Electronic Supplementary Material (ESI) for ChemComm.

A Serendipitous Cascade of Rhodium Vinylcarbenoids with Aminochalcones for the Synthesis of Functionalized Quinolines

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Supplementary Information

A. MATERIALS AND METHODS

Reagents

Reagents and solvents were obtained from Sigma-Aldrich (www.sigma-aldrich.com), Chem-Impex (www.chemimpex.com) or Acros Organics (www.fishersci.com) and used without further purification unless otherwise indicated. Dry solvents (acetonitrile) were obtained from Acros Organics (www.fishersci.com), and dichloromethane was distilled over CaH under N_2 unless otherwise indicated. THF purchased from Sigma-Aldrich was distilled over Na metal with benzophenone indicator. Toluene was obtained from Sigma-Aldrich.

Reactions

All reactions were performed in flame-dried glassware under positive N_2 pressure with magnetic stirring unless otherwise noted. Liquid reagents and solutions were transferred through rubber septa *via* syringes flushed with N_2 prior to use. Cold baths were generated as follows: 0 °C with wet ice/water and −78 °C with dry ice/acetone. Syringe pump addition reactions were conducted using a Harvard Apparatus (Model: 55-1111) syringe pump.

Chromatography

TLC was performed on 0.25 mm E. Merck silica gel 60 F254 plates and visualized under UV light (254 nm) or by staining with potassium permanganate ($KMnO_4$), cerium ammonium molybdenate (CAM), phosphomolybdic acid (PMA), and ninhydrin. Silica flash chromatography was performed on Sorbtech 230–400 mesh silica gel 60.

Analytical Instrumentation

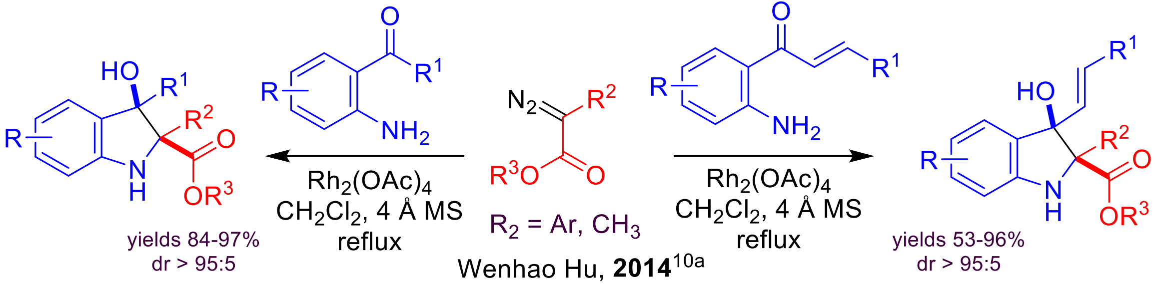
IR spectra were recorded on a Shimadzu IRAffinity-1 FTIR spectrometer with peaks reported in cm^{-1}. NMR spectra were recorded on a Varian VNMRS 300, 400 and 500 MHz NMR spectrometer in $CDCl_3$ unless otherwise indicated. Chemical shifts are expressed in ppm relative to solvent signals: $CDCl_3$ (^1H, 7.26 ppm, ^{13}C, 77.0 ppm); coupling constants are expressed in Hz. NMR spectra were processed using Mnova (www.mestrelab.com/software/mnova-nmr). Mass spectra were obtained on an Advion Expression^L CMS Mass Spectrometer or at the OU Analytical Core Facility on an Agilent 6538 High-Mass-Resolution QTOF Mass Spectrometer and an Agilent 1290 UPLC. X-ray crystallography analysis was carried out at the University of Oklahoma using a Bruker APEX ccd area detector (1) and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) source. Crystal structures were visualized using CCDC Mercury software (http://www.ccdc.cam.ac.uk/products/mercury/).

Nomenclature

N.B.: Atom numbers shown in chemical structures herein correspond to IUPAC nomenclature, which was used to name each compound.

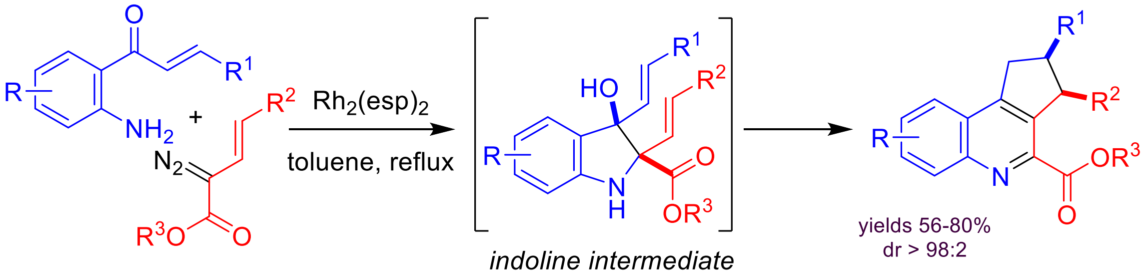
B. PREVIOUS APPROACH TO INDOLINE SCAFFOLD

Previous work

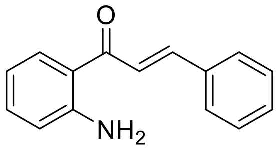


* No example with vinyldiazoacetates

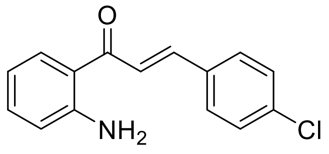
This work



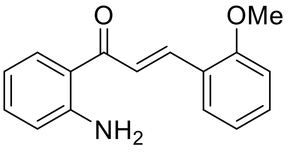
C. Synthesis of 2'-Aminochalcones 1a–1k



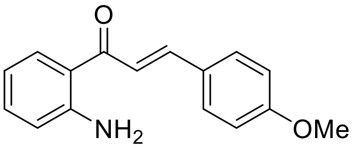
1a[1]



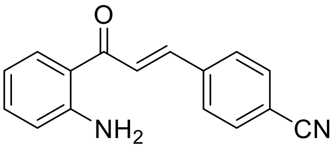
1b[1]



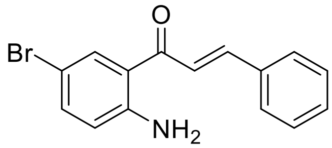
1c[2]



1d[1]



1e[3]



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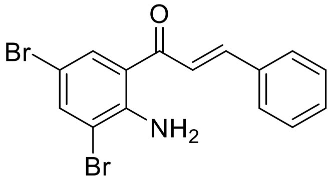
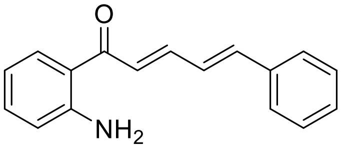
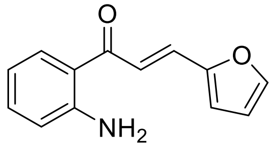


1g[5]

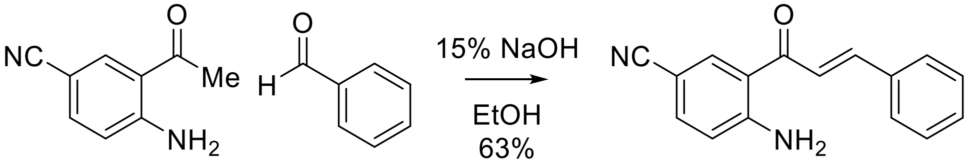


1j[6]



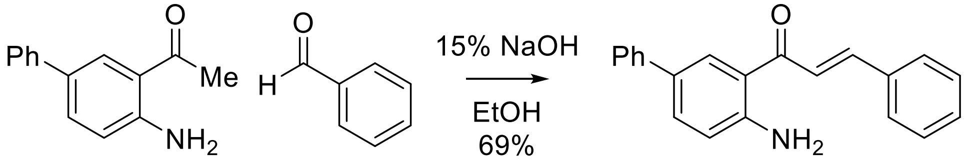
1k[7]

All 2'-aminochalcone starting materials **(1a-1k)**[1-7] were synthesized using known literature protocols except **1h** and **1i**.



1h

4-amino-3-cinnamoylbenzonitrile (1h). 3-acetyl-4-aminobenzonitrile (3.4 mmol) was added to a solution of benzaldehyde (4.1 mmol) in 15 mL of ethanol containing 15 wt % NaOH and stirred at 25 °C for 7 h then the solvent EtOH was removed completely, diluted with 1 M HCl aqueous solution (10 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification of the crude compound over silica gel (gradient elution with 20–25% EtOAc in Hexane) yielded the compound **1h** as a yellow solid {537 mg, 63%, (95% purity) mp 139–140 °C}. **TLC**: R_f 0.25 (4:1 hexanes/EtOAc). **IR** (NaCl): 3435, 3318, 3059, 3028, 2378, 2311, 2218, 1647, 1618, 1570, 1545, 1489, 1449, 1423, 1362, 1335, 1302, 1275, 1227, 1173, 1013, 978, 858, 827, 777, 743, 698, 679, 635. **^{1}H NMR** (400 MHz) δ 8.19 (d, J = 1.9 Hz, 1H), 7.78 (d, J = 12.0 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.53 (d, J = 12.0 Hz, 1H), 7.50 – 7.42 (m, 4H), 6.89 (s, 2H), 6.71 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (101 MHz) δ 190.4, 153.5, 144.8, 136.5, 136.2, 134.6, 130.7, 129.0 (2C), 128.5 (2C), 121.5, 119.4, 118.5, 117.8, 98.2.



1i

(*E*)-1-(4-amino-[1,1'-biphenyl]-3-yl)-3-phenylprop-2-en-1-one (1i). 1-(4-amino-[1,1'-biphenyl]-3-yl)ethan-1-one (1.7 mmol) was added to a solution of benzaldehyde (1.7 mmol) in 15 mL of ethanol containing 15 wt % NaOH and stirred at 25 °C for 24 h then the solvent EtOH was removed completely, diluted with 1 M HCl aqueous solution (10 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification of the crude compound over silica gel (gradient elution with 20–25% EtOAc in Hexane) yielded the compound **1i** as an orange solid (342 mg, 69%, mp 142-143 °C). **TLC**: R_f 0.40 (4:1 hexanes/EtOAc). **IR** (NaCl): 3746, 3470, 3383, 3333, 3059, 3028, 1647, 1620, 1568, 1493, 1479, 1449, 1352, 1331, 1288, 1265, 1202, 1171, 1074, 1007, 974, 854, 827, 764, 734, 696. **^{1}H NMR** (400 MHz) δ 8.08 (d, J = 2.1 Hz, 1H), 7.82 (d, J = 16.0 Hz, 1H), 7.69 (d, J = 16.0 Hz, 1H), 7.67 – 7.65 (m, 2H), 7.61 – 7.55 (m, 3H), 7.49 – 7.41 (m, 5H), 7.37 – 7.31 (m, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.41 (s, 2H). **^{13}C NMR** (101 MHz) δ 191.7, 150.2, 143.2, 140.5, 135.1, 133.2, 130.1, 129.2, 129.0, 128.8 (2C), 128.8 (2C), 128.3 (2C), 126.5, 126.3 (2C), 123.0, 119.2, 117.8.

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5. Khoza, T. A.; Maluleka, M. M.; Mama, N.; Mphahlele, M. J. *Molecules* **2012**, *17*, 14186–14204.
6. Yang, X.-Y.; Tay, W. S.; Li, Y.; Pullarkat, S. A.; Leung, P.-H. *Organometallics* **2015**, *34*, 5196–5201.
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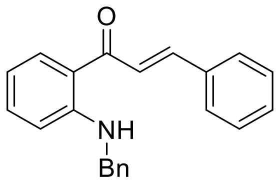
D. SYNTHESIS OF BENZYL PROTECTED 2'-AMINOCHALCONES 1l



1l

Compound **1l** was synthesized using known literature protocol.[8]

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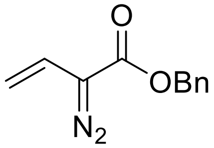
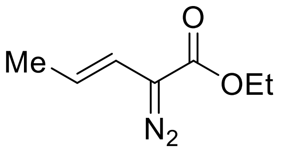
[8] Tang, E.; Chen, B.; Zhang, L.; Li, W.; Lin, J. *Synlett* **2011**, *2011*, 707–711.

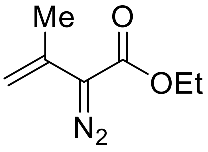
E. SYNTHESIS OF VINYLDIAZOACETATES 2a-2e



2a

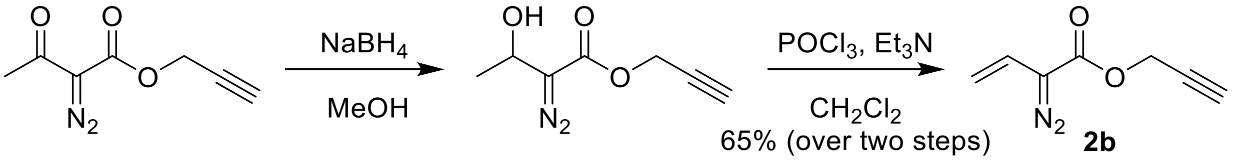


2c

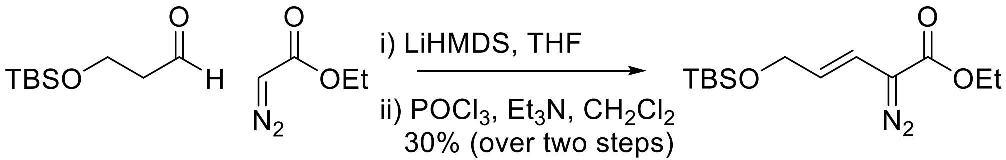


2e

Benzyl 2-diazobut-3-enoate (2a) and ethyl (*E*)-2-diazopent-3-enoate (2c). Compounds were prepared using known literature procedure.[9,10,11]



Prop-2-yn-1-yl 2-diazobut-3-enoate (2b). The solution of keto ester (3.61 mmol) in 12 mL MeOH at 0 °C was slowly added $NaBH_4$ (137 mg, 3.61 mmol). The resulting solution was warmed to room temperature and stirred for 30 min. The MeOH was evaporated and the residue was diluted with water (15 mL) and extracted with EtOAc (50 mL) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by column chromatography (3:1 hexanes/EtOAc) to give alcohol. To a solution of alcohol (3.42 mmol) and Et_3N (4.0 equiv) in 20 mL CH_2Cl_2 at 0 °C was slowly added a solution of $POCl_3$ (0.48 ml, 5.13 mmol, 1.5 equiv) in 5 mL CH_2Cl_2 over 5 minutes. The resulting solution was stirred at 0 °C for 2 h then the reaction mixture was diluted with DCM (10 mL) and water (10 mL). The aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification of the crude compound over silica gel (gradient elution with 5–10% EtOAc in Hexane) yielded the pure compound **2b** (351 mg, 65% over two steps) as a red oil. **IR** (NaCl): 3298, 3951, 2091, 1709, 1616, 1433, 1375, 1306, 1267, 1148, 1099, 1148, 1099, 1032, 978, 920, 880, 743, 681, 644. **^{1}H NMR** (400 MHz) δ 6.15 (dd, J = 17.3, 11.0 Hz, 1H), 5.13 (dd, J = 11.0, 3.3 Hz, 1H), 4.88 (dd, J = 17.6, 3.3 Hz, 1H), 4.80 (s, 2H), 2.49 (s, 1H). **^{13}C NMR** (101 MHz) δ 163.9, 119.9, 107.9, 77.4, 75.2, 52.4 (C=N_2 not observed).



2d

Ethyl (*E*)-5-((tert-butyldimethylsilyl)oxy)-2-diazopent-3-enoate (2d). To a solution of ethyl diazoacetate (1.0 equiv, 0.2 M) in 7 mL anhydrous THF at –78 °C, was added LiHMDS (1.0 equiv, 1 M) in THF. The resulting mixture was stirred for 15 min at –78 °C. 3-((tert-butyldimethylsilyl)oxy)propanal (1.0 equiv, 0.8 M) in THF prepared from known literature protocol was added.[12] The resulting solution was stirred at –78 °C to –20 °C for 2 h. The reaction mixture was quenched by saturated solution of NH_4Cl (10 mL), extracted with EtOAc (30 mL) and the combined layers were dried over Na_2SO_4 and concentrated under reduced pressure to give the crude compound ethyl 5-((tert-butyldimethylsilyl)oxy)-2-diazo-3-hydroxypentanoate

(0.5 mmol, 1.0 equiv), which was redissolved in dry CH_2Cl_2 (3 mL) and Et_3N (2.2 mmol, 4.0 equiv) at 0 °C. Then a solution of $POCl_3$ (0.48 mL, 5.3 mmol) in 3 mL CH_2Cl_2 was added over a period of 5 min. The resulting solution was stirred for 2 h at 0 °C. The reaction mixture was poured into ice water and extracted with CH_2Cl_2 (30 mL). The combined layers were dried over Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification of the crude compound over silica gel (1:49 EtOAc:Hex) yielded the pure compound **2d** (101 mg, 30% over two steps) as a red liquid **TLC**: R_f 0.60 (9:1 hexanes/EtOAc). **IR** (NaCl): 2955, 2932, 2857, 2083, 1707, 1649, 1468, 1371, 1331, 1128, 1103, 1065, 1011, 955, 837, 777, 739. **^{1}H NMR** (400 MHz) δ 6.02 (dt, J = 16.0, 4.0 Hz, 1H), 5.44 (dt, J = 16.0, 8.0 Hz, 1H), 4.29 – 4.23 (m, 4H), 1.29 (t, J = 9.0 Hz, 3H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (101 MHz) δ 165.3, 123.2, 113.2, 63.4, 61.1, 25.9 (3C), 25.8, 18.4, 14.4, -5.2 (2C).

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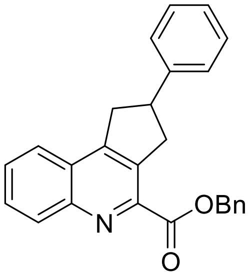
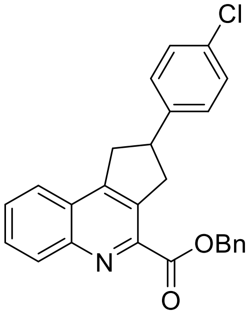
F. GENERAL PROCEDURE FOR THE SYNTHESIS OF QUINOLINES 4a–4p

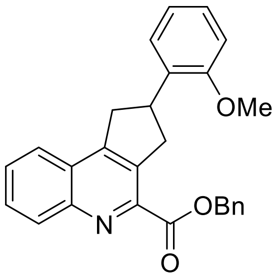
To a stirred solution of 2'-aminochalcone **1** (0.11 mmol) and $Rh_2(esp)_2$ (1 mol%) in 1.1 mL toluene was added a solution of corresponding vinyl diazoacetate **2** (0.22 mmol) in 0.5 mL toluene over 2.5 h *via* syringe pump at room temperature. After the addition was completed, the reaction was left to stir for an additional 30 minutes. The crude reaction mixture was concentrated using rotary evaporation and then purified using flash column chromatography eluting with 1:3 ethyl acetate: hexanes to afford quinoline product **4a–4o**.



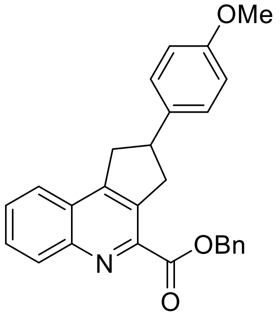
Benzyl 2-phenyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4a). Pale yellow oil (34.0 mg, 77%). **TLC**: R_f 0.34 (4:1 hexanes/EtOAc). **IR** (NaCl): 3738, 3032, 2943, 1718, 1649, 1568, 1500, 1454, 1390, 1317, 1244, 1192, 1157, 1087, 1012, 754, 698. ^{1}**H NMR** (400 MHz) δ 8.32 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.52 (d, J = 6.9 Hz, 2H), 7.40 – 7.31 (m, 8H), 5.53 (s, 2H), 4.01 – 3.79 (m, 3H), 3.56 (dd, J = 16.7, 7.0 Hz, 1H), 3.41 (dd, J = 16.6, 7.4 Hz, 1H). ^{13}**C NMR** (101 MHz) δ 165.7, 151.6, 146.8, 144.9, 144.8, 136.3, 135.8, 131.1, 129.3, 128.6 (2C), 128.6 (2C), 128.5 (2C), 128.5, 128.3, 126.9 (2C), 126.8, 126.5, 123.9, 67.4, 44.3, 41.7, 39.1. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{22}NO_2$ ($[M+H]^+$) 380.1651; found 380.1656.



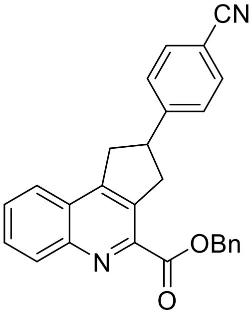
Benzyl 2-(4-chlorophenyl)-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4b). Pale yellow solid (35.0 mg, 74%). Recrystallization from 4:1 hexanes/EtOAc (slow evaporation method) yielded triclinic colorless needles (mp 152-155 °C). **TLC**: R_f 0.18 (4:1 hexanes/EtOAc). **IR** (NaCl): 3062, 3034, 2941, 2370, 1718, 1602, 1579, 1568, 1492, 1454, 1386, 1361, 1317, 1242, 1192, 1157, 1089, 1012, 827, 758, 698. ^{1}**H NMR** (500 MHz) δ 8.31 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.74 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H), 7.64 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.40 – 7.36 (m, 2H), 7.35 – 7.32 (m, 1H), 7.29 – 7.27 (m, 2H), 7.24 – 7.21 (m, 2H), 5.52 (s, 2H), 3.96 (dd, J = 17.2, 8.4 Hz, 1H), 3.89 – 3.78 (m, 2H), 3.51 (dd, J = 17.3, 7.2 Hz, 1H), 3.36 (dd, J = 16.4, 7.2 Hz, 1H). ^{13}**C NMR** (101 MHz) δ 165.6, 151.2, 146.9, 144.7, 143.4, 136.1, 135.8, 132.2, 131.1, 129.4, 128.7 (2C), 128.6, 128.5 (2C), 128.5 (2C), 128.3 (2C), 128.3, 126.7, 123.9, 67.4, 43.7, 41.6, 39.0. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{21}ClNO_2$ ($[M+H]^+$) 414.1261; found 414.1270.



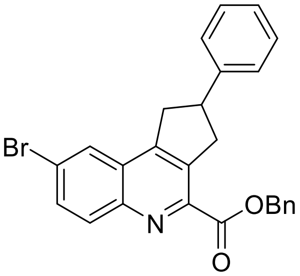
Benzyl 2-(2-methoxyphenyl)-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4c). Pale yellow oil (31.0 mg, 65%). **TLC**: R_f 0.39 (7:3 hexanes/EtOAc). **IR** (NaCl): 3062, 3034, 2943, 2837, 1720, 1598, 1581, 1566, 1492, 1458, 1436, 1388, 1317, 1244, 1192, 1157, 1111, 1087, 1053, 1022, 754, 698. ^{1}**H NMR** (500 MHz) δ 8.31 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.62 (ddd, J = 8.1, 6.7, 1.2 Hz, 1H), 7.52 (d, J = 6.8 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.24 – 7.19 (m, 2H), 6.91 – 6.87 (m, 2H), 5.52 (s, 2H), 4.17 – 4.14 (m, 1H), 3.87 (dd, J = 17.2, 8.7 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, J = 17.0, 8.8 Hz, 1H), 3.60 (dd, J = 17.2, 7.6 Hz, 1H), 3.43 (dd, J = 17.0, 7.8 Hz, 1H). ^{13}**C NMR** (101 MHz) δ 165.8, 157.4, 152.2, 146.7, 144.9, 136.8, 135.9, 132.6, 131.0, 129.1, 128.6, 128.5 (2C), 128.5 (2C), 128.3, 128.2, 127.5, 127.3, 124.1, 120.5, 110.5, 67.3, 55.3, 39.9, 38.7, 37.5. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{24}NO_3$ ($[M+H]^+$) 410.1756; found 410.1768.



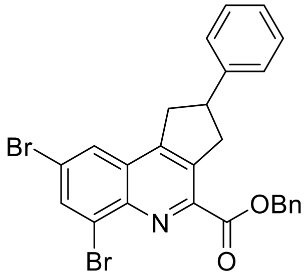
Benzyl 2-(4-methoxyphenyl)-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4d). Orange solid (38.3 mg, 80%, mp 108-111 °C). **TLC**: R_f 0.32 (7:3 hexanes/EtOAc). **IR** (NaCl): 3062, 3034, 2939, 2835, 1718, 1610, 1512, 1456, 1382, 1315, 1246, 1188, 1157, 1087, 1031, 1014, 829, 756. ^{1}**H NMR** (500 MHz) δ 8.31 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.63 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.52 (d, J = 6.8 Hz, 2H), 7.39 – 7.36 (m, 2H), 7.35 – 7.31 (m, 1H), 7.22 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.52 (s, 2H), 3.94 (dd, J = 17.0, 8.4 Hz, 1H), 3.85 (q, J = 8.1 Hz, 1H), 3.80 (s, 3H), 3.78 (t, J = 8.6 Hz, 1H), 3.51 (dd, J = 17.1, 7.4 Hz, 1H), 3.36 (dd, J = 16.5, 7.5 Hz, 1H). ^{13}**C NMR** (101 MHz) δ 165.7, 158.2, 151.7, 146.8, 144.8, 136.9, 136.4, 135.8, 131.1, 129.2, 128.5 (2C), 128.5 (2C), 128.4, 128.3, 127.8 (2C), 126.8, 123.9, 113.9 (2C), 67.4, 55.3, 43.6, 41.8, 39.2. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{24}NO_3$ ($[M+H]^+$) 410.1756; found 410.1762.



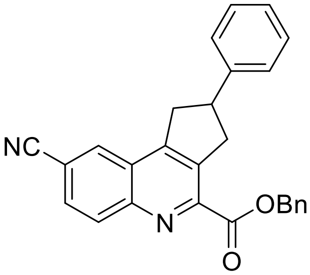
Benzyl 2-(4-cyanophenyl)-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4e). Pale yellow solid (30.3 mg, 62%, mp 165-167 °C). **TLC**: R_f 0.30 (7:3 hexanes/EtOAc). **IR** (NaCl): 3061, 3035, 2926, 2382, 2345, 2225, 1720, 1608, 1502, 1317, 1244, 1192, 1157, 1087, 1012, 839, 756. **^{1}H NMR** (400 MHz) δ 8.32 (d, J = 8.5 Hz, 1H), 7.82 (dd, J = 8.3, 1.4 Hz, 1H), 7.76 (ddd, J = 8.6, 6.8, 1.5 Hz, 1H), 7.66 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.53 – 7.51 (m, 2H), 7.40 – 7.33 (m, 5H), 5.52 (s, 2H), 4.04 – 3.90 (m, 2H), 3.85 (dd, J = 17.0, 8.5 Hz, 1H), 3.54 (dd, J = 16.4, 6.3 Hz, 1H), 3.39 (dd, J = 17.0, 7.1 Hz, 1H). **^{13}C NMR** (101 MHz) δ 165.6, 150.8, 150.6, 146.9, 144.6, 135.7, 132.5 (2C), 131.2, 129.6, 128.8, 128.6 (3C), 128.6 (2C), 128.4, 127.8 (2C), 126.6, 123.8, 118.8, 110.4, 67.5, 44.2, 41.5, 38.8. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{21}N_2O_2$ ($[M+H]^+$) 405.1603; found 405.1601.



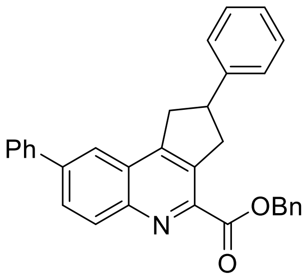
Benzyl 8-bromo-2-phenyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4f). Pale yellow oil (35.0 mg, 76%). **TLC**: R_f 0.32 (4:1 hexanes/EtOAc). **IR** (NaCl): 3062, 3032, 2922, 1722, 1581, 1490, 1292, 1238, 1182, 1012, 827, 754, 698. **^{1}H NMR** (500 MHz) δ 8.17 (d, J = 9.1 Hz, 1H), 7.99 (d, J = 2.2 Hz, 1H), 7.79 (dd, J = 9.1, 2.2 Hz, 1H), 7.51 (d, J = 6.8 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.35 – 7.31 (m, 3H), 7.30 – 7.27 (m, 2H), 7.25 (d, J = 2.6 Hz, 1H), 5.51 (s, 2H), 3.97 (dd, J = 17.1, 8.7 Hz, 1H), 3.91 – 3.88 (m, 1H), 3.76 (dd, J = 17.2, 8.6 Hz, 1H), 3.56 (dd, J = 17.1, 7.3 Hz, 1H), 3.37 (dd, J = 17.0, 7.8 Hz, 1H). **^{13}C NMR** (101 MHz) δ 165.4, 150.8, 145.3, 145.1, 144.6, 137.4, 135.6, 132.9, 132.7, 128.7 (2C), 128.6 (4C), 128.4, 127.9, 126.8 (2C), 126.6, 126.4, 122.9, 67.5, 44.2, 41.6, 38.9. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{20}BrNO_2Na$ ($[M+Na]^+$) 480.0575; found 480.0574.



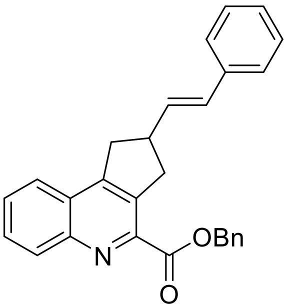
Benzyl 6,8-dibromo-2-phenyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4g). White needles (30.5 mg, 72%, mp 136-137 °C). **TLC**: *R_f* 0.62 (7:3 hexanes/EtOAc). **IR** (NaCl): 3062, 3030, 2943, 2895, 1720, 1676, 1597, 1577, 1544, 1496, 1471, 1454, 1425, 1396, 1361, 1330, 1274, 1182, 1116, 1076, 1026, 956, 908, 856, 777. **^{1}H NMR** (500 MHz) δ 8.17 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 2.1 Hz, 1H), 7.58 – 7.56 (m, 2H), 7.42 – 7.39 (m, 2H), 7.36 – 7.32 (m, 3H), 7.29 – 7.27 (m, 3H), 5.54 – 5.48 (m, 2H), 4.03 – 3.90 (m, 2H), 3.77 (dd, *J* = 17.1, 8.5 Hz, 1H), 3.59 (dd, *J* = 16.9, 7.0 Hz, 1H), 3.37 (dd, *J* = 17.2, 7.6 Hz, 1H). **^{13}C NMR** (126 MHz) δ 165.0, 151.6, 145.4, 144.4, 142.8, 138.5, 135.9, 135.7, 128.7 (2C), 128.6 (2C), 128.4, 128.2, 128.1 (2C), 127.8, 126.8 (2C), 126.7, 126.2, 122.1, 67.3, 44.3, 41.2, 39.1. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{19}Br_2NO_2Na$ ([M+Na]$^+$) 557.9680; found 557.9680.



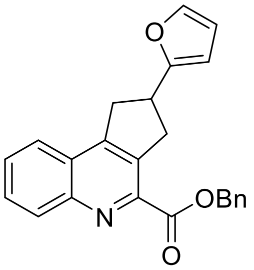
Benzyl 8-cyano-2-phenyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4h). Pale yellow oil {32.7 mg, 67% (95% purity)}. **TLC**: *R_f* 0.38 (7:3 hexanes/EtOAc). **IR** (NaCl): 3062, 3032, 2949, 2225, 1724, 1647, 1608, 1566, 1498, 1454, 1384, 1348, 1307, 1267, 1246, 1184, 1155, 1095, 1053, 1014, 956, 908, 837, 754. **^{1}H NMR** (300 MHz) δ 8.39 (d, *J* = 8.8 Hz, 1H), 8.24 (d, *J* = 1.2 Hz, 1H), 7.86 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.39 – 7.36 (m, 3H), 7.35 – 7.32 (m, 3H), 7.30 – 7.27 (m, 3H), 5.52 (s, 2H), 4.03 – 3.91 (m, 2H), 3.88 – 3.77 (m, 1H), 3.64 – 3.54 (m, 1H), 3.48 – 3.40 (m, 1H). **^{13}C NMR** (101 MHz) δ 165.0, 152.7, 147.6, 147.4, 144.1, 138.2, 135.3, 132.4, 130.6, 129.7, 128.8 (2C), 128.6 (2C), 128.6 (2C), 128.5, 126.8 (2C), 126.8, 126.1, 118.4, 111.9, 67.8, 44.2, 41.5, 38.9. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{21}N_2O_2$ ([M+H]$^+$) 405.1603; found. 405.1603.



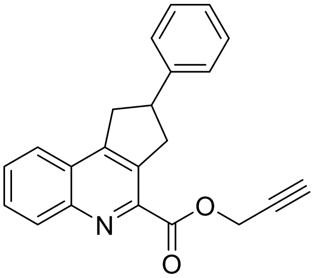
Benzyl 2,8-diphenyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4i). Pale yellow oil (33.8 mg, 74%). **TLC**: R_f 0.19 (4:1 hexanes/EtOAc). **IR** (NaCl): 3399, 3368, 3341, 3059, 3032, 2947, 2924, 1721, 1493, 1452, 1310, 1252, 1182, 1101, 1013, 908, 837, 754. **^{1}H NMR** (400 MHz) δ 8.38 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 9.8 Hz, 2H), 7.74 (d, J = 7.7 Hz, 2H), 7.52 (q, J = 7.7 Hz, 4H), 7.55 – 7.32 (m, 9H), 5.54 (s, 2H), 4.03 – 3.84 (m, 3H), 3.59 (dd, J = 16.9, 6.4 Hz, 1H), 3.46 (dd, J = 15.9, 6.5 Hz, 1H). **^{13}C NMR** (101 MHz) δ 165.7, 151.7, 146.2, 144.9, 144.6, 141.2, 140.1, 136.8, 135.8, 131.5, 129.1, 129.0 (2C), 128.6 (2C), 128.6 (4C), 128.3, 128.1, 127.5 (2C), 127.1, 126.9 (2C), 126.5, 121.6, 67.4, 44.3, 41.7, 39.1. **HRMS** (ESI) *m/z* calcd for $C_{32}H_{26}NO_2$ ([M+H]$^+$) 456.1964; found 456.1964.



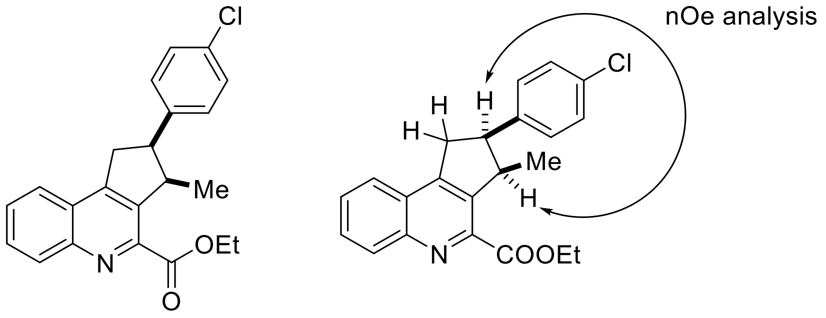
Benzyl (*E*)-2-styryl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4j). Pale yellow oil (35 mg, 72%). **TLC**: R_f 0.45 (7:3 hexanes/EtOAc). **^{1}H NMR** (400 MHz) δ 8.30 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.40 – 7.29 (m, 7H), 7.26 – 7.20 (m, 1H), 6.54 (d, J = 15.7 Hz, 1H), 6.39 (dd, J = 15.8, 7.7 Hz, 1H), 5.53 (s, 2H), 3.76 (dd, J = 16.8, 8.0 Hz, 1H), 3.61 (dd, J = 16.6, 8.3 Hz, 1H), 3.52 – 3.43 (m, 1H), 3.36 (dd, J = 17.0, 7.2 Hz, 1H), 3.21 (dd, J = 16.8, 7.3 Hz, 1H). **^{13}C NMR** (101 MHz) δ 165.7, 151.7, 146.7, 144.9, 137.2, 136.3, 135.8, 133.0, 131.1, 129.8, 129.2, 128.6 (2C), 128.5 (4C), 128.4, 128.3, 127.3, 126.9, 126.1 (2C), 124.0, 67.4, 42.6, 40.1, 37.6. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{24}NO_2$ ([M+H]$^+$) 406.1807; found 406.1806.



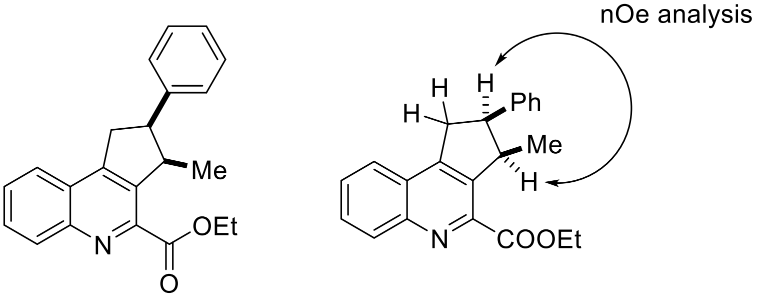
4-((benzyloxy)(l3-oxidaneylidene)methyl)-2-(furan-2-yl)-2,3-dihydro-1H-cyclopenta[c]quinoline (4k). Pale yellow oil (30 mg, 62%). **TLC**: R_f 0.33 (4:1 hexanes/EtOAc). **IR** (NaCl): 3743, 3062, 3034, 2947, 1718, 1560, 1504, 1454, 1425, 1388, 1244, 1192, 1157, 1085, 1012, 756, 736, 698. **^{1}H NMR** (400 MHz) δ 8.30 (d, J = 8.5 Hz, 1H), 7.82 (dd, J = 8.2, 1.4 Hz, 1H), 7.72 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H), 7.63 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.41 – 7.34 (m, 4H), 6.30 (dd, J = 3.2, 1.9 Hz, 1H), 6.11 (d, J = 3.2 Hz, 1H), 5.53 (s, 2H), 3.97 – 3.85 (m, 2H), 3.77 – 3.70 (m, 1H), 3.65 – 3.60 (m, 1H), 3.50 – 3.44 (m, 1H). **^{13}C NMR** (101 MHz) δ 165.6, 157.5, 151.1, 146.7, 144.7, 141.4, 135.9, 135.8, 131.1, 129.3, 128.5 (2C), 128.5 (3C), 128.3, 126.8, 123.9, 110.1, 104.5, 67.4, 39.0, 37.5, 36.5. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{20}NO_3$ ($[M+H]^+$) 370.1443; found 370.1455.



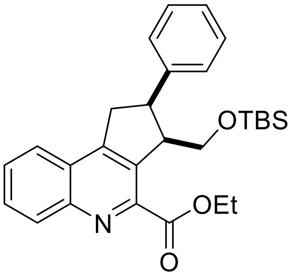
Prop-2-yn-1-yl 2-phenyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4l). Pale yellow oil (34.2 mg, 78%). **TLC**: R_f 0.28 (4:1 hexanes/EtOAc). **IR** (NaCl): 3286, 3061, 3028, 2937, 2846, 2384, 2345, 2038, 1726, 1570, 1498, 1452, 1429, 1386, 1363, 1317, 1242, 1190, 1157, 1087, 1026, 1004, 758, 702, 636. **^{1}H NMR** (400 MHz) δ 8.32 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.75 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H), 7.65 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.34 – 7.33 (m, 4H), 7.27 – 7.23 (m, 1H), 5.06 (d, J = 2.5 Hz, 2H), 4.05 (dd, J = 17.1, 8.5 Hz, 1H), 3.97 – 3.87 (m, 1H), 3.83 (dd, J = 16.7, 8.8 Hz, 1H), 3.61 (dd, J = 17.2, 7.5 Hz, 1H), 3.43 (dd, J = 16.8, 7.8 Hz, 1H), 2.53 (t, J = 2.5 Hz, 1H). **^{13}C NMR** (101 MHz) δ 165.1, 152.0, 146.9, 145.0, 144.0, 136.8, 131.2, 129.6, 128.8, 128.8 (2C), 127.1 (2C), 127.0, 126.7, 124.2, 77.6, 75.5, 53.3, 44.5, 41.8, 39.3. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{18}NO_2$ ($[M+H]^+$) 328.1338; found 328.1339.



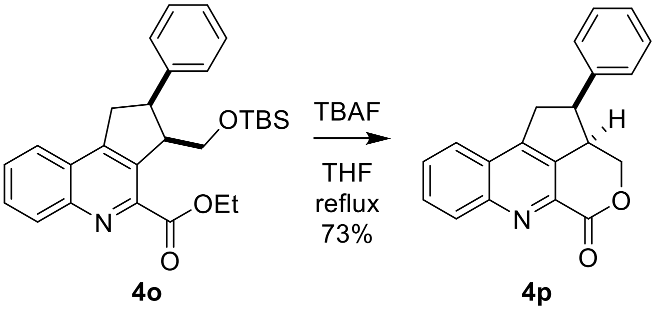
Ethyl-2-(4-chlorophenyl)-3-methyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4m). Orange solid (24.6 mg, 58%). Recrystallization from ethyl acetate (slow evaporation method) yielded triclinic colorless plates (mp 165 – 167 °C). **TLC**: R_f 0.50 (7:3 hexanes/EtOAc). **IR** (NaCl): 3061, 2972, 2930, 2868, 1719, 1568, 1493, 1454, 1371, 1317, 1244, 1188, 1159, 1094, 1032, 1022, 829, 760, 733. **^{1}H NMR** (300 MHz) δ 8.32 (d, J = 9.0 Hz, 1H), 7.91 (dt, J = 8.1, 1.0 Hz, 1H), 7.75 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H), 7.66 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.40 – 7.32 (m, 4H), 4.56 (q, J = 7.1 Hz, 2H), 4.25 (p, J = 7.1 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.58 (d, J = 9 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H), 0.88 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (75 MHz) δ 165.7, 150.6, 146.6, 144.8, 141.9, 138.8, 132.3, 131.1, 129.5 (2C), 129.4, 128.5 (2C), 128.5, 127.0, 124.0, 62.0, 48.8, 43.7, 32.0, 15.4, 14.3. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{21}ClNO_2$ ([M+H]$^+$) 366.1261 ; found 366.1266.



Ethyl-3-methyl-2-phenyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4n). Pale yellow oil (24.8 mg, 56%). **TLC**: R_f 0.30 (4:1 hexanes/EtOAc). **IR** (NaCl): 3061, 2972, 2934, 2903, 1719, 1603, 1570, 1499, 1452, 1371, 1317, 1242, 1190, 1159, 1099, 1032, 864, 779, 754, 700. **^{1}H NMR** (300 MHz) δ 8.31 (ddd, J = 8.5, 1.4, 0.7 Hz, 1H), 7.92 (ddd, J = 8.1, 1.6, 0.7 Hz, 1H), 7.75 (ddd, J = 8.5, 6.8, 1.6 Hz, 1H), 7.66 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.42 – 7.40 (m, 4H), 4.56 (q, J = 6.0 Hz, 2H), 4.27 (p, J = 9.0 Hz, 1H), 4.09 – 3.94 (dt, J = 12.0, 6.0 Hz, 1H), 3.70 – 3.53 (m, 3H), 1.49 (t, J = 9.0 Hz, 3H), 0.89 (d, J = 9.0 Hz, 3H). **^{13}C NMR** (75 MHz) δ 165.7, 150.9, 146.6, 144.8, 142.2, 140.2, 131.0, 129.3, 128.3 (2C), 128.2 (2C), 127.0, 126.5, 124.1, 122.4, 62.0, 49.3, 43.8, 31.9, 15.5, 14.3. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{21}NO_2Na$ ([M+H]$^+$) 332.1651; found 332.1656.

