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Supporting Information

Gold(I)-Catalyzed Dearomative [2+2]-Cycloaddition of Indoles with Activated Allenes: A Combined Experimental–Computational Study

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Supporting Information

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General Methods.

^{1}H-NMR spectra were recorded on Varian 200 (200 MHz) or Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 200 (50 MHz), Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m/z* (rel. intense). LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer. Optical rotations were measured using a Schmidt+Haensch Unipol L1000 polarimeter. Chromatographic purification was done with 240-400 mesh silica gel. Anhydrous THF and DCM were distilled respectively from sodium-benzophenone and P_2O_5 prior to use. Other anhydrous solvents were supplied by Fluka or Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification. Melting points were measured using open glass capillaries in a Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are calibrated by comparison with literature values (Aldrich). The indoles unavailable in commercial were synthesized according to the general procedure for Fisher indole synthesis.[1]

Computational Details.

All the reported DFT computations have been carried out using the software Gaussian 09 series.[2] The M06[3] functional proposed by Truhlar and Zhao was used in all computations. This functional has been demonstrated to provide a better estimate of π-π interactions and reaction energetics[4] with respect to the most

[1] K.S. MacMillan, J. Naidoo, J. Liang, L. Melito, N.S. Williams, L. Morlock, P.J. Huntington, S. Jo Estill, J. Longgood, G.L. Becker, S.L. McKnight, A.A. Pieper, J.K. De Brabander, J.M. Ready, *J. Am. Chem. Soc.* **2011**, *133*, 1428-1437.

[2] Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. Gaussian 09, revision B.01; Gaussian, Inc.: Wallingford CT, 2009

[3] a) Zhao, Y.; Truhlar, D.G. *J. Phys. Chem. A*, **2004**, *108*, 6908-6918. b) Zhao, Y.; Truhlar, D. G. J. Phys. Chem. A, 2005, *109*, 5656-5667. c) Zhao, Y.; Truhlar, D.G. *J. Phys. Chem. B*, **2005**, *109*, 19046-19051. d) Zhao, Y.; Truhlar, D.G. *Acc. Chem. Res.*, **2008**, *41*, 157-167

[4] a) Bottoni, A.; Calvaresi, M.; Ciogli, A.; Cosimelli, B.; Mazzeo, G.; Pisani, L.; Severi, E.; Spinelli, D.; Superchi, S. *Adv. Synth. Catal.* **2013**, *355*, 191-202. b) Giacinto, P.; Bottoni, A.; Calvaresi, M.; Zerbetto, M. *J. Phys. Chem. C*, DOI: 10.1021/jp412456q.

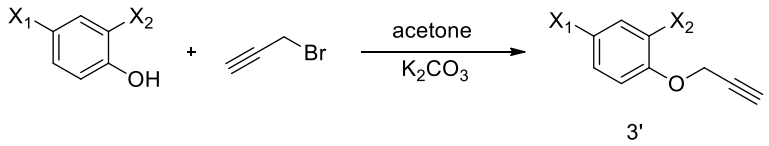
popular DFT Becke's three-parameter exchange functional B3LYP.[5] According to a locally dense basis set (LDBS) approach, the model system has been partitioned into different regions, which were assigned basis sets of different accuracy. All the atoms of the t-Bu groups of the gold ligand (JohnPhos) and of the BOC protecting group have been described by 3-21G* basis set, while the rest of system (except the metal center) has been described by more accurate basis set 6-31G*. Gold atom has been described by the widely used effective core potential (ECP)-type (with pseudopotential) LANL2DZ[6] basis set. The geometries of the various critical points on the potential energy surface were fully optimized with the gradient method available in Gaussian 09. For each stationary point, harmonic vibrational frequencies computations have been performed to determine the nature of the various critical points. The solvent effects have been taken into account during optimization, using the Polarizable Continuum Model (PCM) approach.[7] A value of 8.93 was employed for the toluene dielectric constant ε.

[5] a) Lee, C.; Yang, W.T.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785-789. b) Becke., A.D. *J. Chem. Phys*. **1993**, *98*, 5648-5652.

[6] a) Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 270-283. b) Hay, P.J.; Wadt, W.R. *J. Chem. Phys*. **1985**, *82*, 284-299. c) Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 299C.

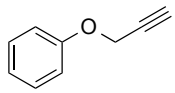
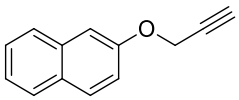
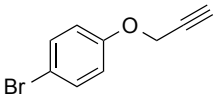
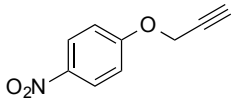
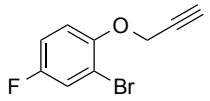
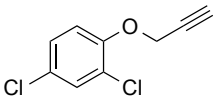
[7] Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.*, **2005**, *105*, 2999-3093.

General Procedure for the synthesis of Propargyl-Phenol Ethers 3'

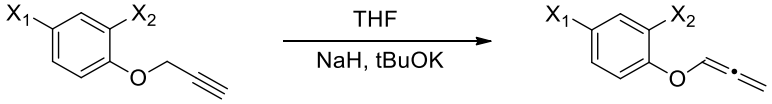


3'

To a stirred solution of phenols (10 mmol) in acetone was added K_2CO_3 (21 mmol) at room temperature. After 15 min propargyl bromide (15 mmol, 1.33 ml) was added dropwise and the mixture was heated under reflux for 3h. It was then quenched with H_2O and evaporated under reduced pressure. The resulting aqueous layer was extracted twice with EtOAc and the organic phase was washed with brine, dried over anhydrous Na_2SO_4, and evaporated *in vacuum*. The residue was purified *via* column chromatography (cHex:AcOEt = 2:1) to gain the desired products as yellow solids.

Propargylaryl ether	Data analysis
	**3a':** Y = 95%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 7.04-7.00 (m, 3H), 4.70 (d, J = 2.0 Hz, 2H), 2.53 (t, J = 2.4Hz, 1H). ***MS:*** 131(M), 103, 65.
	**3b':** Y = 84%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.81-7.76 (m, 3H), 7.47 (t, J = 8.0 1H), 7.38 (t, J = 7.6 1H), 4.83 (d, J = 2.4 Hz, 2H), 2.57 (t, J = 2.4 Hz, 1H). ***MS:*** 181(M),153, 115.
	**3c':** Y = 91%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.38 (d, J = 6.4 Hz, 2H), 6.87 (d, J = 6.4 Hz, 2H), 4.65 (d, J = 2.4 Hz, 2H), 2.50 (t, J = 2.4 Hz, 1H). ***MS:*** 212, 210, 131.
	**3d':** Y = 98%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.20 (d, J = 9.2 Hz, 2H), 7.03 (d, J = 9.1 Hz, 2H), 4.78 (d, J = 2.0 Hz, 2H), 2.57 (t, J = 2.0 Hz, 1H). ***MS:*** 177 (M), 160, 131, 103, 63.
	**3e':** Y = 95%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.6, 2.4 Hz 1H), 7.07-7.00 (m, 2H), 4.75 (d, J = 2.4 Hz, 2H), 2.55 (t, J = 2.4, 1H). ***MS:*** 230 (M), 191, 149, 121, 81.
	**3f':** Y = 97%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.40 (d, J = 2.4 Hz, 1H), 7.21 (dd, J = 9.2, 2.8 Hz, 1H), 7.03 (d, J = 8.8 Hz, 1H), 4.77 (d, J = 2.8 Hz, 1H), 2.56 (t, J = 2.4 Hz, 1H). ***MS:*** 200 (M), 165, 133, 97.

General Procedure for the synthesis of Alkoxyallenes 3



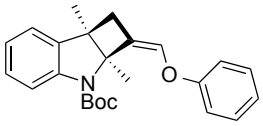
3

Under a nitrogen atmosphere, NaH (4.2 mmol) was suspended into anhydrous THF, followed by addition of propargyl-phenol ethers **3'a-f** (2.5 mmol) with stirring. After 15 min anhydrous *t*-BuOK (0.75 mmol) was added and the mixture was allowed to stir at rt for 5 h. The reaction was quenched by addition of H_2O and evaporated under reduced pressure. The aqueous layer was extracted twice with EtOAc and the resulting organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and evaporated *in vacuum*. Purification by column chromatography (*c*Hex:AcOEt = 8:2) afforded the desired products **3a-f** as yellow oils.

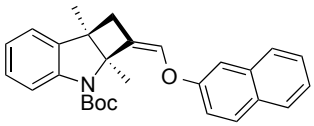
Aryloxyallene 3 = X^1,X^2	**Data analysis**
3a = H,H	Y = 85%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.06-7.04 (m, 3H), 6.85 (t, J = 5.9 Hz, 1H), 5.45 (d, J = 5.9 Hz, 2H). ***MS:*** 131 (M), 103, 77.
3d = β-naphthyl	Y = 86%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.79-7.74 (m, 3H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.39-7.35 (m, 2H), 7.26 (dd, J =2 .8, 9.2 Hz, 1H), 6.96 (t, J = 6.0 Hz, 1H), 5.47 (d, J = 8.0 Hz, 2H) ***MS:*** 181 (M)
3c = Br,H	Y = 90%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 6.80 (t, J = 5.9 Hz, 1H), 5.46 (d, J = 5.9 Hz, 2H). ***MS:*** 212 (M), 183.
3d = NO_2,H	Y = 78%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.23 (d, J = 9.1 Hz, 2H), 7.15 (d, J = 9.1 Hz, 2H), 6.86 (t, J = 5.9 Hz, 1H), 5.54 (d, J = 5.9 Hz, 2H). ***MS:*** 176 (M), 160, 131.
3e = F,Br	Y = 73%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 7.8, 3.0 Hz, 1H), 7.09 (dd, J = 9.0, 5.0 Hz, 1H), 6.99 (ddd, J = 9.0, 7.8, 3.0 Hz, 1H), 6.83 (t, J = 5.9 Hz, 1H), 5.43 (d, J = 5.9 Hz, 1H). ***MS:*** 228 (M), 200, 149.
3f = Cl,Cl	Y = 85%; ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.39 (d, J = 2.4 Hz, 1H), 7.19 (dd, J = 2.4, 8.7 Hz, 1H), 7.08 (d, J = 8.7 Hz, 1H), 6.82 (t, J = 5.9 Hz, 1H), 5.46 (d, J = 5.9 Hz, 2H). ***MS:*** 200 (M), 165, 133.

General procedure for the [2+2]-cycloaddition reaction between indoles and allenamide/ aryloxyallenes (2/3): racemic variant.

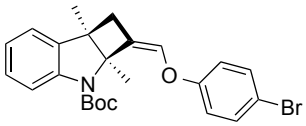
To a stirred solution of [JohnPhosAu(ACN)]SbF_6 (5% mol, 2 mg) in anhydrous DCM (1 ml) at 0 °C, the desired indole (0.05 mmol) and allenamide **2** or aryloxyallenes **3** (0.1 mmol) were added in sequence. The mixture was allowed to stir for 5 h. Removal of the solvent under reduced pressure and purification by column chromatography afforded the desired products.



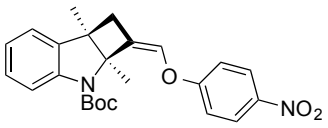
7ba. White solid. Yield = 75%, (*c*Hex:DCM = 8:2). ***Mp:*** 76-78 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.93 (bs, 1H), 7.32 (t, J = 7.6 Hz, 2H) 7.19 (t, J = 7.6 Hz, 1H) 7.11-6.96 (m, 5H), 6.23 (t, J = 1.8 Hz, 1H), 2.80 (dd, J = 13.9, 2.2 Hz, 1H), 2.53 (dd, J = 13.9, 1.5 Hz, 1H), 1.69 (s, 3H), 1.52 (s, 9H), 1.45 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.9, 144.0, 137.4, 137.0, 129.5, 127.8, 122.5, 122.3, 122.0, 116.6, 115.9, 80.9, 74.9, 48.1, 40.3, 28.6, 17.7, 17.4. ***LC-MS*:** 400 (M+Na), 777 (2M +Na). ***Anal. calcd*** for ($C_{24}H_{27}NO_3$: 377.48): C, 76.36; H, 7.21, N, 3.71; Found: C, 76.21, H, 7.10, N, 3.60.



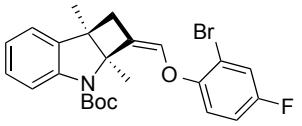
7bb. Pale yellow liquid. Yield = 83%; (*c*Hex:DCM = 98:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.91 (bs, 1H), 7.82-7.79 (m, 2H), 7.75 (d, J = 8.4 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.29- 7.21 (m, 3H), 7.13 (d, J = 7.2 Hz, 1H), 6.99 (t, J = 7.2 Hz, 1H), 6.37 (t, J = 2 Hz, 1H), 2.84 (dd, J =14, 2 Hz, 1H), 2.60 (dd, J = 13.6, 1.6Hz, 1H), 1.72 (s, 3H), 1.50 (s, 9H), 1.47 (s, 3H);. ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 155.5, 144.0, 137.3, 136.9, 134.3, 129.8, 129.6, 127.8, 127.7, 126.9, 126.5, 124.3, 122.4, 122.0, 118.8, 116.0, 110.8, 80.9, 74.9, 48.2, 40.3, 28.6, 17.7, 17.4; ***LC-MS*:** 450(M+Na), 877 (2M +Na). ***Anal. calcd*** for ($C_{28}H_{29}BrNO_3$: 427.54): C, 78.66; H, 6.84, N, 3.28; Found: C, 78.41, H, 6.71, N, 3.15.



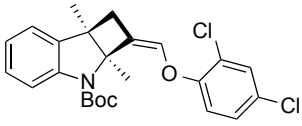
7bc. Light yellow oil. Yield = 96%; (*c*Hex:DCM = 95:5). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.40-7.38 (m, 2H), 7.17 (t, J = 8.8 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.87-6.83 (m, 2H), 6.13 (t, J=1.6 Hz, 1H), 2.77 (dd, J = 2.0, 14.1 Hz, 1H), 2.52 (dd, J = 1.6, 14.1 Hz, 1H), 1.65 (s, 3H), 1.58 (s, 1H), 1.48 (s, 9H), 1.41 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 156.7, 143.90, 137.2, 136.4, 132.5, 132.4, 132.3, 132.3, 127.8, 122.4, 122.1, 118.3, 116.7, 115.96, 114.9, 810, 74.7, 56.0, 48.1, 40.1, 28.6, 17.8, 17.5; ***LC-MS*:** 478 (M+Na), 935 (2M +Na). ***Anal. calcd*** for ($C_{24}H_{26}BrNO_3$: 456.38): C, 63.16; H, 5.74, N, 3.07; Found: C, 63.01, H, 5.61, N, 3.00.



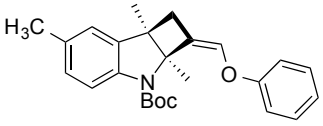
7bd. White solid. Yield = 86%; (*c*Hex:DCM = 8:2). ***Mp:*** 154-157 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.20 (d, J = 9.0 Hz, 2H), 7.77 (s, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.12 (d, J = 7.4 Hz, 1H), 7.07 (d, J = 9.1 Hz, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.24 (t, J=1.6 Hz, 1H), 2.82 (d, J = 14.8 Hz, 1H), 2.58 (d, J = 14.2 Hz, 1H), 1.66 (s, 3H), 1.46 (s, 9H), 1.41 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 162.3, 142.8, 137.0, 134.8, 127.9, 125.8, 122.6, 122.2, 116.2, 115.9, 81.1, 74.6, 39.9, 28.5, 17.8, 17.1. ***LC-MS**:* 445 (M+Na), 867 (2M+Na). ***Anal. calcd*** for ($C_{24}H_{26}N_2O_5$: 422.48): C, 68.23; H, 6.20, N, 6.63; Found: C, 68.06, H, 6.12, N, 6.63.



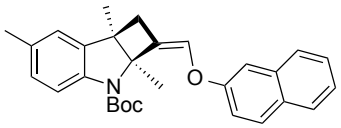
7be. White solid. Yield = 83%. ***Mp*** =118-120 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.29 (dd, J = 7.6, 2.8 Hz, 1H), 7.19-7.14 (m, 1H), 7.07 (dd, J = 7.2, 1.0 Hz, 1H), 6.98-6.89 (m, 3H), 6.07 (t, J = 1.6 Hz, 1H), 2.75 (dd, J = 14.0, 2.0 Hz, 1H), 2.51 (dd, J = 14.0, 1.6 Hz, 1H), 1.75 (s, 3H), 1.43 (s, 3H), 1.41 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) 159.1, 156.7, 151.0, 143.9, 137.4, 137.2, 127.8, 122.4, 122.0, 120.5, 120.3, 118.3, 118.2, 115.9, 115.1, 114.9, 113.3, 113.1, 80.9, 74.8, 48.1, 40.0, 28.4, 17.7, 17.6;**. *LC-MS**:* 497 (M+Na), 519 (M+K). ***Anal. calcd*** for ($C_{24}H_{25}BrFNO_3$: 474.37): C, 60.77; H, 5.31, N, 2.95; Found: C, 60.61, H, 5.13, N, 2.87.



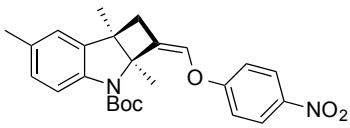
7bf. Light yellow oil. Yield = 95% (*c*Hex:DCM = 8:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.38 (d, J = 2.8 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.10 (d, J = 7.4, 1H), 6.95 (td, J = 8.0, 1.6 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.10 (t, J = 1.6, 1H), 2.80 (dd, J = 14.1, 2.1 Hz, 1H), 2.54 (dd, J = 14.1, 1.5 Hz, 1H), 1.72 (s, 3H), 1.42 (s, 3H), 1.40 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) 152.2, 143.9, 143.6, 140.9, 136.6, 130.1, 127.8, 127.7, 124.6, 122.4, 122.0, 118.1, 115.9, 81.0, 77.3, 77.0, 76.6, 74.8, 40.0, 29.7, 28.4, 17.7, 17.4; ***LC-MS**:* 470 (M+Na), 445 (M+K). ***Anal. calcd*** for ($C_{24}H_{25}Cl_2NO_3$: 446.37): C, 64.58; H, 5.65, N, 3.14; Found: C, 64.41, H, 5.51, N, 3.00.



7ea. White solid. Yield = 76%; (*c*Hex:DCM = 8:2). ***Mp:*** 102-104 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.32-6.90 (m, 7H), 6.21 (t, J = 1.8 Hz, 1H), 2.77 (dd, J = 13.6, 2.0 Hz, 1H), 2.51 (dd, J = 13.8, 1.6 Hz, 1H), 2.29 (s, 3H), 1.65 (s, 3H), 1.48 (s, 9H), 1.40 (d, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) 157.7, 136.8, 131.7, 129.5, 128.2, 122.6, 122.4, 116.6, 115.7, 80.7, 74.9, 40.2, 31.4, 30.2, 29.6, 28.5, 20.8, 17.7, 17.3. ***LC-MS*** 392 (M+H), 414 (M+Na), 430 (M+K), 805 (2M+Na). ***Anal. calcd*** for ($C_{25}H_{29}NO_3$: 391.51): C, 76.70; H, 7.47, N, 3.58; Found: C, 76.55, H, 7.31, N, 3.60.

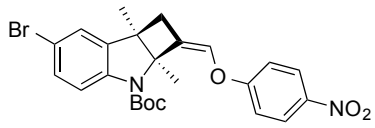


7eb. White solid. Yield = 94%; (*c*Hex:EtOAc = 98:2). ***Mp:*** 112-115 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.77-7.71 (m, 4H), 7.45 (t, J = 8.4 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.26-7.20 (m, 2H), 6.99 (d, J = 8.4 Hz, 1H), 6.91 (s, 1H), 6.34 (t, J=2.0Hz, 1H), 2.81 (dd, J = 2.0, 14.0 Hz, 1H), 2.56 (dd, J = 1.6, 14.0 Hz, 1H), 2.31 (s, 3H), 1.69 (s, 3H), 1.47 (s, 9H), 1.43 (s, 1H). ***^{13}C-NMR*** (100MHz, $CDCl_3$):δ 155.6, 136.8, 134.3, 131.8, 129.8, 129.6, 128.3, 127.7, 126.9, 126.5, 124.3, 122.7, 118.8, 115.7, 110.7, 80.8, 75.0, 28.6, 20.9, 17.7, 17.4. ***LC-MS*:** 442 (M+H), 464 (M+Na), 905 (2M+Na. ***Anal. calcd*** for ($C_{29}H_{31}NO_3$: 441.57): C, 78.88; H, 7.08, N, 3.17; Found: C, 78.62, H, 6.95, N, 3.11.

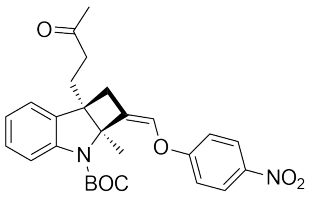


7ed. White solid. Yield = 50%. ***Mp*** = 196-198 °C; ***^{1}H-NMR*** (400 MHz, $CDCl_3$): δ 8.22 (d, J = 9.2 Hz, 2H), 7.67 (bs, 1H), 7.05 (d, J = 9.2 Hz, 2H), 7.00 (d, J = 8.4 Hz, 1H), 6.93 (s, 1H), 6.25 (t, J = 1.6 Hz, 1H), 2.83 (dd, J = 2.0, 14.4 Hz, 1H), 2.59 (d, J = 15.6 Hz, 1H), 2.32 (s, 3H), 1.67 (s, 3H), 1.47 (s, 9H), 1.43 (s, 1H); ***^{13}C-NMR*** (100 MHz, $CDCl_3$): 162.4, 142.6, 141.3, 134.7, 132.1, 128.4, 127.9, 125.8, 122.9, 117.5, 116.2, 115.8, 107.4, 80.9, 74.7, 71.5, 68.8, 39.9, 29.7, 28.6, 20.9, 19.5,

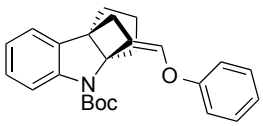
17.8, 17.1, 7.6. ***LC-MS**:* 459 (M+Na), 895 (2M+Na). ***Anal. calcd*** for ($C_{25}H_{28}N_2O_5$: 436.51): C, 68.79; H, 6.47, N, 6.42; Found: C, 68.65, H, 6.29, N, 6.25.



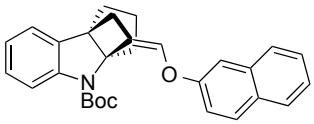
7hd. White solid. Yield = 85%. ***Mp* =** 191-193 °C; ***^{1}H-NMR*** (400 MHz, $CDCl_3$): δ 8.24 (d, J = 9.2 Hz, 2H), 7.69 (bs, 1H), 7.29 (dd, J = 2.0, 8.8 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.28 (s, 1H), 2.85 (dd, J = 2.0, 14.4 Hz, 1H), 2.60 (dd, J = 1.6, 14.4 Hz, 1H), 1.67 (s, 3H), 1.45 (s, 9H), 1.43 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$): 162.2, 142.7, 139.3, 135.1, 130.7, 125.9, 125.8, 125.4, 117.5, 116.3, 116.2, 114.7, 90.3, 81.5, 75.1, 39.9, 28.5, 17.6, 17.1. ***LC-MS**:*525 (M+Na). ***Anal. calcd*** for ($C_{24}H_{25}BrN_2O_5$: 501.38): C, 57.49; H, 5.03, N, 5.59; Found: C, 57.31, H, 5.15, N, 5.31.



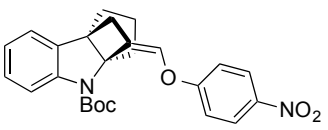
7id. White oil. Yield = 94%. ***^{1}H-NMR*** (400 MHz, $CDCl_3$): δ 8.16 (d, J = 9.2 Hz, 2H), 7.78 (bs, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 6.4 Hz, 1H), 7.01-6.95 (m, 3H), 6.13 (bs, 1H), 2.75 (dd, J = 1.6, 14.4 Hz, 1H), 2.68 (dd, J = 2.0, 14.8 Hz, 1H), 2.43-2.33 (m, 1H), 2.25-2.13 (m, 3H), 2.04 (s, 3H), 1.83 (s, 3H), 1.44 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$): 208.7, 162.1, 162.1, 144.1, 142.7, 134.9, 134.5, 128.3, 126.1, 125.8, 123.3, 123.0, 116.3, 115.6, 81.5, 73.3, 39.46, 38.3, 30.1, 28.4, 26.9, 17.8. ***Anal. calcd*** for ($C_{26}H_{28}N_2O_5$: 448.52): C, 69.63; H, 6.29, N, 6.25; Found: C, 69.51, H, 6.12, N, 6.05



7la: White oil. Yield 54%, (*c*Hex:DCM = 8:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.28 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.9 Hz, 2H), 7.14 (d, J = 6.4 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.98-6.94 (m, 2H), 6.09 (bs, 1H), 2.77(dd, J = 2.0, 15.2 Hz, 1H) 2.66 (dd, J = 2.4, 15.6 Hz, 1H) 2.18 – 2.01 (m, 3H), 1.92-1.89 (m, 3H), 1.72-1.63 (m, 1H), 1.57-1.54 (m, 1H), 1.44 (s, 9H); ***^{13}C-NMR*** 157.7, 129.5, 127.9, 123.6, 122.6, 117.4, 115.7, 80.4, 78.8, 38.1, 36.6, 36.6, 28.2, 28.0; ***LC-MS**:* 412 (M+Na), 801 (2M+Na); ***Anal. calcd*** for ($C_{25}H_{27}NO_3$: 389.50): C, 77.09; H, 6.99, N, 3.60; Found: C, 77.15, H, 7.10, N, 3.55.

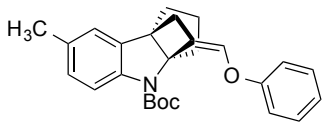


7lb. Pale yellow liquid. Yield = 88%; (*c*Hex:EtOAc = 95:5). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.00 (bs, 1H), 7.81-7.79 (m, 2H), 7.75 (d, J = 8 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.29-7.22 (m, 3H), 7.18 (d, J = 6.4 Hz, 1H), 7.01 (t, J = 6.4 Hz, 1H), 6.25 (bs, 1H), 2.88-2.73 (m, 2H), 2.24-2.20 (m, 2H), 2.13-2.06 (m, 1H), 1.99-1.94 (m, 1H), 1.76-1.70 (m, 1H), 1.59 (d, J = 14.7 Hz, 1H), 1.45 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 155.5, 136.1, 134.3, 130.0, 129.6, 128.0, 127.7, 127.0, 126.5, 124.5, 122.7, 119.2, 115.8, 80.5, 78.9, 38.2, 36.7, 36.6, 28.3, 28.1. ***LC-MS*:** 462 (M+Na), 901 (2M+Na); ***Anal. calcd*** for ($C_{29}H_{29}NO_3$: 439.56): C, 79.24; H, 6.65, N, 3.19; Found: C, 79.03, H, 6.51, N, 3.11.

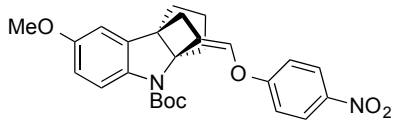


7ld. White solid. Yield = 80%; (*c*Hex:DCM = 95:5). ***Mp* =** 185-187 °C; ***^{1}H-NMR*** (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.8 Hz, 2H), 7.91 (bs, 1H) 7.20 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 1.8 Hz, 1H), 7.06 (d, J = 9.2 Hz, 2H), 6.98 (t, J = 7.6 Hz, 1H), 6.16 (bs, 1H), 2.81 (d, J = 16.0 Hz, 1H), 2.72 (d, J = 15.6 Hz, 1H), 2.21-2.50 (m, 3H), 1.98-1.87 (m, 1H), 1.74-1.65 (m, 1H), 1.57-1.52

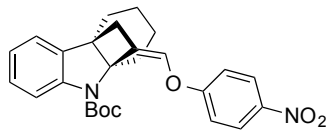
(m, 4H), 1.42 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 206.8, 162.3, 142.8, 136.2, 136.1, 135.9, 135.7, 128.1, 125.8, 123.8, 122.9, 116.8, 115.8, 80.6, 78.7, 36.6, 36.4, 30.9, 28.2, 28.1; ***LC-MS****:* 457 (M+Na). ***Anal. calcd*** for ($C_{25}H_{26}N_2O_5$: 434.49): C, 69.11; H, 6.03, N, 6.45; Found: C, 69.01, H, 6.66, N, 6.63.



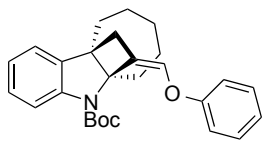
7ma: White oil. Yield = 72% (*c*Hex:DCM = 8:2). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.83 (bs, 1H), 7.28 (t, J = 8.0 Hz, 2H), 7.04-6.93 (m, 5H), 6.08 (bs, 1H), 2.76 (dd, J=2.4, 15.6 Hz, 1H), 2.65 (dd, J=1.6, 15.2 Hz, 1H), 2.29 (s, 3H), 2.22-1.88 (m, 4H), 1.71-1.51 (m, 2H), 1.43 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) 157.7, 138.4, 136.1, 132.1, 129.5, 128.4, 124.2, 122.8, 117.4, 115.5, 80.2, 78.9, 65.8, 38.1, 36.6, 36.5, 28.2, 28.1, 20.8, 15.2; ***LC-MS:*** 426 (M+Na), 442 (M+K), 829 (2M +Na). ***Anal. calcd*** for ($C_{26}H_{29}NO_3$: 403.52): C, 77.39; H, 7.24, N, 3.47; Found: C, 77.50, H, 7.11, N, 3.40.



