν/ cm^{-1} = 1737, 1451, 1202, 1065, 744, 692. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{25}H_{22}NO$: 352.1696, found: 352.1696.

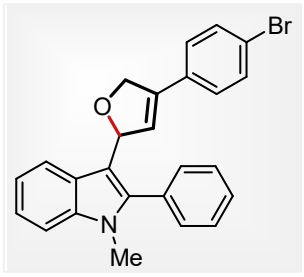
3-(4-([1,1'-Biphenyl]-4-yl)-2,5-dihydrofuran-2-yl)-1-methyl-2-phenyl-1*H*-indole (42, Scheme 5):



The title compound was prepared following **GP-6** using **10** (62.0 mg, 0.15 mmol), obtained as off-white gummy (61.6 mg, 96%). R_f value = 0.51 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, Acetone-D_6) δ/ ppm = 7.69 (d, J = 8.0 Hz, 4H), 7.63 (d, J = 7.8 Hz, 1H), 7.59 – 7.55 (m, 6H), 7.52 – 7.41 (m, 4H), 7.36 (t, J = 7.8 Hz, 1H), 7.20 (t, J = 7.0 Hz, 1H), 7.01 (t, J = 7.7 Hz, 1H), 6.48 (s, 1H), 6.03 (s,

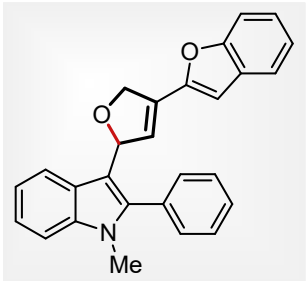
1H), 5.25 (dd, *J* = 11.8, 5.8 Hz, 1H), 5.08 (d, *J* = 11.8 Hz, 1H), 3.63 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, Acetone-D_6) *δ*/ ppm = 141.5, 141.4, 140.4, 139.2, 138.7, 132.8, 132.3, 132.0, 129.9, 129.4, 129.36, 128.5, 128.1, 127.7, 127.5, 125.9, 122.7, 120.9, 120.5, 113.8, 110.7, 83.7, 75.5, 31.2. IR (neat): ν/ cm^{-1} = 1710, 1359, 1219, 1090, 742, 698. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{31}H_{26}NO$: 450.1828, found: 450.1821.

3-(4-(4-Bromophenyl)-2,5-dihydrofuran-2-yl)-1-methyl-2-phenyl-1*H*-indole (43, Scheme 5):



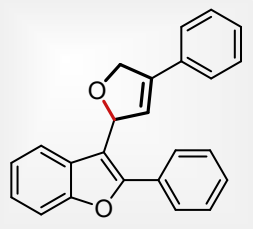
The title compound was prepared following **GP-6** using **12** (62.4 mg, 0.15 mmol), obtained as off-white gummy (59.4 mg, 92%). R_f value = 0.46 (10% EtOAc in hexane). ^{1}H NMR (500 MHz, DMSO-D_6) *δ*/ ppm = 7.59 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 7.1 Hz, 2H), 7.54 – 7.48 (m, 4H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.00 (dt, *J* = 7.9 Hz, 1H), 6.61 (q, *J* = 1.8 Hz, 1H), 5.91 (t, *J* = 5.9 Hz, 1H), 5.12 (ddd, *J* = 12.2, 5.9, 1.9 Hz, 1H), 4.96 (ddd, *J* = 12.2, 4.3, 2.3 Hz, 1H), 3.60 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-D_6) *δ*/ ppm = 138.9, 137.0, 136.9, 131.6, 131.4, 130.7, 130.4, 128.5, 128.45, 128.0, 125.9, 125.7, 121.7, 121.2, 119.5, 119.3, 111.9, 110.1, 82.2, 74.1, 30.7. IR (neat): ν/ cm^{-1} = 1737, 1458, 1245, 1019, 776, 697. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{21}NOBr$: 430.0801, found: 430.0801.

3-(4-(Benzofuran-2-yl)-2,5-dihydrofuran-2-yl)-1-methyl-2-phenyl-1*H*-indole (44, Scheme 5):



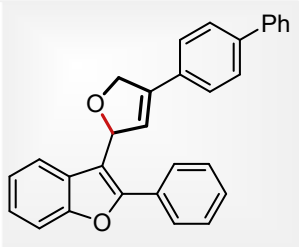
The title compound was prepared following **GP-6** using **27** (56.6 mg, 0.15 mmol), obtained as off-white gummy (54.6 mg, 93%). R_f value = 0.69 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, DMSO-D_6) *δ*/ ppm = 7.66 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.53 (m, 5H), 7.50 (dd, *J* = 8.2, 3.4 Hz, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 6.57 (d, *J* = 1.6 Hz, 1H), 5.97 (t, *J* = 4.0 Hz, 1H), 5.14 (ddd, *J* = 11.8, 5.8, 1.5 Hz, 1H), 4.97 (ddd, *J* = 11.8, 4.0, 2.2 Hz, 1H), 3.61 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-D_6) *δ*/ ppm = 154.2, 149.3, 139.2, 137.0, 130.8, 130.3, 129.1, 128.6, 128.5, 128.3, 126.7, 125.9, 125.2, 123.3, 121.8, 121.4, 119.6, 119.2, 111.3, 111.0, 110.2, 104.8, 82.1, 73.2, 30.7. IR (neat): ν/ cm^{-1} = 1710, 1359, 1219, 1090, 743, 670. HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{27}H_{22}NO_2$: 392.1645, found: 392.1643.

