

Supporting Information

Aminoarylation of Alkynes using Diarylanilines

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1. General methods

Nuclear magnetic resonance spectra were acquired on either 500 MHz (Bruker® AVII+ 500, Bruker AVIII HD 500) or 400 MHz (Bruker AVIII HD 400, Bruker AVIII 400). All ^1H NMR spectra are reported in parts per million (ppm) and were measured relative to the signals at 7.26 ppm (CHCl_3), 2.09 ppm (acetone), 2.54 ppm (DMSO) or 5.32 ppm (CH_2Cl_2). All ^{13}C NMR spectra were reported in ppm relative to residual CHCl_3 (77.36 ppm), acetone (30.60 ppm), DMSO (40.45 ppm), CH_2Cl_2 (53.80 ppm) and were obtained with 1H -decoupling. All ^{19}F chemical shifts were unadjusted from raw data. Data for ^1H NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; br, broad signal), coupling constant (Hz), integration.

High resolution mass spectra were obtained on ThermoFisher Scientific Q-ExactiveTM, Thermo Scientific Exactive plus EMR and Agilent 6530 Q-TOF instruments, using either electrospray ionisation (ESI), atmospheric-pressure chemical ionisation (APCI) as ionisation methods in the positive and negative mode.

Flash column chromatography was carried out by using re-used 10g, 25g or 50g Biotage® Snap Ultra or Biotage Sfär Silica cartridges on a Biotage Isolera Four automated column, using 35-70 μm , 60 Å silica gel for chromatography from ThermoFisher Scientific® or 40-63 μm 60 Å silica gel from Sigma-Aldrich.

Melting points (mp) were recorded on a Griffin melting point apparatus to the nearest degree and are uncorrected.

All air and/or moisture sensitive reactions were performed under an atmosphere of dry nitrogen using anhydrous solvent. All solvents for air sensitive reactions were degassed by bubbling N_2 on the Schlenk line. All commercially available reagents and solvents were used as received without further purification. (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl hex-2-ynoate and (S,Z)-3-(2-((1R,3aS,7aR,E)-1-((2R,5R,E)-5,6-dimethylhept-3-en-2-yl)-7a-methyloctahydro-4H-inden-4-ylidene)ethylidene)-4-methylenecyclohexyl hex-2-ynoate were synthesized based on the literature.¹

2. General procedures

General procedure A – preparation of aniline starting materials

To an oven-dried microwave vial were added aniline (1.2 equiv.), aryl halide (5.0 mmol, 1.0 equiv.), $\text{Pd}(\text{OAc})_2$ (4 mol%), *rac*-Binap (8 mol%) and Cs_2CO_3 (1.4 equiv.). The vial was sealed by a cap and placed on the Schlenk line to evacuate and backfill with N_2 three times. Then toluene (0.5 M) and aryl halide (1.0 equiv.) (if it is liquid) were added by syringe under a flow of N_2 . The mixture was stirred at 120 °C for 18 h. After cooling to room temperature, the mixture was filtered through a pad of Celite and washed with ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel.

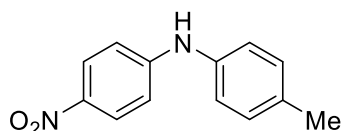
General procedure B – preparation of alkyne starting materials

To a solution of alkyne (10.0 mmol, 1.0 equiv.) in anhydrous THF (0.2M) was dropwise added $n\text{BuLi}$ (1.1 equiv.) at -78 °C under a nitrogen atmosphere and the reaction mixture was stirred at -78 °C for 30 min. Then ethyl chloroformate (1.2 equiv.) was slowly added by syringe and then warmed to room temperature and stirred until complete. The reaction was quenched with saturated NH_4Cl solution and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel.

General procedure C - STR

To an oven-dried microwave vial were added diaryl amine **14** (1.2 equiv.), alkyne **15** (1.0 equiv.) and Cs_2CO_3 (1.5 equiv.). The vial was sealed by a cap and placed on the Schlenk line to evacuate and backfill with N_2 three times. Then dimethylacetamide (0.2 M), alkyne **15** (1.0 equiv.) (if it is liquid) were added by syringe under a flow of N_2 . The mixture was stirred at 70 °C for 18 h. After cooling to room temperature, water and ethyl acetate were added and the phases were separated. The organic phase was washed with brine three times, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel.

3. Compound characterization



4-methyl-N-(4-nitrophenyl)aniline

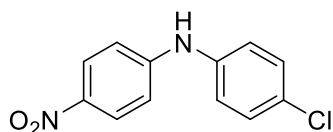
Prepared according to general procedure **A** by using 4-nitroaniline and 1-bromo-4-methylbenzene to yield the titled compound as orange solid (0.79, 72%).

^1H NMR (400 MHz, acetone- d_6) δ 8.39 (s, 1H), 8.12 (d, J = 9.3 Hz, 2H), 7.29 – 7.18 (m, 4H), 7.09 (d, J = 9.3 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 153.1, 140.3, 139.3, 135.2, 131.6, 127.6, 123.5, 114.7, 21.6.

HRMS (+ESI): calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 251.0791, found 251.0794.

mp: 123-125 °C.



4-chloro-N-(4-nitrophenyl)aniline

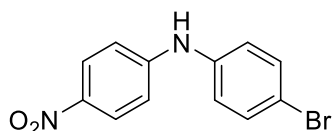
Prepared according to general procedure **A** by using 4-nitroaniline and 1-chloro-4-iodobenzene to yield the titled compound as orange solid (0.84 g, 68%).

^1H NMR (400 MHz, acetone- d_6) δ 8.53 (s, 1H), 8.16 (d, J = 9.3 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.9 Hz, 2H), 7.19 (d, J = 9.2 Hz, 2H).

^{13}C NMR (100 MHz, acetone- d_6) δ 152.0, 141.1, 131.0, 129.4, 127.5, 124.0, 123.9, 115.6.

HRMS (+APCI): calcd for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl}$ $[\text{M}+\text{H}]^+$ 249.0425, found 249.0429.

mp: 160-161 °C.



4-bromo-N-(4-nitrophenyl)aniline

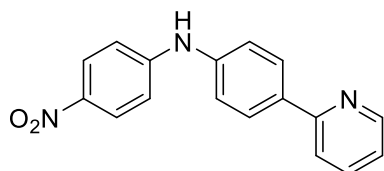
Prepared according to general procedure **A** by using 4-nitroaniline and 1-bromo-4-iodobenzene to yield the titled compound as orange solid (1.10 g, 75%).

^1H NMR (400 MHz, acetone- d_6) δ 8.53 (s, 1H), 8.16 (d, J = 9.2 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 9.2 Hz, 2H).

^{13}C NMR (100 MHz, acetone- d_6) δ 151.8, 141.6, 131.1, 127.5, 124.3, 124.2, 116.8, 115.7.

HRMS (+ESI): calcd for $\text{C}_{12}\text{H}_9\text{N}_2\text{O}_2\text{BrNa}$ $[\text{M}+\text{Na}]^+$ 314.9740, found 314.9745.

mp: 145-147 °C.



4-nitro-N-(4-(pyridin-2-yl)phenyl)aniline

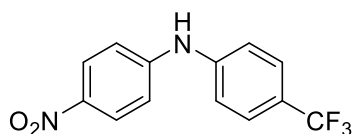
Prepared according to general procedure **A** by using 4-nitroaniline and 2-(4-bromophenyl)pyridine to yield the titled compound as yellow solid (0.78 g, 53%).

¹H NMR (500 MHz, DMSO-*d*₆) 9.52 (s, 1H), 8.67 (d, *J* = 3.8 Hz, 1H), 8.15 (t, *J* = 8.5 Hz, 4H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.87 (td, *J* = 7.7, 1.9 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.33 (ddd, *J* = 7.4, 4.7, 1.1 Hz, 1H), 7.23 – 7.17 (m, 2H).

¹³C NMR (125 MHz, DMSO-*d*₆) δ 156.5, 151.0, 150.4, 142.1, 139.3, 138.1, 134.1, 128.6, 127.1, 123.0, 120.9, 120.5, 115.1.

HRMS (+ESI): calcd for C₁₇H₁₄N₃O₂ [M+H]⁺ 292.1081, found 292.1082.

mp: 186-188 °C.



4-nitro-N-(4-(trifluoromethyl)phenyl)aniline

Prepared according to general procedure **A** by using 4-nitroaniline and 1-iodo-4-(trifluoromethyl)benzene to yield the titled compound as yellow solid (0.84 g, 60%).

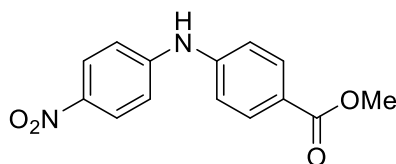
¹H NMR (400 MHz, acetone-*d*₆) δ 8.83 (s, 1H), 8.21 (d, *J* = 9.2 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.35 (d, *J* = 9.2 Hz, 2H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 150.7, 146.3, 142.1, 128.4 (q, *J* = 3.9 Hz), 127.4, 126.3 (q, *J* = 268.8 Hz), 125.1 (q, *J* = 32.4 Hz), 120.7, 117.0.

¹⁹F NMR (235 MHz, acetone-*d*₆) δ -62.3.

HRMS (-ESI): calcd for C₁₃H₈N₂O₂F₃ [M-H]⁻ 281.0543, found 281.0532.

mp: 131-132 °C.



methyl 4-((4-nitrophenyl)amino)benzoate

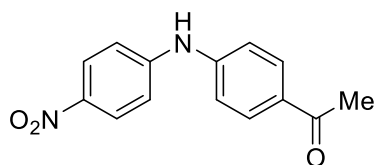
Prepared according to general procedure **A** by using 4-nitroaniline and methyl 4-bromobenzoate to yield the titled compound as yellow solid (0.95 g, 70%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.86 (s, 1H), 8.21 (d, *J* = 9.2 Hz, 2H), 8.02 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 9.2 Hz, 2H), 3.89 (s, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 167.5, 150.5, 147.0, 142.1, 132.7, 127.4, 125.4, 119.7, 117.3, 52.9.

HRMS (-ESI): calcd for C₁₄H₁₁N₂O₄ [M-H]⁻ 271.0724, found 271.0714.

mp: 137-139 °C.



1-(4-((4-nitrophenyl)amino)phenyl)ethan-1-one

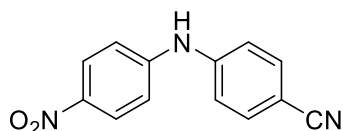
Prepared according to general procedure **A** by using 4-nitroaniline and 1-(4-iodophenyl)ethan-1-one to yield the titled compound as orange solid (0.77 g, 60%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.87 (s, 1H), 8.22 (d, *J* = 9.2 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 9.2 Hz, 2H), 2.58 (s, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 197.0, 150.5, 147.0, 142.1, 133.1, 131.8, 127.4, 119.7, 117.4, 27.2.

HRMS (-ESI): calcd for C₁₄H₁₁N₂O₃ [M-H]⁻ 255.0775, found 255.0763

mp: 142-143 °C.



4-((4-nitrophenyl)amino)benzonitrile

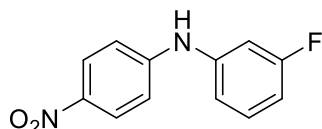
Prepared according to general procedure **A** by using 4-nitroaniline and 4-bromobenzonitrile to yield the titled compound as yellow solid (0.69g, 58%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.96 (s, 1H), 8.24 (d, *J* = 9.2 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 9.3 Hz, 2H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 149.9, 147.1, 142.7, 135.3, 127.3, 120.4, 120.1, 118.0, 106.1.