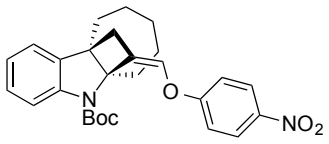
7nd. White oil. Yield = 77%. (*c*Hex:DCM = 95:5); ***^{1}H-NMR*** (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.8 Hz, 2H), 7.84 (bs, 1H), 7.04 (d, J = 8.8 Hz, 2H), 6.75-6.70 (m, 2H), 6.12 (bs, 1H), 3.77 (s, 3H), 2.82 (d, J = 16.0 Hz, 1H), 2.70 (d, J = 16.8 Hz, 1H), 2.19-2.03 (m, 3H), 1.93 (bs, 1H), 1.74-1.67 (m, 1H), 1.55 (s, 1H), 1.38 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 162.3, 155.9, 136.9, 136.3, 125.8, 117.0, 116.3, 112.6, 109.9, 78.9, 55.7, 36.4, 36.2, 31.9, 31.5, 30.2, 29.7, 28.3, 28.1, 26.9, 22.7. ***LC-MS****:* 487 (M+Na). ***Anal. calcd*** for ($C_{26}H_{28}N_2O_6$: 464.52): C, 67.23; H, 6.08, N, 6.03; Found: C, 67.02, H, 6.00, N, 6.21.



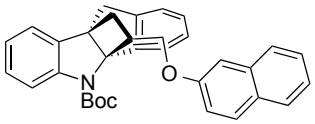
7pd. White solid. Yield = 77%. ***Mp*** **=** 171-174 °C; ***^{1}H-NMR*** (400 MHz, $CDCl_3$): δ 8.22 (d, J=9.2 Hz, 2H), 7.84 (bs, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.07 (d, J = 8.8 Hz, 3H), 6.96 (t, J = 7.2 Hz, 1H), 6.37 (s, 1H), 2.86-2.78 (m, 2H), 2.50 (d, J = 13.2 Hz, 1H), 2.38 (d, J = 13.2 Hz, 1H), 1.75-1.53 (m, 5H), 1.46 (s, 9H), 1.24-1.35 (m, 1H), 1.05 (t, J = 12.8 Hz, 1H), 0.87-0.84 (m, 1H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) 142.5, 134.6, 128.0, 125.9, 122.4, 116.3, 115.8, 81.0, 30.0, 29.7, 29.3, 28.6, 20.9, 20.7. ***LC-MS****:* 471 (M+Na). ***Anal. calcd*** for ($C_{26}H_{28}N_2O_5$: 448.52): C, 69.63; H, 6.29, N, 6.25; Found: C, 69.51, H, 6.12, N, 6.05.



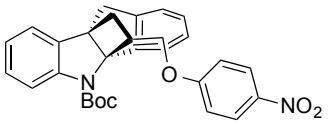
7qa. White oil. Yield = 71% (*c*Hex:DCM = 8:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 7.2 Hz, 2H), 7.19 (t, J = 8.4 Hz, 1H), 7.07-6.92 (m, 5H), 6.08 (t, , J= 2.0, 1H), 3.16 (m, 1H), 2.69 (dd, J = 2.0, 14.8, 1H), 2.61 (dd, J = 2.0, 14.8, 1H), 2.21-2.16 (m, 1H), 1.93 (t, J= 12.8 Hz, 2H), 1.71-1.51 (m, 4H), 1.42 (s, 9H), 1.35-1.24 (m, 2H), 0.98-0.84 (m, 1H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$): 157.7, 145.3, 137.3, 136.5, 129.4, 127.7, 122.6, 122.5, 122.4, 117.1, 116.0, 80.7, 39.1, 36.3, 32.4, 31.5, 29.6, 28.3, 25.6, 24.5; ***LC-MS:*** 440 (M+Na), 857 (2M+Na); ***Anal. calcd*** for ($C_{27}H_{31}NO_3$: 417.55): C, 77.67; H, 7.48, N, 3.35; Found: C, 77.86, H, 7.22, N, 3.41.



7qd. White solid. Yield = 87%. (*c*Hex:DCM = 95:5) ***Mp*** **=** 73-75 °C; ***[1]H-NMR*** (400 MHz, $CDCl_3$): δ 8.16 (d, J = 9.2 Hz, 2H), 7.81(1H, bs), 7.18 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 7.00 (d, J = 8.8 Hz, 3H), 6.10 (bs, 1H), 3.12-3.07 (m, 1H), 2.70 (dd, J = 14.0, 15.2 Hz, 1H), 2.23-2.18 (m, 1H), 1.95-1.89 (m, 2H), 1.68-1.59 (m, 3H), 1.40 (s, 9H), 1.31-1.16 (m, 3H), 0.97-0.89 (m, 1H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 162.4, 144.8, 142.6, 136.12, 134.91, 127.9, 126.7, 125.7, 122.7, 122.7, 116.4, 116.1, 80.9, 53.5, 52.8, 38.9, 36.4, 32.0, 31.5, 30.9, 28.3, 26.9, 25.5, 24.5; ***LC-MS****:* 485 (M+Na), 947 (2M+Na). ***Anal. calcd*** for ($C_{27}H_{30}N_2O_5$: 462.55): C, 70.11; H, 6.54, N, 6.06; Found: C, 70.31, H, 6.76, N, 6.20.



7ub. Pale yellow solid. Yield = 74%; (*c*Hex:EtOAc = 95:5). ***Mp*** **=** 84-86 °C ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 8.27 (bs, 1H), 7.75 (t, J = 9.2 Hz, 3H), 7.66 (d, J = 8.4 Hz, 1H), 7.44-7.33 (m, 3H), 7.23-7.16 (m, 4H), 7.01 (t, J = 7.2 Hz, 1H), 6.30 (t, J=2.0 Hz, 1H), 3.41 (s, 2H), 3.11 (dd, J = 2.0, 14.8 Hz, 1H), 2.90 (dd, J = 1.6, 14.4 Hz, 1H), 1.50 (s, 9H). ***[13]C-NMR*** (100MHz, $CDCl_3$): 155.4, 145.7, 141.19, 136.0, 134.2, 129.9, 129.4, 128.6, 128.1, 127.6, 127.0, 126.7, 126.4, 125.14, 124.3, 122.9, 119.1, 116.6, 81.6, 43.4, 38.4, 28.6. ***LC-MS*****:** 510 (M+Na), 997 (2M+Na). ***Anal. calcd*** for ($C_{33}H_{29}NO_3$: 487.60): C, 81.29; H, 6.00, N, 2.87; Found: C, 81.13, H, 6.21, N, 2.71.

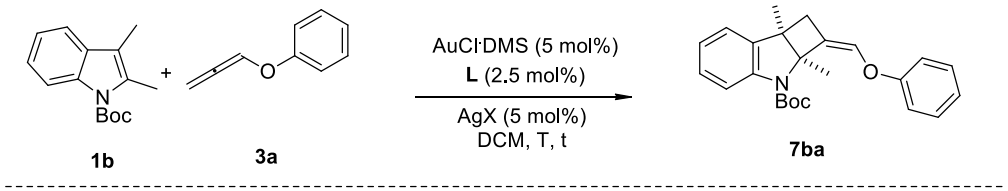


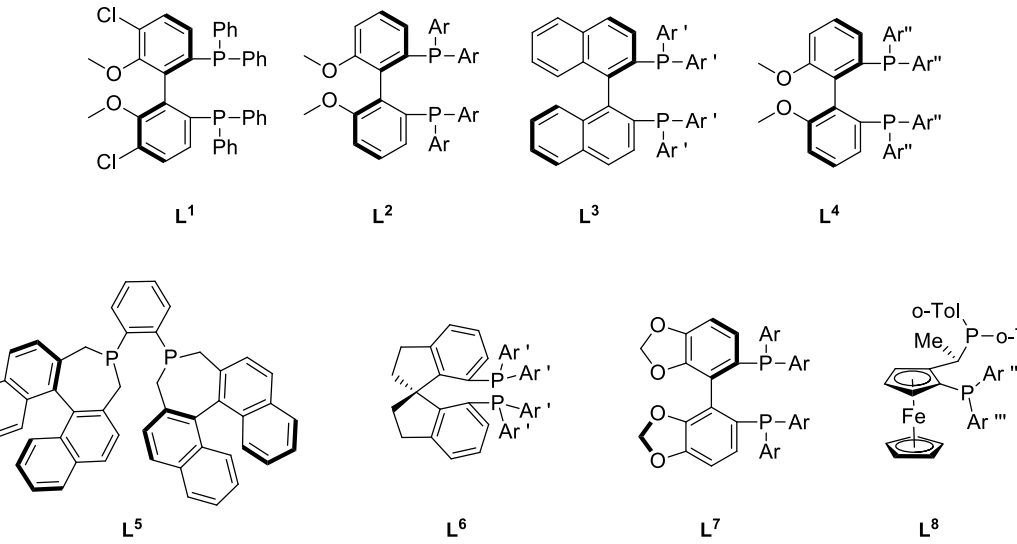
7ud. White oil. Yield = 50%. ***[1]H-NMR*** (400 MHz, $CDCl_3$): δ 8.09 (d, J = 9.2 Hz, 3H), 7.58(bs, 1H), 7.18-7.09 (m, 5H), 6.96-6.89 (m, 3H), 6.14 (t, J= 2.0 Hz, 1H), 3.34 (s, 2H), 3.05 (dd, J = 2.0, 15.2 Hz, 1H), 2.85 (dd, J = 2.0, 15.2 Hz, 1H), 1.50 (s, 9H). ***[13]C-NMR*** (100 MHz, $CDCl_3$): 162.3, 145.6, 140.6, 135.7, 135.1, 128.8, 128.2, 126.9, 125.7, 125.2, 123.9, 123.0, 116.4, 116.2, 81.6, 43.4, 38.3, 29.7, 28.5, 14.2. ***LC-MS****:* 505 (M+Na), 987 (2M+Na). ***Anal. calcd*** for ($C_{29}H_{26}N_2O_5$: 482.54): C, 72.19; H, 5.43, N, 5.81; Found: C, 72.01, H, 5.26, N, 5.61.

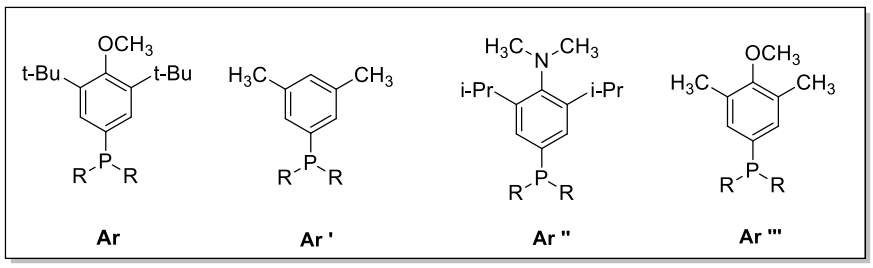
General procedure for the enantioselective [2+2]-cycloaddition reaction.

Under nitrogen atmosphere, AuCl·DMS (1.5 mg, 5 mol%) and (*R*)-DTBM-Segphos (3.0 mg, 2.5 mol%) were dissolved in CH_2Cl_2 (0.5 mL), the solution was stirred at room temperature for 20 min. Then the CH_2Cl_2 was evaporated under reduced pressure, and leave the complex under high vacuum for 20 min. Then, CH_2Cl_2 (1.0 mL) was added and the solution was protected from light by aluminium foil. $AgNTf_2$ (1.9 mg, 5 mol%) was added and the solution was stirred at room temperature for 20 min. Then the mixture was cooled to -20 °C, then substrate **1** (0.1 mmol), and **3** (0.2 mmol) were added in sequence and the mixture stirred at the same temperature for 16 h. Removed the solvent under reduced pressure and the crude was purified by flash column chromatography to give the desired product.

Table S1: Screening of reaction conditions for the enantioselective dearomative cycloaddition of **1b** with **3a**.[a]







Entry	L	AgX	T (°C)	Time (h)	Y %[b]	ee %[c]
1	(*R*)-**L1**	AgOTf	0	5	11	11
2	(*R*)-**L2**	AgOTf	0	5	26	50
3	(*R*)-**L3**	AgOTf	0	5	19	52

4	(*R*)-**L4**	AgOTf	0	5	ND	/
5	(*R*,*R*)-**L5**	AgOTf	0	5	ND	/
6	(*R*)-**L6**	AgOTf	0	5	ND	/
7	(*R*)-**L7**	AgOTf	0	5	60	82
8	(R,S_p)-**L8**	AgOTf	0	5	30	24
9	(*R*)-**L7**	AgOTf	-20	16	72	85
10	(*R*)-**L7**	$AgN(Tf)_2$	0	5	61	84
11	(*R*)-**L7**	$AgN(Tf)_2$	-20	16	35	93
12	(*R*)-**L1**	$AgN(Tf)_2$	0	5	51	11
13	(*R*)-**L2**	$AgN(Tf)_2$	0	5	26	50
14	(*R*)-**L3**	$AgN(Tf)_2$	0	5	19	52
15	(*R*)-**L4**	$AgN(Tf)_2$	0	5	4	/
16	(*R*,*R*)-**L5**	$AgN(Tf)_2$	0	5	/	/
17	(*R*)-**L6**	$AgN(Tf)_2$	0	5	/	/
18	(R,S_p)-**L8**	$AgN(Tf)_2$	0	5	30	24

[a] All reactions were carried out under nitrogen atmosphere in anhydrous solvents (**1b**:**3a**:cat = 1:2:0.05). [b] After flash chromatography (cHex:DCM: 8:2). [c] Determined by HPLC with chiral column. ND = not determined.

(+)-7ba: Yield = 35%, Ee = 93%, $[\alpha]_D$ = +107 °, (*c* = 2.1, $CHCl_3$). ***HPLC:*** AMY-2 98:2 Hex:iPrOH 0.5 mL/min, 40 °C: 9.40 min, 10.31 min.

(+)-7bf: Yield = 65%, Ee = 81%, $[\alpha]_D$ = +100 °, (*c* = 1.4, $CHCl_3$). ***HPLC***: AD, 97.5:2.5 Hex:iPrOH 0.5 mL/min, rt: 7.99 min, 9.27 min.

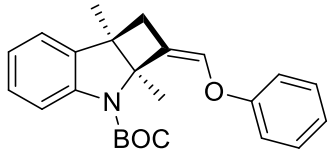
(+)-7ea: Yield = 56%, Ee = 92%, $[\alpha]_D$ = +141°, (*c* = 1.8, $CHCl_3$). ***HPLC*:** AD, 97:3 Hex:iPrOH 0.5 mL/min 40 °C: 8.25 min, 12.21 min.

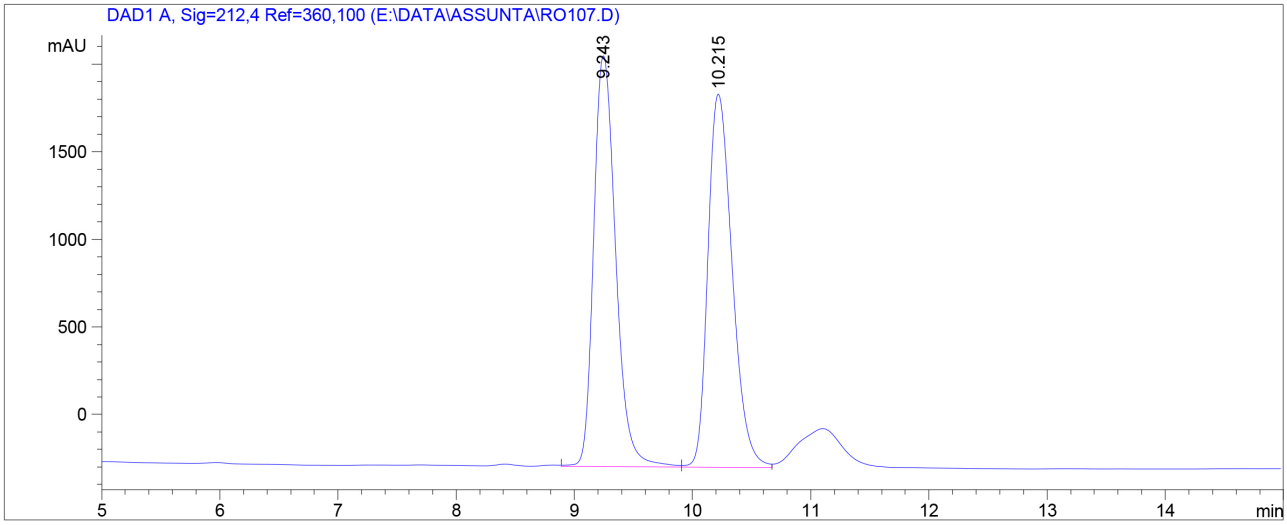
(+)-7la: Yield = 57%, Ee = 87%, $[\alpha]_D$ = +107 °, (*c* = 1.1, $CHCl_3$). ***HPLC***: Amy-2, 95:5 Hex:iPrOH 0.5 mL/min, 40 °C: 9.61 min, 10.79 min.

(+)-7qa: Yield = 73%, Ee = 84%, $[\alpha]_D$ = +110 °, (*c* = 2.9, $CHCl_3$). ***HPLC*:** AD, 90:10 Hex:iPrOH 0.5 mL/min, 40 °C: 6.89 min, 7.62 min.

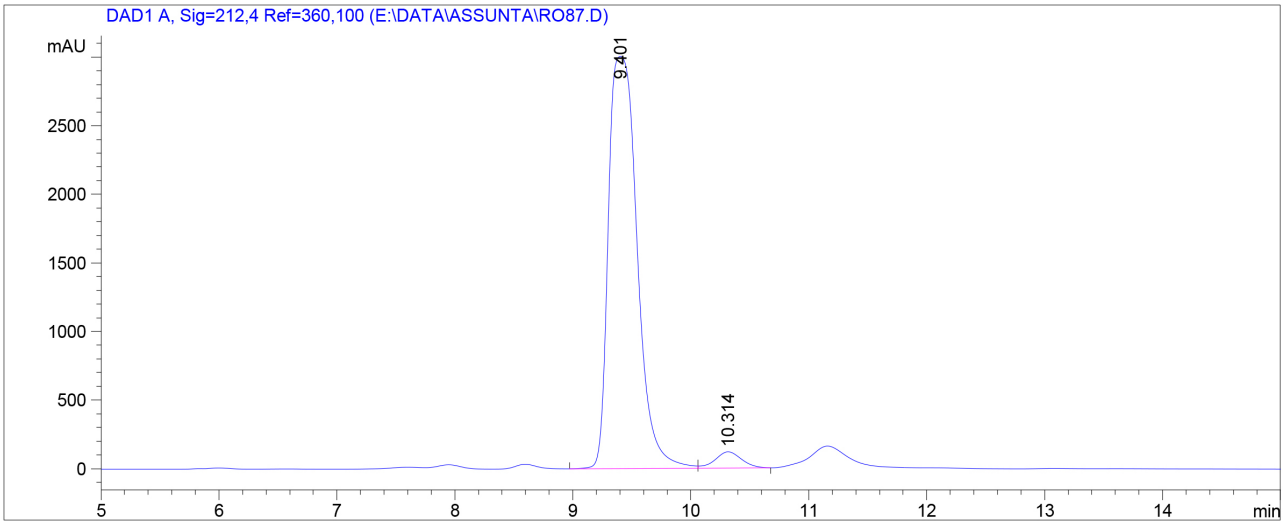
HPLC Spectra

7ba



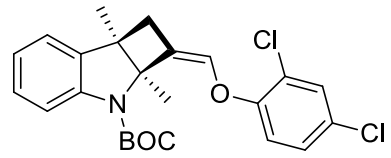


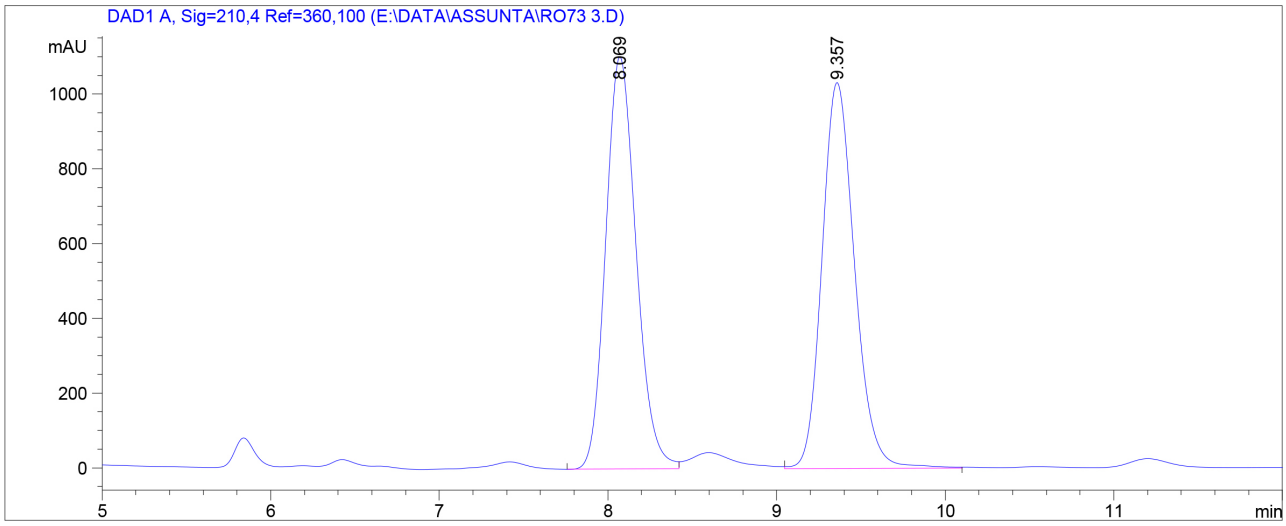
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.243	VV	0.2013	3.04550e4	2347.72876	49.9793
2	10.215	VV	0.2228	3.04803e4	2132.29761	50.0207



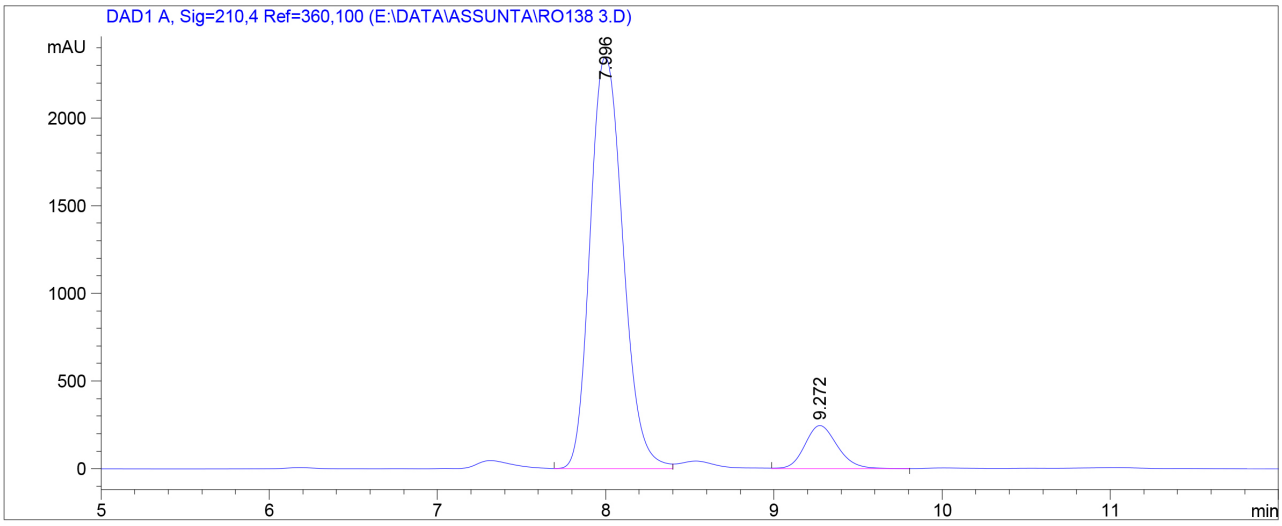
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.401	BV	0.2675	5.08919e4	3006.32739	96.3453
2	10.314	VV	0.2423	1930.49866	120.88380	3.6547

7bf



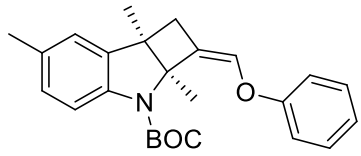


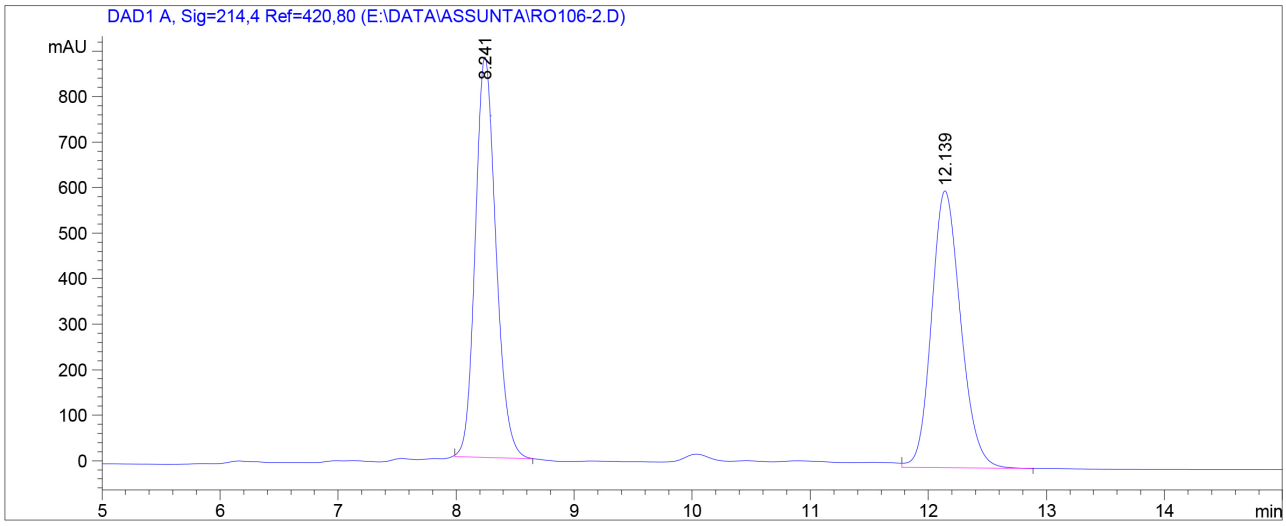
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.069	VV	0.1943	1.38430e4	1103.54529	49.9135
2	9.357	VB	0.2089	1.38910e4	1032.68604	50.0865



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.996	VV	0.2126	3.19308e4	2349.56616	90.4711
2	9.272	VB	0.2088	3363.11304	247.03429	9.5289

7ea





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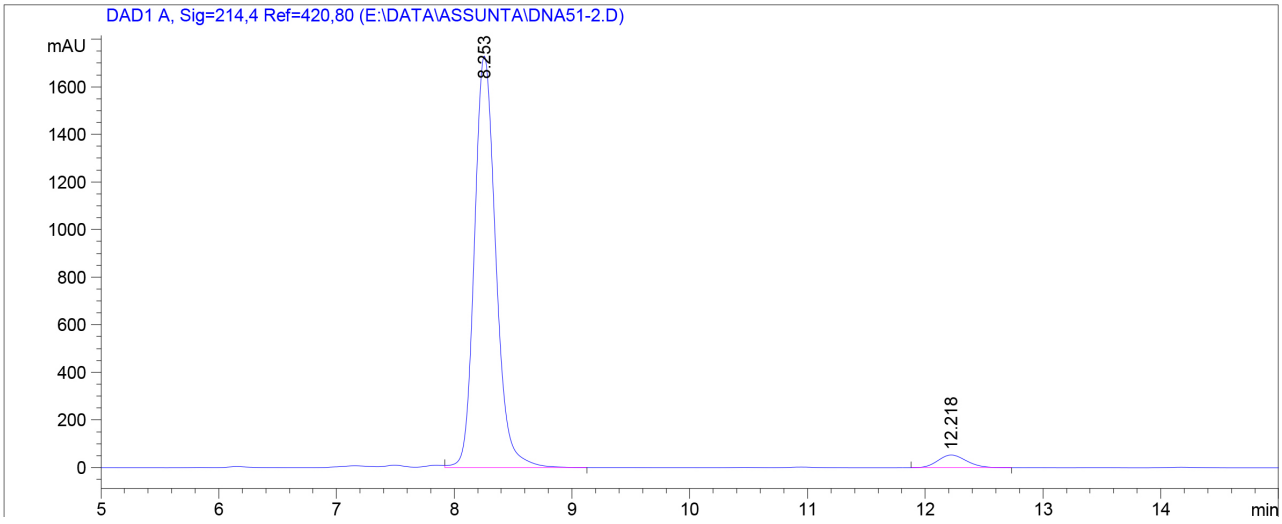
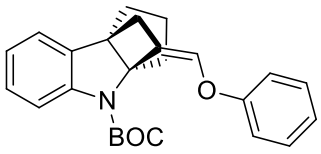
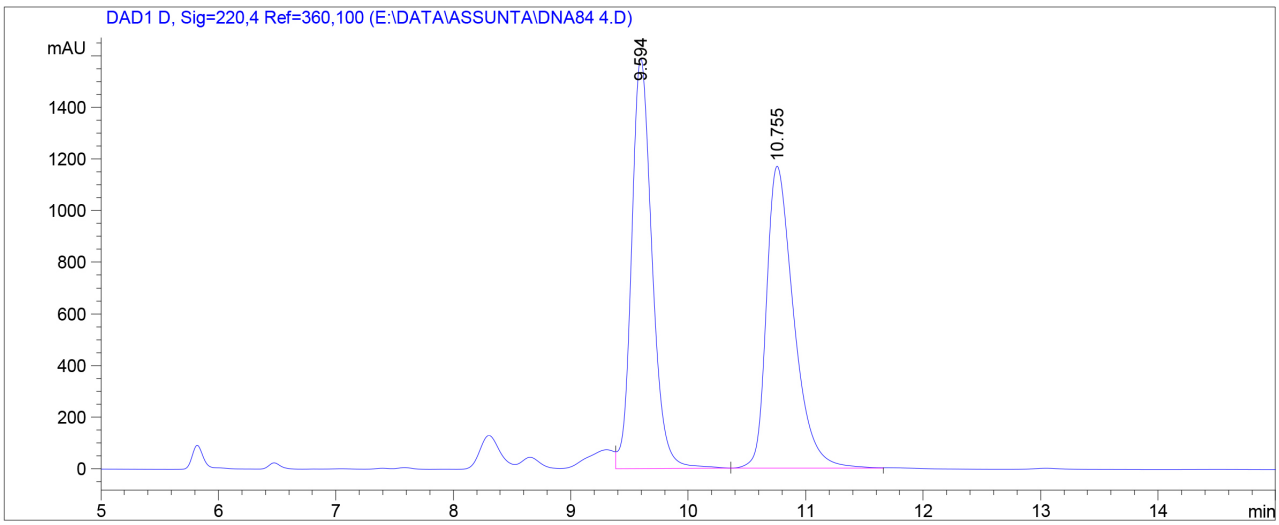
1	8.241	MM	0.2027	1.07128e4	880.80573	50.5316
2	12.139	VB	0.2648	1.04874e4	609.31415	49.4684