2-Phenyl-3-(4-phenyl-2,5-dihydrofuran-2-yl)benzofuran (45, Scheme 5):



The title compound was prepared following **GP-6** using **36** (48.7 mg, 0.15 mmol), obtained as off-white gummy (45.7 mg, 90%). R_f value = 0.39 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, DMSO-D_6) δ/ ppm = 7.80 (d, J = 7.1 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.62 – 7.50 (m, 6H), 7.43 (t, J = 7.2 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 8.3 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 6.72 (d, J = 1.9 Hz, 1H), 6.32 (t, J = 5.7 Hz, 1H), 5.30 (ddd, J = 12.4, 5.8, 2.0 Hz, 1H), 5.14 (ddd, J = 12.4, 4.2, 2.3 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-D_6) δ/ ppm = 153.7, 152.3, 139.3, 131.7, 129.4, 129.39, 129.1, 128.8, 128.5, 127.9, 127.7, 126.2, 124.8, 123.1, 122.9, 120.8, 115.8, 111.3, 80.9, 75.0. IR (neat): ν/ cm^{-1} = 1737, 1665, 1450, 1202, 1065, 744, 692. HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{24}H_{18}O_2Na$: 361.1199, found: 361.1196.

3-(4-([1,1'-Biphenyl]-4-yl)-2,5-dihydrofuran-2-yl)-2-phenylbenzofuran (46, Scheme 5):



The title compound was prepared following **GP-6** using **37** (60.1 mg, 0.15 mmol), obtained as off-white gummy (57.8 mg, 93%). R_f value = 0.81 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, DMSO-D_6) δ/ ppm = 7.81 (d, J = 8.2 Hz, 2H), 7.76 – 7.70 (m, 4H), 7.64 (d, J = 8.2 Hz, 3H), 7.60 (t, J = 7.3 Hz, 2H), 7.54 (d, J = 7.9 Hz, 2H), 7.48 (t, J = 8.2 Hz, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.77 (s, 1H), 6.34 (s, 1H), 5.34 (dd, J = 12.3, 5.7 Hz, 1H), 5.17 (d, J = 12.2 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-D_6) δ/ ppm = 186.9, 153.8, 152.4, 140.2, 139.6, 139.0, 130.9, 129.5, 129.2, 129.1, 128.0, 127.8, 127.1, 126.9, 126.7, 125.1, 124.9, 123.2, 123.1, 120.9, 115.9, 111.4, 81.1, 75.0. IR (neat): ν/ cm^{-1} = 1710, 1524, 1359, 1219, 1090, 748. HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{30}H_{23}O_2$: 415.1693, found: 415.1697.

ESI-11 UV-Visible and fluorescence studies of the synthesized indole derivative (24):

UV-Vis and fluorescence spectra of functionalized indole derivative (**24**) were recorded in CH_2Cl_2 solvent with a concentration of 10^{-5} M.

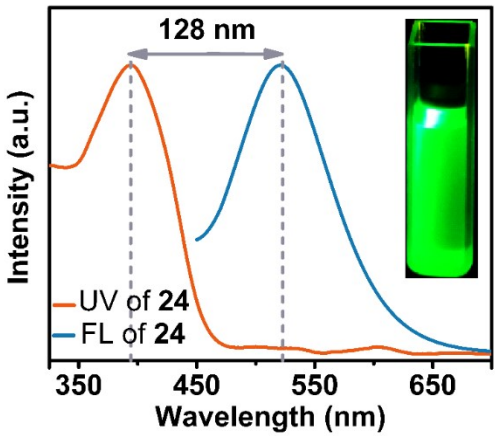


Figure S1. UV-Vis and fluorescence spectrum of indole derivative **24**.

ESI-12 X-Ray crystallographic study for the determination of compound structure:

Single crystal X-ray data for the compound **2**, **33**, **36**, **39** and **1ad** were collected using the detector system [λ (Mo-Kα) = 0.71073 Å] at 293K, graphite monochromator with a ω scan width of 0.3o, crystal-detector distance 60 mm, collimator 0.5 mm. The SMART software[7] was used for the intensity data acquisition and the SAINTPLUS Software[7] was used for the data extraction. In each case, absorption correction was performed with the help of SADABS program,[7] an empirical absorption correction using equivalent reflections was performed with the program. The structure was solved using SHELXS-97[8] and full-matrix least-squares refinement against F2 was carried out using SHELXL-97.[8] All non-hydrogen atoms were refined anisotropically. Aromatic and methyl hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms.

Crystallographic data (including the structure factor) for the structures **2**, **33**, **36**, **39** and **1ad** in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2166456, 2166457, 2166458, 2166459 and2166460. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

X-Ray Crystal Data for Compound 2:

CCDC Number	2166456
Compound identification code	rb007_0m_a
Empirical formula	C24 H19 N O
Formula weight	337.40
Temperature	300 K
Wavelength	0.71073Å
Crystal system	Triclinic
Space group	P -1

Unit cell dimensions	a=5.9743(5) alpha=90.934(4) b=10.7749(9) beta=95.031(4) c=14.3140(13) gamma=105.858(3)
Volume	882.17(13) $Å^3$
Z	2
Density (calculated)	1.270 g/cm^3
Absorption coefficient	0.077 mm-1
F(000)	356.0
Reflections collected	4107
Independent reflections	2765
Completeness to theta = 25.026 °	0.995
Refinement method	Full-matrix least-squares on F2
Max. and min. transmission	0.992 and 0.986
Goodness-of-fit on F2	1.080
R(reflections)	0.0679(2765)
wR2(reflections)	0.1896(4086)
Diffractometer	Xcalibur Gemini Eos CCD

ORTEP-Drawing of Compound 2:

