Supporting Information

Tetrahydroquinolines and Benzazepines through Catalytic Diastereoselective Formal [4+2]-Cycloaddition Reactions Between Donor-Acceptor Cyclopropenes and Imines

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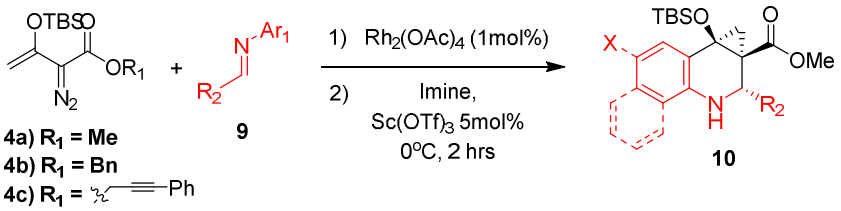
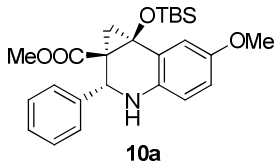
Table of Contents

General	S2
General Synthesis of Tetrahydroquinolines **10a-10r**	S3 – S13
General Synthesis of Benzazepines **15a-15d and 15k**	S13 – S17
Synthesis of Enolsilyldiazoacetate **4c**	S17
^{1}H NMR and ^{13}C NMR spectra	S18 – S41
X-ray crystal structure data for **10r**	S42 – S52

General. Dichloromethane (DCM) was distilled over calcium hydride prior to use. Thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F254 plates. The developed chromatogram was analyzed by UV lamp (254 nm), potassium permanganate ($KMnO_4$) or cerium ammonium molybdate (CAM). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated system on silica gel (230-400 mesh). Metal triflate salts and Brønsted acids were purchased from Aldrich and used as received. Methyl 3-*tert*-butyldimethylsilyloxy-2-diazobut-3-enoate (**4a**) was prepared by the literature methods.[1] Imines were prepared by condensation from the corresponding aldehydes and anilines in CH_2Cl_2 and magnesium sulfate ($MgSO_4$). ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in ppm with the residual $CHCl_3$ signal as the reference, and coupling constants (*J*) are given in hertz. The peak information is described as: br = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite (complex multiplet of magnetically non-equivalent protons). IR spectra were recorded (neat) on a Thermo Nicolet IR200 spectrometer. Melting points were obtained from Electro Thermo Mel-Temp DLX 104. High-resolution mass spectra (HRMS) were performed on a JEOL AccuTOF-ESI mass spectrometer using CsI as the standard.

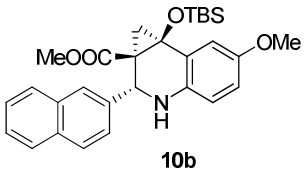


General Procedure for the Synthesis of Tetrahydroquinolines 10a-10p. To a solution containing enoldiazoacetate (**4a-4c)** (0.60 mmol, 1.2 eq.) in 2.0 ml of CH_2Cl_2 under nitrogen atmosphere at 0°C (ice-bath) was added $Rh_2(OAc)_4$ (2.2 mg, 0.0050 mmol, 1.0 mol%), and the resulting solution was stirred for 30 min. The ice bath was then removed, and the reaction solution was stirred at room temperature for an additional 5-10 minutes until the effervescence (evolution of nitrogen) ceased. The reaction was cooled to 0°C with an ice bath, then a solution of imine **9** (0.50 mmol, 1.0 eq.) in 1.0 ml of CH_2Cl_2 was added via syringe, followed by $Sc(OTf)_3$ (12 mg, 0.025 mmol, 5.0 mol%). The reaction solution was stirred for an additional 2 h at 0°C, then concentrated, and the residue was purified by flash chromatography (SiO_2) with hexane and ethyl acetate as the eluent to provide tetrahydroquinolines **10**.



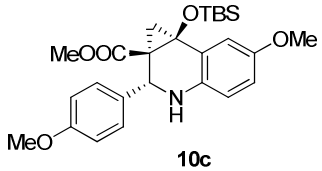
Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-methoxy-2-phenyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10a). The reaction between enoldiazoacetate **4a** and imine **9a** gave **10a** as a single isomer in 92 % isolated yield: white solid, mp = 177-178 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.35 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (comp, 2H), 7.37 – 7.27 (comp, 3H), 7.16 (d, *J* = 2.8 Hz, 1H), 6.66 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.52 (d, *J* = 8.5 Hz, 1H), 4.67 (s, 1H), 3.78 (s, 3H), 3.60 (s, 3H), 3.44 (s, 1H), 2.34 (d, *J* = 6.0 Hz, 1H), 2.12 (d, *J* = 6.0 Hz, 1H), 1.00 (s, 9H), 0.31 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 153.1, 141.5, 136.1, 128.5, 128.1, 127.7, 127.6, 115.7, 113.5,

111.0, 60.5, 55.8, 54.6, 51.7, 47.0, 25.9, 18.4, 17.5, -2.7, -3.3; IR (neat) 3330, 1720 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{25}H_{34}NO_4Si$ $[M+H]^+$ 440.2257, found: 440.2265.



10b

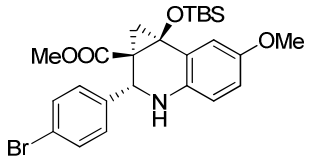
Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-methoxy-2-(naphthalen-2-yl)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10b). Reaction between enoldiazoacetate **4a** and imine **9b** gave **10b** as a single isomer in 92 % yield: white solid, mp = 183-186 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.35 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (comp, 4H), 7.55 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.52 – 7.43 (comp, 2H), 7.19 (d, *J* = 2.8 Hz, 1H), 6.68 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 4.85 (s, 1H), 3.80 (s, 3H), 3.58 (s, 3H), 3.52 (br, 1H), 2.44 (d, *J* = 6.0 Hz, 1H), 2.18 (d, *J* = 6.0 Hz, 1H), 1.00 (s, 9H), 0.33 (s, 3H), 0.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 153.2, 138.9, 136.1, 133.3, 133.2, 128.3, 128.0, 127.7, 127.7, 126.8, 126.1, 126.0, 125.5, 115.7, 113.5, 111.1, 60.6, 55.8, 54.8, 51.7, 46.9, 25.9, 18.4, 17.7, -2.7, -3.3; IR (neat) 3342, 1716 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{29}H_{36}NO_4Si$ $[M+H]^+$ 490.2464, found: 490.2469.



10c

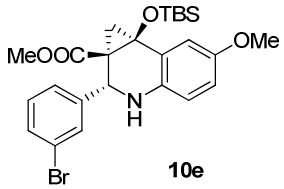
Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-methoxy-2-(4-methoxyphenyl)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10c). Reaction between enoldiazoacetate **4a** and imine **9c** gave **10c** as a single isomer in 88 % yield: white solid, mp = 143-146 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.20 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 2.8 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.65 (dd, *J* = 8.5, 2.9 Hz, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 4.62 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.60 (s, 3H), 3.40 (br, 1H), 2.31

(d, J = 6.0 Hz, 1H), 2.10 (d, J = 6.0 Hz, 1H), 0.99 (s, 9H), 0.31 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 159.4, 153.1, 136.2, 133.6, 128.7, 127.7, 115.6, 113.9, 113.4, 111.0, 60.5, 55.8, 55.2, 53.9, 51.7, 47.0, 25.9, 18.4, 17.4, -2.7, -3.3; IR (neat) 3346, 1716 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{26}H_{36}NO_5Si$ $[M+H]^+$ 470.2363, found: 470.2353.



10d

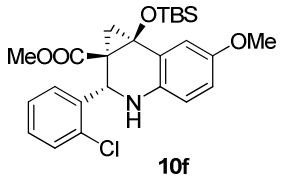
Methyl 2-(4-Bromophenyl)-7b-(*tert*-butyldimethylsilyl)oxy-6-methoxy-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10d). Reaction between enoldiazoacetate **4a** and imine **9d** gave **10d** as a single isomer in 82 % yield: white solid, mp = 158-161 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.35 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 2.8 Hz, 1H), 6.66 (dd, J = 8.5, 2.8 Hz, 1H), 6.53 (d, J = 8.5 Hz, 1H), 4.63 (s, 1H), 3.78 (s, 3H), 3.60 (s, 3H), 3.40 (br, 1H), 2.28 (d, J = 6.0 Hz, 1H), 2.11 (d, J = 6.0 Hz, 1H), 0.99 (s, 9H), 0.30 (s, 3H), 0.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 153.3, 140.6, 135.8, 131.7, 129.4, 127.6, 122.1, 115.8, 113.5, 111.1, 60.7, 55.8, 54.1, 51.8, 46.9, 25.9, 18.4, 17.5, -2.7, -3.3; IR (neat) 3341, 1717 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{25}H_{33}BrNO_4Si$ $[M+H]^+$ 518.1362, found: 518.1355.



10e

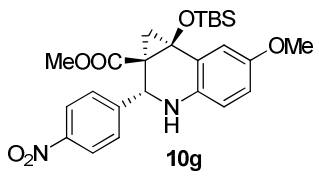
Methyl 2-(3-Bromophenyl)-7b-(*tert*-butyldimethylsilyl)oxy-6-methoxy-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10e). Reaction between enoldiazoacetate **4a** and imine **9e** gave **10e** as a single isomer in 83 % yield: white solid, mp = 167-168 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.35 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, J = 1.8 Hz, 1H), 7.46

– 7.40 (m, 1H), 7.33 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 2.8 Hz, 1H), 6.66 (dd, *J* = 8.5, 2.9 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 4.64 (s, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 3.42 (br, 1H), 2.29 (d, *J* = 6.1 Hz, 1H), 2.13 (d, *J* = 6.1 Hz, 1H), 0.99 (s, 9H), 0.31 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 153.3, 143.9, 135.7, 131.2, 130.7, 130.1, 127.5, 126.4, 122.6, 115.8, 113.6, 111.1, 60.7, 55.8, 54.2, 51.8, 46.9, 25.9, 18.4, 17.6, -2.7, -3.3; IR (neat) 3330, 1719 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{25}H_{33}BrNO_4Si$ $[M+H]^+$ 518.1362, found: 518.1369.



10f

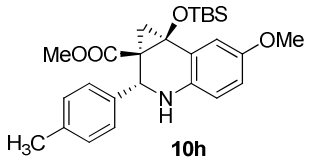
Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-2-(2-chlorophenyl)-6-methoxy-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10f). Reaction between enoldiazoacetate **4a** and imine **9f** gave **10f** as a single isomer in 75 % yield: white solid, mp = 98-101 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.40 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.37 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.30 – 7.20 (comp, 2H), 7.16 (d, *J* = 2.8 Hz, 1H), 6.66 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 5.15 (s, 1H), 3.78 (s, 3H), 3.56 (s, 3H), 3.51 (br, 1H), 2.39 (d, *J* = 5.9 Hz, 1H), 2.30 (d, *J* = 5.9 Hz, 1H), 1.00 (s, 9H), 0.32 (s, 3H), 0.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 168.4, 153.4, 138.4, 136.0, 133.9, 129.7, 129.1, 128.7, 127.9, 127.4, 115.9, 113.5, 111.1, 60.1, 55.8, 51.9, 50.6, 45.1, 25.9, 18.4, 18.3, -2.6, -3.3; IR (neat) 3340, 1738, 1723 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{25}H_{33}ClNO_4Si$ $[M+H]^+$ 474.1867, found: 474.1860.



10g

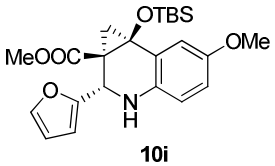
Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-methoxy-2-(4-nitrophenyl)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10g). Reaction

between enoldiazoacetate **4** and imine **9g** gave **10g** as a single isomer in 90 % yield: yellow solid, mp = 195-196 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.20 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 2.8 Hz, 1H), 6.68 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.56 (d, *J* = 8.5 Hz, 1H), 4.79 (s, 1H), 3.79 (s, 3H), 3.61 (s, 3H), 3.46 (br, 1H), 2.31 (d, *J* = 6.1 Hz, 1H), 2.14 (d, *J* = 6.1 Hz, 1H), 0.99 (s, 9H), 0.31 (s, 3H), 0.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 153.6, 148.8, 147.8, 135.3, 128.7, 127.5, 123.7, 116.0, 113.7, 111.1, 60.9, 55.8, 54.3, 51.9, 46.9, 25.8, 18.4, 17.6, -2.7, -3.3; IR (neat) 3359, 1738 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{25}H_{33}N_2O_6Si$ $[M+H]^+$ 485.2108, found: 485.2108.



10h

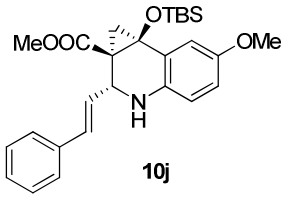
Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-methoxy-2-(*p*-tolyl)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10h). Reaction between enoldiazoacetate **4a** and imine **9h** gave **10h** as a single isomer in 87 % yield: white solid, mp = 176-177 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.40 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, 2H), 7.17 – 7.11 (comp, 3H), 6.65 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 4.63 (s, 1H), 3.78 (s, 3H), 3.60 (s, 3H), 3.40 (br, 1H), 2.34 (s, 3H), 2.31 (d, *J* = 6.0 Hz, 1H), 2.10 (d, *J* = 6.0 Hz, 1H), 0.99 (s, 9H), 0.30 (s, 3H), 0.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 153.1, 138.5, 137.7, 136.2, 129.2, 127.6, 127.5, 115.6, 113.5, 111.0, 60.5, 55.8, 54.3, 51.7, 47.0, 25.9, 21.1, 18.4, 17.4, -2.7, -3.3; IR (neat) 3344, 1715 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{26}H_{36}NO_4Si$ $[M+H]^+$ 454.2414, found: 454.2410.



10i

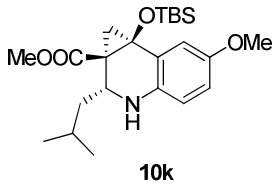
Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-2-(furan-2-yl)-6-methoxy-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10i). Reaction between

enoldiazoacetate **4a** and imine **9i** gave **10i** as a single isomer in 90 % yield: white solid, mp = 100-101 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.30 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 1H), 7.13 (d, *J* = 2.8 Hz, 1H), 6.66 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 6.35 – 6.32 (m, 1H), 6.29 (d, *J* = 3.2 Hz, 1H), 4.85 (s, 1H), 3.77 (s, 3H), 3.67 (s, 3H), 3.60 (br, 1H), 2.23 (d, *J* = 6.2 Hz, 1H), 2.14 (d, *J* = 6.2 Hz, 1H), 0.99 (s, 9H), 0.30 (s, 3H), 0.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 154.2, 153.3, 142.3, 134.9, 127.6, 115.9, 113.6, 111.1, 110.3, 106.4, 60.3, 55.8, 52.0, 48.8, 43.6, 25.9, 18.4, 17.3, -2.7, -3.3; IR (neat) 3336, 1718 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{23}H_{32}NO_5Si$ $[M+H]^+$ 430.2050, found: 430.2044.



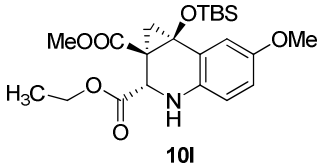
10j

Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-methoxy-2-((*E*)-styryl)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10j). Reaction between enoldiazoacetate **4a** and imine **9j** gave **10j** as a single isomer in 81 % yield: yellow liquid, TLC R_f = 0.35 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.20 (comp, 5H), 7.12 (d, *J* = 2.8 Hz, 1H), 6.70 – 6.61 (comp, 2H), 6.50 (d, *J* = 8.5 Hz, 1H), 6.14 (dd, *J* = 15.9, 7.8 Hz, 1H), 4.34 (d, *J* = 7.8 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.31 (br, 1H), 2.17 (d, *J* = 6.1 Hz, 1H), 2.05 (d, *J* = 6.0 Hz, 1H), 0.99 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 153.1, 136.5, 135.2, 132.6, 128.5, 128.0, 127.8, 127.6, 126.5, 115.6, 113.5, 111.0, 60.3, 55.8, 53.1, 51.8, 44.5, 25.9, 18.4, 16.5, -2.6, -3.3; IR (neat) 3359, 1735 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{27}H_{36}NO_4Si$ $[M+H]^+$ 466.2414, found: 466.2424.



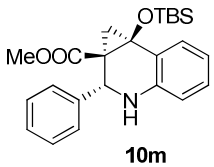
10k

Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-2-isobutyl-6-methoxy-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinoline-1a-carboxylate (10k). Reaction between enoldiazoacetate **4a** and imine **9k** gave **10k** in 75 % yield: yellow liquid, TLC R_f = 0.50 (10:1 hexane/EtOAC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 2.8 Hz, 1H), 6.62 (dd, *J* = 8.5, 2.9 Hz, 1H), 6.49 (d, *J* = 8.5 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.70 (dd, *J* = 5.7, 2.6 Hz, 1H), 3.26 (br, 1H), 1.97 (dd, *J* = 13.5, 6.1 Hz, 2H), 1.80 – 1.62 (m, 1H), 1.45 – 1.25 (m, 2H), 1.00 – 0.93 (comp, 15H), 0.29 (s, 3H), 0.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 152.9, 135.6, 127.7, 115.4, 113.4, 111.0, 59.8, 55.8, 51.7, 47.7, 44.9, 43.3, 25.8, 24.5, 23.7, 21.6, 18.3, 16.2, -2.7, -3.3; IR (neat) 3360, 1736 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{23}H_{38}NO_4Si$ $[M+H]^+$ 420.2570, found: 420.2579.



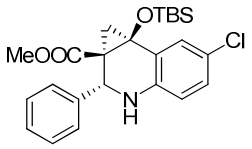
10l

2-Ethyl 1a-Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-methoxy-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a,2-dicarboxylate (10l). Reaction between enoldiazoacetate **4a** and imine **9l** gave **10l** as a single isomer in 45 % yield: yellow solid, mp = 97-99 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.30 (6:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 2.8 Hz, 1H), 6.65 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 4.42 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.11 (d, *J* = 6.3 Hz, 1H), 2.01 (d, *J* = 6.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.98 (s, 9H), 0.28 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 168.4, 153.3, 133.9, 127.2, 116.1, 113.6, 111.0, 61.7, 59.9, 55.7, 53.7, 51.9, 41.9, 25.8, 18.3, 16.9, 13.9, -2.7, -3.3; IR (neat) 3393, 1725 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{22}H_{34}NO_6Si$ $[M+H]^+$ 436.2155, found: 436.2166.



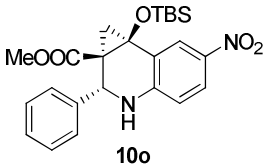
10m

Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-2-phenyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10m). Reaction between enoldiazoacetate **4a** and imine **9m** gave **10m** as a single isomer in 84 % yield: white solid, mp = 155-156 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.40 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.45 – 7.26 (comp, 5H), 7.05 (td, *J* = 7.6, 1.5 Hz, 1H), 6.85 (td, *J* = 7.6, 1.2 Hz, 1H), 6.57 (dd, *J* = 7.8, 1.0 Hz, 1H), 4.74 (s, 1H), 3.62 (br, 1H), 3.59 (s, 3H), 2.28 (d, *J* = 6.0 Hz, 1H), 2.11 (d, *J* = 6.0 Hz, 1H), 0.98 (s, 9H), 0.28 (s, 3H), 0.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 142.3, 141.4, 128.6, 128.1, 127.6, 126.9, 126.6, 125.8, 119.0, 114.7, 60.4, 54.1, 51.7, 47.2, 25.9, 18.4, 17.7, -2.7, -3.4; IR (neat) 3344, 1714 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{24}H_{32}NO_3Si$ $[M+H]^+$ 410.2151, found: 410.2160.



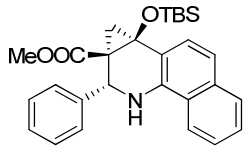
10n

Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-chloro-2-phenyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10n). Reaction between enoldiazoacetate **4a** and imine **9n** gave **10n** as a single isomer in 85 % yield: white solid, mp = 175-177 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.40 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.4 Hz, 1H), 7.42 – 7.28 (comp, 5H), 7.01 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.50 (d, *J* = 8.3 Hz, 1H), 3.64 (br, 1H), 3.61 (s, 3H), 2.27 (d, *J* = 6.1 Hz, 1H), 2.12 (d, *J* = 6.1 Hz, 1H), 0.99 (s, 9H), 0.29 (s, 3H), 0.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 140.9, 140.8, 128.6, 128.3, 127.6, 126.7, 125.9, 124.0, 115.8, 60.1, 54.2, 51.8, 47.1, 25.9, 18.4, 17.8, -2.7, -3.4; IR (neat) 3330, 1718 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{24}H_{31}ClNO_3Si$ $[M+H]^+$ 444.1762, found: 444.1759.



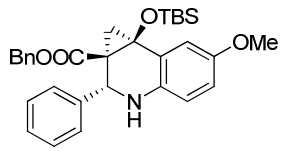
10o

Methyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-nitro-2-phenyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10o). Reaction between enoldiazoacetate **4a** and imine **9o** gave **10o** as a single isomer in 35 % yield: yellow solid, mp = 165-168 °C (recrystallization in dichloromethane and hexane); TLC R_f = 0.20 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.2 Hz, 1H), 7.97 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.40 – 7.33 (comp, 5H), 6.58 (d, *J* = 8.7 Hz, 1H), 4.92 (s, 1H), 4.30 (s, 1H), 3.65 (s, 3H), 2.21 (d, *J* = 6.4 Hz, 1H), 2.14 (d, *J* = 6.4 Hz, 1H), 1.02 (s, 9H), 0.32 (s, 3H), 0.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 167.4, 147.8, 139.9, 139.9, 128.9, 128.7, 127.5, 126.4, 123.6, 122.6, 114.2, 59.9, 53.9, 52.0, 47.0, 25.8, 18.5, 18.3, -2.8, -3.4; IR (neat) 3324, 1720 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{24}H_{31}N_2O_5Si$ $[M+H]^+$ 455.2002, found: 455.2009.



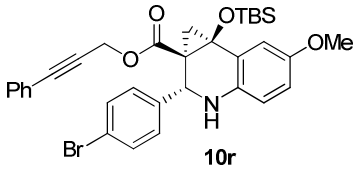
10p

Methyl 7a-(*tert*-Butyldimethylsilyl)oxy-6-phenyl-6,6a,7,7a-tetrahydro-5H-benzo[h]cyclopropa[c]quinoline-6a-carboxylate (10p). Reaction between enoldiazoacetate **4a** and imine **9p** gave **10p** as a single isomer in 81 % yield. white solid; mp = (143-145)°C (recrystallization in dichloromethane and hexane). TLC R_f = 0.50 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (comp, 2H), 7.66 – 7.62 (m, 1H), 7.54 – 7.49 (comp, 2H), 7.46 – 7.35 (comp, 6H), 4.87 (s, 1H), 4.58 (br, 1H), 3.65 (s, 3H), 2.39 (d, *J* = 6.0 Hz, 1H), 2.23 (d, *J* = 6.0 Hz, 1H), 1.05 (s, 9H), 0.33 (s, 1H), 0.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 141.5, 136.9, 132.80, 128.7, 128.6, 128.2, 127.9, 125.3, 125.1, 123.8, 122.2, 121.0, 119.4, 118.0, 60.8, 54.3, 51.7, 48.0, 26.0, 18.7, 18.5, -2.6, -3.4; IR (neat) 3420, 2927, 2855, 1720 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{28}H_{34}NO_3Si$ $[M+H]^+$ 460.2308, found: 460.2311.



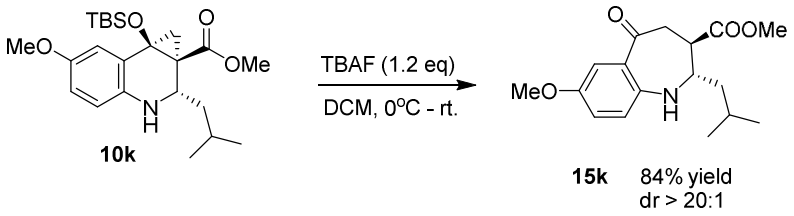
10q

Benzyl 7b-(*tert*-Butyldimethylsilyl)oxy-6-methoxy-2-phenyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinoline-1a-carboxylate (10q). Reaction between enoldiazoacetate **4b** and imine **9a** gave **10q** as a colorless liquid, single isomer in 80 % yield. TLC R_f = 0.50 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (comp, 8H), 7.22 - 7.16 (comp, 3H), 6.69 (dd, *J* = 8.5, 2.9 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 5.08 (s, 2H), 4.69 (s, 1H), 3.83 (s, 3H), 3.47 (br, 1H), 2.41 (d, *J* = 5.9 Hz, 1H), 2.20 (d, *J* = 5.9 Hz, 1H), 1.04 (s, 9H), 0.36 (s, 3H), 0.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 153.2, 141.3, 136.2, 135.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 115.7, 113.5, 111.1, 66.5, 60.7, 55.9, 54.6, 47.0, 26.0, 18.5, 17.8, -2.6, -3.2. IR (neat) 3355, 1731 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{31}H_{38}NO_4Si$ $[M+H]^+$ 516.2570, found: 516.2585.