HRMS (+APCI): calcd for C₁₃H₁₀N₃O₂ [M+H]⁺ 240.0768, found 240.0768.

mp: 207-209 °C.



3-fluoro-N-(4-nitrophenyl)aniline

Prepared according to general procedure **A** by using 4-nitroaniline and 1-fluoro-3-iodobenzene to yield the titled compound as yellow solid (1.10g, 95%).

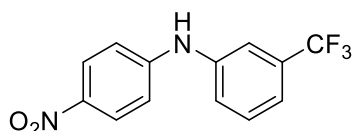
¹H NMR (400 MHz, acetone-*d*₆) δ 8.61 (s, 1H), 8.18 (d, *J* = 9.3 Hz, 2H), 7.48 – 7.39 (m, 1H), 7.26 (d, *J* = 9.3 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.09 (d, *J* = 10.9 Hz, 1H), 6.88 (td, *J* = 8.4, 2.6 Hz, 1H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 165.1 (d, *J* = 242.0 Hz), 151.5, 144.3 (d, *J* = 11.0 Hz), 141.5, 132.7 (d, *J* = 10.0 Hz), 127.5, 117.7 (d, *J* = 3.0 Hz), 116.1, 111.2 (d, *J* = 22.0 Hz), 108.6 (d, *J* = 25.0 Hz),

¹⁹F NMR (235 MHz, acetone-*d*₆) δ -113.2.

HRMS (+ESI): calcd for C₁₂H₉N₂O₂FNa [M+Na]⁺ 255.0540, found 255.0544.

mp: 113-114 °C.



N-(4-nitrophenyl)-3-(trifluoromethyl)aniline

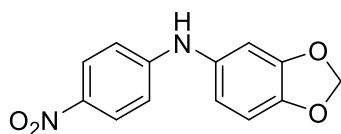
Prepared according to general procedure **A** by using 4-nitroaniline and 1-iodo-3-(trifluoromethyl)benzene to yield the titled compound as yellow solid (0.73 g, 52%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.81 (s, 1H), 8.18 (d, *J* = 9.2 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.59 (s, 1H), 7.47 – 7.40 (m, 1H), 7.27 (d, *J* = 9.2 Hz, 2H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 151.4, 143.3, 141.7, 132.9 (q, *J* = 32.0 Hz), 132.2, 127.5, 125.9 (q, *J* = 270.0 Hz), 125.1, 121.0 (q, *J* = 3.0 Hz), 118.2 (q, *J* = 4.0 Hz), 116.2.

¹⁹F NMR (235 MHz, acetone-*d*₆) δ -63.3.

HRMS (+ESI): calcd for $C_{13}H_9N_2O_2F_3Na$ $[M+Na]^+$ 305.0508, found 305.0512.
mp: 129-130 °C.



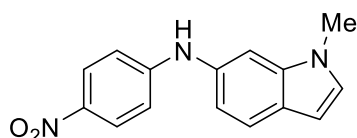
N-(4-nitrophenyl)benzo[d][1,3]dioxol-5-amine

Prepared according to general procedure **A** by using benzo[d][1,3]dioxol-5-amine and 1-iodo-4-nitrobenzene to yield the titled compound as yellow solid (0.57g, 44%).

1H NMR (400 MHz, acetone- d_6) δ 8.30 (s, 1H), 8.11 (d, J = 9.2 Hz, 2H), 7.01 (d, J = 9.3 Hz, 2H), 6.91 (d, J = 8.2 Hz, 1H), 6.87 (d, J = 2.1 Hz, 1H), 6.80 (dd, J = 8.2, 2.2 Hz, 1H), 6.07 (s, 2H).

^{13}C NMR (100 MHz, acetone- d_6) δ 153.7, 150.1, 146.4, 140.2, 135.9, 127.6, 117.6, 114.4, 110.1, 106.2, 103.2.

HRMS (+ESI): calcd for $C_{13}H_{10}N_2O_4Na$ $[M+Na]^+$ 281.0533, found 281.0538.
mp: 125-127 °C.



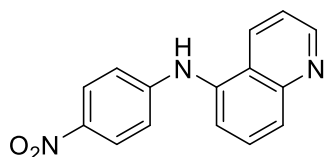
1-methyl-N-(4-nitrophenyl)-1H-indol-6-amine

Prepared according to general procedure **A** by using 4-nitroaniline and 6-bromo-1-methyl-1H-indole to yield the titled compound as yellow solid (0.23 g, 17%).

1H NMR (400 MHz, acetone- d_6) δ 8.45 (s, 1H), 8.11 (d, J = 9.3 Hz, 2H), 7.62 (d, J = 8.3 Hz, 1H), 7.38 (s, 1H), 7.26 (d, J = 3.1 Hz, 1H), 7.10 (d, J = 9.3 Hz, 2H), 7.03 (d, J = 8.4 Hz, 1H), 6.48 (d, J = 3.0 Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 154.3, 139.9, 139.0, 135.8, 131.3, 127.9, 127.6, 123.0, 117.3, 114.3, 105.5, 102.4, 33.7.

HRMS (+ESI): calcd for $C_{15}H_{13}N_3O_2Na$ $[M+Na]^+$ 290.0900, found 290.0905.
mp: 178-180 °C.



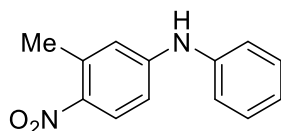
N-(4-nitrophenyl)quinolin-5-amine

Prepared according to general procedure **A** by using 4-nitroaniline and 5-bromoquinoline to yield the titled compound as orange solid (0.53 g, 40%).

1H NMR (400 MHz, acetone- d_6) δ 8.98 (d, J = 4.0 Hz, 1H), 8.66 (s, 1H), 8.50 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 9.3 Hz, 2H), 8.01 (d, J = 8.6 Hz, 1H), 7.88 – 7.80 (m, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.55 (dd, J = 8.6, 4.0 Hz, 1H), 7.05 (d, J = 9.2 Hz, 2H).

^{13}C NMR (100 MHz, acetone- d_6) δ 154.3, 152.5, 151.2, 140.9, 138.2, 132.6, 131.0, 128.9, 127.5, 126.2, 123.1, 122.9, 115.3.

HRMS (+APCI): calcd for $C_{15}H_{12}N_3O_2$ $[M+H]^+$ 266.0924, found 266.0921.
mp: 189-190 °C.



3-methyl-4-nitro-N-phenylaniline

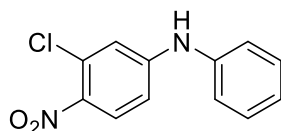
Prepared according to general procedure **A** by using 3-methyl-4-nitroaniline and iodobenzene to yield the titled compound as yellow solid (0.77 g, 68%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.27 (s, 1H), 8.07 (d, *J* = 8.9 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.06 – 6.97 (m, 2H), 2.60 (s, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 151.2, 142.3, 138.6, 131.1, 129.3, 125.0, 122.6, 122.5, 118.5, 113.6, 22.8.

HRMS (+APCI): calcd for C₁₃H₁₂N₂O₂Na [M+Na]⁺ 251.0791, found 251.0794.

mp: 123-124 °C.



3-chloro-4-nitro-N-phenylaniline

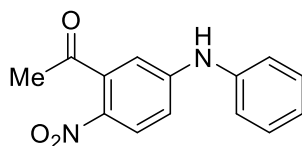
Prepared according to general procedure **A** by using 3-chloro-4-nitroaniline and iodobenzene to yield the titled compound as yellow solid (0.61 g, 49%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.50 (s, 1H), 8.07 (d, *J* = 9.1 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 2.5 Hz, 1H), 7.10 (dd, *J* = 9.1, 2.5 Hz, 1H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 151.9, 141.5, 139.2, 131.3, 131.0, 130.4, 125.9, 123.4, 117.2, 114.0.

HRMS (+APCI): calcd for C₁₂H₁₀N₂O₂Cl [M+H]⁺ 249.0425, found 249.0422.

mp: 130-132 °C.



1-(2-nitro-5-(phenylamino)phenyl)ethan-1-one

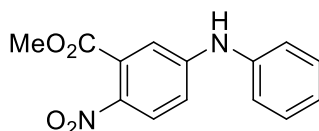
Prepared according to general procedure **A** by using 1-(5-amino-2-nitrophenyl)ethan-1-one and iodobenzene to yield the titled compound as yellow solid (0.79 g, 62%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.62 (s, 1H), 8.11 (d, *J* = 9.2 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.38 – 7.33 (m, 2H), 7.24 – 7.15 (m, 2H), 6.95 (d, *J* = 2.6 Hz, 1H), 2.49 (s, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 201.4, 152.7, 143.7, 141.5, 137.0, 131.3, 128.8, 126.0, 123.4, 115.4, 112.4, 31.4.

HRMS (+APCI): calcd for C₁₄H₁₃N₂O₃ [M+H]⁺ 257.0921, found 257.0911.

mp: 127-128 °C.



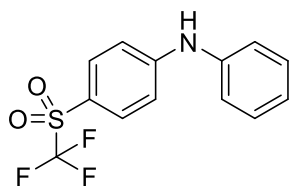
methyl 2-nitro-5-(phenylamino)benzoate

Prepared according to general procedure **A** by using methyl 5-amino-2-nitrobenzoate and iodobenzene to yield the titled compound as orange oil (1.17 g, 86%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.55 (s, 1H), 8.07 (d, *J* = 9.2 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.35 (d, *J* = 7.3 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.14 (d, *J* = 2.6 Hz, 1H), 3.89 (s, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 168.5, 152.1, 141.6, 133.8, 131.3, 128.7, 126.0, 123.4, 116.0, 114.7, 54.0, 31.4.

HRMS (+APCI): calcd for C₁₄H₁₂N₂O₄ [M]⁺ 272.0792, found 272.0790.



N-phenyl-4-((trifluoromethyl)sulfonyl)aniline

Prepared according to general procedure **A** by using methyl 4-((trifluoromethyl)sulfonyl)aniline and iodobenzene to yield the titled compound as white solid (0.39 g, 26%).

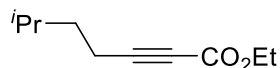
¹H NMR (400 MHz, acetone-*d*₆) δ 8.66 (s, 1H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.40 – 7.34 (m, 2H), 7.30 (d, *J* = 9.0 Hz, 2H), 7.23 (tt, *J* = 7.2, 1.2 Hz, 1H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 154.6, 141.3, 134.7, 131.3, 126.2, 123.8, 121.9 (q, *J* = 323 Hz), 118.2, 115.9.

¹⁹F NMR (235 MHz, acetone-*d*₆) δ -80.5.

HRMS (-APCI): calcd for C₁₃H₉NO₂F₃S [M-H]⁻ 300.0312, found 300.0306.

mp: 121-123 °C.



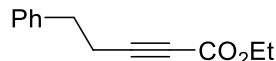
methyl 2-nitro-5-(phenylamino)benzoate

Prepared according to general procedure **B** by using 5-methylhex-1-yne to yield the titled compound as colourless oil (0.85 g, 51%).

