Electronic Supplementary Material (ESI) for ChemComm.

Reductive Cyclizations of Amidines involving Aminal Radicals

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General experimental

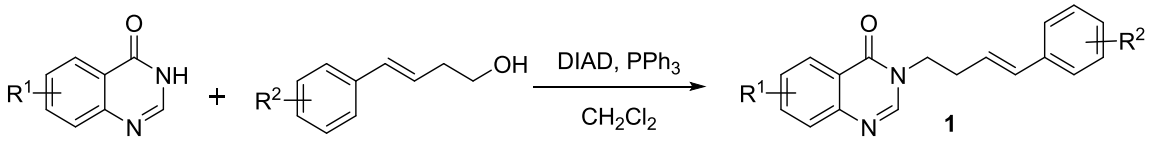
All experiments were performed under nitrogen atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All other chemicals were purchased at the highest commercial grade and used as received. ^{1}H NMR spectra were recorded on NMR spectrometers at 400 MHz and 500 MHz and ^{13}C NMR at 100 MHz and 126 MHz. ^{19}F NMR spectra were obtained at 376 MHz. ^{1}H NMR chemical shifts (δ_H) and ^{13}C NMR chemical shifts (δ_C) are quoted in parts per million (ppm) downfield from trimethylsilane (TMS) and coupling constants (*J*) are quoted in Hertz (Hz). Abbreviations for NMR data are s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sxt (sextet). Infrared (IR) spectra were recorded on a FTIR spectrometer and mass spectra were obtained using positive or negative electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), electron impact ionization (EI) or chemical ionization (CI) techniques. ^{1}H NMR and ^{13}C NMR spectra were assigned with the aid of COSY, HSQC, HMBC, DEPT 135 and nOe NMR techniques and stereochemistry assigned with the aid of X-ray crystallography. Chromatography was carried out using silica gel 60 Angstrom (Å), 240 – 400 mesh. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel, 0.20 mm (Macherey-Nagel, Polygram® Sil G/UV254). TLC plates were visualised by UV absorption, phosphomolybdic acid, vanillin or potassium permanganate solution and heating. Diiodoethane was washed with diethyl ether and sodium thiosulfate before use.

Preparation of samarium diiodide (SmI_2)

An oven-dried flask, equipped with a dry stirrer bar, was flushed with a strong flow of N_2 for 30 minutes and loaded with samarium metal (-40 mesh, 1.4 equiv) and washed diiodoethane (1 equiv). The flask was flushed for another 30 minutes, after which, freshly distilled and degassed THF (0.1 M) was added with stirring. Stirring was continued under a positive pressure of N_2 overnight at room temperature. The mixture was allowed to settle for one hour and titrated prior to use.[1–5]

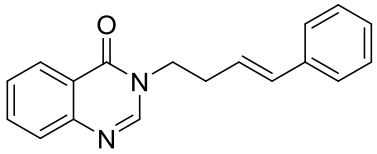
Preparation of starting materials

General procedure A: formation of the cyclization substrates by Mitsunobu reaction[6,7]



To a solution of the amidine (1.0 mmol, 1.0 equiv), alcohol (1.1 mmol, 1.1 equiv) and PPh_3 (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) was added DIAD (diisopropyl azodicarboxylate) (1.5 mmol, 1.5 equiv) dropwise at 0 °C. The mixure was warmed to room temperature and stirred under a N_2 atmosphere for 12 h, then concentrated *in vacuo* to give the crude product, which after purification by chromatography on silica gel, gave the desired product (**1**).

(*E*)-3-(4-Phenylbut-3-en-1-yl)quinazolin-4(3*H*)-one (1a)

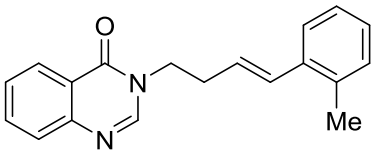


1a

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-phenylbut-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1a** (0.186 g, 0.674 mmol, 67%) as a white solid. M.p. = 135-137 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.34 (1 H, dt, *J* = 8.0, 0.8 Hz, Ar*H*), 8.03 (1 H, s, N=C*H*), 7.65 - 7.83 (2 H, m, Ar*H*), 7.48 - 7.58 (1 H, m, Ar*H*), 7.29 - 7.35 (4 H, m, Ar*H*), 7.24 (1 H, m, Ar*H*), 6.47 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.11 - 6.26 (1 H, m, ArCH=C*H*), 4.15 (2 H, t, *J* = 7.0 Hz, NCH_2CH$_2$), 2.74 (2 H, qd, *J* = 7.2, 1.1 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 148.2 (ArC^q), 146.5 (N=*C*H), 136.8 (ArC^q), 134.2

(Ar*C*H), 133.7 (Ar*C*H=CH), 128.6 (2 × Ar*C*H), 127.6 (Ar*C*H), 127.5 (Ar*C*H), 127.3 (Ar*C*H), 126.7 (Ar*C*H), 126.2 (2 × Ar*C*H), 124.9 (ArCH=*C*H), 122.2 (Ar*C*^{q}), 46.9 (N*C*$H_2$$CH_2$), 32.7 (NC$H_2$*C*$H_2$). **IR (neat, cm^{-1}):** 2935, 1690, 1395, 1259, 1135, 900, 749, 665. **MS (ESI$^+$)** ***m/z*** **(%):** 277.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{17}N_2O$ (M + H$^+$): 277.1335. Found: 277.1336.

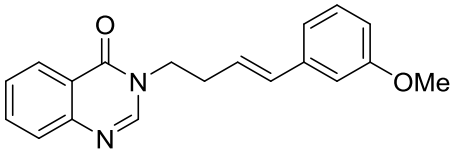
(*E*)-3-(4-(o-Tolyl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1b)



1b

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(o-tolyl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1b** (0.158 g, 0.543 mmol, 54%) as a white solid. M.p. = 104-106.5 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.34 (1 H, dd, *J* = 8.0, 1.3 Hz, Ar*H*), 8.04 (1 H, s, N=C*H*), 7.65 - 7.80 (2 H, m, Ar*H*), 7.42 - 7.59 (1 H, m, Ar*H*), 7.32 - 7.42 (1 H, m, Ar*H*), 7.04 - 7.19 (3 H, m, Ar*H*), 6.63 (1 H, d, *J* = 15.6 Hz, ArC*H*=CH), 5.98 - 6.13 (1 H, m, ArCH=C*H*), 4.16 (2 H, t, *J* = 6.9 Hz, NC$H_2$$CH_2$), 2.76 (2 H, q, *J* = 7.0 Hz, NCH_2CH_2), 2.21 (3 H, s, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 148.2 (Ar*C*^{q}), 146.6 (N=*C*H), 136.1 (Ar*C*^{q}), 135.2 (Ar*C*^{q}), 134.2 (Ar*C*H), 131.8 (Ar*C*H=CH), 130.2 (Ar*C*H), 127.5 (Ar*C*H), 127.5 (Ar*C*H), 127.3 (Ar*C*H), 126.7 (Ar*C*H), 126.3 (ArCH=*C*H), 126.1 (Ar*C*H), 125.7 (Ar*C*H), 122.2 (Ar*C*^{q}), 46.9 (N*C*$H_2$$CH_2$), 32.9 (NC$H_2$*C*$H_2$), 19.6 (*C*$H_3$). **IR (neat, cm^{-1}):** 3019, 1673, 1610, 1474, 1374, 1215, 752, 668. **MS (ESI$^+$)** ***m/z*** **(%):** 291.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{19}N_2O$ (M + H$^+$): 291.1492. Found: 291.1484.

(*E*)-3-(4-(3-Methoxyphenyl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1c)

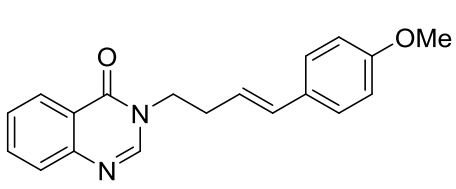


1c

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv),

(*E*)-4-(3-methoxyphenyl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1c** (0.267 g, 0.873 mmol, 87%) as a white solid. M.p. = 87-89.5 ^oC. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.16 - 8.40 (1 H, m, Ar*H*), 8.03 (1 H, s, N=C*H*), 7.61 - 7.82 (2 H, m, Ar*H*), 7.52 (1 H, t, *J* = 7.4 Hz, Ar*H*), 7.21 (1 H, t, *J* = 7.9 Hz, Ar*H*), 6.91 (1 H, d, *J* = 7.8 Hz, Ar*H*), 6.74 - 6.87 (2 H, m, Ar*H*), 6.44 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.09 - 6.25 (1 H, m, ArCH=C*H*), 4.14 (2 H, t, *J* = 7.2 Hz, NCH_2CH$_2$), 3.81 (3 H, s, OCH_3), 2.73 (2 H, q, *J* = 7.1 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 159.8 (Ar*C*^{q}), 148.2 (Ar*C*^{q}), 146.5 (N=*C*H), 138.3 (Ar*C*^{q}), 134.2 (Ar*C*H), 133.6 (Ar*C*H=CH), 129.6 (Ar*C*H), 127.5 (Ar*C*H), 127.3 (Ar*C*H), 126.7 (Ar*C*H), 125.2 (ArCH=*C*H), 122.2 (Ar*C*^{q}), 118.8 (Ar*C*H), 113.1 (Ar*C*H), 111.6 (Ar*C*H), 55.2 (O*C*H$_3$), 46.9 (N*C*H$_2$CH$_2$), 32.7 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3014, 1671, 1610, 1474, 1374, 1216, 1156, 1045, 731, 698. **MS (ESI$^+$) *m/z* (%):** 307.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{19}N_2O_2$ (M + H$^+$): 307.1441. Found: 307.1434.

(*E*)-3-(4-(4-Methoxyphenyl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1d)

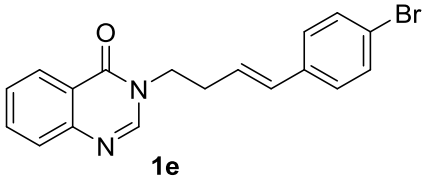


1d

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(4-methoxyphenyl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1d** (0.186 g, 0.608 mmol, 61%) as a white solid. M.p. = 89-92 ^oC. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.34 (1 H, dd, *J* = 7.8, 1.3 Hz, Ar*H*), 8.03 (1 H, s, N=C*H*), 7.61 - 7.85 (2 H, m, Ar*H*), 7.41 - 7.61 (1 H, m, Ar*H*), 7.25 (2 H, d, *J* = 8.8 Hz, Ar*H*), 6.75 - 6.92 (2 H, m, Ar*H*), 6.40 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 5.98 - 6.10 (1 H, m, ArCH=C*H*), 4.13 (2 H, t, *J* = 7.0 Hz, NCH_2CH$_2$), 3.80 (3 H, s, OCH_3), 2.70 (2 H, q, *J* = 6.7 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 159.2 (Ar*C*^{q}),

148.2 (Ar*C*^{q}), 146.5 (N=*C*H), 134.2 (Ar*C*H), 133.1 (Ar*C*H=CH), 129.7 (Ar*C*^{q}), 127.5 (Ar*C*H), 127.3 (2 × Ar*C*H), 127.2 (Ar*C*H), 126.7 (Ar*C*H), 122.6 (ArCH=*C*H), 122.2 (Ar*C*^{q}), 114.0 (2 × Ar*C*H), 55.3 (OCH_3), 47.0 (NCH_2CH_2), 32.7 (NCH_2CH_2). **IR (neat, cm^{-1}):** 3016, 1739, 1673, 1609, 1511, 1374, 1248, 1217, 763. **MS (ESI^{+}) *m/z* (%):** 307.2 (M + H^{+}); **HRMS (ESI^{+}):** calcd. for $C_{19}H_{19}N_2O_2$ (M + H^{+}): 307.1441. Found: 307.1435.

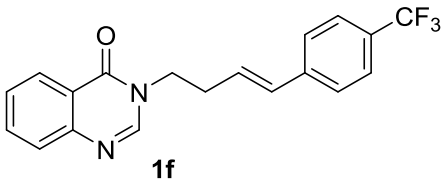
(*E*)-3-(4-(4-Bromophenyl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1e)



1e

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(4-bromophenyl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1e** (0.239 g, 0.675 mmol, 68%) as a white solid. M.p. = 171.8-172.9 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.33 (1 H, dd, *J* = 8.0, 1.0 Hz, Ar*H*), 8.02 (1 H, s, N=C*H*), 7.67 - 7.83 (2 H, m, Ar*H*), 7.47 - 7.58 (1 H, m, Ar*H*), 7.38 - 7.45 (2 H, m, Ar*H*), 7.17 (2 H, m, *J* = 8.3 Hz, Ar*H*), 6.39 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.08 - 6.24 (1 H, m, ArCH=C*H*), 4.14 (2 H, t, *J* = 7.0 Hz, NCH_2CH_2), 2.57 - 2.77 (2 H, m, NCH_2CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 148.1 (Ar*C*^{q}), 146.4 (N=*C*H), 135.8 (Ar*C*^{q}), 134.3 (Ar*C*H), 132.5 (Ar*C*H=CH), 131.7 (2 × Ar*C*H), 127.7 (2 × Ar*C*H), 127.5 (Ar*C*H), 127.3 (Ar*C*H), 126.7 (Ar*C*H), 125.8 (ArCH=*C*H), 122.1 (Ar*C*^{q}), 121.3 (Ar*C*^{q}), 46.7 (NCH_2CH_2), 32.7 (NCH_2CH_2). **IR (neat, cm^{-1}):** 2970, 1740, 1671, 1615, 1474, 1365, 1218, 1156, 1071, 974, 877, 774. **MS (ESI^{+}) *m/z* (%):** 355.1 (M + H^{+}); **HRMS (ESI^{+}):** calcd. for $C_{18}H_{16}N_2OBr$ (M + H^{+}): 355.0441. Found: 355.0433.

(*E*)-3-(4-(4-(Trifluoromethyl)phenyl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1f)

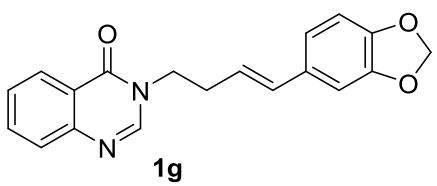


1f

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv),

(*E*)-4-(4-(trifluoromethyl)phenyl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1f** (0.204 g, 0.593 mmol, 59%) as a white solid. M.p. = 162.9-164 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.34 (1 H, dd, *J* = 8.0, 1.3 Hz, Ar*H*), 8.03 (1 H, s, N=C*H*), 7.74 - 7.83 (1 H, m, Ar*H*), 7.66 - 7.74 (1 H, m, Ar*H*), 7.49 - 7.58 (3 H, m, Ar*H*), 7.40 (2 H, d, *J* = 8.0 Hz, Ar*H*), 6.49 (1 H, d, *J* = 16.1 Hz, ArC*H*=CH), 6.31 (1 H, dd, *J* = 15.1, 7.8 Hz, ArCH=C*H*), 4.17 (2 H, t, *J* = 7.0 Hz, NCH_2CH$_2$), 2.77 (2 H, q, *J* = 6.7 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 148.1 (Ar*C*^{q}), 146.3 (N=*C*H), 140.2 (Ar*C*^{q}), 134.3 (Ar*C*H), 132.4 (Ar*C*H=CH), 129.4 (q, *J* = 32.3 Hz, Ar*C*^{q}), 127.8 (ArCH=*C*H), 127.5 (Ar*C*H), 127.4 (Ar*C*H), 126.7 (Ar*C*H), 126.3 (2 × Ar*C*H), 125.5 (q, *J* = 3.0 Hz, 2 × Ar*C*H), 124.0 (q, *J* = 238.4 Hz, *C*F$_3$), 122.1 (Ar*C*^{q}), 46.6 (N*C*H$_2$CH$_2$), 32.8 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 2800, 1739, 1665, 1365, 1217, 1158, 1106, 771, 699. **MS (ESI$^+$) *m/z* (%):** 345.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{16}N_2OF_3$ (M + H$^+$): 345.1209. Found: 345.1204.

(*E*)-3-(4-(Benzo[*d*][1,3]dioxol-5-yl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1g)

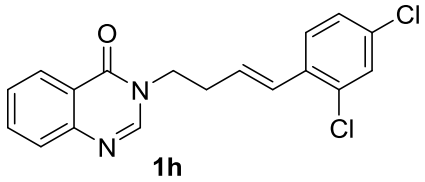


1g

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(benzo[*d*][1,3]dioxol-5-yl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1g** (0.130 g, 0.406 mmol, 41%) as a white solid. M.p. = 177-179 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.34 (1 H, dd, *J* = 8.0, 1.3 Hz, Ar*H*), 8.02 (1 H, s, N=C*H*), 7.67 - 7.80 (2 H, m, Ar*H*), 7.46 - 7.58 (1 H, m, Ar*H*), 6.86 (1 H, s, Ar*H*), 6.73 (2 H, s, Ar*H*), 6.36 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 5.98 - 6.06 (1 H, m, ArCH=C*H*), 5.95 (2 H, s, OCH_2O), 4.13 (2 H, t, *J* = 7.0 Hz, NCH_2CH$_2$), 2.70 (2 H, q, *J* = 7.0 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 148.2 (Ar*C*^{q}), 148.0 (Ar*C*^{q}), 147.2 (Ar*C*^{q}), 146.5 (N=*C*H), 134.2 (Ar*C*H),

133.2 (Ar*C*H=CH), 131.3 (Ar*C*^{q}), 127.5 (Ar*C*H), 127.3 (Ar*C*H), 126.7 (Ar*C*H), 123.0 (ArCH=*C*H), 122.2 (Ar*C*^{q}), 120.8 (Ar*C*H), 108.3 (Ar*C*H), 105.5 (Ar*C*H), 101.1 (O*C*H_2O), 47.0 (N*C*$H_2$$CH_2$), 32.6 (NCH$_2$*C*$H_2$). **IR (neat, cm^{-1}):** 2898, 1679, 1609, 1473, 1444, 1371, 1249, 1037, 929, 775. **MS (ESI$^+$) *m/z* (%):** 321.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{17}N_2O_3$ (M + H$^+$): 321.1234. Found: 321.1232.

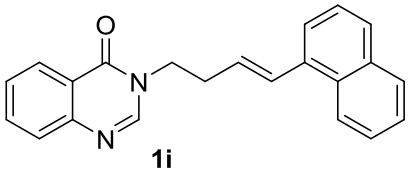
(*E*)-3-(4-(2,4-Dichlorophenyl)but-3-en-1-yl)quinazolin-4(3H)-one (1h)



1h

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(2,4-dichlorophenyl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1h** (0.242 g, 0.703 mmol, 70%) as a white solid. M.p. = 152.5-154 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.33 (1 H, dd, *J* = 8.0, 1.3 Hz, Ar*H*), 8.03 (1 H, s, N=C*H*), 7.66 - 7.82 (2 H, m, Ar*H*), 7.47 - 7.58 (1 H, m, Ar*H*), 7.39 (1 H, d, *J* = 8.3 Hz, Ar*H*), 7.33 (1 H, d, *J* = 2.0 Hz, Ar*H*), 7.18 (1 H, dd, *J* = 8.3, 2.0 Hz, Ar*H*), 6.72 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.16 (1 H, dt, *J* = 15.7, 7.3 Hz, ArCH=C*H*), 4.17 (2 H, t, *J* = 7.0 Hz, NC$H_2$$CH_2$), 2.78 (2 H, qd, *J* = 7.0, 1.3 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 148.2 (Ar*C*^{q}), 146.3 (N=*C*H), 134.3 (Ar*C*H), 133.7 (Ar*C*^{q}), 133.6 (Ar*C*^{q}), 133.3 (Ar*C*^{q}), 129.4 (Ar*C*H), 128.9 (Ar*C*H=CH), 128.6 (ArCH=*C*H), 127.6 (Ar*C*H), 127.5 (Ar*C*H), 127.4 (Ar*C*H), 127.3 (Ar*C*H), 126.7 (Ar*C*H), 122.1 (Ar*C*^{q}), 46.5 (N*C*$H_2$$CH_2$), 32.9 (NCH$_2$*C*$H_2$). **IR (neat, cm^{-1}):** 3027, 1679, 1401, 1216, 750, 691. **MS (ESI$^+$) *m/z* (%):** 345.1 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{15}N_2OCl_2$ (M + H$^+$): 345.0556. Found: 345.0550.

(*E*)-3-(4-(Naphthalen-1-yl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1i)

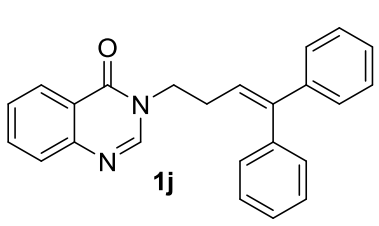


1i

General procedure A was followed: using

quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(naphthalen-1-yl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1i** (0.150 g, 0.460 mmol, 46%) as a white solid. M.p. = 114.5-116 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.37 (1 H, dd, *J* = 7.9, 1.1 Hz, Ar*H*), 8.07 (1 H, s, N=C*H*), 7.67 - 7.94 (5 H, m, Ar*H*), 7.35 - 7.58 (5 H, m, Ar*H*), 7.15 (1 H, d, *J* = 15.6 Hz, ArC*H*=CH), 6.05 - 6.26 (1 H, m, ArCH=C*H*), 4.22 (2 H, t, *J* = 6.9 Hz, NCH_2CH$_2$), 2.86 (2 H, qd, *J* = 7.0, 1.3 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.2 (*C*=O), 148.2 (Ar*C*^{q}), 146.6 (N=*C*H), 134.7 (Ar*C*^{q}), 134.2 (Ar*C*H), 133.5 (Ar*C*^{q}), 131.3 (Ar*C*H=CH), 131.0 (Ar*C*^{q}), 128.5 (Ar*C*H), 128.2 (ArCH=*C*H), 127.9 (Ar*C*H), 127.5 (Ar*C*H), 127.3 (Ar*C*H), 126.7 (Ar*C*H), 126.0 (Ar*C*H), 125.7 (Ar*C*H), 125.6 (Ar*C*H), 123.9 (Ar*C*H), 123.7 (Ar*C*H), 122.2 (Ar*C*^{q}), 46.9 (N*C*H$_2$CH$_2$), 33.0 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3014, 1671, 1610, 1474, 1374, 1215, 968, 743, 668. **MS (ESI$^+$) *m/z* (%):** 327.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{22}H_{19}N_2O$ (M + H$^+$): 327.1492. Found: 327.1485.

3-(4,4-Diphenylbut-3-en-1-yl)quinazolin-4(3*H*)-one (1j)

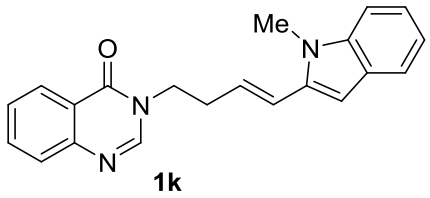


1j

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), 4,4-diphenylbut-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1j** (0.215 g, 0.611 mmol, 61%) as a white solid. M.p. = 99-101 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.27 (1 H, dd, *J* = 8.0, 1.0 Hz, Ar*H*), 7.89 (1 H, s, N=C*H*), 7.74 (1 H, dd, *J*=7.0, 1.5 Hz, Ar*H*), 7.64 - 7.72 (1 H, m, Ar*H*), 7.46 - 7.57 (1 H, m, Ar*H*), 7.17 - 7.29 (8 H, m, Ar*H*), 6.90 - 7.01 (2 H, m, Ar*H*), 6.10 (1 H, t, *J* = 7.7 Hz, C=C*H*), 4.07 (2 H, t, *J* = 6.9 Hz, NCH_2CH$_2$), 2.64 (2 H, q, *J* = 7.0 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 160.9 (*C*=O), 148.1 (Ar*C*^{q}), 146.4 (N=*C*H), 145.5 (Ar*C*^{q}), 141.8 (*C*^{q}),

139.2 (Ar*C*^{q}), 134.1 (Ar*C*H), 129.4 (2 × Ar*C*H), 128.3 (2 × Ar*C*H), 128.2 (2 × Ar*C*H), 127.4 (2 × Ar*C*H), 127.3 (Ar*C*H), 127.2 (2 × Ar*C*H), 127.2 (Ar*C*H), 126.7 (Ar*C*H), 123.5 (C=*C*H), 122.2 (Ar*C*^{q}), 46.5 (N*C*$H_2$$CH_2$), 29.4 (NC$H_2$*C*$H_2$). **IR (neat, cm^{-1}):** 2970, 1739,1365, 1228, 1217, 754. **MS (ESI$^+$) *m/z* (%):** 353.2 (M + H^+); **HRMS (ESI$^+$):** calcd. for $C_{24}H_{20}N_2ONa$ (M + Na^+): 375.1468. Found: 375.1463.

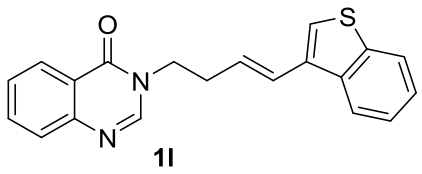
(*E*)-3-(4-(1-Methyl-1*H*-indol-2-yl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1k)



1k

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(1-methyl-1*H*-indol-2-yl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1k** (0.179 g, 0.544 mmol, 54%) as a white solid. M.p. = 150-152 ^{o}C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ ppm 8.26 - 8.39 (1 H, m, Ar*H*), 8.04 (1 H, s, N=C*H*), 7.75 - 7.83 (1 H, m, Ar*H*), 7.66 - 7.75 (1 H, m, Ar*H*), 7.49 - 7.60 (2 H, m, Ar*H*), 7.25 (1 H, d, *J* = 8.4 Hz, Ar*H*), 7.15 - 7.21 (1 H, m, Ar*H*), 7.02 - 7.13 (1 H, m, Ar*H*), 6.60 (1 H, s, Ar*H*), 6.51 (1 H, d, *J* = 15.7 Hz, ArC*H*=CH), 6.12 - 6.32 (1 H, m, ArCH=C*H*), 4.18 (2 H, t, *J* = 6.9 Hz, NC$H_2$$CH_2$), 3.62 (3 H, s, NC$H_3$), 2.79 (2 H, q, *J* = 6.9 Hz, NCH_2CH_2). **^{13}C NMR (126 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 148.2 (Ar*C*^{q}), 146.5 (N=*C*H), 137.7 (Ar*C*^{q}), 137.5 (Ar*C*^{q}), 134.3 (Ar*C*H), 127.8 (ArCH=*C*H), 127.7 (Ar*C*^{q}), 127.5 (Ar*C*H), 127.4 (Ar*C*H), 126.7 (Ar*C*H), 122.8 (Ar*C*H=CH), 122.1 (Ar*C*^{q}), 121.6 (Ar*C*H), 120.3 (Ar*C*H), 119.8 (Ar*C*H), 109.1 (Ar*C*H), 98.8 (Ar*C*H), 46.7 (N*C*$H_2$$CH_2$), 33.0 (NC$H_2$*C*$H_2$), 29.8 (N*C*$H_3$). **IR (neat, cm^{-1}):** 3014, 2346, 1736, 1670, 1611, 1474, 1370, 1216, 749, 700, 668. **MS (ESI$^+$) *m/z* (%):** 330.2 (M + H^+); **HRMS (ESI$^+$):** calcd. for $C_{21}H_{20}N_3O$ (M + H^+): 330.1601. Found: 330.1596.

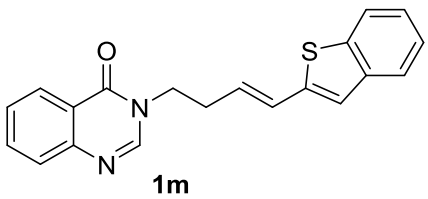
(*E*)-3-(4-(Benzo[*b*]thiophen-3-yl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1l)



1l

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(benzo[*b*]thiophen-3-yl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1l** (0.122 g, 0.367 mmol, 37%) as a light yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.30 - 8.40 (1 H, m, Ar*H*), 8.06 (1 H, s, N=C*H*), 7.80 - 7.90 (1 H, m, Ar*H*), 7.66 - 7.80 (3 H, m, Ar*H*), 7.46 - 7.57 (1 H, m, Ar*H*), 7.32 - 7.42 (3 H, m, Ar*H*), 6.70 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.13 - 6.34 (1 H, m, ArCH=C*H*), 4.19 (2 H, t, *J* = 7.0 Hz, NCH_2CH$_2$), 2.74 - 2.85 (2 H, m, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 148.2 (ArC^q), 146.5 (N=*C*H), 140.4 (ArC^q), 137.5 (ArC^q), 134.3 (Ar*C*H), 133.6 (ArC^q), 127.5 (Ar*C*H), 127.3 (Ar*C*H), 126.8 (ArCH=*C*H), 126.7 (Ar*C*H), 126.0 (Ar*C*H=CH), 124.4 (Ar*C*H), 124.2 (Ar*C*H), 122.9 (Ar*C*H), 122.2 (ArC^q), 121.9 (Ar*C*H), 121.8 (Ar*C*H), 46.8 (NCH$_2$CH$_2$), 33.1 (NCH$_2$$CH_2$). **IR (neat, cm^{-1}):** 1671, 1609, 1473, 1374, 1155, 908, 731, 698. **MS (ESI$^+$) *m/z* (%):** 333.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{20}H_{17}N_2OS$ (M + H$^+$): 333.1056. Found: 333.1053.

(*E*)-3-(4-(Benzo[*b*]thiophen-2-yl)but-3-en-1-yl)quinazolin-4(3*H*)-one (1m)

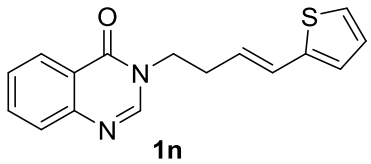


1m

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(benzo[*b*]thiophen-2-yl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1m** (0.167 g, 0.503 mmol, 50%) as a light yellow solid. M.p. = 172.6-174 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.33 - 8.40 (1 H, m, Ar*H*), 8.04 (1 H, s, N=C*H*), 7.68 - 7.83 (3 H, m, Ar*H*), 7.64 - 7.68 (1 H, m, Ar*H*), 7.46 - 7.58 (1 H, m, Ar*H*), 7.28 - 7.34 (2 H, m, Ar*H*), 7.06 (1 H, s, Ar*H*), 6.68 (1 H, d, *J* = 15.6 Hz,

ArC*H*=CH), 6.04 - 6.20 (1 H, m, ArCH=C*H*), 4.16 (2 H, t, *J* = 7.0 Hz, NCH_2CH$_2$), 2.76 (2 H, d, *J* = 7.0 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 161.1 (*C*=O), 148.2 (Ar*C*^{q}), 146.4 (N=*C*H), 141.9 (Ar*C*^{q}), 140.0 (Ar*C*^{q}), 138.7 (Ar*C*^{q}), 134.3 (Ar*C*H), 127.6 (Ar*C*H), 127.5 (Ar*C*H=CH), 127.3 (Ar*C*H and ArCH=*C*H), 126.7 (Ar*C*H), 124.7 (Ar*C*H), 124.4 (Ar*C*H), 123.4 (Ar*C*H), 122.5 (Ar*C*H), 122.2 (Ar*C*H), 122.2 (Ar*C*^{q}), 46.7 (N*C*H$_2$CH$_2$), 32.6 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 2969, 1737, 1666, 1609, 1472, 1365, 1224, 955, 772, 737, 697. **MS (ESI$^+$) *m/z* (%):** 333.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{20}H_{17}N_2OS$ (M + H$^+$): 333.1056. Found: 333.1056.

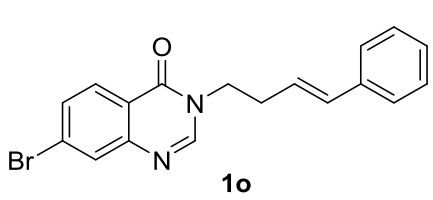
(*E*)-3-(4-(Thiophen-2-yl)but-3-en-1-yl)quinazolin-4(3H)-one (1n)



1n

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-(thiophen-2-yl)but-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1n** (0.114 g, 0.404 mmol, 40%) as a light yellow solid. M.p. = 103.1-105 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ ppm 8.35 (1 H, dd, *J* = 7.9, 1.1 Hz, Ar*H*), 8.04 (1 H, s, N=C*H*), 7.68 - 7.82 (2 H, m, Ar*H*), 7.47 - 7.59 (1 H, m, Ar*H*), 7.14 (1 H, d, *J* = 5.3 Hz, Ar*H*), 6.95 (1 H, dd, *J* = 5.3, 3.5 Hz, Ar*H*), 6.89 (1 H, d, *J* = 3.3 Hz, Ar*H*), 6.60 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.0 - 6.1 (1 H, m, ArCH=C*H*), 4.14 (2 H, t, *J* = 7.2 Hz, NCH_2CH$_2$), 2.71 (2 H, dd, *J* = 7.3, 1.0 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 161.1 (*C*=O), 148.2 (Ar*C*^{q}), 146.4 (N=*C*H), 141.8 (Ar*C*^{q}), 134.2 (Ar*C*H), 127.5 (Ar*C*H), 127.3 (Ar*C*H), 127.3 (Ar*C*H), 126.8 (Ar*C*H=CH), 126.7 (Ar*C*H), 125.4 (Ar*C*H), 124.5 (ArCH=*C*H), 124.1 (Ar*C*H), 122.2 (Ar*C*^{q}), 46.9 (N*C*H$_2$CH$_2$), 32.5 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3013, 1670, 1610, 1474, 1375, 1323, 1217, 1105. 959, 753, 698. **MS (ESI$^+$) *m/z* (%):** 283.1 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{16}H_{15}N_2OS$ (M + H$^+$): 283.0900. Found: 283.0893.

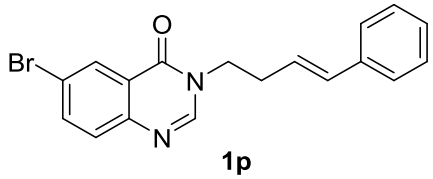
(*E*)-7-Bromo-3-(4-phenylbut-3-en-1-yl)quinazolin-4(3*H*)-one (1o)



1o

General procedure A was followed: using 7-bromoquinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-phenylbut-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1o** (0.200 g, 0.563 mmol, 56%) as a white solid. M.p. = 155-156.8 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.19 (1 H, d, *J* = 8.5 Hz, Ar*H*), 8.03 (1 H, s, N=C*H*), 7.89 (1 H, d, *J* = 1.8 Hz, Ar*H*), 7.63 (1 H, dd, *J* = 8.5, 1.8 Hz, Ar*H*), 7.30 - 7.35 (4 H, m, Ar*H*), 7.22 - 7.27 (1 H, m, Ar*H*), 6.46 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.13 - 6.24 (1 H, m, ArCH=C*H*), 4.14 (2 H, t, *J* = 7.0 Hz, NCH_2CH$_2$), 2.74 (2 H, q, *J* = 7.0 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 160.6 (*C*=O), 149.2 (ArC^q), 147.6 (N=*C*H), 136.7 (ArC^q), 133.9 (Ar*C*H=CH), 130.7 (Ar*C*H), 130.3 (Ar*C*H), 129.0 (ArC^q), 128.6 (2 × Ar*C*H), 128.2 (Ar*C*H), 127.6 (Ar*C*H), 126.2 (2 × Ar*C*H), 124.6 (ArCH=*C*H), 121.0 (ArC^q), 47.0 (N*C*H$_2$CH$_2$), 32.6 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 2969, 2346, 1736, 1664, 1365, 1228, 882, 775, 663. **MS (ESI$^+$) *m/z* (%):** 356.3 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{16}N_2OBr$ (M + H$^+$): 355.0441. Found: 355.0432.

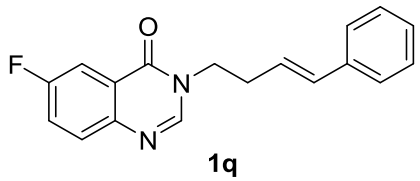
(*E*)-6-Bromo-3-(4-phenylbut-3-en-1-yl)quinazolin-4(3*H*)-one (1p)



1p

General procedure A was followed: using 6-bromoquinazolin-4(3H)-one (1.0 mmol, 1.0 equiv), (*E*)-4-phenylbut-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1p** (0.231 g, 0.651 mmol, 65%) as a white solid. M.p. = 97-98.5 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.46 (1 H, d, *J* = 2.3 Hz, Ar*H*), 8.02 (1 H, s, N=C*H*), 7.83 (1 H, dd, *J* = 8.5, 2.3 Hz, Ar*H*), 7.58 (1 H, d, *J* = 8.8 Hz, Ar*H*), 7.29 - 7.35 (4 H, m, Ar*H*), 7.13 - 7.25 (1 H, m, Ar*H*), 6.45 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.02 - 6.25 (1 H, m,

ArCH=C*H*), 4.14 (2 H, t, *J* = 7.0 Hz, NC*H*$_2$CH$_2$), 2.72 (2 H, q, *J* = 7.2 Hz, NCH$_2$C*H*$_2$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 159.9 (*C*=O), 147.0 (Ar*C*^{q}), 146.8 (N=*C*H), 137.4 (Ar*C*H), 136.7 (Ar*C*^{q}), 133.9 (Ar*C*H=CH), 129.3 (Ar*C*H), 129.3 (Ar*C*H), 128.6 (2 × Ar*C*H), 127.6 (Ar*C*H), 126.2 (2 × Ar*C*H), 124.6 (ArCH=*C*H), 123.5 (Ar*C*^{q}), 120.9 (Ar*C*^{q}), 47.0 (N*C*H$_2$CH$_2$), 32.6 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 2970, 1739, 1365, 1228, 1217, 754. **MS (ESI$^+$) *m/z* (%):** 355.1 (M$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{16}N_2OBr$ (M + H$^+$): 355.0441. Found: 355.0430.



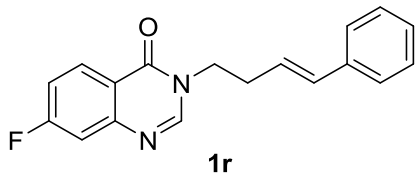
1q

(*E*)-6-Fluoro-3-(4-phenylbut-3-en-1-yl)quinazolin-4(3H)-one (1q)

General procedure A was followed: using 6-fluoroquinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-phenylbut-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1q** (0.230 g, 0.782 mmol, 78%) as a white solid. M.p. = 121-123.3 °C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ ppm 7.92 - 8.04 (2 H, m, N=C*H* and Ar*H*), 7.72 (1 H, dd, *J* = 8.9, 4.9 Hz, Ar*H*), 7.48 (1 H, td, *J* = 8.5, 3.0 Hz, Ar*H*), 7.28 - 7.35 (4 H, m, Ar*H*), 7.19 - 7.26 (1 H, m, Ar*H*), 6.46 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.10 - 6.24 (1 H, m, ArCH=C*H*), 4.15 (2 H, t, *J* = 7.0 Hz, NC*H*$_2$CH$_2$), 2.73 (2 H, qd, *J* = 7.1, 1.0 Hz, NCH$_2$C*H*$_2$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 161.2 (d, *J* = 249.5 Hz, *C*F), 160.4 (*C*=O), 145.7 (N=*C*H), 144.8 (Ar*C*^{q}), 136.8 (Ar*C*^{q}), 133.8 (Ar*C*H=CH), 130.0 (d, *J* = 8.1 Hz, Ar*C*H), 128.6 (2 × Ar*C*H), 127.6 (Ar*C*H), 126.2 (2 × Ar*C*H), 124.7 (ArCH=*C*H), 123.5 (d, *J* = 8.1 Hz, Ar*C*^{q}), 122.8 (d, *J* = 24.2 Hz, Ar*C*H), 111.6 (d, *J* = 24.2 Hz, Ar*C*H), 47.0 (N*C*H$_2$CH$_2$), 32.7 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3024, 1739, 1674, 1607, 1486, 1374, 1269, 1216, 966, 836, 749. **MS (ESI$^+$) *m/z* (%):** 295.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{16}N_2OF$ (M + H$^+$): 295.1241. Found: 295.1235.

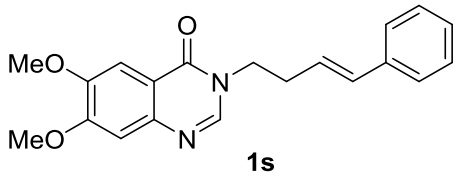
(*E*)-7-Fluoro-3-(4-phenylbut-3-en-1-yl)quinazolin-4(3*H*)-one (1r)

General procedure A was followed: using 7-fluoroquinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-phenylbut-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1r** (0.203 g, 0.690 mmol, 69%) as a white solid. M.p. = 143.7-144.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.34 (1 H, dd, *J* = 8.9, 6.1 Hz, Ar*H*), 8.03 (1 H, s, N=C*H*), 7.28 - 7.37 (5 H, m, Ar*H*), 7.20 - 7.27 (2 H, m, Ar*H*), 6.46 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.09 - 6.24 (1 H, m, ArCH=C*H*), 4.14 (2 H, t, *J* = 7.0 Hz, NCH_2CH$_2$), 2.73 (2 H, q, *J* = 6.7 Hz, NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 166.4 (d, *J* = 255.5 Hz, *C*F), 160.4 (*C*=O), 150.3 (d, *J* = 13.1 Hz, ArC^q), 147.7 (N=*C*H), 136.8 (ArC^q), 133.8 (Ar*C*H=CH), 129.5 (d, *J* = 11.1 Hz, Ar*C*H), 128.6 (2 × Ar*C*H), 127.6 (Ar*C*H), 126.2 (2 × Ar*C*H), 124.7 (ArCH=*C*H), 118.9 (d, *J* = 2.0 Hz, ArC^q), 116.1 (d, *J* = 23.2 Hz, Ar*C*H), 112.9 (d, *J* = 21.2 Hz, Ar*C*H), 46.9 (N*C*H$_2$CH$_2$), 32.7 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3016, 1676, 1606, 1477, 1373, 1216, 1126, 960, 870, 753. **MS (ESI$^+$) *m/z* (%):** 295.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{16}N_2OF$ (M + H$^+$): 295.1241. Found: 295.1235.



1r

(*E*)-6,7-Dimethoxy-3-(4-phenylbut-3-en-1-yl)quinazolin-4(3*H*)-one (1s)

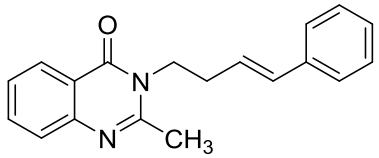


1s

General procedure A was followed: using 6,7-dimethoxyquinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-phenylbut-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1s** (0.217 g, 0.646 mmol, 65%) as a white solid. M.p. = 111-112.3 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ ppm 7.95 (1 H, s, N=C*H*), 7.65 (1 H, s, Ar*H*), 7.29 - 7.36 (4 H, m, Ar*H*), 7.20 - 7.26 (1 H, m, Ar*H*), 7.10 (1 H, s, Ar*H*), 6.46 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.10 - 6.24 (1 H, m, ArCH=C*H*), 4.14 (2 H, t, *J* = 6.9 Hz,

NC*H*$_2$CH$_2$), 4.02 (3 H, s, C*H*$_3$), 4.00 (3 H, s, C*H*$_3$), 2.73 (2 H, q, *J* = 6.9 Hz, NCH$_2$C*H*$_2$). **^{13}C NMR (126 MHz, CDCl$_3$):** δ ppm 160.5 (*C*=O), 154.9 (Ar*C*^{q}), 149.4 (Ar*C*^{q}), 145.3 (N=*C*H), 144.5 (Ar*C*^{q}), 136.9 (Ar*C*^{q}), 133.6 (Ar*C*H=CH), 128.6 (2 × Ar*C*H), 127.5 (Ar*C*H), 126.2 (2 × Ar*C*H), 125.0 (ArCH=*C*H), 115.6 (Ar*C*^{q}), 107.9 (Ar*C*H), 105.6 (Ar*C*H), 56.3 (2 × *C*H$_3$), 46.9 (N*C*H$_2$CH$_2$), 32.8 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3024, 2969, 2249, 1661, 1610, 1499, 1376, 1270, 1217, 1123, 1017, 968, 729. MS **(ESI$^+$) *m/z* (%):** 337.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{20}H_{21}N_2O_3$ (M + H$^+$): 337.1547. Found: 337.1537.

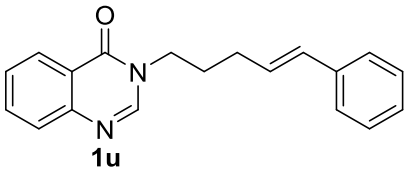
(*E*)-2-Methyl-3-(4-phenylbut-3-en-1-yl)quinazolin-4(3*H*)-one (1t)



1t

General procedure A was followed: using 2-methylquinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-4-phenylbut-3-en-1-ol (1.1 mmol, 1.1 equiv), PPh$_3$ (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1t** (0.158 g, 0.545 mmol, 55%) as a white solid. M.p. = 69-71.1 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ ppm 8.27 (1 H, dd, *J* = 8.0, 1.3 Hz, Ar*H*), 7.68 - 7.82 (1 H, m, Ar*H*), 7.59 - 7.65 (1 H, m, Ar*H*), 7.40 - 7.50 (1 H, m, Ar*H*), 7.29 - 7.37 (4 H, m, Ar*H*), 7.20 - 7.27 (1 H, m, Ar*H*), 6.50 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.24 (1 H, dt, *J* = 15.8, 7.3 Hz, ArCH=C*H*), 4.17 - 4.29 (2 H, m, NC*H*$_2$CH$_2$), 2.63 - 2.73 (5 H, m, NCH$_2$C*H*$_2$ and C*H*$_3$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 162.0 (*C*=O), 153.9 (Ar*C*^{q}), 147.3 (Ar*C*^{q}), 136.9 (Ar*C*^{q}), 134.3 (Ar*C*H), 133.0 (Ar*C*H=CH), 128.6 (2 × Ar*C*H), 127.5 (Ar*C*H), 126.8 (Ar*C*H), 126.7 (Ar*C*H), 126.4 (Ar*C*H), 126.1 (2 × Ar*C*H), 125.3 (ArCH=*C*H), 120.5 (Ar*C*^{q}), 44.4 (N*C*H$_2$CH$_2$), 32.1 (NCH$_2$*C*H$_2$), 23.4 (*C*H$_3$). **IR (neat, cm^{-1}):** 2970, 1738, 1690, 1608, 1472, 1373, 920, 773, 698. **MS (ESI$^+$) *m/z* (%):** 291.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{19}N_2O$ (M + H$^+$): 291.1492. Found: 291.1492.

(*E*)-3-(5-Phenylpent-4-en-1-yl)quinazolin-4(3*H*)-one (1u)



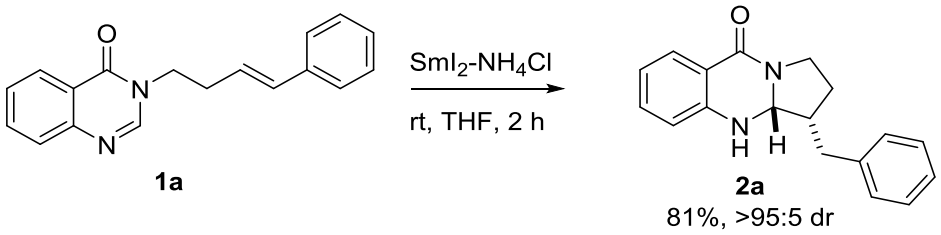
1u

General procedure A was followed: using quinazolin-4(3*H*)-one (1.0 mmol, 1.0 equiv), (*E*)-5-phenylpent-4-en-1-ol (1.1 mmol, 1.1 equiv), PPh_3 (1.5 mmol, 1.5 equiv) and DIAD (1.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (10 mL) for 12 h. The mixture was purified by chromatography (40% EtOAc/hexanes) and gave **1u** (0.192 g, 0.662 mmol, 66%) as a white solid. M.p. = 115-117 ^{o}C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ ppm 8.33 (1 H, dd, *J* = 8.0, 1.4 Hz, Ar*H*), 8.05 (1 H, s, N=C*H*), 7.70 - 7.80 (2 H, m, Ar*H*), 7.47 - 7.55 (1 H, m, Ar*H*), 7.27 - 7.37 (4 H, m, Ar*H*), 7.15 - 7.24 (1 H, m, Ar*H*), 6.46 (1 H, d, *J* = 15.8 Hz, ArC*H*=CH), 6.21 (1 H, dt, *J* = 15.8, 6.9 Hz, ArCH=C*H*), 4.02 - 4.12 (2 H, m, NCH_2CH$_2$), 2.27 - 2.40 (2 H, m, ArCH=CH$_2$CH_2), 2.03 (2 H, quin, *J* = 7.3 Hz, NCH$_2$CH_2). **^{13}C NMR (126 MHz, $CDCl_3$):** δ ppm 161.1 (*C*=O), 148.2 (ArC^q), 146.6 (N=*C*H), 137.2 (ArC^q), 134.2 (Ar*C*H), 131.3 (Ar*C*H=CH), 128.5 (2 × Ar*C*H), 127.5 (Ar*C*H), 127.3 (2 × Ar*C*H), 127.2 (Ar*C*H), 126.7 (ArCH=*C*H), 126.0 (2 × Ar*C*H), 122.2 (ArC^q), 46.6 (N*C*H$_2$CH$_2$), 29.9 (ArCH=CH*C*H$_2$), 28.6 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 2970, 1738, 1670, 1608, 1365, 1217, 773. **MS (ESI$^+$) *m/z* (%):** 313.1 (M + Na$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{18}N_2OK$ (M + K$^+$): 329.1051. Found: 329.1045.