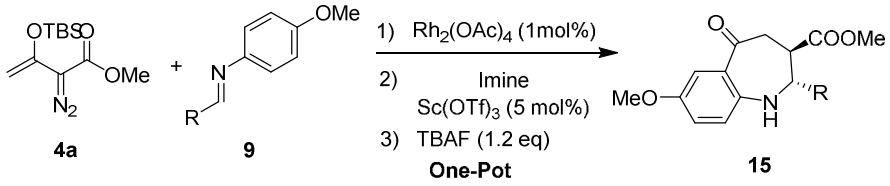


10r

3-Phenylprop-2-yn-1-yl 2-(4-Bromophenyl)-7b-(*tert*-butyldimethylsilyl)oxy-6-methoxy-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*c*]quinoline-1a-carboxylate (10r). Reaction between **4c** and **9d** gave **10r** in 91% yield: colorless solid, mp = 160-161 °C; TLC R_f = 0.30 (10:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (comp, 9H), 7.16 (d, *J* = 2.8 Hz, 1H), 6.67 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 4.92 (d, *J* = 15.6 Hz, 1H), 4.76 (d, *J* = 15.6 Hz, 1H), 4.70 (s, 1H), 3.79 (s, 3H), 3.43 (s, 1H), 2.33 (d, *J* = 6.0 Hz, 1H), 2.15 (d, *J* = 6.0 Hz, 1H), 0.99 (s, 9H), 0.31 (s, 3H), 0.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 153.3, 140.3, 135.8, 131.8, 131.6, 129.6, 128.7, 128.3, 127.5, 122.1, 115.8, 113.6, 111.1, 86.6, 82.8, 61.0, 55.8, 54.0, 53.0, 46.8, 25.9, 18.4, 17.6, -2.6, -3.2; IR (neat) 3355, 2854, 1736 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{33}H_{37}BrNO_4Si$ $[M+H]^+$ 618.1675, found: 618.1680.



Procedure for the Synthesis of 1*H*-Benzazepine 15k. To a solution containing tetrahydroquinoline **10k** (120 mg, 0.30 mmol) in 2.0 ml of CH_2Cl_2 at 0°C was added tetra-*n*-butylammonium fluoride (TBAF) (1.0M) (0.30 ml, 1.2eq) via syringe. The reaction was stirred for 1 h at 0°C and one additional h at room temperature. The solvent was evaporated, and the residue purified by flash chromatography (SiO_2) with hexane and ethyl acetate as the eluent to provide benzazepine **15k** as a single isomer in 84% yield: yellow liquid; TLC R_f = 0.35 (4:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 3.1 Hz, 1H), 6.93 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 3.99 (br, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.45 - 3.40 (m, 1H), 3.25 (dd, *J* = 12.0, 7.5 Hz, 1H), 2.98 - 2.91 (m, 1H), 2.84 (dd, *J* = 12.0, 3.2 Hz, 1H), 1.70 - 1.65 (m, 1H), 1.57 - 1.50 (m, 1H), 1.40 – 1.31 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 173.2, 153.3, 147.1, 125.4, 122.3, 120.2, 110.5, 59.9, 55.7, 54.1, 52.0, 44.0, 43.7, 25.5, 23.4, 21.6. IR (neat) 3376, 1734, 1655 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{17}H_{24}NO_4$ $[M+H]^+$ 306.1705, found: 306.1716.



General Procedure for One-Pot Synthesis of 1*H*-Benzazepines (15a-15d). To a solution containing enoldiazoacetate **4a** (150 mg, 0.60 mmol, 1.2 eq) in 2.0 ml of CH_2Cl_2 under nitrogen atmosphere at 0°C (ice-bath) was added $Rh_2(OAc)_4$ (2.2 mg, 0.0050 mmol, 1.0 mol%) and stirred for 30 minutes. Then the ice bath was removed and the reaction solution was stirred at room temperature for additional 5-10 min until the effervescence (evolution of nitrogen) ceased. The reaction was cooled to 0°C with an ice bath, then a solution of imine **9** (0.50 mmol, 1 eq) in 1.0 ml of CH_2Cl_2 was added via

syringe, followed by $Sc(OTf)_3$ (12 mg, 0.025 mmol, 5.0 mol%). The reaction was stirred for additional 2 h at 0°C. Then a solution of tetra-*n*-butylammonium fluoride (TBAF) (1.0 M, 0.60 ml, 1.2 eq) was added via syringe and stirred for 1 h at 0°C. The ice bath was removed, and the reaction solution was stirred for 1 h at room temperature. The solvent was evaporated, and the residue was purified by flash chromatography (SiO_2) with hexane and ethyl acetate as the eluent to provide benzazepines **15**.

The **s**tereochemistry of the major isomer of **15** was assigned to be *anti* based on ^{1}HNMR NOE experiments. Although correlations between H2 and H3, and H2 and H4 were observed, there was no correlation between H_1 and H_2 (Figure 1).

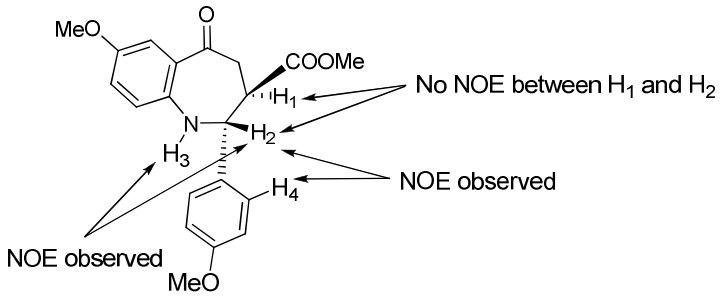
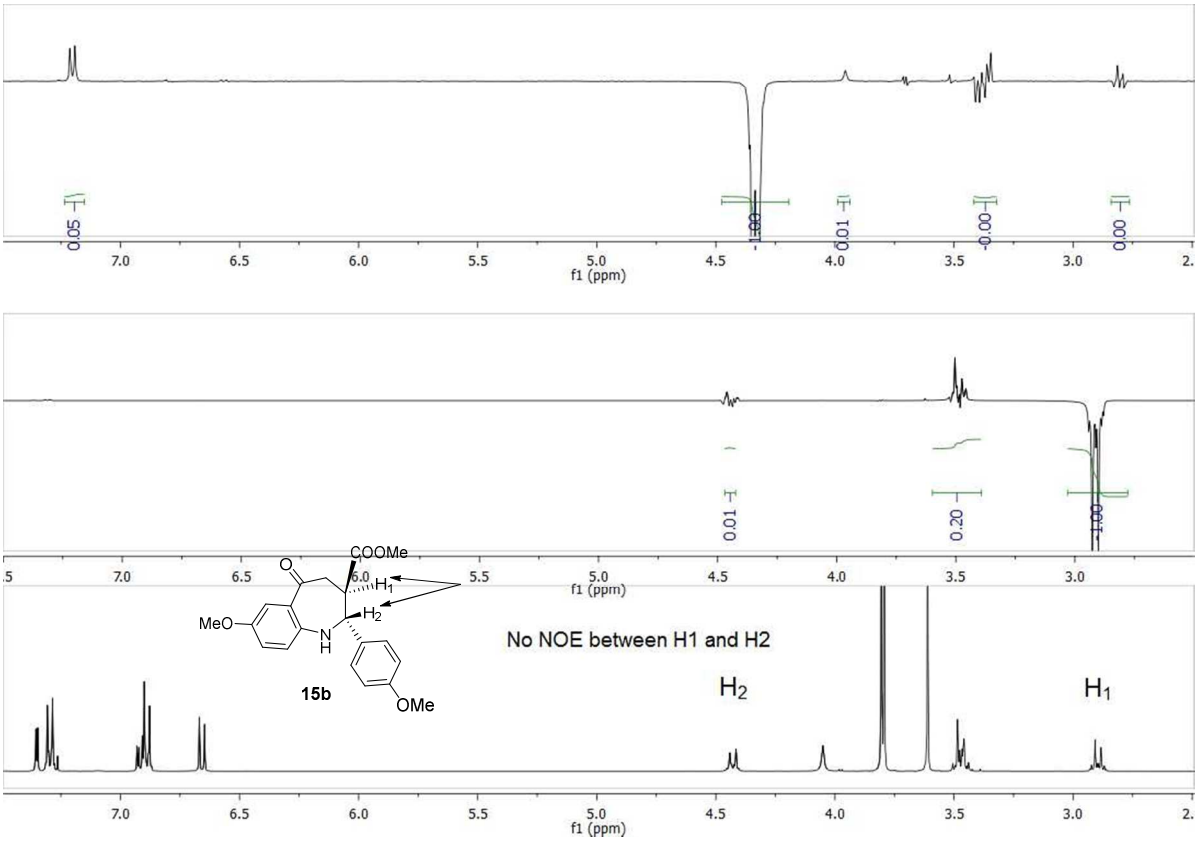
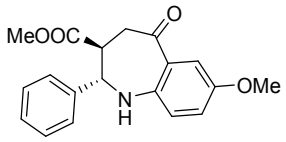


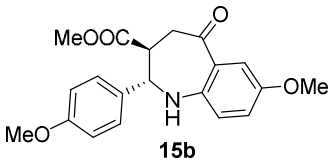
Figure 1. NOE experiments.





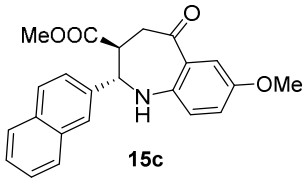
15a

Methyl 7-Methoxy-5-oxo-2-phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine-3-carboxylate (15a). Yellow solid, mp = 152-154 °C; TLC R_f = 0.30 (4:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (comp, 6H), 6.92 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.67 (d, *J* = 8.7 Hz, 1H), 4.52 – 4.45 (m, 1H), 4.10 (br, 1H), 3.79 (s, 3H), 3.61 (s, 3H), 3.53 – 3.44 (m, 2H), 2.95 – 2.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 172.4, 153.6, 147.1, 141.3, 129.1, 128.4, 126.9, 125.3, 122.3, 120.5, 110.6, 66.5, 55.7, 54.4, 52.0, 43.8; IR (neat) 3342, 1739, 1649 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{19}H_{20}NO_4$ $[M+H]^+$ 326.1392, found: 326.1399.



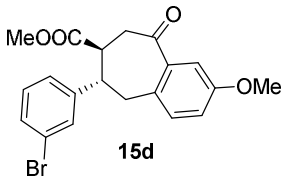
15b

Methyl 7-Methoxy-2-(4-methoxyphenyl)-5-oxo-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine-3-carboxylate (15b). Colorless solid, mp = 156-157 °C; TLC R_f = 0.20 (2:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 3.0 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.94 – 6.85 (comp, 3H), 6.66 (d, *J* = 8.7 Hz, 1H), 4.47 – 4.38 (m, 1H), 4.04 (br, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.61 (s, 3H), 3.51 – 3.43 (m, 2H), 2.94 – 2.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 172.4, 159.5, 153.5, 147.2, 133.3, 128.1, 125.2, 122.2, 120.4, 114.4, 110.6, 66.0, 55.7, 55.3, 54.5, 52.0, 43.8; IR (neat) 3357, 2957, 2834, 1724, 1657 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{20}H_{22}NO_5$ $[M+H]^+$ 356.1498, found: 356.1505.



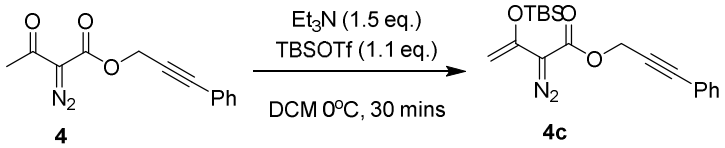
15c

Methyl 7-Methoxy-2-(naphthalen-2-yl)-5-oxo-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine-3-carboxylate (15c). Isolated as a mixture of isomer 13:1(anti/syn): yellow solid, mp = 64-70 °C; TLC R_f = 0.20 (4:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.78 (comp, 4H), 7.51 (dd, *J* = 5.4, 4.1 Hz, 3H), 7.39 (d, *J* = 3.0 Hz, 1H), 6.93 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.67 (d, *J* = 8.7 Hz, 1H), 4.68 (d, *J* = 10.9 Hz, 1H), 4.20 (br, 1H), 3.80 (s, 3H), 3.66 – 3.51 (comp, 5H), 2.96 (dd, *J* = 12.1, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 172.4, 153.6, 147.0, 138.4, 133.2, 133.1, 129.1, 128.0, 127.7, 126.6, 126.4, 126.2, 125.4, 124.5, 122.3, 120.6, 110.6, 66.6, 55.7, 54.2, 52.0, 43.8; IR (neat) 3347, 1732, 1661 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{23}H_{22}NO_4$ $[M+H]^+$ 376.1549, found: 376.1555.



15d

Methyl 2-(3-Bromophenyl)-7-methoxy-5-oxo-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine-3-carboxylate (15d). Isolated as a mixture of inseparable isomers (9:1). TLC R_f = 0.25 (4:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 1.8 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.34 (d, *J* = 3.0 Hz, 1H), 7.32 - 7.21 (m, 3H), 6.93 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 4.48 (d, *J* = 8.3, 1H), 4.07 (br, 1H), 3.79 (s, 3H), 3.63 (s, 3H), 3.51 – 3.41 (m, 2H), 2.99 – 2.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 172.1, 153.7, 146.5, 143.5, 131.6, 130.6, 129.9, 125.8, 125.5, 123.1, 122.3, 120.7, 110.7, 65.7, 55.7, 54.0, 52.1, 43.6; IR (neat) 3354, 1733, 1662 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{19}H_{19}BrNO_4$ $[M+H]^+$ 404.0497, found: 404.0452.



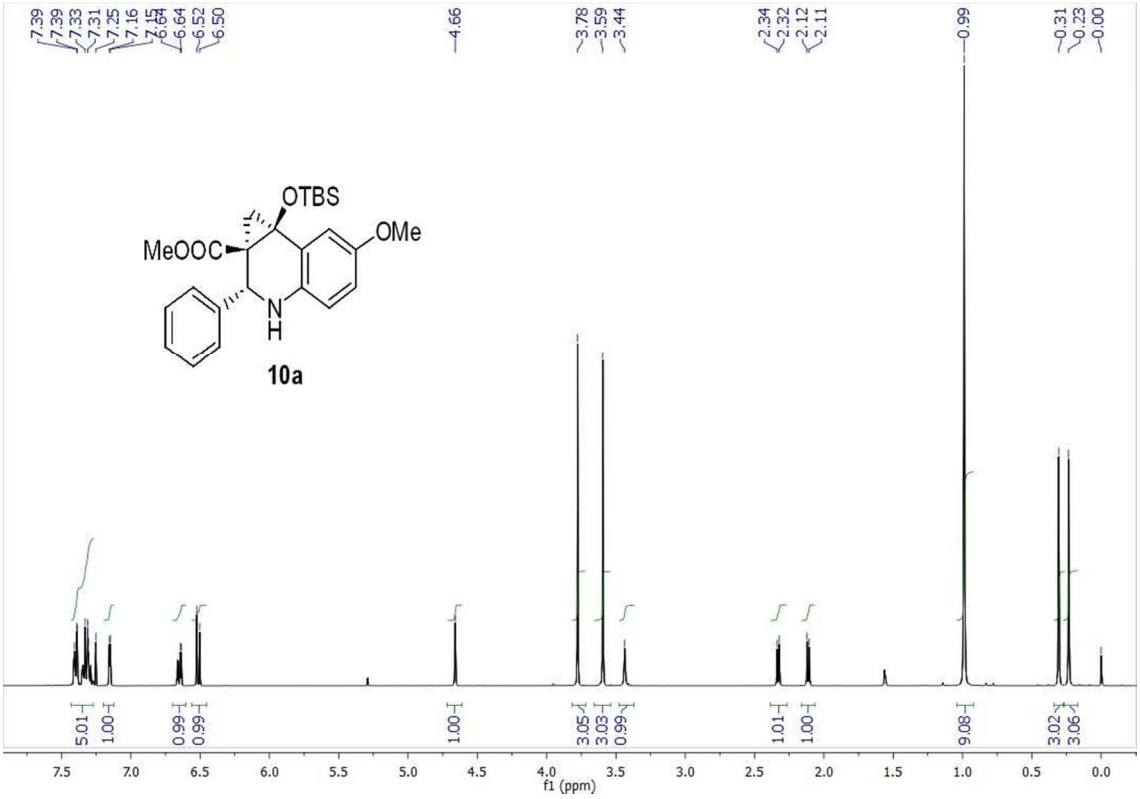
4 4c

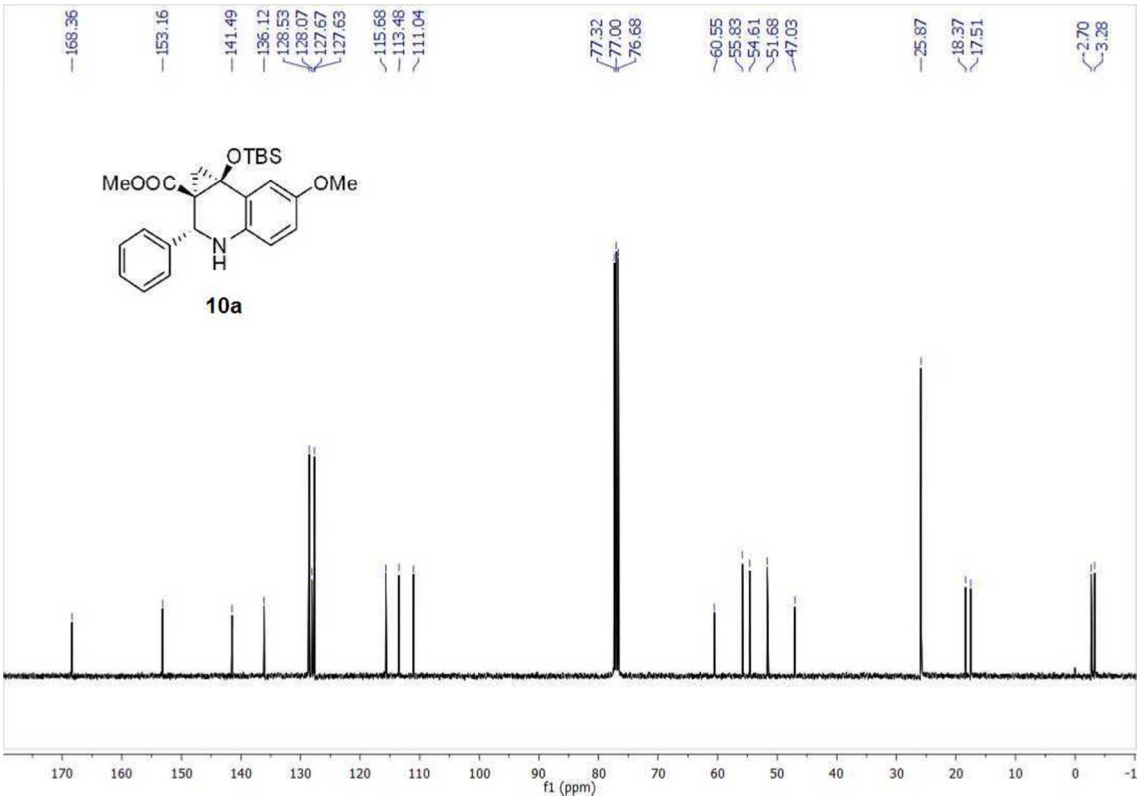
Procedure for the Synthesis of 4c. A solution of **4**[2] (0.50 gram, 2.0 mmol) in 15 ml DCM at 0°C was added triethylamine (0.42 ml, 1.5 eq.). Then *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) (0.50 ml, 1.1 eq.) was added drop-wise. The reaction was stirred at 0°C for 30 minutes, and then diluted with 80 ml of hexane. The solution was washed 3 times with saturated sodium bicarbonate, dried over $NaSO_4$, filtered, and concentrated to provide **4c** in 94% yield as an orange liquid. The product was used without further purification. IR (neat) 2103, 1712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.29 (comp, 5H), 5.06 (comp, 3H), 4.30 (d, *J* = 2.2 Hz, 1H), 0.95 (s, 9H), 0.26 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 140.5, 131.9, 128.8, 128.3, 122.1, 90.6, 86.6, 82.9, 52.9, 25.6, 18.1, -4.7.

References:

(1) Davies, H. M. L.; Ahmed, G.; Churchill, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 10774-10780.

(2) Padwa, A.; Dean, C. D.; Fairfax, J. D.; Xu, L. S. *J. Org. Chem.* **1993**, *58*, 4646-4655.