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.253	VB	0.1952	2.18313e4	1730.37183	95.9512
2	12.218	BB	0.2639	921.21088	53.75893	4.0488

7la





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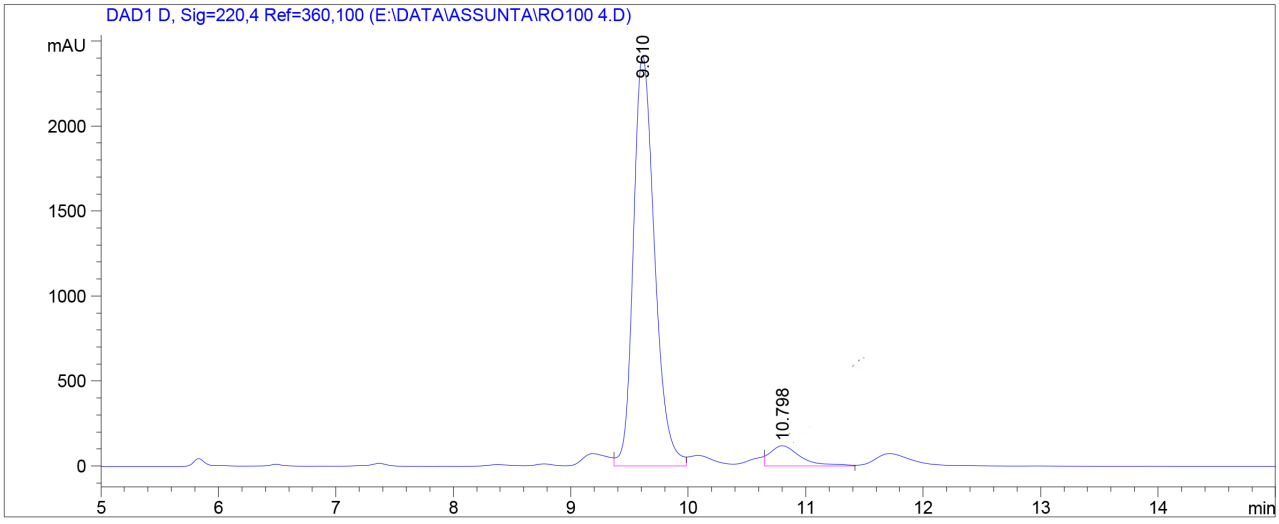
1	9.594	VV	0.1858	1.93439e4	1591.57739	50.5108
2	10.755	VB	0.2448	1.89526e4	1171.01929	49.4892



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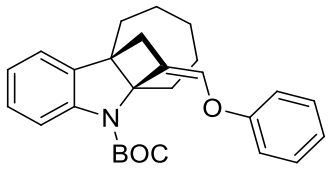
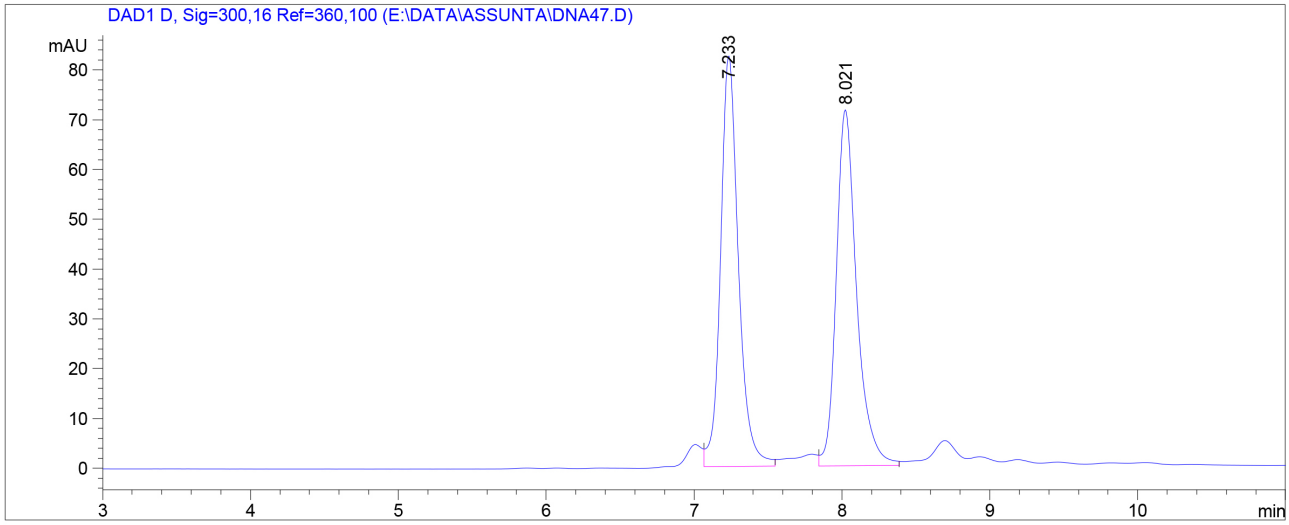
1	9.610	VV	0.1927	3.03885e4	2416.20410	93.2866
2	10.798	FM	0.3042	2186.92261	119.83054	6.7134

7qa





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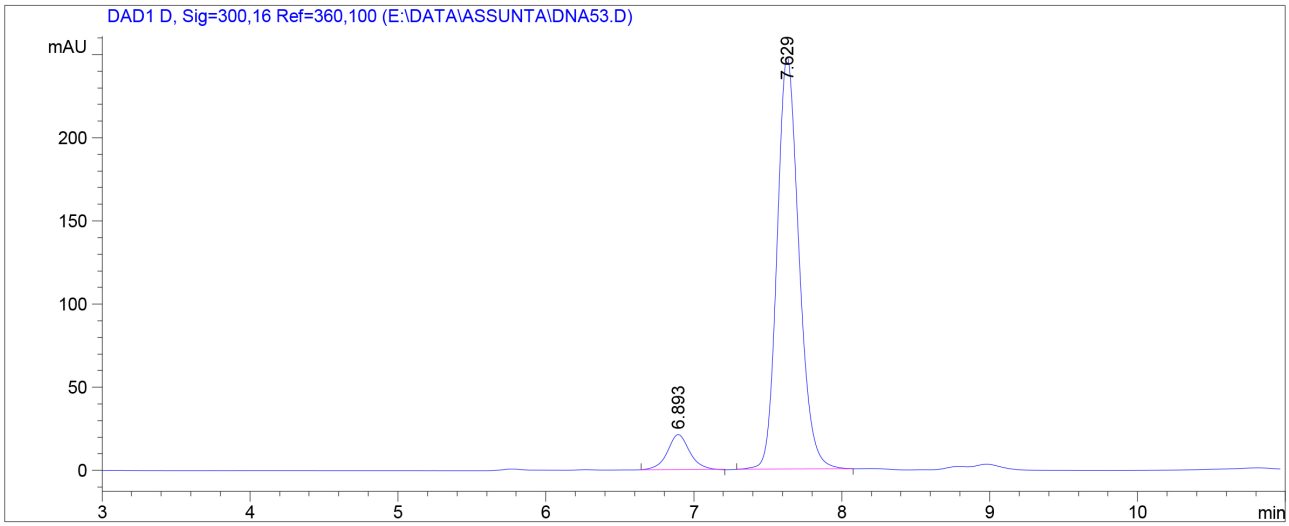
1	8.801	VV	0.1918	2.34371e4	1901.92725	49.5024
2	9.574	VV	0.2256	2.39083e4	1625.55518	50.4976



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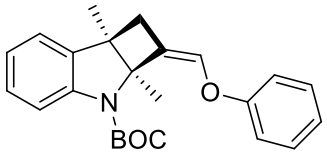
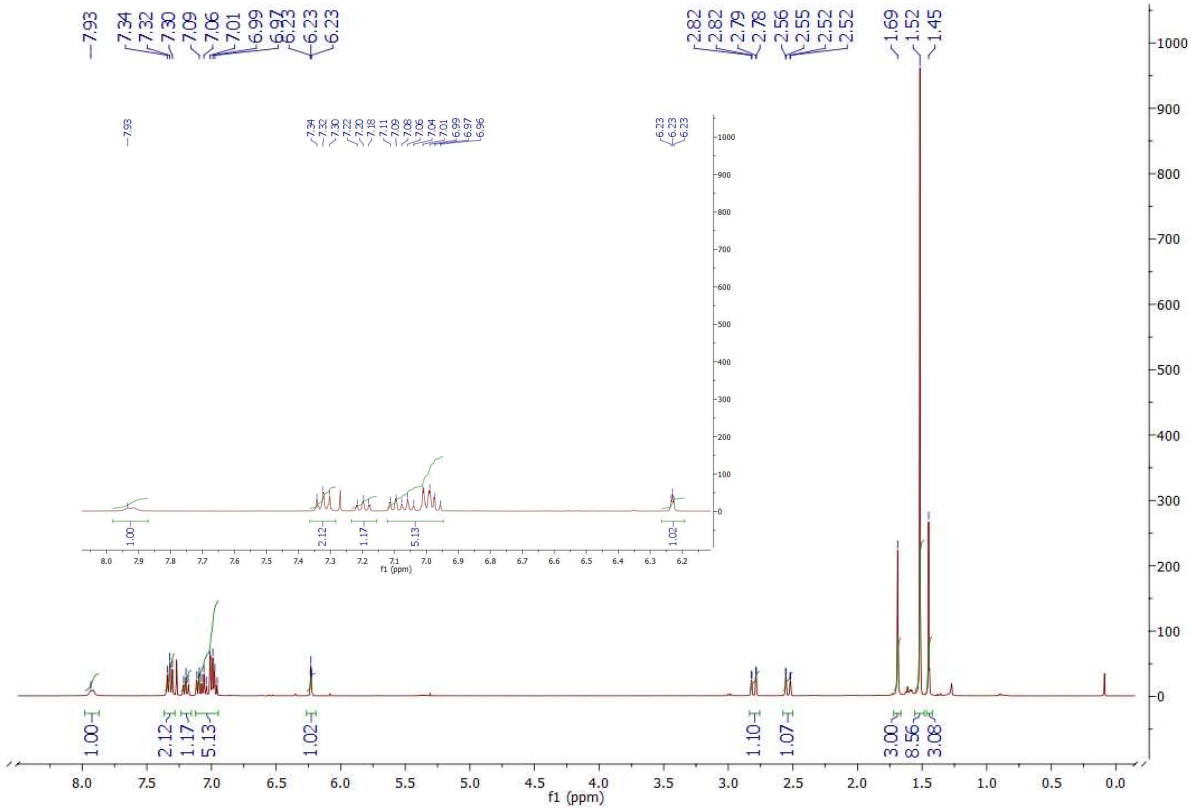
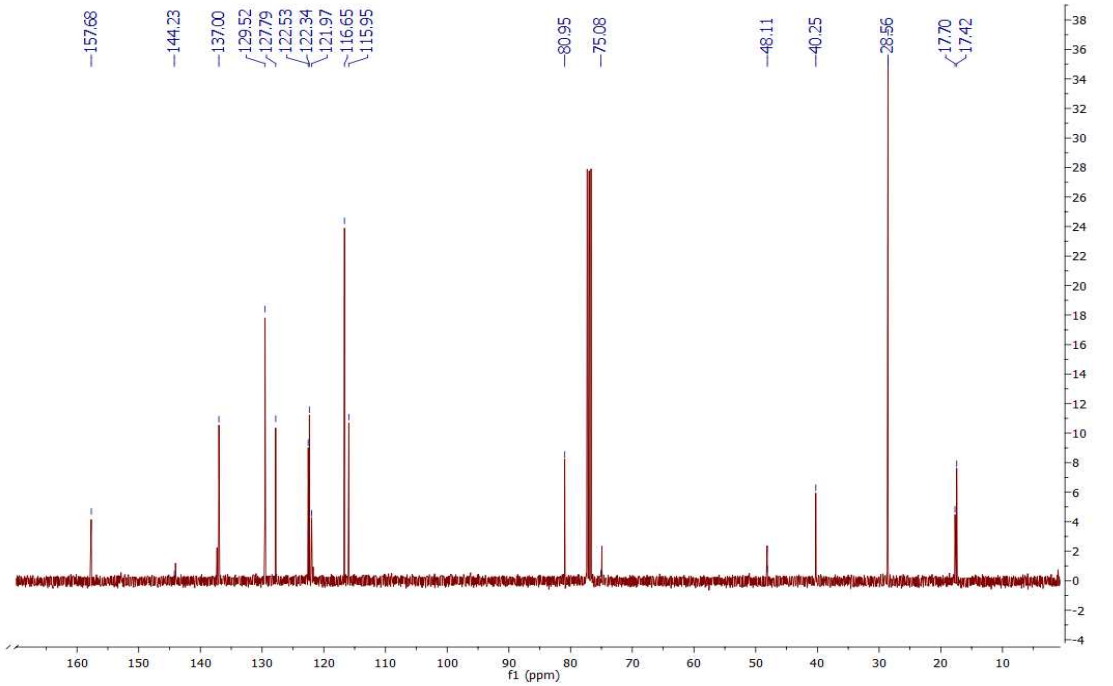
1	6.893	BB	0.1592	223.92596	21.19970	8.0655
2	7.629	BB	0.1581	2552.40137	247.86354	91.9345

NMR spectra

7ba







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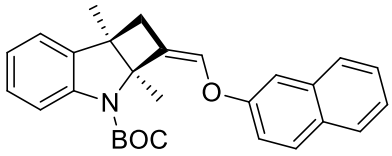
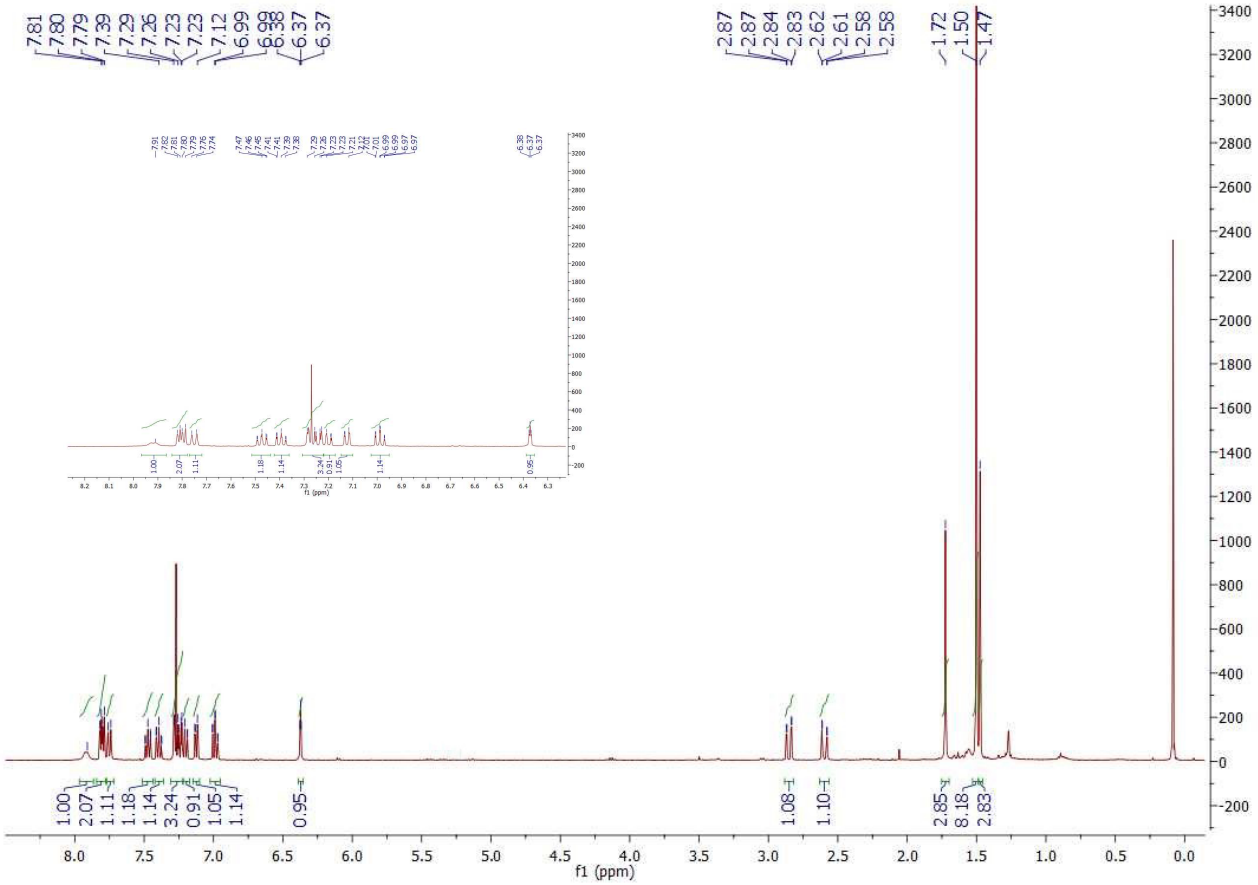

N
BOC
O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7.29
7.26
7.23
7.23
7.12
6.99
6.98
6.37
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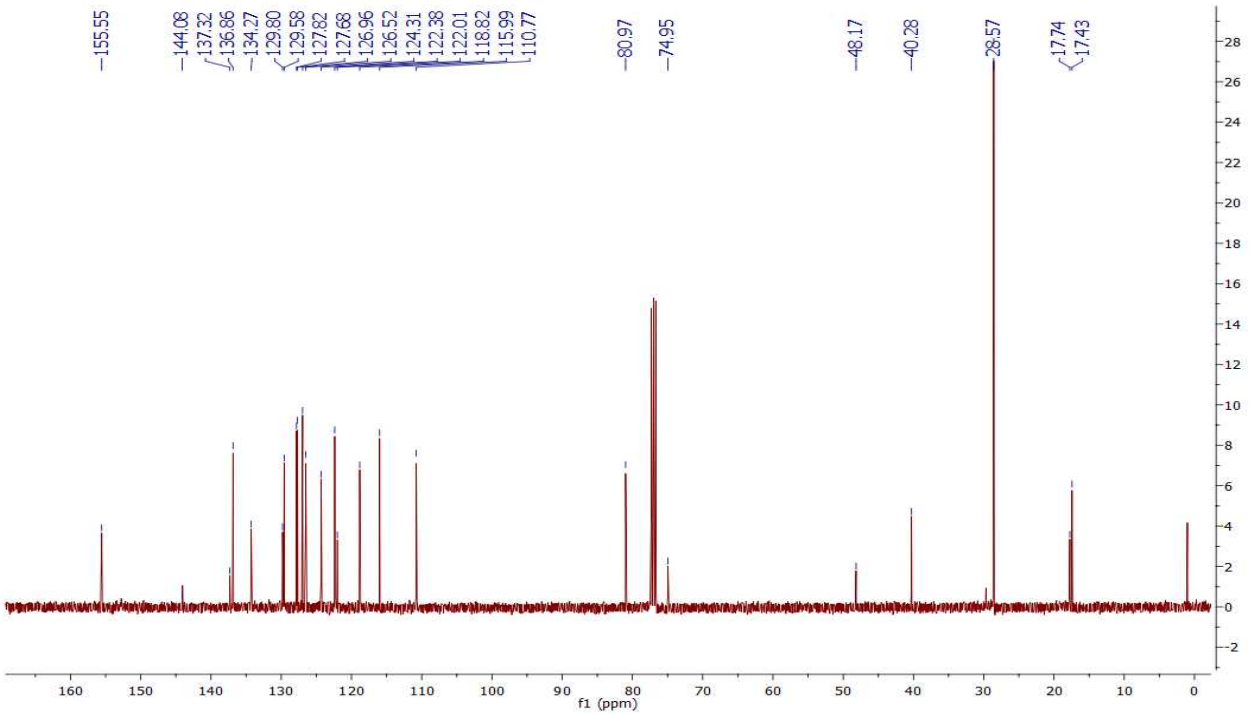
2.87
2.87
2.84
2.83
2.62
2.61
2.58
2.58
1.72
1.50
1.47
1.00
2.07
1.11
1.18
1.14
3.24
0.91
1.05
1.14
0.95
1.08
1.10
2.85
8.18
2.83
f1 (ppm)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129.58
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126.52
124.31
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122.01
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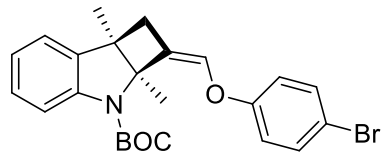
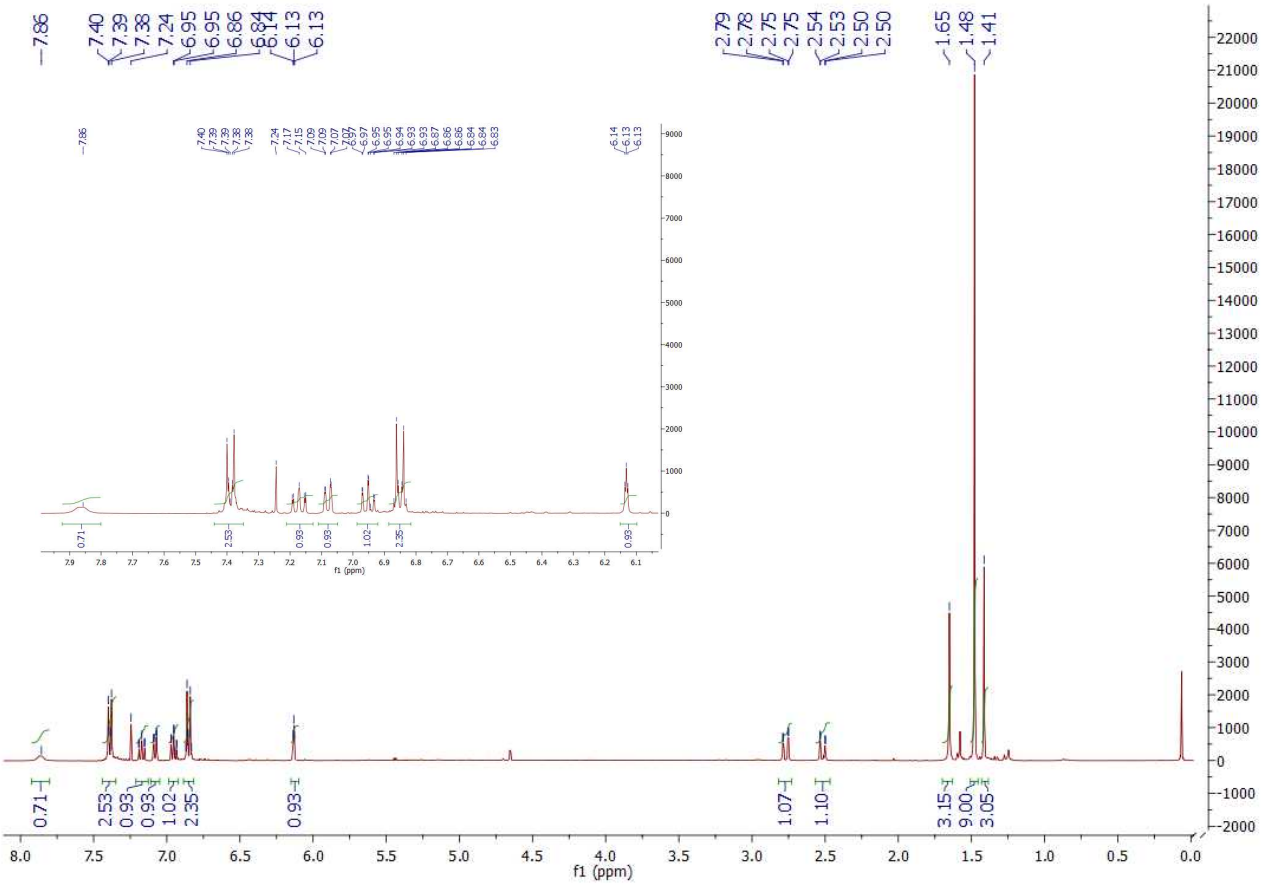
28.57
17.74
17.43
f1 (ppm)

7bc


N
BOC
O
Br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7.24
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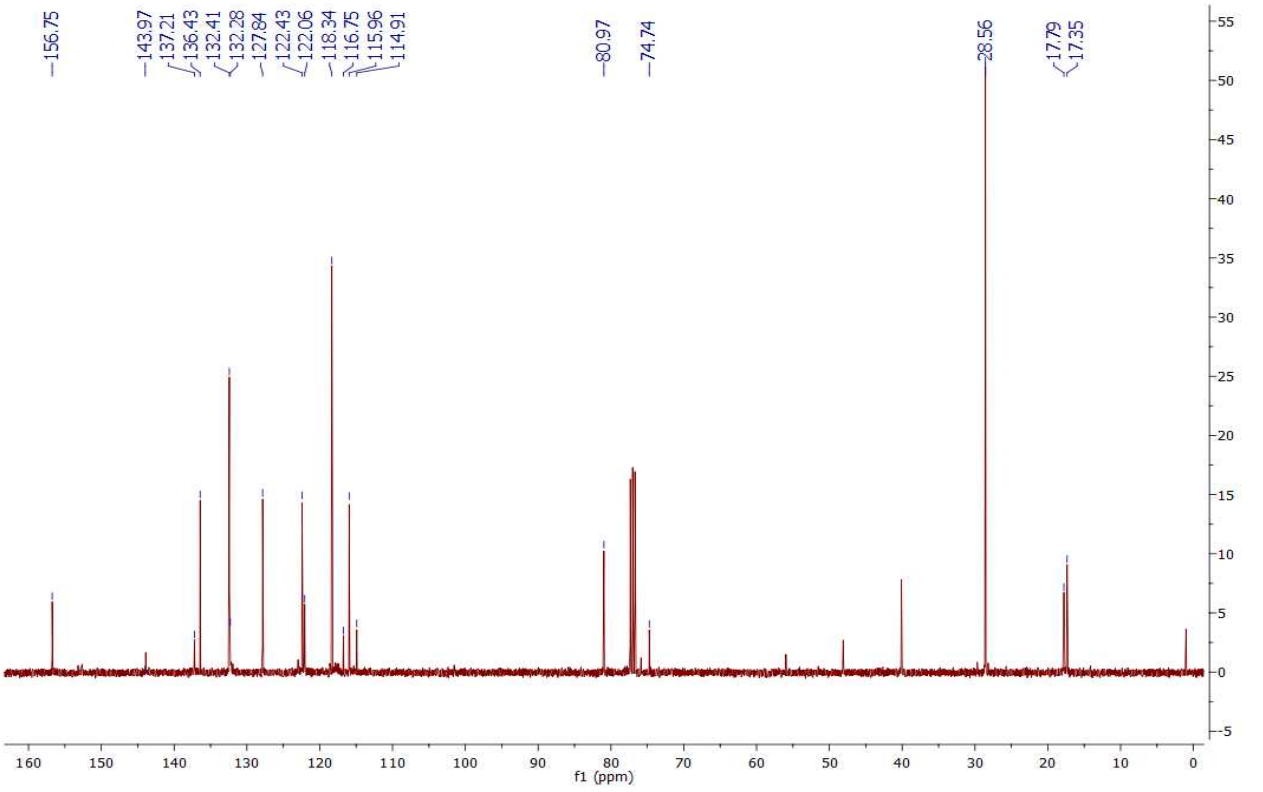
6.86
6.84
6.14
6.13
2.79
2.78
2.75
2.54
2.53
2.50
1.65
1.48
1.41
0.71
2.53
0.93
0.93
1.02
2.35
0.93
1.07
1.10
3.15
9.00
3.05
f1 (ppm)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132.28
127.84
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122.06
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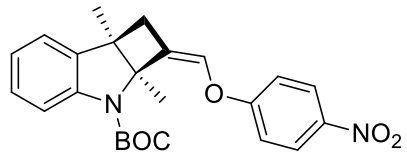
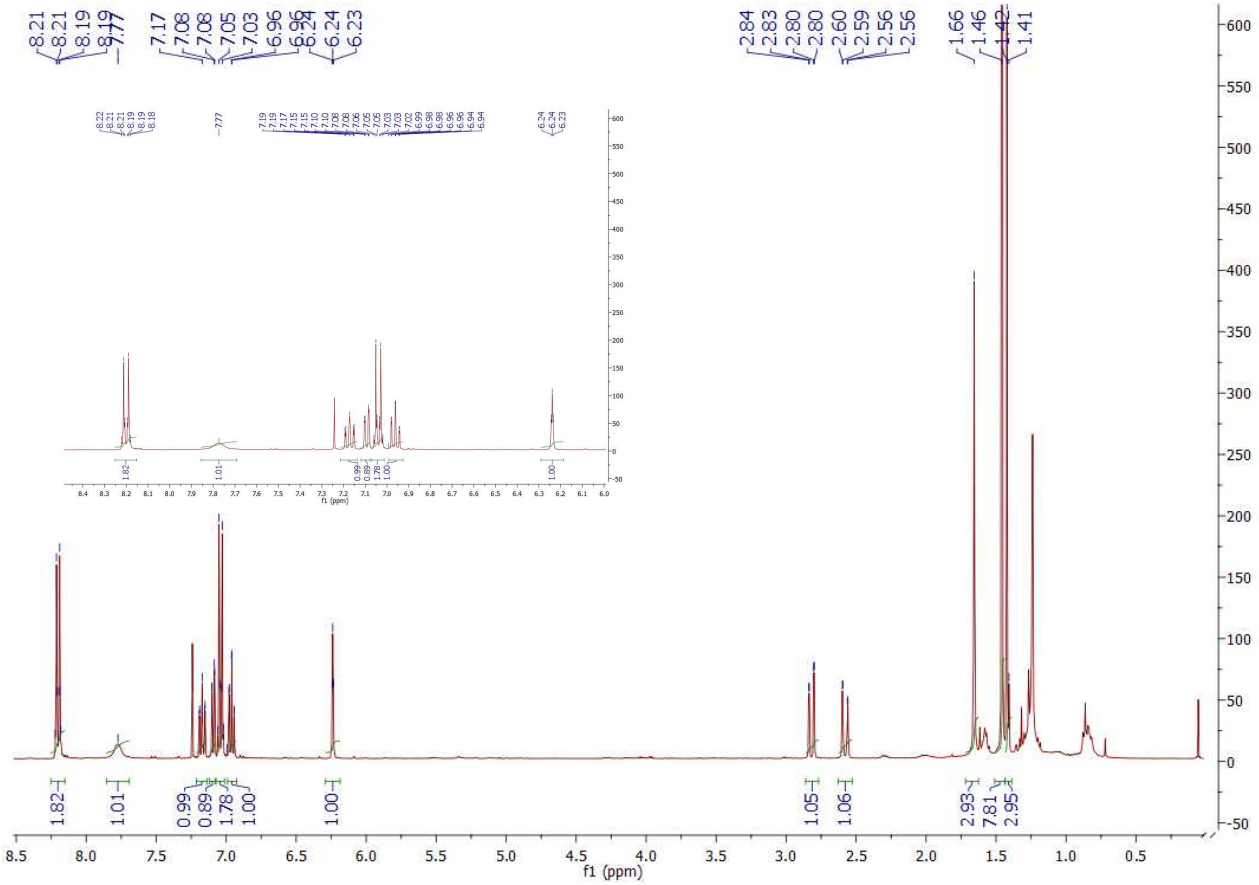
28.56
17.79
17.35
f1 (ppm)