¹H NMR (400 MHz, acetone-*d*₆) δ 4.20 (q, *J* = 7.1 Hz, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.79 – 1.69 (m, 1H), 1.54 – 1.47 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.96 (s, 3H), 0.95 (s, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 154.8, 90.3, 74.7, 62.8, 37.9, 28.7, 23.0, 17.6, 15.1.

HRMS (+ESI): calcd for C₁₀H₁₆O₂Na [M+Na]⁺ 191.1043, found 191.1045.



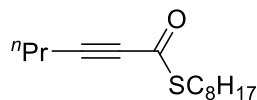
ethyl 5-phenylpent-2-ynoate

Prepared according to general procedure **B** by using but-3-yn-1-ylbenzene to yield the titled compound as colourless oil (1.37 g, 68%).

¹H NMR (400 MHz, CDCl₃) δ 7.34 (dd, *J* = 8.3, 6.4 Hz, 2H), 7.29 – 7.19 (m, 3H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 153.8, 139.8, 128.7, 128.5, 126.8, 88.4, 73.9, 61.9, 34.0, 21.0, 14.2.

HRMS (+ESI): calcd for C₁₃H₁₄O₂Na [M+Na]⁺ 225.0886, found 225.0888.



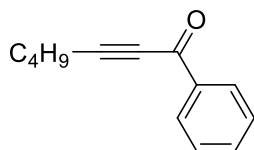
S-octyl hex-2-ynethioate

To a solution of hex-2-ynoic acid (4.0 mmol, 1.0 equiv.) and DMAP (0.1 equiv.) in DCM (50 mL) were added EDC·HCl (1.5 equiv.) and octane-1-thiol (1.1 equiv.) at 0 °C. Then the reaction was warmed to room temperature. Upon completion monitored by the TLC, water was added and the phases were separated. Then the aqueous phase was extracted with DCM (x3). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the titled compound as colourless oil (0.46 g, 48%).

¹H NMR (500 MHz, acetone-*d*₆) δ 3.00 (t, *J* = 7.3 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 1.68 – 1.58 (m, 4H), 1.46 – 1.38 (m, 2H), 1.37 – 1.28 (m, 8H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (125 MHz, acetone-*d*₆) δ 177.1, 96.3, 80.2, 33.2, 30.8, 30.57, 30.10, 24.0, 22.5, 21.7, 15.1, 14.3.

HRMS (+ESI): calcd for C₁₄H₂₄OSNa [M+Na]⁺ 263.1440, found 263.1443.



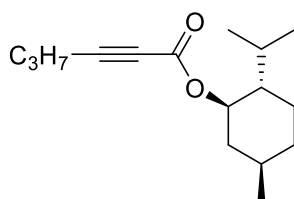
1-phenylhept-2-yn-1-one

To an oven-dried microwave vial were added PdCl₂(PPh₃)₂ (0.5 mol%) and CuI (2.5 mol%). The vial was sealed by a cap and placed on the Schlenk line to evacuate and backfill with N₂ three times. Then Et₃N (10 mL), benzoyl chloride (5 mmol, 1.0 equiv.) and hex-1-yne (1.25 equiv.) were added. The mixture was stirred at room temperature. After 24 h, Et₂O was added and the reaction was quenched with 3 M HCl. Then the organic layer was washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The mixture was purified by column chromatography on silica gel to afford the titled compound as light brown oil (0.76 g, 82%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.17 (d, *J* = 7.1 Hz, 2H), 7.73 (t, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 2.62 (t, *J* = 7.1 Hz, 2H), 1.71 (p, *J* = 7.0 Hz, 2H), 1.56 (h, *J* = 7.3 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 178.8, 138.7, 135.6, 130.7, 130.4, 98.0, 80.9, 31.4, 23.5, 19.8, 14.5.

HRMS (+ESI): calcd for C₁₃H₁₄ONa [M+Na]⁺ 209.0937, found 209.0940.



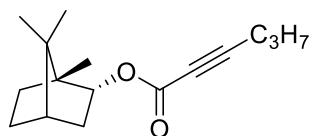
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl hex-2-ynoate

To a solution of hex-2-ynoic acid (4.0 mmol, 1.0 equiv.) and DMAP (0.2 equiv.) in DCM (50 mL) were added EDC·HCl (1.2 equiv.) and L-Menthol (1.1 equiv.) at 0 °C. Then the reaction was warmed to room temperature. Upon completion monitored by the TLC, water was added and the phases were separated. Then the aqueous phase was extracted with DCM (x3). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the titled compound as colourless oil (0.93 g, 93%).

¹H NMR (400 MHz, acetone-*d*₆) δ 4.78 (td, *J* = 10.9, 4.4 Hz, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.00 (dtd, *J* = 11.9, 4.1, 1.8 Hz, 1H), 1.92 (pd, *J* = 7.0, 2.7 Hz, 1H), 1.78 – 1.70 (m, 2H), 1.63 (h, *J* = 7.3 Hz, 2H), 1.58 – 1.50 (m, 1H), 1.46 (ddt, *J* = 12.6, 10.8, 3.1 Hz, 1H), 1.21 – 0.87 (m, 12H), 0.81 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 154.5, 90.2, 76.9, 75.0, 48.5, 42.2, 35.6, 32.9, 27.8, 24.9, 23.0, 22.6, 21.7, 21.4, 17.4, 14.4.

HRMS (+ESI): calcd for C₁₆H₂₆O₂Na [M+Na]⁺ 273.1825, found 273.1828.



(1R,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl hex-2-ynoate

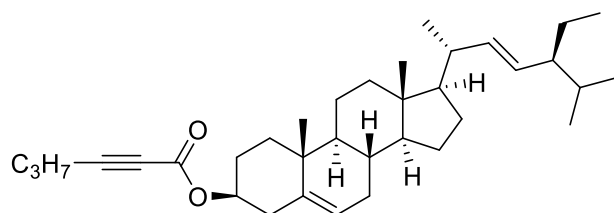
To a solution of hex-2-ynoic acid (4.0 mmol, 1.0 equiv.) and DMAP (0.2 equiv.) in DCM (50 mL)

were added EDC·HCl (1.2 equiv.) and (-)-Borneol (1.1 equiv.) at 0 °C. Then the reaction was warmed to room temperature. Upon completion monitored by the TLC, water was added and the phases were separated. Then the aqueous phase was extracted with DCM (x3). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the titled compound as colourless oil (0.87 g, 87%).

¹H NMR (400 MHz, acetone-*d*₆) δ 4.97 (ddd, *J* = 10.0, 3.6, 2.2 Hz, 1H), 2.45 – 2.35 (m, 3H), 1.98 (ddd, *J* = 12.7, 9.4, 4.5 Hz, 1H), 1.82 (ttt, *J* = 12.2, 4.4, 3.2 Hz, 1H), 1.74 (t, *J* = 4.5 Hz, 1H), 1.64 (h, *J* = 7.3 Hz, 2H), 1.39 (dddd, *J* = 12.7, 11.8, 4.5, 2.2 Hz, 1H), 1.29 (ddd, *J* = 12.1, 9.4, 4.4 Hz, 1H), 1.09 – 1.02 (m, 4H), 0.97 (s, 3H), 0.94 (s, 3H), 0.89 (s, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 155.2, 90.2, 82.7, 75.1, 50.3, 49.3, 46.4, 38.0, 29.3, 28.5, 22.6, 21.5, 20.7, 19.8, 14.5, 14.4.

HRMS (+ESI): calcd for C₁₆H₂₄O₂Na [M+Na]⁺ 271.1669, found 271.1672.



(3S,8S,9S,10R,13R,14S,17R)-17-((2R,5S,E)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl hex-2-ynoate

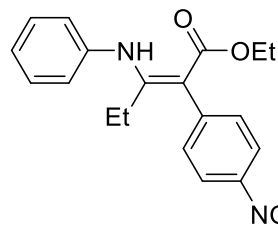
To a solution of hex-2-ynoic acid (4.0 mmol, 1.0 equiv.) and DMAP (0.2 equiv.) in DCM (50 mL) were added EDC·HCl (1.2 equiv.) and Stigmasterol (1.1 equiv.) at 0 °C. Then the reaction was warmed to room temperature. Upon completion monitored by the TLC, water was added and the phases were separated. Then the aqueous phase was extracted with DCM (x3). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the titled compound as white solid (1.32 g, 65%).

¹H NMR (400 MHz, CD₂Cl₂) δ 5.39 (d, *J* = 5.1 Hz, 1H), 5.18 (dd, *J* = 15.2, 8.5 Hz, 1H), 5.04 (dd, *J* = 15.1, 8.6 Hz, 1H), 4.68 – 4.55 (m, 1H), 2.40 – 2.25 (m, 4H), 2.12 – 1.93 (m, 3H), 1.93 – 1.82 (m, 2H), 1.76 – 1.39 (m, 12H), 1.34 – 0.91 (m, 17H), 0.89 – 0.76 (m, 9H), 0.71 (s, 3H).

¹³C NMR (100 MHz, CD₂Cl₂) δ 153.5, 139.9, 138.8, 129.7, 123.2, 89.2, 76.1, 73.8, 57.2, 56.4, 51.7, 50.5, 42.6, 40.9, 40.1, 38.3, 37.4, 37.0, 32.33, 32.30, 32.26, 29.3, 28.0, 25.8, 24.7, 21.6, 21.4, 21.2, 20.9, 19.5, 19.2, 13.6, 12.4, 12.2.

HRMS (+ESI): calcd for C₃₅H₅₄O₂Na [M+Na]⁺ 529.4016, found 529.4016

mp: 135-136 °C.



ethyl (Z)-2-(4-nitrophenyl)-3-(phenylamino)pent-2-enoate

Prepared according to general procedure **C** by using 4-nitro-N-phenylaniline (1.2 equiv.), ethyl pent-2-ynoate (0.2 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (49.5 mg, 73%).

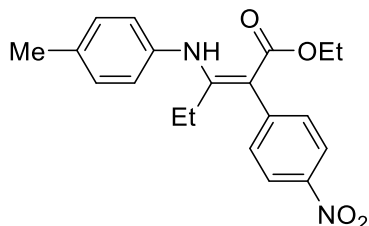
¹H NMR (400 MHz, acetone-*d*₆) δ 11.34 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.42 (m, 2H), 7.38 – 7.27 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.35 (q, *J* = 7.5 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.7, 165.1, 148.1, 147.7, 140.9, 135.0, 131.0, 127.5,

127.3, 124.5, 99.3, 60.8, 23.8, 15.4, 13.3.

HRMS (-ESI): calcd for $C_{19}H_{19}N_2O_4$ $[M-H]^-$ 339.1364, found 339.1366.

mp: 104-105 °C.



ethyl (Z)-2-(4-nitrophenyl)-3-(p-tolylamino)pent-2-enoate

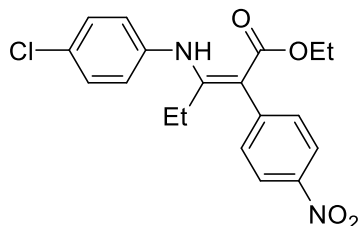
Prepared according to general procedure **C** by using 4-methyl-N-(4-nitrophenyl)aniline (1.2 equiv.), ethyl pent-2-ynoate (0.2 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow solid (18.2 mg, 26%).