Reductive Cyclizations of Amidines involving Aminal Radicals

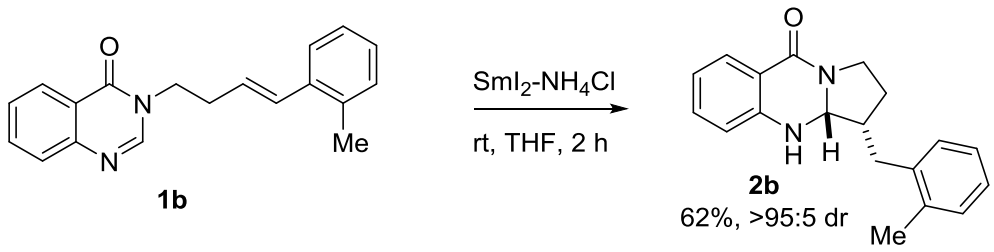
General procedure B: SmI_2 mediated radical cyclization to give bicyclic products (2)

An oven-dried vial containing a stirrer bar was charged with the substrate **1** (0.1 mmol, 1 equiv) and NH_4Cl (0.3 mmol, 3 equiv), then placed under a positive pressure of nitrogen. THF (0.05 M, typically, 2.0 mL) was added, followed by addition of the fresh SmI_2 solution slowly over 1 h. After the specified time (typically, 1 h), the reaction was quenched by bubbling air through the mixture before dilution with CH_2Cl_2 (30 mL) and aqueous HCl (0.1 M, 20 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic phases were dried over Mg_2SO_4, filtered and concentrated. The crude product was purified by chromatography on silica gel.



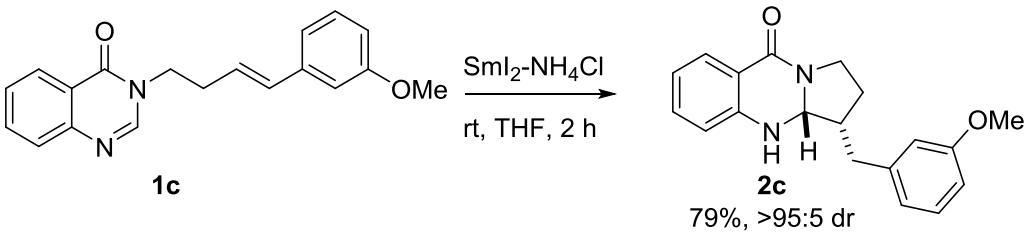
(3*S*,3a*R*)-3-Benzyl-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2a). According to the general procedure B, using **1a** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2a** (22.5 mg, 0.0809 mmol, 81%, >95:5 dr) as a white solid. M.p. = 244-246 ^oC. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.92 (1 H, dd, *J* = 7.8, 1.3 Hz, Ar*H*), 7.17 - 7.38 (6 H, m, Ar*H*), 6.83 - 6.93 (1 H, m, Ar*H*), 6.67 (1 H, d, *J* = 8.0 Hz, Ar*H*), 5.18 (1 H, d, *J* = 5.3 Hz, NHC*H*), 4.31 (1 H, s, N*H*), 3.85 (1 H, dt, *J* = 11.9, 7.7 Hz, 1 H from NCH_2CH$_2$), 3.61 (1 H, ddd, *J* = 12.2, 8.1, 4.5 Hz, 1 H from NCH_2CH$_2$), 3.10 (1 H, dd, *J* = 13.8, 5.5 Hz, 1 H from ArCH_2CH), 2.70 -

2.80 (1 H, m, ArCH$_2$C*H*), 2.65 (dd, *J* = 13.8, 9.8 Hz, 1 H from ArC*H*$_2$CH), 1.87 - 1.96 (1 H, m, 1 H from NCH$_2$C*H*$_2$), 1.77 - 1.87 (1 H, m, 1 H from NCH$_2$C*H*$_2$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 162.5 (C=O), 147.5 (Ar*C*^{q}), 139.7 (Ar*C*^{q}), 133.0 (Ar*C*H), 128.9 (2 × Ar*C*H), 128.7 (2 × Ar*C*H), 128.3 (Ar*C*H), 126.5 (Ar*C*H), 119.7 (Ar*C*H), 117.6 (Ar*C*^{q}), 114.9 (Ar*C*H), 71.9 (NH*C*H), 43.4 (ArCH$_2$*C*H), 42.8 (N*C*H$_2$CH$_2$), 33.8 (Ar*C*H$_2$CH), 26.8 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3269, 2945, 1628, 1482, 1434, 1216, 906, 727, 647. **MS (ESI$^+$) *m/z* (%):** 279.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{19}N_2O$ (M + H$^+$): 279.1492. Found: 279.1496.

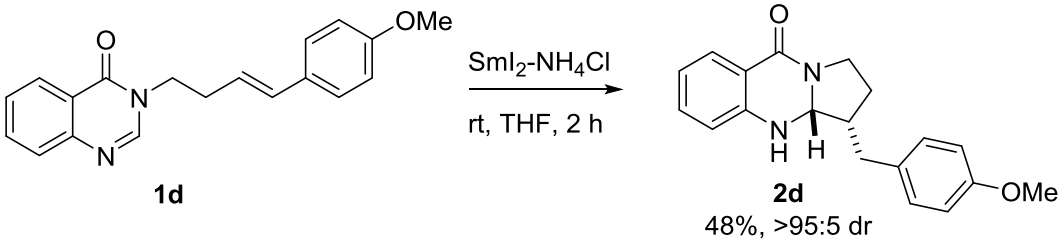


(3*S*,3a*R*)-3-(2-Methylbenzyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2b). According to the general procedure B, using **1b** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2b** (18.0 mg, 0.0616 mmol, 62%, >95:5 dr) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$):** δ ppm 7.92 (1 H, d, *J* = 7.8 Hz, Ar*H*), 7.27 - 7.32 (1 H, m, Ar*H*), 7.13 - 7.23 (4 H, m, Ar*H*), 6.89 (1 H, t, *J* = 7.5 Hz, Ar*H*), 6.68 (1 H, d, *J* = 8.0 Hz, Ar*H*), 5.21 (1 H, d, *J* = 5.3 Hz, NHC*H*), 4.33 (1 H, s, N*H*), 3.75 - 3.94 (1 H, m, 1 H from NC*H*$_2$CH$_2$), 3.64 (1 H, ddd, *J* = 12.2, 8.2, 4.3 Hz, 1 H from NC*H*$_2$CH$_2$), 3.11 (1 H, dd, *J* = 14.3, 5.3 Hz, 1 H from ArC*H*$_2$CH), 2.76 (1 H, dd, *J* = 10.3, 4.8 Hz, ArCH$_2$C*H*), 2.56 - 2.70 (1 H, m, 1 H from ArC*H*$_2$CH), 2.36 (3 H, s, C*H*$_3$), 1.76 - 1.97 (2 H, m, NCH$_2$C*H*$_2$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 162.5 (C=O), 147.5 (Ar*C*^{q}), 137.9 (Ar*C*^{q}), 136.4 (Ar*C*^{q}), 133.0 (Ar*C*H), 130.6 (Ar*C*H), 129.2 (Ar*C*H), 128.3 (Ar*C*H), 126.5 (Ar*C*H), 126.2 (Ar*C*H), 119.7 (Ar*C*H), 117.6 (Ar*C*^{q}), 114.9 (Ar*C*H), 72.1 (NH*C*H), 42.8 (N*C*H$_2$CH$_2$), 42.1 (ArCH$_2$*C*H), 30.7 (Ar*C*H$_2$CH), 26.8 (NCH$_2$*C*H$_2$), 19.7 (*C*H$_3$). **IR (neat, cm^{-1}):** 2969, 2346, 1736, 1671, 1618, 1450, 1216, 752, 690. **MS (ESI$^+$) *m/z* (%):**

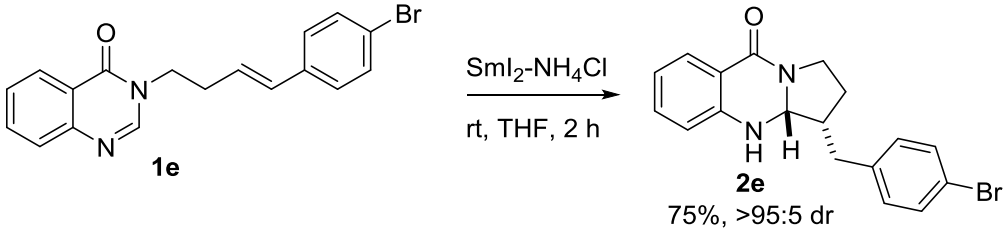
293.2 (M + H^+); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{21}N_2O$ (M + H^+): 293.1648. Found: 293.1635.



(3*S*,3a*R*)-3-(3-Methoxybenzyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2c). According to the general procedure B, using **1c** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2c** (24.3 mg, 0.0789 mmol, 79%, >95:5 dr) as a white solid. M.p. = 172-174 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.86 - 7.95 (1 H, m, Ar*H*), 7.21 - 7.32 (2 H, m, Ar*H*), 6.84 - 6.92 (1 H, m, Ar*H*), 6.73 - 6.84 (3 H, m, Ar*H*), 6.66 (1 H, d, *J* = 8.0 Hz, Ar*H*), 5.17 (1 H, d, *J* = 5.5 Hz, NHC*H*), 4.31 (1 H, s, N*H*), 3.83 - 3.89 (1 H, m, 1 H from NCH_2CH$_2$), 3.81 (3 H, s, OCH_3), 3.60 (1 H, ddd, *J* = 12.2, 8.1, 4.5 Hz, 1 H from NCH_2CH$_2$), 3.07 (1 H, dd, *J* = 13.9, 5.9 Hz, 1 H from ArCH_2CH), 2.69 - 2.80 (1 H, m, ArCH$_2$C*H*), 2.55 - 2.69 (1 H, m, 1 H from ArCH_2CH), 1.86 - 1.97 (1 H, m, 1 H from NCH$_2$CH_2), 1.67 - 1.86 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 162.5 (C=O), 159.9 (ArC^q), 147.5 (ArC^q), 141.3 (ArC^q), 133.0 (Ar*C*H), 129.7 (Ar*C*H), 128.3 (Ar*C*H), 121.2 (Ar*C*H), 119.7 (Ar*C*H), 117.6 (ArC^q), 114.9 (Ar*C*H), 114.8 (Ar*C*H), 111.5 (Ar*C*H), 71.9 (NH*C*H), 55.2 (OCH_3), 43.3 (ArCH$_2$*C*H), 42.8 (N*C*H$_2$CH$_2$), 33.8 (Ar*C*H$_2$CH), 26.8 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3284, 3004, 1739, 1633, 1485, 1434, 1365, 1217, 754. **MS (ESI$^+$) *m/z* (%):** 309.2 (M + H^+); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{21}N_2O_2$ (M + H^+): 309.1598. Found: 309.1588.

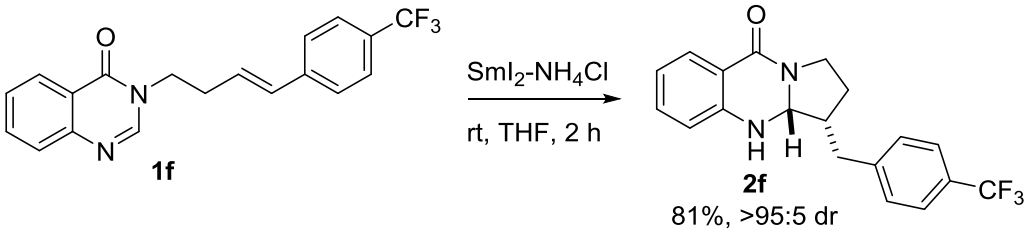


(3*S*,3a*R*)-3-(4-Methoxybenzyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2d). According to the general procedure B, using **1d** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2d** (14.8 mg, 0.0481 mmol, 48%, >95:5 dr) as a white solid. M.p. = 187-191.2 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.88 - 7.94 (1 H, m, Ar*H*), 7.26 (1 H, d, *J* = 1.5 Hz, Ar*H*), 7.15 (2 H, d, *J* = 8.8 Hz, Ar*H*), 6.86 - 6.91 (3 H, m, Ar*H*), 6.65 (1 H, d, *J* = 8.0 Hz, Ar*H*), 5.16 (1 H, d, *J* = 5.3 Hz, NHC*H*), 4.20 (1 H, s, N*H*), 3.78 - 3.88 (4 H, m, 1 H from NCH_2CH$_2$ and OCH_3), 3.60 (1 H, ddd, *J* = 12.2, 8.0, 4.6 Hz, 1 H from NCH_2CH$_2$), 3.03 (1 H, dd, *J* = 13.9, 5.9 Hz, 1 H from ArCH_2CH), 2.71 (1 H, dd, *J* = 10.3, 5.0 Hz, ArCH$_2$C*H*), 2.57 - 2.67 (1 H, m, 1 H from ArCH_2CH), 1.86 - 1.97 (1 H, m, 1 H from NCH$_2$CH_2), 1.76 - 1.86 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 162.5 (C=O), 158.2 (Ar*C*^{q}), 147.4 (Ar*C*^{q}), 132.9 (Ar*C*H), 131.5 (Ar*C*^{q}), 129.8 (2 × Ar*C*H), 128.3 (Ar*C*H), 119.8 (Ar*C*H), 117.7 (Ar*C*^{q}), 114.9 (Ar*C*H), 114.1 (2 × Ar*C*H), 71.8 (NH*C*H), 55.3 (O*C*H$_3$), 43.6 (ArCH$_2$*C*H), 42.8 (N*C*H$_2$CH$_2$), 32.9 (Ar*C*H$_2$CH), 26.9 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3738, 2966, 2331, 1736, 1639, 1512, 1436, 1216, 763. **MS (ESI^{+}) *m/z* (%):** 309.2 (M + H^{+}); **HRMS (ESI^{+}):** calcd. for $C_{19}H_{21}N_2O_2$ (M + H^{+}): 309.1598. Found: 309.1591.



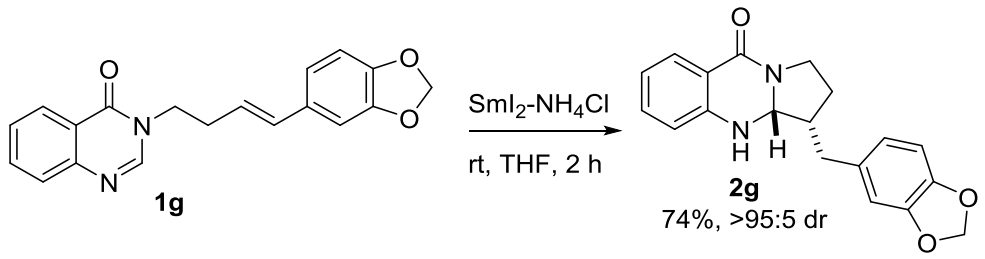
(3*S*,3a*R*)-3-(4-Bromobenzyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2e).

According to the general procedure B, using **1e** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2e** (26.7 mg, 0.0748 mmol, 75%, >95:5 dr) as a white solid. M.p. = 126-127.3 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.87 - 7.95 (1 H, m, Ar*H*), 7.45 (2 H, m, *J* = 8.3 Hz, Ar*H*), 7.27 - 7.33 (1 H, m, Ar*H*), 7.09 (2 H, m, *J* = 8.3 Hz, Ar*H*), 6.88 (1 H, t, *J* = 7.4 Hz, Ar*H*), 6.67 (1 H, d, *J* = 8.0 Hz, Ar*H*), 5.19 (1 H, d, *J* = 5.3 Hz, NHC*H*), 4.32 (1 H, s, N*H*), 3.79 (1 H, dt, *J* = 12.0, 8.0 Hz, 1 H from NCH_2CH$_2$), 3.62 (1 H, ddd, *J* = 12.1, 8.5, 3.8 Hz, 1 H from NCH_2CH$_2$), 3.06 (1 H, dd, *J* = 13.9, 5.4 Hz, 1 H from ArCH_2CH), 2.69 (1 H, dd, *J* = 9.4, 5.4 Hz, ArCH$_2$C*H*), 2.51 - 2.63 (1 H, m, 1 H from ArCH_2CH), 1.83 - 1.96 (1 H, m, 1 H from NCH$_2$CH_2), 1.71 - 1.83 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 162.5 (C=O), 147.4 (Ar*C*^{q}), 138.7 (Ar*C*^{q}), 133.1 (Ar*C*H), 131.8 (2 × Ar*C*H), 130.7 (2 × Ar*C*H), 128.2 (Ar*C*H), 120.3 (Ar*C*^{q}), 119.8 (Ar*C*H), 117.5 (Ar*C*^{q}), 114.9 (Ar*C*H), 71.9 (NH*C*H), 43.3 (ArCH$_2$*C*H), 42.6 (N*C*H$_2$CH$_2$), 33.2 (Ar*C*H$_2$CH), 26.4 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 2966, 2247, 1667, 1620, 1487, 1467, 1383, 1071, 1011, 907, 773. **MS (ESI$^+$) *m/z* (%):** 357.1 (M^+); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{18}N_2OBr$ ($M + H^+$): 357.0597. Found: 357.0595.



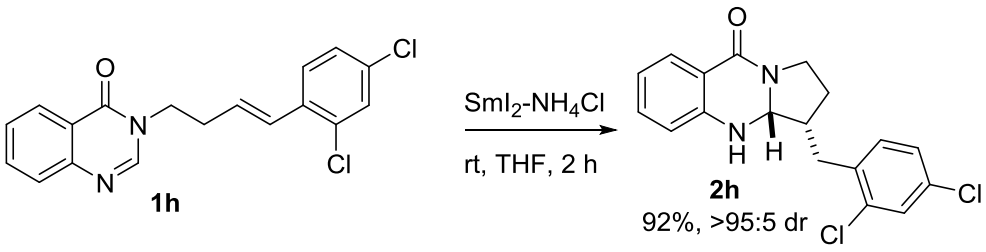
(3*S*,3a*R*)-3-(4-(Trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2f). According to the general procedure B, using **1f** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2f** (28.0 mg, 0.0809 mmol, 81%, >95:5 dr) as a white solid. M.p. = 193.4-195 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.91 (1 H, dd, *J* = 7.8, 1.5 Hz, Ar*H*), 7.58

(2 H, d, *J* = 8.0 Hz, Ar*H*), 7.28 - 7.37 (3 H, m, Ar*H*), 6.82 - 6.94 (1 H, m, Ar*H*), 6.69 (1 H, d, *J* = 7.8 Hz, Ar*H*), 5.22 (1 H, d, *J* = 5.0 Hz, NHC*H*), 4.41 (1 H, s, N*H*), 3.73 - 3.88 (1 H, m, 1 H from NCH_2CH$_2$), 3.65 (1 H, ddd, *J* = 12.0, 8.5, 3.8 Hz, 1 H from NCH_2CH$_2$), 3.18 (1 H, dd, *J* = 13.4, 4.6 Hz, 1 H from ArCH_2CH), 2.57 - 2.82 (2 H, m, ArCH$_2$C*H* and 1 H from ArCH_2CH), 1.83 - 1.99 (1 H, m, 1 H from NCH$_2$CH_2), 1.65 - 1.83 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 162.5 (C=O), 147.4 (ArC^q), 144.0 (ArC^q), 133.1 (Ar*C*H), 129.3 (2 × Ar*C*H), 128.9 (q, *J* = 32.3 Hz, ArC^q), 128.2 (Ar*C*H), 125.6 (q, *J* = 4.0 Hz, 2 × Ar*C*H), 124.2 (q, *J* = 272.7 Hz, *C*F$_3$), 119.8 (Ar*C*H), 117.4 (ArC^q), 114.9 (Ar*C*H), 72.0 (NH*C*H), 43.3 (ArCH$_2$*C*H), 42.5 (N*C*H$_2$CH$_2$), 33.5 (Ar*C*H$_2$CH), 26.2 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3269, 3004, 1739, 1633, 1483, 1435, 1324, 1216, 1122, 1067, 743. **MS (ESI$^+$)** ***m/z*** **(%):** 347.2 (M$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{18}N_2OF_3$ (M + H$^+$): 347.1366. Found: 347.1361.



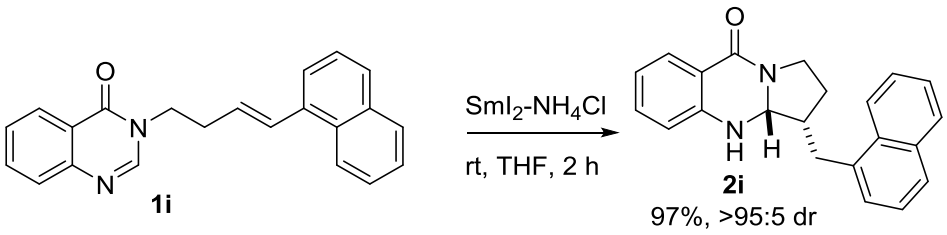
(3*S*,3a*R*)-3-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2g). According to the general procedure B, using **1g** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2g** (23.9 mg, 0.0742 mmol, 74%, >95:5 dr) as a white solid. M.p. = 223-224.5 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ ppm 7.91 (1 H, d, *J* = 7.5 Hz, Ar*H*), 7.30 (1 H, d, *J* = 1.5 Hz, Ar*H*), 6.88 (1 H, t, *J* = 7.4 Hz, Ar*H*), 6.78 (1 H, d, *J* = 7.8 Hz, Ar*H*), 6.62 - 6.74 (3 H, m, Ar*H*), 5.96 (2 H, s, OCH_2O), 5.16 (1 H, d, *J* = 5.5 Hz, NHC*H*), 4.26 (1 H, s, N*H*), 3.83 (1 H, dt, *J* = 12.0, 7.7 Hz, 1 H from NCH_2CH$_2$), 3.60 (1 H, ddd, *J* = 12.2, 8.0, 4.6 Hz, 1 H from NCH_2CH$_2$), 3.01 (1 H, dd, *J* = 13.9, 5.6 Hz, 1 H from ArCH_2CH), 2.68 (1 H, dd, *J* =

10.5, 5.0 Hz, ArCH$_2$C*H*), 2.50 - 2.63 (1 H, m, 1 H from ArC*H*$_2$CH), 1.86 - 1.96 (1 H, m, 1 H from NCH$_2$C*H*$_2$), 1.73 - 1.86 (1 H, m, 1 H from NCH$_2$C*H*$_2$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 162.5 (C=O), 148.0 (Ar*C*^{q}), 147.4 (Ar*C*^{q}), 146.2 (Ar*C*^{q}), 133.3 (Ar*C*^{q}), 133.0 (Ar*C*H), 128.3 (Ar*C*H), 121.7 (Ar*C*H), 119.8 (Ar*C*H), 117.7 (Ar*C*^{q}), 114.9 (Ar*C*H), 109.0 (Ar*C*H), 108.4 (Ar*C*H), 101.0 (O*C*H$_2$O), 71.8 (NH*C*H), 43.5 (ArCH$_2$*C*H), 42.8 (N*C*H$_2$CH$_2$), 33.5 (Ar*C*H$_2$CH), 26.7 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3291, 2924, 1635, 1487, 1442, 1215, 1039, 757. **MS (ESI$^+$) *m/z* (%):** 323.3 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{19}N_2O_3$ (M + H$^+$): 323.1390. Found: 323.1386.

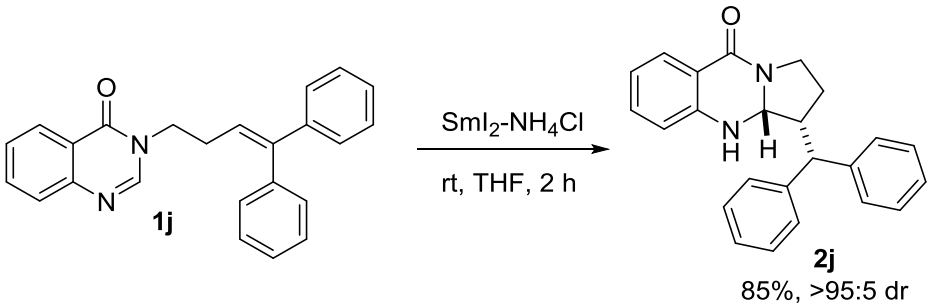


(3*S*,3a*R*)-3-(2,4-Dichlorobenzyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2h). According to the general procedure B, using **1h** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2h** (32.0 mg, 0.0922 mmol, 92%, >95:5 dr) as a white solid. M.p. = 218.4-220 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ ppm 7.93 (1 H, d, *J* = 7.8 Hz, Ar*H*), 7.43 (1 H, d, *J* = 2.0 Hz, Ar*H*), 7.29 - 7.35 (1 H, m, Ar*H*), 7.14 - 7.25 (2 H, m, Ar*H*), 6.91 (1 H, t, *J* = 7.5 Hz, Ar*H*), 6.72 (1 H, d, *J* = 8.0 Hz, Ar*H*), 5.23 (1 H, d, *J* = 5.0 Hz, NHC*H*), 4.23 (1 H, s, N*H*), 3.76 - 3.91 (1 H, m, 1 H from NC*H*$_2$CH$_2$), 3.60 - 3.71 (1 H, m, 1 H from NC*H*$_2$CH$_2$), 3.24 (1 H, dd, *J* = 13.9, 4.4 Hz, 1 H from ArC*H*$_2$CH), 2.71 - 2.82 (1 H, m, ArCH$_2$C*H*), 2.57 - 2.71 (1 H, m, 1 H from ArC*H*$_2$CH), 1.84 - 1.96 (1 H, m, 1 H from NCH$_2$C*H*$_2$), 1.80 (1 H, dd, *J* = 7.0, 3.5 Hz, 1 H from NCH$_2$C*H*$_2$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ ppm 162.4 (C=O), 147.2 (Ar*C*^{q}), 136.1 (Ar*C*^{q}), 134.9 (Ar*C*^{q}), 133.1 (Ar*C*H), 133.1 (Ar*C*^{q}), 132.1 (Ar*C*H), 129.6 (Ar*C*H), 128.3 (Ar*C*H), 127.2 (Ar*C*H), 119.9 (Ar*C*H), 117.5 (Ar*C*^{q}), 114.8 (Ar*C*H), 72.1

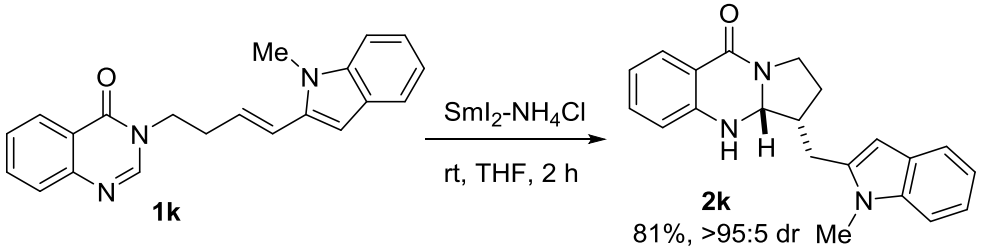
(NH*C*H), 42.5 (N*C*H$_2$CH$_2$), 41.7 (ArCH$_2$*C*H), 30.9 (Ar*C*H$_2$CH), 25.9 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3229, 2970, 1739, 1625, 1435, 1365, 1216, 769. **MS (ESI$^+$) *m/z* (%):** 347.1 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{17}N_2OCl_2$ (M + H$^+$): 347.0712. Found: 347.0706.



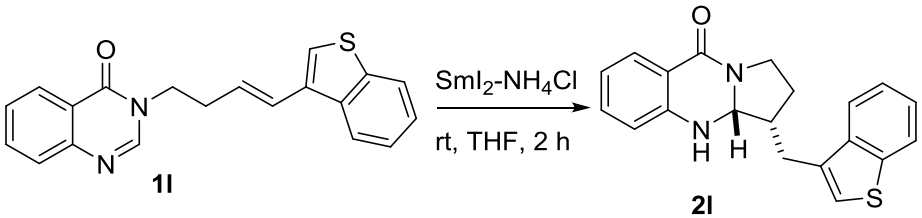
(3*S*,3a*R*)-3-(Naphthalen-1-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2i). According to the general procedure B, using **1i** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2i** (31.9 mg, 0.0972 mmol, 97%, >95:5 dr) as a light yellow solid. M.p. = 202.6-203.4 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.03 - 8.11 (1 H, m, Ar*H*), 7.87 - 7.97 (2 H, m, Ar*H*), 7.79 (1 H, d, *J* = 8.0 Hz, Ar*H*), 7.49 - 7.57 (2 H, m, Ar*H*), 7.41 - 7.48 (1 H, m, Ar*H*), 7.34 - 7.40 (1 H, m, Ar*H*), 7.28 - 7.33 (1 H, m, Ar*H*), 6.84 - 6.95 (1 H, m, Ar*H*), 6.71 (1 H, d, *J* = 8.0 Hz, Ar*H*), 5.26 (1 H, d, *J* = 5.0 Hz, NHC*H*), 4.47 (1 H, s, N*H*), 3.94 (1 H, dt, *J* = 12.0, 7.9 Hz, 1 H from NC*H*$_2$CH$_2$), 3.54 - 3.68 (2 H, m, 1 H from NC*H*$_2$CH$_2$ and 1 H from ArC*H*$_2$CH), 2.99 - 3.07 (1 H, m, 1 H from ArC*H*$_2$CH), 2.94 (1 H, dd, *J* = 10.0, 5.0 Hz, ArCH$_2$C*H*), 1.79 - 1.92 (2 H, m, NCH$_2$C*H*$_2$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 162.6 (C=O), 147.5 (Ar*C*^{q}), 135.7 (Ar*C*^{q}), 134.1 (Ar*C*^{q}), 133.1 (Ar*C*H), 131.9 (Ar*C*^{q}), 129.1 (Ar*C*H), 128.3 (Ar*C*H), 127.4 (Ar*C*H), 126.9 (Ar*C*H), 126.1 (Ar*C*H), 125.8 (Ar*C*H), 125.5 (Ar*C*H), 123.5 (Ar*C*H), 119.8 (Ar*C*H), 117.6 (Ar*C*^{q}), 115.0 (Ar*C*H), 72.1 (NH*C*H), 42.8 (N*C*H$_2$CH$_2$), 42.5 (ArCH$_2$*C*H), 30.5 (Ar*C*H$_2$CH), 26.9 (NCH$_2$*C*H$_2$). ν_{max} (thin film/cm^{-1}): 3268, 2945, 1629, 1482, 1434, 1216, 1029, 791, 763. **MS (ESI$^+$) *m/z* (%):** 329.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{22}H_{21}N_2O$ (M + H$^+$): 329.1648. Found: 329.1641.



(3*R*,3a*R*)-3-Benzhydryl-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2j). According to the general procedure B, using **1j** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2j** (30.0 mg, 0.0847 mmol, 85%, >95:5 dr) as a white solid. M.p. = 186-187.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.76 - 7.86 (1 H, m, Ar*H*), 7.46 (2 H, d, *J* = 7.3 Hz, Ar*H*), 7.31 - 7.41 (2 H, m, Ar*H*), 7.21 - 7.29 (5 H, m, Ar*H*), 7.11 - 7.21 (2 H, m, Ar*H*), 6.75 - 6.87 (1 H, m, Ar*H*), 6.30 (1 H, d, *J* = 7.8 Hz, Ar*H*), 5.08 (1 H, d, *J* = 7.0 Hz, NHC*H*), 4.16 (1 H, d, *J* = 11.8 Hz, Ph_2C*H*CH), 4.05 (1 H, ddd, *J* = 11.6, 6.7, 2.8 Hz, 1 H from NCH_2CH_2), 3.81 (1 H, s, N*H*), 3.29 - 3.41 (1 H, m, Ph_2CHC*H*), 3.26 (1 H, ddd, *J* = 11.7, 9.8, 6.7 Hz, 1 H from NCH_2CH_2), 1.60 - 1.78 (2 H, m, NCH_2CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 162.1 (C=O), 147.5 (ArC^q), 143.1 (ArC^q), 142.3 (ArC^q), 132.7 (Ar*C*H), 129.6 (2 × Ar*C*H), 128.9 (2 × Ar*C*H), 128.4 (Ar*C*H), 127.6 (2 × Ar*C*H), 127.5 (Ar*C*H), 127.4 (2 × Ar*C*H), 126.9 (Ar*C*H), 120.0 (Ar*C*H), 117.9 (ArC^q), 115.1 (Ar*C*H), 70.5 (NH*C*H), 51.8 (Ph_2*C*HCH), 47.1 (Ph_2CH*C*H), 44.5 (N*C*H_2CH_2), 29.7 (NCH_2*C*H_2). **IR (neat, cm^{-1}):** 3358, 2970, 1739, 1652, 1427, 1365, 1217, 772. **MS (ESI$^+$) *m/z* (%):** 355.2 (M + H^+); **HRMS (ESI$^+$):** calcd. for $C_{24}H_{23}N_2O$ (M + H^+): 355.1805. Found: 355.1800.

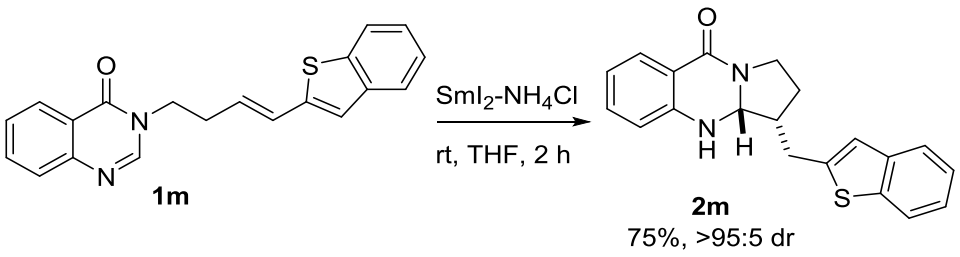


(3*R*,3a*R*)-3-((1-Methyl-1H-indol-2-yl)methyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2k). According to the general procedure B, using **1k** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2k** (26.8 mg, 0.0810 mmol, 81%, >95:5 dr) as a white solid. M.p. = 200-201.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.92 (1 H, dd, *J* = 7.8, 1.3 Hz, Ar*H*), 7.58 (1 H, d, *J* = 7.8 Hz, Ar*H*), 7.28 - 7.36 (1 H, m, Ar*H*), 7.18 - 7.27 (2 H, m, Ar*H*), 7.10 - 7.17 (1 H, m, Ar*H*), 6.82 - 6.92 (1 H, m, Ar*H*), 6.60 (1 H, d, *J* = 8.0 Hz, Ar*H*), 6.33 (1 H, s, Ar*H*), 5.26 (1 H, d, *J* = 5.5 Hz, NHC*H*), 4.43 (1 H, s, N*H*), 3.83 - 3.91 (1 H, m, 1 H from NCH_2CH$_2$), 3.68 - 3.71 (3 H, m, CH_3), 3.61 - 3.68 (1 H, m, 1 H from NCH_2CH$_2$), 3.24 (1 H, dd, *J* = 15.9, 7.2 Hz, 1 H from ArCH_2CH), 2.95 (1 H, td, *J* = 5.9, 4.5 Hz, ArCH$_2$C*H*), 2.80 (1 H, dd, *J* = 16.1, 7.5 Hz, 1 H from ArCH_2CH), 2.04 - 2.17 (1 H, m, 1 H from NCH$_2$CH_2), 1.93 - 2.03 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 162.5 (C=O), 147.4 (Ar*C*^{q}), 138.8 (Ar*C*^{q}), 137.5 (Ar*C*^{q}), 133.1 (Ar*C*H), 128.2 (Ar*C*H), 127.7 (Ar*C*^{q}), 121.2 (Ar*C*H), 119.9 (Ar*C*H), 119.7 (Ar*C*H), 119.7 (Ar*C*H), 117.3 (Ar*C*^{q}), 115.0 (Ar*C*H), 109.0 (Ar*C*H), 99.2 (Ar*C*H), 71.8 (NH*C*H), 42.7 (N*C*H$_2$CH$_2$), 41.0 (ArCH$_2$*C*H), 29.7 (*C*H$_3$), 27.8 (NCH$_2$*C*H$_2$), 25.5 (Ar*C*H$_2$CH). **IR (neat, cm^{-1}):** 3293, 2927, 1634, 1467, 1432, 1334, 1217, 749. **MS (ESI$^+$) *m/z* (%):** 332.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{21}H_{22}N_3O$ (M + H$^+$): 332.1757. Found: 332.1746.



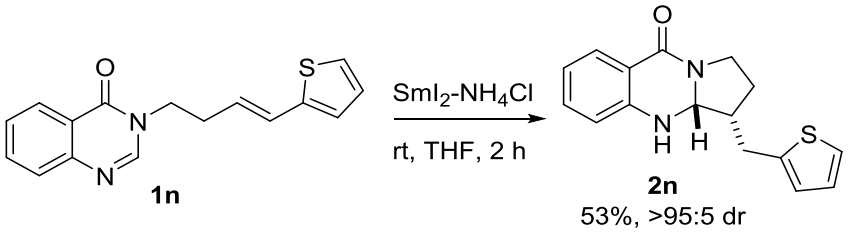
(3*S*,3a*R*)-3-(Benzo[*b*]thiophen-3-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2l). According to the general procedure B, using **1l** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1

h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2l** (21.5 mg, 0.0644 mmol, 64%, >95:5 dr) as a light yellow solid. M.p. = 275-276.3 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ ppm 7.87 - 7.99 (2 H, m, Ar*H*), 7.73 - 7.82 (1 H, m, Ar*H*), 7.33 - 7.47 (2 H, m, Ar*H*), 7.27 - 7.31 (1 H, m, Ar*H*), 7.17 (1 H, s, Ar*H*), 6.89 (1 H, t, *J* = 7.4 Hz, Ar*H*), 6.66 (1 H, d, *J* = 7.9 Hz, Ar*H*), 5.24 (1 H, d, *J* = 5.0 Hz, NHC*H*), 4.41 (1 H, s, N*H*), 3.88 (1 H, dt, *J* = 12.0, 7.9 Hz, 1 H from NC$H_2$$CH_2$), 3.64 (1 H, ddd, *J* = 12.2, 8.3, 4.4 Hz, 1 H from NC$H_2$$CH_2$), 3.23 - 3.39 (1 H, m, 1 H from ArCH_2CH), 2.82 - 2.99 (2 H, m, ArCH_2C*H* and 1 H from ArCH_2CH), 1.94 - 2.04 (1 H, m, 1 H from NCH_2CH_2), 1.85 - 1.93 (1 H, m, 1 H from NCH_2CH_2). **^{13}C NMR (126 MHz, $CDCl_3$):** δ ppm 162.5 (C=O), 147.4 (Ar*C*^{q}), 140.6 (Ar*C*^{q}), 138.8 (Ar*C*^{q}), 134.2 (Ar*C*^{q}), 133.1 (Ar*C*H), 128.3 (Ar*C*H), 124.6 (Ar*C*H), 124.2 (Ar*C*H), 123.1 (Ar*C*H), 122.3 (Ar*C*H), 121.6 (Ar*C*H), 119.8 (Ar*C*H), 117.5 (Ar*C*^{q}), 115.0 (Ar*C*H), 71.9 (NH*C*H), 42.7 (N*C*$H_2$$CH_2$), 41.7 (Ar$CH_2$*C*H), 27.3 (N$CH_2$*C*$H_2$), 26.7 (Ar*C*$H_2$CH). **IR (neat, cm^{-1}):** 3295, 2928, 1667, 1611, 1467, 1383, 1334, 907, 727, 695. **MS (ESI$^+$) *m/z* (%):** 335.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{20}H_{19}N_2OS$ (M + H$^+$): 335.1213. Found: 335.1208.



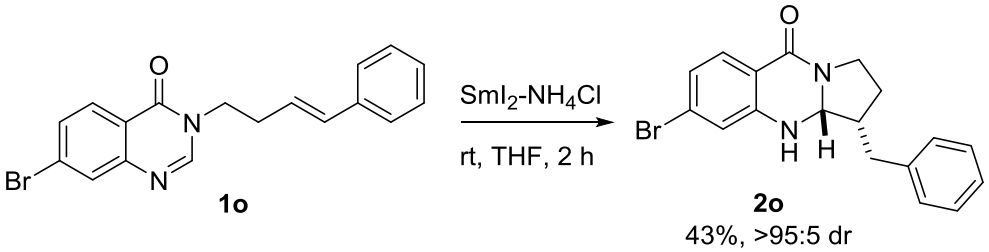
(3*R*,3a*R*)-3-(Benzo[*b*]thiophen-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2m). According to the general procedure B, using **1m** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2m** (25.0 mg, 0.0748 mmol, 75%, >95:5 dr) as a light yellow solid. M.p. = 232.1-234 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ ppm 7.92 (1 H, d, *J* = 7.6 Hz, Ar*H*), 7.80 (1 H, d, *J* = 7.9 Hz, Ar*H*), 7.71 (1 H, d, *J* = 7.9 Hz, Ar*H*), 7.28 - 7.42 (3 H, m, Ar*H*), 7.10

(1 H, s, Ar*H*), 6.89 (1 H, t, *J* = 7.6 Hz, Ar*H*), 6.67 (1 H, d, *J* = 7.9 Hz, Ar*H*), 5.24 (1 H, d, *J* = 5.0 Hz, NHC*H*), 4.36 (1 H, s, N*H*), 3.86 (1 H, dt, *J* = 12.0, 7.9 Hz, 1 H from NCH_2CH$_2$), 3.65 (1 H, ddd, *J* = 12.2, 8.3, 4.4 Hz, 1 H from NCH_2CH$_2$), 3.38 (1 H, dd, *J* = 15.3, 6.1 Hz, 1 H from ArCH_2CH), 2.99 (1 H, dd, *J* = 15.3, 9.3 Hz, 1 H from ArCH_2CH), 2.77 - 2.89 (1 H, m, ArCH$_2$C*H*), 1.97 - 2.11 (1 H, m, 1 H from NCH$_2$CH_2), 1.87 - 1.97 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (126 MHz, CDCl$_3$):** δ ppm 162.4 (C=O), 147.3 (Ar*C*^{q}), 143.4 (Ar*C*^{q}), 140.0 (Ar*C*^{q}), 139.4 (Ar*C*^{q}), 133.1 (Ar*C*H), 128.3 (Ar*C*H), 124.4 (Ar*C*H), 124.0 (Ar*C*H), 123.0 (Ar*C*H), 122.2 (Ar*C*H), 122.1 (Ar*C*H), 119.9 (Ar*C*H), 117.5 (Ar*C*^{q}), 114.9 (Ar*C*H), 71.7 (NH*C*H), 43.5 (ArCH$_2$*C*H), 42.6 (N*C*H$_2$CH$_2$), 29.2 (Ar*C*H$_2$CH), 26.9 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3297, 2932, 1638, 1482, 905, 712, 649. **MS (ESI$^+$) *m/z* (%):** 335.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{20}H_{19}N_2OS$ (M + H$^+$): 335.1213. Found: 335.1209.



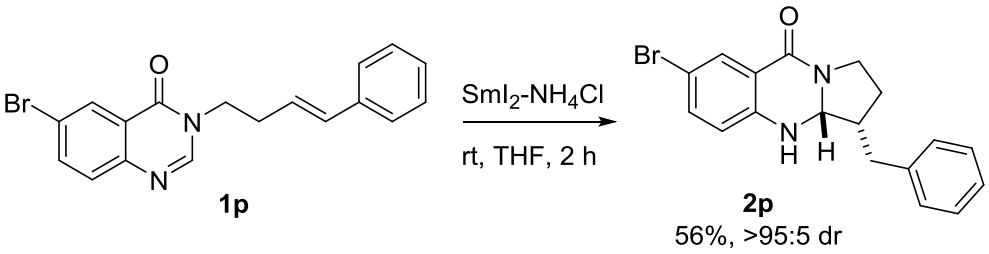
(3*R*,3a*R*)-3-(Thiophen-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2n). According to the general procedure B, using **1n** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2n** (15.1 mg, 0.0532 mmol, 53%, >95:5 dr) as a light yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$):** δ ppm 7.84 - 7.94 (1 H, m, Ar*H*), 7.26 - 7.31 (1 H, m, Ar*H*), 7.17 - 7.21 (1 H, m, Ar*H*), 6.97 (1 H, dd, *J* = 5.0, 3.5 Hz, Ar*H*), 6.86 - 6.92 (2 H, m, Ar*H*), 6.66 (1 H, d, *J* = 7.8 Hz, Ar*H*), 5.19 (1 H, d, *J* = 5.5 Hz, NHC*H*), 4.31 (1 H, s, N*H*), 3.83 (1 H, dt, *J* = 12.0, 7.8 Hz, 1 H from NCH_2CH$_2$), 3.61 (1 H, ddd, *J* = 12.2, 8.1, 4.5 Hz, 1 H from NCH_2CH$_2$), 3.30 (1 H, dd, *J* = 15.3, 6.5 Hz, 1 H from ArCH_2CH), 2.87 - 3.02 (1 H, m, 1 H from ArCH_2CH), 2.62 - 2.82 (1 H, m, ArCH$_2$C*H*), 1.80 - 2.10 (2 H, m, NCH$_2$CH_2). **^{13}C NMR (101**

MHz, $CDCl_3$): δ ppm 162.4 (C=O), 147.4 (Ar*C*^{q}), 142.3 (Ar*C*^{q}), 133.0 (Ar*C*H), 128.3 (Ar*C*H), 127.1 (Ar*C*H), 125.5 (Ar*C*H), 124.0 (Ar*C*H), 119.8 (Ar*C*H), 117.5 (Ar*C*^{q}), 114.9 (Ar*C*H), 71.6 (NH*C*H), 44.0 (ArCH$_2$*C*H), 42.7 (N*C*H$_2$CH$_2$), 28.3 (Ar*C*H$_2$CH), 27.1 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 2969, 2346, 1678, 1612, 1467, 1386, 1217, 753, 695. **MS (ESI^+) *m/z* (%):** 285.1 (M + H^+); **HRMS (ESI^+):** calcd. for $C_{16}H_{17}N_2OS$ (M + H^+): 285.1056. Found: 285.1048.