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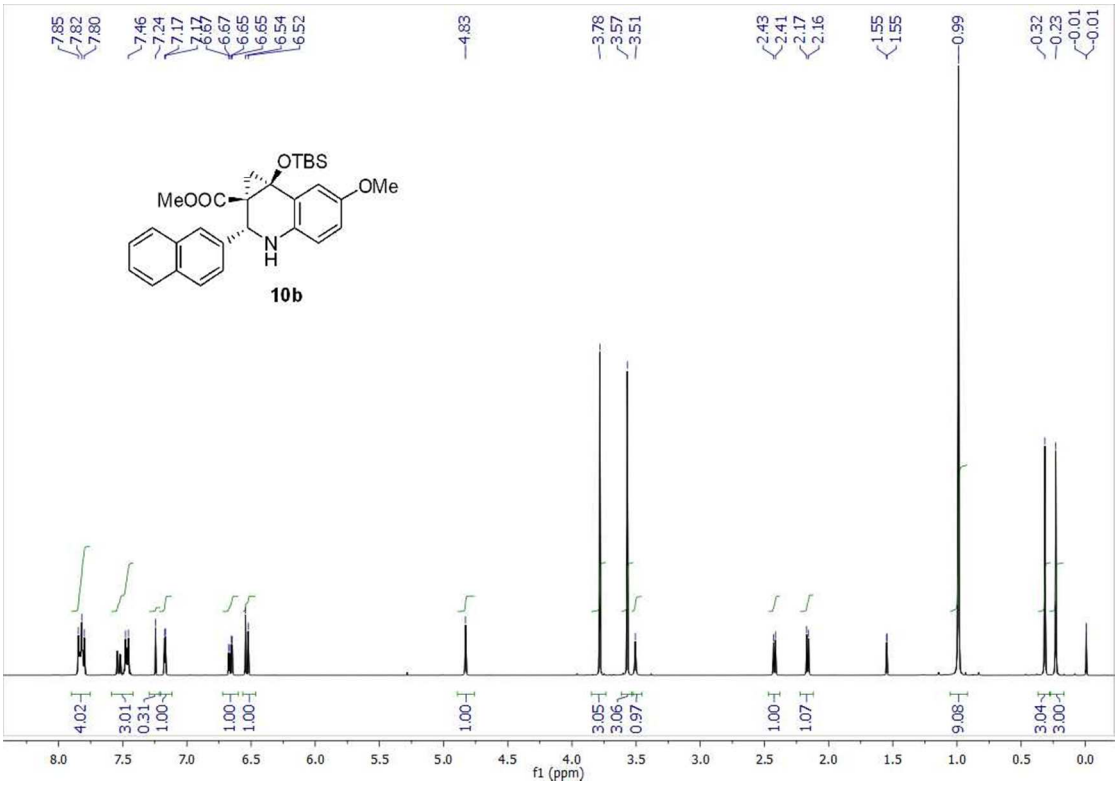
10a
f1 (ppm)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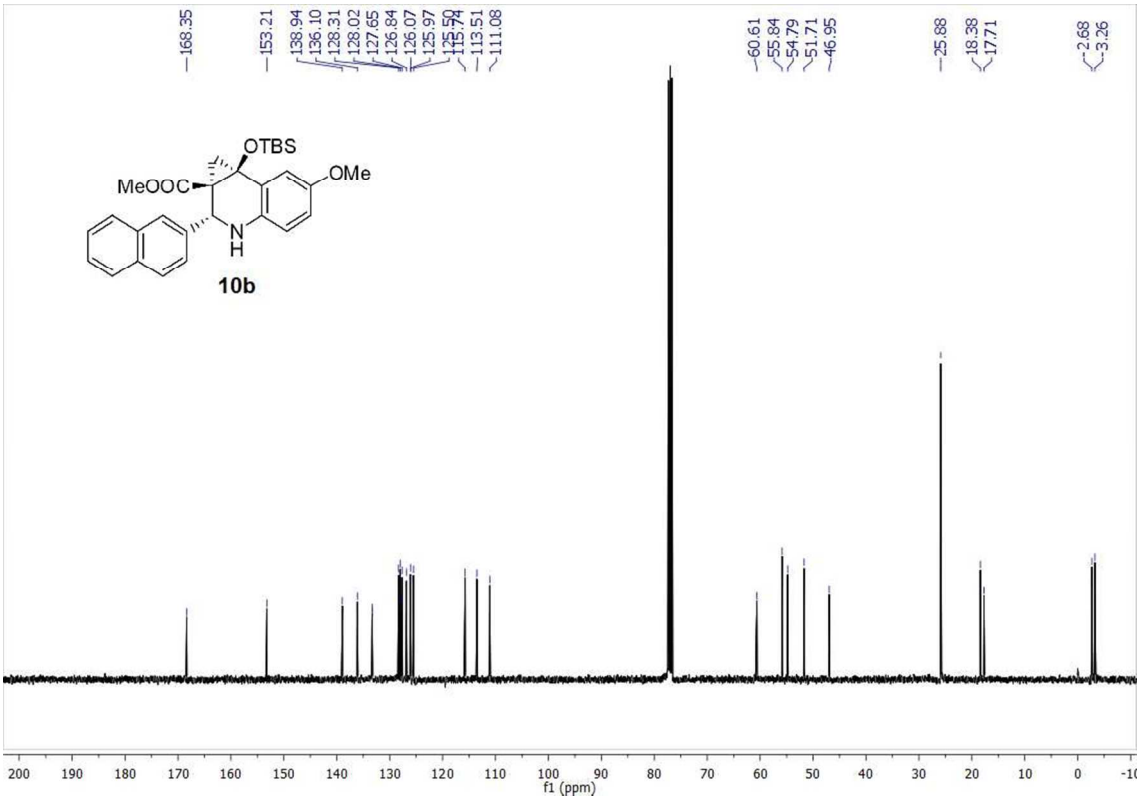
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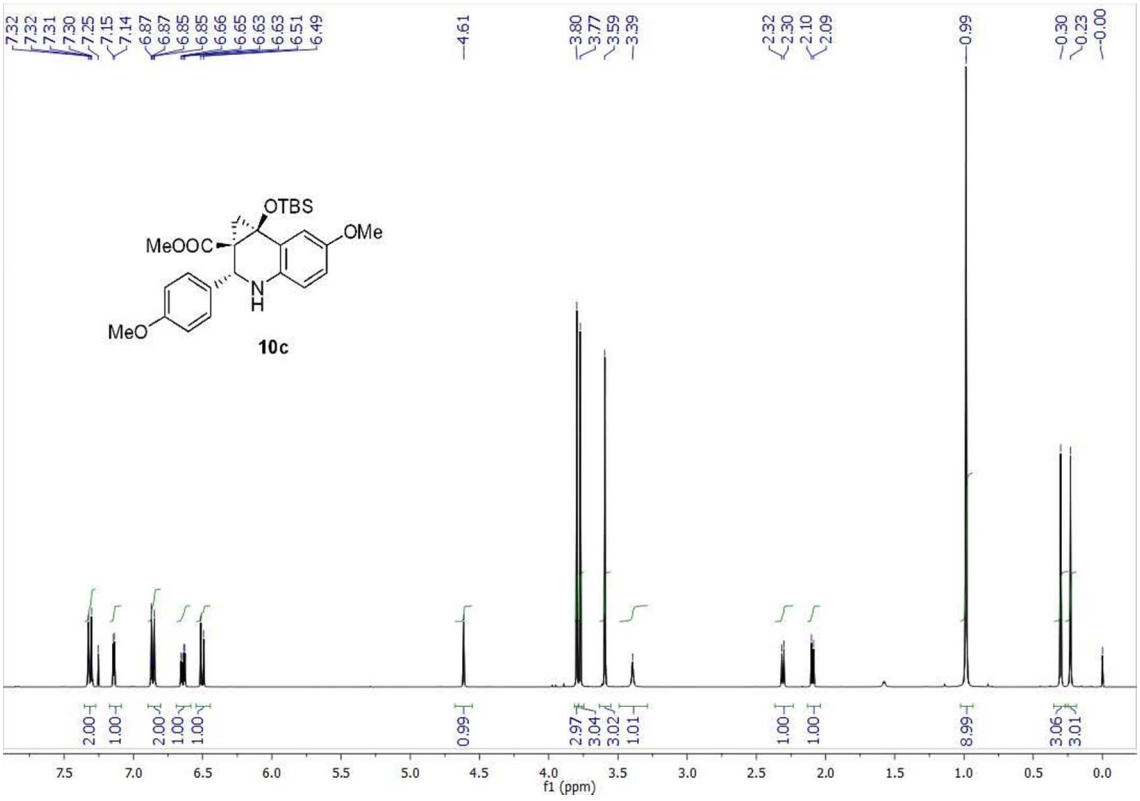
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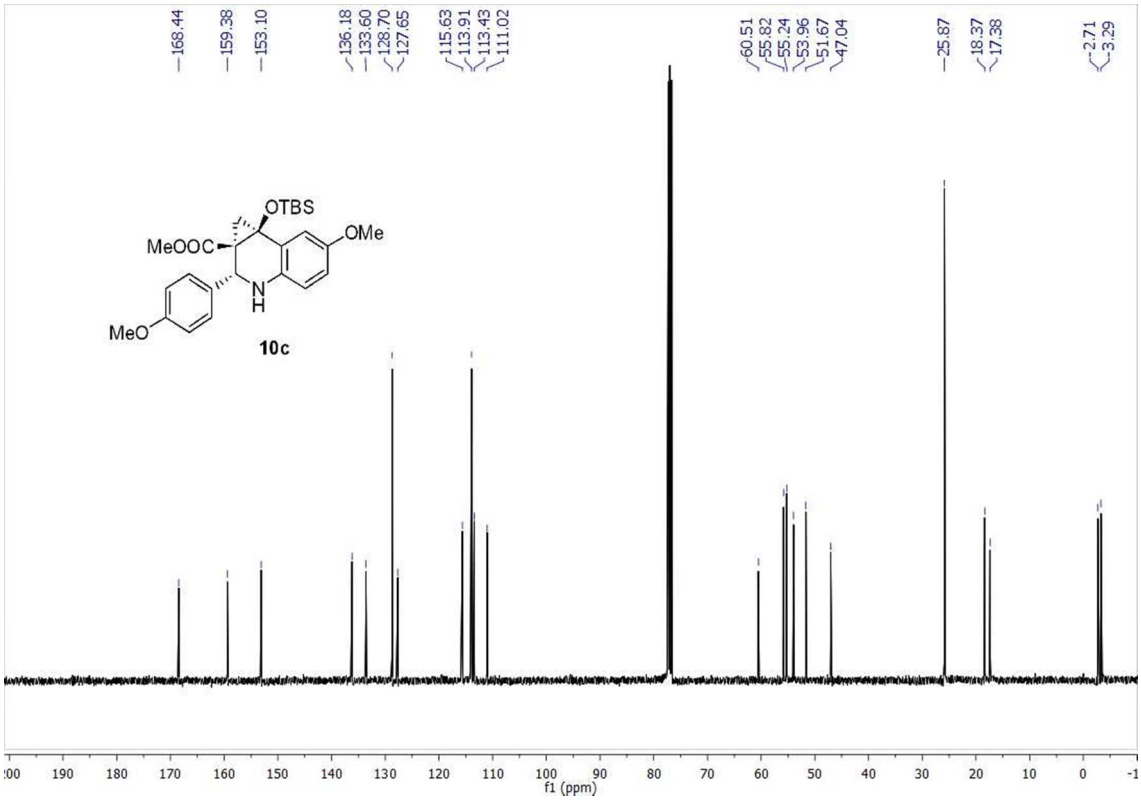
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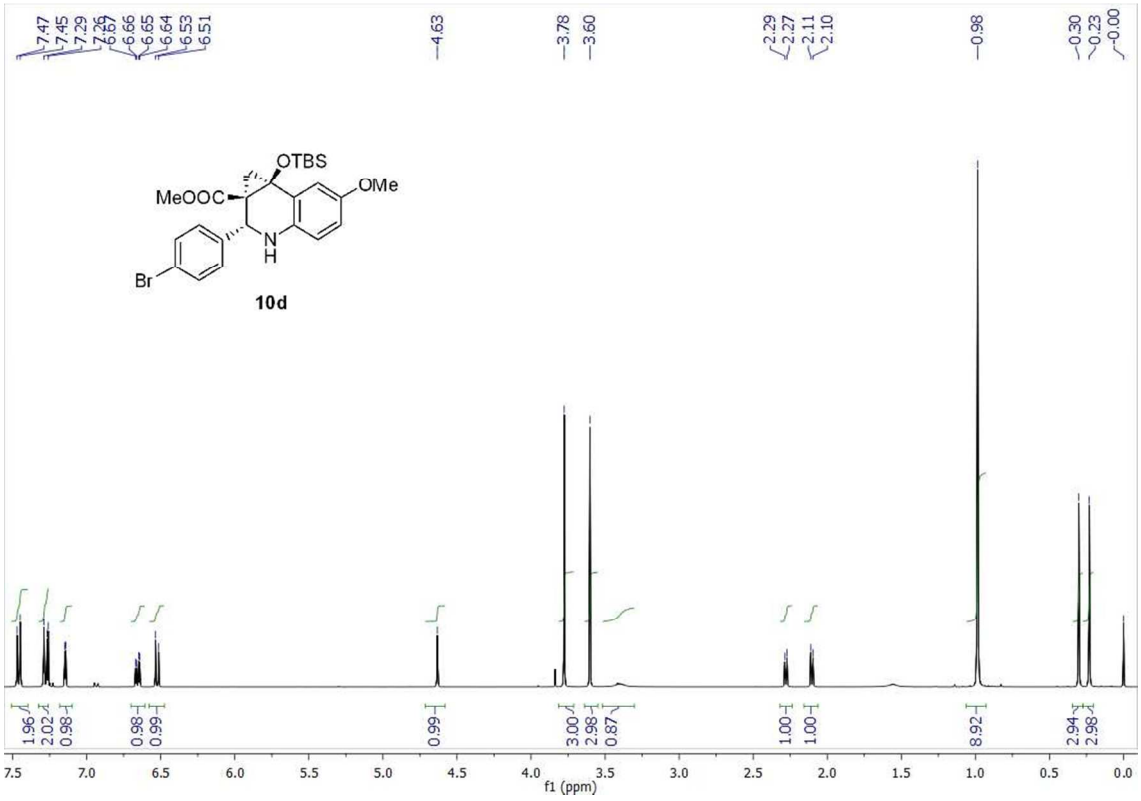
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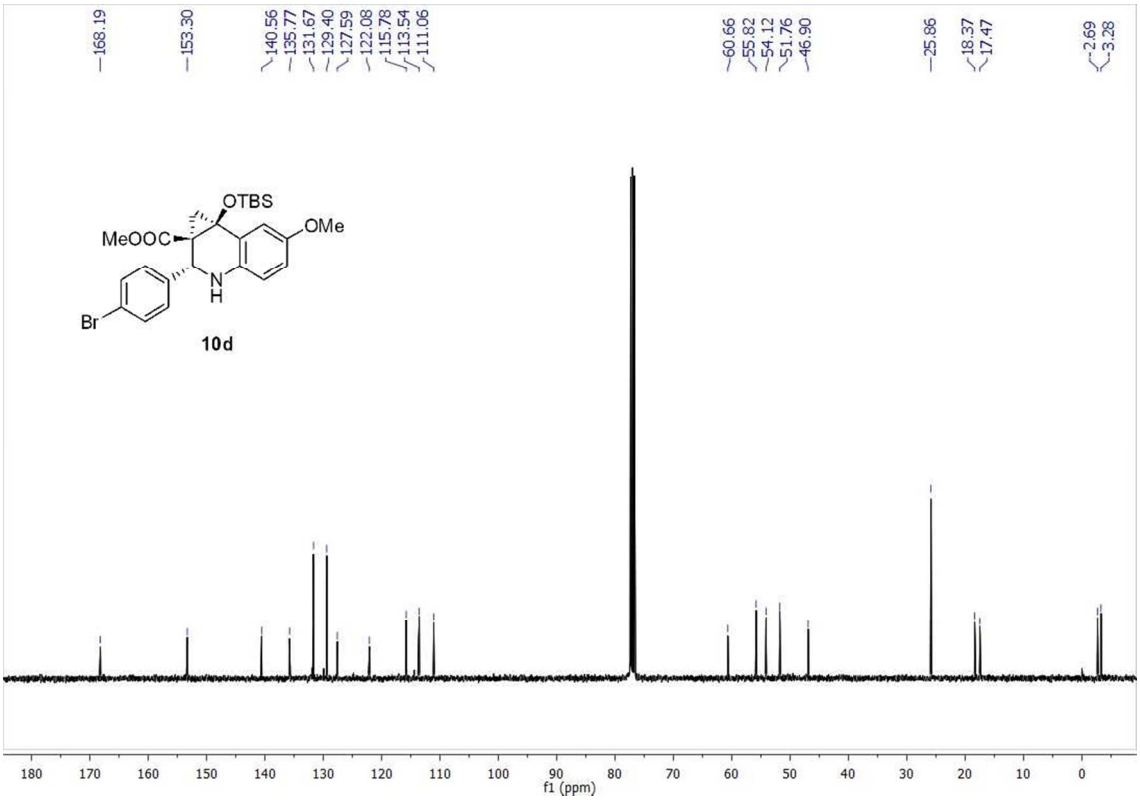
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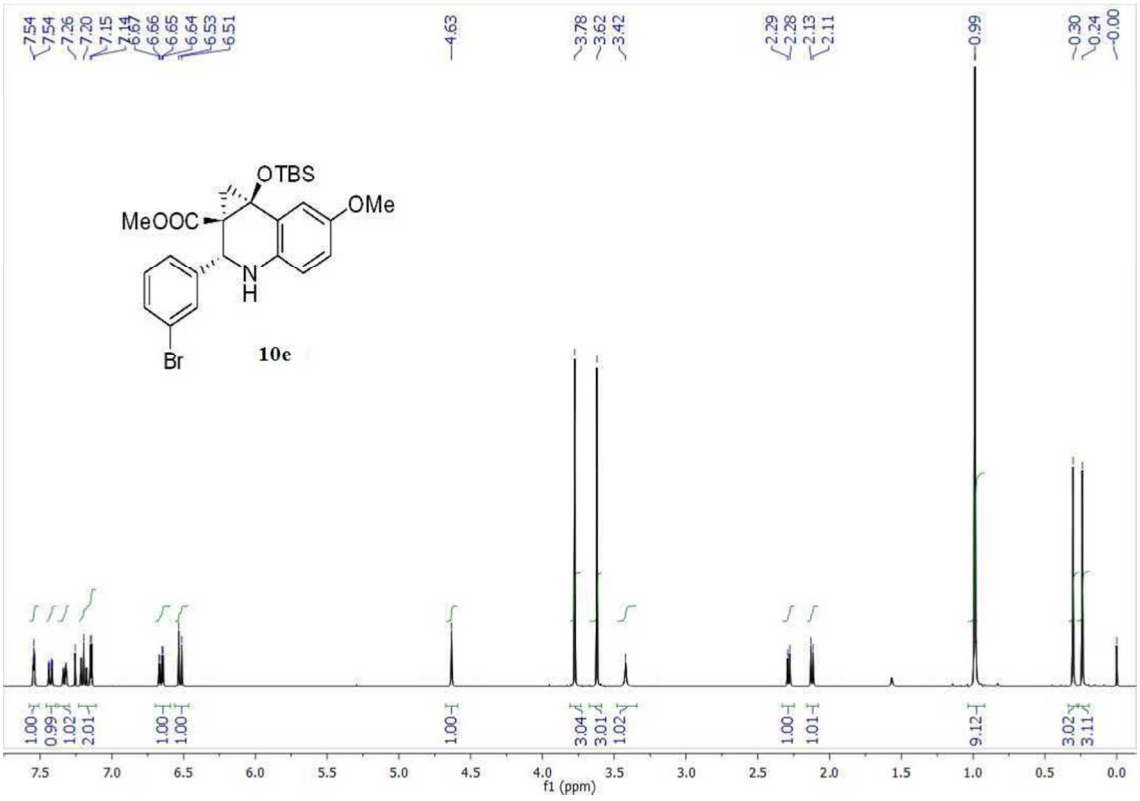
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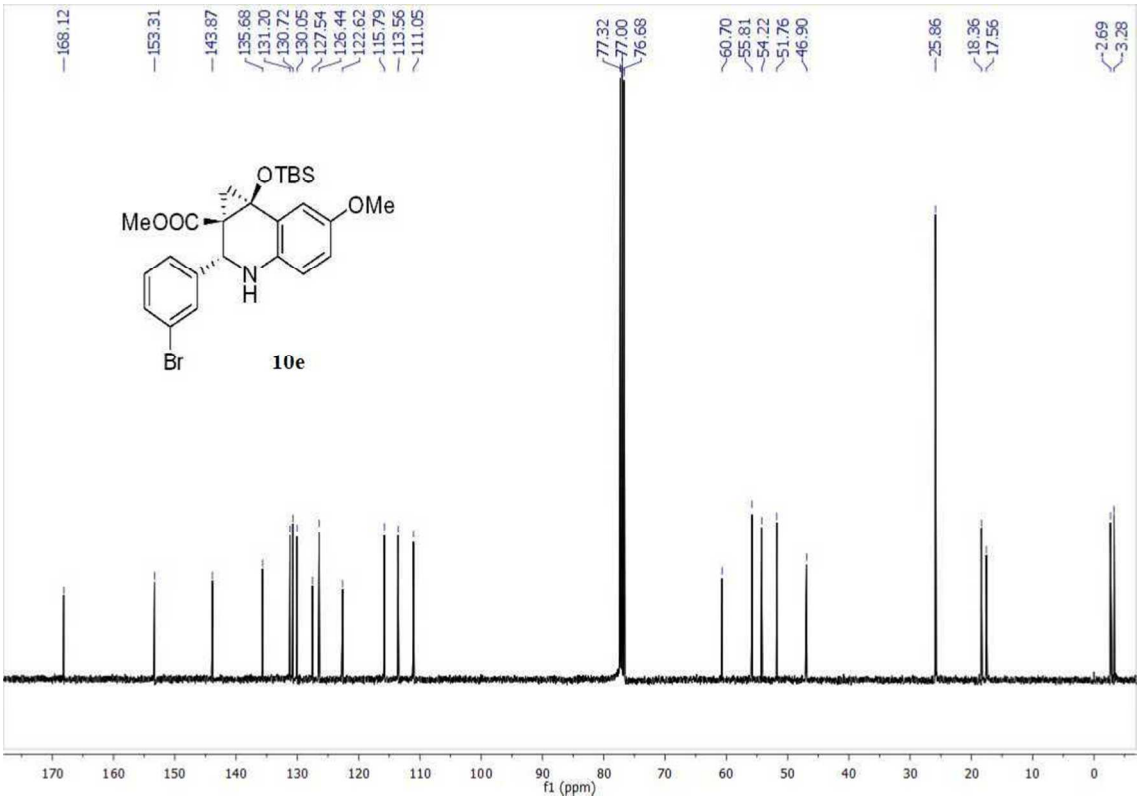
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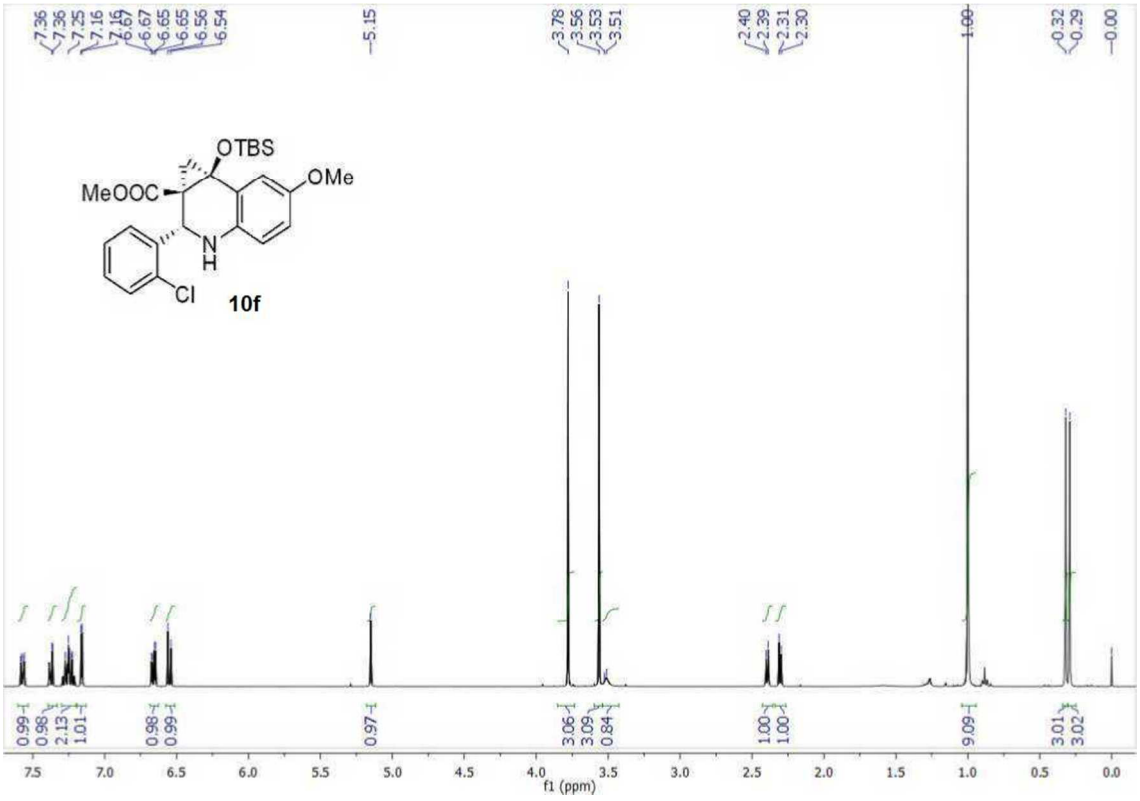
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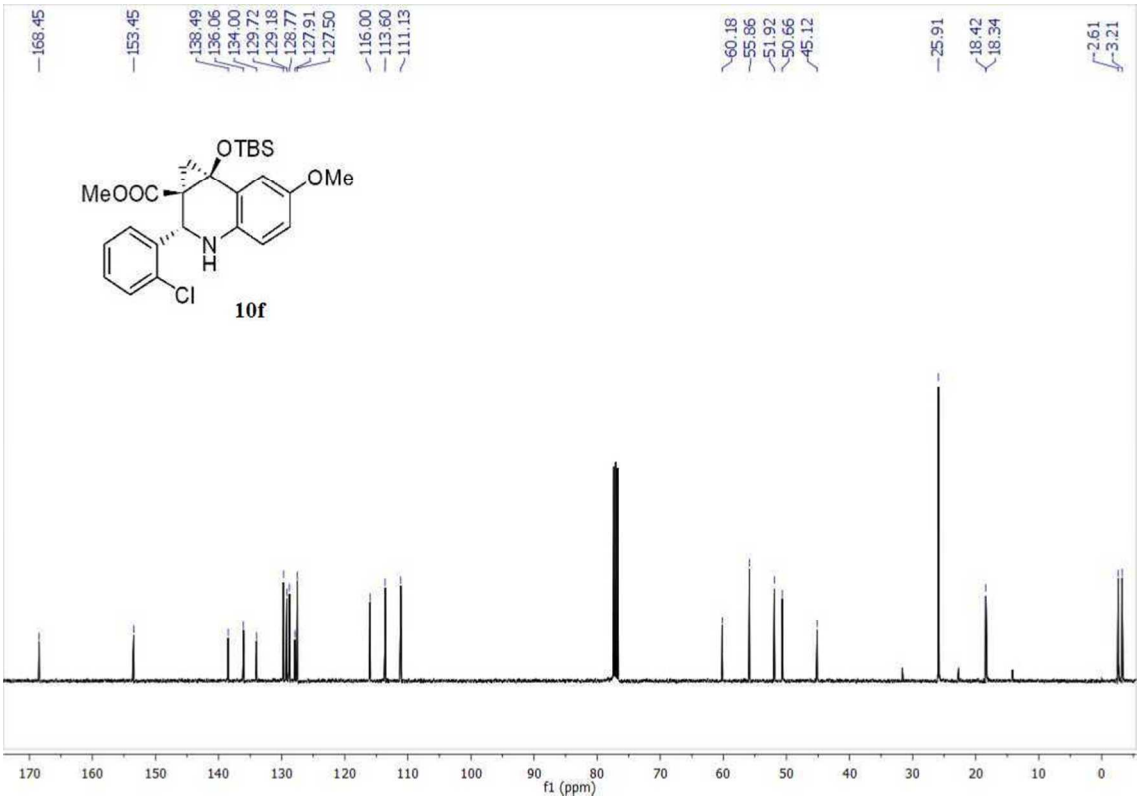
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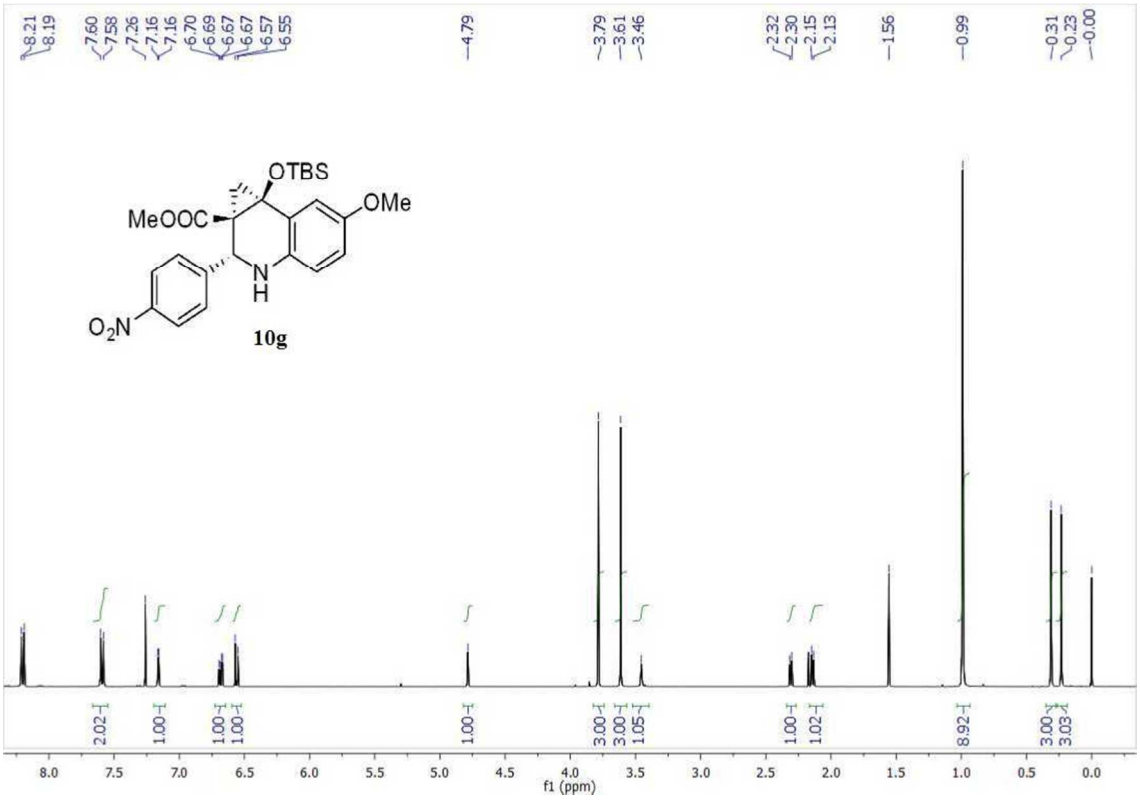
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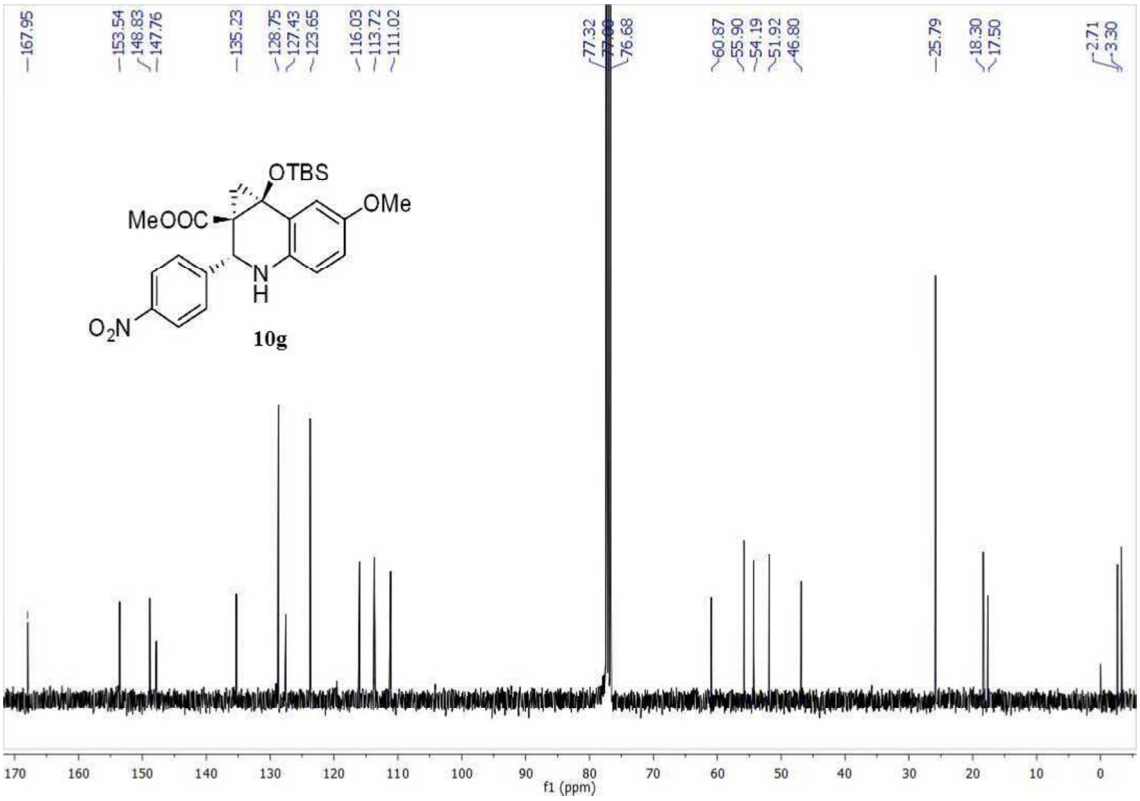