1H NMR (400 MHz, acetone- d_6) δ 11.08 (s, 1H), 8.07 (d, J = 11.4 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 3.93 (q, J = 7.1 Hz, 2H), 2.21 (s, 3H), 2.13 (q, J = 7.5 Hz, 2H), 0.96 (t, J = 7.1 Hz, 3H), 0.60 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 170.7, 165.6, 148.0, 147.9, 138.2, 137.4, 135.0, 131.5, 127.5, 124.4, 98.7, 60.7, 23.8, 21.7, 15.5, 13.3.

HRMS (-ESI): calcd for $C_{20}H_{21}N_2O_4$ $[M-H]^-$ 353.1516, found 353.1519.

mp: 123-125 °C.



ethyl (Z)-3-((4-chlorophenyl)amino)-2-(4-nitrophenyl)pent-2-enoate

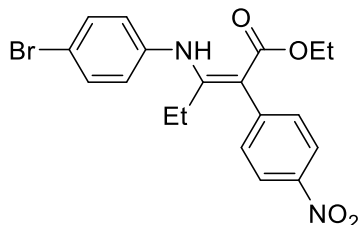
Prepared according to general procedure **C** by using 4-chloro-N-(4-nitrophenyl)aniline (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and KOH (1.5 equiv.) to yield the titled compound as yellow solid (48.2 mg, 43%).

1H NMR (400 MHz, acetone- d_6) δ 11.27 (s, 1H), 8.25 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 4.11 (q, J = 7.0 Hz, 2H), 2.34 (q, J = 7.5 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H), 0.79 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 170.7, 164.6, 148.2, 147.5, 140.0, 134.9, 132.3, 131.0, 128.8, 124.5, 100.2, 60.9, 23.8, 15.4, 13.3.

HRMS (+ESI): calcd for $C_{19}H_{19}N_2O_4ClNa$ $[M+Na]^+$ 397.0926, found 397.0923.

mp: 88-89 °C.



ethyl (Z)-3-((4-bromophenyl)amino)-2-(4-nitrophenyl)pent-2-enoate

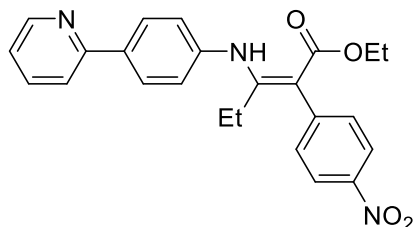
Prepared according to general procedure **C** by using 4-bromo-N-(4-nitrophenyl)aniline (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and KOH (1.5 equiv.) to yield the titled compound as yellow solid (56.3 mg, 45%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.27 (s, 1H), 8.25 (d, *J* = 7.0 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 2.35 (q, *J* = 7.6 Hz, 2H), 1.13 (t, *J* = 7.0 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.7, 164.5, 148.2, 147.4, 140.5, 134.9, 134.0, 129.0, 124.5, 120.0, 100.3, 60.9, 23.8, 15.4, 13.3.

HRMS (-ESI): calcd for C₁₉H₁₈N₂O₄Br [M-H]⁻ 417.0455, found 417.0440.

mp: 94-96 °C.



ethyl (Z)-2-(4-nitrophenyl)-3-((4-(pyridin-2-yl)phenyl)amino)pent-2-enoate

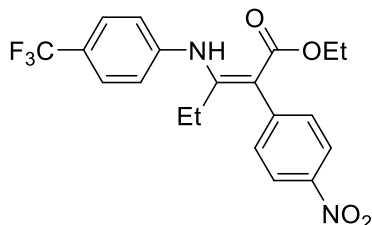
Prepared according to general procedure **C** by using ethyl (Z)-2-(4-nitrophenyl)-3-((4-(pyridin-2-yl)phenyl)amino)pent-2-enoate (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and KOH (1.5 equiv.) to yield the titled compound as yellow solid (45.0 mg, 36%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.44 (s, 1H), 8.71 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 8.26 (d, *J* = 8.9 Hz, 2H), 8.23 (d, *J* = 8.7 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.90 (td, *J* = 7.7, 1.9 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 7.4, 4.8 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.44 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.8, 164.7, 157.6, 151.3, 148.2, 147.6, 141.8, 138.6, 138.0, 135.0, 129.3, 126.7, 124.5, 123.9, 121.4, 100.2, 60.9, 24.0, 15.4, 13.3.

HRMS (+ESI): calcd for C₂₄H₂₄N₃O₄ [M+H]⁺ 418.1767, found 418.1768.

mp: 121-122 °C.



ethyl (Z)-2-(4-nitrophenyl)-3-((4-(trifluoromethyl)phenyl)amino)pent-2-enoate

Prepared according to general procedure **C** by using 4-nitro-N-(4-(trifluoromethyl)phenyl)aniline (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (85.6 mg, 70%).

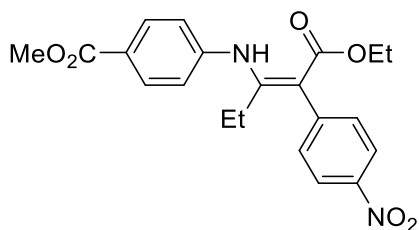
¹H NMR (400 MHz, acetone-*d*₆) δ 11.47 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.46 (q, *J* = 7.5 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.7, 163.5, 148.3, 147.1, 145.0, 134.8, 128.1 (q, *J* = 3.8 Hz), 126.09 (q, *J* = 263.0 Hz), 126.05, 124.6, 102.0, 61.2, 24.0, 15.3, 13.3.

¹⁹F NMR (235 MHz, acetone-*d*₆) δ -62.6.

HRMS (-ESI): calcd for C₂₀H₁₈N₂O₄F₃ [M-H]⁻ 407.1221, found 407.1288.

mp: 93-94 °C.



methyl (Z)-4-((1-ethoxy-2-(4-nitrophenyl)-1-oxopent-2-en-3-yl)amino)benzoate

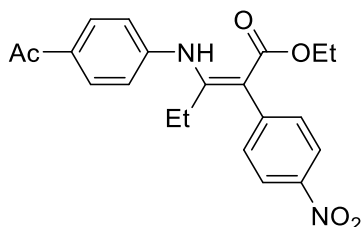
Prepared according to general procedure **C** by using methyl 4-((4-nitrophenyl)amino)benzoate (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow solid (76.4 mg, 64%).

^1H NMR (400 MHz, acetone- d_6) δ 11.51 (s, 1H), 8.27 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 4.12 (q, J = 7.0 Hz, 2H), 3.92 (s, 3H), 2.48 (q, J = 7.5 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H), 0.85 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 170.7, 167.4, 163.4, 148.3, 147.2, 145.7, 134.8, 132.4, 127.9, 125.0, 124.5, 102.1, 61.2, 53.1, 24.1, 15.3, 13.2.

HRMS (+ESI): calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 421.1383, found 421.1385.

mp: 102-104 °C.



ethyl (Z)-3-((4-acetylphenyl)amino)-2-(4-nitrophenyl)pent-2-enoate

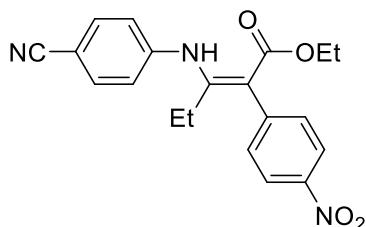
Prepared according to general procedure **C** by using methyl 1-(4-((4-nitrophenyl)amino)phenyl)ethan-1-one (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow solid (73.3 mg, 64%).

^1H NMR (400 MHz, acetone- d_6) δ 11.52 (s, 1H), 8.27 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 4.13 (q, J = 7.0 Hz, 2H), 2.61 (s, 3H), 2.49 (q, J = 7.5 Hz, 2H), 1.13 (t, J = 7.0 Hz, 3H), 0.85 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 197.4, 170.7, 163.4, 148.3, 147.1, 145.5, 135.2, 134.8, 131.4, 124.9, 124.5, 102.1, 61.2, 27.3, 24.1, 15.4, 13.3.

HRMS (+ESI): calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 405.1432, found 405.1435.

mp: 103-104 °C.



ethyl (Z)-3-((4-cyanophenyl)amino)-2-(4-nitrophenyl)pent-2-enoate

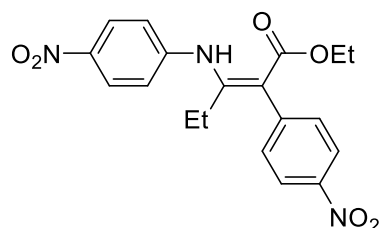
Prepared according to general procedure **C** by using 4-((4-nitrophenyl)amino)benzonitrile (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow gum (77.7 mg, 71%).

^1H NMR (400 MHz, acetone- d_6) δ 11.50 (s, 1H), 8.27 (d, J = 8.9 Hz, 2H), 7.83 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.9 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 4.13 (q, J = 7.0 Hz, 2H), 2.49 (q, J = 7.5 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H), 0.86 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 170.6, 162.7, 148.3, 146.9, 145.7, 135.1, 134.7, 125.3,

124.6, 120.0, 108.9, 103.4, 61.3, 24.1, 15.3, 13.2.

HRMS (-ESI): calcd for $C_{20}H_{18}N_3O_4$ $[M-H]^-$ 364.1305, found 364.1397.



ethyl (Z)-2-(4-nitrophenyl)-3-((4-nitrophenyl)amino)pent-2-enoate

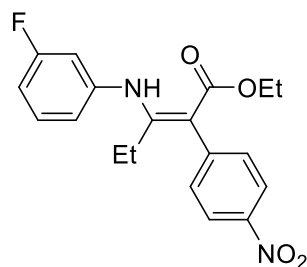
Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), ethyl pent-2-ynoate (0.2 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow solid (66.6 mg, 87%).

1H NMR (400 MHz, $CDCl_3$) δ 11.58 (s, 1H), 8.24 – 8.21 (m, 4H), 7.39 (d, J = 7.1 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 2.38 (q, J = 7.5 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H), 0.86 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 160.6, 147.1, 146.0, 144.9, 144.0, 132.9, 125.6, 123.6, 122.8, 102.8, 60.7, 23.01, 14.6, 12.7.

HRMS (+ESI): calcd for $C_{19}H_{19}N_3O_6Na$ $[M+Na]^+$ 408.1166, found 408.1171.

mp: 77-79 °C



ethyl (Z)-3-((3-fluorophenyl)amino)-2-(4-nitrophenyl)pent-2-enoate

Prepared according to general procedure **C** by using 3-fluoro-N-(4-nitrophenyl)aniline (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow solid (62.3 mg, 58%).

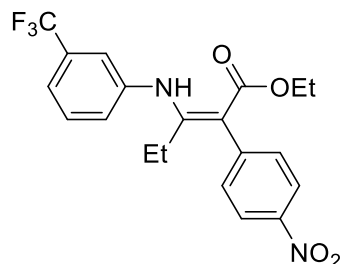
1H NMR (400 MHz, acetone- d_6) δ 11.34 (s, 1H), 8.26 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.9 Hz, 2H), 7.54 – 7.42 (m, 1H), 7.15 (t, J = 8.7 Hz, 2H), 7.06 (t, J = 8.5 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.40 (q, J = 7.5 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H), 0.82 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 170.7, 165.9, 164.3, 163.5, 148.2, 147.4, 143.0 (d, J = 10 Hz), 134.9, 132.4 (d, J = 9 Hz), 124.4, 122.7 (d, J = 3 Hz), 113.7 (d, J = 23 Hz), 100.7, 61.0, 23.9, 15.4, 13.3.

^{19}F NMR (235 MHz, acetone- d_6) δ -113.1.

