Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Selective Construction of Quaternary Stereocentres in Radical Cyclisation Cascades Triggered by Electron-Transfer Reduction of Amide-Type Carbonyls

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Contents

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 125 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 ionisation (ESI), atmospheric pressure chemical ionisation (APCI), electron impact ionisation (EI) or chemical ionisation (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. Flash column 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.

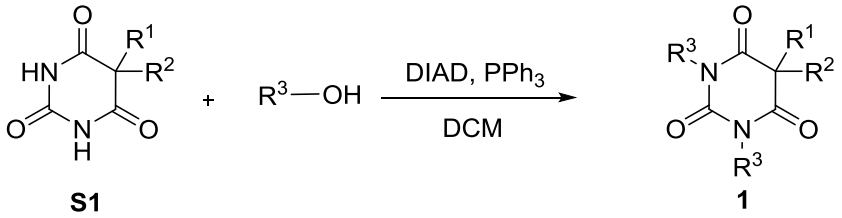
For details of the preparation of related compounds (and associated characterisation data) in Table 2 (**1a-c**, **1e**, **2a-c**, **2e**, **3a-c**, **3e**), see: H.-M. Huang and D. J. Procter, *J. Am. Chem. Soc.*, 2016, **138**, 7770.

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 diiodoethane (1 equiv). The flask was flushed for another 30 minutes, after which freshly distilled and degassed THF (0.1 M) was added under 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]

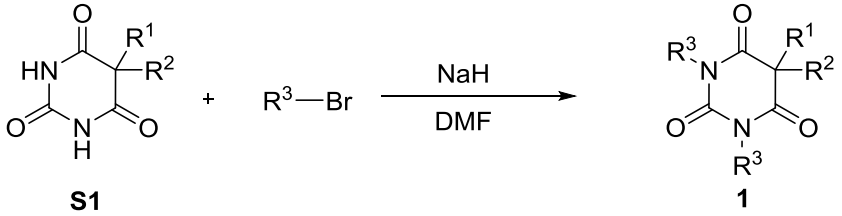
Preparation of starting materials

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



To a solution of the barbituric acid (1.0 mmol, 1.0 equiv), alcohol (2.2 mmol, 2.2 equiv) and PPh_3 (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) was added DIAD (diisopropyl azodicarboxylate) (3.0 mmol, 3.0 equiv) dropwise at 0 ^oC. The mixure was warmed to room temperature and stirred under a N_2 atmosphere for 24 h, then concentrated *in vacuo* to give the crude product, which after purification by flash chromatography on silica gel gave the desired product.

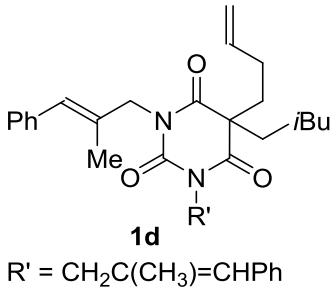
General procedure B: formation of the cascade substrates by *N*-alkylation with an alkyl halide[8]



NaH (60%) (2.2 mmol, 2.2 equiv) was added to an oven-dried flask under N_2, and then DMF (4 mL) was added and the mixture cooled to 0 ℃. The barbiturate derivative was added. After the generation of H_2, the alkyl halide (2.2 mmol, 2.2 equiv) was added, and the reaction mixture was allowed to stir at 80 ^oC for 16 h. After cooling to room temperature, H_2O (5 mL) and ethyl acetate (20 mL) were added. The organic phases were combined, washed with brine (× 5), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash

column chromatography.

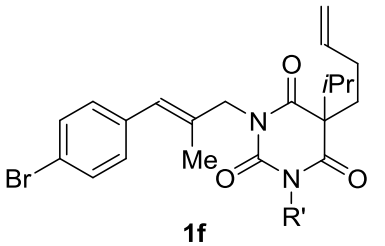
5-(But-3-en-1-yl)-5-isopentyl-1,3-bis((*E*)-2-methyl-3-phenylallyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1d)



General procedure A was followed: using 5-(but-3-enyl)-5-isopentylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-2-methyl-3-phenylprop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0 equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by chromatography (10% EtOAc/hexanes) and gave **1d** (0.442 g, 0.863 mmol, 86%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.26 - 7.32 (5 H, m, Ar*H*), 7.18 - 7.23 (5 H, m, Ar*H*), 6.43 (2 H, s, 2 × C(CH$_3$)C*H*Ar), 5.61 - 5.75 (1 H, m, C*H*=CH$_2$), 4.88 - 5.00 (2 H, m, CH=C*H*$_2$), 4.65 (4 H, d, *J* = 6.72 Hz, 2 × NC*H*$_2$), 2.15 - 2.21 (2 H, m, CH$_2$C*H*$_2$CH=CH$_2$), 1.96 - 2.09 (4 H, m, CH$_2$C*H*$_2$CH(CH$_3$)$_2$ and C*H*$_2$CH$_2$CH=CH$_2$), 1.92 (6 H, s, 2 × C(C*H*$_3$)CHAr), 1.46 (1 H, m, C*H*(CH$_3$)$_2$), 1.02 - 1.10 (2 H, m, C*H*$_2$CH$_2$CH(CH$_3$)$_2$), 0.79 (6 H, d, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.7 (2 × NC(O)C), 150.8 (NC(O)N), 137.0 (2 × *C*(CH$_3$)CHAr), 136.5 (CH$_2$CH$_2$*C*H=CH$_2$), 132.0 (2 × Ar*C*^{q}), 128.9 (4 × Ar*C*H), 128.1 (4 × Ar*C*H), 127.2 (2 × C(CH$_3$)*C*HAr), 126.6 (2 × Ar*C*H), 116.0 (CH$_2$CH$_2$CH=*C*H$_2$), 56.4 (*C*^{q}), 48.7 (2 × NCH$_2$), 39.0 (CH$_2$*C*H$_2$CH=CH$_2$), 38.8 (CH$_2$*C*H$_2$CH(CH$_3$)$_2$), 34.0 (*C*H$_2$CH$_2$CH(CH$_3$)$_2$), 29.8 (*C*H$_2$CH$_2$CH=CH$_2$), 28.1 (*C*H(CH$_3$)$_2$), 22.2 (CH(*C*H$_3$)$_2$), 16.6 (2 × C(*C*H$_3$)CHAr). ν_{max} (thin film/cm^{-1}): 2955, 1673, 1430, 1397, 1269, 1182, 916, 762, 740, 697. MS (ESI$^+$) *m/z* (%): 513.3 (M + H$^+$); HRMS (ESI$^+$) calcd. for $C_{33}H_{41}N_2O_3$ (M + H$^+$): 513.3117. Found: 513.3118.

1,3-Bis((*E*)-3-(4-bromophenyl)-2-methylallyl)-5-(but-3-enyl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1f)

General procedure A was followed: using

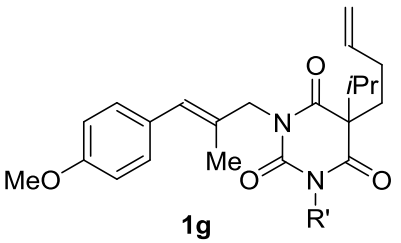


1f

R' = $CH_2C(CH_3)=CH(4\text{-}BrC_6H_4)$

5-(but-3-enyl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-3-(4-bromophenyl)-2-methylprop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0 equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by chromatography (10% EtOAc/hexanes) and gave **1f** (0.500 g, 0.722 mmol, 72%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.38 - 7.45 (4 H, m, Ar*H*), 7.00 - 7.07 (4 H, m, Ar*H*), 6.36 (2 H, s, 2 × ArC*H*=C), 5.65 - 5.74 (1 H, m, CH_2=C*H*), 4.89 - 4.95 (2 H, m, CH_2=CH), 4.62 (4 H, s, 2 × NCH_2), 2.33 - 2.40 (1 H, m, C*H*$(CH_3)_2$), 2.17 - 2.25 (2 H, m, CH_2=CHC$H_2$$CH_2$), 1.91 - 1.98 (2 H, m, CH_2=$CHCH_2$CH_2), 1.88 (6 H, s, 2 × CH=CCH_3), 1.02 (6 H, d, *J* = 6.9 Hz, CH(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.0 (2 × N*C*(O)C), 151.0 (N*C*(O)N), 136.8 (CH_2=*C*H), 135.9 (2 × ArCH=*C*), 133.1 (2 × Ar*C*^{q}), 131.3 (4 × ArC*H*), 130.4 (4 × ArC*H*), 126.3 (2 × Ar*C*H=C), 120.5 (2 × Ar*C*^{q}), 115.9 (*C*H_2=CH), 59.7 (*C*^{q}), 48.6 (2 × N*C*H_2), 39.2 (*C*H$(CH_3)_2$), 34.9 (CH_2=CH*C*H_2), 30.2 (CH_2=$CHCH_2$*C*H_2), 18.0 (CH(*C*H_3)$_2$), 16.6 (2 × CH=C*C*H_3). ν_{max} (thin film/cm^{-1}): 2969, 2938, 1659, 1486, 1430, 1394, 1284, 1184, 1073, 1009, 911, 771. MS (ESI$^+$) *m/z* (%): 677.1 (M + Cl$^-$); HRMS (ESI$^+$) calcd. for $C_{31}H_{35}N_2O_3Br_2$ (M + H$^+$): 641.1009. Found: 641.1005.

5-(But-3-enyl)-5-isopropyl-1,3-bis((*E*)-3-(4-methoxyphenyl)-2-methylallyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1g)



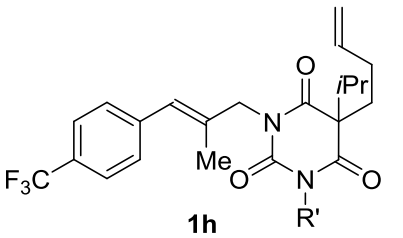
1g

R' = $CH_2C(CH_3)=CH(4\text{-}MeOC_6H_4)$

General procedure A was followed: using 5-(but-3-enyl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-1-(3-chloro-2-methylprop-1-enyl)-4-methoxybenzene (2.2 mmol, 2.2 equiv), NaH (2.2 mmol, 2.2 equiv) in anhydrous DMF (4 mL) at 80 ^{o}C for 16 h. The mixture was purified by chromatography (20% EtOAc/hexanes) and gave **1g** (0.246 g, 0.452 mmol, 45%) as a colourless oil. ^{1}H NMR (500

MHz, $CDCl_3$) δ ppm 7.11 - 7.15 (4 H, m, Ar*H*), 6.81 - 6.86 (4 H, m, Ar*H*), 6.40 (2 H, s, 2 × ArC*H*=C), 5.66 - 5.74 (1 H, m, CH_2=C*H*), 4.90 - 4.97 (2 H, m, CH_2=CH), 4.63 (4 H, s, 2 × NCH_2), 3.80 (6 H, s, 2 × OCH_3), 2.33 - 2.39 (1 H, m, C*H*(CH_3)$_2$), 2.17 - 2.22 (2 H, m, CH_2=CHCH_2CH$_2$), 1.92 - 1.98 (2 H, m, CH_2=CHCH$_2$CH_2), 1.90 (6 H, s, 2 × CH=CCH_3), 1.01 (6 H, d, *J* = 6.9 Hz, CH(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.1 (2 × NC(O)C), 158.2 (2 × ArC^q), 151.1 (N*C*(O)N), 136.9 (CH_2=*C*H), 130.5 (2 × ArCH=*C*), 130.1 (4 × Ar*C*H), 129.7 (2 × ArC^q), 127.2 (2 × Ar*C*H=C), 115.8 (*C*H_2=CH), 113.5 (4 × ArC*H*), 59.7 (*C*^{q}), 55.2 (2 × O*C*H_3), 48.9 (2 × N*C*H_2), 39.2 (*C*H(CH_3)$_2$), 34.9 (CH_2=CH*C*H_2), 30.1 (CH_2=CHCH$_2$*C*H$_2$), 18.0 (CH(*C*H_3)$_2$), 16.6 (2 × CH=C*C*H_3). ν_{max} (thin film/cm^{-1}): 2936, 2835, 1673, 1607, 1510, 1430, 1396, 1249, 1176, 1034, 909, 842, 730. MS (ESI$^+$) *m/z* (%): 545.3 (M + H$^+$); HRMS (ESI$^+$) calcd. for $C_{33}H_{40}N_2O_5Na$ (M + Na$^+$): 567.2829. Found: 567.2826.

5-(But-3-en-1-yl)-5-isopropyl-1,3-bis((*E*)-2-methyl-3-(4-(trifluoromethyl)phenyl)allyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1h)



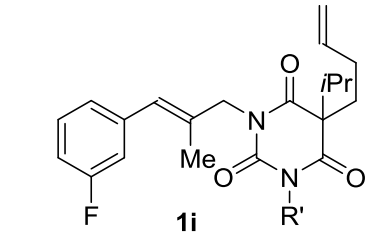
1h

R' = $CH_2C(CH_3)$=CH(4-$CF_3C_6H_4$)

General procedure A was followed: using 5-(but-3-enyl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-3-(4-trifluoromethylphenyl)-2-methylprop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0 equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by chromatography (10% EtOAc/hexanes) and gave **1h** (0.330 g, 0.532 mmol, 53%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.54 (4 H, d, *J* = 8.3 Hz, Ar*H*), 7.27 (4 H, d, *J* = 8.0 Hz, Ar*H*), 6.44 (2 H, s, 2 × ArC*H*=C), 5.60 - 5.79 (1 H, m, CH_2=C*H*), 4.85 - 4.99 (2 H, m, CH_2=CH), 4.66 (4 H, s, 2 × NCH_2), 2.31 - 2.43 (1 H, m, C*H*(CH_3)$_2$), 2.16 - 2.28 (2 H, m, CH_2=CHCH_2CH$_2$), 1.92 - 2.02 (2 H, m, CH_2=CHCH$_2$CH_2), 1.93 (6 H, s, 2 × CH=CCH_3), 1.03 (6 H, d, *J* = 6.8 Hz, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.0 (2 × NC(O)C), 151.0 (N*C*(O)N), 140.6 (2 × ArCH=*C*), 136.7 (CH_2=*C*H), 134.5 (2 × ArC^q), 129.0 (4 ×

ArC*H*), 128.7 (q, *J* = 32 Hz, 2 × Ar*C*^{q}), 126.1 (2 × ArC*H*), 125.1 (q, *J* = 4 Hz, 2 × ArC*H*), 124.1 (q, *J* = 271 Hz, 2 × *C*F_3), 116.0 (*C*H_2=CH), 59.8 (*C*^{q}), 48.6 (2 × N*C*H_2), 39.3 (*C*H(CH_3)$_2$), 34.9 (CH_2=CH*C*H_2), 30.2 (CH_2=CHCH_2*C*H_2), 18.0 (CH(*C*H_3)$_2$), 16.6 (2 × CH=C*C*H_3). ν_{max} (thin film/cm^{-1}): 2974, 1683, 1231, 1395, 1318, 1164, 1122, 1067, 1016, 908, 859, 731. MS (ESI$^+$) *m/z* (%): 659.2 (M + K^+); HRMS (ESI$^+$) calcd. for $C_{33}H_{34}N_2O_3F_6Cl$ (M + Cl^-): 655.2168. Found: 655.2164.

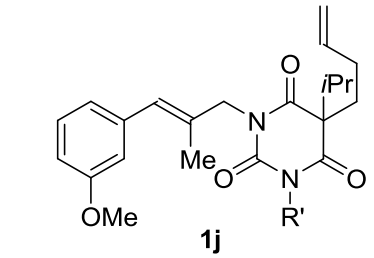
5-(But-3-en-1-yl)-1,3-bis((*E*)-3-(3-fluorophenyl)-2-methylallyl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1i)



R' = $CH_2C(CH_3)$=CH(3-FC_6H_4)

General procedure A was followed: using 5-(but-3-enyl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-3-(3-fluorophenyl)prop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0 equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by chromatography (10% EtOAc/hexanes) and gave **1i** (0.371 g, 0.713 mmol, 71%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.19 - 7.29 (2 H, m, Ar*H*), 6.85 - 6.98 (6 H, m, Ar*H*), 6.40 (2 H, s, 2 × ArC*H*=C), 5.63 - 5.79 (1 H, m, CH_2=C*H*), 4.82 - 5.02 (2 H, m, C*H*$_2$=CH), 4.64 (4 H, s, 2 × NC*H*$_2$), 2.32 - 2.43 (1 H, m, C*H*(CH_3)$_2$), 2.17 - 2.27 (2 H, m, CH_2=CHC*H*$_2$CH$_2$), 1.93 - 2.00 (2 H, m, CH_2=CHCH$_2$C*H*$_2$), 1.91 (6 H, s, 2 × CH=CC*H*$_3$), 1.03 (6 H, d, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.0 (2 × N*C*(O)C), 162.6 (d, *J* = 246 Hz, 2 × Ar*C*^{q}), 151.0 (N*C*(O)N), 139.2 (d, *J* = 8.8 Hz, 2 × Ar*C*^{q}), 136.8 (CH_2=*C*H), 133.5 (2 × ArCH=*C*), 129.6 (d, *J* = 7.6 Hz, 2 × Ar*C*H), 126.4 (d, *J* = 2.5 Hz, 2 × Ar*C*H), 124.6 (d, *J* = 2.5 Hz, 2 × Ar*C*H), 115.9 (*C*H_2=CH), 115.5 (d, *J* = 21.4 Hz, 2 × Ar*C*H), 59.7 (*C*^{q}), 48.6 (2 × N*C*H_2), 39.3 (*C*H(CH_3)$_2$), 34.9 (CH_2=CH*C*H_2), 30.2 (CH_2=CHCH$_2$*C*H_2), 18.0 (CH(*C*H_3)$_2$), 16.6 (2 × CH=C*C*H_3). ν_{max} (thin film/cm^{-1}): 2971, 1655, 1580, 1430, 1394, 1280, 1253, 1143, 949, 879, 756, 689. MS (ESI$^+$) *m/z* (%): 521.2 (M + H^+); HRMS (ESI$^+$) calcd. for $C_{31}H_{34}N_2O_3F_2Na$ (M + Na^+): 543.2430. Found: 543.2428.

5-(But-3-en-1-yl)-5-isopropyl-1,3-bis((*E*)-3-(3-methoxyphenyl)-2-methylallyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1j)



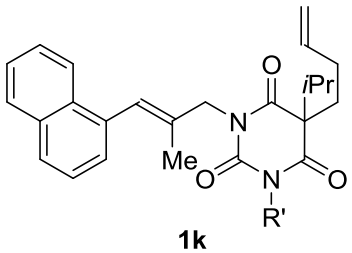
1j

R' = $CH_2C(CH_3)=CH(3\text{-}MeOC_6H_4)$

General procedure B was followed: using 5-(but-3-enyl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-1-(3-chloro-2-methylprop-1-en-1-yl)-3-methoxybenzene (2.2 mmol, 2.2 equiv), NaH (2.2 mmol, 2.2 equiv) in anhydrous DMF (4 mL) at 80 ^{o}C for 16 h. The mixture was purified by chromatography (20% EtOAc/hexanes) and gave **1j** (0.219 g, 0.402 mmol, 40%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.21 (2 H, t, *J* = 7.9 Hz, Ar*H*), 6.72 - 6.81 (6 H, m, Ar*H*), 6.43 (2 H, s, 2 × ArC*H*=C), 5.63 - 5.77 (1 H, m, CH_2=C*H*), 4.90 - 4.98 (2 H, m, CH_2=CH), 4.64 (4 H, s, 2 × NCH_2), 3.77 (6 H, s, 2 × OCH_3), 2.33 - 2.40 (1 H, m, C*H*$(CH_3)_2$), 2.17 - 2.24 (2 H, m, CH_2=CHCH_2CH_2), 1.94 - 2.00 (2 H, m, CH_2=CHCH_2CH_2), 1.92 (6 H, s, 2 × CH=CCH_3), 1.02 (6 H, d, *J* = 7.0 Hz, CH(C$H_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.0 (2 × N*C*(O)C), 159.4 (2 × ArC^q), 151.1 (N*C*(O)N), 138.5 (2 × ArCH=*C*), 136.9 (CH_2=*C*H), 132.4 (2 × ArC^q), 129.1 (2 × Ar*C*H), 127.4 (2 × Ar*C*H=C), 121.4 (2 × Ar*C*H), 115.9 (*C*H_2=CH), 114.3 (2 × Ar*C*H), 112.2 (2 × Ar*C*H), 59.7 (C^q), 55.2 (2 × OCH_3), 48.7 (2 × NCH_2), 39.3 (*C*H$(CH_3)_2$), 34.9 (CH_2=CH*C*H_2), 30.2 (CH_2=CHCH_2*C*H_2), 18.0 (CH(*C*$H_3)_2$), 16.7 (2 × CH=C*C*H_3). ν_{max} (thin film/cm^{-1}): 2938, 1635, 1576, 1429, 1394, 1273, 1159, 1044, 910, 782, 694. MS (ESI^+) *m/z* (%): 545.3 (M + H^+); HRMS (ESI^+) calcd. for $C_{33}H_{40}N_2O_5Na$ (M + Na^+): 567.2829. Found: 567.2822.

5-(But-3-en-1-yl)-5-isopropyl-1,3-bis((*E*)-2-methyl-3-(naphthalen-1-yl)allyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1k)

General procedure A was followed: using 5-(but-3-enyl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv),

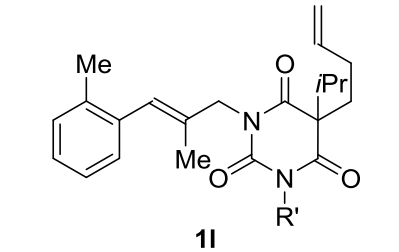


1k

R' = $CH_2C(CH_3)=CHC_{10}H_7$

(*E*)-2-methyl-3-(naphthalen-2-yl)prop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0 equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by chromatography (10% EtOAc/hexanes) and gave **1k** (0.349 g, 0.598 mmol, 60%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.89 - 7.96 (2 H, m, Ar*H*), 7.80 - 7.87 (2 H, m, Ar*H*), 7.75 (2 H, d, *J* = 8.3 Hz, Ar*H*), 7.36 - 7.48 (6 H, m, Ar*H*), 7.25 (2 H, d, *J* = 7.0 Hz, Ar*H*), 6.94 (2 H, s, 2 × ArC*H*=C), 5.63 - 5.82 (1 H, m, CH_2=C*H*), 4.89 - 4.97 (2 H, m, CH_2=CH), 4.82 (4 H, s, 2 × NCH_2), 2.41 - 2.49 (1 H, m, C*H*$(CH_3)_2$), 2.27 - 2.33 (2 H, m, CH_2=CHC$H_2$$CH_2$), 1.97 - 2.05 (2 H, m, CH_2=CHCH_2CH_2), 1.76 (6 H, s, 2 × CH=CCH_3), 1.08 (6 H, d, *J* = 7.0 Hz, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.2 (2 × N*C*(O)C), 151.3 (N*C*(O)N), 136.9 (CH_2=*C*H), 134.5 (2 × ArCH=*C*), 133.8 (2 × ArC^q), 133.5 (2 × ArC^q), 132.0 (2 × ArC^q), 128.3 (2 × Ar*C*H), 127.3 (2 × Ar*C*H), 126.4 (2 × Ar*C*H), 126.4 (2 × Ar*C*H=C), 126.0 (2 × Ar*C*H), 125.8 (2 × Ar*C*H), 125.2 (2 × Ar*C*H), 125.1 (2 × Ar*C*H), 115.9 (*C*H_2=CH), 59.8 (C^q), 48.5 (2 × N*C*H_2), 39.4 (*C*H$(CH_3)_2$), 34.9 (CH_2=CH*C*H_2), 30.2 (CH_2=CHCH_2*C*H_2), 18.1 (CH(*C*H_3)$_2$), 16.5 (2 × CH=C*C*H_3). ν_{max} (thin film/cm^{-1}): 3058, 2937, 1645, 1430, 1393, 1283, 1184, 907, 781, 730. MS (ESI$^+$) *m/z* (%): 585.3 (M + H$^+$); HRMS (ESI$^+$) calcd. for $C_{39}H_{40}N_2O_3Na$ (M + Na$^+$): 607.2931. Found: 607.2926.

5-(But-3-en-1-yl)-5-isopropyl-1,3-bis((*E*)-2-methyl-3-(o-tolyl)allyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1l)



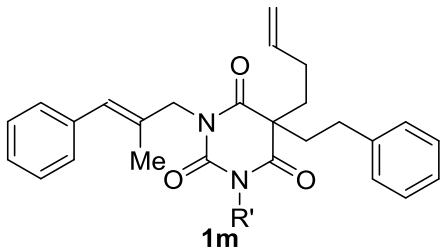
1l

R' = $CH_2C(CH_3)=CH(2\text{-}MeC_6H_4)$

General procedure A was followed: using 5-(but-3-enyl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-2-methyl-3-(o-tolyl)prop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0 equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by

chromatography (10% EtOAc/hexanes) and gave **1l** (0.299 g, 0.584 mmol, 58%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.10 - 7.17 (6 H, m, Ar*H*), 7.05 - 7.10 (2 H, m, Ar*H*), 6.49 (2 H, s, 2 × ArC*H*=C), 5.66 - 5.75 (1 H, m, CH_2=C*H*), 4.90 - 4.97 (2 H, m, CH_2=CH), 4.67 (4 H, s, 2 × NCH_2), 2.34 - 2.41 (1 H, m, C*H*(CH_3)$_2$), 2.16 - 2.25 (8 H, m, 2 × ArCH_3 and CH_2=CHC$H_2$$CH_2$), 1.91 - 1.98 (2 H, m, CH_2=CHCH_2CH_2), 1.73 (6 H, s, 2 × CH=CCH_3), 1.03 (6 H, d, *J* = 6.9 Hz, CH(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.1 (2 × N*C*(O)C), 151.1 (N*C*(O)N), 136.8 (CH_2=*C*H), 136.4 (2 × ArCH=*C*), 136.4 (2 × Ar*C*^{q}), 132.0 (2 × Ar*C*^{q}), 129.7 (2 × Ar*C*H), 129.1 (2 × Ar*C*H), 127.4 (2 × Ar*C*H=C), 126.9 (2 × Ar*C*H), 125.3 (2 × Ar*C*H), 115.8 (*C*H_2=CH), 59.7 (*C*^{q}), 48.4 (2 × N*C*H_2), 39.3 (*C*H(CH_3)$_2$), 34.8 (CH_2=CH*C*H_2), 30.1 (CH_2=CHCH_2*C*H_2), 19.8 (2 × Ar*C*H_3), 18.0 (CH(*C*H_3)$_2$), 16.2 (2 × CH=C*C*H_3). ν_{max} (thin film/cm^{-1}): 2938, 1612, 1429, 1395, 1283, 1184, 1046, 910, 742. MS (ESI^{+}) *m/z* (%): 513.3 (M + H^{+}); HRMS (ESI^{+}) calcd. for $C_{33}H_{41}N_2O_3$ (M + H^{+}): 513.3112. Found: 513.3109.

5-(But-3-en-1-yl)-1,3-bis((*E*)-2-methyl-3-phenylallyl)-5-phenethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1m)



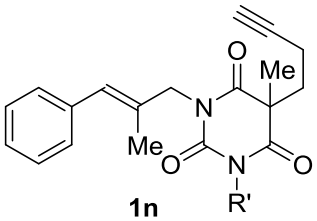
1m

R' = $CH_2C(CH_3)=CHC_6H_5$

General procedure A was followed: using 5-(but-3-en-1-yl)-5-phenethylpyrimidine-2,4,6(1*H*,3*H*,5H)-trione (1.0 mmol, 1.0 equiv), (*E*)-2-methyl-3-phenylprop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0 equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by chromatography (10% EtOAc/hexanes) and gave **1m** (0.289 g, 0.528 mmol, 53%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.14 - 7.33 (13 H, m, Ar*H*), 7.03 - 7.11 (2 H, m, Ar*H*), 6.48 (2 H, s, 2 × ArC*H*=C), 5.62 - 5.73 (1 H, m, CH_2=C*H*), 4.90 - 4.98 (2 H, m, CH_2=CH), 4.63 (4 H, s, 2 × NCH_2), 2.47 - 2.59 (2 H, m, ArCH_2), 2.33 - 2.43 (2 H, m, ArCH_2CH_2), 2.15 - 2.24 (2 H, m, CH_2=CHC$H_2$$CH_2$), 1.99 - 2.10 (2 H, m, CH_2=CHCH_2CH_2),

1.93 (6 H, s, 2 × CH=CCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.3 (2 × NC(O)C), 150.7 (NC(O)N), 139.7 (ArC^q), 137.0 (2 × ArCH=C), 136.3 (CH_2=CH), 132.0 (2 × ArC^q), 128.9 (4 × ArCH), 128.5 (2 × ArCH), 128.3 (2 × ArCH), 128.1 (4 × ArCH), 127.5 (2 × ArCH=C), 126.6 (2 × ArCH), 126.5 (ArCH), 116.1 (CH_2=CH), 56.2 (C^q), 48.8 (2 × NCH_2), 41.7 (ArCH_2CH_2), 39.2 (CH_2=CHCH_2), 31.5 (ArCH_2CH_2), 29.6 (CH_2=CHCH_2CH_2), 16.6 (2 × CH=CCH_3). ν_{max} (thin film/cm^{-1}): 3024, 2936, 1667, 1430, 1398, 1168, 1021, 917, 741, 696. MS (ESI$^+$) *m/z* (%): 547.2 (M + H$^+$); HRMS (ESI$^+$) calcd. for $C_{36}H_{38}N_2O_3Na$ (M + Na$^+$): 569.2775. Found: 569.2771.

5-(But-3-yn-1-yl)-5-methyl-1,3-bis((*E*)-2-methyl-3-phenylallyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1n)

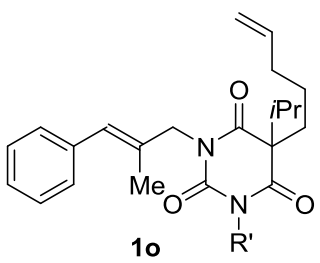


1n

[R' = $CH_2C(CH_3)$=CHPh]

General procedure A was followed: using 5-(but-3-yn-1-yl)-5-methylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-2-methyl-3-phenylprop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0 equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by chromatography (10% EtOAc/hexanes) and gave **1n** (0.232 g, 0.51 mmol, 51%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28 - 7.32 (4 H, m, ArH), 7.19 - 7.22 (6 H, m, ArH), 6.40 (2 H, s, 2 × C(Ar)CH=C), 4.58 - 4.68 (4 H, m, 2 × NCH_2), 2.36 - 2.39 (2 H, m, CH_2CH_2C≡CH), 2.25 - 2.29 (2 H, m, CH_2CH_2C≡CH), 1.92 (1 H, m, CH_2C≡CH), 1.91 (6 H, m, 2 × CH=CCH_3), 1.62 (3 H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.5 (2 × NC(O)C), 150.6 (NC(O)N), 137.1 (2 × CH=C^q(CH_3)), 132.0 (2 × ArC^q), 129.0 (4 × ArCH), 128.1 (2 × ArCH), 126.7 (2 × ArCH), 126.6 (2 × ArC^qCH=C), 81.8 (CH_2C≡CH), 70.8 (CH_2C≡CH), 51.1 (C^q), 48.7 (2 × NCH_2CH=CH_2), 29.9 (CH_2CH_2C≡CH), 27.1 (C(O)CCH_3), 16.4 (C=CCH_3), 14.8 (CH_2C≡CH). ν_{max} (thin film/cm^{-1}): 3431, 2973, 2112, 1680, 1429, 1395, 759. MS (ESI$^+$) *m/z* (%): 455 (M + H$^+$, 100); HRMS (ESI) calcd. for $C_{29}H_{30}N_2O_3Na$ (M + Na$^+$): 477.2149. Found: 477.2145.

5-Isopropyl-1,3-bis((*E*)-2-methyl-3-phenylallyl)-5-(pent-4-en-1-yl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1o)



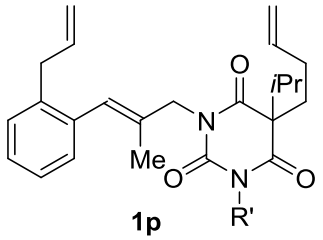
1o

[R' = $CH_2C(CH_3)$=CHPh]

General procedure A was followed: using 5-isopropyl-5-(pent-4-en-1-yl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-2-methyl-3-phenylprop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0 equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by chromatography (10% EtOAc/hexanes) and gave **1o** (0.224 g, 0.45 mmol, 22%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28 - 7.34 (4 H, m, Ar*H*), 7.19 - 7.25 (6 H, m, Ar*H*), 6.47 (2 H, s, 2 × C(Ar)C*H*=C), 5.72 (1 H, m, C*H*=CH_2), 4.92 - 5.02 (2 H, m, CH=CH_2), 4.70 (4 H, s, 2 × NCH_2), 2.36 - 2.48 (1 H, m, C*H*$(CH_3)_2$), 2.12 - 2.19 (2 H, m, C$H_2CH_2CH_2$CH=CH_2), 2.07 (2 H, q, *J* = 7.3 Hz, $CH_2CH_2CH_2$CH=CH_2), 1.95 (6 H, s, 2 × CH=CCH_3), 1.25 - 1.36 (2 H, m, $CH_2CH_2CH_2$CH=CH_2), 1.07 (6 H, d, *J* = 6.8 Hz, CH(C$H_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.2 (2 × N*C*(O)C), 151.0 (N*C*(O)N), 137.5 ($CH_2CH_2CH_2$C*H*=CH_2), 137.1 (2 × CH=$C^q(CH_3)$), 132.1 (2 × ArC^q), 129.0 (4 × Ar*C*H), 128.1 (2 × Ar*C*H), 127.2 (2 × Ar*C*H), 127.1 (2 × ArC^q*C*H=C), 126.6 (2 × Ar*C*H), 115.3 ($CH_2CH_2CH_2CH$=CH_2), 60.2 (*C*$CH_2CH_2CH_2$), 48.7 (2 × NCH_2), 39.0 (*C*H$(CH_3)_2$), 35.4 (*C*$H_2CH_2CH_2$CH=CH_2), 33.7 (CH_2CH_2*C*H_2CH=CH_2), 25.2 (CH_2*C*H_2CH_2CH=CH_2), 18.1 (2 × C=C*C*H_3), 16.6 (C(*C*$H_3)_2$). ν_{max} (thin film/cm^{-1}): 2971, 1679, 1429, 1393, 1278, 740, 697. MS (ESI$^+$) *m/z* (%): 499 (M + H$^+$, 100); HRMS (ESI) calcd. for $C_{32}H_{38}N_2O_3Na$ (M + Na$^+$): 521.2780. Found: 521.2775.

1,3-Bis((*E*)-3-(2-allylphenyl)-2-methylallyl)-5-(but-3-en-1-yl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1p)

General procedure A was followed: using 5-(but-3-en-1-yl)-5-isopropylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (1.0 mmol, 1.0 equiv), (*E*)-3-(2-allylphenyl)-2-methylprop-2-en-1-ol (2.2 mmol, 2.2 equiv), PPh_3 (3.0 mmol, 3.0



1p

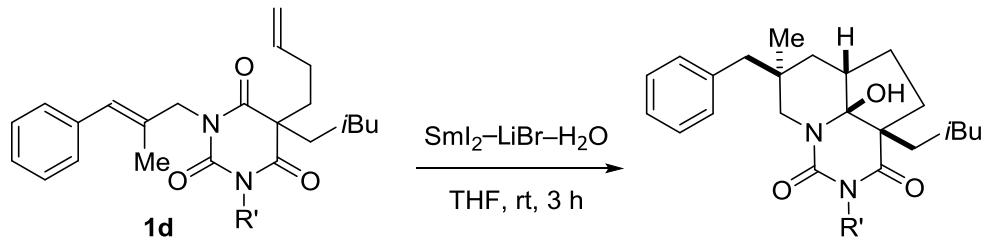
[R' = $CH_2C(CH_3)=CH(2\text{-}CH_2CH=CH_2C_6H_4)$]

equiv) and DIAD (3.0 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (10 mL) for 24 h. The mixture was purified by chromatography (10% EtOAc/hexanes) and gave **1p** (0.410 g, 0.73 mmol, 73%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.16 - 7.34 (8 H, m, Ar*H*), 6.63 (2 H, s, 2 × ArC*H*=C), 5.97 (2 H, m, 2 × $ArCH_2CH$=CH_2), 5.73 - 5.87 (1 H, m, CH_2CH_2CH=CH_2), 4.99 - 5.11 (6 H, m, 4 H from CH_2CH_2CH=CH_2 and 2 H from CH_2CH=CH_2), 4.75 (4 H, s, 2 × NCH_2), 3.39 (4 H, d, *J* = 6.3 Hz, 2 × $C(Ar)CH_2CH$=CH_2), 2.39 - 2.53 (1 H, m, $CH(CH_3)_2$), 2.27 - 2.34 (2 H, m, CCH_2CH_2CH=CH_2), 1.98 - 2.07 (2 H, m, CCH_2CH_2CH=CH_2), 1.81 (6 H, s, 2 × CH=$C(CH_3)$), 1.09 - 1.15 (6 H, d, *J* = 1.3 Hz $CH(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.1 (2 × NC(O)C), 151.1 (NC(O)N), 138.3 (2 × $C(Ar)CH_2CH$=CH_2), 138.3 (2 × $CH=C^q(CH_3)$), 136.9 (2 × $C(Ar)^qCH_2CH$=CH_2), 136.8 ($CH_2CH_2CH_2CH$=CH_2), 132.6 (2 × ArC^q), 129.5 (2 × ArCH), 129.1 (2 × ArCH), 127.2 (2 × ArCH), 127.1 (2 × ArC^qCH=C), 125.9 (2 × ArCH), 115.8 (2 × $C(Ar)CH_2CH$=CH_2), 115.7 (CCH_2CH_2CH=CH_2), 59.7 ($CCH_2CH_2CH_2$), 48.4 (2 × NCH_2), 39.3 ($CH(CH_3)$), 37.6 (2 × $C(Ar)CH_2CH$=CH_2), 34.8 (CCH_2CH_2CH=CH_2), 30.2 (CCH_2CH_2CH=CH_2), 18.1 (2 × C=CCH_3), 16.3 ($C(CH_3)_2$). ν_{max} (thin film/cm^{-1}): 2976, 1682, 1429, 1396, 914, 751. MS (ESI$^+$) *m/z* (%): 565 (M + H$^+$, 100); HRMS (ESI) calcd. for $C_{37}H_{45}N_2O_3$ (M + H$^+$): 565.3425. Found: 565.3428.