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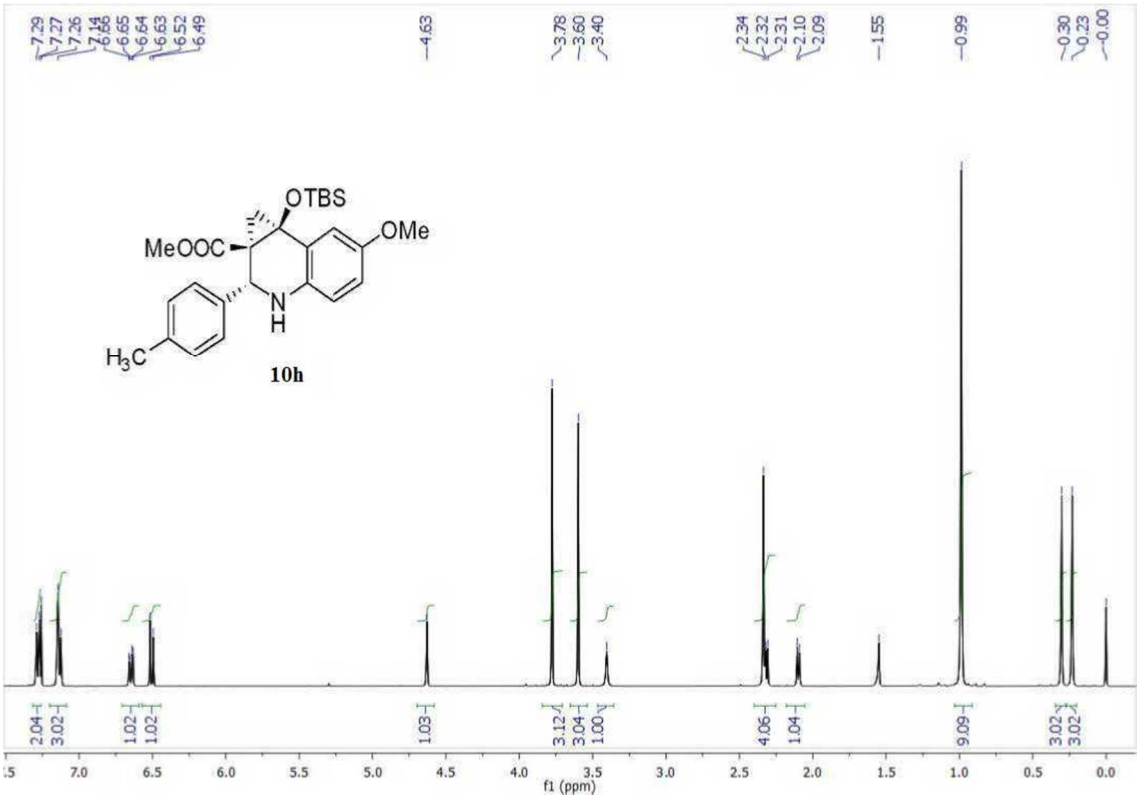
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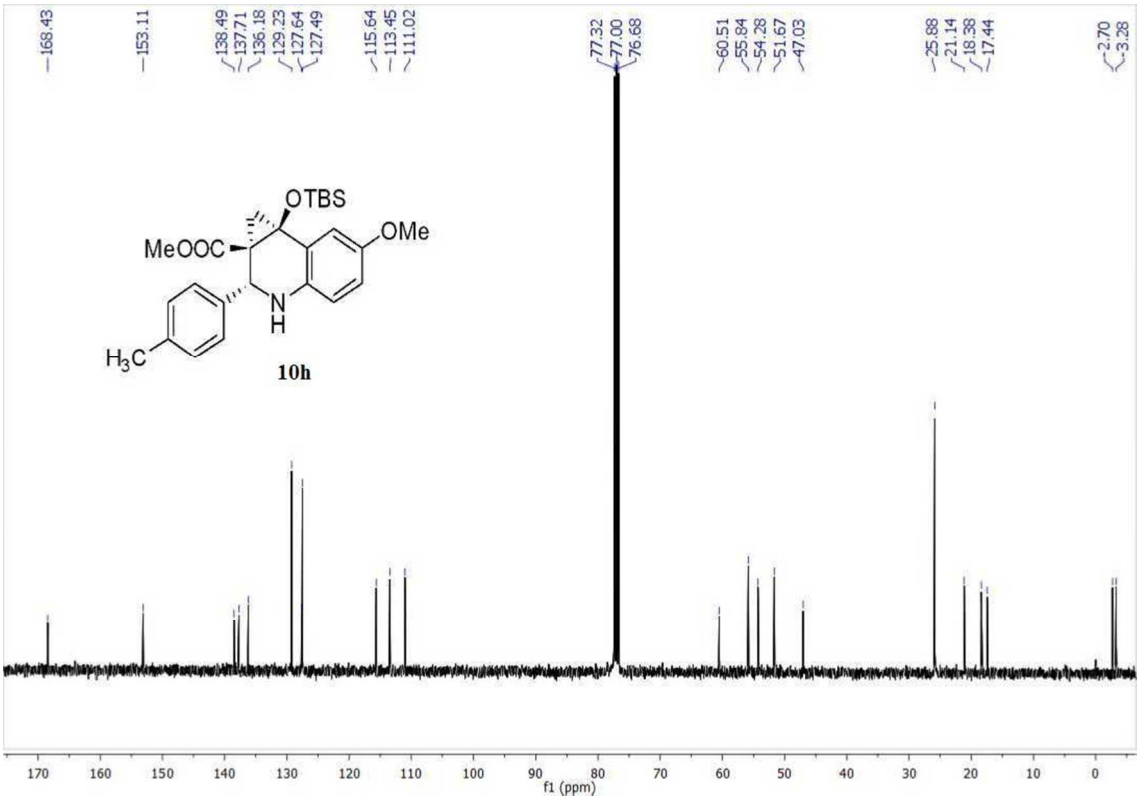
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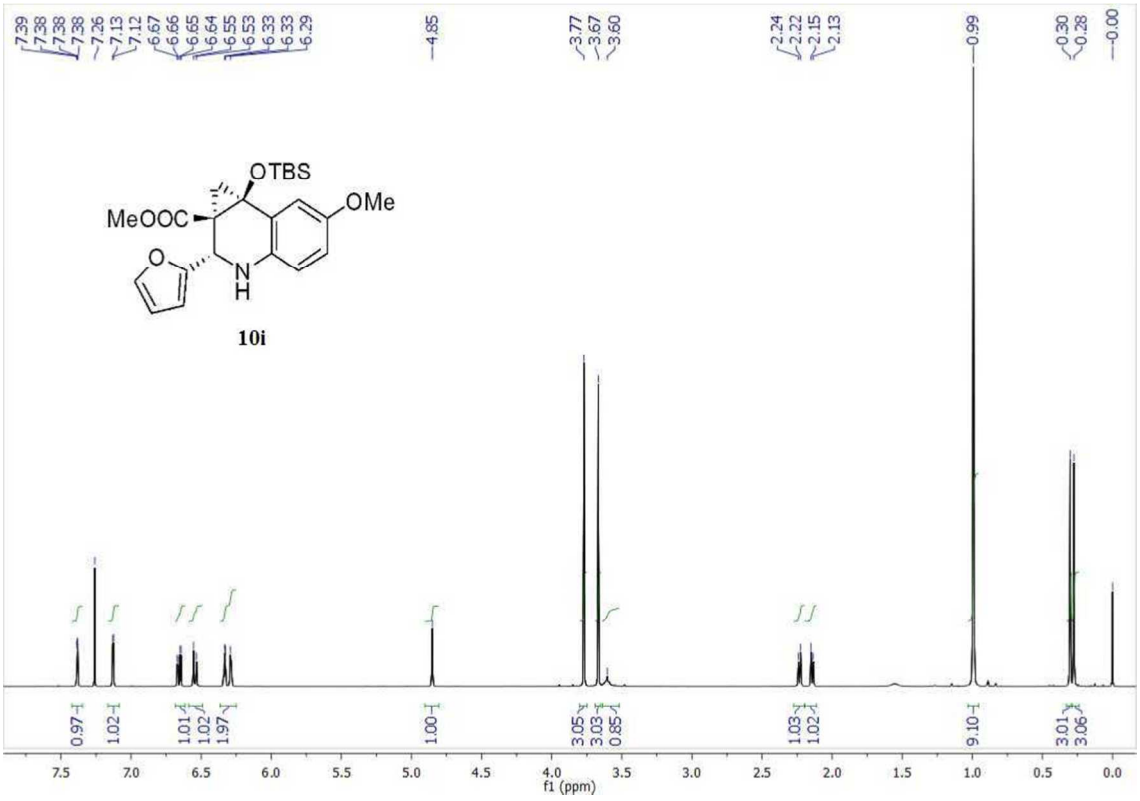
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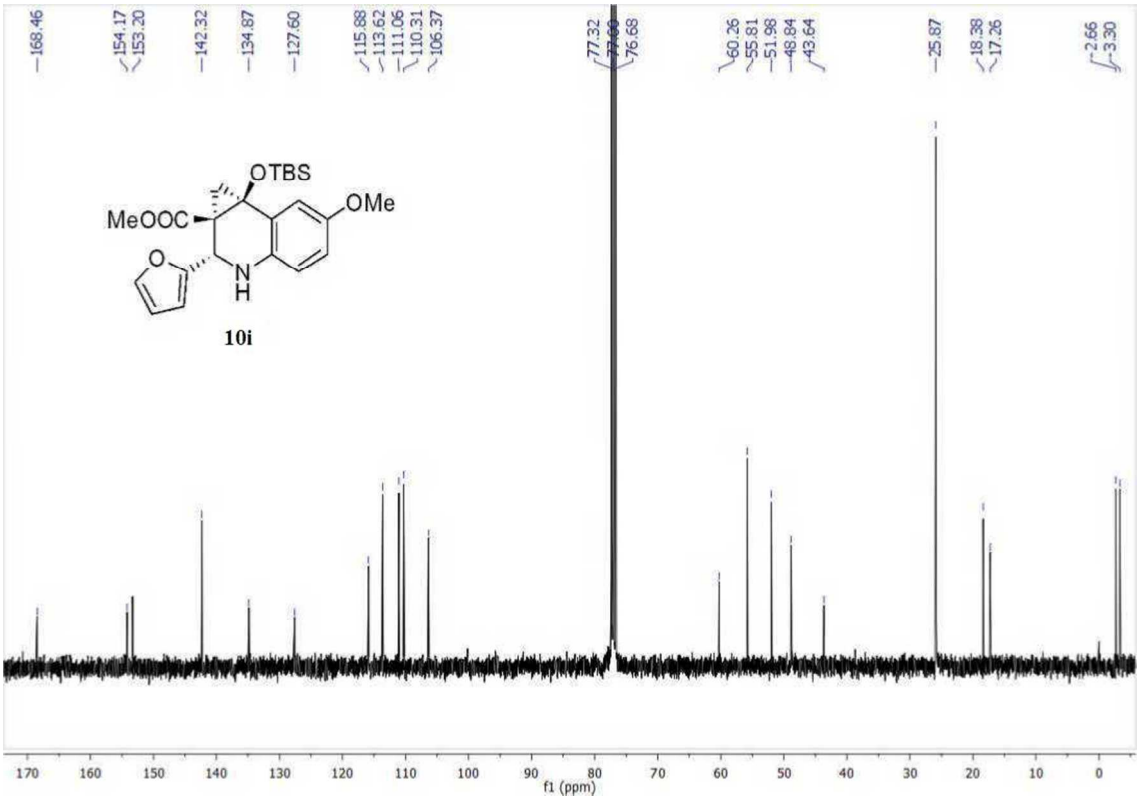
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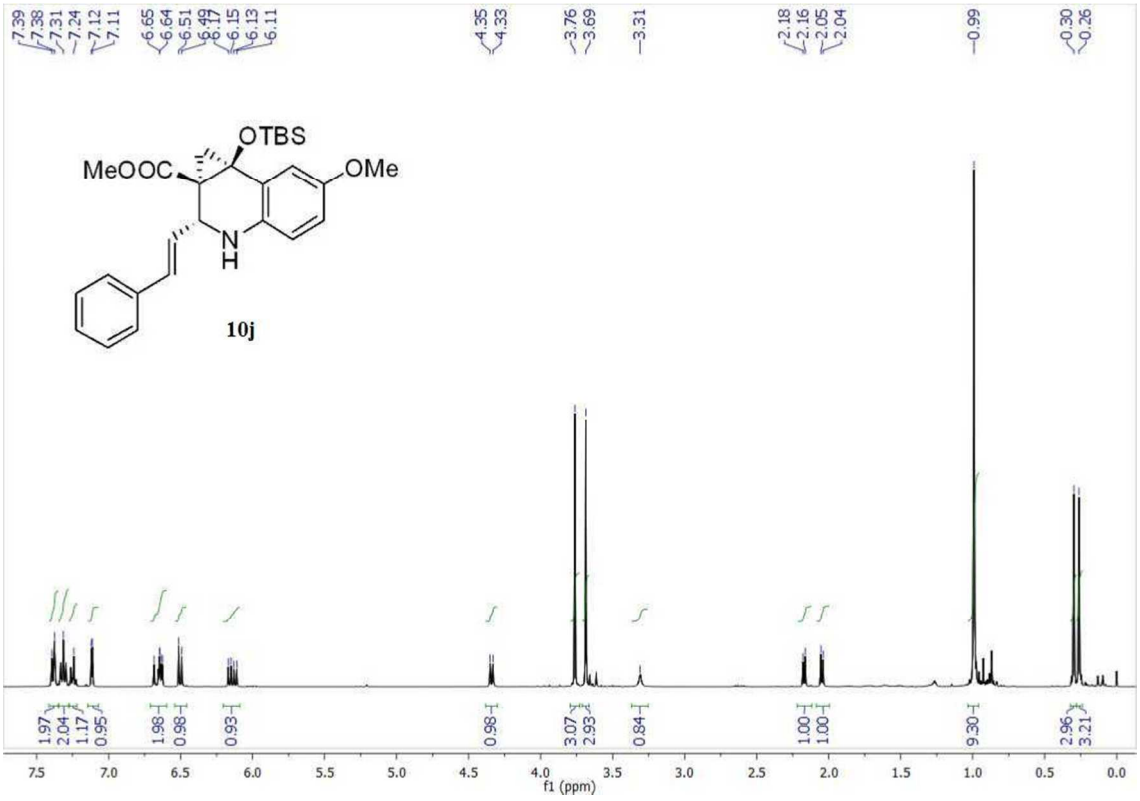
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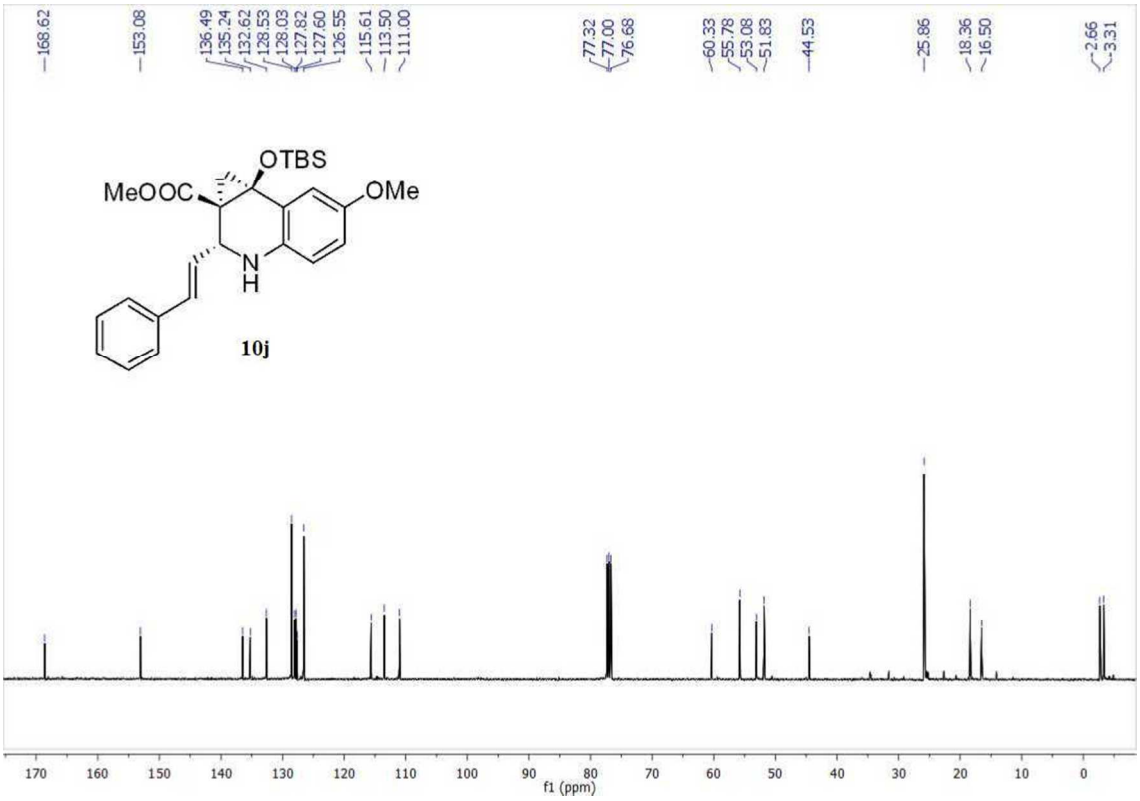
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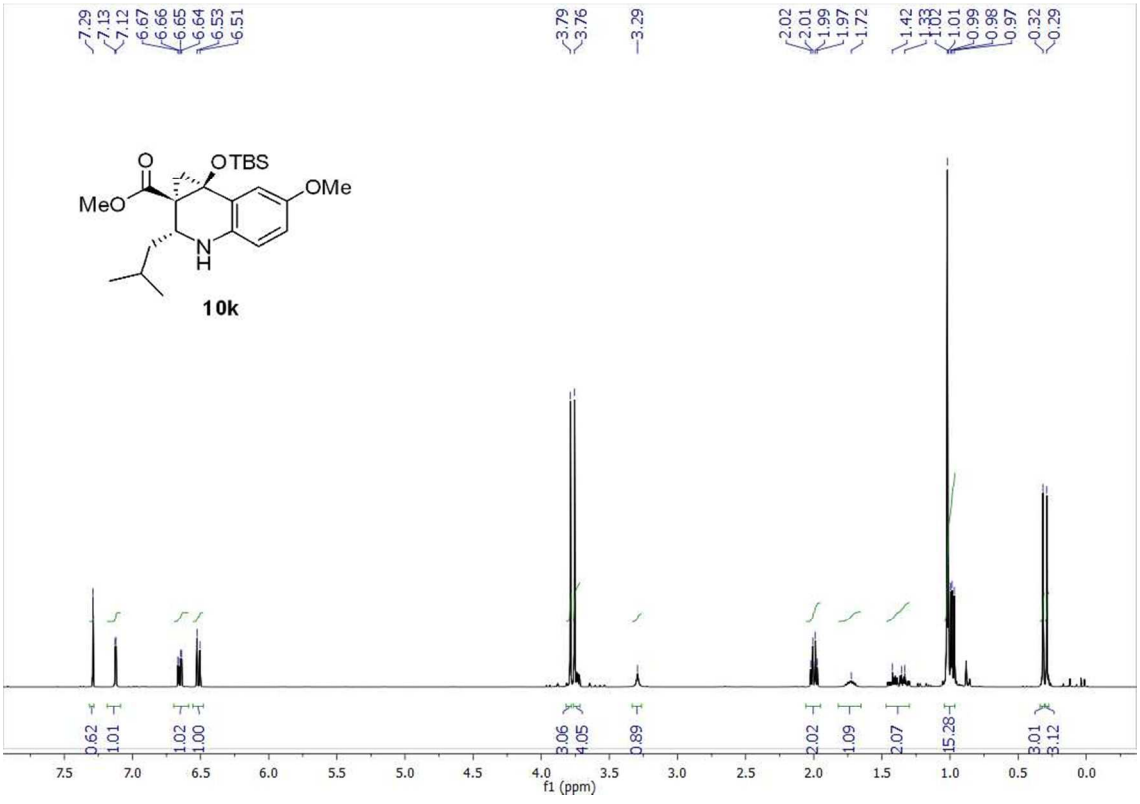
10j
f1 (ppm)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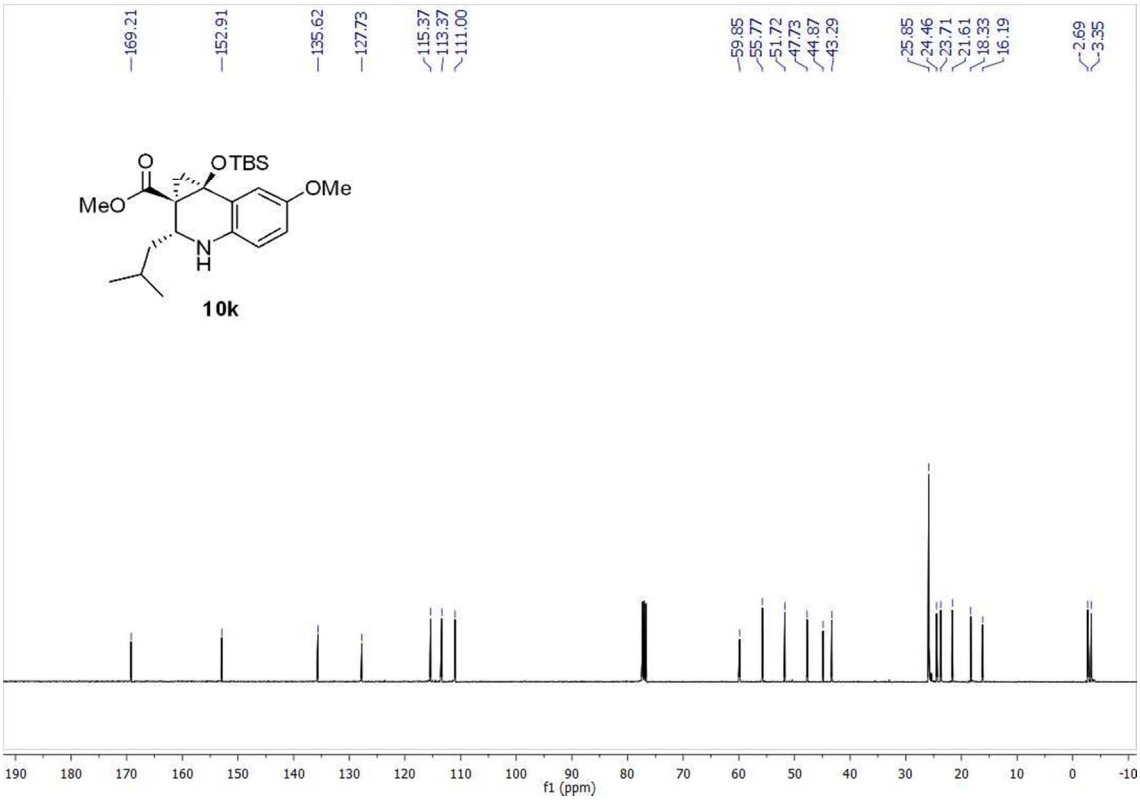
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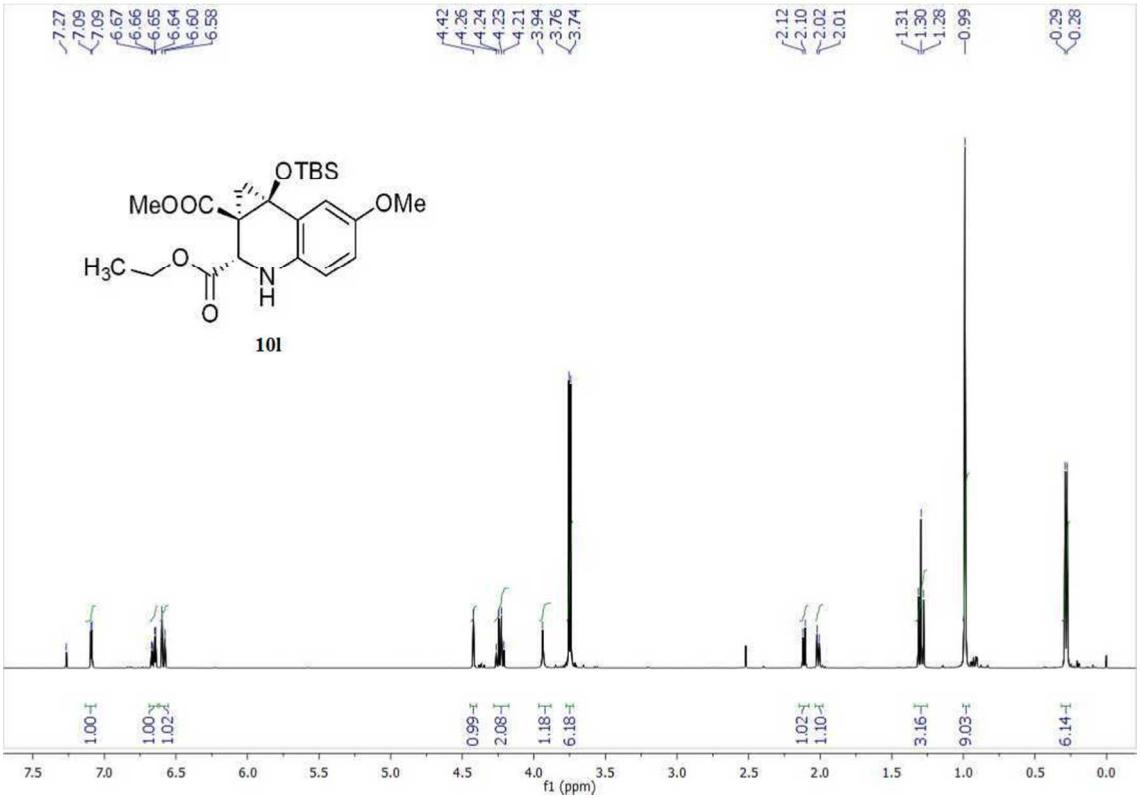
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H
O
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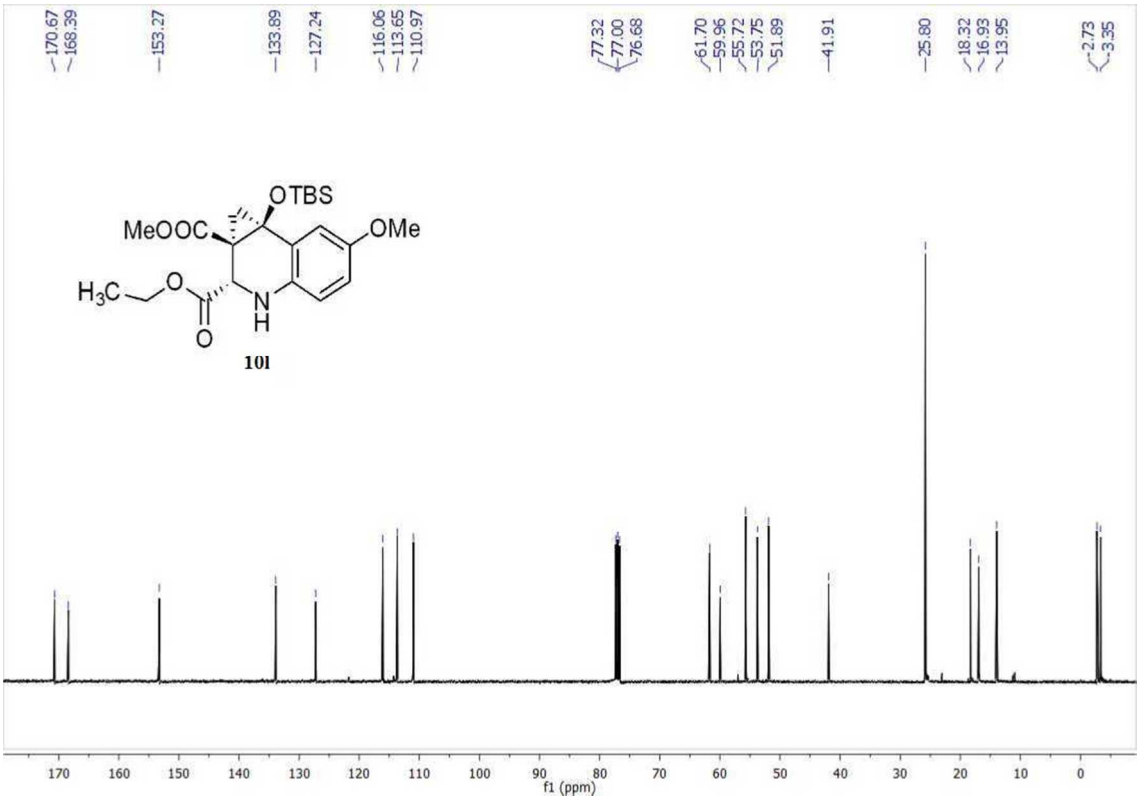
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H
O
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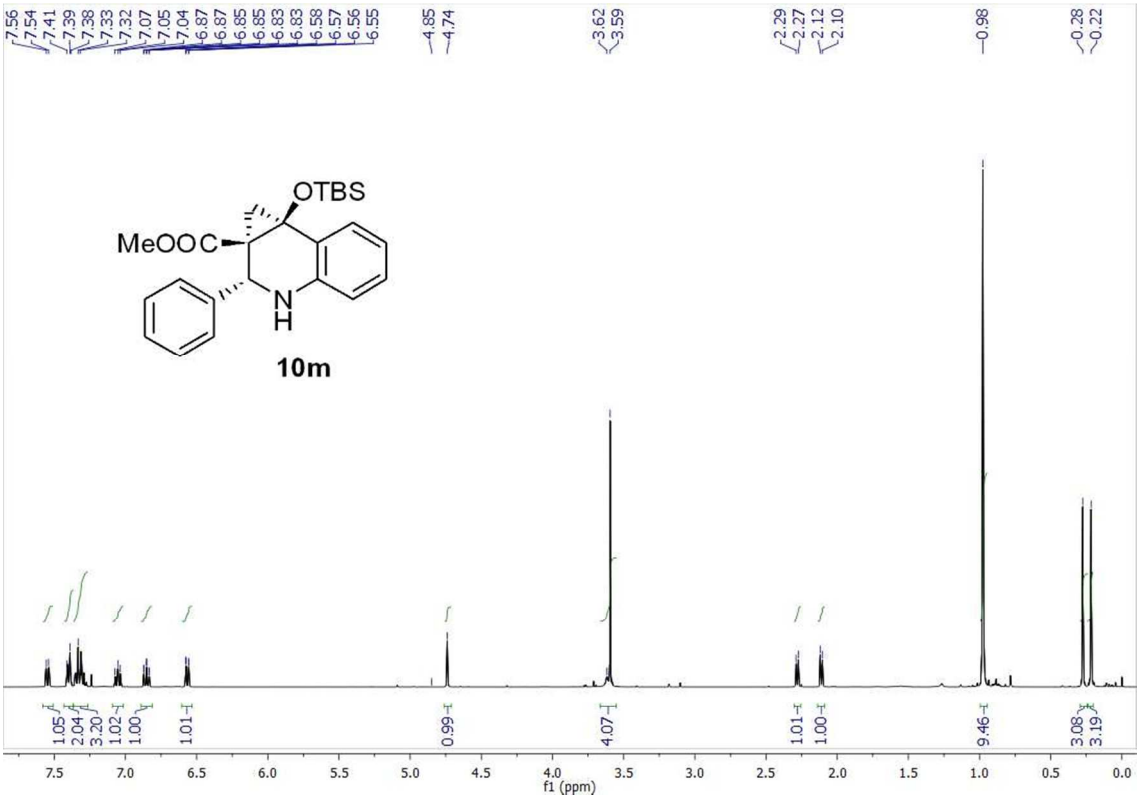