HRMS (-ESI): calcd for $C_{19}H_{18}N_2O_4F$ $[M-H]^-$ 357.1274, found 357.1277.

mp: 92-94 °C.



ethyl (Z)-2-(4-nitrophenyl)-3-((3-(trifluoromethyl)phenyl)amino)pent-2-enoate

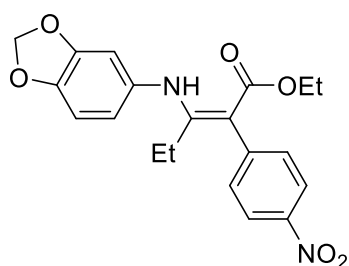
Prepared according to general procedure **C** by using N-(4-nitrophenyl)-3-(trifluoromethyl)aniline (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow oil (66.2 mg, 54%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.38 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 2H), 7.74 – 7.56 (m, 6H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.39 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.7, 164.1, 148.3, 147.3, 142.1, 134.9, 132.8 (q, *J* = 32.1 Hz), 132.0, 130.6, 125.7 (q, *J* = 270.2 Hz), 124.5, 123.6 (q, *J* = 3.8 Hz), 123.4 (q, *J* = 3.8 Hz), 101.2, 61.1, 23.9, 15.4, 13.2.

¹⁹F NMR (235 MHz, acetone-*d*₆) δ -63.2.

HRMS (-ESI): calcd for C₂₀H₁₈N₂O₄F₃ [M-H]⁻ 407.1224, found 407.1302.



ethyl (Z)-3-(benzo[d][1,3]dioxol-5-ylamino)-2-(4-nitrophenyl)pent-2-enoate

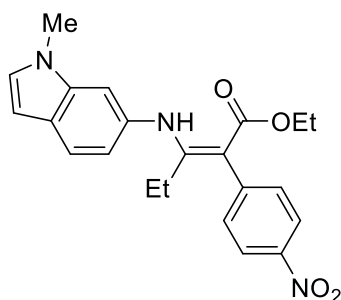
Prepared according to general procedure **C** by using N-(4-nitrophenyl)benzo[d][1,3]dioxol-5-amine (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (26.5 mg, 23%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.11 (s, 1H), 8.24 (d, *J* = 8.9 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 2.1 Hz, 1H), 6.81 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.10 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.28 (q, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.7, 165.9, 149.9, 148.0, 147.9, 147.8, 135.0, 134.7, 124.4, 121.4, 109.7, 109.4, 103.5, 98.6, 60.7, 23.9, 15.5, 13.4.

HRMS (-ESI): calcd for C₂₀H₁₉N₂O₆ [M-H]⁻ 383.1261, found 383.1262.

mp: 103-105 °C.



ethyl (Z)-3-((1-methyl-1H-indol-6-yl)amino)-2-(4-nitrophenyl)pent-2-enoate

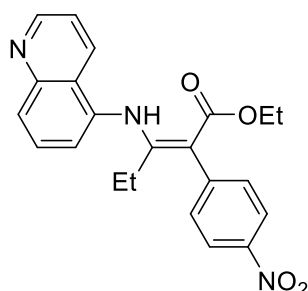
Prepared according to general procedure **C** by using 1-methyl-N-(4-nitrophenyl)-1H-indol-6-amine (1.2 equiv.), ethyl pent-2-ynoate (0.17 mmol) and KOH (1.5 equiv.) to yield the titled compound as yellow solid (18.7 mg, 28%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.40 (s, 1H), 8.25 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.39 (s, 1H), 7.31 (d, *J* = 3.1 Hz, 1H), 7.02 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.90 (s, 3H), 2.35 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.8, 166.4, 148.2, 148.0, 138.7, 135.1, 134.5, 131.9, 128.8, 124.4, 122.5, 120.0, 109.1, 102.3, 97.9, 60.6, 33.8, 24.0, 15.5, 13.6.

HRMS (+ESI): calcd for C₂₂H₂₃N₃O₄Na [M+Na]⁺ 416.1581, found 416.1585.

mp: 120-121 °C.



ethyl (Z)-2-(4-nitrophenyl)-3-(quinolin-5-ylamino)pent-2-enoate

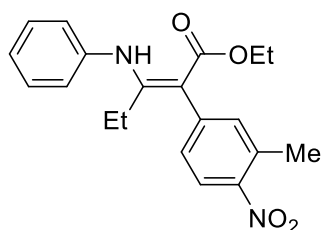
Prepared according to general procedure **C** by using N-(4-nitrophenyl)quinolin-5-amine (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (23.4 mg, 20%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.53 (s, 1H), 9.02 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 7.69 – 7.63 (m, 4H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.24 (q, *J* = 7.5 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.68 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 171.1, 166.1, 152.6, 150.8, 148.2, 147.5, 137.1, 135.0, 132.4, 130.6, 130.0, 127.6, 126.3, 124.5, 123.7, 100.1, 61.0, 24.4, 15.4, 13.7.

HRMS (+ESI): calcd for C₂₂H₂₁N₃O₄ [M+Na]⁺ 414.1424, found 414.1422.

mp: 108-110 °C.



ethyl (Z)-2-(3-methyl-4-nitrophenyl)-3-(phenylamino)pent-2-enoate

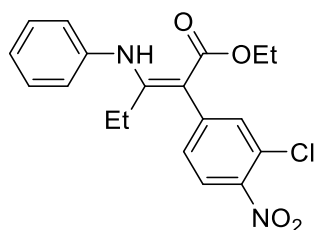
Prepared according to general procedure **C** by using 3-methyl-4-nitro-N-phenylaniline (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (21.2 mg, 20%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.30 (s, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.40 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.29 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 2.34 (q, *J* = 7.6 Hz, 2H), 1.14 (t, *J* = 7.0 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.9, 165.1, 149.2, 145.8, 141.1, 138.1, 134.3, 132.6, 131.0, 127.4, 127.3, 125.7, 99.4, 60.7, 23.9, 21.1, 15.5, 13.4.

HRMS (+ESI): calcd for C₂₀H₂₂N₂O₄Na [M+H]⁺ 377.1472, found 377.1471.

mp: 73-74 °C.



ethyl (Z)-2-(3-chloro-4-nitrophenyl)-3-(phenylamino)pent-2-enoate

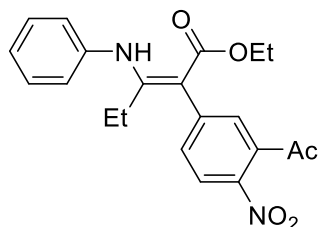
Prepared according to general procedure **C** by using 3-chloro-4-nitro-N-phenylaniline (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound

as yellow gum (50.5 mg, 45%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.33 (s, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.64 (s, 1H), 7.53 – 7.46 (m, 3H), 7.35 – 7.30 (m, 3H), 4.12 (q, *J* = 7.0 Hz, 2H), 2.37 (q, *J* = 7.5 Hz, 2H), 1.15 (t, *J* = 6.8 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.5, 165.6, 147.9, 146.7, 140.8, 136.7, 133.8, 131.0, 127.6, 127.4, 126.7, 98.3, 60.9, 23.9, 15.5, 13.3.

HRMS (+ESI): calcd for C₁₉H₁₉N₂O₄ClNa [M+Na]⁺ 397.0926, found 397.0932.



ethyl (Z)-2-(3-acetyl-4-nitrophenyl)-3-(phenylamino)pent-2-enoate

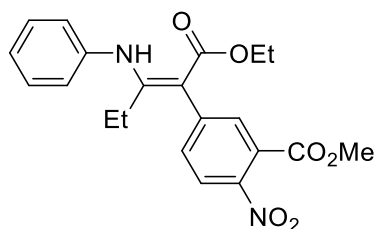
Prepared according to general procedure **C** by using 1-(2-nitro-5-(phenylamino)phenyl)ethan-1-one (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as brown solid (59.5 mg, 52%).

¹H NMR (400 MHz, acetone-*d*₆) δ 1.36 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.34 – 7.30 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 2.38 (q, *J* = 7.5 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 200.5, 170.5, 165.5, 147.0, 145.9, 140.8, 138.7, 136.2, 133.0, 131.0, 127.6, 127.4, 125.5, 98.6, 60.9, 30.73, 23.9, 15.4, 13.3.

HRMS (+ESI): calcd for C₂₁H₂₂N₂O₅Na [M+Na]⁺ 405.1421, found 405.1424.

mp: 116–117 °C.



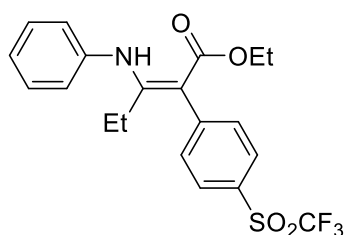
methyl (Z)-5-(1-ethoxy-1-oxo-3-(phenylamino)pent-2-en-2-yl)-2-nitrobenzoate

Prepared according to general procedure **C** by using methyl 2-nitro-5-(phenylamino)benzoate (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow oil (52.5 mg, 44%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.34 (s, 1H), 8.04 (dt, *J* = 8.6, 1.0 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.50 – 7.46 (m, 2H), 7.36 – 7.30 (m, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 2.35 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.5, 167.2, 165.6, 148.0, 146.2, 140.8, 137.4, 135.0, 131.0, 128.7, 127.6, 127.4, 125.3, 98.3, 60.9, 54.2, 23.9, 15.4, 13.3.

HRMS (+ESI): calcd for C₂₁H₂₂N₂O₆Na [M+Na]⁺ 421.1370, found 421.1372.



ethyl (Z)-3-(phenylamino)-2-(4-((trifluoromethyl)sulfonyl)phenyl)pent-2-enoate

Prepared according to general procedure **C** by using N-phenyl-4-((trifluoromethyl)sulfonyl)aniline (1.2 equiv.), ethyl pent-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (38.4 mg, 30%).

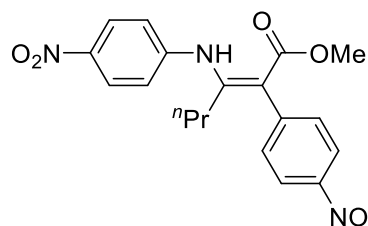
¹H NMR (400 MHz, acetone-*d*₆) δ 11.36 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.35 – 7.31 (m, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.36 (q, *J* = 7.5 Hz, 2H), 1.13 (t, *J* = 7.0 Hz, 3H), 0.78 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.5, 165.5, 150.4, 140.9, 135.9, 131.8, 131.0, 129.8, 127.7, 127.4, 122.7 (q, *J* = 324 Hz), 99.1, 60.9, 23.9, 15.4, 13.2.

¹⁹F NMR (235 MHz, acetone-*d*₆) δ -80.0.

HRMS (+ESI): calcd for C₂₀H₂₀NO₄F₃SNa [M+Na]⁺ 450.0957, found 450.0961.

mp: 90-91 °C.



methyl (Z)-2-(4-nitrophenyl)-3-((4-nitrophenyl)amino)hex-2-enoate

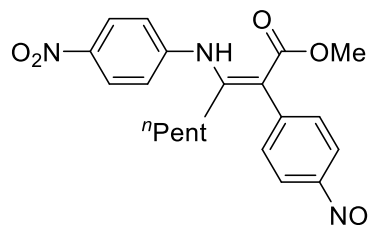
Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), methyl hex-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (84.3 mg, 73%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.55 (s, 1H), 8.31 (d, *J* = 9.1 Hz, 2H), 8.28 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H), 3.64 (s, 3H), 2.55 – 2.48 (m, 2H), 1.39 – 1.30 (m, 2H), 0.67 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 171.0, 160.8, 148.5, 147.9, 146.7, 145.3, 134.7, 126.8, 124.7, 124.2, 104.8, 52.5, 32.8, 22.4, 14.5.