Radical cyclisation cascades that construct quaternary all carbon stereocentres mediated by SmI_2-H_2O-LiBr

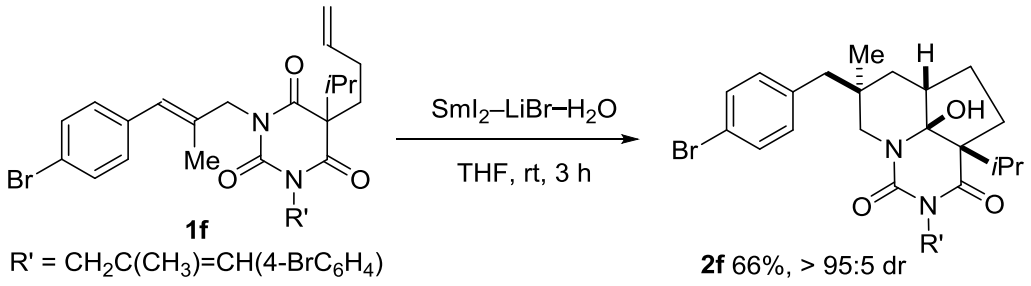
General procedure C: SmI_2-H_2O-LiBr mediated radical cyclisation cascades to give hemiaminal products (2)

To an oven-dried vial charged with anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) was added freshly prepared SmI_2 (0.3 mmol, 3.0 mL, 0.1 M, 3 equiv) in THF, under a nitrogen atmosphere. The solution was stirred for 30 min at room temperature. An oven-dried vial containing a stir bar was charged with substrate (0.1 mmol, 1 equiv) and placed under a positive pressure of nitrogen. THF (0.05 M, typically, 2.0 mL) and water (typically, 100 equiv) were added, followed by the syringe pump addition of the mixture of SmI_2 and LiBr over 1 h with vigorous stirring. After the specified time (typically, 3 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.



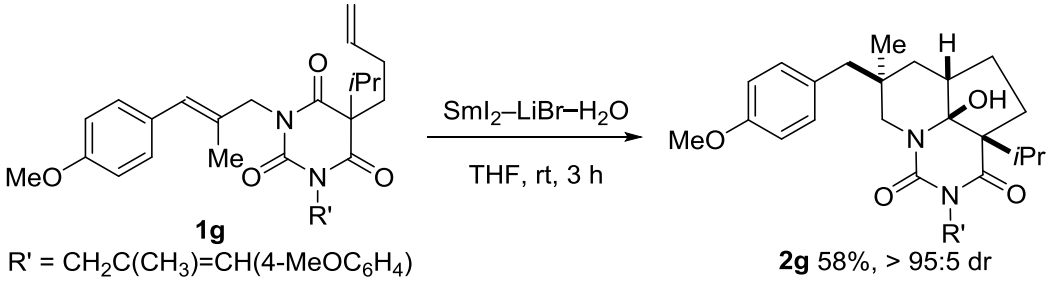
(2a*S*,2a^1*S*,7R,8a*S*)-7-Benzyl-2a^1-hydroxy-2a-isopentyl-7-methyl-4-((*E*)-2-methyl-3-phenylallyl)octahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (2d). According to the general procedure C, **1d** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 3 h and purification by chromatography (1/4 EtOAc/hexanes), gave **2d** (36 mg, 0.070 mmol, 70%, >

95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.27 - 7.33 (4 H, m, Ar*H*), 7.19 - 7.25 (3 H, m, Ar*H*), 7.14 - 7.19 (3 H, m, Ar*H*), 6.26 (1 H, s, C(CH_3)=C*H*Ar), 4.52 (2 H, d, *J* = 3.5 Hz, NCH_2), 4.12 (1 H, dd, *J* = 13.1, 2.3 Hz, 1 H from NCH_2), 3.01 (1 H, d, *J* = 13.1 Hz, 1 H from NCH_2), 2.60 (2 H, s, CH_2Ar), 2.56 - 2.59 (1 H, m, $CH_2CH_2CHCH_2$), 2.15 (1 H, s, O*H*), 2.03 - 2.13 (1 H, m, 1 H from C$H_2CH_2CH(CH_3)_2$), 1.90 - 2.03 (3 H, m, 1 H from C$H_2CH_2CH(CH_3)_2$ and 1 H from C$H_2CH_2CHCH_2$ and 1 H from $CH_2CH_2CHCH_2$), 1.86 (3 H, s, CH=CCH_3), 1.62 - 1.79 (3 H, m, 1 H from $CH_2CH_2CH(CH_3)_2$ and 1 H from C$H_2CH_2CHCH_2$ and 1 H from $CH_2CH_2CHCH_2$), 1.43 - 1.58 (3 H, m, 1 H from C$H(CH_3)_2$ and 1 H from $CH_2CH_2CHCH_2$ and 1 H from $CH_2CH_2CHCH_2$), 1.30 (1 H, dd, *J* = 6.8, 3.5 Hz, 1 H from $CH_2CH_2CH(CH_3)_2$), 1.04 (3 H, s, CH_3), 0.92 (6 H, dd, *J* = 6.5, 4.5 Hz, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.5 (N*C*(O)C), 152.5 (N*C*(O)N), 137.7 (ArCH=*C*), 137.0 (Ar*C*^{q}), 133.5 (Ar*C*^{q}), 130.6 (2 × Ar*C*H), 129.0 (2 × Ar*C*H), 128.0 (2 × Ar*C*H), 127.9 (2 × Ar*C*H), 126.4 (Ar*C*H), 126.2 (Ar*C*H), 124.8 (C=*C*HAr), 91.6 (*C*OH), 55.2 (*C*^{q}), 49.1 (*C*H_2Ar), 48.2 (N*C*H_2), 47.6 (N*C*H_2), 42.3 ($CH_2CH_2CHCH_2$), 34.9 (*C*$H_2CH(CH_3)_2$), 34.8 ($CH_2CH_2CHCH_2$), 34.4 (*C*$H_2CH_2CH(CH_3)_2$), 33.7 (*C*^{q}), 30.7 (*C*$H_2CH_2CHCH_2$), 29.1 (C*H*$(CH_3)_2$), 26.5 ($CH_2CH_2CHCH_2$), 23.0 (*C*H_3), 22.6 (*C*H_3), 22.5 (*C*H_3), 16.3 (*C*H_3). ν_{max} (thin film/cm^{-1}): 3409, 2955, 1705, 1664, 1440, 1367, 1259, 1021, 909, 733, 700. MS (ESI^{+}) *m/z* (%): 513.3 (M+H^{+}, 100); HRMS (ESI^{+}) calcd. for $C_{33}H_{43}N_2O_3$ (M + H^{+}): 515.3268. Found: 515.3266.



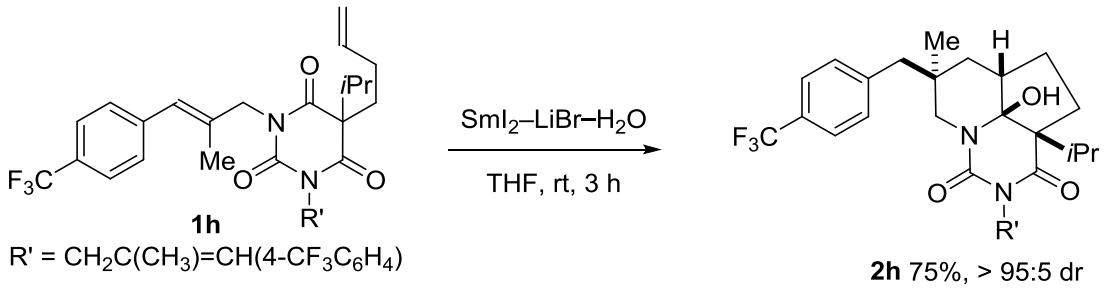
(2a*R*,2a^{1}*S*,7*R*,8a*S*)-7-(4-Bromobenzyl)-4-((*E*)-3-(4-bromophenyl)-2-methylallyl)-2a^{1}-hydroxy-2a-isopropyl-7-methyloctahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (2f). According to the general procedure C, **1f** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL,

0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 3 h and purification by chromatography (1/4 EtOAc/hexanes), gave **2f** (43 mg, 0.066 mmol, 66%, >95:5 dr) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.37 - 7.45 (4 H, m, Ar*H*), 6.94 - 7.10 (4 H, m, Ar*H*), 6.20 (1 H, s, ArC*H*=C), 4.43 - 4.56 (2 H, m, CH=C(CH_3)CH_2N), 4.07 (1 H, d, *J* = 13.2 Hz, 1 H from NCH_2), 3.10 (1 H, d, *J* = 13.6 Hz, 1 H from NCH_2), 2.52 - 2.63 (2 H, m, ArCH_2), 2.43 - 2.48 (1 H, m, COHC*H*), 2.13 - 2.28 (3 H, m, C*H*(CH_3)$_2$ and 1 H from C(O)CC$H_2$$CH_2$ and CO*H*), 1.87 - 2.03 (2 H, m, 1 H from C(O)CC$H_2$$CH_2$ and 1 H from C(O)CCH_2CH_2), 1.83 (3 H, s, CH=CCH_3), 1.75 (1 H, dd, *J* = 14.3, 6.5 Hz, 1 H from CHCH_2), 1.31 - 1.39 (1 H, m, 1 H from C(O)CCH_2CH_2), 1.16 - 1.26 (4 H, m, 1 H from CHCH_2 and CH_3(CH_3)CH), 1.11 (3 H, d, *J* = 6.9 Hz, CH_3(CH_3)CH), 1.00 (3 H, s, ArCH_2CCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.3 (N*C*(O)C), 152.7 (N*C*(O)N), 136.5 (ArCH=*C*), 136.2 (Ar*C*^{q}), 134.5 (Ar*C*^{q}), 132.2 (2 × Ar*C*H), 131.2 (2 × Ar*C*H), 131.1 (2 × Ar*C*H), 130.5 (2 × Ar*C*H), 124.1 (Ar*C*H=C), 120.5 (Ar*C*^{q}), 120.1 (Ar*C*^{q}), 91.9 (*C*OH), 58.4 (*C*^{q}), 48.4 (NCH_2C(CH_3)CH_2), 47.5 (NCH_2C(CH_3)=CH), 47.3 (ArCH_2), 44.0 (COHCH), 36.0 (COHCHCH_2), 34.0 (*C*^{q}), 33.9 (C(*i*Pr)$CH_2$$CH_2$), 31.0 (*C*H($CH_3$)$_2$), 27.7 (C(*i*Pr)$CH_2$$CH_2$), 24.7 (Ar$CH_2CCH_3$), 19.8 (CH(*C*$H_3$)$CH_3$), 19.7 (CH($CH_3$)*C*$H_3$), 16.4 (CH=C*C*$H_3$). ν_{max} (thin film/cm^{-1}): 2228, 2031, 2007, 1219, 908, 772, 623. MS (ESI$^+$) *m/z* (%): 679.0 (M+Cl$^-$, 100); HRMS (ESI$^+$) calcd. for $C_{31}H_{35}N_2O_3Br_2$ (M - H$^+$): 641.1009. Found: 641.1016.



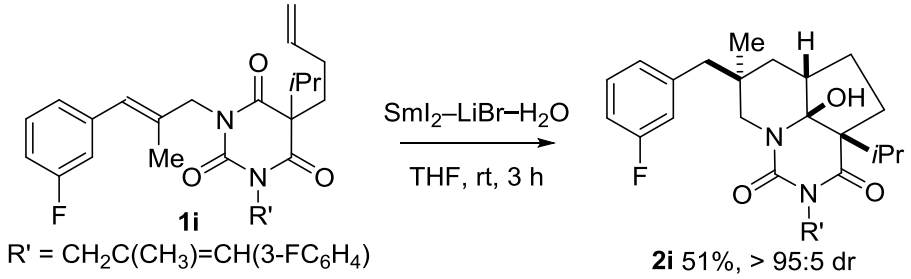
(2a*R*,2a^1*S*,7*R*,8a*S*)-2a^1-Hydroxy-2a-isopropyl-7-(4-methoxybenzyl)-4-((*E*)-3-(4-methoxyphenyl)-2-methylallyl)-7-methyloctahydro-3H-4,5a-diazaacenaphthylene-3,5(4H)-dione (2g). According to the general procedure C, **1g** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv),

stirring for 3 h, and purification by chromatography (1/4 EtOAc/hexanes), gave **2g** (32 mg, 0.058 mmol, 58%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.12 - 7.16 (2 H, m, Ar*H*), 7.05 - 7.09 (2 H, m, Ar*H*), 6.82 - 6.85 (4 H, m, Ar*H*), 6.25 (1 H, s, ArC*H*=C), 4.45 - 4.60 (2 H, m, CH=C(CH_3)CH_2N), 4.08 (1 H, dd, *J* = 13.3, 1.3 Hz, 1 H from NCH_2), 3.80 (6 H, s, 2 × OCH_3), 3.11 (1 H, d, *J* = 13.3 Hz, 1 H from NCH_2), 2.57 (2 H, d, *J* = 5.0 Hz, ArCH_2), 2.39 - 2.50 (1 H, m, COHC*H*), 2.15 - 2.30 (2 H, m, C*H*(CH_3)$_2$ and 1 H from C(O)CCH_2CH_2), 2.10 (1 H, s, CO*H*), 1.92 - 1.99 (2 H, m, 1 H from C(O)CCH_2CH_2 and 1 H from C(O)CCH_2CH_2), 1.85 (3 H, s, CH=CCH_3), 1.76 (1 H, dd, *J* = 14.3, 6.3 Hz, 1 H from CHCH_2), 1.31 - 1.39 (1 H, m, 1 H from C(O)CCH_2CH_2), 1.17 - 1.22 (4 H, m, 1 H from CHCH_2 and CH_3(CH_3)CH), 1.11 (3 H, d, *J* = 6.8 Hz, CH_3(CH_3)CH), 1.01 (3 H, s, ArCH_2CCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.3 (N*C*(O)C), 158.2 (Ar*C*^{q}), 157.9 (Ar*C*^{q}), 152.8 (N*C*(O)N), 132.0 (ArCH=*C*), 131.5 (2 × Ar*C*H), 130.3 (Ar*C*^{q}), 130.1 (2 × Ar*C*H) , 129.3 (Ar*C*^{q}), 125.0 (Ar*C*H=C), 113.5 (2 × Ar*C*H), 113.4 (2 × Ar*C*H), 91.9 (*C*OH), 58.5 (*C*^{q}), 55.2 (2 × O*C*H_3), 48.4 (N*C*H_2), 47.7 (N*C*H_2C(CH_3)=CH), 47.1 (Ar*C*H_2), 44.2 (COH*C*H), 36.1 (CH*C*H_2), 34.1 (*C*^{q}), 33.9 (C(*i*Pr)*C*H_2CH_2), 31.0 (*C*H(CH_3)$_2$), 27.8 (C(*i*Pr)CH_2*C*H_2), 24.9 (*C*H_3), 19.8 (CH(*C*H_3)CH_3), 19.7 (CH(CH_3)*C*H_3), 16.4 (CH=C*C*H_3). ν_{max} (thin film/cm^{-1}): 3431, 2932, 1645, 1510, 1438, 1366, 1230, 1177, 1034, 909, 824, 730. MS (ESI$^+$) *m/z* (%): 547.3 (M + H$^+$, 100); HRMS (ESI$^+$) calcd. for $C_{33}H_{42}N_2O_5Na$ (M + Na$^+$): 569.2986. Found: 569.2981.



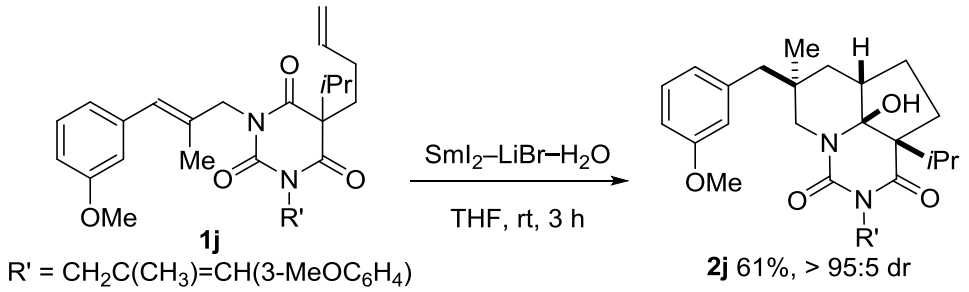
(2a*R*,2a^1*S*,7*R*,8a*S*)-2a^1-Hydroxy-2a-isopropyl-7-methyl-4-((*E*)-2-methyl-3-(4-(trifluoromethyl)phenyl)allyl)-7-(4-(trifluoromethyl)benzyl)octahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (2h). According to the general procedure C, **1h** (0.10 mmol), SmI_2 (0.30 mmol,

3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 3 h and purification by chromatography (1/4 EtOAc/hexanes), gave **2h** (47 mg, 0.075 mmol, 75%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.54 (4 H, t, *J* = 7.3 Hz, Ar*H*), 7.19 - 7.34 (4 H, m, Ar*H*), 6.29 (1 H, s, ArC*H*=C), 4.47 - 4.58 (2 H, m, CH=C(CH_3)CH_2N), 4.04 - 4.16 (1 H, m, 1 H from NCH_2), 3.14 (1 H, d, *J* = 13.3 Hz 1 H from NCH_2), 2.60 - 2.76 (2 H, m, ArCH_2), 2.41 - 2.56 (1 H, m, C*H*), 2.33 (1 H, s, CO*H*), 2.16 - 2.30 (2 H, m, 1 H from C(O)CCH_2CH$_2$ and CH_3(CH_3)C*H*), 1.90 - 2.06 (2 H, m, 1 H from C(O)CCH_2CH$_2$ and 1 H from CHCH_2), 1.86 (3 H, s, CH=CCH_3), 1.79 (1 H, dd, *J* = 14.3, 6.3 Hz, 1 H from C(O)CCH$_2$CH_2), 1.31 - 1.43 (1 H, m, 1 H from CHCH_2), 1.26 (1 H, d, *J* = 5.0 Hz, 1 H from C(O)CCH$_2$CH_2), 1.21 (3 H, d, *J* = 6.8 Hz, CH_3(CH_3)CH), 1.13 (3 H, d, *J* = 6.8 Hz, CH_3(CH_3)CH), 1.02 (3 H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.3 (N*C*(O)C), 152.8 (N*C*(O)N), 141.3 (Ar*C*^{q}), 141.2 (Ar*C*^{q}), 135.9 (ArCH=*C*), 130.8 (2 × Ar*C*H), 129.1 (4 × Ar*C*H), 128.6 (q, *J* = 32 Hz, 2 ×Ar*C*^{q}), 124.9 (q, *J* = 3.0 Hz, 2 × Ar*C*H), 124.3 (q, *J* = 270 Hz, 2 ×Ar*C*^{q}), 123.9 (Ar*C*H=C), 92.0 (*C*OH), 58.4 (*C*^{q}), 48.5 (NCH_2), 47.7 (NCH_2C(CH_3)=CH), 47.5 (ArCH_2), 44.0 (*C*H), 36.0 (CHCH_2), 34.1 (*C*^{q}), 33.9 (C(*i*Pr)*C*H$_2$CH$_2$), 30.9 (*C*H(CH_3)$_2$), 27.7 (C(*i*Pr)CH$_2$*C*H$_2$), 24.6 (*C*H$_3$), 19.8 (CH(*C*H$_3$)CH$_3$), 19.7 (CH(CH_3)*C*H$_3$), 16.4 (CH=C*C*H$_3$). ν_{max} (thin film/cm^{-1}): 2966, 1673, 1344, 1164, 1067, 908, 732. MS (ESI$^+$) *m/z* (%): 623.2 (M + H$^+$, 100); HRMS (ESI$^+$) calcd. for $C_{33}H_{37}N_2O_3F_6$ (M + H$^+$): 623.2703. Found: 627.2702.



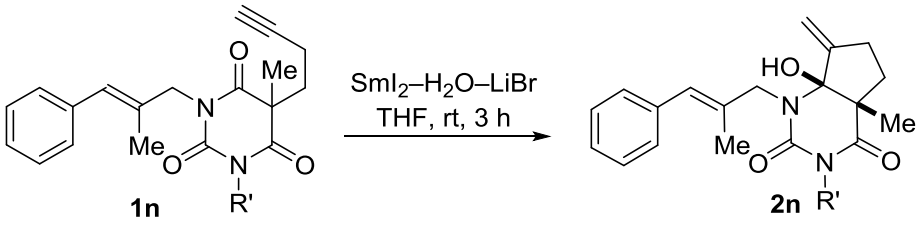
(2a*R*,2a^1*S*,7*R*,8a*S*)-7-(3-Fluorobenzyl)-4-((*E*)-3-(3-fluorophenyl)-2-methylallyl)-2a^1-hydroxy-2a-isopropyl-7-methyloctahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (2i). According to the general procedure C, **1i** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv),

stirring for 3 h and purification by chromatography (1/4 EtOAc/hexanes), gave **2i** (27 mg, 0.051 mmol, 51%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.19 - 7.28 (2 H, m, Ar*H*), 6.81 - 7.01 (6 H, m, Ar*H*), 6.24 (1 H, s, ArC*H*=C), 4.43 - 4.59 (2 H, m, CH=C(CH_3)CH_2N), 4.09 (1 H, dd, *J* = 13.3, 1.5 Hz, 1 H from NCH_2), 3.12 (1 H, d, *J* = 13.6 Hz, 1 H from NCH_2), 2.59 - 2.65 (2 H, m, ArCH_2), 2.39 - 2.52 (1 H, m, C*H*), 2.31 (1 H, s, CO*H*), 2.14 - 2.29 (2 H, m, 1 H from C(O)CCH_2CH$_2$ and CH_3(CH_3)C*H*), 1.89 - 2.03 (2 H, m, 1 H from C(O)CCH_2CH$_2$ and 1 H from CHCH_2), 1.86 (3 H, s, CH=CCH_3), 1.78 (1 H, dd, *J* = 14.3, 6.3 Hz, 1 H from C(O)CCH$_2$CH_2), 1.32 - 1.42 (1 H, m, 1 H from CHCH_2), 1.23 - 1.28 (1 H, m, 1 H from C(O)CCH$_2$CH_2), 1.20 (3 H, d, *J* = 7.0 Hz, CH_3(CH_3)CH), 1.13 (3 H, d, *J* = 6.8 Hz, CH_3(CH_3)CH), 1.03 (3 H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.3 (N*C*(O)C), 162.6 (d, *J* = 244 Hz, ArC^q), 162.5 (d, *J* = 244 Hz, ArC^q), 152.7 (N*C*(O)N), 139.9 (d, *J* = 11 Hz, ArC^q), 139.8 (d, *J* = 11 Hz, ArC^q), 134.9 (C^q), 129.4 (d, *J* = 4 Hz, Ar*C*H), 129.3 (d, *J* = 4 Hz, Ar*C*H), 126.2 (d, *J* = 2 Hz, Ar*C*H=C), 124.7 (d, *J* = 3 Hz, Ar*C*H), 124.1 (d, *J* = 2 Hz, Ar*C*H), 117.3 (d, *J* = 21 Hz, Ar*C*H), 115.6 (d, *J* = 22 Hz, Ar*C*H), 113.4 (d, *J* = 21 Hz, Ar*C*H), 113.1 (d, *J* = 21 Hz, Ar*C*H), 91.9 (*C*OH), 58.4 (C^q), 48.4 (N*C*H$_2$), 47.7 (N*C*H$_2$C(CH_3)=CH), 47.5 (Ar*C*H$_2$), 44.0 (*C*H), 36.1 (CH*C*H$_2$), 34.1 (C^q), 33.9 (C(*i*Pr)*C*H$_2$CH$_2$), 30.9 (*C*H(CH_3)$_2$), 27.7 (C(*i*Pr)CH$_2$*C*H$_2$), 24.7 (*C*H$_3$), 19.8 (CH(*C*H$_3$)CH$_3$), 19.7 (CH(CH_3)*C*H$_3$), 16.5 (CH=C*C*H$_3$). ν_{max} (thin film/cm^{-1}): 3432, 2931, 1703, 1659, 1582, 1439, 1367, 1254, 1143, 1020, 910, 734. MS (ESI$^+$) *m/z* (%): 523.2 (M + H$^+$, 100); HRMS (ESI$^+$) calcd. for $C_{31}H_{36}N_2O_3F_2Na$ (M + Na$^+$): 545.2586. Found: 545.2581.



(2a*R*,2a^1*S*,7*R*,8a*S*)-2a^1-Hydroxy-2a-isopropyl-7-(3-methoxybenzyl)-4-((*E*)-3-(3-methoxyp -henyl)-2-methylallyl)-7-methyloctahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione

(2j). According to the general procedure C, **1j** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 3 h and purification by chromatography (1/4 EtOAc/hexanes), gave **2j** (33 mg, 0.061 mmol, 61%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.17 - 7.24 (2 H, m, Ar*H*), 6.68 - 6.83 (6 H, m, Ar*H*), 6.27 (1 H, s, C(CH_3)=C*H*Ar), 4.51 (2 H, s, NC*H*$_2$), 4.07 - 4.13 (1 H, m, 1 H from NC*H*$_2$), 3.78 (3 H, s, OC*H*$_3$), 3.80 (3 H, s, OC*H*$_3$), 3.13 (1 H, d, *J* = 13.3 Hz, 1 H from NC*H*$_2$), 2.59 (2 H, d, *J* = 2.0 Hz, C*H*$_2$Ar), 2.40 - 2.51 (1 H, m, C*H*), 2.32 (1 H, s, CO*H*), 2.17 - 2.29 (2 H, m, 1 H from C*H*$_2$CH$_2$CHCH$_2$ and C*H*(CH_3)$_2$), 1.88 - 2.01 (2 H, m, 1 H from C*H*$_2$CH$_2$CHCH$_2$ and 1 H from CH$_2$C*H*$_2$CHCH$_2$), 1.87 (3 H, s, =C(C*H*$_3$)), 1.80 (1 H, dd, *J* = 14.2, 6.4 Hz, 1 H from CH$_2$CH$_2$CHC*H*$_2$), 1.35 (1 H, d, *J* = 7.5 Hz, 1 H from CH$_2$C*H*$_2$CHCH$_2$), 1.25 (1 H, d, *J* = 4.3 Hz, 1 H from CH$_2$CH$_2$CHC*H*$_2$), 1.20 (3 H, d, *J* = 7.0 Hz, C*H*$_3$), 1.12 (3 H, d, *J* = 6.8 Hz, C*H*$_3$), 1.04 (3 H, s, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.4 (N*C*(O)C), 159.2 (2 × Ar*C*^{q}), 152.8 (N*C*(O)N), 139.1 (ArCH=*C*), 138.9 (Ar*C*^{q}), 133.8 (Ar*C*^{q}), 128.9 (2 × Ar*C*H), 125.1 (Ar*C*H=C), 123.1 (Ar*C*H), 121.5 (Ar*C*H), 116.8 (Ar*C*H), 114.5 (Ar*C*H), 111.8 (Ar*C*H), 111.3 (Ar*C*H), 91.9 (*C*OH), 58.4 (*C*^{q}), 55.2 (2 × O*C*H$_3$), 48.6 (N*C*H$_2$), 48.0 (Ar*C*H$_2$), 47.5 (N*C*H$_2$C(CH_3)=CH), 44.1 (*C*H), 36.2 (CH*C*H$_2$), 34.1 (*C*^{q}), 33.9 (C(*i*Pr)*C*H$_2$CH$_2$), 31.0 (*C*H(CH_3)$_2$), 27.8 (C(*i*Pr)CH$_2$*C*H$_2$), 25.0 (*C*H$_3$), 19.8 (*C*H$_3$), 19.7 (*C*H$_3$), 16.5 (CH=C*C*H$_3$). ν_{max} (thin film/cm^{-1}): 3430, 1936, 1644, 1581, 1435, 1366, 1258, 1156, 1049, 908, 732, 696. MS (ESI$^+$) *m/z* (%): 547.3 (M + H$^+$, 100); HRMS (ESI$^+$) calcd. for $C_{33}H_{42}N_2O_5Na$ (M + Na$^+$): 559.2986. Found: 569.2980.



1n [R' = $CH_2C(CH_3)$=CHPh] **2n** 26%, >95:5 dr

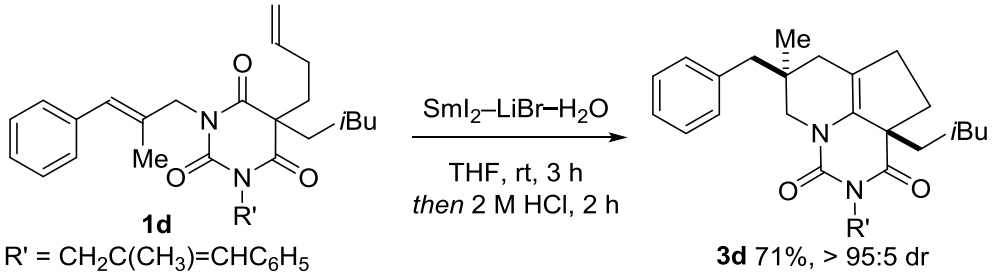
(4a*S*,7a*S*)-7a-Hydroxy-4a-methyl-1,3-bis((*E*)-2-methyl-3-phenylallyl)-7-methylenehexahydro-2*H*-cyclopenta[*d*]pyrimidine-2,4(3*H*)-dione (2n). According to the general procedure

C, **1n** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 3 h and purification by chromatography (1/4 EtOAc/hexanes), gave **2n** (12.8 mg, 0.026 mmol, 26%, >95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.29 - 7.36 (4 H, m, Ar*H*), 7.15 - 7.26 (6 H, m, Ar*H*), 6.33 (2 H, d, *J* = 6.3 Hz, 2 × ArC*H*=C(CH_3)), 5.38 - 5.47 (1 H, m, 1 H from C=CH_2), 5.31 (1 H, s, 1 H from C=CH_2), 4.59 (2 H, s, NCH_2), 4.35 (1 H, d, *J* = 16.1 Hz, 1 H from NCH_2), 4.23 (1 H, d, *J* = 16.1 Hz, 1 H from NCH_2), 2.60 (1 H, s, OH), 2.47 - 2.55 (2 H, m, CH_2CH_2C=CH_2), 2.19 (1 H, m, 1 H from CH_2CH_2C=CH_2), 1.85 - 1.90 (7 H, m, 1 H from CH_2CH_2C=CH_2 and 2 × CH_3), 1.30 (3 H, s, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 172.6 (N*C*(O)C), 152.7 (N*C*(O)N), 149.3 (*C*=CH_2), 137.7 (ArC^q), 137.3 (ArC^q), 135.5 (=C^q), 133.4 (=C^q), 129.0 (2 × ArC*H*), 128.9 (ArC*H*), 128.8 (ArC*H*), 128.2 (ArC*H*), 128.0 (ArC*H*), 126.5 (ArC*H*), 126.2 (ArC*H*), 125.7 (ArC*H*), 124.8 (ArC*H*), 112.2 (C=*C*H_2), 92.5 (*C*OH), 50.9 (C^q), 50.4 (N*C*H_2), 47.6 (N*C*H_2), 32.7 (CH_2CH_2C=CH_2), 26.0 (CH_2CH_2C=CH_2), 17.5 (*C*H_3), 16.2 (*C*H_3), 16.0 (*C*H_3). ν_{max} (thin film/cm^{-1}): 3398, 2942, 1710, 1652, 1444, 1358, 1253, 699. MS (ESI^-) *m/z* (%): 491 (M + Cl^-, 100); HRMS (ESI^+) calcd. for $C_{29}H_{33}N_2O_3$ (M + H^+): 457.2486. Found: 457.2490.

General procedure D: SmI_2-LiBr-H_2O mediated radical cyclisation cascades to give enamine products (3)

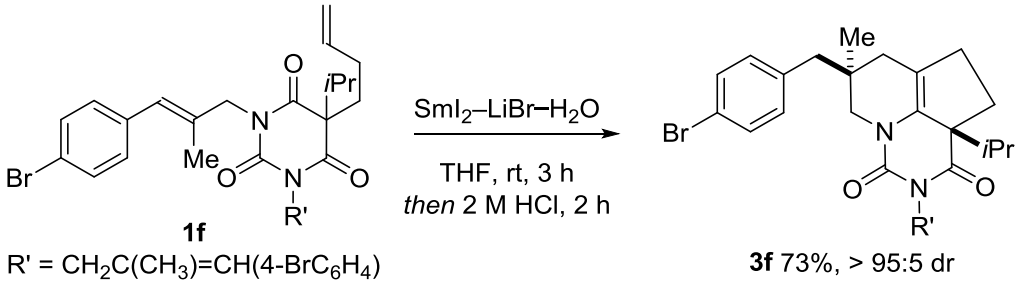
To an oven-dried flask charged with anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) was added freshly prepared SmI_2 (0.3 mmol, 3.0 mL, 0.1 M) in THF, under a nitrogen atmosphere. The solution was stirred for 30 min at room temperature. To an oven-dried vial containing a stir bar was added substrate (0.1 mmol, 1 equiv) and the vial placed under a positive pressure of nitrogen. THF (0.05 M, typically, 2.0 mL) and water (typically, 100 equiv) were added, followed by syringe pump addition of the mixture of SmI_2 and LiBr over 1 h with vigorous stirring. After 3 h, HCl (2 M in Et_2O, 2 mL) was added and the resulting solution stirred for 2 h. The reaction was then diluted with CH_2Cl_2 (30 mL) and HCl (0.1 M, 20 mL). The aqueous

layer was extracted with CH_2Cl_2 (3 × 20 mL), the organic layers were combined, dried over Mg_2SO_4 and concentrated. The crude product was purified by chromatography on silica gel.