f1 (ppm)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H
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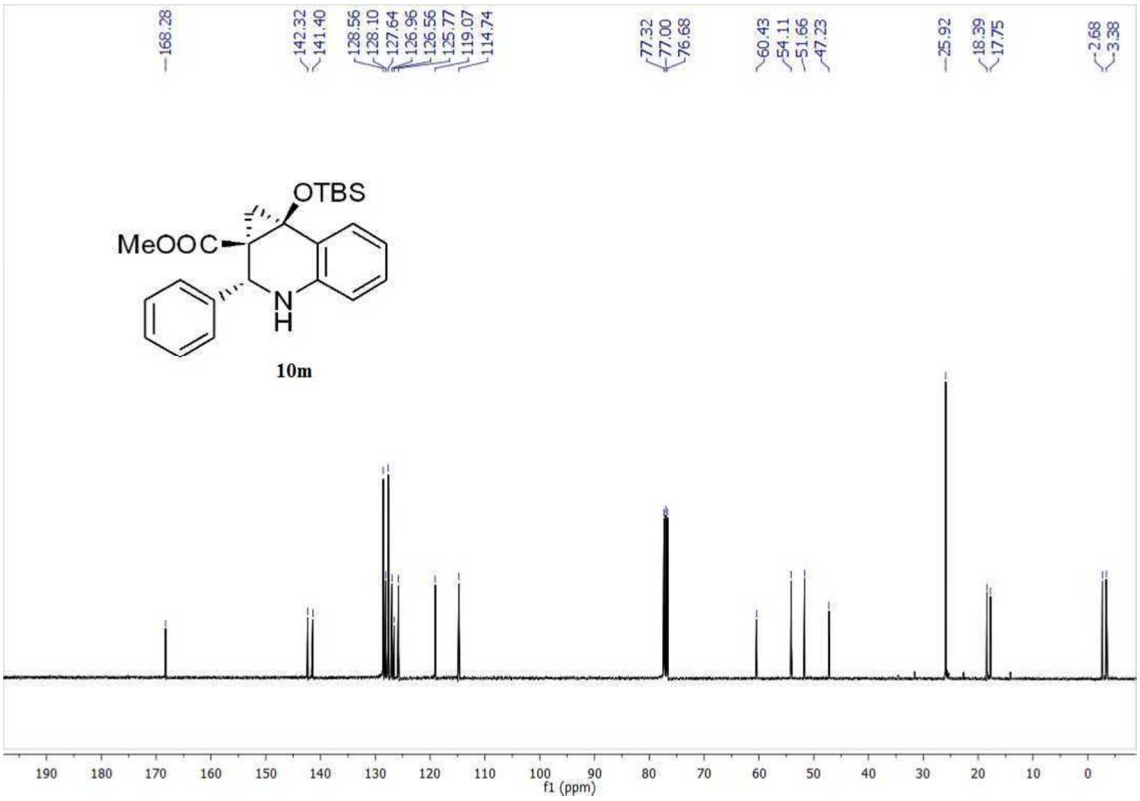
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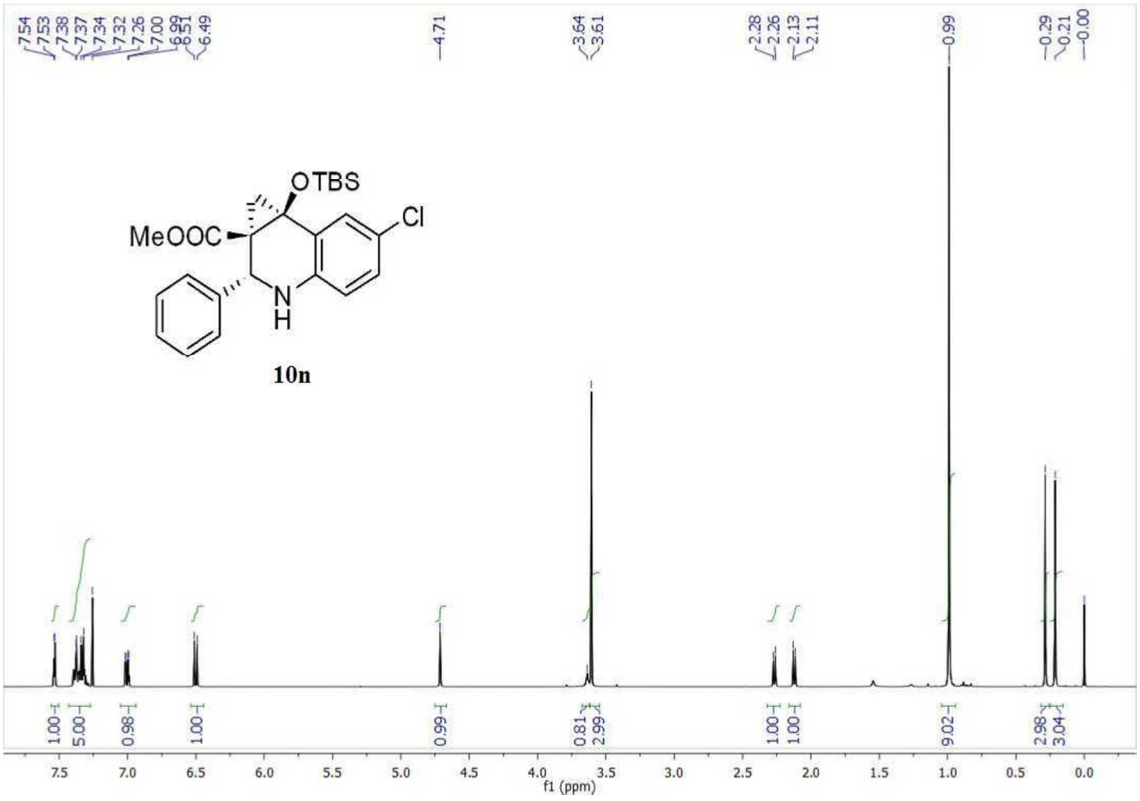
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2.13
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H
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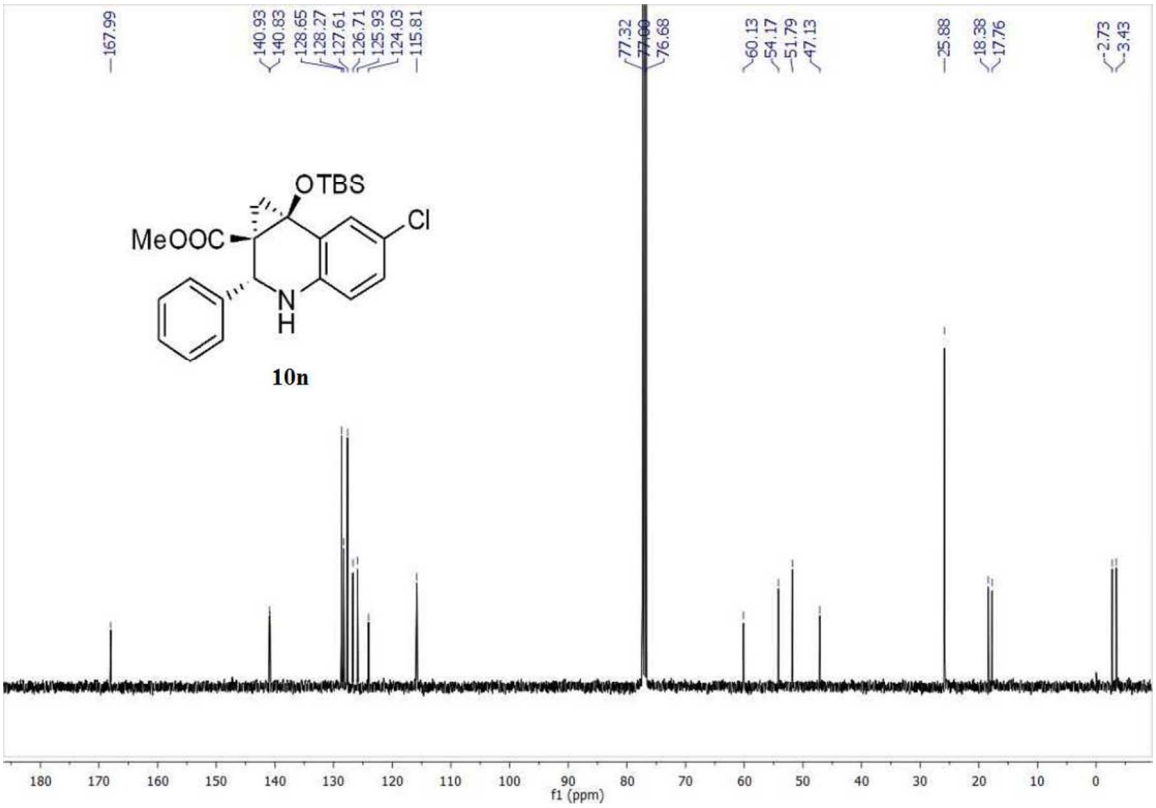
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N
H
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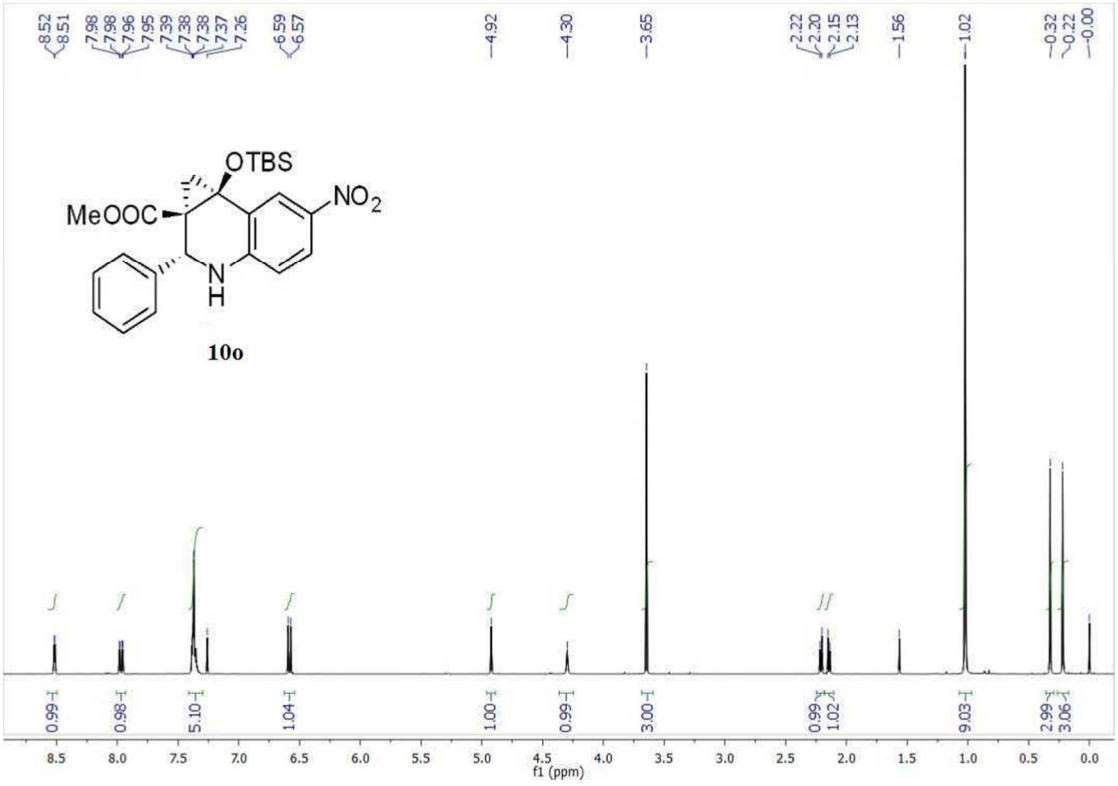
f1 (ppm)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4.30
3.65
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2.20
2.15
2.13
1.56
1.02
0.32
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0.00
OTBS
MeOOC
NO2
N
H
10o
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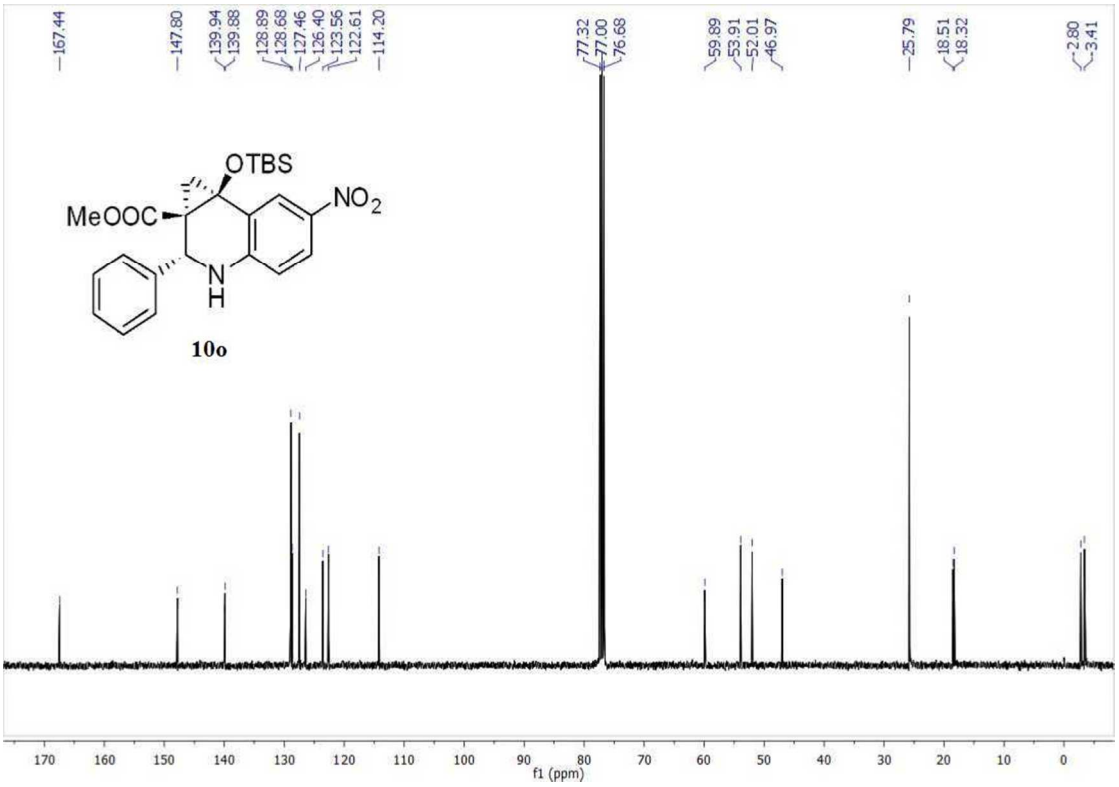
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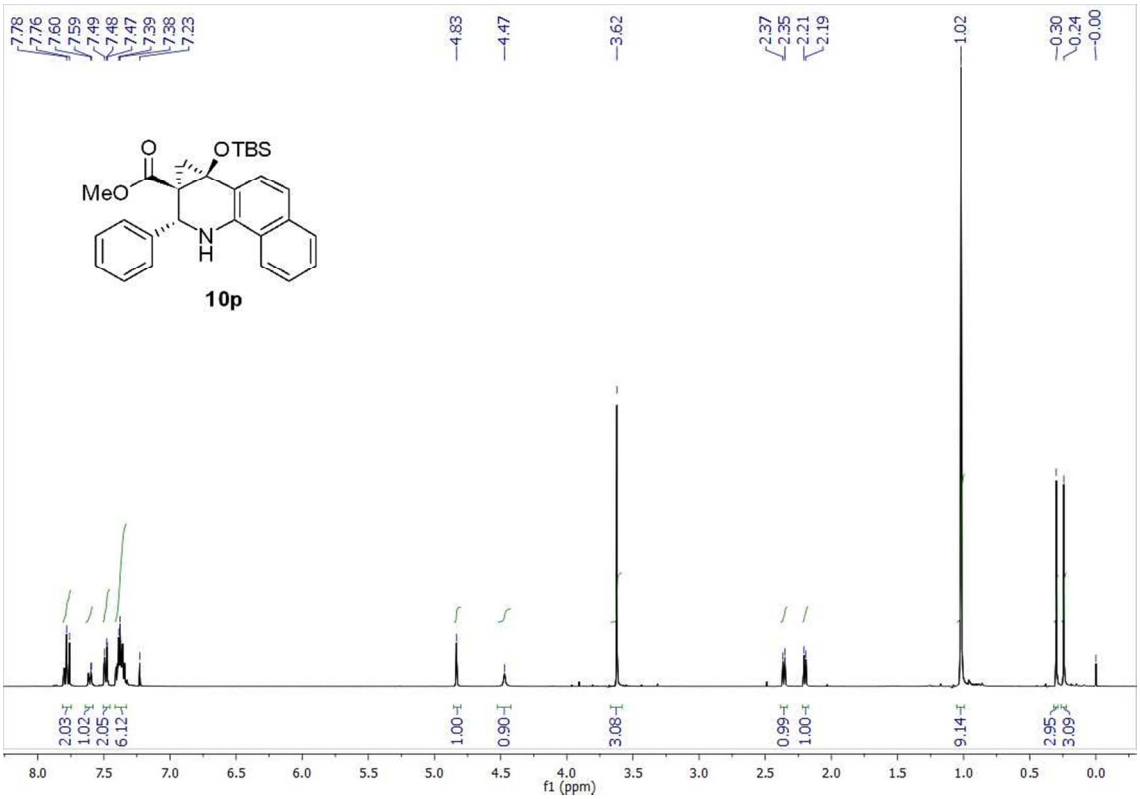
f1 (ppm)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0.30