7bd


N
BOC
O
NO2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7.08
7.08
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7.03
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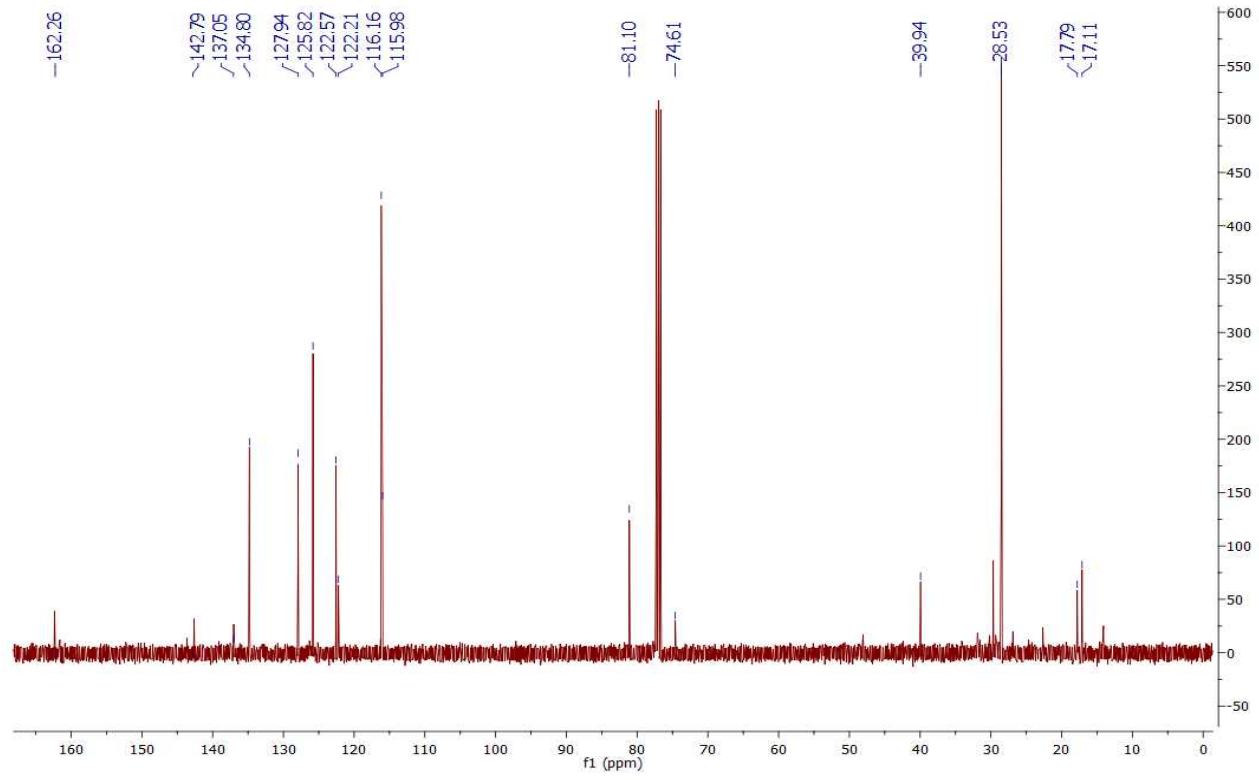
2.80
2.80
2.60
2.59
2.56
2.56
1.66
1.46
1.42
1.41
1.82
1.01
0.99
0.89
1.78
1.00
1.00
1.05
1.06
2.93
7.81
2.95
f1 (ppm)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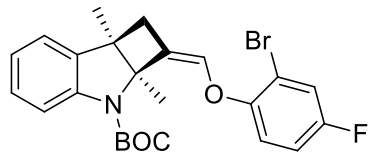
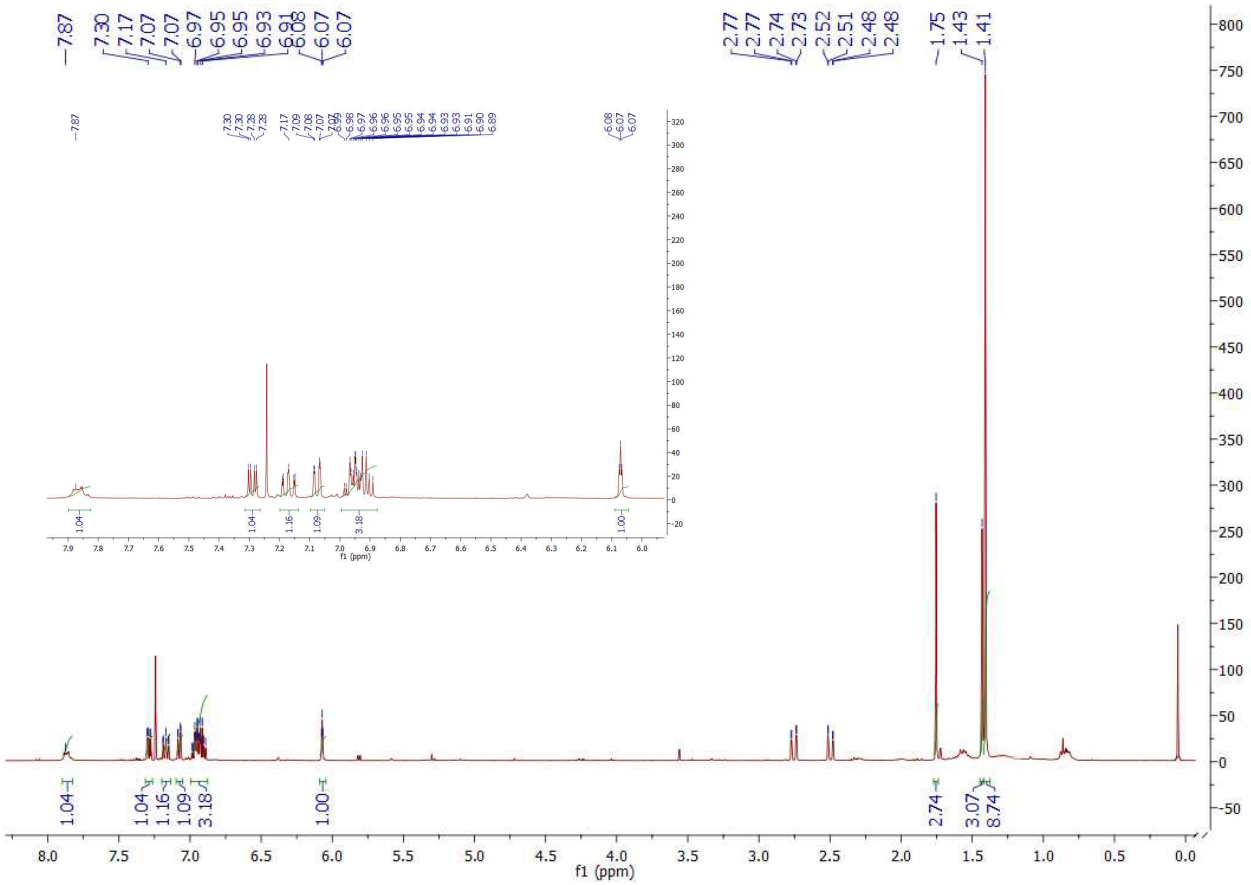
17.79
17.11
f1 (ppm)

7be


Br
O
N
BOC
F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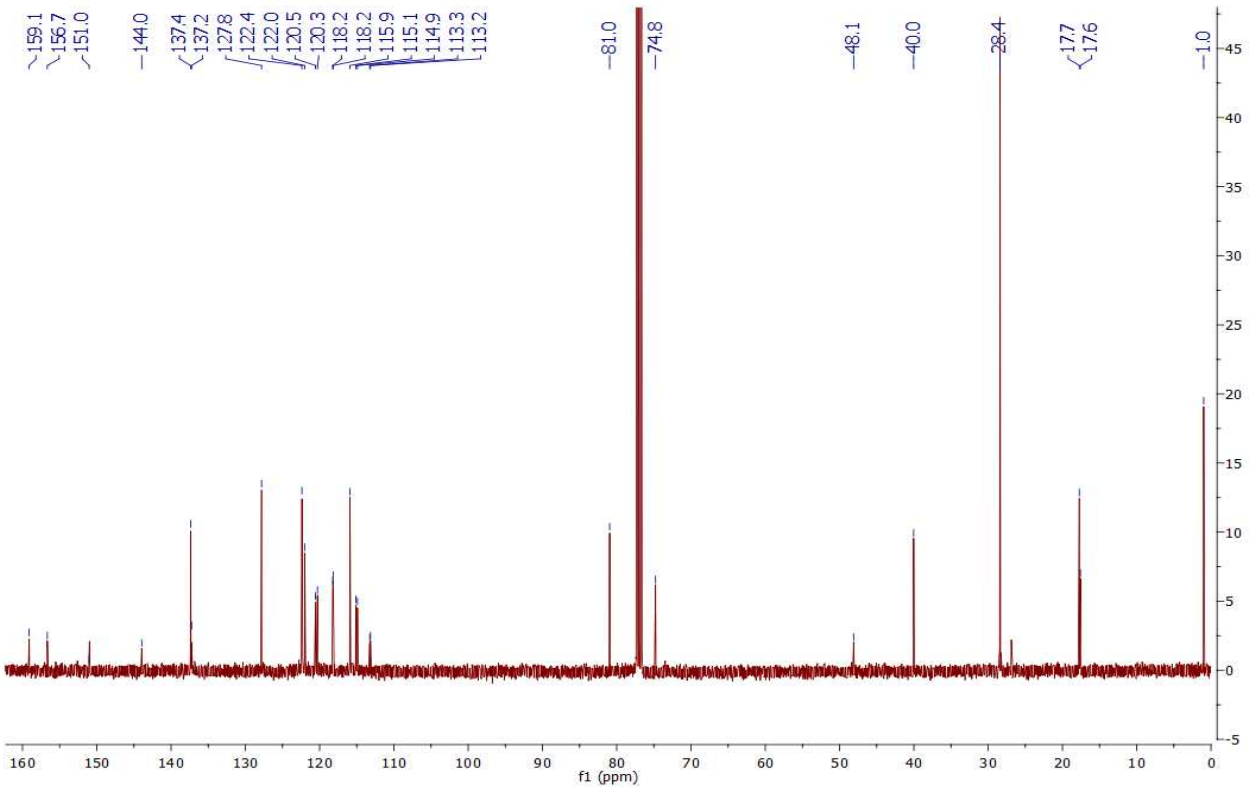
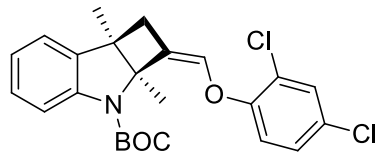
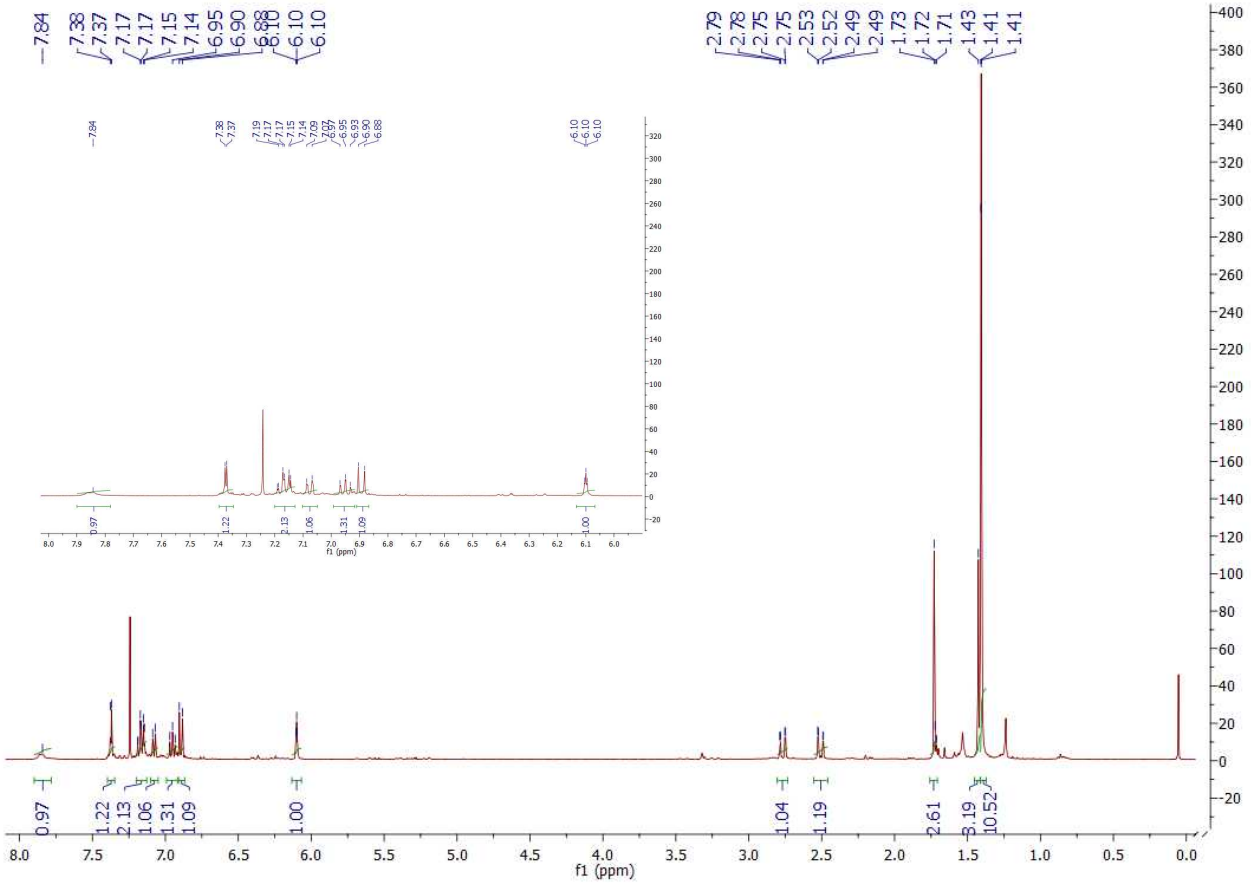
7.17
7.07
7.07
6.97
6.95
6.93
6.91
6.08
6.07
6.07
2.77
2.77
2.74
2.73
2.52
2.51
2.48
2.48
1.75
1.43
1.41
1.04
1.04
1.16
1.09
3.18
1.00
2.74
3.07
8.74
f1 (ppm)


159.1
156.7
151.0
144.0
137.4
137.2
127.8
122.4
122.0
120.5
120.3
118.2
118.2
115.9
115.1
114.9
113.3
113.2
81.0
74.8
48.1
40.0
28.4
17.7
17.6
-1.0
f1 (ppm)

7bf


Cl
O
N
BOC
Cl


7.84
7.38
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7.17
7.15
7.14
6.95
6.90
6.88
6.10
6.10
2.79
2.78
2.75
2.75
2.53
2.52
2.49
2.49
1.73
1.72
1.71
1.43
1.41
1.41
0.97
1.22
2.13
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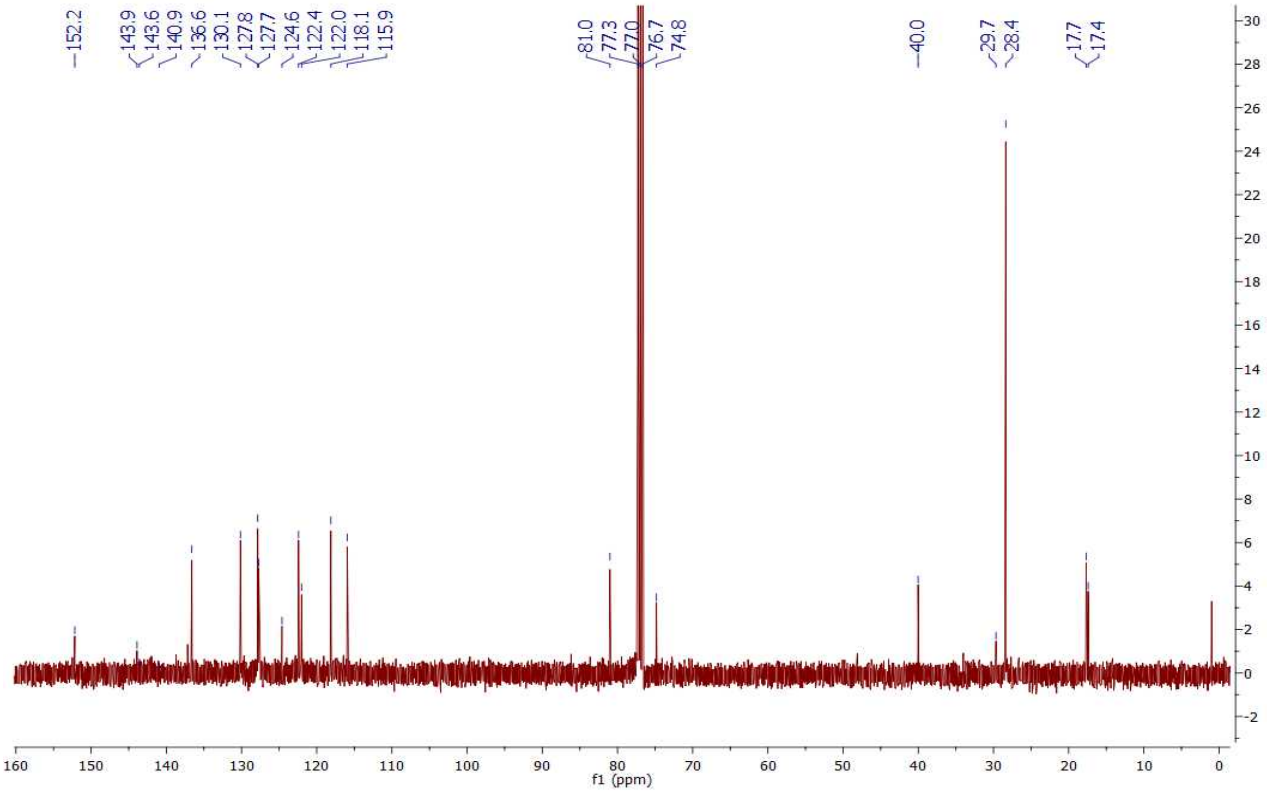
1.31
1.09
1.00
1.04
1.19
2.61
3.19
10.52
f1 (ppm)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143.9
143.6
140.9
136.6
130.1
127.8
127.7
124.6
122.4
122.0
118.1
115.9
81.0
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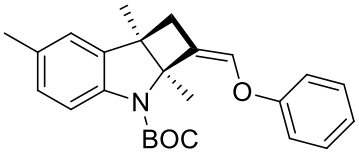
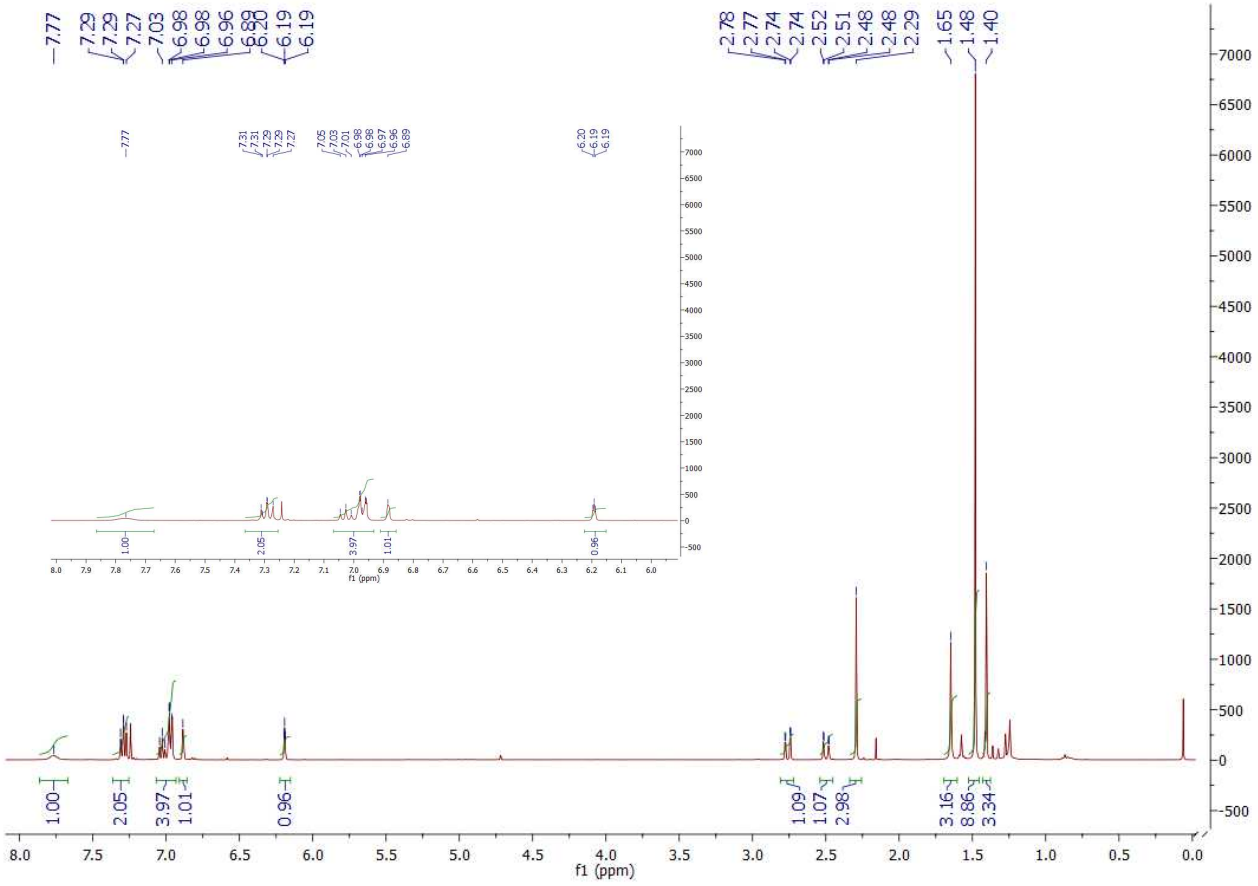
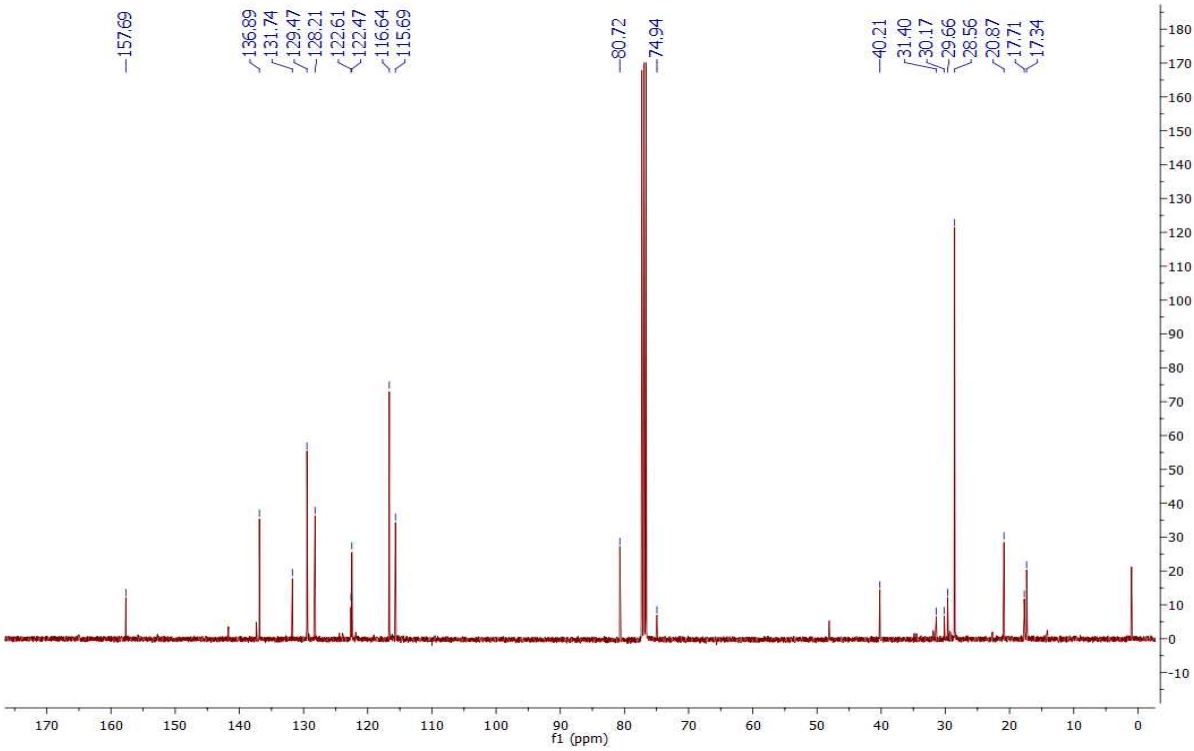
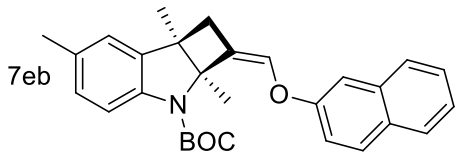
77.0
76.7
74.8
40.0
29.7
28.4
17.7
17.4
f1 (ppm)