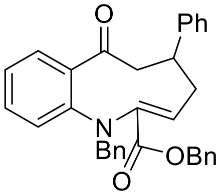


Ethyl-3-(((tert-butyldimethylsilyl)oxy)methyl)-2-phenyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4o). White oil (45.8 mg, 74%). **TLC**: R_f 0.50 (8:2 hexanes/EtOAc). **IR** (NaCl): 3854, 3744, 3618, 2951, 2930, 2887, 2857, 1717, 1647, 1562, 1504, 1464, 1368, 1317, 1248, 1186, 1157, 1119, 1094, 1061, 1030, 837, 777, 698. **^{1}H NMR** (400 MHz) δ 8.31 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.0 Hz 1H), 7.75 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.66 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.33 – 7.29 (m, 1H), 4.55 (qd, J = 7.1, 2.2 Hz, 2H), 4.18 (d, J = 8.1 Hz, 1H), 4.03 (dt, J = 11.8, 8.0 Hz, 1H), 3.92 – 3.83 (m, 2H), 3.55 – 3.48 (m, 2H), 1.49 (t, J = 7.1 Hz, 3H), 0.49 (s, 9H), -0.33 (s, 3H), -0.59 (s, 3H). **^{13}C NMR** (101 MHz) δ 166.1, 154.2, 146.6, 139.9, 137.4, 130.9, 129.3, 128.7 (2C), 128.3, 128.3, 128.2 (2C), 126.8, 126.6, 124.0, 62.8, 61.9, 51.6, 49.1, 35.3, 25.4 (3C), 17.7, 14.4, -6.1, -6.3. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{36}NO_3Si$ ($[M+H]^+$) 462.2464; found 462.2461.



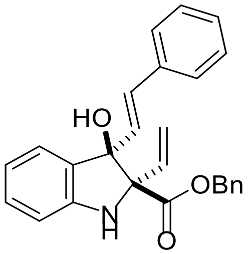
Ethyl-3-(((tert-butyldimethylsilyl)oxy)methyl)-2-phenyl-2,3-dihydro-1H-cyclopenta[c]quinoline-4-carboxylate (4p). To a solution of **4o** (0.06 mmol, 0.03 M) in THF was added tetrabutylammonium fluoride solution (4.0 equiv, 1.0 M) in THF at 0 °C. Reaction was then refluxed 4 h and then quenched with water. The aqueous layer was extracted with EtOAc (3 × 5 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification of the crude compound over silica gel (elution with 100% EtOAc) yielded the compound **4p** as a pale yellow oil (13.8 mg, 73%). **TLC**: R_f 0.1 (5% MeOH/EtOAc). **IR** (NaCl): 3408, 3059, 2928, 2880, 1730, 1663, 1589, 1452, 1387, 1240, 1188, 1159, 1074, 1043, 760, 735, 702. **^{1}H NMR** (400 MHz) δ 8.27 (d, J = 8.5 Hz, 1H), 8.04 – 7.98 (d, J = 9.0 Hz, 1H), 7.85 (t, J = 7.7 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 6.0 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 3.0 Hz, 1H), 4.53 (q, J = 6.4 Hz, 1H), 4.12 (dt, J = 12.1, 7.9 Hz, 1H), 3.96 – 3.86 (m, 2H), 3.62 (dd, J = 16.5, 7.9 Hz, 1H), 3.52 (dd, J = 11.0, 6.6 Hz, 1H). **^{13}C NMR** (101 MHz) δ 164.8, 156.8, 143.8, 142.6, 138.7, 137.7, 131.1, 129.3, 128.7 (2C), 128.0 (2C), 127.5, 127.1, 126.3, 124.6, 62.8, 50.3, 48.8, 33.7. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{15}NO_2Na$ ($[M+H]^+$) 302.1181; found 302.1178.

G. SYNTHESIS OF AZACYCLE 5a



Benzyl (*Z*)-1-benzyl-7-oxo-5-phenyl-4,5,6,7-tetrahydro-1H-benzo[b]azonine-2-carboxylate (5a). To a stirred solution of **1l** (0.11 mmol) and $Rh_2(esp)_2$ (1 mol%) in 1.1 mL toluene was added a solution of vinyl diazoacetate **2a** (0.22 mmol) in 0.5 mL toluene over 2.5 h *via* syringe pump at reflux. After the addition was completed, the reaction was left to stir at refluxing temperature for an additional 30 minutes. The crude reaction mixture was concentrated using rotary evaporation and then purified using flash column chromatography eluting with 10-15% ethyl acetate: hexanes to afford azacycle product **5a** as a pale yellow oil {(20 mg, 38% (95% purity)}. **TLC**: R_f 0.42 (4:1 hexanes/EtOAc). **IR** (NaCl): 3782, 3030, 2390, 2309, 1721, 1686, 1595, 1485, 1449, 1240, 1163, 1142, 1034, 750, 698. **^{1}H NMR** (500 MHz) δ 7.44 (d, J = 6.9 Hz, 2H), 7.40 – 7.27 (m, 9H), 7.24 – 7.15 (m, 6H), 7.12 (d, J = 8.2 Hz, 1H), 7.00 – 6.92 (m, 2H), 5.10 (d, J = 12.4 Hz, 1H), 5.03 – 4.92 (m, 2H), 4.40 (d, J = 14.2 Hz, 1H), 3.65 – 3.56 (m, 1H), 3.46 (t, J = 12.1 Hz, 1H), 2.87 (td, J = 12.1, 9.7 Hz, 1H), 2.44 (d, J = 13.3 Hz, 1H), 2.07 – 2.00 (m, 1H). **^{13}C NMR** (101 MHz) δ 206.1, 163.9, 146.7, 145.3, 142.5, 140.7, 137.2, 135.6, 134.6, 131.3, 128.7 (2C), 128.7 (2C), 128.6 (2C), 128.4 (2C), 128.1, 128.0 (2C), 127.8, 127.6, 126.6, 126.6 (2C), 121.0, 118.3, 66.7, 55.9, 49.4, 41.7, 34.9. **HRMS** (ESI) *m/z* calcd for $C_{33}H_{29}NO_3Na$ ($[M+Na]^+$) 510.2045; found 510.2061.

H. SYNTHESIS OF INDOLINE INTERMEDIATE 6a



Methyl (2*R*, 3*R*)-2-((*E*)-buta-1,3-dien-1-yl)-3-hydroxy-3-((*E*)-2-oxo-4-phenylbut-3-en-1-yl)tetrahydrofuran-2-carboxylate (6a). To a stirred solution of 2'-aminochalcone **1a** (0.11 mmol) and $Rh_2(esp)_2$ (1 mol%) in 1.1 mL CH_2Cl_2 was added a solution of vinyldiazoacetate **2a** (0.22 mmol) in 0.5 mL CH_2Cl_2 over 2.5 h *via* syringe pump at room temperature. After the addition was completed, the reaction was left to stir for an additional 30 minutes. The crude reaction mixture was concentrated using rotary evaporation and then purified using flash column chromatography eluting with 1:3 ethyl acetate: hexanes to afford aldol product **5a** as a liquid (29 mg, 65%). **TLC**: R_f 0.24 (7:3 hexanes/EtOAc). **IR** (NaCl): 3375, 3030, 2363, 2338, 1734, 1605, 1476, 1464, 1373, 1275, 1258, 1171, 1128, 1057, 976, 910, 743, 694, 669, 652. **^{1}H NMR** (400 MHz) δ 7.42 – 7.27 (m, 9H), 7.22 (t, J = 8.1 Hz, 2H), 7.11 (d, J = 7.5 Hz, 1H), 6.90 – 6.77 (m, 3H), 6.40 (d, J = 16.0 Hz, 1H), 6.18 (dd, J = 17.1, 10.4 Hz, 1H), 5.44 – 5.29 (m, 2H), 5.18 (dd, J = 11.4, 4.5 Hz, 2H), 4.64 (s, 1H). **^{13}C NMR** (101 MHz) δ 170.9, 149.1, 136.6, 135.8, 135.3, 131.5, 130.5, 130.4, 128.5 (2C), 128.5 (2C), 128.2, 128.1 (2C), 127.7 (2C), 126.7 (2C), 124.8, 119.9, 115.8, 110.9, 85.8, 80.4, 67.4. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{23}NO_3Na$ ($[M+Na]^+$) 420.1576; found 420.1581. Relative stereochemistry was assigned based on previous literature reports.[13]

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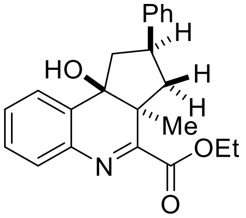
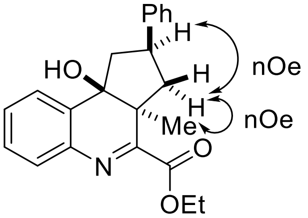
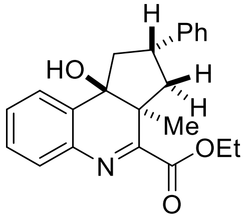
[13] Jing, C.; Xing, D.; Hu, W. *Chemical Communications* **2014**, *50*, 951–953.

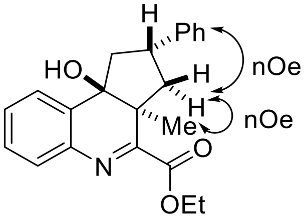
I. SYNTHESIS OF QUINOLINE CASCADE INTERMEDIATE 7a–7b





Prepared using general procedure D. Benzyl-9b-hydroxy-3a-methyl-2-phenyl-2,3,3a,9b-tetrahydro-1H-cyclopenta[c]quinoline-4-carboxylate (7a, major diastereomer). Yellow oil (34 mg, 72%) as a 1.4:1 mixture of diastereromers **7a** and **7b**. **TLC**: R_f 0.25 (4:1 hexanes/EtOAc). **IR** (NaCl): 2976, 2938, 2378, 2315, 1722, 1678, 1603, 1514, 1454, 1393, 1369, 1315, 1294, 1265, 1215, 1163, 1128, 1111, 1043, 858, 772, 752, 702. **^{1}H NMR** (400 MHz) δ 7.66 – 7.64 (m, 1H), 7.56 – 7.54 (m, 1H), 7.39 – 7.37 (m, 2H), 7.33 – 7.28 (m, 4H), 7.22 – 7.16 (m, 1H), 4.55 – 4.45 (m, 1H), 4.45 – 4.35 (m, 1H), 3.22 – 3.11 (m, 1H), 2.73 (dd, J = 13.4, 7.5 Hz, 1H), 2.42 (dd, J = 15.0, 11.5 Hz, 1H), 2.30 – 2.26 (m, 1H), 2.13 (dd, J = 15.1, 6.2 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.44 (t, J = 7.0 Hz, 2H), 1.30 (s, 3H). **^{13}C NMR** (101 MHz) δ 167.3, 165.2, 145.7, 140.1, 133.5, 129.9, 128.8, 128.6, 128.5 (2C), 127.2 (2C), 126.2, 123.8, 80.9, 61.9, 51.6, 49.5, 44.5, 43.1, 15.3, 14.3. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{24}NO_3$ ($[M+H]^+$) 350.1756; found 350.1756.

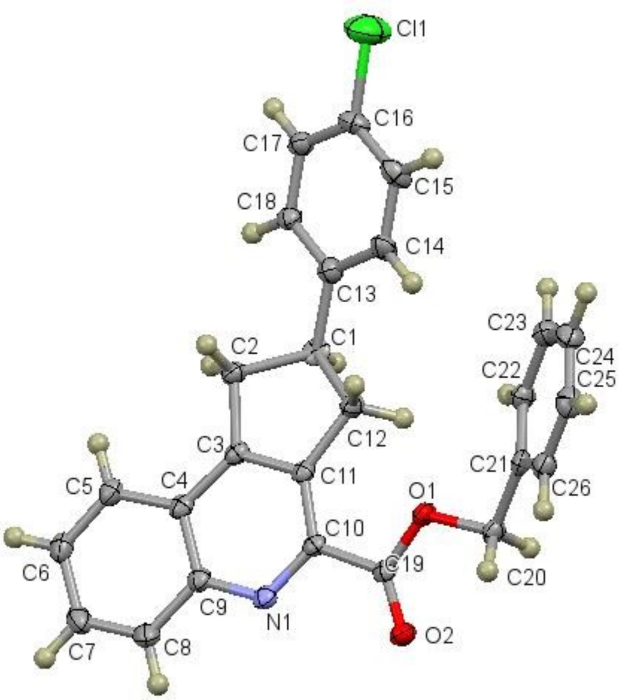


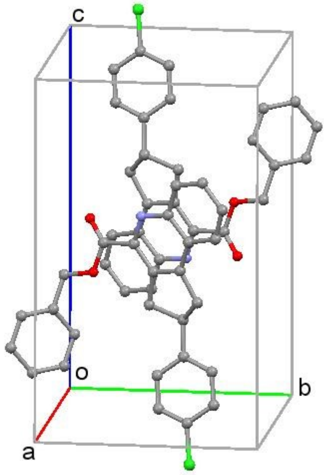


Benzyl-9b-hydroxy-3a-methyl-2-phenyl-2,3,3a,9b-tetrahydro-1H-cyclopenta[c]quinoline-4-carboxylate (7b, minor diastereomer). Yellow oil. **TLC**: R_f 0.19 (4:1 hexanes/EtOAc). **IR** (NaCl): 2978, 2936, 2361, 2334, 1719, 1649, 1558, 1539, 1508, 1456, 1369, 1290, 1238, 1042, 756, 700. **^{1}H NMR** (400 MHz) δ 7.69 – 7.67 (m, 1H), 7.60 – 7.57 (m, 1H), 7.42 – 7.37 (m, 2H), 7.24 (d, J = 7.4 Hz, 2H), 7.20 – 7.12 (m, 3H), 4.47 – 4.39 (m, 1H), 4.36 – 4.28 (m, 1H), 3.65 – 3.56 (m, 1H), 2.61 (dd, J = 14.7, 10.5 Hz, 1H), 2.41 (dd, J = 14.8, 7.1 Hz, 1H), 2.27 (dd, J = 13.6, 7.3 Hz, 1H), 2.05 (dd, J = 13.5, 11.5 Hz, 1H), 1.90 (s, 1H), 1.40 (s, 3H), 1.36 (t, J = 7.1 Hz, 2H). **^{13}C NMR** (101 MHz) δ 167.5, 165.3, 144.7, 139.8, 132.9, 130.0, 129.2, 128.8, 128.5 (2C), 127.1 (2C), 126.2, 124.5, 81.7, 61.9, 50.3, 49.0, 45.2, 39.8, 17.6, 14.2. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{24}NO_3$ ($[M+H]^+$) 350.1756; found 350.1759.

J. X-RAY DIFFRACTION DATA FOR QUINOLINES 4b and 4m

Compound: **4b**
Sample: KC-695
CCDC 1553211
User: Kiran Chinthapally
Formula: $C_{26}\ H_{20}\ Cl\ N\ O_2$





Comment

The selected crystal was twinned by a 2-fold rotation around the [1 0 0] axis with a refined twin ratio of 0.4865(13). A large peak in the difference map occurred near C1. Attempts to model it as a ring flip were unsuccessful. It is most likely an artifact of the twinning. The displacement ellipsoids were drawn at the 50% probability level.

EXPERIMENTAL

A colourless, needle-shaped crystal of dimensions 0.08 x 0.10 x 0.48 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).[15] The sample was cooled to 100(2) K. Cell parameters were determined from a non-linear, least squares fit of 5350 peaks in the range $2.34 < \theta < 26.93°$. A total of 30817 data were measured in the range $1.376 < \theta < 27.547°$ using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method giving minimum and maximum transmission factors of 0.902 and 0.983.[16] The data were merged to form a set of 8336 independent data with R(int) = 0.0395 and a coverage of 100.0 %.

The triclinic space group $P1$ was determined by statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.[17] The positions of hydrogens were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms. A total of 272 parameters were refined against 8336 data to give $wR(F^2) = 0.1543$ and S = 0.997 for weights of $w = 1/[\sigma^2(F^2) + (0.0700 P)^2 + 0.6000 P]$, where $P = [F_o2 + 2F_c2] / 3$. The final R(F) was 0.0623 for the 6344 observed, $[F > 4\sigma(F)]$, data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 1.014 and -0.424 e/Å^3, respectively.

Table 1. Crystal data and structure refinement for KC-695.

Empirical formula	$C_{26} H_{20} Cl N O_2$	
Formula weight	413.88	
Crystal system	triclinic	
Space group	$P1$	
Unit cell dimensions	a = 7.528(3) Å	α= 92.924(5)°
	b = 9.407(3) Å	β= 101.019(5)°
	c = 15.201(5) Å	γ= 110.770(5)°
Volume	979.6(6) Å^3	
Z, Z'	2, 1	
Density (calculated)	1.403 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	432	
Absorption coefficient	0.219 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.983 and 0.902	

Theta range for data collection	1.376 to 27.547°
Reflections collected	30817
Independent reflections	8336 [R(int) = 0.0395]
Data / restraints / parameters	8336 / 0 / 272
$wR(F^2$ all data)	$wR2 = 0.1543$
$R(F$ obsd data)	$R1 = 0.0623$
Goodness-of-fit on F^2	0.997
Observed data [I > 2σ(I)]	6344
Largest and mean shift / s.u.	0.000 and 0.000
Largest diff. peak and hole	1.014 and -0.424 e/Å^3

$wR2 = \{ \Sigma [w(F_o2 - F_c2)2] / \Sigma [w(F_o 2)2] \}1/2$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for KC-695. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	0.86399(14)	0.67332(10)	-0.07021(5)	0.0473(2)
O(1)	0.4567(2)	0.17649(19)	0.39042(12)	0.0221(4)
O(2)	0.4074(2)	0.1541(2)	0.53141(12)	0.0244(4)
N(1)	0.7135(3)	0.4323(2)	0.58834(14)	0.0213(4)
C(1)	0.7022(4)	0.6186(3)	0.30395(19)	0.0281(6)
C(2)	0.8822(3)	0.7111(3)	0.38061(17)	0.0211(5)
C(3)	0.8390(3)	0.6274(3)	0.46059(17)	0.0191(5)
C(4)	0.9250(3)	0.6785(3)	0.55301(17)	0.0206(5)
C(5)	1.0750(3)	0.8235(3)	0.58693(18)	0.0235(5)
C(6)	1.1470(4)	0.8644(3)	0.67801(18)	0.0266(6)
C(7)	1.0739(4)	0.7639(3)	0.73993(19)	0.0303(6)
C(8)	0.9312(4)	0.6222(3)	0.70933(18)	0.0279(6)
C(9)	0.8536(3)	0.5750(3)	0.61537(17)	0.0219(5)
C(10)	0.6406(3)	0.3884(3)	0.50076(16)	0.0184(5)
C(11)	0.6960(3)	0.4833(3)	0.43338(16)	0.0182(5)
C(12)	0.6277(4)	0.4557(3)	0.33189(17)	0.0215(5)
C(13)	0.7438(4)	0.6271(3)	0.20962(18)	0.0266(6)
C(14)	0.6939(5)	0.4981(3)	0.14707(19)	0.0396(7)
C(15)	0.7298(5)	0.5118(4)	0.0612(2)	0.0439(8)

C(16)	0.8149(4)	0.6562(3)	0.03727(17)	0.0288(6)
C(17)	0.8624(4)	0.7850(3)	0.09665(17)	0.0247(5)
C(18)	0.8281(4)	0.7691(3)	0.18263(18)	0.0251(5)
C(19)	0.4878(3)	0.2274(3)	0.47797(16)	0.0188(5)
C(20)	0.3117(3)	0.0231(3)	0.35939(17)	0.0217(5)
C(21)	0.3305(3)	-0.0238(3)	0.26643(17)	0.0212(5)
C(22)	0.3344(4)	0.0730(3)	0.19960(17)	0.0247(5)
C(23)	0.3548(4)	0.0296(3)	0.11462(19)	0.0302(6)
C(24)	0.3680(4)	-0.1117(3)	0.09519(19)	0.0309(6)
C(25)	0.3597(4)	-0.2093(3)	0.16082(19)	0.0293(6)
C(26)	0.3422(4)	-0.1653(3)	0.24658(18)	0.0250(5)

Table 3. Bond lengths [Å] and angles [°] for KC-695.

Cl(1)-C(16)	1.746(3)	C(11)-C(12)	1.508(3)
O(1)-C(19)	1.339(3)	C(12)-H(12A)	0.9900
O(1)-C(20)	1.453(3)	C(12)-H(12B)	0.9900
O(2)-C(19)	1.204(3)	C(13)-C(18)	1.381(4)
N(1)-C(10)	1.322(3)	C(13)-C(14)	1.393(4)
N(1)-C(9)	1.363(3)	C(14)-C(15)	1.387(4)
C(1)-C(13)	1.525(4)	C(14)-H(14)	0.9500
C(1)-C(12)	1.546(4)	C(15)-C(16)	1.382(4)
C(1)-C(2)	1.552(4)	C(15)-H(15)	0.9500
C(1)-H(1)	1.0000	C(16)-C(17)	1.367(4)
C(2)-C(3)	1.507(3)	C(17)-C(18)	1.385(3)
C(2)-H(2A)	0.9900	C(17)-H(17)	0.9500
C(2)-H(2B)	0.9900	C(18)-H(18)	0.9500
C(3)-C(11)	1.380(3)	C(20)-C(21)	1.506(3)
C(3)-C(4)	1.410(3)	C(20)-H(20A)	0.9900
C(4)-C(5)	1.419(3)	C(20)-H(20B)	0.9900
C(4)-C(9)	1.433(3)	C(21)-C(26)	1.387(4)
C(5)-C(6)	1.367(4)	C(21)-C(22)	1.396(4)
C(5)-H(5)	0.9500	C(22)-C(23)	1.387(4)
C(6)-C(7)	1.415(4)	C(22)-H(22)	0.9500
C(6)-H(6)	0.9500	C(23)-C(24)	1.389(4)
C(7)-C(8)	1.370(4)	C(23)-H(23)	0.9500
C(7)-H(7)	0.9500	C(24)-C(25)	1.385(4)
C(8)-C(9)	1.418(4)	C(24)-H(24)	0.9500
C(8)-H(8)	0.9500	C(25)-C(26)	1.392(4)
C(10)-C(11)	1.419(3)	C(25)-H(25)	0.9500
C(10)-C(19)	1.515(3)	C(26)-H(26)	0.9500

C(19)-O(1)-C(20)	116.27(18)	C(11)-C(3)-C(4)	120.5(2)
C(10)-N(1)-C(9)	118.3(2)	C(11)-C(3)-C(2)	111.1(2)
C(13)-C(1)-C(12)	115.5(2)	C(4)-C(3)-C(2)	128.4(2)
C(13)-C(1)-C(2)	113.7(2)	C(3)-C(4)-C(5)	124.3(2)
C(12)-C(1)-C(2)	104.5(2)	C(3)-C(4)-C(9)	116.6(2)
C(13)-C(1)-H(1)	107.6	C(5)-C(4)-C(9)	119.1(2)
C(12)-C(1)-H(1)	107.6	C(6)-C(5)-C(4)	120.2(2)
C(2)-C(1)-H(1)	107.6	C(6)-C(5)-H(5)	119.9
C(3)-C(2)-C(1)	102.9(2)	C(4)-C(5)-H(5)	119.9
C(3)-C(2)-H(2A)	111.2	C(5)-C(6)-C(7)	120.9(2)
C(1)-C(2)-H(2A)	111.2	C(5)-C(6)-H(6)	119.5
C(3)-C(2)-H(2B)	111.2	C(7)-C(6)-H(6)	119.5
C(1)-C(2)-H(2B)	111.2	C(8)-C(7)-C(6)	120.3(3)
H(2A)-C(2)-H(2B)	109.1	C(8)-C(7)-H(7)	119.8

C(6)-C(7)-H(7)	119.8
C(7)-C(8)-C(9)	120.5(2)
C(7)-C(8)-H(8)	119.8
C(9)-C(8)-H(8)	119.8
N(1)-C(9)-C(8)	118.2(2)
N(1)-C(9)-C(4)	122.8(2)
C(8)-C(9)-C(4)	119.0(2)
N(1)-C(10)-C(11)	123.6(2)
N(1)-C(10)-C(19)	114.0(2)
C(11)-C(10)-C(19)	122.3(2)
C(3)-C(11)-C(10)	118.2(2)
C(3)-C(11)-C(12)	110.4(2)
C(10)-C(11)-C(12)	131.4(2)
C(11)-C(12)-C(1)	103.4(2)
C(11)-C(12)-H(12A)	111.1
C(1)-C(12)-H(12A)	111.1
C(11)-C(12)-H(12B)	111.1
C(1)-C(12)-H(12B)	111.1
H(12A)-C(12)-H(12B)	109.1
C(18)-C(13)-C(14)	117.6(2)
C(18)-C(13)-C(1)	119.1(2)
C(14)-C(13)-C(1)	123.2(2)
C(15)-C(14)-C(13)	121.1(3)
C(15)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(16)-C(15)-C(14)	119.2(3)
C(16)-C(15)-H(15)	120.4
C(14)-C(15)-H(15)	120.4
C(17)-C(16)-C(15)	121.0(2)
C(17)-C(16)-Cl(1)	119.8(2)
C(15)-C(16)-Cl(1)	119.2(2)
C(16)-C(17)-C(18)	119.0(2)
C(16)-C(17)-H(17)	120.5
C(18)-C(17)-H(17)	120.5
C(13)-C(18)-C(17)	122.1(3)
C(13)-C(18)-H(18)	119.0
C(17)-C(18)-H(18)	119.0
O(2)-C(19)-O(1)	124.5(2)
O(2)-C(19)-C(10)	124.8(2)
O(1)-C(19)-C(10)	110.65(19)
O(1)-C(20)-C(21)	107.38(18)
O(1)-C(20)-H(20A)	110.2
C(21)-C(20)-H(20A)	110.2
O(1)-C(20)-H(20B)	110.2
C(21)-C(20)-H(20B)	110.2
H(20A)-C(20)-H(20B)	108.5
C(26)-C(21)-C(22)	119.5(2)
C(26)-C(21)-C(20)	119.7(2)
C(22)-C(21)-C(20)	120.8(2)
C(23)-C(22)-C(21)	120.3(2)
C(23)-C(22)-H(22)	119.8
C(21)-C(22)-H(22)	119.8
C(22)-C(23)-C(24)	120.1(3)
C(22)-C(23)-H(23)	120.0
C(24)-C(23)-H(23)	120.0
C(25)-C(24)-C(23)	119.7(3)
C(25)-C(24)-H(24)	120.1
C(23)-C(24)-H(24)	120.1
C(24)-C(25)-C(26)	120.4(3)
C(24)-C(25)-H(25)	119.8
C(26)-C(25)-H(25)	119.8
C(21)-C(26)-C(25)	120.0(2)
C(21)-C(26)-H(26)	120.0
C(25)-C(26)-H(26)	120.0

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for KC-695. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	75(1)	52(1)	23(1)	8(1)	22(1)	28(1)
O(1)	23(1)	16(1)	22(1)	1(1)	8(1)	1(1)

O(2)	26(1)	22(1)	24(1)	5(1)	10(1)	5(1)
N(1)	18(1)	23(1)	23(1)	3(1)	8(1)	6(1)
C(1)	28(1)	25(1)	33(2)	4(1)	11(1)	11(1)
C(2)	22(1)	18(1)	23(1)	4(1)	9(1)	5(1)
C(3)	18(1)	18(1)	25(1)	5(1)	9(1)	8(1)
C(4)	19(1)	20(1)	25(1)	2(1)	9(1)	8(1)
C(5)	20(1)	21(1)	29(1)	1(1)	8(1)	6(1)
C(6)	19(1)	25(1)	32(1)	-4(1)	6(1)	5(1)
C(7)	26(1)	38(2)	22(1)	-4(1)	4(1)	8(1)
C(8)	25(1)	34(2)	23(1)	2(1)	9(1)	6(1)
C(9)	18(1)	24(1)	23(1)	0(1)	7(1)	6(1)
C(10)	16(1)	20(1)	21(1)	4(1)	7(1)	7(1)
C(11)	17(1)	18(1)	20(1)	2(1)	7(1)	7(1)
C(12)	23(1)	17(1)	22(1)	2(1)	7(1)	4(1)
C(13)	30(1)	24(1)	22(1)	2(1)	5(1)	5(1)
C(14)	68(2)	21(2)	24(2)	7(1)	7(1)	11(1)
C(15)	84(2)	26(2)	23(2)	0(1)	10(2)	23(2)
C(16)	41(2)	36(2)	17(1)	7(1)	10(1)	20(1)
C(17)	26(1)	24(1)	24(1)	7(1)	9(1)	7(1)
C(18)	26(1)	24(1)	25(1)	1(1)	10(1)	6(1)
C(19)	16(1)	22(1)	21(1)	4(1)	6(1)	10(1)
C(20)	21(1)	16(1)	25(1)	2(1)	6(1)	2(1)
C(21)	15(1)	19(1)	23(1)	1(1)	3(1)	0(1)
C(22)	26(1)	17(1)	26(1)	1(1)	6(1)	3(1)
C(23)	33(1)	28(2)	25(1)	6(1)	7(1)	5(1)
C(24)	31(1)	34(2)	26(1)	-2(1)	9(1)	9(1)
C(25)	26(1)	27(1)	34(2)	-2(1)	6(1)	11(1)
C(26)	21(1)	23(1)	28(1)	4(1)	4(1)	5(1)

Table 5. Hydrogen coordinates and isotropic displacement parameters for KC-695.

	x	y	z	U(eq)
H(1)	0.5999	0.6627	0.3061	0.034
H(2A)	1.0039	0.7093	0.3658	0.025
H(2B)	0.8936	0.8189	0.3920	0.025
H(5)	1.1254	0.8923	0.5462	0.028
H(6)	1.2476	0.9616	0.7000	0.032
H(7)	1.1239	0.7949	0.8030	0.036
H(8)	0.8840	0.5550	0.7514	0.034
H(12A)	0.4838	0.4075	0.3135	0.026

H(12B)	0.6850	0.3894	0.3046	0.026
H(14)	0.6342	0.3990	0.1635	0.047
H(15)	0.6964	0.4230	0.0193	0.053
H(17)	0.9180	0.8839	0.0792	0.030
H(18)	0.8637	0.8585	0.2243	0.030
H(20A)	0.1793	0.0227	0.3571	0.026
H(20B)	0.3347	-0.0492	0.4011	0.026
H(22)	0.3231	0.1689	0.2123	0.030
H(23)	0.3597	0.0966	0.0697	0.036
H(24)	0.3828	-0.1413	0.0371	0.037
H(25)	0.3659	-0.3069	0.1472	0.035
H(26)	0.3383	-0.2323	0.2915	0.030

Table 6. Torsion angles [°] for KC-695.

C(13)-C(1)-C(2)-C(3)	-153.1(2)
C(12)-C(1)-C(2)-C(3)	-26.3(2)
C(1)-C(2)-C(3)-C(11)	17.0(3)
C(1)-C(2)-C(3)-C(4)	-163.3(2)
C(11)-C(3)-C(4)-C(5)	178.9(2)
C(2)-C(3)-C(4)-C(5)	-0. 8(4)
C(11)-C(3)-C(4)-C(9)	-1. 1(3)
C(2)-C(3)-C(4)-C(9)	179.2(2)
C(3)-C(4)-C(5)-C(6)	178.7(2)
C(9)-C(4)-C(5)-C(6)	-1.3(3)
C(4)-C(5)-C(6)-C(7)	-0.1(4)
C(5)-C(6)-C(7)-C(8)	1.2(4)
C(6)-C(7)-C(8)-C(9)	-0.7(4)
C(10)-N(1)-C(9)-C(8)	179.8(2)
C(10)-N(1)-C(9)-C(4)	-0.2(3)
C(7)-C(8)-C(9)-N(1)	179.3(2)
C(7)-C(8)-C(9)-C(4)	-0.7(4)
C(3)-C(4)-C(9)-N(1)	1.7(3)
C(5)-C(4)-C(9)-N(1)	-178.3(2)
C(3)-C(4)-C(9)-C(8)	-178.3(2)
C(5)-C(4)-C(9)-C(8)	1.7(3)
C(9)-N(1)-C(10)-C(11)	-1.9(3)
C(9)-N(1)-C(10)-C(19)	179.33(19)
C(4)-C(3)-C(11)-C(10)	-0.8(3)
C(2)-C(3)-C(11)-C(10)	178.9(2)
C(4)-C(3)-C(11)-C(12)	-180.0(2)
C(2)-C(3)-C(11)-C(12)	-0.2(3)
N(1)-C(10)-C(11)-C(3)	2.5(3)
C(19)-C(10)-C(11)-C(3)	-178.9(2)
N(1)-C(10)-C(11)-C(12)	-178.6(2)
C(19)-C(10)-C(11)-C(12)	0.1(4)
C(3)-C(11)-C(12)-C(1)	-16.8(3)
C(10)-C(11)-C(12)-C(1)	164.2(2)
C(13)-C(1)-C(12)-C(11)	152.0(2)
C(2)-C(1)-C(12)-C(11)	26.4(2)
C(12)-C(1)-C(13)-C(18)	-173.9(2)
C(2)-C(1)-C(13)-C(18)	-53.1(3)
C(12)-C(1)-C(13)-C(14)	8.7(4)
C(2)-C(1)-C(13)-C(14)	129.5(3)
C(18)-C(13)-C(14)-C(15)	0.8(5)
C(1)-C(13)-C(14)-C(15)	178.2(3)
C(13)-C(14)-C(15)-C(16)	-0.7(5)
C(14)-C(15)-C(16)-C(17)	-0.5(5)
C(14)-C(15)-C(16)-Cl(1)	178.9(3)
C(15)-C(16)-C(17)-C(18)	1.5(4)
Cl(1)-C(16)-C(17)-C(18)	-177.9(2)
C(14)-C(13)-C(18)-C(17)	0.2(4)
C(1)-C(13)-C(18)-C(17)	-177.3(2)
C(16)-C(17)-C(18)-C(13)	-1.3(4)
C(20)-O(1)-C(19)-O(2)	1.4(3)
C(20)-O(1)-C(19)-C(10)	-179.62(18)
N(1)-C(10)-C(19)-O(2)	14.5(3)
C(11)-C(10)-C(19)-O(2)	-164.2(2)
N(1)-C(10)-C(19)-O(1)	-164.42(19)
C(11)-C(10)-C(19)-O(1)	16.8(3)
C(19)-O(1)-C(20)-C(21)	-168.04(19)
O(1)-C(20)-C(21)-C(26)	130.7(2)
O(1)-C(20)-C(21)-C(22)	-49.9(3)
C(26)-C(21)-C(22)-C(23)	-1.6(4)
C(20)-C(21)-C(22)-C(23)	179.0(2)
C(21)-C(22)-C(23)-C(24)	1.1(4)
C(22)-C(23)-C(24)-C(25)	0.4(4)
C(23)-C(24)-C(25)-C(26)	-1.3(4)
C(22)-C(21)-C(26)-C(25)	0.6(4)
C(20)-C(21)-C(26)-C(25)	-180.0(2)
C(24)-C(25)-C(26)-C(21)	0.8(4)

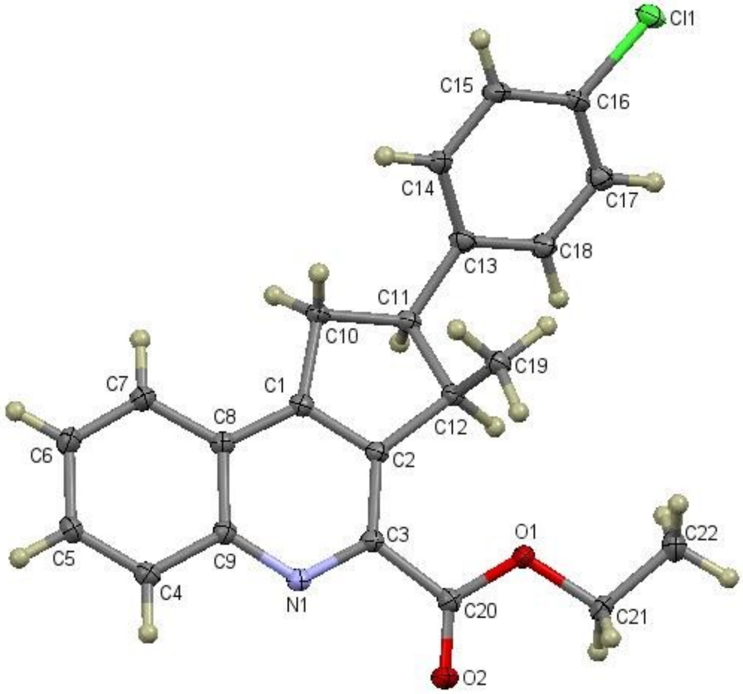
Table 7. Hydrogen bonds for KC-695[Å and °].

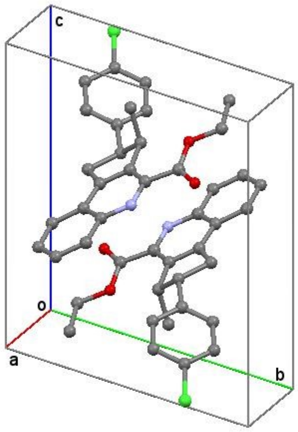
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(8)-H(8)...Cl(1)#1	0.95	2.93	3.518(3)	121.3

C(20)-H(20B)...O(2)#2	0.99	2.55	3.383(3)	141.9

Symmetry transformations used to generate equivalent atoms:
#1 x, y, z+1 #2 -x+1, -y, -z+1

Compound: **4m**
Sample: Massaro_N_2017_280
CCDC 1553212
User: Nicholas Massaro
Formula: $C_{22}H_{20}ClNO_2$





Comment

The displacement ellipsoids were drawn at the 50% probability level.

EXPERIMENTAL

A colourless, plate-shaped crystal of dimensions 0.07 x 0.20 x 0.34 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).[15] The sample was cooled to 100(2) K. Cell parameters were determined from a non-linear least squares fit of 4628 peaks in the range $2.19 < \theta < 28.55°$. A total of 23600 data were measured in the range $1.866 < \theta < 30.549°$ using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method giving minimum and maximum transmission factors of 0.926 and 0.984.[16] The data were merged to form a set of 5374 independent data with R(int) = 0.0535 and a coverage of 100.0 %.

The triclinic space group $P1$ was determined by statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.[17] The positions of hydrogens were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. A total of 237 parameters were refined against 5374 data to give wR(F^2) = 0.1446 and S = 1.001 for weights of $w = 1/[\sigma^2(F^2) + (0.0900\ P)^2]$, where $P = [F_o2 + 2F_c2] / 3$. The final R(F) was 0.0472 for the 3878 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.690 and -0.362 e/Å^3, respectively.

Acknowledgment
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16. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, and D. Stalke (2015). *J. Appl. Cryst., 48*, 3-10.
17. (a) G. M. Sheldrick (2015). *Acta Cryst., A71*, 3-8. (b) G. M. Sheldrick (2015). *Acta Cryst., C71*, 3-8.

Table 1. Crystal data and structure refinement for Massaro_N_2017_280.

Empirical formula	$C_{22} H_{20} Cl N O_2$	
Formula weight	365.84	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 8.1448(13) Å	α= 107.878(3)°
	b = 10.1417(16) Å	β= 104.781(3)°
	c = 12.1318(19) Å	γ= 99.492(3)°
Volume	889.4(2) $Å^3$	
Z, Z'	2, 1	
Density (calculated)	1.366 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	384	
Absorption coefficient	0.231 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.984 and 0.926	
Theta range for data collection	1.866 to 30.549°	
Reflections collected	23600	
Independent reflections	5374 [R(int) = 0.0535]	
Data / restraints / parameters	5374 / 0 / 237	
$wR(F^2$ all data)	$wR2$ = 0.1446	
$R(F$ obsd data)	$R1$ = 0.0472	
Goodness-of-fit on F^2	1.001	
Observed data [I > 2σ(I)]	3878	
Largest and mean shift / s.u.	0.000 and 0.000	
Largest diff. peak and hole	0.690 and -0.362 $e/Å^3$	

$wR2 = \{ \Sigma [w(F_o2 - F_c2)^2] / \Sigma [w(F_o 2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for Massaro_N_2017_280. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	-0.19680(5)	0.22348(4)	0.94769(4)	0.02391(12)
O(1)	0.68778(15)	0.69645(11)	0.81811(10)	0.0200(2)
O(2)	0.87015(16)	0.75442(12)	0.71966(11)	0.0246(3)
N(1)	0.76874(17)	0.47443(13)	0.56267(11)	0.0152(3)
C(1)	0.4604(2)	0.28776(16)	0.54583(14)	0.0161(3)
C(2)	0.52367(19)	0.42367(15)	0.63462(14)	0.0141(3)
C(3)	0.67974(19)	0.51485(15)	0.63891(14)	0.0144(3)
C(4)	0.8082(2)	0.29542(16)	0.39756(14)	0.0176(3)
C(5)	0.7523(2)	0.16015(17)	0.30955(15)	0.0195(3)
C(6)	0.5975(2)	0.06146(17)	0.29682(15)	0.0210(3)
C(7)	0.4996(2)	0.09925(17)	0.37249(15)	0.0196(3)
C(8)	0.5535(2)	0.23902(16)	0.46473(14)	0.0160(3)
C(9)	0.7095(2)	0.33837(16)	0.47714(14)	0.0153(3)
C(10)	0.2914(2)	0.20826(16)	0.55164(15)	0.0180(3)
C(11)	0.2314(2)	0.33117(16)	0.62906(14)	0.0166(3)
C(12)	0.4071(2)	0.44611(16)	0.71509(14)	0.0155(3)
C(13)	0.1114(2)	0.29435(16)	0.69810(14)	0.0165(3)
C(14)	0.0647(2)	0.15918(17)	0.70514(15)	0.0187(3)
C(15)	-0.0323(2)	0.13539(17)	0.78000(15)	0.0205(3)
C(16)	-0.0839(2)	0.24800(17)	0.84781(15)	0.0181(3)
C(17)	-0.0455(2)	0.38254(17)	0.83894(15)	0.0195(3)
C(18)	0.0512(2)	0.40391(17)	0.76444(15)	0.0188(3)
C(19)	0.4869(2)	0.41947(17)	0.83264(14)	0.0192(3)
C(20)	0.7580(2)	0.66777(16)	0.72816(14)	0.0168(3)
C(21)	0.7471(2)	0.84297(16)	0.90605(15)	0.0204(3)
C(22)	0.6334(3)	0.85342(19)	0.98677(16)	0.0270(4)

Table 3. Bond lengths [Å] and angles [°] for Massaro_N_2017_280.