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O
OTBS
MeO
N
H
10p
2.03
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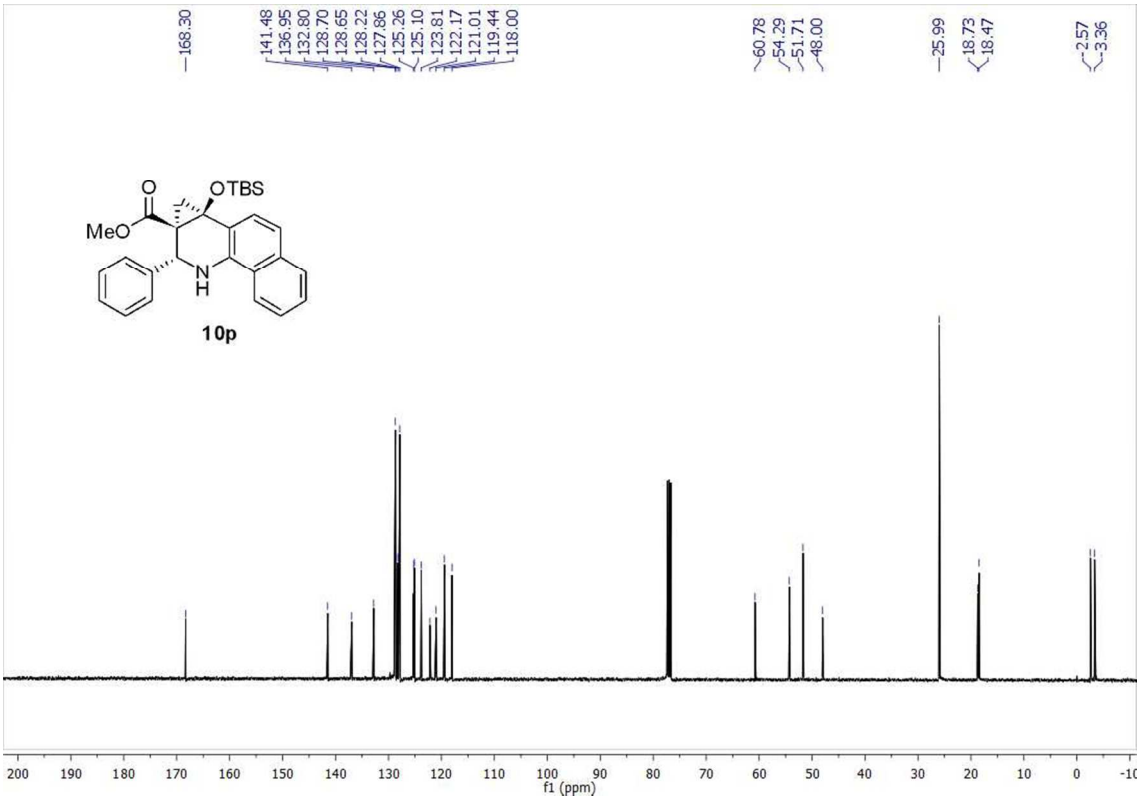
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54.29
51.71
48.00
25.99
18.73
18.47
2.57
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MeO
N
H
10p
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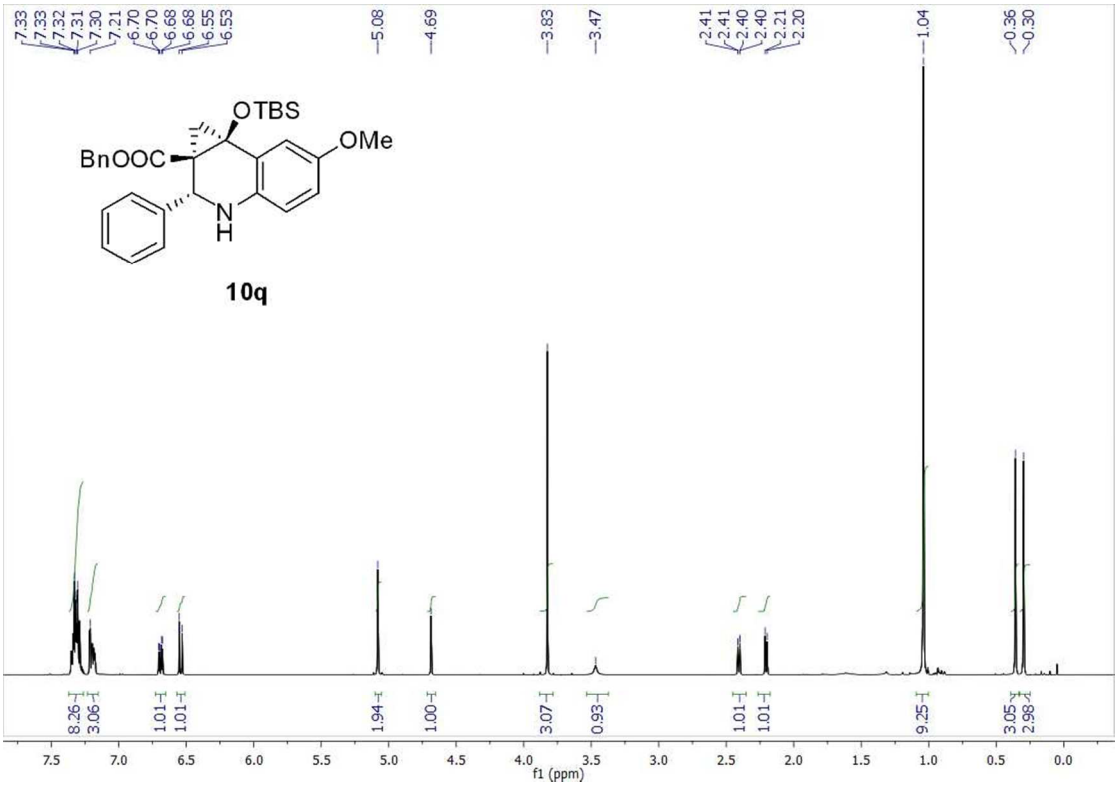
f1 (ppm)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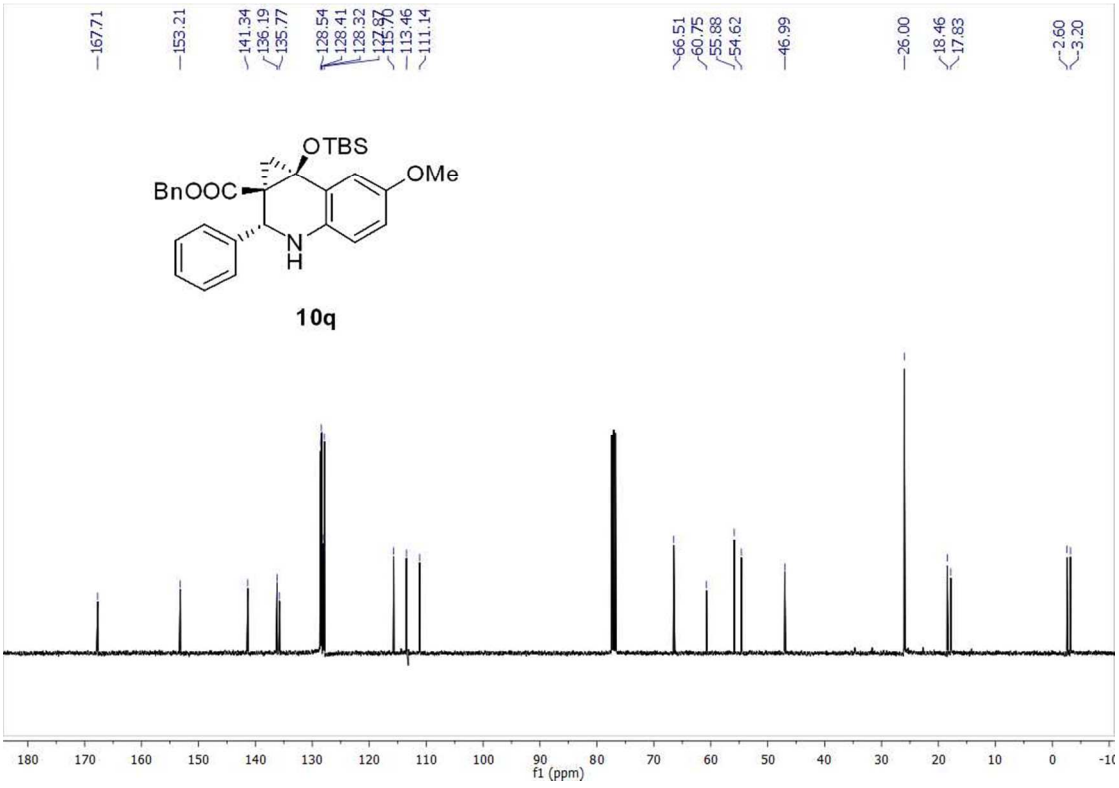
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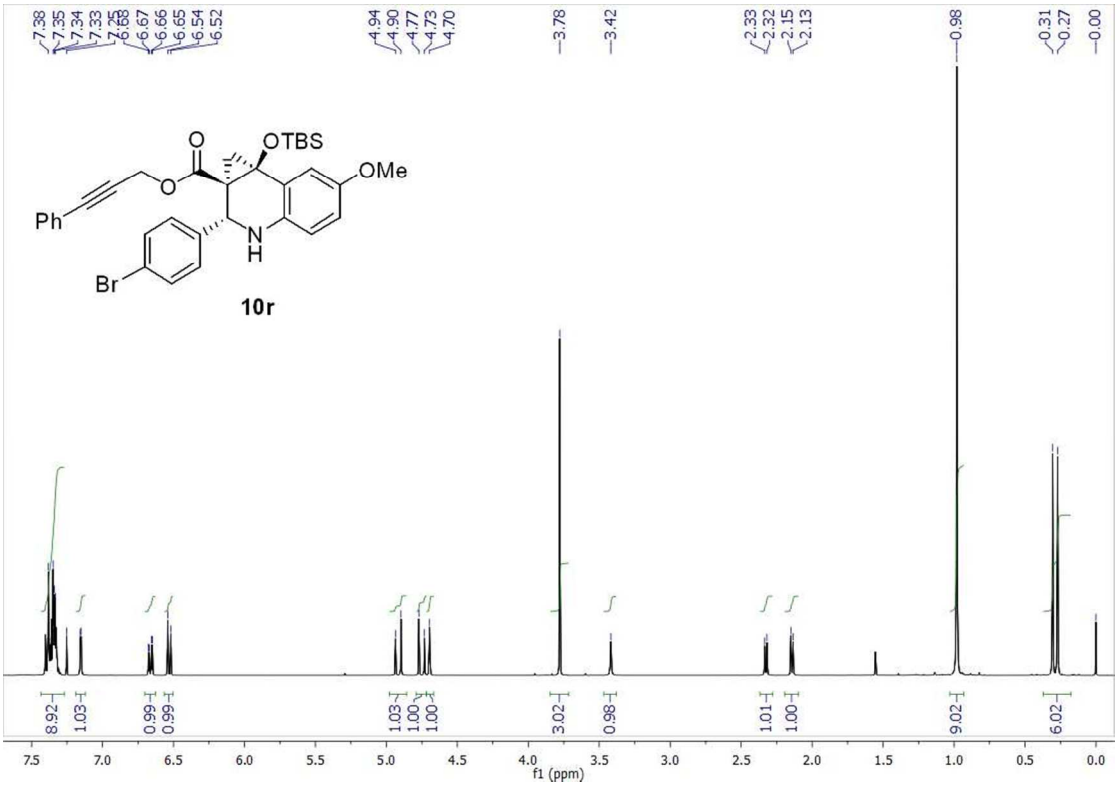
f1 (ppm)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3.78
3.42
2.33
2.32
2.15
2.13
0.98
0.31
0.27
0.00
OTBS
OMe
Ph
Br
N
H
O
10r
8.92
1.03
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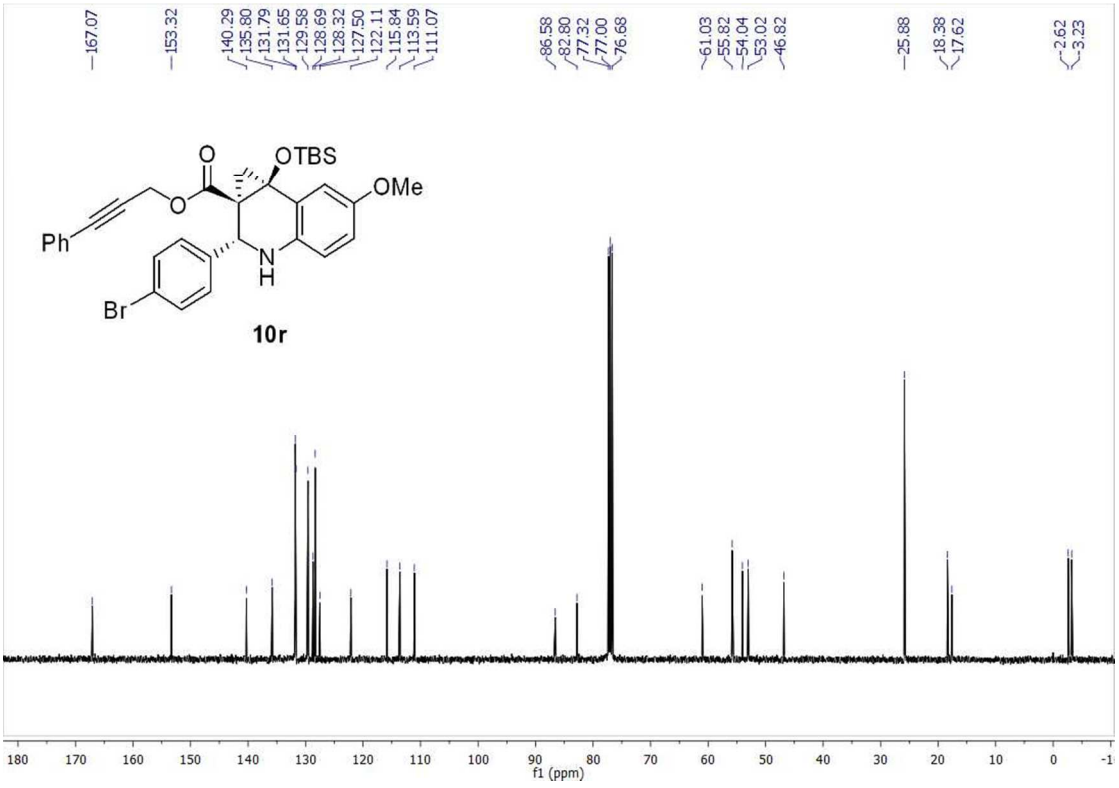
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Ph
Br
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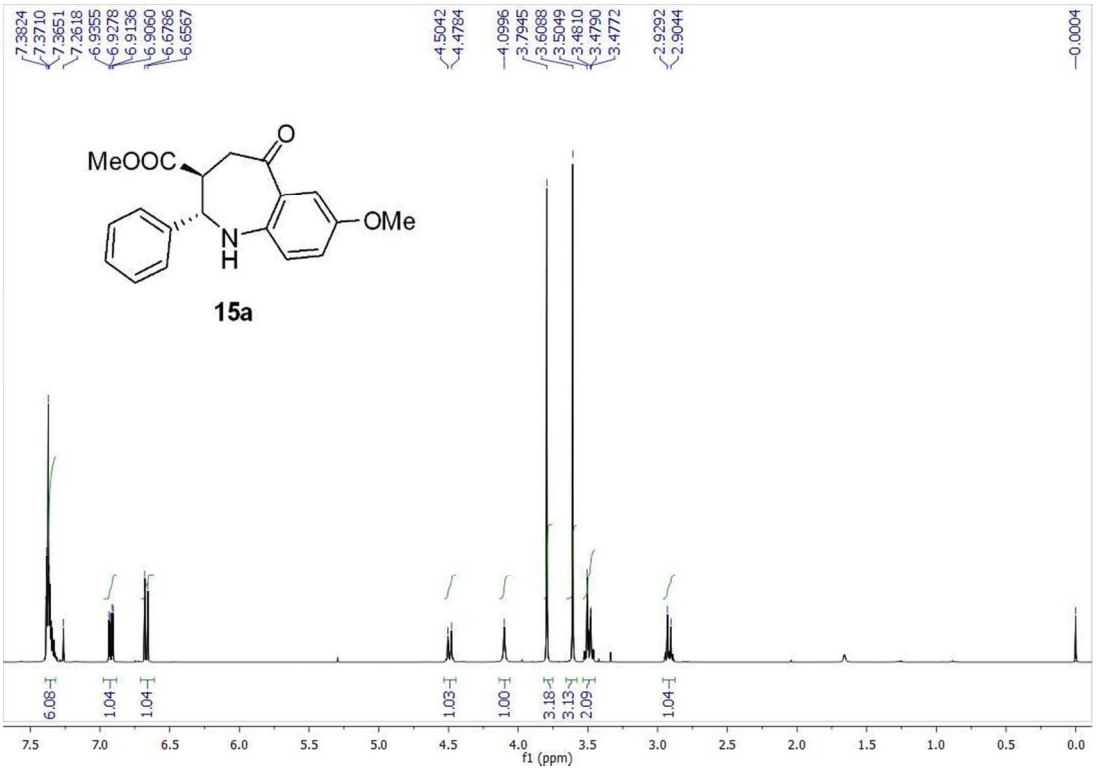
10r
f1 (ppm)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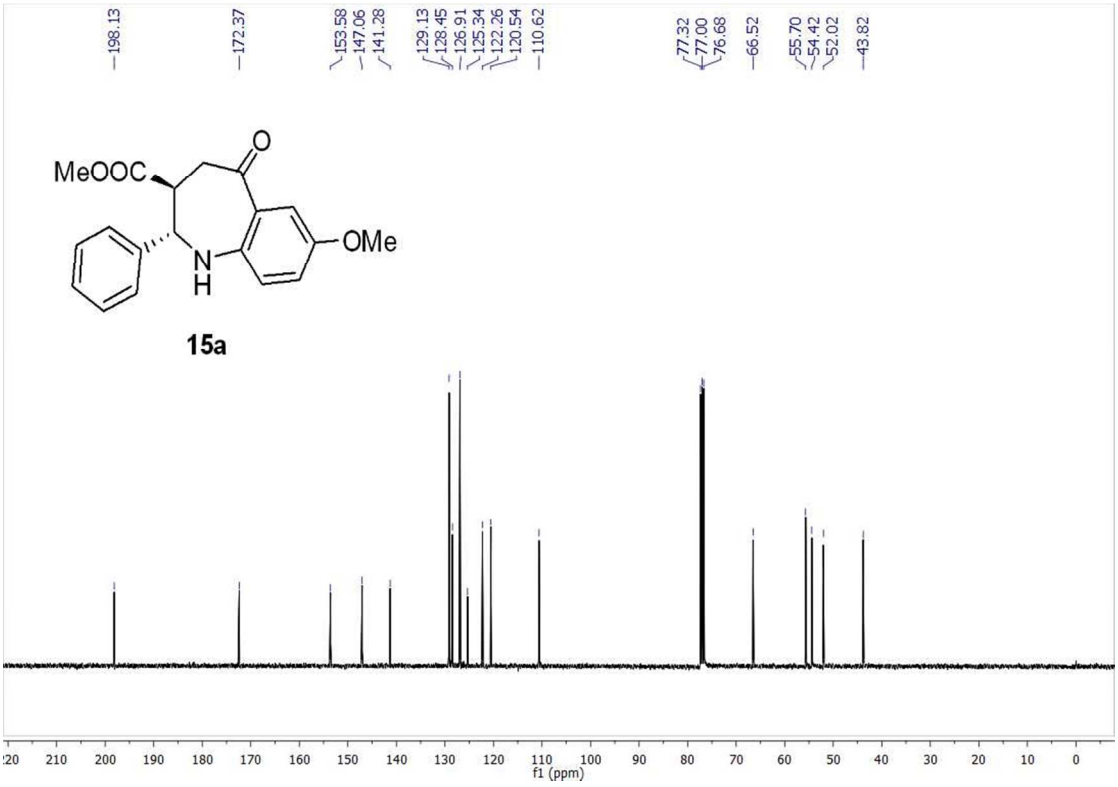