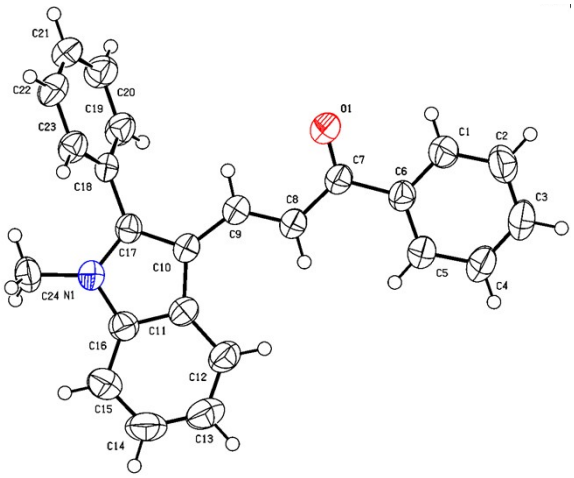


Figure S2. Thermal ellipsoidal plot of compound **2** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius.

X-Ray Crystal Data for Compound 33:

CCDC Number	2166457
Compound identification code	Rb 32
Empirical formula	C25 H21 N O3
Formula weight	383.43
Temperature	298 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a= 11.0647(2) alpha= 111.413(2) b= 12.8133(2) beta= 91.060(1) c= 15.8157(3) gamma= 102.444(1)
Volume	2026.78(7) $Å^3$
Z	4
Density (calculated)	1.257 g/cm^3
Absorption coefficient	0.082 mm^{-1}
F(000)	808.0
Reflections collected	7179
Independent reflections	5150
Completeness to theta = 25.025°	0.999
Refinement method	Full-matrix least-squares on F2
Max. and min. transmission	0.992 and 0.985
Goodness-of-fit on F2	1.048
R(reflections)	0.0464(5150)
wR2(reflections)	0.1279(7171)
Diffractometer	Xcalibur Gemini Eos CCD

ORTEP-Drawing of Compound 33:

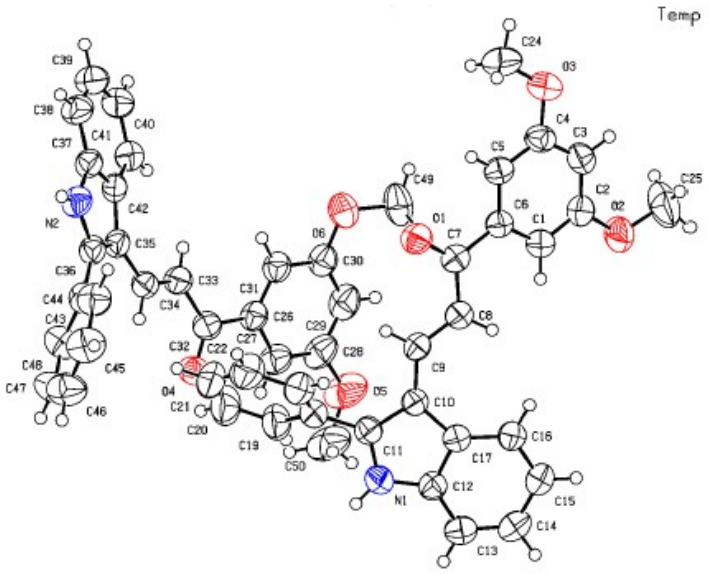


Figure S3. Thermal ellipsoidal plot of compound **33** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius**.**

X-Ray Crystal Data for Compound 36:

CCDC Number	2166458
Compound identification code	rb016_0ma_a
Empirical formula	C23 H16 O2
Formula weight	324.36
Temperature	300 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a= 11.716(6) alpha= 90 b= 14.621(7) beta= 107.26(2) c= 10.413(5) gamma= 90
Volume	1703.4(15) $Å^3$
Z	4
Density (calculated)	1.265 g/cm^3
Absorption coefficient	0.080 mm^{-1}
F(000)	680.0
Reflections collected	3018
Independent reflections	1800
Completeness to theta = 25.025°	0.914
Refinement method	Full-matrix least-squares on F2
Max. and min. transmission	0.992 and 0.986
Goodness-of-fit on F2	1.313
R(reflections)	0.1195(1800)

wR2(reflections)	0.3502(2759)
Diffractometer	Xcalibur Gemini Eos CCD

ORTEP-Drawing of Compound 36:

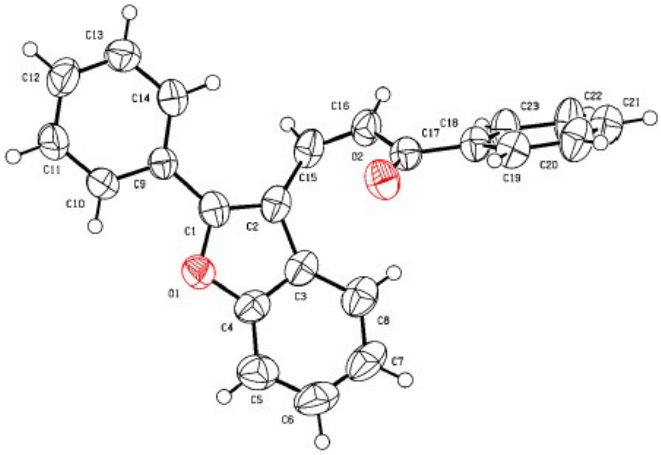


Figure S4. Thermal ellipsoidal plot of compound **36** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius**.**

X-Ray Crystal Data for Compound 39:

CCDC Number	2166459
Compound identification code	RB100
Empirical formula	C19 H19 N O3
Formula weight	309.35
Temperature	297 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a= 10.6702(4) alpha= 90 b= 9.9677(4) beta= 109.575(5) c= 15.8095(8) gamma= 90
Volume	1584.28(13) $Å^3$

Z	4
Density (calculated)	1.297 g/cm^3
Absorption coefficient	0.088 mm^{-1}
F(000)	656.0
Reflections collected	3514
Independent reflections	2236
Completeness to theta = 25.025°	0.924
Refinement method	Full-matrix least-squares on F2
Max. and min. transmission	0.996 and 0.995
Goodness-of-fit on F2	1.060
R(reflections)	0.0495(2236)
wR2(reflections)	0.1437(3248)
Diffractometer	Xcalibur Gemini Eos CCD

ORTEP-Drawing of Compound 39:

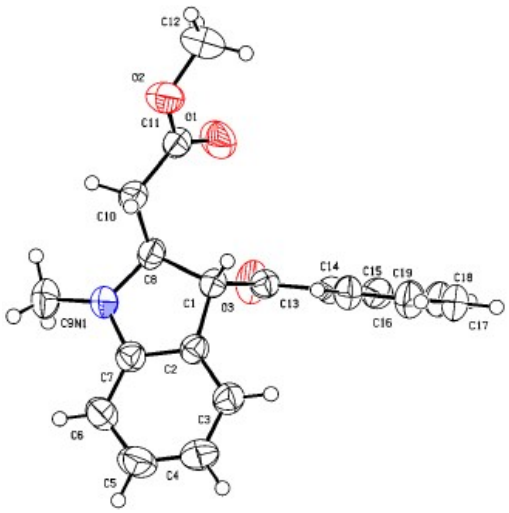


Figure S5. Thermal ellipsoidal plot of compound **39** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius**.**

X-Ray Crystal Data for Compound 1ad:

CCDC Number	2166460
Compound identification code	Rb38

Empirical formula	C26 H21 N O3
Formula weight	395.44
Temperature	298 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a= 19.4449(8) alpha= 90 b= 5.9085(2) beta= 116.246(5) c= 19.6048(8) gamma= 90
Volume	2020.19(16) $Å^3$
Z	4
Density (calculated)	1.300 g/cm^3
Absorption coefficient	0.085 mm^{-1}
F(000)	832.0
Reflections collected	4408
Independent reflections	2574
Completeness to theta = 25.025°	0.958
Refinement method	Full-matrix least-squares on F2
Max. and min. transmission	0.992 and 0.985
Goodness-of-fit on F2	1.053
R(reflections)	0.0514(2574)
wR2(reflections)	0.1502(4222)
Diffractometer	Xcalibur Gemini Eos CCD

ORTEP-1ad : **Drawing of Compound**

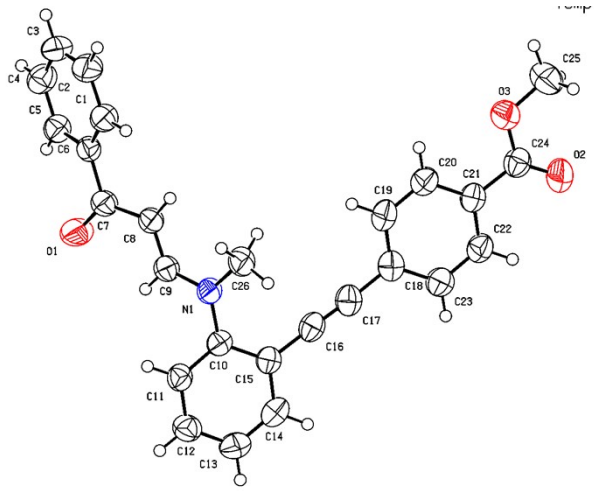


Figure S6. Thermal ellipsoidal plot of compound **1ad** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius**.**

ESI-13 HRMS studies to support the proposed mechanism:

The reaction for the formation of indole **2** from **1aa** was conducted separately in presence of TfOH and $MeSO_3H$. After 30mins, HRMS analysis has been performed for both the reactions to identify few intemediates.