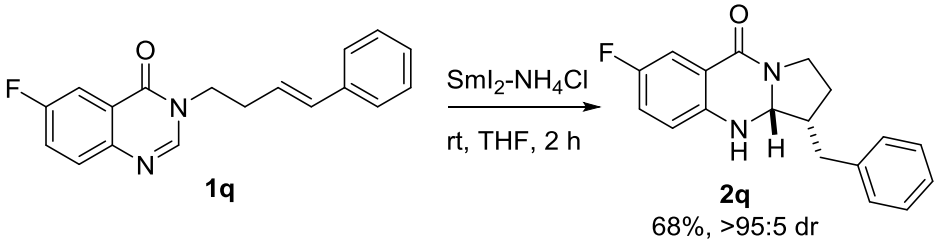


(3*S*,3a*R*)-3-Benzyl-6-bromo-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2o). According to the general procedure B, using **1o** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2o** (15.3 mg, 0.0430 mmol, 43%, >95:5 dr) as a white solid. M.p. = 200-202 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.92 (1 H, d, *J* = 7.0 Hz, Ar*H*), 7.29 - 7.37 (2 H, m, Ar*H*), 7.21 - 7.26 (3 H, m, Ar*H*), 6.88 (1 H, t, *J* = 7.5 Hz, Ar*H*), 6.66 (1 H, d, *J* = 8.0 Hz, Ar*H*), 5.18 (1 H, d, *J* = 5.5 Hz, NHC*H*), 4.28 (1 H, s, N*H*), 3.85 (1 H, dt, *J* = 12.0, 7.8 Hz, 1 H from NC*H*$_2$CH$_2$), 3.61 (1 H, ddd, *J* = 12.0, 8.0, 4.5 Hz, 1 H from NC*H*$_2$CH$_2$), 3.10 (1 H, dd, *J* = 13.6, 5.5 Hz, 1 H from ArC*H*$_2$CH), 2.72 - 2.84 (1 H, m, ArCH$_2$C*H*), 2.55 - 2.72 (1 H, m, 1 H from ArC*H*$_2$CH), 1.87 - 1.97 (1 H, m, 1 H from NCH$_2$C*H*$_2$), 1.77 - 1.87 (1 H, m, 1 H from NCH$_2$C*H*$_2$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 162.5 (C=O), 147.4 (Ar*C*^{q}), 139.7 (Ar*C*^{q}), 133.0 (Ar*C*H), 128.9 (2 × Ar*C*H), 128.7 (Ar*C*^{q} and Ar*C*H), 128.3 (Ar*C*H), 126.5 (Ar*C*H), 119.7 (Ar*C*H), 117.6 (Ar*C*^{q}), 114.9 (Ar*C*H), 71.9 (NH*C*H), 43.4 (ArCH$_2$*C*H), 42.8 (N*C*H$_2$CH$_2$), 33.8 (Ar*C*H$_2$CH), 26.8 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3274, 3025, 2944. 1629, 1483, 1434, 907, 729, 697. **MS (ESI^+) *m/z* (%):** 357.2 (M + H^+); **HRMS (ESI^+):** calcd. for $C_{18}H_{18}N_2OBr$ (M +

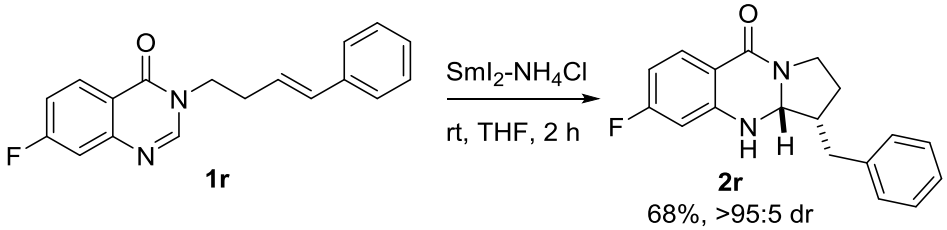
H^+): 357.0597. Found: 357.0585.



(3*S*,3a*R*)-3-Benzyl-7-bromo-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2p). According to the general procedure B, using **1p** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2p** (20.0 mg, 0.0562 mmol, 56%, >95:5 dr) as a white solid. M.p. = 213.4-215 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 8.01 (1 H, d, *J* = 2.3 Hz, Ar*H*), 7.30 - 7.38 (3 H, m, Ar*H*), 7.19 - 7.26 (3 H, m, Ar*H*), 6.55 (1 H, d, *J* = 8.5 Hz, Ar*H*), 5.15 (1 H, d, *J* = 5.5 Hz, NHC*H*), 4.35 (1 H, s, N*H*), 3.82 (1 H, dt, *J* = 12.0, 8.0 Hz, 1 H from NCH_2CH$_2$), 3.60 (1 H, ddd, *J* = 12.2, 8.1, 4.5 Hz, 1 H from NCH_2CH$_2$), 3.07 (1 H, dd, *J* = 13.9, 5.9 Hz, 1 H from ArCH_2CH), 2.71 - 2.81 (1 H, m, ArCH$_2$C*H*), 2.60 - 2.70 (1 H, m, 1 H from ArCH_2CH), 1.86 - 1.98 (1 H, m, 1 H from NCH$_2$CH_2), 1.77 - 1.86 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.2 (C=O), 146.3 (ArC^q), 139.4 (ArC^q), 135.6 (Ar*C*H), 130.8 (Ar*C*H), 128.8 (2 × Ar*C*H), 128.8 (2 × Ar*C*H), 126.6 (Ar*C*H), 119.2 (ArC^q), 116.6 (Ar*C*H), 111.8 (ArC^q), 71.9 (NH*C*H), 43.3 (ArCH$_2$*C*H), 42.9 (N*C*H$_2$CH$_2$), 33.8 (Ar*C*H$_2$CH), 26.8 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3265, 3001, 2346, 1735,1634, 1492, 1450, 1365, 1216, 752, 662. **MS (ESI$^+$) *m/z* (%):** 357.2 (M + H^+); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{18}N_2OBr$ (M + H^+): 357.0597. Found: 357.0590.

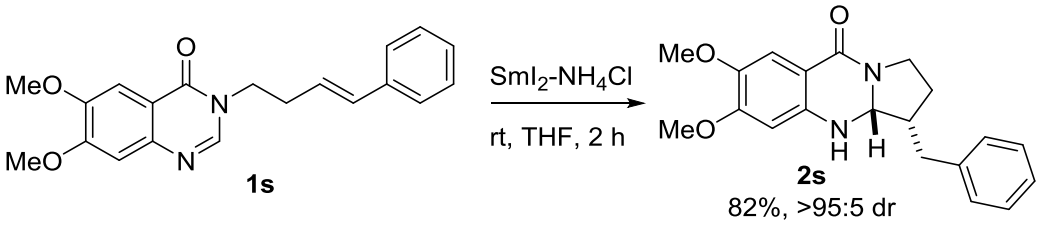


(3*S*,3a*R*)-3-Benzyl-7-fluoro-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2q). According to the general procedure B, using **1q** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2q** (20.0 mg, 0.0676 mmol, 68%, >95:5 dr) as a white solid. M.p. = 175.1-176 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.61 (1 H, dd, *J* = 8.8, 3.0 Hz, Ar*H*), 7.31 - 7.40 (2 H, m, Ar*H*), 7.21 - 7.26 (3 H, m, Ar*H*), 7.01 (1 H, td, *J* = 8.4, 2.8 Hz, Ar*H*), 6.63 (1 H, dd, *J* = 8.7, 4.1 Hz, Ar*H*), 5.14 (1 H, d, *J* = 5.5 Hz, NHC*H*), 4.15 (1 H, s, N*H*), 3.84 (1 H, dt, *J* = 12.0, 7.7 Hz, 1 H from NCH_2CH_2), 3.60 (1 H, ddd, *J* = 12.2, 8.0, 4.6 Hz, 1 H from NCH_2CH_2), 3.08 (1 H, dd, *J* = 13.8, 5.8 Hz, 1 H from $ArCH_2CH$), 2.72 - 2.82 (1 H, m, $ArCH_2CH$), 2.62 - 2.71 (1 H, m, 1 H from $ArCH_2CH$), 1.87 - 1.98 (1 H, m, 1 H from NCH_2CH_2), 1.77 - 1.87 (1 H, m, 1 H from NCH_2CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 161.5 (C=O), 156.9 (d, *J* = 239.4 Hz, CF), 143.6 (d, *J* = 2.0 Hz, ArC^q), 139.5 (ArC^q), 128.8 (2 × ArCH), 128.8 (2 × ArCH), 126.6 (ArCH), 120.2 (d, *J* = 24.2 Hz, ArCH), 119.0 (d, *J* = 7.0 Hz, ArC^q), 116.3 (d, *J* = 7.1 Hz, ArCH), 114.3 (d, *J* = 25.3 Hz, ArCH), 72.1 (NHCH), 43.3 ($ArCH_2CH$), 42.9 (NCH_2CH_2), 33.8 ($ArCH_2CH$), 27.0 (NCH_2CH_2). **IR (neat, cm^{-1}):** 3271, 2944, 1634, 1494, 1451, 1252, 1193, 908, 732. **MS (ESI$^+$) *m/z* (%):** 297.2 ($M + H^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{18}N_2OF$ ($M + H^+$): 297.1398. Found: 297.1387.



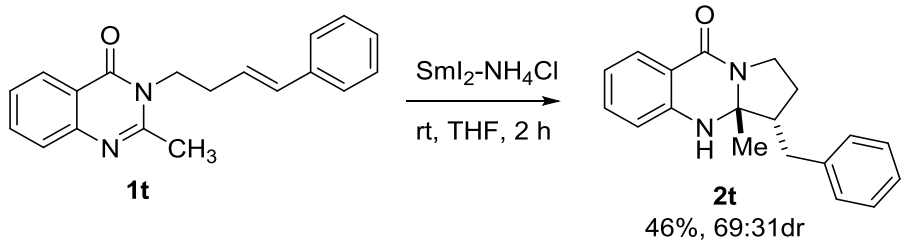
(3*S*,3a*R*)-3-Benzyl-6-fluoro-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2r). According to the general procedure B, using **1r** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2r**

(20.1 mg, 0.0679 mmol, 68%, >95:5 dr) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.89 (1 H, dd, *J* = 8.5, 6.5 Hz, Ar*H*), 7.31 - 7.38 (2 H, m, Ar*H*), 7.18 - 7.27 (3 H, m, Ar*H*), 6.55 (1 H, td, *J* = 8.7, 2.3 Hz, Ar*H*), 6.35 (1 H, dd, *J* = 10.0, 2.3 Hz, Ar*H*), 5.19 (1 H, d, *J* = 5.3 Hz, NHC*H*), 4.55 (1 H, s, N*H*), 3.82 (1 H, dt, *J* = 11.9, 8.0 Hz, 1 H from NCH_2CH$_2$), 3.60 (1 H, ddd, *J* = 12.1, 8.2, 4.3 Hz, 1 H from NCH_2CH$_2$), 3.08 (1 H, dd, *J* = 14.1, 5.8 Hz, 1 H from ArCH_2CH), 2.69 - 2.81 (1 H, m, ArCH$_2$C*H*), 2.56 - 2.69 (1 H, m, 1 H from ArCH_2CH), 1.88 - 1.97 (1 H, m, 1 H from NCH$_2$CH_2), 1.75 - 1.88 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 166.0 (d, *J* = 252.5 Hz, CF), 161.9 (C=O), 149.4 (d, *J* = 12.1 Hz, ArC^q), 139.5 (ArC^q), 130.7 (d, *J* = 11.1 Hz, Ar*C*H), 128.9 (2 × Ar*C*H), 128.8 (2 × Ar*C*H), 126.5 (Ar*C*H), 113.8 (d, *J* = 2.0 Hz, ArC^q), 107.1 (d, *J* = 24.2 Hz, Ar*C*H), 101.4 (d, *J* = 25.3 Hz, Ar*C*H), 72.0 (NH*C*H), 43.3 (ArCH$_2$*C*H), 42.7 (N*C*H$_2$CH$_2$), 33.7 (Ar*C*H$_2$CH), 26.7 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3026, 2360, 2249, 1673, 1612, 1478, 1442, 1281, 1144, 908, 776. **MS (ESI$^+$) *m/z* (%):** 297.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{18}N_2OF$ (M + H$^+$): 297.1398. Found: 297.1386.



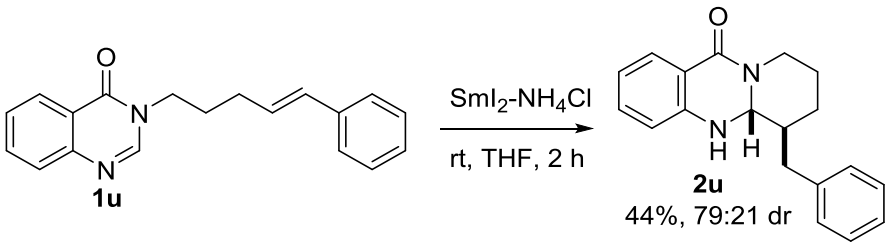
(3*S*,3a*R*)-3-Benzyl-6,7-dimethoxy-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2s). According to the general procedure B, using **1s** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2s** (27.6 mg, 0.0817 mmol, 82%, >95:5 dr) as a white solid. M.p. = 169.4-170.2 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ ppm 7.40 (1 H, s, Ar*H*), 7.30 - 7.36 (2 H, m, Ar*H*), 7.15 - 7.26 (3 H, m, Ar*H*), 6.21 (1 H, s, Ar*H*), 5.11 (1 H, d, *J* = 5.4 Hz, NHC*H*), 4.14 (1 H, s, N*H*), 3.86 (3 H, s, CH_3), 3.85 (3 H, s, CH_3), 3.75 - 3.83 (1 H, m, 1 H from NCH_2CH$_2$),

3.58 (1 H, ddd, *J* = 12.2, 8.0, 4.7 Hz, 1 H from NCH_2CH$_2$), 3.08 (1 H, dd, *J* = 13.7, 5.5 Hz, 1 H from ArCH_2CH), 2.73 (1 H, dd, *J* = 10.2, 5.2 Hz, ArCH$_2$C*H*), 2.59 - 2.69 (1 H, m, 1 H from ArCH_2CH), 1.85 - 1.93 (1 H, m, 1 H from NCH$_2$CH_2), 1.74 - 1.84 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (126 MHz, CDCl$_3$):** δ ppm 162.6 (C=O), 153.4 (Ar*C*^{q}), 143.4 (Ar*C*^{q}), 142.7 (Ar*C*^{q}), 139.7 (Ar*C*^{q}), 128.8 (2 × Ar*C*H), 128.7 (2 × Ar*C*H), 126.5 (Ar*C*H), 110.0 (Ar*C*H), 109.9 (Ar*C*^{q}), 98.8 (Ar*C*H), 72.3 (NH*C*H), 56.3 (O*C*H$_3$), 56.0 (O*C*H$_3$), 43.4 (ArCH$_2$*C*H), 42.7 (N*C*H$_2$CH$_2$), 33.8 (Ar*C*H$_2$CH), 27.0 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3256, 2936, 1611, 1451, 1265, 1223, 1114, 1014, 910, 727, 645. **MS (ESI$^+$) *m/z* (%):** 339.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{20}H_{23}N_2O_3$ (M + H$^+$): 339.1703. Found: 339.1691.



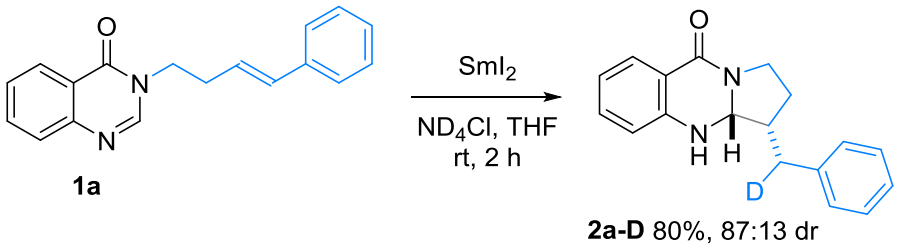
(3*S*,3a*R*)-3-Benzyl-3a-methyl-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2t). According to the general procedure B, using **1t** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2t** (13.5 mg, 0.0462 mmol, 46%, 69:31 dr) as a white solid. M.p. = 221-223 ^{o}C. **^{1}H NMR (500 MHz, CDCl$_3$):** δ ppm 7.91 (1 H, d, *J* = 7.6 Hz, Ar*H*), 7.28 - 7.36 (3 H, m, Ar*H*), 7.19 - 7.26 (3 H, m, Ar*H*), 6.85 (1 H, t, *J* = 7.6 Hz, Ar*H*), 6.62 (1 H, d, *J* = 7.9 Hz, Ar*H*), 4.13 (1 H, s, N*H*), 3.92 (1 H, dt, *J* = 12.3, 7.7 Hz, 1 H from NCH_2CH$_2$), 3.55 (1 H, ddd, *J* = 12.5, 8.4, 4.7 Hz, 1 H from NCH_2CH$_2$), 3.12 (1 H, dd, *J* = 13.1, 4.9 Hz, 1 H from ArCH_2CH), 2.51 - 2.64 (2 H, m, 1 H from ArCH_2CH and ArCH$_2$C*H*), 1.95 - 2.04 (1 H, m, 1 H from NCH$_2$CH_2), 1.74 - 1.80 (1 H, m, 1 H from NCH$_2$CH_2), 1.48 (3 H, s, CH_3). **^{13}C NMR (126 MHz, CDCl$_3$):** δ ppm 161.5 (C=O), 145.8 (Ar*C*^{q}), 140.0 (Ar*C*^{q}), 133.1 (Ar*C*H), 129.0 (2 × Ar*C*H), 128.7 (2 × Ar*C*H), 128.2 (Ar*C*H), 126.4 (Ar*C*H), 119.1 (Ar*C*H), 116.1 (Ar*C*^{q}), 114.9 (Ar*C*H), 77.5 (*C*^{q}),

50.5 (ArCH$_2$*C*H), 42.7 (N*C*H$_2$CH$_2$), 35.6 (Ar*C*H$_2$CH), 26.9 (*C*H$_3$), 26.8 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3269, 2970, 1612, 1484, 1417, 1217, 750. **MS (ESI$^+$) *m/z* (%):** 293.2 (M + H$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{21}N_2O$ (M + H$^+$): 293.1648. Found: 293.1646.



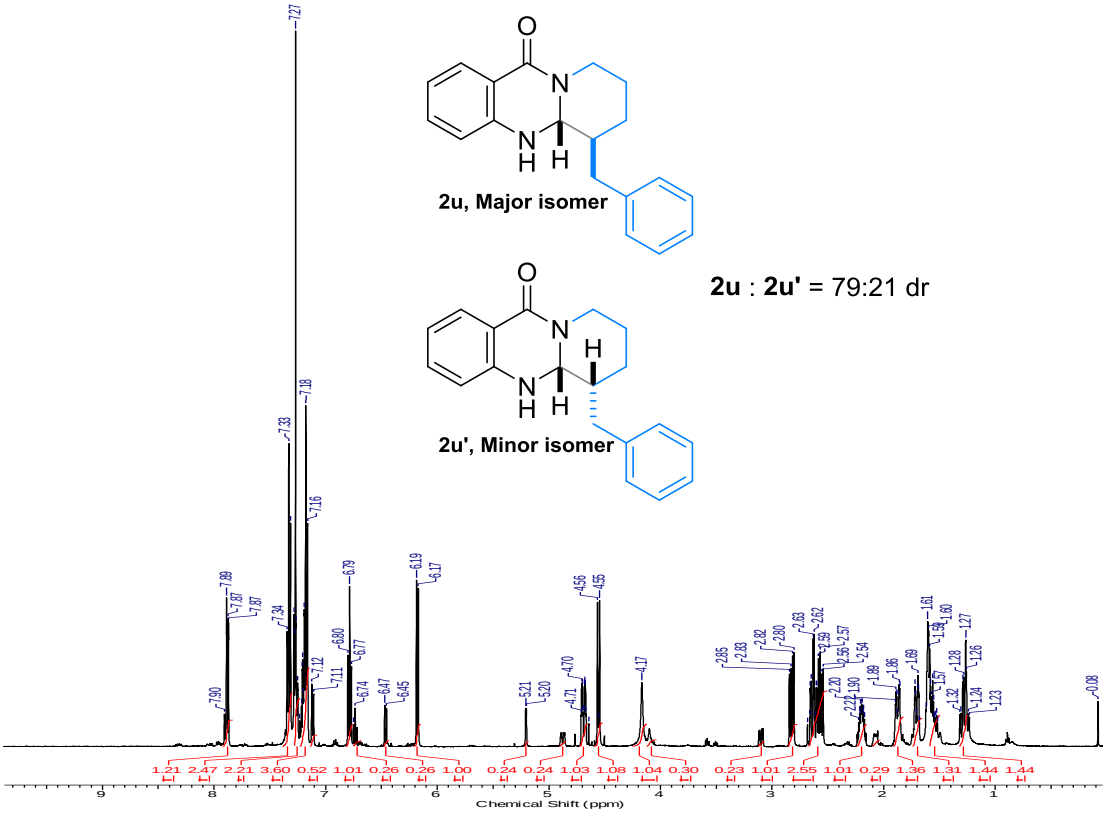
(5a*R*,6*S*)-6-Benzyl-5,5a,6,7,8,9-hexahydro-11H-pyrido[2,1-*b*]quinazolin-11-one (2u). According to the general procedure B, using **1u** (0.10 mmol), SmI_2 (0.50 mmol, 5 equiv, 5.0 mL, 0.10 M) and NH_4Cl (16 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2u** (12.9 mg, 0.0442 mmol, 44%, 79:21 dr) as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$):** (major diastereomer only) δ ppm 7.83 - 7.92 (1 H, m, Ar*H*), 7.30 - 7.39 (2 H, m, Ar*H*), 7.23 - 7.28 (2 H, m, Ar*H*), 7.14 - 7.23 (2 H, m, Ar*H*), 6.75 - 6.82 (1 H, m, Ar*H*), 6.18 (1 H, d, *J* = 7.9 Hz, Ar*H*), 4.69 (1 H, ddt, *J* = 13.5, 4.3, 2.0, 2.0 Hz, 1 H from NC*H*$_2$), 4.55 (1 H, d, *J* = 9.3 Hz, NHC*H*), 4.17 (1 H, s, N*H*), 2.83 (1 H, dd, *J* = 13.7, 6.8 Hz, 1 H from ArC*H*$_2$CH), 2.51 - 2.68 (2 H, m, 1 H from ArC*H*$_2$CH and 1 H from NC*H*$_2$), 2.15 - 2.25 (1 H, m, ArCH$_2$C*H*), 1.83 - 1.92 (1 H, m, 1 H from NCH$_2$CH$_2$C*H*$_2$), 1.66 - 1.74 (1 H, m, 1 H from NCH$_2$C*H*$_2$CH$_2$), 1.50 - 1.59 (1 H, m, 1 H from NCH$_2$C*H*$_2$CH$_2$), 1.25 - 1.32 (1 H, m, 1 H from NCH$_2$CH$_2$C*H*$_2$). **^{13}C NMR (126 MHz, $CDCl_3$):** (major diastereomer only) δ ppm 163.6 (C=O), 145.1 (Ar*C*^{q}), 139.2 (Ar*C*^{q}), 133.3 (Ar*C*H), 128.97 (2 × Ar*C*H), 128.87 (2 × Ar*C*H), 128.4 (Ar*C*H), 126.6 (Ar*C*H), 118.8 (Ar*C*H), 115.1 (Ar*C*^{q}), 114.1 (Ar*C*H), 74.3 (NH*C*H), 43.14 (N*C*H$_2$), 43.10 (ArCH$_2$*C*H), 39.4 (Ar*C*H$_2$CH), 30.1 (NCH$_2$CH$_2$*C*H$_2$), 24.1 (NCH$_2$*C*H$_2$CH$_2$). **IR (neat, cm^{-1}):** 3303, 2940, 1738, 1612, 1365, 1229, 750. **MS (ESI$^+$) *m/z* (%):** 331.1 (M + K$^+$); **HRMS (ESI$^+$):** calcd. for $C_{19}H_{21}N_2O$ (M + H$^+$): 293.1648. Found: 293.1644.

Deuterium Labelling Experiment

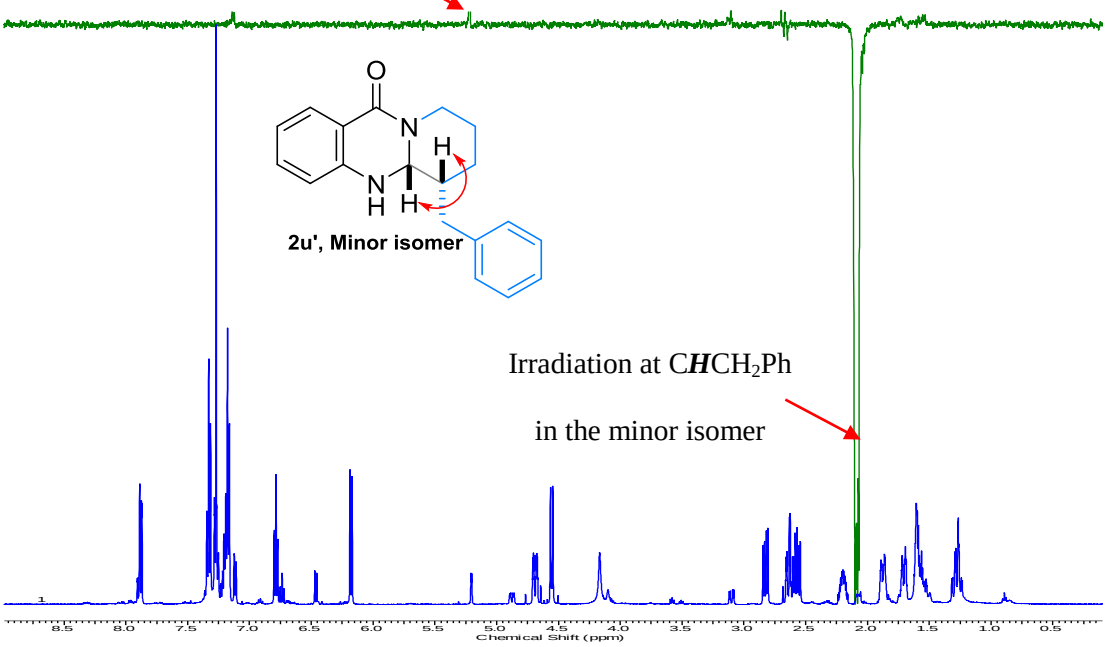


(3*S*,3a*R*)-3-(Phenylmethyl-*d*)-2,3,3a,4-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (2a-D). According to the general procedure B, using **1a** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M) and ND_4Cl (18 mg, 0.3 mmol, 3 equiv) with a slow addition over 1 h, stirring at room temperature for 1 h and purification by chromatography (50% EtOAc/hexanes), gave **2a-D** (22.3 mg, 0.0799 mmol, 80%, 83:17 dr) as a yellow solid. M.p. = 165-167 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ ppm 7.92 (1 H, dd, *J* = 7.8, 1.3 Hz, Ar*H*), 7.17 - 7.38 (6 H, m, Ar*H*), 6.83 - 6.93 (1 H, m, Ar*H*), 6.67 (1 H, d, *J* = 8.0 Hz, Ar*H*), 5.18 (1 H, d, *J* = 5.3 Hz, NHC*H*), 4.31 (1 H, s, N*H*), 3.85 (1 H, dt, *J* = 11.9, 7.7 Hz, 1 H from NCH_2CH$_2$), 3.61 (1 H, ddd, *J* = 12.2, 8.1, 4.5 Hz, 1 H from NCH_2CH$_2$), 2.70 - 2.80 (1 H, m, ArCH$_2$C*H*), 2.66 (d, *J* = 9.9 Hz, 1 H from ArC*H*DCH), 1.87 - 1.96 (1 H, m, 1 H from NCH$_2$CH_2), 1.77 - 1.87 (1 H, m, 1 H from NCH$_2$CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ ppm 162.5 (C=O), 147.5 (ArC^q), 139.7 (ArC^q), 133.0 (Ar*C*H), 128.9 (2 × Ar*C*H), 128.7 (2 × Ar*C*H), 128.3 (Ar*C*H), 126.5 (Ar*C*H), 119.7 (Ar*C*H), 117.6 (ArC^q), 114.9 (Ar*C*H), 71.9 (NH*C*H), 43.4 (ArCHD*C*H), 42.8 (N*C*H$_2$CH$_2$), 33.5 (t, *J* = 19.2 Hz, Ar*C*HDCH), 26.8 (NCH$_2$*C*H$_2$). **IR (neat, cm^{-1}):** 3268, 2970, 1738, 1632, 1435, 1365, 1217, 758. **MS (ESI$^+$) *m/z* (%):** 318.1 (M + K$^+$); **HRMS (ESI$^+$):** calcd. for $C_{18}H_{17}DN_2OK$ (M + K$^+$): 318.1113. Found: 318.1107.

NOE Study for 2u

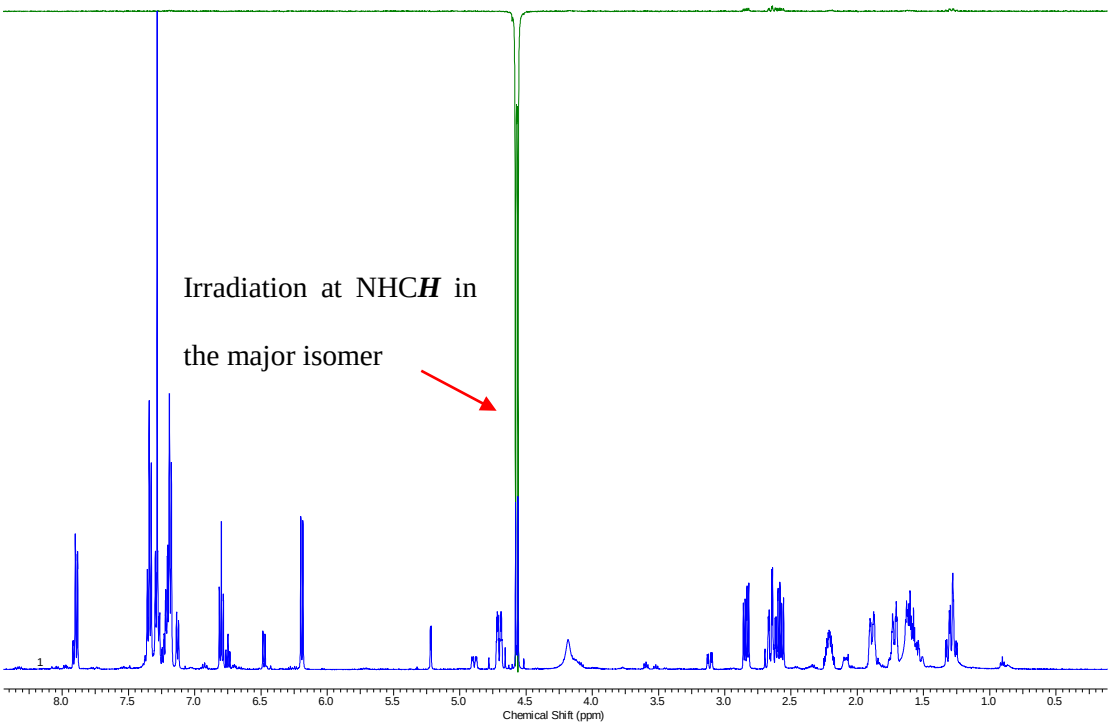


NHC***H*** in the minor isomer

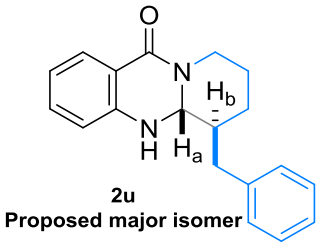


Irradiation at C***H***CH_2Ph

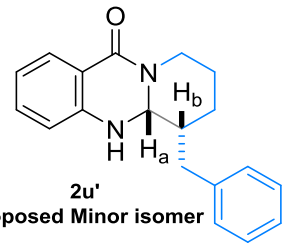
in the minor isomer



When we irraditated the C***H***CH_2Ph in the minor isomer, we observed the NOE peak (2%) of the NHC***H*** in the minor isomer. However, when we irraditated the NHC***H*** in the major isomer, we did not observe any NOE peak for the C***H***CH_2Ph in the major isomer. So we propose the following stereochemistry:

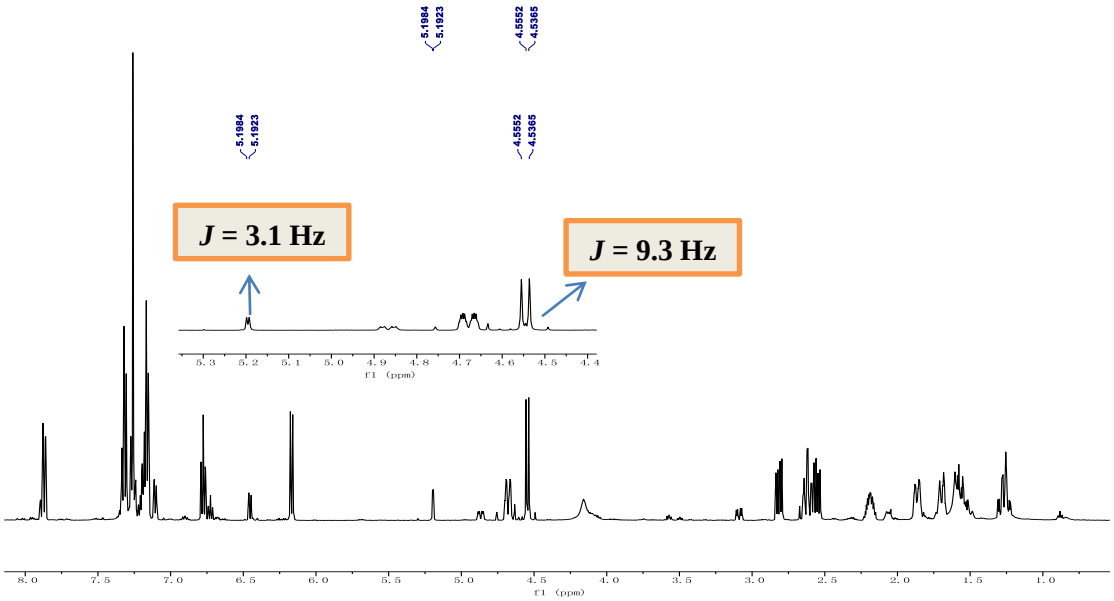


2u
Proposed major isomer



2u'
Proposed Minor isomer

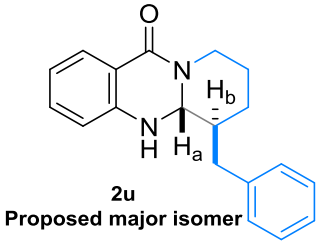
Proposed Stereochemistry of 2u



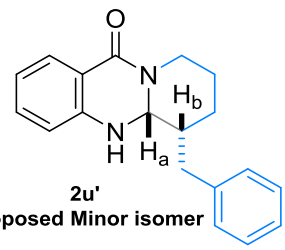
From the ^{1}H NMR spectra, the *J* value coupling constant of H_a in the major isomer is 9.3 Hz, the *J* value coupling constant of H_a in the minor isomer is 3.1 Hz.

The 3D chemical structures of the major and minor isomers for **2u** were calculated using MM2 minimization in Chem3D (version 16.0.1.4, Perkin Elmer) and the 3D mol files exported to MSpin (version 2.3.2-694, MestReLab Research S. L.). ^{3}J H_a,H_b coupling values were calculated using the Karplus option in the JCoupling tool of MSpin.[8] When H_a and H_b are *anti*, *J* value coupling constant is calculated as 9.3 Hz which matches the major isomer (*J* = 9.3 Hz), see Figure S 1. When H_a and H_b are *syn*, *J* value coupling constant is calculated as 4.9 Hz which matches the minor isomer (*J* = 3.1 Hz), see Figure S 2.

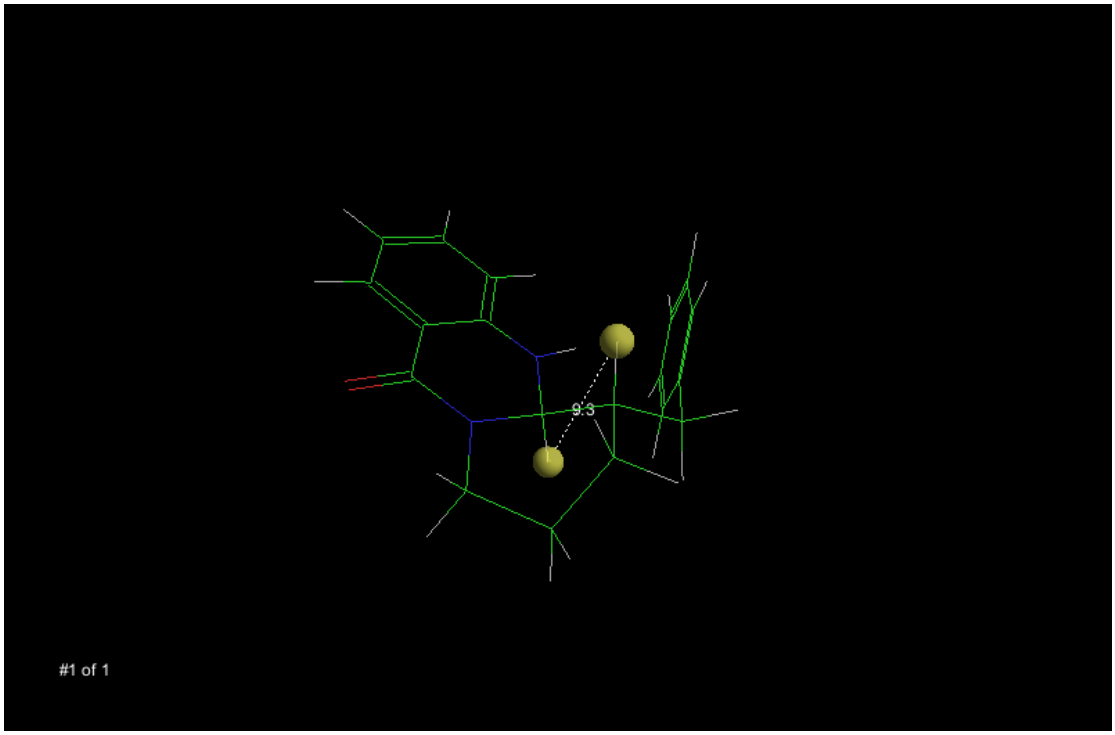
We therefore propose the following stereochemistry and it matches the results we observe from NOE study:



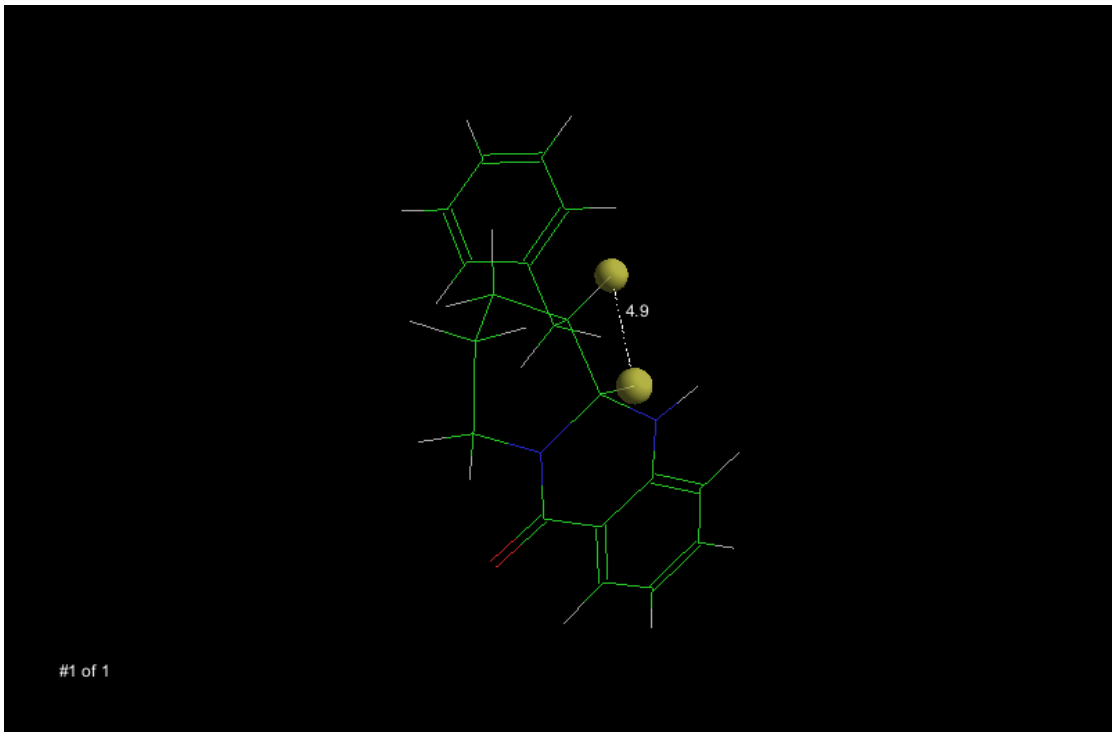
2u
Proposed major isomer



2u'
Proposed Minor isomer



Figture S1. Calculated *J* value coupling constant when the H_a and H_b are *anti*.



Figture S2. Calculated *J* value coupling constant when the H_a and H_b are *syn*.

X-ray structure of 2a

CCDC 1846530

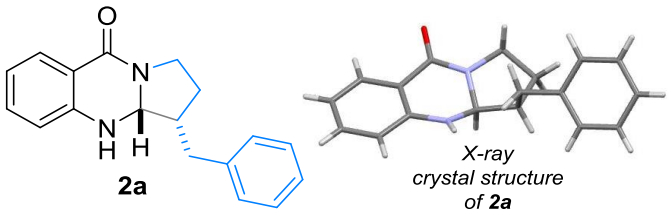


Table S1. Crystal data and details of data collection and refinement for compound **2a**

Bond precision:	C-C = 0.0034 A	Wavelength = 0.71073	
Cell:	a = 22.8586(15)	b = 5.0654(4)	c = 13.0500(8)
	alpha = 90	beta = 98.008(6)	gamma = 90
Temperature:	150 K		
	Calculated	Reported	
Volume	1496.30(18)	1496.30(18)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	$C_{18}H_{18}N_2O$	$2(C_{18}H_{18}N_2O)$	
Sum formula	$C_{18}H_{18}N_2O$	$C_{36}H_{36}N_4O_2$	
Mr	278.34	556.69	
Dx,g cm-3	1.236	1.236	
Z	4	2	
Mu (mm-1)	0.078	0.078	
F000	592.0	592.0	
F000’	592.22		
h,k,lmax	31,6,17	29,6,17	
Nref	3987	3345	
Tmin,Tmax	0.981,0.992	0.554,1.000	

Tmin’	0.977	
Correction method= MULTI-SCAN		
Data completeness= 0.839		Theta(max)= 29.064
R(reflections)= 0.0628(2129)		wR2(reflections)= 0.1540(3345)
S = 1.023		Npar= 190

X-ray structure of 2g

CCDC 1846531

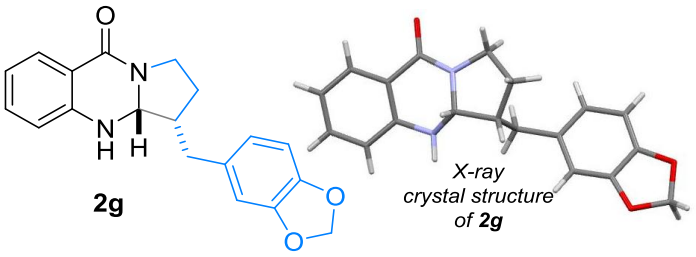


Table S2. Crystal data and details of data collection and refinement for compound **2g**

Bond precision:	C-C = 0.0030 A	Wavelength = 0.71073	
Cell:	a = 11.0010(11)	b = 6.9737(7)	c = 20.129(2)
	alpha = 90	beta = 93.637(9)	gamma = 90
Temperature:	150 K		
	Calculated	Reported	
Volume	1541.1(3)	1541.3(3)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	$C_{19}H_{18}N_2O_3$	$C_{19}H_{18}N_2O_3$	
Sum formula	$C_{19}H_{18}N_2O_3$	$C_{19}H_{18}N_2O_3$	
Mr	322.35	322.35	
Dx,g cm-3	1.389	1.389	
Z	4	4	
Mu (mm-1)	0.095	0.095	
F000	680.0	680.0	
F000’	680.31		
h,k,lmax	13,8,24	13,8,24	
Nref	2830	2826	

Tmin,Tmax	0.989,0.991	0.747,1.000
Tmin’	0.963	
Correction method= MULTI-SCAN		
Data completeness= 0.999		Theta(max)= 25.342
R(reflections)= 0.0577(1996)		wR2(reflections)= 0.1287(2826)
S = 1.055		Npar= 220

X-ray structure of 2t

CCDC 1846532

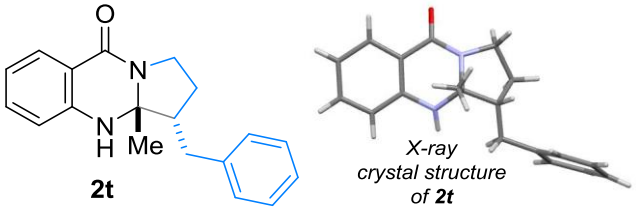


Table S3. Crystal data and details of data collection and refinement for compound **2t**

Bond precision:	C-C = 0.0061 A	Wavelength = 0.71073	
Cell:	a = 41.133(3)	b = 13.3359(14)	c = 11.1564(8)
	alpha = 90	beta = 90	gamma = 90
Temperature:	150 K		
	Calculated	Reported	
Volume	6119.8(9)	6119.8(9)	
Space group	C m c 21	C m c 21	
Hall group	C 2c -2	C 2c -2	
Moiety formula	$C_{19}H_{20}N_2O$ [+ solvent]	$C_{19}H_{20}N_2O$	
Sum formula	$C_{19}H_{20}N_2O$ [+ solvent]	$C_{19}H_{20}N_2O$	
Mr	292.37	292.37	
Dx,g cm-3	0.635	0.635	
Z	8	8	
Mu (mm-1)	0.040	0.040	
F000	1248.0	1248.0	
F000’	1248.46		

h,k,lmax	56,18,15	55,17,15
Nref	8366[4395]	7118
Tmin,Tmax	0.986,0.992	0.159,1.000
Tmin’	0.980	
Correction method= MULTI-SCAN		
Data completeness= 1.62/0.85		Theta(max)= 29.136
R(reflections)= 0.0785(4664)		wR2(reflections)= 0.2542(7118)
S = 1.010		Npar= 200

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[1] P. Girard, J.-L. Namy, H. B. Kagan, *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698.

[2] T. Imamoto, M. Ono, *Chem. Lett.* **1987**, 501–502.