Cl(1)-C(16)	1.7477(15)	C(11)-C(13)	1.512(2)
O(1)-C(20)	1.3345(18)	C(11)-C(12)	1.561(2)
O(1)-C(21)	1.4514(18)	C(11)-H(11)	1.0000
O(2)-C(20)	1.2068(18)	C(12)-C(19)	1.533(2)
N(1)-C(3)	1.3252(19)	C(12)-H(12)	1.0000
N(1)-C(9)	1.3636(19)	C(13)-C(14)	1.396(2)
C(1)-C(2)	1.377(2)	C(13)-C(18)	1.398(2)
C(1)-C(8)	1.412(2)	C(14)-C(15)	1.395(2)
C(1)-C(10)	1.506(2)	C(14)-H(14)	0.9500
C(2)-C(3)	1.422(2)	C(15)-C(16)	1.384(2)

C(2)-C(12)	1.521(2)	C(15)-H(15)	0.9500
C(3)-C(20)	1.508(2)	C(16)-C(17)	1.392(2)
C(4)-C(5)	1.370(2)	C(17)-C(18)	1.382(2)
C(4)-C(9)	1.422(2)	C(17)-H(17)	0.9500
C(4)-H(4)	0.9500	C(18)-H(18)	0.9500
C(5)-C(6)	1.416(2)	C(19)-H(19A)	0.9800
C(5)-H(5)	0.9500	C(19)-H(19B)	0.9800
C(6)-C(7)	1.372(2)	C(19)-H(19C)	0.9800
C(6)-H(6)	0.9500	C(21)-C(22)	1.503(2)
C(7)-C(8)	1.423(2)	C(21)-H(21A)	0.9900
C(7)-H(7)	0.9500	C(21)-H(21B)	0.9900
C(8)-C(9)	1.429(2)	C(22)-H(22A)	0.9800
C(10)-C(11)	1.546(2)	C(22)-H(22B)	0.9800
C(10)-H(10A)	0.9900	C(22)-H(22C)	0.9800
C(10)-H(10B)	0.9900		
C(20)-O(1)-C(21)	116.54(12)	C(6)-C(5)-H(5)	119.5
C(3)-N(1)-C(9)	118.56(13)	C(7)-C(6)-C(5)	120.70(15)
C(2)-C(1)-C(8)	120.26(14)	C(7)-C(6)-H(6)	119.7
C(2)-C(1)-C(10)	111.44(13)	C(5)-C(6)-H(6)	119.7
C(8)-C(1)-C(10)	128.31(14)	C(6)-C(7)-C(8)	119.91(15)
C(1)-C(2)-C(3)	118.49(14)	C(6)-C(7)-H(7)	120.0
C(1)-C(2)-C(12)	109.99(13)	C(8)-C(7)-H(7)	120.0
C(3)-C(2)-C(12)	131.50(14)	C(1)-C(8)-C(7)	123.86(14)
N(1)-C(3)-C(2)	123.10(14)	C(1)-C(8)-C(9)	116.91(14)
N(1)-C(3)-C(20)	113.30(13)	C(7)-C(8)-C(9)	119.23(14)
C(2)-C(3)-C(20)	123.58(13)	N(1)-C(9)-C(4)	117.99(14)
C(5)-C(4)-C(9)	119.84(15)	N(1)-C(9)-C(8)	122.63(14)
C(5)-C(4)-H(4)	120.1	C(4)-C(9)-C(8)	119.38(14)
C(9)-C(4)-H(4)	120.1	C(1)-C(10)-C(11)	102.30(12)
C(4)-C(5)-C(6)	120.94(15)	C(1)-C(10)-H(10A)	111.3
C(4)-C(5)-H(5)	119.5	C(11)-C(10)-H(10A)	111.3

C(1)-C(10)-H(10B)	111.3	C(18)-C(17)-C(16)	118.91(14)
C(11)-C(10)-H(10B)	111.3	C(18)-C(17)-H(17)	120.5
H(10A)-C(10)-H(10B)	109.2	C(16)-C(17)-H(17)	120.5
C(13)-C(11)-C(10)	117.95(12)	C(17)-C(18)-C(13)	121.84(14)
C(13)-C(11)-C(12)	112.67(12)	C(17)-C(18)-H(18)	119.1
C(10)-C(11)-C(12)	104.03(12)	C(13)-C(18)-H(18)	119.1
C(13)-C(11)-H(11)	107.2	C(12)-C(19)-H(19A)	109.5
C(10)-C(11)-H(11)	107.2	C(12)-C(19)-H(19B)	109.5
C(12)-C(11)-H(11)	107.2	H(19A)-C(19)-H(19B)	109.5
C(2)-C(12)-C(19)	110.35(12)	C(12)-C(19)-H(19C)	109.5
C(2)-C(12)-C(11)	101.46(12)	H(19A)-C(19)-H(19C)	109.5
C(19)-C(12)-C(11)	112.74(12)	H(19B)-C(19)-H(19C)	109.5
C(2)-C(12)-H(12)	110.7	O(2)-C(20)-O(1)	123.76(14)
C(19)-C(12)-H(12)	110.7	O(2)-C(20)-C(3)	124.42(14)
C(11)-C(12)-H(12)	110.7	O(1)-C(20)-C(3)	111.82(12)
C(14)-C(13)-C(18)	117.83(14)	O(1)-C(21)-C(22)	106.61(13)
C(14)-C(13)-C(11)	123.85(14)	O(1)-C(21)-H(21A)	110.4
C(18)-C(13)-C(11)	118.22(13)	C(22)-C(21)-H(21A)	110.4
C(15)-C(14)-C(13)	121.21(14)	O(1)-C(21)-H(21B)	110.4
C(15)-C(14)-H(14)	119.4	C(22)-C(21)-H(21B)	110.4
C(13)-C(14)-H(14)	119.4	H(21A)-C(21)-H(21B)	108.6
C(16)-C(15)-C(14)	119.18(14)	C(21)-C(22)-H(22A)	109.5
C(16)-C(15)-H(15)	120.4	C(21)-C(22)-H(22B)	109.5
C(14)-C(15)-H(15)	120.4	H(22A)-C(22)-H(22B)	109.5
C(15)-C(16)-C(17)	120.94(14)	C(21)-C(22)-H(22C)	109.5
C(15)-C(16)-Cl(1)	120.18(12)	H(22A)-C(22)-H(22C)	109.5
C(17)-C(16)-Cl(1)	118.88(12)	H(22B)-C(22)-H(22C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for

Massaro_N_2017_280. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	26(1)	22(1)	31(1)	11(1)	19(1)	5(1)
O(1)	25(1)	12(1)	21(1)	1(1)	14(1)	-1(1)
O(2)	26(1)	16(1)	30(1)	3(1)	17(1)	-2(1)
N(1)	16(1)	14(1)	16(1)	6(1)	7(1)	3(1)

C(1)	16(1)	16(1)	16(1)	6(1)	7(1)	2(1)
C(2)	13(1)	15(1)	16(1)	6(1)	6(1)	3(1)
C(3)	15(1)	13(1)	16(1)	6(1)	7(1)	3(1)
C(4)	16(1)	18(1)	19(1)	6(1)	8(1)	4(1)
C(5)	20(1)	19(1)	20(1)	5(1)	11(1)	5(1)
C(6)	21(1)	17(1)	21(1)	1(1)	9(1)	2(1)
C(7)	19(1)	17(1)	20(1)	3(1)	8(1)	1(1)
C(8)	16(1)	15(1)	16(1)	5(1)	6(1)	2(1)
C(9)	15(1)	15(1)	16(1)	5(1)	5(1)	4(1)
C(10)	18(1)	15(1)	20(1)	2(1)	10(1)	-1(1)
C(11)	16(1)	16(1)	19(1)	7(1)	8(1)	2(1)
C(12)	16(1)	13(1)	18(1)	5(1)	9(1)	2(1)
C(13)	13(1)	18(1)	18(1)	7(1)	6(1)	2(1)
C(14)	18(1)	15(1)	23(1)	4(1)	10(1)	1(1)
C(15)	21(1)	16(1)	27(1)	8(1)	12(1)	1(1)
C(16)	15(1)	19(1)	22(1)	7(1)	10(1)	2(1)
C(17)	18(1)	19(1)	25(1)	8(1)	10(1)	6(1)
C(18)	18(1)	17(1)	24(1)	8(1)	10(1)	4(1)
C(19)	18(1)	21(1)	18(1)	7(1)	8(1)	1(1)
C(20)	17(1)	16(1)	18(1)	6(1)	8(1)	5(1)
C(21)	22(1)	13(1)	21(1)	-1(1)	9(1)	-1(1)
C(22)	32(1)	22(1)	24(1)	1(1)	16(1)	4(1)

Table 5. Hydrogen coordinates and isotropic displacement parameters for Massaro_N_2017_280.

	x	y	z	U(eq)
H(4)	0.9127	0.3604	0.4054	0.021
H(5)	0.8183	0.1321	0.2563	0.023
H(6)	0.5610	-0.0319	0.2352	0.025
H(7)	0.3961	0.0322	0.3633	0.024
H(10A)	0.3120	0.1386	0.5922	0.022
H(10B)	0.2036	0.1570	0.4689	0.022
H(11)	0.1680	0.3735	0.5722	0.020
H(12)	0.3897	0.5450	0.7350	0.019
H(14)	0.0997	0.0820	0.6581	0.022
H(15)	-0.0627	0.0430	0.7844	0.025
H(17)	-0.0851	0.4584	0.8834	0.023
H(18)	0.0774	0.4956	0.7581	0.023
H(19A)	0.4104	0.4340	0.8834	0.029

H(19B)	0.6036	0.4867	0.8782	0.029
H(19C)	0.4978	0.3207	0.8115	0.029
H(21A)	0.7343	0.9115	0.8633	0.025
H(21B)	0.8724	0.8653	0.9554	0.025
H(22A)	0.5096	0.8286	0.9364	0.041
H(22B)	0.6669	0.9517	1.0466	0.041
H(22C)	0.6495	0.7867	1.0299	0.041

Table 6. Torsion angles [°] for Massaro_N_2017_280.

C(8)-C(1)-C(2)-C(3)	2.7(2)	C(1)-C(10)-C(11)-C(12)	-30.06(14)
C(10)-C(1)-C(2)-C(3)	-177.90(12)	C(1)-C(2)-C(12)-C(19)	97.50(15)
C(8)-C(1)-C(2)-C(12)	-176.07(13)	C(3)-C(2)-C(12)-C(19)	-81.01(19)
C(10)-C(1)-C(2)-C(12)	3.37(17)	C(1)-C(2)-C(12)-C(11)	-22.23(15)
C(9)-N(1)-C(3)-C(2)	-1.0(2)	C(3)-C(2)-C(12)-C(11)	159.26(14)
C(9)-N(1)-C(3)-C(20)	-179.57(12)	C(13)-C(11)-C(12)-C(2)	160.66(11)
C(1)-C(2)-C(3)-N(1)	-1.1(2)	C(10)-C(11)-C(12)-C(2)	31.77(13)
C(12)-C(2)-C(3)-N(1)	177.32(14)	C(13)-C(11)-C(12)-C(19)	42.64(17)
C(1)-C(2)-C(3)-C(20)	177.36(13)	C(10)-C(11)-C(12)-C(19)	-86.25(14)
C(12)-C(2)-C(3)-C(20)	-4.2(2)	C(10)-C(11)-C(13)-C(14)	6.1(2)
C(9)-C(4)-C(5)-C(6)	-0.4(2)	C(12)-C(11)-C(13)-C(14)	-115.15(17)
C(4)-C(5)-C(6)-C(7)	0.1(2)	C(10)-C(11)-C(13)-C(18)	-177.58(14)
C(5)-C(6)-C(7)-C(8)	0.1(2)	C(12)-C(11)-C(13)-C(18)	61.16(18)
C(2)-C(1)-C(8)-C(7)	178.43(14)	C(18)-C(13)-C(14)-C(15)	-2.7(2)
C(10)-C(1)-C(8)-C(7)	-0.9(2)	C(11)-C(13)-C(14)-C(15)	173.61(15)
C(2)-C(1)-C(8)-C(9)	-2.2(2)	C(13)-C(14)-C(15)-C(16)	0.4(2)
C(10)-C(1)-C(8)-C(9)	178.49(14)	C(14)-C(15)-C(16)-C(17)	2.3(2)
C(6)-C(7)-C(8)-C(1)	179.37(15)	C(14)-C(15)-C(16)-Cl(1)	-177.07(12)
C(6)-C(7)-C(8)-C(9)	0.0(2)	C(15)-C(16)-C(17)-C(18)	-2.4(2)
C(3)-N(1)-C(9)-C(4)	-178.74(13)	Cl(1)-C(16)-C(17)-C(18)	176.93(12)
C(3)-N(1)-C(9)-C(8)	1.5(2)	C(16)-C(17)-C(18)-C(13)	-0.1(2)
C(5)-C(4)-C(9)-N(1)	-179.34(13)	C(14)-C(13)-C(18)-C(17)	2.6(2)
C(5)-C(4)-C(9)-C(8)	0.5(2)	C(11)-C(13)-C(18)-C(17)	-173.96(14)
C(1)-C(8)-C(9)-N(1)	0.1(2)	C(21)-O(1)-C(20)-O(2)	2.8(2)
C(7)-C(8)-C(9)-N(1)	179.51(13)	C(21)-O(1)-C(20)-C(3)	-176.97(12)
C(1)-C(8)-C(9)-C(4)	-179.71(13)	N(1)-C(3)-C(20)-O(2)	12.5(2)
C(7)-C(8)-C(9)-C(4)	-0.3(2)	C(2)-C(3)-C(20)-O(2)	-166.08(14)
C(2)-C(1)-C(10)-C(11)	17.25(16)	N(1)-C(3)-C(20)-O(1)	-167.71(12)
C(8)-C(1)-C(10)-C(11)	-163.37(15)	C(2)-C(3)-C(20)-O(1)	13.7(2)
C(1)-C(10)-C(11)-C(13)	-155.67(13)	C(20)-O(1)-C(21)-C(22)	172.55(13)

Table 7. Hydrogen bonds for Massaro_N_2017_280 [Å and °].

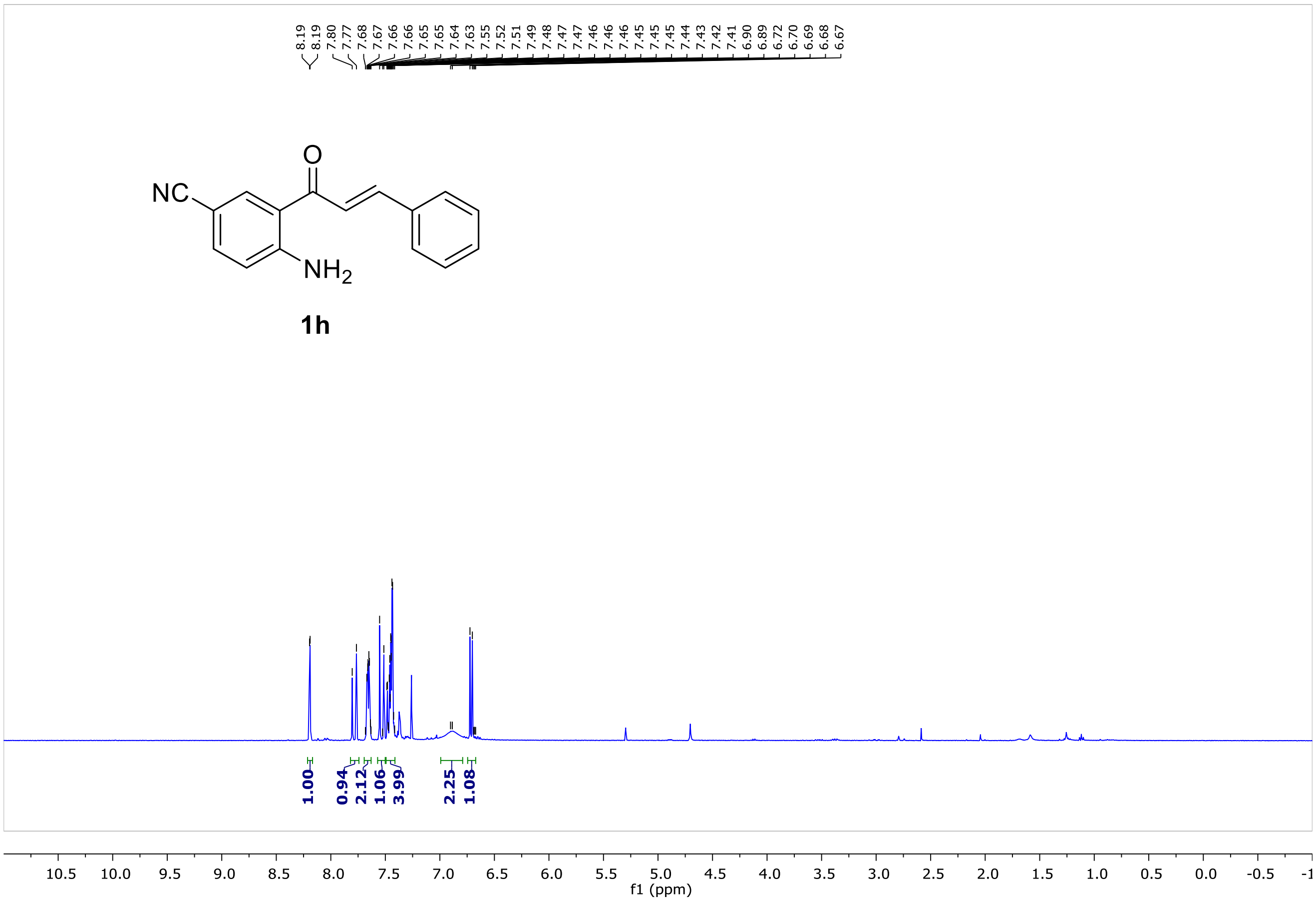
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(21)-H(21A)...Cl(1)#1	0.99	2.92	3.6687(17)	133.5

Symmetry transformations used to generate equivalent atoms:

#1 x+1, y+1, z

K. ^{1}H-NMR, ^{13}C-NMR, COSY, HSQC, AND NOE SPECTRA

Massaro_N_2017_155t16_PROTON_01 — Massaro_N_2017_155t16 —



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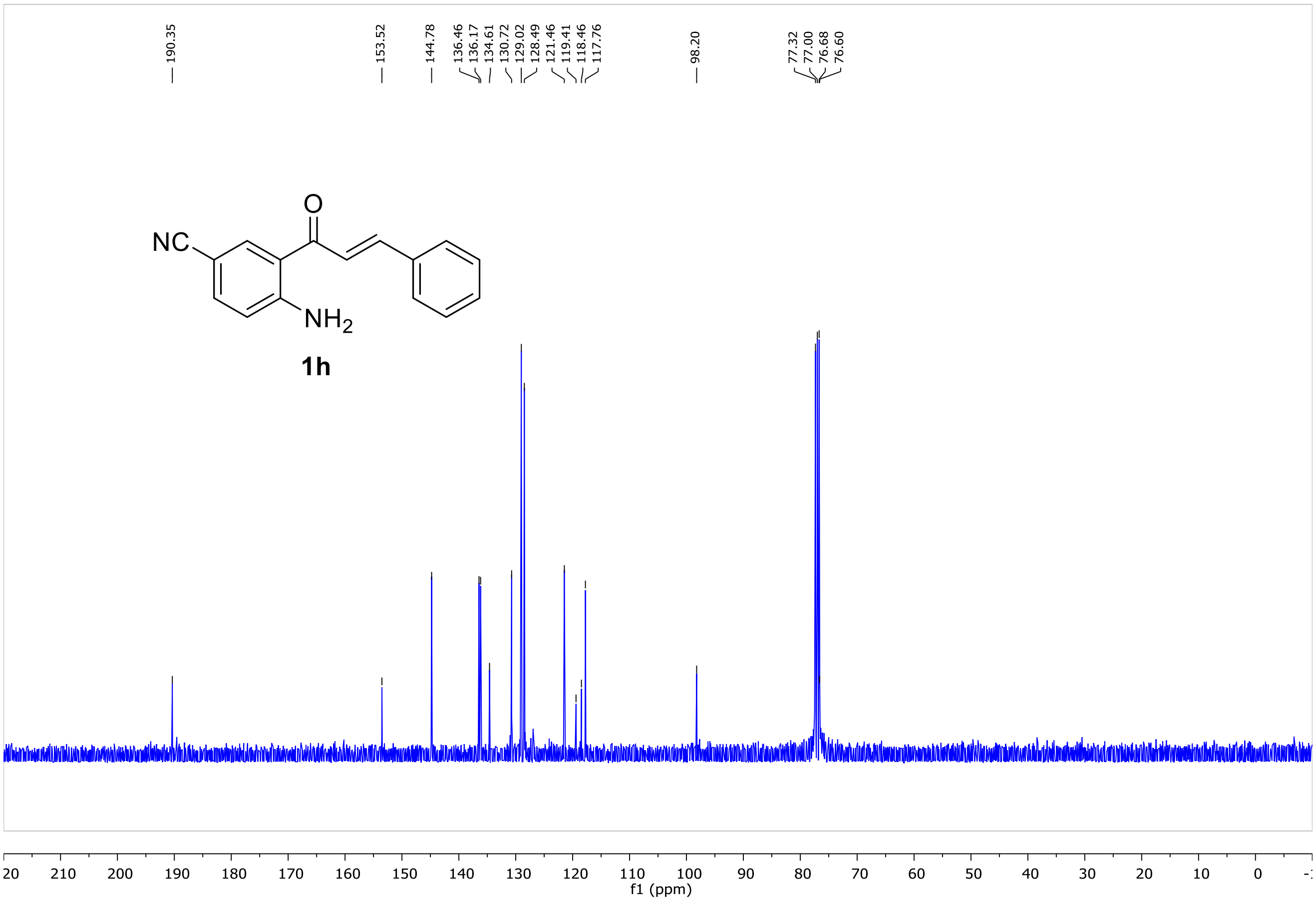

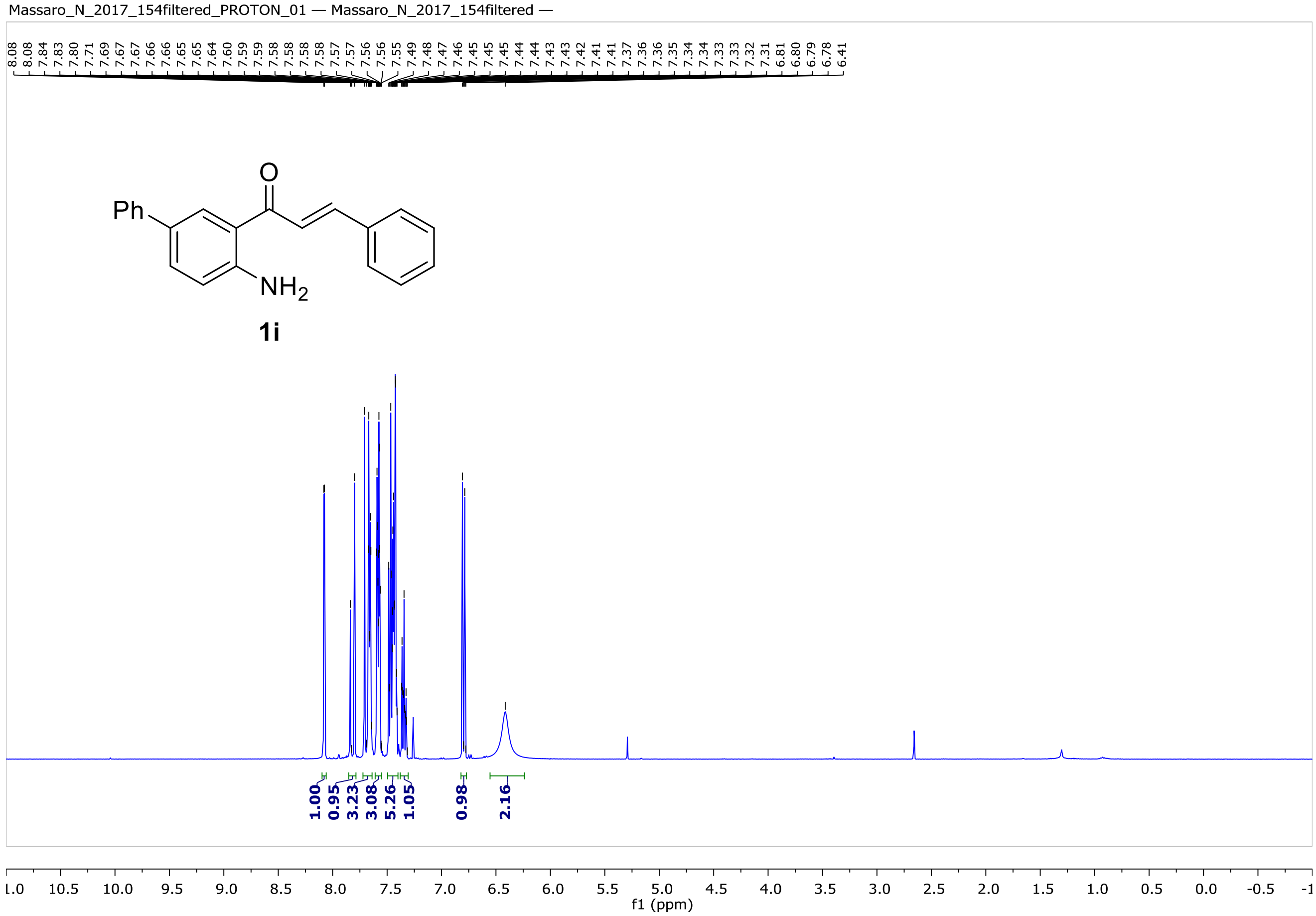
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7.33
7.32
7.31
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6.80
6.79
6.78
6.41
Ph
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NH2
1i
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0.95
3.23
3.08
5.26
1.05
0.98
2.16
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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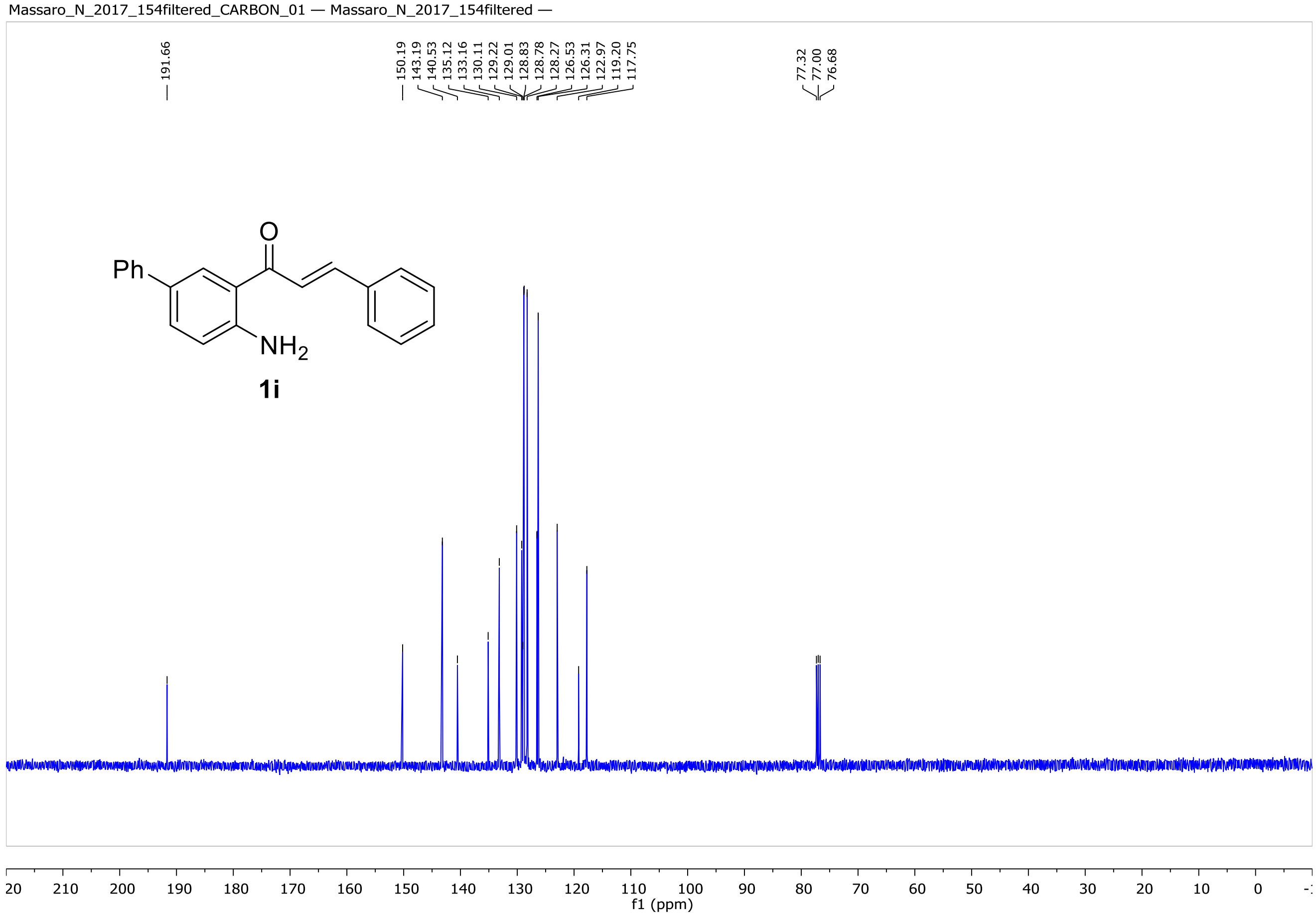
-1
f1 (ppm)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129.22
129.01
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128.78
128.27
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126.31
122.97
119.20
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77.00
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Ph
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NH2
1i
20
210
200
190
180
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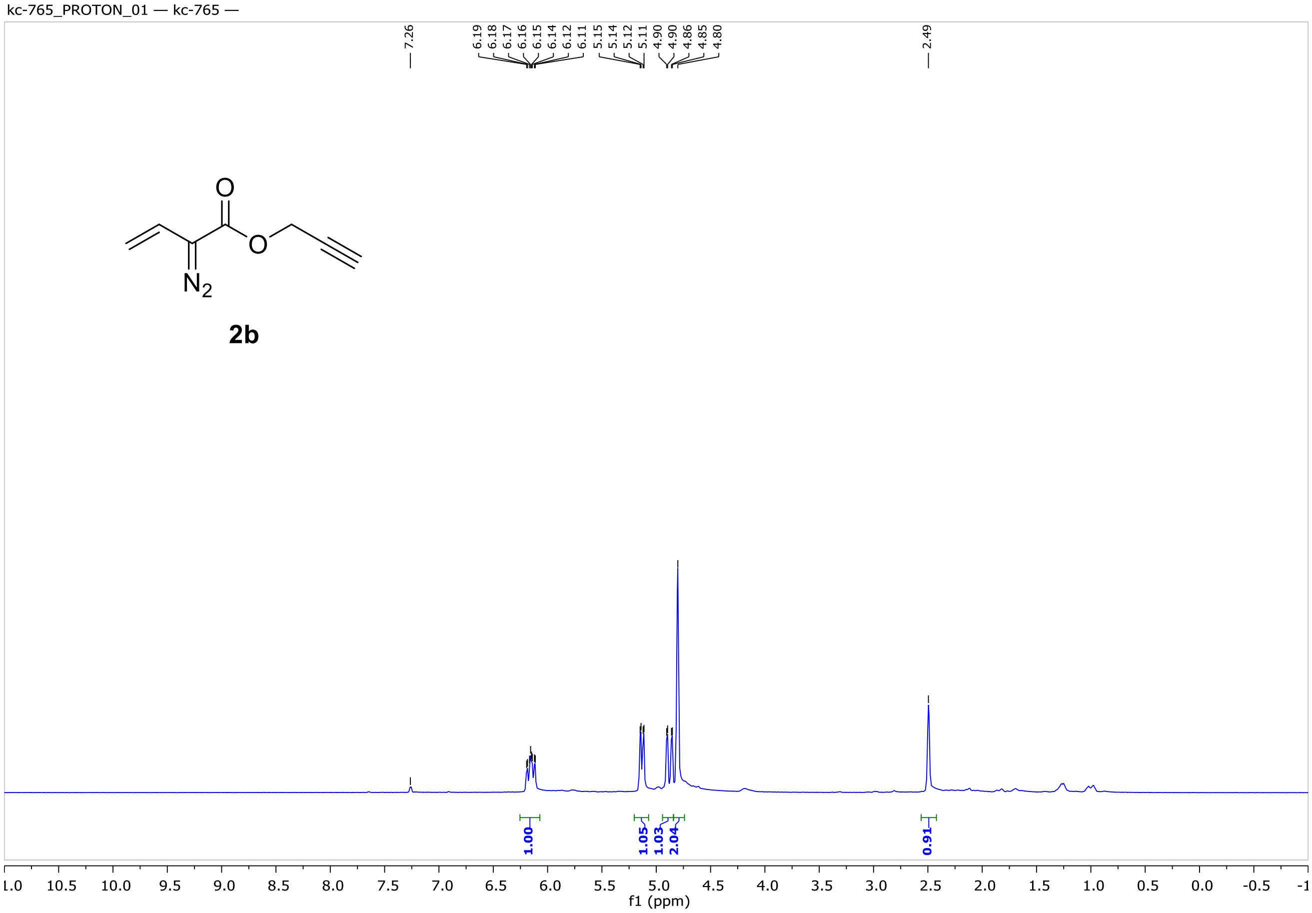
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4.90
4.86
4.85
4.80
2.49
O
O
N2
2b
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2.04
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7.5
7.0
6.5
6.0
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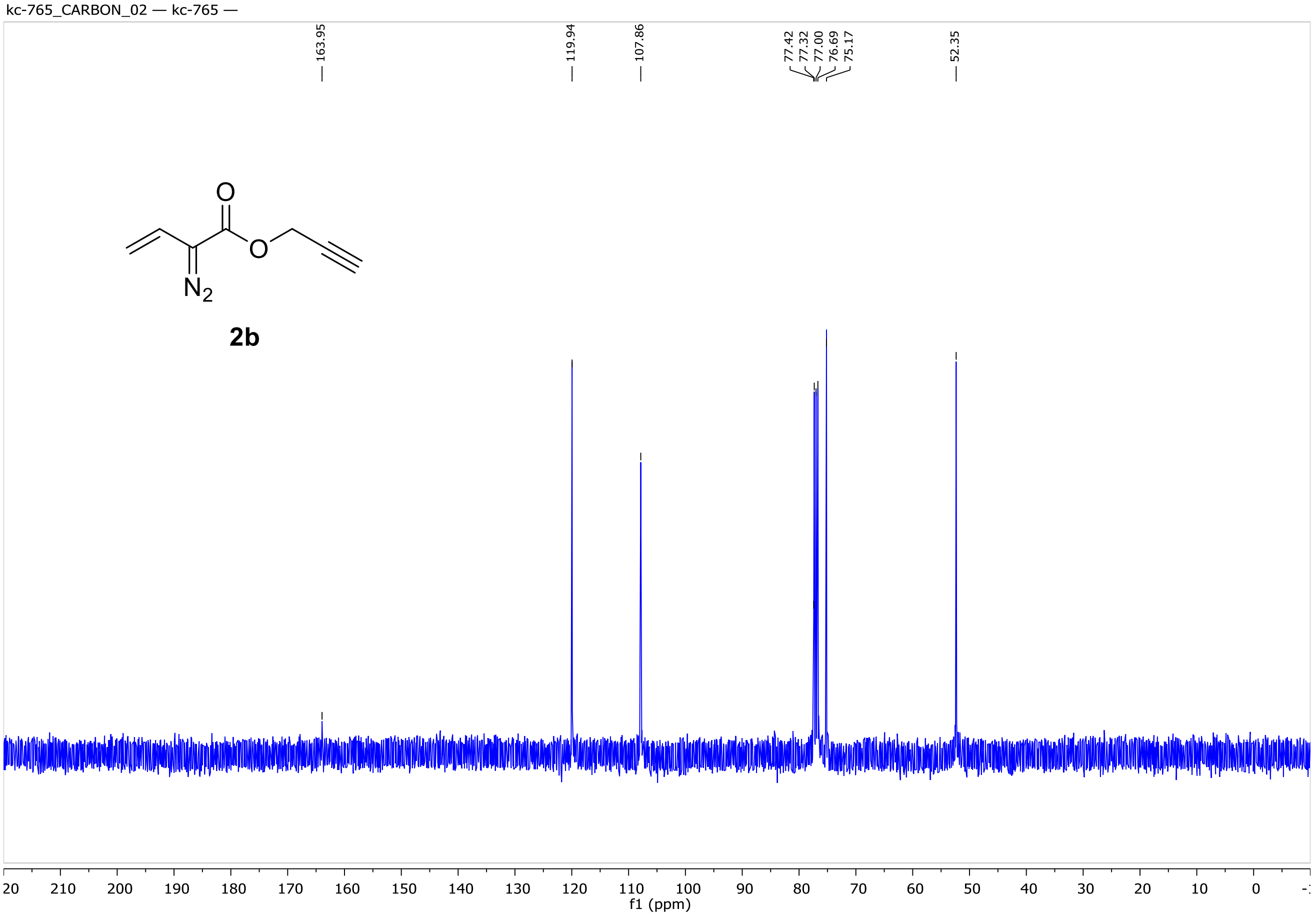
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O
N2
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
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20
10
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f1 (ppm)

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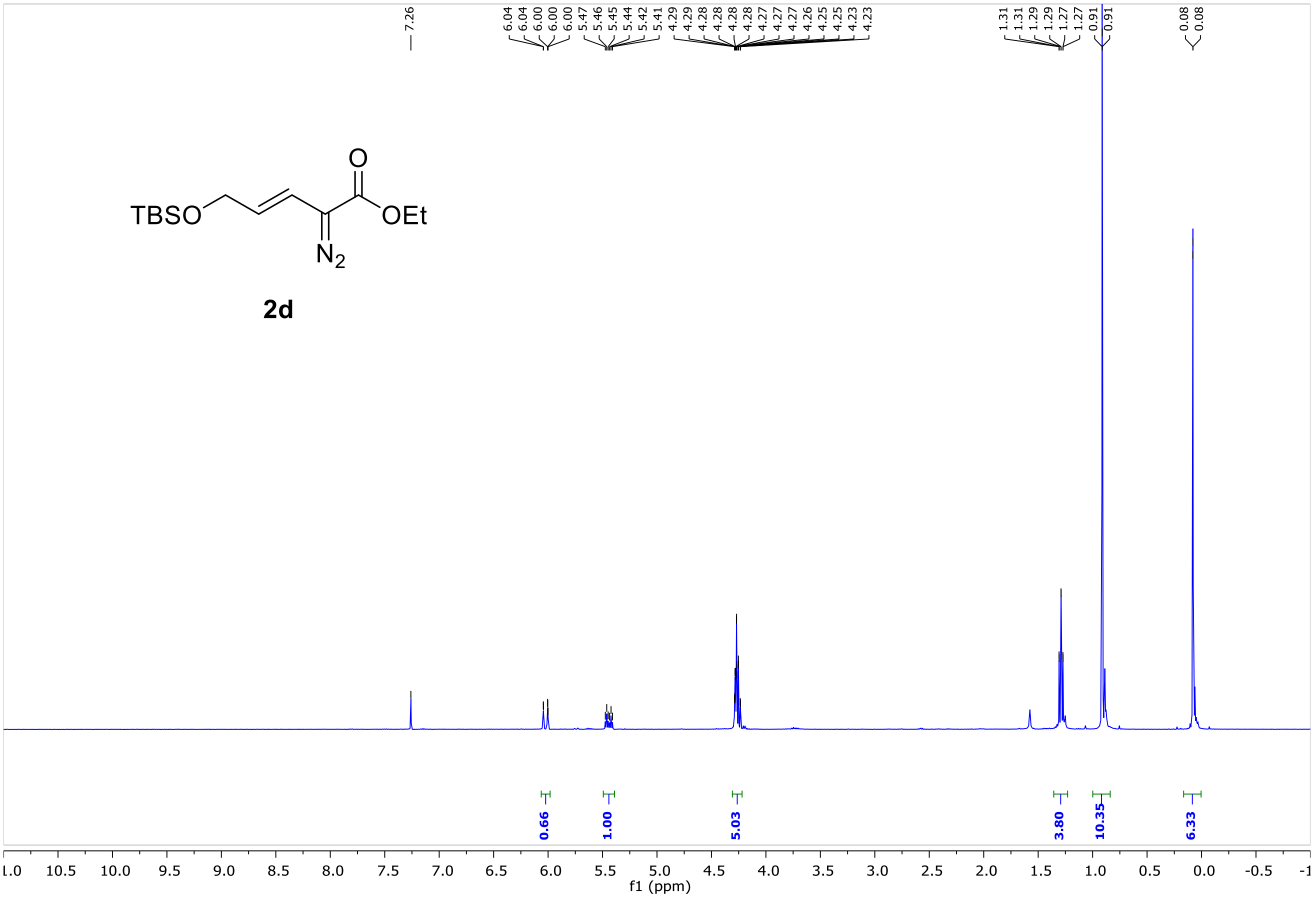

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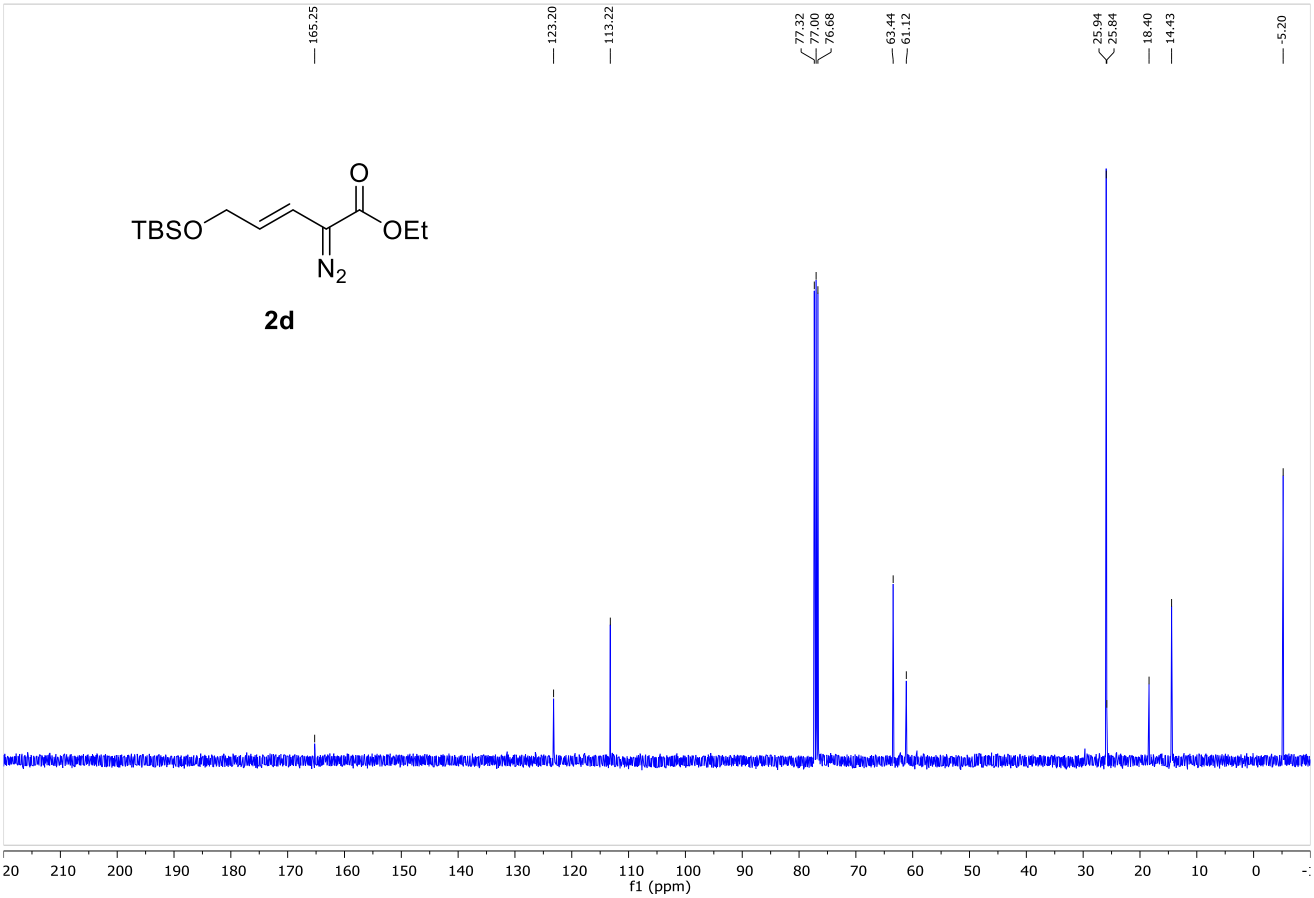