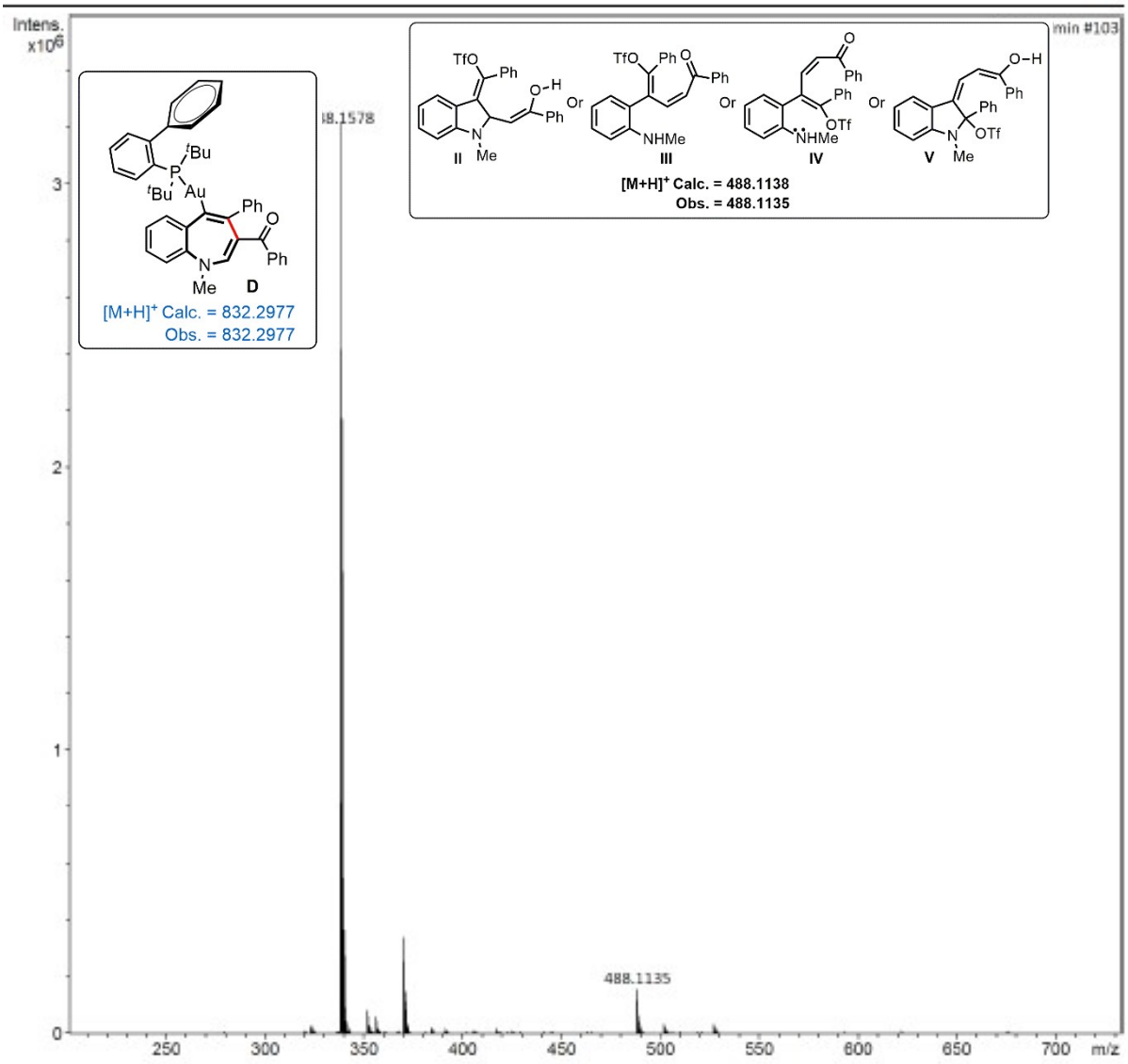


Figure S7. Full HRMS spectrum of crude reaction mixture of TfOH catalysis for intermediate **II/III/IV/V**.

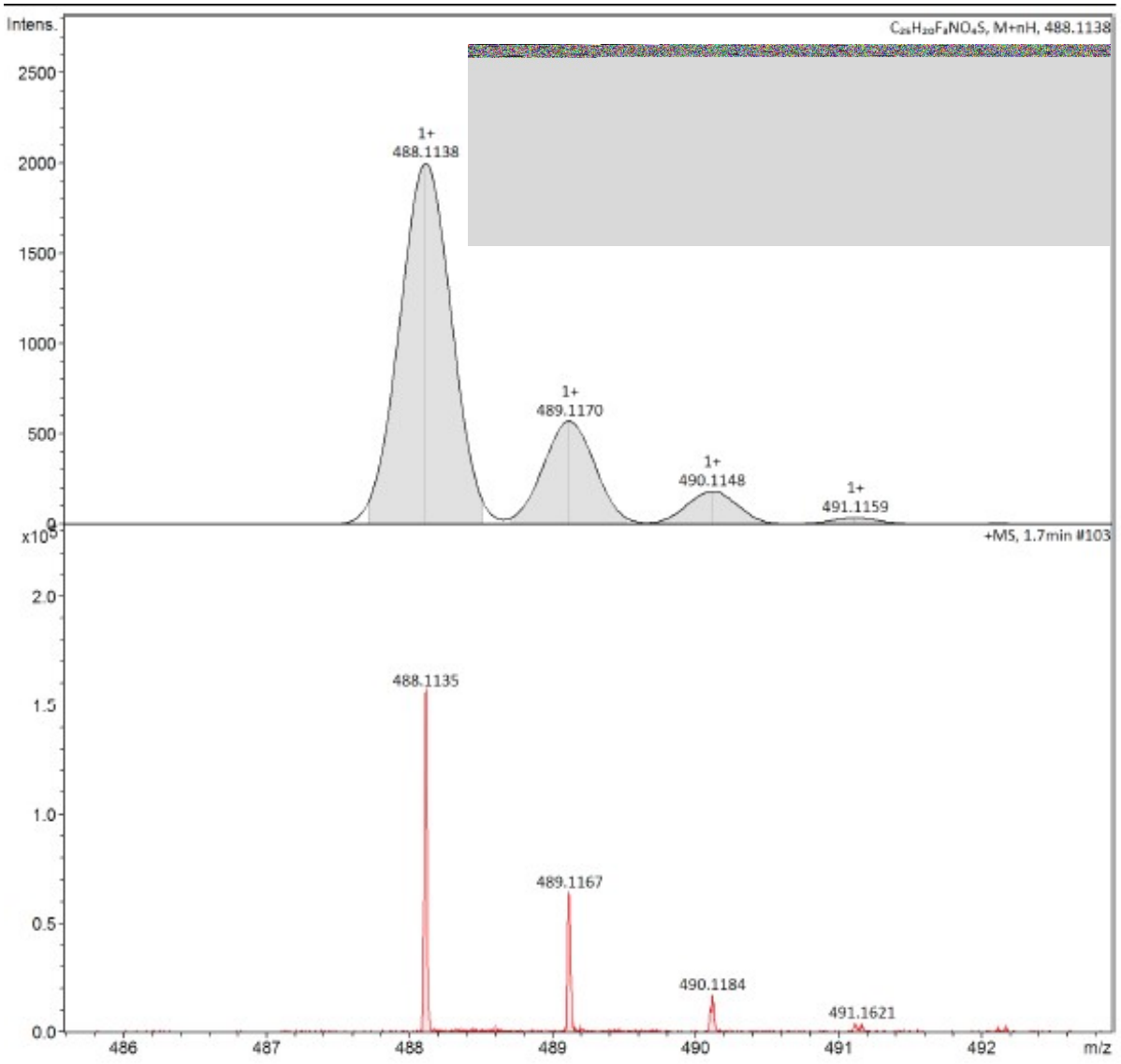


Figure S8. Simulated HRMS spectrum of crude reaction mixture of TfOH catalysis for intermediate **II/III/IV/V**.