HRMS (+ESI): calcd for C₁₉H₁₉N₃O₆Na [M+Na]⁺ 408.1166, found 408.1170.

mp: 137-139 °C.



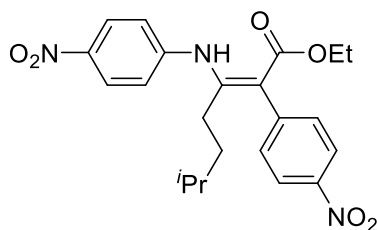
methyl (Z)-2-(4-nitrophenyl)-3-((4-nitrophenyl)amino)oct-2-enoate

Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), methyl oct-2-ynoate (0.3 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as orange gum (84.3 mg, 73%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.56 (s, 1H), 8.32 (d, *J* = 9.1 Hz, 2H), 8.29 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 3.64 (s, 3H), 2.57 – 2.49 (m, 2H), 1.37 – 1.29 (m, 2H), 1.06 – 0.99 (m, 4H), 0.67 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.9, 161.2, 148.5, 147.8, 146.7, 145.3, 134.7, 126.7, 124.7, 124.4, 104.5, 52.5, 32.5, 30.77, 28.5, 23.1, 14.6.

HRMS (+ESI): calcd for C₂₁H₂₃N₃O₆Na [M+Na]⁺ 436.1479, found 436.1481.



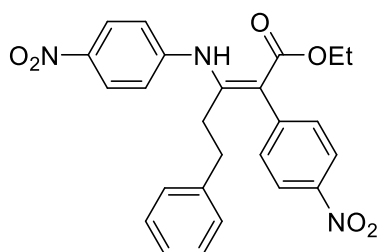
ethyl (Z)-6-methyl-2-(4-nitrophenyl)-3-((4-nitrophenyl)amino)hept-2-enoate

Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), ethyl 6-methylhept-2-ynoate (0.3 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow oil (63.4 mg, 50%).

^1H NMR (400 MHz, acetone- d_6) δ 11.56 (s, 1H), 8.32 (d, J = 9.0 Hz, 2H), 8.29 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 9.0 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 2.58 – 2.47 (m, 2H), 1.30 – 1.19 (m, 3H), 1.14 (t, J = 7.1 Hz, 3H), 0.57 (d, J = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, acetone- d_6) δ 170.5, 161.4, 148.4, 147.8, 146.8, 145.3, 134.8, 126.7, 124.6, 104.7, 61.5, 37.9, 29.2, 28.9, 22.8, 15.3.

HRMS (-ESI): calcd for $\text{C}_{22}\text{H}_{24}\text{N}_3\text{O}_6$ $[\text{M}-\text{H}]^-$ 426.1688, found 426.1705.



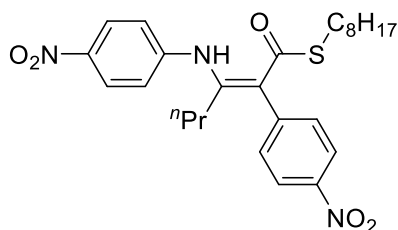
ethyl (Z)-2-(4-nitrophenyl)-3-((4-nitrophenyl)amino)-5-phenylpent-2-enoate

Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), ethyl 5-phenylpent-2-ynoate (0.3 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow oil (47.0 mg, 34%).

^1H NMR (400 MHz, acetone- d_6) δ 11.51 (s, 1H), 8.34 (d, J = 9.0 Hz, 2H), 8.25 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 9.1 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.19 – 7.15 (m, 3H), 6.85 – 6.79 (m, 2H), 4.14 (q, J = 7.0 Hz, 2H), 2.84 (t, J = 7.2 Hz, 2H), 2.59 (t, J = 7.2 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 170.5, 159.4, 148.4, 147.8, 146.6, 145.4, 141.5, 134.7, 130.0, 129.7, 127.9, 126.8, 124.58, 124.56, 105.7, 61.5, 34.7, 33.21, 15.25.

HRMS (+ESI): calcd for $\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 484.1479, found 484.1486.



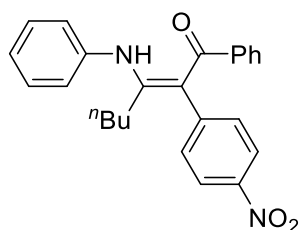
S-octyl (Z)-2-(4-nitrophenyl)-3-((4-nitrophenyl)amino)hex-2-enethioate

Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), S-octyl hex-2-ynethioate (0.2 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow oil (38.9 mg, 39%).

^1H NMR (500 MHz, acetone- d_6) δ 12.23 (s, 1H), 8.35 (d, J = 4.9 Hz, 2H), 8.33 (d, J = 5.2 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 9.0 Hz, 2H), 2.89 – 2.85 (m, 4H), 2.41 – 2.34 (m, 2H), 1.59 – 1.53 (m, 2H), 1.37 – 1.29 (m, 10H), 0.90 (t, J = 6.9 Hz, 3H), 0.66 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, acetone- d_6) δ 192.3, 158.4, 149.4, 147.3, 145.8, 145.7, 136.4, 126.7, 125.2, 124.9, 113.2, 33.3, 33.1, 31.2, 30.81, 30.63, 30.58, 30.39, 24.0, 22.4, 15.1, 14.6.

HRMS (-ESI): calcd for $C_{26}H_{32}N_3O_5S$ $[M-H]^-$ 498.2083, found 498.2110.



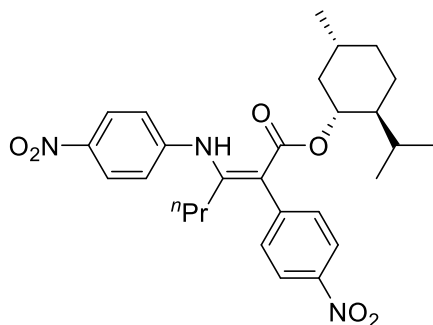
(Z)-2-(4-nitrophenyl)-3-((4-nitrophenyl)amino)-1-phenylhept-2-en-1-one

Prepared according to general procedure **C** by using 4-nitro-N-phenylaniline (1.2 equiv.), 1-phenylhept-2-yn-1-one (0.3 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as orange gum (26.4 mg, 22%).

1H NMR (400 MHz, acetone- d_6) δ 14.33 (s, 1H), 8.11 (d, J = 8.8 Hz, 2H), 7.56 – 7.50 (m, 4H), 7.47 – 7.37 (m, 3H), 7.25 – 7.13 (m, 5H), 2.54 – 2.43 (m, 2H), 1.29 – 1.19 (m, 2H), 0.95 (q, J = 7.3 Hz, 2H), 0.51 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 194.0, 168.4, 149.5, 147.8, 144.0, 140.2, 136.0, 131.1, 130.3, 129.6, 129.0, 128.3, 127.6, 124.4, 110.2, 31.2, 23.6, 14.1.

HRMS (+ESI): calcd for $C_{25}H_{24}N_2O_3Na$ $[M+Na]^+$ 423.1687, found 423.1685.



(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl amino)hex-2-enoate

(Z)-2-(4-nitrophenyl)-3-((4-nitrophenyl)-

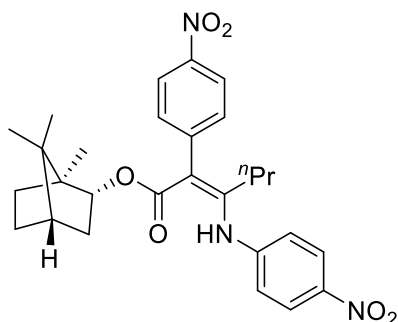
Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl hex-2-ynoate (0.2 mmol) and Cs_2CO_3 (1.5 equiv.) to yield the titled compound as yellow solid (53.9 mg, 53%).

1H NMR (400 MHz, acetone- d_6) δ 11.61 (s, 1H), 8.31 (d, J = 6.1 Hz, 2H), 8.29 (d, J = 5.8 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H), 4.72 (td, J = 10.6, 4.4 Hz, 1H), 2.54 – 2.50 (m, 2H), 2.10 – 2.01 (m, 1H), 1.74 – 1.59 (m, 3H), 1.55 – 1.44 (m, 1H), 1.41 – 1.30 (m, 3H), 1.12 – 1.08 (m, 1H), 0.91 (d, J = 6.5 Hz, 3H), 0.87 – 0.81 (m, 2H), 0.78 (d, J = 7.1 Hz, 3H), 0.74 (d, J = 7.0 Hz, 3H), 0.69 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, acetone- d_6) δ 170.1, 160.3, 148.4, 148.0, 146.9, 145.0, 134.7, 126.8, 124.6, 123.9, 105.6, 75.4, 48.5, 42.4, 35.6, 33.0, 32.9, 27.7, 24.8, 23.1, 22.4, 21.6, 17.5, 14.6.

HRMS (+ESI): calcd for $C_{28}H_{35}N_3O_6Na$ $[M+Na]^+$ 532.2423, found 532.2424.

mp: 112–113 °C.



**(1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl
nitrophenyl)-mino)hex-2-enoate**

(Z)-2-(4-nitrophenyl)-3-((4-

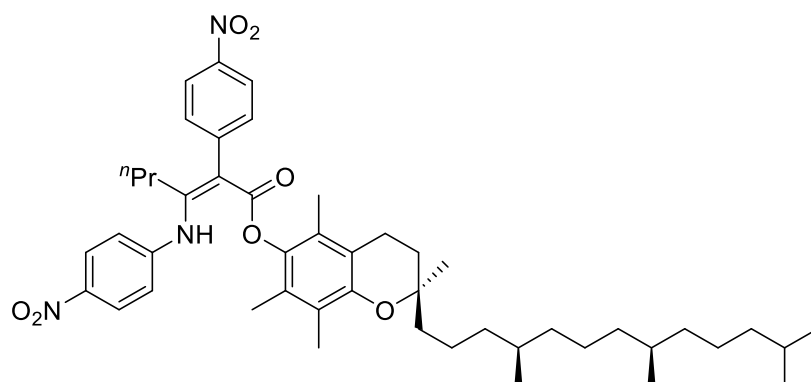
Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), (1R,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl hex-2-ynoate (0.2 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (80.0 mg, 79%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.57 (s, 1H), 8.32 (t, *J* = 8.9 Hz, 4H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 9.1 Hz, 2H), 4.89 (ddd, *J* = 9.8, 3.4, 2.0 Hz, 1H), 2.57 – 2.53 (m, 2H), 2.41 – 2.33 (m, 1H), 1.66 – 1.58 (m, 2H), 1.42 – 1.30 (m, 3H), 1.20 – 1.13 (m, 1H), 1.05 – 1.02 (m, 1H), 1.00 – 0.97 (m, 1H), 0.92 (s, 3H), 0.84 (s, 3H), 0.73 (s, 3H), 0.70 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 170.7, 160.2, 148.4, 147.9, 147.0, 145.1, 134.7, 126.8, 124.6, 123.9, 105.7, 81.1, 50.08, 50.06, 49.0, 46.4, 38.6, 32.9, 29.1, 28.2, 22.4, 20.6, 19.9, 14.6, 14.50.

