General methods and experimental procedure

Unless otherwise noted all reagents were obtained from commercial suppliers and used without further purification. Chromatography columns were prepared using Fisher Chemicals 60A 35–70 micron silica gel. Nuclear magnetic resonance spectra were recorded using Bruker DPX300 and DPX500 MHz spectrometers. Chemical shifts are reported in parts per million (δ) downfield relative to the internal reference tetramethylsilane (TMS). Unless otherwise specified NMR spectra were recorded in deuterochloroform at room temperature. Abbreviations used: Ar = aromatic, d = doublet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, q = quartet, s = singlet, t = triplet. Mass spectra were recorded using a micromass ZMD 2000 spectrometer employing the electrospray (ES+) ionisation technique. Accurate molecular masses (HRMS) were obtained from Waters LCT, GCT or Bruker MicroTof spectrometers. Infra-red spectra were recorded using a Perkin-Elmer FT-IR spectrometer. IR spectra of liquids were recorded as thin films on sodium chloride plates. IR spectra of solids were recorded using dichloromethane as solvent on sodium chloride plates. Melting points are uncorrected. Compounds **6**, **10** and **14** contains trace of ethyl acetate (NMR)

Method A: General procedure for copper catalysed click reaction

To a stirred solution of **4a** (1.0 mmol), sodium ascorbate (0.3 mmol) and $CuSO_4$ (0.01 mmol) in $^tBuOH/H_2O$ (4 mL, 1:1) was added benzyl azide (1.0 mmol) dropwise over 2 minutes. The reaction was stirred at RT for 12 hours and monitored via TLC. Upon completion the reaction was concentrated *in vacuo* in order to remove ^tBuOH. The resultant residue was diluted with ethyl acetate (20 mL) and washed with H_2O (50 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield a crude product which was purified by column chromatography (gradient elution of hexane/ethyl acetate).

Method B: General procedure for palladium catalysed cyclisation – Cross coupling

5a (1.0 mmol), boronic acid (2.0 mmol), $Pd(PPh_3)_4$ (5 mol%) and Cs_2CO_3 (3.0 mmol) were dissolved in dioxane/H_2O (15:1, 3.0 mL) with stirring. The reaction mixture was stirred for 6 hours at 90 °C and monitored via TLC. Upon completion the reaction was diluted with ethyl acetate (30 mL) and washed with H_2O (20 mL). The organic phase was dried over Na_2SO_4,

filtered and concentrated *in vacuo* to yield a crude product which was purified by column chromatography (gradient elution of hexane/ethyl acetate).

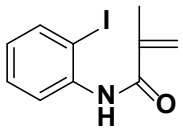
Method C: General procedure for one-pot copper catalysed click reaction and palladium catalysed cyclisation – Cross coupling

4a (1.0 mmol), benzyl azide (1.0 mmol) and CuI (5 mol%) were dissolved in dioxane/H_2O (3.2 mL) with stirring. The reaction mixture was stirred for 12 hours at 90 °C and monitored via TLC. Upon completion boronic acid (2.0 mmol), $Pd(PPh_3)_4$ (5 mol%) and Cs_2CO_3 (3.0 mmol) were added and the reaction stirred for a further 12 hours. Upon completion the reaction was diluted with ethyl acetate (30 mL) and washed with H_2O (20 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield a crude product which was purified by column chromatography (gradient elution of hexane/ethyl acetate).

Method D: General procedure for palladium catalysed cyclisation-carbonylation-amination

5a (1.0 mmol), Cs_2CO_3 (3.0 mmol), Palladium acetate (10 mol%), furyl phosphine (20 mol%) and amine (1.5 mmol) were dissolved in 15 mL toluene with stirring under a CO balloon. The mixture was stirred for 100 °C for 10 hours and the reaction monitored via TLC. On completion the mixture was diluted with ethyl acetate, filtered and concentrated *in vacuo*. The crude product was seprated using column chromatography (gradient elution of hexane/ethyl acetate)

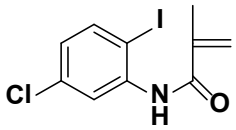
Compound A1



To a stirred solution of 2-iodoaniline (5.0 g, 22.8 mmol) and triethylamine (0.24 mL, 25.1 mmol) in anhydrous CH_2Cl_2 (150 mL) was added methacryloyl chloride (2.5 mL, 25.1 mmol) dropwise over 5 mins and the reaction stirred at RT for 10 hours. The reaction was quenched by the addition of H_2O (100 mL) and the aqueous phase extracted with CH_2Cl_2 (2 x 50 mL). Organic

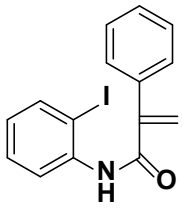
phases were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield brown oil. The resultant oil was used without further purification.

Compound A2



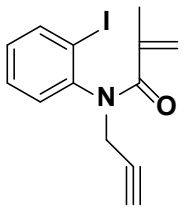
To a stirred solution of 5-chloro-2-iodoaniline (0.538g, 2.1mmol) and triethylamine (0.234g, 2.31 mmol) in 100 mL DCM, methacrolyl chloride was added (0.241g, 2.31 mmol). The mixture was stirred over ice for 1 hour. The mixture was then stirred at room temperature overnight. The mixture was then quenched with 100 mL water. The aqueous phase was separated with two 100 mL washes of DCM. The organic phases were combined and dried with anhdyous sodium sulphate. The liquid was filtered off and concentrated *in vacuo* to give brown oil which was used without further purification.

Compound A3



To a stirred solution of 2-phenylacrylic acid (1.0 g, 6.75 mmol) in anhydrous THF (50 mL) was added glucosez (0.86 g, 6.41 mmol) and the reaction stirred at RT for 2 hours. 2-iodoanaline (1.48 g, 6.75 mmol) was added and the reaction stirred for a further 12 hours. The reaction was quenched by the addition of H_2O (100 mL) and the aqueous phase extracted with CH_2Cl_2 (2 x 50 mL). Organic phases were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield brown oil. The resultant oil was used without further purification.

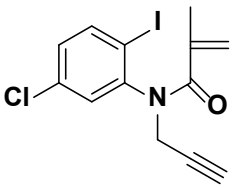
Compound 4a



To a stirred solution of compound **A1** (22.8 mmol) and sodium hydride (0.84 g, 20.9 mmol) in anhydrous DMF (100 mL) was added propargyl bromide (3.60 mL, 32.3 mmol). The solution was stirred at RT for 1 hour, quenched by the addition of H_2O (100 mL) and the aqueous phase extracted with diethyl ether (4 x 100 mL). Organic phases were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield a brown syrup. The resulting syrup was purified by column chromatography (gradient elution of hexane/ethyl acetate 8:2) to yield compound **4a** as a yellow solid (2.90 g, 34 % over 2 steps).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (1H, dd, J = 7.8, 1.5 Hz, Ar***H***), 7.42-7.27 (2H, m, Ar***H***), 7.06 (1H, td, J = 8.5, 1.5 Hz, Ar***H***), 5.13 (1H, s, C=C***H***), 5.03 (1H, s, C=C***H***), 5.10 (1H, d, J = 15.0 Hz, NC***H***), 3.95 (1H, d, J = 15.0 Hz, NC***H***), 2.20 (1H, s, alkyl***H***), 1.83 (3H, s, C***H*****$_3$**). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 171.2, 147.1, 140.1, 139.3, 131.1, 129.8, 129.1, 119.8, 86.2, 72.6, 71.5, 37.8, 20.4. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 1656, 1631. **H.R.M.S.** [ES+] Found: 347.9862 (MNa^+); $C_{13}H_{12}INO$ requires 347.9856 (MNa^+). **M.pt:** 63-64 °C

Compound 4b

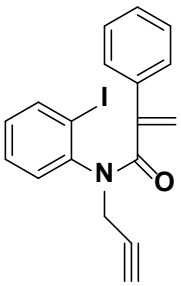


To a stirred solution of crude **A2** (assuming 1.5g, 4.7 mmol are all product) and 60% sodium hydride (0.187 g, 4.7 mmol) in anhydrous DMF (100 mL), 80% propargyl bromide (3.60 mL, 7.04 mmol) was added. The solution was stirred at RT for 1 hour, quenched by the addition of H_2O (100 mL) and the aqueous phase extracted with diethyl ether (4 x 100 mL). The organic phases were combined, dried over Na_2SO_4, filtered and subsequently concentrated *in vacuo* to

yield a brown liquid which was purified by column chromatography (gradient elution of hexane/ethyl acetate 8:2) to yield compound **4b** as a colourless solid (0.80 g, 47 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (1H, d, J = 8.25 Hz, Ar***H***), 7.29 (1H, s, Ar***H***), 7.07 (1H, dd, J = 8.7, 2.3 Hz, Ar***H***), 5.10 (2H, s, C=C***H***), 5.03 (1H, d, J = 14.7 Hz, NC***H***H), 3.95 (1H, d, J = 15.6 Hz, NCH***H***), 2.25 (1H, s, alkyne***H***), 1.87 (3H, s, C***H*****$_3$**). **^{13}C NMR** (75.5 MHz, $CDCl_3$): 170.9, 145.2, 140.7, 139.4, 134.9, 131.1, 130.0, 120.0 97.0, 78.1, 73.1, 37.7, 20.4. **ν_{max}/cm^{-1}**; 3302, 1662, 1631, 1571, 1462. **H.R.M.S.** [ES+] Found: 359.9642 (MH^+); $C_{13}H_{11}ICINO$ requires 3599647 (MH^+). **M.pt:** 62-64 °C

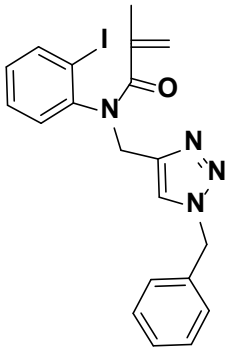
Compound 4c



To a stirred solution of **A3** (assume 6.75 mmol) and sodium hydride (245.7 mg, 6.14 mmol) in anhydrous DMF (100 mL) was added propargyl bromide (1.1 mL, 9.45 mmol). The solution was stirred at RT for 1 hour, quenched by the addition of H_2O (100 mL) and the aqueous phase extracted with diethyl ether (4 x 100 mL). Organic phases were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield a brown syrup. The resulting syrup was purified by column chromatography (gradient elution of hexane/ethyl acetate 8:2) to yield compound **4c** as yellow oil (1.67 g, 64 % over 2 steps).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (1H, dd, J = Hz, Ar***H***), 7.31-7.23 (6H, m, Ar***H***), 7.01-6.70 (2H, m, Ar***H***), 5.6 (1H, s, C=CH), 5.43 (1H, s, C=CH), 5.2 (1H, dd, J = 17.3, 2.5 Hz, NC***H***H), 3.9 2 (1H, dd, J = 17.3, 2.5 Hz, NCH***H***), 2.2 (1H, t, J = 2.5 Hz, alkyne***H***).

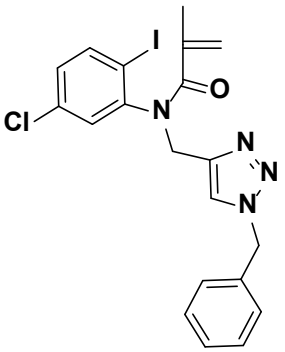
Compound 5a



Prepared by general procedure Method A from compound **4a** (326.0 mg, 1.0 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 7:3) to yield compound **5a** as a clear gel (403.4 mg, 88 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (1H, dd, J = 8.4, 1.5 Hz, Ar***H***), 7.65 (1H, s, triazole***H***), 7.40-7.22 (5H, m, Ar***H***), 7.10-6.94 (2H, m, Ar***H***), 5.6 (1H, d, J = 15.0 Hz, NC***H*****HPh**), 5.5 (1H, d, C**H*****H***Ph) 5.3 (1H, d, J = 15.0 Hz, NC***H***), 5.0 (1H, s, C=C***H*****$_2$**), 4.5 (1H, d, J = 15.0 HzNC*H*) 1.53 (s C***H*****$_3$**), **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 171.3, 140.0, 134.7, 133.5, 130.8, 129.5, 129.3, 129.2, 129.1, 128.7, 128.0, 124.1, 124.0, 119.8, 99.3, 54.1, 44.6, 20.5. **ν_{max}/cm^{-1}**; 3069, 2901, 1651, 1625. **H.R.M.S.** [ES+] Found: 481.0513 (MNa^+); $C_{20}H_{19}IN_4O$ requires 481.0496 (MNa^+).

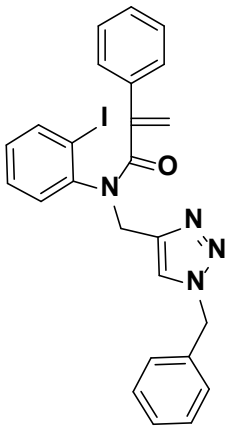
Compound 5b



Prepared by general procedure Method A from compound **4b** (359.0 mg, 1.0 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 4:1) to yield compound **5b** as a colourless solid (201.0 mg, 41.0 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ7.75 (1H, d, J = 9.2, Ar***H***), 7.63 (1H, s, triazole***H***), 7.39-7.32 (3H, m, Ar***H***), 7.25 (2H, m, Ar***H***), 6.99 (2H, m, Ar***H***), 5.57 (1H, d, J = 15.1 Hz, NC***H***HPh), 5.47 (1H, d, J = 15.1 Hz, NCH***H***Ph) 5.28 (1H, d, J = 14.7 Hz, NC***H***H), 5.05 (1H, s, C=CH***H***), 5.00 (1H, s, C=C***H***H), 4.49 (1H, d, J = 14.7 Hz, NCH***H***), 1.81 (3H, s, C***H*****$_3$**). **^{13}C NMR** (75.5 MHz, $CDCl_3$): 171.1, 143.5, 140.7, 139.5, 135.0, 134.7, 130.9, 129.7, 129.3, 129.1, 128.7, 128.0, 126.4, 126.2, 123.9, 120.2, 97.3, 54.2, 44.6, 20.4**. ν_{max}/cm^{-1}**; 1655, 1629, 1497, 1461**. H.R.M.S.** [ES+] Found: 515.0123 (MNa^+). $C_{20}H_{18}ICIN_4O$ requires 515.0112 (MNa^+). **M.pt:** 103-105 °C

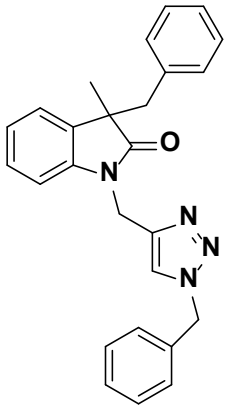
Compound 5c



Prepared by general procedure Method A from compound **4c** (238.4 mg, 0.62 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 7:3) to yield compound **5c** as a clear gel (179.4 mg, 56 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (1H, s, triazole***H***), 6.49 (1H, d, J = 7.6 Hz, Ar***H***), 5.59 (1H, s, C=C***H***), 5.53 (2H, s, NC***HH***Ph), 5.48 (1H, d, J = 14.7 Hz, NC***H***H), 5.34 (1H, s, C=C***H***), 4.39 (1H, d, J = 14.7 Hz, NCH***H***). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.0, 145.2, 143.8, 143.7, 139.6, 136.8, 134.8, 134.4, 131.4, 129.9, 129.4, 129.1, 128.9, 128.8, 128.6, 128.3, 128.0, 125.9, 100.1, 54.2, 44.1. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 1709, 1611. **H.R.M.S.** [ES+] Found: 543.0664 (MNa^+); $C_{25}H_{21}IN_4O$ requires 543.0652 (MNa^+).

Compound 6

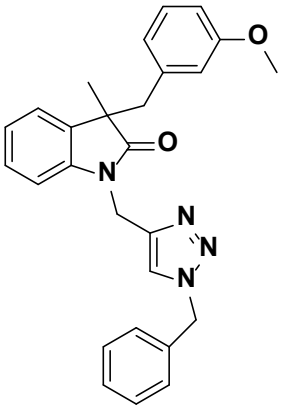


Prepared by general procedure Method B from **5a** (70.0 mg, 0.15 mmol) and phenylboronic acid (37.2 mg, 0.31 mmol) to yield compound **6** as a yellow oil (51.2 mg, 82 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.26 (4H, m, Ar***H***), 7.16-7.04 (4H, m, Ar***H***), 6.97-6.77 (5H, m, Ar***H***), 6.68 (1H, dd, J = 7.8, 1.5 Hz, Ar***H***), 6.09 (1H, s, triazole***H***), 5.39 (1H, d, J = 15.1 Hz, NC***H***HPh), 5.29 (1H, d, J = 15.1 Hz, NCH***H***Ph), 5.15 (1H, d, J = 15.9, NC***H***H), 4.57 (1H, d, J = 15.9 Hz, NCH***H***), 3.19 (1H, d, J = 13.1 Hz, C***H***H), 3.07 (1H, d, J = 13.1 Hz, CH***H***), 1.51 (3H, s, C***H*****$_3$**). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 179.2, 143.4, 141.7, 136.7, 134.8, 132.8, 130.1, 128.6, 128.0, 127.9, 127.7, 127.4, 126.3, 123.1, 122.5, 121.8, 109.3, 53.8, 50.1, 44.2, 35.7, 23.9. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 1709, 1611. **H.R.M.S.** [ES+] Found: 431.1846 (MNa^+); $C_{26}H_{24}N_4O$ requires 431.1842 (MNa^+).

Alternatively compound **6** was synthesized using the general procedure Method C in 62 % yield.

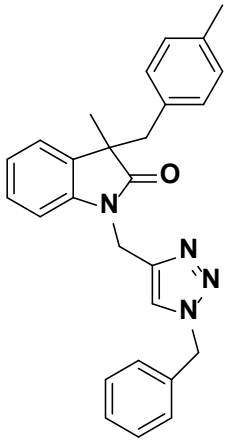
Compound 7



Prepared by general procedure Method B from **5a** (70.0 mg, 0.15 mmol) and (3-methoxyphenyl) boronic acid (46.5 mg, 0.31 mmol) to yield compound **7** as a white solid (46.9 mg, 70 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.27 (4H, m, Ar***H***), 7.16-7.06 (4H, m, Ar***H***), 6.79 (1H, app. t, J = 7.2 Hz, Ar***H***), 6.68 (1H, dd, Ar***H***), 6.55 (1H, ddd, J = 7.0, 2.4, 1.0 Hz, Ar***H***), 6.44 (1H, dt, J = 6.3, 6.2, 1.2 Hz, Ar***H***), 6.25 (1H, dd, Ar***H***), 6.23 (1H, s, triazole***H***), 5.42 (1H, d, J = 14.9 Hz, NC***H***HPh), 5.29 (1H, d, J = 14.9 Hz, NCH***H***Ph), 5.16 (1H, d, J = 15.9 Hz, NC***H***H), 4.58 (1H, d, J = 15.9 Hz, NCH***H***), 3.40 (3H, s, OC***H*****$_3$**), 3.18 (1H, d, J = 12.9 Hz, C***H***H), 3.07 (1H, d, J = 12.9 Hz, CH***H***), 1.52 (3H, s, C***H*****$_3$**). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 179.2, 143.4, 141.7, 136.7, 134.8, 132.8, 130.1, 129.6, 129.0, 128.6, 127.9, 127.6, 127.4, 126.3, 123.1, 122.5, 121.8, 115.4, 109.3, 53.8, 50.1, 44.3, 35.7, 24.8, 23.9. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 2351, 1710, 1612. **H.R.M.S.** [ES+] Found: 461.1947 (MNa^+). $C_{27}H_{26}N_4O_2$ requires 461.1948 (MNa^+). **M.pt:** 92-94 °C.