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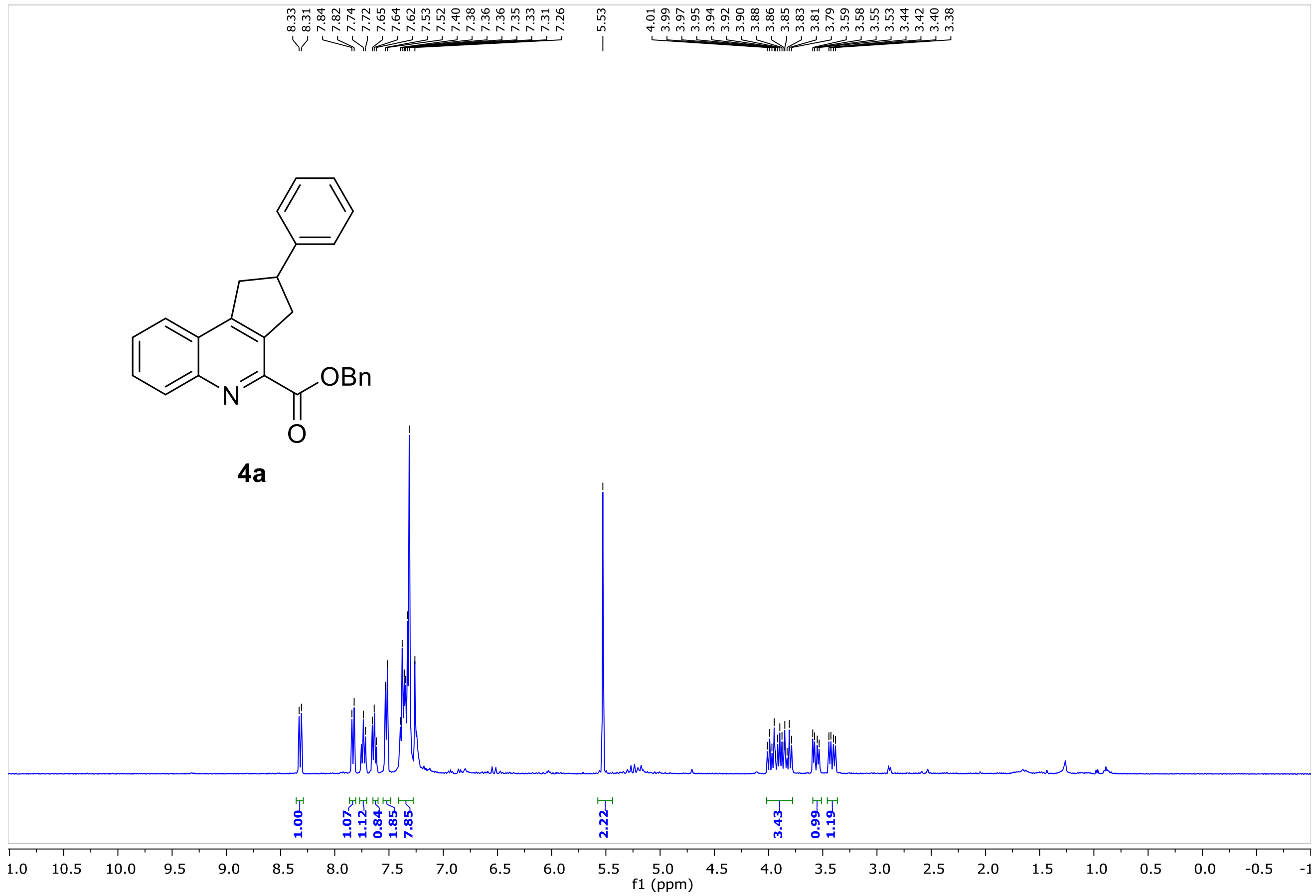

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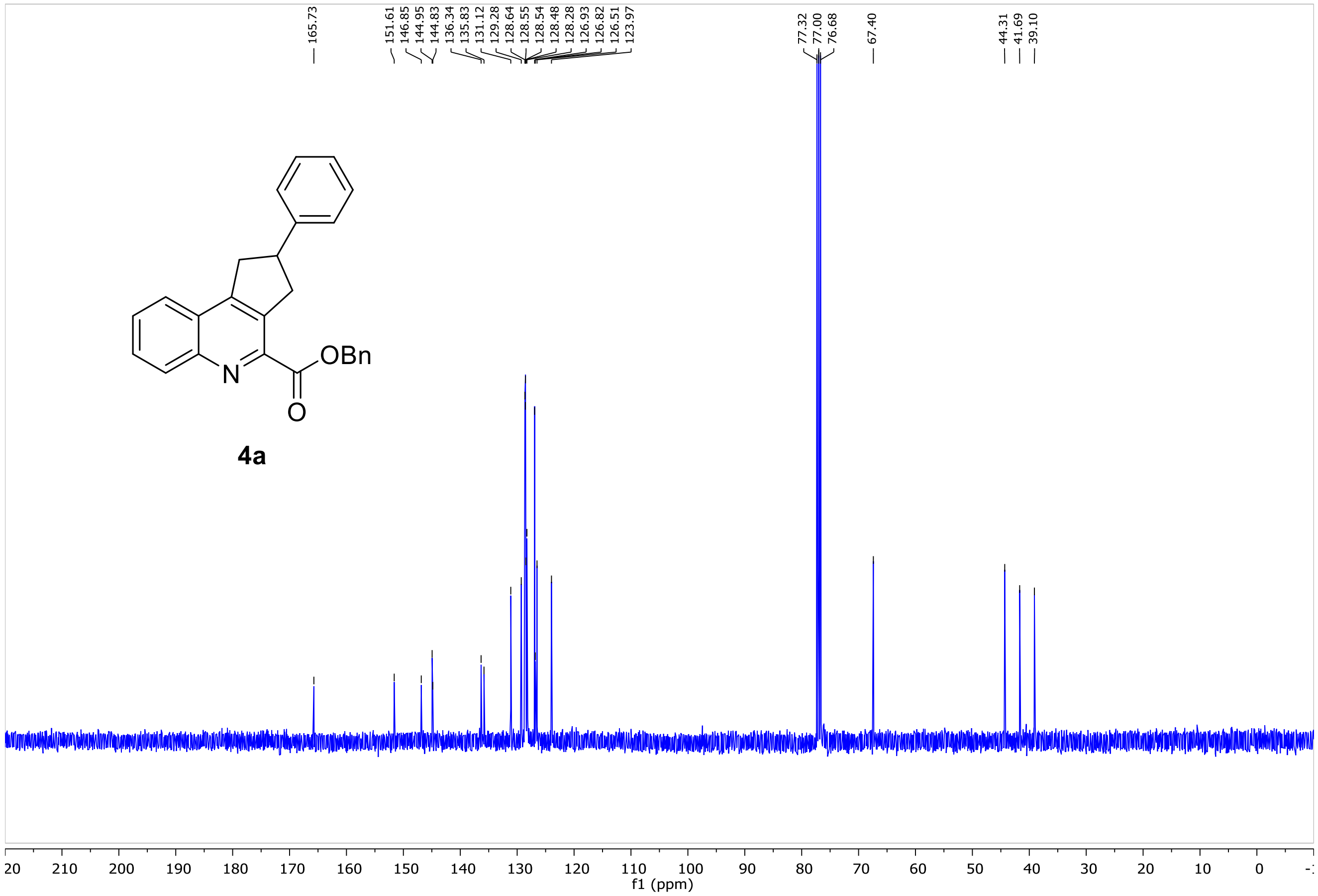

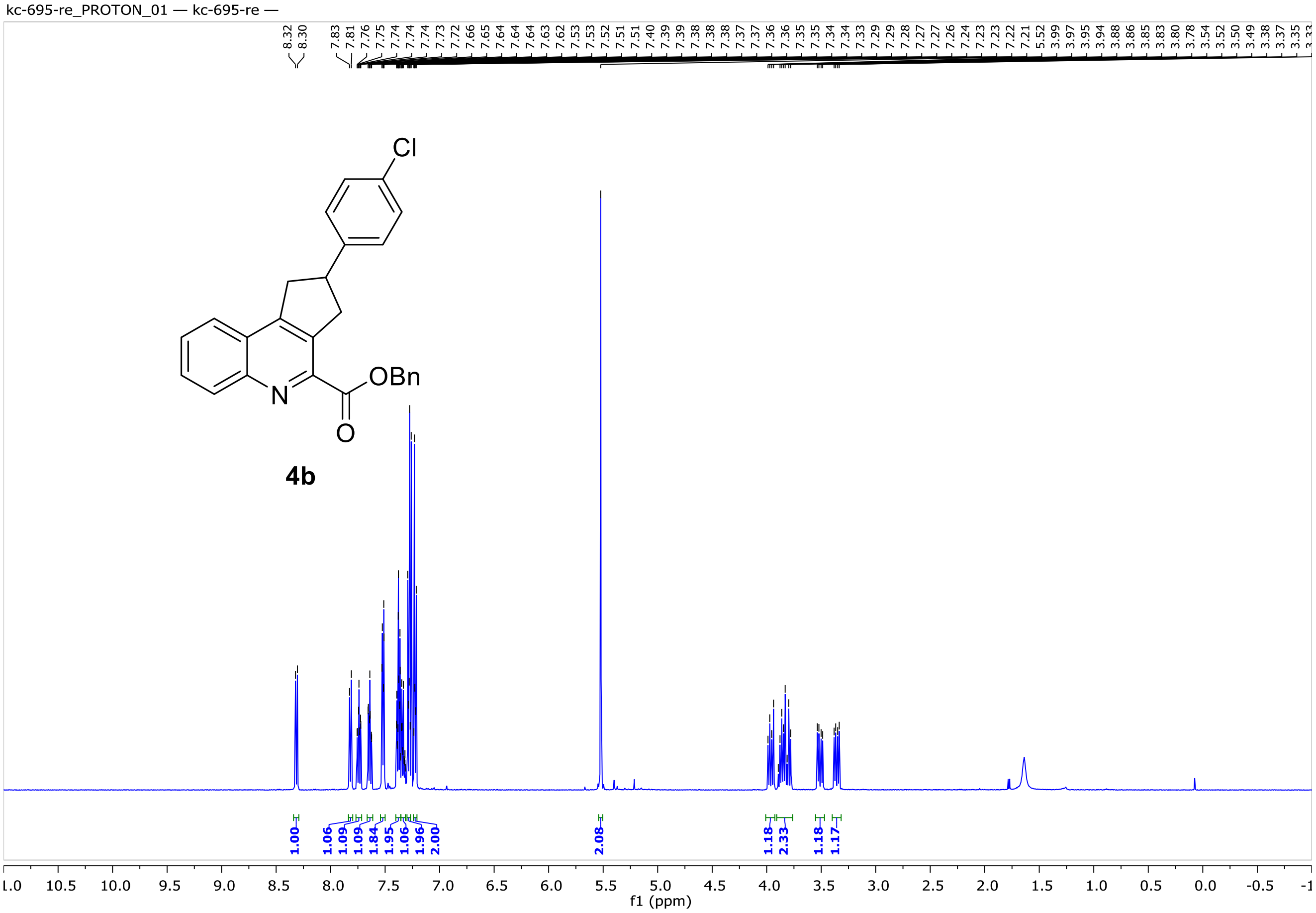
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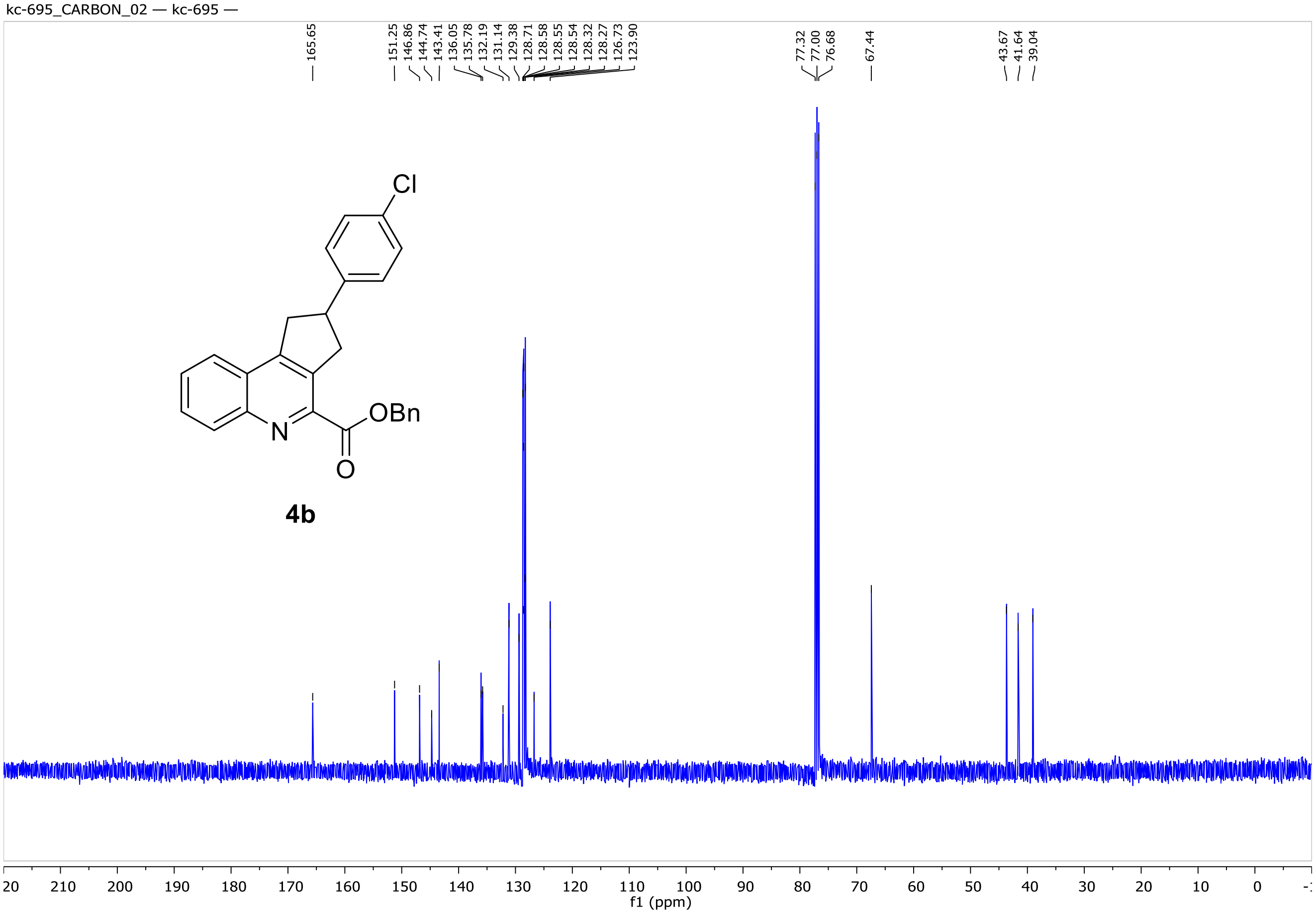
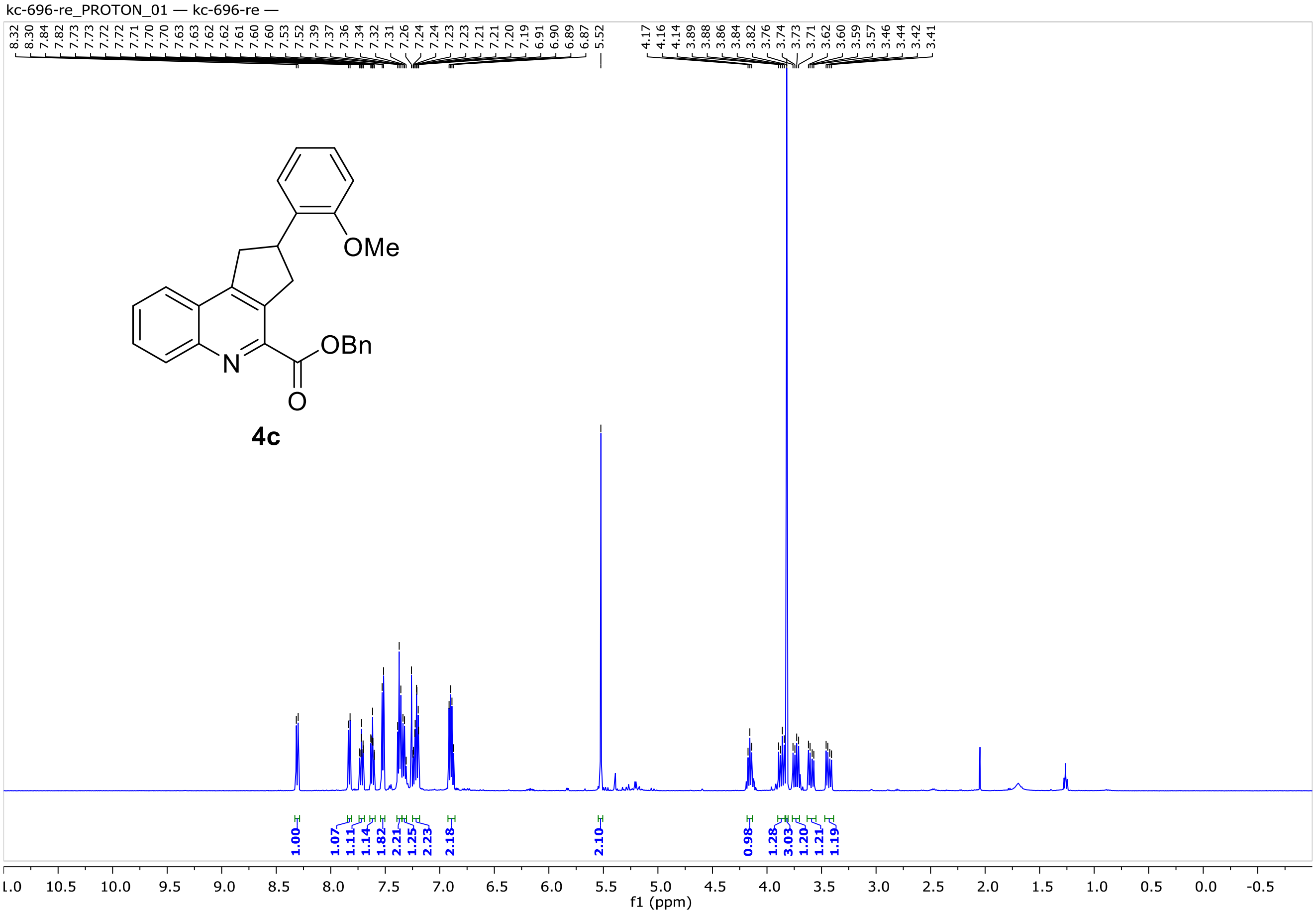
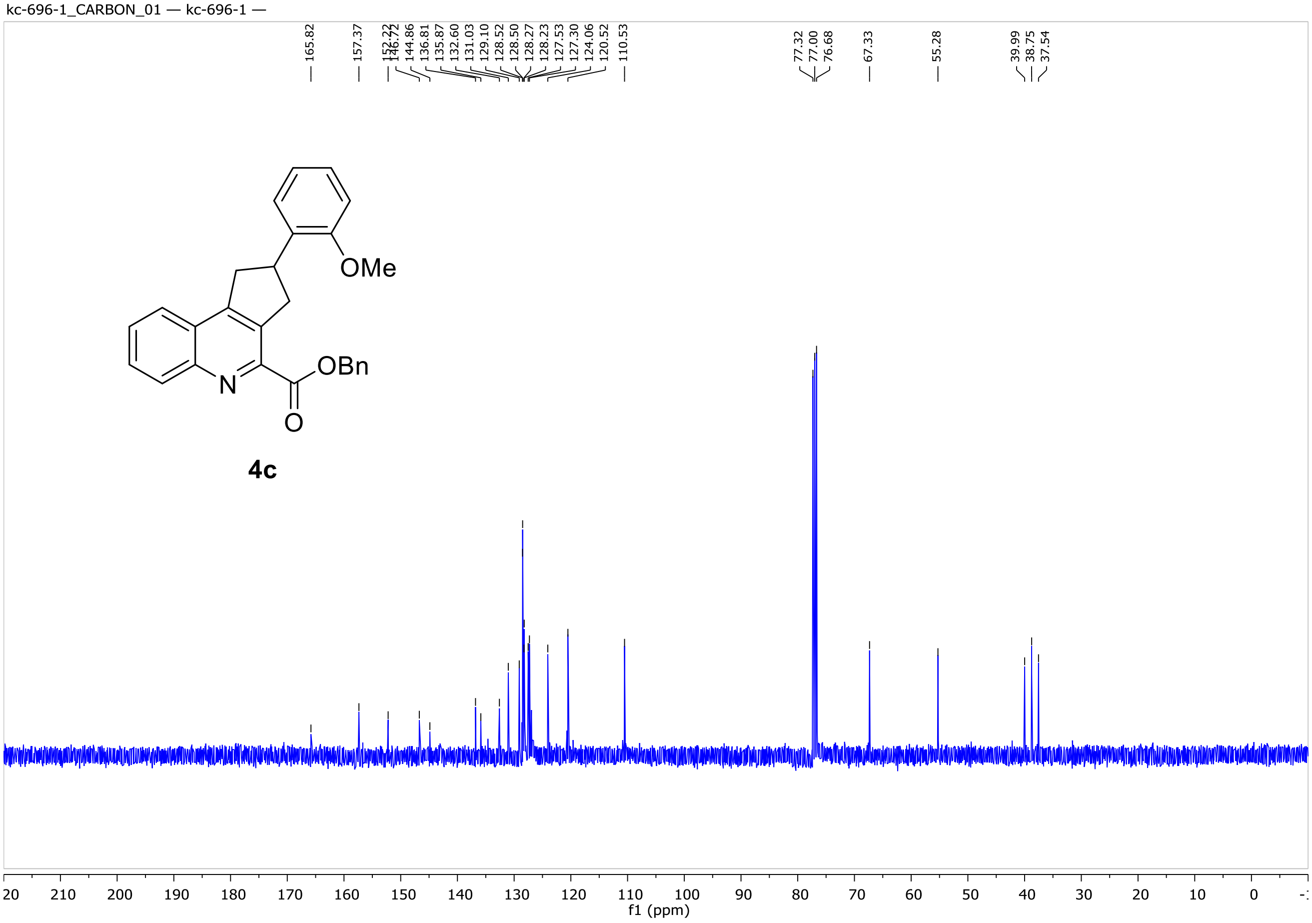
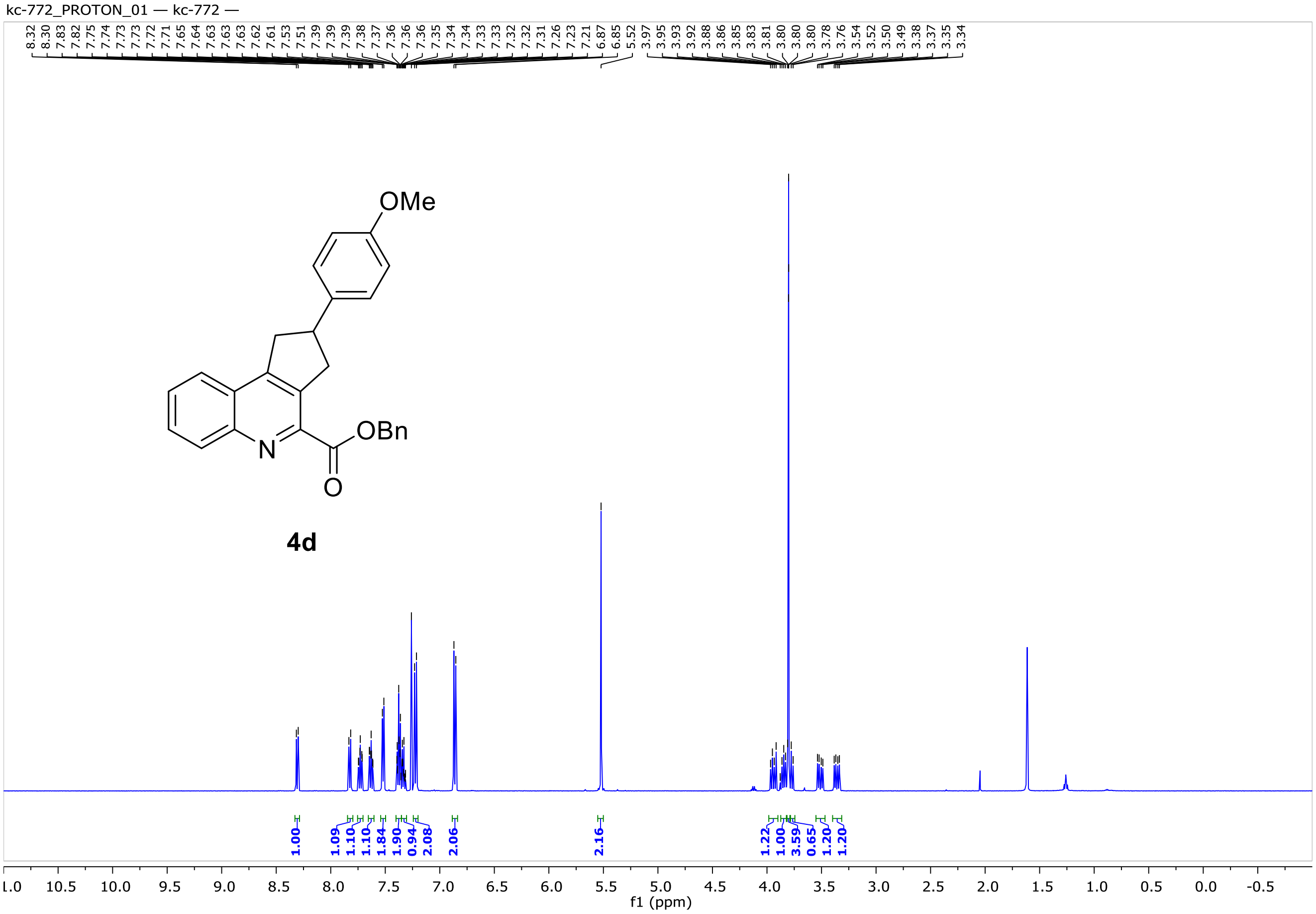
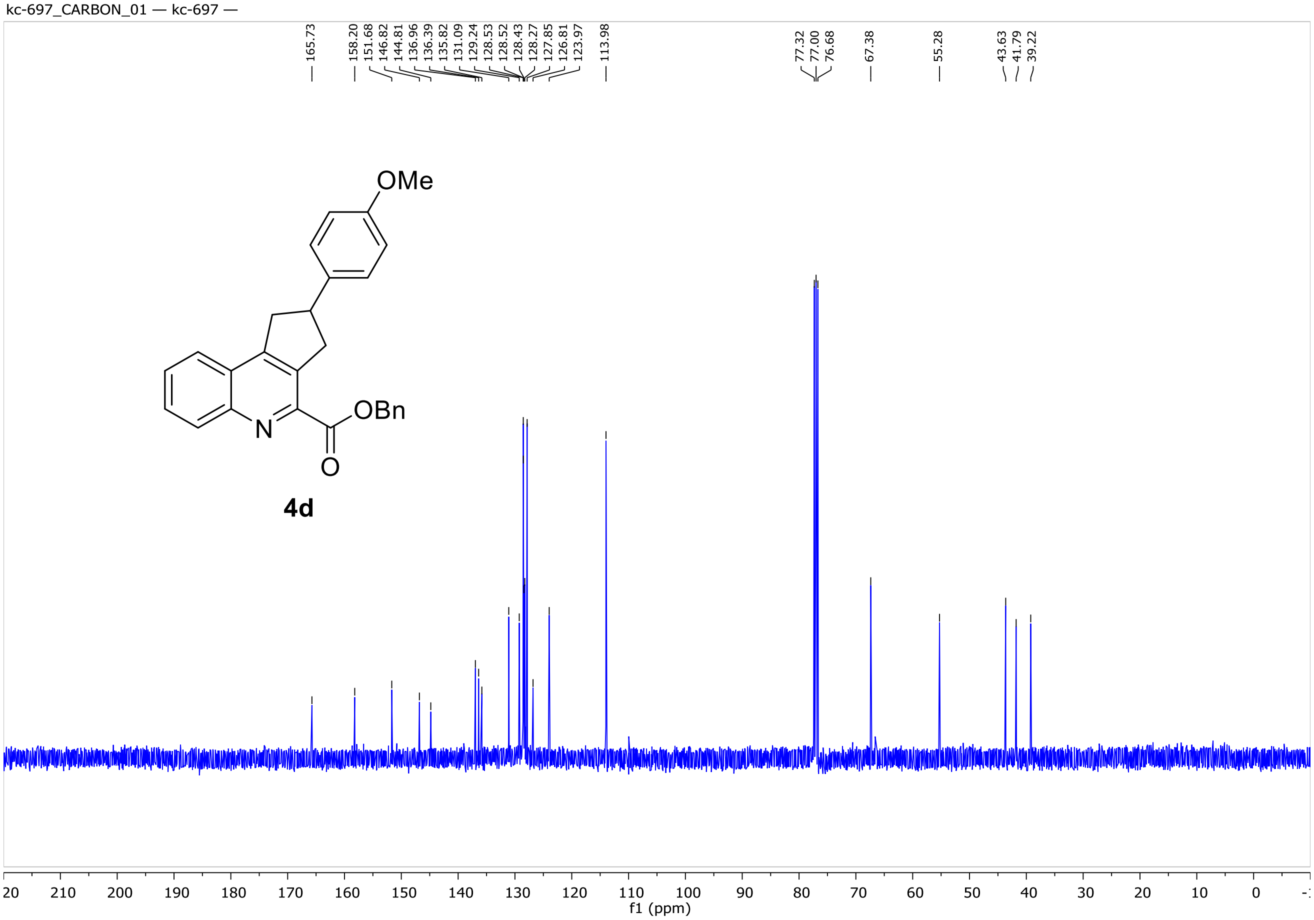
7.23
7.23
7.22
7.21
5.52
3.99
3.97
3.95
3.94
3.88
3.86
3.85
3.83
3.80
3.78
3.54
3.52
3.50
3.49
3.38
3.37
3.35
Cl
N
OBn
O
4b
1.00
1.06
1.09
1.09
1.84
1.95
1.06
1.96
2.00
2.08
1.18
2.33
1.18
1.17
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

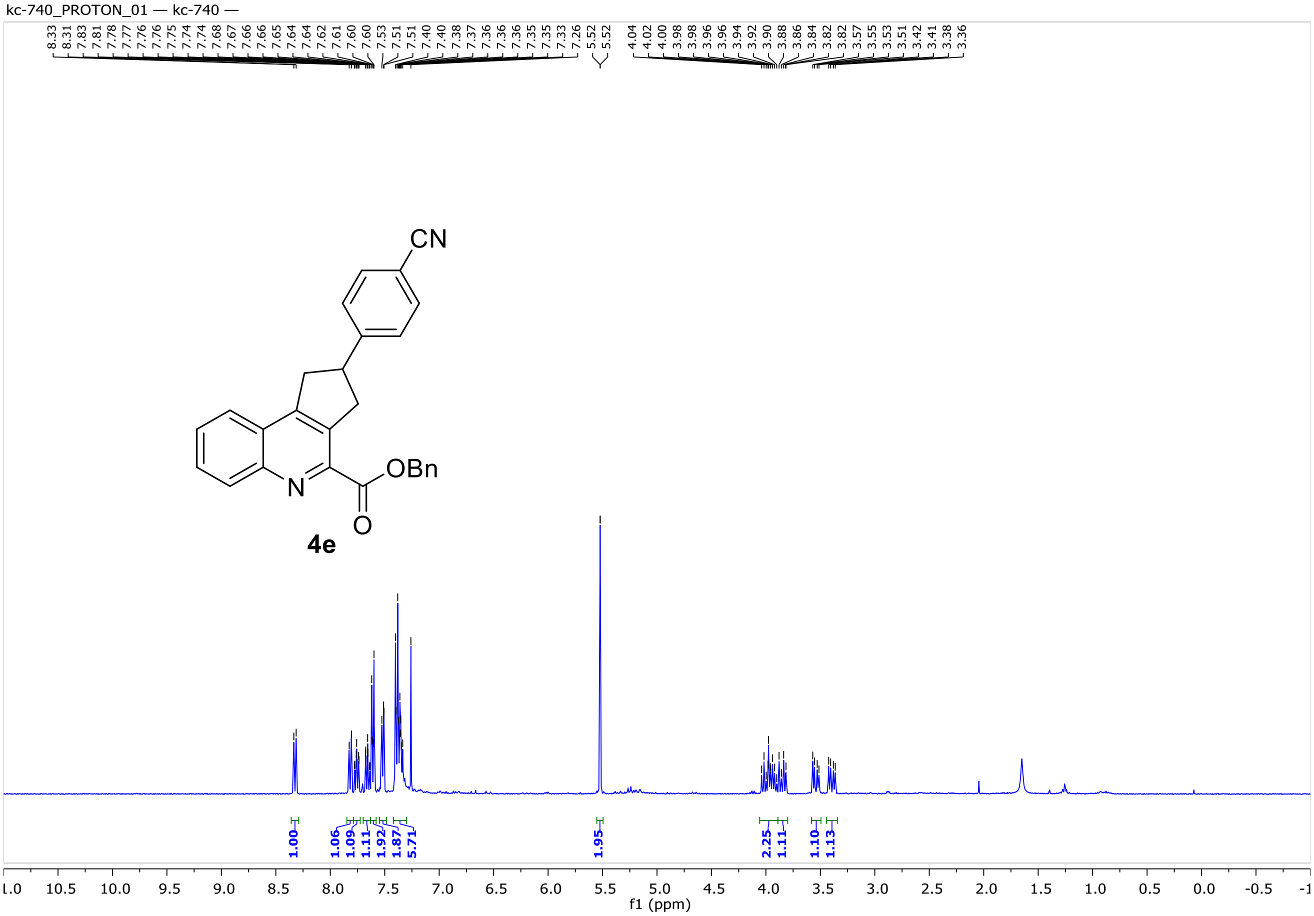

kc-695_CARBON_02 — kc-695 —
165.65
151.25
146.86
144.74
143.41
136.05
135.78
132.19
131.14
129.38
128.71
128.58
128.55
128.54
128.32
128.27
126.73
123.90
77.32
77.00
76.68
67.44
43.67
41.64
39.04
Cl
N
OBn
O
4b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

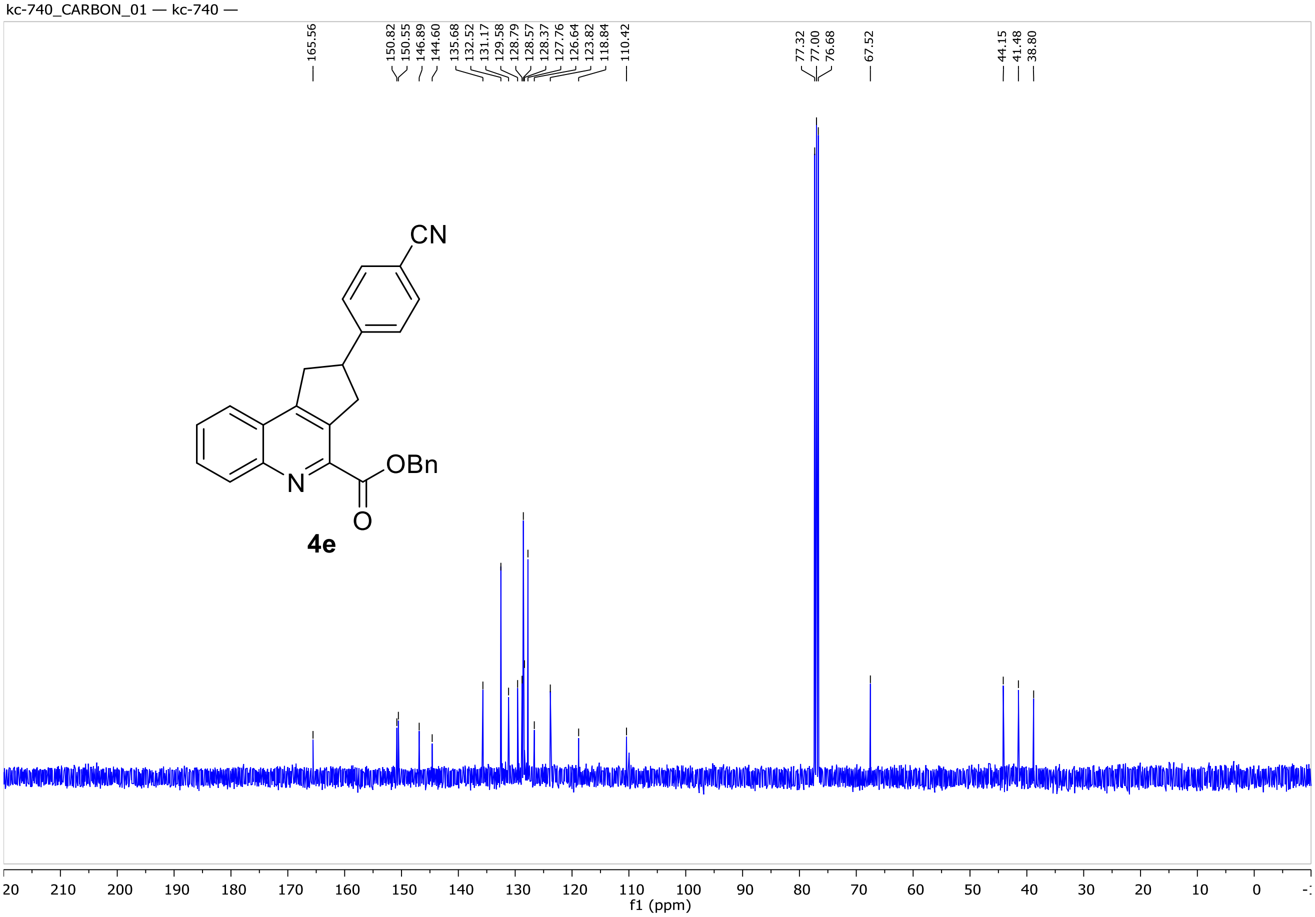

kc-696-re_PROTON_01 — kc-696-re —
8.32 8.30 7.84 7.82 7.73 7.73 7.72 7.72 7.71 7.70 7.70 7.63 7.63 7.62 7.61 7.60 7.60 7.53 7.52 7.39 7.37 7.36 7.34 7.32 7.31 7.26 7.24 7.24 7.23 7.23 7.21 7.21 7.20 7.19 6.91 6.90 6.89 6.87 5.52
4.17 4.16 4.14 3.89 3.88 3.86 3.84 3.82 3.76 3.74 3.73 3.71 3.62 3.60 3.59 3.57 3.46 3.44 3.42 3.41
OMe
OBn
N
O
4c
1.00 1.07 1.11 1.14 1.82 2.21 1.25 2.23 2.18 2.10 0.98 1.28 3.03 1.20 1.21 1.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

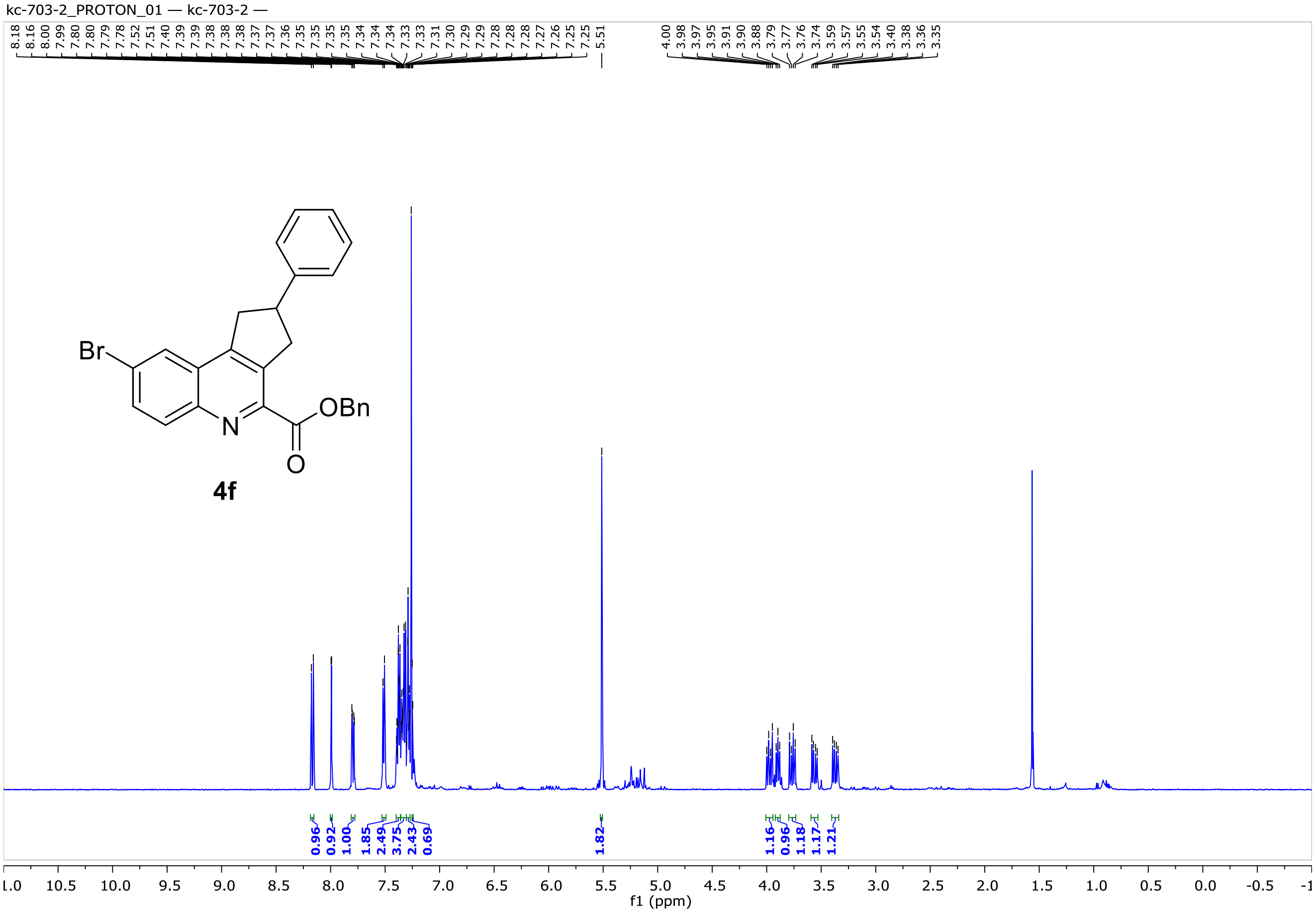

kc-696-1_CARBON_01 — kc-696-1 —
165.82 157.37 152.22 146.72 144.86 136.81 135.87 132.60 131.03 129.10 128.52 128.50 128.27 128.23 127.53 127.30 124.06 120.52 110.53
77.32 77.00 76.68 67.33 55.28 39.99 38.75 37.54
OMe
OBn
N
O
4c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