HRMS (+ESI): calcd for C₂₈H₃₃N₃O₆Na [M+Na]⁺ 530.2266, found 530.2265.

mp: 140-142 °C.



**(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl
nitrophenyl)-3-((4-nitrophenyl)amino)hex-2-enoate**

(Z)-2-(4-

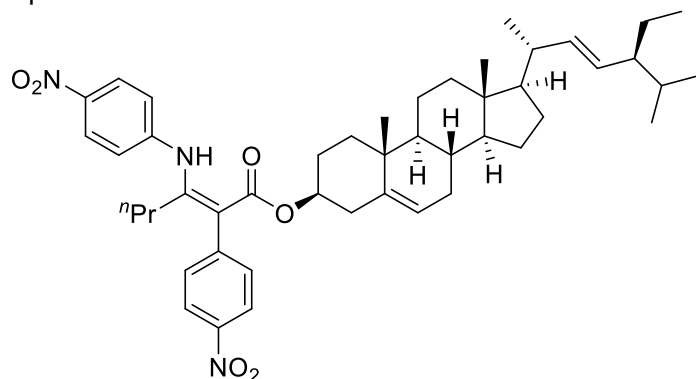
Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl hex-2-ynoate (0.2 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (108.0 mg, 69%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.61 (s, 1H), 8.36 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 9.1 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 9.1 Hz, 2H), 2.66 – 2.54 (m, 4H), 2.11 – 2.07 (m, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.82 (dt, *J* = 12.3, 6.8 Hz, 2H), 1.56 (dt, *J* = 18.3, 7.0 Hz, 3H), 1.49 – 1.39 (m, 5H), 1.38 – 1.23 (m, 11H), 1.22 – 1.07 (m, 6H), 0.89 (p, *J* = 6.4 Hz, 13H), 0.73 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 169.1, 162.6, 150.6, 148.7, 147.4, 146.8, 145.4, 142.3, 134.8, 128.3, 126.8, 125.0, 124.4, 123.9, 119.0, 103.5, 76.8, 40.8, 38.9, 38.84, 38.79, 38.74, 38.71, 34.22, 34.18, 33.0, 29.4, 26.3, 25.84, 25.80, 25.1, 24.7, 23.8, 23.7, 22.5, 21.9, 20.9, 20.8, 20.7, 14.7, 14.1, 13.2, 12.7.

HRMS (-ESI): calcd for C₄₇H₆₄N₃O₇ [M-H]⁻ 782.4785, found 782.4788.

mp: 51-52 °C.



(3S,8S,9S,10R,13R,14S,17R)-17-((2R,5S,E)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (Z)-2-(4-nitrophenyl)-3-((4-nitrophenyl)amino)hex-2-enoate

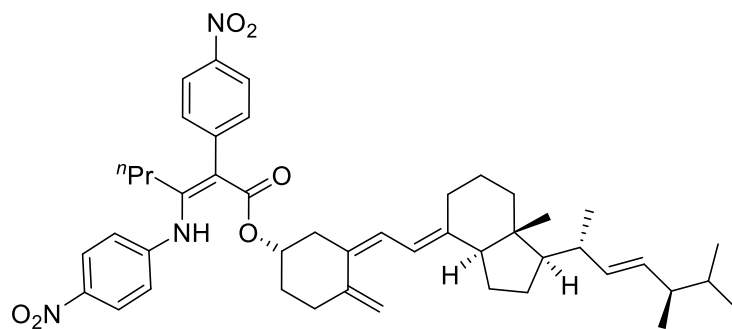
Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), (3S,8S,9S,10R,13R,14S,17R)-17-((2R,5S,E)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl hex-2-ynoate (0.2 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow solid (96.3 mg, 63%).

¹H NMR (400 MHz, CD₂Cl₂) δ 11.60 (s, 1H), 8.21 (d, *J* = 5.1 Hz, 2H), 8.19 (d, *J* = 4.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 9.0 Hz, 2H), 5.35 (dd, *J* = 4.8, 2.4 Hz, 1H), 5.17 (dd, *J* = 15.1, 8.6 Hz, 1H), 5.03 (dd, *J* = 15.1, 8.6 Hz, 1H), 4.62 – 4.54 (m, 1H), 2.37 – 2.33 (m, 2H), 2.23 (ddd, *J* = 13.0, 5.0, 2.2 Hz, 1H), 2.12 – 1.90 (m, 4H), 1.82 (dt, *J* = 13.2, 3.5 Hz, 1H), 1.78 – 1.66 (m, 2H), 1.49 – 0.89 (m, 24H), 0.86 – 0.79 (m, 10H), 0.69 (s, 3H), 0.64 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CD₂Cl₂) δ 169.1, 159.2, 147.1, 146.5, 145.4, 144.0, 140.2, 138.8, 133.2, 129.7, 125.6, 123.4, 122.9, 122.8, 104.0, 74.5, 57.2, 56.4, 51.7, 50.5, 42.6, 40.9, 40.1, 38.5, 37.4, 37.0, 32.3, 32.3, 32.2, 31.8, 29.3, 28.1, 25.8, 24.7, 21.5, 21.4, 21.2, 19.5, 19.2, 13.7, 12.4, 12.2.

HRMS (-ESI): calcd for C₄₇H₆₂N₃O₆ [M-H]⁻ 764.4668, found 764.4668.

mp: 126-128 °C.



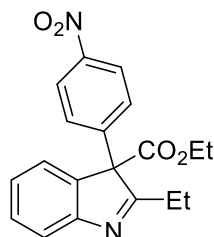
(S,Z)-3-(2-((1R,3aS,7aR,E)-1-((2R,5R,E)-5,6-dimethylhept-3-en-2-yl)-7a-methyloctahydro-4H-inden-4-ylidene)ethylidene)-4-methylenecyclohexyl (Z)-2-(4-nitrophenyl)-3-((4-nitrophenyl)amino)hex-2-enoate

Prepared according to general procedure **C** by using bis(4-nitrophenyl)amine (1.2 equiv.), (S,Z)-3-(2-((1R,3aS,7aR,E)-1-((2R,5R,E)-5,6-dimethylhept-3-en-2-yl)-7a-methyloctahydro-4H-inden-4-ylidene)ethylidene)-4-methylenecyclohexyl hex-2-ynoate (0.2 mmol) and Cs₂CO₃ (1.5 equiv.) to yield the titled compound as yellow gum (107.5 mg, 72%).

¹H NMR (400 MHz, acetone-*d*₆) δ 11.57 (s, 1H), 8.31 (d, *J* = 9.1 Hz, 2H), 8.16 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 6.08 (d, *J* = 11.2 Hz, 1H), 5.92 (d, *J* = 11.1 Hz, 1H), 5.34 – 5.24 (m, 2H), 5.17 – 5.13 (m, 1H), 5.00 (s, 1H), 4.72 (s, 1H), 2.84 – 2.84 (m, 1H), 2.55 – 2.45 (m, 3H), 2.34 (dd, *J* = 13.8, 5.0 Hz, 1H), 2.16 – 1.70 (m, 10H), 1.59 – 1.31 (m, 10H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 6H), 0.69 (t, *J* = 7.4 Hz, 3H), 0.60 (s, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 169.7, 160.3, 148.0, 147.8, 146.9, 146.5, 145.0, 142.7, 137.4, 136.4, 134.5, 133.4, 126.8, 124.3, 123.8, 123.5, 119.2, 113.1, 105.6, 72.2, 58.0, 57.8, 47.2, 44.5, 43.2, 42.1, 41.9, 34.6, 32.9, 32.7, 32.7, 29.3, 25.1, 23.7, 22.4, 21.1, 20.8, 18.9, 14.6, 13.3.

HRMS (+ESI): calcd for C₄₆H₅₉N₃O₆ [M+Na]⁺ 772.4285, found 772.4286.



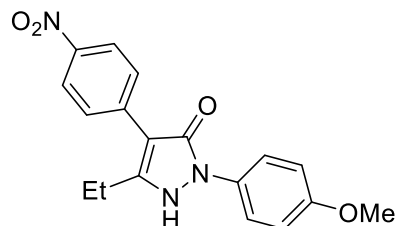
ethyl 2-ethyl-3-(4-nitrophenyl)-3H-indole-3-carboxylate

Prepared by adaptation of a literature procedure.² To an oven-dried microwave vial were added ethyl (Z)-2-(4-nitrophenyl)-3-(phenylamino)pent-2-enoate (0.2 mmol, 1.0 equiv.), iodine (1.1 equiv.) and K₂CO₃ (1.2 equiv.). The vial was sealed by a cap and placed on the Schlenk line to evacuate and backfill with N₂ three times. Then DMF (1.0 mL) was added by syringe. The mixture was stirred at 100 °C for 1 h. After cooling to room temperature, water and ethyl acetate were added and the phases were separated. The organic phase was washed with brine three times, followed by dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel to yield the titled compound as oil (17.2 mg, 25%).

¹H NMR (400 MHz, acetone-*d*₆) δ 8.26 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.55 (td, *J* = 7.6, 1.3 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.41 – 7.33 (m, 3H), 4.42 – 4.20 (m, 2H), 2.95 – 2.83 (m, 1H), 2.47 – 2.3 (m, 1H), 1.27 (t, *J* = 5.2 Hz, 3H), 1.23 (t, *J* = 4.8 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 169.7, 160.3, 148.0, 147.8, 146.9, 146.5, 145.0, 142.7, 137.4, 136.4, 134.5, 133.4, 126.8, 124.3, 123.8, 123.5, 119.2, 113.1, 105.6, 72.2, 58.0, 57.8, 47.2, 44.5, 43.2, 42.1, 41.9, 34.6, 32.9, 32.7, 32.7, 29.3, 25.1, 23.7, 22.4, 21.1, 20.8, 18.9, 14.6, 13.3.

HRMS (+ESI): calcd for C₁₉H₁₉N₂O₄ [M+H]⁺ 339.1339, found 339.1346.



ethyl 2-ethyl-3-(4-nitrophenyl)-3H-indole-3-carboxylate

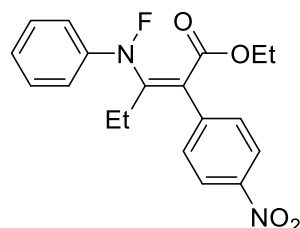
Prepared by adaptation of a literature procedure.³ To a solution of ethyl (Z)-2-(4-nitrophenyl)-3-(phenylamino)pent-2-enoate (0.2 mmol, 1.0 equiv.) in EtOH was added (4-methoxyphenyl)hydrazine hydrogen chloride (1.0 equiv.). The vial was sealed by a cap then the mixture was refluxed for overnight. After cooling to room temperature, the mixture was poured into cold water. The resulting solid was filtered and washed with EtOH to yield the titled compound as light yellow solid (27.8 mg, 41%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.32 – 8.25 (m, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 9.1 Hz, 2H), 3.83 (s, 3H), 3.39 (brs, 1H), 2.83 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 158.3, 151.6, 145.3, 141.5, 128.5, 124.6, 124.0, 115.1, 102.6, 56.3, 31.6, 21.4, 13.3.