Compound 8



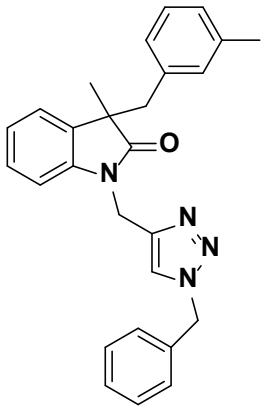
Prepared by general procedure Method B from **5a** (70.0 mg, 0.15 mmol) and p-tolylboronic acid (41.5 mg, 0.31 mmol) to yield compound **8** as a clear oil (57.4 mg, 89 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.30 (3H, m, Ar***H***), 7.21 (1H, dd, J = 8.5, 1.2 Hz, Ar***H***), 7.12 (1H, td, J = 8.0, 1.5 Hz, Ar***H***), 7.05-7.03 (3H, m, Ar***H***), 6.76 (2H, d, J = 7.5 Hz, Ar***H***), 6.71 (2H, d, J = 7.5 Hz, Ar***H***), 6.70 (1H, d, J = 8.0 Hz, Ar***H***), 6.51 (1H, s, triazole***H***), 5.37 (1H, d, J = 15.1 Hz, NC***H***HPh), 5.33 (1H, d, J = 15.1 Hz, NCH***H***Ph), 5.06 (1H, d, J = 16.0 Hz, NC***H***H), 4.67 (1H, d, J = 16.0 Hz, NCH***H***), 3.13 (1H, d, J = 12.8 Hz, C***H***H), 3.03 (1H, d, J = 12.8 Hz,

CH***H***), 2.15 (3H, s, C***H*****$_3$**Ar), 1.48 (3H, s, C***H*****$_3$**). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 179.5, 143.5, 141.7, 135.7, 134.7, 133.5, 132.9, 130.0, 129.1, 129.0, 128.4, 127.8, 127.4, 123.2, 122.4, 122.2, 109.3, 53.8, 49.9, 43.8, 35.7, 23.7, 21.1. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 1707, 1611. **H.R.M.S.** [ES+] Found: 445.1996 (MNa^+). $C_{27}H_{26}N_4O$ requires 445.1999 (MNa^+).

Alternatively compound **8** was synthesized using the general procedure Method C in 80 % yield.

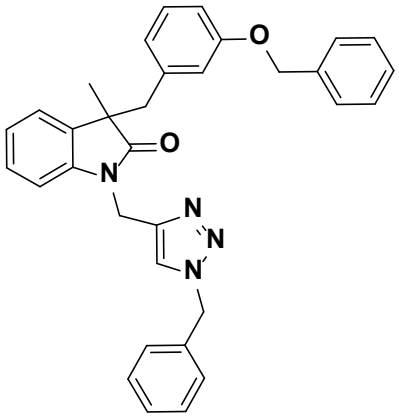
Compound 9



Prepared by general procedure Method B from **5a** (50.0 mg, 0.11 mmol) and m-tolylboronic acid (29.7 mg, 0.22 mmol) to yield compound **9** as a white solid (40.6 mg, 88 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.24 (4H, m, Ar***H***), 7.16-7.04 (4H, m, Ar***H***), 6.81-6.74 (2H, m, Ar***H***), 6.46 (1H, d, J = 8.0 Hz, Ar***H***), 6.63 (1H, s, Ar***H***), 6.56 (1H, d, J = 7.0 Hz, Ar***H***), 6.13 (1H, s, triazole***H***), 5.39 (1H, d, J = 14.9 Hz, NC***H***HPh), 5.29 (1H, d, J = 14.9 Hz, NCH***H***Ph), 5.13 (1H, d, J = 15.8 Hz, NC***H***H), 4.60 (1H, d, J = 15.8 Hz, NCH***H***), 3.13 (1H, d, J = 13.4 Hz, C***H***H), 3.04 (1H, d, J = 13.4 Hz, CH***H***), 2.00 (3H, s, C***H*****$_3$**Ar), 1.50 (3H, s, C***H*****$_3$**). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 179.5, 143.5, 142.3, 137.2, 136.6, 135.0, 132.9, 131.0, 129.0, 128.6, 128.4, 127.9, 127.5, 127.3, 127.0, 123.1, 122.4, 121.8, 109.3, 53.8, 50.0, 44.3, 35.7, 23.8, 21.0. **ν_{max}/cm^{-1}**; 2917, 1709, 1611. **H.R.M.S.** [ES+] Found: 445.2006 (MNa^+). $C_{27}H_{26}N_4O$ requires 445.1999 (MNa^+). **M.pt:** 94-96 °C.

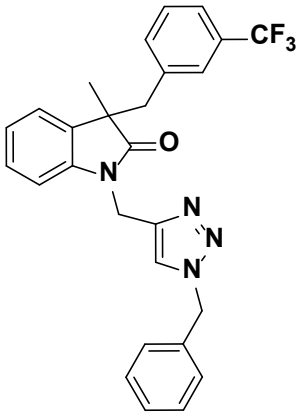
Compound 10



Prepared by general procedure Method B from **5a** (50.0 mg, 0.11 mmol) and 3-(benzyloxy)phenylboronic acid (49.8 mg, 0.22 mmol) to yield compound **10** as a clear oil (45.1 mg, 80 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.24 (9H, m, Ar***H***), 7.14 (1H, app. td, J = 7.8, 1.4 Hz, Ar***H***), 7.09 (1H, app. td, J = 7.8, 1.4 Hz, Ar***H***), 7.05-7.03 (2H, m, Ar***H***), 6.76-6.70 (2H, m, Ar***H***), 6.60 (1H, dd, J = 7.3, 1.8 Hz, Ar***H***), 6.43 (1H, br. d, J = 7.3 Hz, Ar***H***), 6.39-6.38 (1H, m, Ar***H***), 6.23 (1H, s, triazole***H***), 5.29 (1H, d, J = 15.1 Hz, NC***H***HPh), 5.16 (1H, d, J = 15.1 Hz, NCH***H***Ph), 5.14 (1H, d, J = 16.8 Hz, NC***H***H), 4.70 (1H, d, J = 11.6, OC***H***H), 4.59 (1H, d, J = 11.6 Hz, OCH***H***), 4.57 (1H, d, J = 16.8 Hz, NCH***H***), 3.17 (1H, d, J = 13.3 Hz, C***H***H), 3.06 (1H, d, J = 13.3 Hz, CH***H***), 1.51(3H, s, C***H$_3$***). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 179.1, 158.1, 143.3, 141.9, 138.2, 136.8, 134.8, 133.0, 128.9, 128.7, 128.6, 128.5, 128.0, 127.5, 127.4, 123.4, 123.1, 122.8, 122.5, 121.8, 115.5, 114.1, 109.4, 69.8, 53.7, 50.0, 44.4, 35.7, 23.9. **ν_{max}/cm^{-1}**; 2919, 1709, 1611. **H.R.M.S.** [ES+] Found: 537.2267 (MNa^+); $C_{33}H_{30}N_4O_2$ requires 537.2261 (MNa^+).

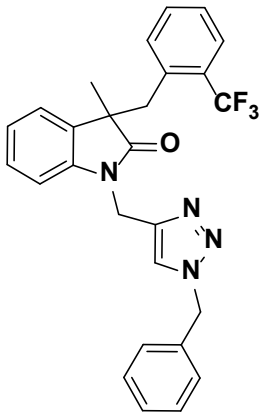
Compound 11



Prepared by general procedure Method B from **5a** (62.0 mg, 0.14 mmol) and 3-(trifluoromethyl)phenylboronic acid (51.4 mg, 0.27 mmol) to yield compound **11** as a clear oil (40 mg, 62 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-6.88 (12H, m, Ar***H***), 6.80 (1H, d, J = 7.8 Hz, Ar***H***), 6.58 (1H, s, triazole***H***), 5.42 (1H, d, J = 15.1 Hz, NC***H***HPh), 5.33 (1H, d, J = 15.1 Hz, NCH***H***Ph), 4.95 (1H, d, J = 15.6 Hz, NC***H***H), 4.65 (1H, d, J = 15.6 Hz, NCH***H***), 3.22 (1H, d, J = 13.2 Hz, C***H***H), 3.08 (1H, d, J = 13.2 Hz, CH***H***), 1.51 (3H, s, C***H*****$_3$**). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 178.9, 143.2, 141.7, 137.3, 134.6, 133.3, 133.1, 129.1, 128.7, 128.3, 128.0, 127.9, 127.7, 126.7, 123.0, 122.8, 122.6, 121.7, 121.4, 109.5, 53.9, 49.8, 44.0, 35.5, 23.5. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 1708, 1612. **H.R.M.S.** [ES+] Found: 499.1728 (MNa^+); $C_{27}H_{23}F_3N_4O$ requires 499.1716 (MNa^+).

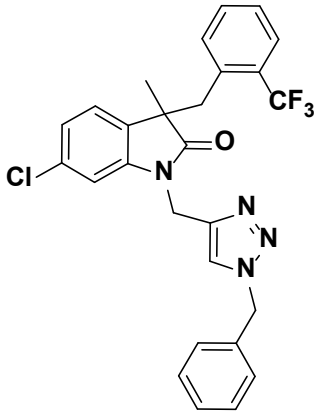
Compound 12



Prepared by general procedure Method B from **5a** (65.0 mg, 0.14 mmol) and 2-(trifluoromethyl)phenylboronic acid (53.9 mg, 0.28 mmol) to yield compound **12** as a clear oil (58.8 mg, 87 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (1H, d, J = 8.0 Hz, Ar***H***), 7.36-7.33 (3H, m, Ar***H***), 7.24 (1H, s, Ar***H***), 7.22-7.21 (2H, m, Ar***H***), 7.15 (1H, ddd, , Ar***H***), 7.10-7.01 (1H, m, Ar***H***), 7.02 (1H, d, J = 8.0 Hz, Ar***H***), 6.96-6.90 (3H, m, Ar***H***), 6.90 (1H, s, triazole***H***), 5.45 (2H, s, NC***HH***Ph), 5.10 (1H, d, J = 15.6 Hz, NC***H***H), 4.88 (1H, d, J = 15.6 Hz, NCH***H***), 3.39 (1H, d, J = 14.9 Hz, C***H***H), 3.33 (1H, d, J = 14.9 Hz, CH***H***), 1.46 (3H, s, C***H*****$_3$**). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 179.9, 143.2, 141.6, 136.0, 134.4, 132.9, 132.7, 131.0, 130.4, 129.2, 128.9, 128.1, 128.0, 126.5, 123.4, 122.7, 122.6, 122.3, 122.2, 109.3, 54.2, 48.5, 38.5, 35.6, 25.1. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 1709, 1611. **H.R.M.S.** [ES+] Found: 499.1731 (MNa^+); $C_{27}H_{23}F_3N_4O$ requires 499.1716 (MNa^+).

Compound 13

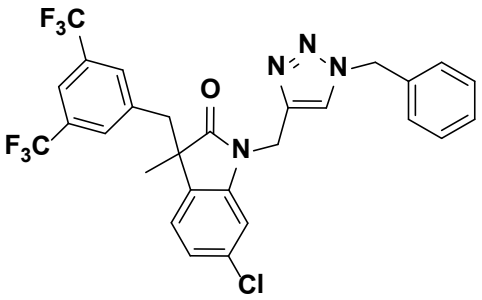


Prepared by general procedure Method B from **5b** (60mg, 0.12mmol) and 2-(trifluoromethyl)phenylboronic acid (47mg, 0.24mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 1:1) to yield compound **13** as a colourless solid (60 mg, 90 % yield)

^{1}H NMR (500 MHz, $CDCl_3$): 7.47 (1H, d, J= 7.8Hz, Ar***H***), 7.38-7.36 (4H, m, Ar***H***), 7.24-7.23 (2H, m, Ar***H***), 7.12-7.09 (1H, t, J = 7.3, Ar***H***), 7.02 (1H, d, J = 1.8 Hz, Ar***H***), 6.96-6.95 (1H, d, J = 7.8 Hz, Ar***H***), 6.93(1H, s, triazole***H***), 6.92-6.88 (1H, m, Ar***H***), 6.84 (1H, d, J = 7.8Hz, Ar***H***), 5.48 (2H, s, NC***HH***Ph), 5.08 (1H, d, J = 15.6, NC***H***H), 4.84 (1H, d, J = 15.6 Hz, NCH***H***), 3.38

(1H, d, J = 15.1 Hz, C***H***H), 3.31 (1H, d, J = 15.1 Hz, CH***H***), 1.44 (3H, s, C***H*****3**). **^{13}C NMR** (75.5 MHz, $CDCl_3$): 180.0, 142.8, 142.7, 135.6, 134.3, 133.8, 131.2, 131.0, 130.3, 129.2, 129.0, 128.9, 128.04, 126.7, 126.2, 126.1, 126.1, 125.3, 124.4, 123.2, 122.6, 122.2, 109.9, 54.3, 48.4, 38.4, 35.7, 25.0. **ν_{max}/cm^{-1}**; 2830, 1717, 1610, 1490. **H.R.M.S.** [ES+] Found: 511.1512 (MH^+). $C_{27}H_{22}ClF_3N_4O$ requires 511.1507 (MH^+). **M.pt:** 97-99 °C.

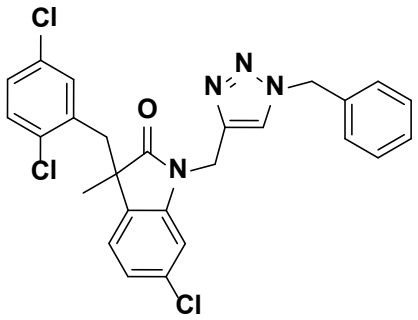
Compound 14



Prepared by general procedure Method B from **5b** (50mg, 0.1 mmol) and 3.5-bis(trifluoromethyl) benzeneboronic acid. Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 2:3) to yield compound **14** as a colourless gel (48.2mg, 82 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (1H, s, Ar***H***), 7.38-7.33 (3H, m, Ar***H***), 7.25 (2H, s, Ar***H***), 7.20-7.19 (2H, m, Ar***H***), 7.13 (1H, s, triazole***H***), 7.10 (1H, d, J = 7.8 Hz, Ar***H***), 7.07-7.04 (1H, m, Ar***H***), 7.00 (1H, d, J = 1.4 Hz, Ar***H***), 5.45 (1H, d, J = 15.1 Hz, NC***H***HPh), 5.40 (1H, d, J = 15.1 Hz, NCH***H***Ph), 4.75 (1H, d, J = 15.6, NC***H***H), 4.64 (1H, d, J = 15.6 Hz, NCH***H***), 3.27 (1H, d, J = 13.1 Hz, C***H***H), 3.09 (1H, d, J = 13.1 Hz, CH***H***), 1.48(3H, s, C***H*****3**). **^{13}C NMR** (75.5 MHz, $CDCl_3$): 178.6, 142.9, 142.5, 138.4, 134.6, 134.4, 130.9, 129.9, 129.9, 129.7, 129.1 128.8, 128.0, 124.1, 123.8, 122.7, 122.0, 110.5, 54.2, 495, 43.7, 35.4, 23.0. **ν_{max}/cm^{-1}**: 3054, 2986, 1717, 1610, 1490. **H.R.M.S.** [ES+] Found: 579.1385 (MH^+). $C_{28}H_{21}ClF_6N_4O$ requires 579.1381 (MH^+).

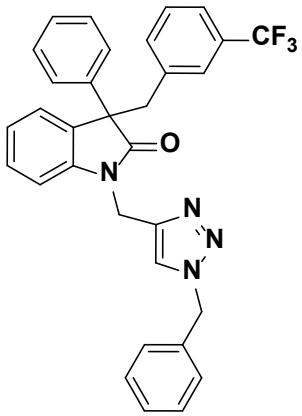
Compound 15



Prepared by general procedure Method B from **5b** (33mg, 0.067 mmol) and 2,5-dichlorobenzeneboronic acid (27mg, 0.134 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 7:3) to yield compound **15** as a colourless solid (27mg, 79% yield)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.34 (3H, m, Ar***H***), 7.25 (1H, s, triazole***H***), 7.20-7.19 (2H, m, Ar***H***), 7.1 (1H, d, J = 7.8 Hz, Ar***H***), 7.05 (1H, d, J = 2.3 Hz, Ar***H***), 7.03 (1H, d, J = 8.7 Hz, Ar***H***), 6.99 (1H, d, J = 1.4 Hz, Ar***H***), 6.96 (1H, dd, J = 8.0, 1.6 Hz, Ar***H***), 6.93 (1H, dd, J = 8.5, 2.5 Hz, Ar***H***), 5.50 (1H, d, J = 14.9 Hz, NC***H***HPh), 5.45 (1H, d, J = 14.9 Hz, NCH***H***Ph), 5.07 (1H, d, J = 16.0 Hz, NC***H***H), 4.79 (1H, d, J = 15.8 Hz, NCH***H***), 3.36 (1H, d, J = 13.8 Hz, C***H***H), 3.17 (1H, d, J = 13.8 Hz, CH***H***), 1.46 (3H, s, C***H*****$_3$**). **^{13}C NMR** (75.5 MHz, $CDCl_3$): 179.3, 142.8, 142.7, 136.1, 134.5, 134.0, 132.9, 131.8, 131.0, 130.6, 130.0, 129.1, 128.8, 128.2, 127.9, 124.9, 122.4, 122.2, 110.0, 54.2, 49.3, 39.3, 35.8, 23.9. **ν_{max}/cm^{-1}**; 3688, 2685, 1714, 1610, 1490. **H.R.M.S.** [ES+] Found: 511.086525 (MH^+); $C_{30}H_{25}ClN_4O$ requires 511.085371 (MH^+). **M.pt:** 107-109 °C.