(2a*S*,7*S*)-7-Benzyl-2a-isopentyl-7-methyl-4-((*E*)-2-methyl-3-phenylallyl)-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3d). According to the general procedure D, **1d** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), LiBr (521 mg, 6.0 mmol) and H_2O (0.18 mL, 100 equiv), stirring for 3 h, addition of HCl (2 M in Et_2O, 2 mL), stirring for 2 h and purification by chromatography (1/4 EtOAc/hexanes), gave **3d** (35 mg, 0.071 mmol, 71%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28 - 7.34 (4 H, m, Ar*H*), 7.22 - 7.26 (1 H, m, Ar*H*), 7.14 - 7.22 (5 H, m, Ar*H*), 6.26 (1 H, s, C(CH_3)=C*H*Ar), 4.54 (1 H, d, *J* = 14.6 Hz, 1 H from NCH_2), 4.42 (1 H, d, *J* = 15.1 Hz, 1 H from NCH_2), 3.96 (1 H, d, *J* = 12.3 Hz, 1 H from NCH_2), 3.11 (1 H, d, *J* = 12.5 Hz, 1 H from NCH_2), 2.68 (2 H, d, *J* = 4.8 Hz, CH_2Ar), 2.45 (1 H, d, *J* = 8.5 Hz, 1 H from CCH_2(*i*Bu)CH_2CH_2), 2.17 - 2.26 (2 H, m, 1 H from CCH_2(*i*Bu)CH_2CH_2 and 1 H from CCH_2(*i*Bu)CH_2CH_2), 2.07 - 2.17 (2 H, m, 1 H from CCH_2(*i*Bu)CH_2CH_2 and 1 H from CH_2), 1.83 - 1.87 (3 H, m, CH_3), 1.66 - 1.77 (2 H, m, CH_2CH(CH_3)$_2$), 1.57 - 1.63 (1 H, m, 1 H from CH_2), 1.37 - 1.48 (1 H, m, CH_2C*H*(CH_3)$_2$), 1.19 - 1.29 (1 H, m, 1 H from C$H_2$$CH_2$CH($CH_3$)$_2$), 1.11 - 1.17 (1 H, m, 1 H from C$H_2$$CH_2$CH($CH_3$)$_2$), 0.90 (3 H, s, C$H_3$), 0.81 (6 H, d, *J* = 10.9 Hz, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.9 (N*C*(O)C), 151.3 (N*C*(O)N), 137.7 (ArCH=*C*), 136.9 (Ar*C*^{q}), 133.7 (Ar*C*^{q}), 131.0 (*C*^{q}), 130.5 (2 × Ar*C*H), 128.9 (2 × Ar*C*H), 128.1 (2 × Ar*C*H), 127.9 (2 × Ar*C*H), 126.6 (Ar*C*H), 126.2 (Ar*C*H), 125.2 (CH_2C(CH_3)=*C*HAr), 117.6 (*C*^{q}), 53.4 (*C*^{q}), 51.4 (N*C*H_2), 47.8 (N*C*H_2), 46.6 (*C*H_2Ar), 35.4 (*C*H_2CH(CH_3)$_2$), 35.3 (*C*H_2), 34.1 (*C*^{q}), 33.1 (*C*$H_2$$CH_2$CH($CH_3$)$_2$), 31.4 (CC$H_2$(*i*Bu)C$H_2CH_2$),

30.9 ($CCH_2(i\text{Bu})CH_2CH_2$), 28.3 ($CH(CH_3)_2$), 22.8 ($CH_3$), 22.5 ($CH_3$), 22.4 ($CH_3$), 16.3 ($CH_3$). ν_{max} (thin film/cm^{-1}): 2954, 1676, 1419, 1327, 1169, 753, 700. MS (ESI^+) *m/z* (%): 497.3 (M + H^+, 100); HRMS (ESI^+) calcd. for $C_{33}H_{41}N_2O_2$ (M + H^+): 497.3163. Found: 497.3162.



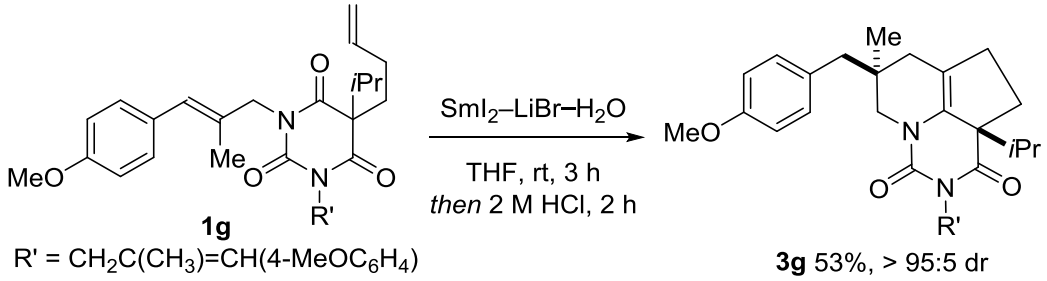
1f

R' = $CH_2C(CH_3)$=CH(4-BrC_6H_4)

3f 73%, > 95:5 dr

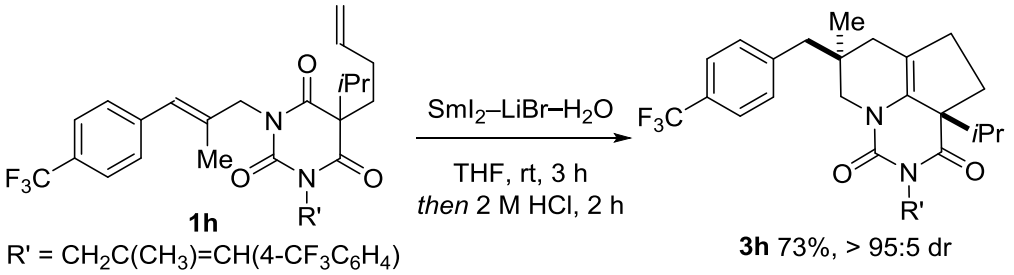
(2a*R*,7*S*)-7-(4-Bromobenzyl)-4-((*E*)-3-(4-bromophenyl)-2-methylallyl)-2a-isopropyl-7-methyl-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3f). According to the general procedure D, **1f** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), LiBr (521 mg, 6.0 mmol) and H_2O (0.18 mL, 100 equiv), stirring for 3 h, addition of HCl (2 M in Et_2O, 2 mL), stirring for 2 h and purification by chromatography (1/4 EtOAc/hexanes), gave **3f** (46 mg, 0.073 mmol, 73%, >95:5 dr) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.36 - 7.46 (4 H, m, Ar*H*), 7.04 (4 H, m, Ar*H*), 6.17 (1 H, s, ArC*H*=C), 4.51 (1 H, d, *J* = 15.5 Hz, 1 H from CH=C(CH_3)CH_2N), 4.39 (1 H, d, *J* = 15.1 Hz, 1 H from CH=C(CH_3)CH_2N), 3.97 - 4.05 (1 H, m, 1 H from NCH_2), 3.02 (1 H, d, *J* = 12.6 Hz, 1 H from NCH_2), 2.58 - 2.69 (2 H, m, ArCH_2), 2.34 - 2.44 (1 H, m, 1 H from C(*i*Pr)CH_2CH_2), 2.09 - 2.25 (4 H, m, 1 H from C(*i*Pr)CH_2CH_2 and C(*i*Pr)CH_2 and 1 H from CH_2), 2.05 (1 H, m, C$H(CH_3)_2$), 1.82 (3 H, s, CH=CCH_3), 1.70 (1 H, d, *J* = 17.0 Hz, 1 H from CH_2), 0.94 (3 H, d, *J* = 6.6 Hz, CH_3(CH_3)CH), 0.89 (3 H, d, *J* = 6.9 Hz, CH_3(CH_3)CH), 0.84 (3 H, s, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 173.6 (N*C*(O)C), 151.3 (N*C*(O)N), 136.6 (ArCH=*C*), 135.7 (ArC^q), 134.8 (ArC^q), 132.1 (2 × Ar*C*H), 131.3 (2 × Ar*C*H), 131.1 (2 × Ar*C*H), 130.5 (2 × Ar*C*H), 130.0 (C^q), 124.2 (Ar*C*H=C), 120.7 (ArC^q), 120.0 (ArC^q), 118.9 (C^q), 57.8 (C^q), 51.3 (NCH_2), 48.0 (NCH_2C(CH_3)=CH), 46.3 (ArCH_2), 35.6 (CH_2), 34.7 ($CH(CH_3)_2$), 34.1 (C^q), 32.6 (C(*i*Pr)$CH_2$$CH_2$), 26.9 (C(*i*Pr)$CH_2$$CH_2$), 22.4 ($CH_3$), 17.6 (CH($CH_3$)$CH_3$), 17.1 (CH($CH_3$)$CH_3$), 16.3 (CH=C$CH_3$). ν_{max} (thin film/cm^{-1}): 2962, 1760, 1486, 1418, 1327, 1175,

1071, 1010, 907, 729. MS (ESI^+) *m/z* (%): 625.3 ($M+H^+$, 100); HRMS (ESI^+) calcd. for $C_{31}H_{35}N_2O_2Br_2$ ($M + H^+$): 625.1060. Found: 625.1056.

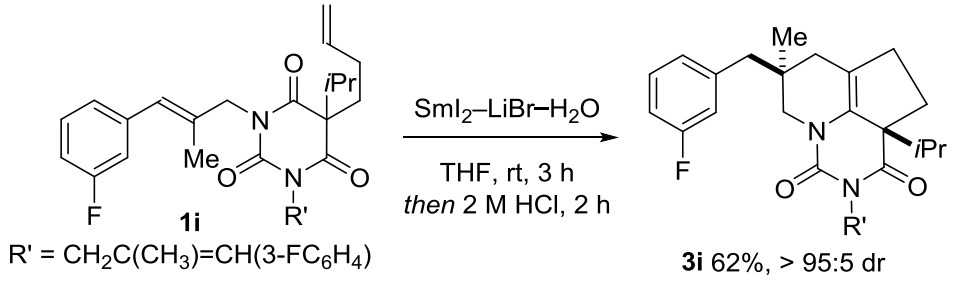


(2a*R*,7*S*)-2a-Isopropyl-7-(4-methoxybenzyl)-4-((*E*)-3-(4-methoxyphenyl)-2-methylallyl)-7-methyl-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3g). According to the general procedure D, **1g** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), LiBr (521 mg, 6.0 mmol) and H_2O (0.18 mL, 100 equiv), stirring for 3 h, addition of HCl (2 M in Et_2O, 2 mL), stirring for 2 h and purification by chromatography (1/4 EtOAc/hexanes), gave **3g** (28 mg, 0.053 mmol, 53%, > 95:5 dr) as a white solid. M.p. = 76 - 77.3 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.10 - 7.15 (2 H, m, Ar*H*), 7.05 - 7.10 (2 H, m, Ar*H*), 6.80 - 6.87 (4 H, m, Ar*H*), 6.22 (1 H, s, ArC*H*=C), 4.37 - 4.54 (2 H, m, CH=C(CH_3)CH_2N), 3.99 - 4.05 (1 H, m, 1 H from NCH_2), 3.79 - 3.82 (6 H, s, 2 × OCH_3), 3.03 (1 H, d, *J* = 12.3 Hz, 1 H from NCH_2), 2.58 - 2.67 (2 H, m, ArCH_2), 2.33 - 2.45 (1 H, m, 1 H from C(*i*Pr)CH_2CH_2), 1.99 - 2.25 (5 H, m, 1 H from C(*i*Pr)CH_2CH_2 and C(*i*Pr)CH_2 and C*H*(CH_3)$_2$ and 1 H from CH_2), 1.84 (3 H, s, CH=CCH_3), 1.63 - 1.73 (1 H, m, 1 H from CH_2), 0.86 - 0.96 (6 H, m, CH(CH_3)$_2$), 0.85 (3 H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.7 (N*C*(O)C), 158.3 (ArC^q), 157.9 (ArC^q), 151.4 (N*C*(O)N), 132.2 (ArCH=*C*), 131.4 (2 × Ar*C*H), 130.3 (ArC^q), 130.1 (2 × Ar*C*H), 129.9 (ArC^q), 128.9 (C^q), 125.0 (Ar*C*H=C), 119.1 (C^q), 113.6 (2 × Ar*C*H), 113.4 (2 × Ar*C*H), 57.8 (C^q), 55.2 (2 × O*C*H_3), 51.3 (N*C*H_2), 48.2 (N*C*H_2C(CH_3)=CH), 46.1 (Ar*C*H_2), 35.6 (*C*H_2), 34.7 (*C*H(CH_3)$_2$), 34.2 (C^q), 32.6 (C(*i*Pr)CH_2*C*H_2), 26.8 (C(*i*Pr)*C*H_2CH$_2$), 22.5 (*C*H_3), 17.7 (CH(*C*H_3)CH$_3$), 17.1 (CH(CH$_3$)*C*H$_3$), 16.3 (CH=C*C*H_3). ν_{max} (thin film/cm^{-1}): 2959, 1670, 1509, 1418, 1245, 1175, 1034, 908, 839, 729. MS (ESI^+) *m/z* (%): 529.3 ($M+H^+$, 100); HRMS (ESI^+) calcd. for

$C_{33}H_{41}N_2O_4$ (M + H^+): 529.3061. Found: 529.3056.



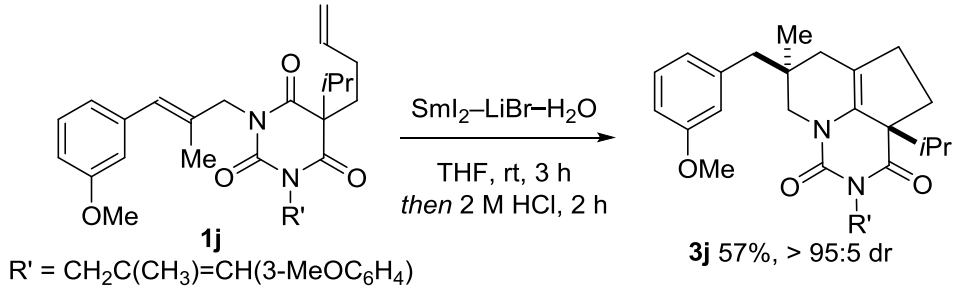
(2a*R*,7*S*)-2a-Isopropyl-7-methyl-4-((*E*)-2-methyl-3-(4-(trifluoromethyl)phenyl)allyl)-7-(4-(trifluoromethyl)benzyl)-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3h). According to the general procedure D, **1h** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), LiBr (521 mg, 6.0 mmol) and H_2O (0.18 mL, 100 equiv), stirring for 3 h, addition of HCl (2 M in Et_2O, 2 mL), stirring for 2 h and purification by chromatography (1/4 EtOAc/hexanes), gave **3h** (44 mg, 0.073 mmol, 73%, > 95:5 dr) as a white solid. M.p. = 85.6 – 86.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.49 - 7.62 (4 H, m, Ar*H*), 7.23 - 7.29 (4 H, m, Ar*H*), 6.26 (1 H, s, ArC*H*=C), 4.54 (1 H, d, *J* = 15.6 Hz, 1 H from CH=C(CH_3)CH_2N), 4.42 (1 H, d, *J* = 15.3 Hz, 1 H from CH=C(CH_3)CH_2N), 4.05 (1 H, d, *J* = 12.5 Hz, 1 H from NCH_2), 3.07 (1 H, d, *J* = 12.3 Hz, 1 H from NCH_2), 2.69 - 2.83 (2 H, m, ArCH_2), 2.32 - 2.47 (1 H, m, 1 H from CH_2), 2.11 - 2.28 (4 H, m, C(*i*Pr)CH_2CH_2 and C(*i*Pr)C$H_2$$CH_2$), 1.85 (3 H, s, CH=CC$H_3$), 1.73 (1 H, d, *J* = 17.1 Hz, 1 H from CH_2), 0.86 - 0.96 (9 H, m, CH(CH_3)$_2$ and CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.6 (N*C*(O)C), 151.3 (N*C*(O)N), 141.3 (ArC^q), 140.9 (ArC^q), 136.2 (C^q), 130.7 (2 × Ar*C*H), 130.0 (C^q), 129.1 (4 × Ar*C*H), 128.6 (q, *J* = 54 Hz, 2 × ArC^q), 125.1 (q, *J* = 4 Hz, Ar*C*H), 124.9 (q, *J* = 4 Hz, Ar*C*H), 124.7 (q, *J* = 263 Hz, 2 × ArC^q), 123.9 (Ar*C*H=C), 118.9 (C^q), 57.9 (C^q), 51.3 (NCH_2), 47.9 (NCH_2C(CH_3)=CH), 46.7 (ArCH_2), 35.8 (CH_2), 34.7 (*C*H(CH_3)$_2$), 34.2 (C^q), 32.6 (C(*i*Pr)$CH_2$$CH_2$), 26.8 (C(*i*Pr)*C*$H_2$$CH_2$), 22.3 ($CH_3$), 17.6 (CH(*C*$H_3$)$CH_3$), 17.1 (CH($CH_3$)*C*$H_3$), 16.3 (CH=C*C*$H_3$). ν_{max} (thin film/cm^{-1}): 2966, 1675, 1419, 1365, 1122, 1067, 1018, 852, 748. MS (ESI$^+$) *m/z* (%): 605.2 (M + H^+, 100); HRMS (ESI$^+$) calcd. for $C_{33}H_{35}N_2O_2F_6$ (M + H^+): 605.2597. Found: 605.2596.



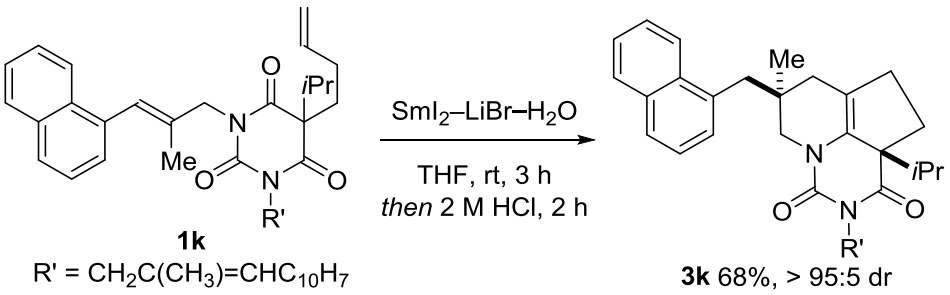
R' = $CH_2C(CH_3)=CH(3\text{-}FC_6H_4)$

3i 62%, > 95:5 dr

(2a*R*,7*S*)-7-(4-Fluorobenzyl)-4-((*E*)-3-(4-fluorophenyl)-2-methylallyl)-2a-isopropyl-7-methyl-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3i). According to the General procedure D, **1i** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), LiBr (521 mg, 6.0 mmol) and H_2O (0.18 mL, 100 equiv), stirring for 3 h, addition of HCl (2 M in Et_2O, 2 mL), stirring for 2 h and purification by chromatography (1/4 EtOAc/hexanes), gave **3i** (31 mg, 0.062 mmol, 62%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.15 - 7.30 (2 H, m, Ar*H*), 6.72 - 7.01 (6 H, m, Ar*H*), 6.21 (1 H, s, ArC*H*=C), 4.46 - 4.57 (1 H, m, 1 H from CH=C(CH_3)CH_2N), 4.29 - 4.46 (1 H, m, 1 H from CH=C(CH_3)CH_2N), 4.04 (1 H, dd, *J* = 12.4, 1.4 Hz, 1 H from NCH_2), 3.04 (1 H, d, *J* = 12.5 Hz, 1 H from NCH_2), 2.56 - 2.77 (2 H, m, ArCH_2), 2.29 - 2.49 (1 H, m, 1 H from CH_2), 1.98 - 2.28 (4 H, m, C(*i*Pr)CH_2CH$_2$ and C(*i*Pr)CH$_2$CH_2), 1.85 (3 H, s, CH_3), 1.72 (1 H, d, *J* = 17.3 Hz, 1 H from CH_2), 0.93 - 0.99 (3 H, m, CH(CH_3)$_2$), 0.82 - 0.90 (6 H, m, CH(CH_3)$_2$ and CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.6 (N*C*(O)C), 162.6 (d, *J* = 244 Hz, 2 × Ar*C*^{q}), 151.3 (N*C*(O)N), 140.0 (d, *J* = 8 Hz, Ar*C*^{q}), 139.2 (d, *J* = 8 Hz, Ar*C*^{q}), 135.2 (*C*^{q}), 130.0 (*C*^{q}), 129.6 (d, *J* = 8 Hz, Ar*C*H), 129.4 (d, *J* = 7 Hz, Ar*C*H), 126.2 (d, *J* = 3 Hz, Ar*C*H), 124.7 (d, *J* = 3 Hz, Ar*C*H=C), 124.2 (d, *J* = 2 Hz, Ar*C*H), 119.0 (*C*^{q}), 117.3 (d, *J* = 20 Hz, Ar*C*H), 115.5 (d, *J* = 21 Hz, Ar*C*H), 113.6 (d, *J* = 20 Hz, Ar*C*H), 113.1 (d, *J* = 21 Hz, Ar*C*H), 57.8 (*C*^{q}), 51.3 (N*C*H$_2$), 48.0 (NCH$_2$C(CH_3)=CH), 46.7 (Ar*C*H$_2$), 35.7 (*C*H$_2$), 34.7 (*C*H(CH_3)$_2$), 34.2 (*C*^{q}), 32.6 (C(*i*Pr)CH$_2$*C*H$_2$), 26.8 (C(*i*Pr)*C*H$_2$CH$_2$), 22.4 (*C*H$_3$), 17.6 (CH(*C*H$_3$)CH$_3$), 17.1 (CH(CH_3)*C*H$_3$), 16.3 (CH=C*C*H$_3$). ν_{max} (thin film/cm^{-1}): 2963, 1671, 1581, 1419, 1254, 1143, 908, 731. MS (ESI$^+$) *m/z* (%): 505.2 (M+H$^+$, 100); HRMS (ESI$^+$) calcd. for $C_{31}H_{34}N_2O_2F_2Na$ (M + Na$^+$): 527.2481. Found: 527.2476.

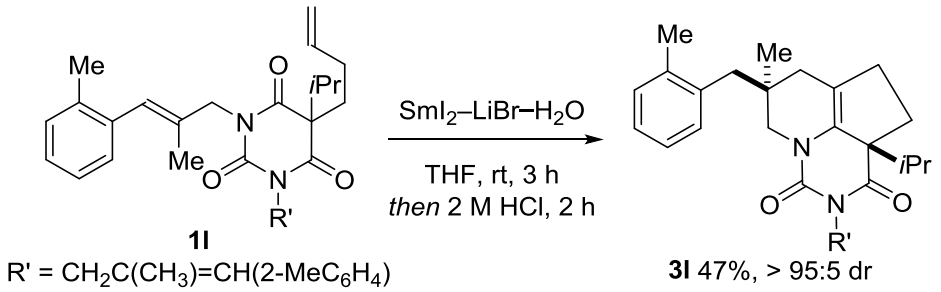


(2a*R*,7*S*)-2a-Isopropyl-7-(3-methoxybenzyl)-4-((*E*)-3-(3-methoxyphenyl)-2-methylallyl)-7-methyl-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3j). According to the general procedure D, **1j** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 2 h, addition of HCl (2 M in Et_2O, 2 mL), stirring for 3 h and purification by chromatography (1/4 EtOAc/hexanes), gave **3j** (30 mg, 0.057 mmol, 57%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.16 - 7.25 (2 H, m, Ar*H*), 6.69 - 6.83 (6 H, m, Ar*H*), 6.24 (1 H, s, C(CH_3)=C*H*Ar), 4.37 - 4.56 (2 H, m, CH=C(CH_3)CH_2N), 4.01 - 4.07 (1 H, m, 1 H from NCH_2), 3.81 (3 H, s, OCH_3), 3.78 (3 H, s, OCH_3), 3.06 (1 H, d, *J* = 12.5 Hz, 1 H from NCH_2), 2.66 (2 H, d, *J* = 3.3 Hz, ArCH_2), 2.32 - 2.45 (1 H, m, 1 H from C(*i*Pr)CH_2CH_2), 2.15 - 2.26 (3 H, m, 1 H from C(*i*Pr)CH_2CH_2 and C(*i*Pr)C$H_2$$CH_2$), 2.01 - 2.15 (2 H, m, C*H*(CH_3)$_2$ and 1 H from CH_2), 1.85 (3 H, s, =C(CH_3)), 1.72 (1 H, d, *J* = 17.3 Hz, 1 H from CH_2), 0.92 - 0.97 (3 H, m, CH_3), 0.89 (6 H, d, *J* = 3.4 Hz, 2 × CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.6 (N*C*(O)C), 159.3 (Ar*C*^{q}), 159.3 (Ar*C*^{q}), 151.4 (N*C*(O)N), 139.1 (*C*(CH_3)=CHAr), 138.4 (Ar*C*^{q}), 134.1 (Ar*C*^{q}), 129.9 (*C*^{q}), 129.1 (Ar*C*H), 128.9 (Ar*C*H), 125.2 (C(CH_3)=*C*HAr), 123.0 (Ar*C*H), 121.5 (Ar*C*H), 119.1 (*C*^{q}), 116.7 (Ar*C*H), 114.3 (Ar*C*H), 111.9 (Ar*C*H), 111.5 (Ar*C*H), 57.8 (*C*^{q}), 55.2 (O*C*H_3), 55.2 (O*C*H_3), 51.4 (N*C*H_2), 48.0 (N*C*H_2), 47.0 (*C*H_2Ar), 35.8 (*C*H_2), 34.7 (*C*H(CH_3)$_2$), 34.2 (*C*^{q}), 32.6 (C(*i*Pr)CH_2*C*H_2), 26.9 (C(*i*Pr)*C*$H_2$$CH_2$), 22.7 (*C*$H_3$), 17.7 (*C*$H_3$), 17.1 (*C*$H_3$), 16.4 (*C*$H_3$). ν_{max} (thin film/cm^{-1}): 2960, 1672, 1598, 1420, 1259, 1156, 1047, 908, 746, 695. MS (ESI$^+$) *m/z* (%): 529.3 (M+H$^+$, 100); HRMS (ESI$^+$) calcd. for $C_{33}H_{41}N_2O_4$ (M + H$^+$): 529.3061. Found: 529.3057.



(2a*R*,7*S*)-2a-Isopropyl-7-methyl-4-((*E*)-2-methyl-3-(naphthalen-1-yl)allyl)-7-(naphthalen-1-ylmethyl)-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3k). According to the general procedure D, **1k** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 3 h, addition of HCl (2 M in Et_2O, 2 mL), stirring for 2 h and purification by chromatography (1/4 EtOAc/hexanes), gave **3k** (39 mg, 0.068 mmol, 68%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.12 (1 H, d, *J* = 8.3 Hz, Ar*H*), 7.86 - 7.94 (2 H, m, Ar*H*), 7.82 (2 H, t, *J* = 8.4 Hz, Ar*H*), 7.74 (1 H, d, *J* = 8.0 Hz, Ar*H*), 7.33 - 7.58 (8 H, m, Ar*H*), 6.67 (1 H, s, C(CH_3)=C*H*Ar), 4.64 - 4.70 (1 H, m, 1 H from CH=C(CH_3)CH_2N), 4.51 - 4.58 (1 H, m, 1 H from CH=C(CH_3)CH_2N), 4.18 - 4.26 (1 H, m, 1 H from NCH_2), 3.23 (2 H, d, *J* = 3.5 Hz, ArCH_2), 3.14 - 3.20 (1 H, m, 1 H from NCH_2), 2.27 - 2.43 (2 H, m, 1 H from CH_2 and 1 H from C(*i*Pr)CH_2CH_2), 2.12 - 2.27 (3 H, m, 1 H from C(*i*Pr)CH_2CH_2 and C(*i*Pr)C$H_2$$CH_2$), 2.04 - 2.11 (1 H, m, C*H*(CH_3)$_2$), 1.80 (1 H, d, *J* = 17.1 Hz, 1 H from CH_2CH_2CCH_2), 1.68 (3 H, s, =(CH_3)), 0.97 (3 H, d, *J* = 6.8 Hz, CH_3), 0.93 (3 H, s, CH_3), 0.88 (3 H, d, *J* = 6.8 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.8 (N*C*(O)C), 151.5 (N*C*(O)N), 135.4 (*C*(CH_3)=CHAr), 135.2 (Ar*C*^{q}), 134.0 (Ar*C*^{q}), 133.4 (Ar*C*^{q}), 133.4 (Ar*C*^{q}), 133.2 (Ar*C*^{q}), 132.1 (Ar*C*^{q}), 129.9 (*C*^{q}), 129.1 (Ar*C*H), 128.9 (Ar*C*H), 128.1 (Ar*C*H), 127.6 (Ar*C*H), 126.9 (Ar*C*H), 126.5 (Ar*C*H), 125.9 (Ar*C*H), 125.7 (Ar*C*H), 125.7 (Ar*C*H), 125.5 (Ar*C*H), 125.5 (Ar*C*H), 125.2 (Ar*C*H), 125.1 (Ar*C*H), 124.5 (Ar*C*H), 123.6 (C(CH_3)=*C*HAr), 119.4 (*C*^{q}), 57.9 (*C*^{q}), 51.6 (N*C*H_2), 47.7 (N*C*H_2), 42.0 (*C*H_2Ar), 36.1 (*C*H_2), 35.3 (*C*^{q}), 34.7 (*C*H(CH_3)$_2$), 32.7 (C(*i*Pr)CH_2*C*H_2), 27.1 (C(*i*Pr)*C*$H_2$$CH_2$), 23.5 (*C*$H_3$), 17.8 (*C*$H_3$), 17.3 (*C*$H_3$), 16.2 (*C*$H_3$). ν_{max} (thin film/cm^{-1}): 2962, 1672, 1420, 1327, 1175, 908, 781, 731. MS (ESI$^+$) *m/z* (%): 569.3 (M+H$^+$, 100); HRMS (ESI$^+$) calcd. for $C_{39}H_{41}N_2O_2$ (M + H$^+$): 569.3163. Found:

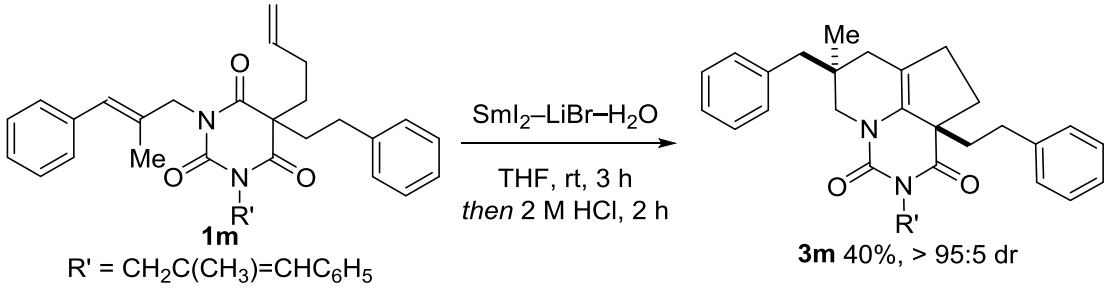
569.3163.



1l
R' = $CH_2C(CH_3)=CH(2\text{-}MeC_6H_4)$

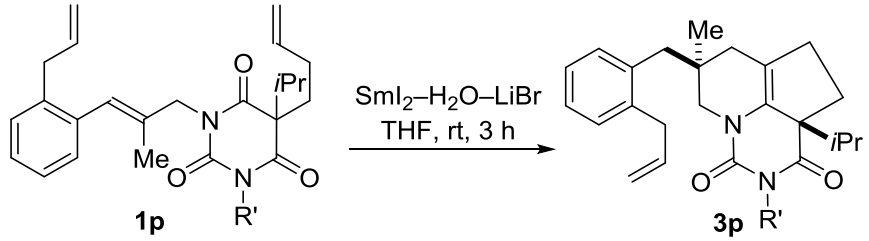
3l 47%, > 95:5 dr

(2a*R*,7*S*)-2a-Isopropyl-7-methyl-4-((*E*)-2-methyl-3-(o-tolyl)allyl)-7-(2-methylbenzyl)-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3l). According to the general procedure D, **1l** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 3 h, addition of HCl (2 M in Et_2O, 2 mL), stirring for 2 h and purification by chromatography (1/4 EtOAc/hexanes), gave **3l** (23 mg, 0.047 mmol, 47%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.05 - 7.21 (8 H, m, Ar*H*), 6.28 (1 H, s, C(CH_3)=C*H*Ar), 4.58 (1 H, dd, *J* = 14.9, 0.9 Hz, 1 H from CH=C(CH_3)CH_2N), 4.41 (1 H, dd, *J* = 15.1, 0.8 Hz, 1 H from CH=C(CH_3)CH_2N), 4.09 (1 H, dd, *J* = 12.5, 1.3 Hz, 1 H from NCH_2), 3.10 (1 H, d, *J* = 12.5 Hz, 1 H from NCH_2), 2.75 (2 H, d, *J* = 6.3 Hz, ArCH_2), 2.38 - 2.45 (1 H, m, 1 H from C(*i*Pr)CH_2CH_2), 2.36 (3 H, s, Ar*C*H_3), 2.20 - 2.23 (2 H, m, 1 H from C(*i*Pr)CH_2CH_2 and 1 H from $CH_2CH_2CCH_2$), 2.17 - 2.20 (4 H, m, 1 H from C(*i*Pr)CH_2CH_2 and Ar*C*H_3), 2.12 - 2.17 (1 H, m, 1 H from C(*i*Pr)CH_2CH_2), 2.00 - 2.09 (1 H, m, C*H*(CH_3)$_2$), 1.79 (1 H, d, *J* = 17.1 Hz, 1 H from CH_2), 1.67 (3 H, s, =C(CH_3)), 0.95 (3 H, d, *J* = 6.8 Hz, CH_3), 0.86 - 0.90 (6 H, m, 2 × CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.6 (N*C*(O)C), 151.4 (N*C*(O)N), 137.1 (*C*(CH_3)=CHAr), 137.0 (Ar*C*^{q}), 136.5 (Ar*C*^{q}), 135.5 (Ar*C*^{q}), 133.6 (Ar*C*^{q}), 131.5 (Ar*C*H), 130.8 (Ar*C*H), 129.9 (*C*^{q}), 129.6 (Ar*C*H), 129.3 (Ar*C*H), 126.7 (Ar*C*H), 126.5 (Ar*C*H), 125.6 (Ar*C*H), 125.2 (Ar*C*H), 124.9 (C(CH_3)=*C*HAr), 119.1 (*C*^{q}), 57.8 (*C*^{q}), 51.3 (NCH_2), 47.8 (NCH_2), 42.8 (*C*H_2Ar), 35.8 (*C*H_2), 35.4 (*C*^{q}), 34.7 (*C*H(CH_3)$_2$), 32.6 (C(*i*Pr)CH_2*C*H_2), 27.1 (C(*i*Pr)*C*H_2CH_2), 22.8 (*C*H_3), 20.6 (*C*H_3), 19.8 (*C*H_3), 17.7 (*C*H_3), 17.2 (*C*H_3), 15.9 (*C*H_3). ν_{max} (thin film/cm^{-1}): 2962, 1673, 1402, 1293, 1175, 908, 732. MS (ESI$^+$) *m/z* (%): 569.3 (M+H$^+$, 100); HRMS (ESI$^+$) calcd. for $C_{33}H_{41}N_2O_2$ (M + H$^+$): 497.3163. Found: 497.3156.