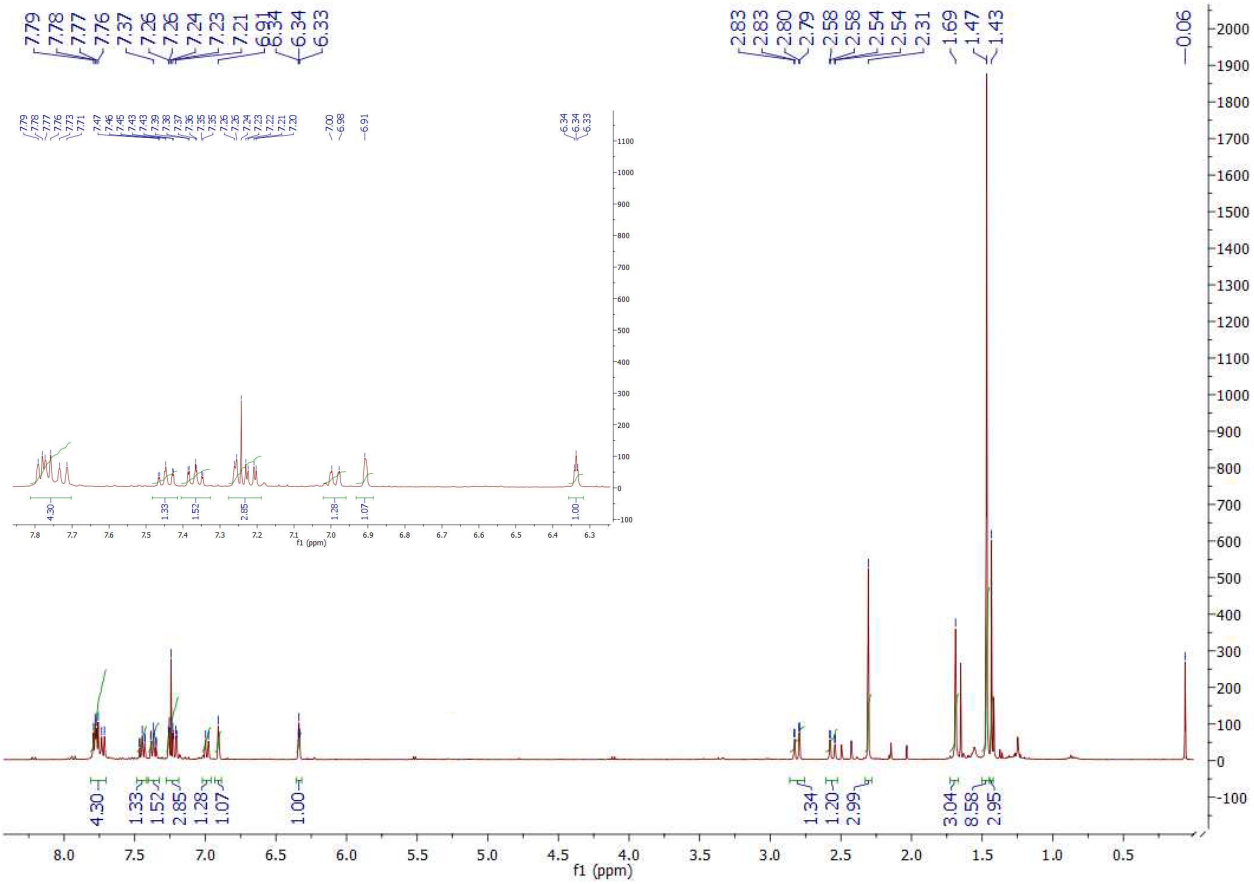
7ea

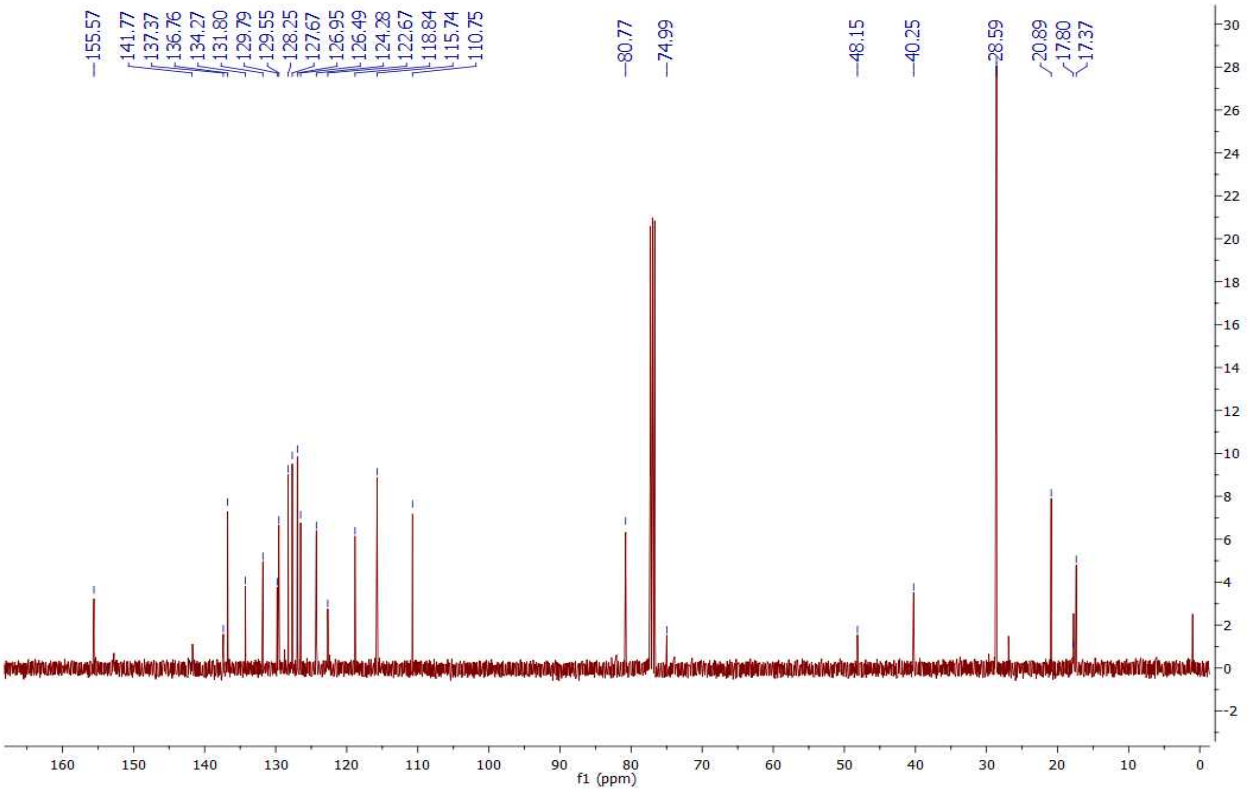

N
BOC
O


7.77
7.29
7.29
7.27
7.03
6.98
6.98
6.96
6.89
6.20
6.19
6.19
2.78
2.77
2.74
2.74
2.52
2.51
2.48
2.48
2.29
1.65
1.48
1.40
1.00
2.05
3.97
1.01
0.96
1.09
1.07
2.98
3.16
8.86
3.34
f1 (ppm)


157.69
136.89
131.74
129.47
128.21
122.61
122.47
116.64
115.69
80.72
74.94
40.21
31.40
30.17
29.66
28.56
20.87
17.71
17.34
f1 (ppm)


7eb
N
BOC
O


7.79
7.78
7.77
7.76
7.37
7.26
7.26
7.24
7.23
7.21
6.34
6.34
6.33
2.83
2.83
2.80
2.79
2.58
2.58
2.54
2.54
2.31
1.69
1.47
1.43
0.06
4.30
1.33
1.52
2.85
1.28
1.07
1.00
1.34
1.20
2.99
3.04
8.58
2.95
f1 (ppm)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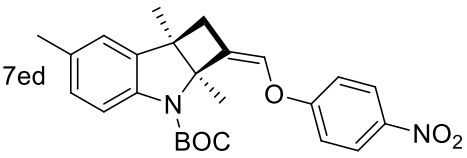
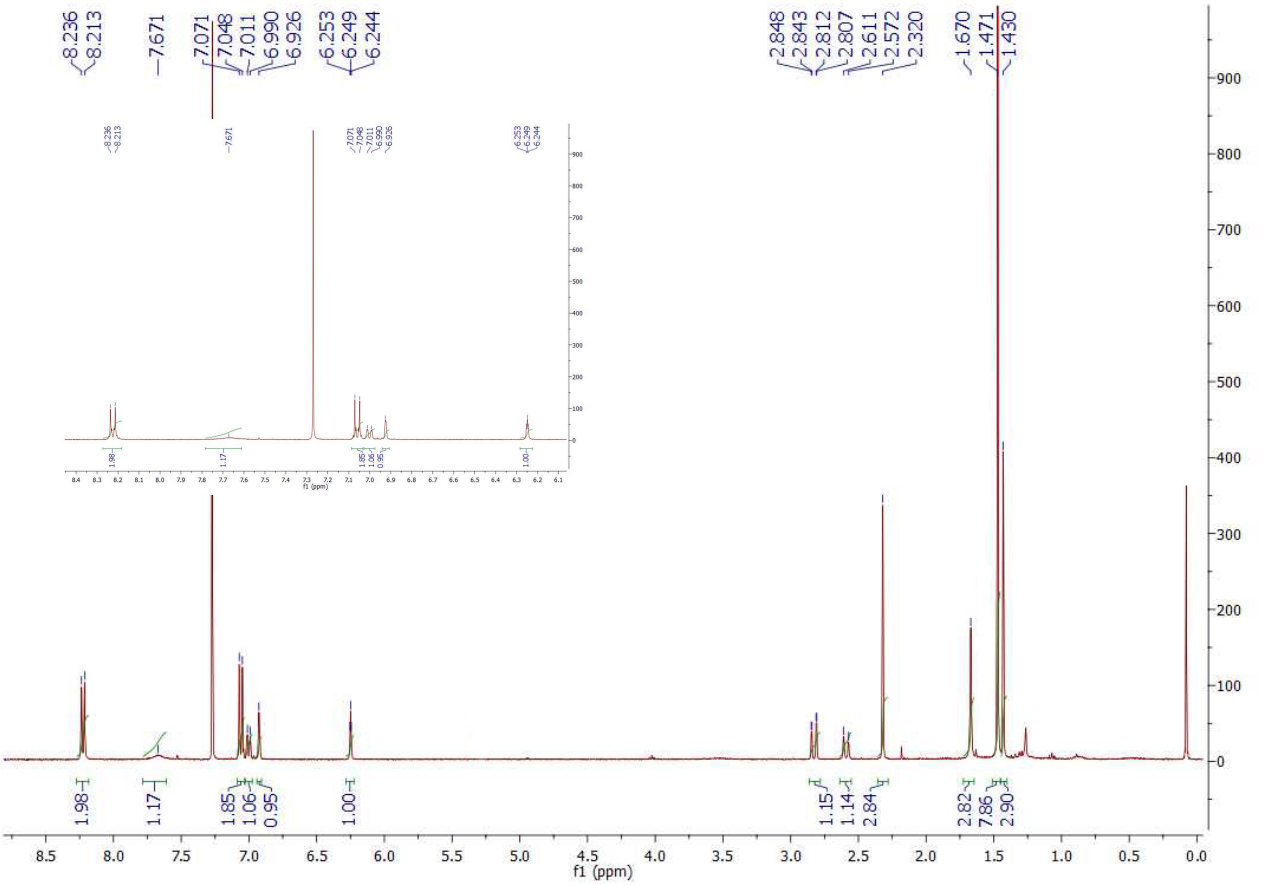
141.77
137.37
136.76
134.27
131.80
129.79
129.55
128.25
127.67
126.95
126.49
124.28
122.67
118.84
115.74
110.75
80.77
74.99
48.15
40.25
28.59
20.89
17.80
17.37
f1 (ppm)


7ed
N
BOC
O
NO2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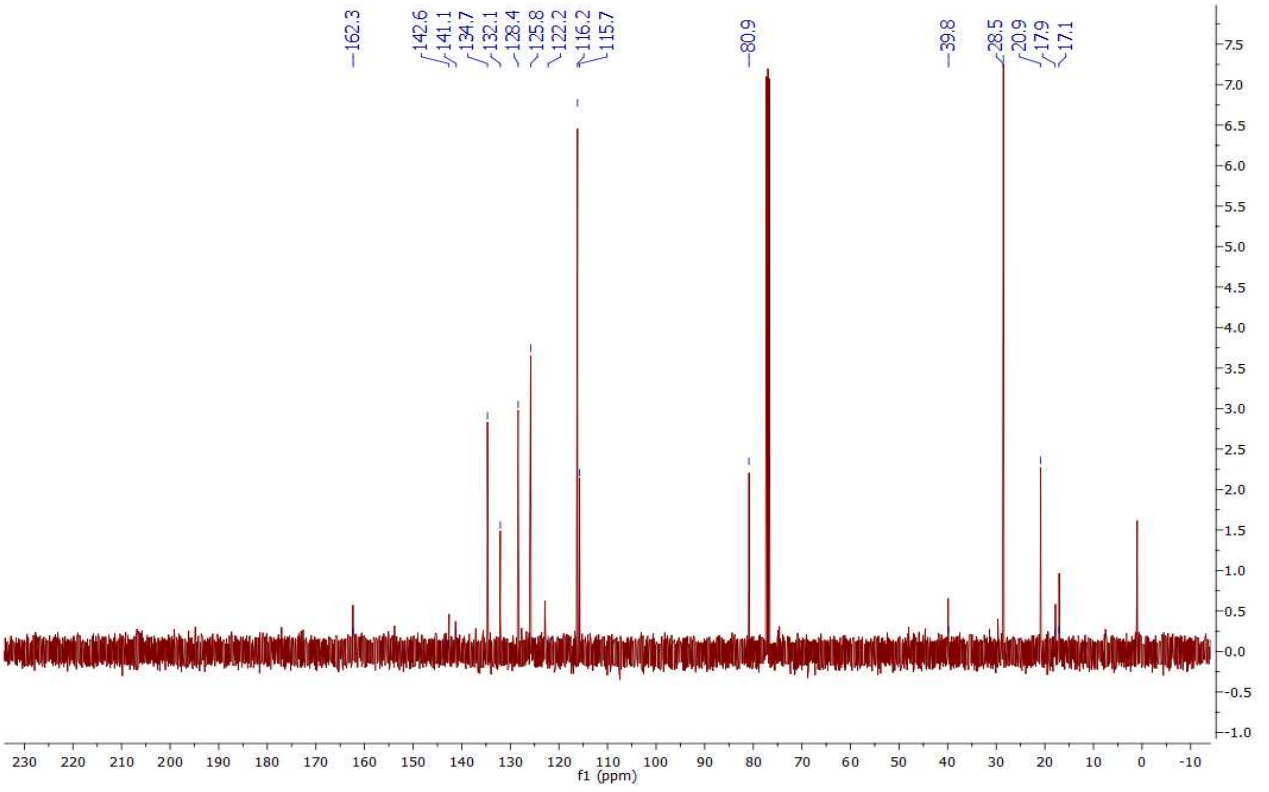
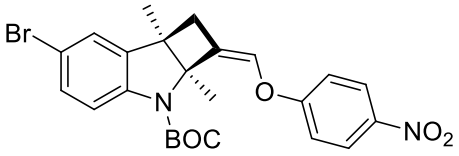
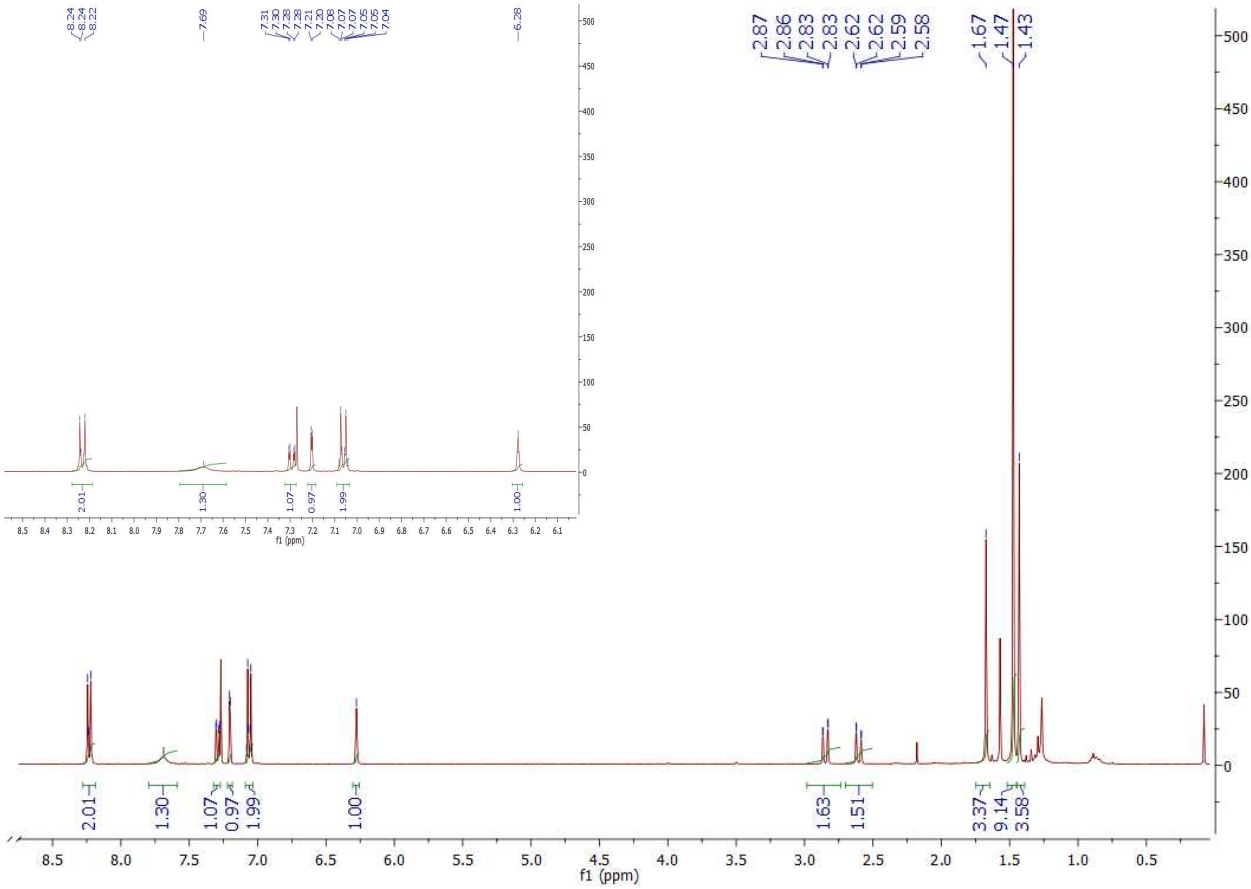
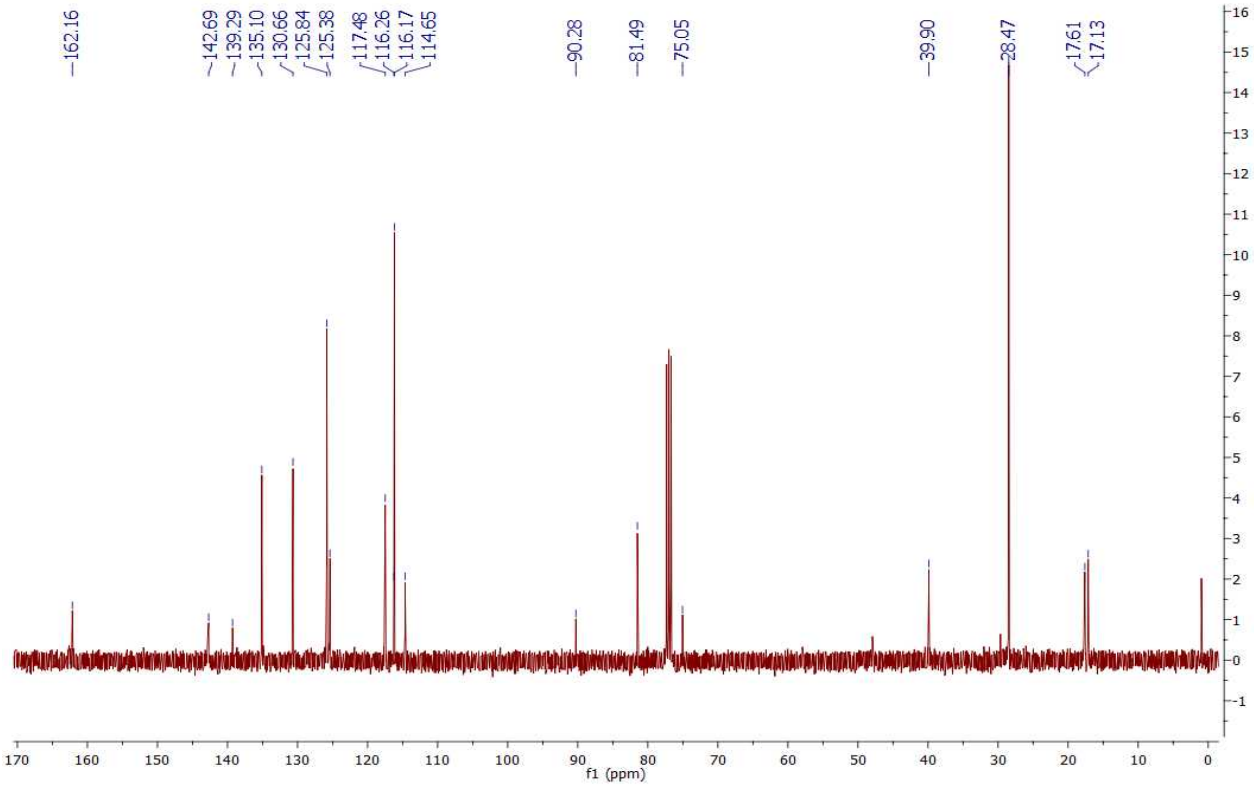
8.213
7.671
7.071
7.048
7.011
6.990
6.926
6.253
6.249
6.244
2.848
2.843
2.812
2.807
2.611
2.572
2.320
1.670
1.471
1.430
1.98
1.17
1.85
1.06
0.95
1.00
1.15
1.14
2.84
2.82
7.86
2.90
f1 (ppm)


162.3
142.6
141.1
134.7
132.1
128.4
125.8
122.2
116.2
115.7
80.9
39.8
28.5
20.9
17.9
17.1
f1 (ppm)

7hd


Br
N
BOC
O
NO2


8.24
8.24
8.22
7.69
7.31
7.30
7.28
7.28
7.21
7.20
7.08
7.07
7.07
7.05
7.05
7.04
6.28
2.87
2.86
2.83
2.83
2.62
2.62
2.59
2.58
1.67
1.47
1.43
2.01
1.30
1.07
0.97
1.99
1.00
1.63
1.51
3.37
9.14
3.58
f1 (ppm)


162.16
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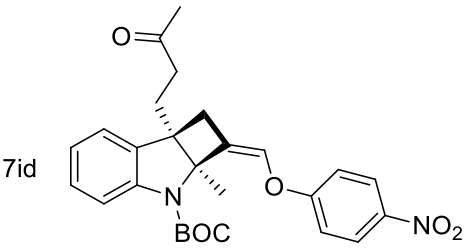
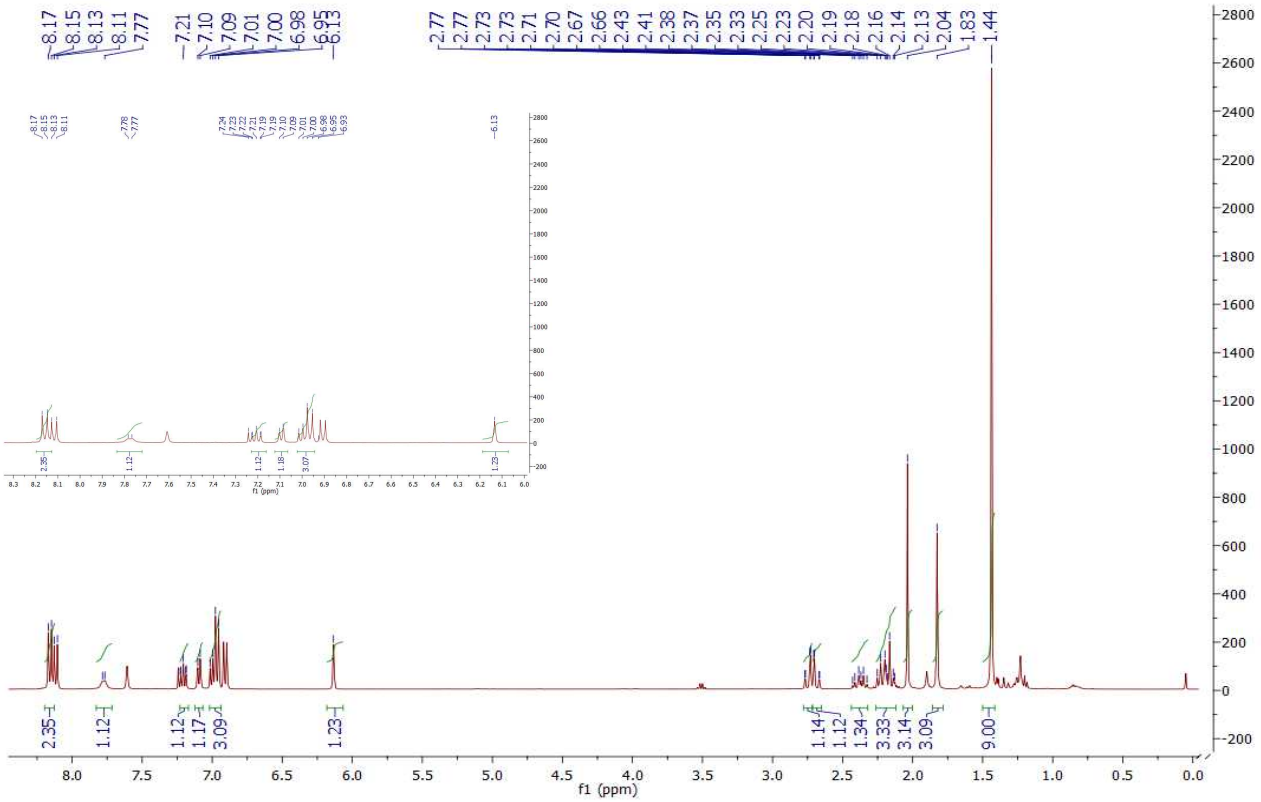
139.29
135.10
130.66
125.84
125.38
117.48
116.26
116.17
114.65
90.28
81.49
75.05
39.90
28.47
17.61
17.13
f1 (ppm)

7id


O
N
BOC
O
NO2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8.15
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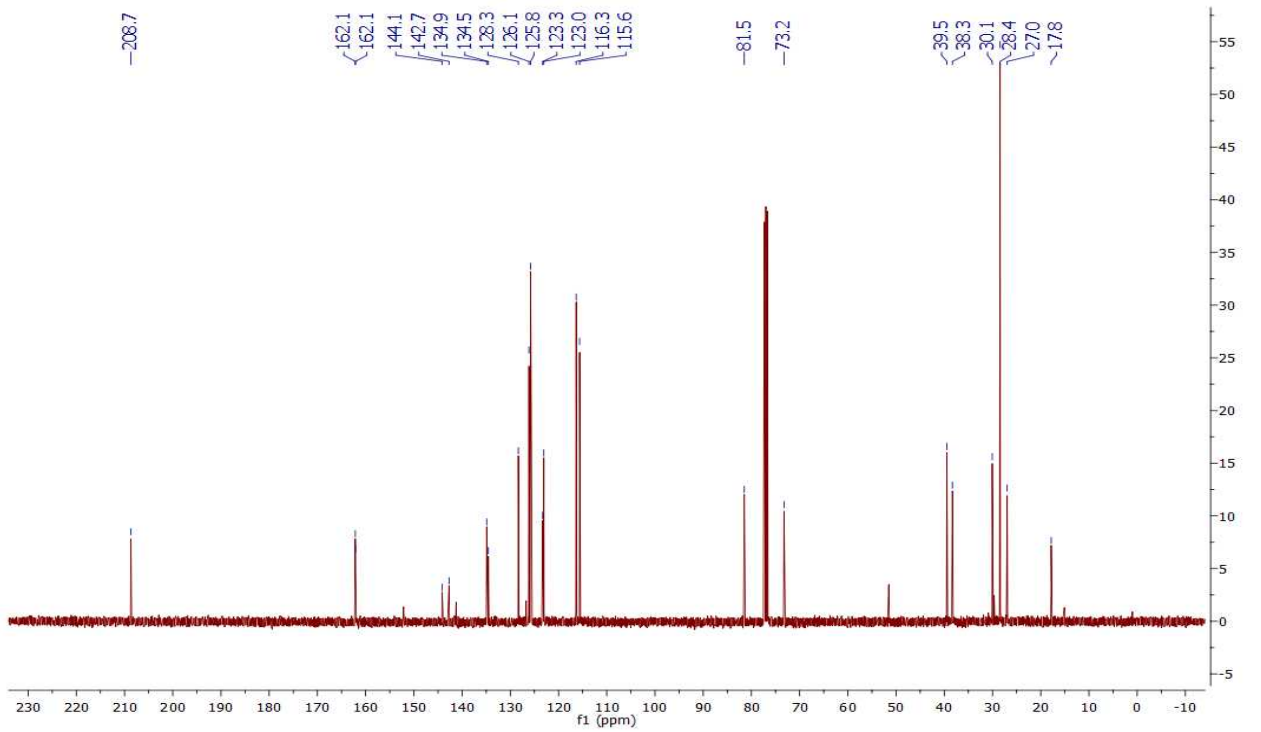
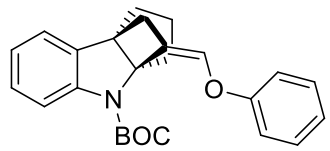
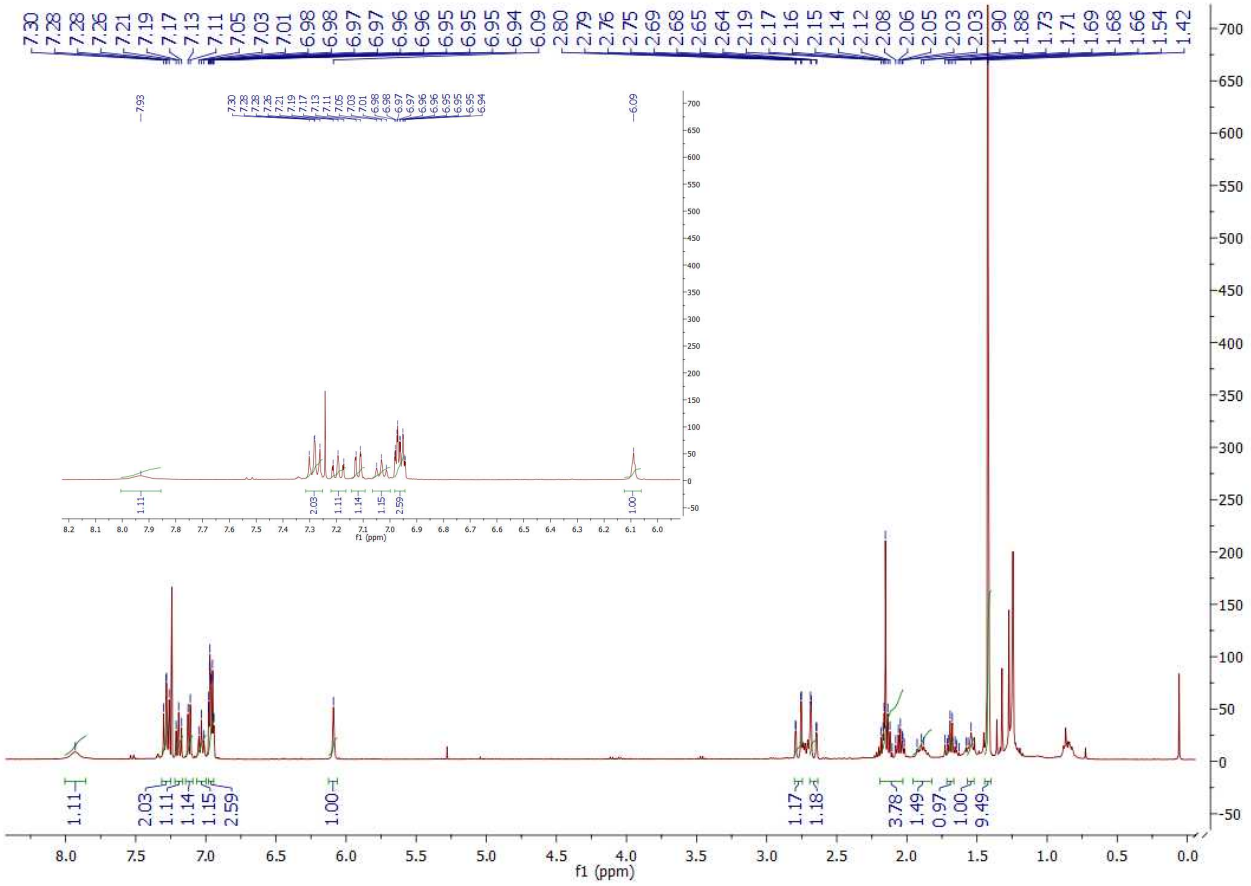
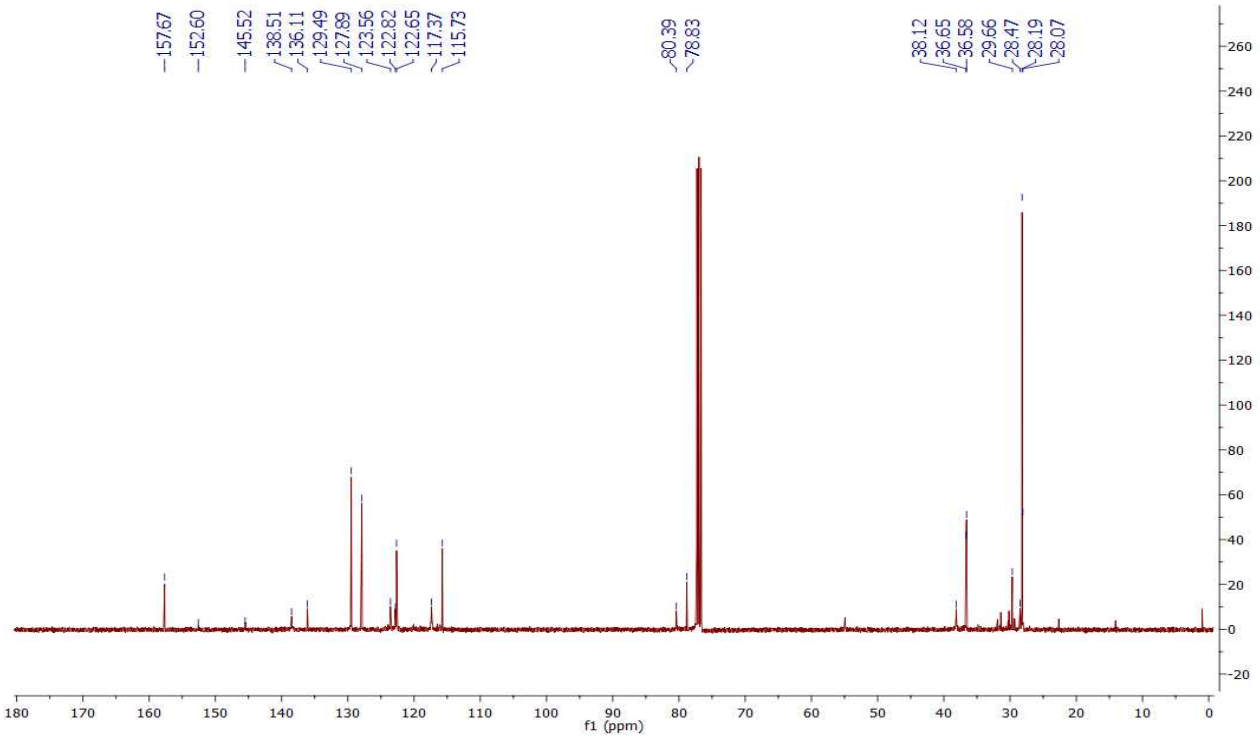
8.11
7.77
7.21
7.10
7.09
7.01
7.00
6.98
6.95
6.13
2.77
2.77
2.73
2.73
2.71
2.70
2.67
2.66
2.43
2.41
2.38
2.37
2.35
2.33
2.25
2.23
2.20
2.19
2.18
2.16
2.14
2.13
2.04
1.83
1.44
2.35
1.12
1.12
1.17
3.09
1.23
1.14
1.12
1.34
3.33
3.14
3.09
9.00
f1 (ppm)