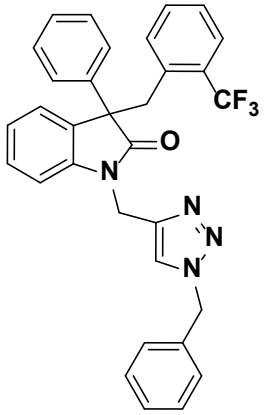
Compound 16



Prepared by general procedure Method B from **5c** (60.0 mg, 0.12 mmol) and 3-(trifluoromethyl)phenylboronic acid (43.8 mg, 0.23 mmol) to yield compound **16** as a clear oil (40.4 mg, 65 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (2H, d, J = 7.3 Hz, Ar***H***), 7.34-7.27 (7H, m, Ar***H***), 7.23-7.09 (5H, m, Ar***H***), 7.07-6.99 (2H, m, Ar***H***), 6.93 (1H, app.t, J = 7.8 Hz, Ar***H***), 6.86 (1H, d, J = 7.8 Hz, Ar***H***), 6.69 (1H, s, triazole***H***), 5.41 (1H, d, J = 15.1 Hz, NC***H***HPh), 5.34 (1H, d, J = 15.1 Hz, NCH***H***Ph), 4.82 (1H, d, J = 15.6 Hz, NC***H***H), 4.70 (1H, d, J = 15.6 Hz, NCH***H***), 3.79 (1H, d, J = 12.8 Hz, C***H***H), 3.50 (1H, d, J = 12.8 Hz, CH***H***). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 177.0, 143.1, 142.3, 139.4, 136.8, 134.6, 133.6, 130.4, 129.9, 129.1, 128.8, 128.7, 128.0, 127.7, 127.1, 127.0, 125.3, 125.0, 123.3, 123.2, 122.8, 122.7, 121.9, 109.8, 57.9, 54.0, 43.4, 35.7. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 1711, 1603. **H.R.M.S.** [ES+] Found: 561.1881(MNa^+); $C_{32}H_{25}F_3N_4O$ requires 561.1873 (MNa^+).

Compound 17

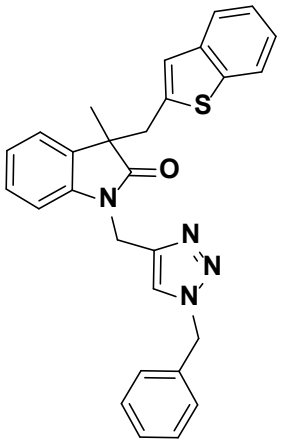


Prepared by general procedure Method B from **5c** (55.0 mg, 0.11 mmol) and 2-(trifluoromethyl)phenylboronic acid (40.1 mg, 0.21 mmol) to yield compound **17** as a clear oil (40.9 mg, 72 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (3H, m, Ar***H***), 7.38-7.14 (9H, m, Ar***H***), 7.12-7.02 (2H, m, Ar***H***), 6.97-6.88 (1H, app.t, J = 7.3 Hz, Ar***H***), 6.86-6.80 (2H, m, Ar***H***), 6.73 (1H, d, J = 7.8 Hz, Ar***H***), 6.72 (1H, s, triazole***H***), 5.44 (2H, s, NC***HH***Ph), 5.05 (1H, d, J = 15.6 Hz, NC***H***H), 4.90 (1H, d, J = 15.6 Hz, NCH***H***), 3.83 (2H, s, C***HH***). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 177.9, 143.2, 142.2, 139.9, 135.9, 139.3, 134.9, 134.3, 131.0, 130.3, 130.0, 129.7, 129.2, 128.8, 128.7, 128.5,

128.0, 127.7, 127.3, 126.6, 126.0, 122.5, 122.2, 109.6, 56.6, 54.3, 38.8, 35.8. ν_{max}/cm^{-1}; 2685, 2521, 2410, 1711, 1603. **H.R.M.S.** [ES+] Found: 561.1864 (MNa^+). $C_{32}H_{25}F_3N_4O$ requires 561.1873 (MNa^+).

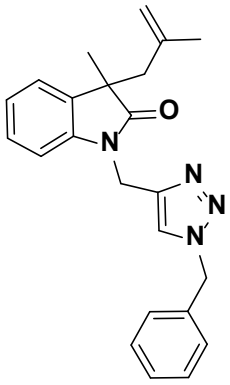
Compound 18



Prepared by general procedure Method B from **5a** (50.0 mg, 0.11 mmol) and benzo[b]thiophene-2-boronic acid (38.8 mg, 0.22 mmol) to yield compound **18** as a white solid (44.6 mg, 88 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (1H, d, J = 8.0 Hz, Ar***H***), 7.46 (1H, d, J = 8.0 Hz, Ar***H***), 7.36 (1H, d, J = 7.0 Hz, Ar***H***), 7.31-7.20 (5H, m, Ar***H***), 7.17 (1H, d, J = 8.0 Hz, Ar***H***), 7.15 (1H, d, J = 8.0 Hz, Ar***H***), 6.90 (1H, s, thiozole***H***), 6.86-6.82 (2H, m, Ar***H***), 6.75 (1H, d, J = 8.0 Hz, Ar***H***), 5.95 (1H, s, triazole***H***), 5.23 (1H, d, J = 15.6 Hz, NC***H***HPh), 4.71 (1H, d, J = 15.6 Hz, NC***H***H), 4.59 (1H, d, J = 15.6 Hz, NCH***H***), 4.41 (1H, d, J = 15.6 Hz, NCH***H***Ph), 3.61 (1H, d, J = 14.2 Hz, C***H***H), 3.36 (1H, d, J = 14.2 Hz, CH***H***), 1.55 (3H, s, C***H$_3$***). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 178.7, 143.1, 142.3, 140.0, 139.8, 139.2, 134.9, 132.4, 128.8, 128.6, 128.3, 127.2, 124.2, 123.9, 123.6, 123.5, 123.1, 122.9, 122.1, 121.8, 109.7, 53.1, 49.6, 39.5, 35.8, 24.1. ν_{max}/cm^{-1}; 2919, 1710, 1611. **H.R.M.S.** [ES+] Found: 487.1575 (MNa^+); $C_{27}H_{26}N_4O$ requires 487.1563 (MNa^+). **M.pt:** 147-149 °C.

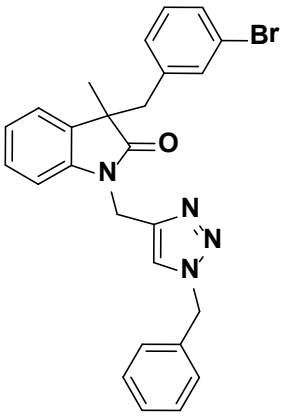
Compound 19



Prepared by general procedure Method B from **5a** (70.0 mg, 0.15 mmol) and potassium trifluoro(prop-1-enyl)borate (45.2 mg, 0.31 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 7:3) to yield compound **19** as a yellow oil (43.2 mg, 76 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.10 (9H, m, Ar***H***), 7.31 (1H, s, triazole***H***), 5.48 (1H, d, J = 14.9 Hz, NC***H***HPh), 5.42 (1H, d, J = 14.9 Hz, NCH***H***Ph), 5.12 (1H, d, J = 15.6 Hz, NC***H***H), 4.84 (1H, d, J = 15.6 Hz, NCH***H***), 4.37 (1H, s, C=C***H***), 4.24 (1H, s, C=C***H***), 2.67 (1H, d, J = 13.8 Hz, C***H***H), 2.44 (1H, d, J = 13.8 Hz, CH***H***), 1.35 (3H, s, C=C***H*****$_3$**), 1.08 (3H, s, C***H*****$_3$**). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 179.8, 143.6, 141.2, 140.1, 134.3, 133.4, 129.1, 128.8, 128.2, 128.0, 123.0, 122.3, 119.7, 114.2, 109.3, 54.3, 48.6, 45.6, 35.5, 24.9, 20.5. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 1708, 1612. **H.R.M.S.** [ES+] Found: 373.2020 (MNa^+); $C_{23}H_{25}N_4O$ requires 373.2023 (MNa^+).

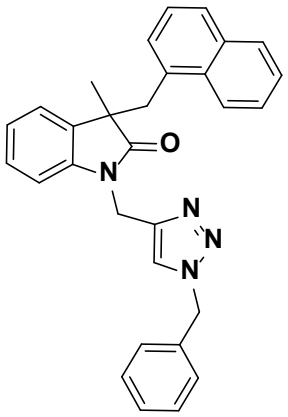
Compound 20



Prepared by general procedure Method C from **4a** (81.3 mg, 0.25 mmol) and 3-bromophenylboronic acid (100.4mg, 0.5 mmol) to yield compound **20** as a clear oil (94.1 mg,77 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.30 (3H, m, Ar***H***), 7.27-7.06 (5H, m, Ar***H***), 7.02-7.00 (2H, m, Ar***H***), 6.79 (1H, d, J = 7.5 Hz, Ar***H***), 6.68-6.23 (2H, m, Ar***H***), 6.60 (1H, s, triazole***H***), 5.45 (1H, d, J = 15.1 Hz, NC***H***HPh), 5.38 (1H, d, J = 15.1 Hz, NCH***H***Ph), 5.09 (1H, d, J = 16.0 Hz, NC***H***H), 4.61 (1H, d, J = 16.0 Hz, NCH***H***), 3.13 (1H, d, J = 12.8 Hz, C***H***H), 3.01 (1H, d, J = 12.8 Hz, CH***H***), 1.49 (3H, s, C***H*****$_3$**). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 178.9, 143.3, 141.8, 138.9, 134.8, 132.8, 130.0, 129.4, 129.2, 129.0, 128.6, 128.5, 128.2, 127.6, 123.0, 122.6, 121.9, 121.4, 109.5, 53.9, 49.9, 43.8, 35.6, 23.8. **ν_{max}/cm^{-1}**: 2685, 2521, 2410, 1709, 1611. **H.R.M.S.** [ES+] Found: 509.0943 (MNa^+). $C_{26}H_{23}BrN_4O$ requires 509.0947 (MNa^+).

Compound 21

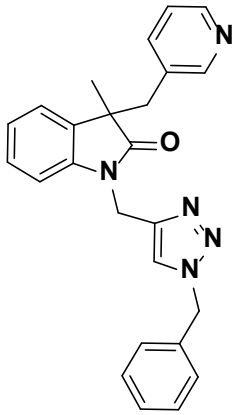


Prepared by general procedure Method C from **4a** (81.3 mg, 0.25 mmol) and 1-naphthaleneboronic acid (86.1 mg, 0.50 mmol) to yield compound **21** as an off white solid (90.6 mg, 79 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (1H, d, J = 8.6 Hz, Ar***H***), 7.64 (1H, dd, J = 8.4, 1.3 Hz, Ar***H***), 7.47-7.39 (2H, m, Ar***H***), 7.36-7.30 (4H, m, Ar***H***), 7.19 (2H, dd, J = 7.3, 0.9 Hz, Ar***H***), 7.09-7.02 (2H, m, Ar***H***), 7.00-6.95 (2H, m, Ar***H***), 6.88 (1H, dd, J = 7.3, 0.9 Hz, Ar***H***), 6.68 (1H, d, J = 7.8 Hz, Ar***H***), 5.92 (1H, s, triazole***H***), 5.32 (1H, d, J = 15.4 Hz, NC***H***HPh), 5.22 (1H, d, J = 15.4 Hz, NCH***H***Ph), 5.02 (1H, d, J = 15.8 Hz, NC***H***H), 4.52 (1H, d, J = 15.8 Hz, NCH***H***), 3.79 (1H, d, J = 13.7 Hz, C***H***H), 3.45 (1H, d, J = 13.7 Hz, CH***H***), 1.59 (3H, s, C***H*****$_3$**). **^{13}C NMR** (125

MHz, $CDCl_3$): δ 179.6, 143.3, 141.8, 134.8, 133.4, 132.9, 132.8, 132.3, 129.0, 128.6, 128.0, 127.9, 127.4, 127.1, 126.5, 125.6, 125.5, 125.0, 124.8, 123.7, 122.3, 121.7, 109.2, 53.7, 49.8, 39.8, 35.6, 23.9. **ν_{max}/cm^{-1}**; 2685, 2521, 2410, 1709, 1611. **H.R.M.S.** [ES+] Found: 481.2000 (MNa^+); $C_{30}H_{26}N_4O$ requires 481.1999 (MNa^+). **M.pt:** 73-75 °C

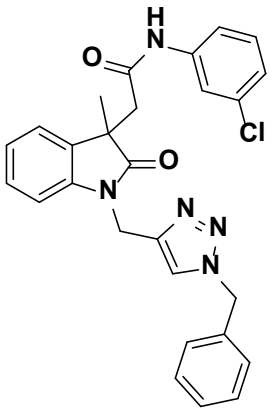
Compound 22



Prepared by general procedure Method C from **4a** (81.3 mg, 0.25 mmol) and 3-pyridinylboronic acid (61.5 mg, 0.50 mmol) to yield compound **22** as a clear oil (39.2 mg, 38 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (3H, d, J = 4.6 Hz, Ar***H***), 7.29-7.21 (4H, m, Ar***H***), 7.22-7.13 (3H, m, Ar***H***), 7.08 (1H, app.t, J = 7.3 Hz, Ar***H***), 6.96 (1H, d, J = 7.3 Hz, Ar***H***), 6.84 (1H, d, J = 7.8 Hz, Ar***H***), 6.77 (1H, s, triazole***H***), 5.46 (1H, d, J = 14.7 Hz, NC***H***HPh), 5.40 (1H, d, J = 14.7 Hz, NCH***H***Ph), 5.01 (1H, d, J = 15.6 Hz, NC***H***H), 4.62 (1H, d, J = 15.6 Hz, NCH***H***), 3.19 (1H, d, J = 13.3 Hz, C***H***H), 3.01 (1H, d, J = 13.3 Hz, CH***H***), 1.51 (3H, s, C***H$_3$***). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 178.8, 151.2, 143.0, 141.7, 136.9, 134.7, 131.9, 129.1, 128.8, 128.7, 128.4, 127.8, 123.7, 123.1, 122.9, 122.7, 122.1, 109.5, 54.0, 49.8, 41.5, 35.5, 23.5. **ν_{max}/cm^{-1}**; 2627, 2410, 1713, 1533. **H.R.M.S.** [ES+] Found: 410.1982 (MNa^+). $C_{25}H_{24}N_5O$ requires 410.1975 (MNa^+).

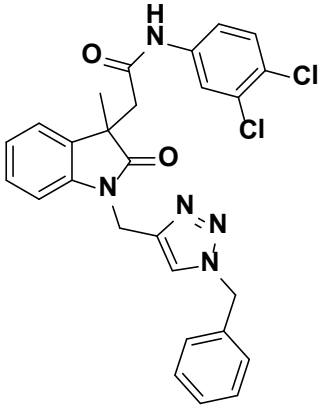
Compound 23



Prepared by general procedure Method D from **5a** (100mg, 0.22 mmol) and *m*-chloroaniline (42.24mg, 0.33 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 1:4) to yield compound **23** as a colourless gel (64.7 mg, 61 % yield)

^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (1H, s, N***H***), 7.6 (1H, s, Ar***H***), 7.56 (1H, s, triazole***H***), 7.30-7.29 (3H, m, Ar***H***), 7.24-7.12 (6H, m, Ar***H***), 7.07 (1H, t , J = 7.6 Hz, Ar***H***), 7.02-7.01 (1H, m, Ar***H***), 6.99 (1H, d, J = 7.8 Hz, Ar***H***), 5.42 (1H, d, J = 14.7 Hz, NC***H***HPh), 5.32 (1H, d, J = 14.7 Hz, NCH***H***Ph) , 5.26 (1H, d, J = 15.6 Hz, NCH***H***), 4.90 (1H, d, J = 15.8 Hz, NC***H***H), 3.04(1H, d, J = 15.8 Hz, C***H***HCO), 2.88 (1H, d, J = 15.4 Hz, CH***H***CO), 1.48 (3H, s, C***H$_3$***). **^{13}C NMR** (75.5 MHz, $CDCl_3$): 180.3, 167.3, 143.0, 141.4, 139.0, 134.6, 134.5, 133.0, 129.9, 129.0, 128.6, 128.5, 127.9, 124.2, 123.2, 122.7, 122.3, 119.9, 117.7, 109.9, 54.2, 46.0, 44.9, 36.0, 24.0. **ν_{max}/cm^{-1}**; 2984, 1702, 1613, 1595, 1469. **H.R.M.S.** [ES+] Found: 486.169836 (MH^+). $C_{27}H_{25}ClN_5O_2$ requires 486.169129 (MH^+).

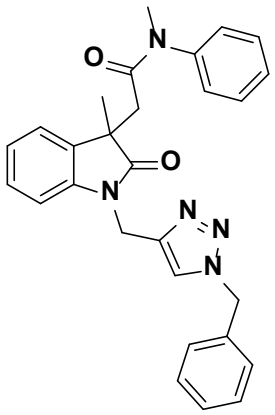
Compound 24



Prepared by general procedure Method D from **5a** (114mg, 0.25 mmol) and 3,4-dichloroaniline (60mg, 0.375 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 1:4) to yield compound **24** as a colourless solid (77 mg, 60 % yield)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62(1H, s, N***H***), 7.71 (1H, s, Ar***H***), 7.51 (1H, s, triazole***H***), 7.32-7.31 (3H, m, Ar***H***), 7.28 (1H, d, J = 8.7 Hz, Ar***H***), 7.24 (2H, d, J = 7.3, Ar***H***), 7.18-7.15 (3H, m, Ar***H***), 7.09 (1H, t, J= 7.6 Hz, Ar***H***), 7.05 (1H, d, J = 7.8 Hz, Ar***H***), 5.44 (1H, d, J = 14.9 Hz, NC***H***HPh), 5.36 (1H, d, J = 14.9 Hz, NCH***H***Ph) , 5.20 (1H, d, J = 16.0 Hz, NCH***H***), 4.93 (1H, d, J = 16.0 Hz, NC***H***H), 2.99 (1H, d, J = 15.4 Hz, C***H***HCO), 2.84 (1H, d, J = 15.4 Hz, CH***H***CO), 1.47 (3H, s, C***H$_3$***). **^{13}C NMR** (75.5 MHz, $CDCl_3$): 180.5, 167.5, 142.9, 141.3, 137.3, 134.5, 133.0, 132.6, 130.4, 129.1, 128.7, 128.5, 127.8, 127.3, 123.4, 122.6, 122.3, 121.5, 119.0, 109.9, 54.2, 46.0, 44.6, 35.9, 23.8. **ν_{max}/cm^{-1}**; 2986, 1696, 1613, 1592, 1469. **H.R.M.S.** [ES+] Found:: 520.130352 (MH^+). $C_{27}H_{25}ClN_5O_2$ requires 520.130157 (MH^+). **M.pt:** 63-65 °C.