(2a*R*,7*S*)-7-Benzyl-7-methyl-4-((*E*)-2-methyl-3-phenylallyl)-2a-phenethyl-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3m). According to the general procedure D, **1m** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 3 h, addition of HCl (2 M in Et_2O, 2 mL), stirring for 2 h and purified by chromatography (1/4 EtOAc/hexanes), gave **3m** (21 mg, 0.040 mmol, 40%, > 95:5 dr) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.27 - 7.34 (4 H, m, Ar*H*), 7.18 - 7.25 (6 H, m, Ar*H*), 7.12 - 7.17 (3 H, m, Ar*H*), 7.04 - 7.09 (2 H, m, Ar*H*), 6.26 (1 H, s, C(CH_3)=C*H*Ar), 4.55 (1 H, d, *J* = 15.8 Hz, 1 H from CH=C(CH_3)CH_2N), 4.43 (1 H, d, *J* = 15.8 Hz, 1 H from CH=C(CH_3)CH_2N), 3.95 (1 H, d, *J* = 12.5 Hz, 1 H from NCH_2), 2.92 (1 H, d, *J* = 12.5 Hz, 1 H from NCH_2), 2.58 - 2.71 (4 H, m, 2 × ArCH_2), 2.46 - 2.57 (1 H, m, 1 H from $CH_2CH_2CCH_2$), 2.20 - 2.38 (3 H, m, 1 H from $CH_2CH_2CCH_2$ and $CH_2CH_2CCH_2$), 2.08 - 2.17 (1 H, m, 1 H from CH_2), 1.99 - 2.08 (1 H, m, 1 H from ArCH$_2$CH_2), 1.92 - 1.99 (1 H, m, 1 H from ArCH$_2$CH_2), 1.88 (3 H, s, =C(CH_3)), 1.71 (1 H, d, *J* = 16.6 Hz, 1 H from $CH_2CH_2CCH_2$), 0.90 (3 H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.6 (N*C*(O)C), 151.1 (N*C*(O)N), 140.9 (*C*(CH_3)=CHAr), 137.5 (Ar*C*^{q}), 136.8 (Ar*C*^{q}), 133.7 (Ar*C*^{q}), 130.6 (2 × Ar*C*H), 129.0 (2 × Ar*C*H), 128.5 (2 × Ar*C*H), 128.2 (2 × Ar*C*H), 128.2 (*C*^{q}), 128.0 (3 × Ar*C*H), 126.6 (Ar*C*H), 126.3 (2 × Ar*C*H), 126.1 (Ar*C*H), 124.9 (C(CH_3)=*C*HAr), 118.4 (*C*^{q}), 53.5 (*C*^{q}), 51.2 (N*C*H$_2$), 47.8 (N*C*H$_2$), 46.7 (*C*H$_2$Ar), 38.7 (*C*H$_2$CH$_2$Ar), 35.4 (*C*H$_2$), 34.0 (*C*^{q}), 31.5 (CH$_2$*C*H$_2$CCH$_2$), 30.9 (*C*H$_2$CH$_2$CCH$_2$ and ArCH$_2$), 22.9 (*C*H$_3$), 16.4 (*C*H$_3$). ν_{max}(thin film/cm^{-1}): 2926, 1674, 1420, 1327, 1149, 908, 732, 699. MS (ESI$^+$) *m/z* (%): 531.3 (M+H$^+$, 100); HRMS (ESI$^+$) calcd. for $C_{36}H_{39}N_2O_2$ (M + H$^+$):

531.3006. Found: 531.3006.



(2a*R*,7*S*)-7-(2-Allylbenzyl)-4-((*E*)-3-(2-allylphenyl)-2-methylallyl)-2a-isopropyl-7-methyl-1,2,2a,6,7,8-hexahydro-3*H*-4,5a-diazaacenaphthylene-3,5(4*H*)-dione (3p). According to the general procedure C, **1p** (0.10 mmol), SmI_2 (0.30 mmol, 3 equiv, 3.0 mL, 0.10 M), anhydrous LiBr (521 mg, 6.0 mmol, 60 equiv) and H_2O (0.18 mL, 100 equiv), stirring for 3 h and purification by chromatography (1/4 EtOAc/hexanes), gave **3p** (21 mg, 0.039 mmol, 39%, 83:17 dr) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.07 - 7.23 (8 H, m, Ar*H*), 6.30 (1 H, s, ArC*H*=), 5.81 - 5.99 (2 H, m, 2 × CH_2CH=CH_2), 5.08 (1 H, dd, *J* = 10.1, 1.3 Hz, 1 H from CH_2CH=CH_2), 4.90 - 5.02 (3 H, m, 1 H from CH_2CH=CH_2 and CH_2CH=CH_2), 4.56 (1 H, d, *J* = 15.4 Hz, 1 H from NCH_2), 4.40 (1 H, d, *J* = 15.1 Hz, 1 H from NCH_2), 4.09 (1 H, d, *J* = 12.3 Hz, 1 H from NCH_2), 3.44 - 3.48 (1 H, m, 1 H from CH_2CH=CH_2), 3.22 - 3.33 (3 H, m, 1 H from CH_2CH=CH_2 and CH_2CH=CH_2), 3.10 (1 H, d, *J* = 12.6 Hz, 1 H from NCH_2), 2.76 (2 H, q, *J* = 13.9 Hz, CH_2Ar), 2.34 - 2.43 (1 H, m, 1 H from CH_2), 2.10 - 2.26 (4 H, m, 1 H from CH_2, 1 H from CH_2CH_2C=, 1 H from CH_2CH_2C= and CH(CH_3)$_2$), 1.98 - 2.08 (1 H, m, 1 H from CH_2CH_2C=), 1.78 (1 H, m, 1 H from CH_2CH_2C=), 1.63 - 1.68 (3 H, m, CH_3), 0.92 - 0.97 (3 H, d, *J* = 10.0 Hz, CH(CH_3)$_2$), 0.88 - 0.92 (3 H, d, *J* = 5.0 Hz, CH(CH_3)$_2$), 0.86 (3 H, s, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 173.6 (N*C*(O)C), 151.4 (N*C*(O)N), 138.8 (*C*H=CH_2), 138.3 (*C*H=CH_2), 137.1 (C^q), 137.0 (C^q), 136.8 (C^q), 135.1 (C^q), 134.1 (C^q), 131.7 (Ar*C*H), 130.1 (Ar*C*H), 130.0 (C^q), 129.6 (Ar*C*H), 128.9 (Ar*C*H), 126.9 (Ar*C*H), 126.8 (Ar*C*H), 126.0 (Ar*C*H), 125.7 (Ar*C*H), 124.3 (Ar*C*H=), 119.0 (C^q), 116.0 (CH=*C*H_2), 115.4 (CH=*C*H_2), 57.8 (C^q), 51.4 (N*C*H_2), 47.6 (N*C*H_2), 42.2 (*C*H_2), 37.6 (*C*H_2), 37.6 (*C*H_2), 36.0 (*C*H_2), 35.1 (C^q), 34.7 (*C*H(*C*H_3)$_2$), 32.6 (*C*H_2), 27.2 (*C*H_2), 22.8 (*C*H_3), 17.7 (*C*H_3), 17.3 (*C*H_3), 16.0 (*C*H_3). ν_{max} (thin film/cm^{-1}): 2962, 1683, 1432, 1293, 1125, 918, 752. MS (ESI$^+$)

m/z (%): 549.4 ($M+H^+$, 100); HRMS (ESI^+) calcd. for $C_{37}H_{45}N_2O_2$ ($M + H^+$): 549.3476. Found: 549.3469.

X-ray structure of 3i

CCDC 1529301

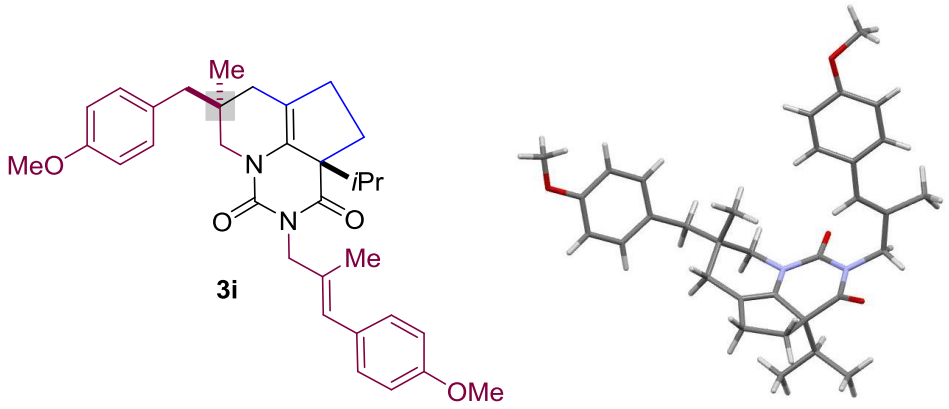


Table S1. Crystal data and details of data collection and refinement for compound **3i**

Bond precision:	C-C = 0.0041 A	Wavelength = 0.71073	
Cell:	a = 11.4817(6)	b = 11.8623(7)	c = 11.8623(7)
	alpha = 76.664(5)	beta = 63.649(6)	gamma = 70.861(5)
Temperature:	150 K		
	Calculated	Reported	
Volume	1422.43(16)	1422.42(16)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	$C_{33}H_{40}N_2O_4$	$C_{33}H_{40}N_2O_4$	
Sum formula	$C_{33}H_{40}N_2O_4$	$C_{33}H_{40}N_2O_4$	
Mr	528.67	528.67	
Dx,g cm-3	1.234	1.234	
Z	2	2	
Mu (mm-1)	0.081	0.081	
F000	568.0	568.0	

F000’	568.24	
h,k,lmax	15,16,17	15,14,16
Nref	8068	6621
Tmin,Tmax	0.992,0.998	0.855,1.000
Tmin’	0.992	
Correction method= MULTI-SCAN		
Data completeness= 0.821		Theta(max)= 29.687
R(reflections)= 0.0741(3806)		wR2(reflections)= 0.2091(6621)
S = 1.069		Npar= 368

X-ray structure of 3j

CCDC 1529302

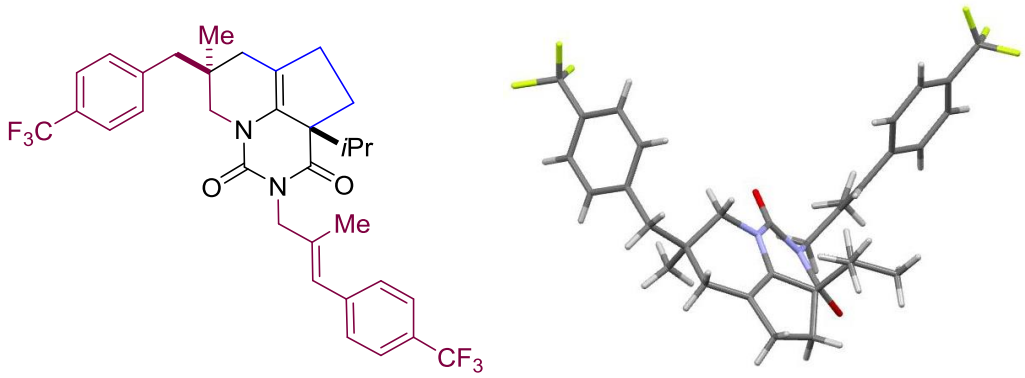


Table S2. Crystal data and details of data collection and refinement for compound **3j**

Bond precision:	C-C = 0.0059 A	Wavelength = 0.71073	
Cell:	a = 11.6196(7)	b = 13.8475(8)	c = 21.0449(12)
	alpha = 89.100(5)	beta = 83.969(5)	gamma = 83.670(5)
Temperature:	150 K		
	Calculated	Reported	
Volume	3346.9(3)	3346.9(3)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	$C_{33}H_{34}F_6N_2O_2$, 0.274(C_6H_{14}), 0.226(C_5H_{11}), 0.226(CH_3)	2($C_{33}H_{34}F_6N_2O_2$), $C_{2.81}H_{6.52}$,$C_{3.19}H_{7.48}$	
Sum formula	$C_{36}H_{41}F_6N_2O_2$	$C_{72}H_{82}F_{12}N_4O_4$	
Mr	647.71	1295.41	
Dx,g cm-3	1.285	1.285	

Z	4	2
Mu (mm-1)	0.102	0.102
F000	1364.0	1364.0
F000’	1364.83	
h,k,lmax	15,19,28	15,18,26
Nref	18213	14966
Tmin,Tmax	0.982,0.990	0.882,1.000
Tmin’	0.970	
Correction method= MULTI-SCAN		
Data completeness= 0.822		Theta(max)= 29.254
R(reflections)= 0.0950(7852)		wR2(reflections)= 0.2787(14966)
S = 1.034		Npar= 866

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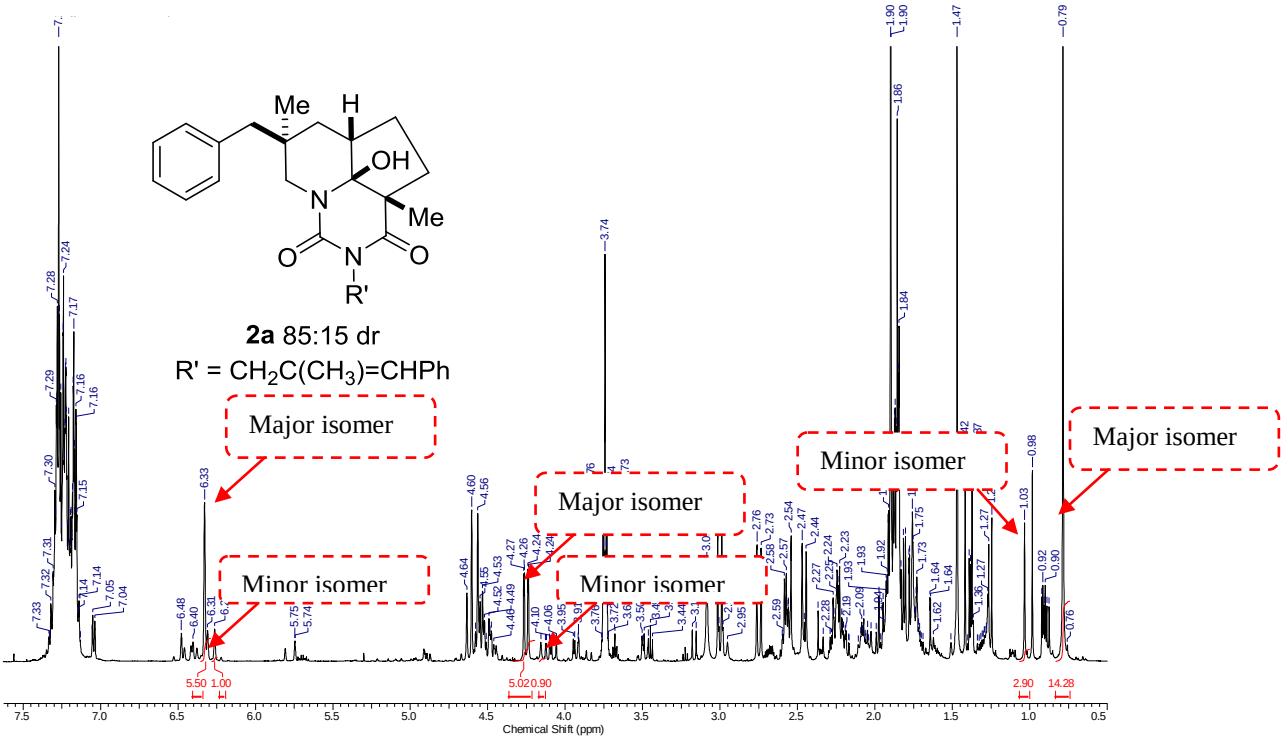
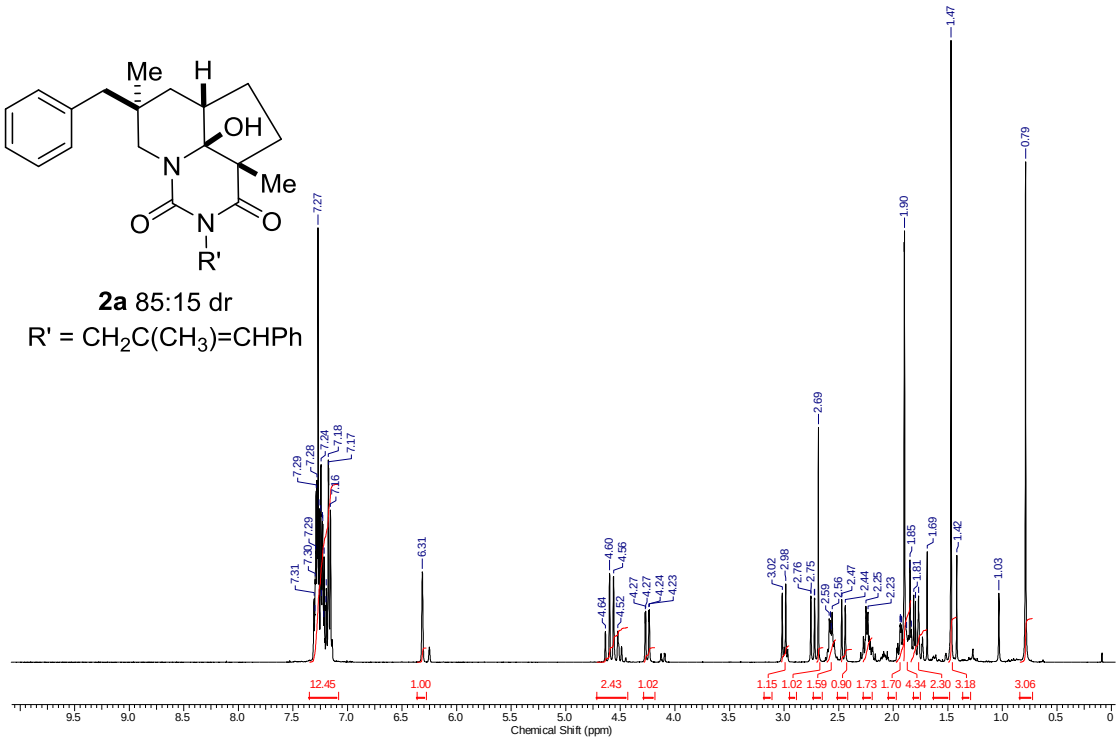
Crude ^{1}H NMR Spectra of Compounds 2a and 3a

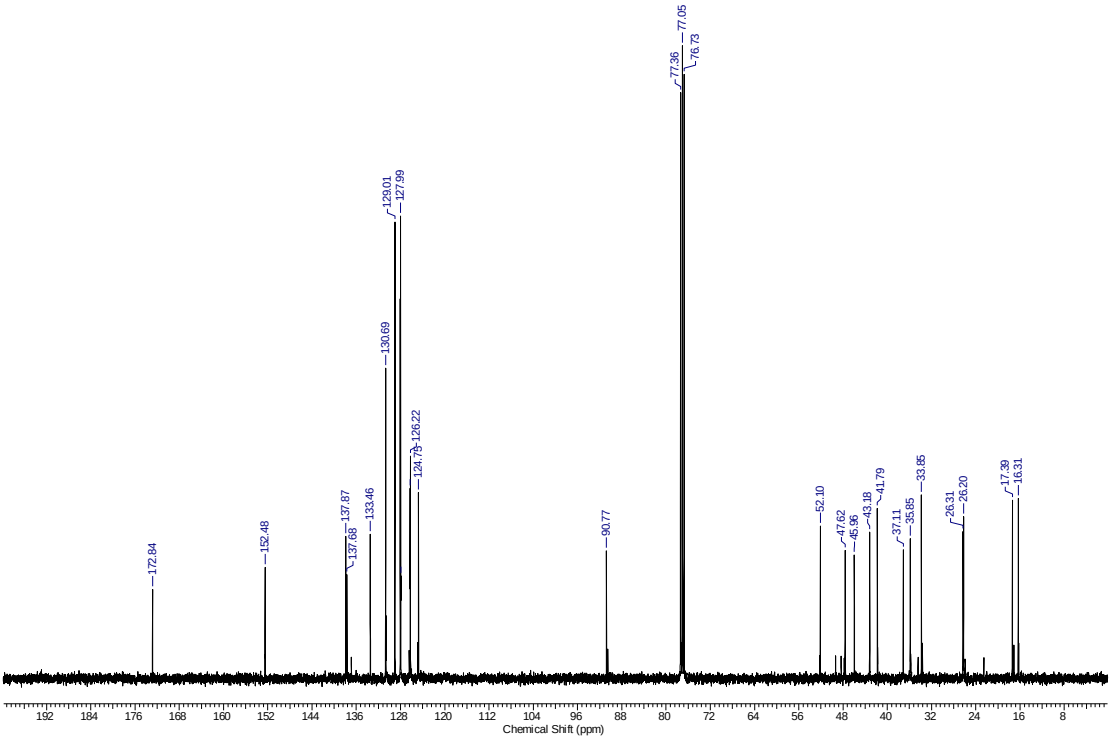
Crude ^{1}H NMR (500 MHz, $CDCl_3$)



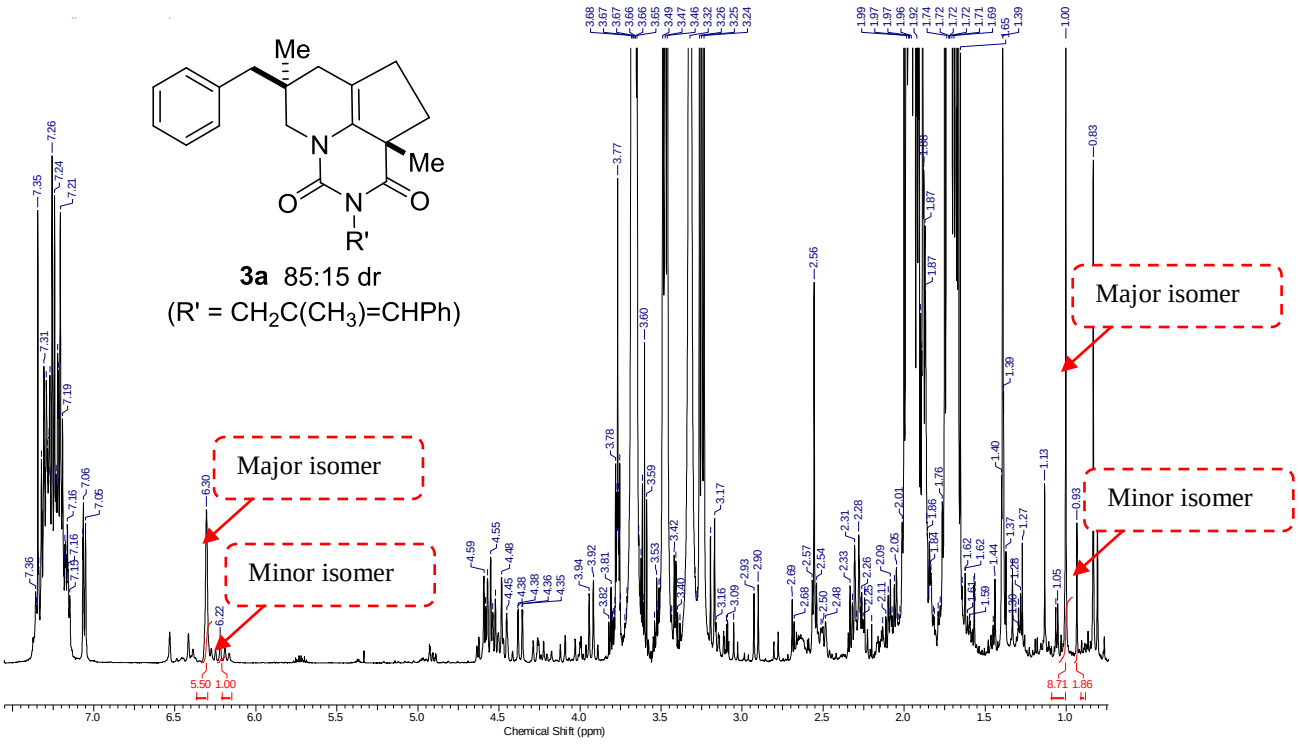
Purified ^{1}H NMR (400 MHz, $CDCl_3$)



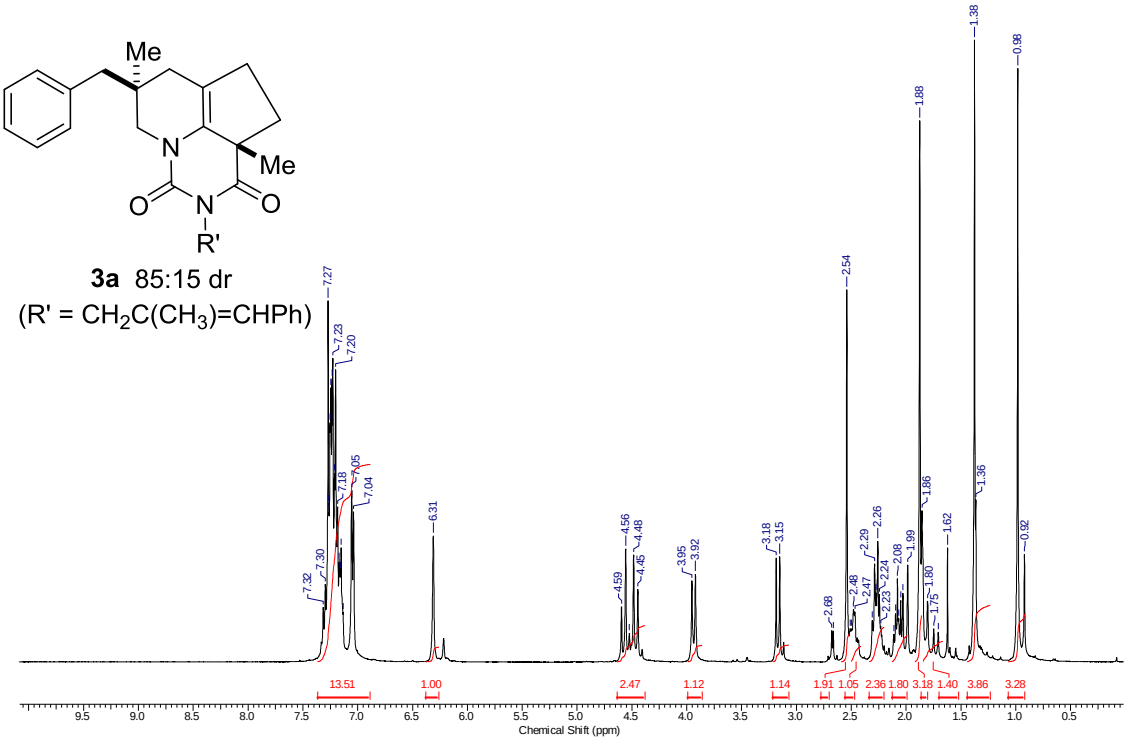
Purified ^{13}C NMR (100 MHz, $CDCl_3$)



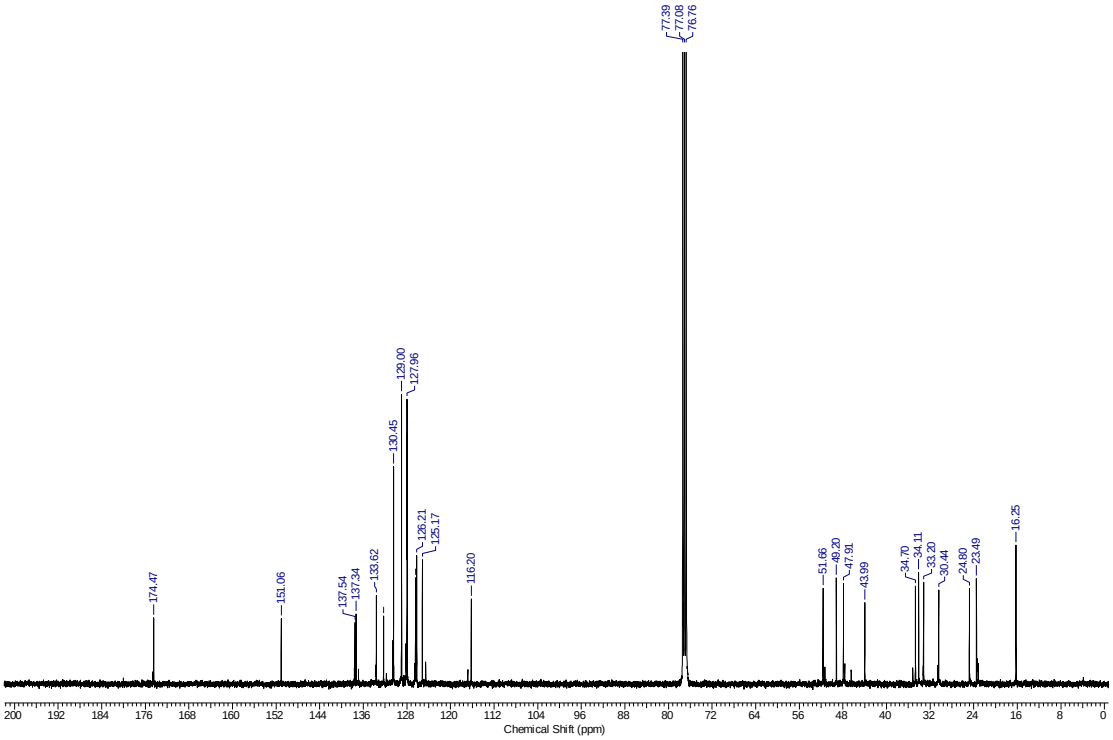
Crude ^{1}H NMR (500 MHz, $CDCl_3$)



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

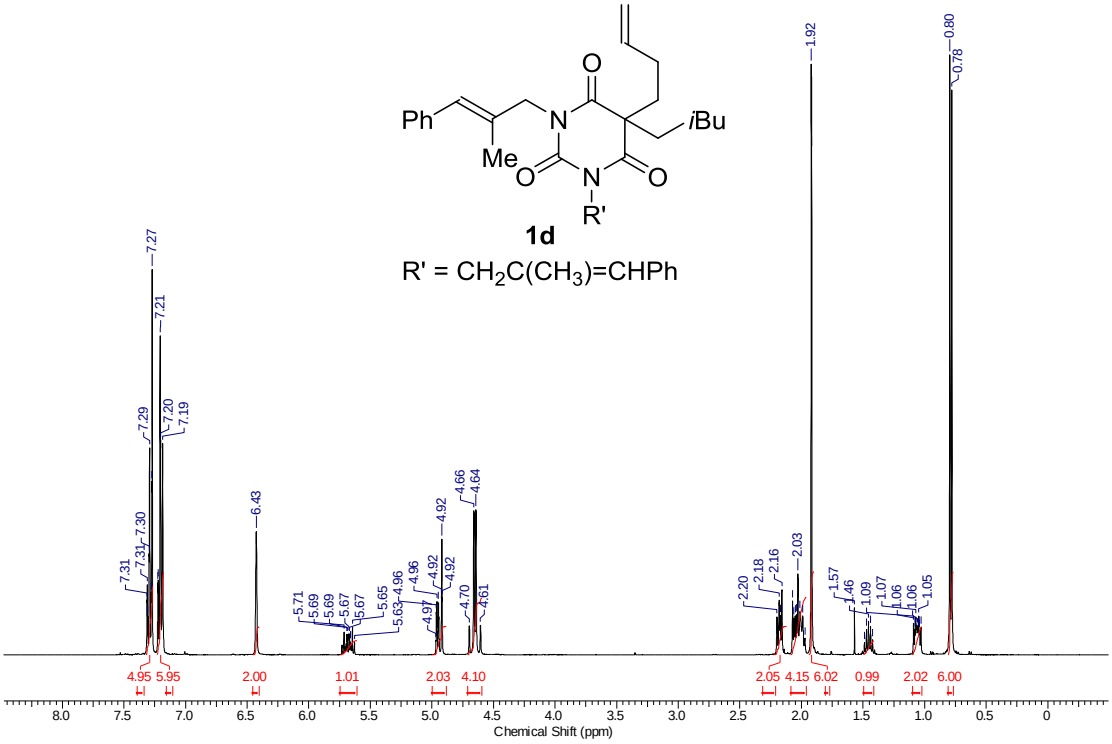


Purified ^{13}C NMR (100 MHz, $CDCl_3$)

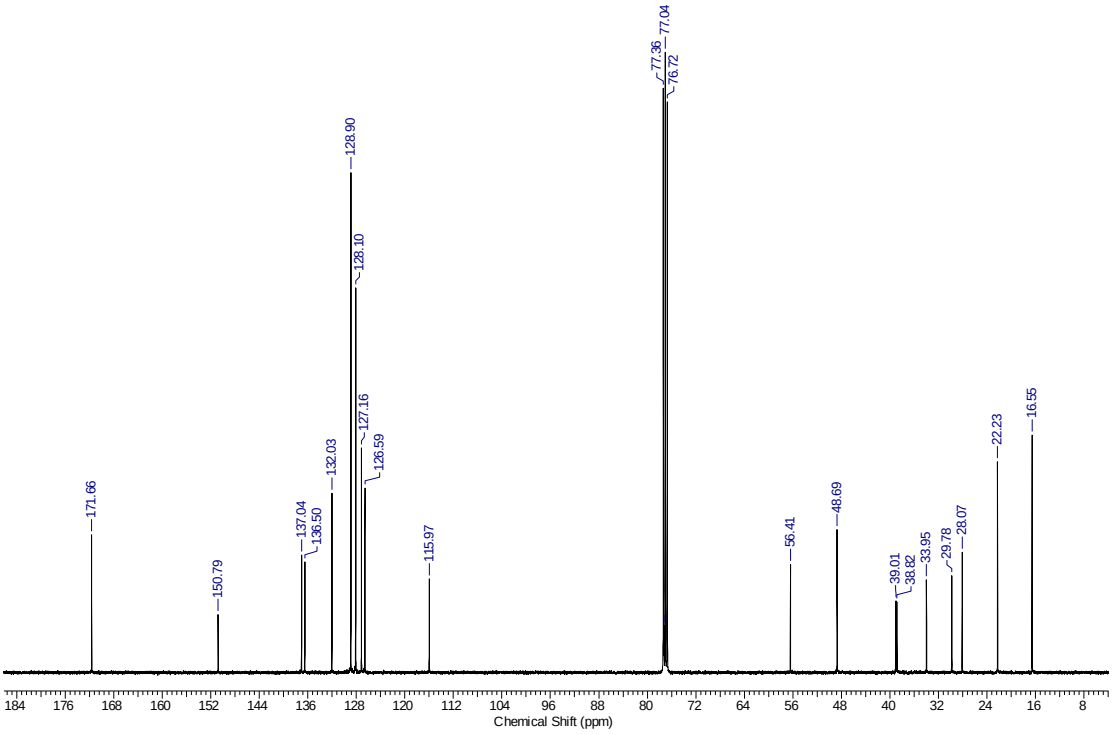


^{1}H and ^{13}C NMR Spectra of Compounds

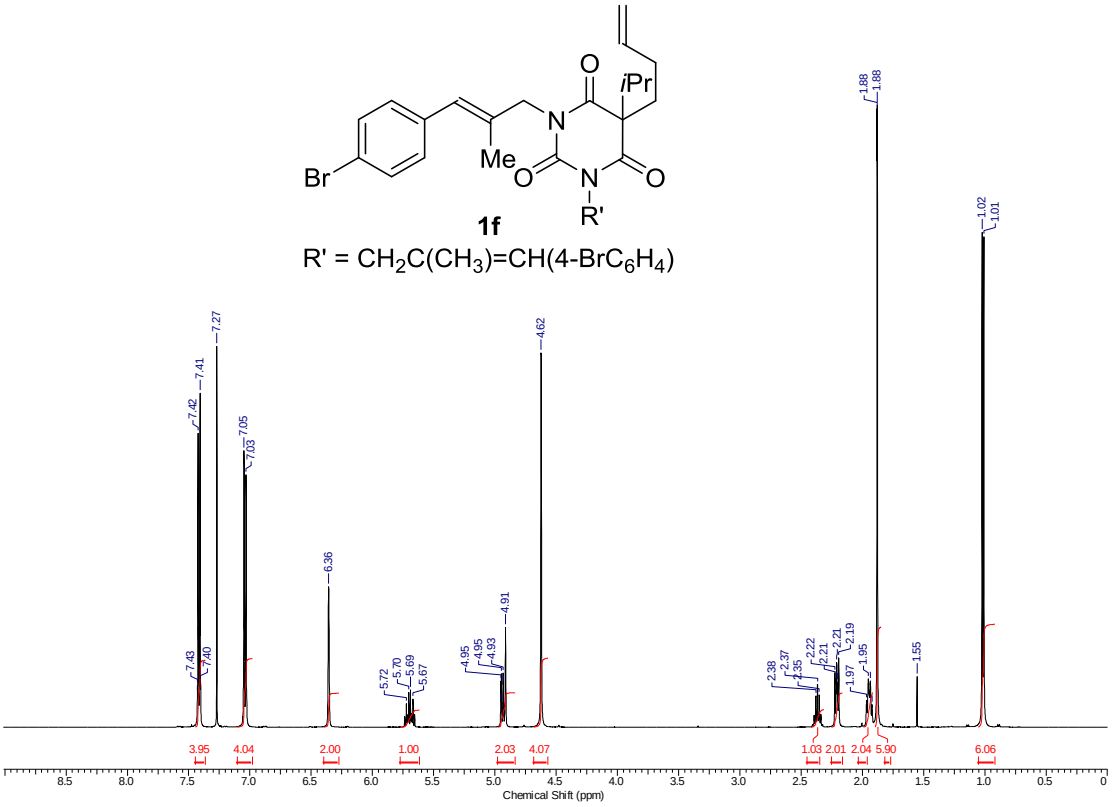
^{1}H NMR (400 MHz, $CDCl_3$)



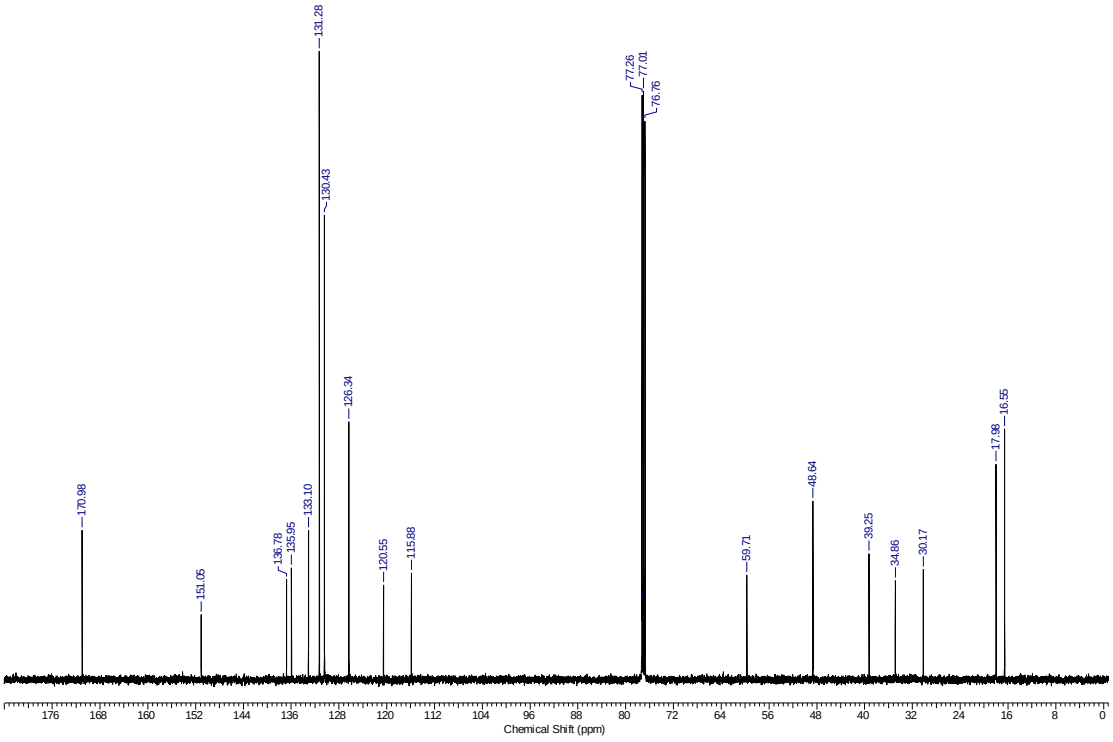
^{13}C NMR (101 MHz, $CDCl_3$)