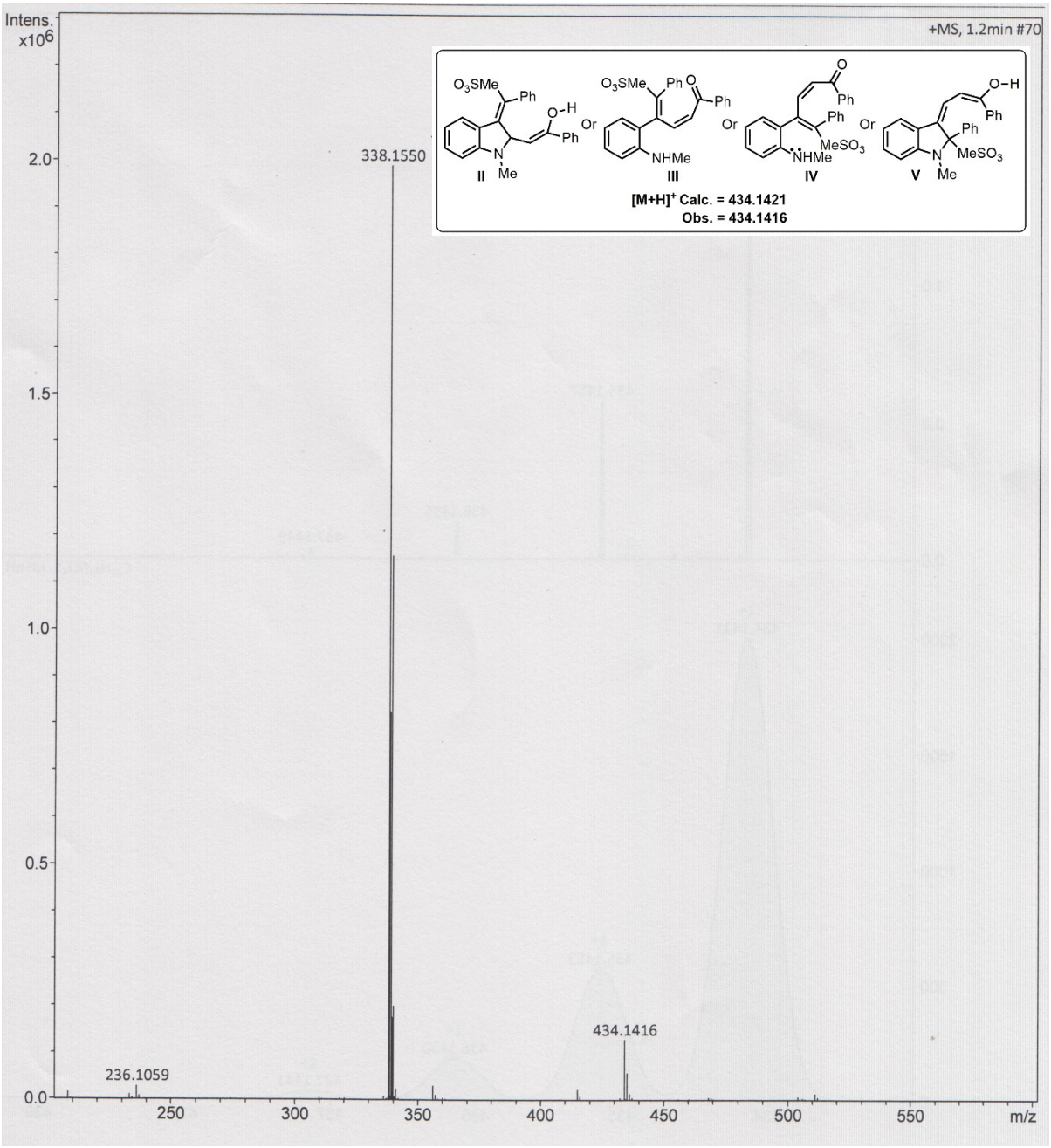


Figure S9. Full HRMS spectrum of crude reaction mixture of $MeSO_3H$ catalysis for intermediate **II/III/IV/V**.