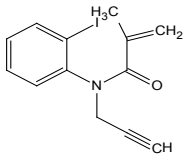
Compound 25



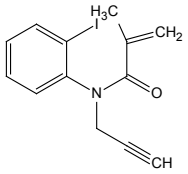
Prepared by general procedure Method D from **5a** (100 mg, 0.31 mmol) and N-methylaniline (40mg, 0.372 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 3:7) to yield compound **25** as a colourless gel (50.8 mg, 50 % yield)

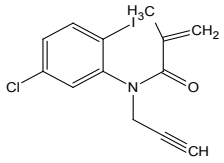
^{1}H NMR (500 MHz, $CDCl_3$): 7.97 (1H, s, triazole***H***), 7.45 (1H, D, J = 7.3 Hz, Ar***H***), 7.40-7.37 (1H, m, Ar***H***), 7.29-7.28 (3H, m, Ar***H***), 7.21-7.13 (6H, m, Ar***H***), 7.01-6.98 (2H, m, Ar***H***), 7.82 (1H, d, J = 7.8 Hz, Ar***H***), 5.52 (1H, d, J = 15.1 Hz, NC***H***HPh), , 5.38 (2H, d, J = 16.5 Hz,

NC***H***HPh, NC***H***H), 4.88 (1H, d, J = 16.0 Hz, NCH***H***) 2.96, (3H, s, N***CH₃***), 2.85(1H, d, J = 16.8 Hz, C***H***HCO), 2.68 (1H, d, J = 16.8 Hz, CH***H***CO), 1.16 (3H, s, C***H₃***). **^{13}C NMR** (75.5 MHz, $CDCl_3$): 180.5, 168.7, 148.9, 148.9, 143.7, 142.4, 134.8, 133.9, 130.0, 128.9, 128.5, 128.0, 127.7, 127.4, 123.6, 123.4, 123.3, 122.2, 121.2, 109.4, 51.2, 45.9, 41.6, 37.1, 36.2, 25.2. **ν_{max}/cm^{-1}**; 3135, 2928, 1715, 1655, 1613, 1467. **H.R.M.S.** [ES+] Found: 466.2257 (MH^+); $C_{30}H_{25}ClN_4O$ requires 466.238 (MH^+).



4





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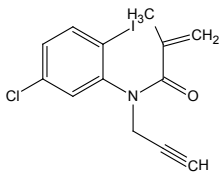

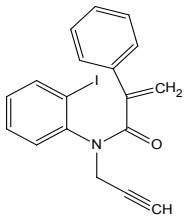

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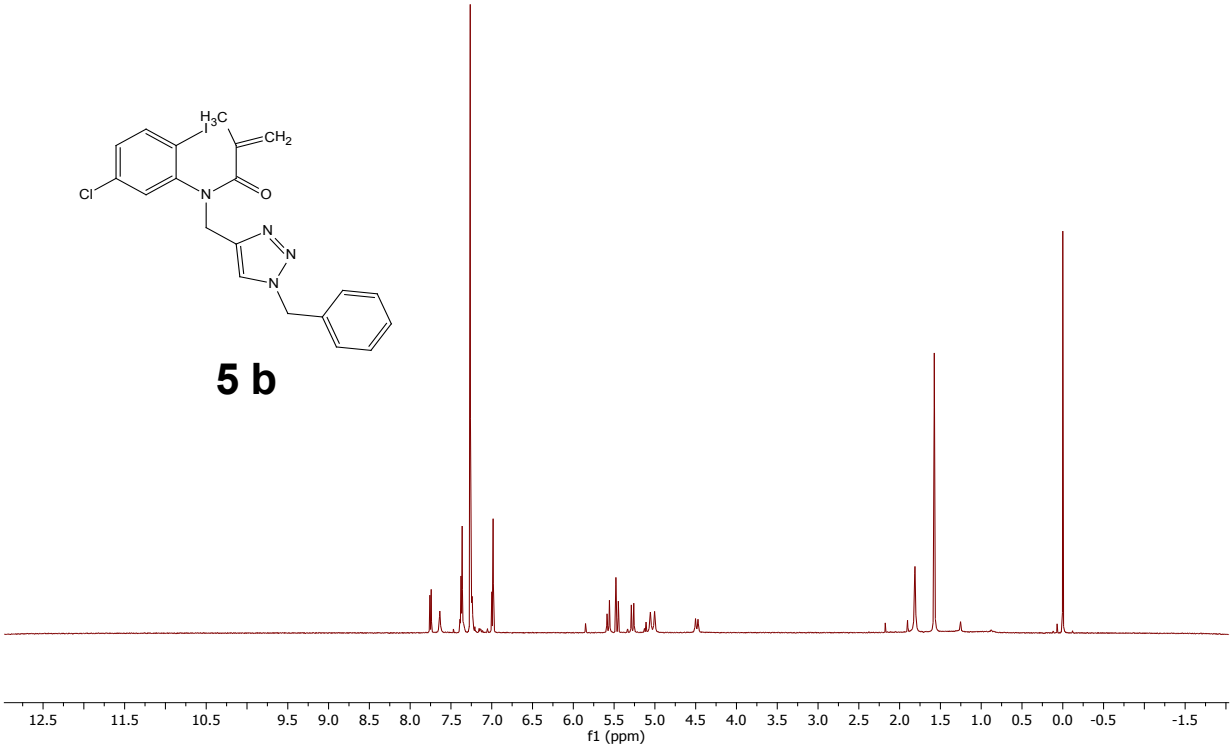
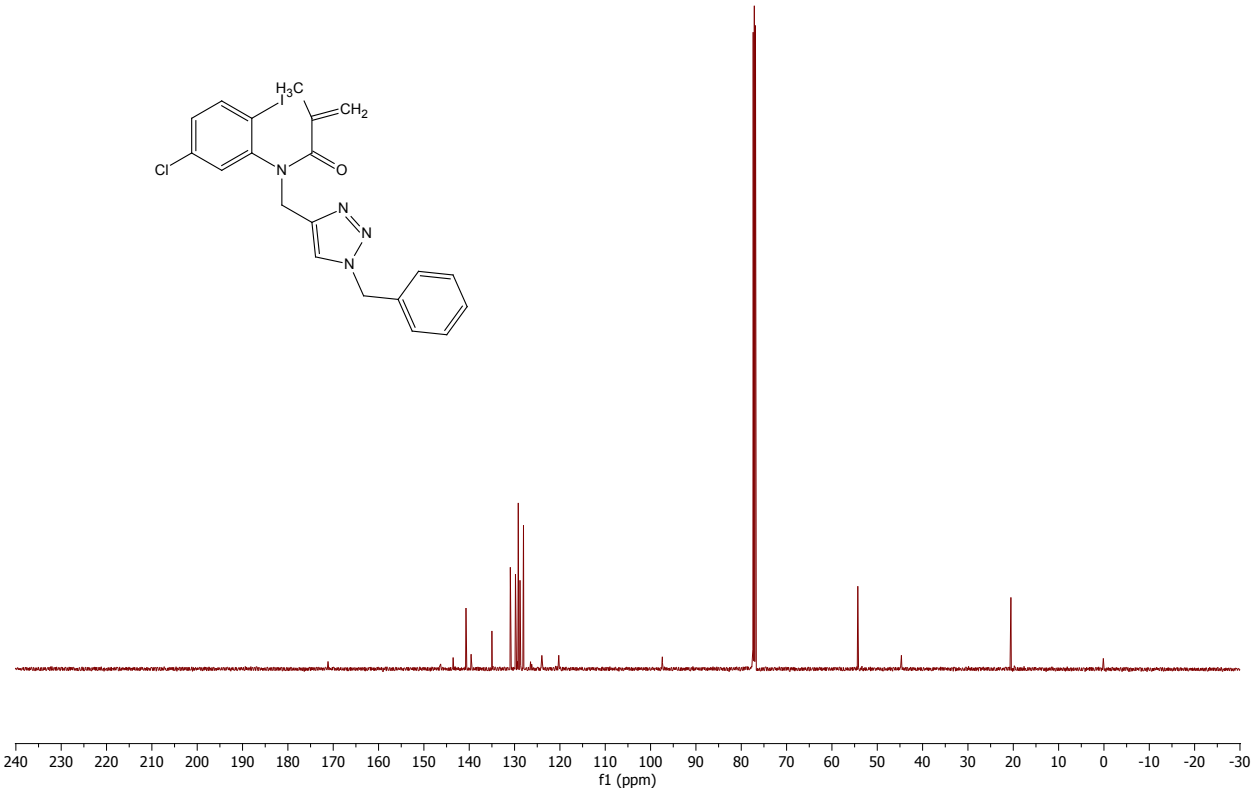
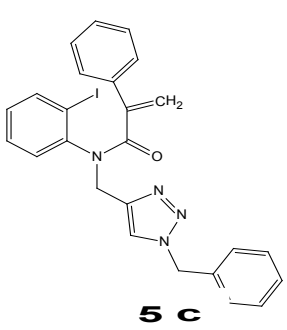


5 b





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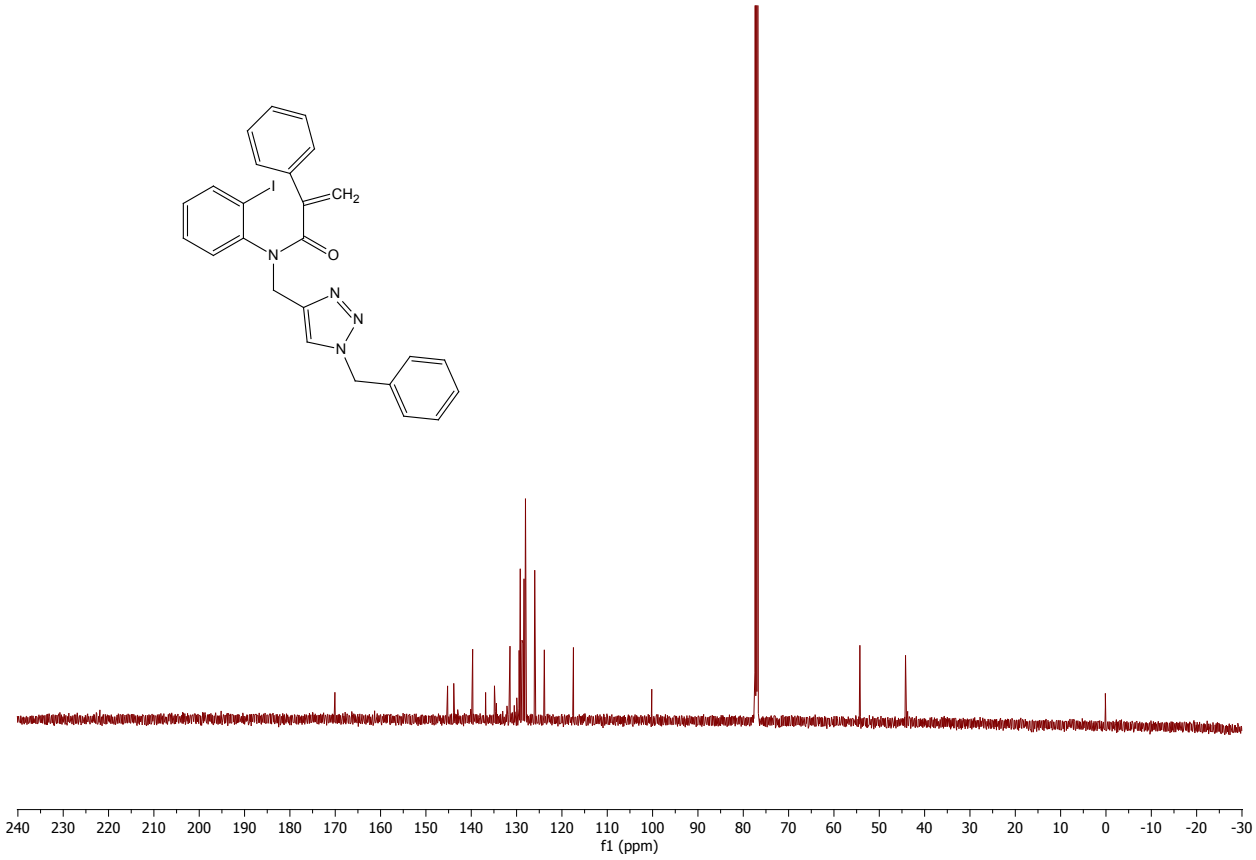

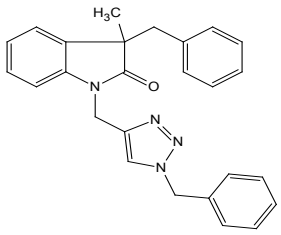

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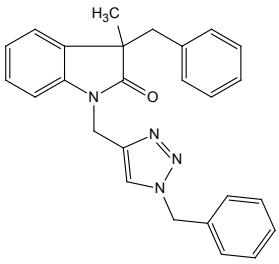

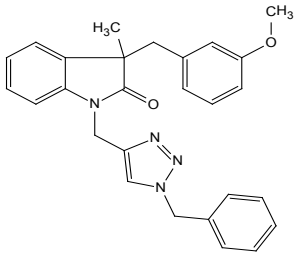

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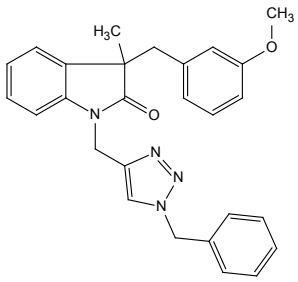

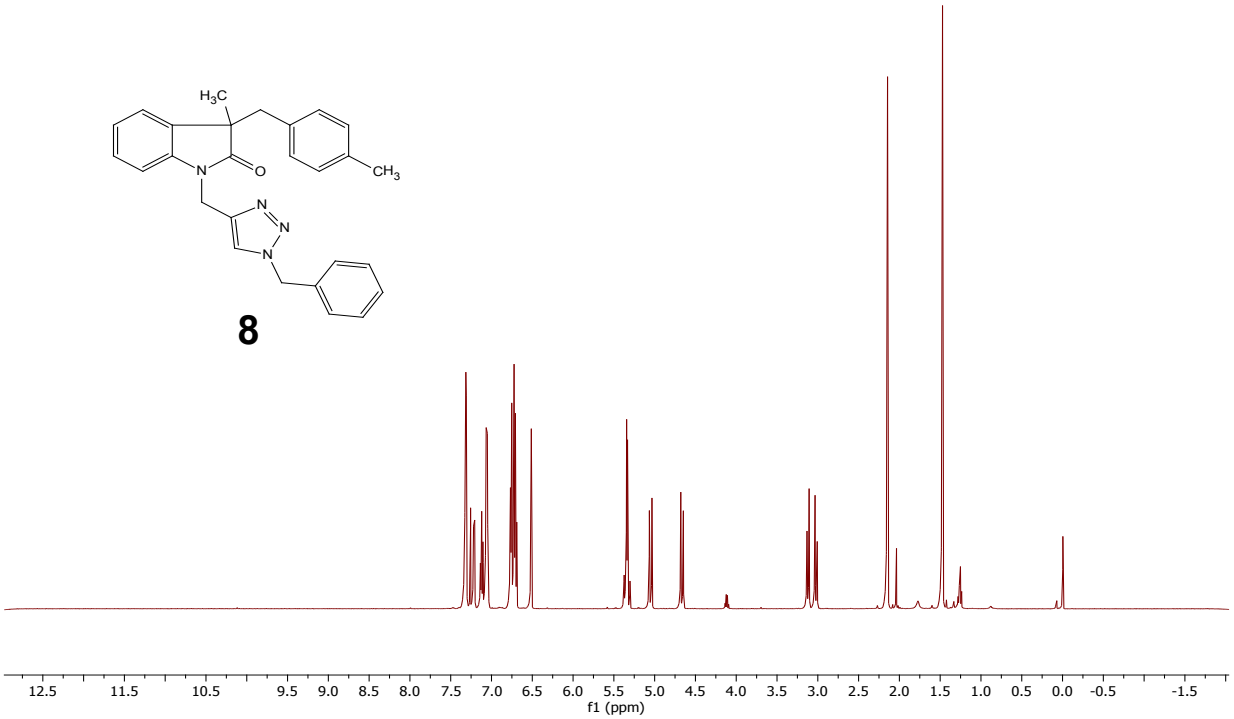

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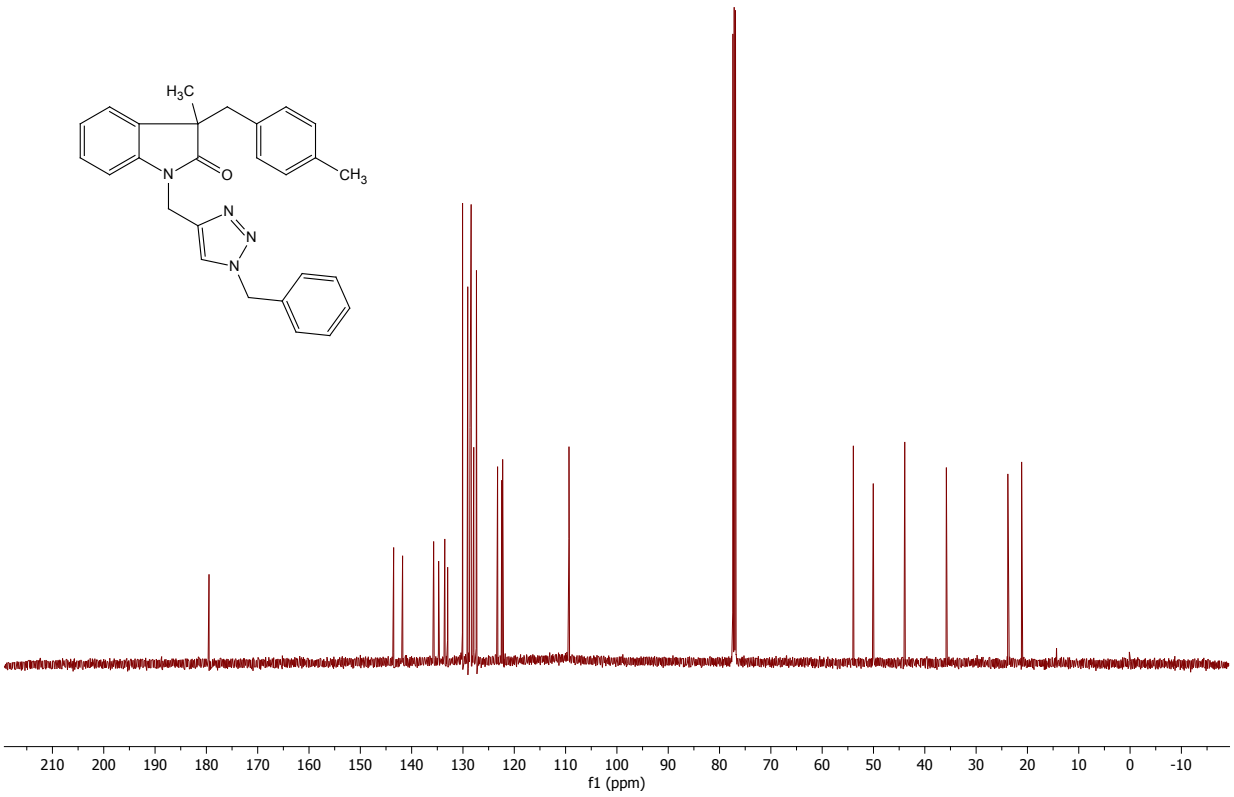