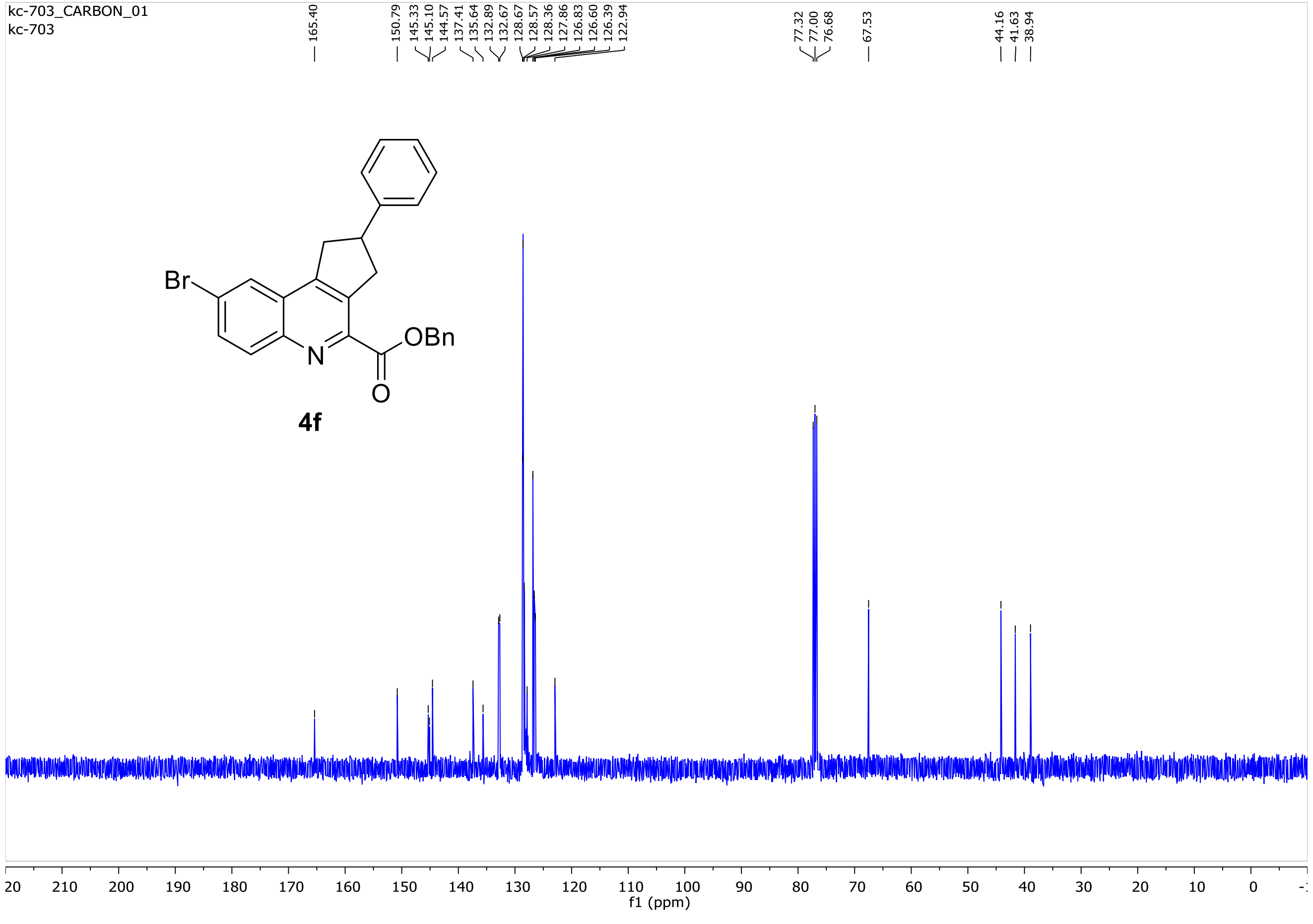

kc-772_PROTON_01 — kc-772 —
8.32 8.30 7.83 7.82 7.75 7.74 7.73 7.73 7.72 7.71 7.65 7.64 7.63 7.63 7.63 7.62 7.61 7.53 7.51 7.39 7.39 7.39 7.38 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.26 7.23 7.21 6.87 6.85 5.52 3.97 3.95 3.93 3.92 3.88 3.86 3.85 3.83 3.81 3.80 3.80 3.80 3.78 3.76 3.54 3.52 3.50 3.49 3.38 3.37 3.35 3.34
OMe
N
OBn
O
4d
1.00 1.09 1.10 1.10 1.84 1.90 0.94 2.08 2.06 2.16 1.22 1.00 3.59 0.65 1.20 1.20
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

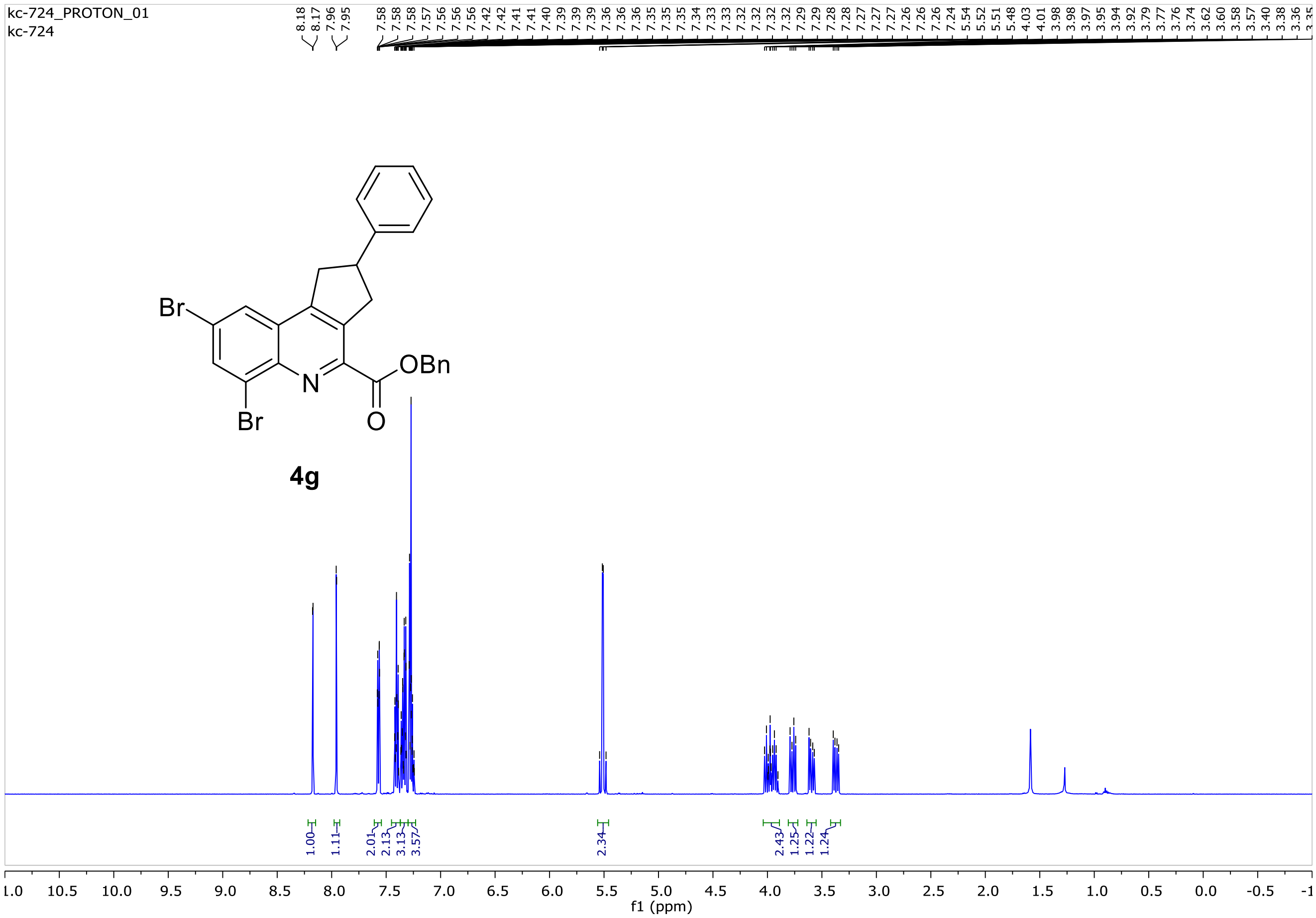

kc-697_CARBON_01 — kc-697 —
165.73 158.20 151.68 146.82 144.81 136.96 136.39 135.82 131.09 129.24 128.53 128.52 128.43 128.27 127.85 126.81 123.97 113.98 77.32 77.00 76.68 67.38 55.28 43.63 41.79 39.22
OMe
N
OBn
O
4d
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

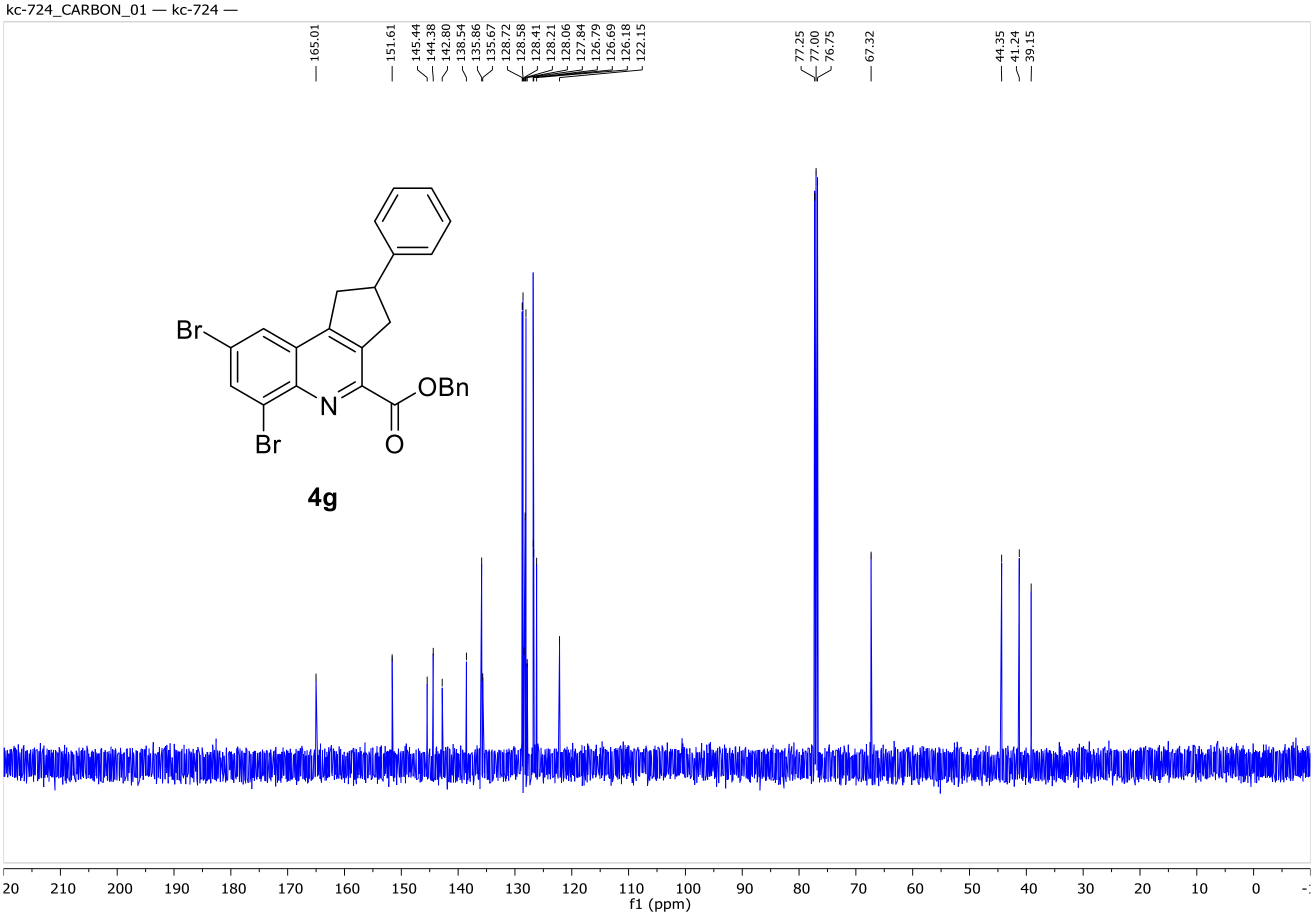

kc-740_PROTON_01 — kc-740 —
8.33
8.31
7.83
7.81
7.78
7.77
7.76
7.76
7.75
7.74
7.74
7.68
7.67
7.66
7.66
7.65
7.64
7.64
7.62
7.61
7.60
7.60
7.53
7.51
7.51
7.40
7.38
7.37
7.36
7.36
7.36
7.35
7.35
7.33
7.26
5.52
5.52
4.04
4.02
4.00
3.98
3.98
3.96
3.94
3.92
3.90
3.88
3.86
3.84
3.82
3.82
3.57
3.55
3.53
3.51
3.42
3.41
3.38
3.36
CN
OBn
N
O
4e
1.00
1.06
1.09
1.11
1.92
1.87
5.71
1.95
2.25
1.11
1.10
1.13
f1 (ppm)

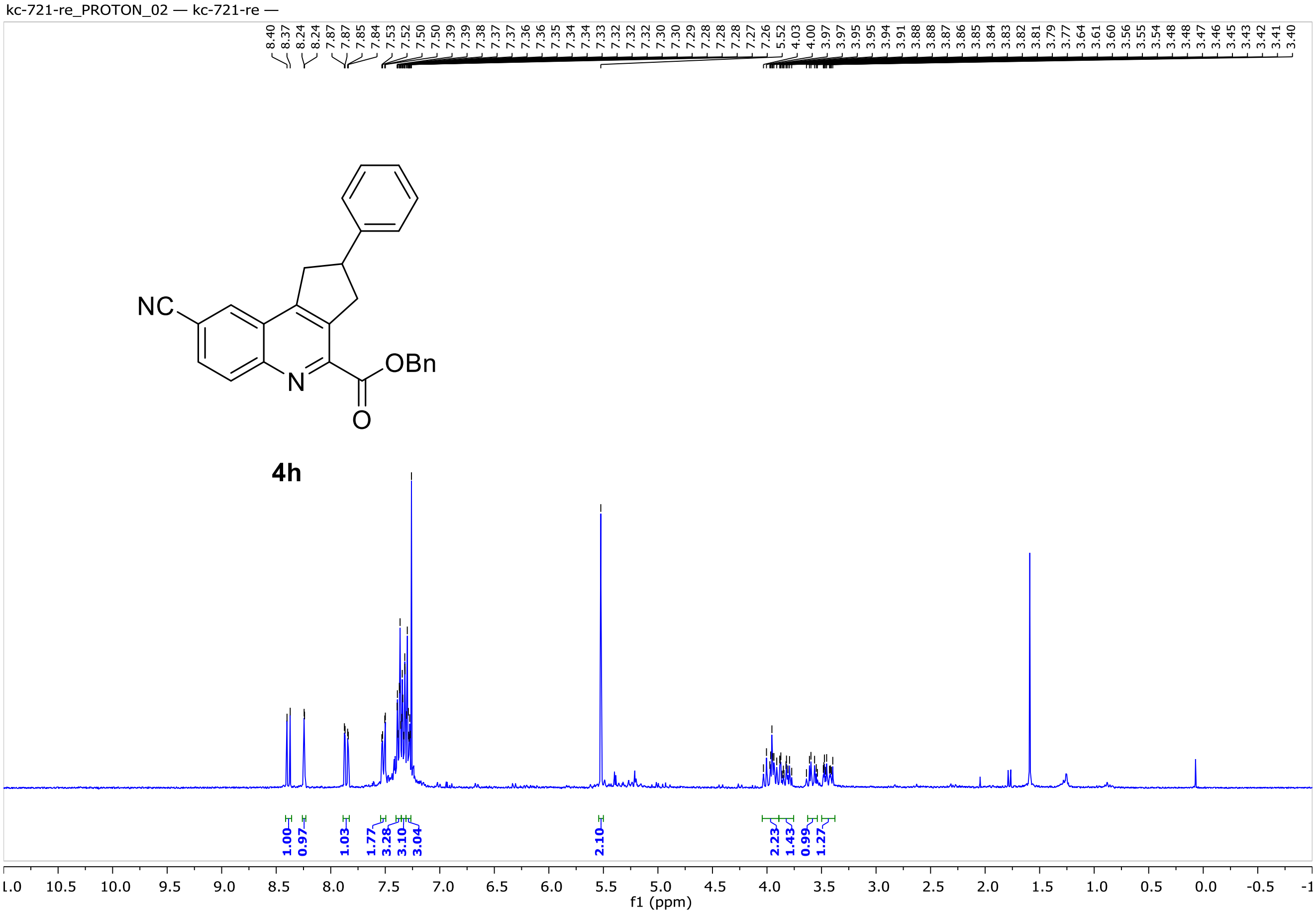

kc-740_CARBON_01 — kc-740 —
165.56
150.82
150.55
146.89
144.60
135.68
132.52
131.17
129.58
128.79
128.57
128.37
127.76
126.64
123.82
118.84
110.42
77.32
77.00
76.68
67.52
44.15
41.48
38.80
CN
OBn
N
O
4e
f1 (ppm)

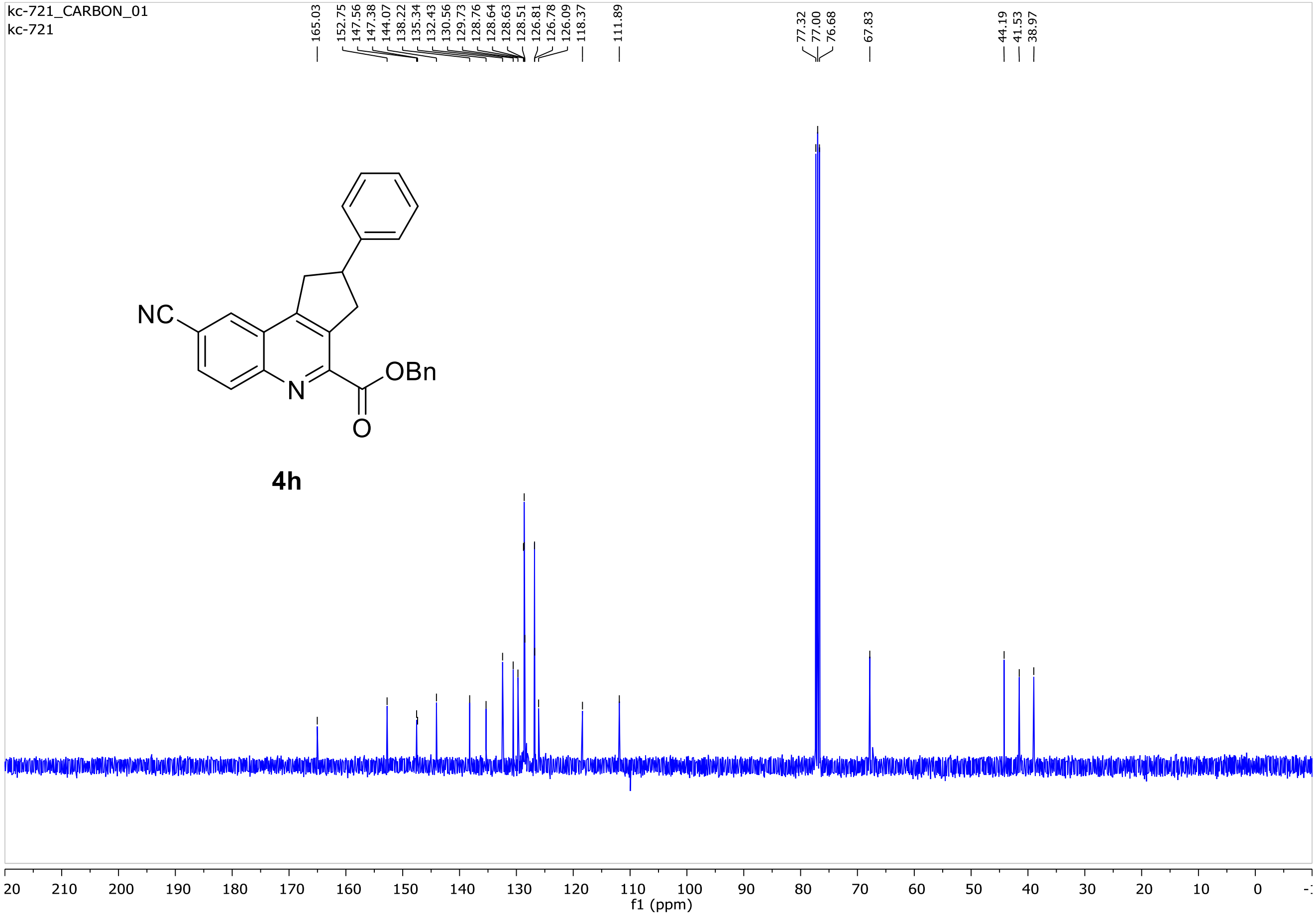

kc-703-2_PROTON_01 — kc-703-2 —
8.18
8.16
8.00
7.99
7.80
7.80
7.79
7.78
7.52
7.51
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.31
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.26
7.25
7.25
5.51
4.00
3.98
3.97
3.95
3.91
3.90
3.88
3.79
3.77
3.76
3.74
3.59
3.57
3.55
3.54
3.40
3.38
3.36
3.35
Br
N
OBn
O
4f
0.96
0.92
1.00
1.85
2.49
3.75
2.43
0.69
1.82
1.16
0.96
1.18
1.17
1.21
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

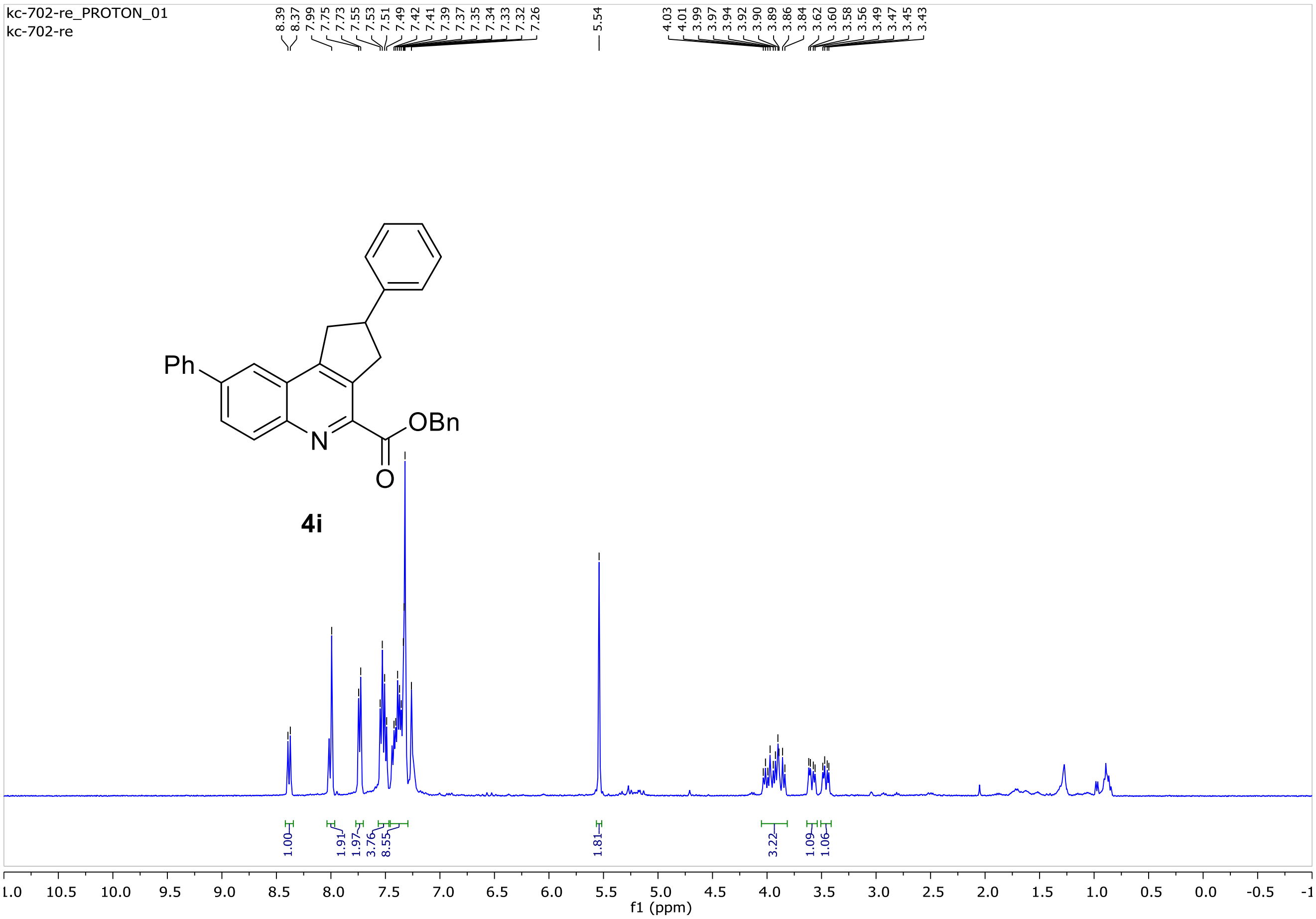

kc-703_CARBON_01
kc-703
165.40
150.79
145.33
145.10
144.57
137.41
135.64
132.89
132.67
128.67
128.57
128.36
127.86
126.83
126.60
126.39
122.94
77.32
77.00
76.68
67.53
44.16
41.63
38.94
Br
N
OBn
O
4f
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


kc-724_PROTON_01
kc-724
8.18
8.17
7.96
7.95
7.58
7.58
7.58
7.57
7.56
7.56
7.56
7.42
7.42
7.41
7.40
7.39
7.39
7.39
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.32
7.32
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.26
7.24
5.54
5.52
5.51
5.48
4.03
4.01
3.98
3.98
3.97
3.95
3.94
3.92
3.79
3.77
3.76
3.74
3.62
3.60
3.58
3.57
3.40
3.38
3.36
3.3
Br
Br
N
OBn
O
4g
1.00
1.11
2.01
2.13
3.13
3.57
2.34
2.43
1.25
1.22
1.24
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

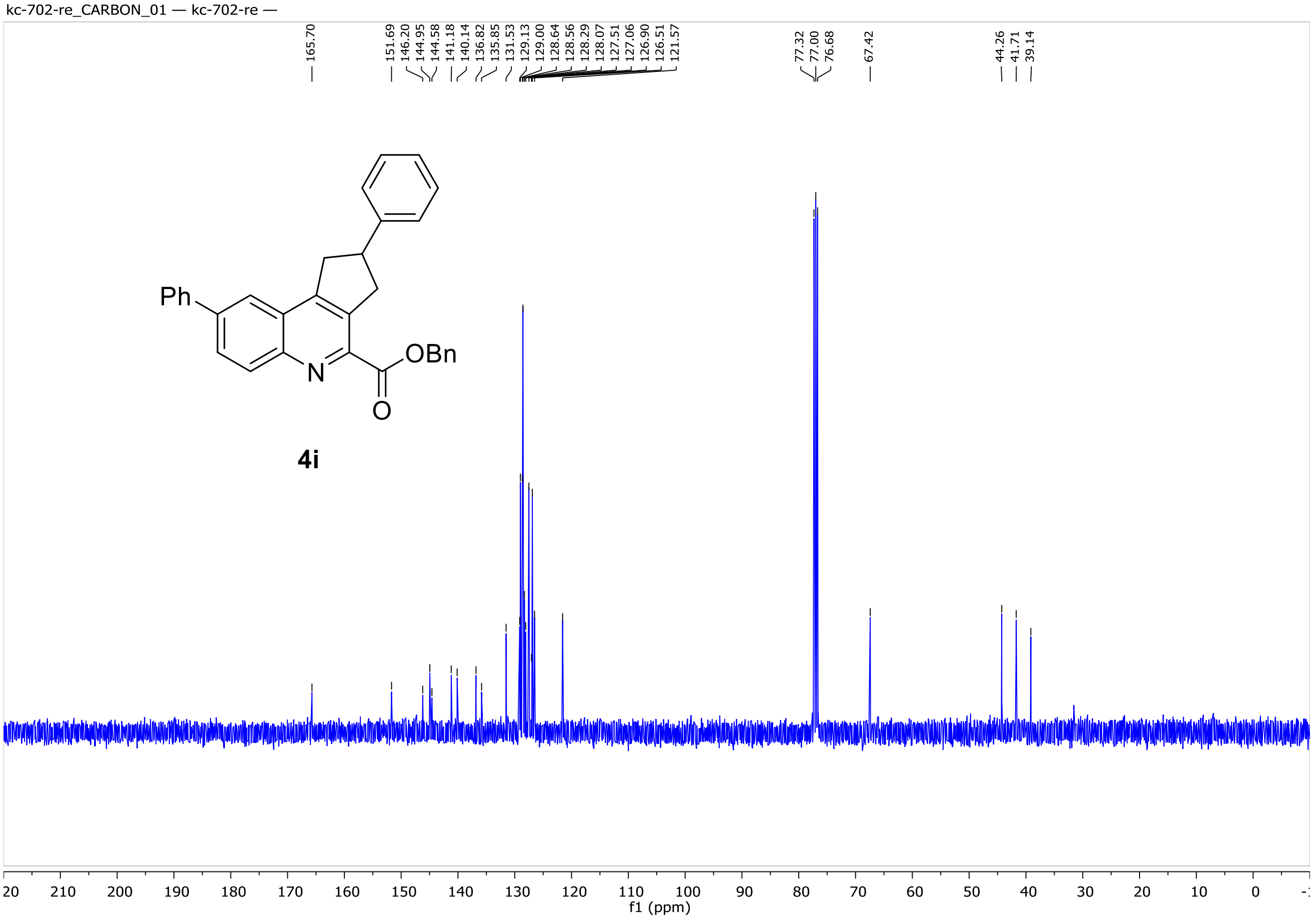

kc-724_CARBON_01 — kc-724 —
165.01
151.61
145.44
144.38
142.80
138.54
135.86
135.67
128.72
128.58
128.41
128.21
128.06
127.84
126.79
126.69
126.18
122.15
77.25
77.00
76.75
67.32
44.35
41.24
39.15
Br
Br
N
OBn
O
4g
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


kc-721-re_PROTON_02 — kc-721-re —
8.40
8.37
8.24
8.24
7.87
7.87
7.85
7.84
7.53
7.52
7.50
7.50
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.32
7.30
7.30
7.29
7.28
7.28
7.28
7.27
7.26
5.52
4.03
4.00
3.97
3.97
3.95
3.95
3.94
3.91
3.88
3.88
3.87
3.86
3.85
3.84
3.83
3.82
3.81
3.79
3.77
3.64
3.61
3.60
3.56
3.55
3.54
3.48
3.48
3.47
3.46
3.45
3.43
3.42
3.41
3.40
NC
N
OBn
O
4h
1.00
0.97
1.03
1.77
3.28
3.10
3.04
2.10
2.23
1.43
0.99
1.27
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

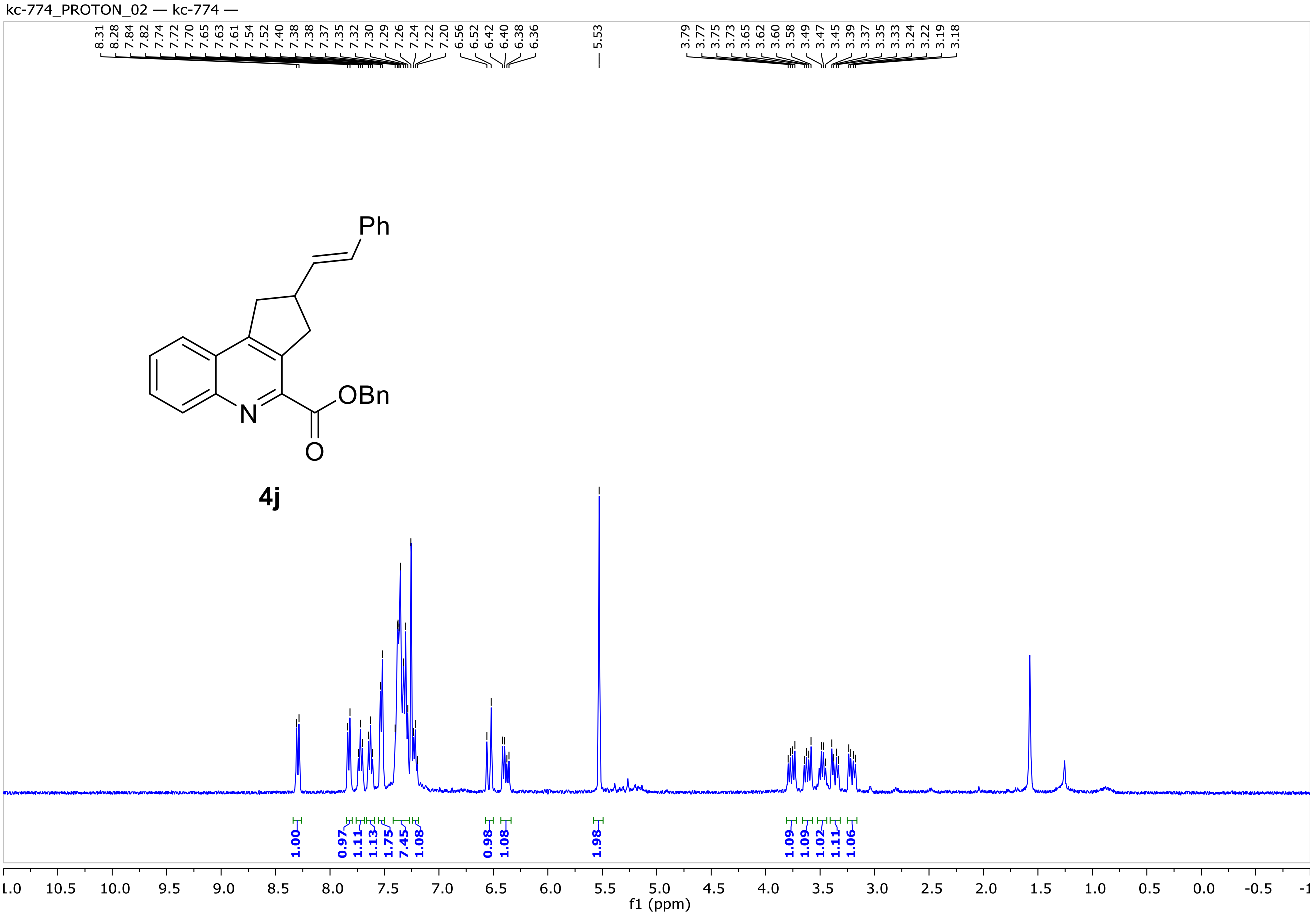

kc-721_CARBON_01
kc-721
165.03
152.75
147.56
147.38
144.07
138.22
135.34
132.43
130.56
129.73
128.76
128.64
128.63
128.51
126.81
126.78
126.09
118.37
111.89
77.32
77.00
76.68
67.83
44.19
41.53
38.97
NC
N
OBn
O
4h
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

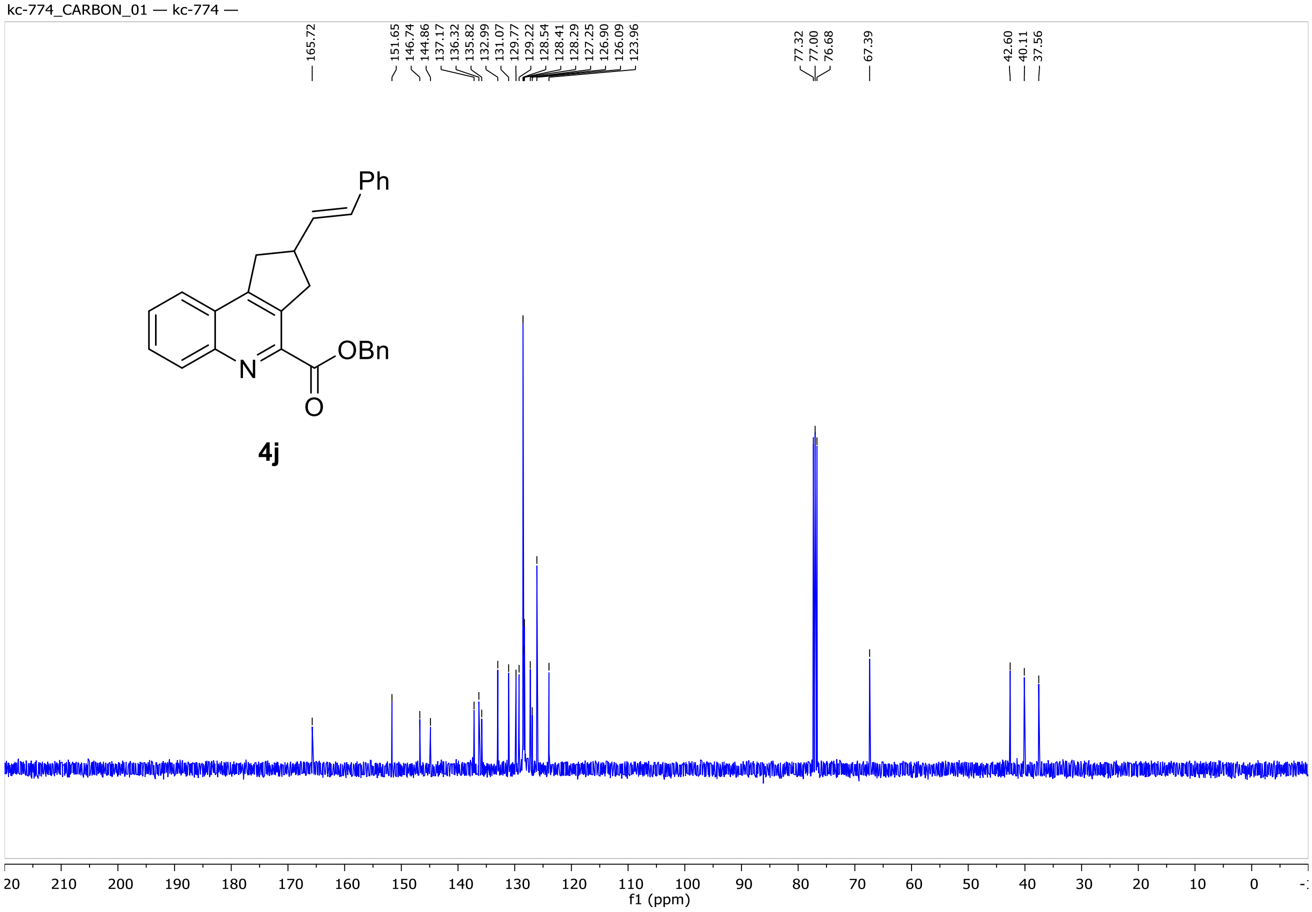

kc-702-re_PROTON_01
kc-702-re
8.39
8.37
7.99
7.75
7.73
7.55
7.53
7.51
7.49
7.42
7.41
7.39
7.37
7.35
7.34
7.33
7.32
7.26
5.54
4.03
4.01
3.99
3.97
3.94
3.92
3.90
3.89
3.86
3.84
3.62
3.60
3.58
3.56
3.49
3.47
3.45
3.43
Ph
OBn
N
O
1.00
1.91
1.97
3.76
8.55
1.81
3.22
1.09
1.06
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