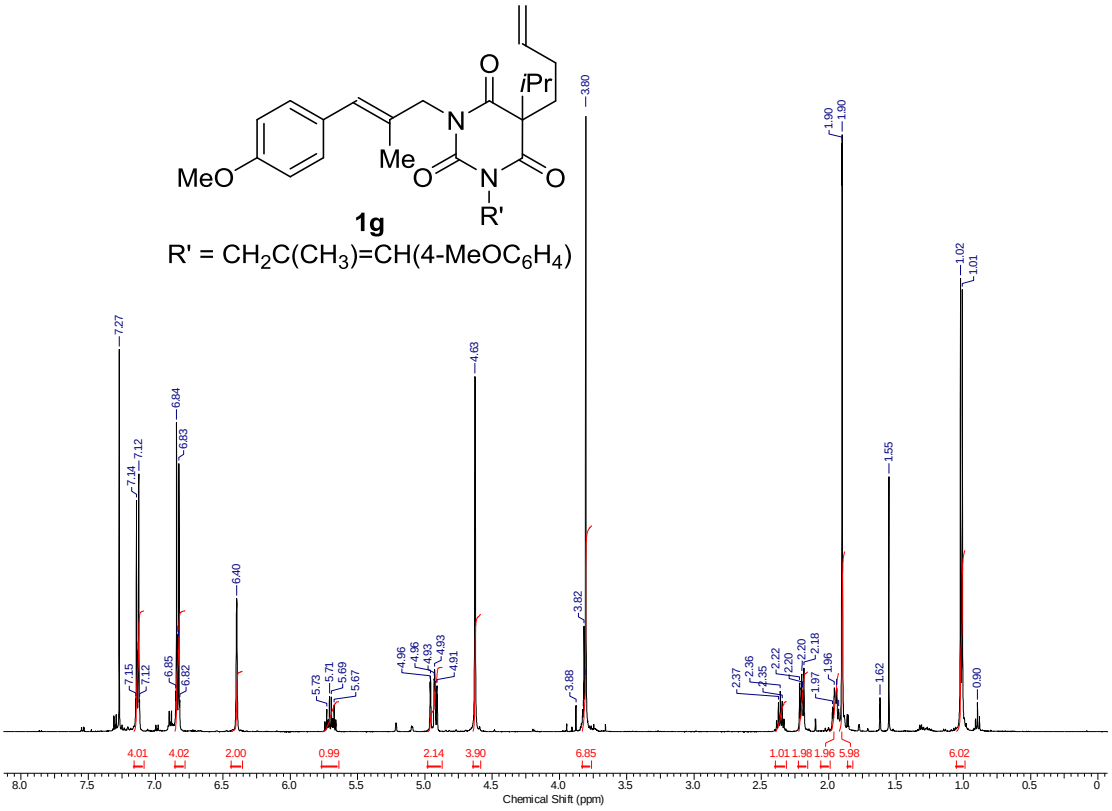
^{1}H NMR (500 MHz, $CDCl_3$)



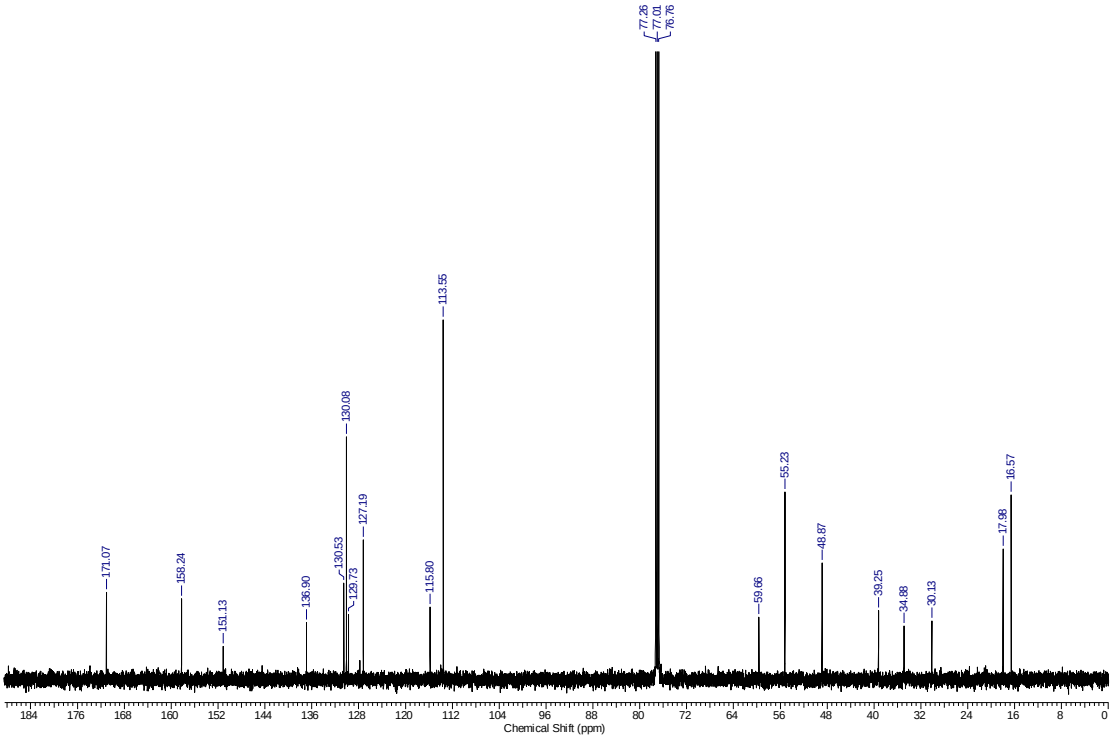
^{13}C NMR (125 MHz, $CDCl_3$)



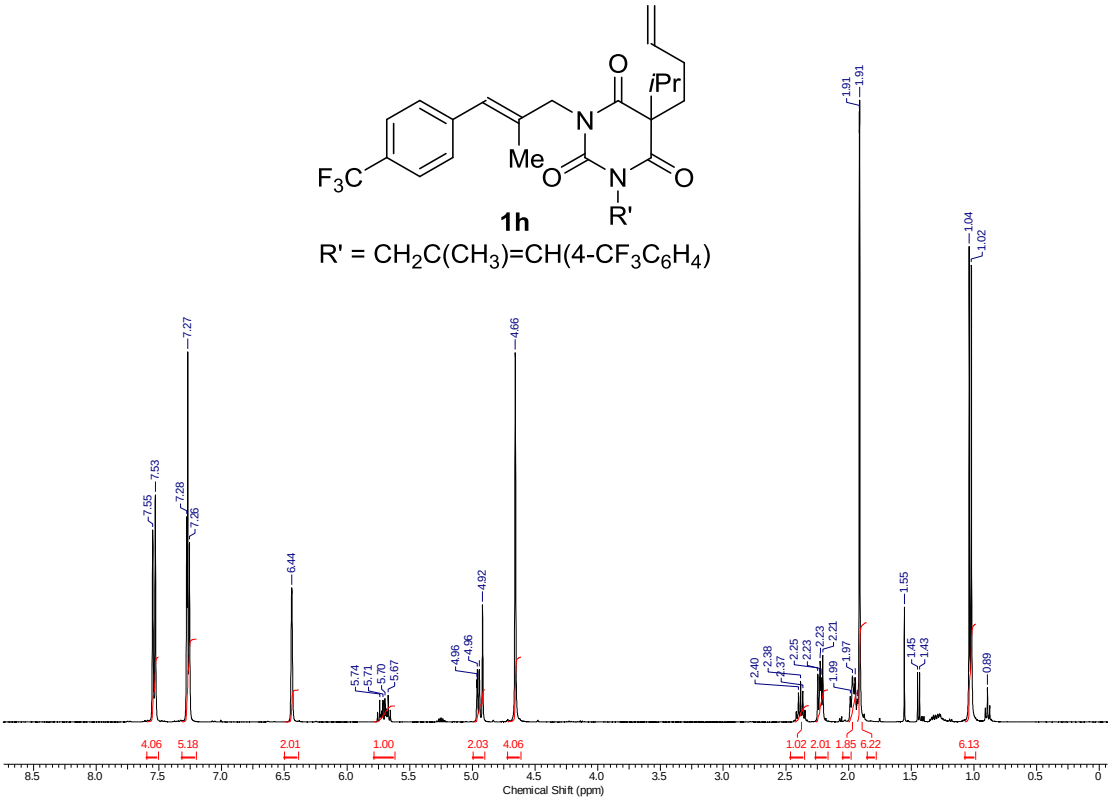
^{1}H NMR (500 MHz, $CDCl_3$)



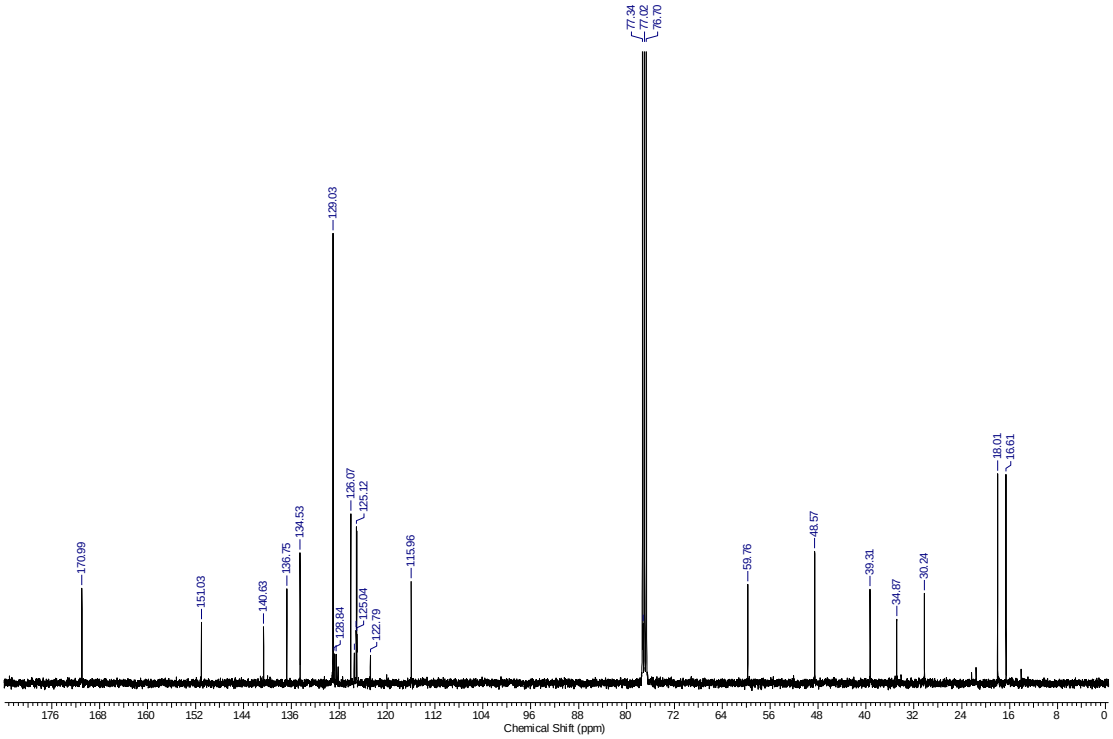
^{13}C NMR (125 MHz, $CDCl_3$)



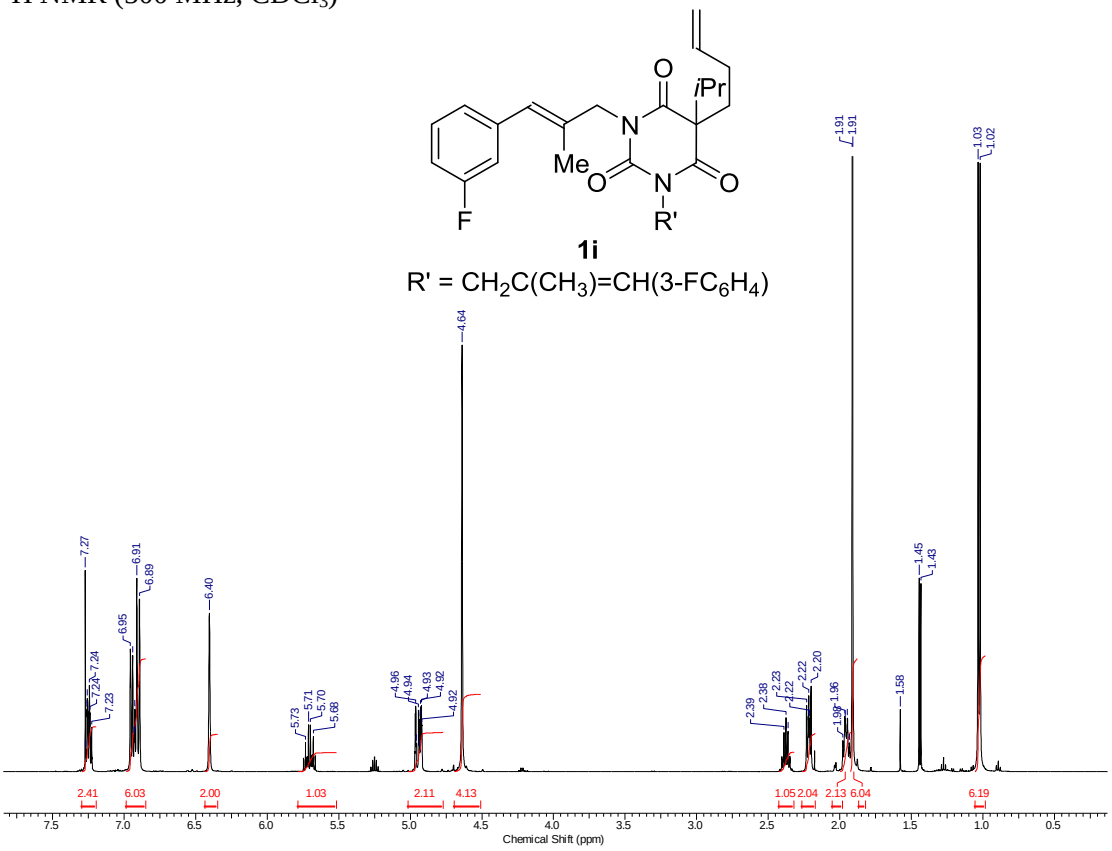
^{1}H NMR (400 MHz, $CDCl_3$)



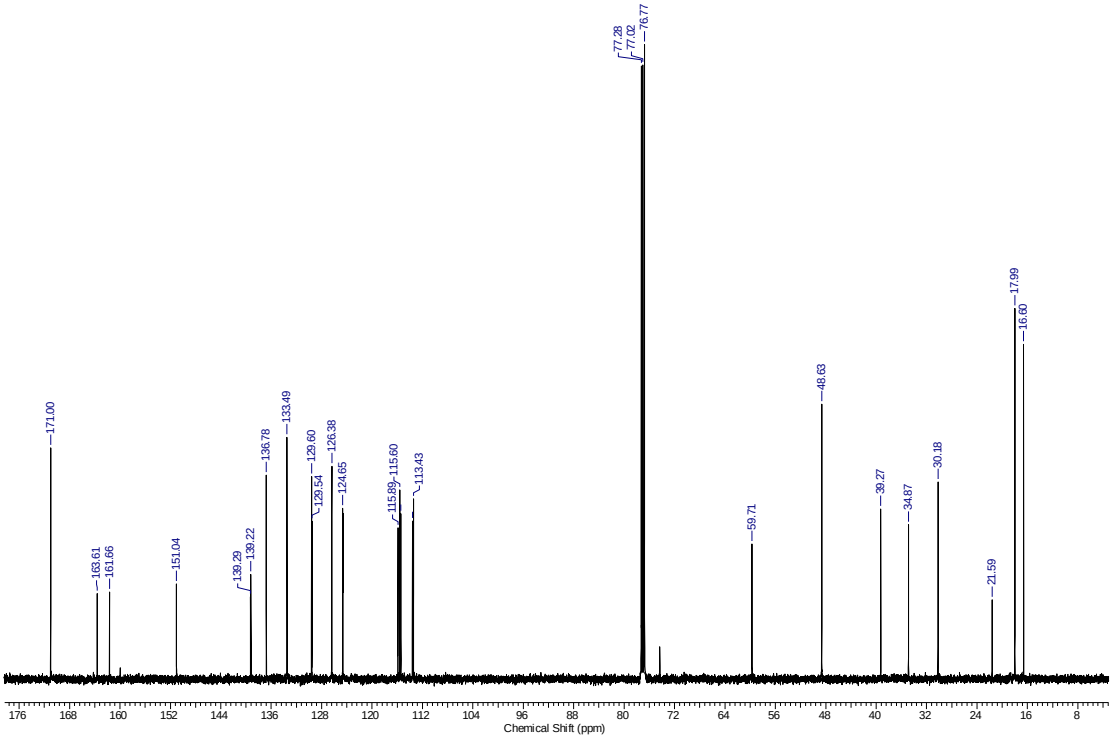
^{13}C NMR (101 MHz, $CDCl_3$)



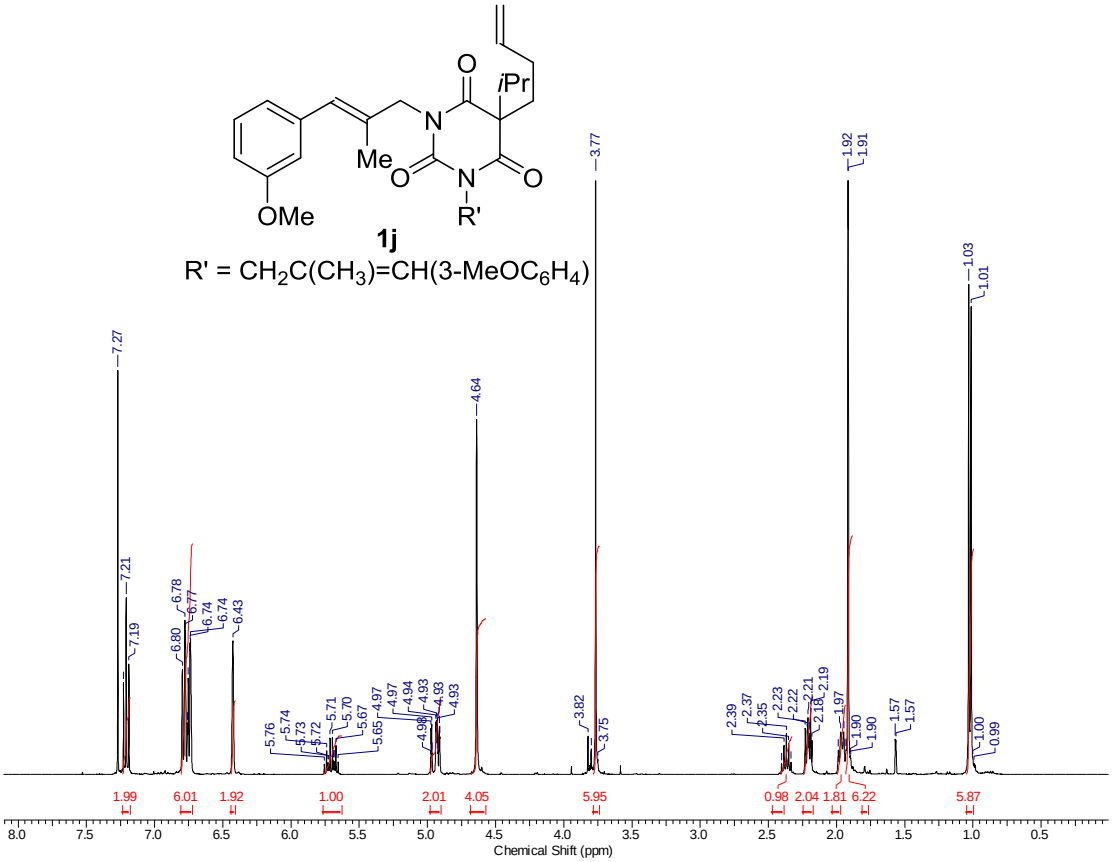
^{1}H NMR (500 MHz, $CDCl_3$)



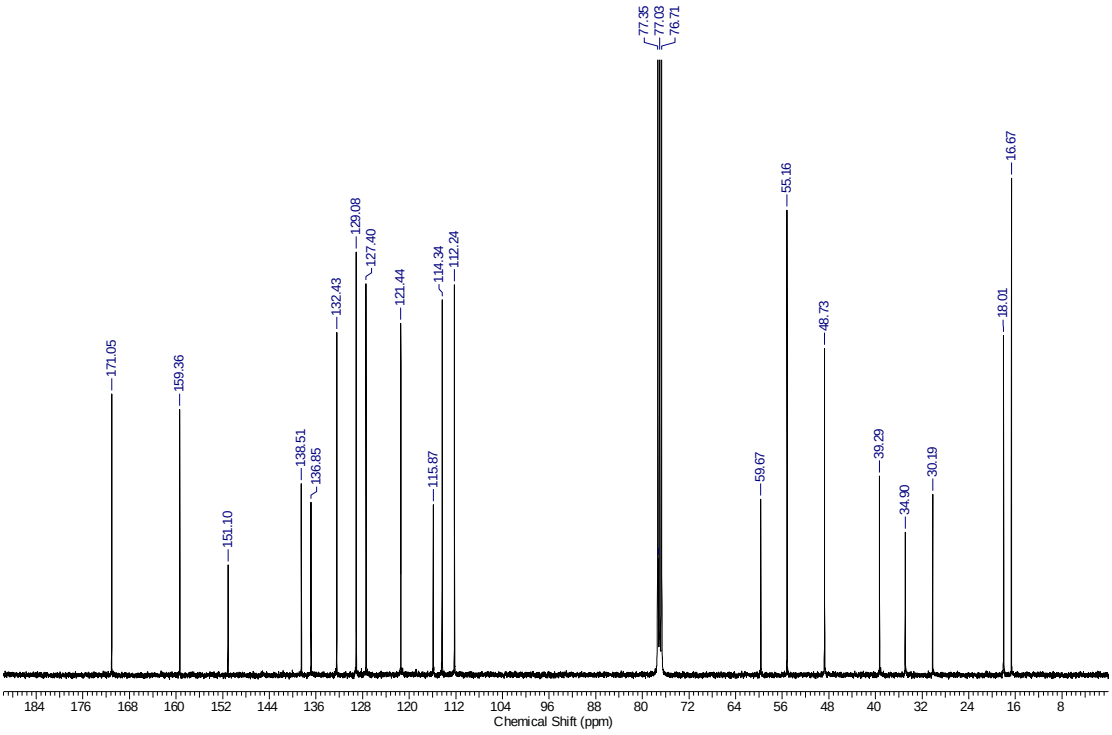
^{13}C NMR (126 MHz, $CDCl_3$)



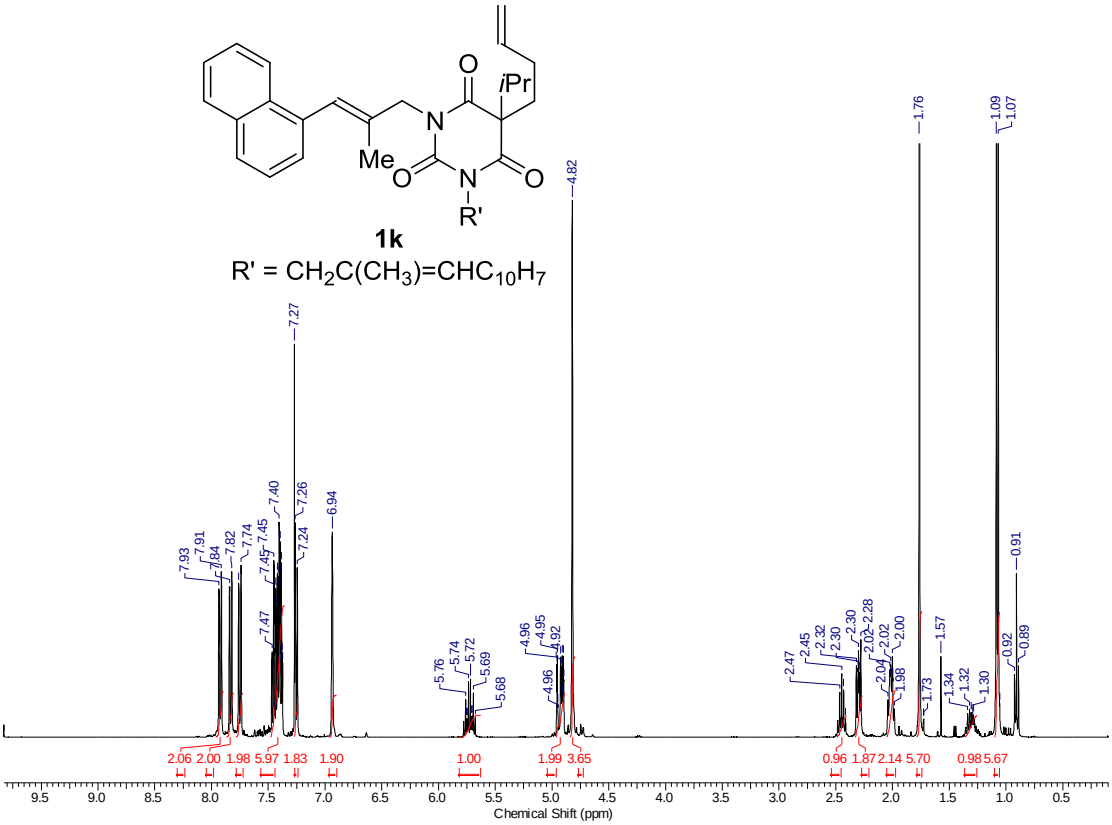
^{1}H NMR (400 MHz, $CDCl_3$)



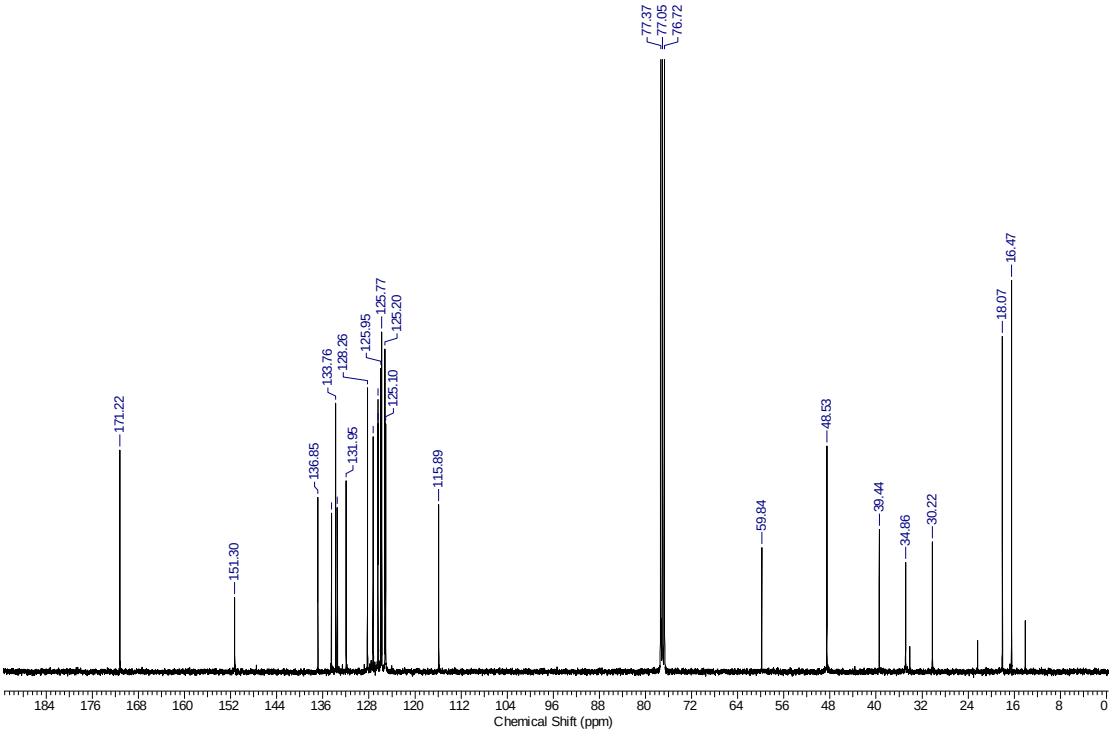
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



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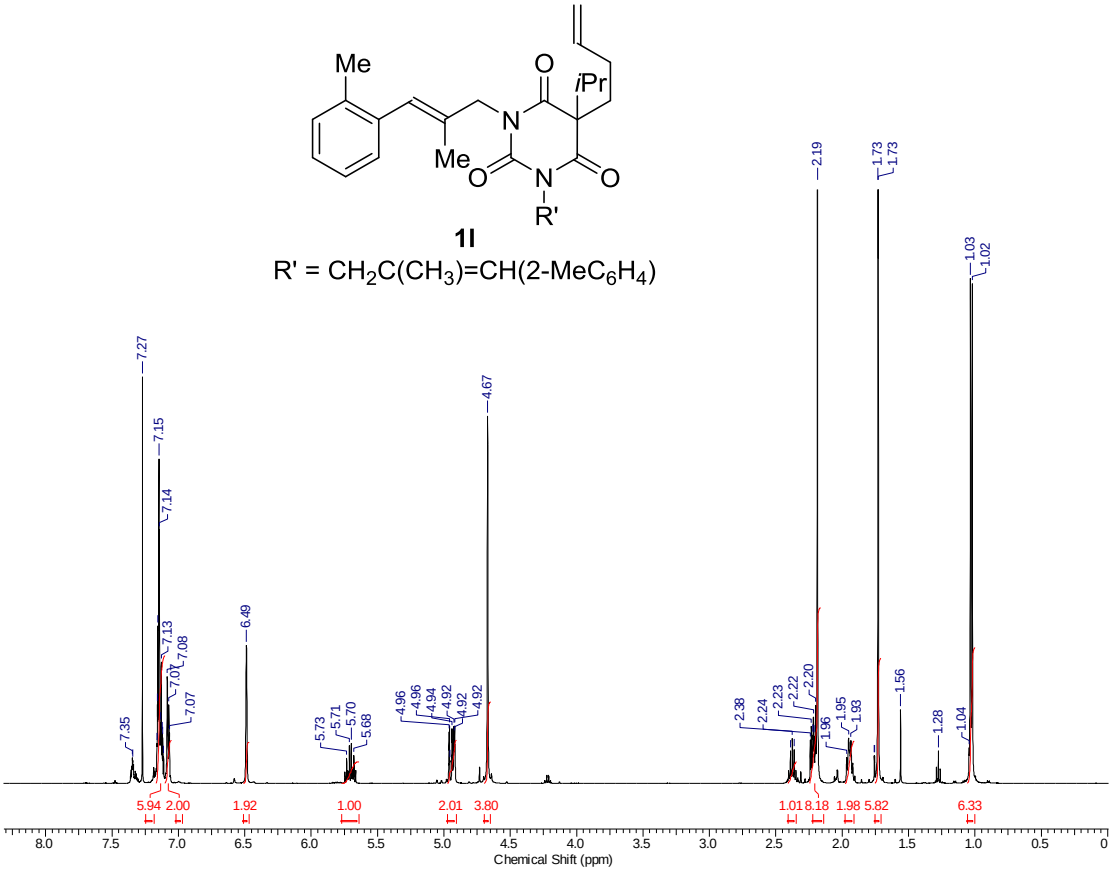
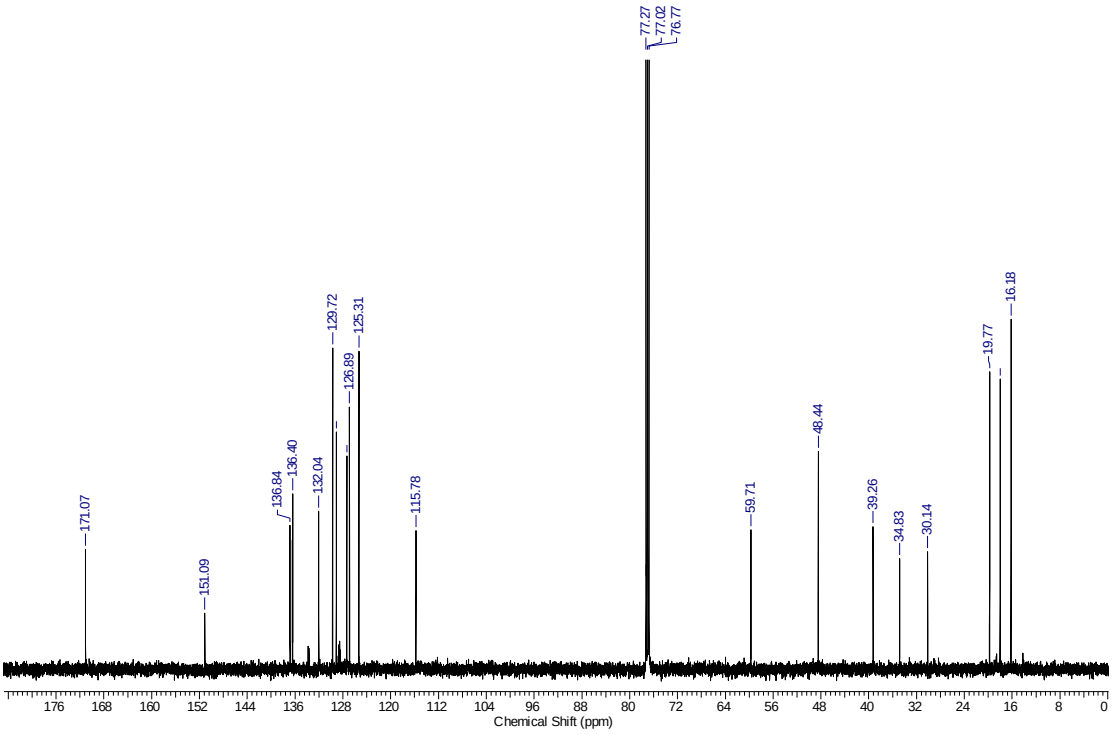
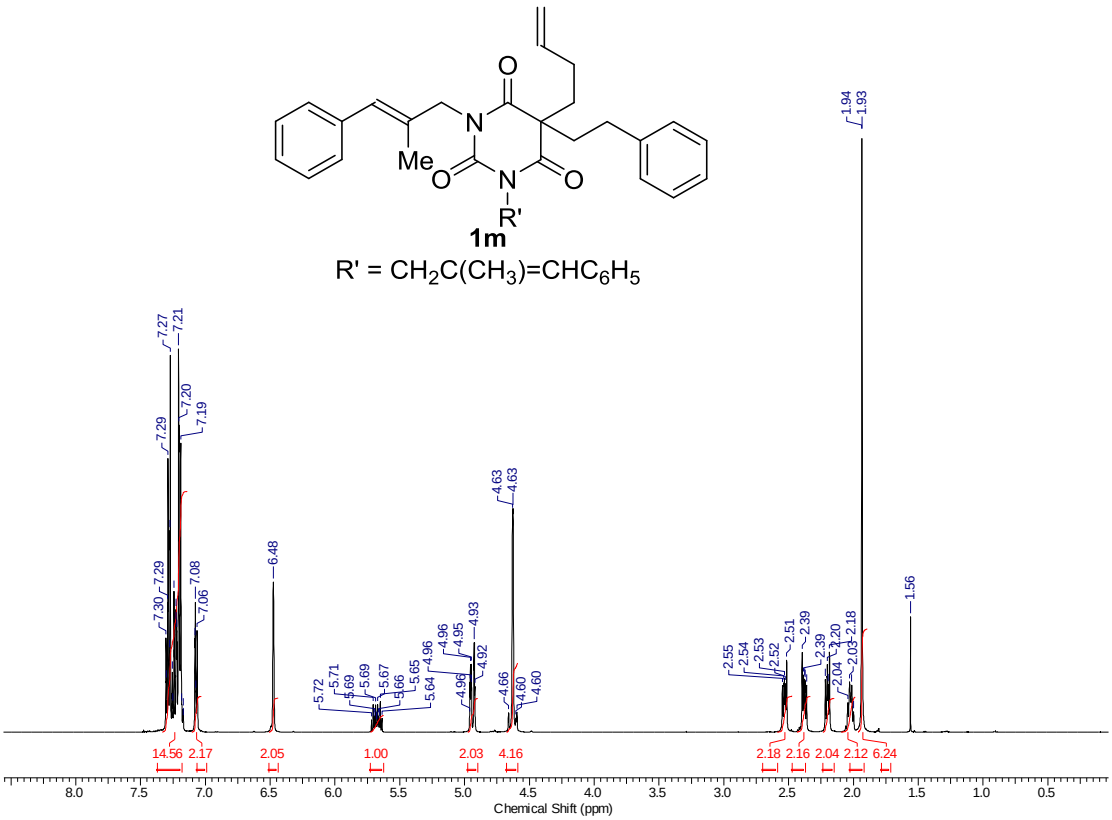