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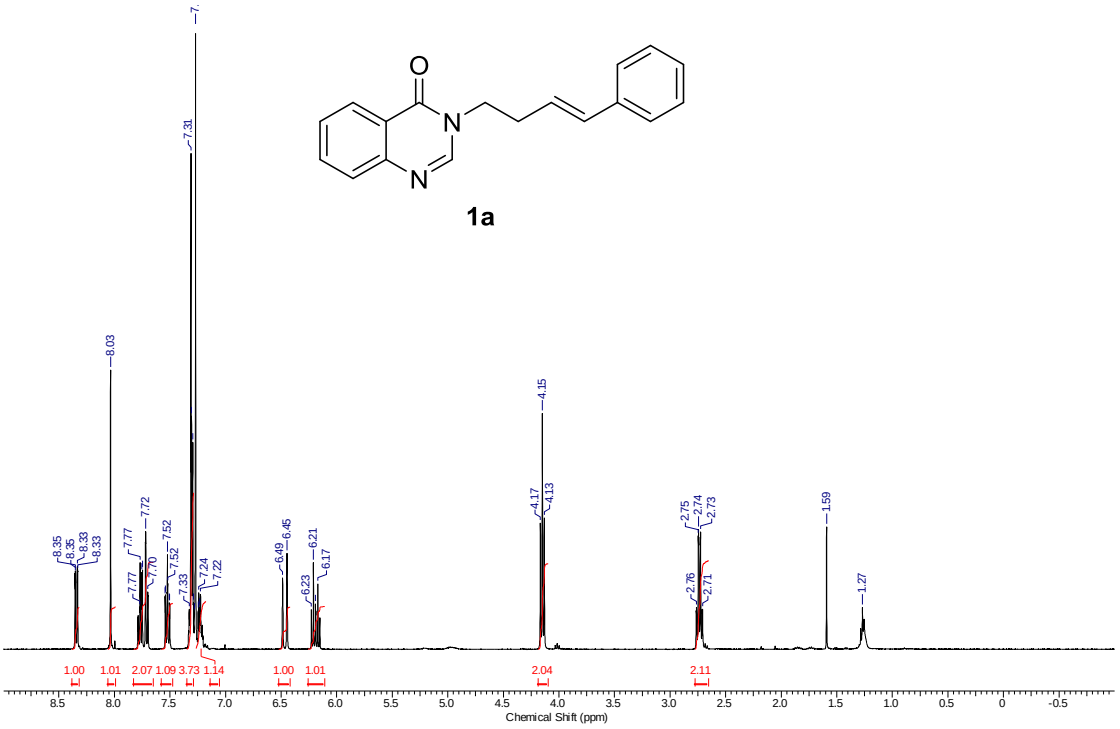
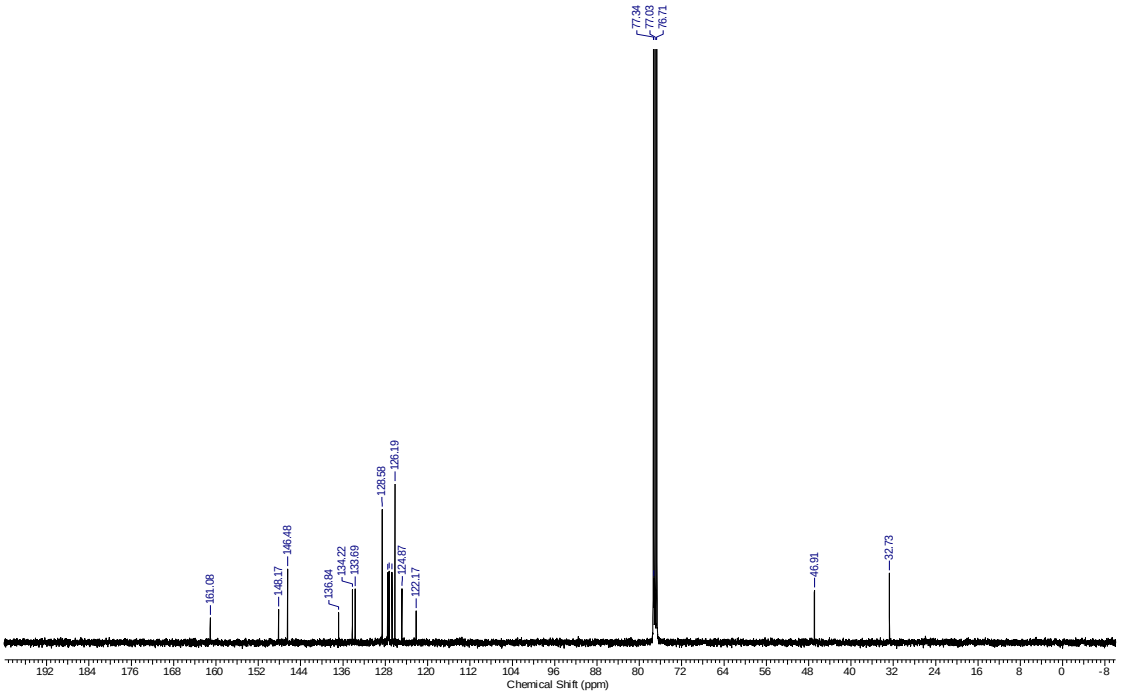
[8] M. Karplus, *J. Am. Chem. Soc.* **1963**, *85*, 2870–2871.

^{1}H and ^{13}C NMR Spectra of Compounds

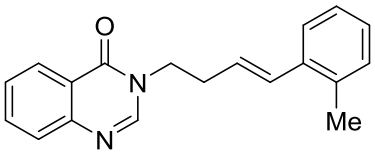
^{1}H NMR (400 MHz, $CDCl_3$)



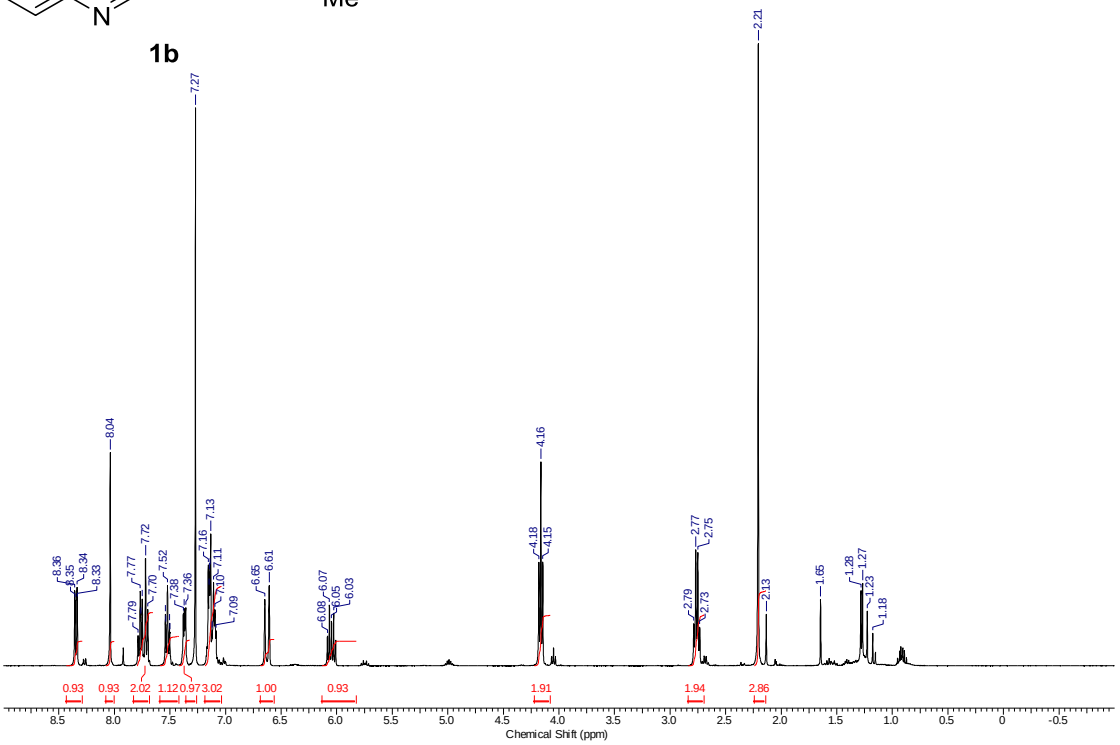
^{13}C NMR (101 MHz, $CDCl_3$)



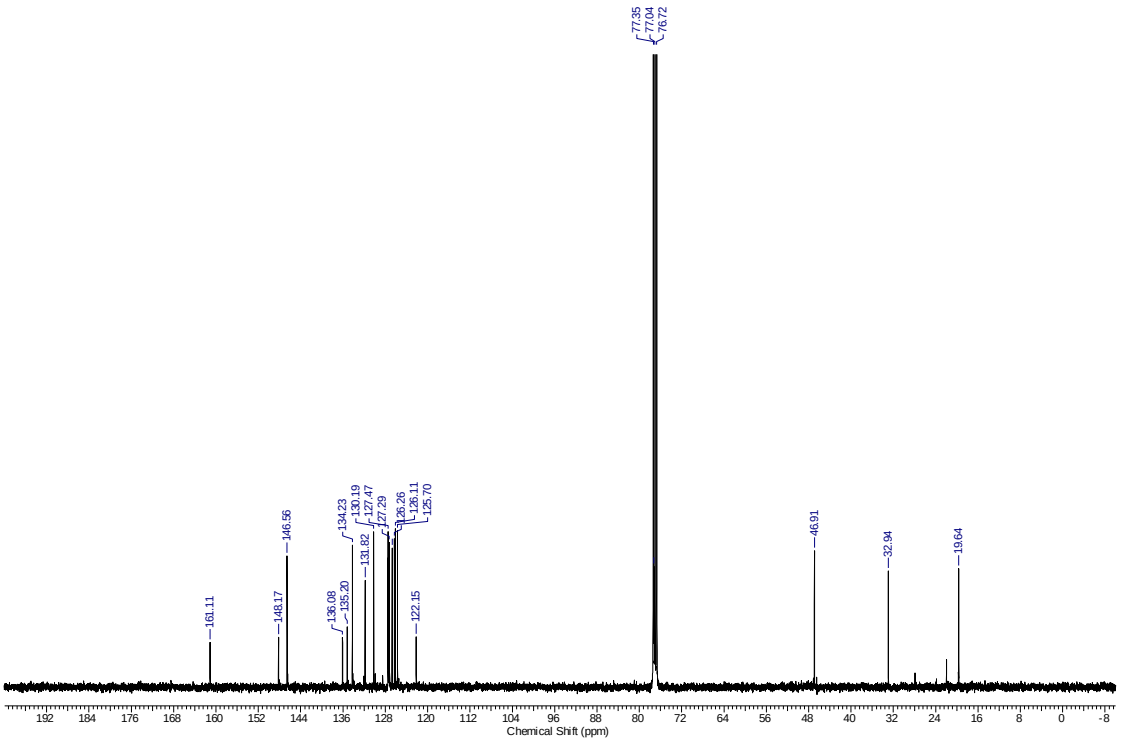
^{1}H NMR (400 MHz, $CDCl_3$)



1b



^{13}C NMR (101 MHz, $CDCl_3$)



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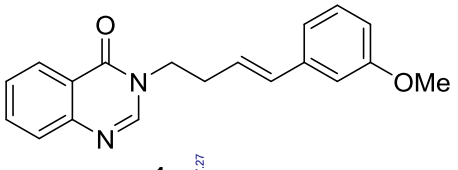
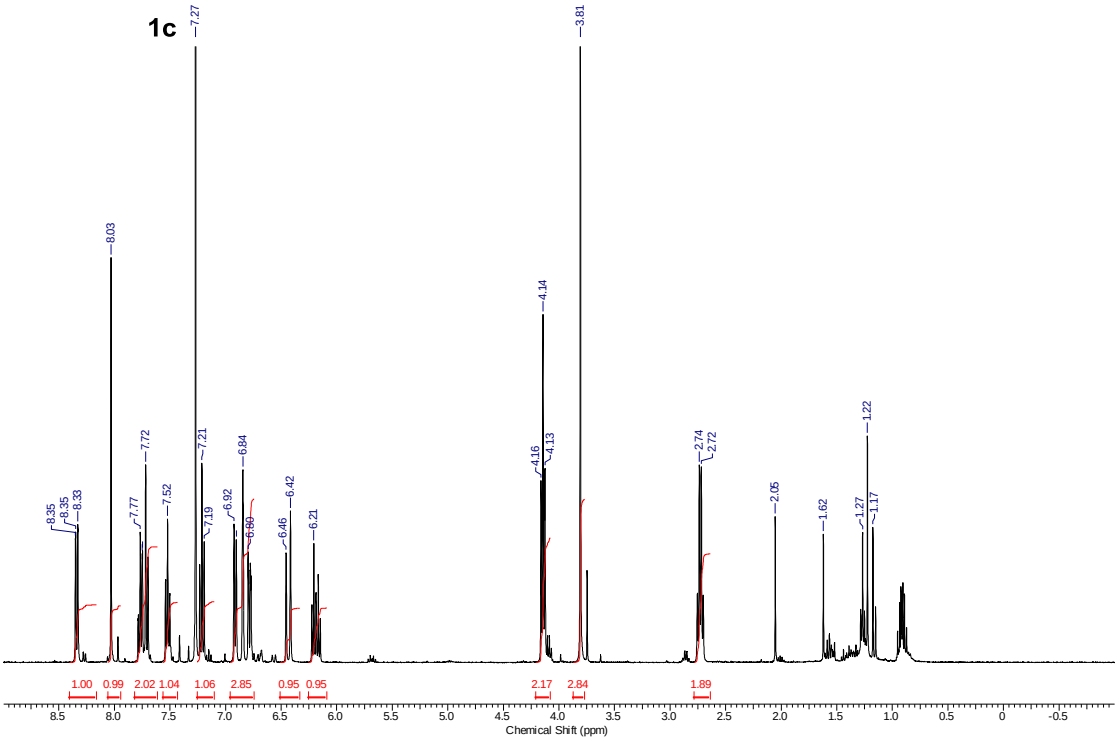
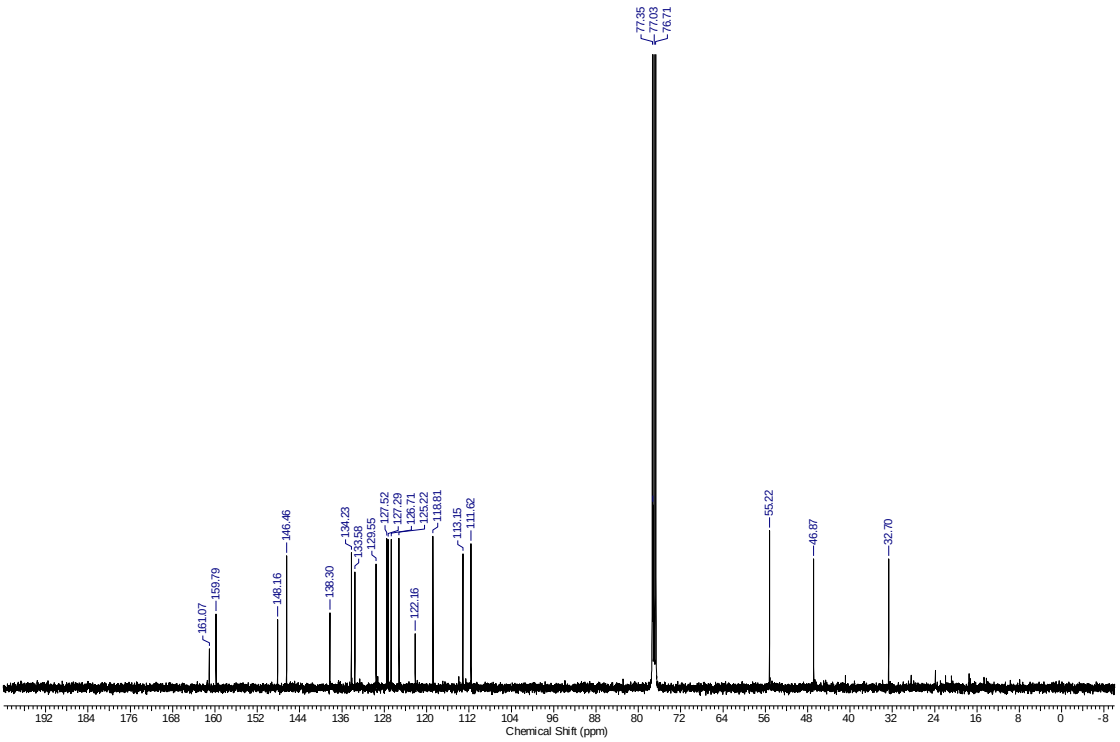
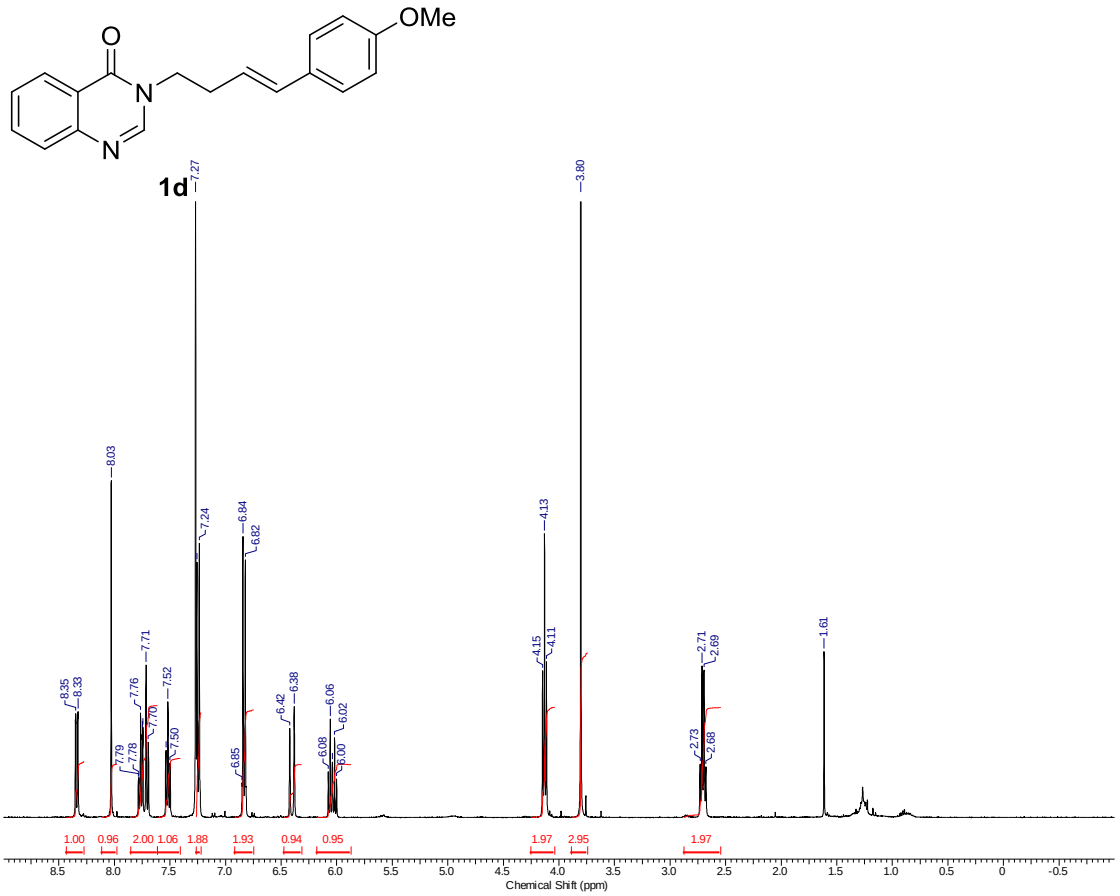




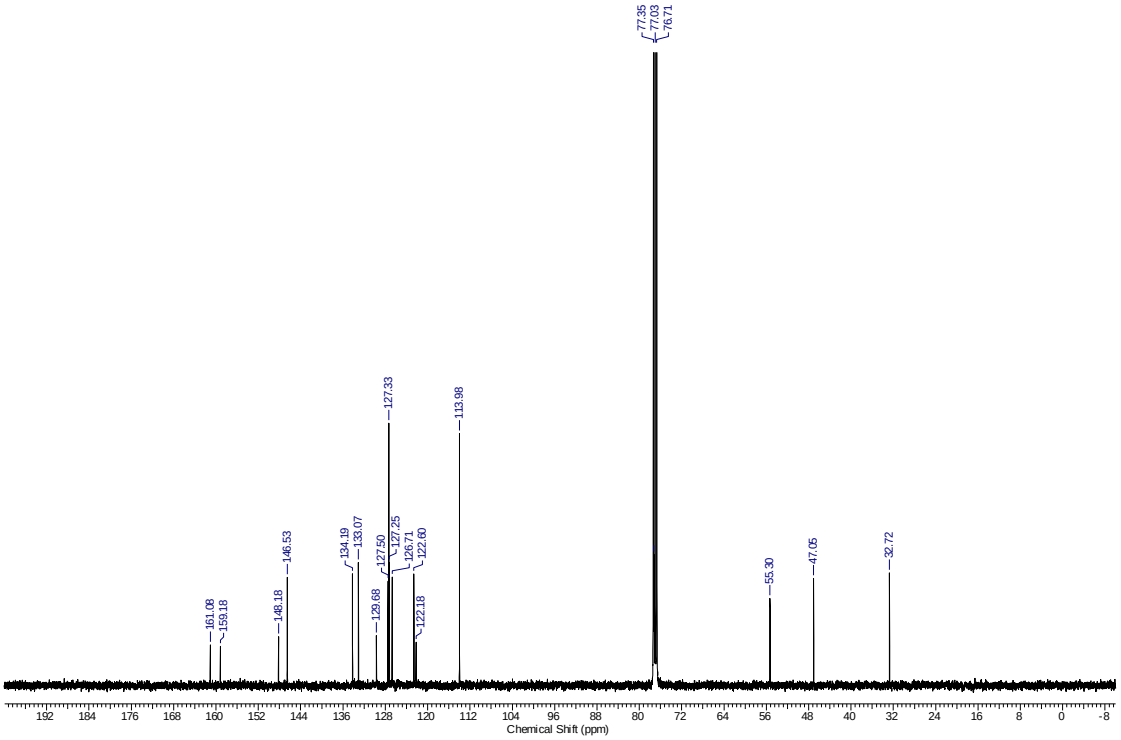
^{13}C NMR (101 MHz, $CDCl_3$)



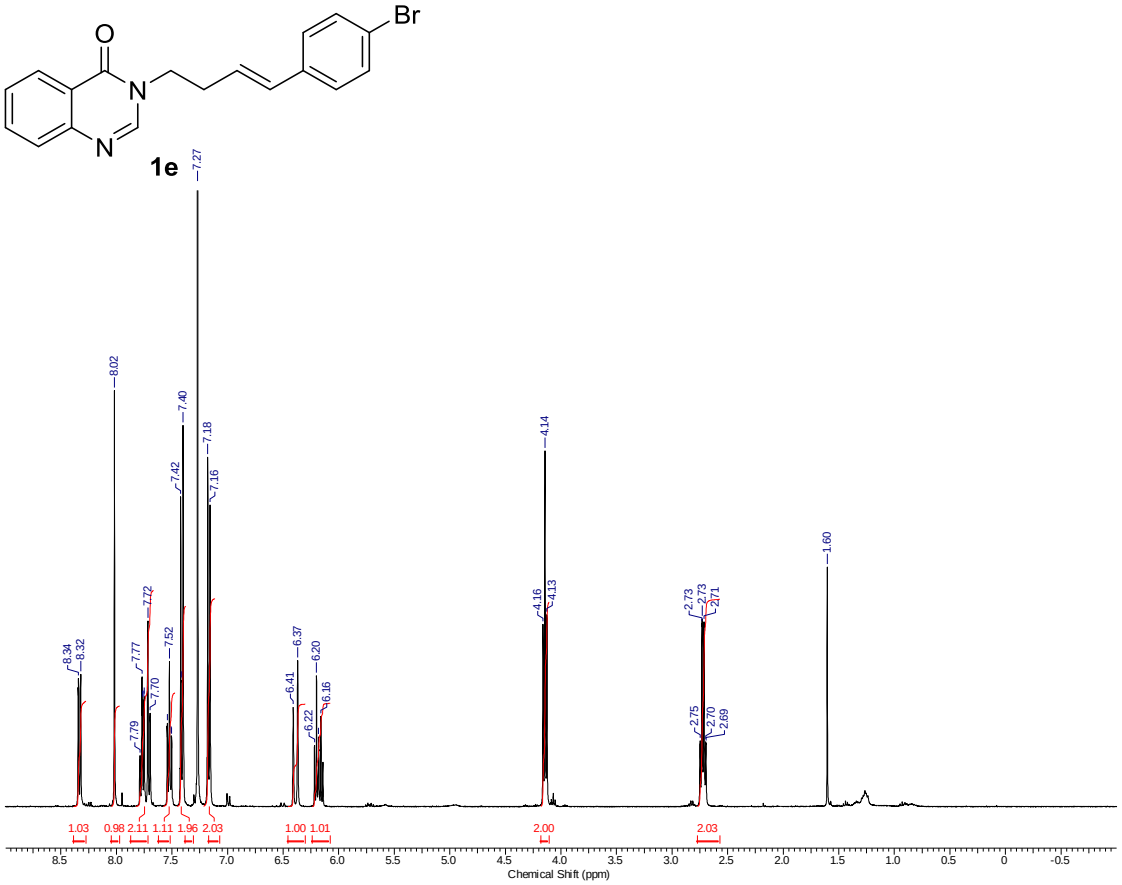
^{1}H NMR (400 MHz, $CDCl_3$)



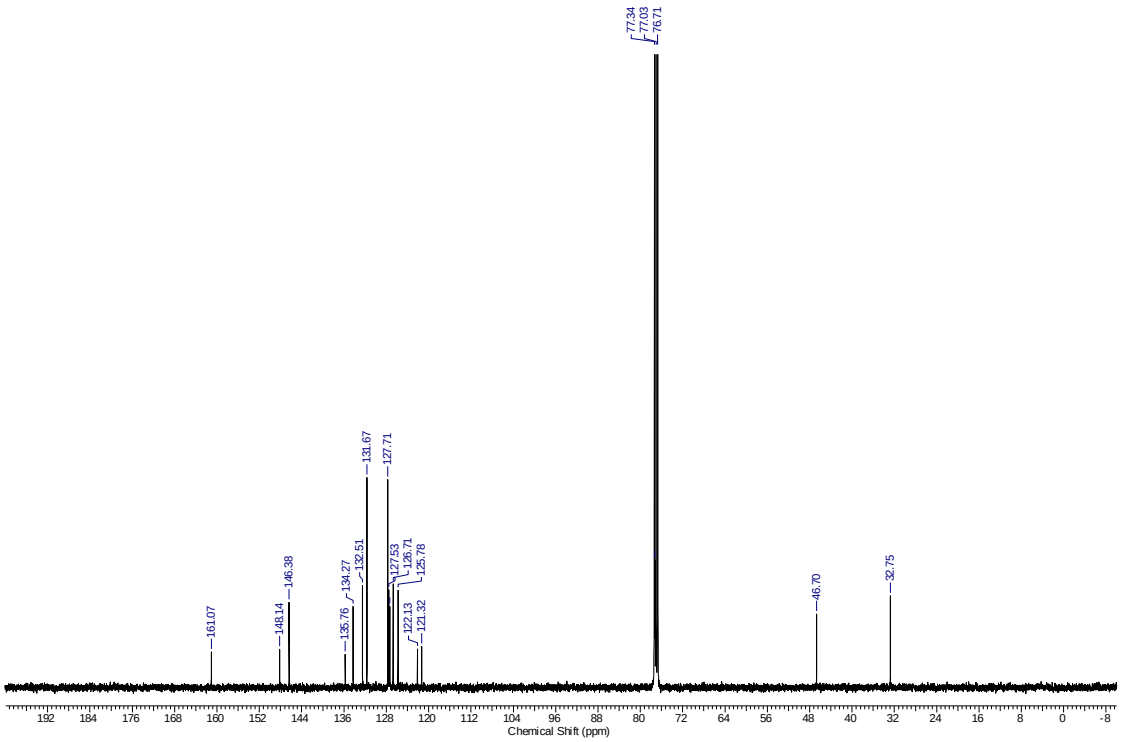
^{13}C NMR (101 MHz, $CDCl_3$)



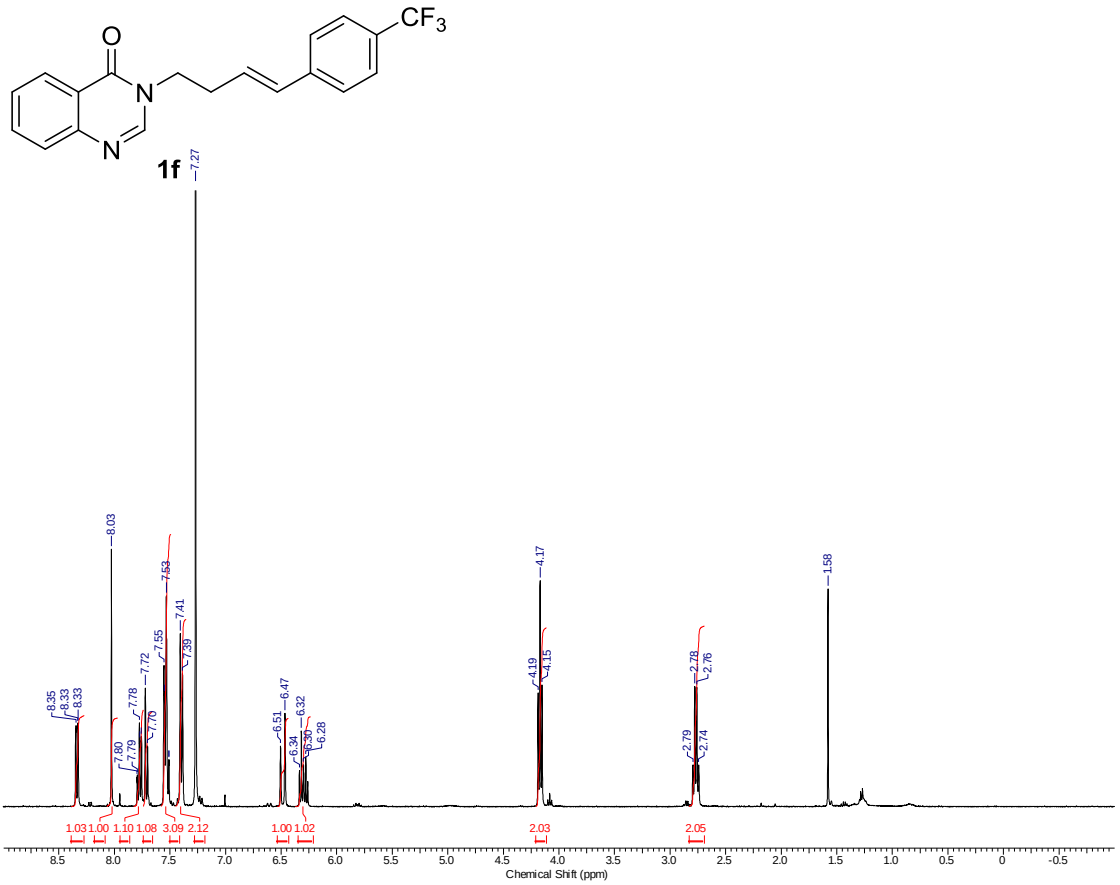
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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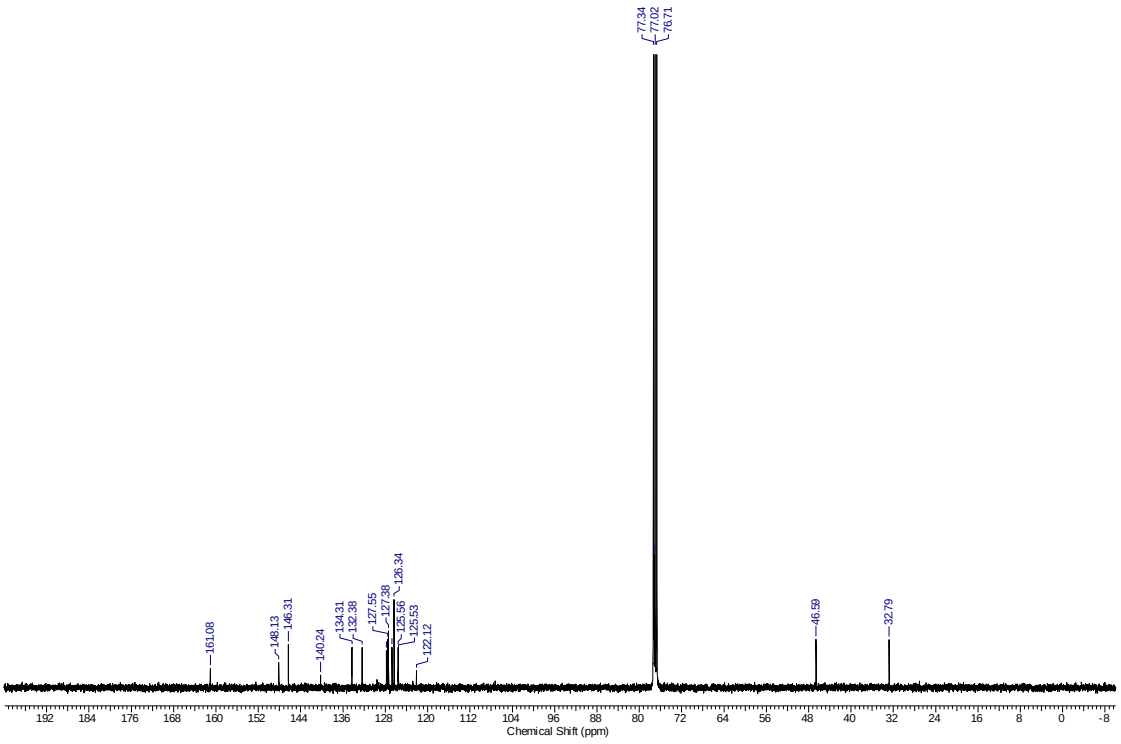
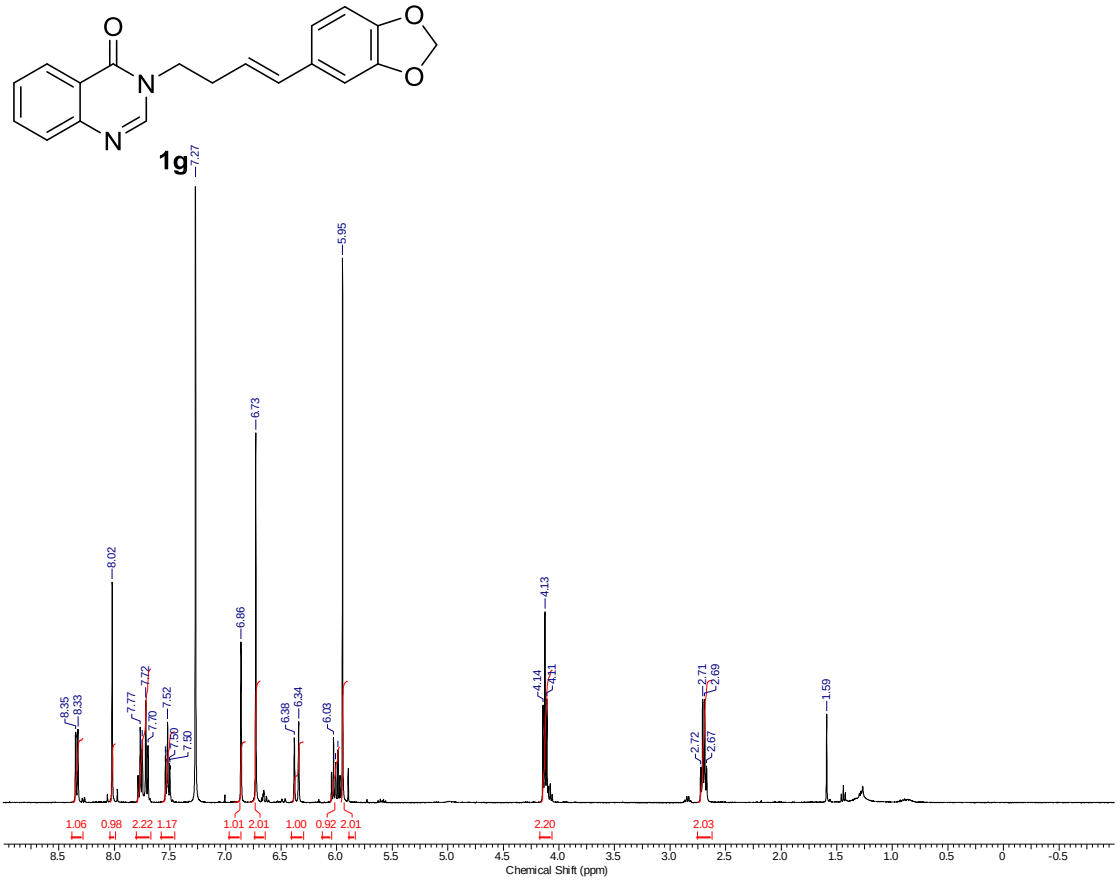


^{1}H NMR (400 MHz, $CDCl_3$)



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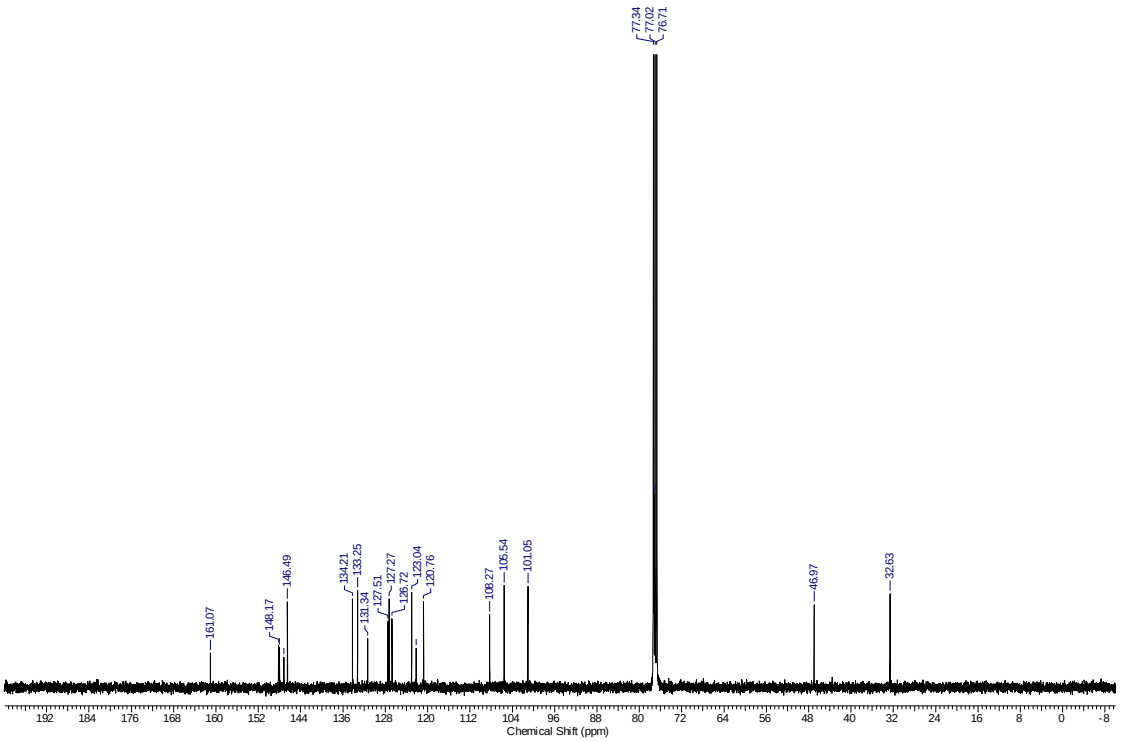
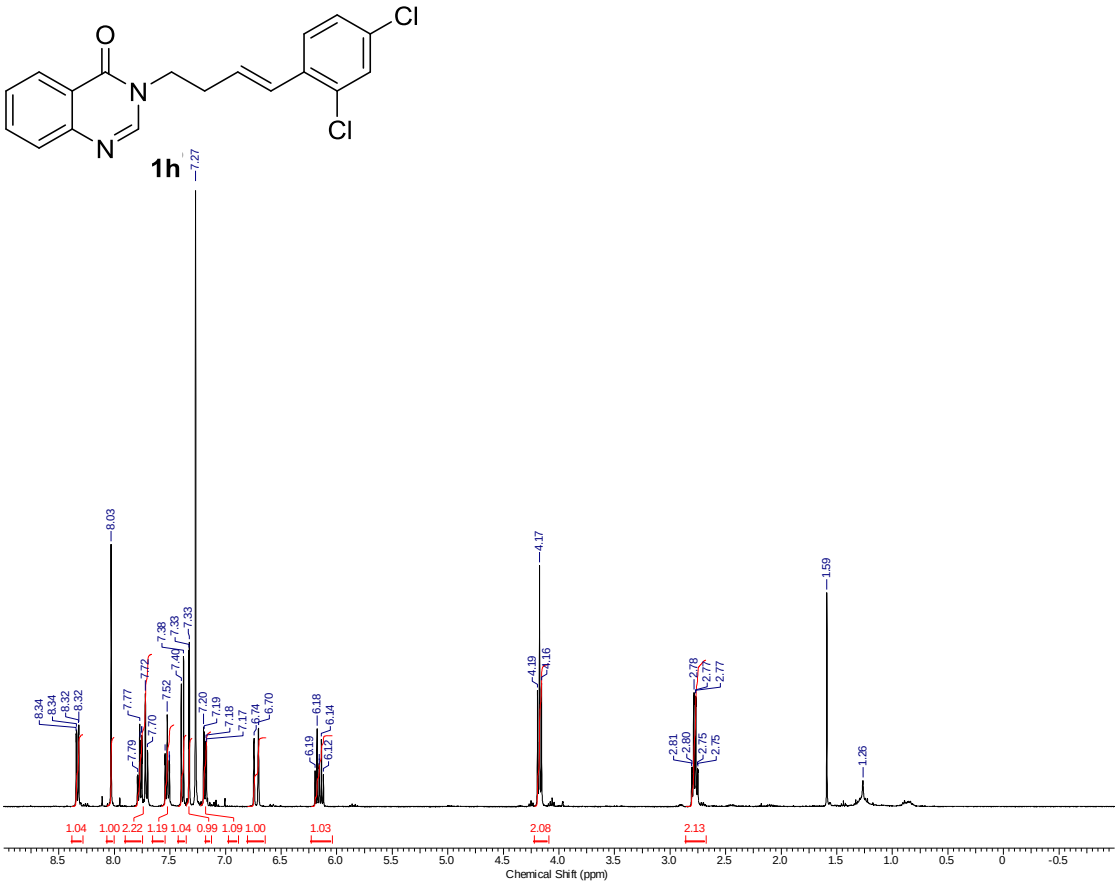
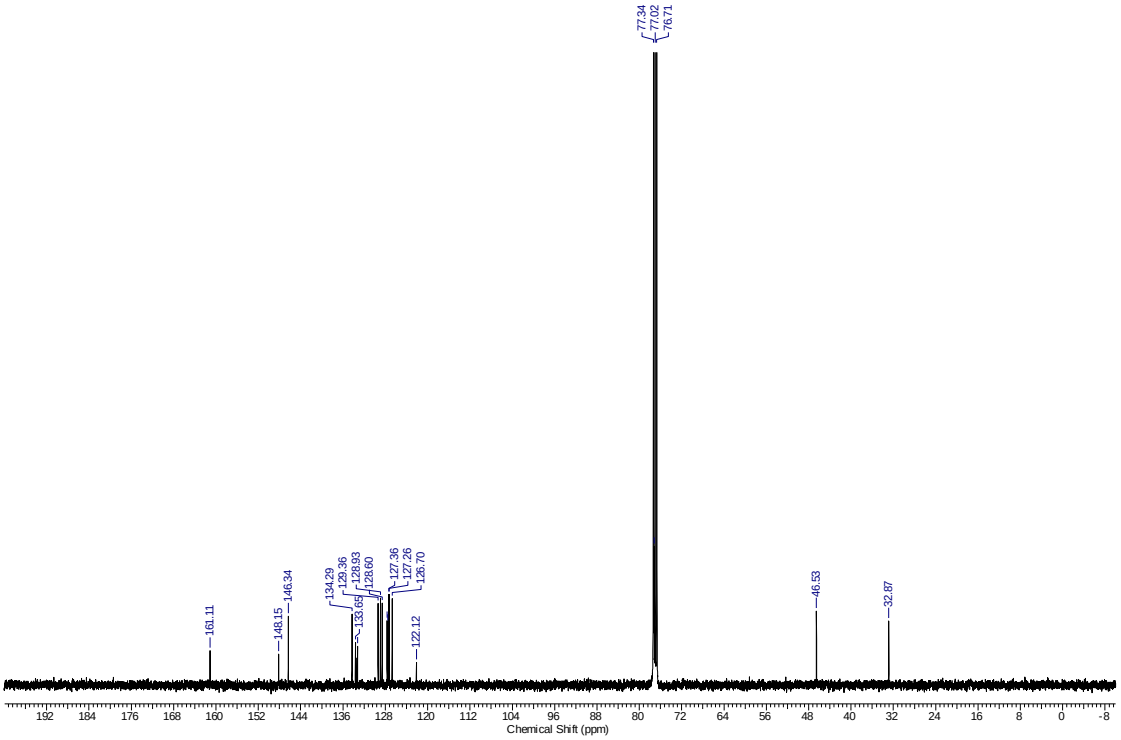


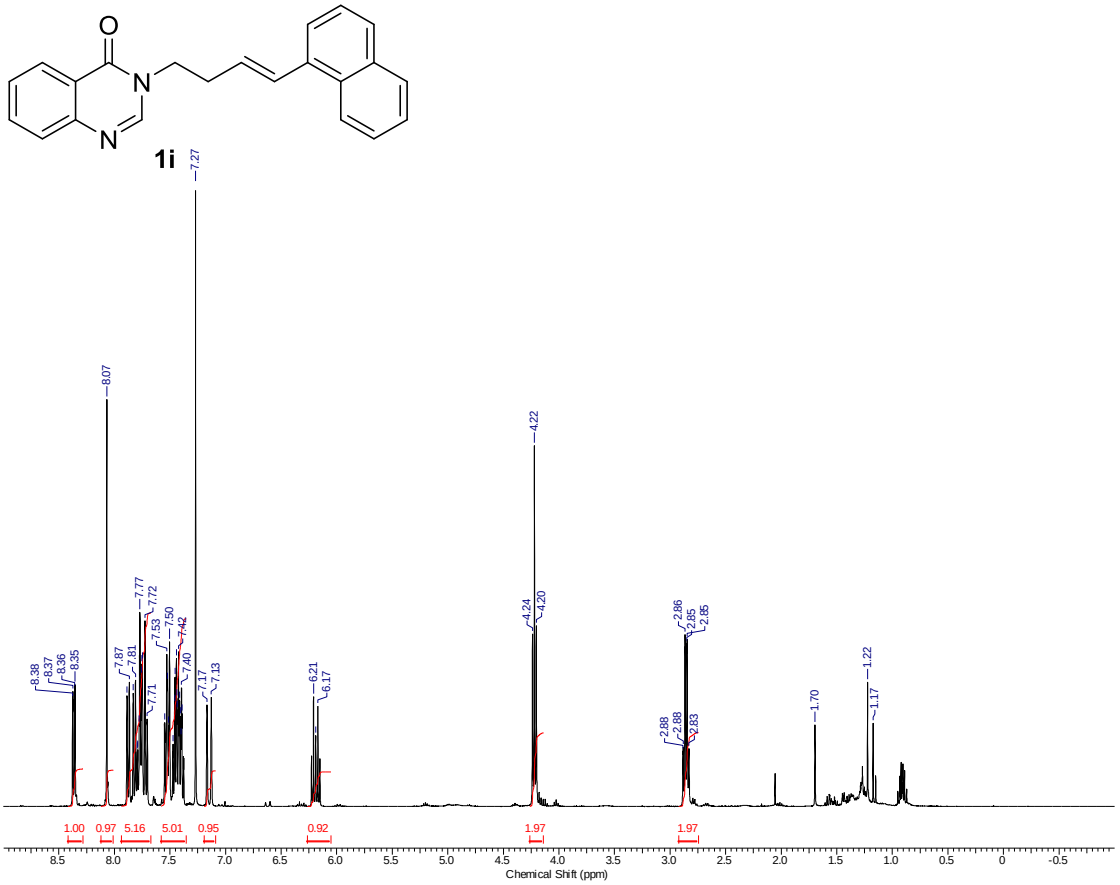
^{1}H NMR (400 MHz, $CDCl_3$)



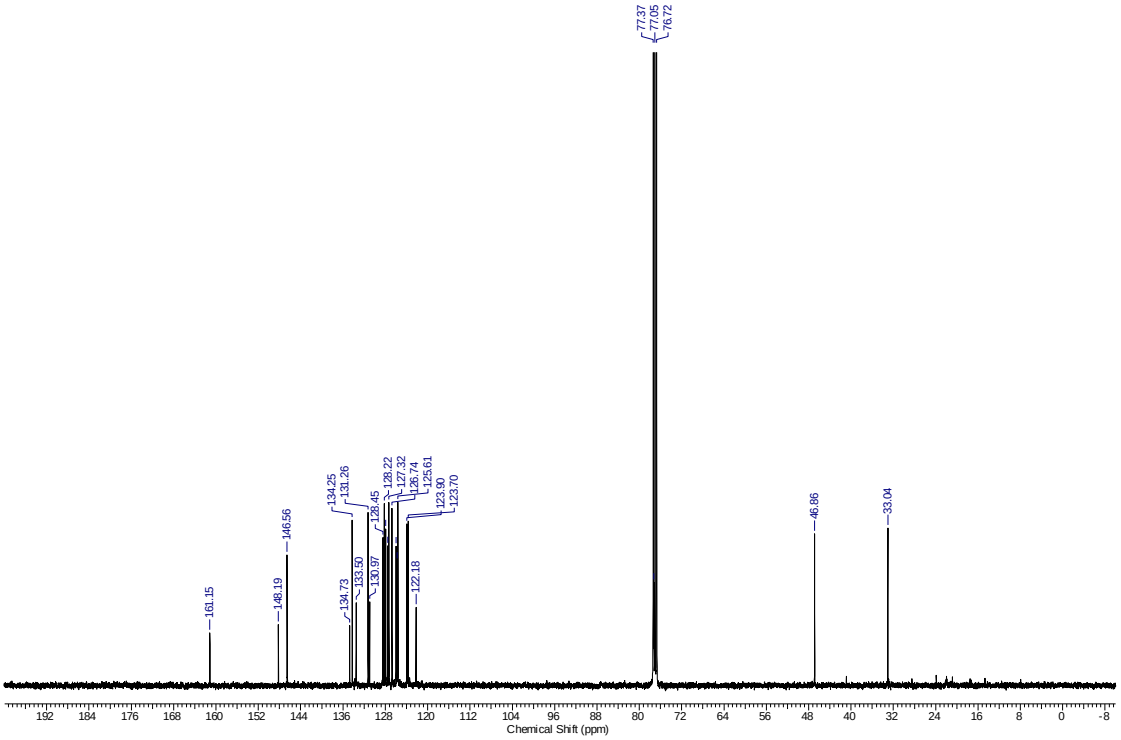
^{13}C NMR (101 MHz, $CDCl_3$)