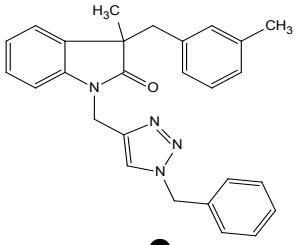

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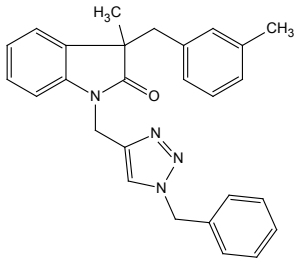

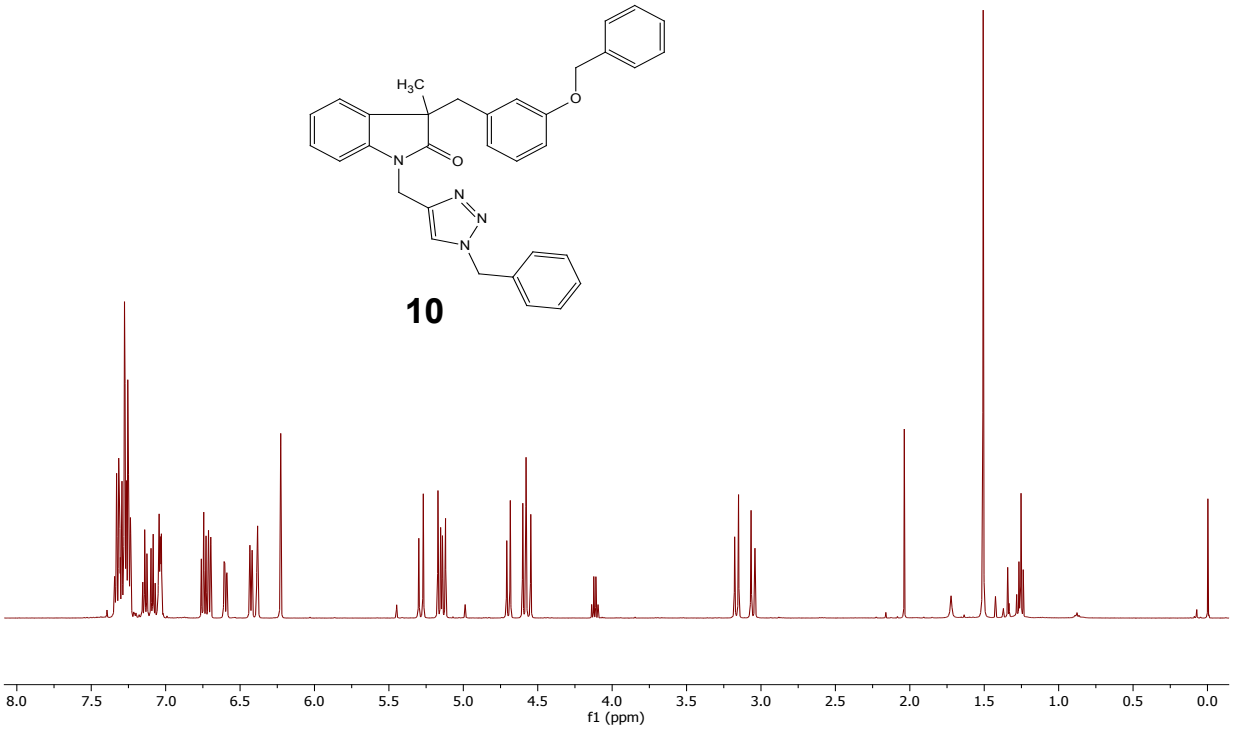

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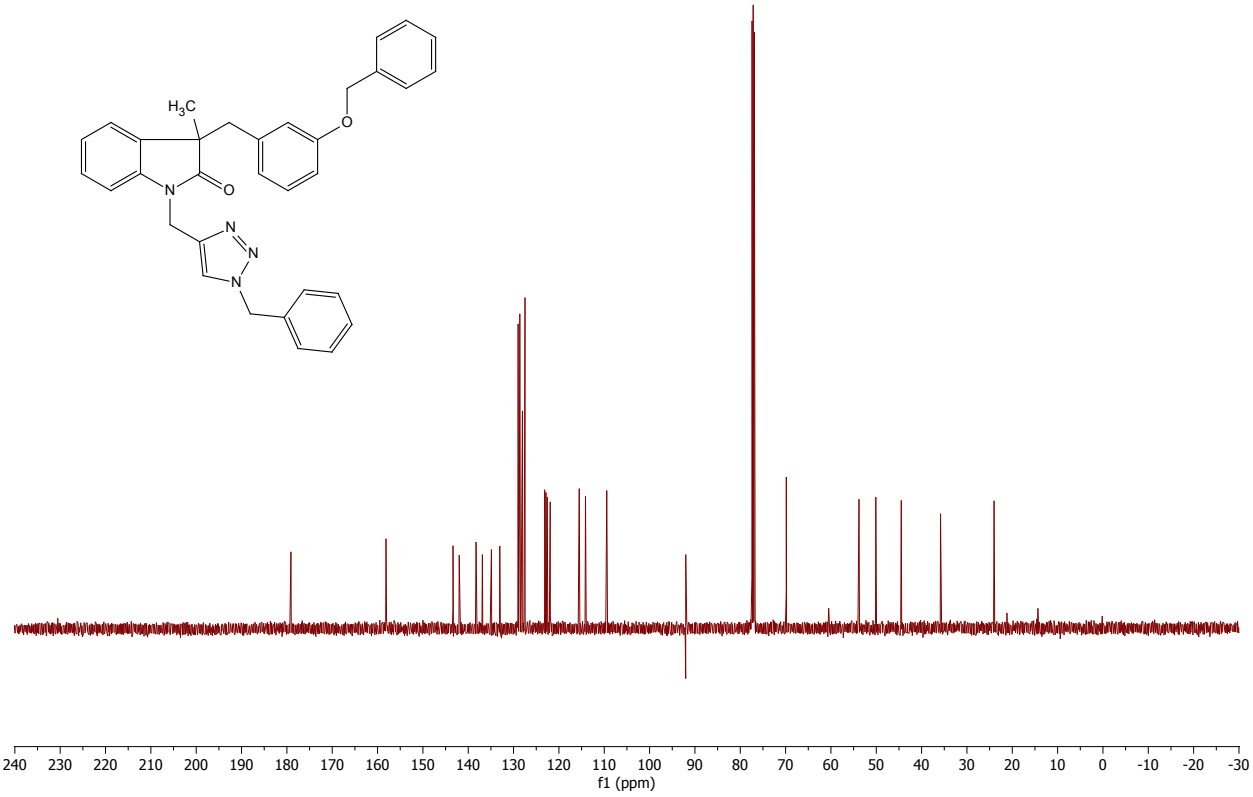
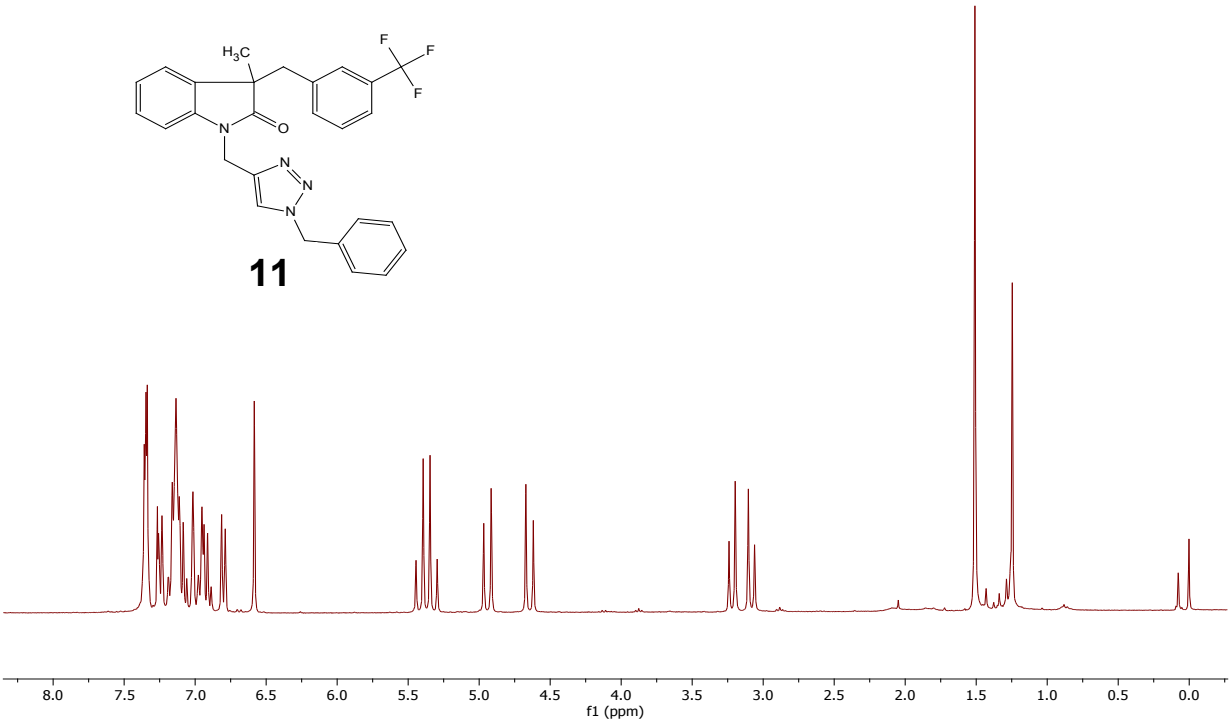
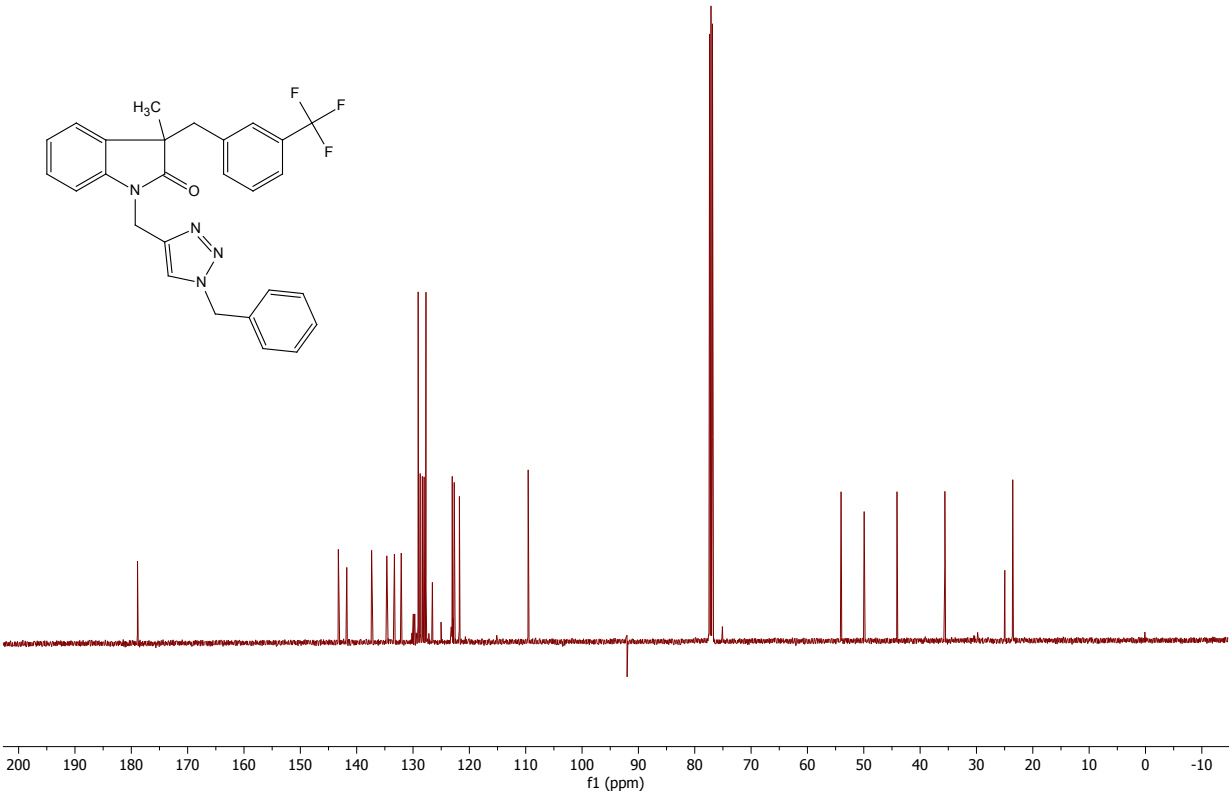
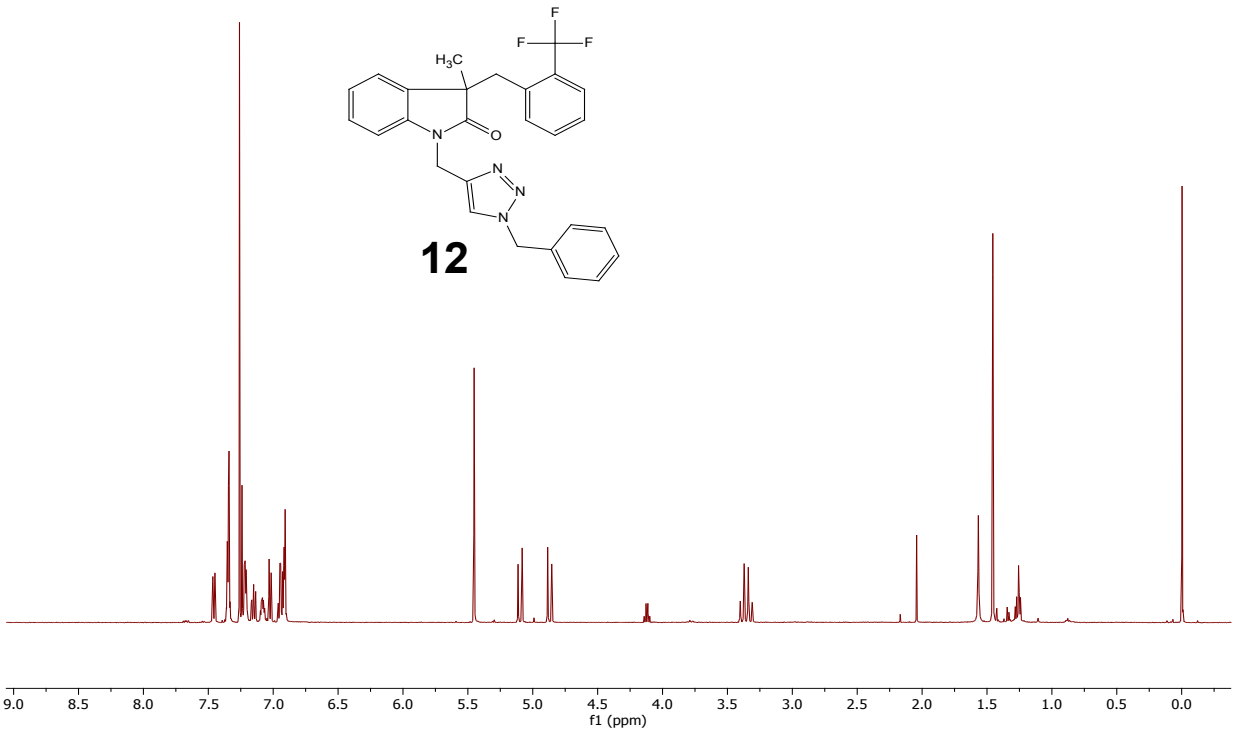
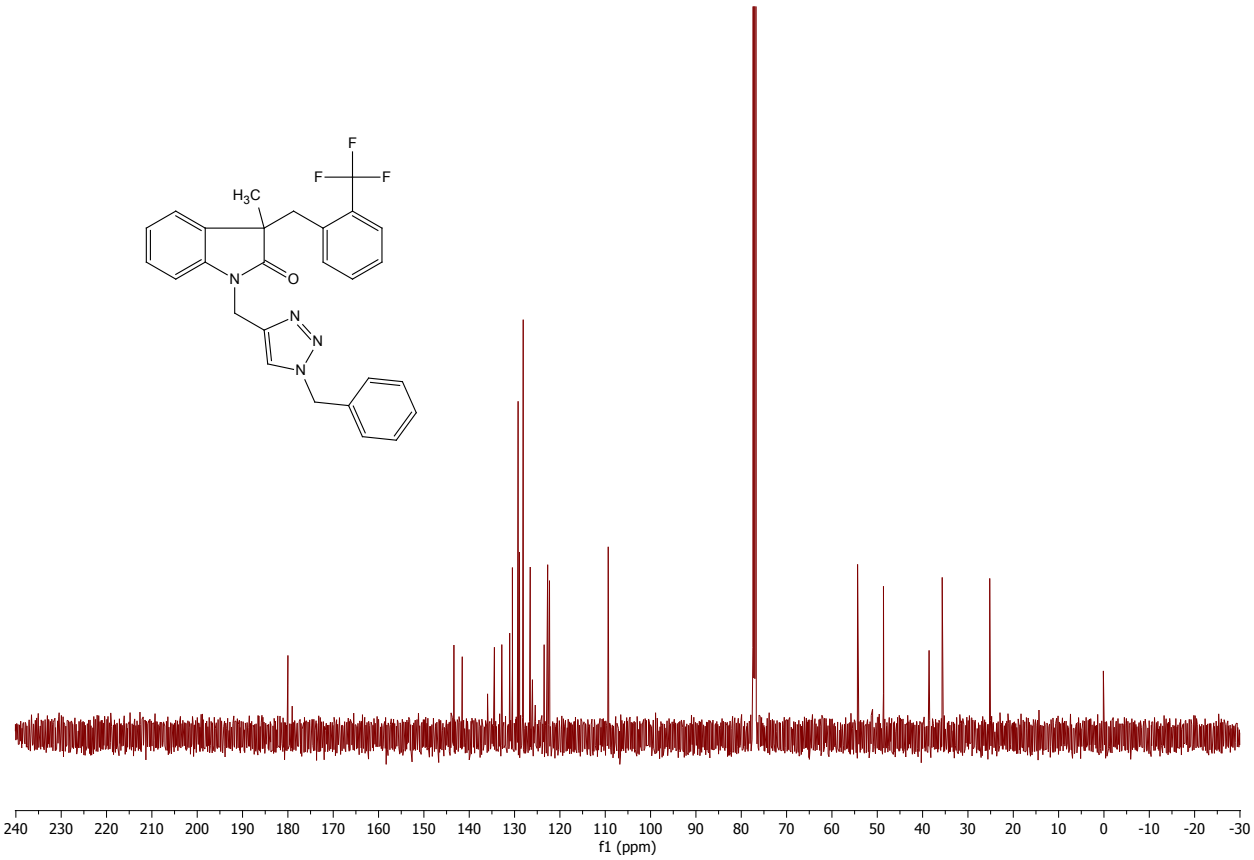