^{13}C NMR (126 MHz, $CDCl_3$)



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



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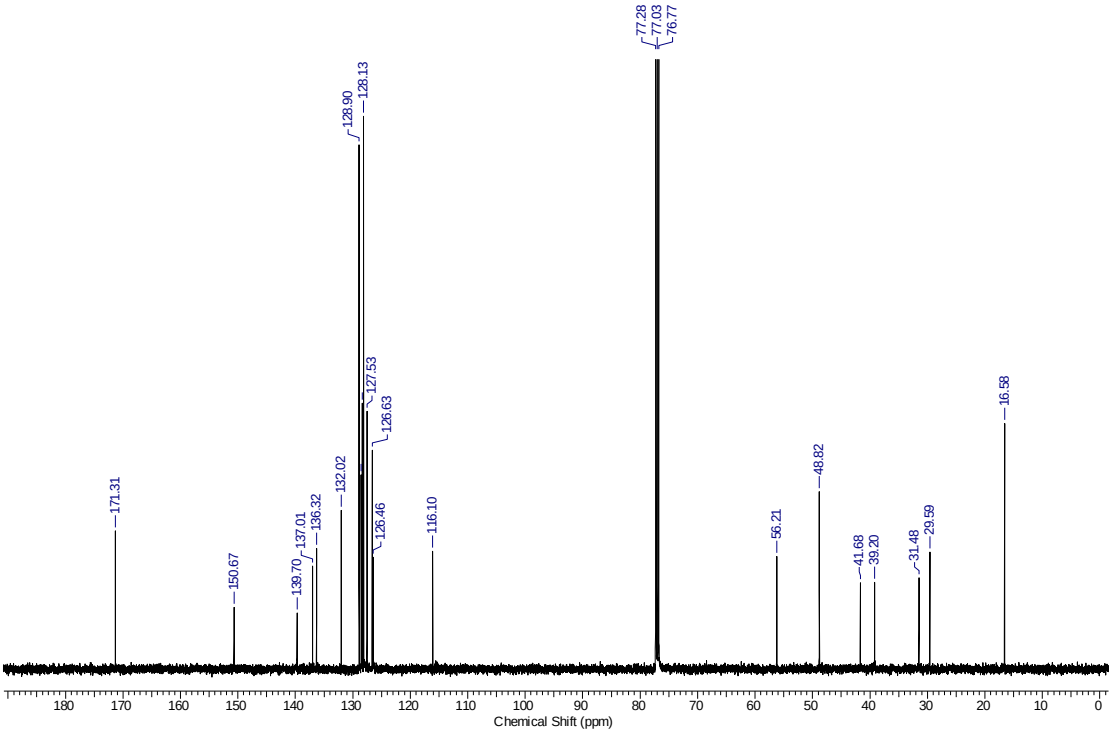
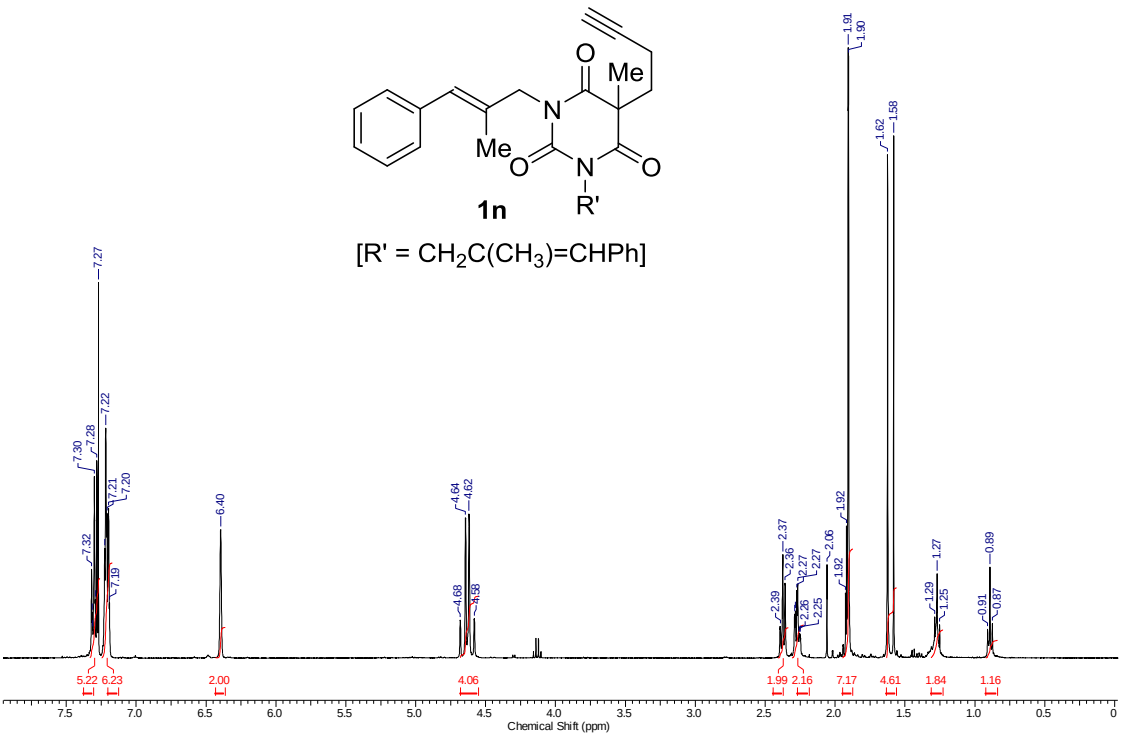
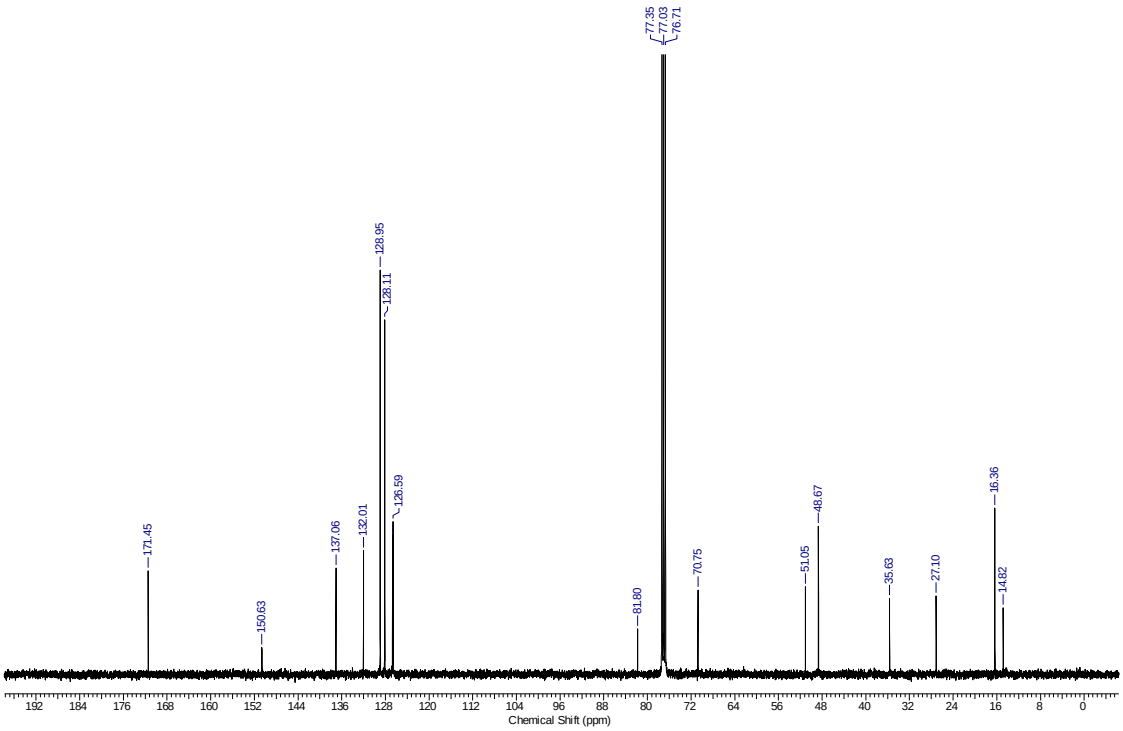


^{1}H NMR (400 MHz, $CDCl_3$)



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



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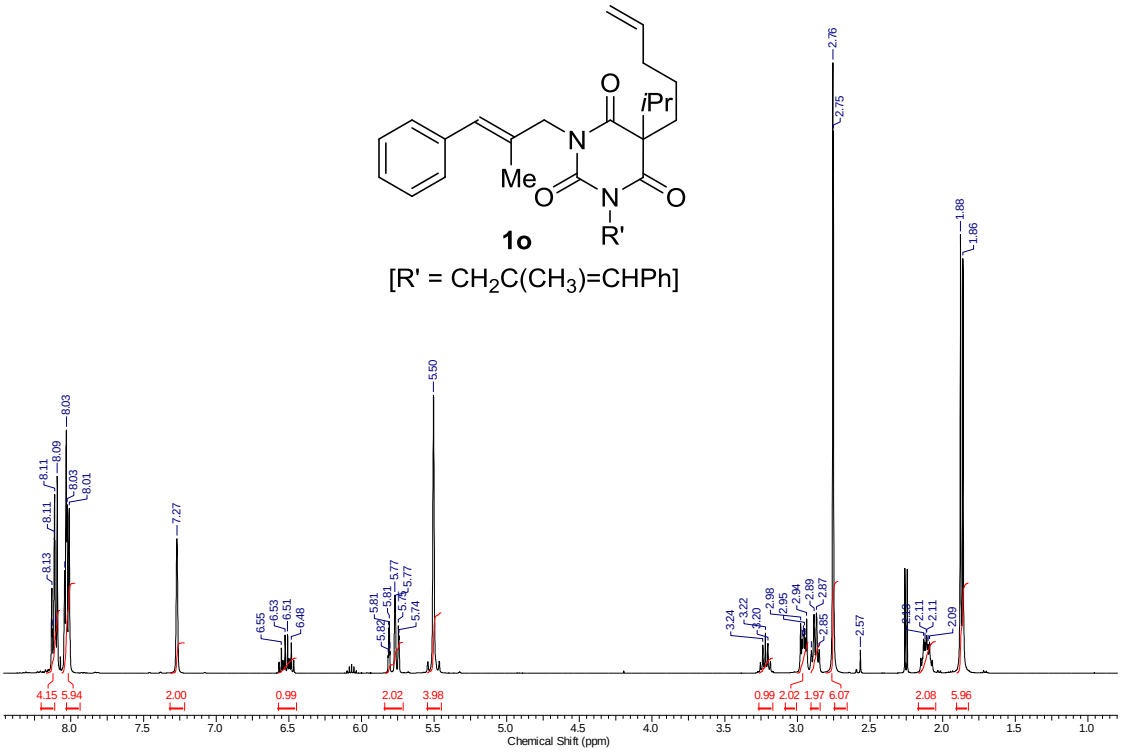
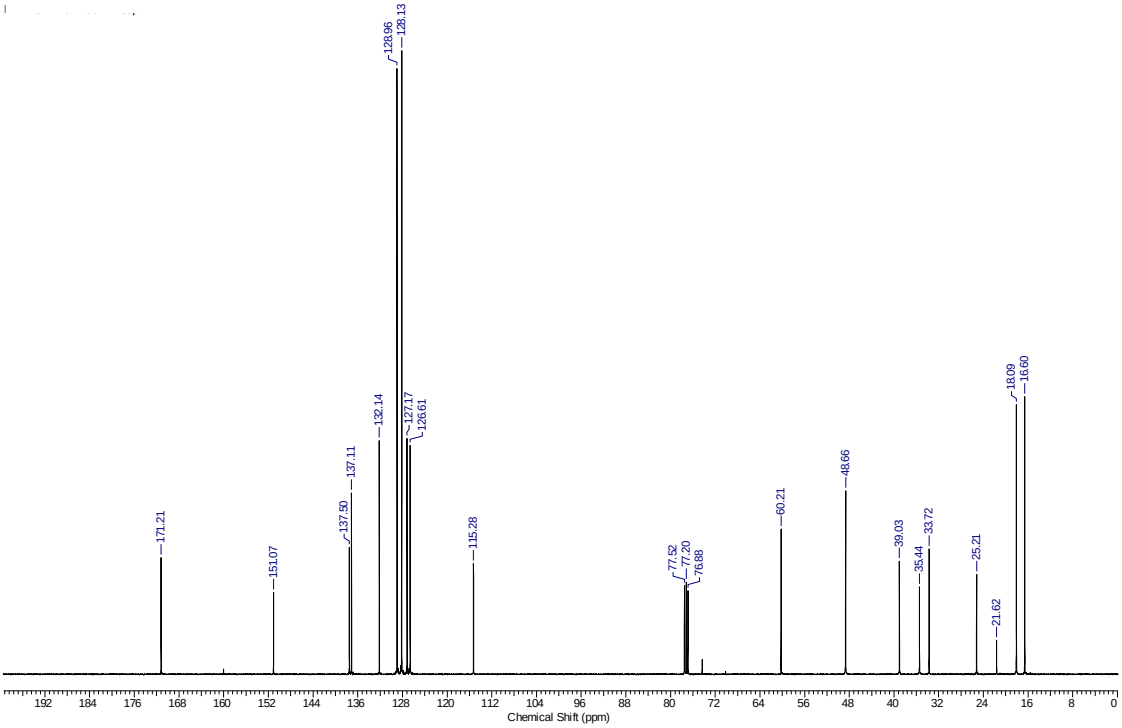


^{13}C NMR (101 MHz, $CDCl_3$)



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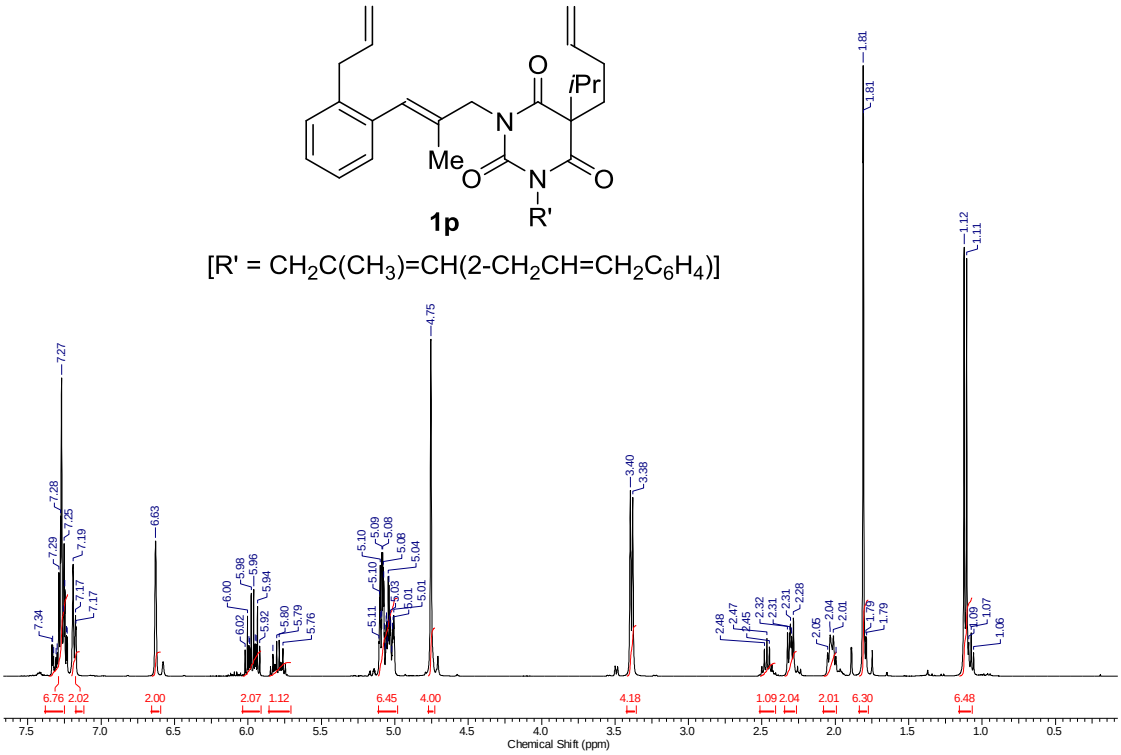
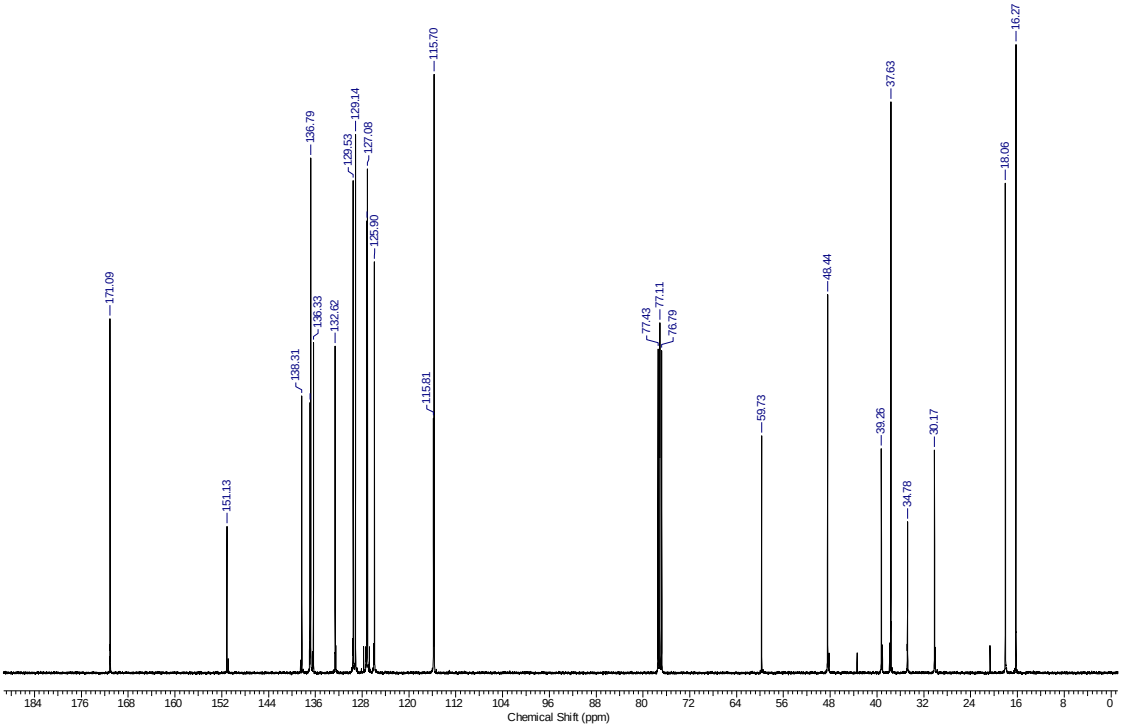
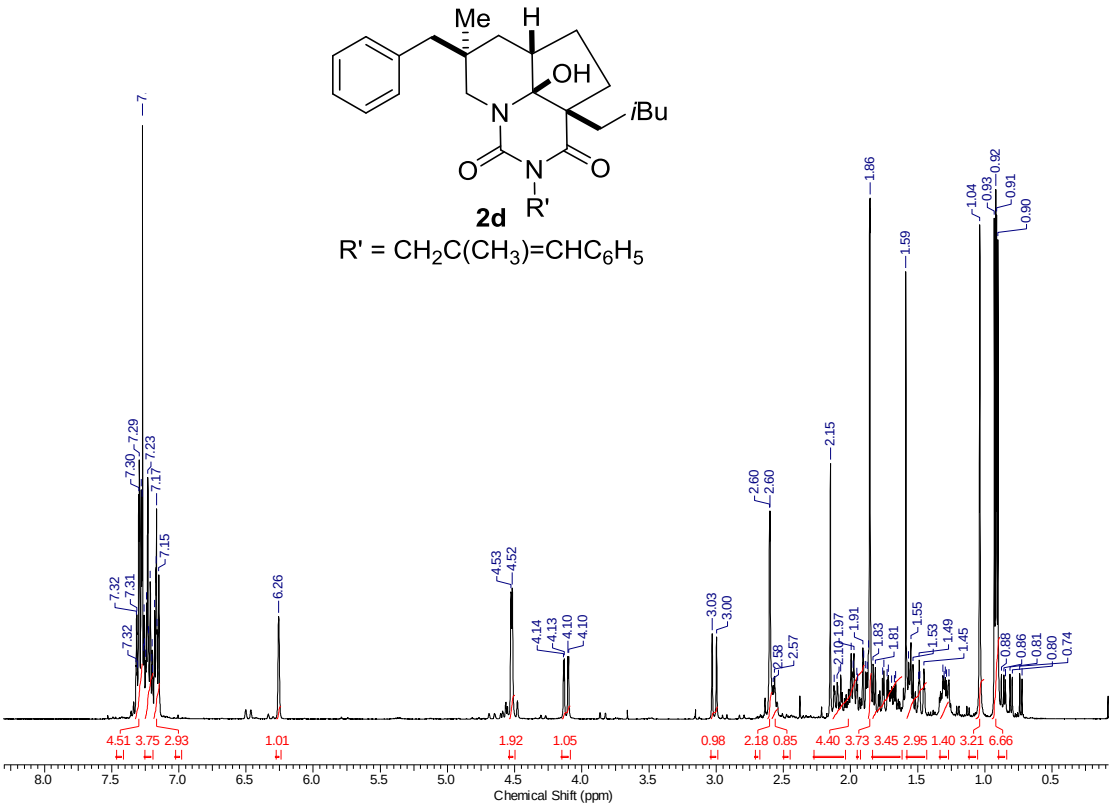


^{13}C NMR (101 MHz, $CDCl_3$)



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



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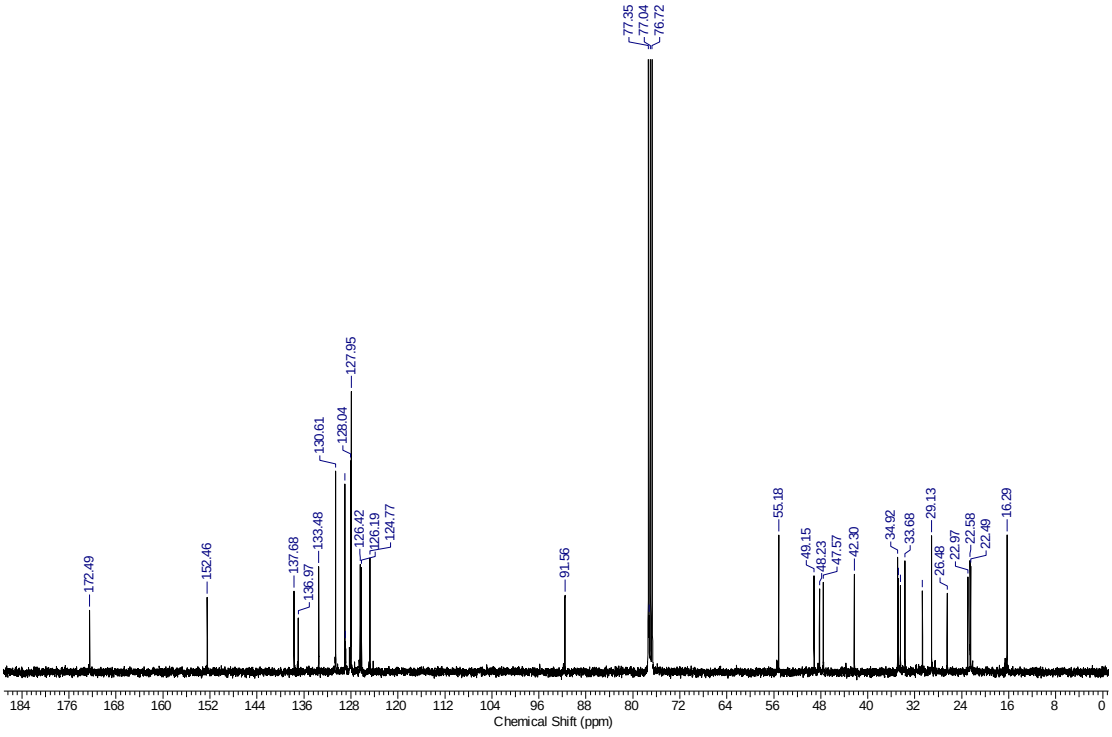

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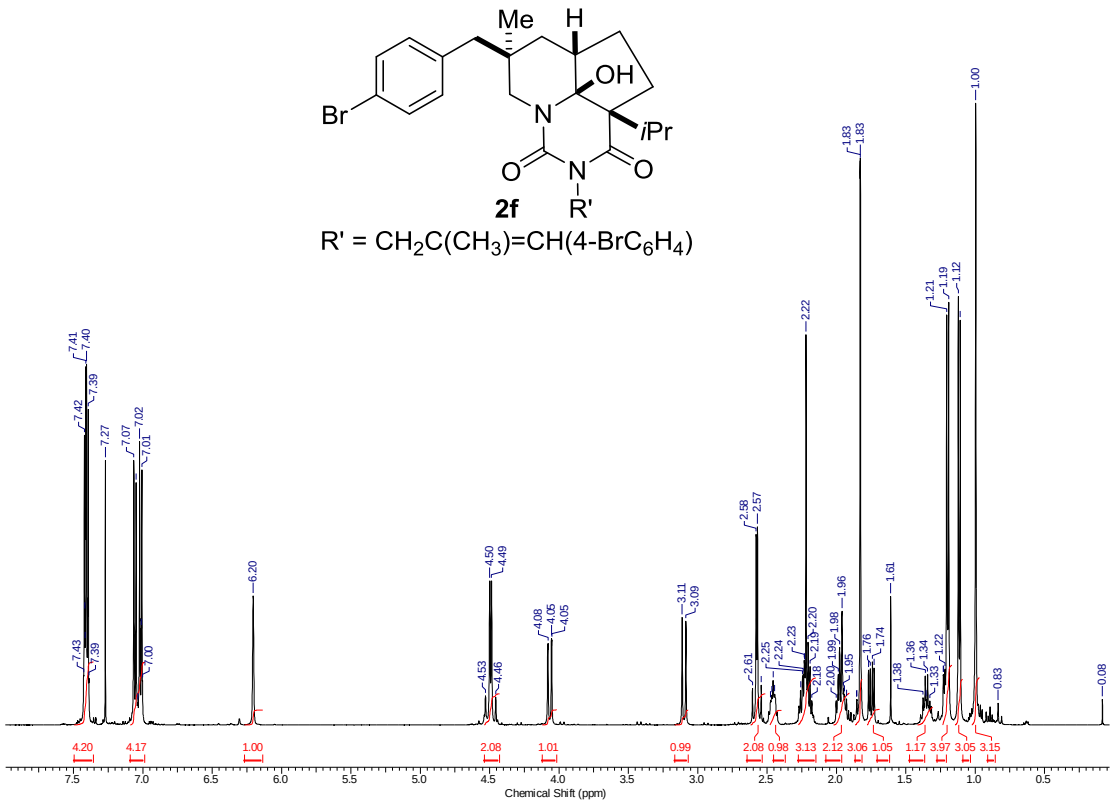
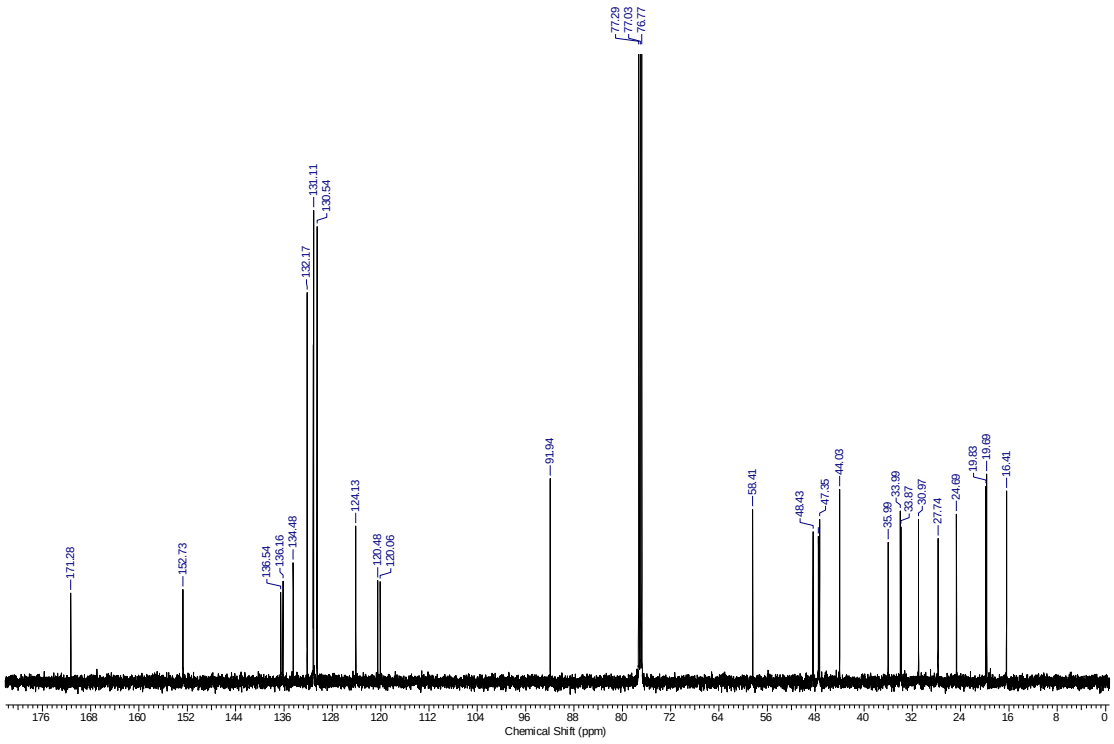


^{13}C NMR (125 MHz, $CDCl_3$)



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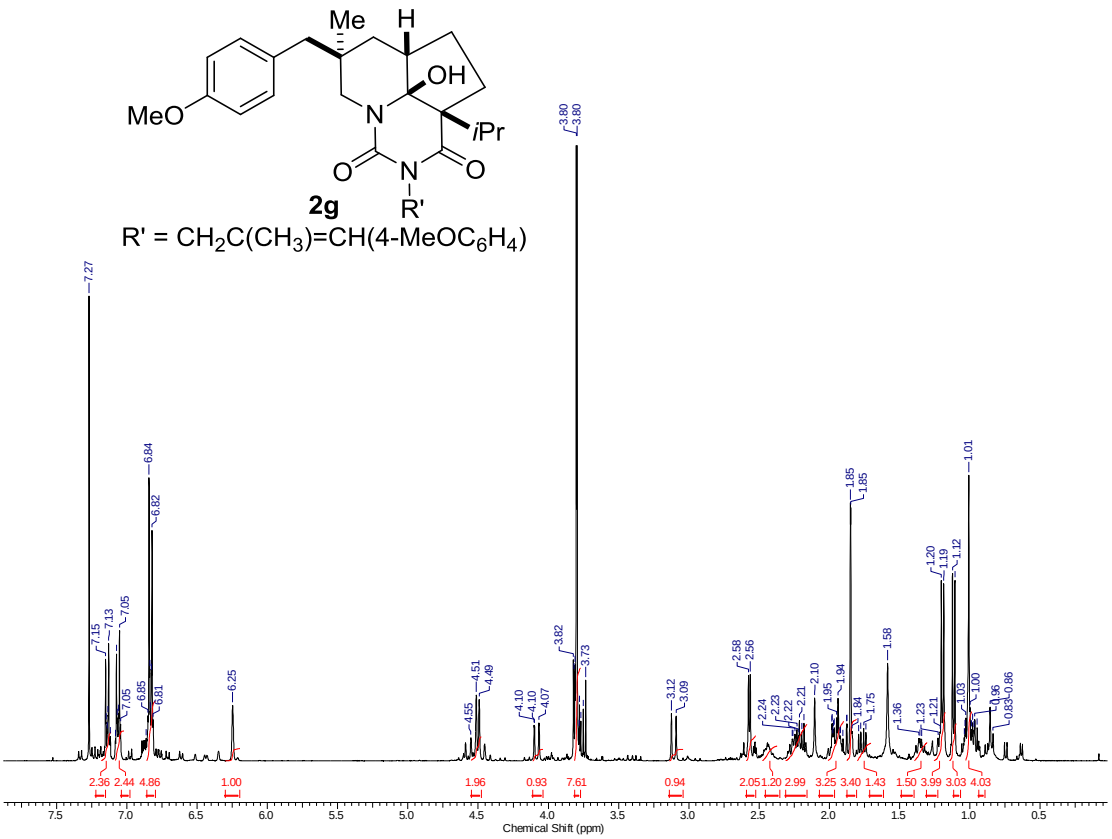

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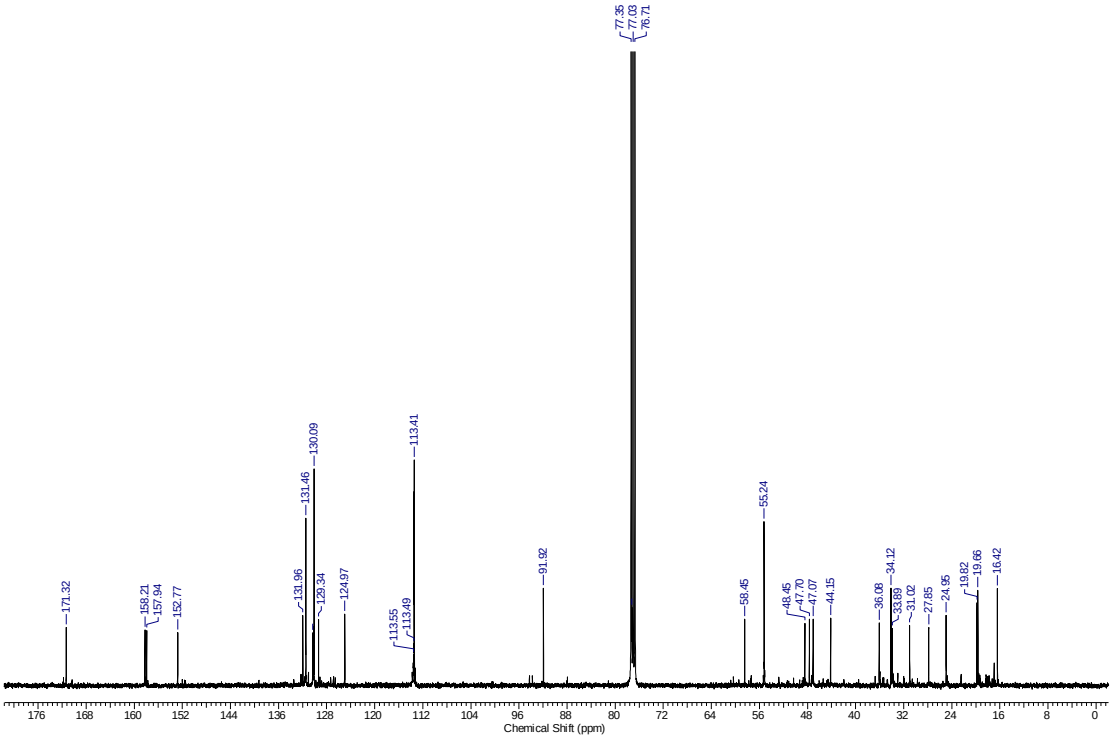