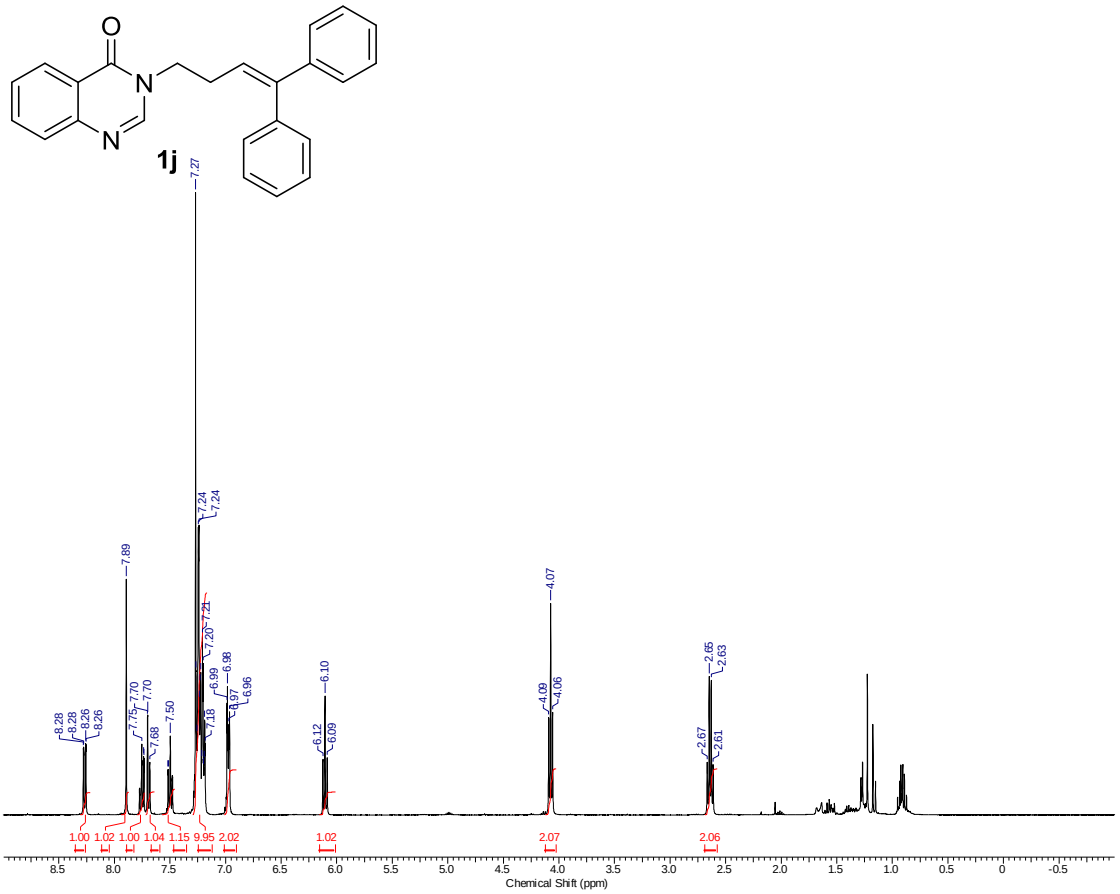
^{1}H NMR (400 MHz, $CDCl_3$)



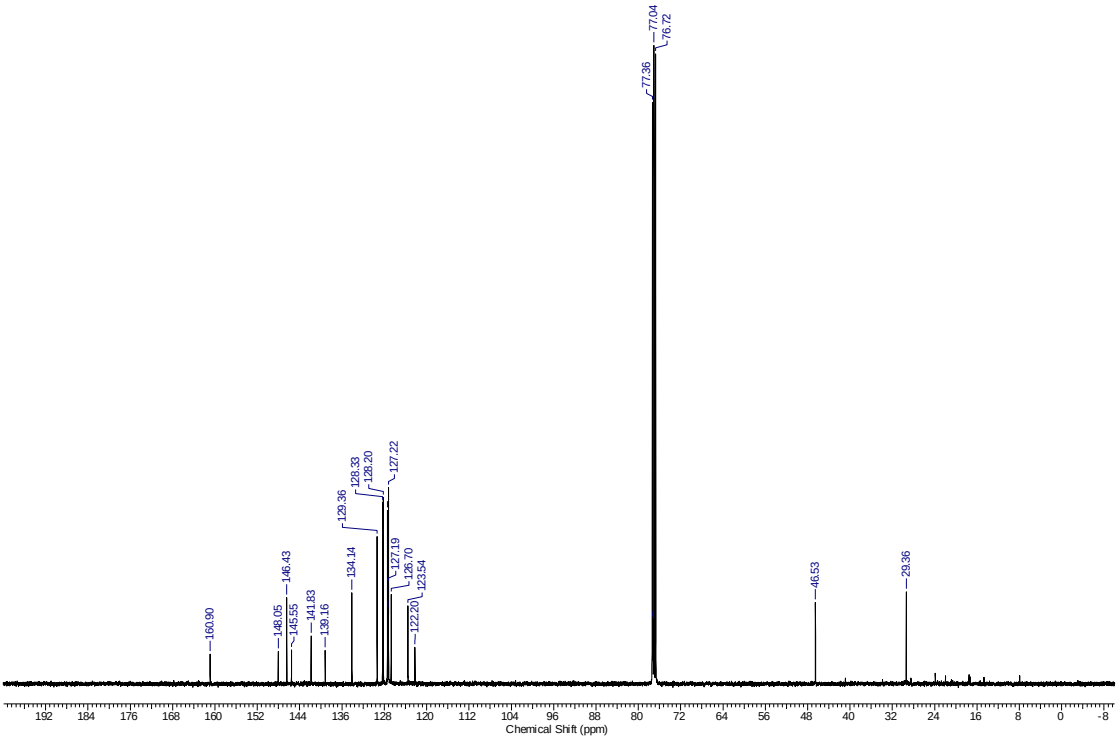
^{13}C NMR (101 MHz, $CDCl_3$)



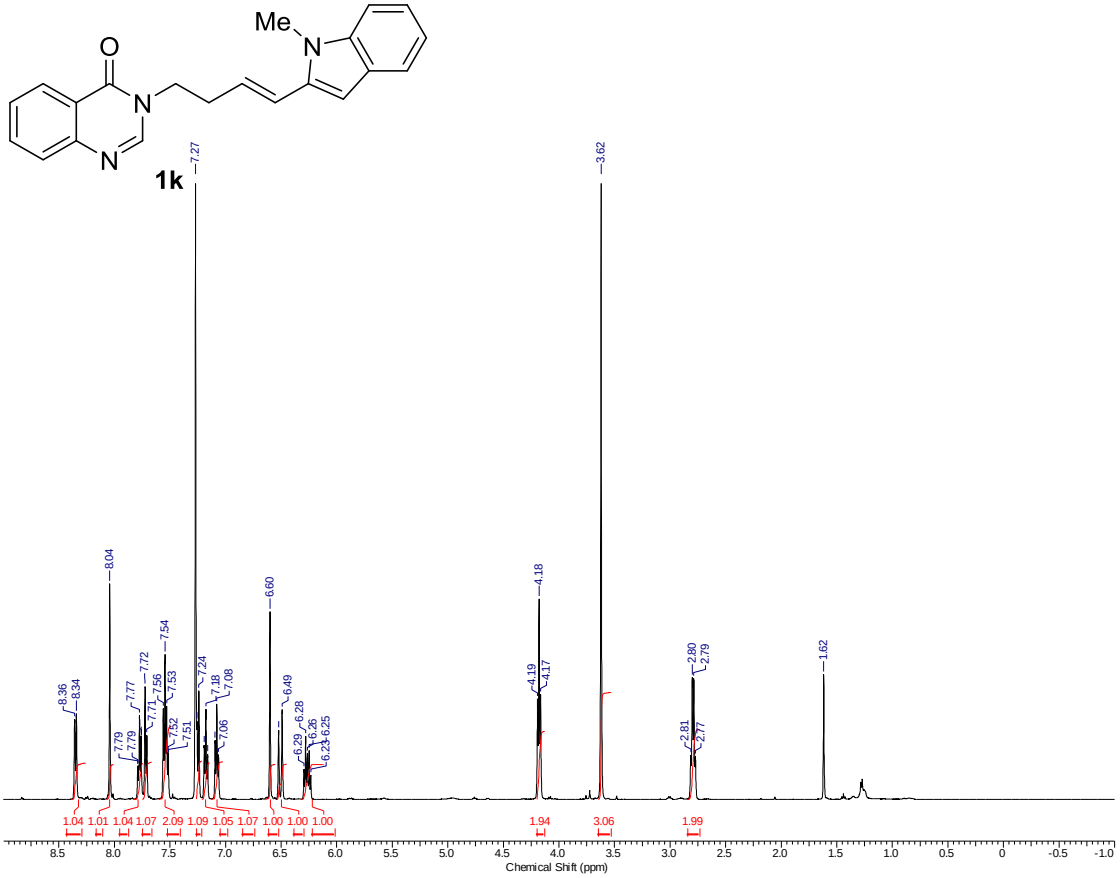
^{1}H NMR (400 MHz, $CDCl_3$)



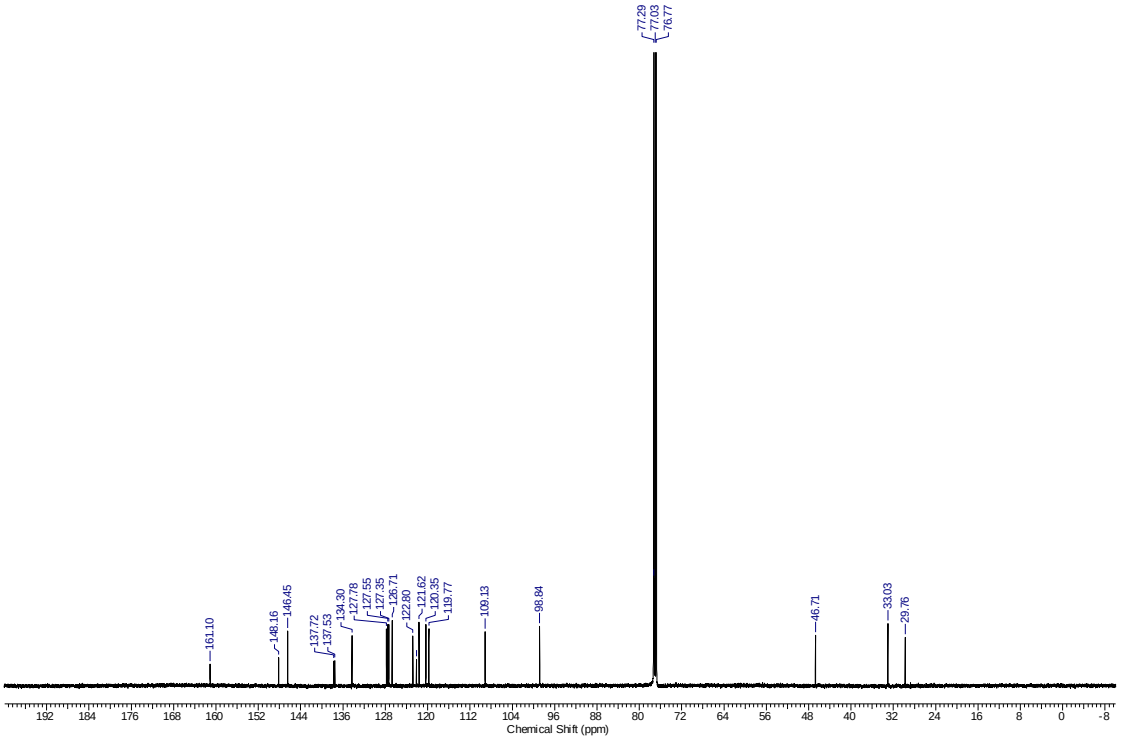
^{13}C NMR (101 MHz, $CDCl_3$)



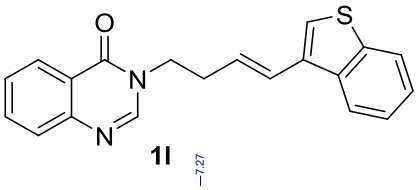
^{1}H NMR (500 MHz, $CDCl_3$)



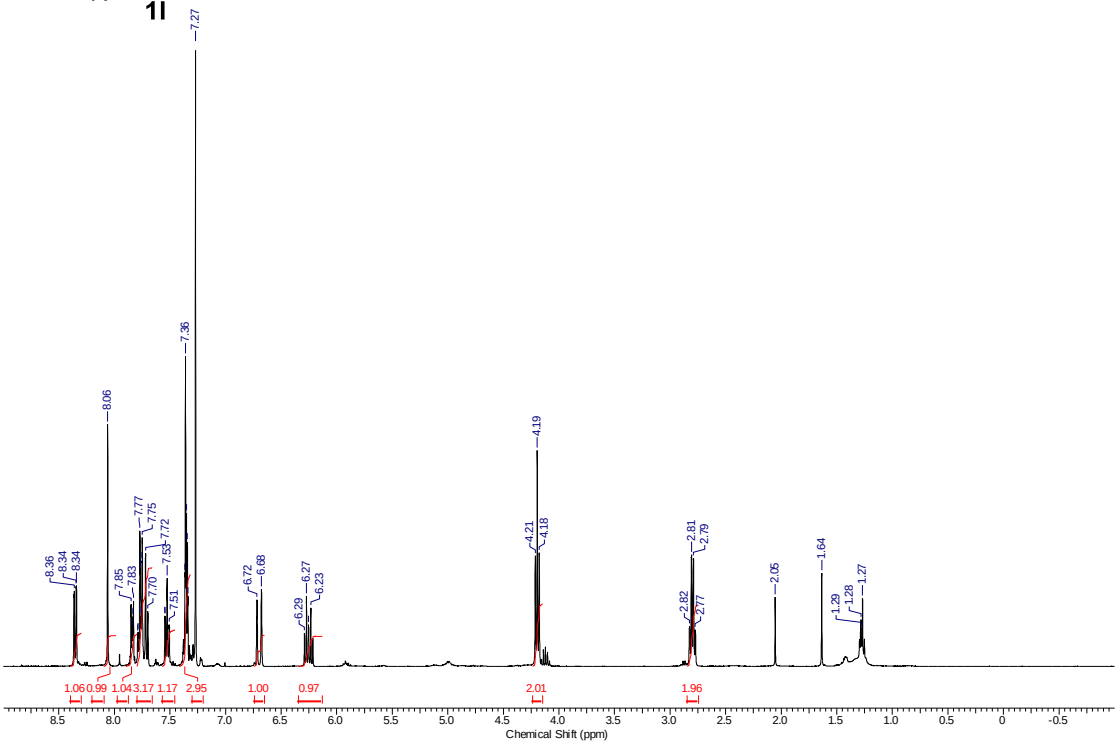
^{13}C NMR (126 MHz, $CDCl_3$)



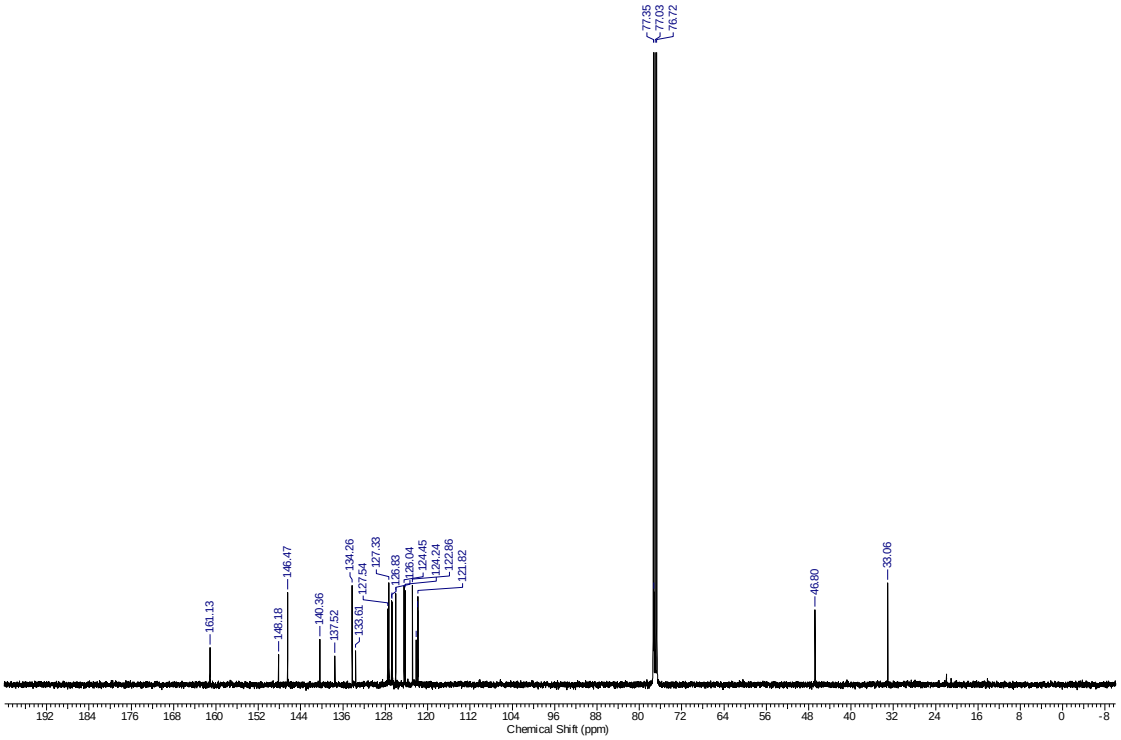
^{1}H NMR (400 MHz, $CDCl_3$)



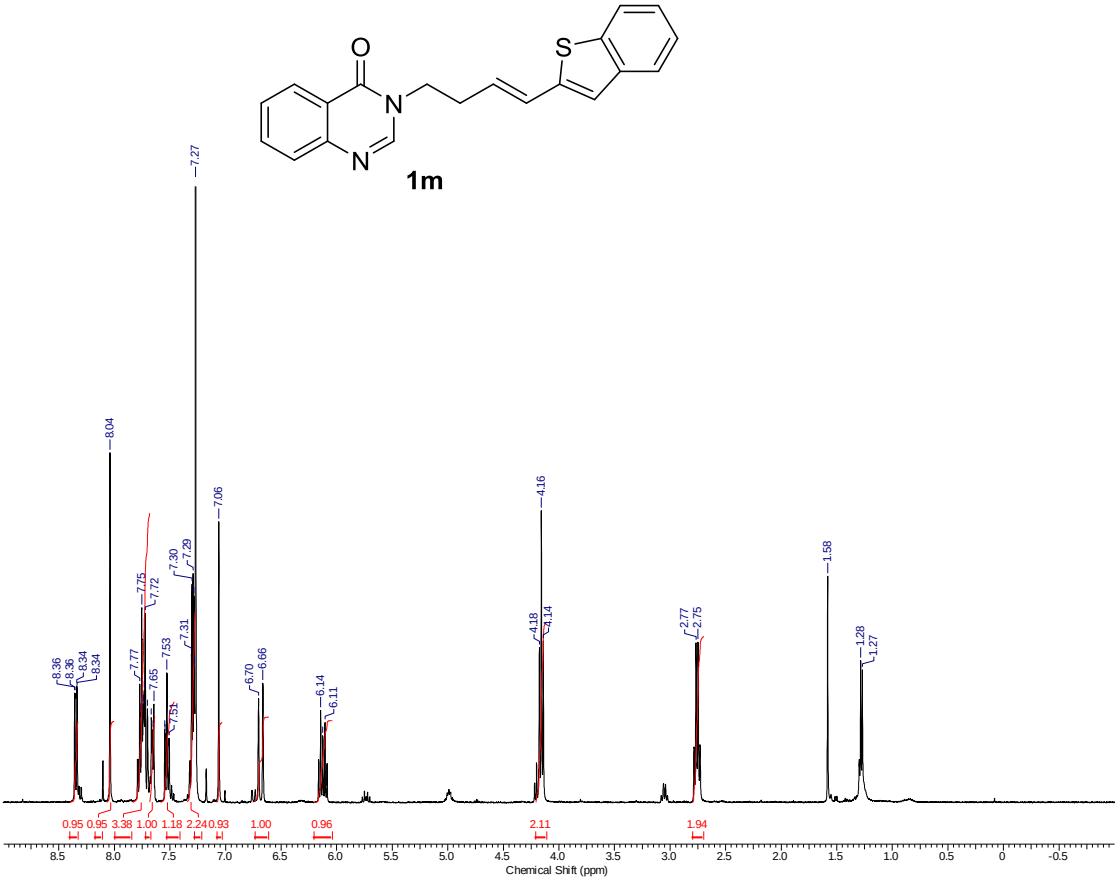
1l



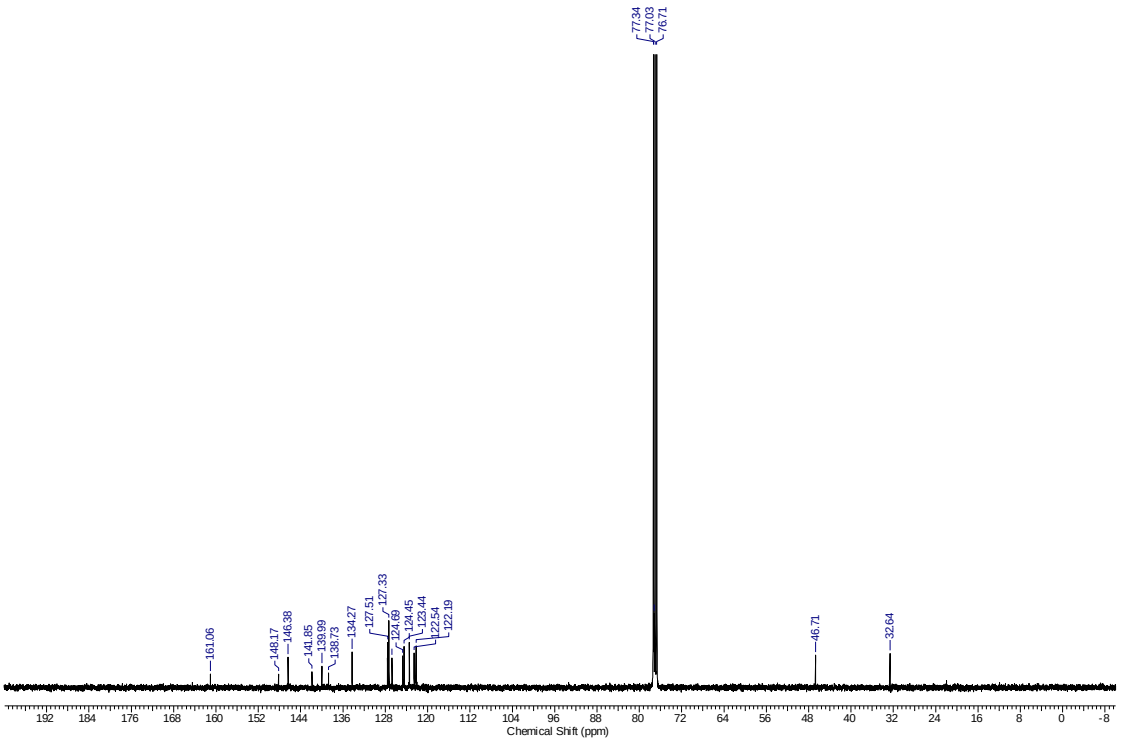
^{13}C NMR (101 MHz, $CDCl_3$)



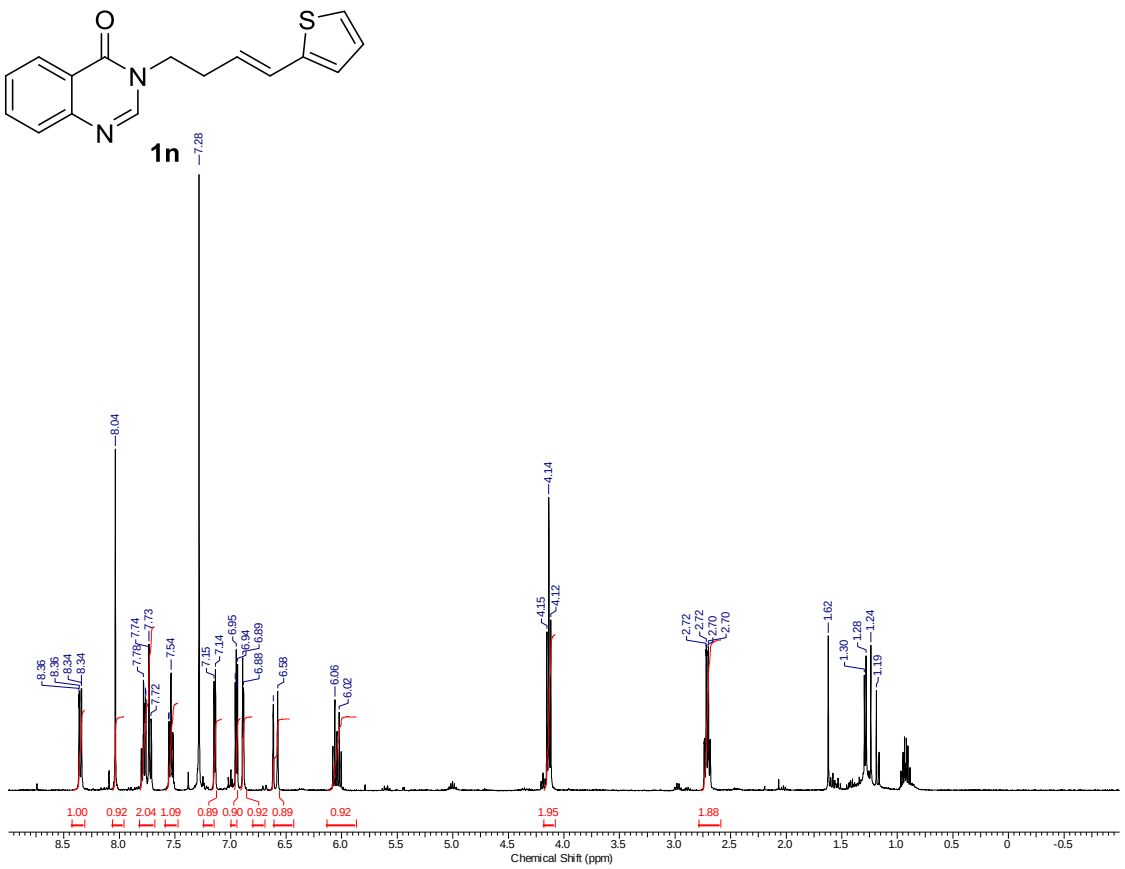
^{1}H NMR (400 MHz, $CDCl_3$)



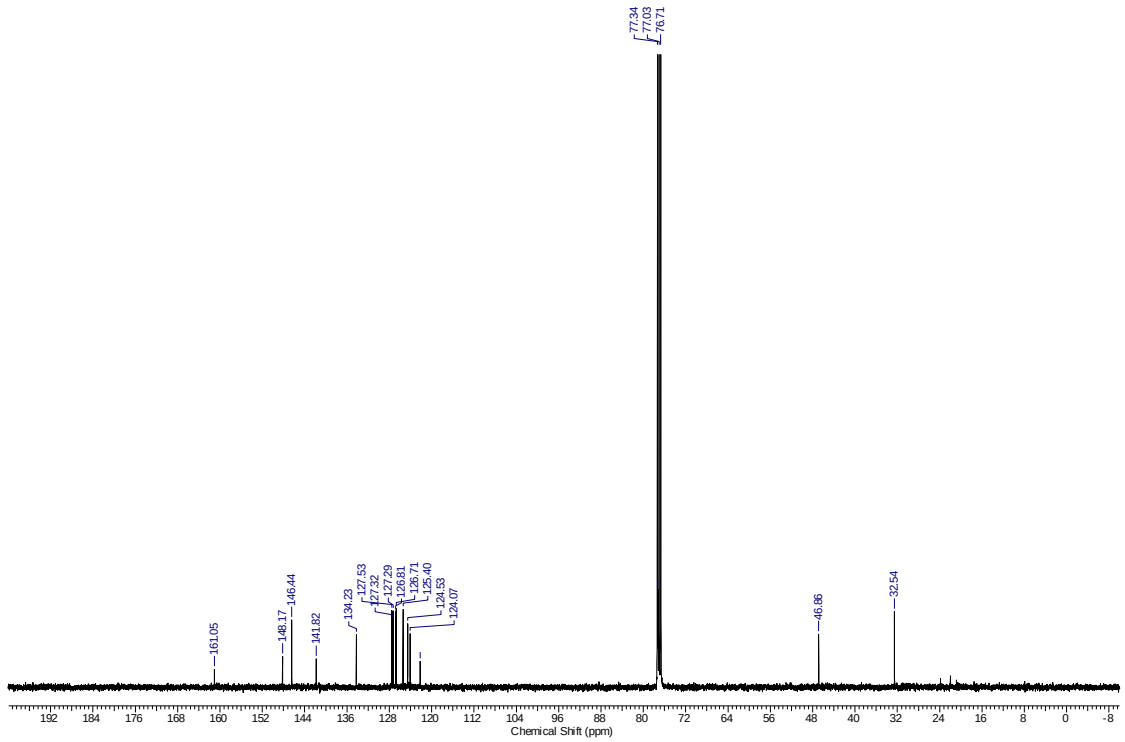
^{13}C NMR (101 MHz, $CDCl_3$)



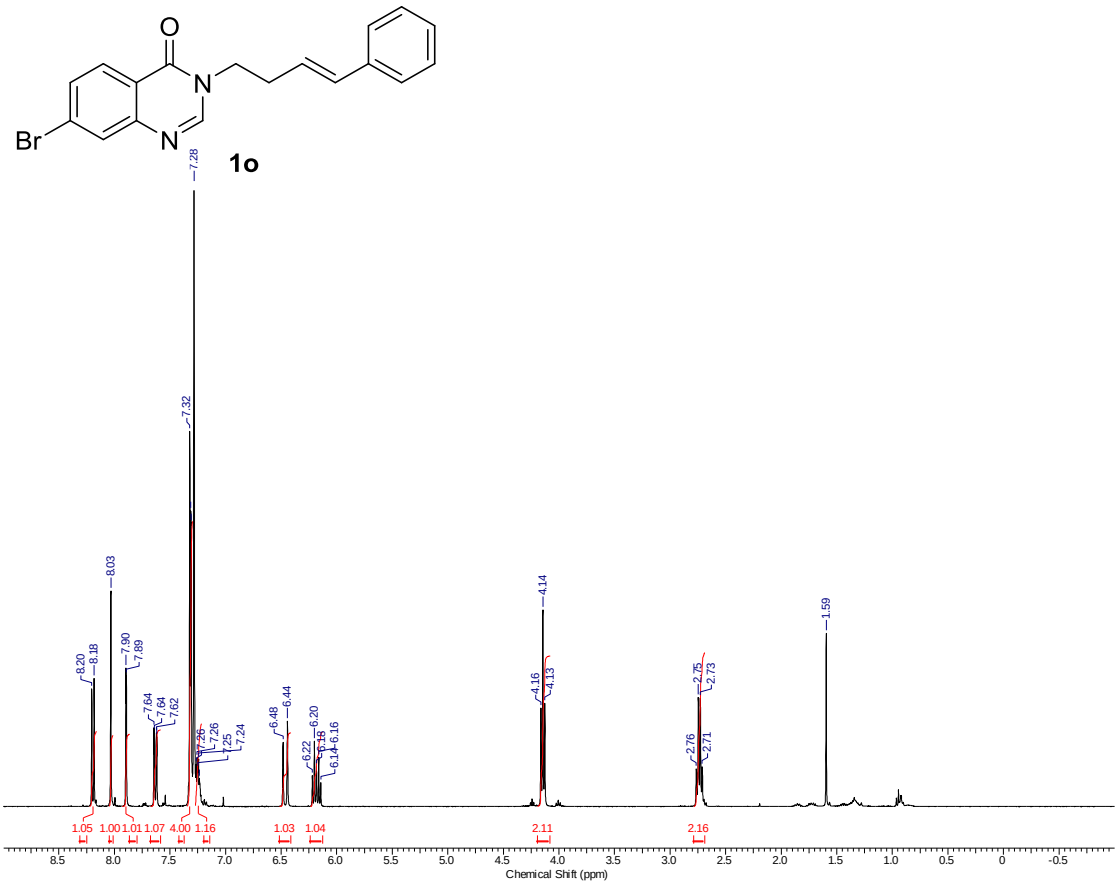
^{1}H NMR (400 MHz, $CDCl_3$)



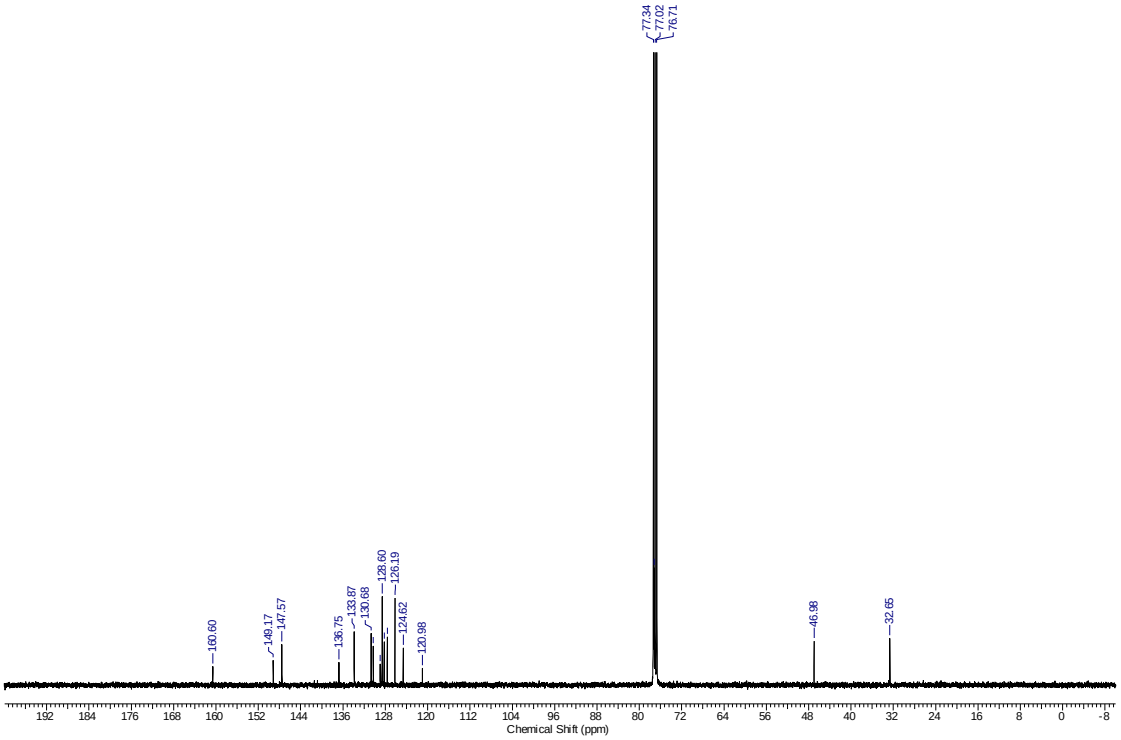
^{13}C NMR (101 MHz, $CDCl_3$)



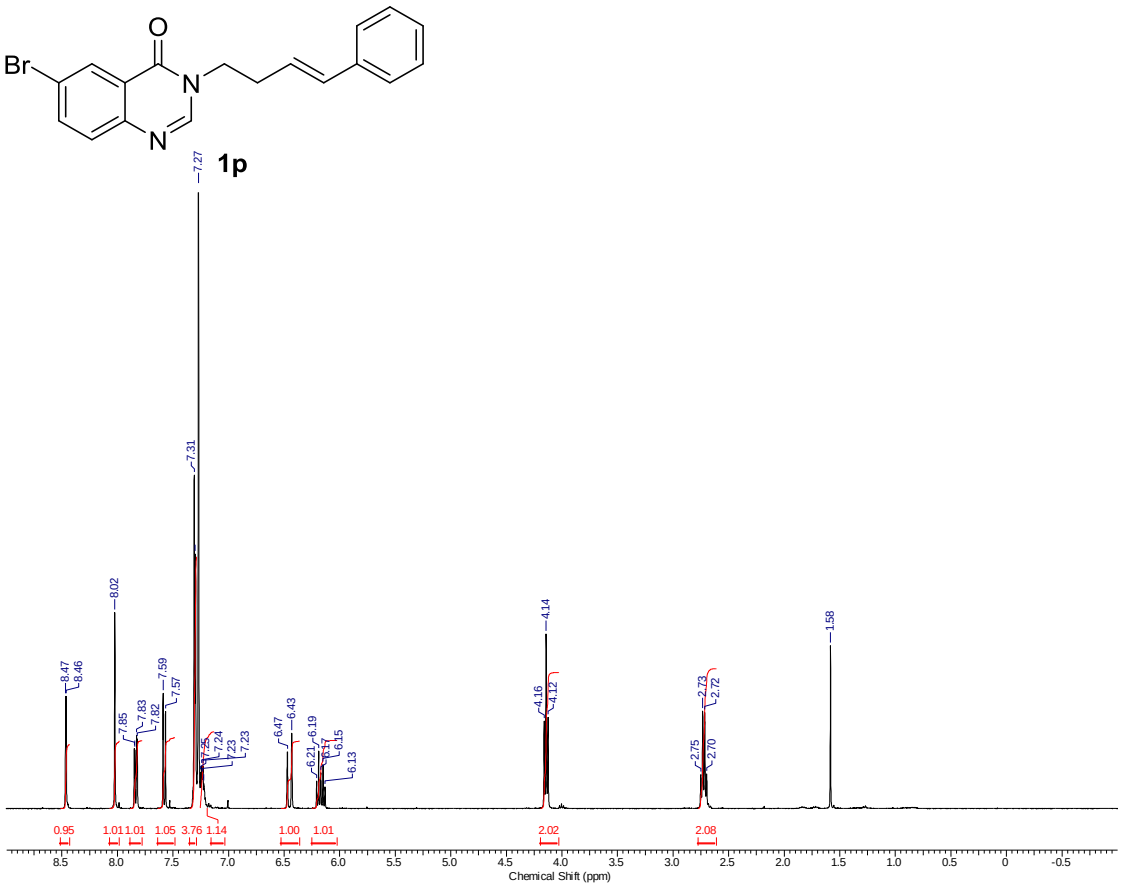
^{1}H NMR (400 MHz, $CDCl_3$)



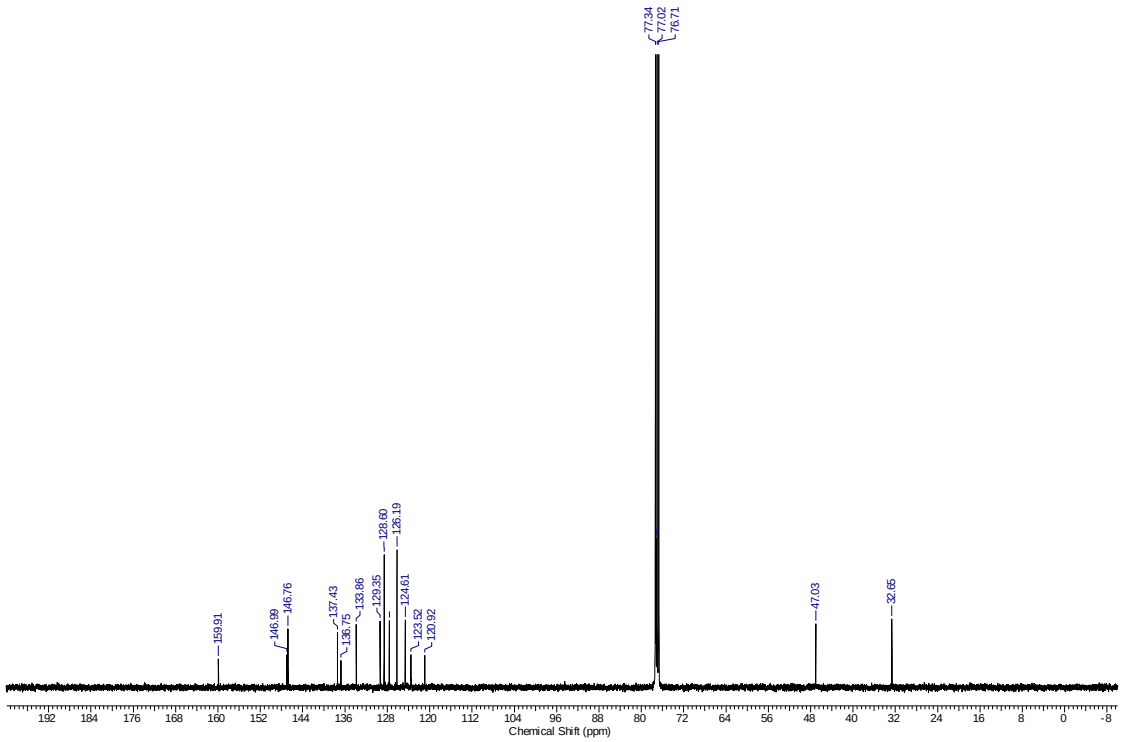
^{13}C NMR (101 MHz, $CDCl_3$)c



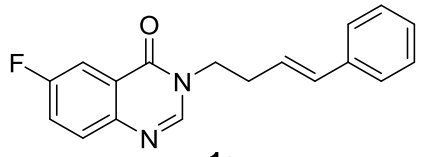
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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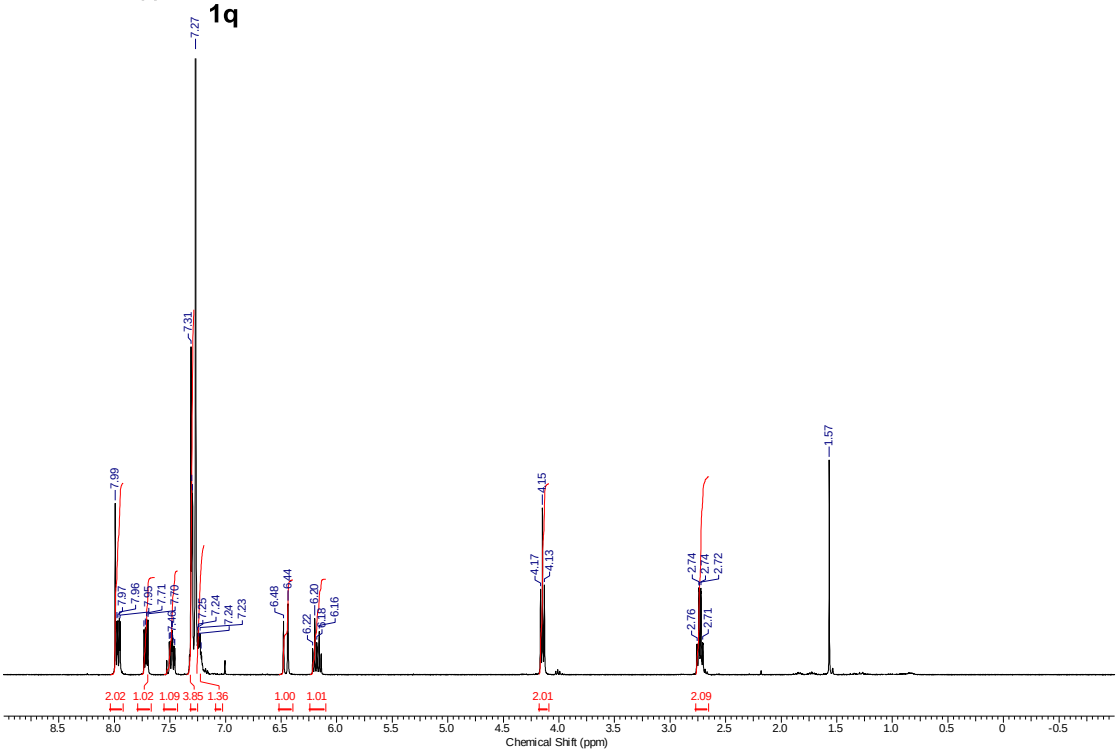
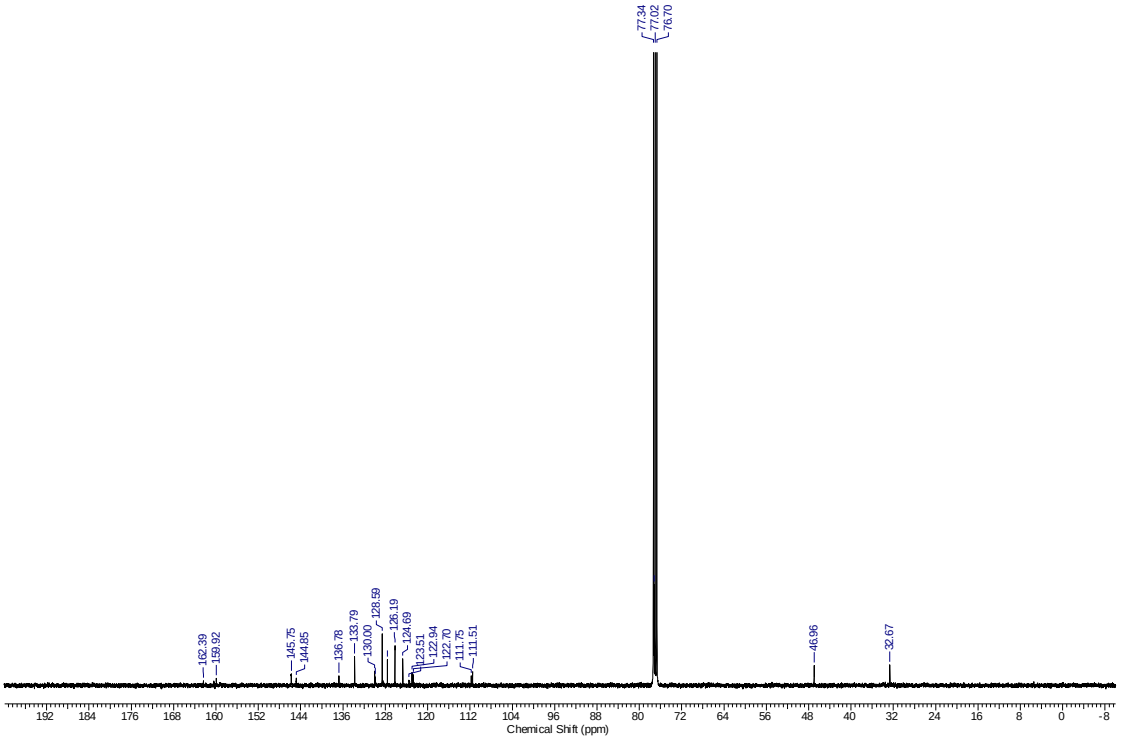
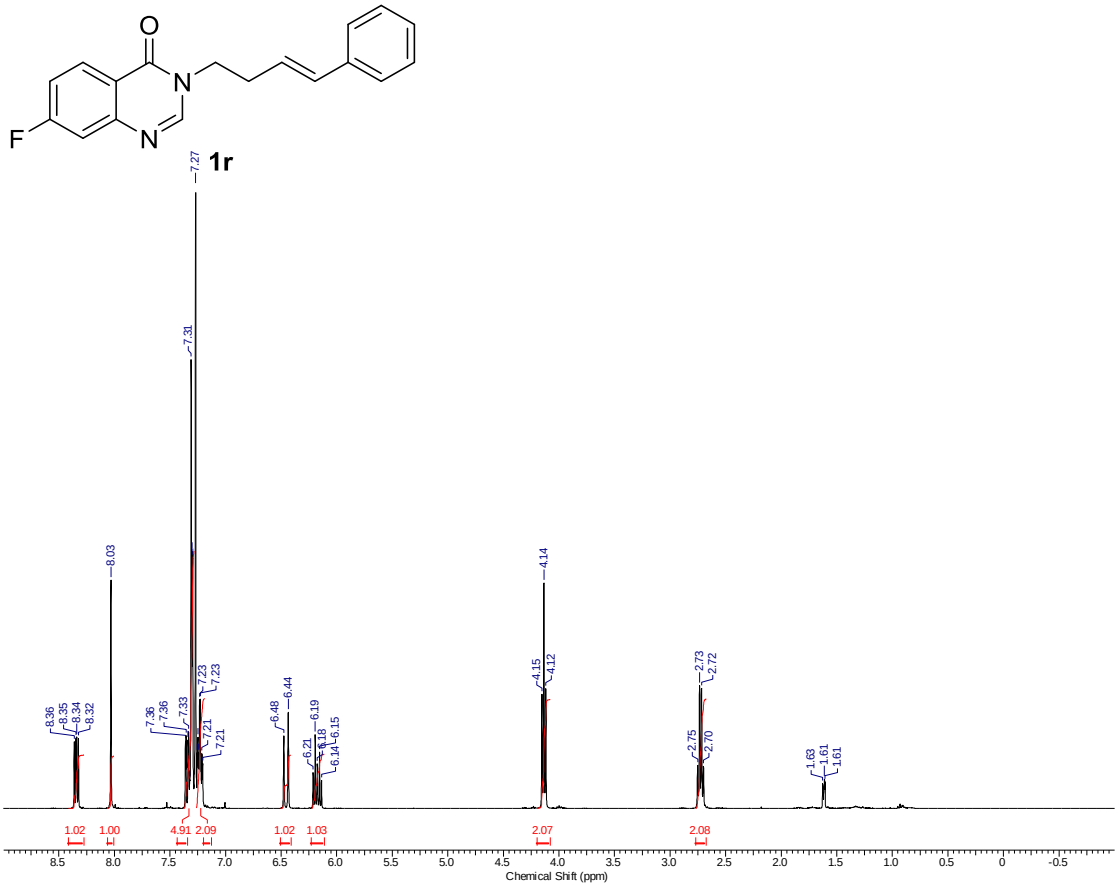