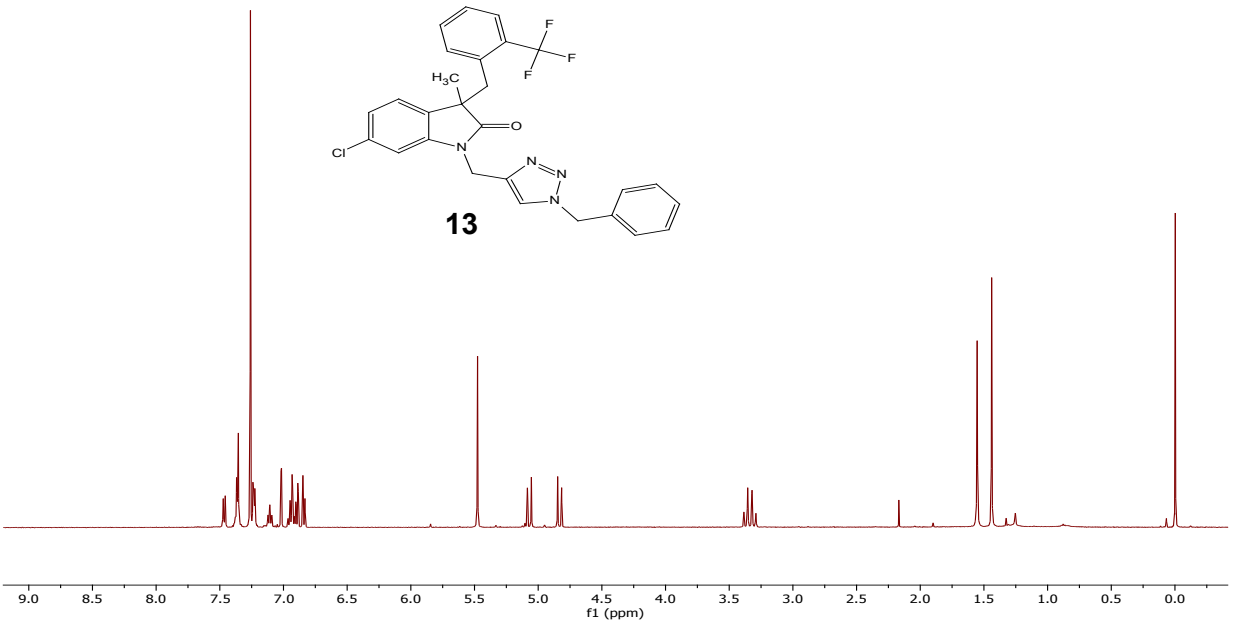


11









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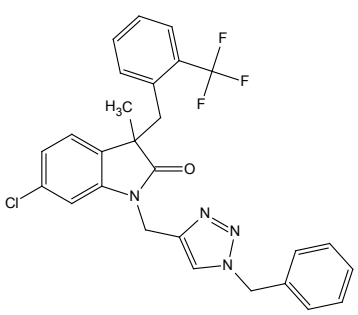
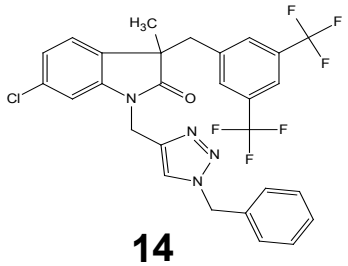
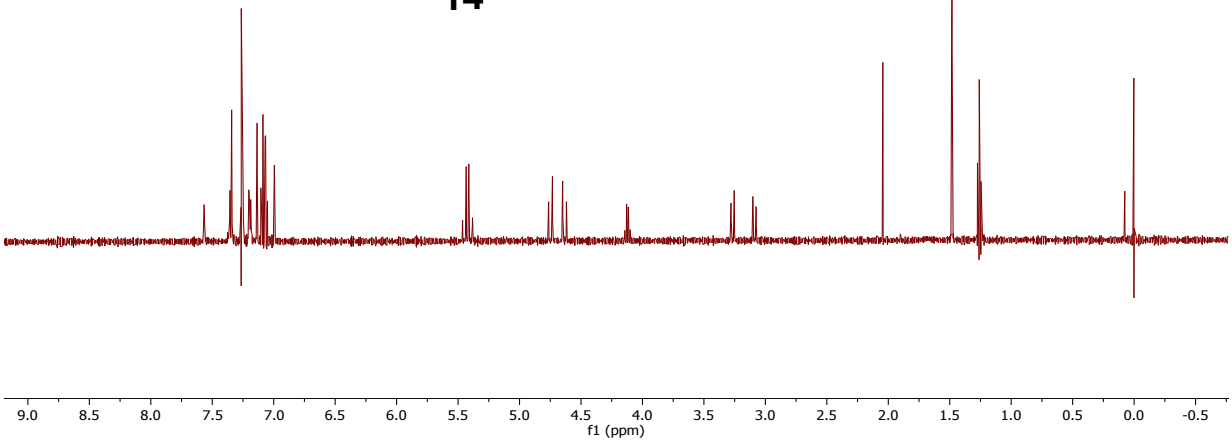
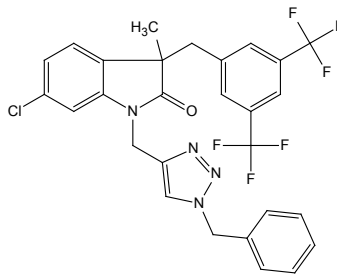
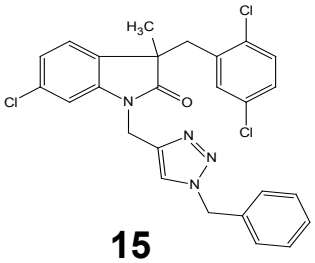




14







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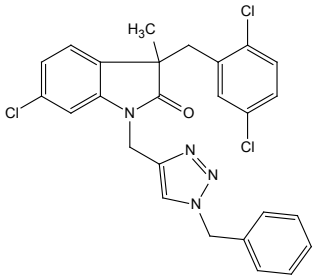