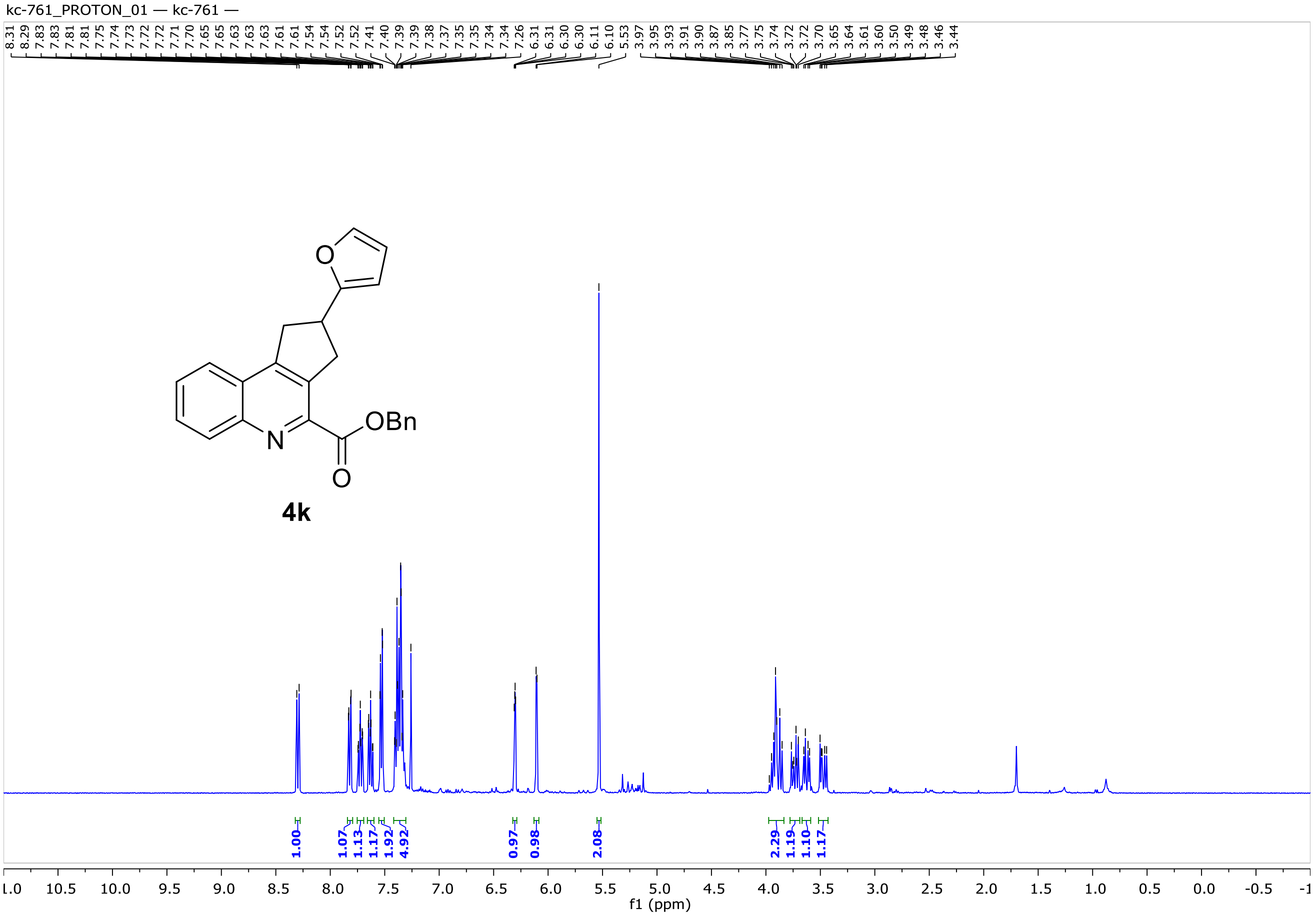
4i

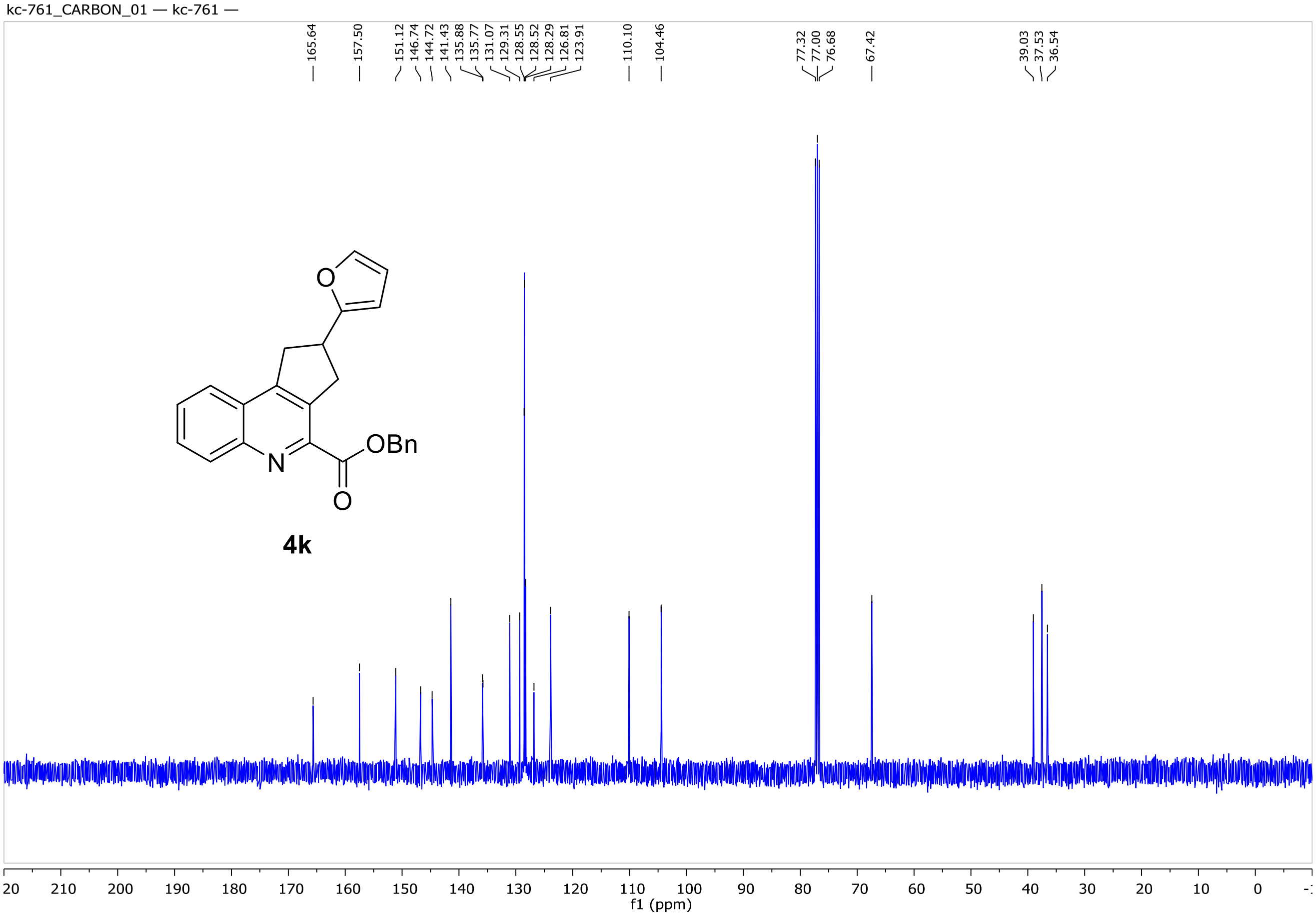

kc-702-re_CARBON_01 — kc-702-re —
165.70
151.69
146.20
144.95
144.58
141.18
140.14
136.82
135.85
131.53
129.13
129.00
128.64
128.56
128.29
128.07
127.51
127.06
126.90
126.51
121.57
77.32
77.00
76.68
67.42
44.26
41.71
39.14
Ph
OBn
N
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

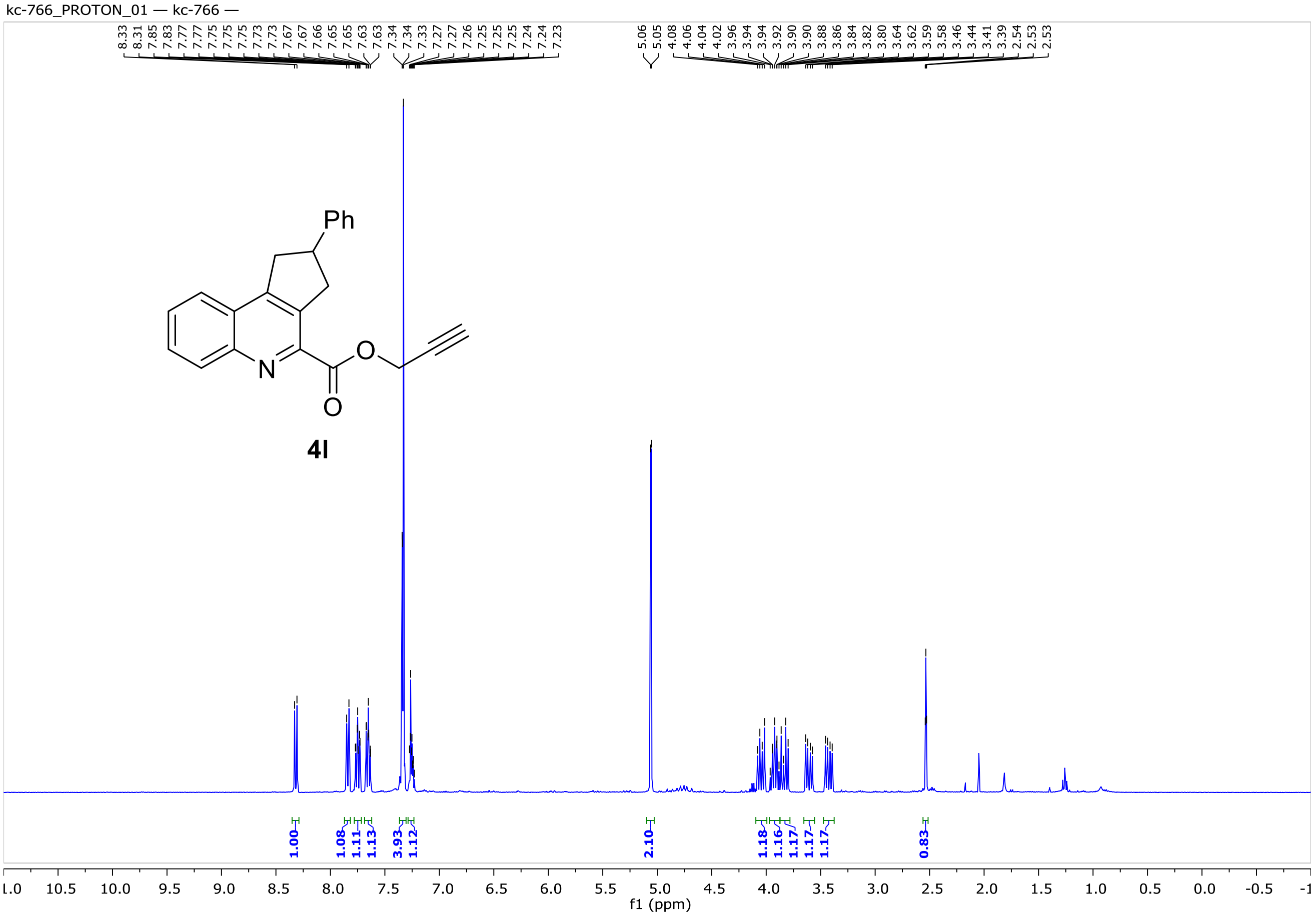
4i

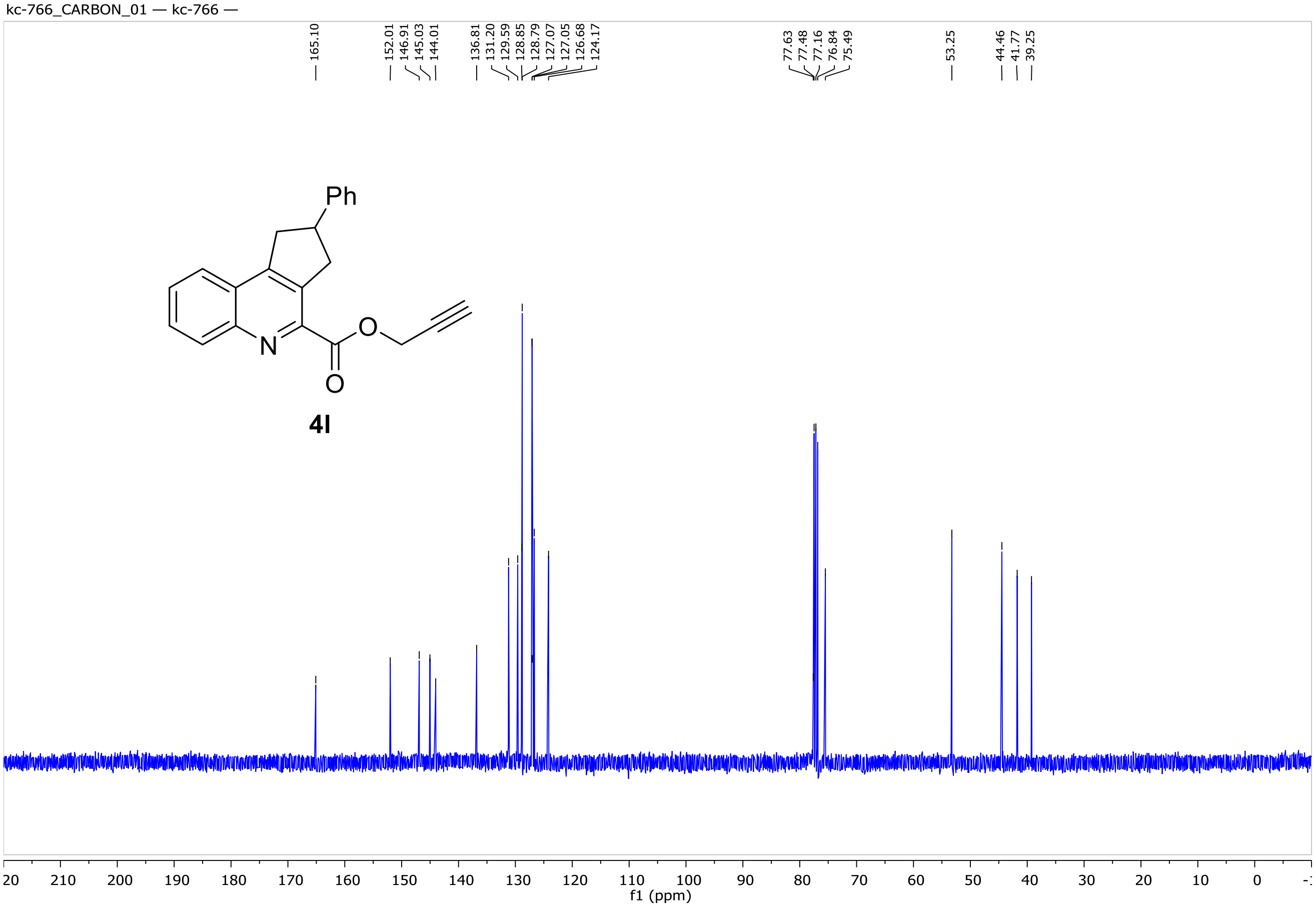

kc-774_PROTON_02 — kc-774 —
8.31 8.28 7.84 7.82 7.74 7.72 7.70 7.65 7.63 7.61 7.54 7.52 7.40 7.38 7.38 7.37 7.35 7.32 7.30 7.29 7.26 7.24 7.22 7.20 6.56 6.52 6.42 6.40 6.38 6.36
5.53
3.79 3.77 3.75 3.73 3.65 3.62 3.60 3.58 3.49 3.47 3.45 3.39 3.37 3.35 3.33 3.24 3.22 3.19 3.18
Ph
OBn
N
O
4j
1.00 0.97 1.11 1.13 1.75 7.45 1.08 0.98 1.08 1.98 1.09 1.09 1.02 1.11 1.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

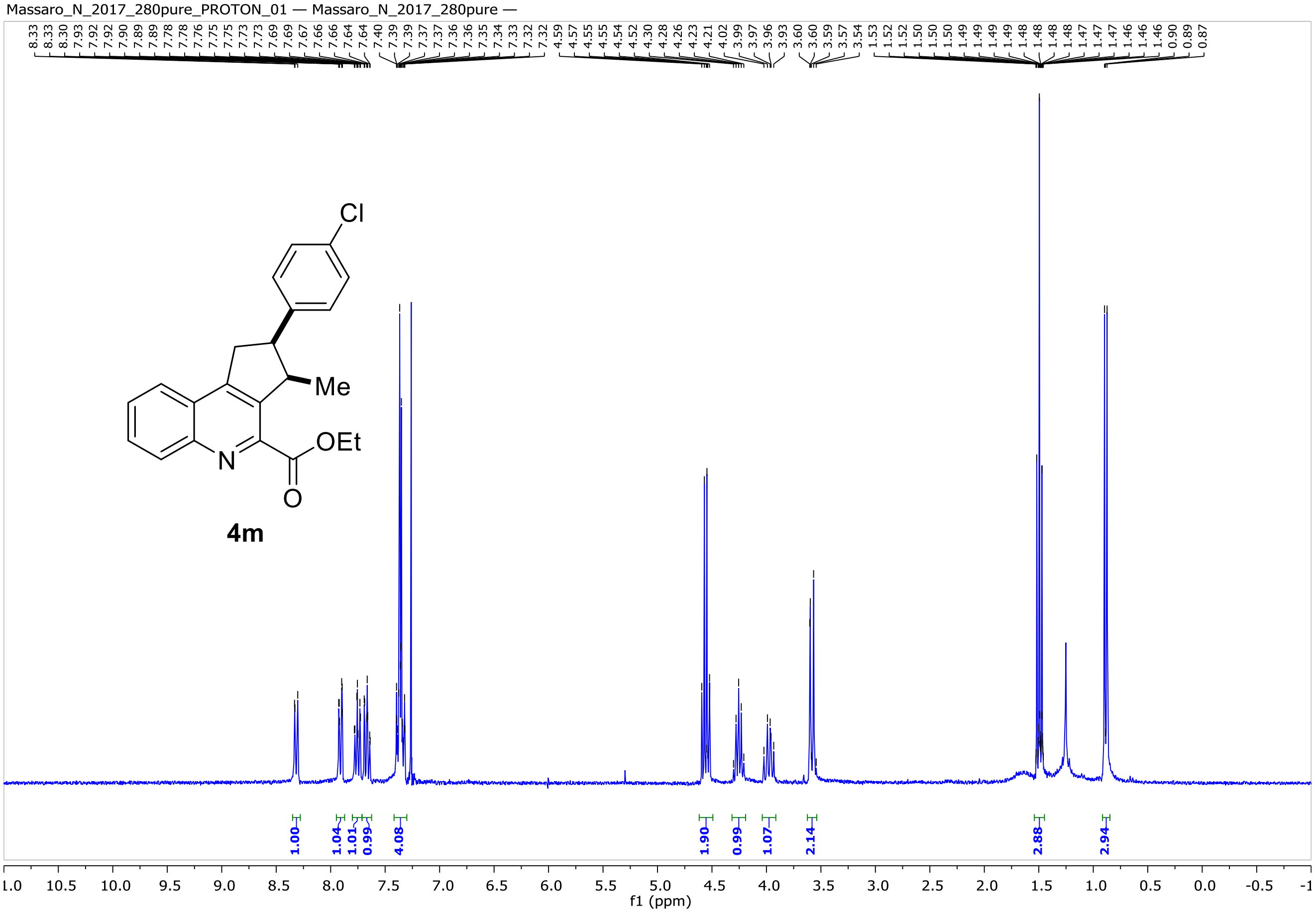

kc-774_CARBON_01 — kc-774 —
165.72
151.65 146.74 144.86 137.17 136.32 135.82 132.99 131.07 129.77 129.22 128.54 128.41 128.29 127.25 126.90 126.09 123.96
77.32 77.00 76.68
67.39
42.60 40.11 37.56
Ph
OBn
N
O
4j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

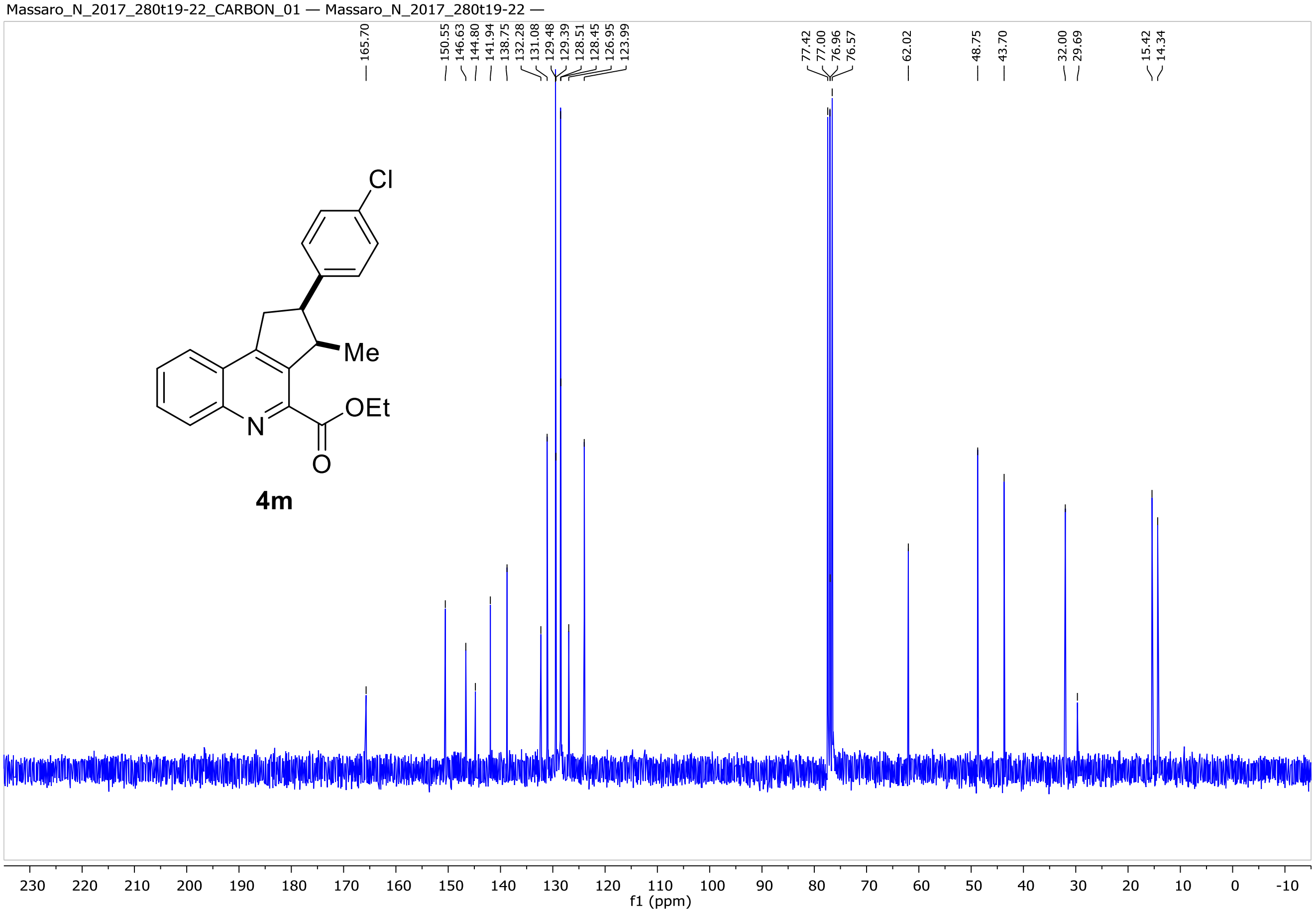

kc-761_PROTON_01 — kc-761 —
8.31
8.29
7.83
7.83
7.81
7.81
7.75
7.74
7.73
7.72
7.72
7.71
7.70
7.65
7.65
7.63
7.63
7.63
7.61
7.61
7.54
7.54
7.52
7.52
7.41
7.40
7.39
7.39
7.38
7.37
7.35
7.35
7.34
7.34
7.26
6.31
6.31
6.30
6.30
6.11
6.10
5.53
3.97
3.95
3.93
3.91
3.90
3.87
3.85
3.77
3.75
3.74
3.72
3.72
3.70
3.65
3.64
3.61
3.60
3.50
3.49
3.48
3.46
3.44
O
N
OBn
O
4k
1.00
1.07
1.13
1.17
1.92
4.92
0.97
0.98
2.08
2.29
1.19
1.10
1.17
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


kc-761_CARBON_01 — kc-761 —
165.64
157.50
151.12
146.74
144.72
141.43
135.88
135.77
131.07
129.31
128.55
128.52
128.29
126.81
123.91
110.10
104.46
77.32
77.00
76.68
67.42
39.03
37.53
36.54
O
N
OBn
O
4k
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

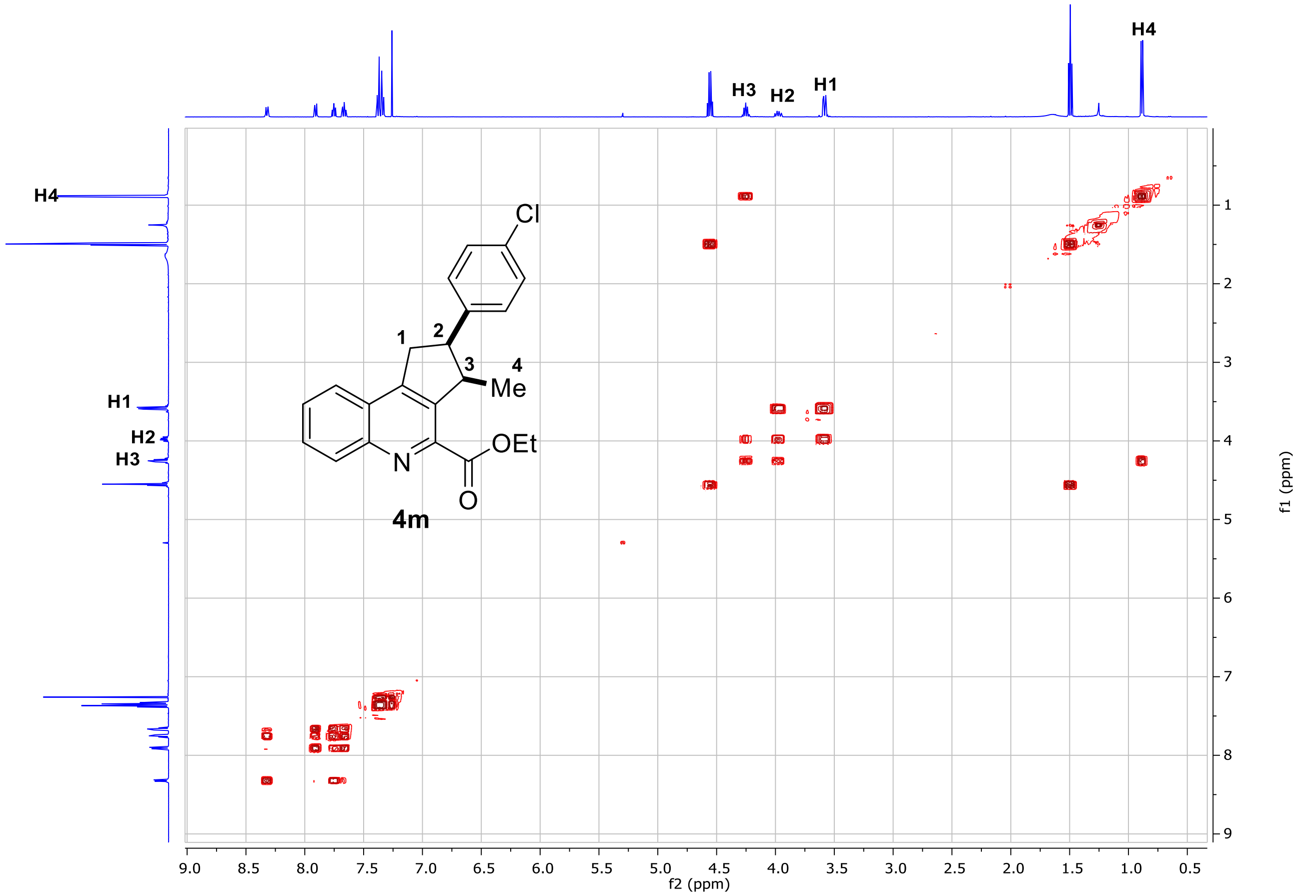

kc-766_PROTON_01 — kc-766 —
8.33
8.31
7.85
7.83
7.77
7.77
7.75
7.75
7.75
7.73
7.73
7.67
7.66
7.65
7.65
7.63
7.63
7.34
7.34
7.33
7.27
7.27
7.26
7.25
7.25
7.25
7.24
7.24
7.23
5.06
5.05
4.08
4.06
4.04
4.02
3.96
3.94
3.94
3.92
3.90
3.90
3.88
3.86
3.84
3.82
3.80
3.64
3.62
3.59
3.58
3.46
3.44
3.41
3.39
2.54
2.53
2.53
Ph
N
O
O
4l
1.00
1.08
1.11
1.13
3.93
1.12
2.10
1.18
1.16
1.17
1.17
1.17
0.83
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


kc-766_CARBON_01 — kc-766 —
165.10
152.01
146.91
145.03
144.01
136.81
131.20
129.59
128.85
128.79
127.07
127.05
126.68
124.17
77.63
77.48
77.16
76.84
75.49
53.25
44.46
41.77
39.25
Ph
N
O
O
4l
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

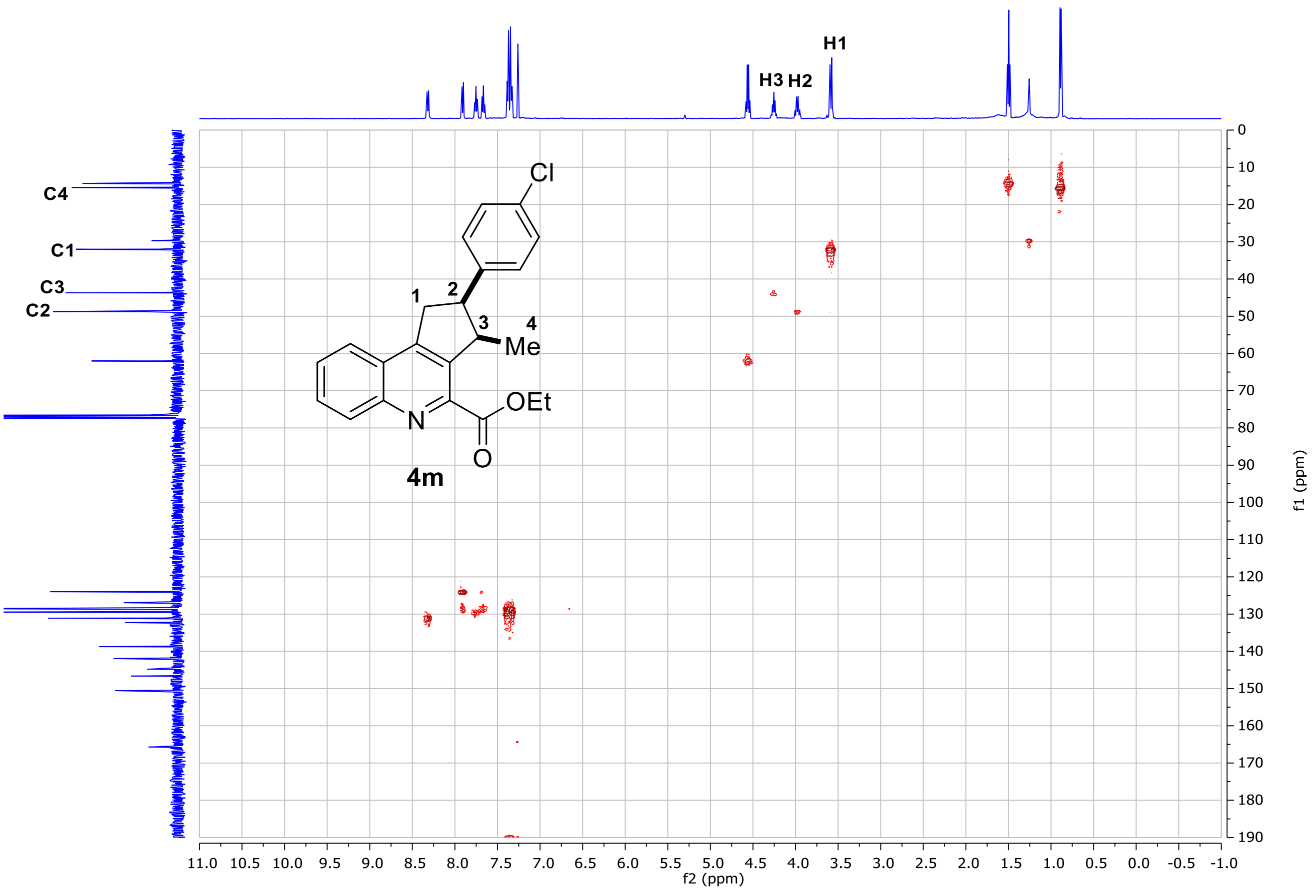

Massaro_N_2017_280pure_PROTON_01 — Massaro_N_2017_280pure —
8.33
8.33
8.30
7.93
7.92
7.92
7.90
7.89
7.89
7.78
7.78
7.76
7.75
7.75
7.73
7.73
7.69
7.69
7.67
7.66
7.66
7.64
7.64
7.40
7.39
7.39
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.32
7.32
4.59
4.57
4.55
4.55
4.54
4.52
4.30
4.28
4.26
4.23
4.21
4.02
3.99
3.97
3.96
3.93
3.60
3.60
3.59
3.57
3.54
1.53
1.52
1.52
1.50
1.50
1.50
1.49
1.49
1.49
1.49
1.48
1.48
1.48
1.48
1.47
1.47
1.47
1.46
1.46
1.46
0.90
0.89
0.87
Cl
Me
OEt
N
O
4m
1.00
1.04
1.01
0.99
4.08
1.90
0.99
1.07
2.14
2.88
2.94
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

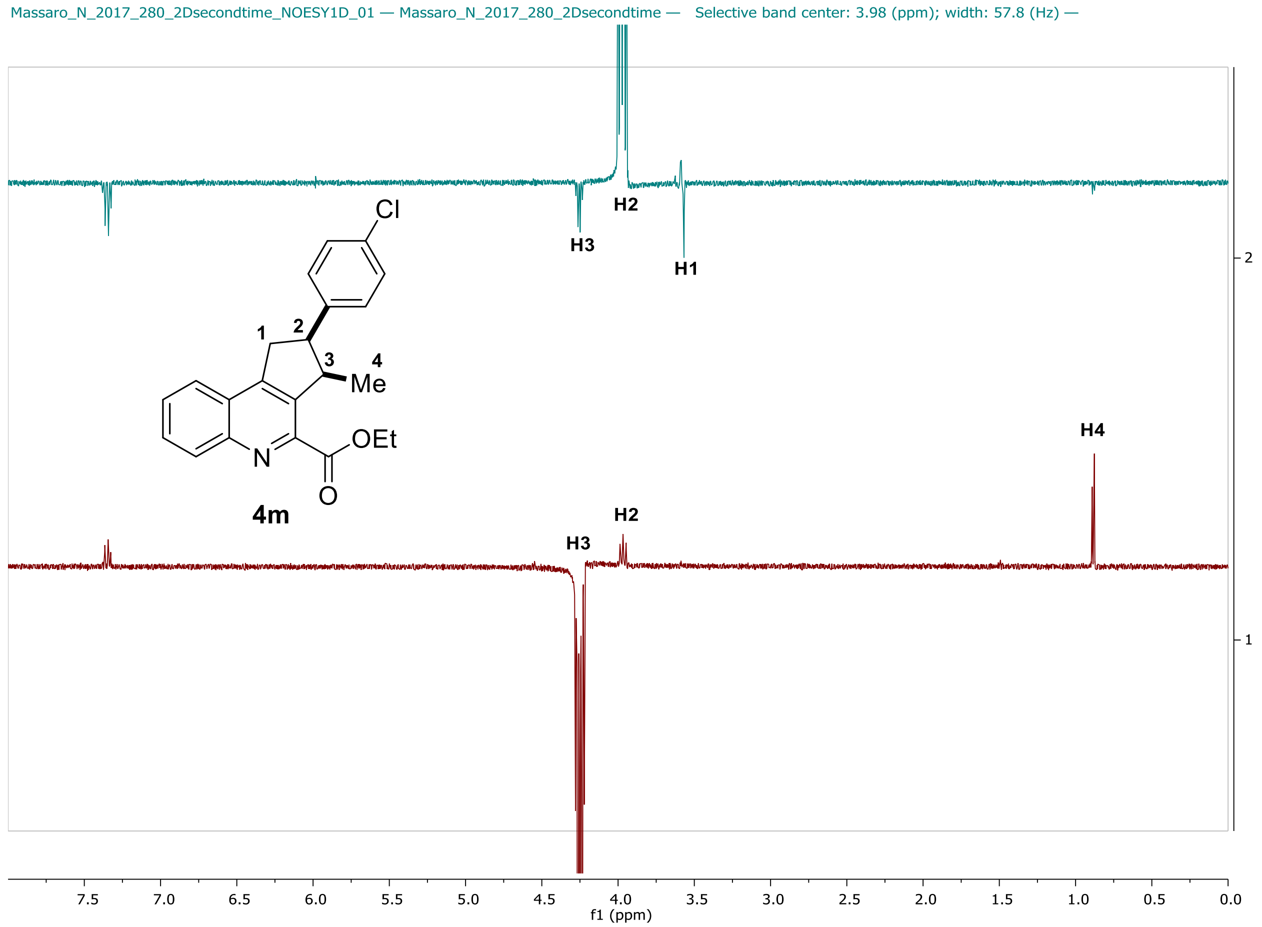

Massaro_N_2017_280t19-22_CARBON_01 — Massaro_N_2017_280t19-22 —
165.70
150.55
146.63
144.80
141.94
138.75
132.28
131.08
129.48
129.39
128.51
128.45
126.95
123.99
77.42
77.00
76.96
76.57
62.02
48.75
43.70
32.00
29.69
15.42
14.34
Cl
Me
OEt
N
O
4m
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Massaro_N_2017_280_2D_COSY_01 — Massaro_N_2017_280_2D — Selective band center: 3.98 (ppm); width: 69.5 (Hz) —

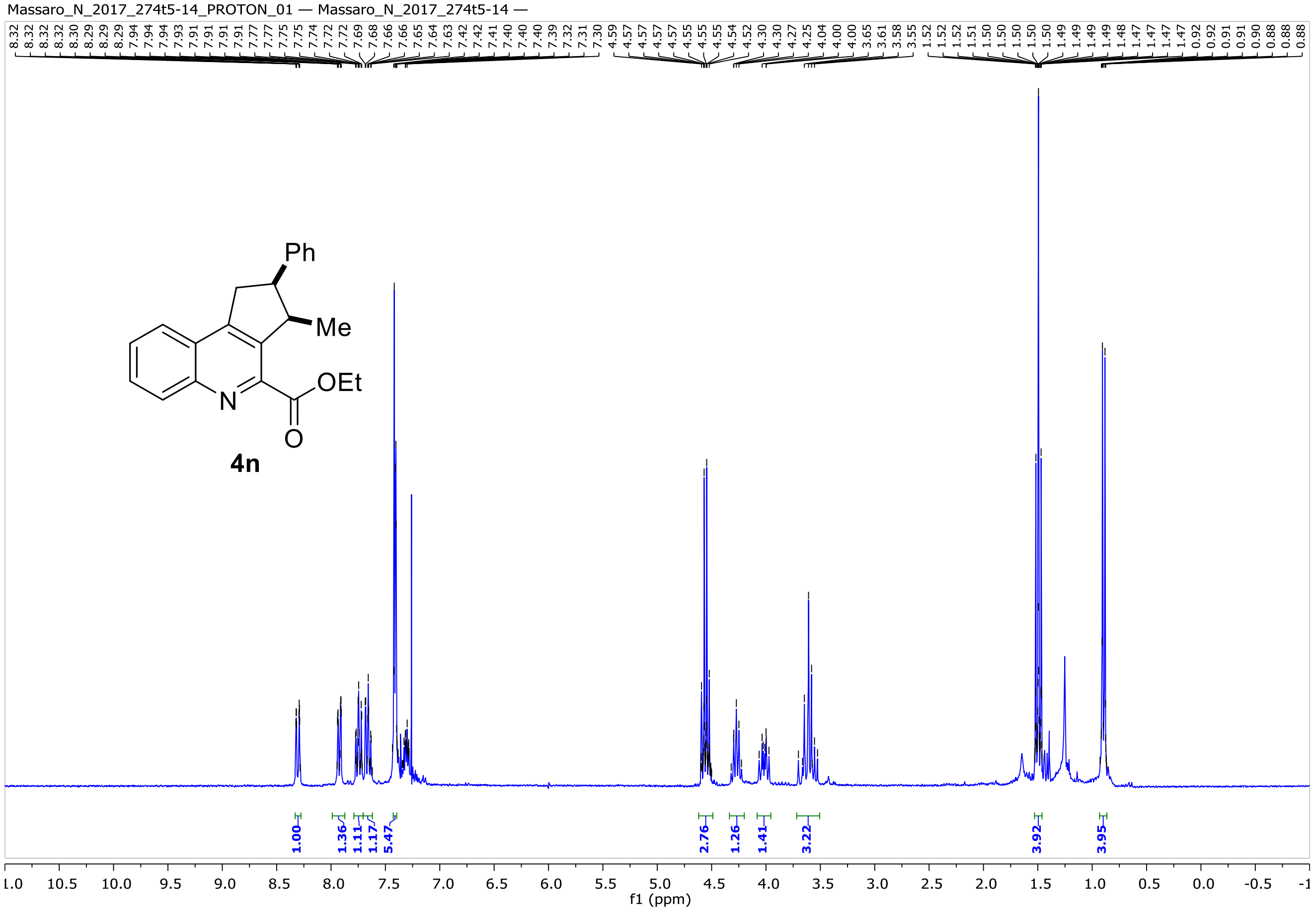


Massaro_N_2017_280_2D_HSQCAD_01 — Massaro_N_2017_280_2D —



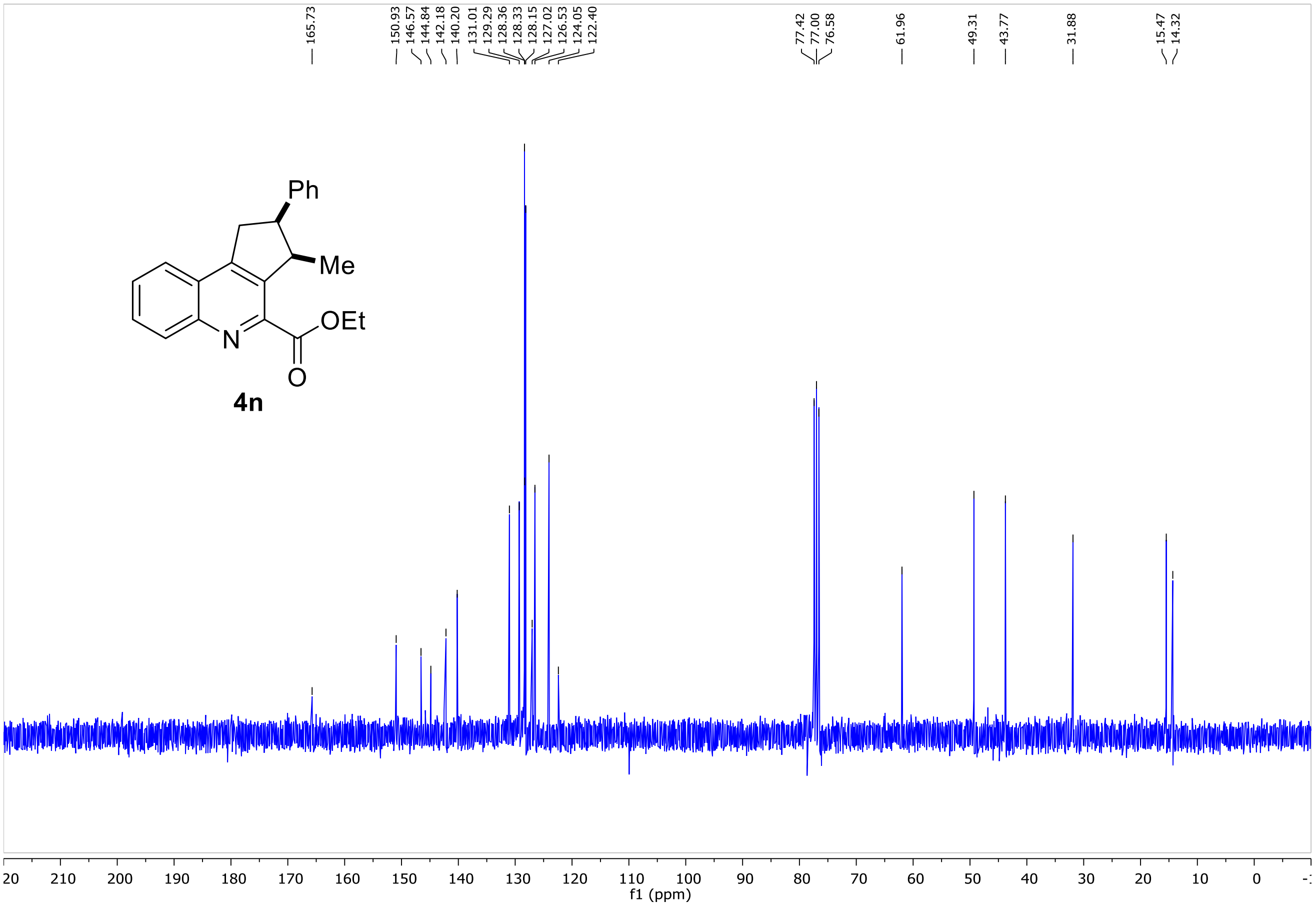

Massaro_N_2017_280_2Dsecondtime_NOESY1D_01 — Massaro_N_2017_280_2Dsecondtime — Selective band center: 3.98 (ppm); width: 57.8 (Hz) —
H2
H3
H1
Cl
1
2
3
4
Me
N
OEt
O
H4
H2
H3
2
1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4m