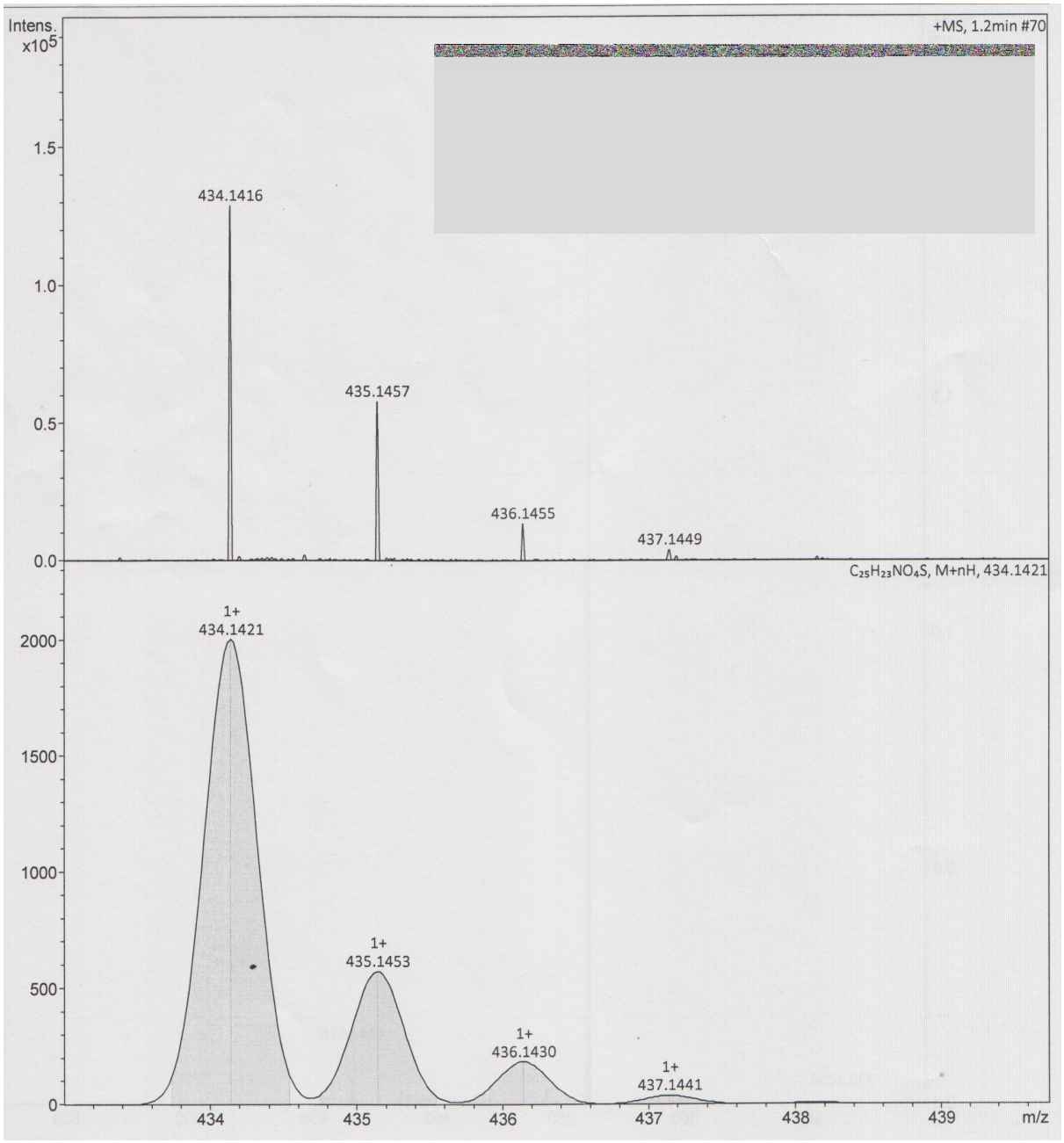


Figure S10. Simulated HRMS spectrum of crude reaction mixture of $MeSO_3H$ catalysis for intermediate **II/III/IV/V**.