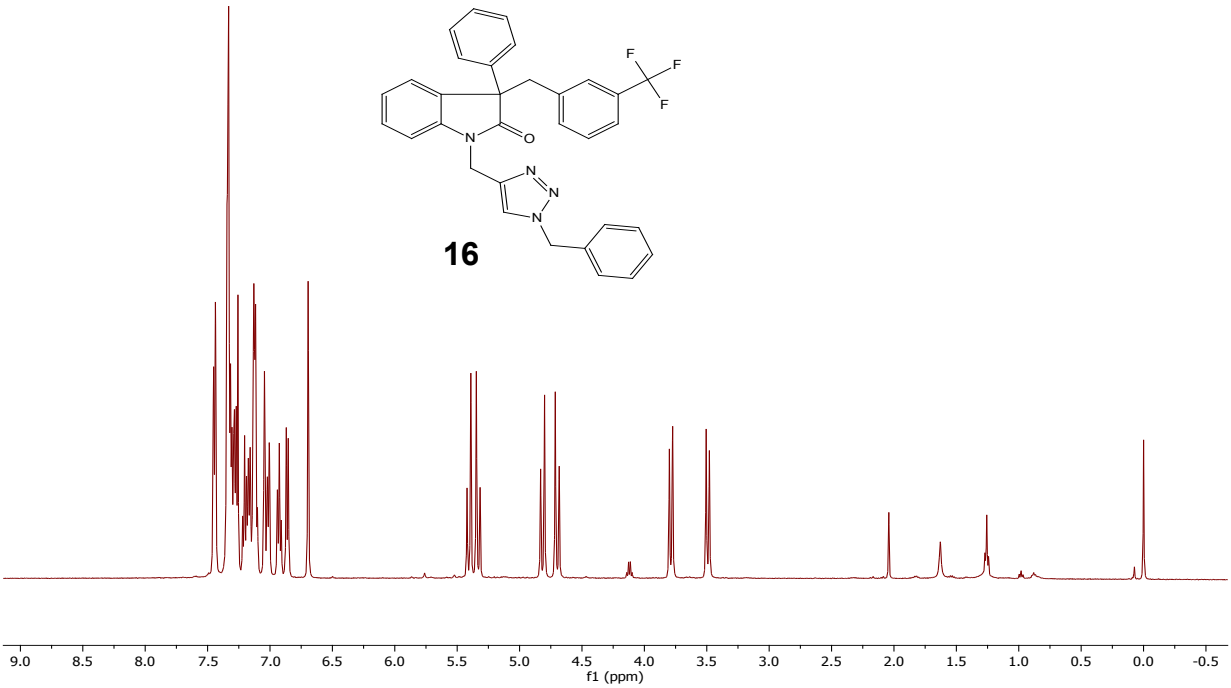

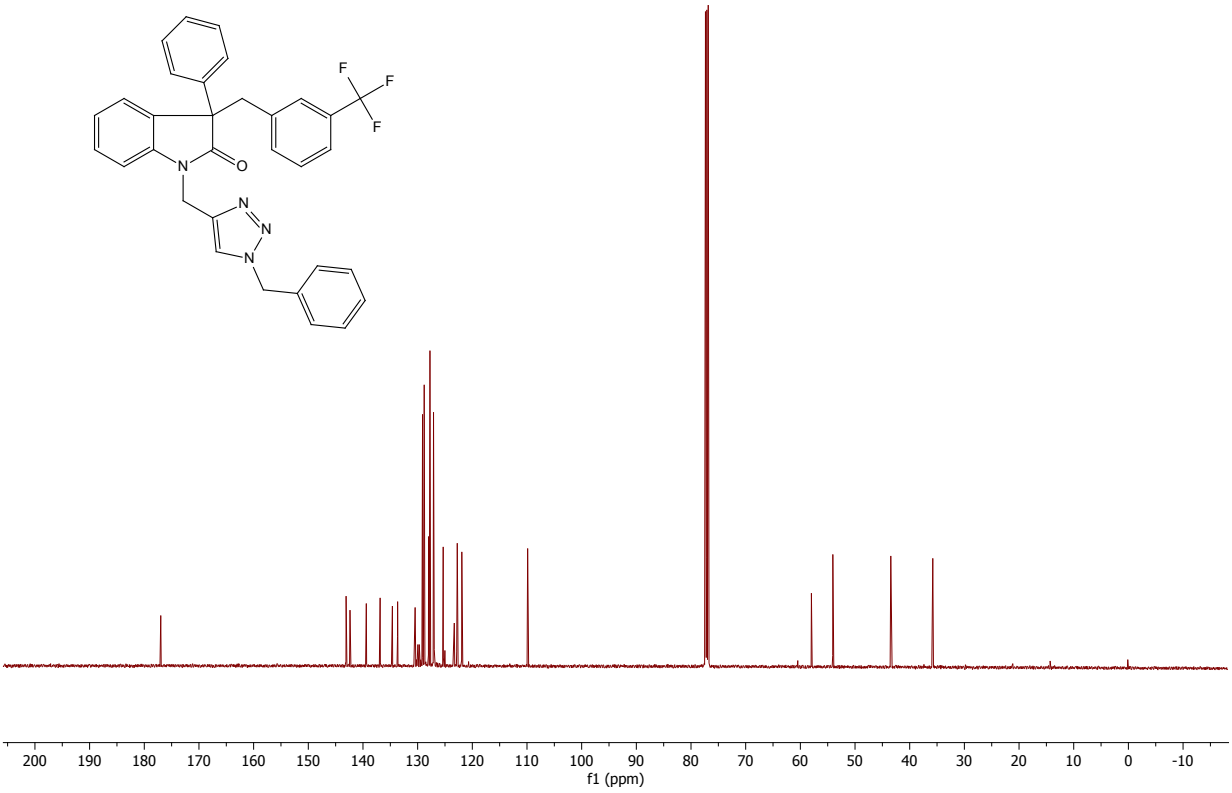

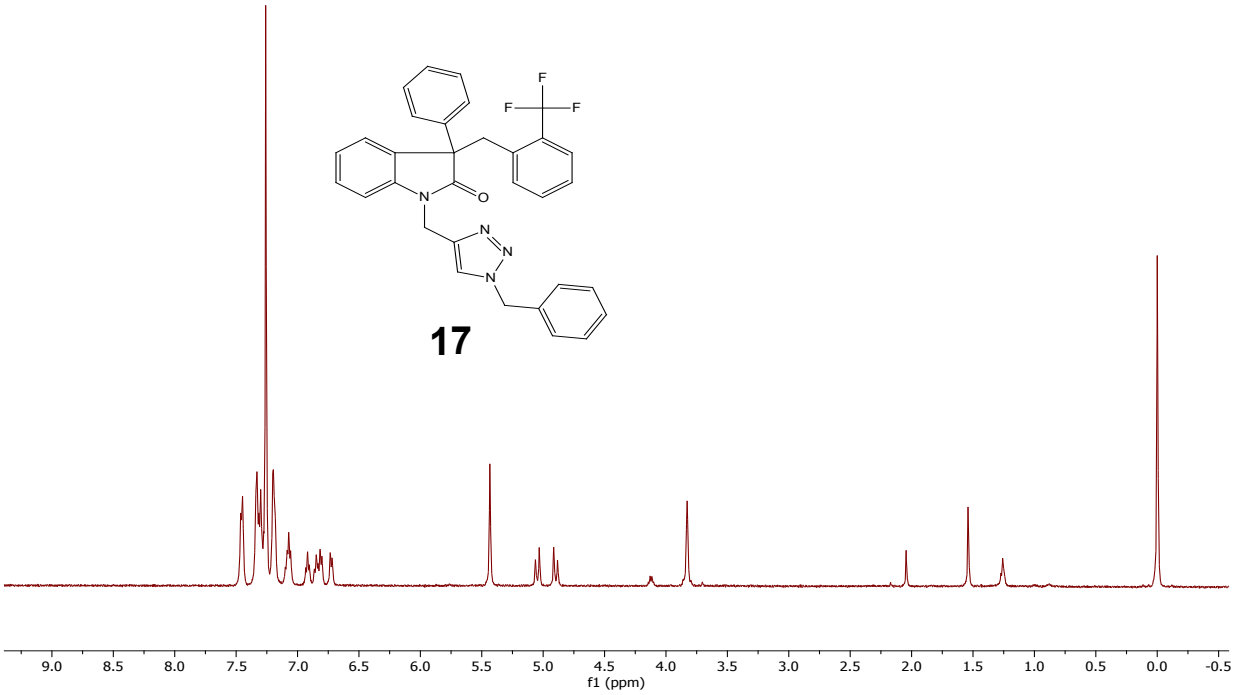

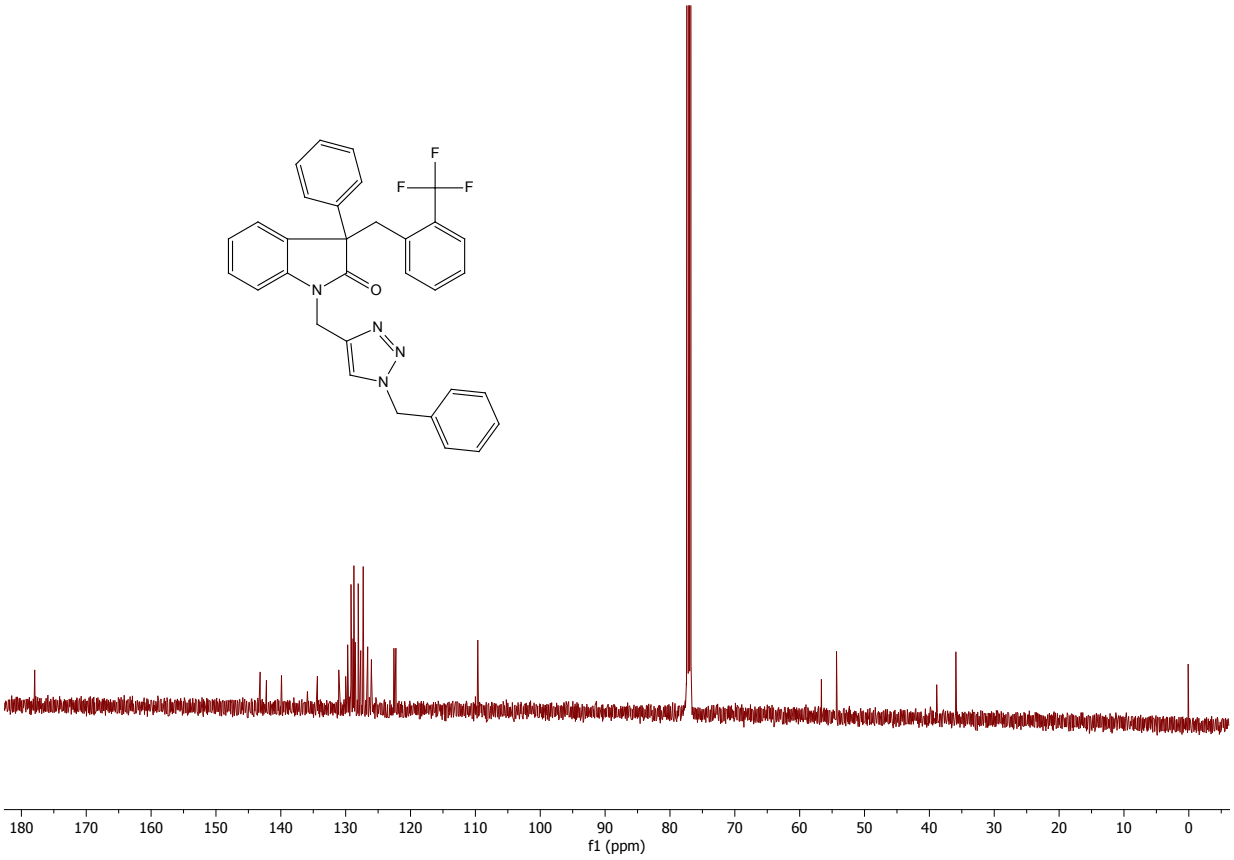

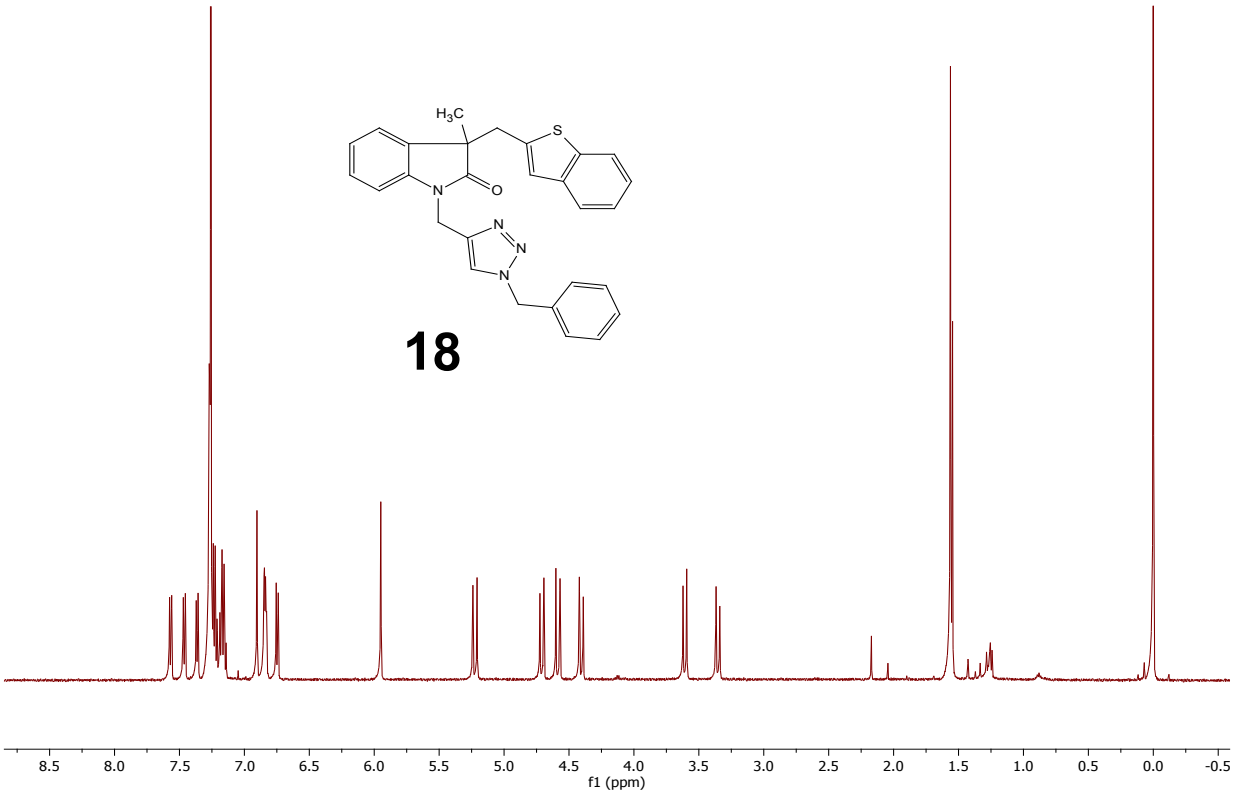

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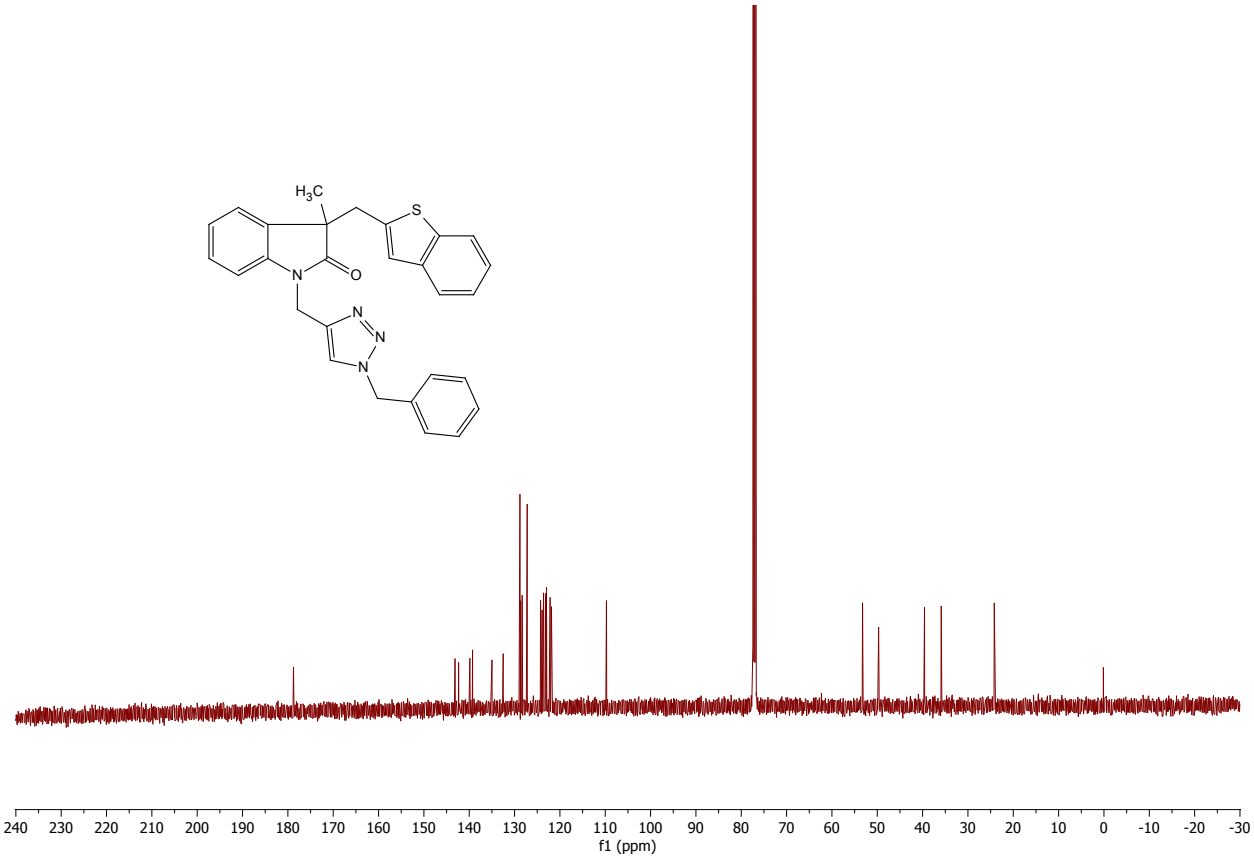

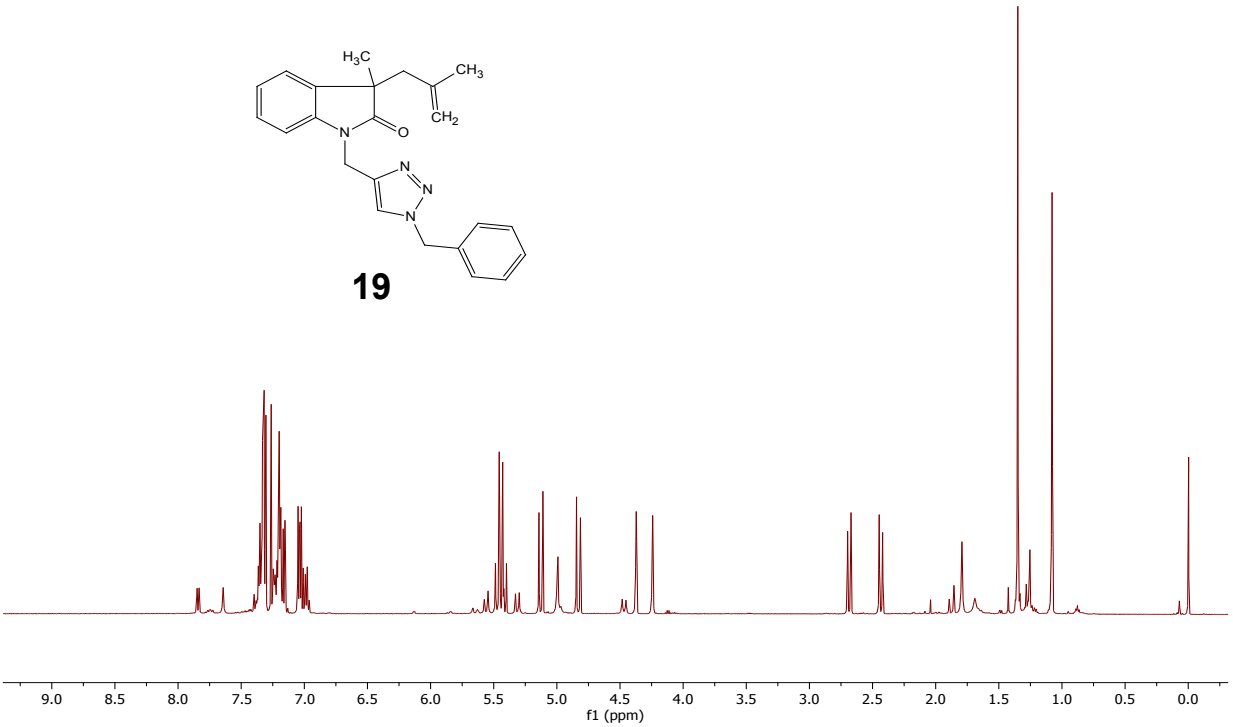

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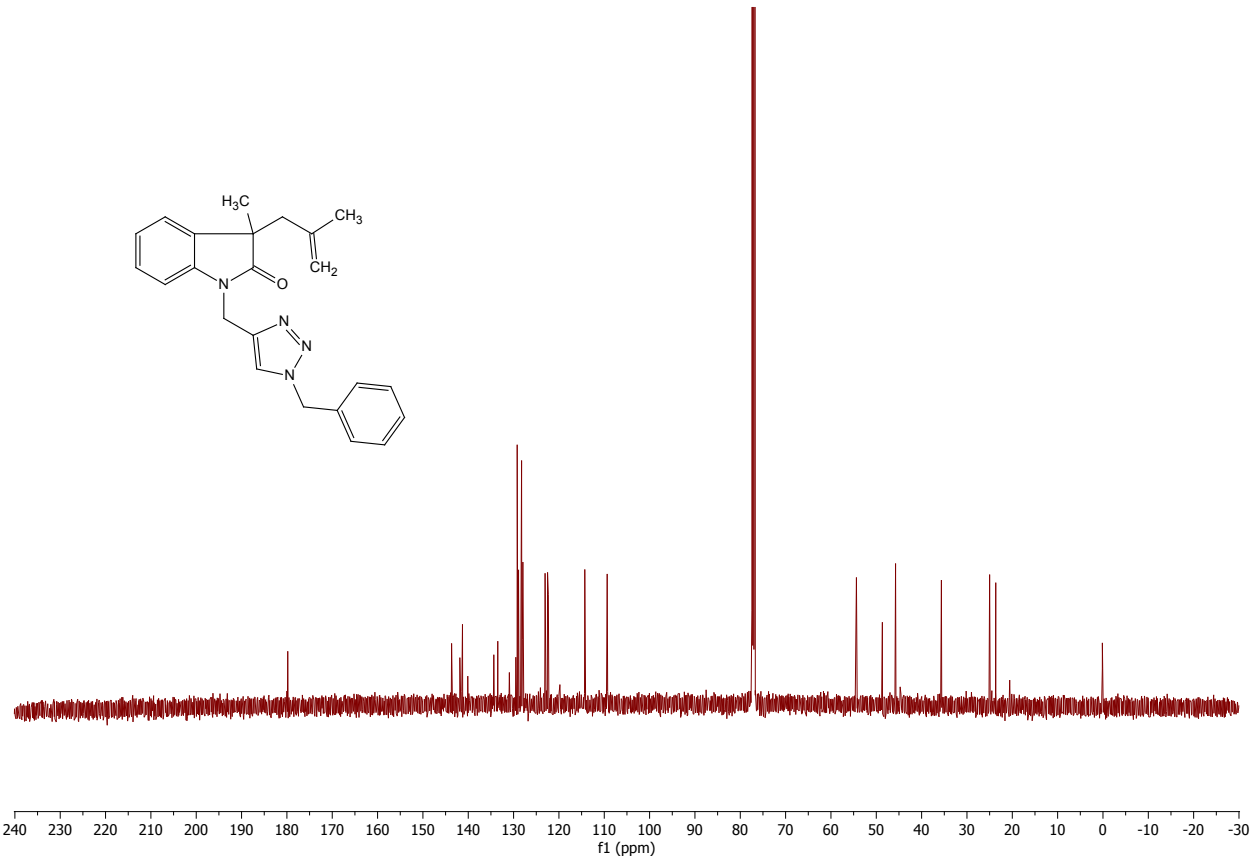

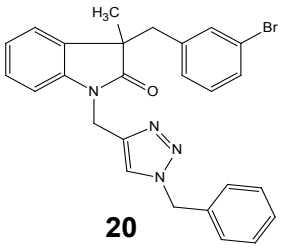

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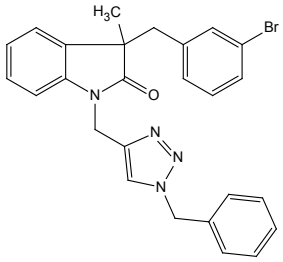