208.7
162.1
162.1
144.1
142.7
134.9
134.5
128.3
126.1
125.8
123.3
123.0
116.3
115.6
81.5
73.2
39.5
38.3
30.1
28.4
27.0
17.8
f1 (ppm)

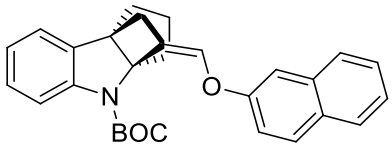
7la

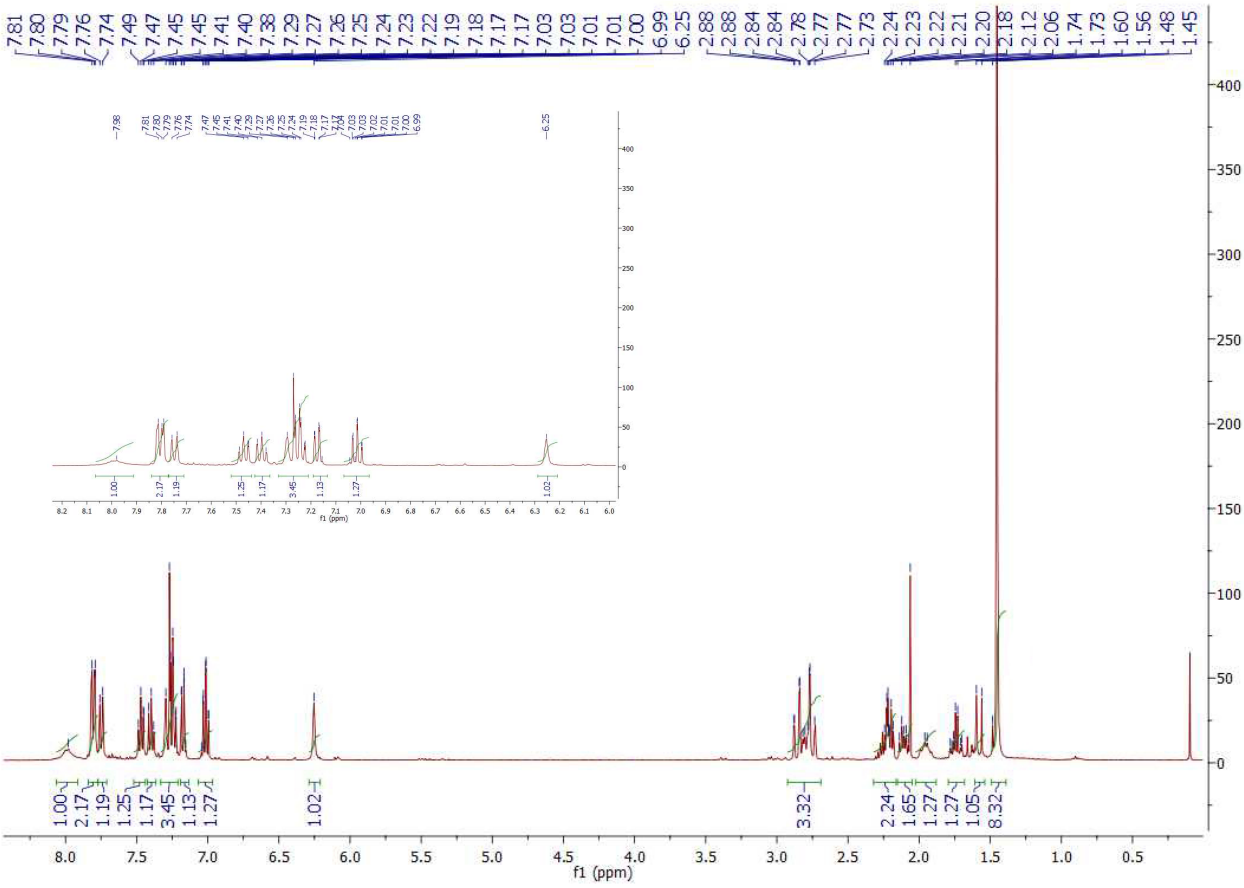


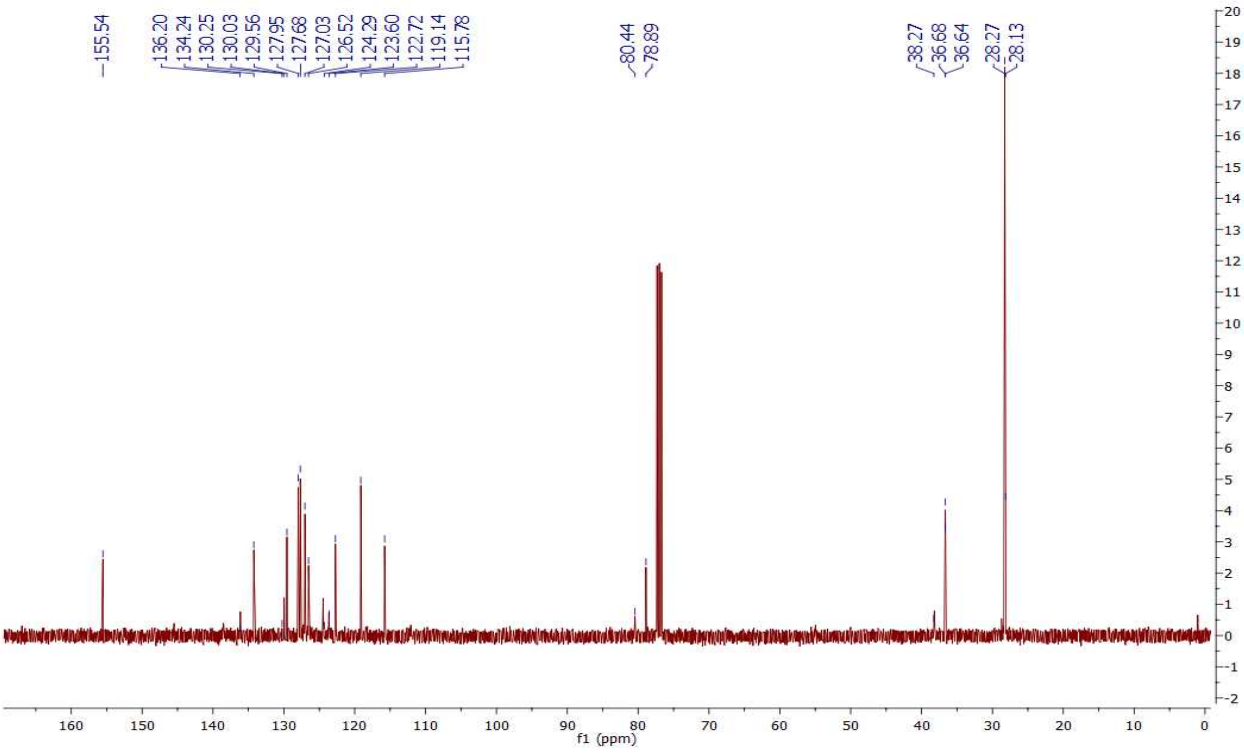




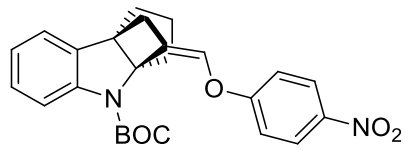
7Ib

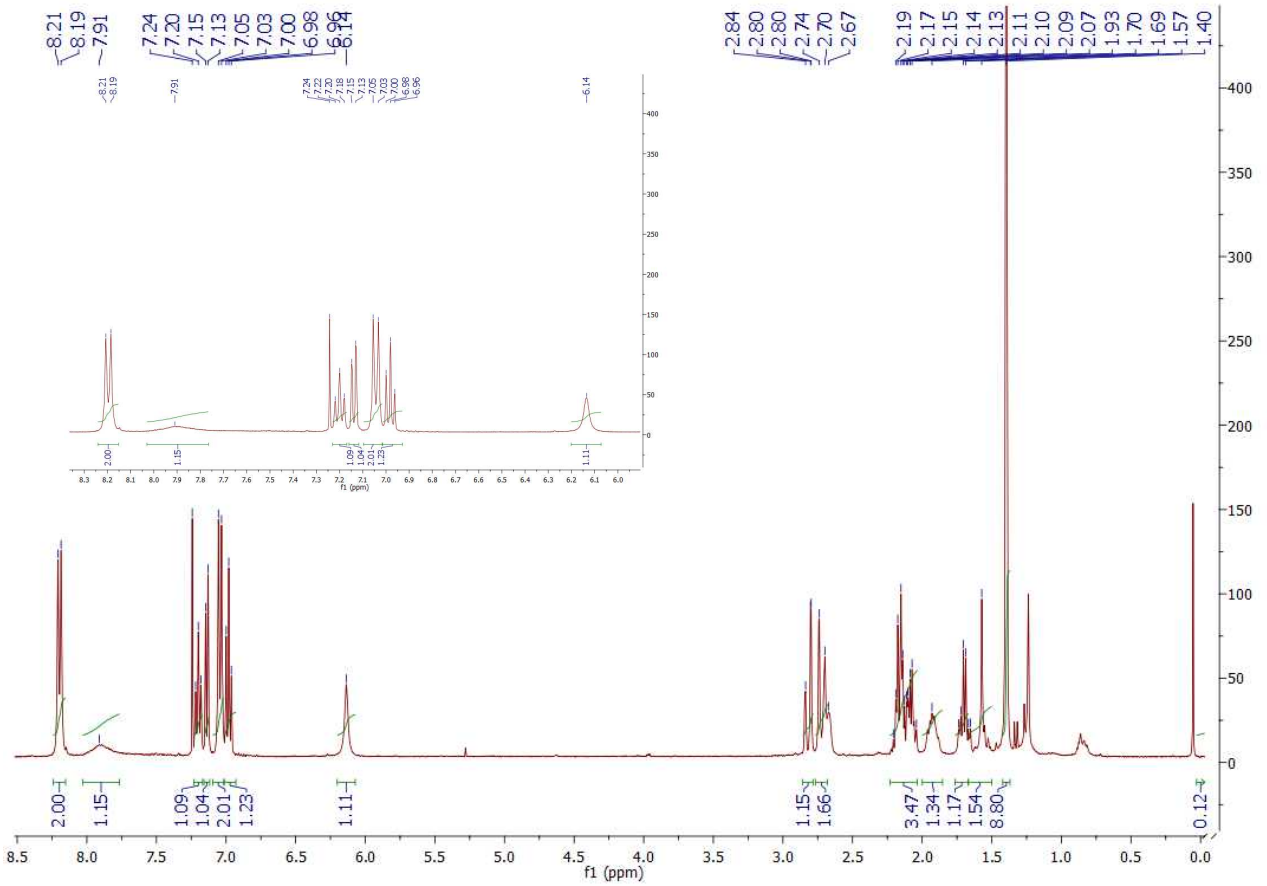

N
BOC
O


7.81 7.80 7.79 7.76 7.74 7.49 7.47 7.45 7.45 7.41 7.40 7.38 7.29 7.27 7.26 7.25 7.24 7.23 7.22 7.19 7.18 7.17 7.17 7.03 7.03 7.01 7.01 7.00 6.99 6.25 2.88 2.88 2.84 2.84 2.78 2.77 2.77 2.73 2.24 2.23 2.22 2.21 2.20 2.18 2.12 2.06 1.74 1.73 1.60 1.56 1.48 1.45
1.00 2.17 1.19 1.25 1.17 3.45 1.13 1.27 1.02 3.32 2.24 1.65 1.27 1.27 1.05 8.32
f1 (ppm)


155.54 136.20 134.24 130.25 130.03 129.56 127.95 127.68 127.03 126.52 124.29 123.60 122.72 119.14 115.78 80.44 78.89 38.27 36.68 36.64 28.27 28.13
f1 (ppm)

7ld


O
N
BOC
NO2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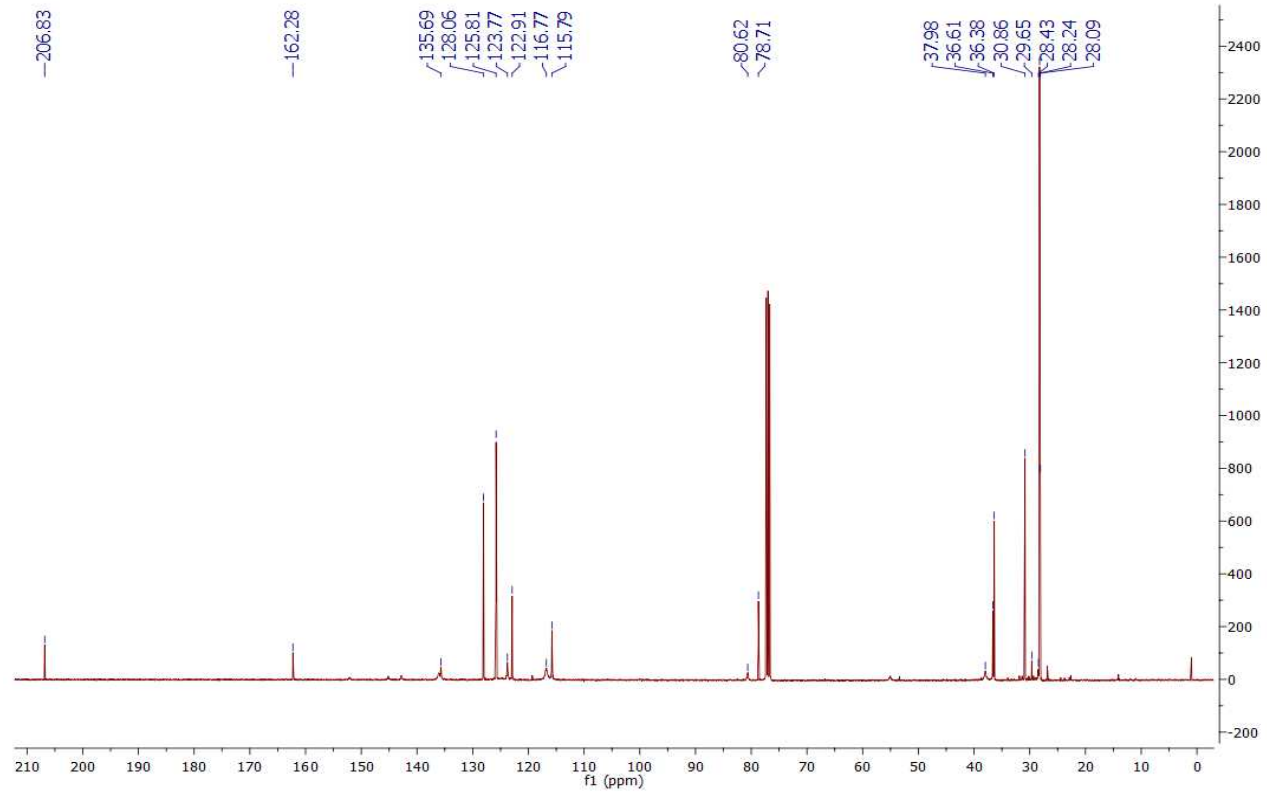
7.20
7.15
7.13
7.05
7.03
7.00
6.98
6.96
6.14
2.84
2.80
2.74
2.70
2.67
2.19
2.17
2.15
2.14
2.13
2.11
2.10
2.09
2.07
1.93
1.70
1.69
1.57
1.40
2.00
1.15
1.09
1.04
2.01
1.23
1.11
1.15
1.66
3.47
1.34
1.17
1.54
8.80
0.12
f1 (ppm)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128.06
125.81
123.77
122.91
116.77
115.79
80.62
78.71
37.98
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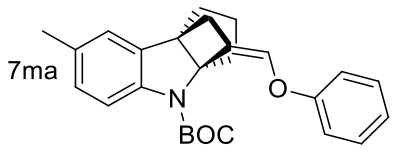
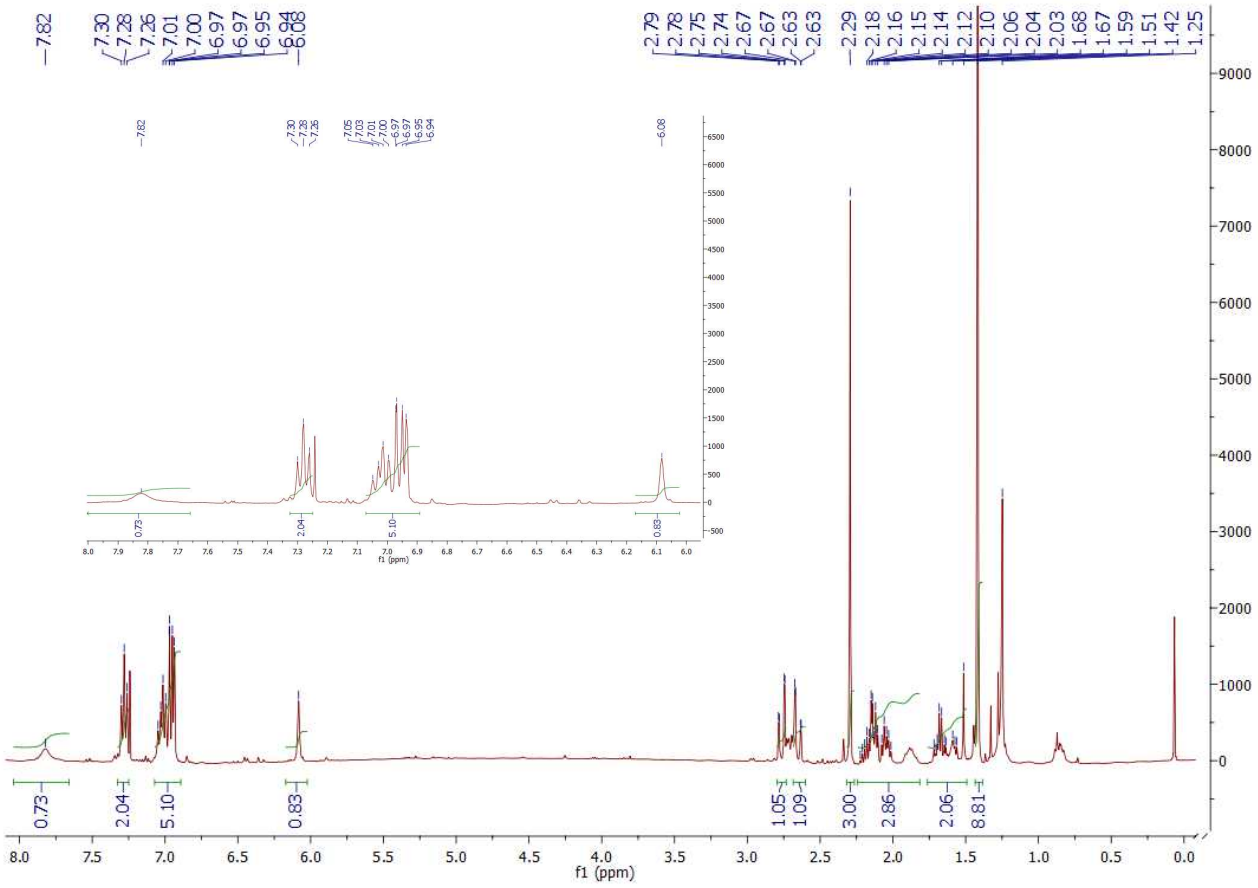
29.65
28.43
28.24
28.09
f1 (ppm)


7ma
O
N
BOC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7.00
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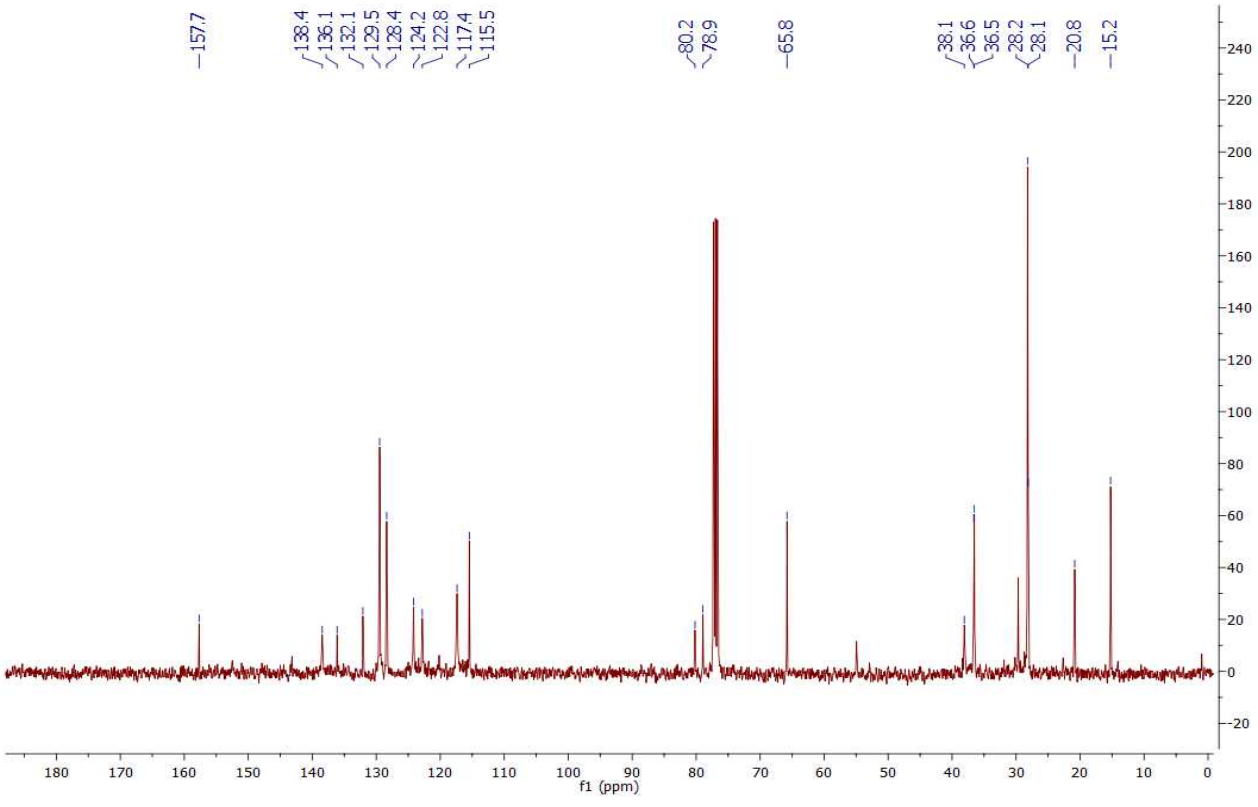
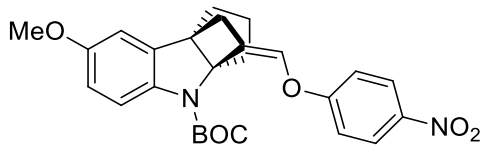
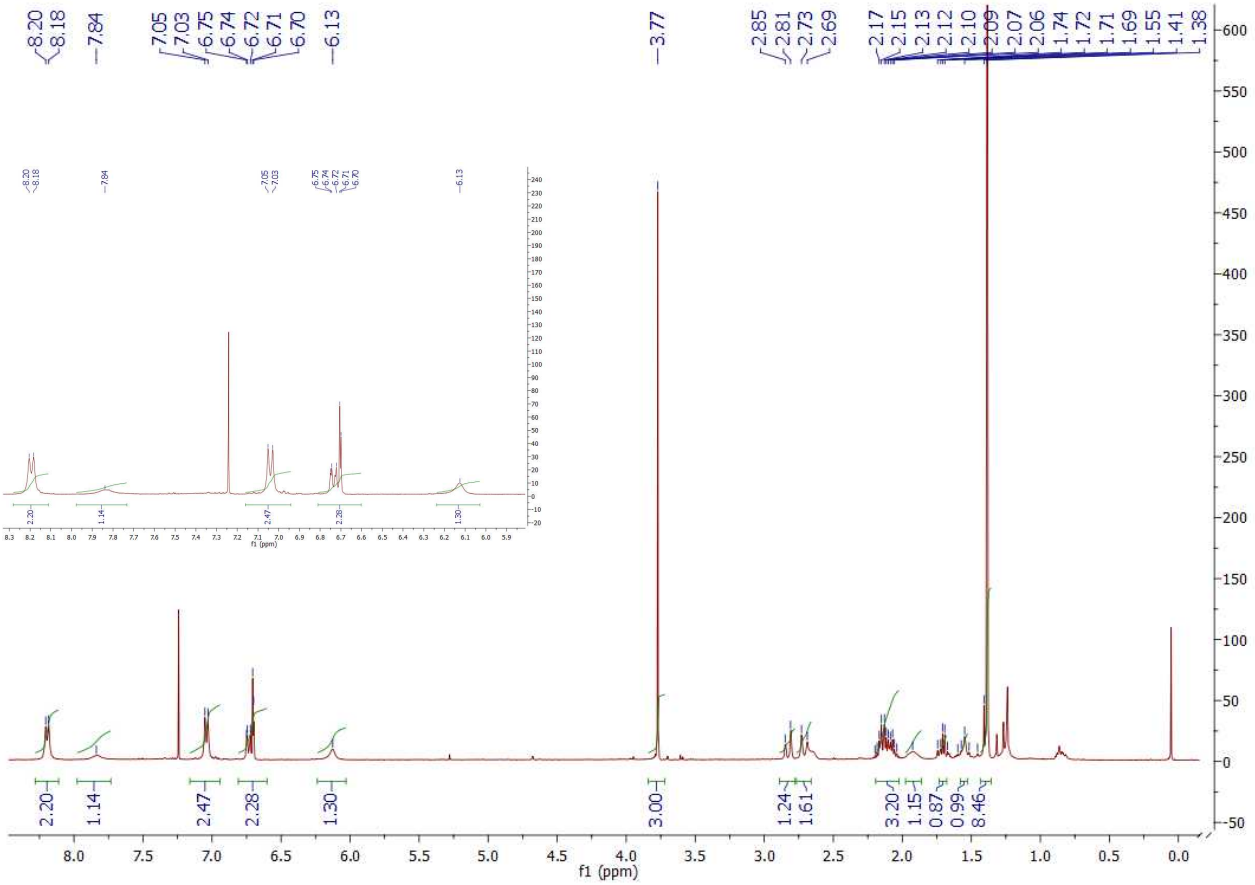
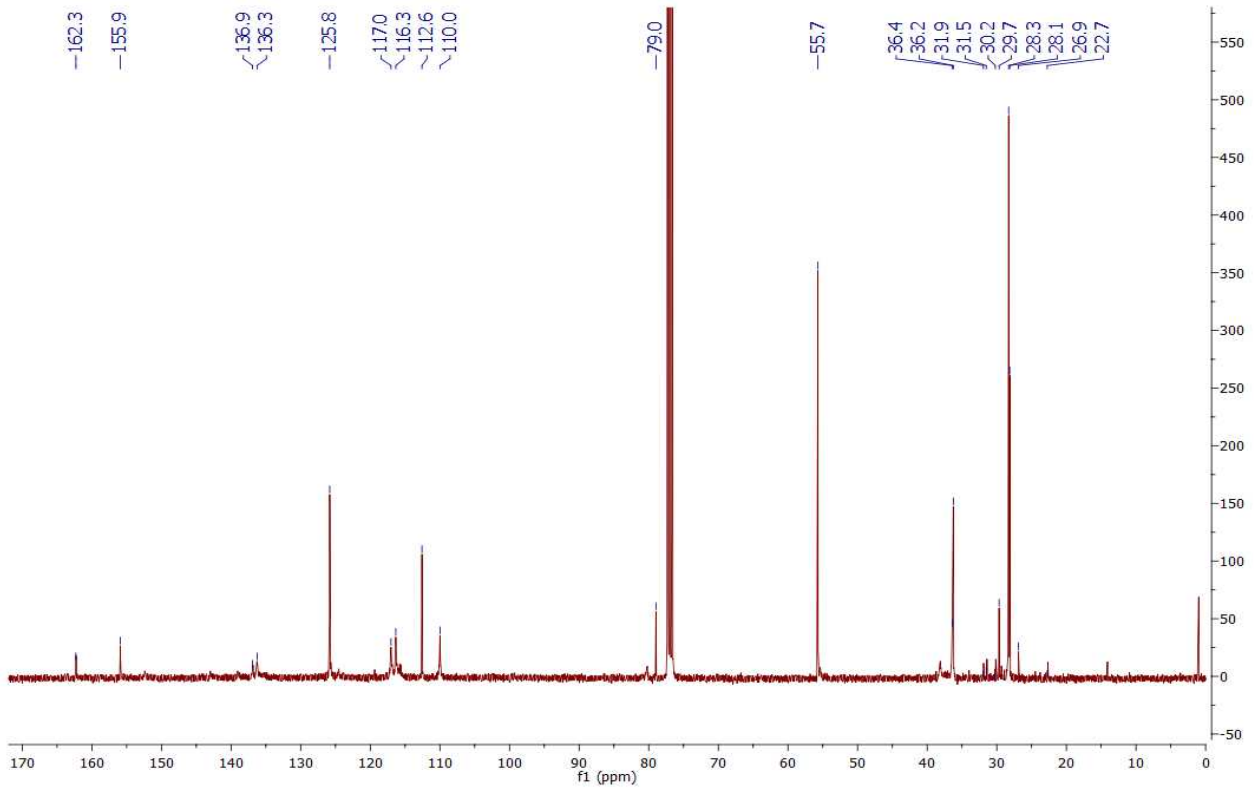
6.95
6.94
6.08
2.79
2.78
2.75
2.74
2.67
2.67
2.63
2.63
2.29
2.18
2.16
2.15
2.14
2.12
2.10
2.06
2.04
2.03
1.68
1.67
1.59
1.51
1.42
1.25
0.73
2.04
5.10
0.83
1.05
1.09
3.00
2.86
2.06
8.81
f1 (ppm)