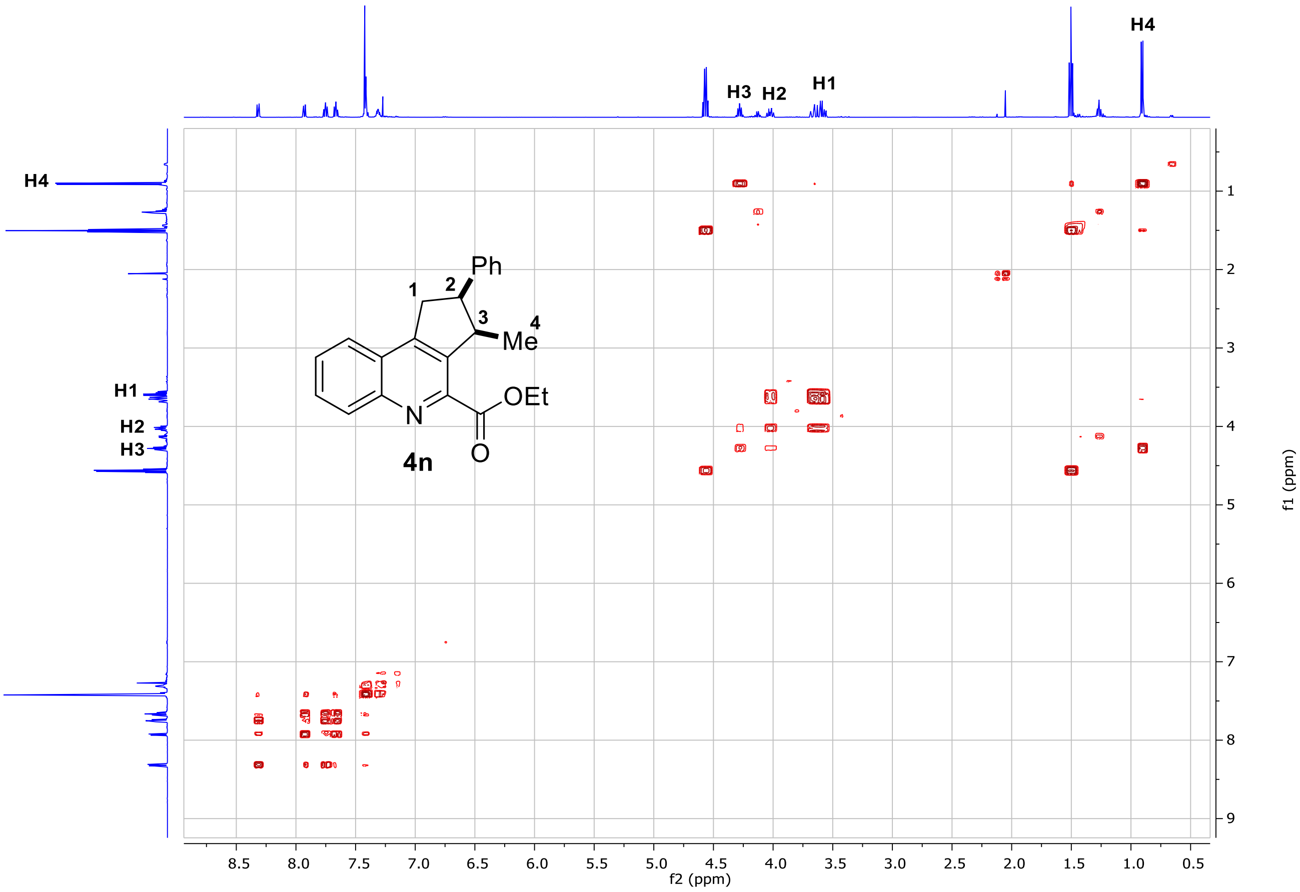

Massaro_N_2017_274t5-14_PROTON_01 — Massaro_N_2017_274t5-14 —
8.32 8.32 8.32 8.32 8.30 8.29 8.29 8.29 7.94 7.94 7.94 7.93 7.91 7.91 7.91 7.91 7.77 7.77 7.75 7.75 7.74 7.72 7.72 7.69 7.68 7.66 7.66 7.65 7.64 7.63 7.42 7.41 7.40 7.40 7.40 7.39 7.32 7.31 7.30
4.59 4.57 4.57 4.57 4.55 4.55 4.55 4.54 4.52 4.30 4.30 4.27 4.25 4.04 4.00 4.00 3.65 3.61 3.58 3.55
1.52 1.52 1.52 1.51 1.50 1.50 1.50 1.50 1.50 1.49 1.49 1.49 1.48 1.47 1.47 1.47 1.47 0.92 0.92 0.91 0.91 0.90 0.88 0.88 0.88
Ph
Me
N
OEt
O
1.00
1.36
1.11
1.17
5.47
2.76
1.26
1.41
3.22
3.92
3.95
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

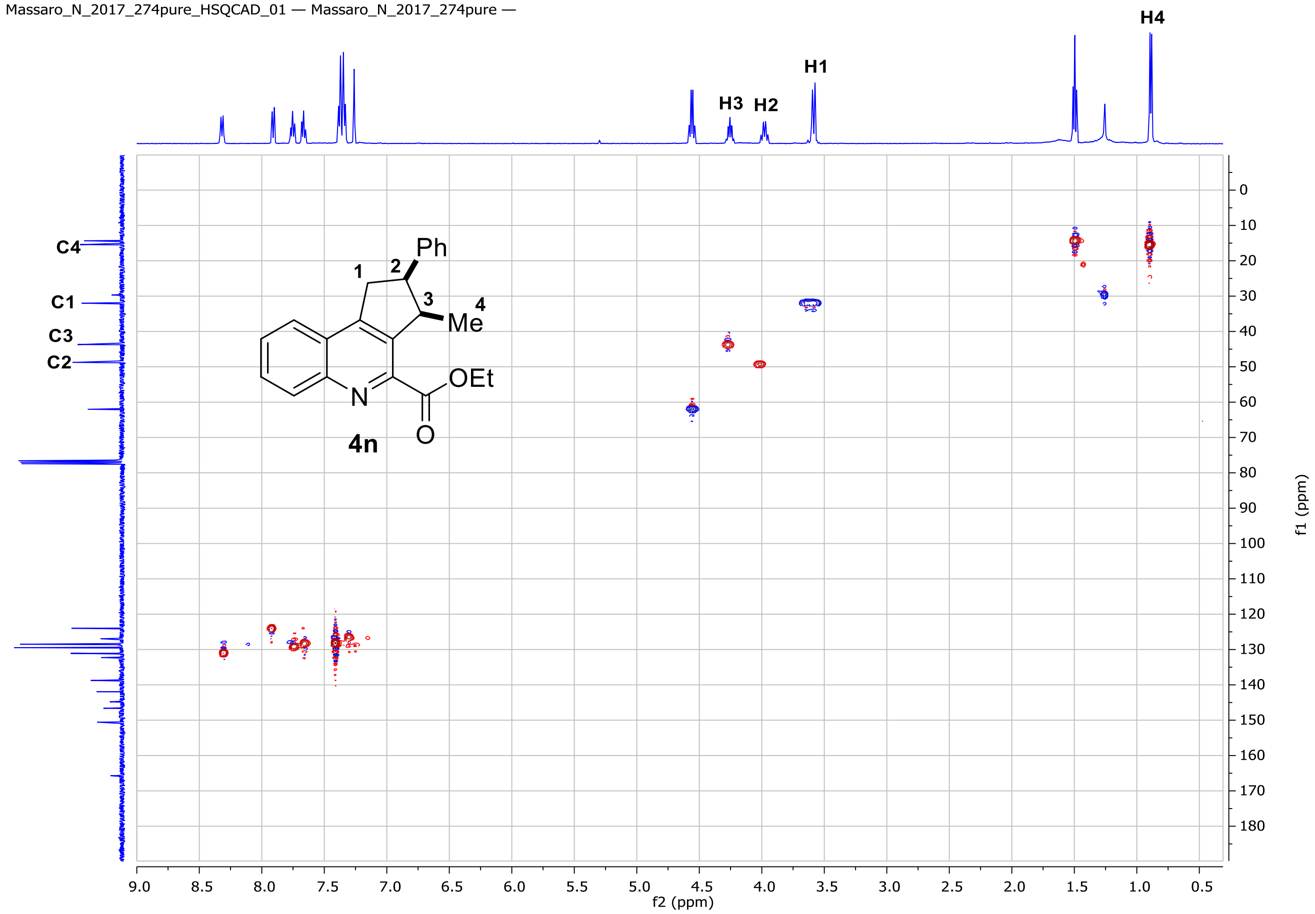
4n

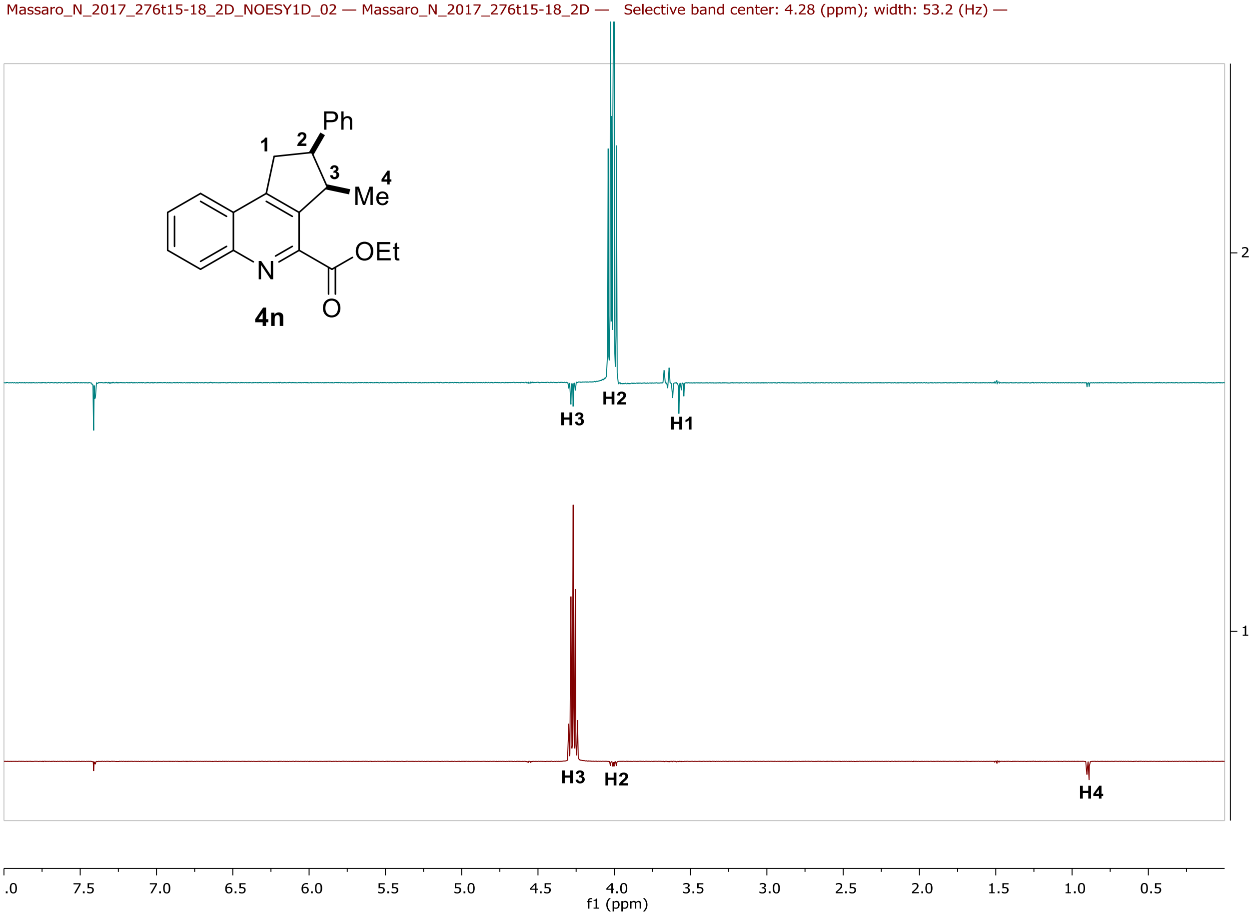
Massaro_N_2017_276t15-18_CARBON_01 — Massaro_N_2017_276t15-18 —

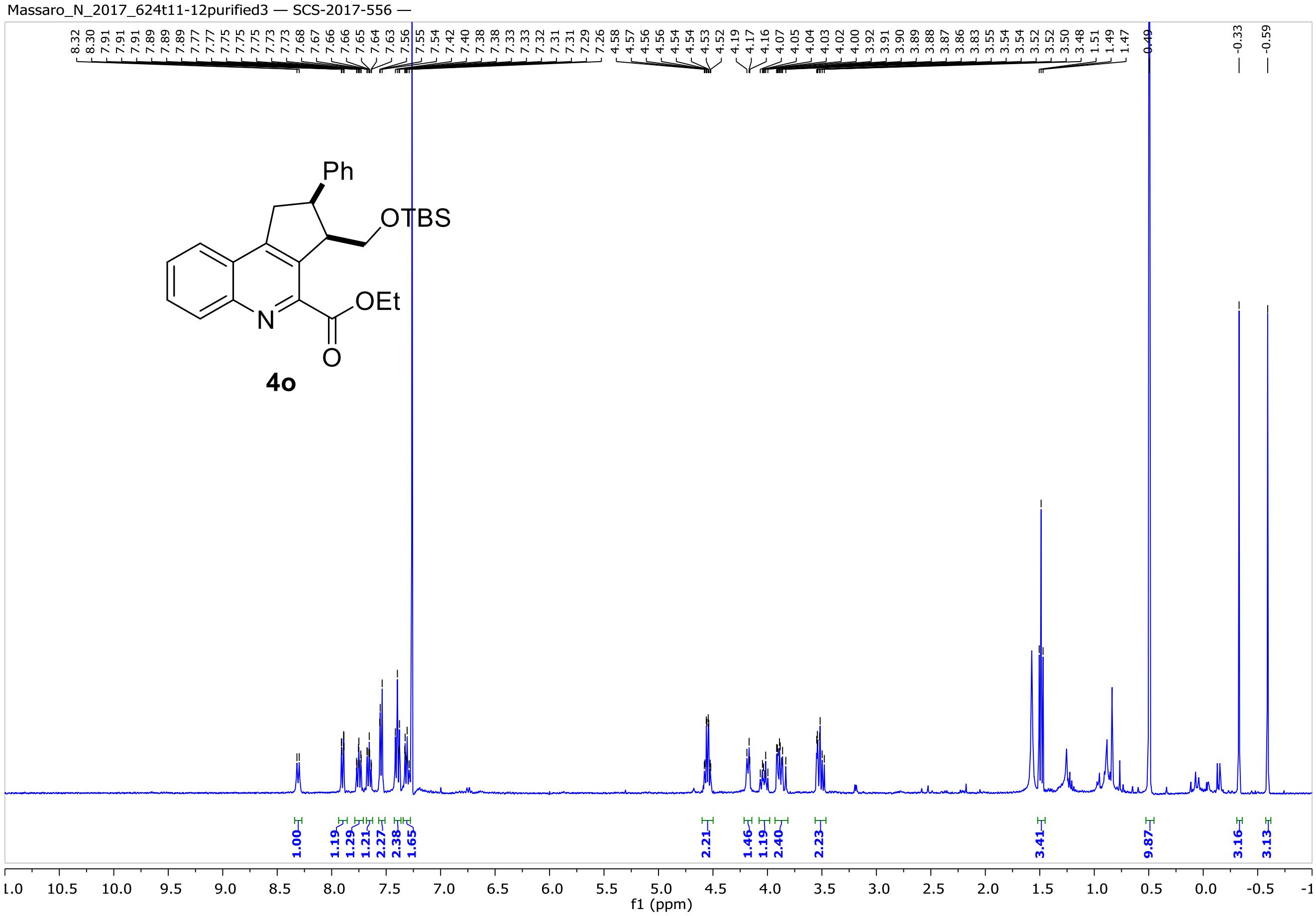


Massaro_N_2017_276t15-18_2D_COSY_01 — Massaro_N_2017_276t15-18_2D — Selective band center: 4.02 (ppm); width: 50.3 (Hz) —

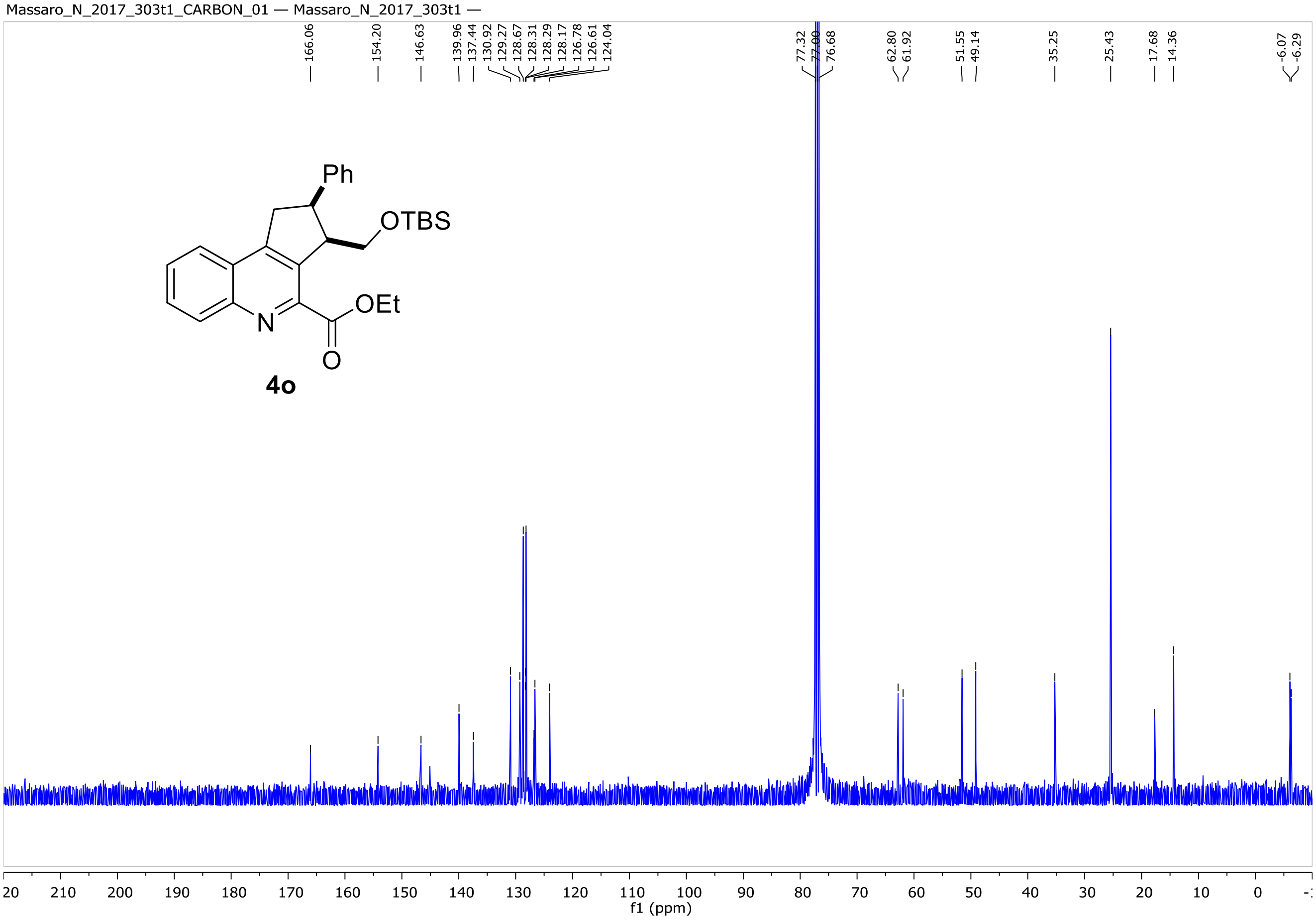



Massaro_N_2017_274pure_HSQCAD_01 — Massaro_N_2017_274pure —
H4
H1
H3
H2
C4
C1
C3
C2
1
2
Ph
3
4
Me
N
OEt
O
4n
f2 (ppm)
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

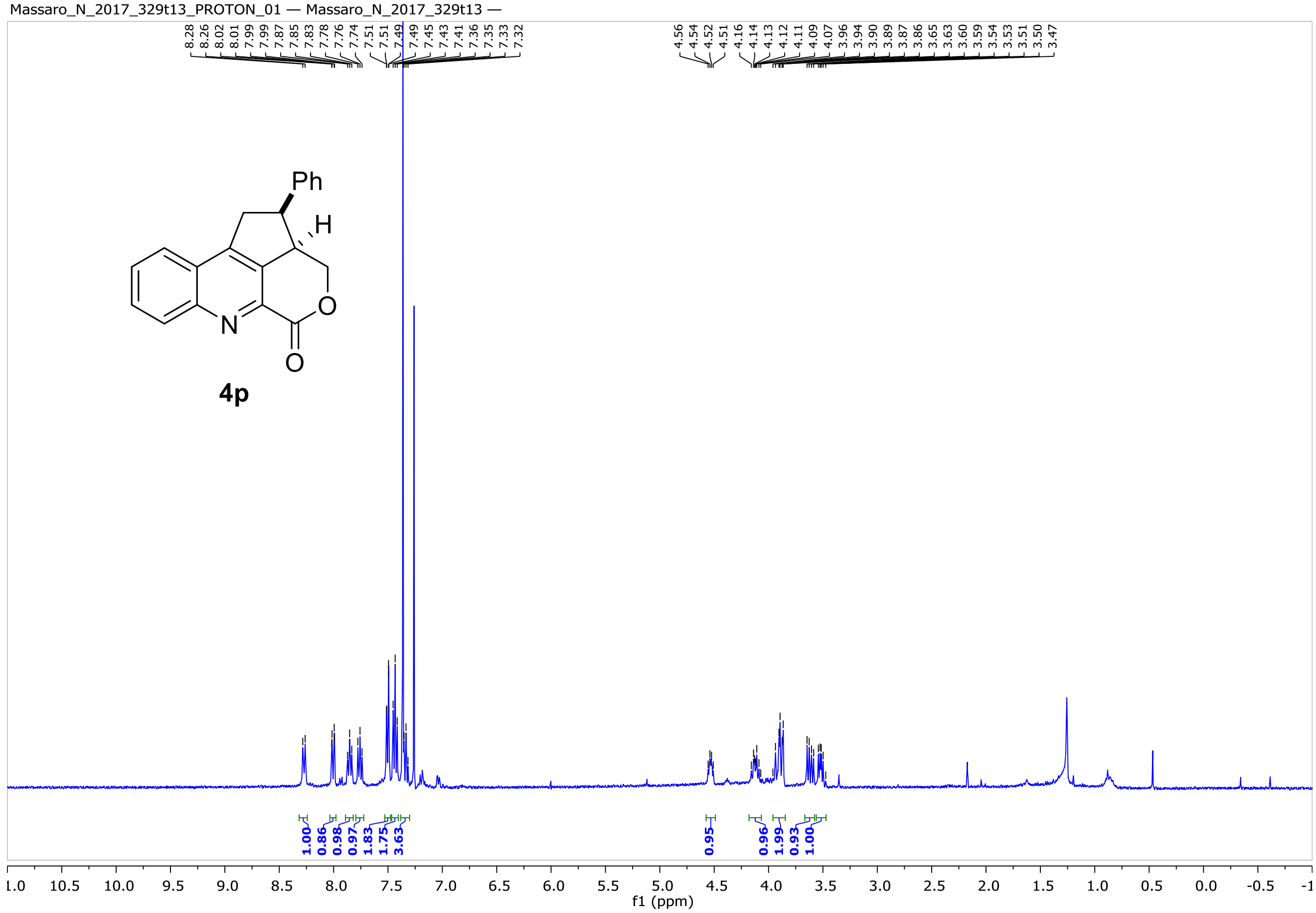

Massaro_N_2017_276t15-18_2D_NOESY1D_02 — Massaro_N_2017_276t15-18_2D — Selective band center: 4.28 (ppm); width: 53.2 (Hz) —
1
2
Ph
3
4
Me
N
OEt
O
4n
H3
H2
H1
H3
H2
H4
2
1
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

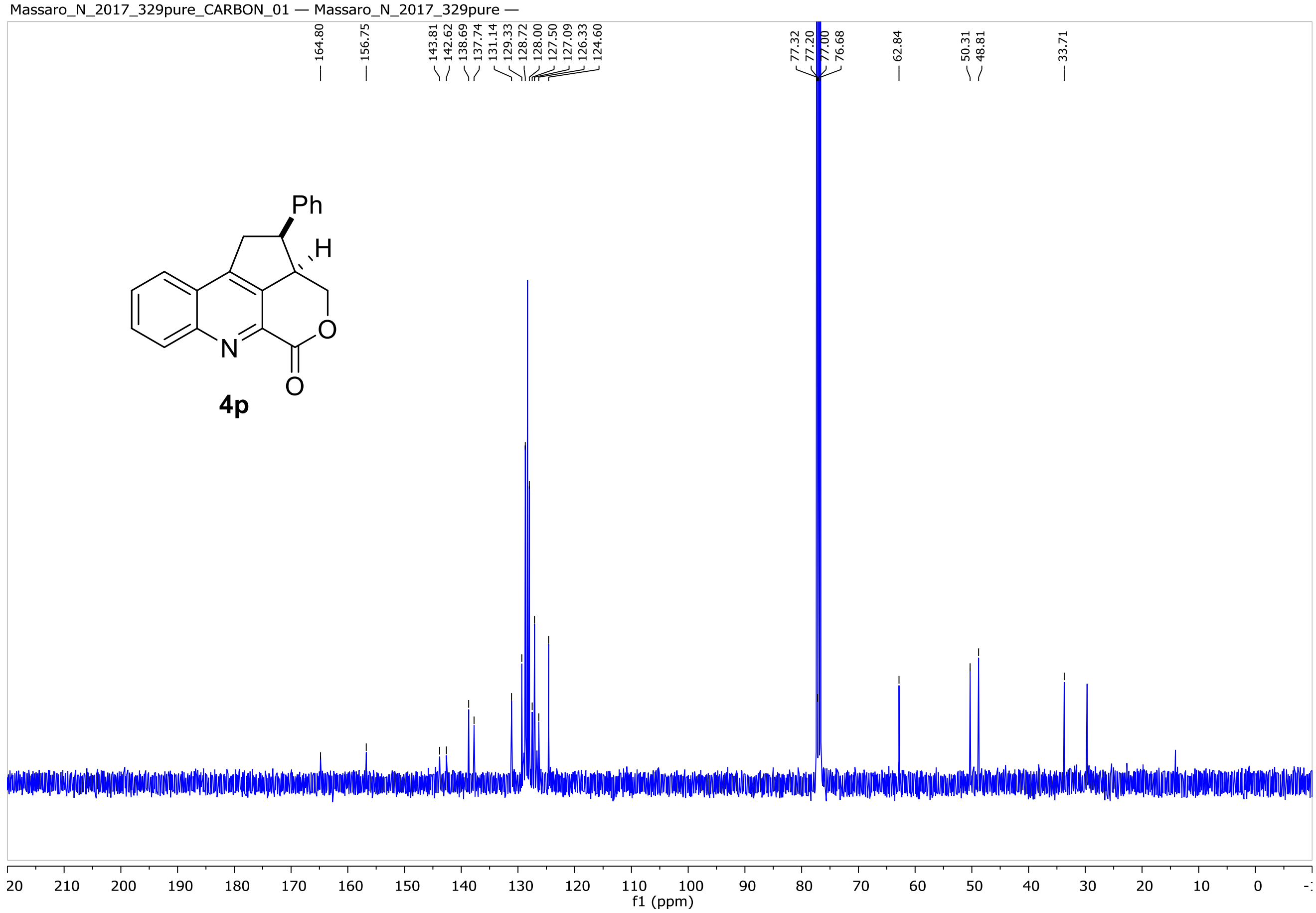

Massaro_N_2017_624t11-12purified3 — SCS-2017-556 —
8.32
8.30
7.91
7.91
7.89
7.89
7.77
7.77
7.75
7.75
7.73
7.73
7.68
7.67
7.66
7.65
7.64
7.63
7.56
7.55
7.54
7.42
7.40
7.38
7.38
7.33
7.32
7.31
7.31
7.29
7.26
4.58
4.57
4.56
4.56
4.54
4.54
4.53
4.52
4.19
4.17
4.16
4.07
4.05
4.04
4.03
4.02
4.00
3.92
3.91
3.90
3.89
3.88
3.87
3.86
3.83
3.55
3.54
3.54
3.52
3.52
3.50
3.48
1.51
1.49
1.47
0.49
-0.33
-0.59
Ph
OTBS
OEt
N
O
1.00
1.19
1.29
1.21
2.27
2.38
1.65
2.21
1.46
1.19
2.40
2.23
3.41
9.87
3.16
3.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

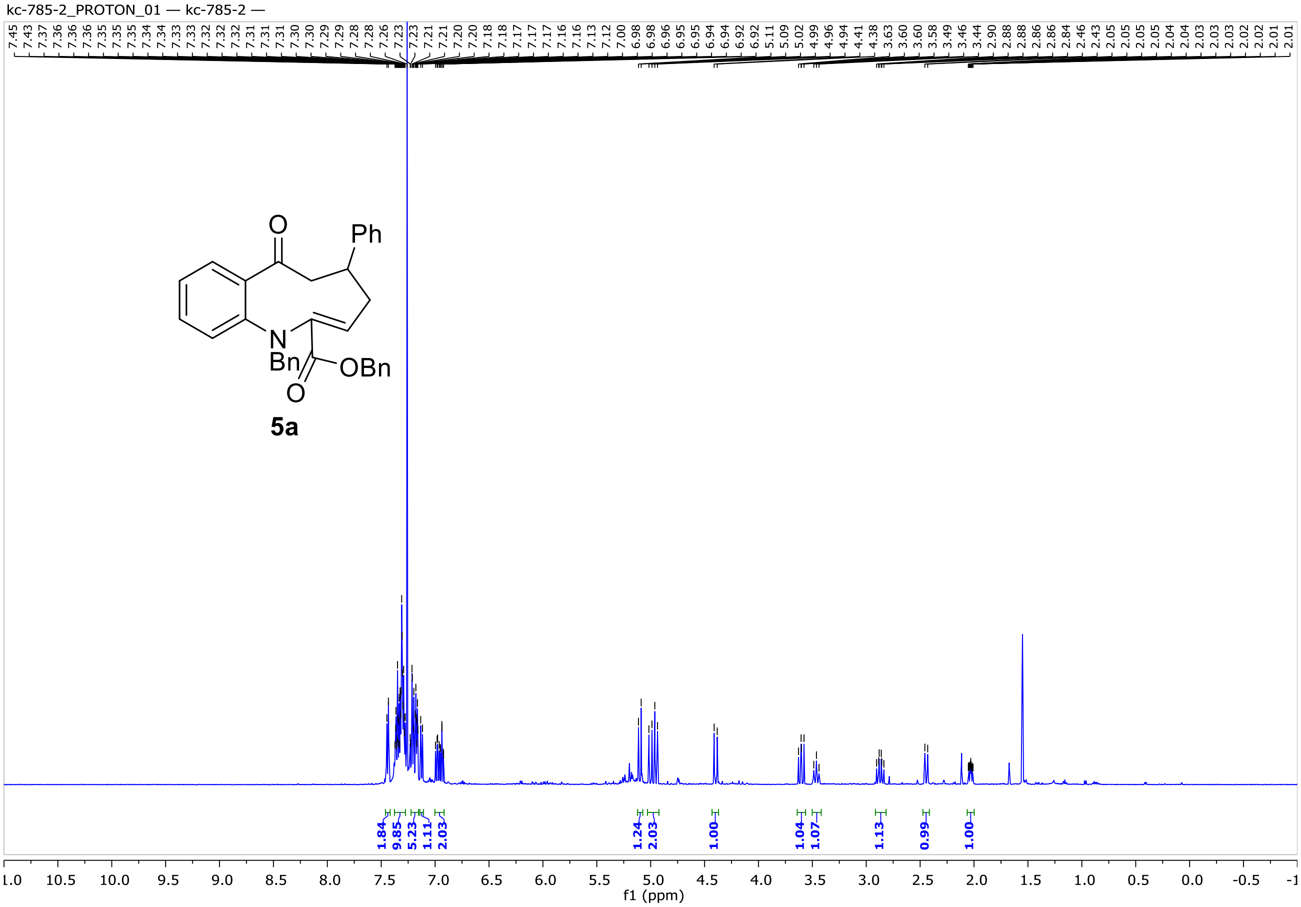
4o

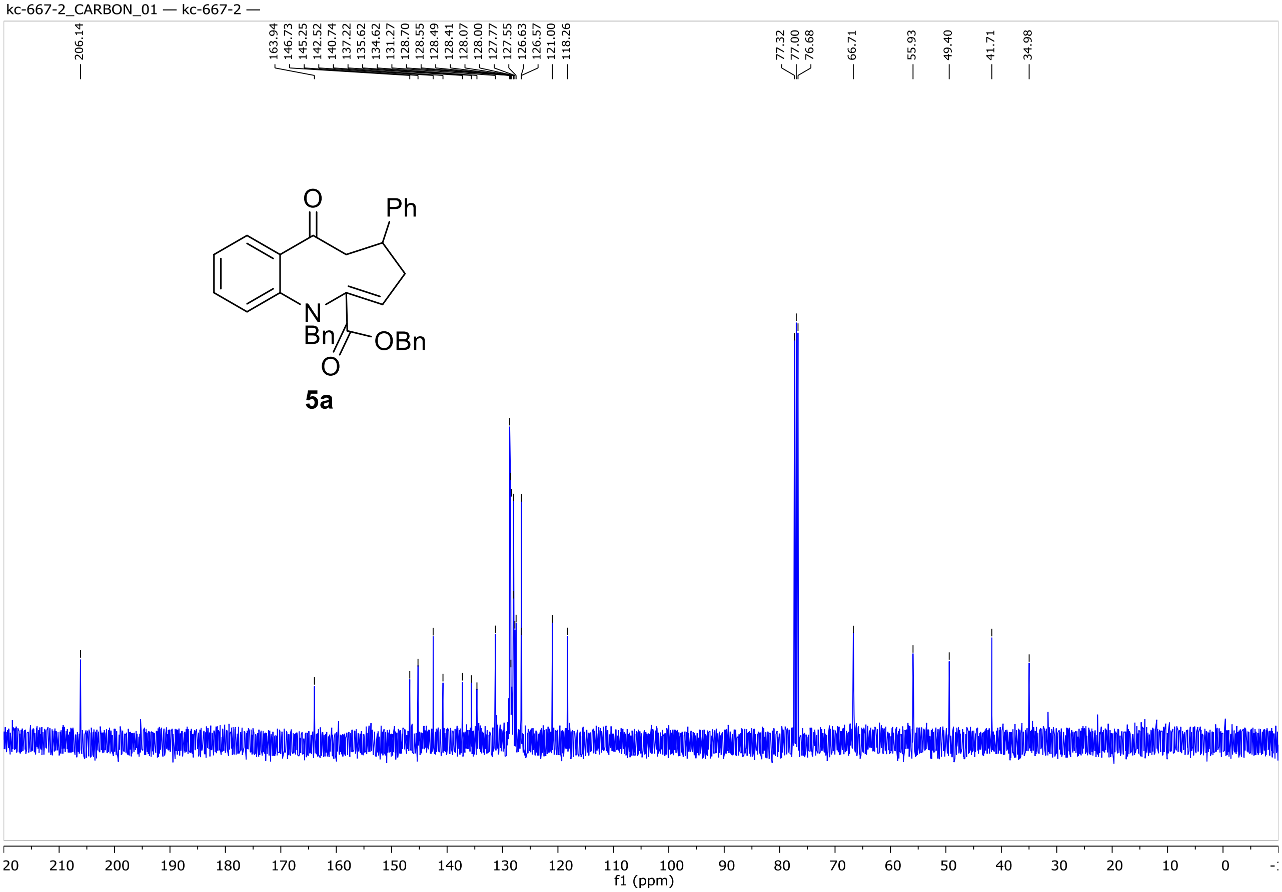

Massaro_N_2017_303t1_CARBON_01 — Massaro_N_2017_303t1 —
166.06
154.20
146.63
139.96
137.44
130.92
129.27
128.67
128.31
128.29
128.17
126.78
126.61
124.04
77.32
77.00
76.68
62.80
61.92
51.55
49.14
35.25
25.43
17.68
14.36
-6.07
-6.29
Ph
OTBS
OEt
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

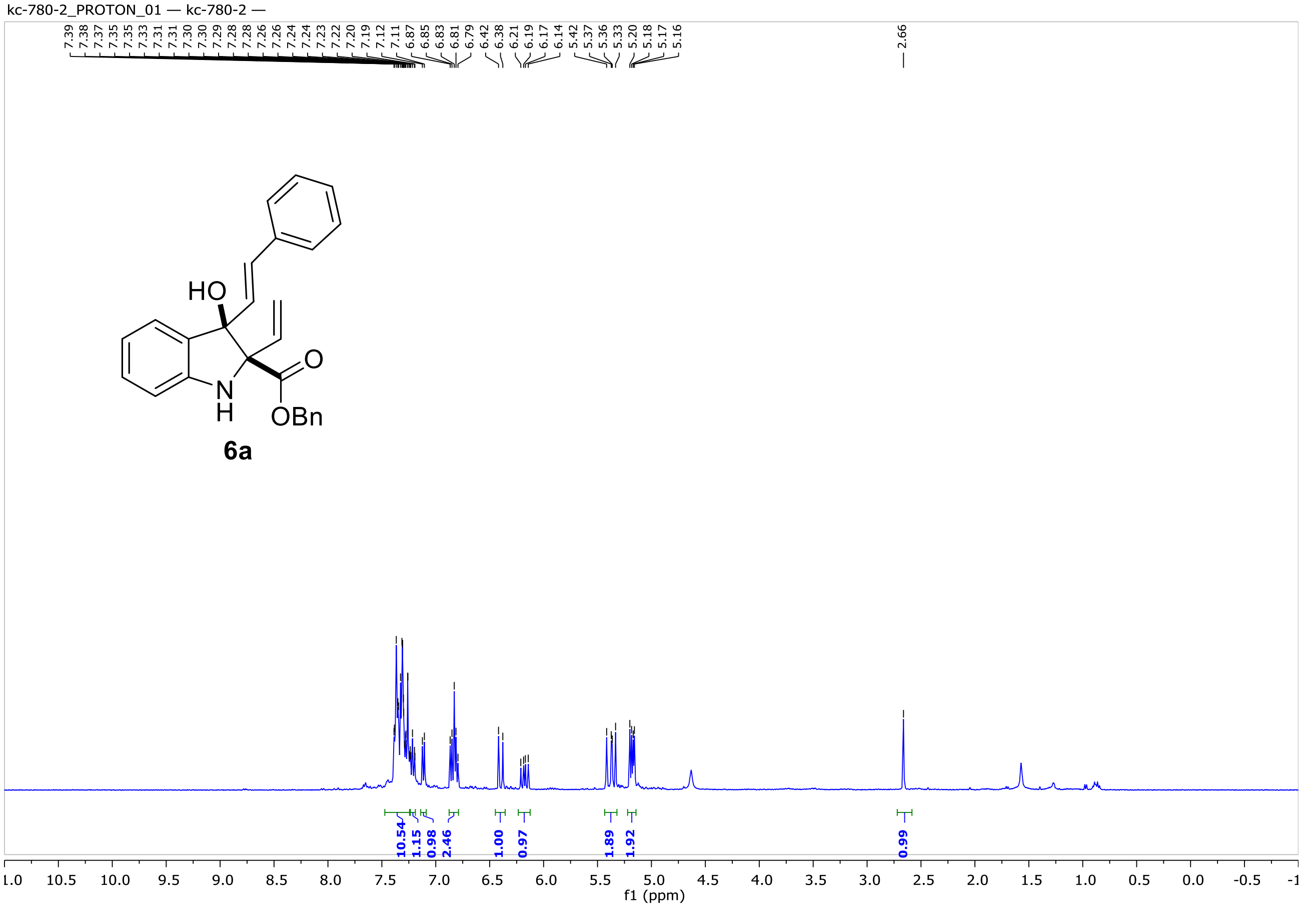
4o

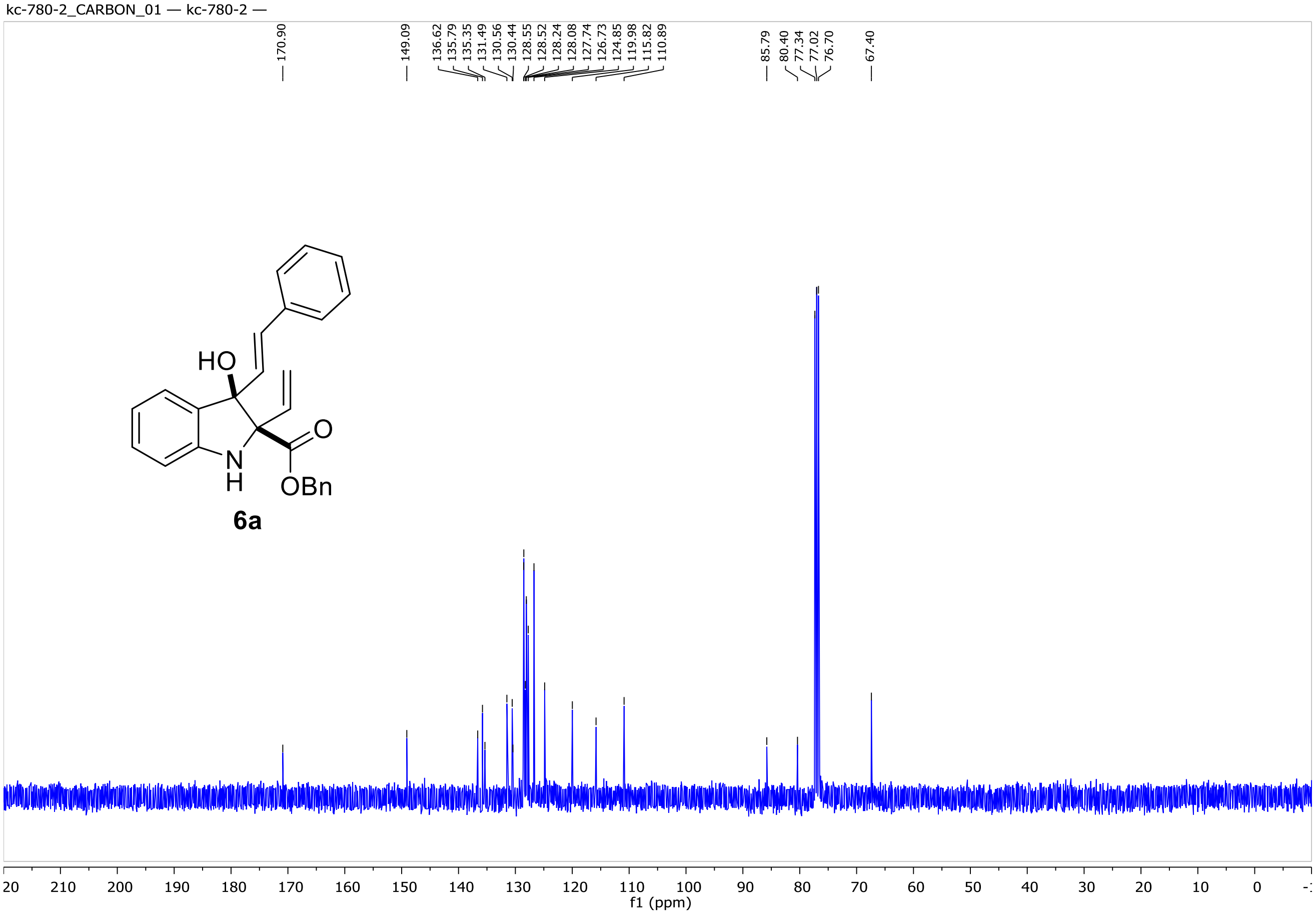

Massaro_N_2017_329t13_PROTON_01 — Massaro_N_2017_329t13 —
8.28 8.26 8.02 8.01 7.99 7.99 7.87 7.85 7.83 7.78 7.76 7.74 7.51 7.51 7.49 7.49 7.45 7.43 7.41 7.36 7.35 7.33 7.32
4.56 4.54 4.52 4.51 4.16 4.14 4.13 4.12 4.11 4.09 4.07 3.96 3.94 3.90 3.89 3.87 3.86 3.65 3.63 3.60 3.59 3.54 3.53 3.51 3.50 3.47
Ph
H
N
O
O
4p
1.00
0.86
0.98
0.97
1.83
1.75
3.63
0.95
0.96
1.99
0.93
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