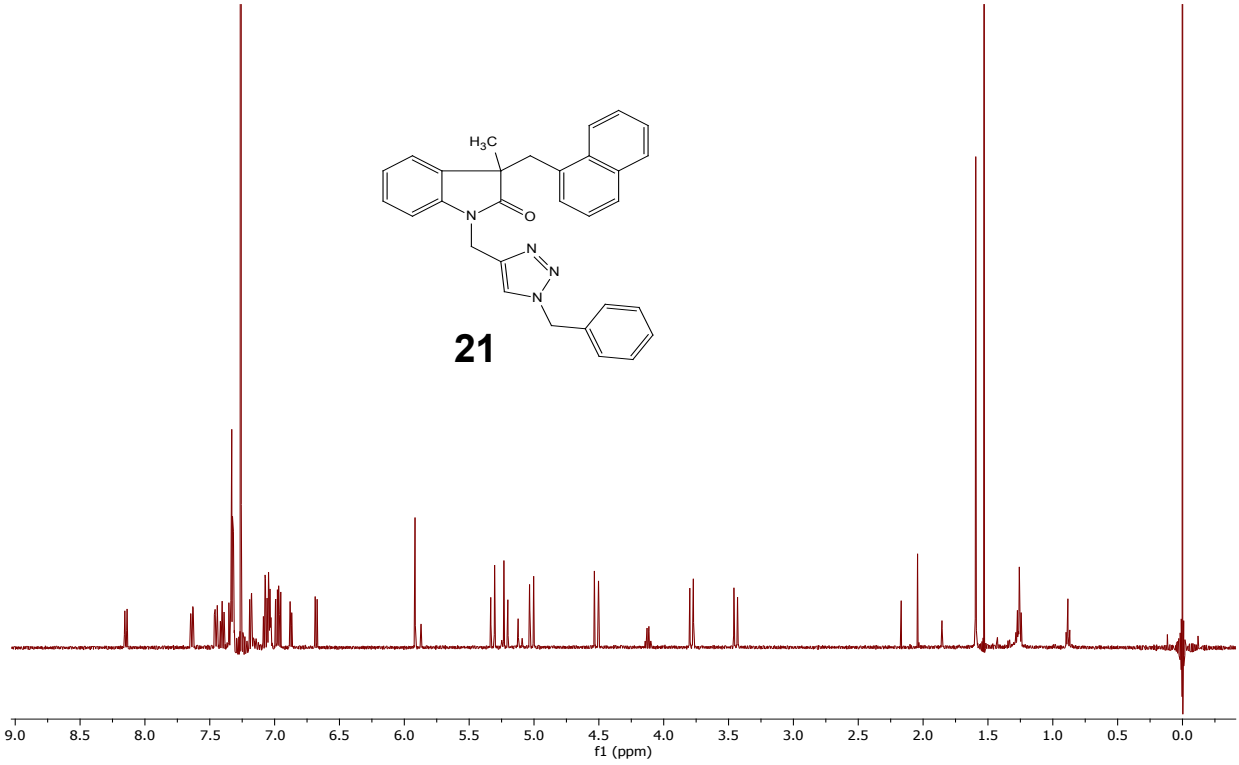

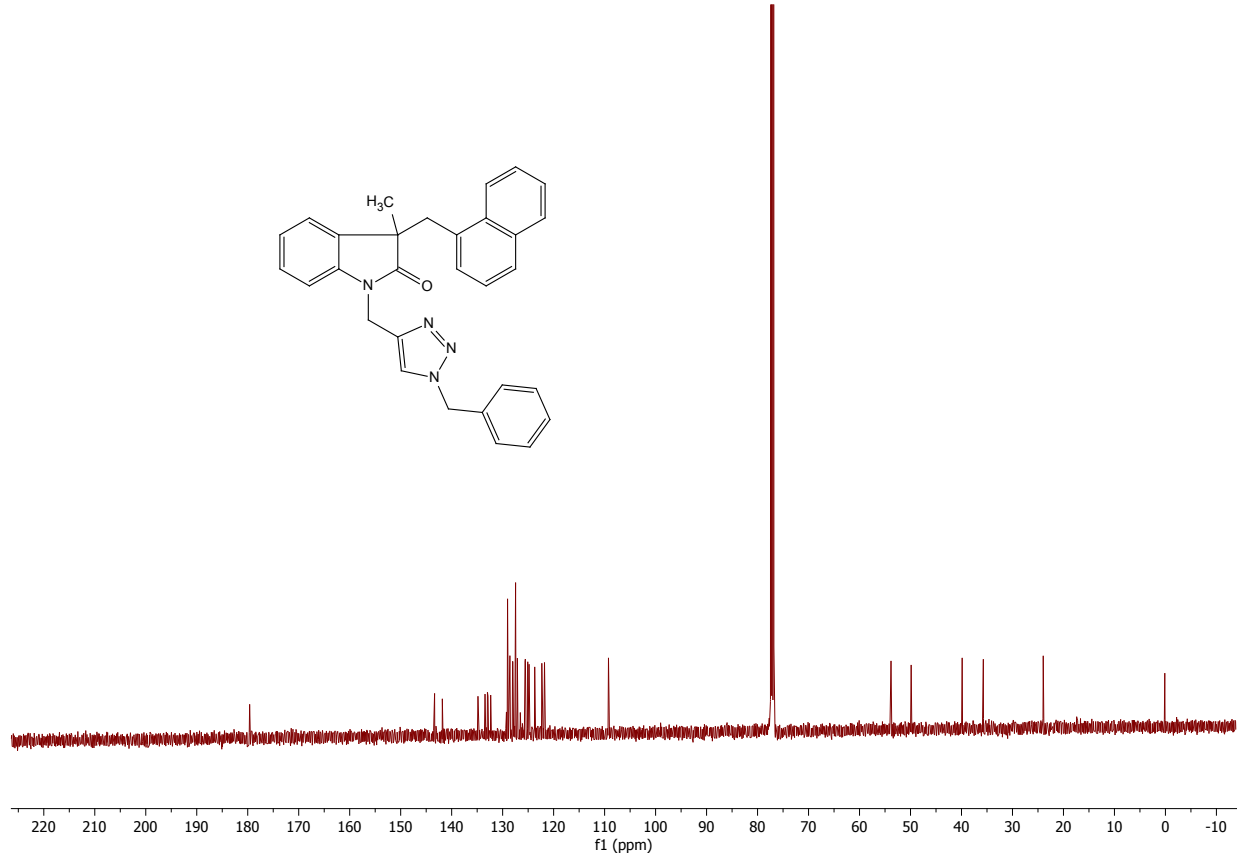

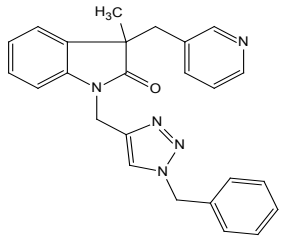

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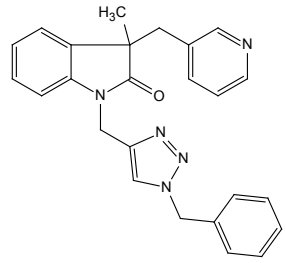

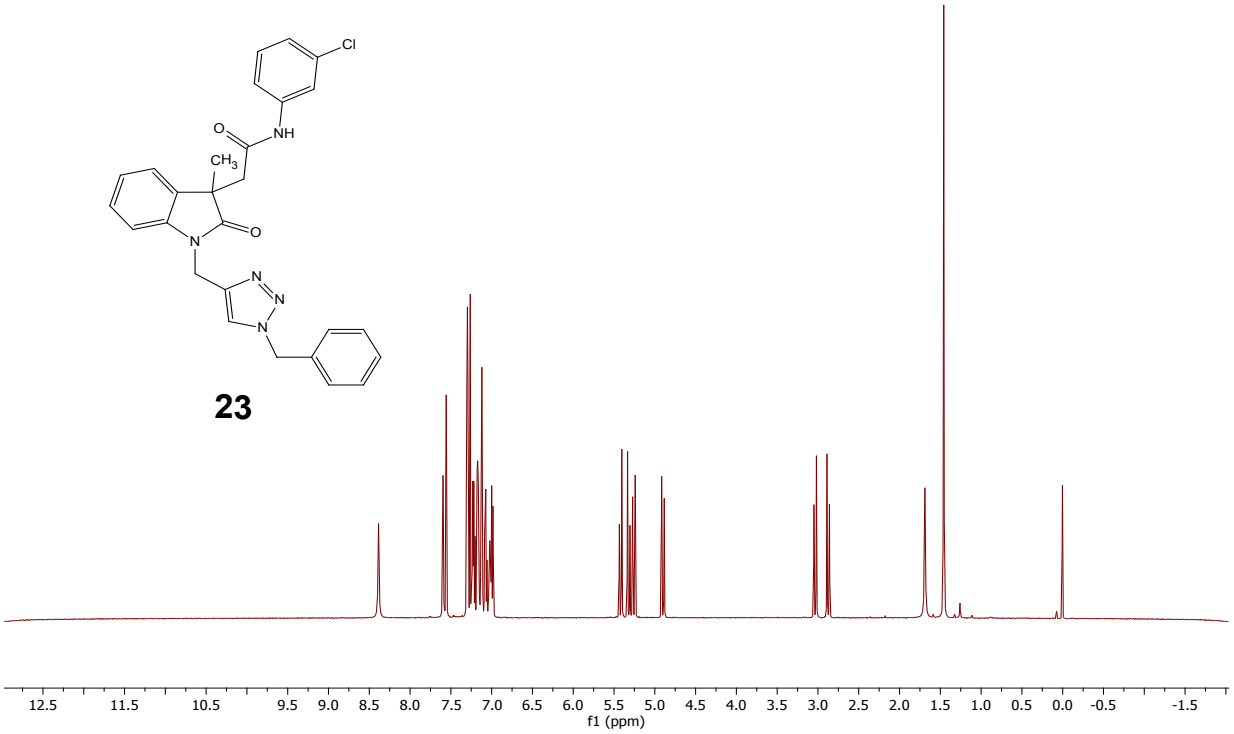

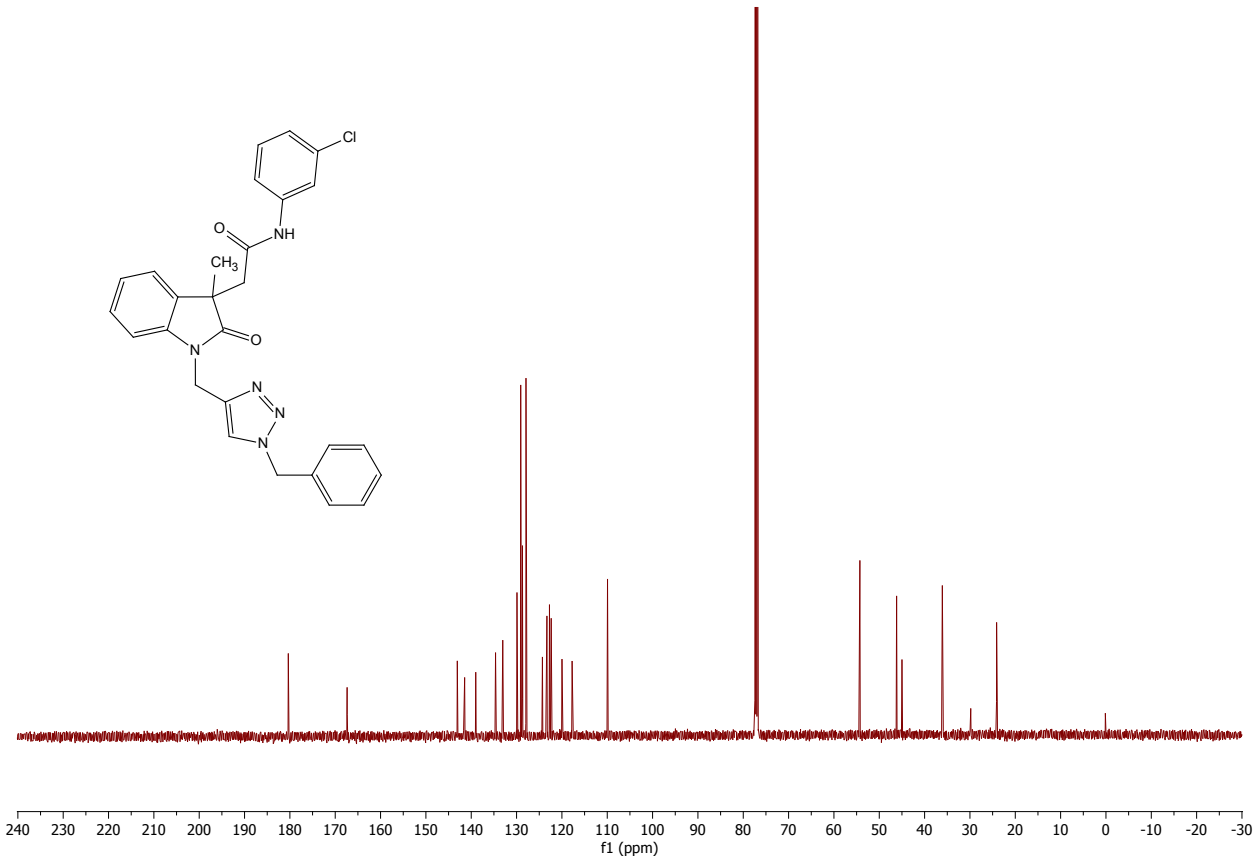

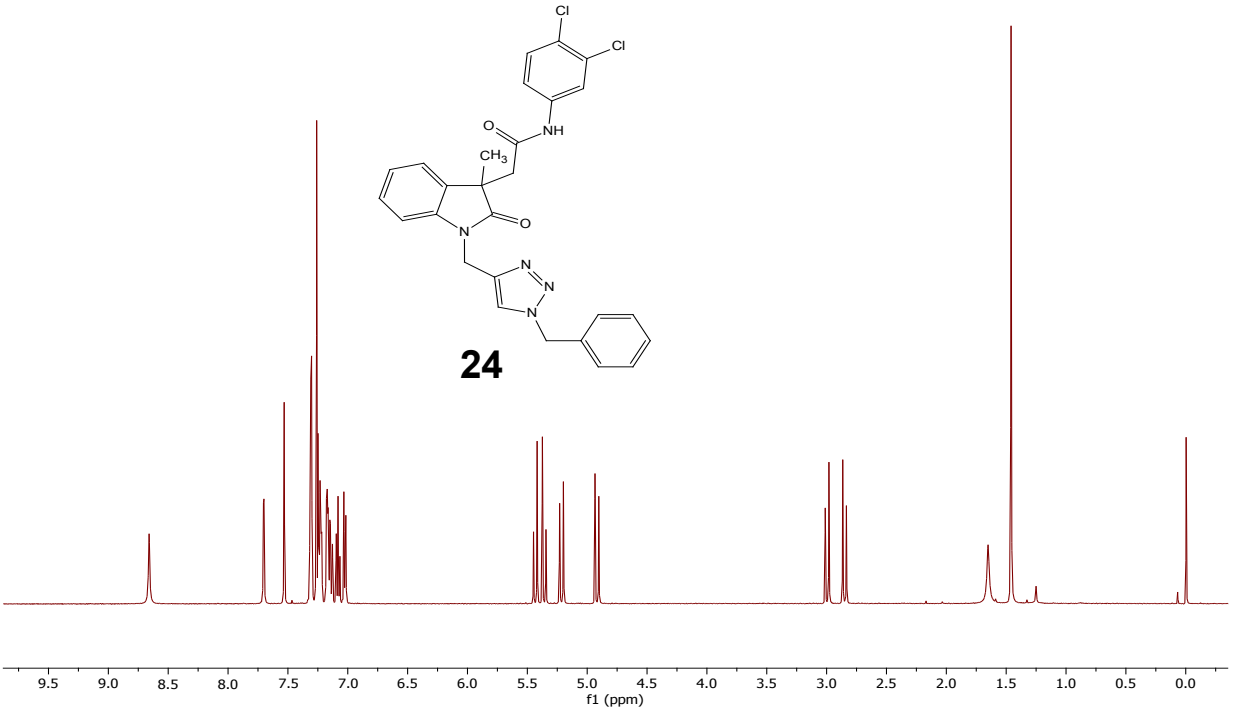

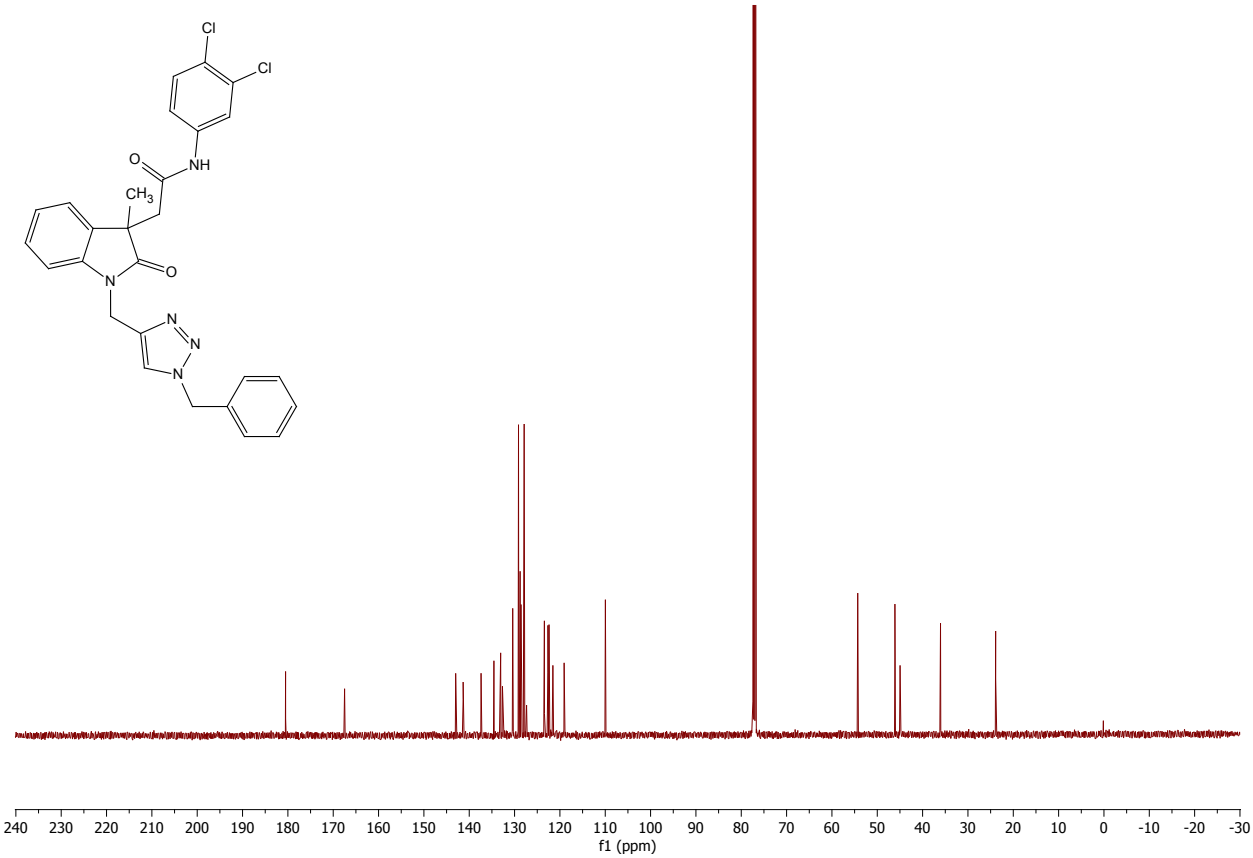

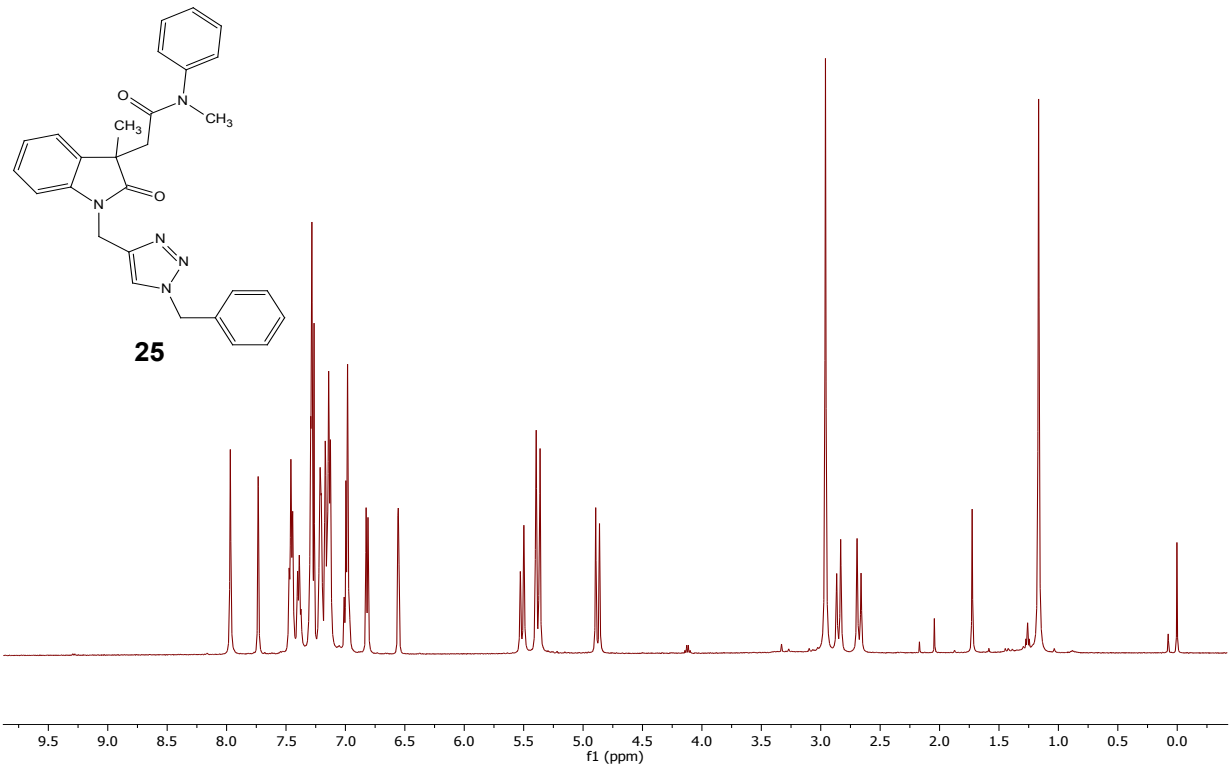

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