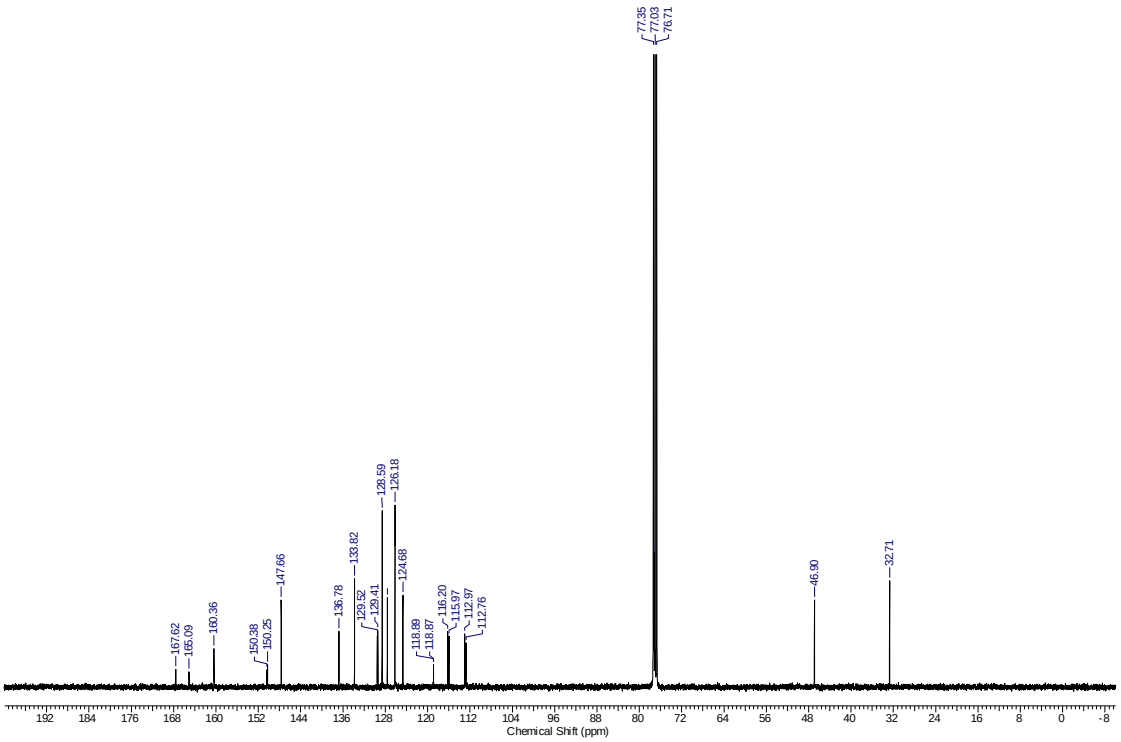
^{13}C NMR (101 MHz, $CDCl_3$)c



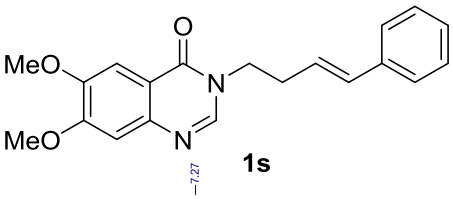
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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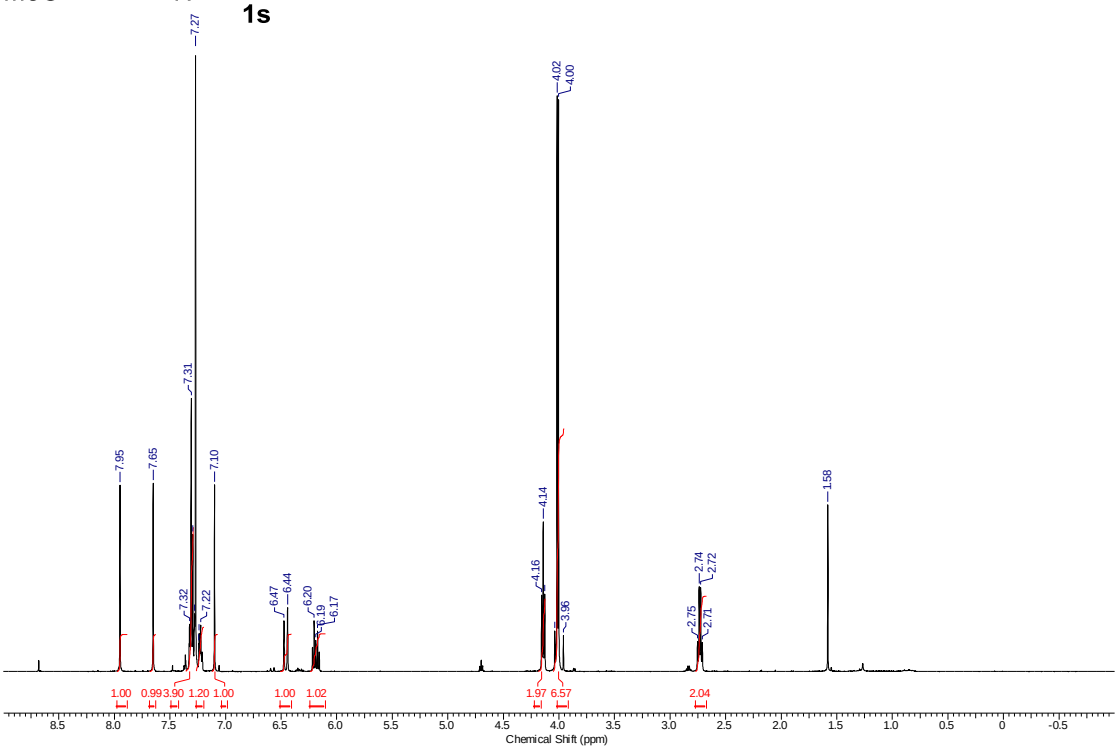
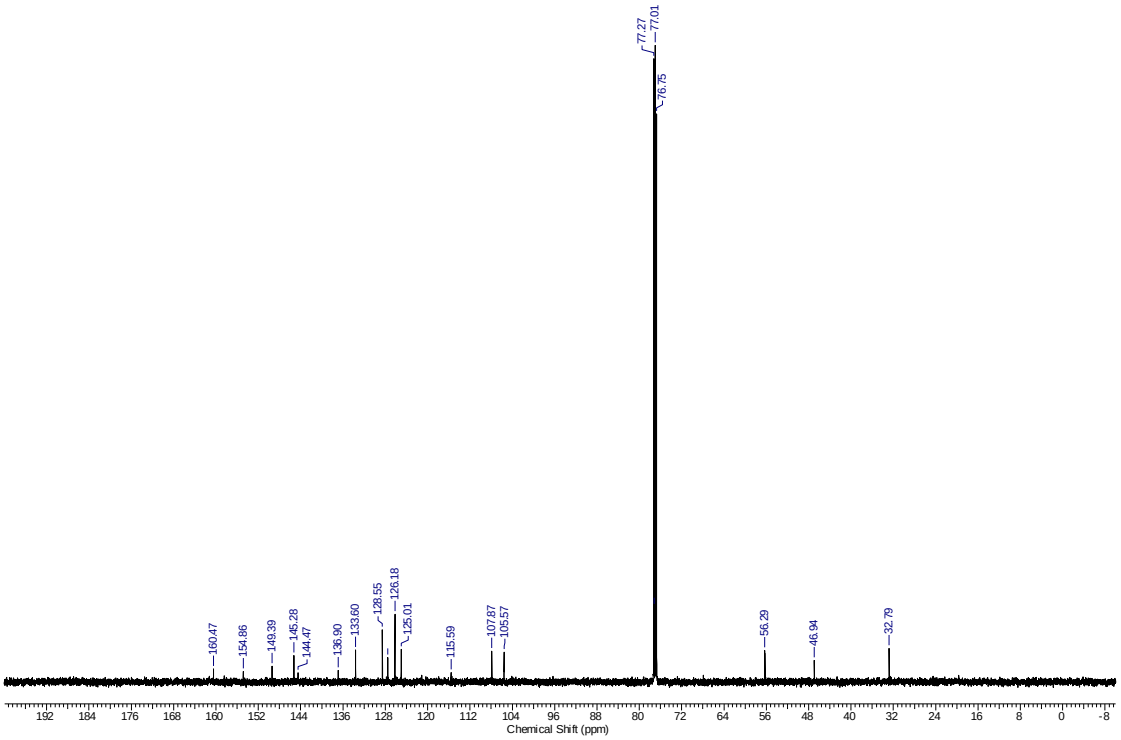
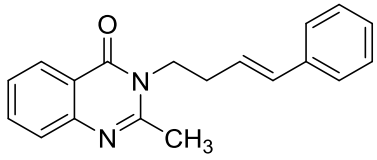


^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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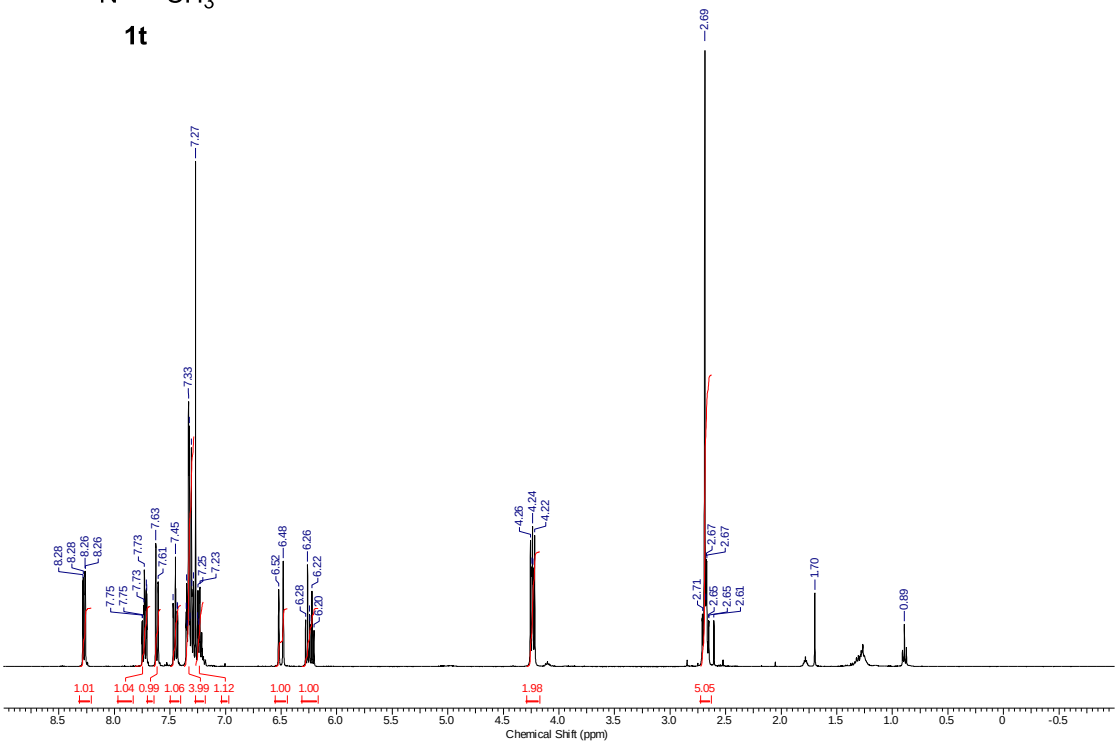
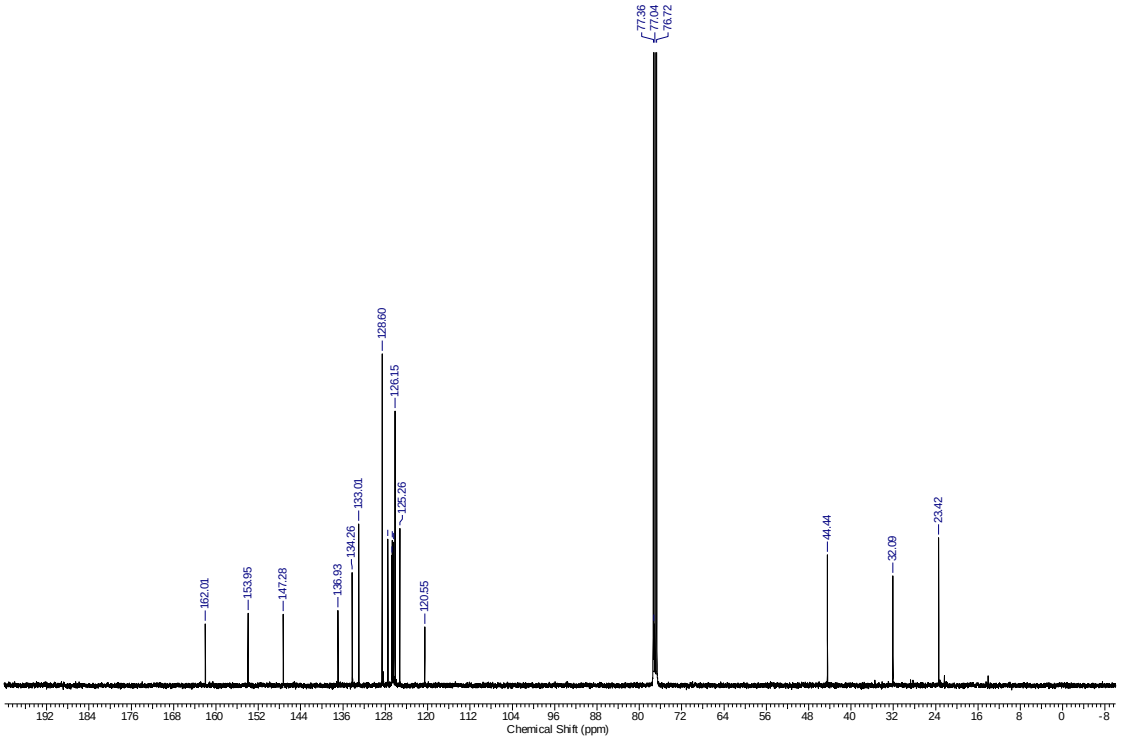
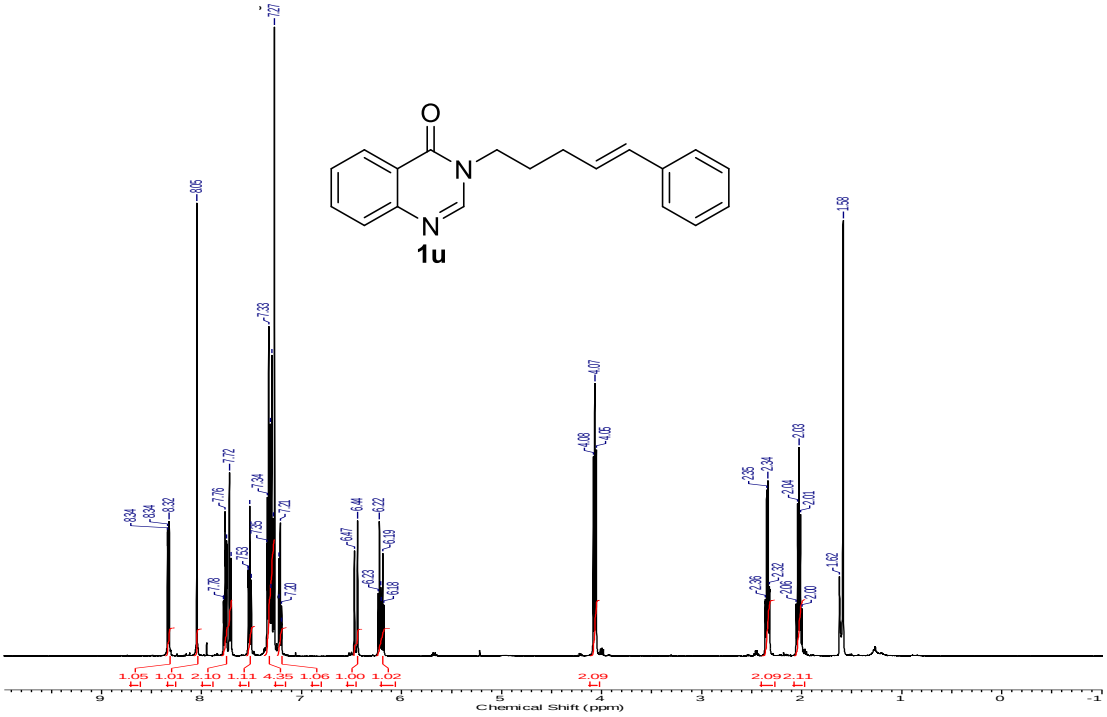


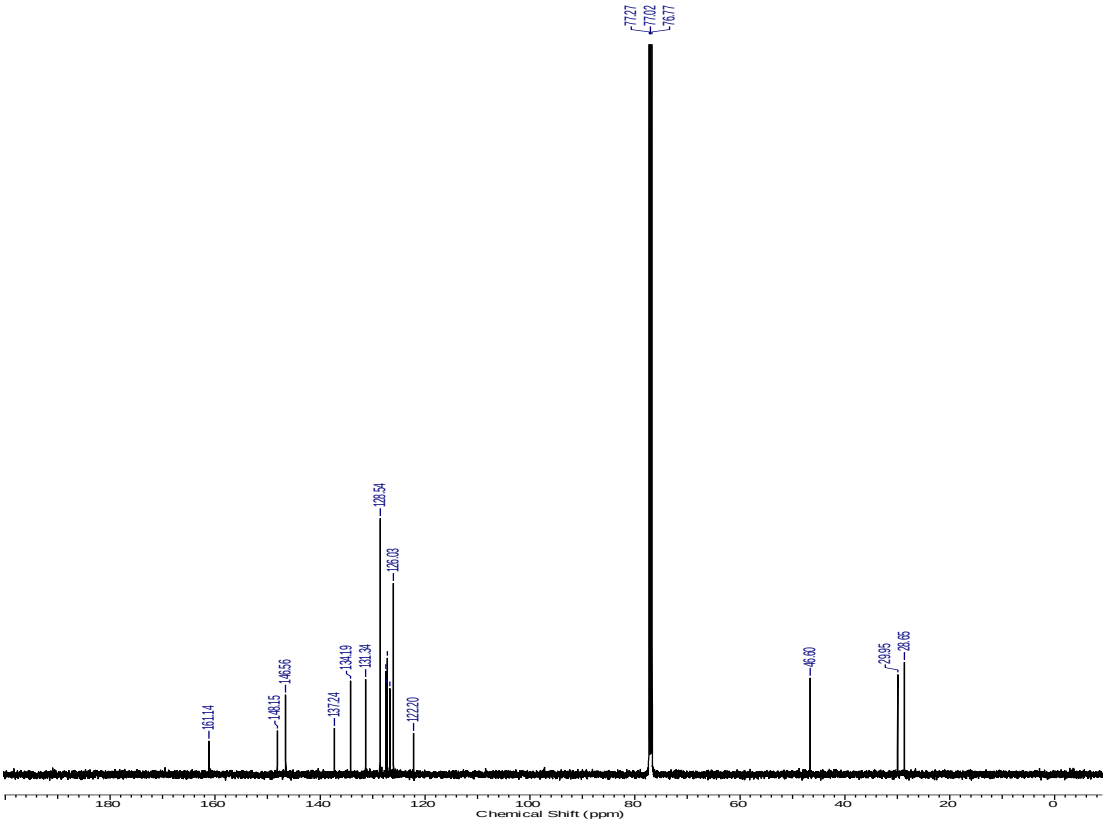
^{13}C NMR (101 MHz, $CDCl_3$)



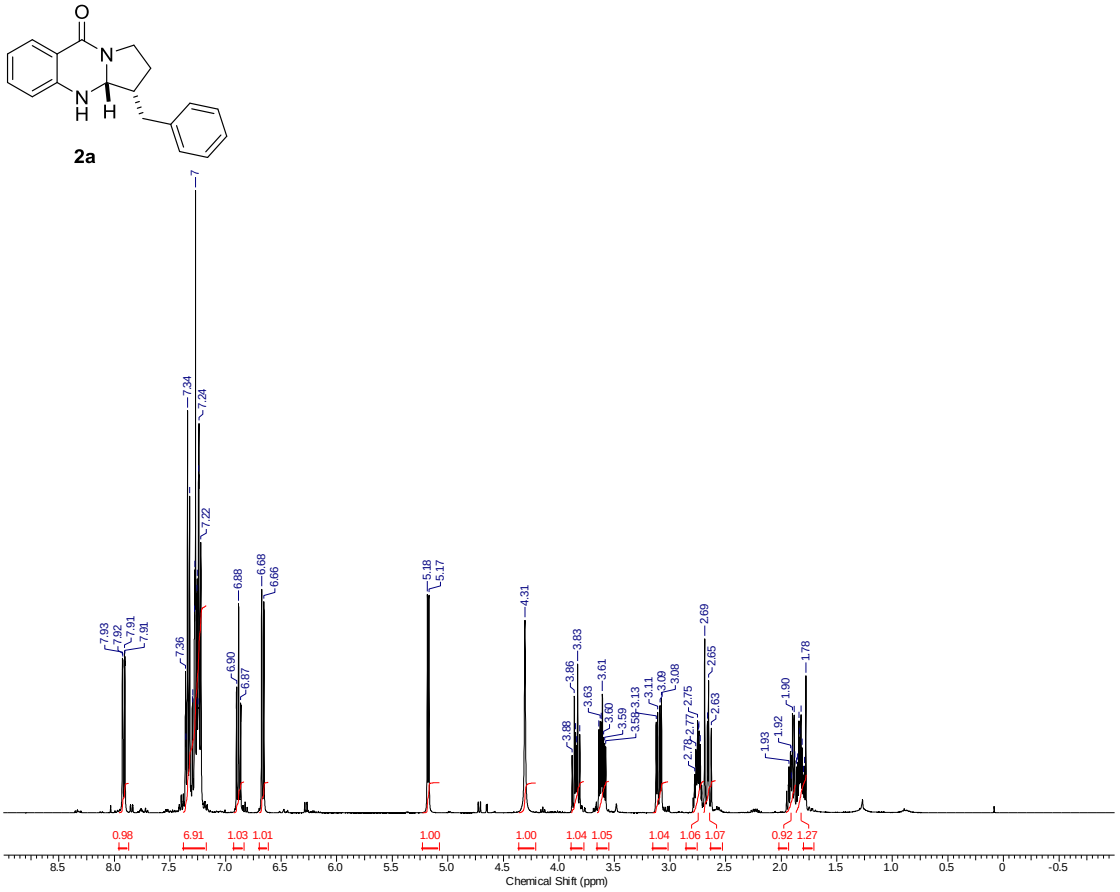
^{1}H NMR (500 MHz, $CDCl_3$)



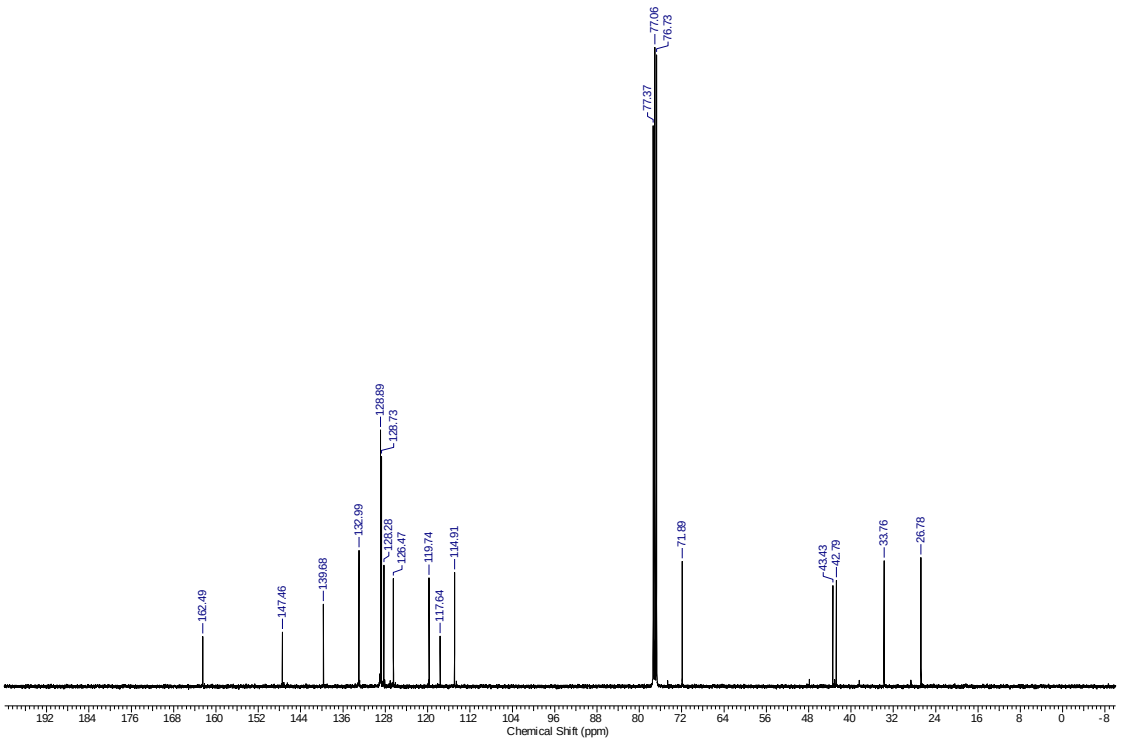
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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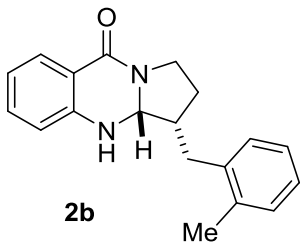

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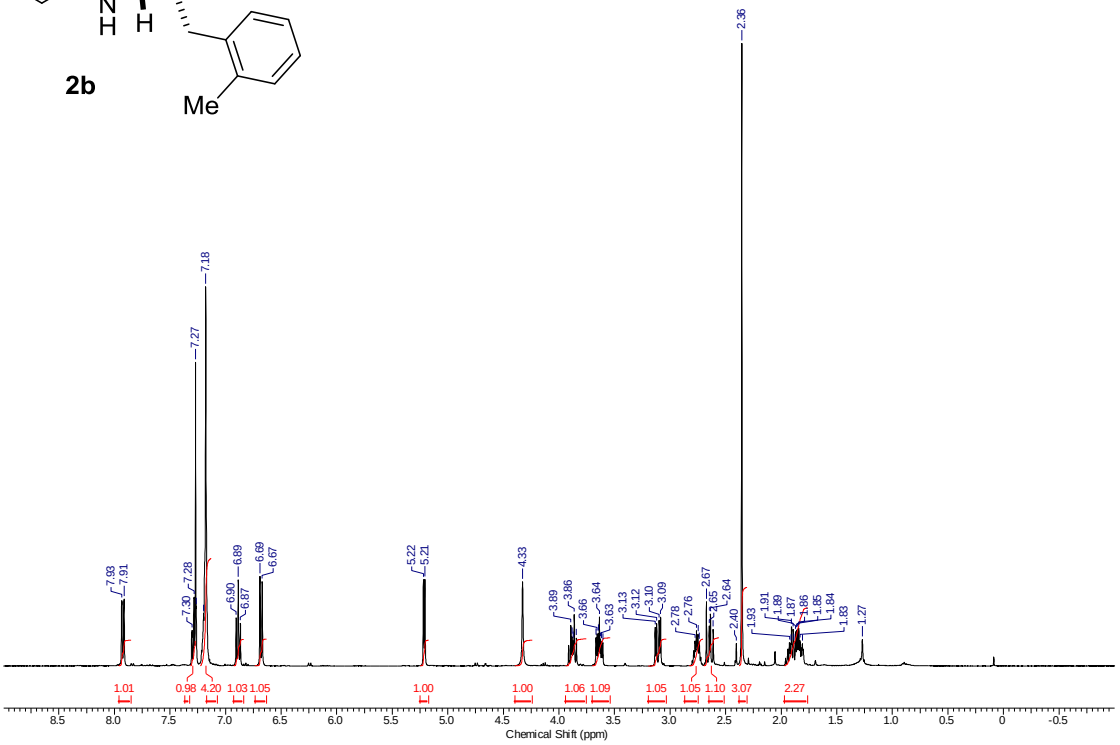
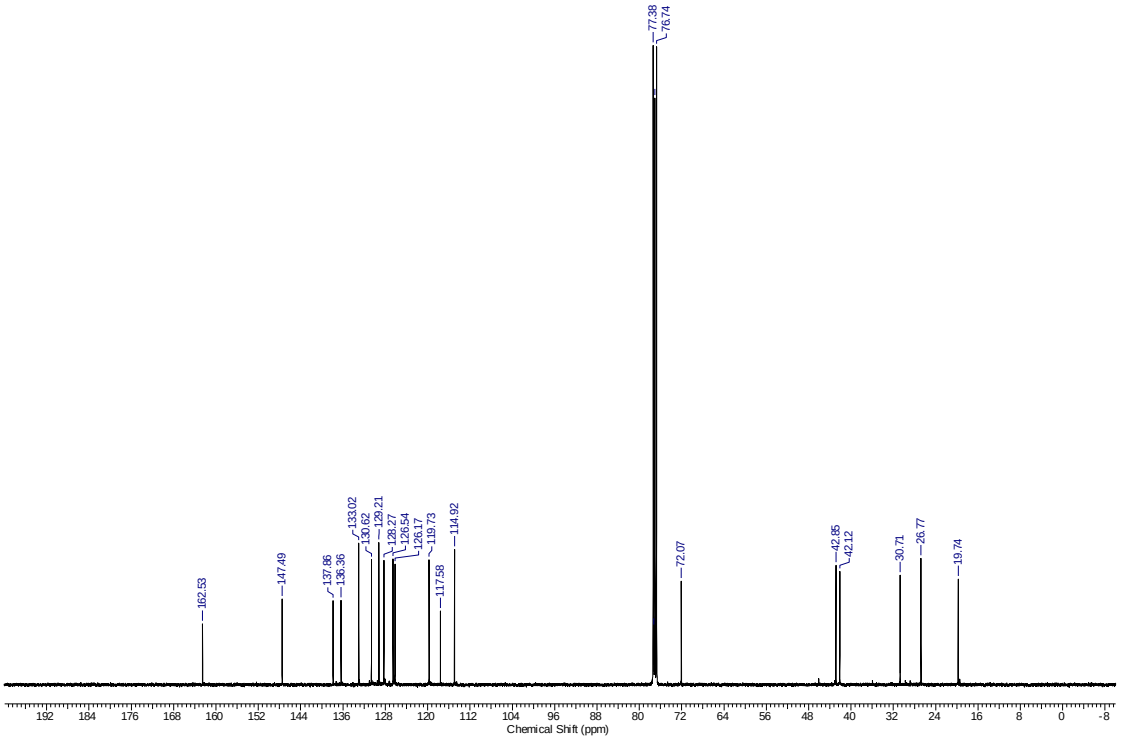


^{13}C NMR (101 MHz, $CDCl_3$)



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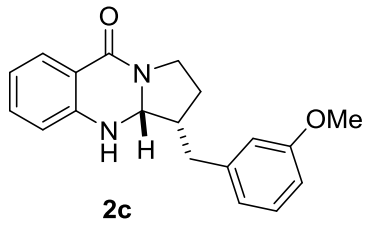

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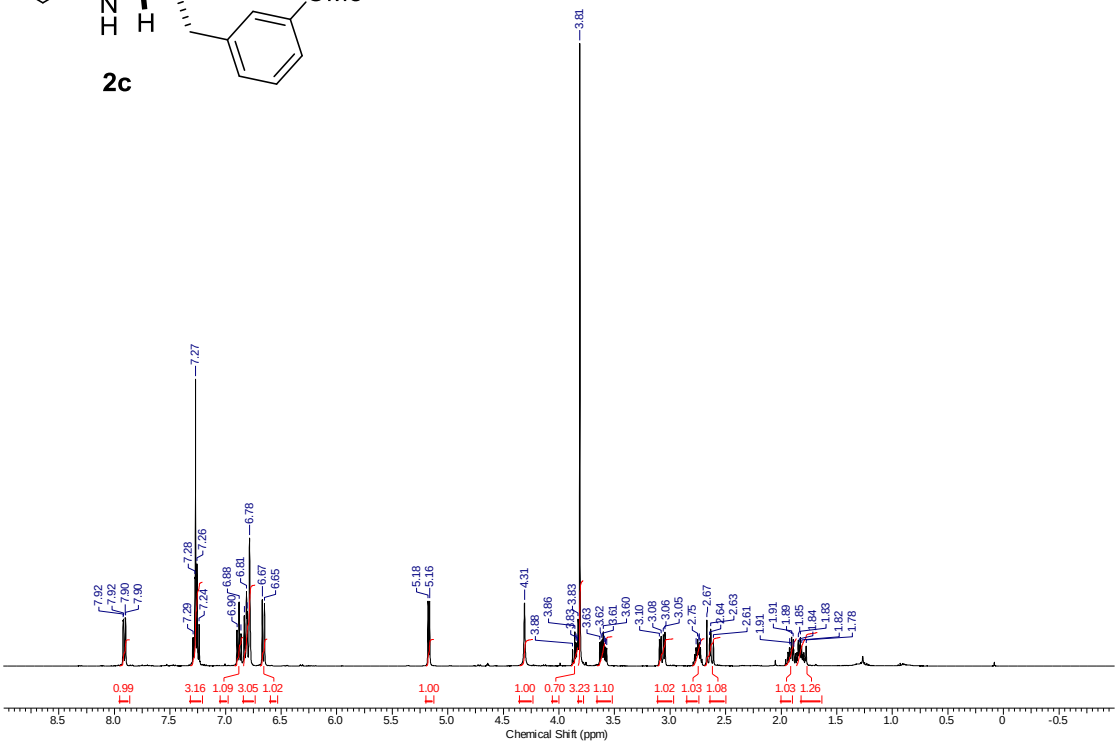
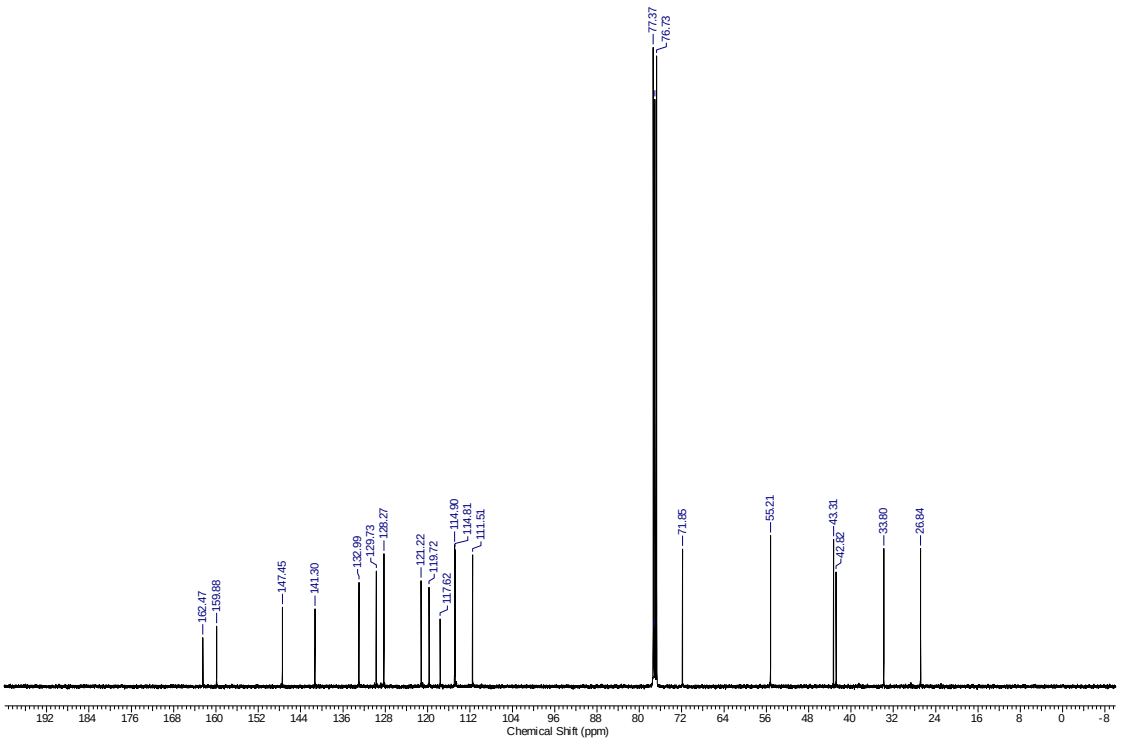
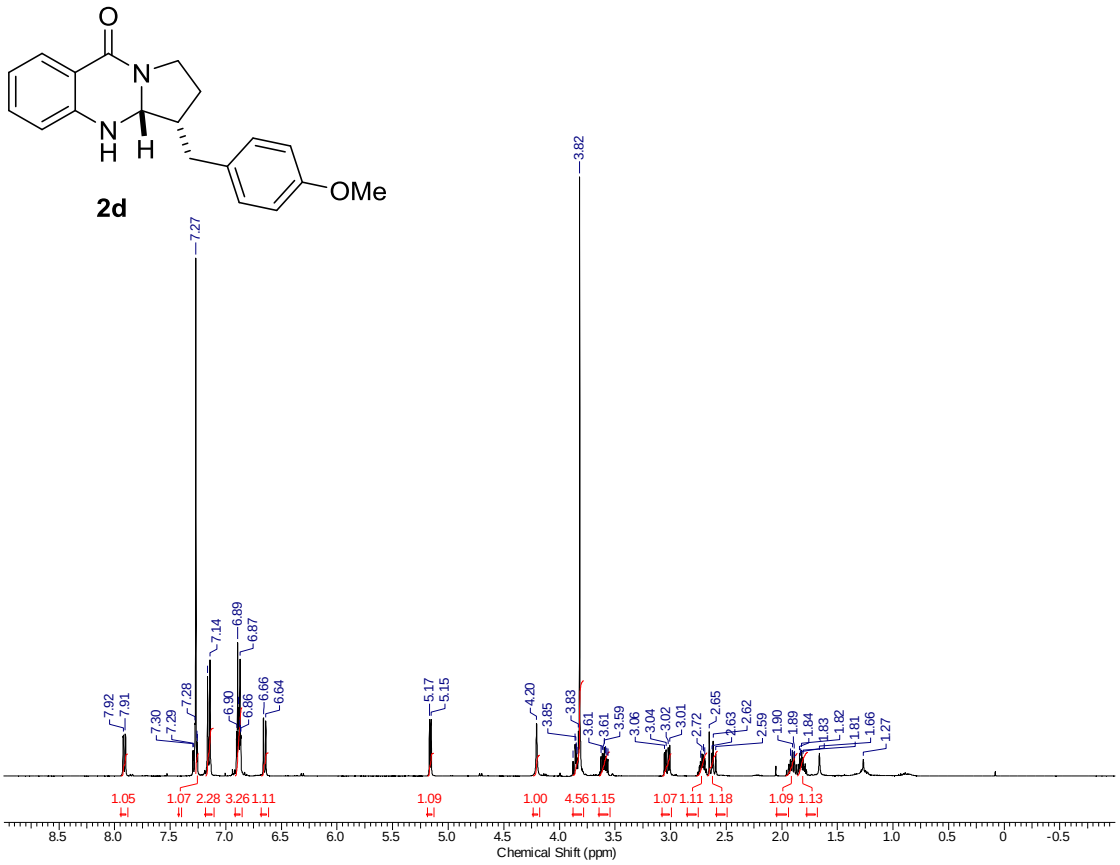


^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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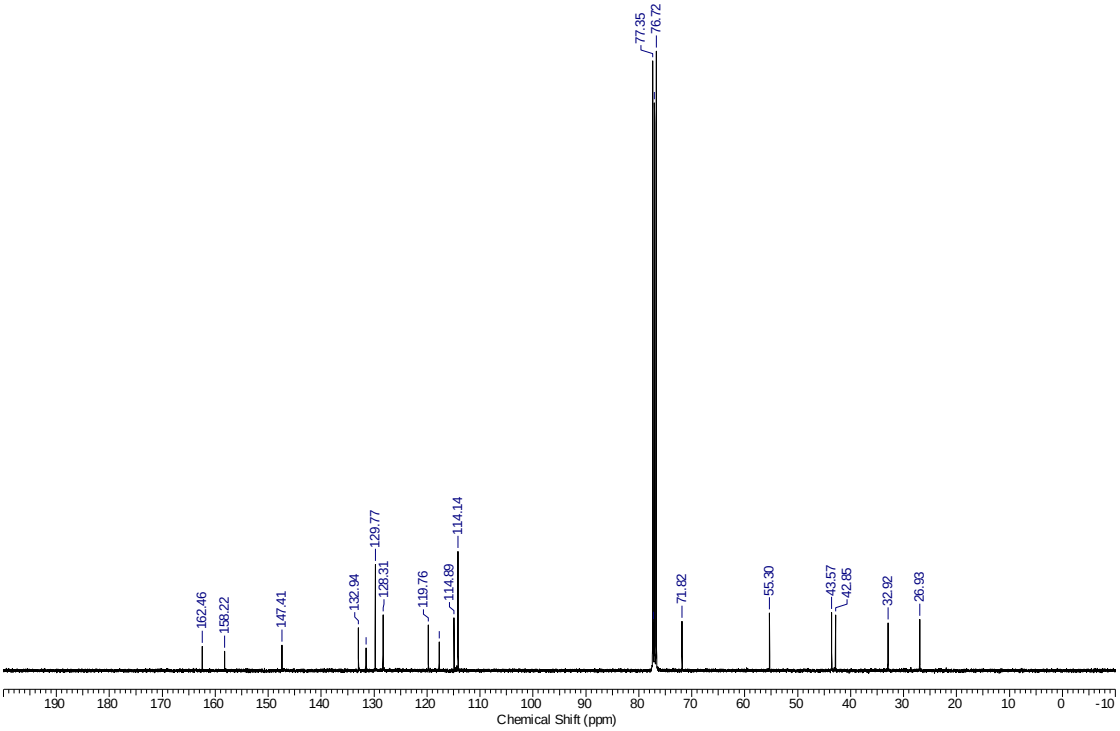
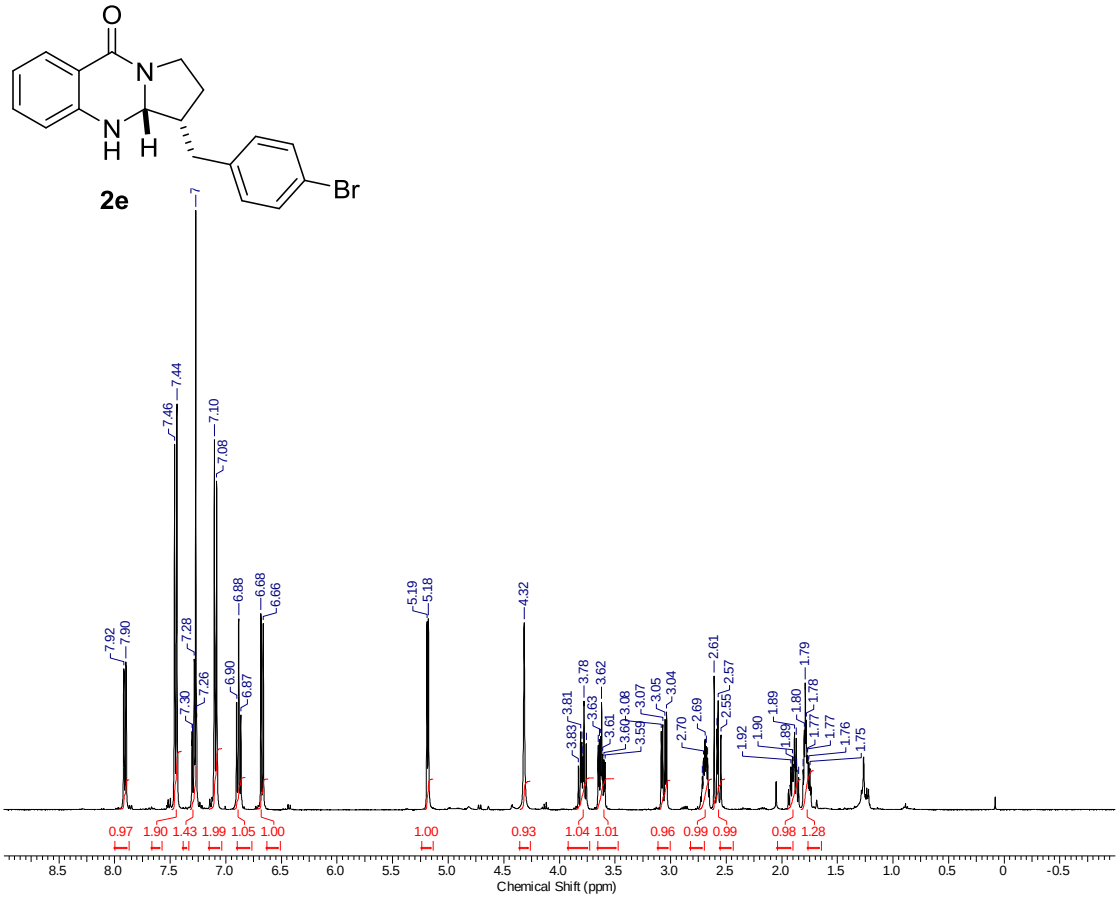


^{1}H NMR (400 MHz, $CDCl_3$)