Massaro_N_2017_329pure_CARBON_01 — Massaro_N_2017_329pure —
164.80
156.75
143.81 142.62 138.69 137.74 131.14 129.33 128.72 128.00 127.50 127.09 126.33 124.60
77.32 77.20 77.00 76.68
62.84
50.31 48.81
33.71
Ph
H
N
O
O
4p
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

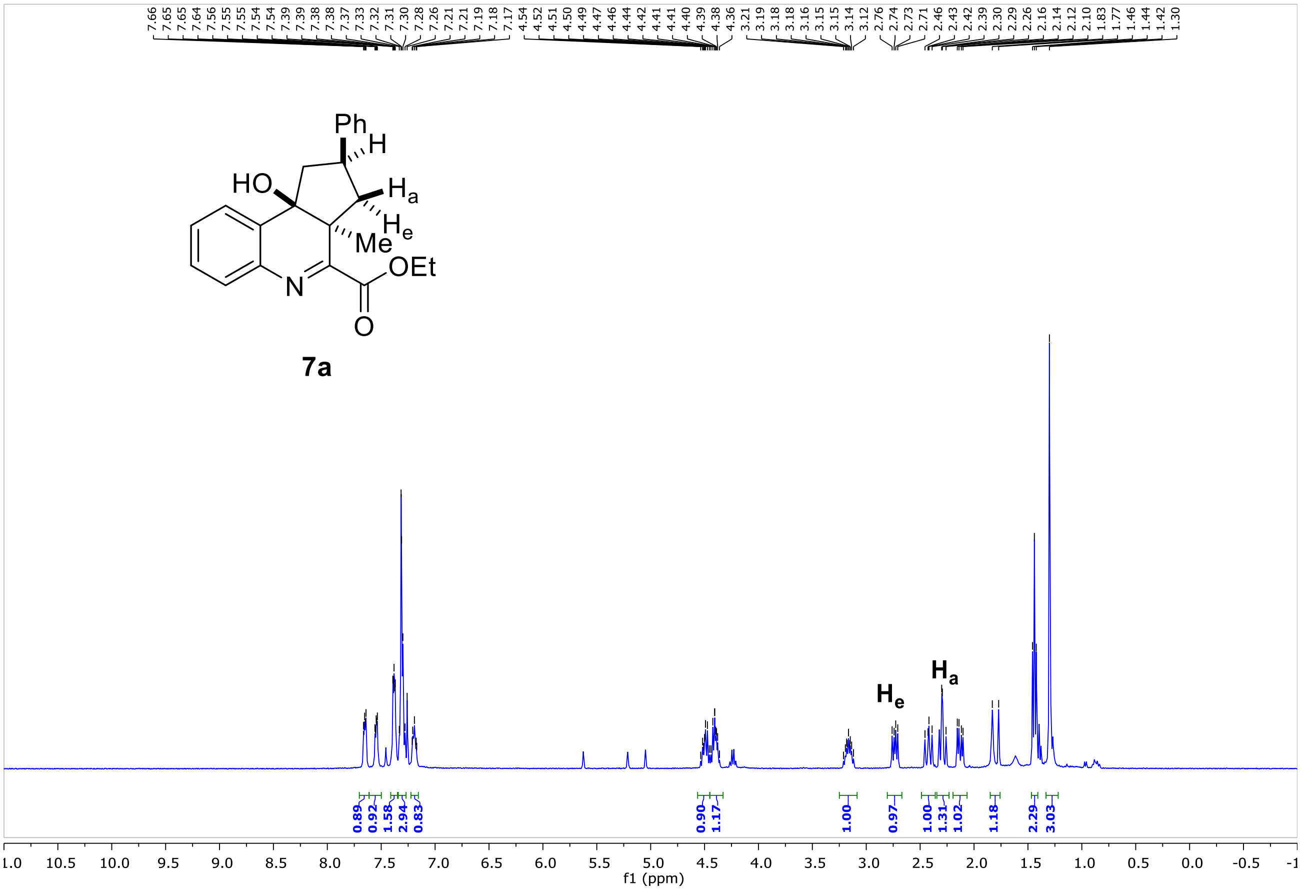

kc-785-2_PROTON_01 — kc-785-2 —
7.45 7.43 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.26 7.23 7.23 7.21 7.21 7.20 7.20 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.13 7.12 7.00 6.98 6.98 6.96 6.95 6.95 6.94 6.94 6.92 6.92 5.11 5.09 5.02 4.99 4.96 4.94 4.41 4.38 3.63 3.60 3.60 3.58 3.49 3.46 3.44 2.90 2.88 2.88 2.86 2.86 2.84 2.46 2.43 2.05 2.05 2.05 2.04 2.04 2.03 2.03 2.03 2.02 2.02 2.01 2.01
O
Ph
N
Bn
OBn
O
5a
1.84
9.85
5.23
1.11
2.03
1.24
2.03
1.00
1.04
1.07
1.13
0.99
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


kc-667-2_CARBON_01 — kc-667-2 —
206.14
163.94 146.73 145.25 142.52 140.74 137.22 135.62 134.62 131.27 128.70 128.55 128.49 128.41 128.07 128.00 127.77 127.55 126.63 126.57 121.00 118.26
77.32 77.00 76.68
66.71
55.93
49.40
41.71
34.98
O
Ph
N
Bn
OBn
O
5a
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

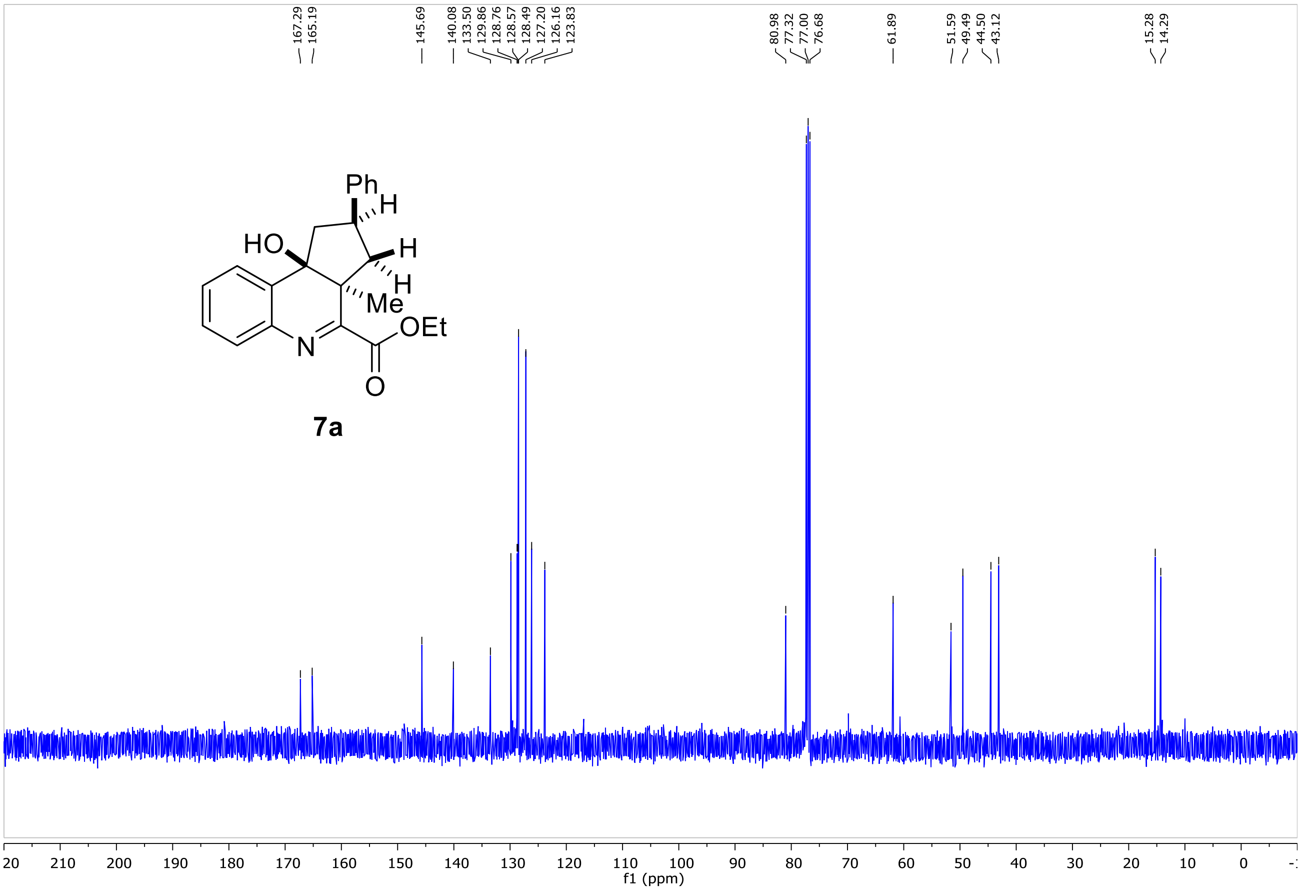

kc-780-2_PROTON_01 — kc-780-2 —
7.39
7.38
7.37
7.35
7.35
7.33
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.26
7.26
7.24
7.24
7.23
7.22
7.20
7.19
7.12
7.11
6.87
6.85
6.83
6.81
6.79
6.42
6.38
6.21
6.19
6.17
6.14
5.42
5.37
5.36
5.33
5.20
5.18
5.17
5.16
2.66
HO
O
N
H
OBn
6a
10.54
1.15
0.98
2.46
1.00
0.97
1.89
1.92
0.99
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


kc-780-2_CARBON_01 — kc-780-2 —
170.90
149.09
136.62
135.79
135.35
131.49
130.56
130.44
128.55
128.52
128.24
128.08
127.74
126.73
124.85
119.98
115.82
110.89
85.79
80.40
77.34
77.02
76.70
67.40
HO
O
N
H
OBn
6a
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:
f1 (ppm)

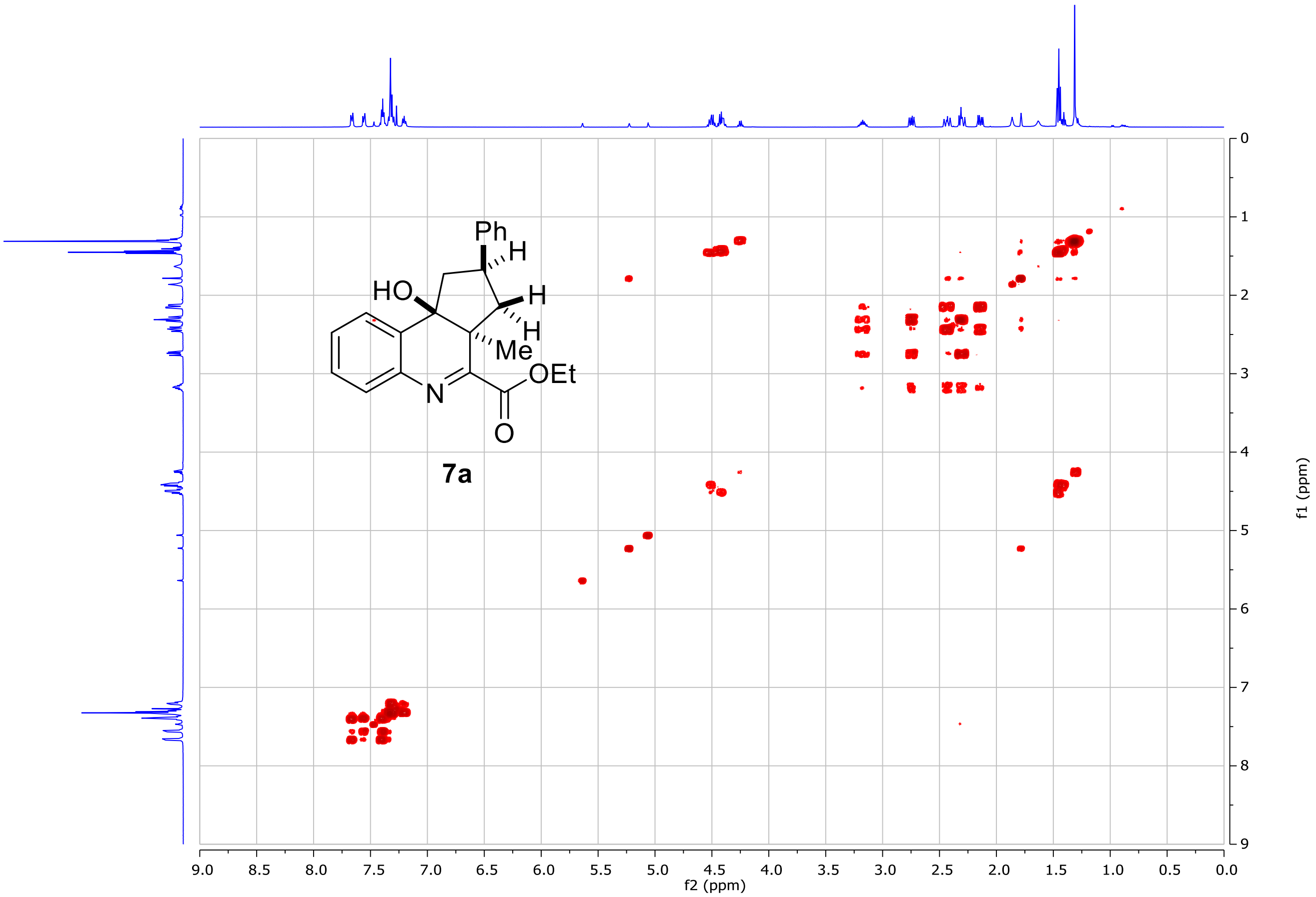
kc-801-tolune_PROTON_02 — kc-801-tolune —



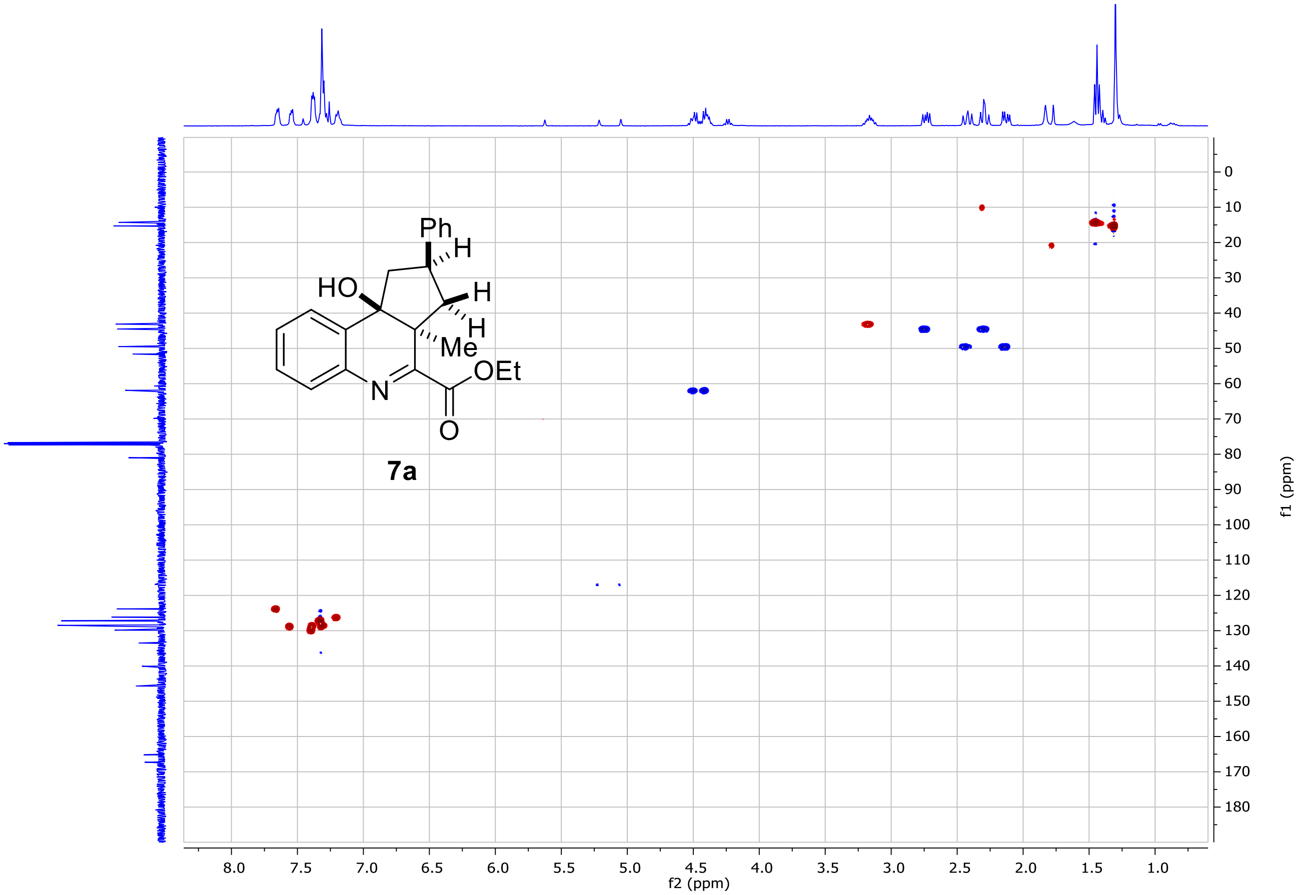
kc-801-toluene-l_CARBON_01 — kc-801-toluene-l —

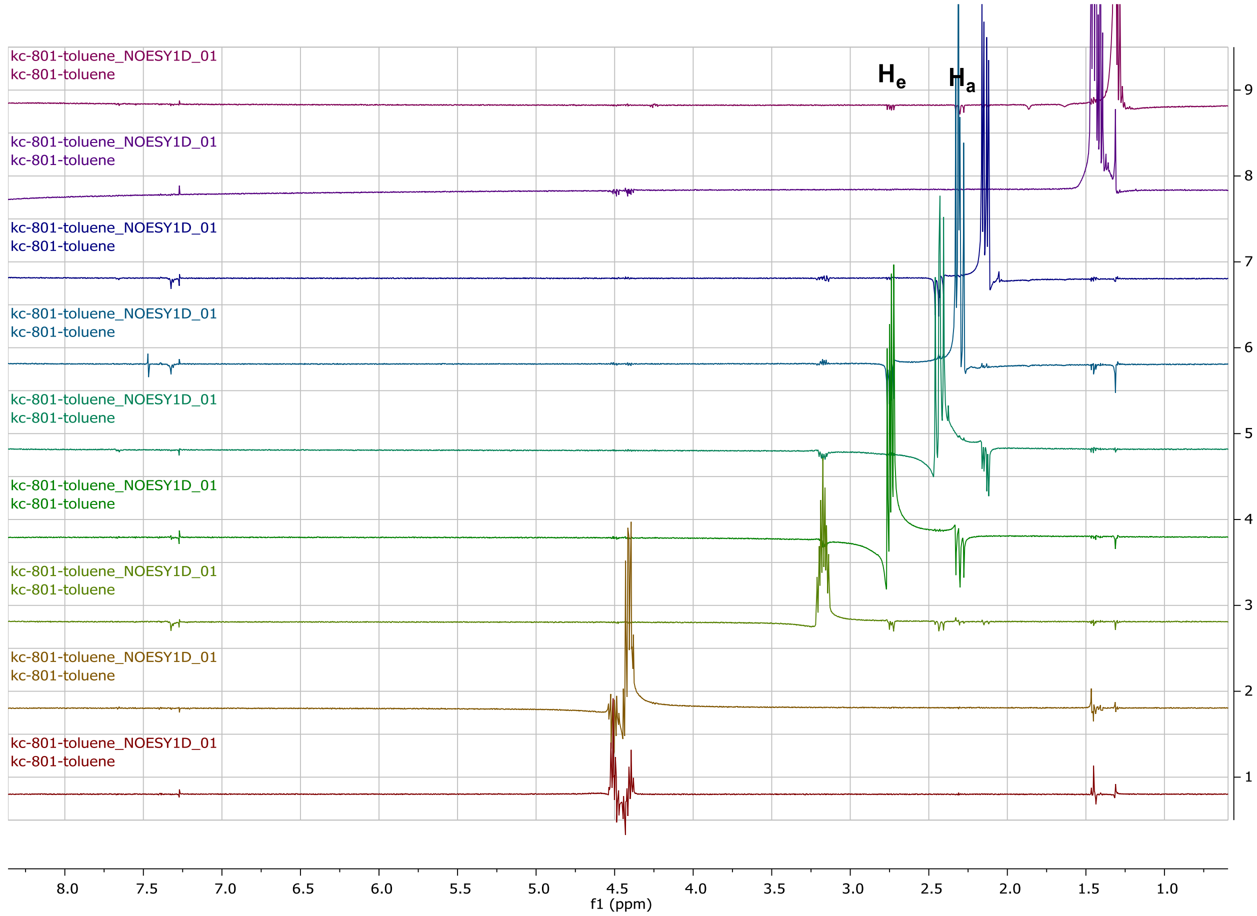


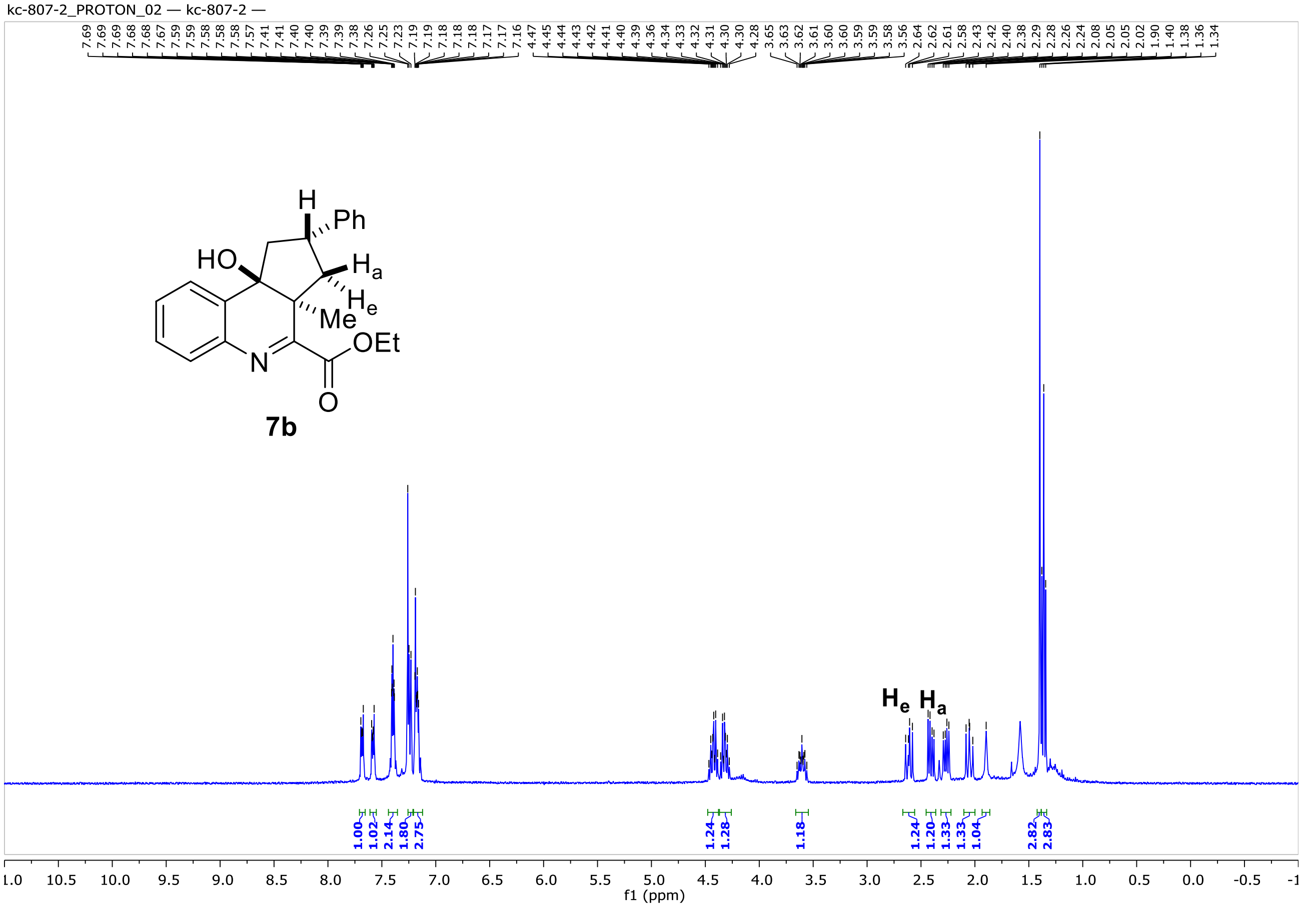
kc-801-toluene-1_COSY_01 — kc-801-toluene-1 —

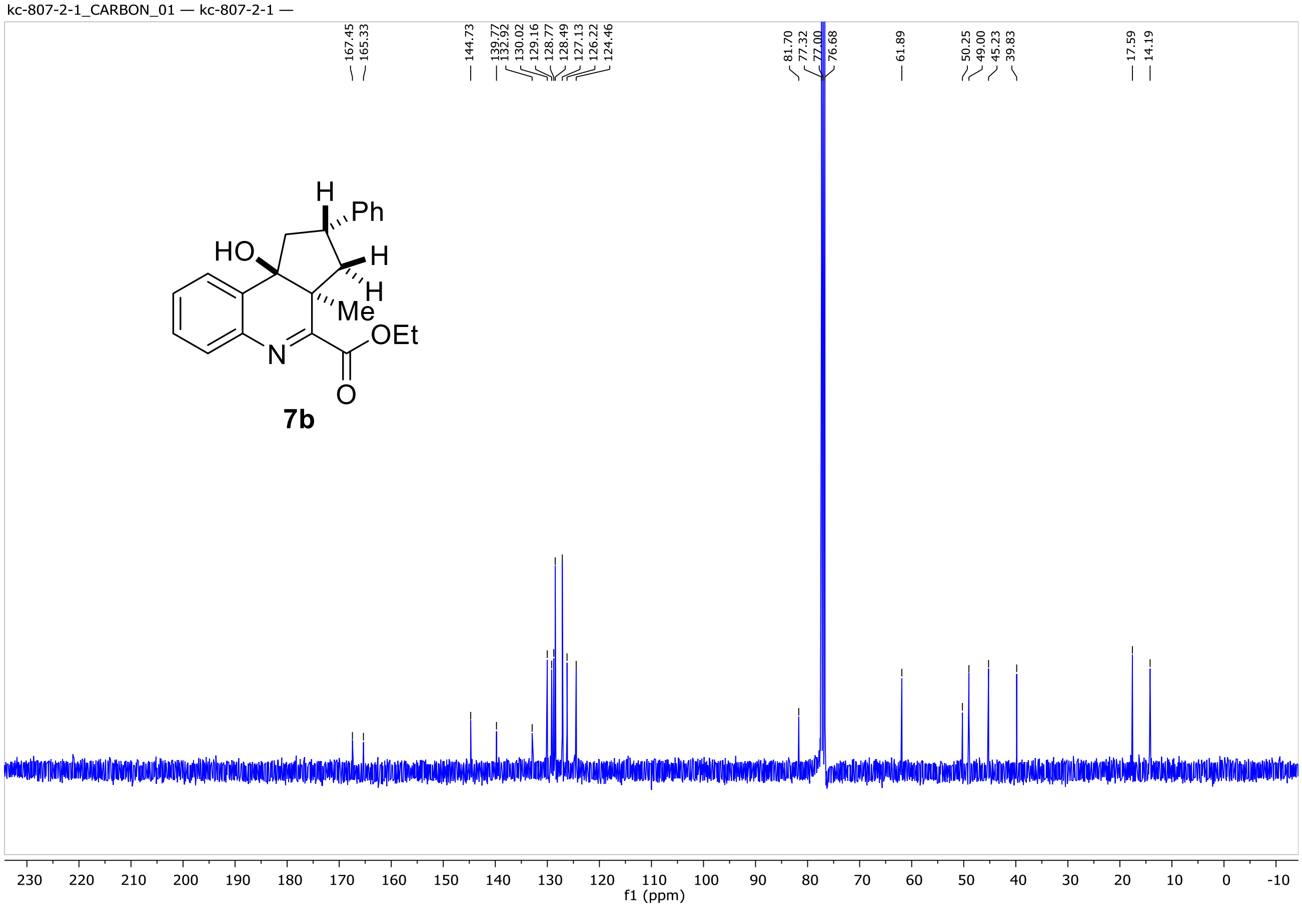


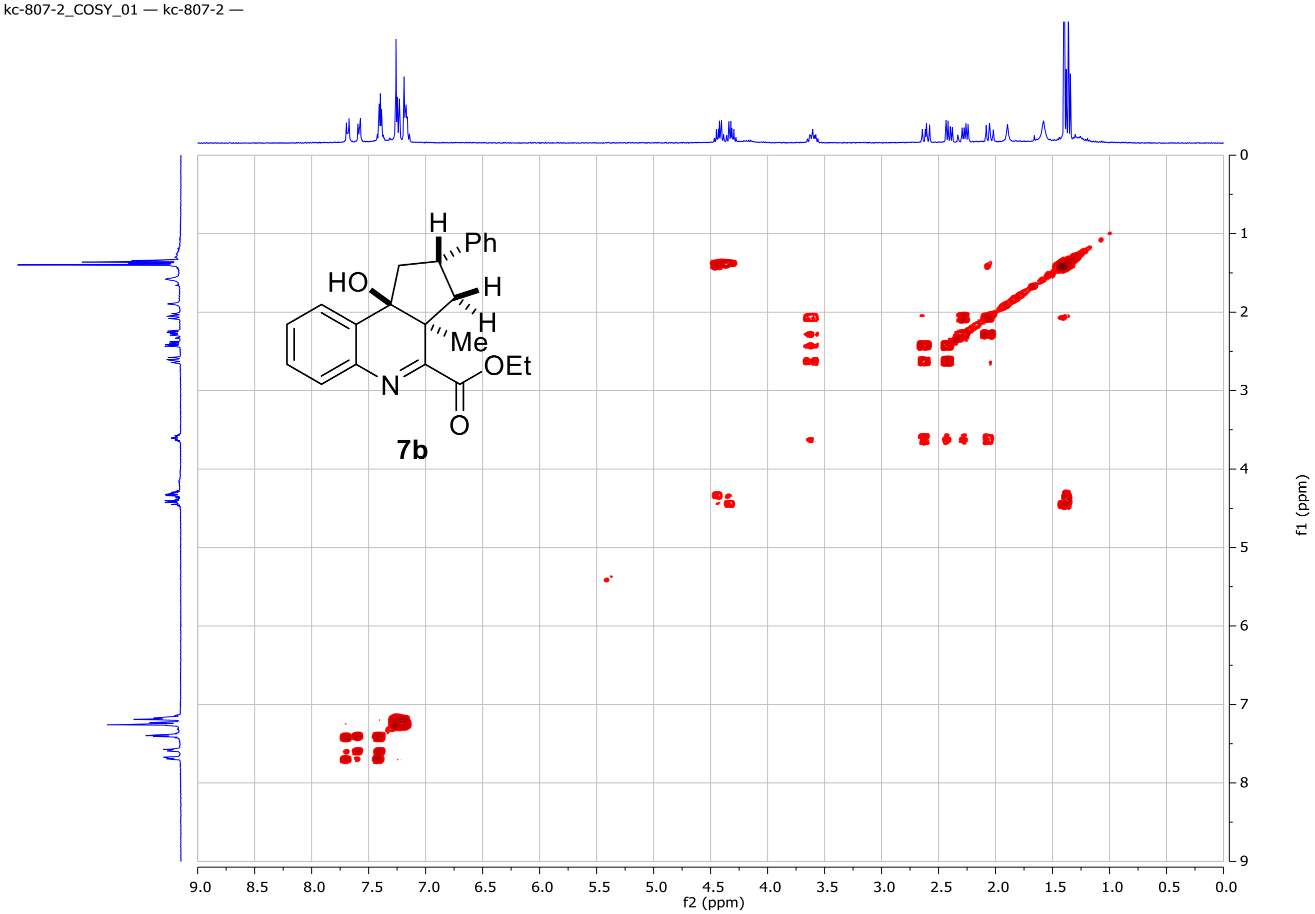
kc-801-toluene_HSQCAD_01 — kc-801-toluene —

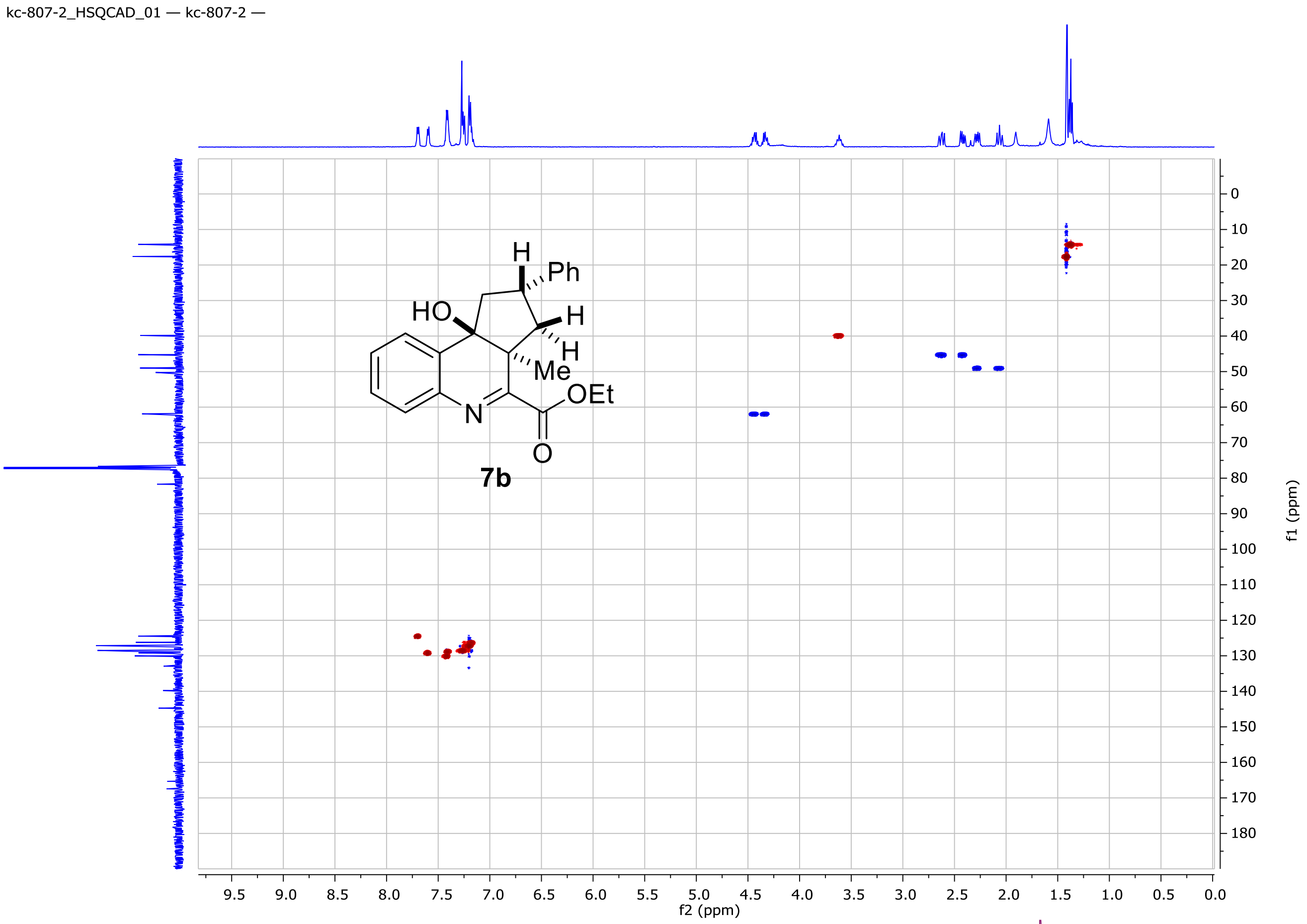


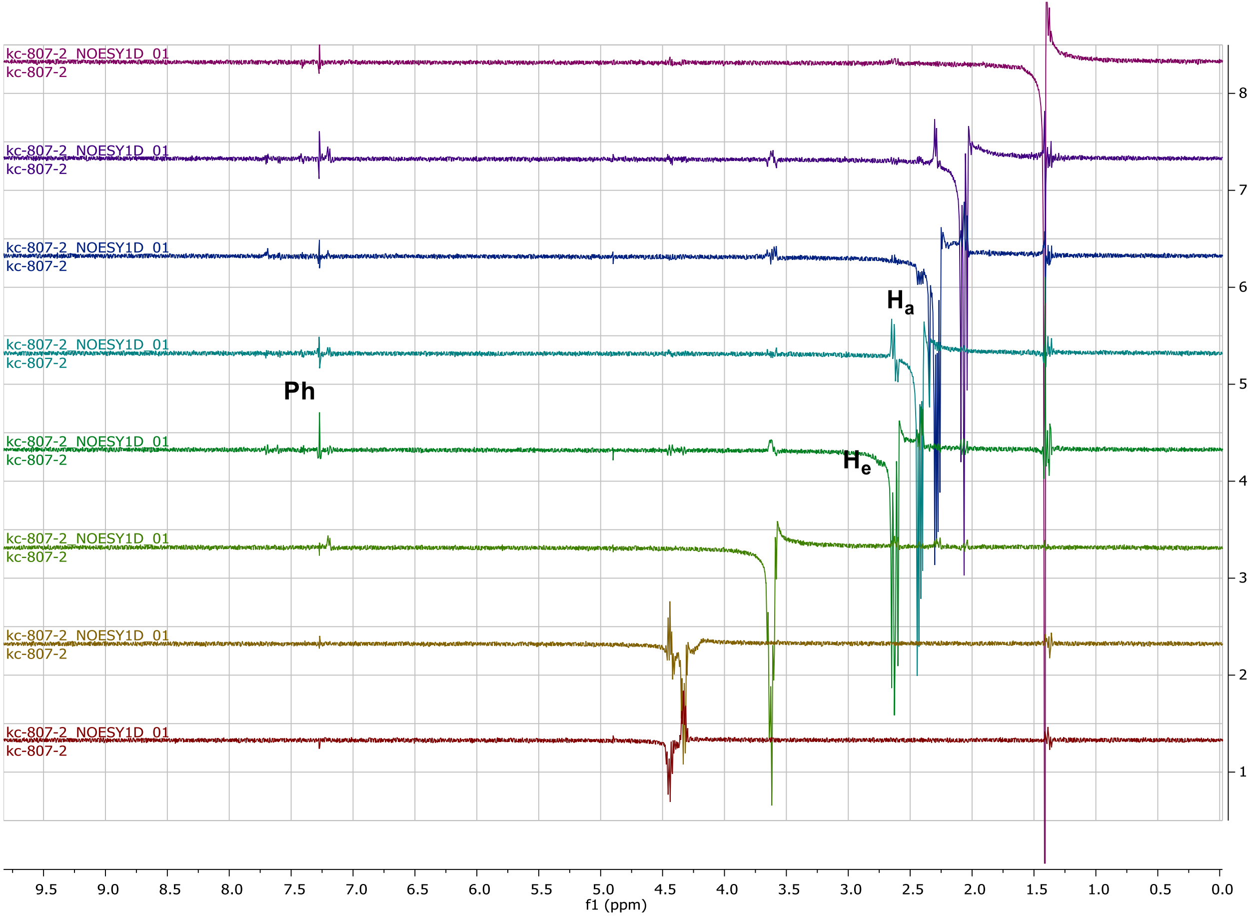

kc-801-toluene_NOESY1D_01
kc-801-toluene
He
Ha
9
8
7
6
5
4
3
2
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


kc-807-2_PROTON_02 — kc-807-2 —
7.69 7.69 7.69 7.68 7.68 7.67 7.59 7.59 7.58 7.58 7.58 7.58 7.57 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.26 7.25 7.23 7.19 7.19 7.18 7.18 7.18 7.17 7.16 4.47 4.45 4.44 4.43 4.42 4.41 4.40 4.39 4.36 4.34 4.33 4.32 4.31 4.30 4.30 4.28 3.65 3.63 3.62 3.61 3.60 3.59 3.59 3.58 3.56 2.64 2.62 2.61 2.58 2.43 2.42 2.40 2.38 2.29 2.28 2.26 2.24 2.08 2.05 2.02 1.90 1.40 1.38 1.36 1.34
H
Ph
HO
Ha
He
Me
N
OEt
O
7b
He
Ha
1.00 1.02 2.14 1.80 2.75 1.24 1.28 1.18 1.24 1.20 1.33 1.33 1.04 2.82 2.83
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


kc-807-2-1_CARBON_01 — kc-807-2-1 —
167.45
165.33
144.73
139.77
132.92
130.02
129.16
128.77
128.49
127.13
126.22
124.46
81.70
77.32
77.00
76.68
61.89
50.25
49.00
45.23
39.83
17.59
14.19
H
Ph
HO
H
H
Me
N
OEt
O
7b
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


kc-807-2_COSY_01 — kc-807-2 —
H
Ph
HO
H
H
Me
N
OEt
O
7b
0
1
2
3
4
5
6
7
8
9
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)


kc-807-2_HSQCAD_01 — kc-807-2 —
H
Ph
HO
H
H
Me
N
OEt
O
7b
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
f1 (ppm)


kc-807-2_NOESY1D_01
kc-807-2
kc-807-2_NOESY1D_01
kc-807-2
kc-807-2_NOESY1D_01
kc-807-2
kc-807-2_NOESY1D_01
kc-807-2
Ph
kc-807-2_NOESY1D_01
kc-807-2
kc-807-2_NOESY1D_01
kc-807-2
kc-807-2_NOESY1D_01
kc-807-2
kc-807-2_NOESY1D_01
kc-807-2
Ha
He
8 7 6 5 4 3 2 1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)