HRMS (+ESI): calcd for C₁₈H₁₇N₃O₄Na [M+Na]⁺ 362.1111, found 362.1115.

mp: 94–95 °C.



ethyl (Z)-3-(fluoro(phenyl)amino)-2-(4-nitrophenyl)pent-2-enoate

Prepared by adaptation of a literature procedure.⁴ To a solution of ethyl (Z)-2-(4-nitrophenyl)-3-(phenylamino)pent-2-enoate (0.2 mmol, 1.0 equiv.) in DCM/H₂O (v/v = 1:1, 4 mL) was added selectfluor (5.0 equiv.). The vial was sealed by a cap and the mixture was stirred at room temperature for 72 h. Then the mixture was extracted with DCM (3 mL x 3). The organic layers were combined, dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel to yield the titled compound as yellow solid (40.1 mg, 56%).

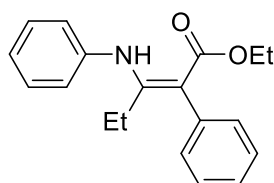
¹H NMR (500 MHz, acetone-*d*₆) 8.39 (d, *J* = 8.3 Hz, 2H), 8.05 – 7.98 (m, 2H), 7.45 – 7.37 (m, 2H), 7.16 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.87 – 6.80 (m, 2H), 4.43 – 4.33 (m, 1H), 2.50 – 2.31 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 0.94 (td, *J* = 7.7, 0.9 Hz, 3H).

¹³C NMR (125 MHz, acetone-*d*₆) δ 172.7 (d, *J* = 22.2 Hz), 167.8 (d, *J* = 20.2 Hz), 150.6, 150.0, 143.8 (d, *J* = 18.2 Hz), 130.7, 129.3 (d, *J* = 7.8 Hz), 125.6, 124.7 (d, *J* = 1.5 Hz), 119.9, 100.4 (d, *J* = 152.4 Hz), 64.1, 24.4, 15.0, 12.8 (d, *J* = 1.8 Hz).

¹⁹F NMR (471 MHz, acetone-*d*₆) δ -165.1,

HRMS (+ESI): calcd for C₁₉H₂₀N₂O₄F [M+H]⁺ 359.1414, found 359.1413.

mp: 69–70 °C.

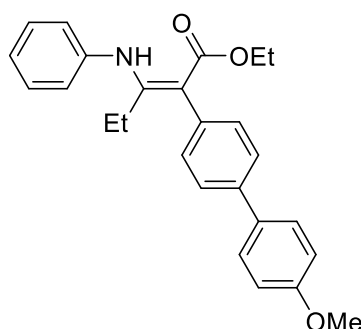


Prepared by adaptation of a literature procedure.⁵ To an oven-dried microwave vial were added ethyl (Z)-2-(4-nitrophenyl)-3-(phenylamino)pent-2-enoate (0.2 mmol, 1.0 equiv.), Pd(OAc)₂ (5 mol%), Brettphos (10 mol%) and K₃PO₄ (2.5 equiv.). The vial was sealed by a cap and placed on the Schlenk line to evacuate and backfill with N₂ three times. Then 1,4-dioxane (1.5 mL) and isopropanol (1.5 equiv.) were added by syringe. The mixture was stirred at 130 °C for overnight. After cooling to room temperature, the reaction was filtered through celite and concentrated. The residue was purified by column chromatography on silica gel to yield the titled compound as colourless oil (44.0 mg, 75%).

¹H NMR (400 MHz, acetone-*d*₆) 11.25 (s, 1H), 7.48 – 7.42 (m, 2H), 7.37 (tt, *J* = 7.2, 1.0 Hz, 2H), 7.31 – 7.24 (m, 6H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.31 (q, *J* = 7.5 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 171.7, 164.3, 141.5, 139.9, 133.7, 130.9, 129.4, 127.8, 126.9, 126.9, 101.5, 60.4, 23.8, 15.5, 13.5.

HRMS (+APCI): calcd for C₁₉H₂₂NO₂ [M+H]⁺ 296.1645, found 296.1644.



ethyl (Z)-2-(4'-methoxy-[1,1'-biphenyl]-4-yl)-3-(phenylamino)pent-2-enoate

Prepared by adaptation of a literature procedure.⁶ To an oven-dried microwave vial were added ethyl (Z)-2-(4-nitrophenyl)-3-(phenylamino)pent-2-enoate (0.2 mmol, 1.0 equiv.), (4-methoxyphenyl)boronic acid (1.5 equiv.), Pd(OAc)₂ (5 mol%), Brettphos (20 mol%), 18-crown-6 (10 mol%) and K₃PO₄ (3.0 equiv.). The vial was sealed by a cap and placed on the Schlenk line to evacuate and backfill with N₂ three times. Then 1,4-dioxane (1.0 mL) was added by

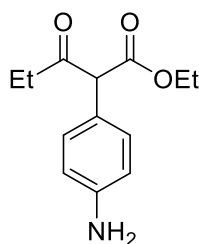
syringe. The mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the reaction was filtered through celite and concentrated. The residue was purified by column chromatography on silica gel to yield the titled compound as white solid (49.0 mg, 61%).

¹H NMR (400 MHz, acetone-*d*₆) 11.28 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.34 – 7.25 (m, 5H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 2.37 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 171.7, 164.5, 161.0, 141.6, 140.0, 138.4, 134.7, 134.2, 130.9, 129.4, 127.4, 127.0, 126.9, 115.9, 101.0, 60.5, 56.4, 23.9, 15.6, 13.5.

HRMS (+ESI): calcd for C₂₆H₂₇NO₄Na [M+Na]⁺ 424.1883, found 424.1890.

mp: 79–80 °C.



ethyl 2-(4-aminophenyl)-3-oxopentanoate

To an oven-dried microwave vial were added ethyl (Z)-2-(4-nitrophenyl)-3-(phenylamino)pent-2-enoate (0.2 mmol, 1.0 equiv.), Fe filings (5.0 equiv.) and NH₄Cl (2.5 equiv.). The vial was sealed by a cap and then EtOH/H₂O (v/v = 3:1, 6.4 mL) was added by syringe. The mixture was stirred at 60 °C for 4 h. After cooling to room temperature, the mixture was filtered and concentrated under reduced pressure. Then water and ethyl acetate were added and the phases were separated. The organic phase was washed with brine, dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel to yield the titled compound as yellow oil (44.7 mg, 95%).

¹H NMR (400 MHz, acetone-*d*₆) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 4.74 (d, *J* = 7.2 Hz, 3H), 4.17 (qd, *J* = 7.1, 1.8 Hz, 2H), 2.53 (q, *J* = 7.3 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (100 MHz, acetone-*d*₆) δ 206.2, 170.7, 149.9, 131.8, 122.9, 115.9, 65.1, 62.1, 35.6, 15.2, 8.9.

HRMS (+ESI): calcd for C₁₃H₁₇NO₃Na [M+Na]⁺ 258.1101, found 258.1104.

4. References

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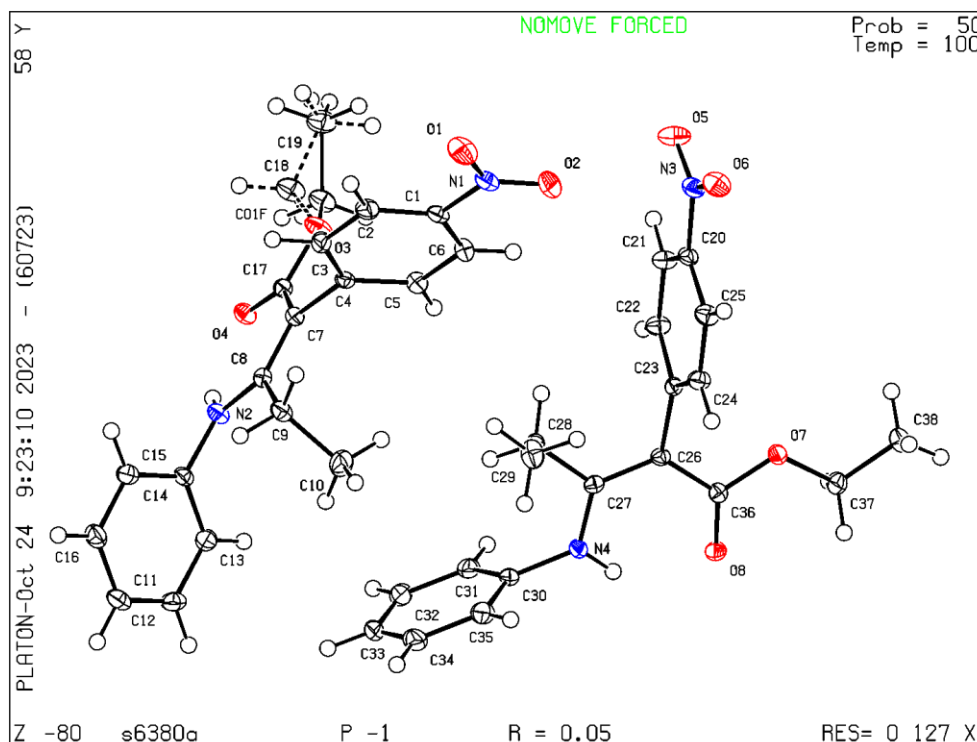
5. X-ray crystallography of 17a

Data collection: X-ray diffraction data for compound **17a** was collected on Agilent Supernova diffractometer using MoK α ($\lambda = 0.71073\text{\AA}$) radiation, equipped with CCD plate detector and an Agilent Crysosystem nitrogen flow gas system, at a temperature of 100K. Data were collected and reduced using CrysAlisPro v42.^{REF1} Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.

Crystal structure determination and refinements: The crystal structure was solved and refined against all F^2 values using the SHELX and Olex2 suite of programmes.^{REF2} Coordinates for all non-hydrogen atoms were freely refined and atomic displacement parameters were freely refined anisotropically. Isotropic thermal parameters were allowed to freely refine. Hydrogen atoms were refined using idealised geometries (riding model) and assigned fixed isotropic displacement parameters.

The structure presented with a disorder ethoxy group in one of the molecules. This was modelled as a two-component disorder, refined so that the sum of the occupancies is equal to 1. Similar 1,2- bond distance, atomic displacement parameters and rigid bond restraints were applied on the disordered part of ethoxy group.

Crystallographic data for X have been deposited in Cambridge Crystallographic Data Centre, with deposition number CCDC 2342281. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).



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Table S1. Crystallographic information for sample **17a**

Identification code	17a
Empirical formula	$C_{19}H_{20}N_2O_4$
Formula weight	340.37
Temperature/K	99.7(7)
Crystal system	triclinic
Space group	P-1
a/Å	8.1324(3)
b/Å	11.0134(5)
c/Å	20.2400(8)
$\alpha/^\circ$	77.534(4)
$\beta/^\circ$	79.396(4)
$\gamma/^\circ$	80.934(4)
Volume/Å ³	1726.67(13)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.309
μ/mm^{-1}	0.093
F(000)	720
Crystal size/mm ³	0.19 × 0.17 × 0.1
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	6.676 to 63.176
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -29 ≤ l ≤ 29
Reflections collected	60067
Independent reflections	10899 [R_{int} = 0.0639, R_{sigma} = 0.0474]
Data/restraints/parameters	10899/25/473
Goodness-of-fit on F^2	1.032
Final R indexes [$ I \geq 2\sigma(I)$]	R_1 = 0.0514, wR_2 = 0.1119
Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1232
Largest diff. peak/hole / e Å ⁻³	0.380/-0.313

REF1. Rigaku Oxford Diffraction, (2024), CrysAlisPro Software system, version 1.171.42a, Rigaku Corporation, Wroclaw, Poland

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6. NMR spectra