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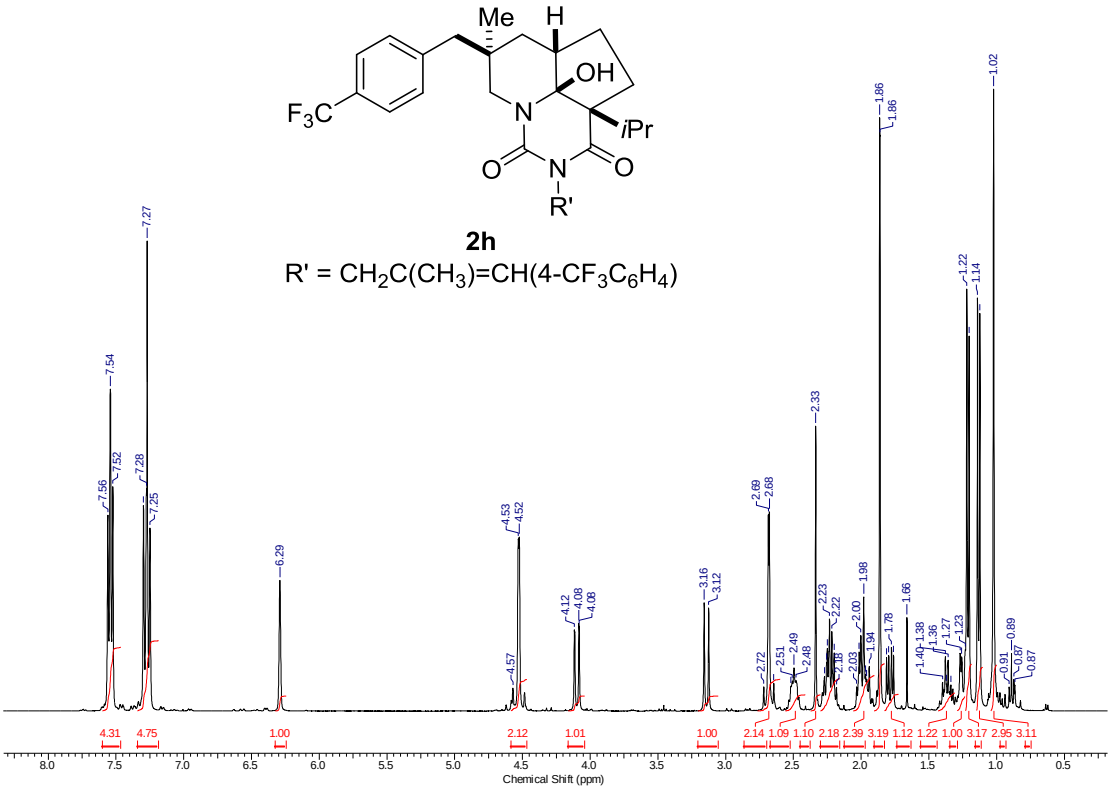

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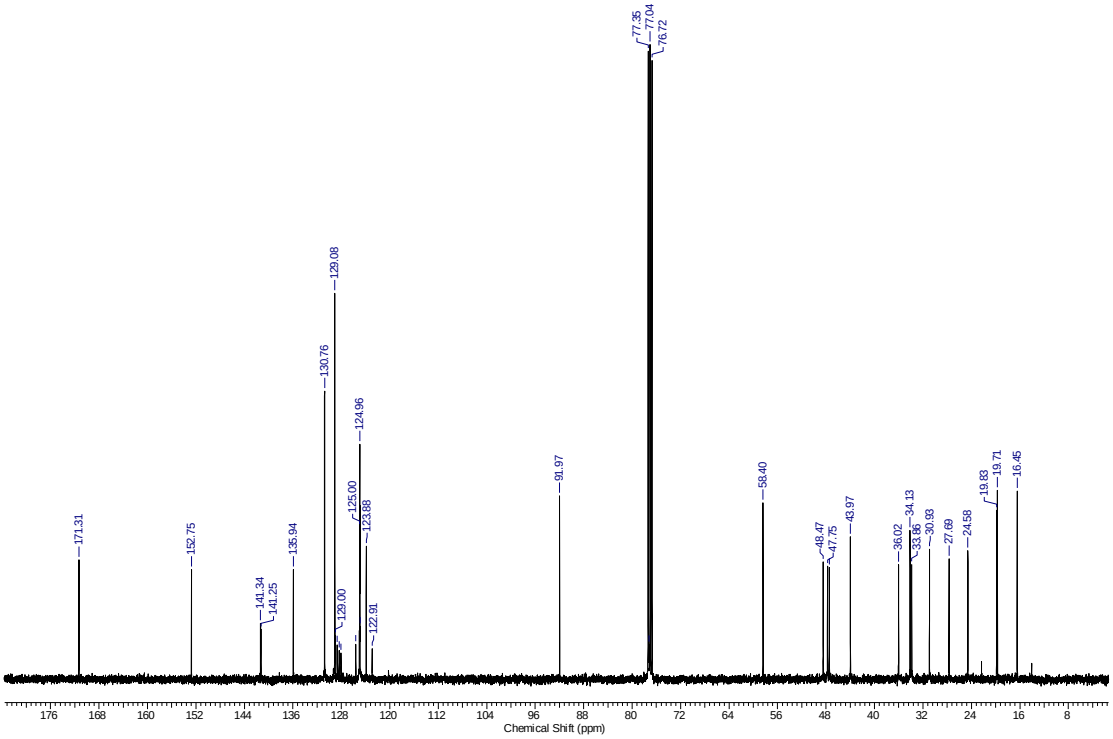

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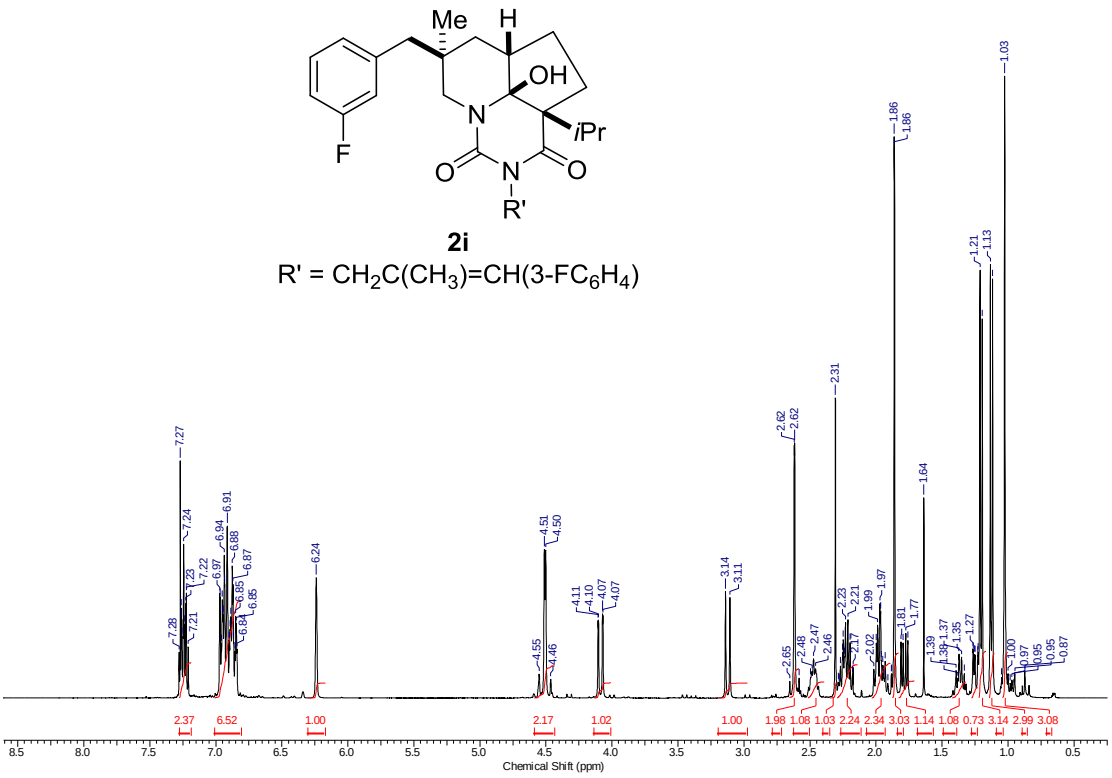

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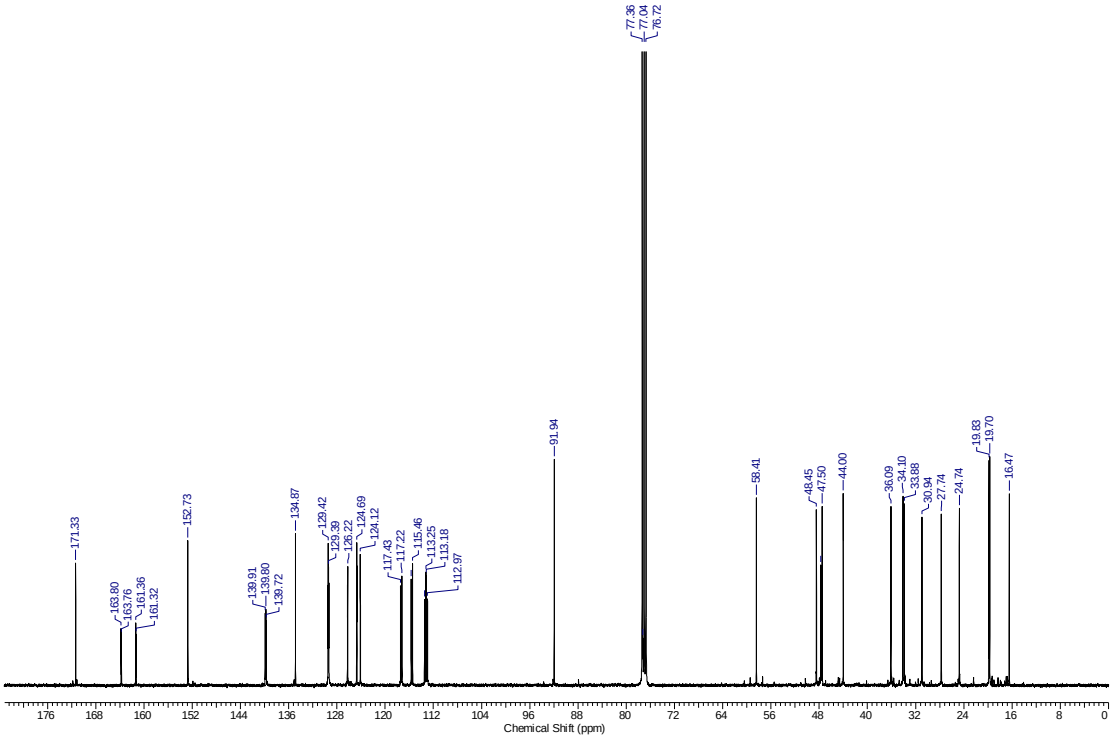

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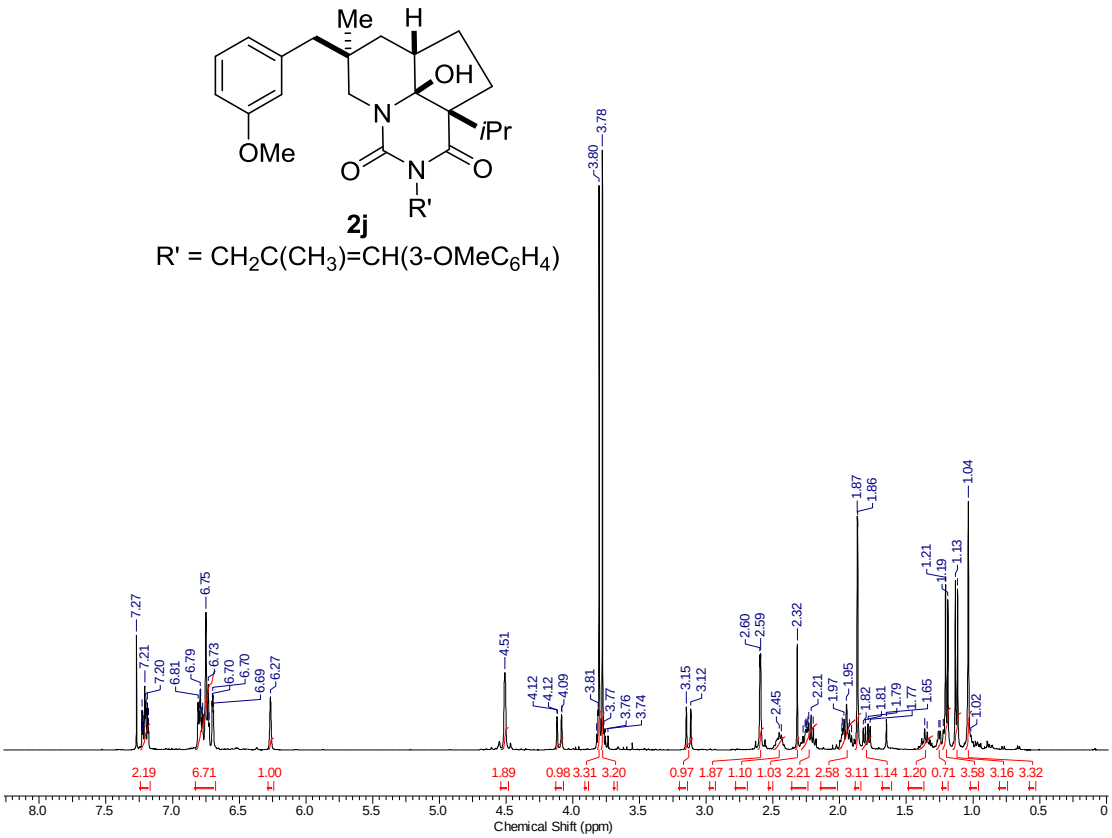

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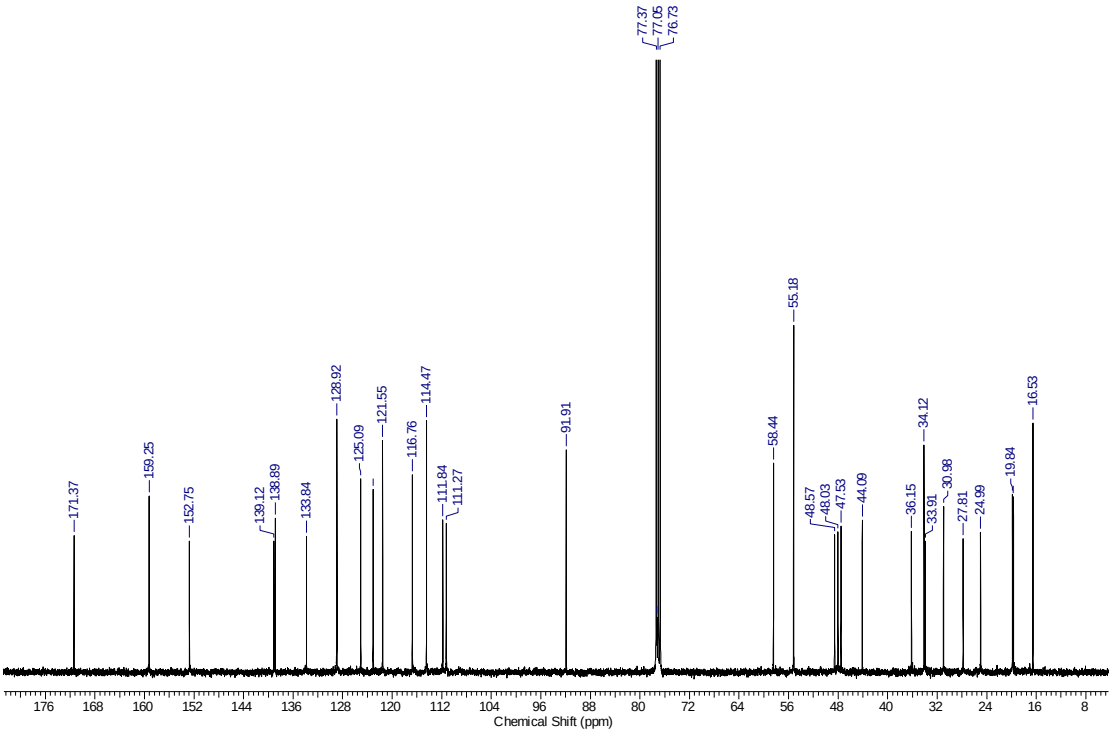

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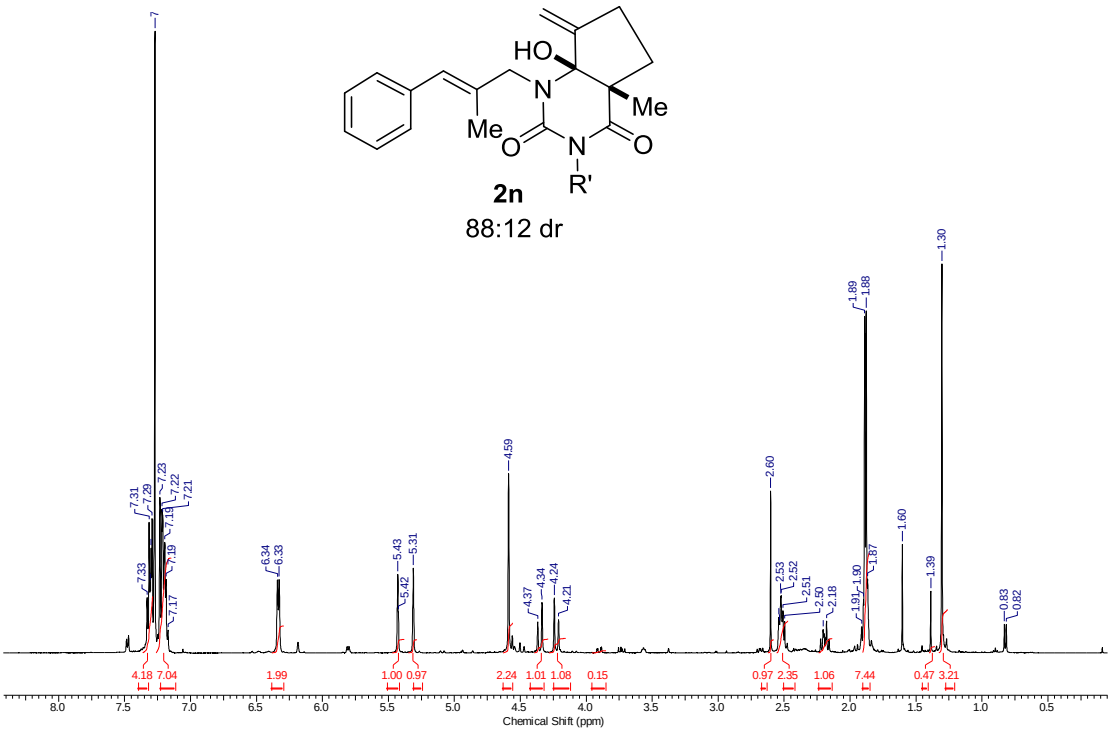

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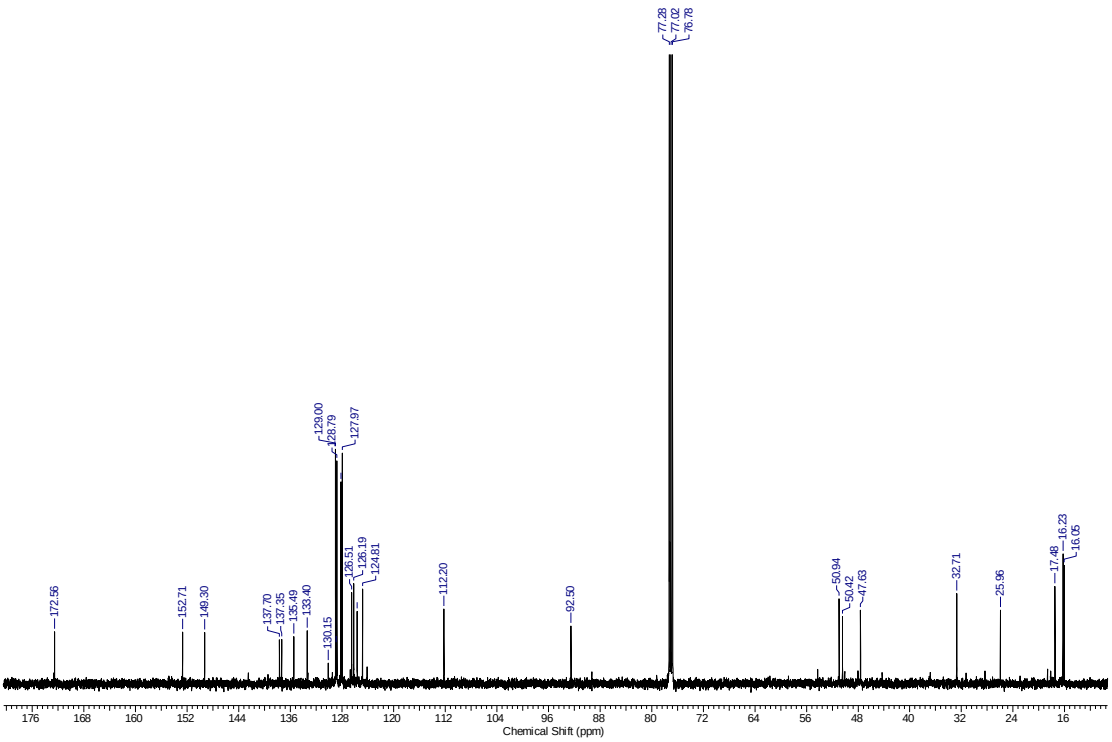

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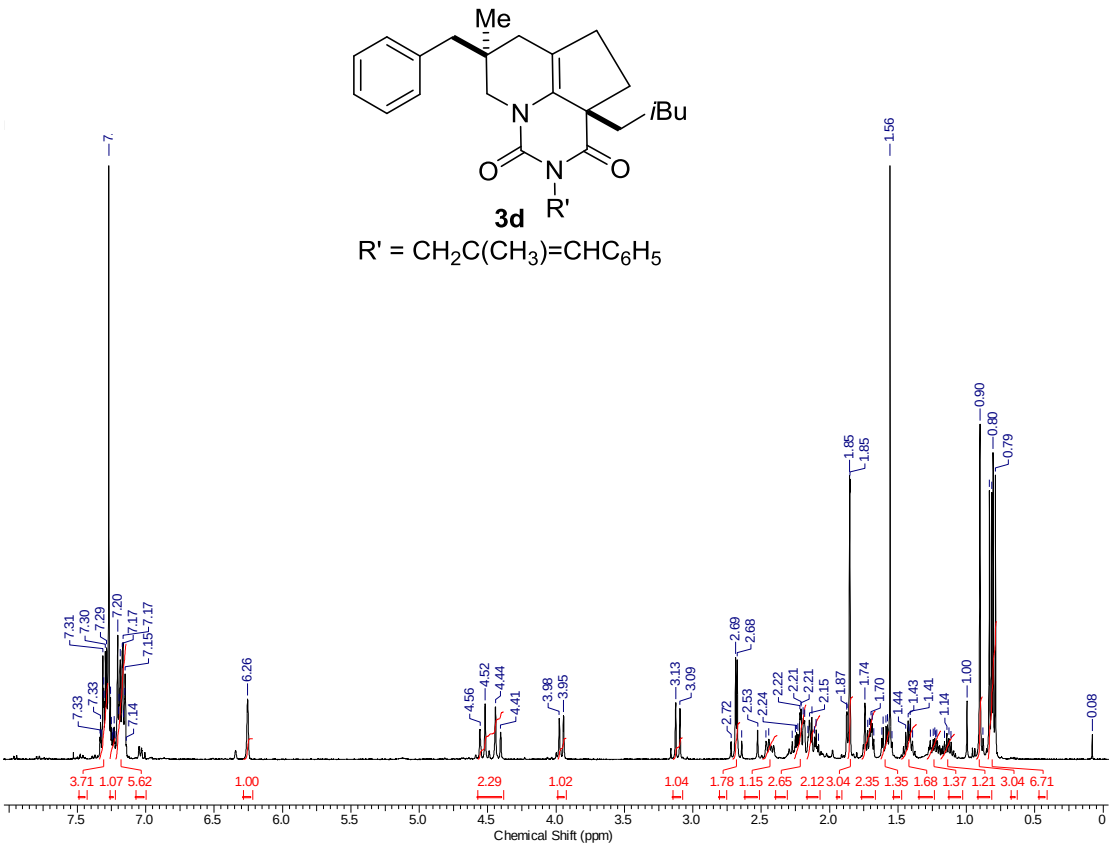

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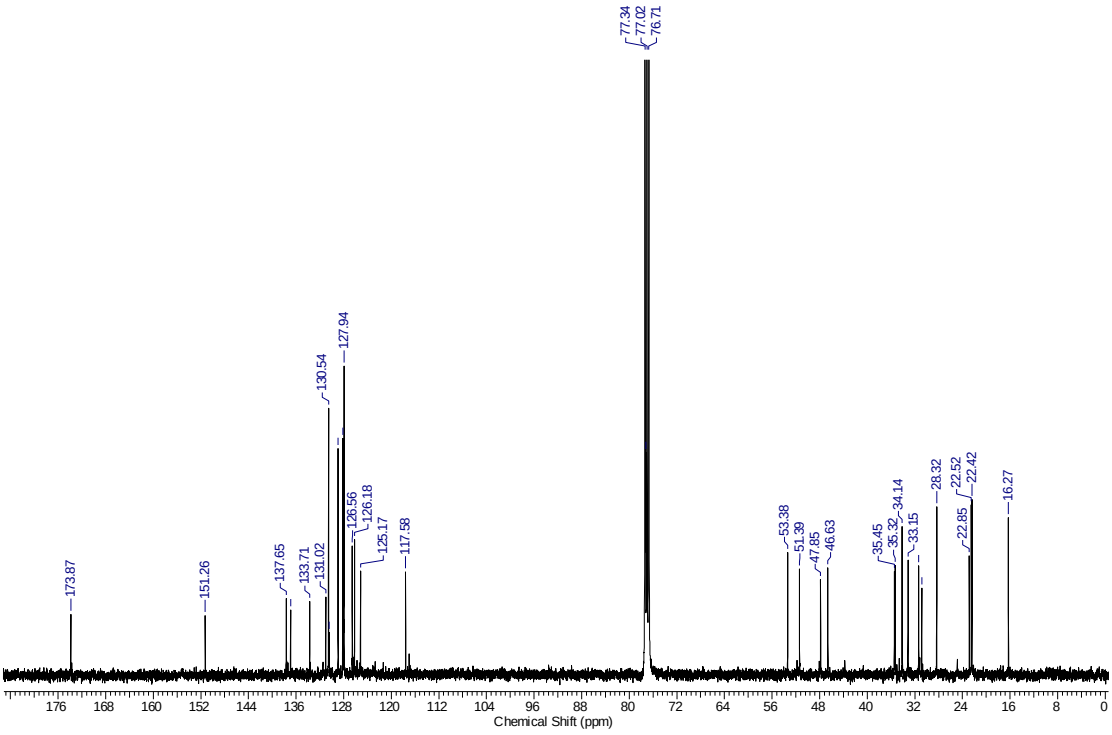

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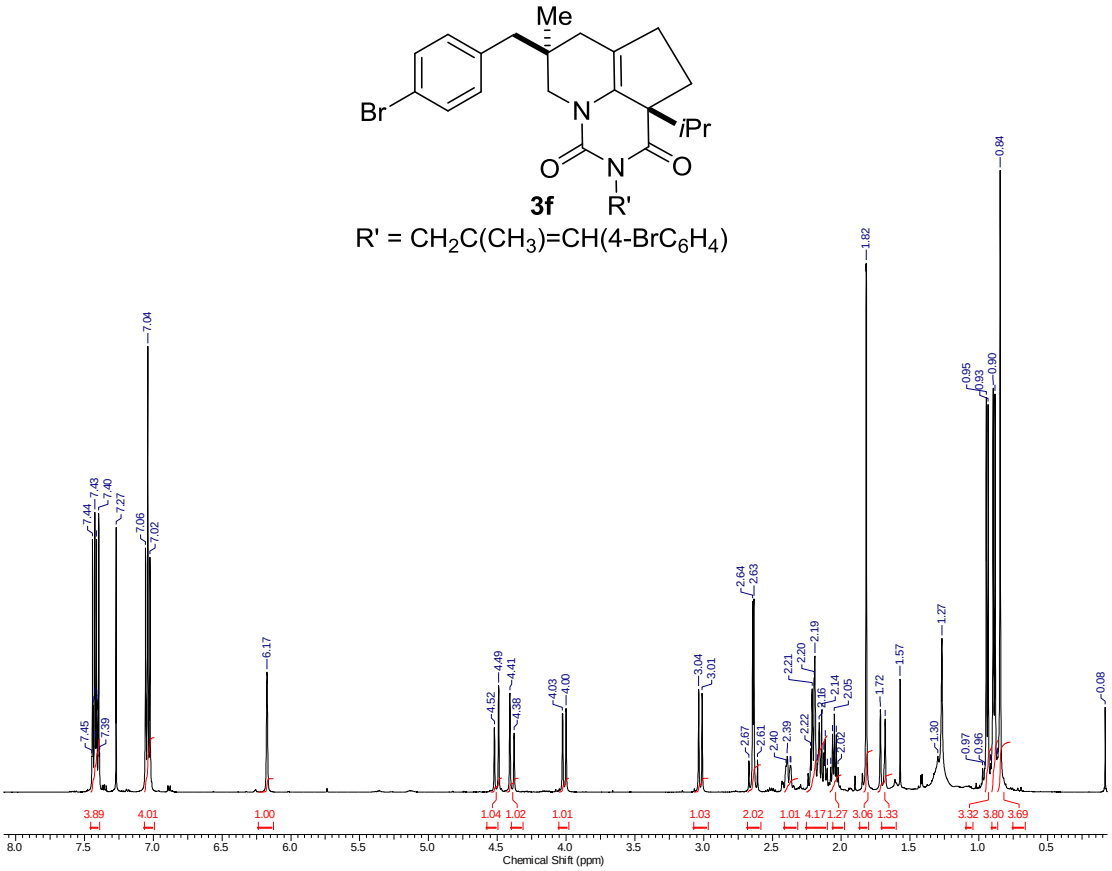

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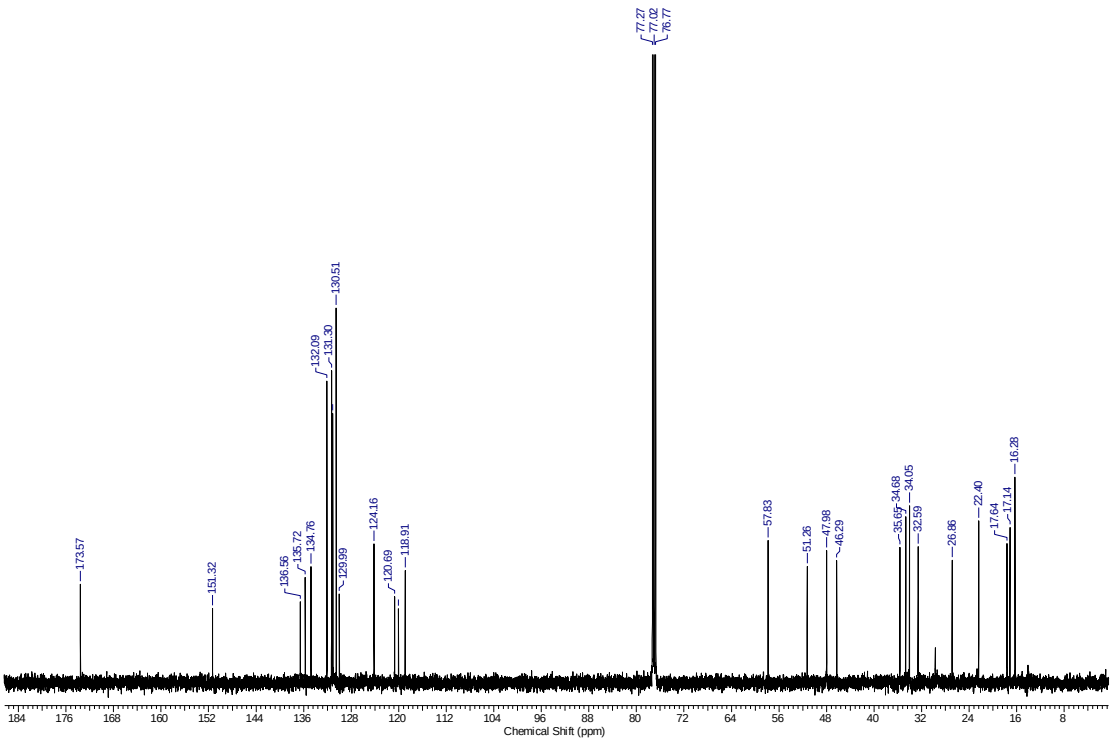

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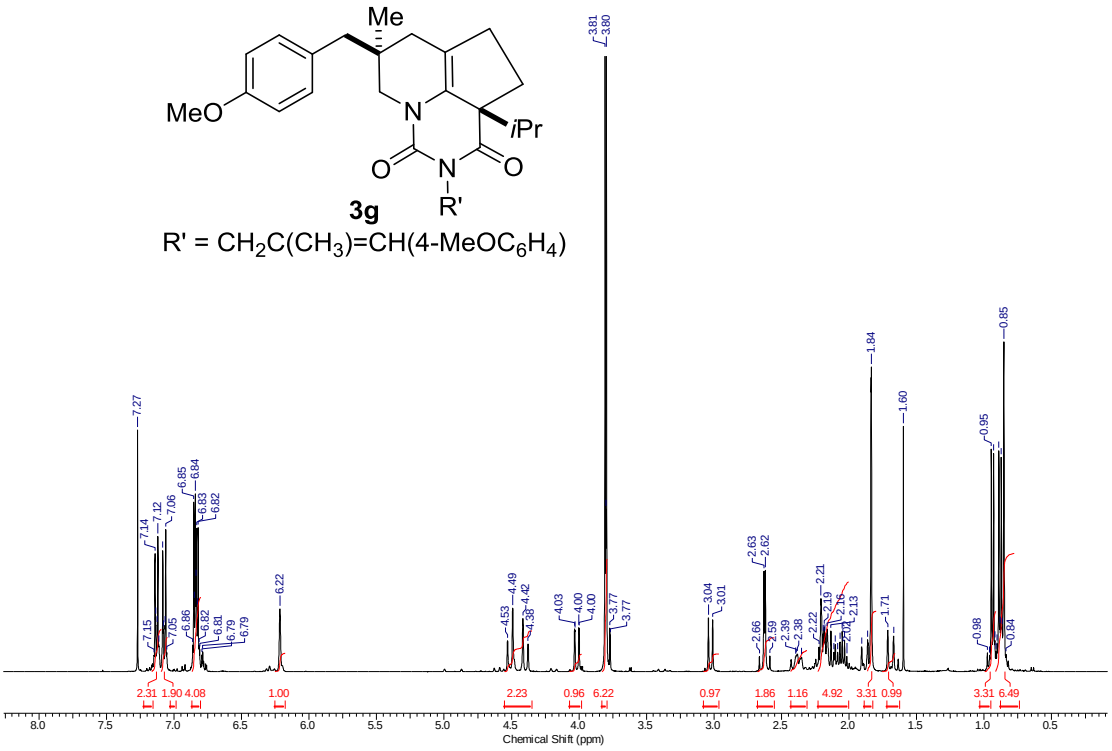

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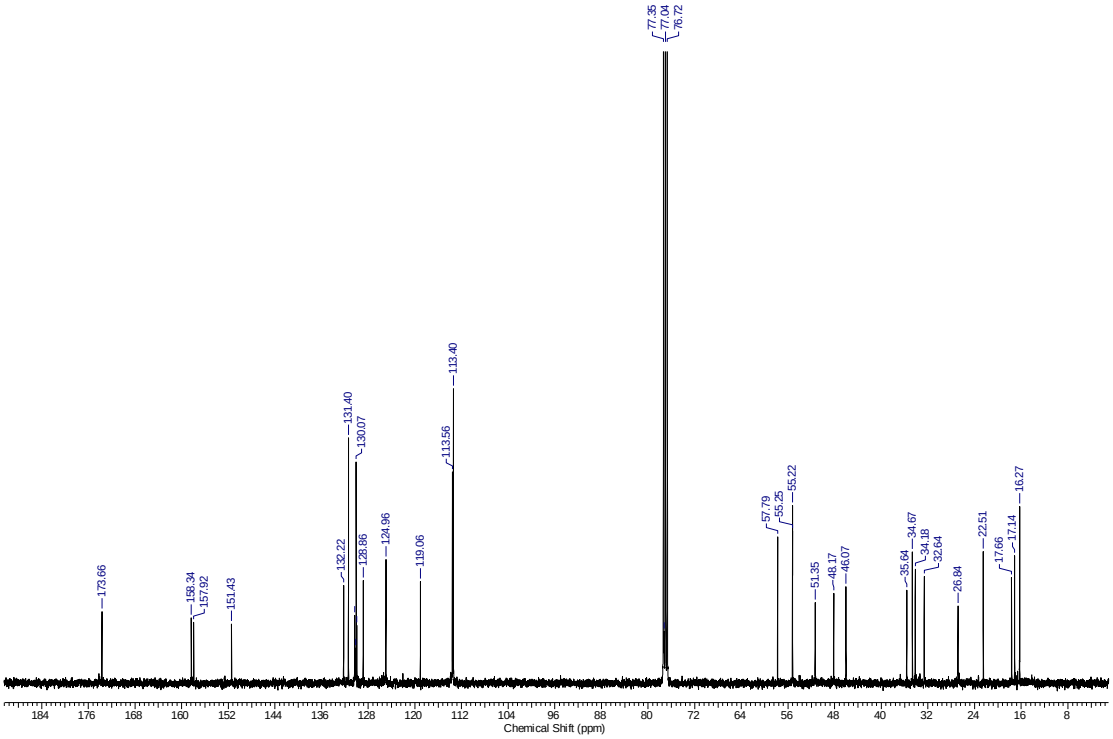