157.7
138.4
136.1
132.1
129.5
128.4
124.2
122.8
117.4
115.5
80.2
78.9
65.8
38.1
36.6
36.5
28.2
28.1
20.8
15.2
f1 (ppm)

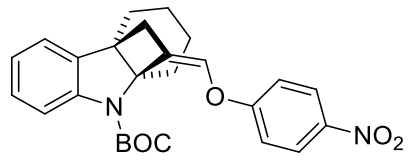
7nd

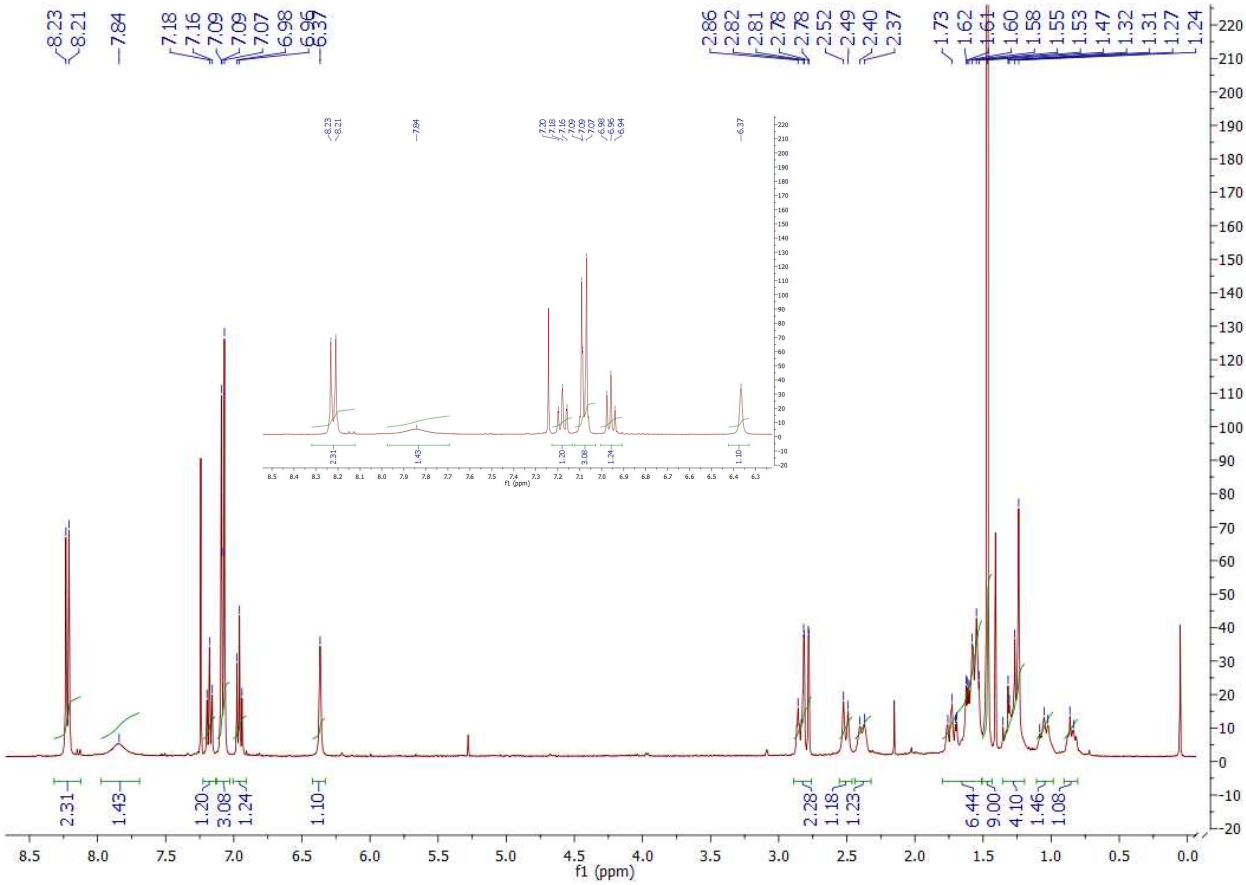

MeO
N
BOC
O
NO2


8.20
8.18
7.84
7.05
7.03
6.75
6.74
6.72
6.71
6.70
6.13
3.77
2.85
2.81
2.73
2.69
2.17
2.15
2.13
2.12
2.10
2.09
2.07
2.06
1.74
1.72
1.71
1.69
1.55
1.41
1.38
2.20
1.14
2.47
2.28
1.30
3.00
1.24
1.61
3.20
1.15
0.87
0.99
8.46
f1 (ppm)


162.3
155.9
136.9
136.3
125.8
117.0
116.3
112.6
110.0
79.0
55.7
36.4
36.2
31.9
31.5
30.2
29.7
28.3
28.1
26.9
22.7
f1 (ppm)

7pd


N
BOC
O
NO2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8.21
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7.18
7.16
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7.09
7.07
6.98
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6.37
2.86
2.82
2.81
2.78
2.52
2.49
2.40
2.37
1.73
1.62
1.61
1.60
1.58
1.55
1.53
1.47
1.32
1.31
1.27
1.24
2.31
1.43
1.20
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1.24
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2.28
1.18
1.23
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4.10
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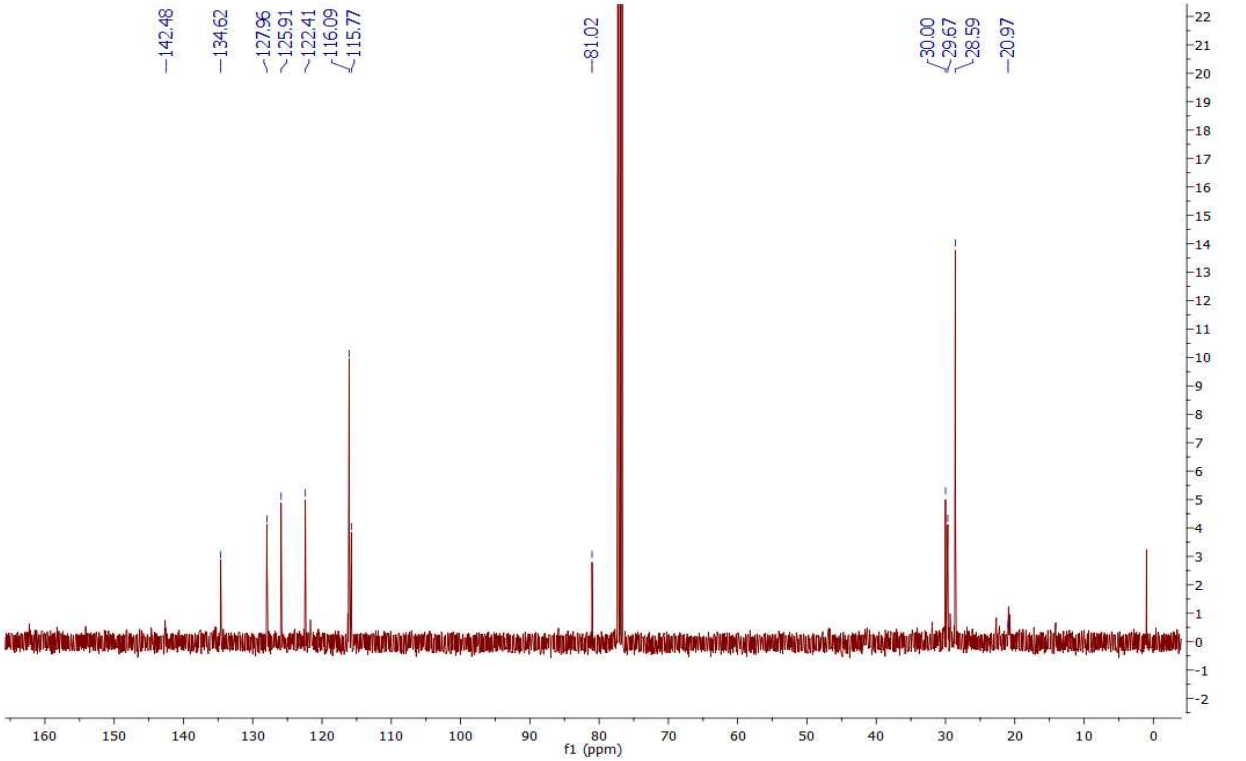
1.08
f1 (ppm)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127.96
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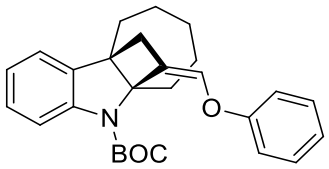
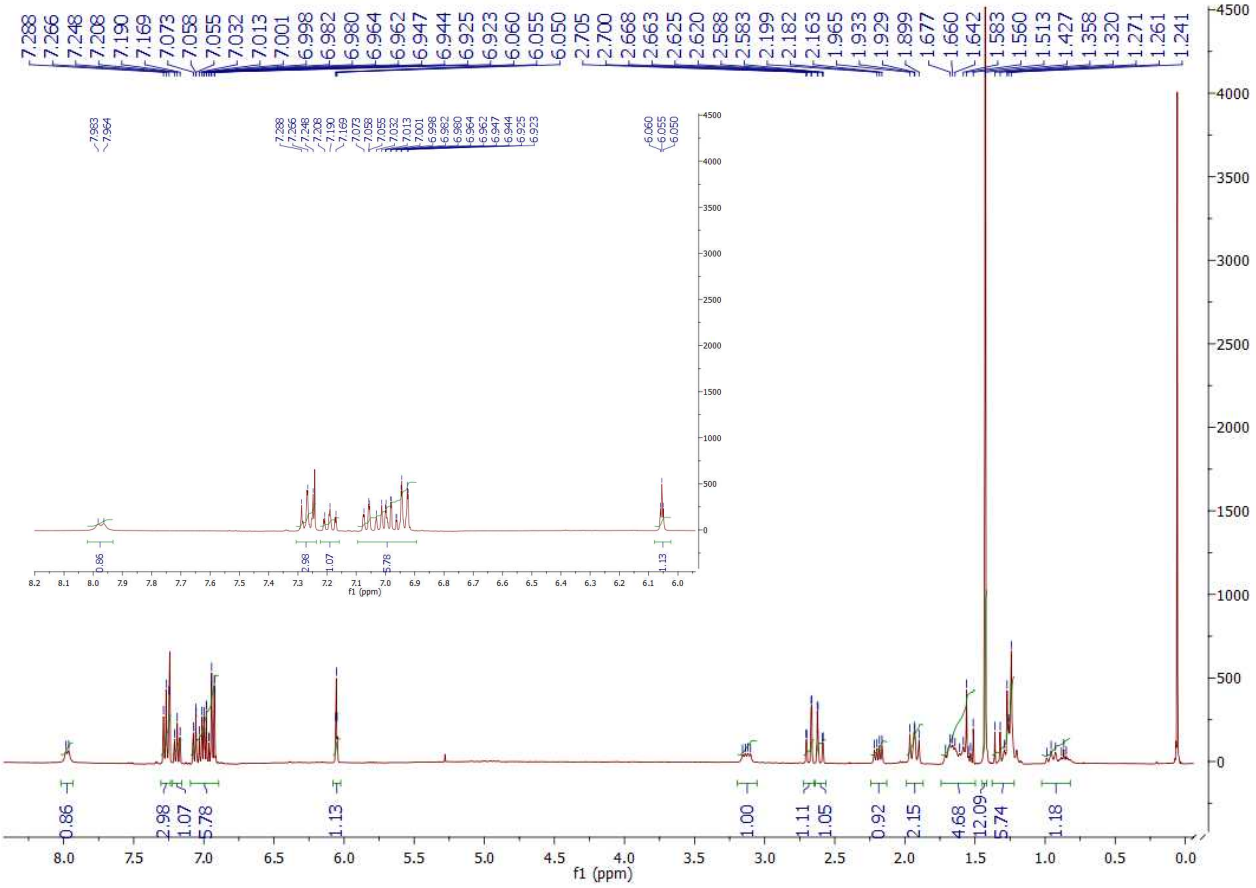
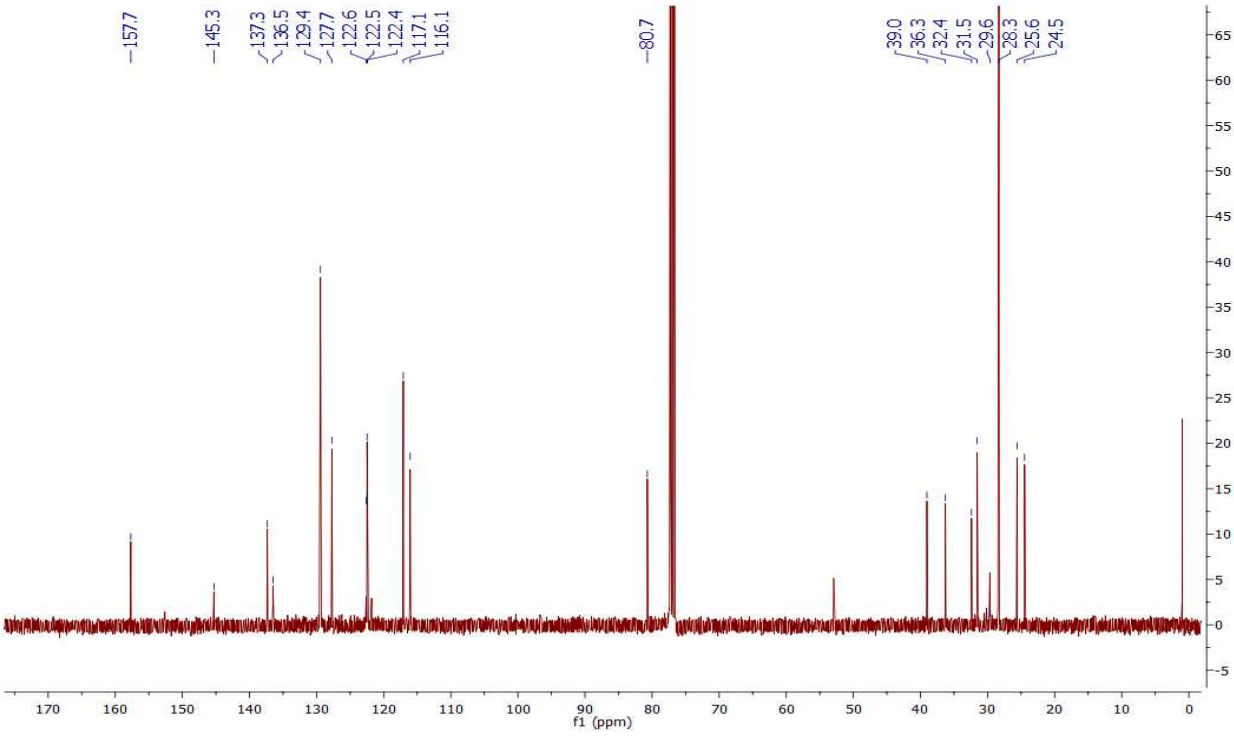
116.09
115.77
81.02
30.00
29.67
28.59
20.97
f1 (ppm)

7qa







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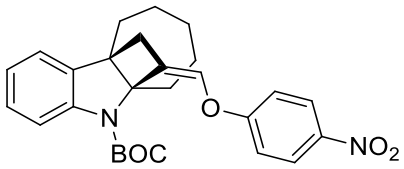

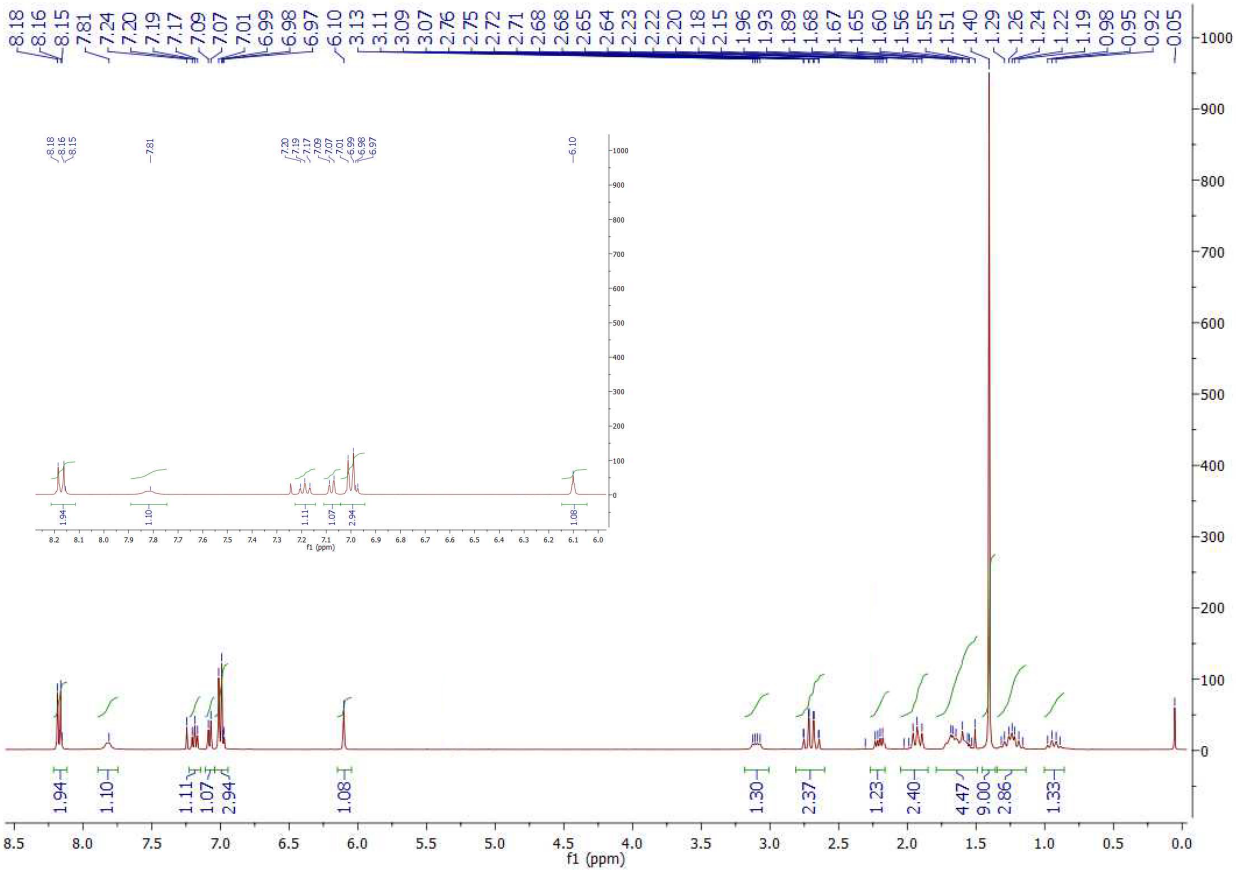

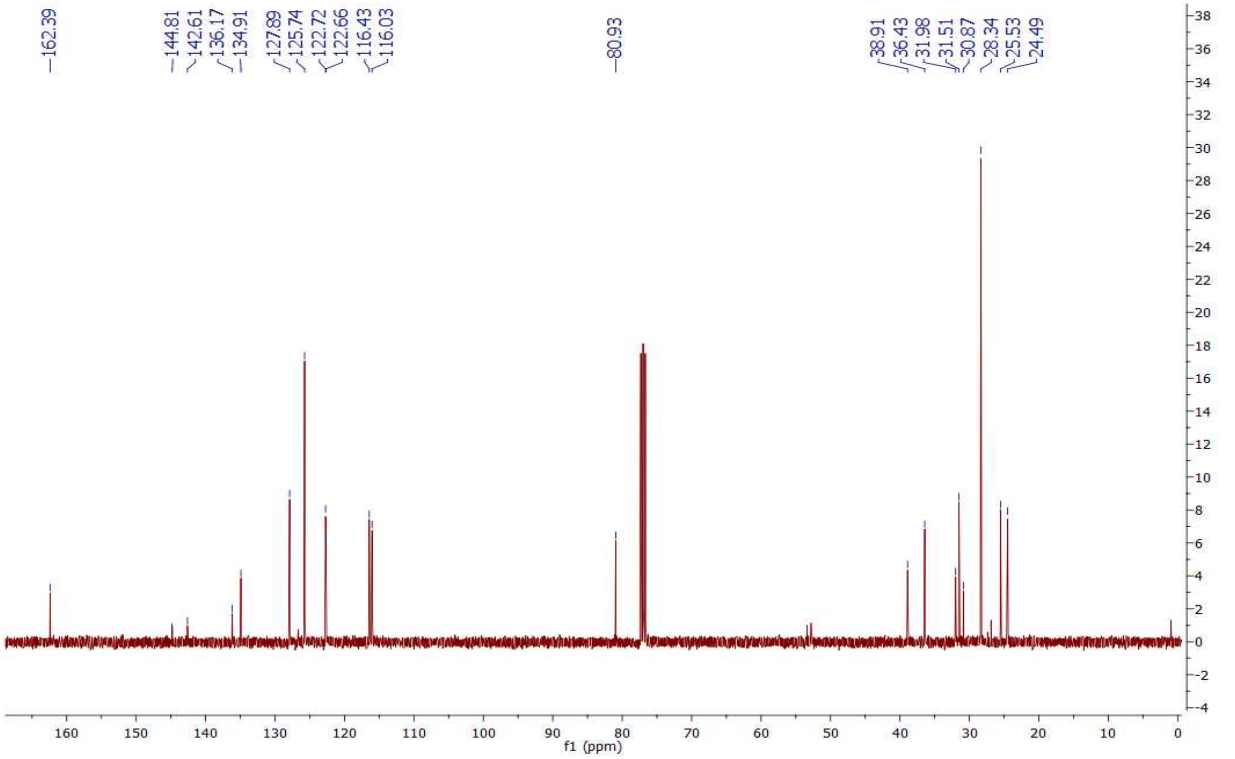

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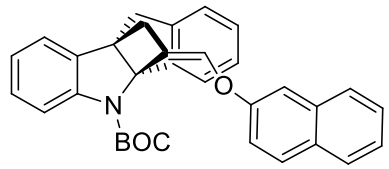
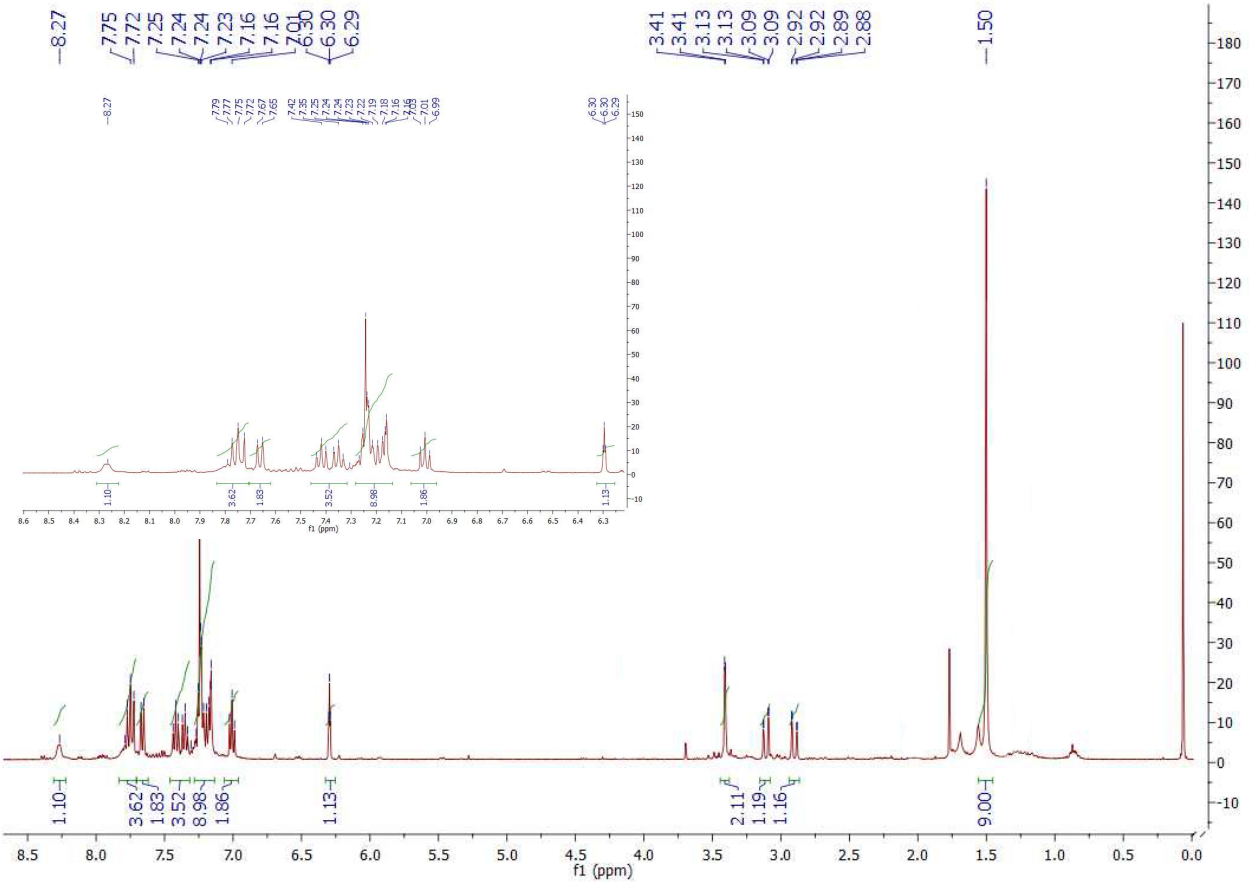