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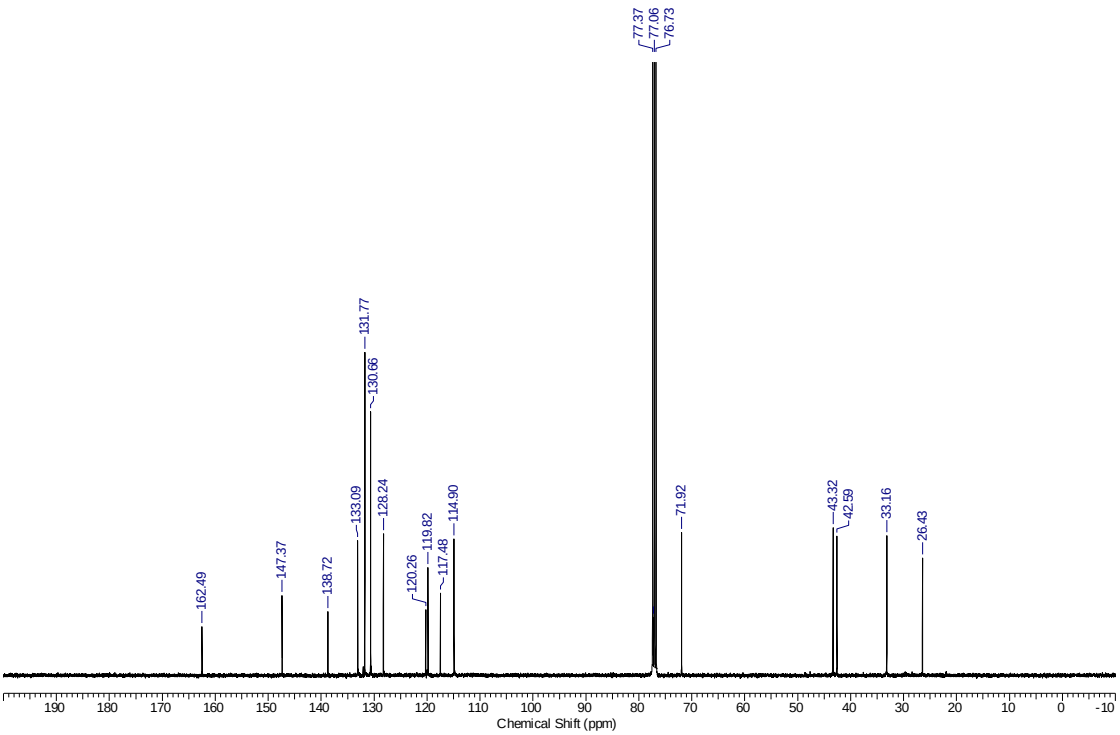

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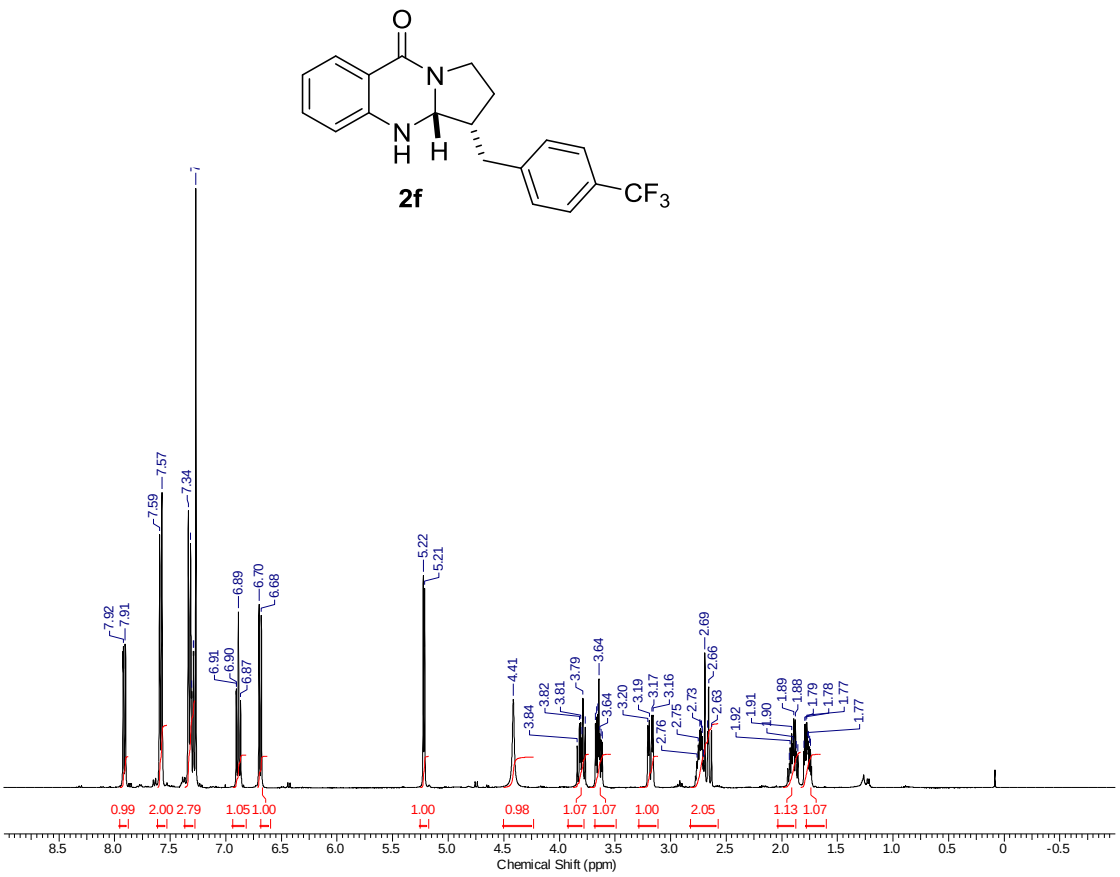

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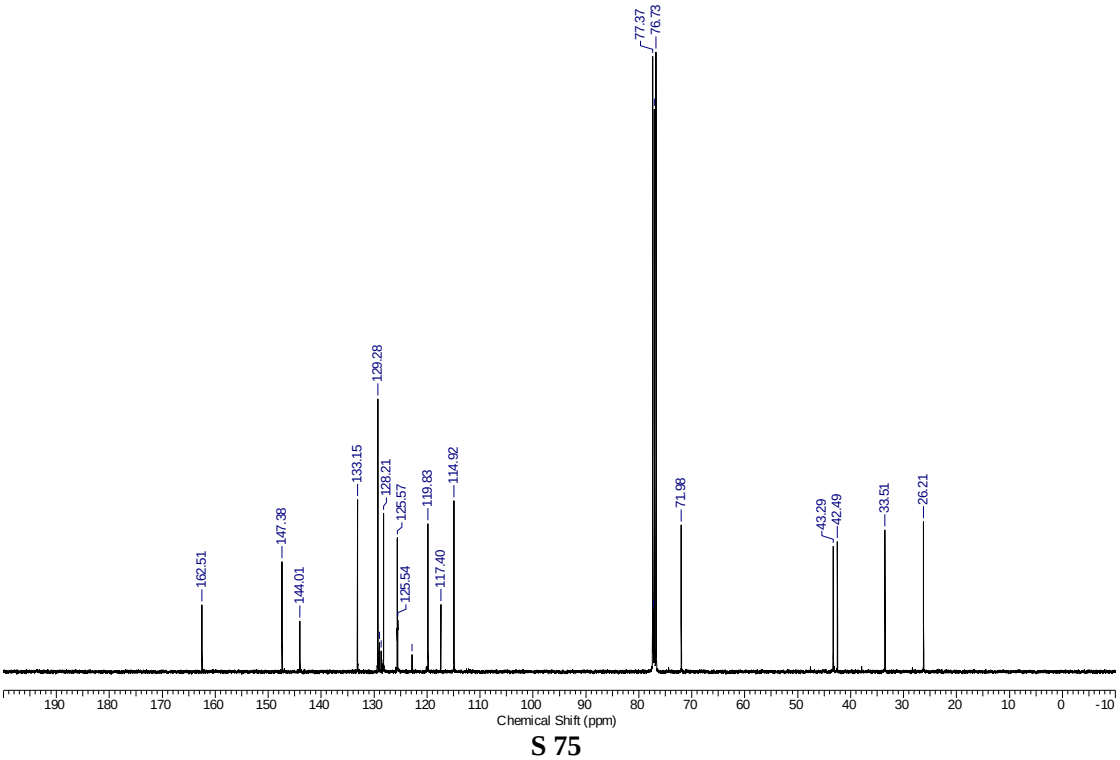

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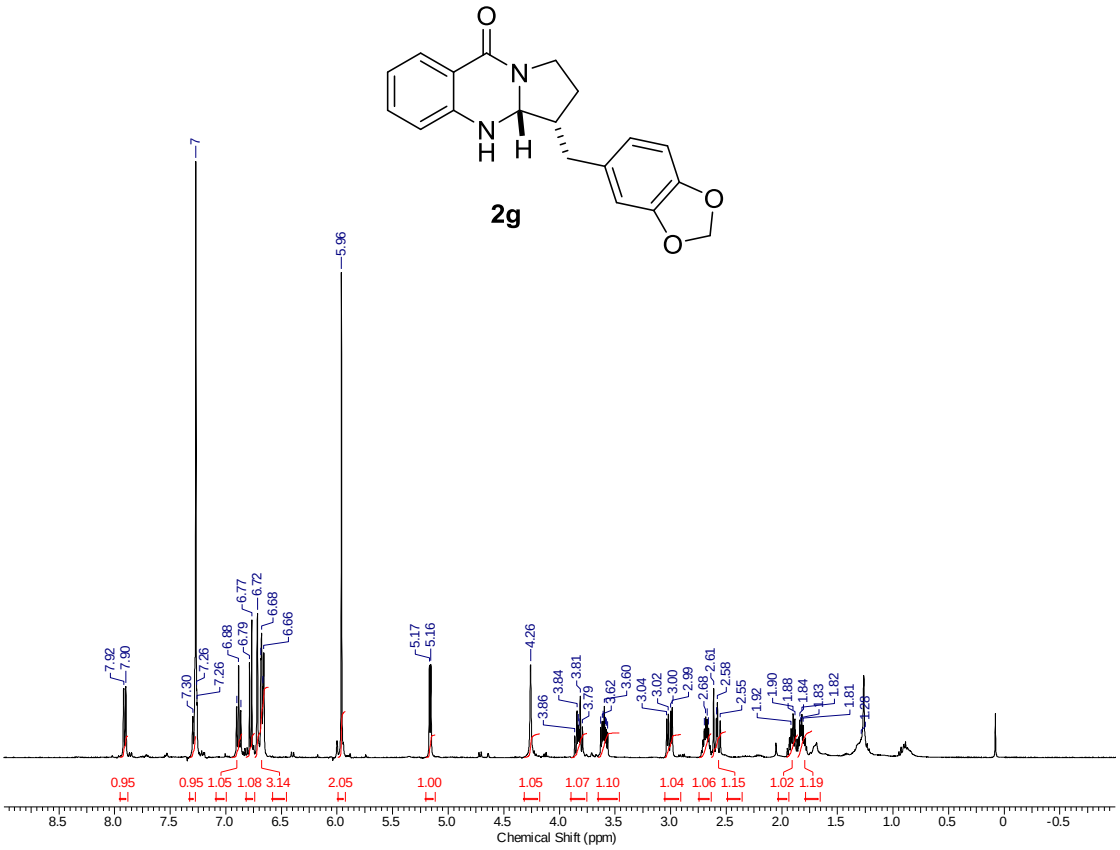

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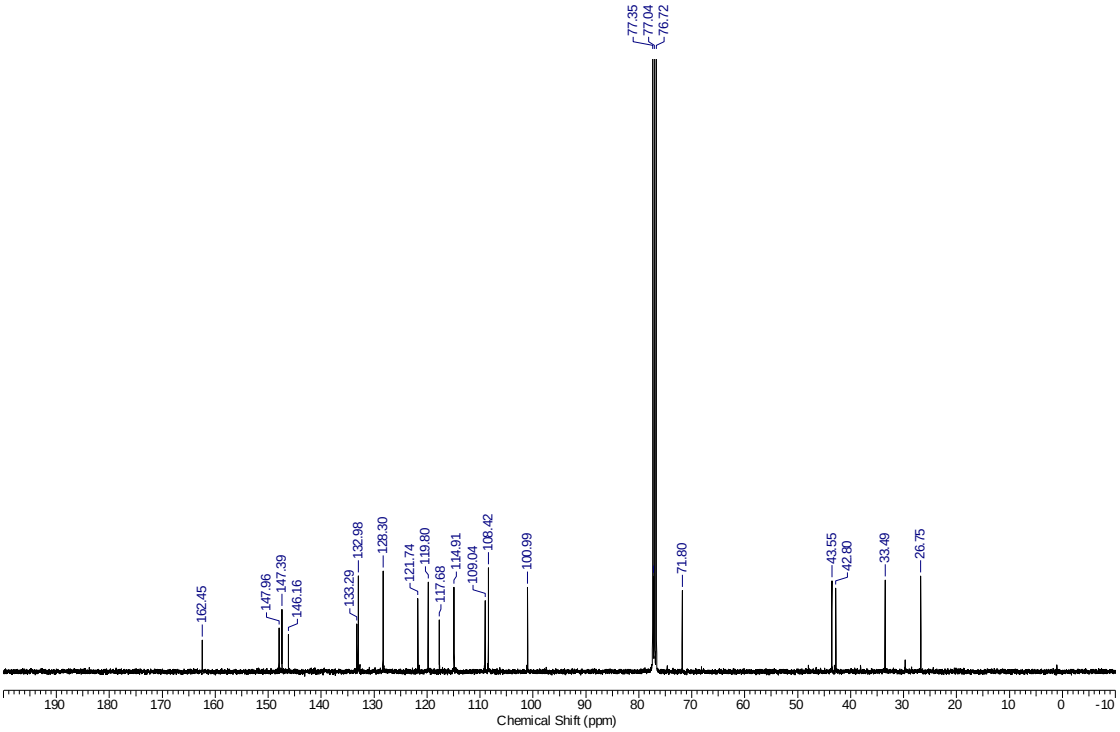

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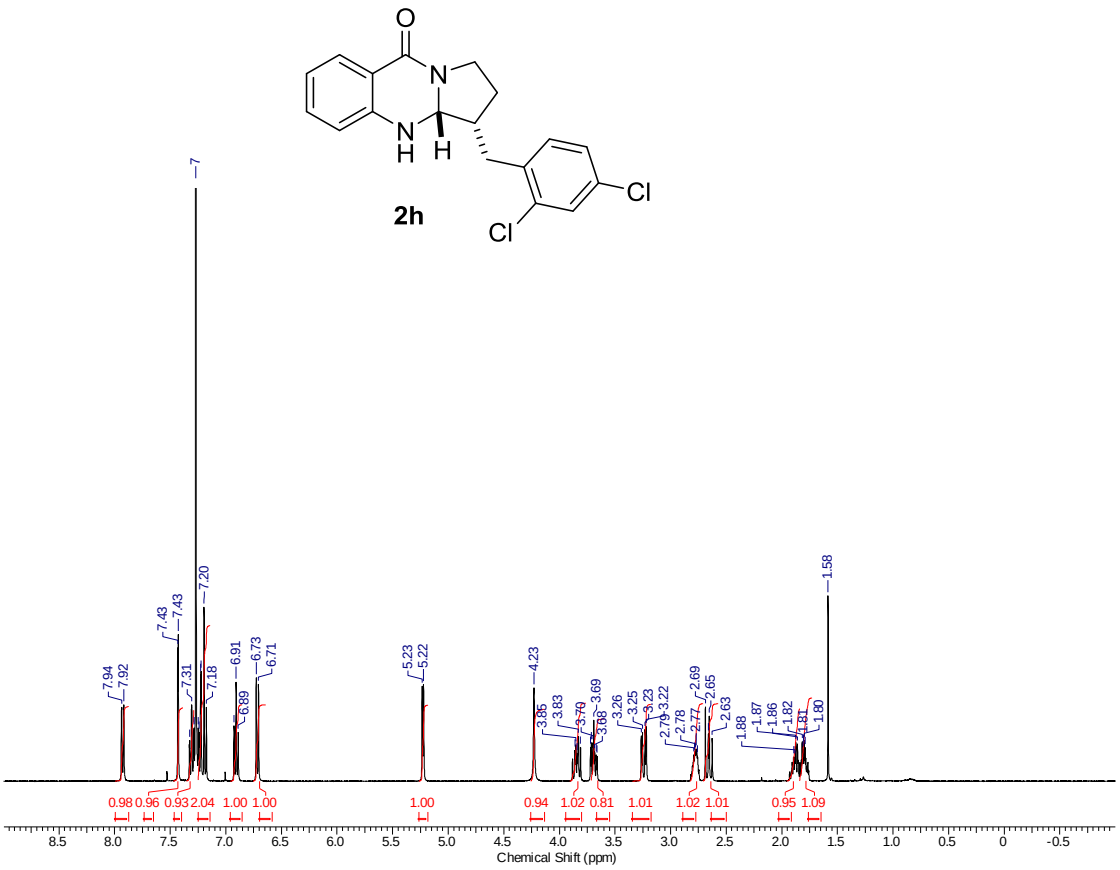

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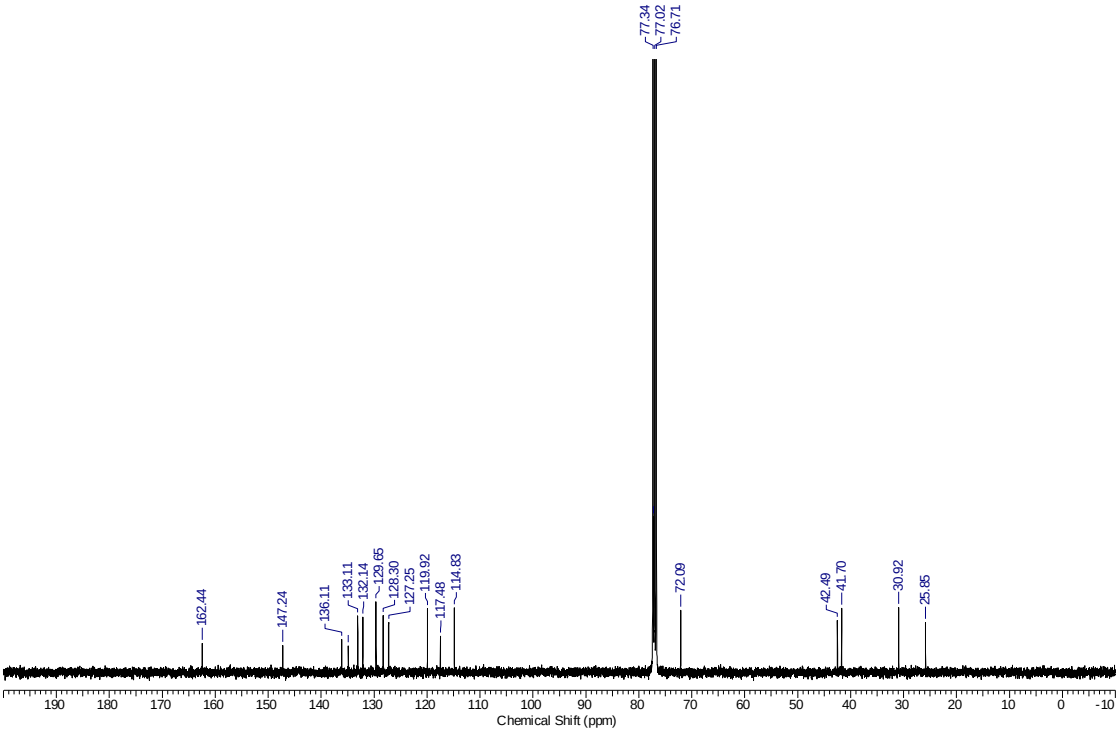

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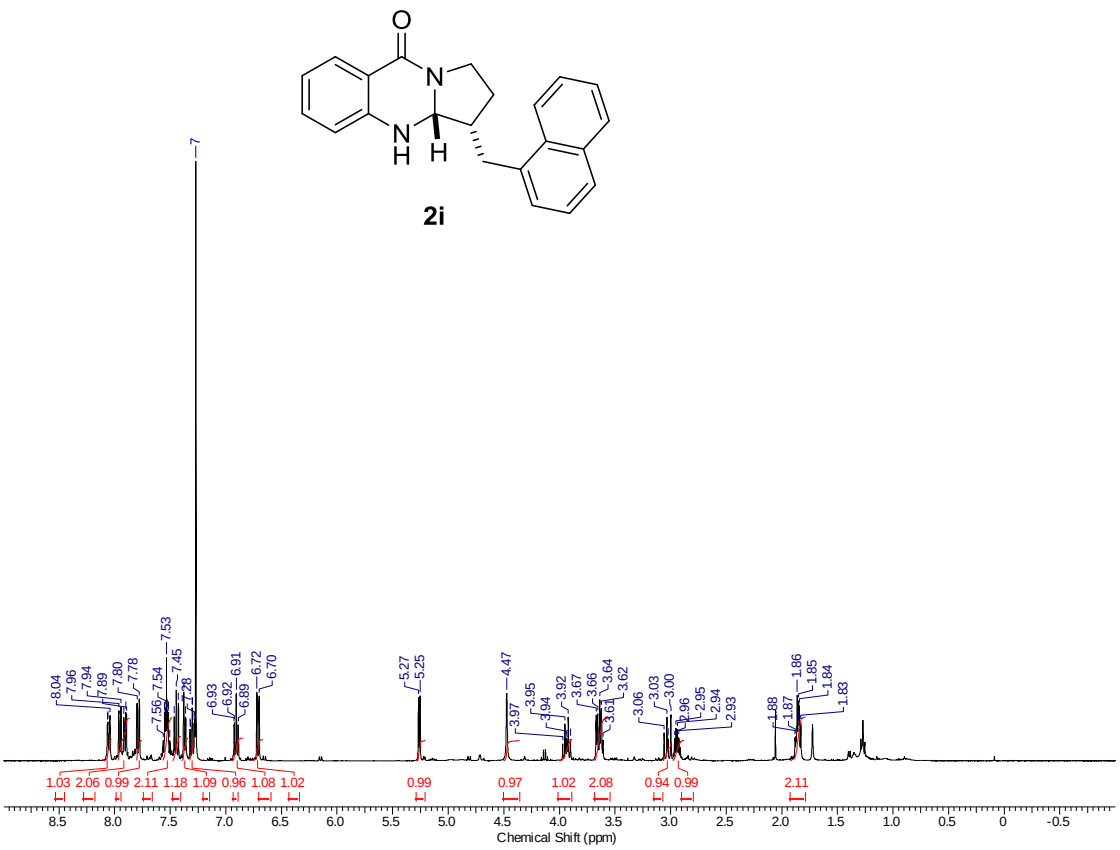

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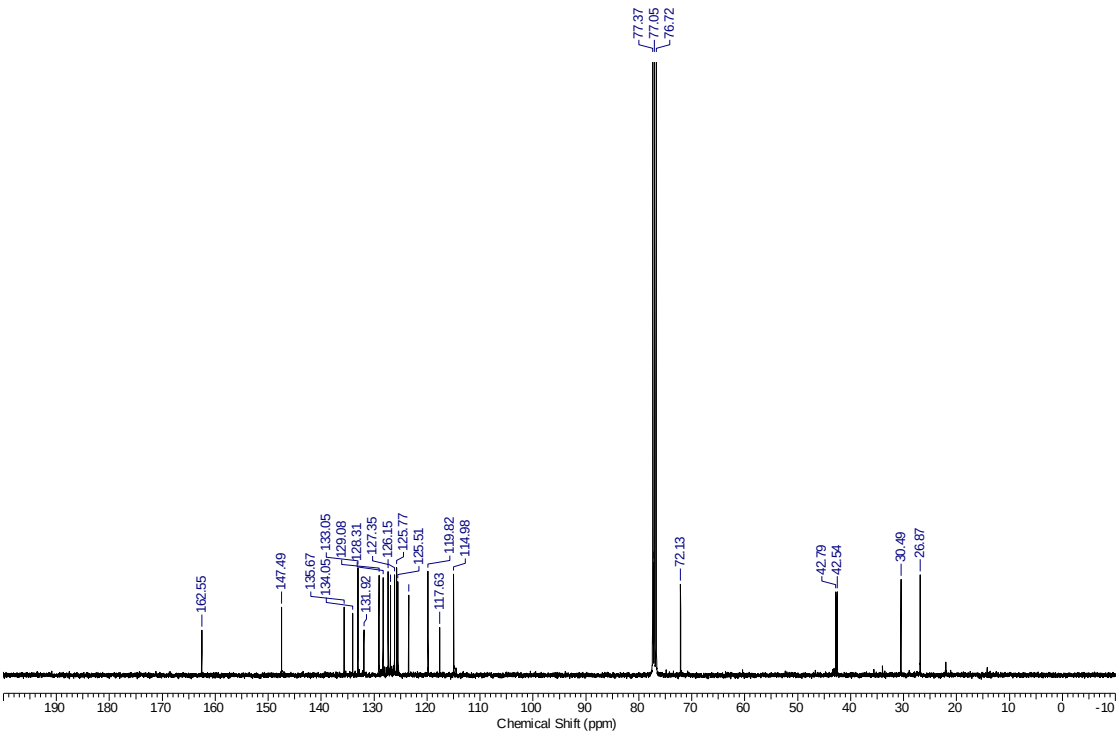

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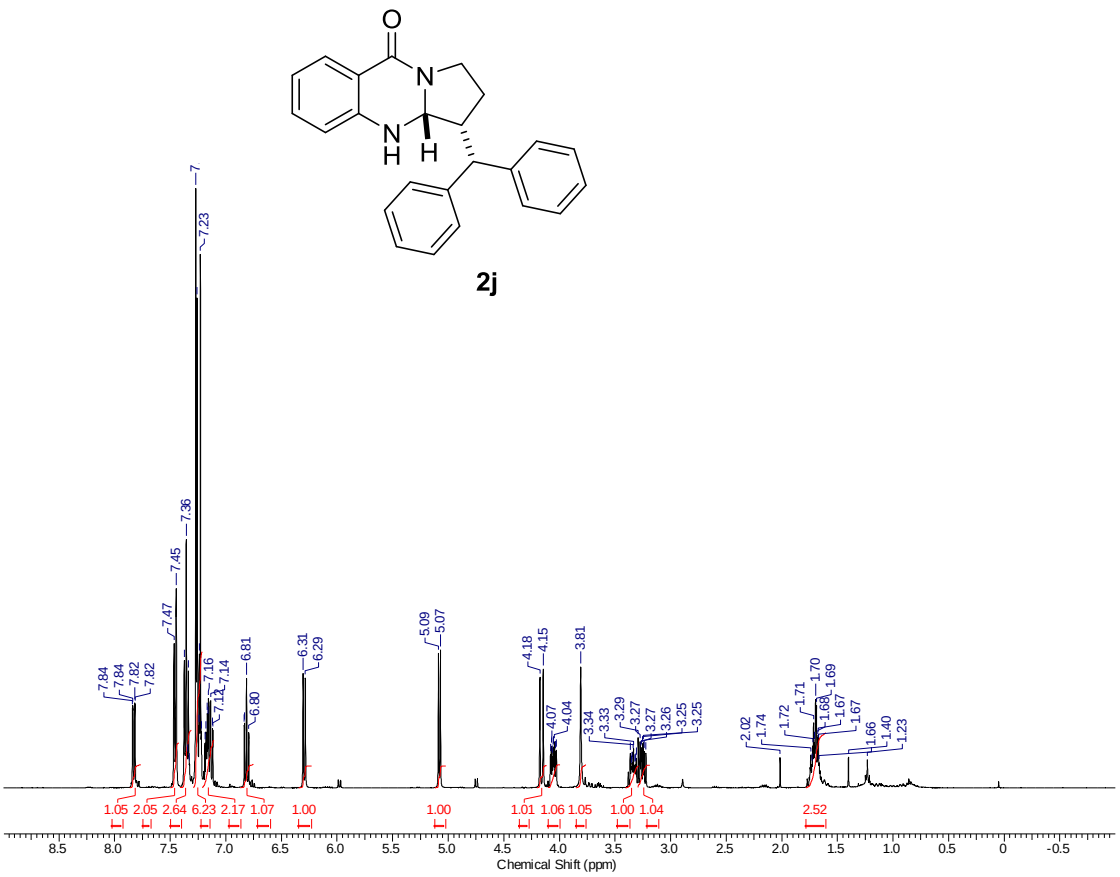

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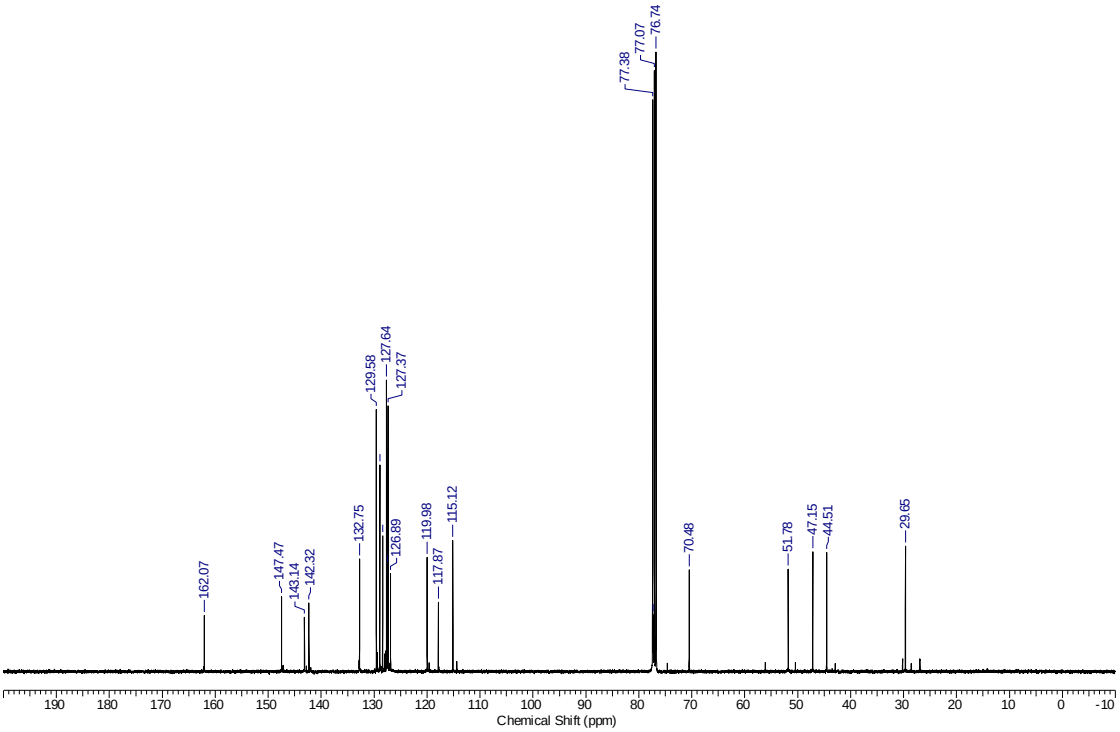

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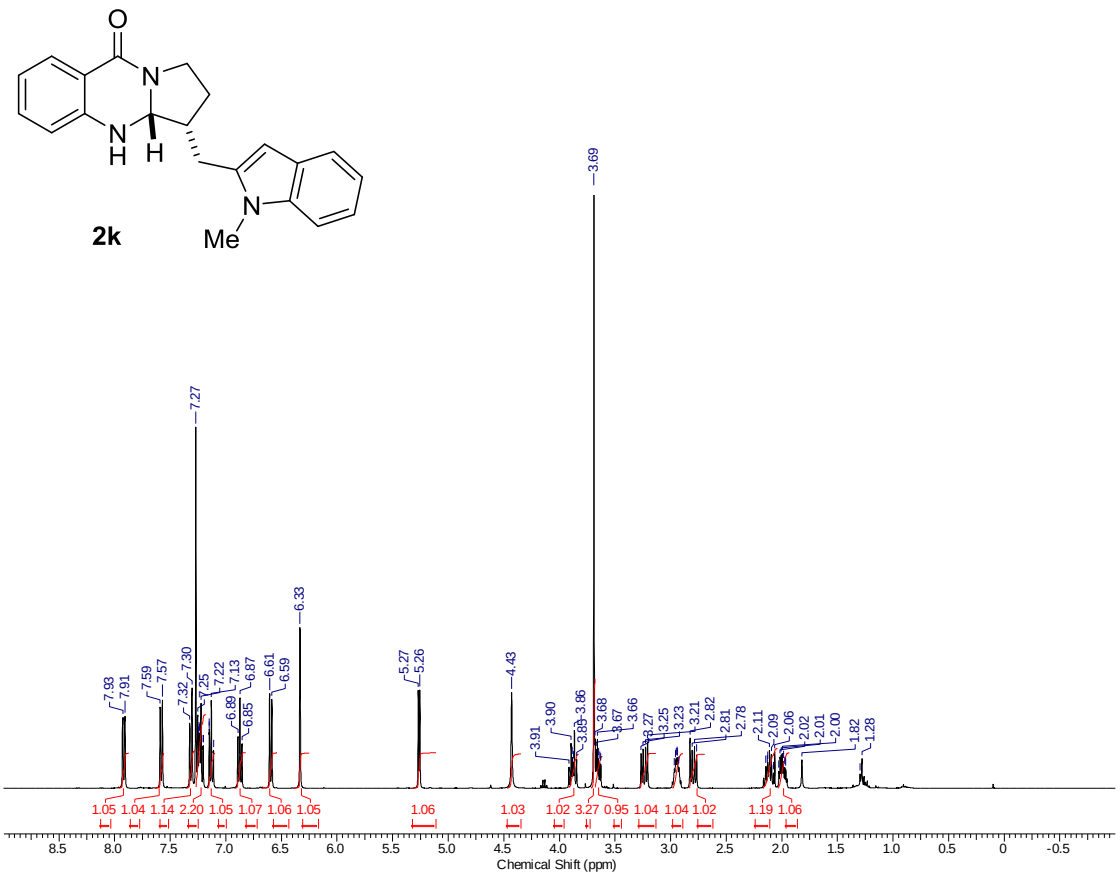
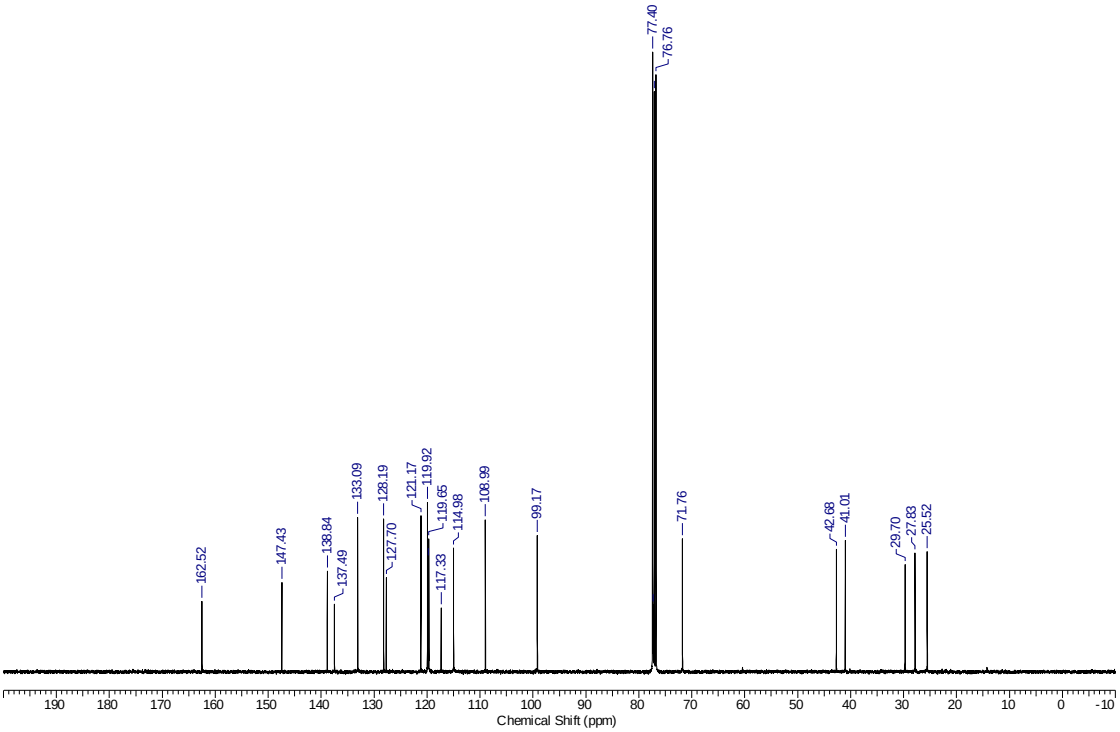
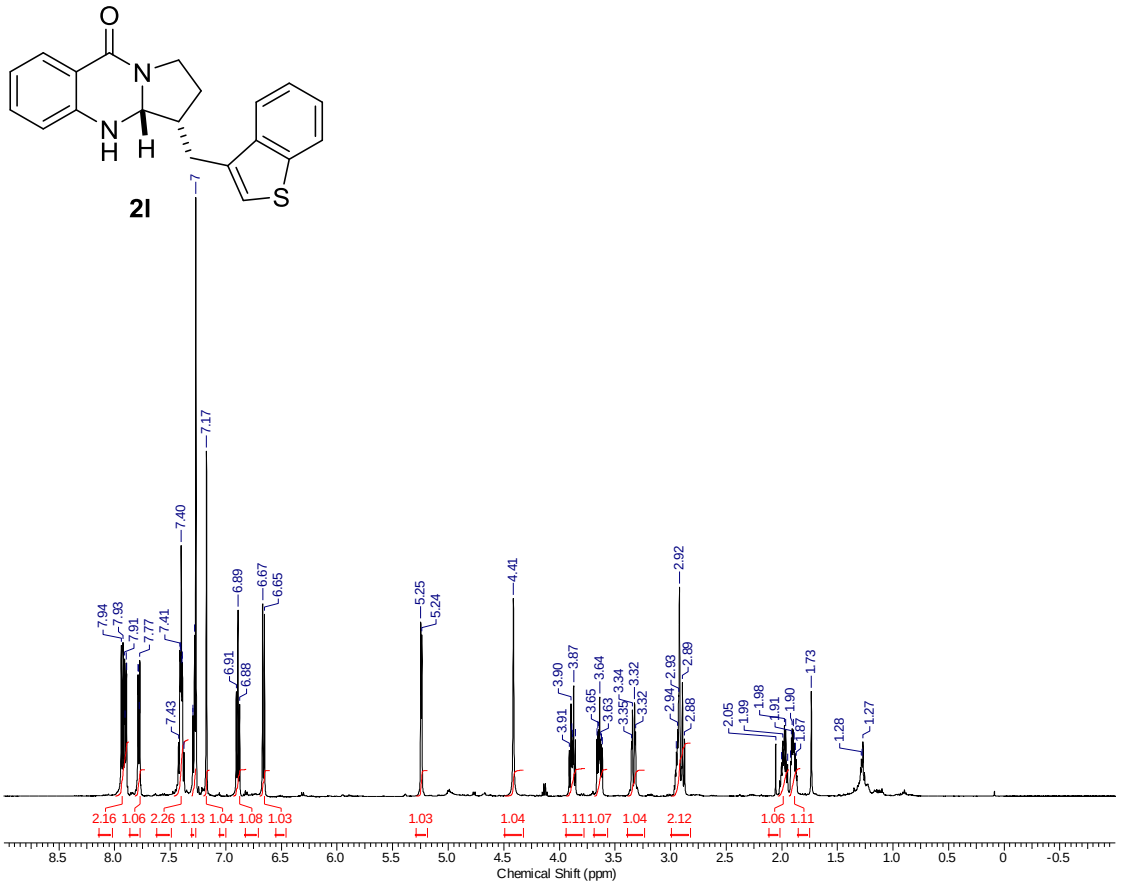


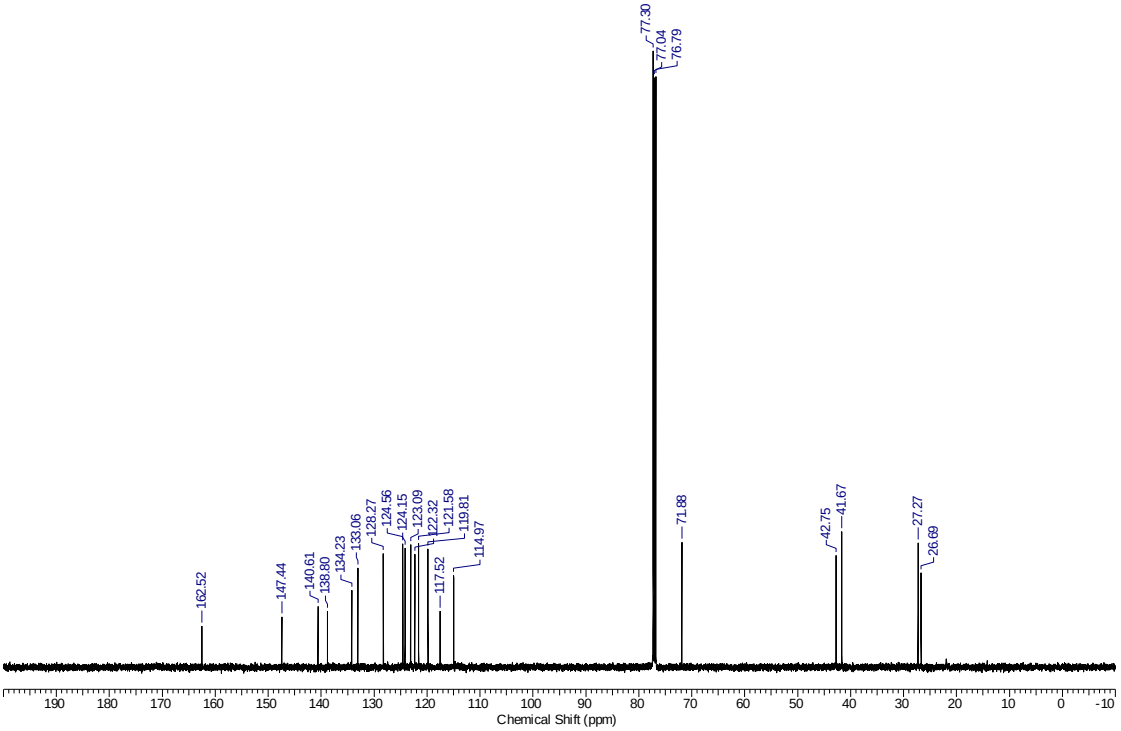
^{13}C NMR (101 MHz, $CDCl_3$)



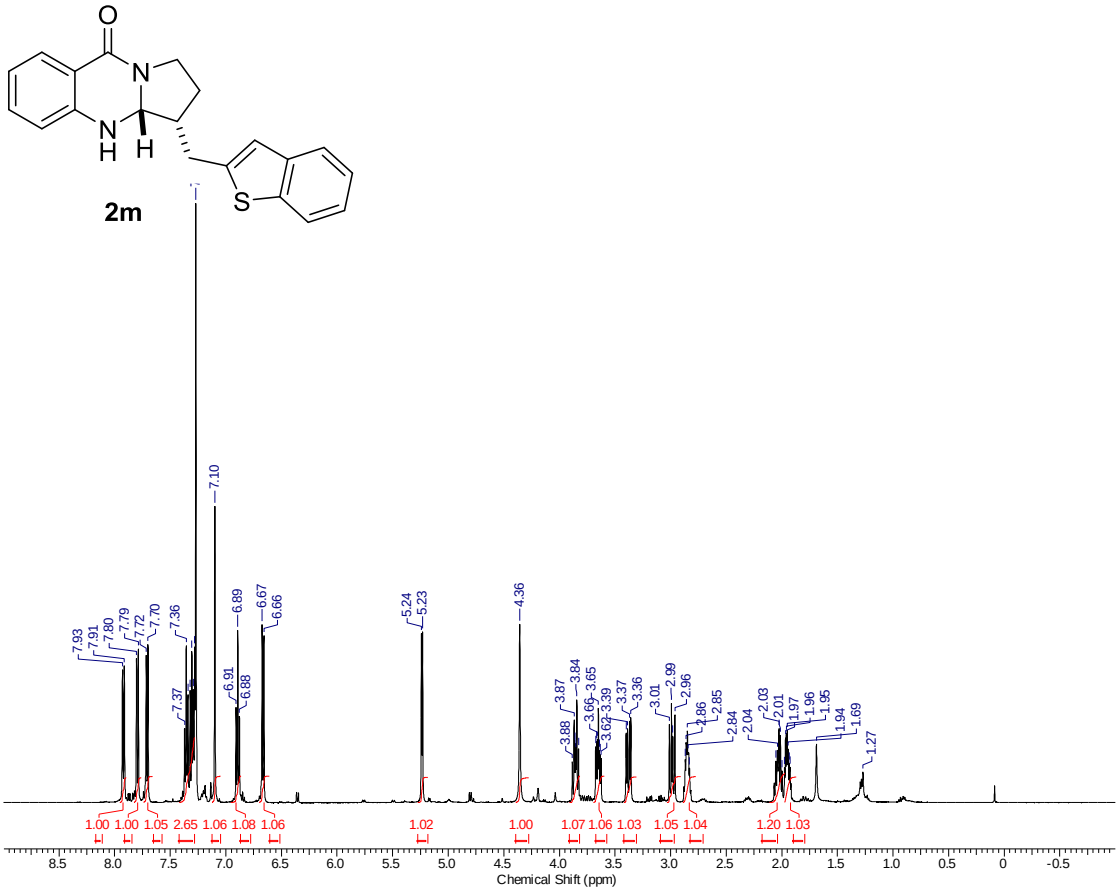
^{1}H NMR (500 MHz, $CDCl_3$)



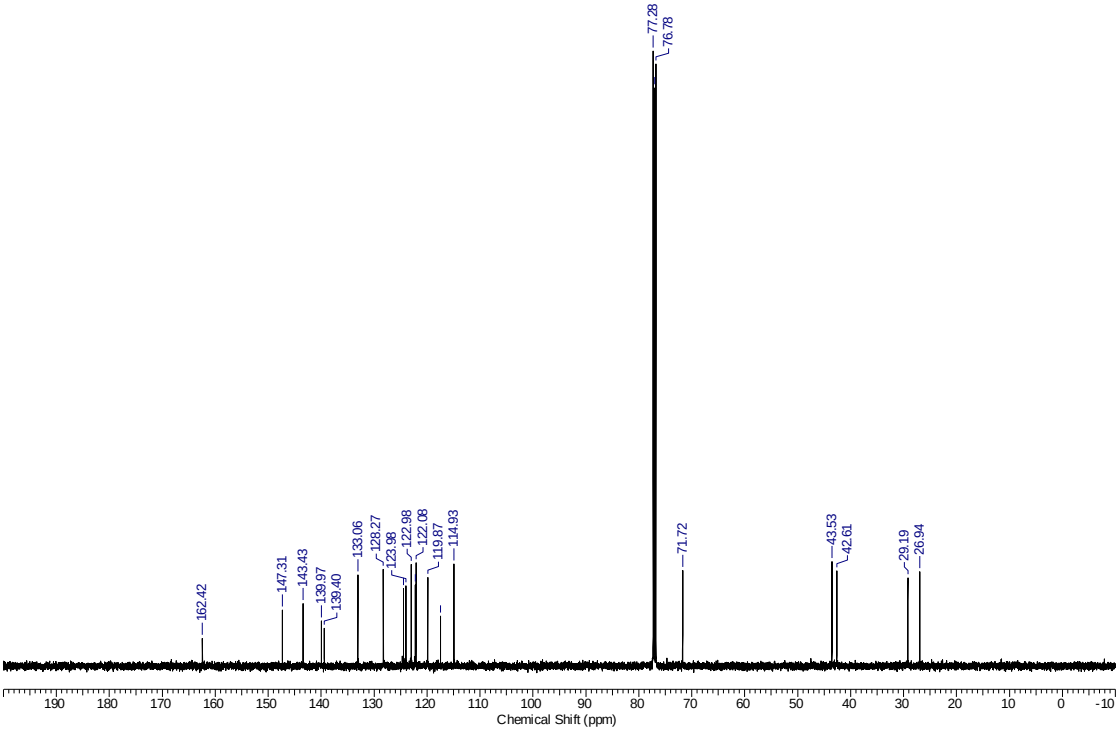
^{13}C NMR (126 MHz, $CDCl_3$)