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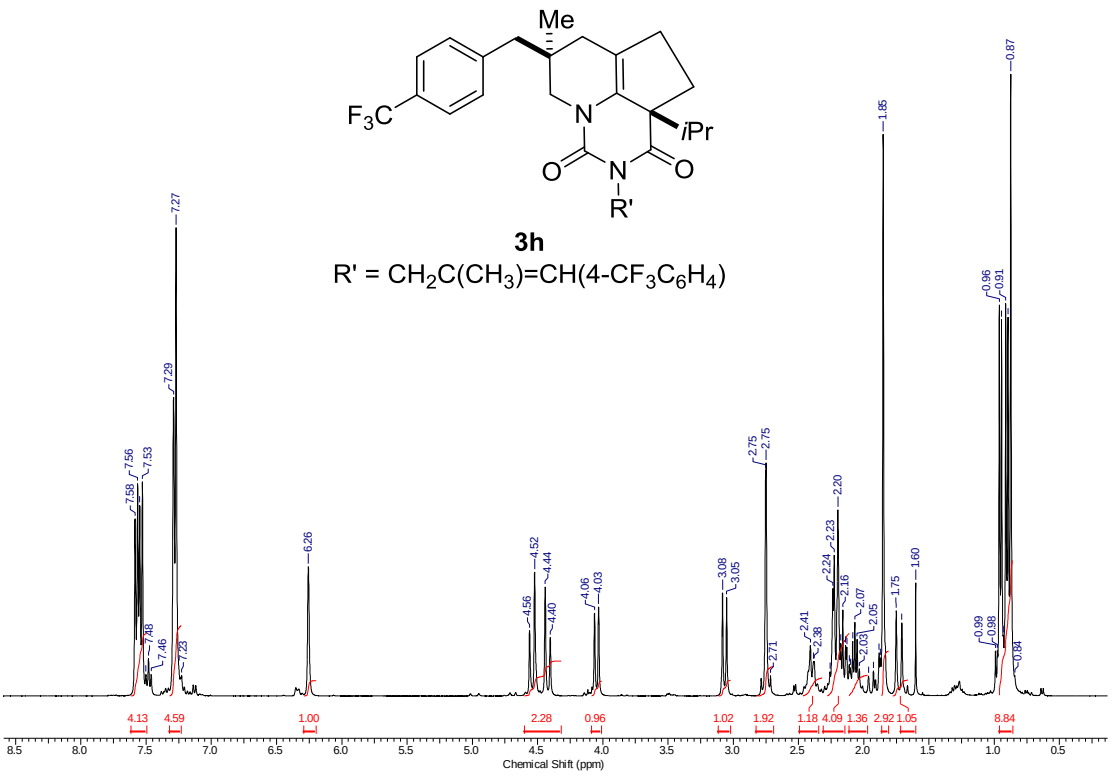

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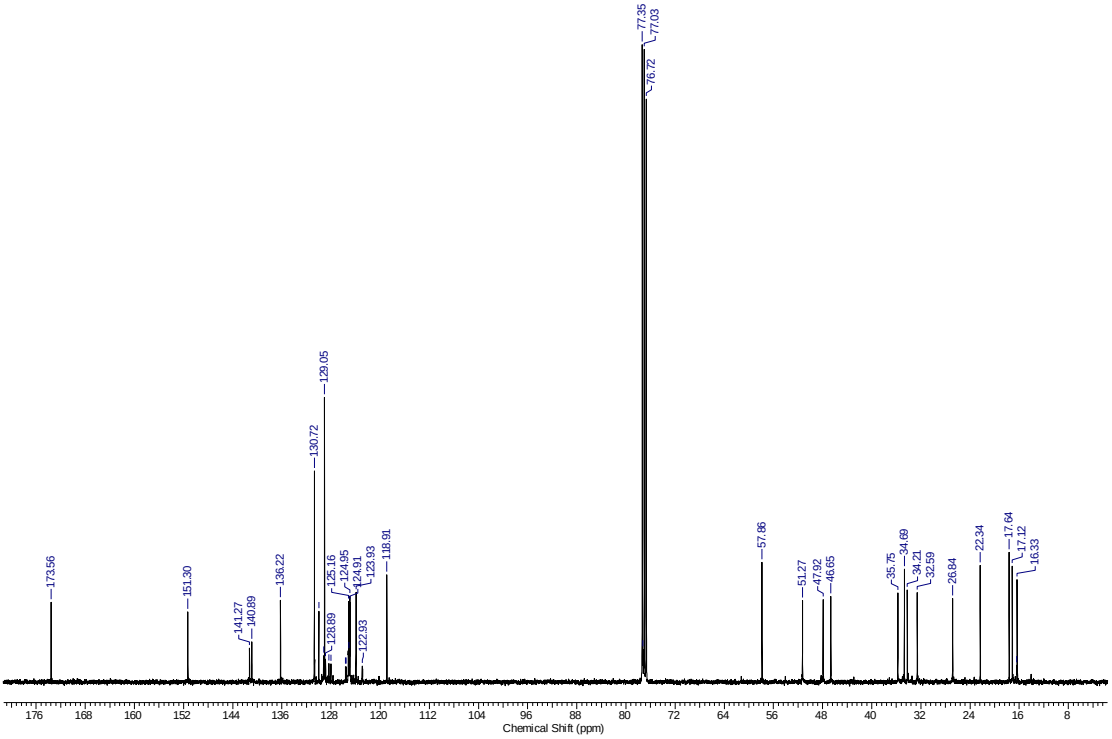

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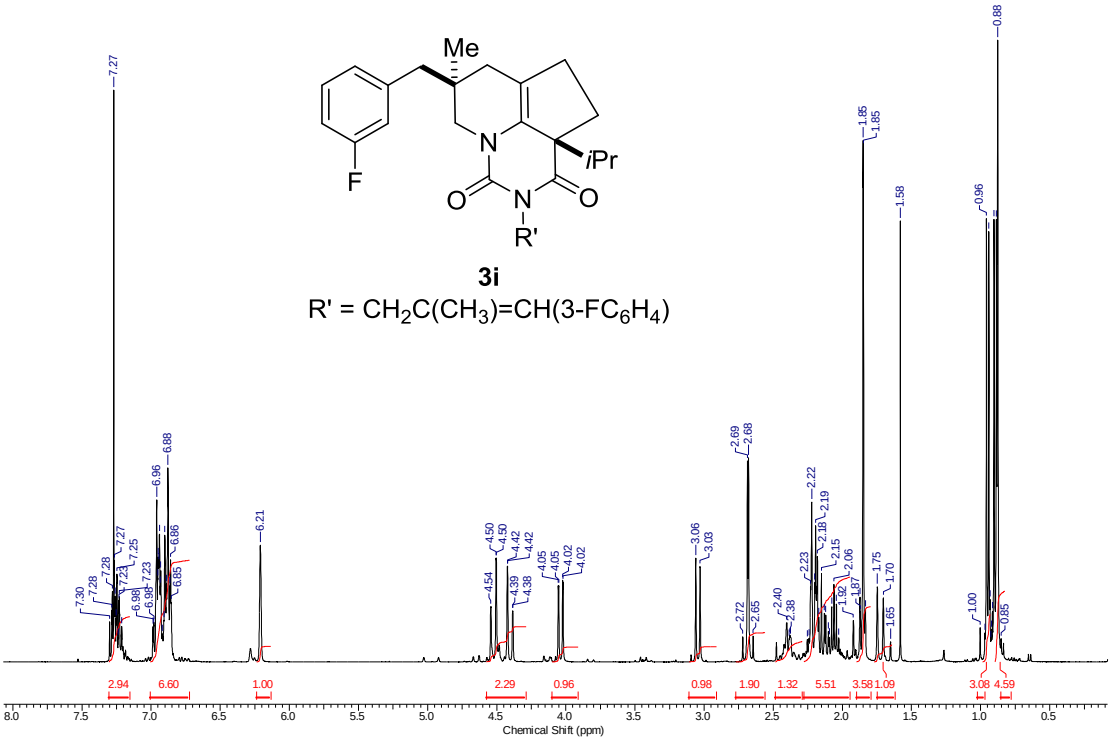
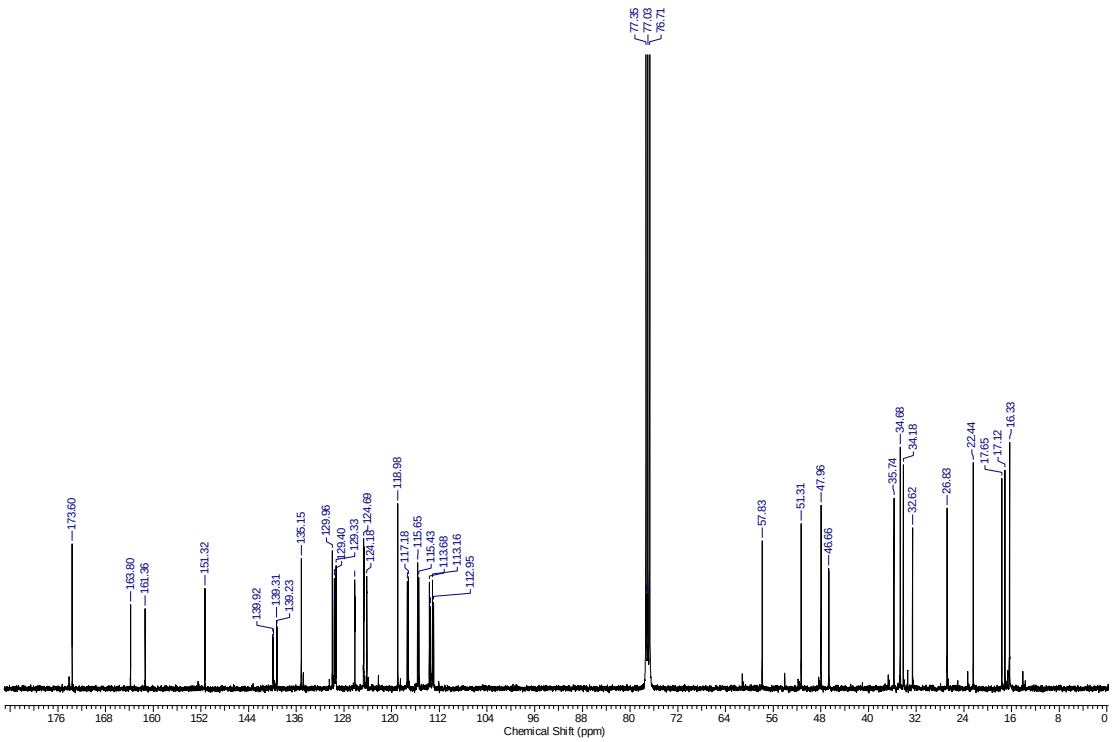
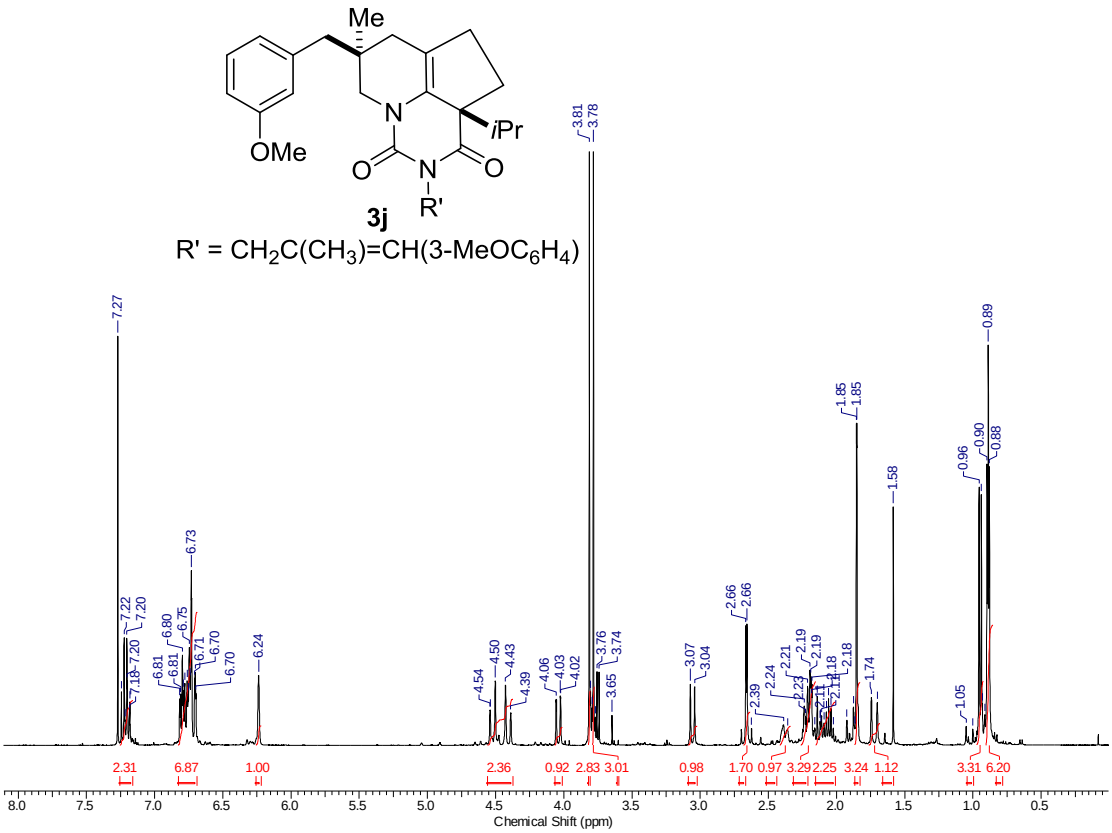


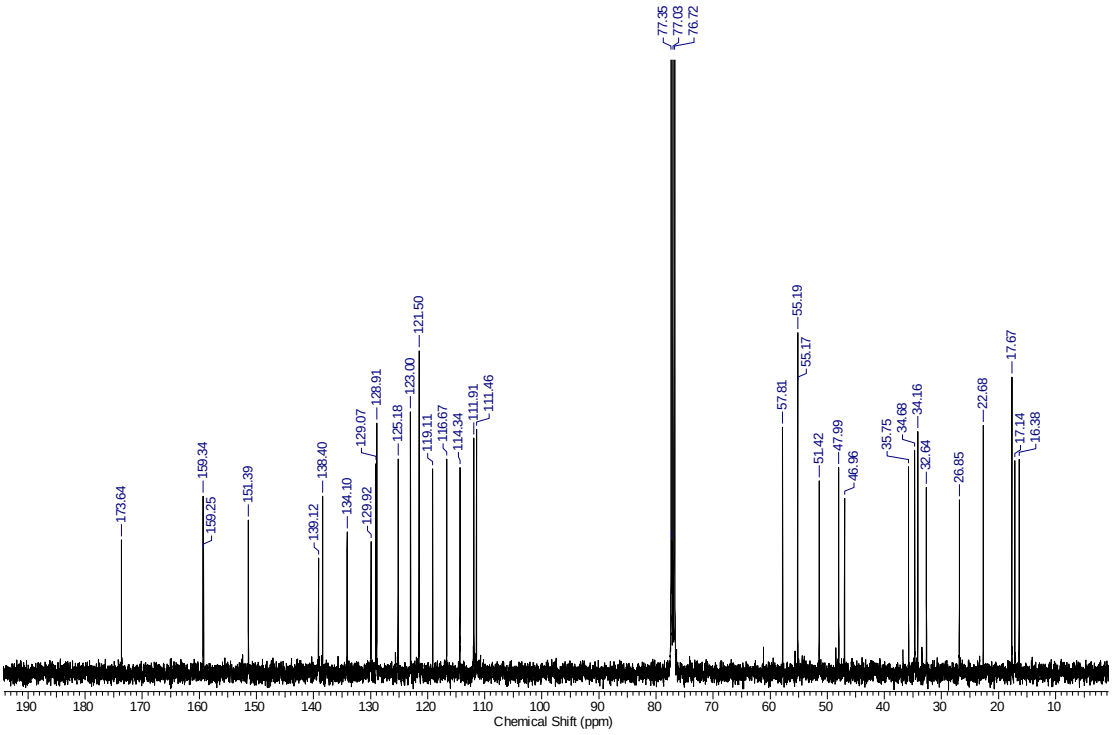
^{13}C NMR (101 MHz, $CDCl_3$)



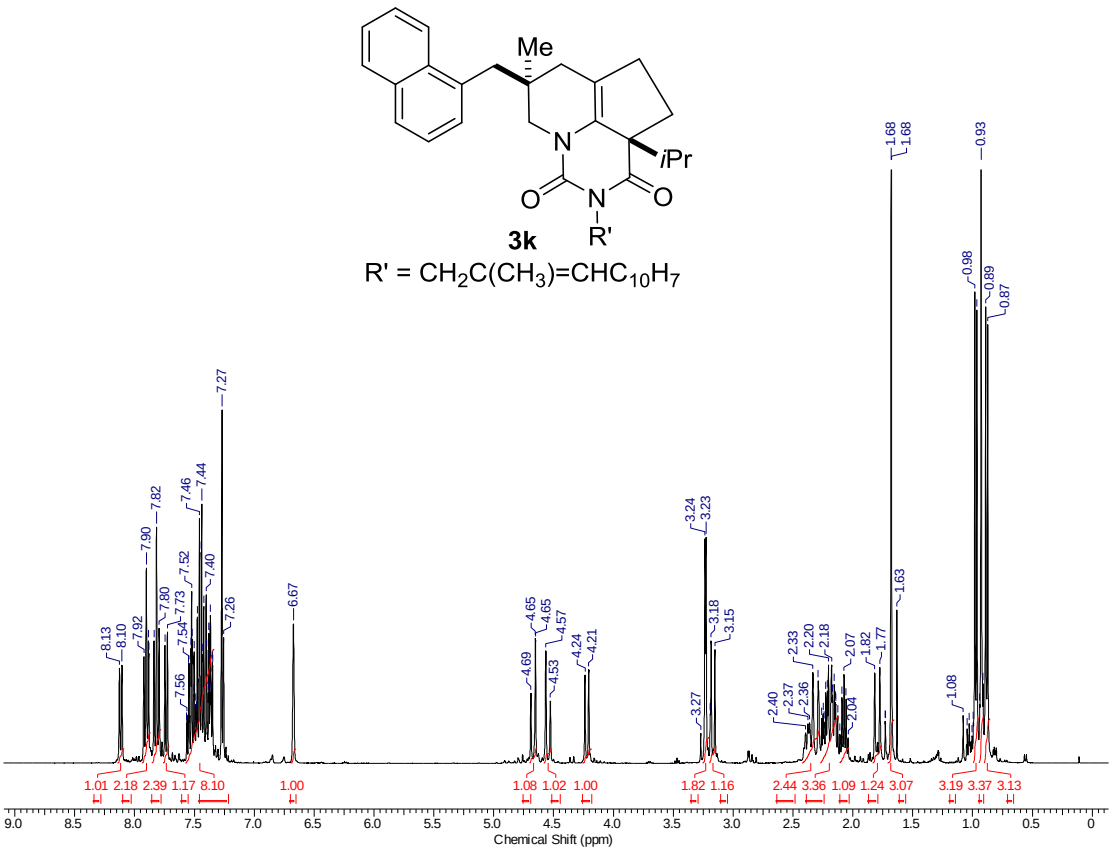
^{1}H NMR (400 MHz, $CDCl_3$)



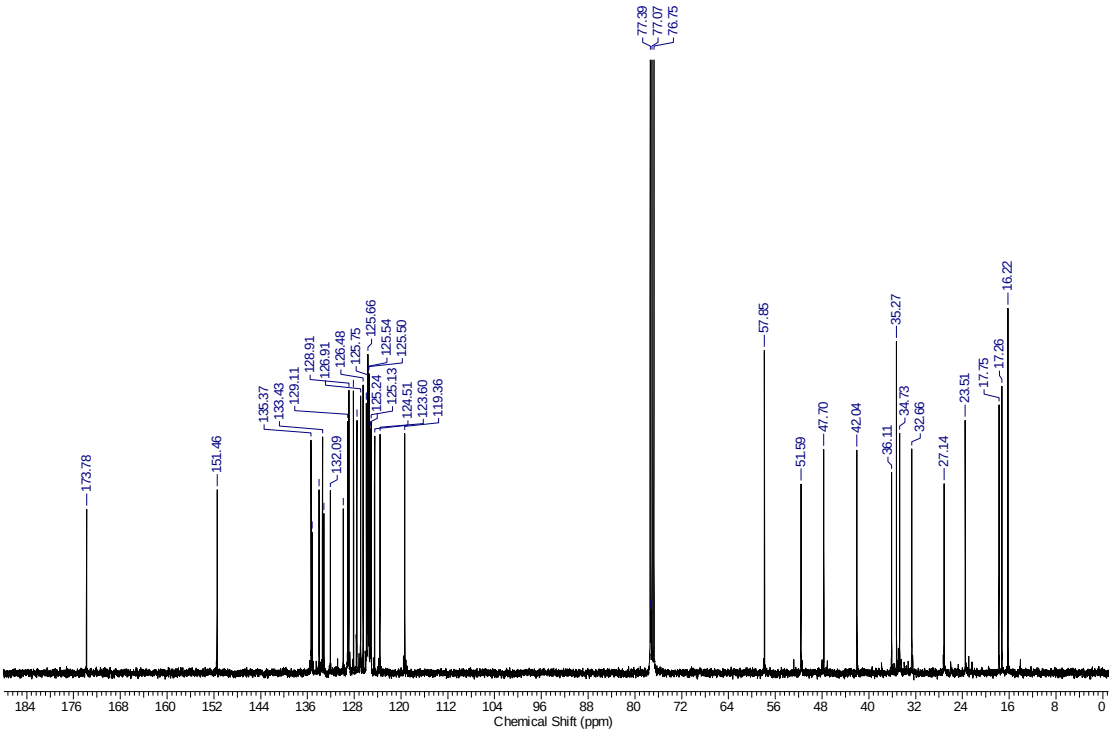
^{13}C NMR (101 MHz, $CDCl_3$)



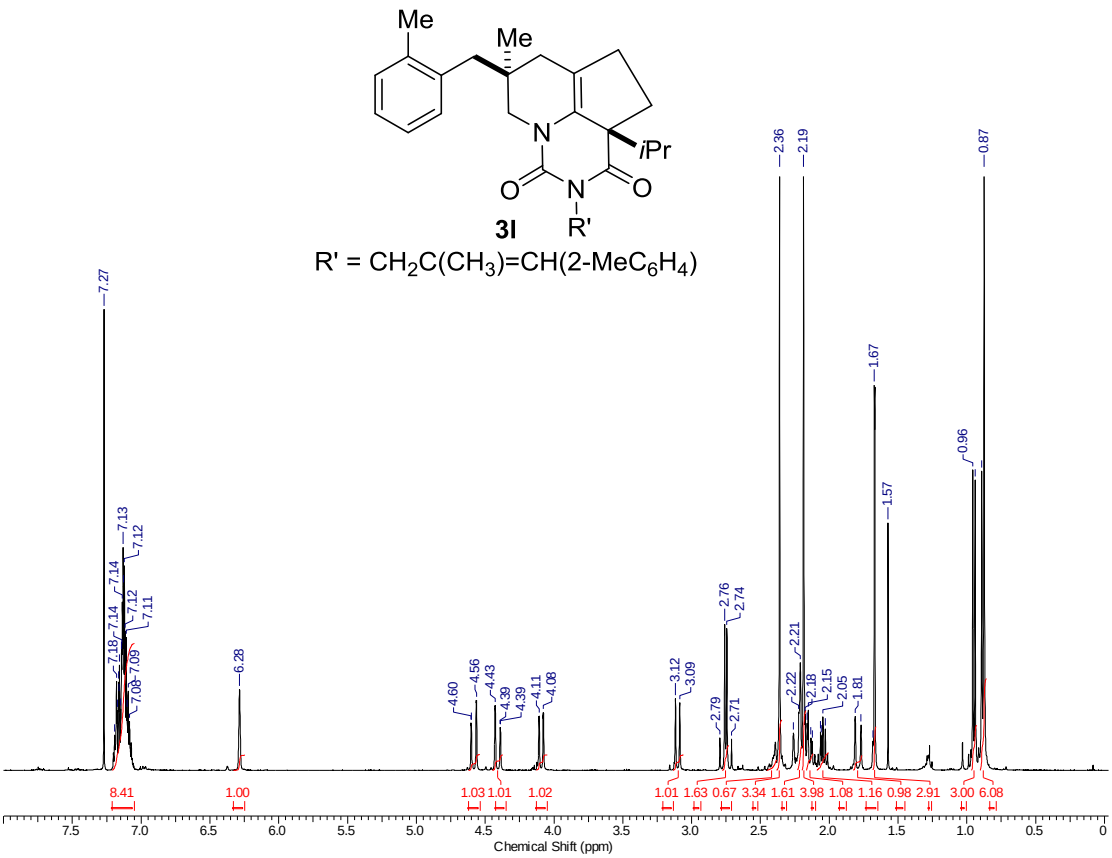
^{1}H NMR (400 MHz, $CDCl_3$)



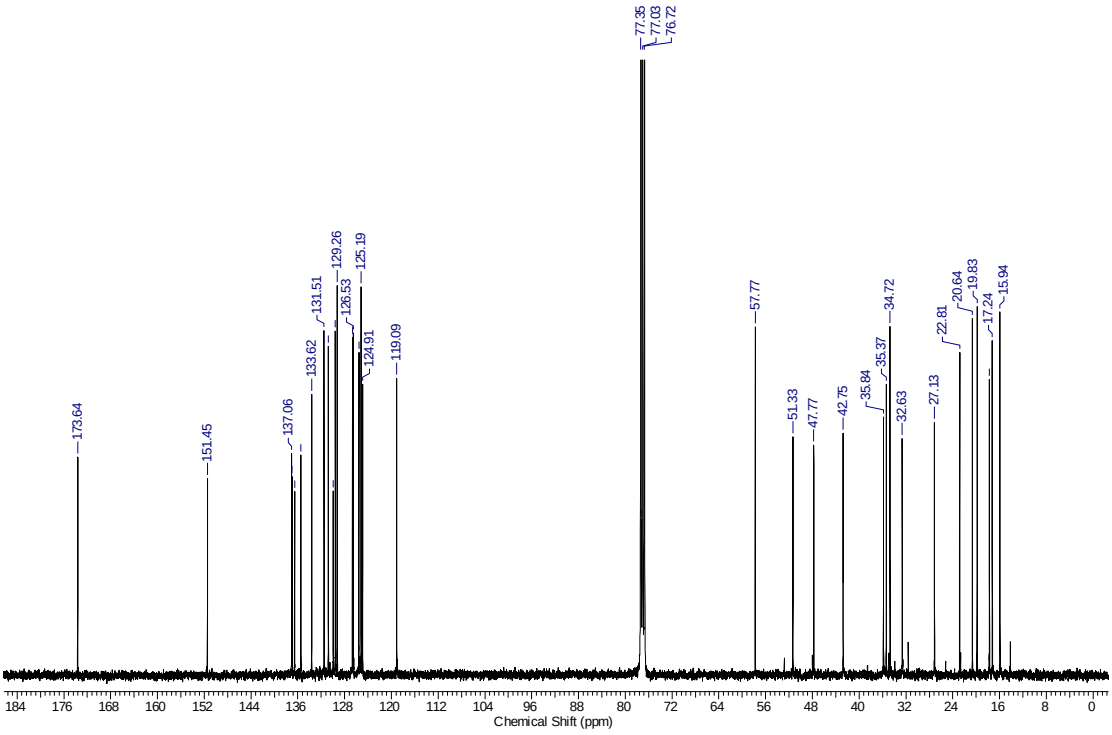
^{13}C NMR (101 MHz, $CDCl_3$)



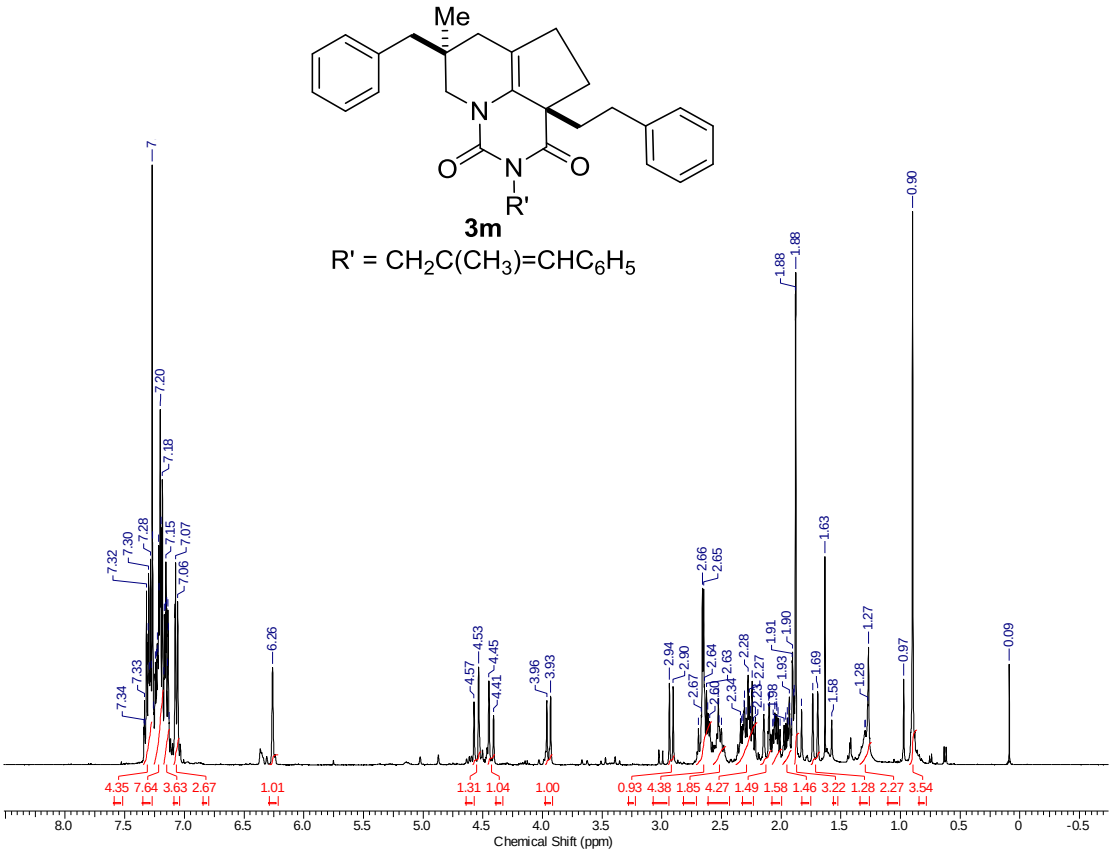
^{1}H NMR (400 MHz, $CDCl_3$)



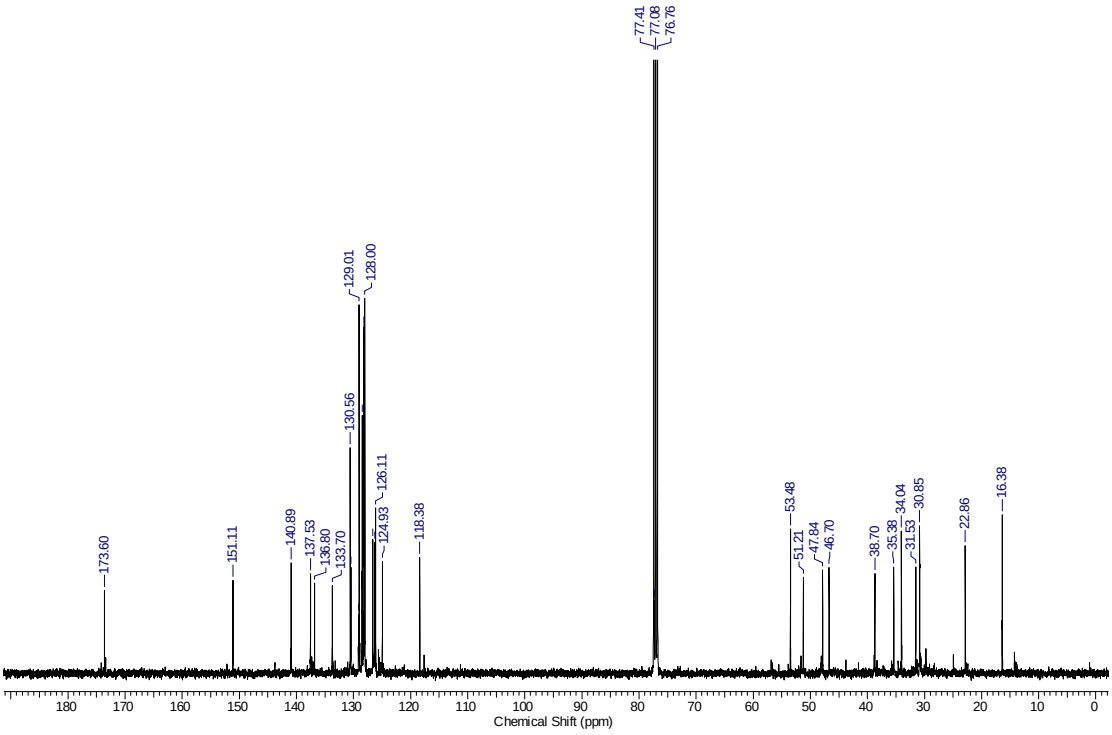
^{13}C NMR (101 MHz, $CDCl_3$)



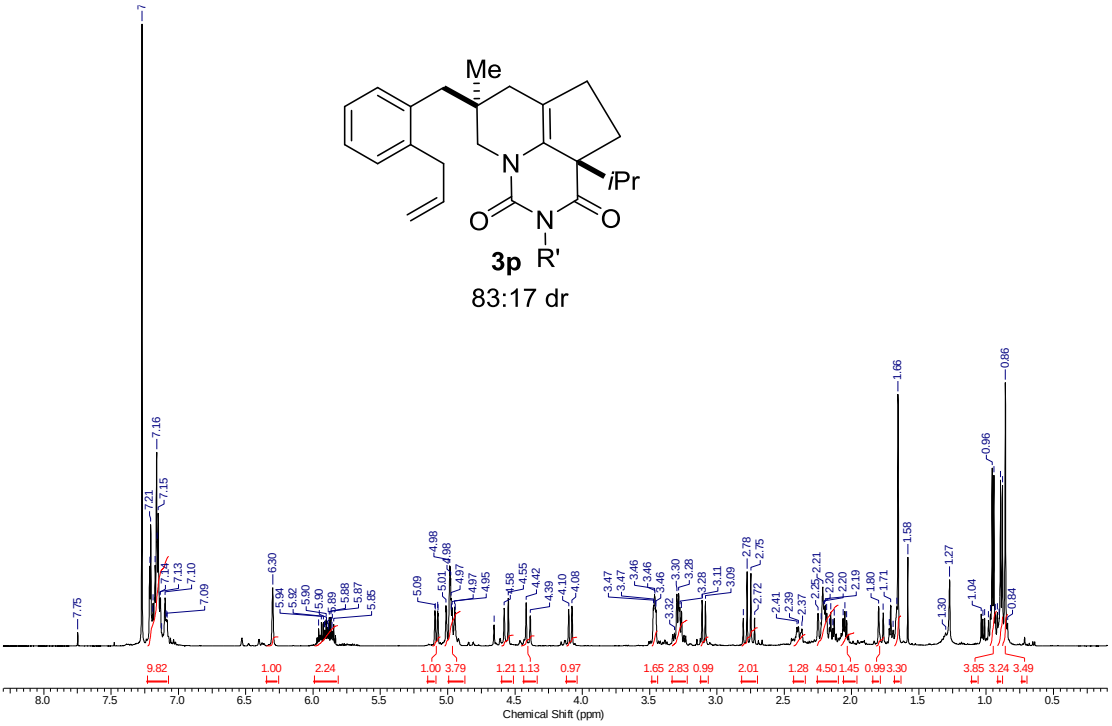
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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