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O
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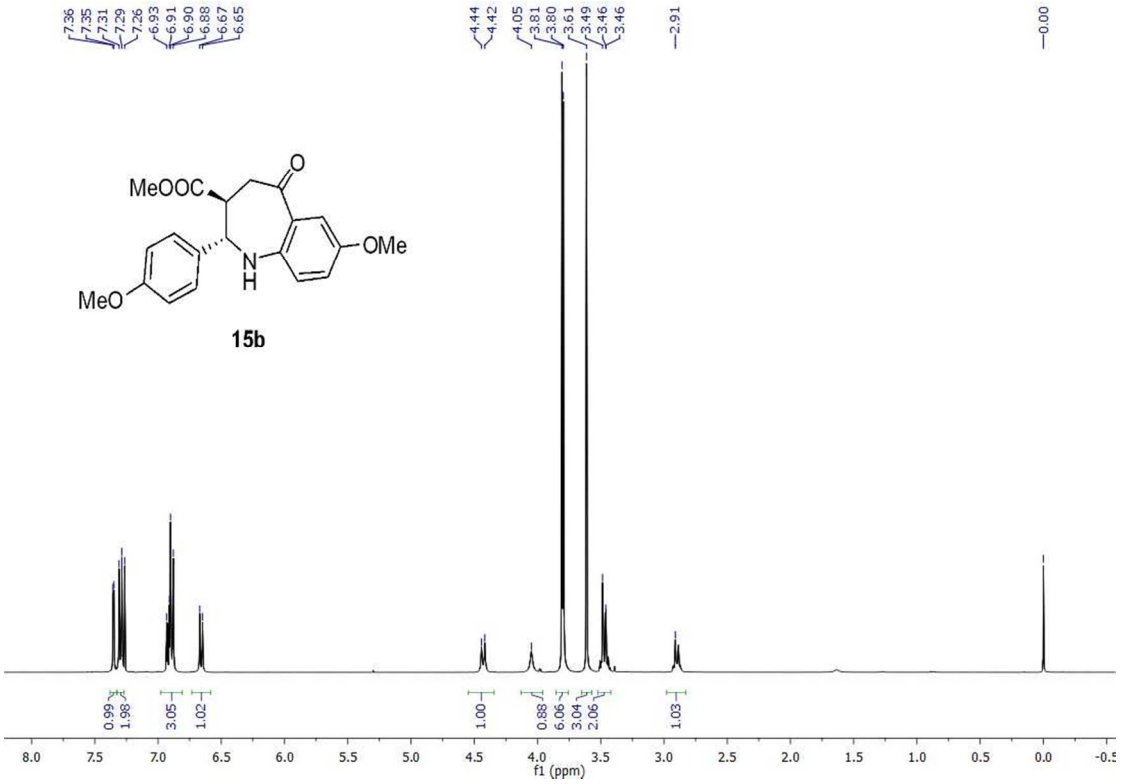
15a
f1 (ppm)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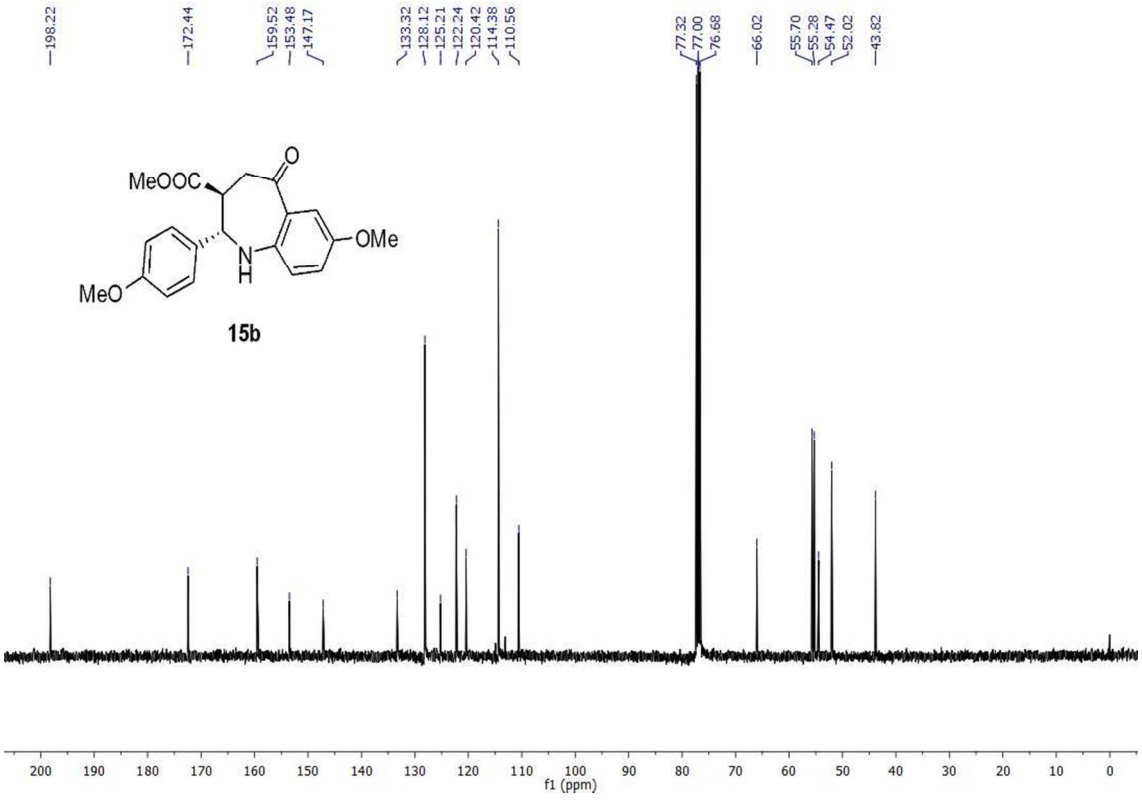
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66.02
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52.02
43.82
MeOOC
O
OMe
N
H
MeO
15b
200
190
180
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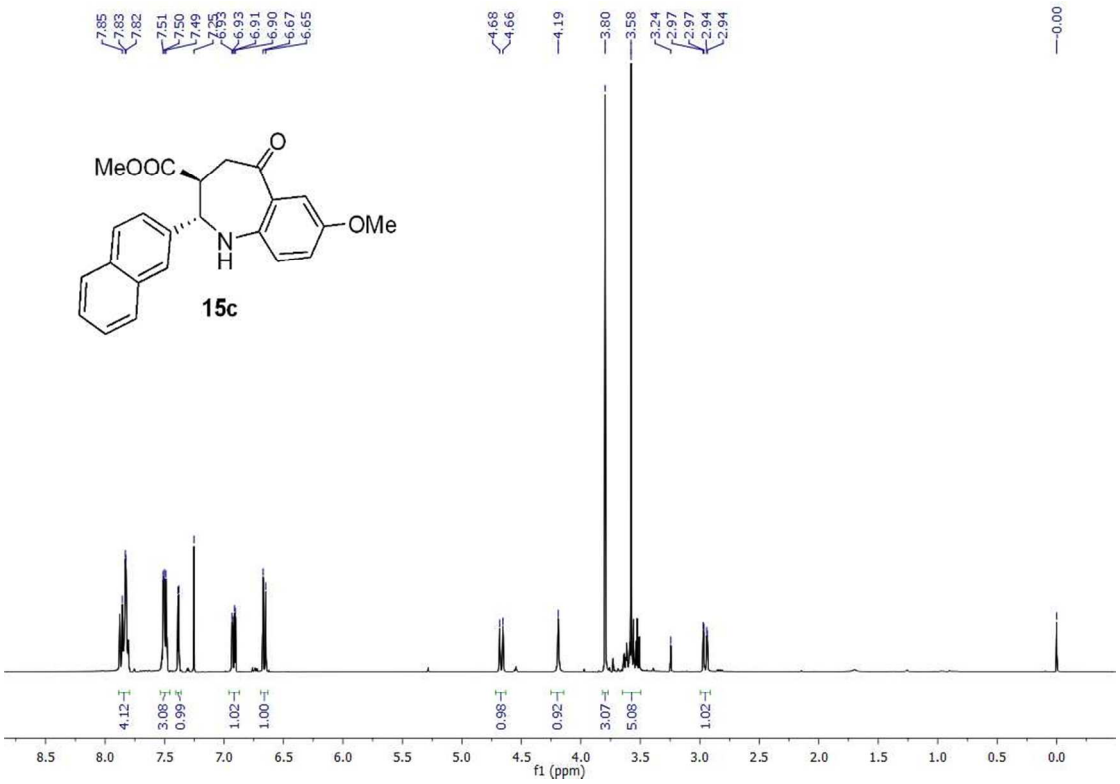
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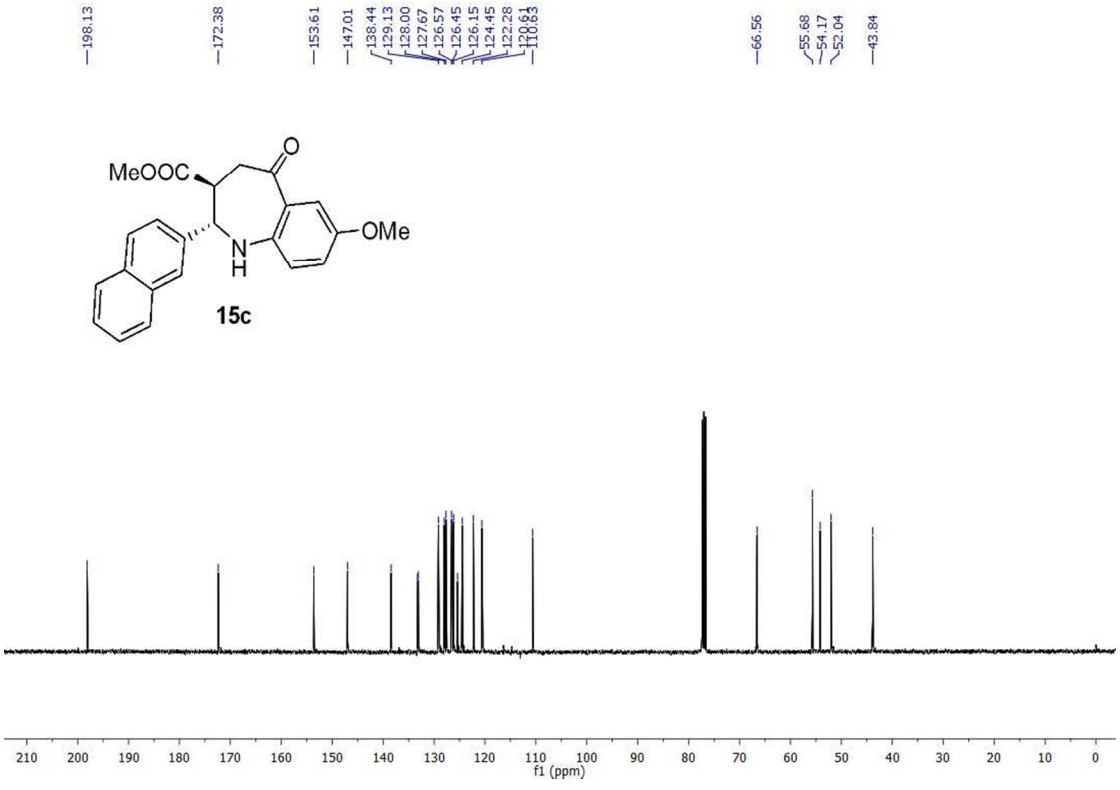
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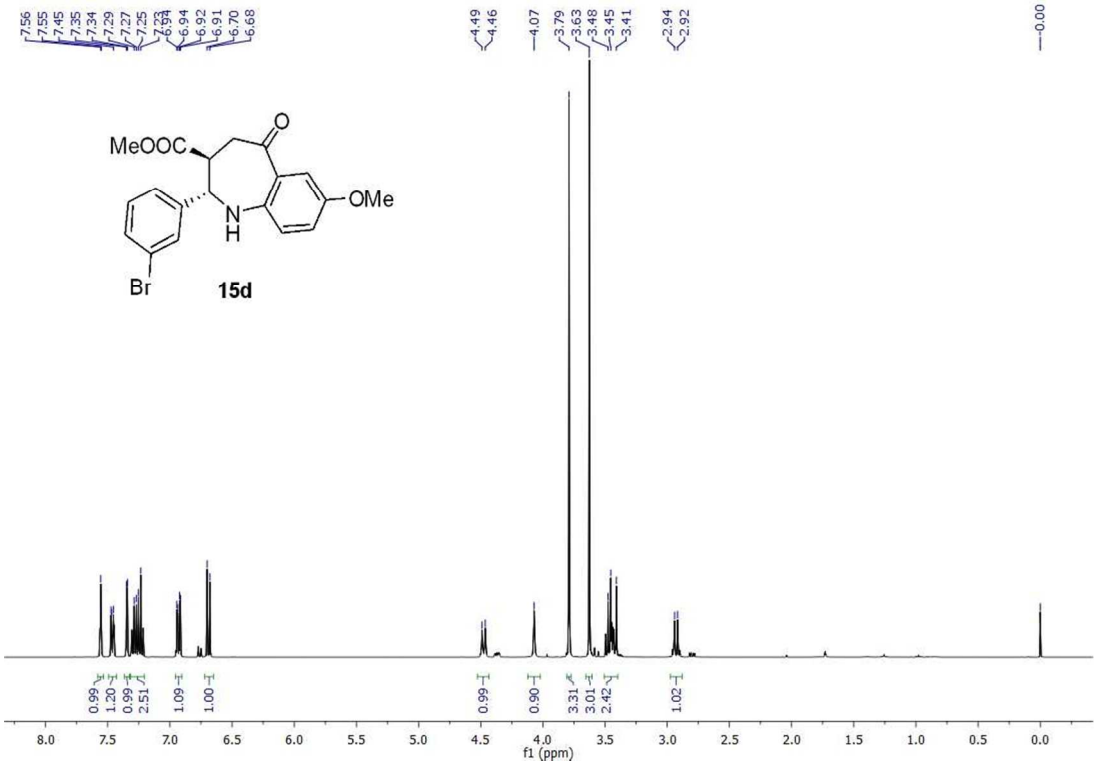
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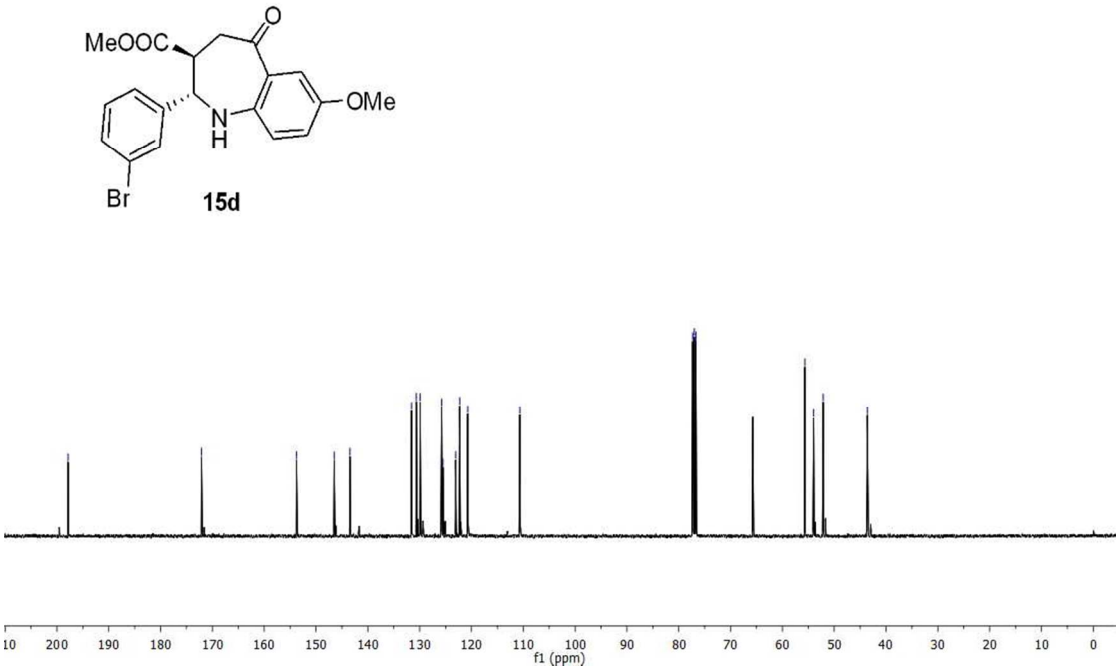
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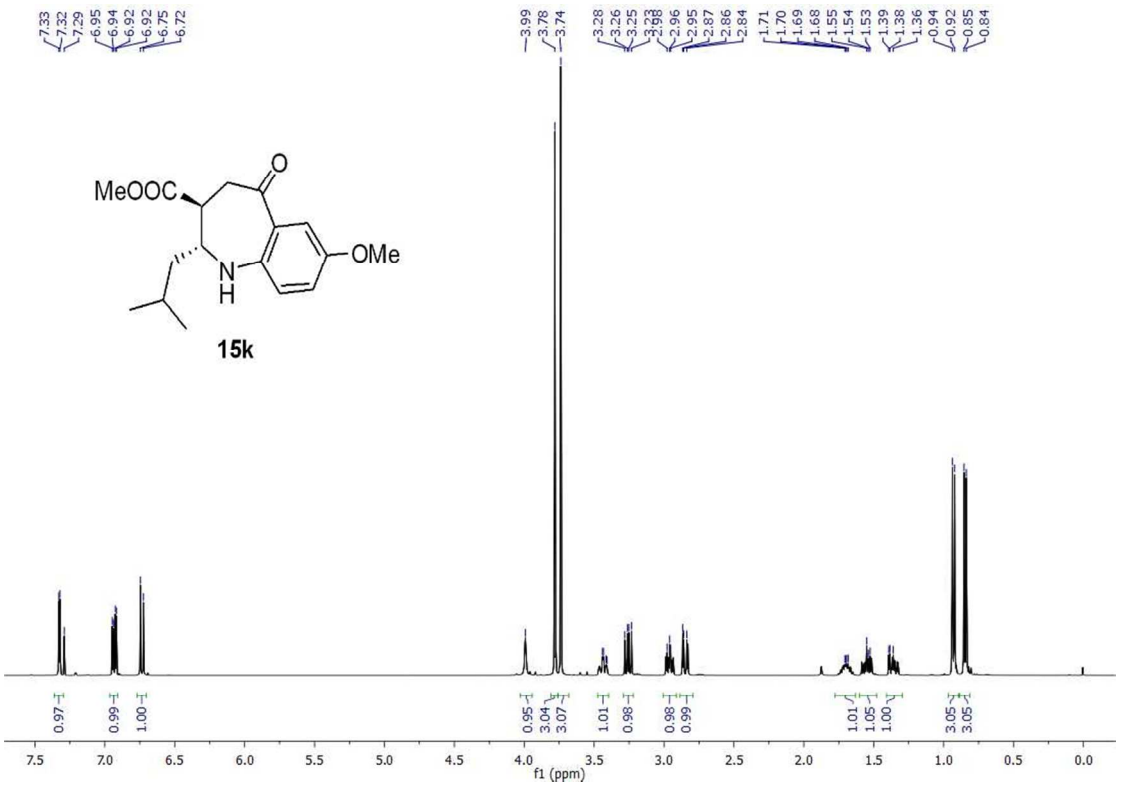
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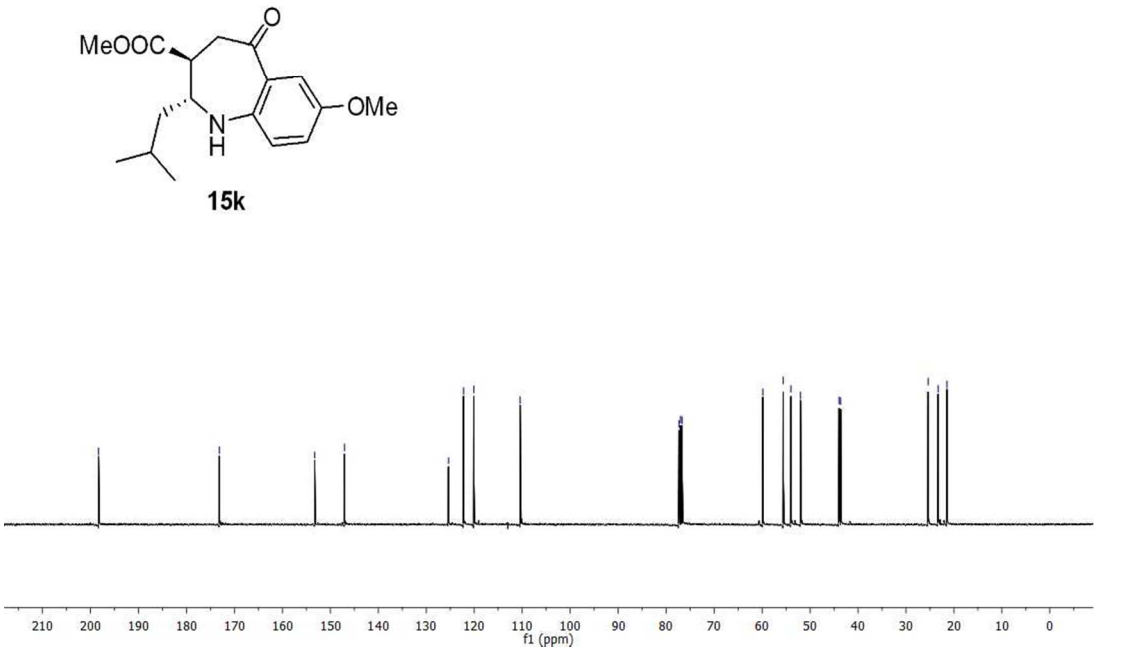
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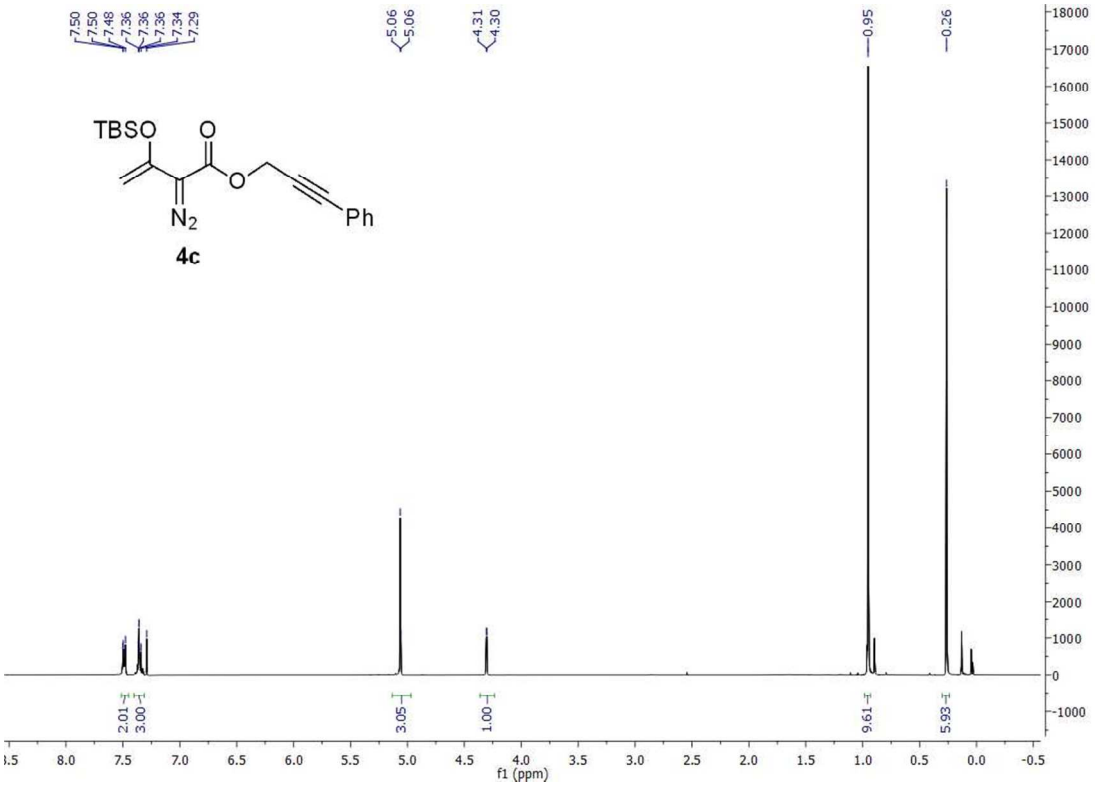
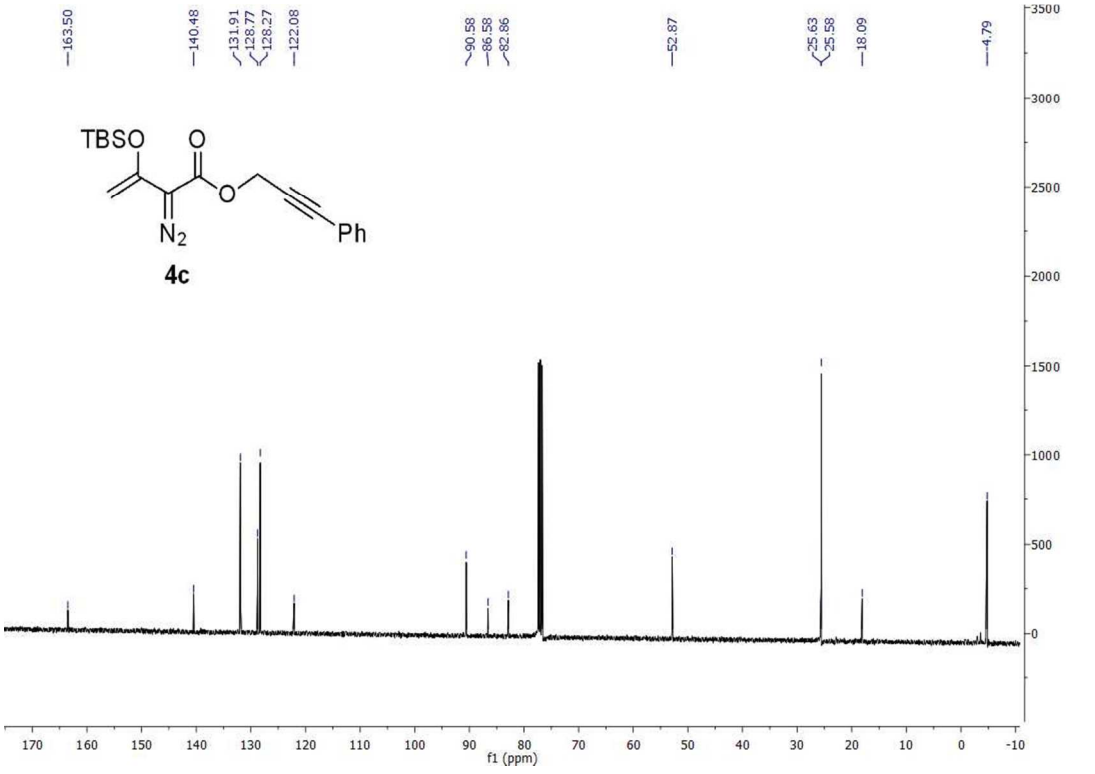
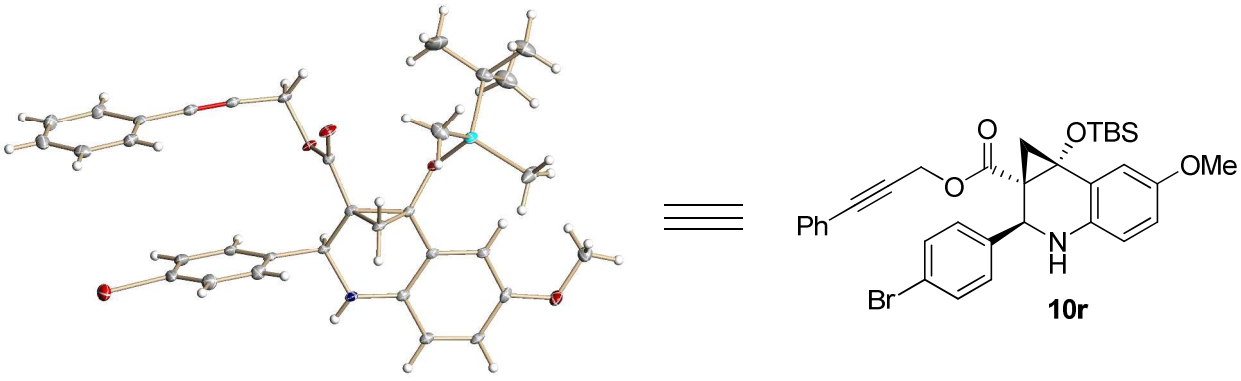