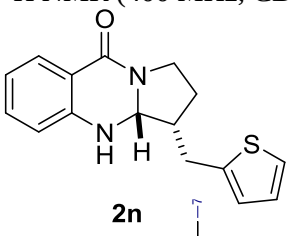
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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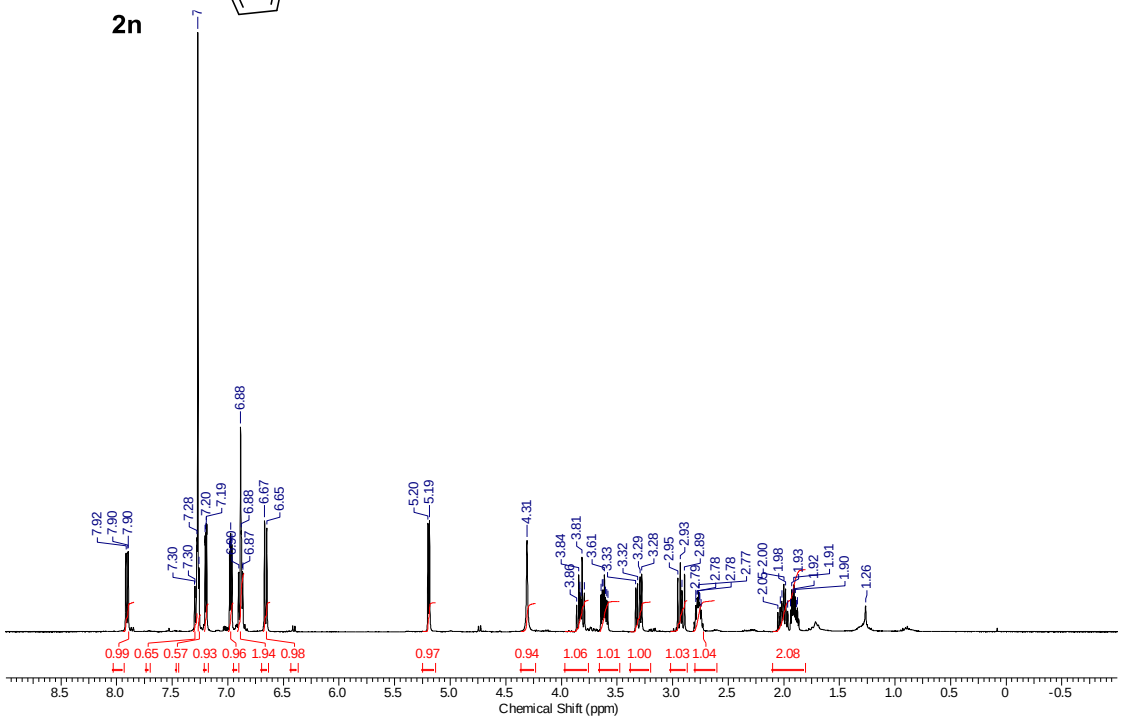
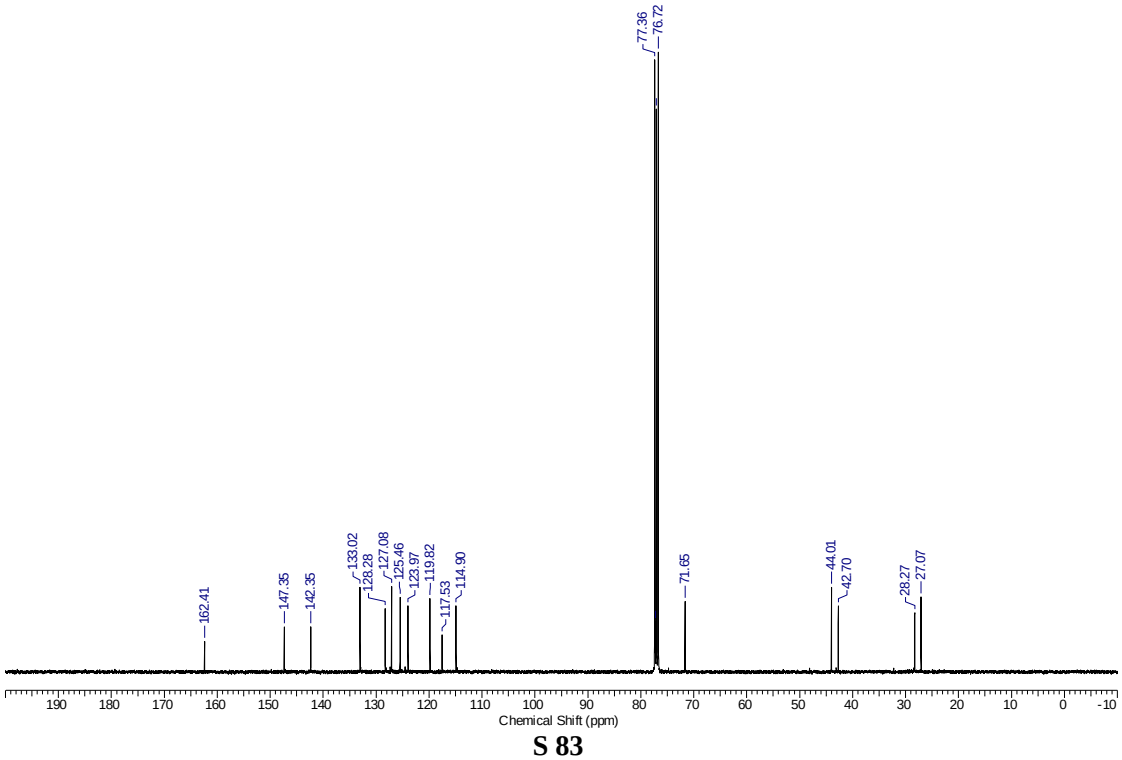
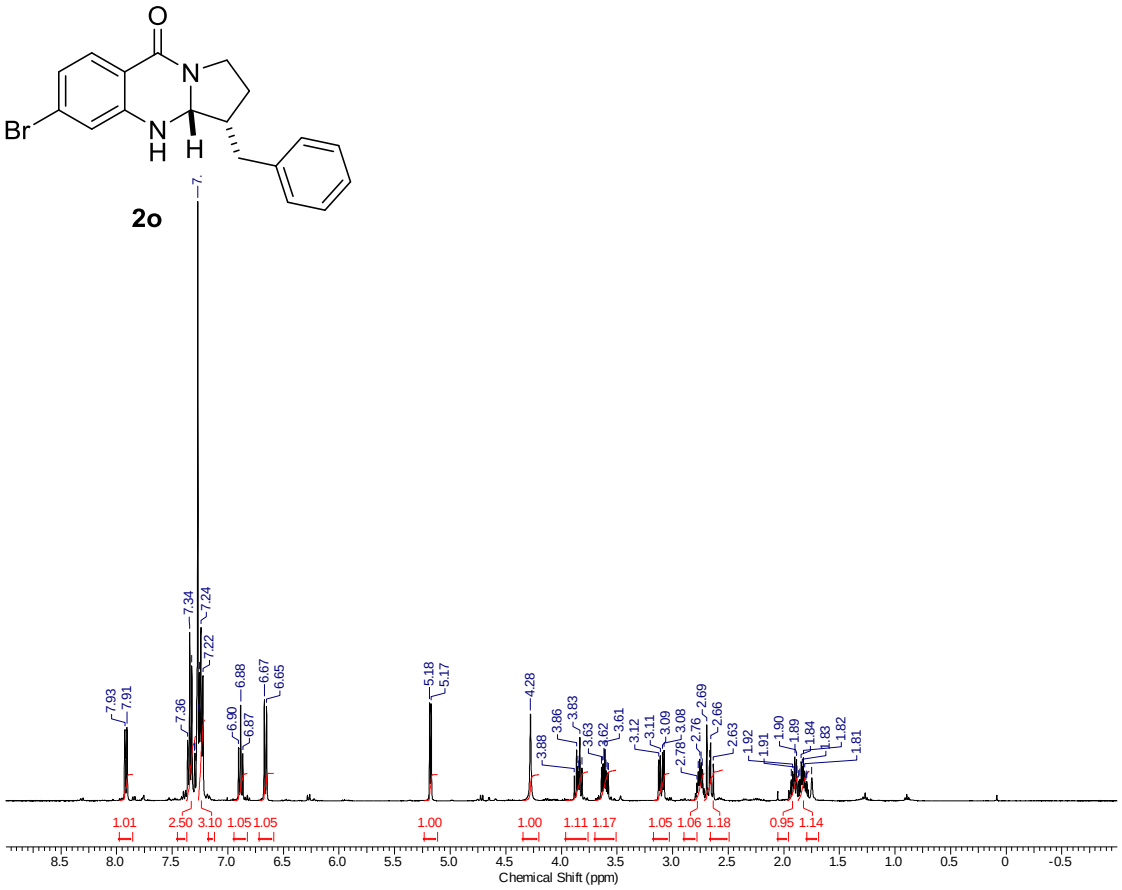


^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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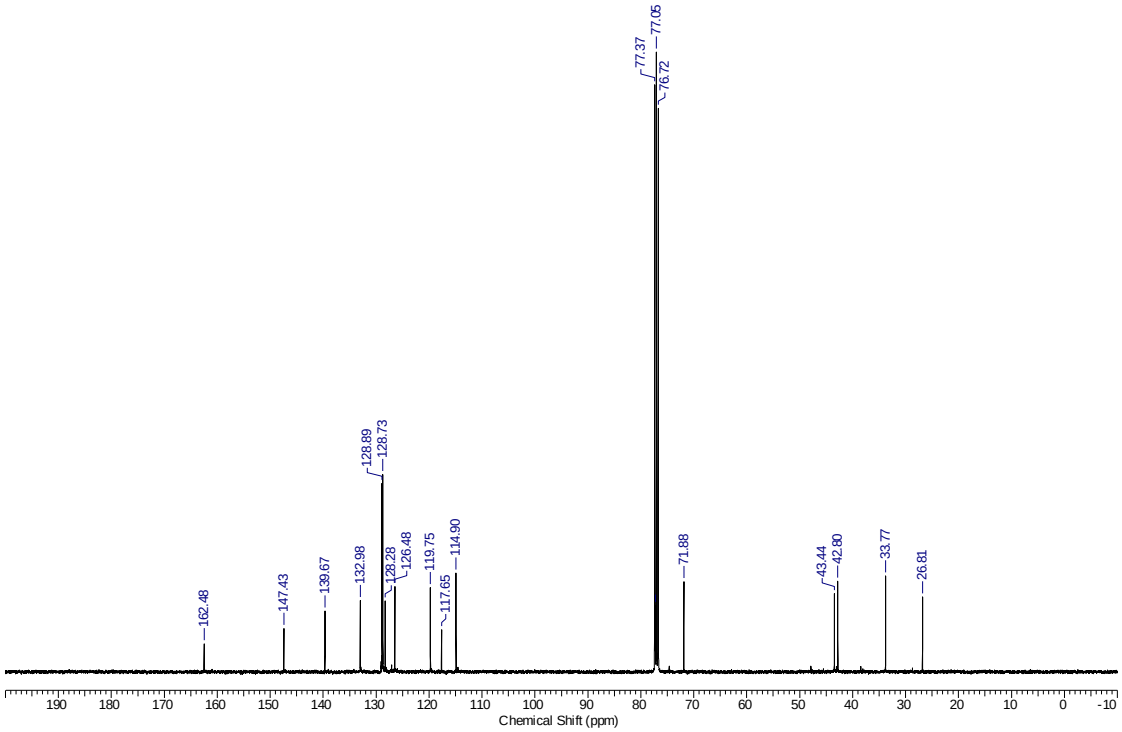

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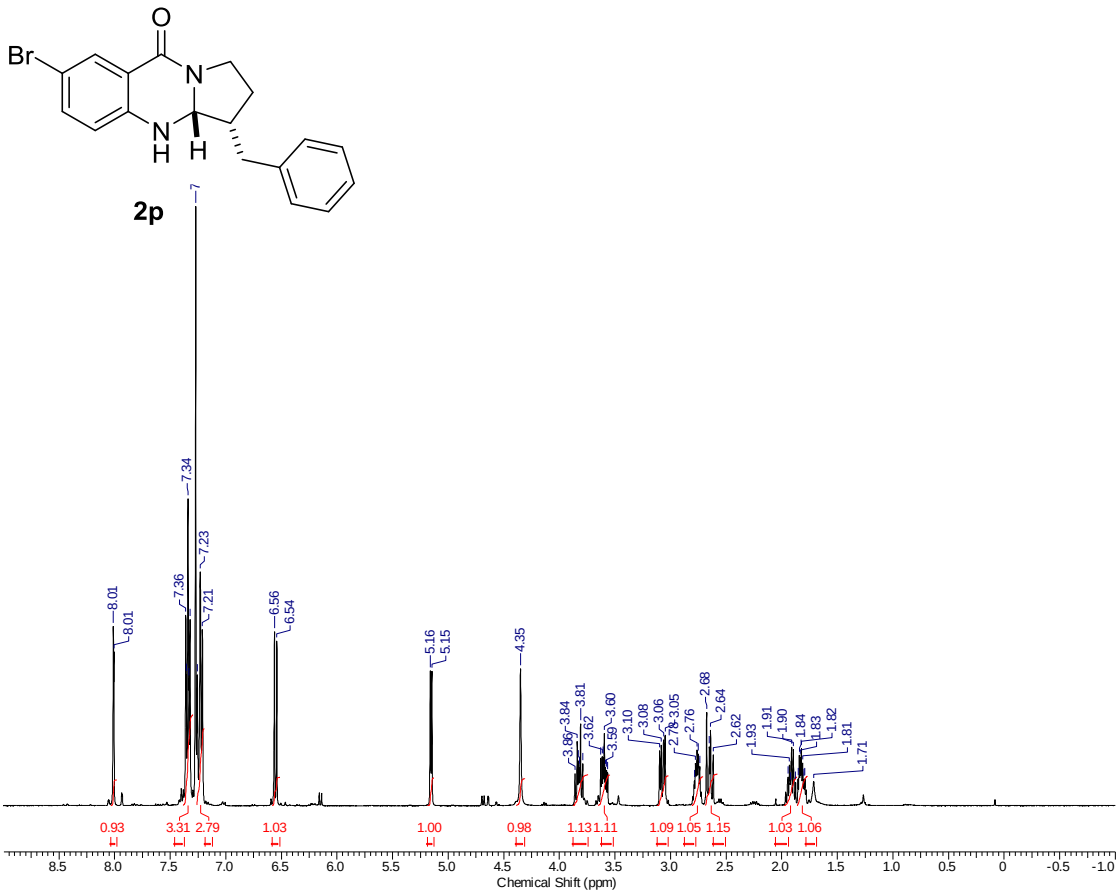

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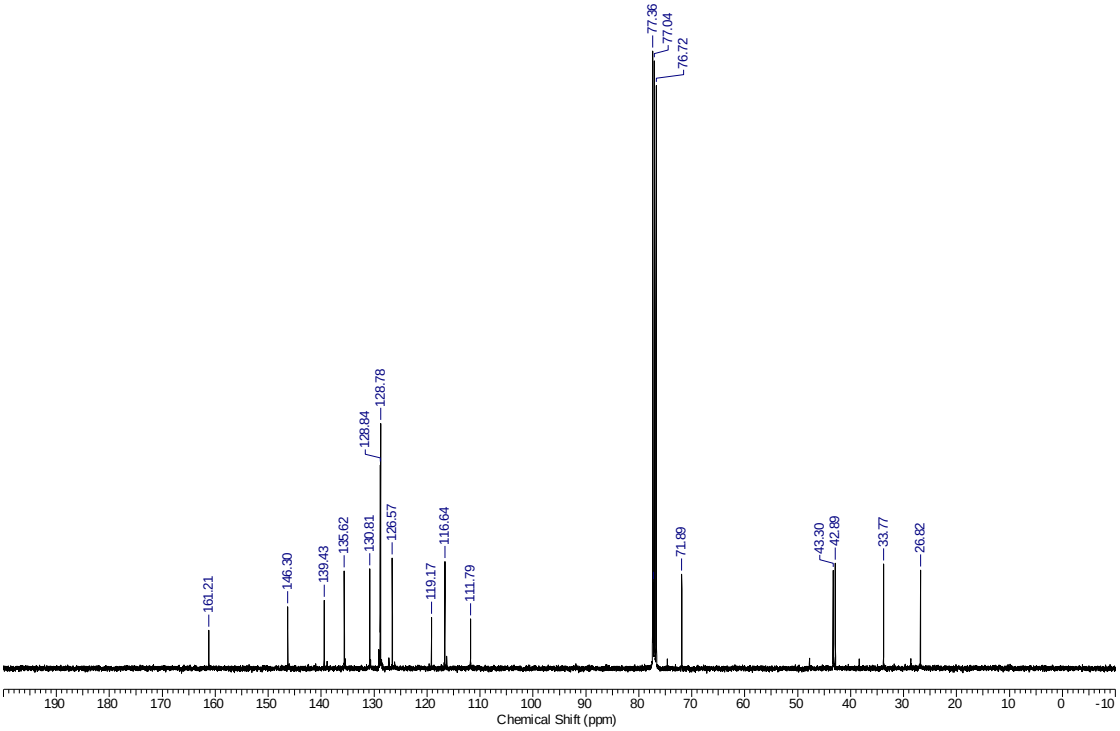

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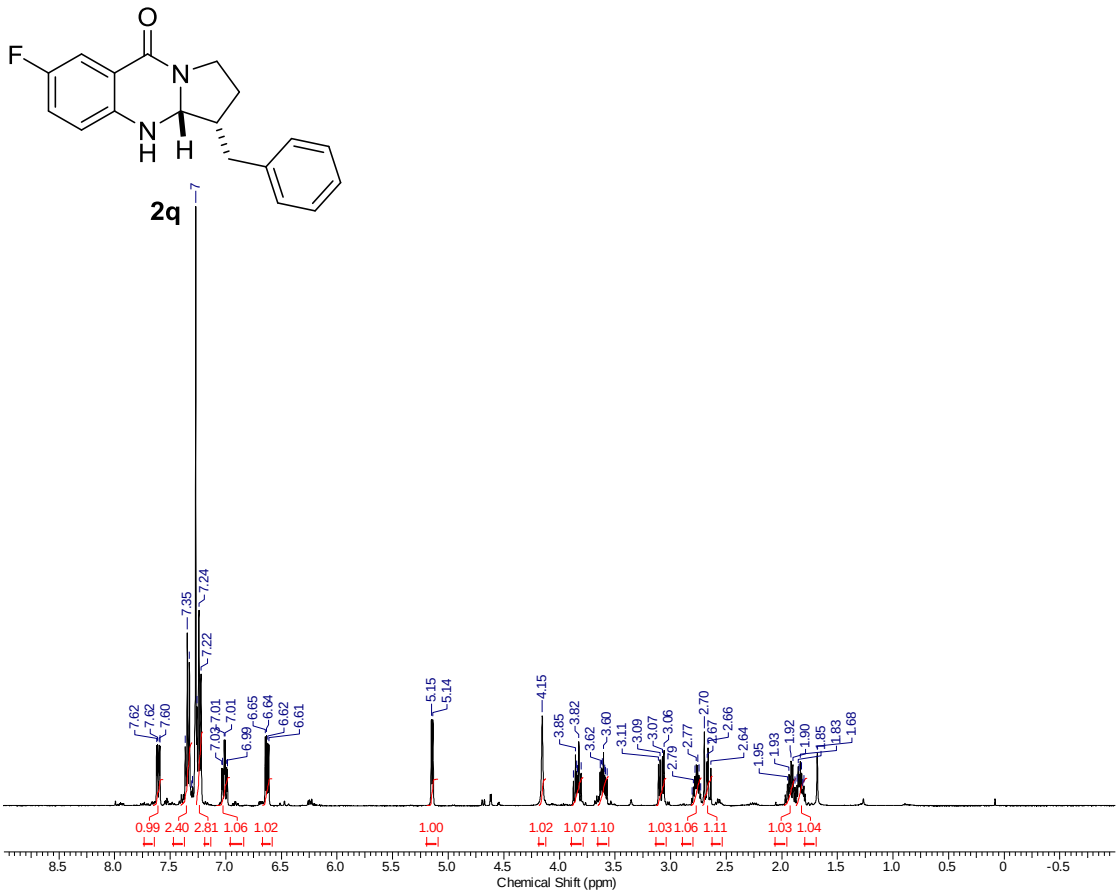

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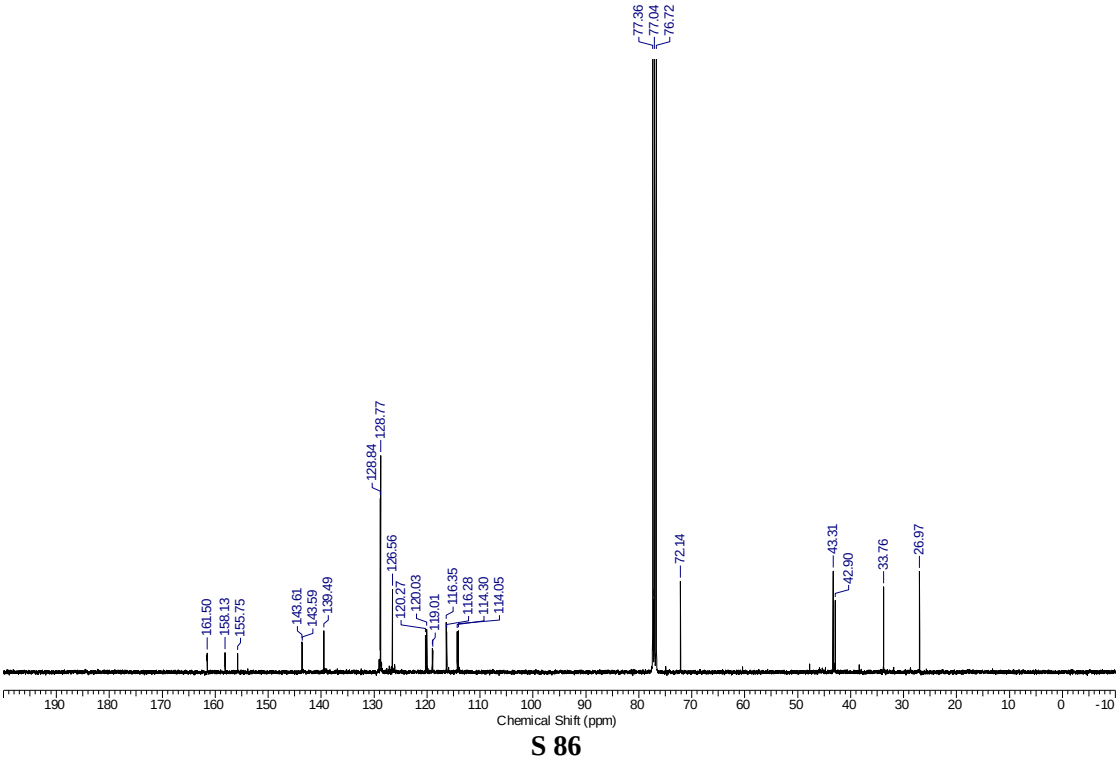
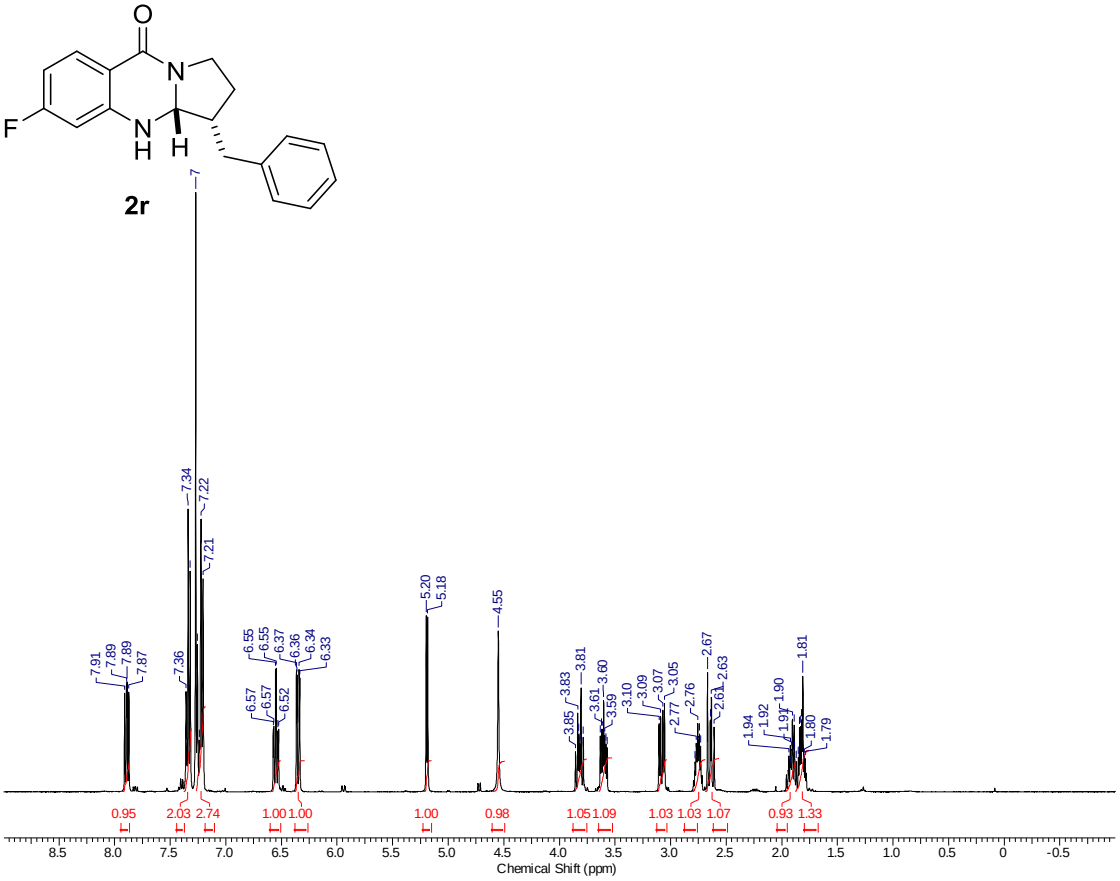
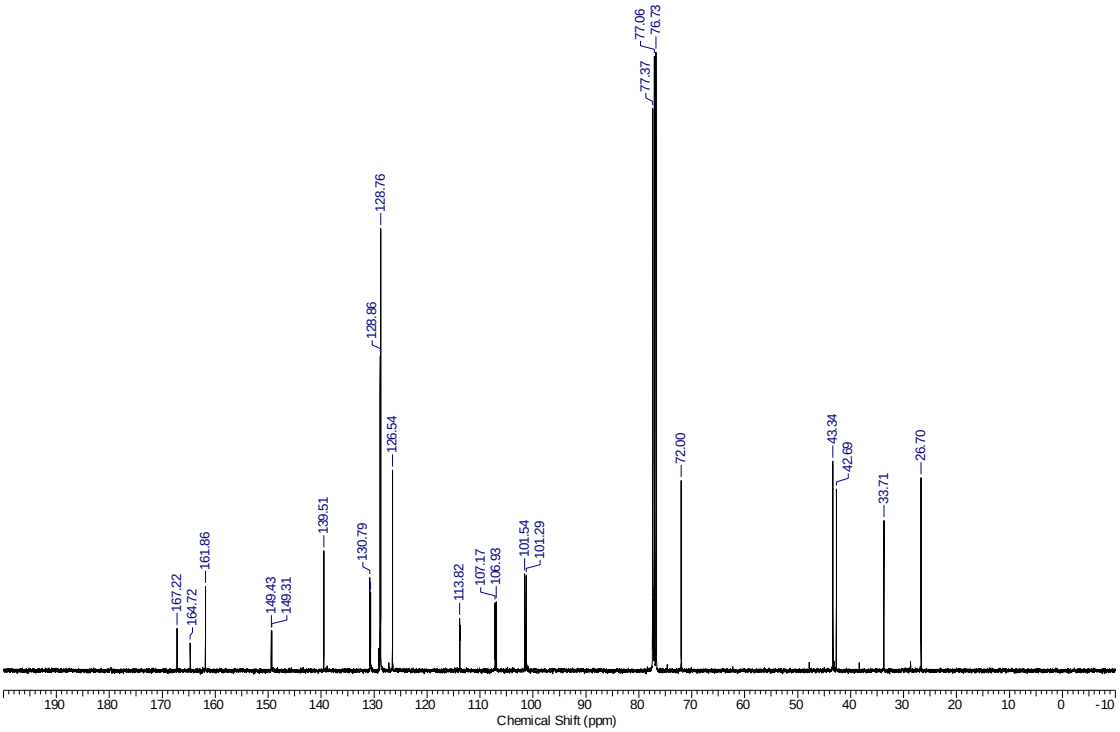


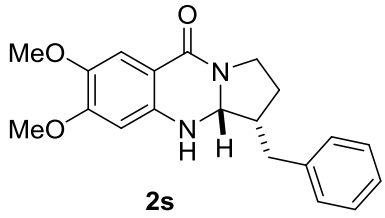
^{1}H NMR (400 MHz, $CDCl_3$)



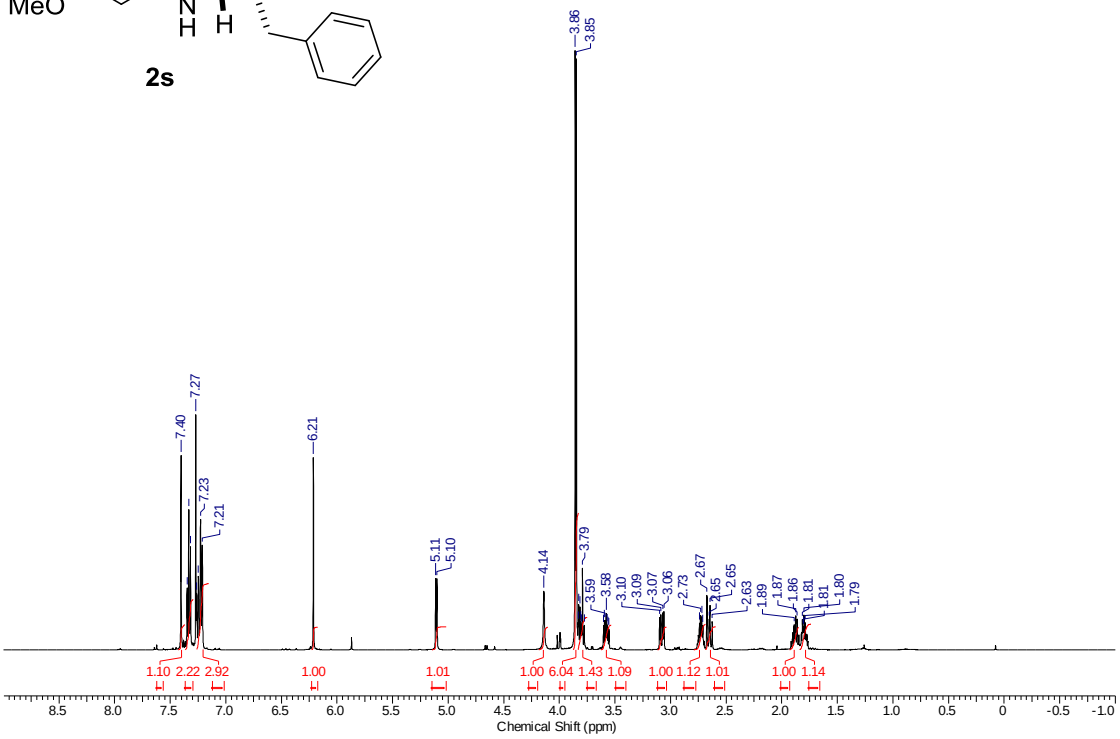
^{13}C NMR (101 MHz, $CDCl_3$)



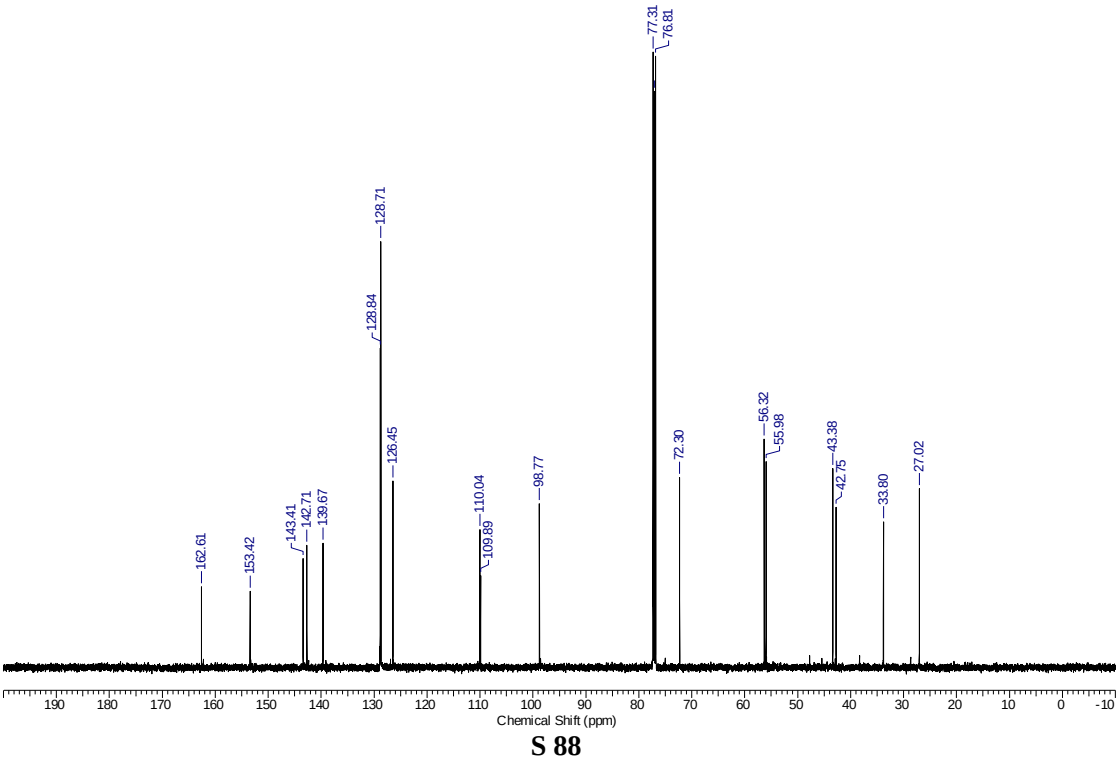
^{1}H NMR (500 MHz, $CDCl_3$)



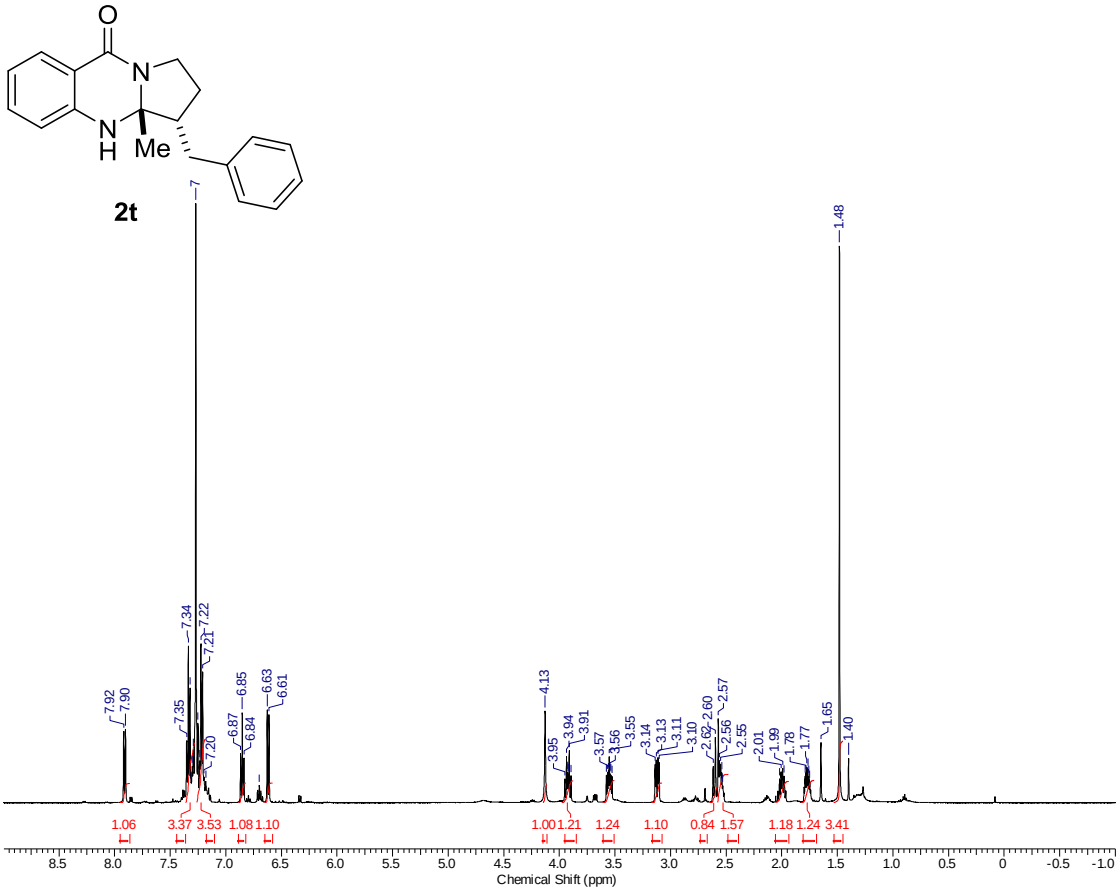
2s



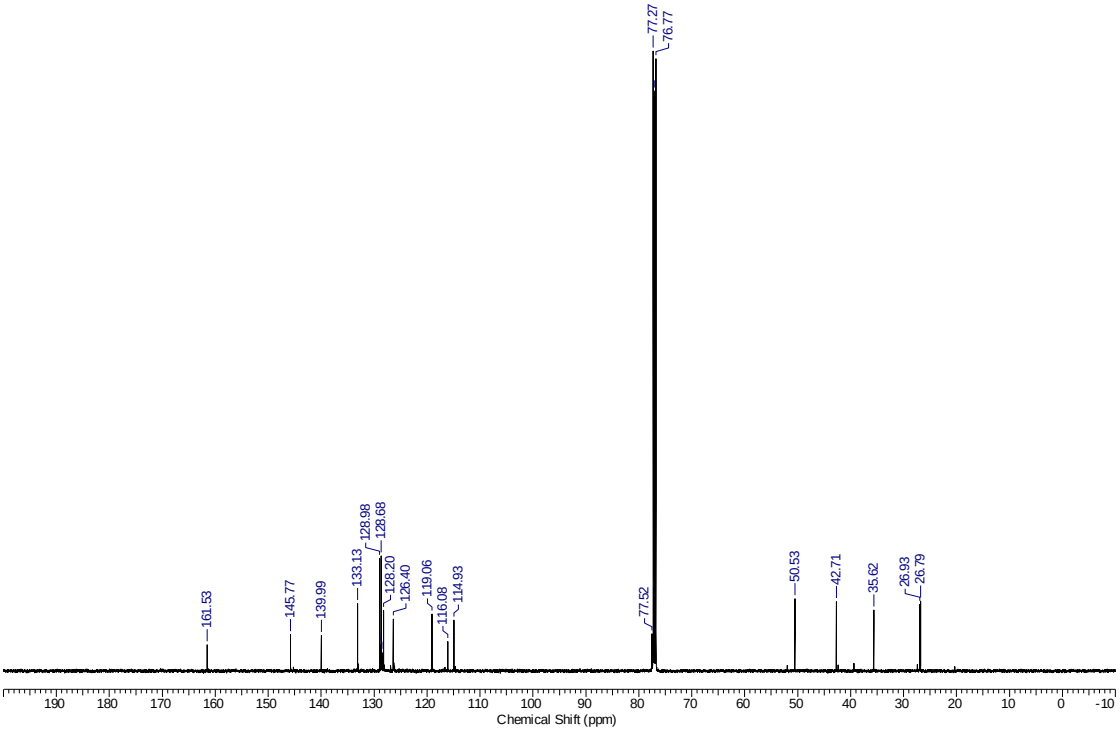
^{13}C NMR (126 MHz, $CDCl_3$)



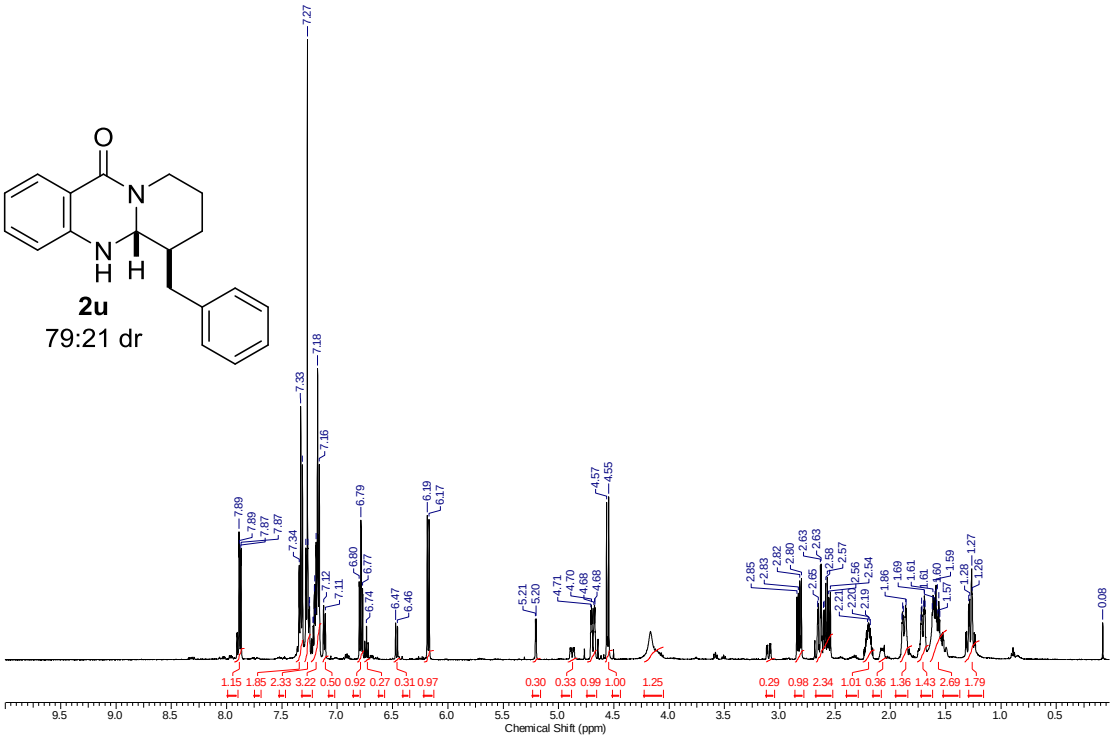
^{1}H NMR (500 MHz, $CDCl_3$)



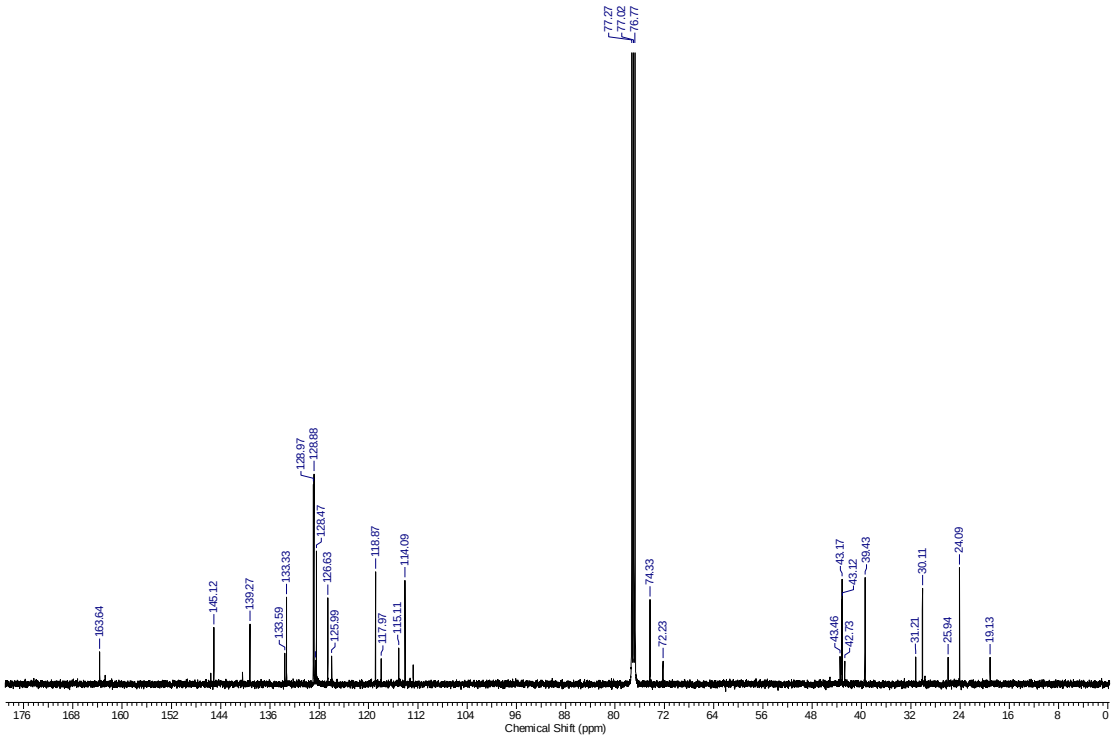
^{13}C NMR (126 MHz, $CDCl_3$)



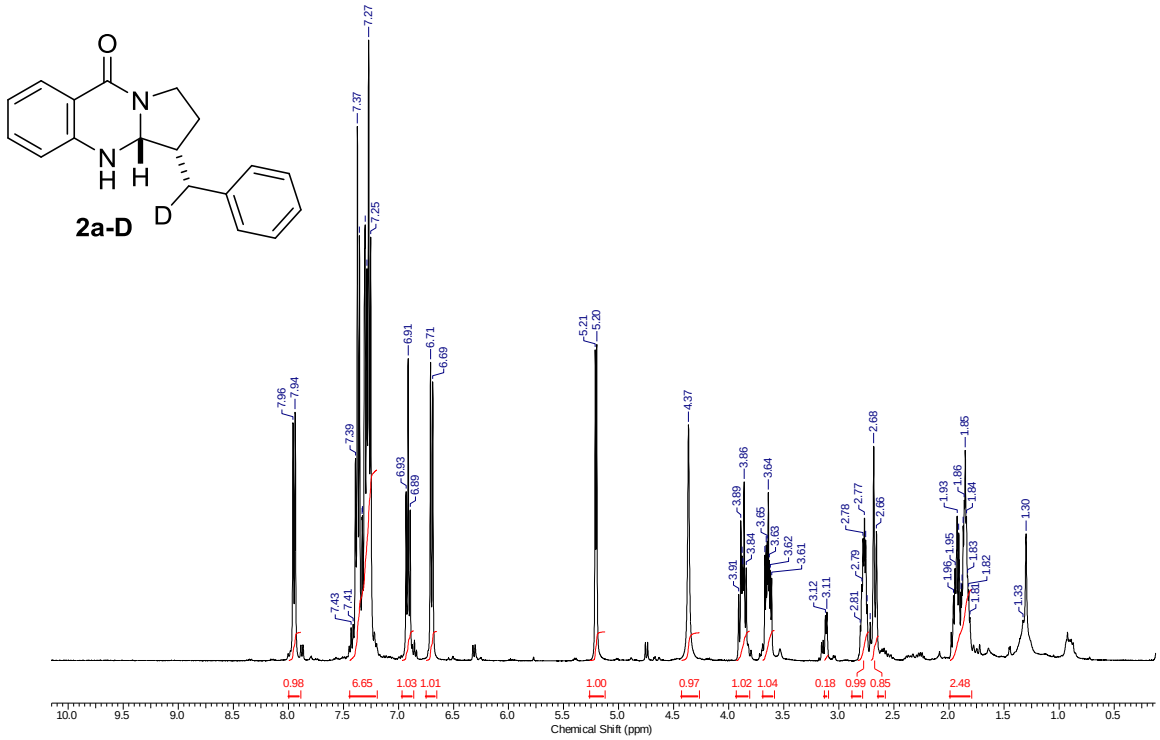
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)