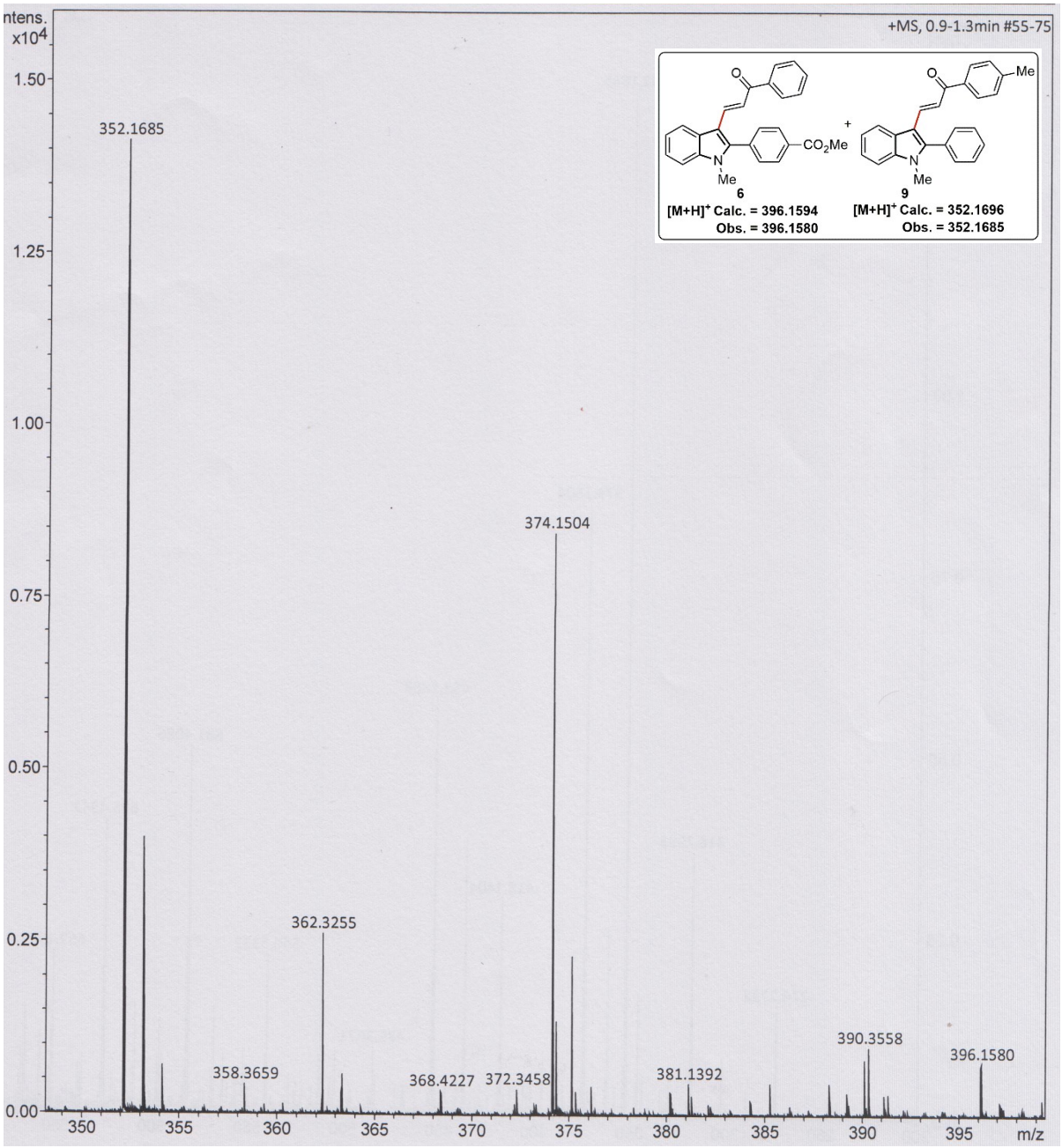


Figure S11. HRMS spectrum of cross-over experiment.

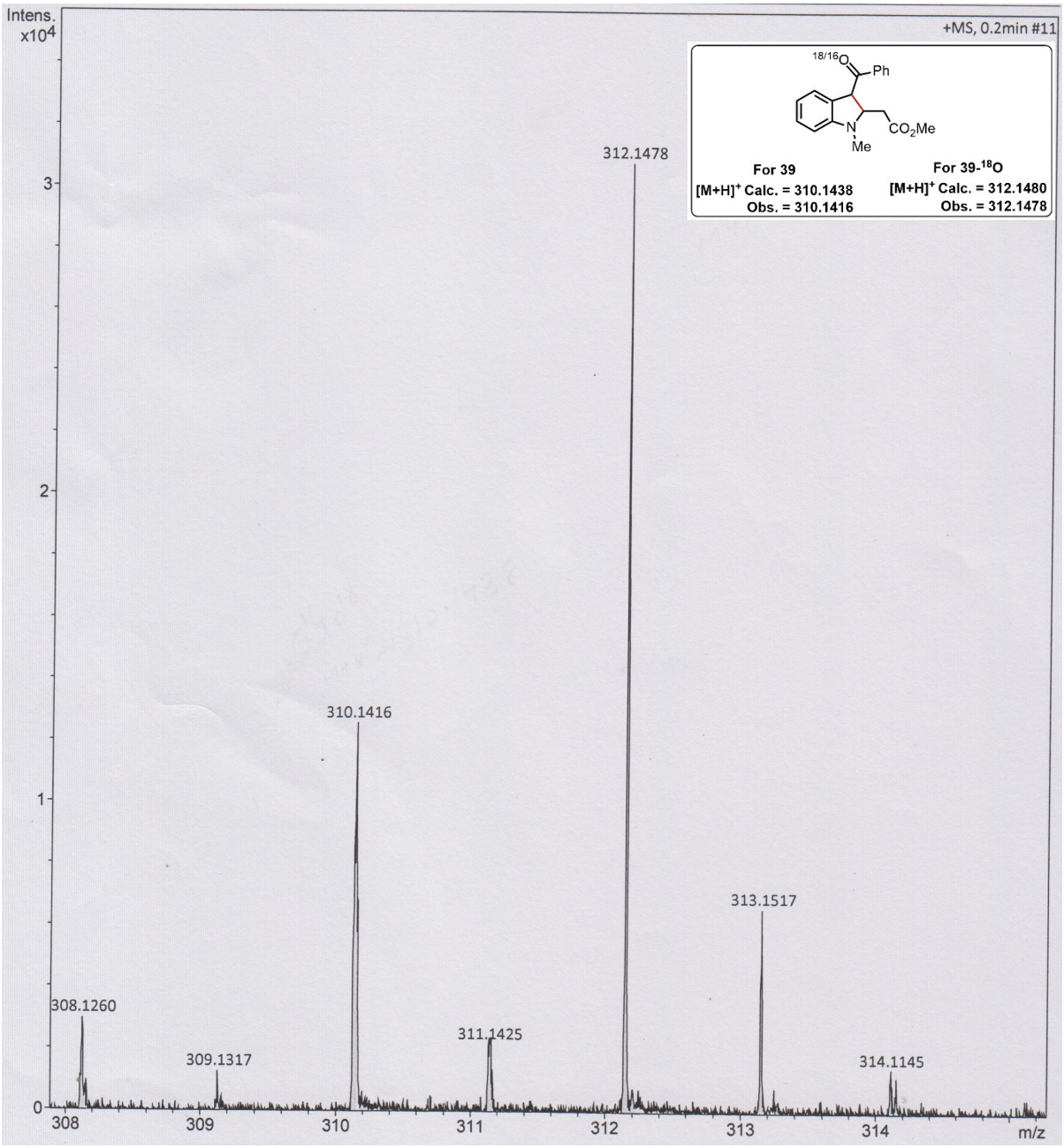


Figure S12. HRMS spectrum of ^{18}O levelling experiment.

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