Crystal Structure Report for 10r



A colorless prism-like specimen of $C_{31}H_{34}O_3Si$ with approximate dimensions 0.25 mm × 0.41 mm × 0.46 mm was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoKα sealed tube (λ = 0.71073 Å). Data collection temperature was 150 K.

The total exposure time was 5.05 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 22695 reflections to a maximum θ angle of 30.00° (0.71 Å resolution), of which 7682 were independent (average redundancy 2.954, completeness = 99.4%, R_{int} = 1.71%, R_{sig} = 1.76%) and 6769 (88.12%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.4638(4) Å, b = 10.2914(5) Å, c = 14.8643(7) Å, α = 74.9167(7)°, β = 86.8223(7)°, γ = 71.4086(7)°, V = 1324.30(11) Å^3, are based upon the refinement of the XYZ-centroids of 9986 reflections above 20 σ(I) with 4.520° < 2θ < 65.16°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9020 and 0.9710.

The structure was solved and refined using the Bruker SHELXTL Software Package using the space group P -1, with Z = 2 for the formula unit, $C_{31}H_{34}O_3Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 442 variables converged at R_1 = 3.75% for the observed data and wR_2 = 7.82% for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 0.404 e$^-$/Å^3 and the largest hole was -0.332 e$^-$/Å^3 with an RMS deviation of 0.041 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.210 g/cm^3 and F(000), 516 e$^-$.

APEX2 Version 2010.11-3 (Bruker AXS Inc.).
SAINT Version 7.68A (Bruker AXS Inc., 2009).
SADABS Version 2008/1 (G. M. Sheldrick, Bruker AXS Inc.).
XPREP Version 2008/2 (G. M. Sheldrick, Bruker AXS Inc.).
XS Version 2008/1 (Sheldrick, G. M. *Acta Cryst.* **2008**. *A64*, 112-122).
XL Version 2012/4 (Sheldrick, G. M. **2012** University of Gottingen, Germany).
Platon (Spek, A. L. *Acta Cryst.* **1990**. *A46*, C-34).

Table 1. Sample and crystal data for UM2350.

Identification code	2350	
Chemical formula	$C_{31}H_{34}O_3Si$	
Formula weight	482.67	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.25 × 0.41 × 0.46 mm	
Crystal habit	colorless prism	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.4638(4) Å	α = 74.9167(7)°
	b = 10.2914(5) Å	β = 86.8223(7)°
	c = 14.8643(7) Å	γ = 71.4086(7)°
Volume	1324.30(11) $Å^3$	
Z	2	
Density (calculated)	1.210 Mg/cm^3	
Absorption coefficient	0.119 mm^{-1}	
F(000)	516	

Table 2. Data collection and structure refinement for UM2350.

Diffractometer	Bruker APEX-II CCD
Radiation source	sealed tube, MoKα
Theta range for data collection	2.16 to 30.00°
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-20 \le l \le 20$
Reflections collected	22695
Independent reflections	7682 [R(int) = 0.0171]
Coverage of independent reflections	99.4%
Absorption correction	multi-scan
Max. and min.	0.9710 and 0.9020

transmission		
Structure solution technique	direct methods	
Structure solution program	ShelXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	ShelXL-2012 (Sheldrick, 2012)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7682 / 0 / 442	
Goodness-of-fit on F^2	1.000	
Final R indices	6769 data; I>2σ(I)	$R_1 = 0.0375$, $wR_2 = 0.0763$
	all data	$R_1 = 0.0430$, $wR_2 = 0.0782$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0100P)^2+0.7550P]$, $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.404 and -0.332 eÅ^{-3}	
R.M.S. deviation from mean	0.041 eÅ^{-3}	

$R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})| / \Sigma[F_o^2]$
$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$
$\text{GOOF} = S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for UM2350.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.31429(11)	0.47995(10)	0.20584(7)	0.01973(18)
O2	0.43122(8)	0.38683(8)	0.16096(5)	0.02195(15)
C3	0.38453(11)	0.40713(11)	0.07048(7)	0.02038(18)
C4	0.26753(11)	0.52677(11)	0.04318(7)	0.02128(19)
C5	0.15048(12)	0.59422(11)	0.96970(7)	0.0252(2)
O5	0.14632(10)	0.57631(9)	0.89202(6)	0.0357(2)

	x/a	y/b	z/c	U(eq)
C6	0.02558(13)	0.69824(12)	0.00993(8)	0.0274(2)
C7	0.05565(11)	0.64932(11)	0.11684(7)	0.02217(19)
C8	0.22778(11)	0.59739(10)	0.12214(7)	0.01955(18)
Si1	0.27057(3)	0.23594(3)	0.31744(2)	0.02237(7)
O1	0.22270(8)	0.40339(8)	0.25331(5)	0.02264(15)
C11	0.28090(18)	0.11868(15)	0.23927(10)	0.0393(3)
C12	0.45368(15)	0.18129(15)	0.37992(10)	0.0380(3)
C13	0.11485(13)	0.23217(12)	0.40172(8)	0.0271(2)
C14	0.97067(16)	0.25121(19)	0.35050(11)	0.0437(3)
C15	0.0858(2)	0.35123(18)	0.45121(11)	0.0473(4)
C16	0.15756(19)	0.08882(17)	0.47483(11)	0.0468(4)
C21	0.38723(12)	0.53036(11)	0.27273(7)	0.02194(19)
C22	0.29318(14)	0.61577(13)	0.32504(8)	0.0298(2)
C23	0.35255(16)	0.66663(15)	0.38689(9)	0.0378(3)
C24	0.50575(17)	0.63126(15)	0.39785(9)	0.0386(3)
C25	0.59933(14)	0.54594(14)	0.34685(9)	0.0334(3)
C26	0.54093(13)	0.49582(12)	0.28354(8)	0.0263(2)
C31	0.46713(11)	0.29572(10)	0.02566(7)	0.02074(19)
C32	0.58818(12)	0.18380(11)	0.07281(8)	0.0245(2)
C33	0.66460(12)	0.07596(12)	0.03143(8)	0.0270(2)
C34	0.62178(13)	0.07915(12)	0.94283(8)	0.0269(2)
C35	0.50360(13)	0.19084(12)	0.89498(8)	0.0276(2)
C36	0.42605(12)	0.29939(12)	0.93566(7)	0.0250(2)
C41	0.97946(11)	0.76001(11)	0.16844(7)	0.0232(2)
C42	0.86581(13)	0.74123(13)	0.22882(8)	0.0301(2)
C43	0.79438(15)	0.84131(15)	0.27772(9)	0.0369(3)
C44	0.83611(14)	0.96164(14)	0.26699(9)	0.0348(3)
C45	0.94812(14)	0.98270(13)	0.20622(9)	0.0322(2)
C46	0.01917(12)	0.88279(12)	0.15728(8)	0.0282(2)

Table 4. Bond lengths (Å) for UM2350.

C1-O1	1.3959(12)	C1-O2	1.4705(12)
C1-C21	1.5189(14)	C1-C8	1.5422(13)
O2-C3	1.3815(12)	C3-C4	1.3517(14)
C3-C31	1.4622(14)	C4-C5	1.4667(14)

C4-C8	1.5059(14)	C5-O5	1.2204(13)
C5-C6	1.5326(16)	C6-C7	1.5498(15)
C6-H6A	0.986(15)	C6-H6B	0.976(15)
C7-C41	1.5085(15)	C7-C8	1.5436(14)
C7-H7	0.978(13)	C8-H8	0.984(12)
Si1-O1	1.6669(8)	Si1-C11	1.8595(13)
Si1-C12	1.8620(14)	Si1-C13	1.8840(12)
C11-H11A	0.974(19)	C11-H11B	0.967(19)
C11-H11C	0.974(19)	C12-H12A	0.957(18)
C12-H12B	0.990(19)	C12-H12C	0.952(19)
C13-C14	1.5320(19)	C13-C15	1.5329(17)
C13-C16	1.5346(18)	C14-H14A	1.002(18)
C14-H14B	0.976(19)	C14-H14C	1.010(19)
C15-H15A	0.989(19)	C15-H15B	0.966(19)
C15-H15C	1.023(19)	C16-H16A	1.002(19)
C16-H16B	0.978(19)	C16-H16C	1.011(19)
C21-C26	1.3909(15)	C21-C22	1.3963(15)
C22-C23	1.3893(17)	C22-H22	0.972(15)
C23-C24	1.386(2)	C23-H23	0.959(16)
C24-C25	1.3806(19)	C24-H24	0.968(17)
C25-C26	1.3962(16)	C25-H25	0.980(15)
C26-H26	0.955(14)	C31-C32	1.3991(14)
C31-C36	1.4015(14)	C32-C33	1.3883(15)
C32-H32	0.955(14)	C33-C34	1.3885(16)
C33-H33	0.949(14)	C34-C35	1.3860(17)
C34-H34	0.956(14)	C35-C36	1.3899(15)
C35-H35	0.963(14)	C36-H36	0.944(14)
C41-C42	1.3910(15)	C41-C46	1.3972(15)
C42-C43	1.3918(18)	C42-H42	0.952(15)
C43-C44	1.385(2)	C43-H43	0.974(16)
C44-C45	1.3875(18)	C44-H44	0.960(15)
C45-C46	1.3902(16)	C45-H45	0.952(16)
C46-H46	0.979(15)		

Table 5. Bond angles (°) for UM2350.

O1-C1-O2	108.52(8)	O1-C1-C21	110.76(8)

O2-C1-C21	108.99(8)	O1-C1-C8	110.22(8)
O2-C1-C8	102.82(7)	C21-C1-C8	115.07(8)
C3-O2-C1	108.65(7)	C4-C3-O2	111.51(9)
C4-C3-C31	133.66(9)	O2-C3-C31	114.81(8)
C3-C4-C5	139.76(10)	C3-C4-C8	109.11(9)
C5-C4-C8	109.70(9)	O5-C5-C4	129.99(10)
O5-C5-C6	124.57(10)	C4-C5-C6	105.44(9)
C5-C6-C7	105.42(8)	C5-C6-H6A	107.1(8)
C7-C6-H6A	110.9(8)	C5-C6-H6B	111.3(8)
C7-C6-H6B	113.7(9)	H6A-C6-H6B	108.2(12)
C41-C7-C8	116.13(9)	C41-C7-C6	114.74(9)
C8-C7-C6	101.12(8)	C41-C7-H7	109.2(7)
C8-C7-H7	107.5(7)	C6-C7-H7	107.4(7)
C4-C8-C1	102.48(8)	C4-C8-C7	102.71(8)
C1-C8-C7	121.07(8)	C4-C8-H8	110.3(7)
C1-C8-H8	109.1(7)	C7-C8-H8	110.4(7)
O1-Si1-C11	108.55(6)	O1-Si1-C12	112.05(5)
C11-Si1-C12	109.28(7)	O1-Si1-C13	104.37(5)
C11-Si1-C13	111.20(6)	C12-Si1-C13	111.29(6)
C1-O1-Si1	128.87(6)	Si1-C11-H11A	109.0(11)
Si1-C11-H11B	111.5(11)	H11A-C11-H11B	109.9(15)
Si1-C11-H11C	110.7(11)	H11A-C11-H11C	108.0(15)
H11B-C11-H11C	107.7(15)	Si1-C12-H12A	109.1(11)
Si1-C12-H12B	110.6(10)	H12A-C12-H12B	108.5(14)
Si1-C12-H12C	113.3(11)	H12A-C12-H12C	108.7(15)
H12B-C12-H12C	106.6(14)	C14-C13-C15	108.47(12)
C14-C13-C16	108.67(12)	C15-C13-C16	109.06(12)
C14-C13-Si1	110.55(8)	C15-C13-Si1	110.68(9)
C16-C13-Si1	109.36(9)	C13-C14-H14A	110.2(10)
C13-C14-H14B	111.3(11)	H14A-C14-H14B	108.8(14)
C13-C14-H14C	110.7(10)	H14A-C14-H14C	108.3(14)
H14B-C14-H14C	107.5(14)	C13-C15-H15A	110.2(10)
C13-C15-H15B	109.7(11)	H15A-C15-H15B	105.9(15)
C13-C15-H15C	112.2(10)	H15A-C15-H15C	109.8(14)
H15B-C15-H15C	108.9(15)	C13-C16-H16A	110.8(10)
C13-C16-H16B	110.1(11)	H16A-C16-H16B	106.0(15)
C13-C16-H16C	111.5(11)	H16A-C16-H16C	109.1(14)

H16B-C16-H16C	109.1(15)	C26-C21-C22	119.43(10)
C26-C21-C1	123.23(9)	C22-C21-C1	117.34(9)
C23-C22-C21	120.31(11)	C23-C22-H22	120.1(9)
C21-C22-H22	119.5(8)	C24-C23-C22	120.07(12)
C24-C23-H23	121.0(10)	C22-C23-H23	119.0(10)
C25-C24-C23	119.89(11)	C25-C24-H24	119.8(10)
C23-C24-H24	120.3(10)	C24-C25-C26	120.55(12)
C24-C25-H25	120.6(9)	C26-C25-H25	118.8(9)
C21-C26-C25	119.75(11)	C21-C26-H26	119.6(8)
C25-C26-H26	120.7(8)	C32-C31-C36	119.38(10)
C32-C31-C3	119.97(9)	C36-C31-C3	120.64(9)
C33-C32-C31	120.15(10)	C33-C32-H32	120.6(8)
C31-C32-H32	119.2(8)	C32-C33-C34	120.14(10)
C32-C33-H33	119.2(9)	C34-C33-H33	120.7(9)
C35-C34-C33	120.09(10)	C35-C34-H34	119.5(9)
C33-C34-H34	120.4(9)	C34-C35-C36	120.35(10)
C34-C35-H35	120.3(8)	C36-C35-H35	119.3(8)
C35-C36-C31	119.87(10)	C35-C36-H36	120.7(8)
C31-C36-H36	119.4(8)	C42-C41-C46	118.31(10)
C42-C41-C7	119.82(10)	C46-C41-C7	121.87(10)
C41-C42-C43	120.95(12)	C41-C42-H42	118.9(9)
C43-C42-H42	120.2(9)	C44-C43-C42	120.18(12)
C44-C43-H43	121.5(10)	C42-C43-H43	118.3(10)
C43-C44-C45	119.56(11)	C43-C44-H44	121.5(9)
C45-C44-H44	118.9(9)	C44-C45-C46	120.20(12)
C44-C45-H45	121.1(9)	C46-C45-H45	118.7(9)
C45-C46-C41	120.79(11)	C45-C46-H46	119.4(8)
C41-C46-H46	119.8(8)		

Table 6. Torsion angles (°) for UM2350.

O1-C1-O2-C3	93.98(9)	C21-C1-O2-C3	-145.32(8)
C8-C1-O2-C3	-22.78(10)	C1-O2-C3-C4	15.16(11)
C1-O2-C3-C31	-163.36(8)	O2-C3-C4-C5	-164.21(12)
C31-C3-C4-C5	13.9(2)	O2-C3-C4-C8	-0.13(12)
C31-C3-C4-C8	178.01(11)	C3-C4-C5-O5	-22.7(2)
C8-C4-C5-O5	173.26(12)	C3-C4-C5-C6	157.27(13)

C8-C4-C5-C6	-6.75(11)	O5-C5-C6-C7	161.65(11)
C4-C5-C6-C7	-18.34(11)	C5-C6-C7-C41	161.07(9)
C5-C6-C7-C8	35.28(10)	C3-C4-C8-C1	-13.81(11)
C5-C4-C8-C1	155.34(8)	C3-C4-C8-C7	-140.09(9)
C5-C4-C8-C7	29.06(11)	O1-C1-C8-C4	-94.17(9)
O2-C1-C8-C4	21.36(9)	C21-C1-C8-C4	139.72(9)
O1-C1-C8-C7	19.18(12)	O2-C1-C8-C7	134.71(9)
C21-C1-C8-C7	-106.93(11)	C41-C7-C8-C4	-163.31(9)
C6-C7-C8-C4	-38.45(10)	C41-C7-C8-C1	83.45(12)
C6-C7-C8-C1	-151.69(9)	O2-C1-O1-Si1	41.17(11)
C21-C1-O1-Si1	-78.43(10)	C8-C1-O1-Si1	153.07(7)
C11-Si1-O1-C1	-87.41(10)	C12-Si1-O1-C1	33.37(10)
C13-Si1-O1-C1	153.92(8)	O1-Si1-C13-C14	69.07(10)
C11-Si1-C13-C14	-47.78(11)	C12-Si1-C13-C14	-169.88(10)
O1-Si1-C13-C15	-51.15(11)	C11-Si1-C13-C15	-167.99(11)
C12-Si1-C13-C15	69.91(12)	O1-Si1-C13-C16	-171.32(9)
C11-Si1-C13-C16	71.83(11)	C12-Si1-C13-C16	-50.27(11)
O1-C1-C21-C26	122.08(10)	O2-C1-C21-C26	2.76(13)
C8-C1-C21-C26	-112.08(11)	O1-C1-C21-C22	-58.10(12)
O2-C1-C21-C22	-177.42(9)	C8-C1-C21-C22	67.73(12)
C26-C21-C22-C23	0.43(17)	C1-C21-C22-C23	-179.40(11)
C21-C22-C23-C24	-0.8(2)	C22-C23-C24-C25	0.3(2)
C23-C24-C25-C26	0.6(2)	C22-C21-C26-C25	0.46(16)
C1-C21-C26-C25	-179.73(10)	C24-C25-C26-C21	-0.96(18)
C4-C3-C31-C32	178.72(11)	O2-C3-C31-C32	-3.19(14)
C4-C3-C31-C36	-1.50(18)	O2-C3-C31-C36	176.60(9)
C36-C31-C32-C33	-1.39(16)	C3-C31-C32-C33	178.40(10)
C31-C32-C33-C34	0.38(17)	C32-C33-C34-C35	0.71(17)
C33-C34-C35-C36	-0.78(17)	C34-C35-C36-C31	-0.24(17)
C32-C31-C36-C35	1.31(16)	C3-C31-C36-C35	-178.47(10)
C8-C7-C41-C42	-130.10(10)	C6-C7-C41-C42	112.34(12)
C8-C7-C41-C46	50.18(14)	C6-C7-C41-C46	-67.38(13)
C46-C41-C42-C43	-0.68(17)	C7-C41-C42-C43	179.59(11)
C41-C42-C43-C44	-0.17(19)	C42-C43-C44-C45	0.90(19)
C43-C44-C45-C46	-0.77(19)	C44-C45-C46-C41	-0.10(18)
C42-C41-C46-C45	0.82(17)	C7-C41-C46-C45	-179.46(10)

Table 7. Anisotropic atomic displacement parameters (Å^2) for UM2350.

The anisotropic atomic 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}
C1	0.0198(4)	0.0195(4)	0.0186(4)	-0.0053(3)	-0.0002(3)	-0.0040(3)
O2	0.0213(3)	0.0236(3)	0.0182(3)	-0.0069(3)	-0.0020(3)	-0.0016(3)
C3	0.0220(4)	0.0229(4)	0.0170(4)	-0.0050(3)	0.0000(3)	-0.0082(4)
C4	0.0237(5)	0.0218(4)	0.0184(4)	-0.0045(4)	-0.0010(4)	-0.0074(4)
C5	0.0277(5)	0.0233(5)	0.0226(5)	-0.0028(4)	-0.0048(4)	-0.0072(4)
O5	0.0406(5)	0.0380(5)	0.0238(4)	-0.0086(3)	-0.0099(3)	-0.0039(4)
C6	0.0254(5)	0.0265(5)	0.0256(5)	-0.0041(4)	-0.0069(4)	-0.0029(4)
C7	0.0198(4)	0.0210(4)	0.0241(5)	-0.0036(4)	-0.0018(4)	-0.0056(4)
C8	0.0197(4)	0.0190(4)	0.0187(4)	-0.0035(3)	-0.0013(3)	-0.0052(3)
Si1	0.02759(14)	0.01949(13)	0.01944(13)	-0.00541(10)	0.00134(10)	-0.00641(11)
O1	0.0233(3)	0.0208(3)	0.0220(3)	-0.0026(3)	-0.0001(3)	-0.0067(3)
C11	0.0561(9)	0.0352(6)	0.0381(7)	-0.0213(6)	0.0175(6)	-0.0233(6)
C12	0.0328(6)	0.0353(6)	0.0354(7)	0.0028(5)	-0.0069(5)	-0.0048(5)
C13	0.0339(6)	0.0268(5)	0.0217(5)	-0.0072(4)	0.0045(4)	-0.0110(4)
C14	0.0339(7)	0.0617(9)	0.0374(7)	-0.0145(7)	0.0049(6)	-0.0170(7)
C15	0.0634(10)	0.0520(9)	0.0419(8)	-0.0295(7)	0.0249(7)	-0.0293(8)
C16	0.0525(9)	0.0404(7)	0.0376(7)	0.0053(6)	0.0100(6)	-0.0149(7)
C21	0.0261(5)	0.0213(4)	0.0178(4)	-0.0036(4)	-0.0017(4)	-0.0074(4)
C22	0.0301(6)	0.0319(6)	0.0277(5)	-0.0121(4)	-0.0012(4)	-0.0062(5)
C23	0.0464(7)	0.0394(7)	0.0320(6)	-0.0192(5)	0.0004(5)	-0.0115(6)
C24	0.0511(8)	0.0443(7)	0.0297(6)	-0.0128(5)	-0.0058(5)	-0.0238(6)
C25	0.0333(6)	0.0411(7)	0.0293(6)	-0.0047(5)	-0.0054(5)	-0.0191(5)
C26	0.0266(5)	0.0295(5)	0.0228(5)	-0.0045(4)	-0.0007(4)	-0.0106(4)
C31	0.0219(4)	0.0218(4)	0.0195(4)	-0.0059(4)	0.0025(3)	-0.0081(4)
C32	0.0247(5)	0.0260(5)	0.0222(5)	-0.0077(4)	0.0004(4)	-0.0060(4)
C33	0.0249(5)	0.0249(5)	0.0299(5)	-0.0087(4)	0.0017(4)	-0.0050(4)
C34	0.0284(5)	0.0269(5)	0.0309(6)	-0.0140(4)	0.0078(4)	-0.0120(4)
C35	0.0323(6)	0.0329(6)	0.0233(5)	-0.0121(4)	0.0030(4)	-0.0144(5)
C36	0.0271(5)	0.0268(5)	0.0213(5)	-0.0063(4)	0.0000(4)	-0.0084(4)
C41	0.0187(4)	0.0235(5)	0.0234(5)	-0.0034(4)	-0.0028(4)	-0.0030(4)
C42	0.0272(5)	0.0312(6)	0.0291(6)	-0.0028(4)	0.0020(4)	-0.0093(4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C43	0.0327(6)	0.0444(7)	0.0290(6)	-0.0074(5)	0.0086(5)	-0.0088(5)
C44	0.0343(6)	0.0384(6)	0.0277(6)	-0.0136(5)	-0.0003(5)	-0.0020(5)
C45	0.0309(6)	0.0303(6)	0.0365(6)	-0.0128(5)	-0.0024(5)	-0.0071(5)
C46	0.0229(5)	0.0285(5)	0.0331(6)	-0.0087(4)	0.0026(4)	-0.0075(4)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for UM2350.

	x/a	y/b	z/c	U(eq)
H6A	0.0353(16)	0.7934(16)	-0.0159(10)	0.035(4)
H6B	-0.0725(16)	0.7004(15)	-0.0088(10)	0.035(4)
H7	0.0223(14)	0.5663(14)	0.1407(9)	0.024(3)
H8	0.2661(14)	0.6784(13)	0.1112(9)	0.022(3)
H11A	0.372(2)	0.1097(19)	0.2046(13)	0.062(3)
H11B	0.278(2)	0.026(2)	0.2741(13)	0.062(3)
H11C	0.197(2)	0.1592(19)	0.1945(13)	0.062(3)
H12A	0.479(2)	0.083(2)	0.4127(13)	0.059(3)
H12B	0.533(2)	0.1937(19)	0.3353(13)	0.059(3)
H12C	0.454(2)	0.2349(19)	0.4232(13)	0.059(3)
H14A	-0.113(2)	0.2552(19)	0.3950(13)	0.060(3)
H14B	-0.056(2)	0.338(2)	0.3001(13)	0.060(3)
H14C	-0.017(2)	0.169(2)	0.3221(13)	0.060(3)
H15A	0.010(2)	0.3432(19)	0.4993(13)	0.061(3)
H15B	0.176(2)	0.3408(19)	0.4841(13)	0.061(3)
H15C	0.052(2)	0.450(2)	0.4057(13)	0.061(3)
H16A	0.074(2)	0.0827(19)	0.5188(13)	0.062(3)
H16B	0.174(2)	0.012(2)	0.4445(13)	0.062(3)
H16C	0.251(2)	0.0727(19)	0.5118(13)	0.062(3)
H22	0.1857(17)	0.6382(15)	0.3186(10)	0.036(4)
H23	0.2860(18)	0.7241(17)	0.4227(11)	0.047(4)
H24	0.5475(18)	0.6645(17)	0.4421(11)	0.049(5)
H25	0.7079(17)	0.5191(16)	0.3546(10)	0.040(4)
H26	0.6055(15)	0.4377(14)	0.2477(10)	0.031(3)
H32	0.6158(15)	0.1814(14)	0.1342(10)	0.029(3)
H33	0.7441(16)	-0.0011(15)	0.0652(10)	0.035(4)

	x/a	y/b	z/c	U(eq)
H34	0.6724(16)	0.0038(15)	-0.0852(10)	0.033(4)
H35	0.4757(16)	0.1950(15)	-0.1673(10)	0.034(4)
H36	0.3456(16)	0.3758(15)	-0.0966(10)	0.032(4)
H42	-0.1631(16)	0.6586(16)	0.2361(10)	0.037(4)
H43	-0.2835(18)	0.8233(17)	0.3201(11)	0.048(4)
H44	-0.2103(17)	1.0310(16)	0.3011(11)	0.043(4)
H45	-0.0228(17)	1.0656(16)	0.1966(11)	0.042(4)
H46	0.0975(16)	0.8993(15)	0.1142(10)	0.036(4)