N
BOC
O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7.16
7.16
7.01
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6.30
6.29
3.41
3.41
3.13
3.13
3.09
3.09
2.92
2.92
2.89
2.88
1.50
1.10
3.62
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3.52
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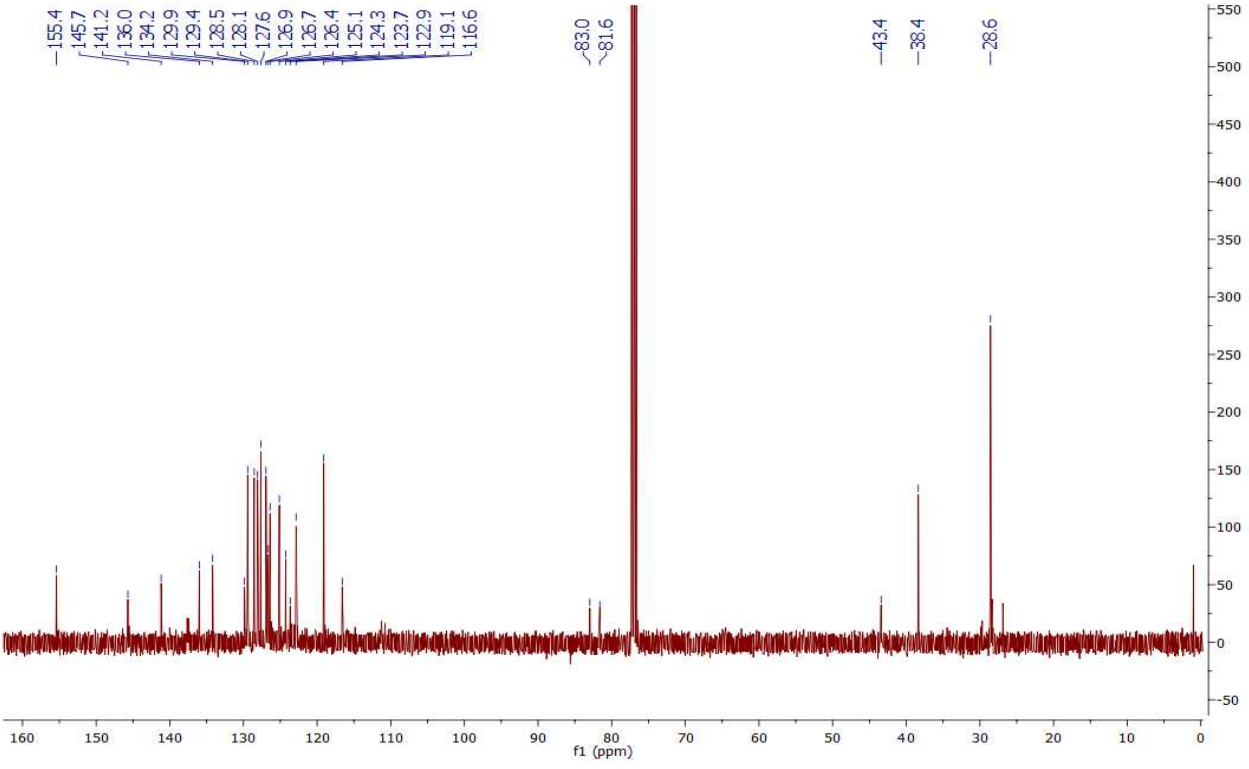
1.86
1.13
2.11
1.19
1.16
9.00
f1 (ppm)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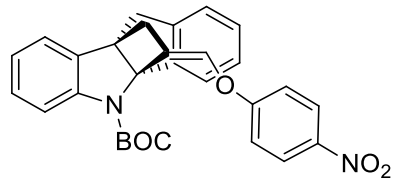
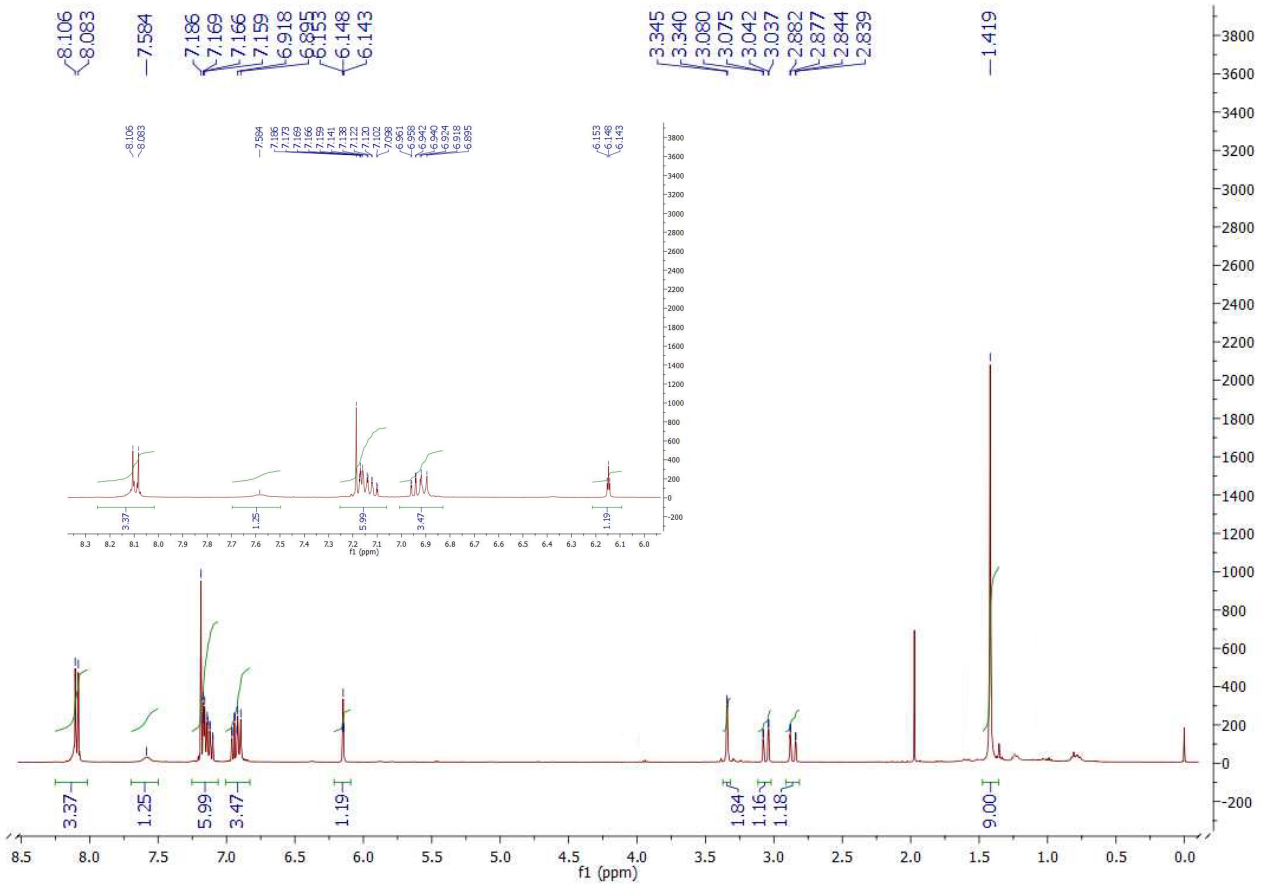
145.7
141.2
136.0
134.2
129.9
129.4
128.5
128.1
127.6
126.9
126.7
126.4
125.1
124.3
123.7
122.9
119.1
116.6
83.0
81.6
43.4
38.4
28.6
f1 (ppm)

7ud


O
N
BOC
NO2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7.166
7.159
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6.895
6.153
6.148
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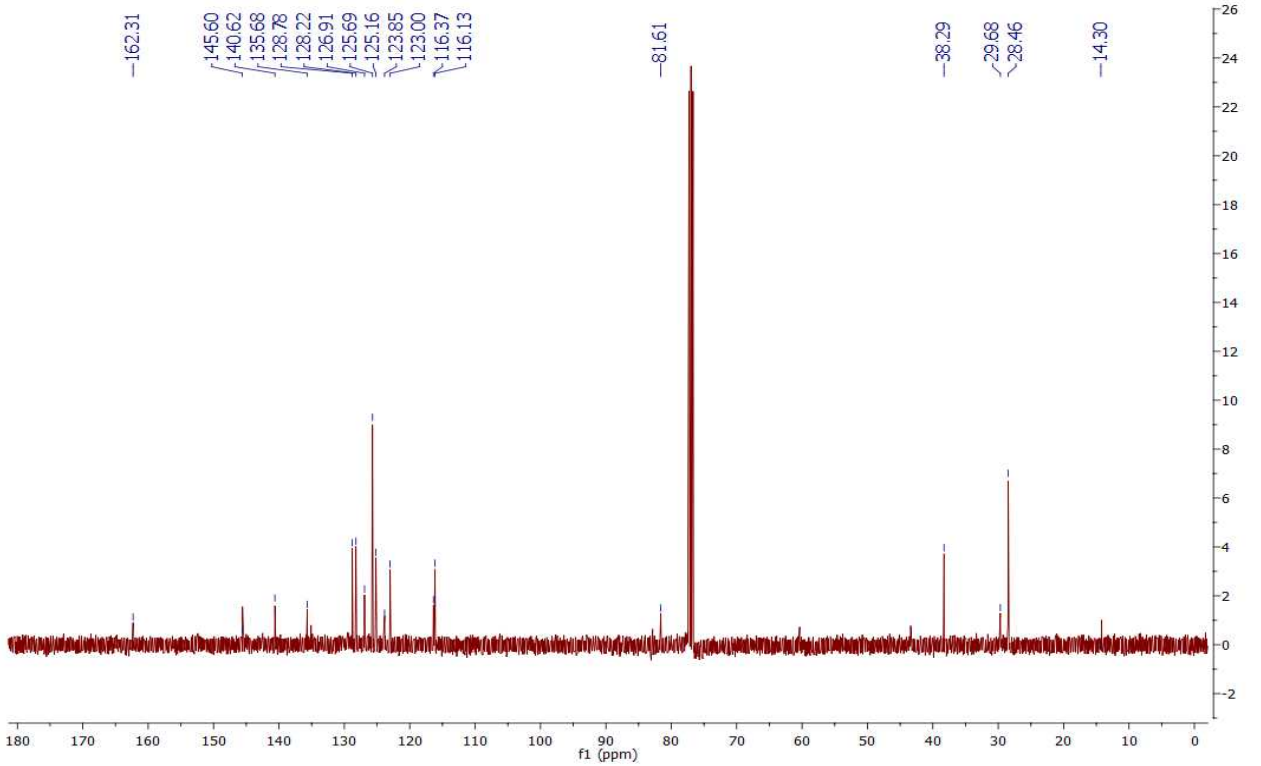
3.345
3.340
3.080
3.075
3.042
3.037
2.882
2.877
2.844
2.839
1.419
3.37
1.25
5.99
3.47
1.19
1.84
1.16
1.18
9.00
f1 (ppm)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135.68
128.78
128.22
126.91
125.69
125.16
123.85
123.00
116.37
116.13
81.61
38.29
29.68
28.46
14.30
f1 (ppm)

Computational details

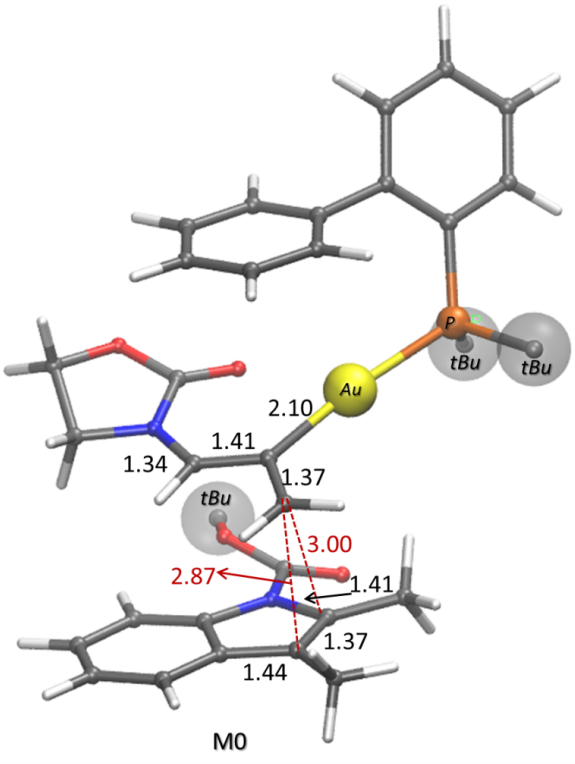

Figure S1. A 3D representation of the encounter complex **M0**. Bond lengths are given in Å.

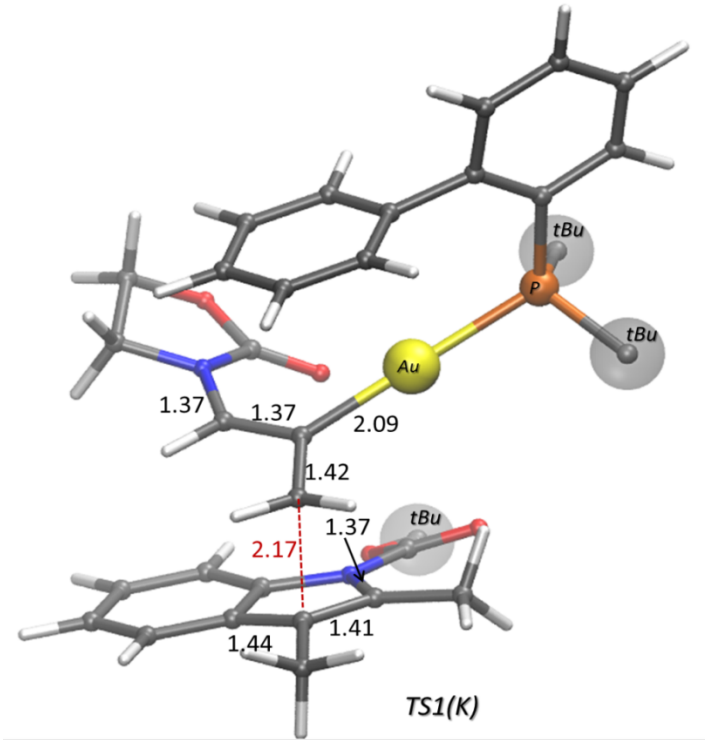

Figure S2. A 3D representation of transition state **TS1(K)**. Bond lengths are given in Å.

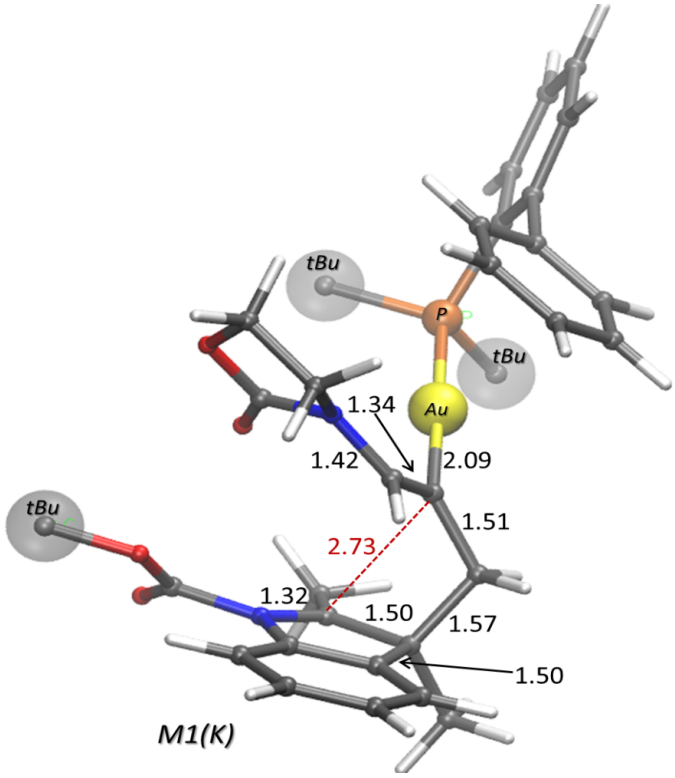

Figure S3. A 3D representation of the intermediate **M1(K)**. Bond lengths are given in Å.

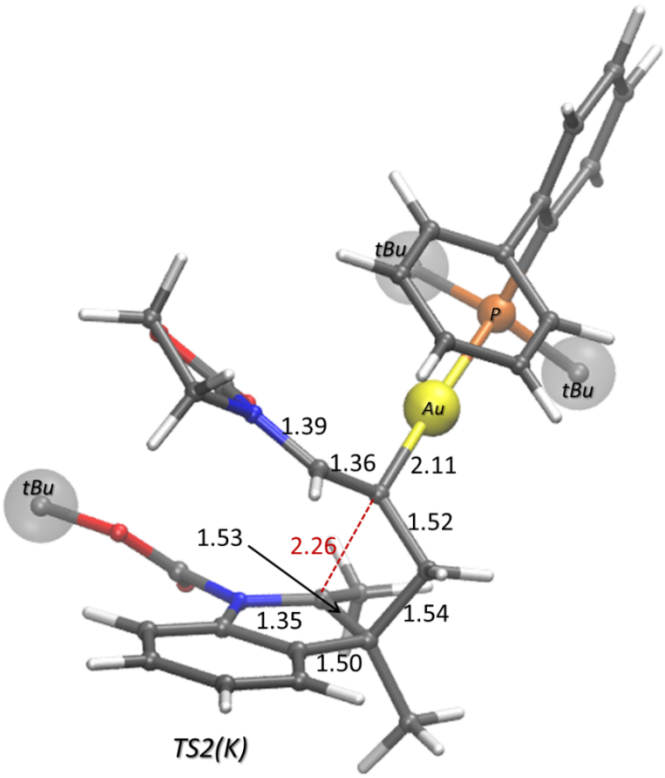

Figure S4. A 3D representation of transition state **TS2(K)**. Bond lengths are given in Å.

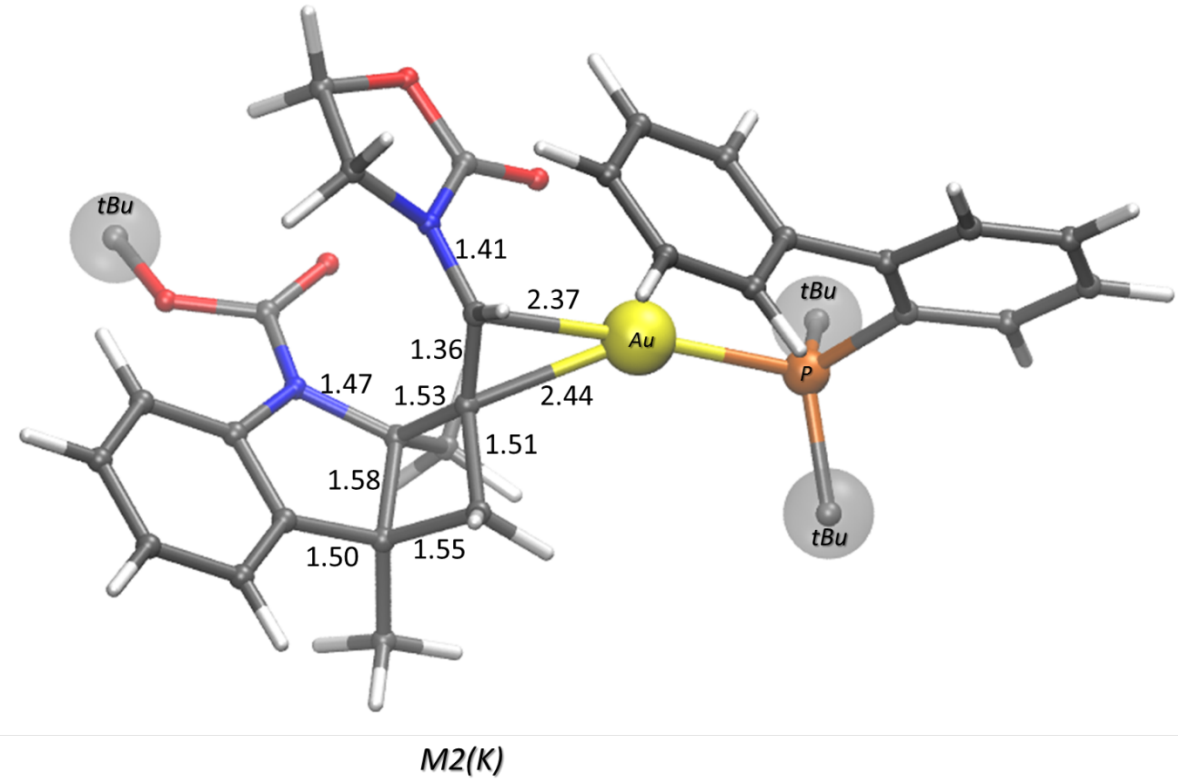

Figure S5. A 3D representation of the final adduct **M2(K)**. Bond lengths are given in Å.

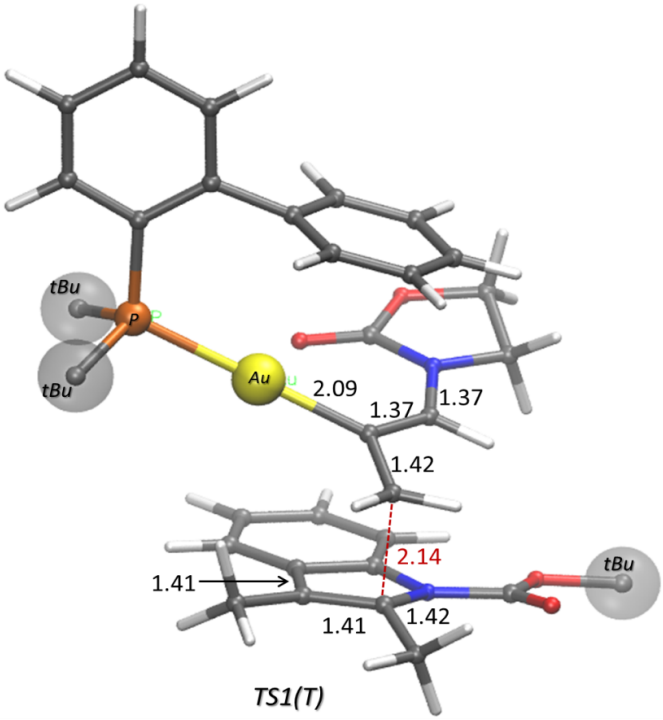

Figure S6. A 3D representation of transition state **TS1(T)**. Bond lengths are given in Å.

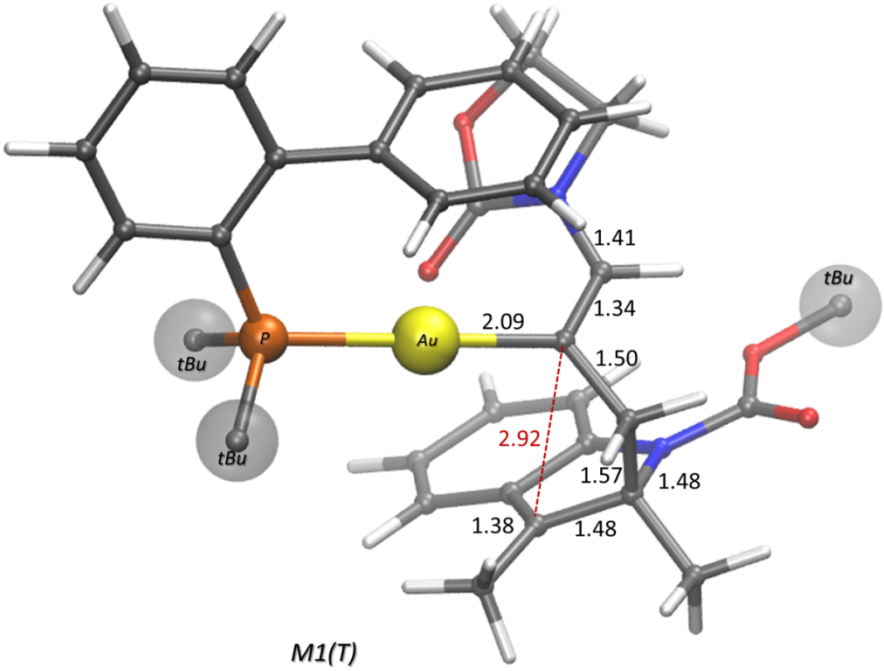

Figure S7. A 3D representation of the intermediate **M1(T)**. Bond lengths are given in Å.

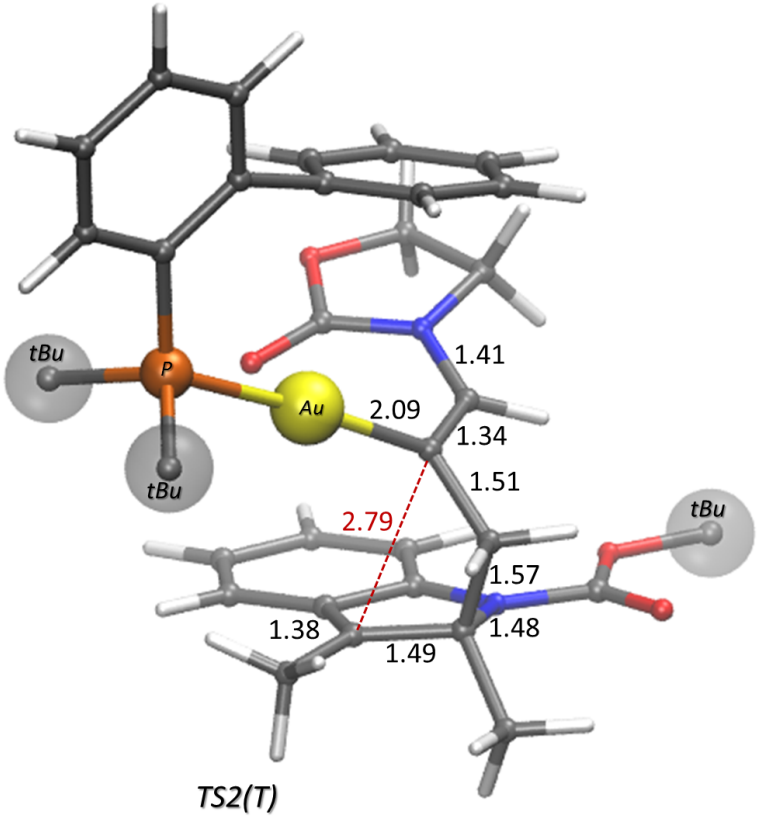

Figure S8. A 3D representation of transition state **TS2(T)**. Bond lengths are given in Å.

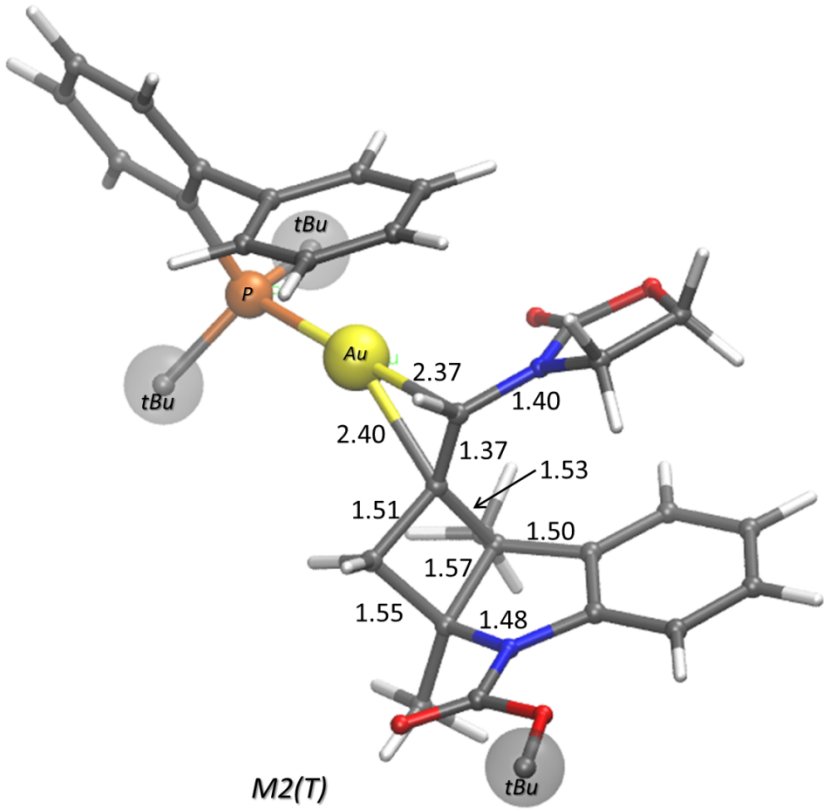

Figure S9. A 3D representation of the final adduct **M2(T)**. Bond lengths are given in Å

Table S2. Cartesian coordinates (Å) for the various computed critical points. Total energy values in hartrees.

M1-π
scf done: -1690.583942

C	-0.352697	1.336100	-0.633012
C	-1.249743	2.037155	0.080391
C	0.733351	1.045276	-1.320030
N	1.103930	-0.141676	-1.940182
C	0.256099	-1.120256	-2.390632
O	0.964217	-2.070115	-3.014895
O	-0.953694	-1.159179	-2.286785
H	-1.169320	2.110408	1.168818
H	-2.007273	2.661801	-0.398366
H	1.483371	1.833452	-1.414812
Au	-2.081974	-0.134311	-0.096603
P	-3.924245	-1.540690	0.460087
C	-3.473533	-2.997184	1.478754
C	-4.486512	-3.909789	1.816090
C	-4.214287	-5.094030	2.485379
C	-2.902410	-5.402504	2.823578
C	-1.888102	-4.513221	2.500906
C	-2.144492	-3.304418	1.840071
H	-5.517108	-3.700902	1.545672
H	-5.026793	-5.773728	2.732792
H	-2.667976	-6.330396	3.341235
H	-0.858571	-4.742277	2.774013
C	-0.948651	-2.446275	1.613636
C	2.466511	-0.358305	-2.410371
H	3.184292	-0.250460	-1.588834
H	2.719288	0.359892	-3.201767
C	2.372030	-1.796403	-2.918777
H	2.808119	-2.519180	-2.220445
C	-0.721340	-1.309308	2.399743
C	0.480713	-0.611868	2.305815
C	1.474346	-1.047130	1.432505
C	1.253903	-2.172370	0.642371
C	0.050304	-2.866459	0.728598
H	-1.486330	-0.990094	3.108248
H	0.649947	0.259962	2.935802
H	2.423755	-0.515863	1.375149
H	2.036285	-2.535794	-0.024022
H	-0.119538	-3.753696	0.117642
H	2.813630	-1.941044	-3.906959
C	-5.134001	-0.514989	1.473268
C	-4.329479	0.043684	2.670363
C	-5.629591	0.665919	0.614442
C	-6.354621	-1.262400	2.045315
H	-3.943805	-0.765870	3.306434
H	-3.491344	0.671224	2.335091
H	-5.003795	0.664323	3.278170
H	-6.296338	0.330288	-0.189406
H	-6.197792	1.348158	1.263139
H	-4.791348	1.227934	0.177269

H	-6.978736	-0.524536	2.570651
H	-6.970310	-1.727689	1.267192
H	-6.054798	-2.021459	2.777289
C	-4.626018	-2.214129	-1.154829
C	-4.660665	-1.079182	-2.204878
C	-3.619178	-3.283311	-1.641522
C	-6.030589	-2.837206	-1.075647
H	-5.379849	-0.293815	-1.942423
H	-3.668744	-0.626755	-2.338473
H	-4.968018	-1.517624	-3.165192
H	-3.598803	-4.153430	-0.972833
H	-3.937582	-3.620025	-2.638726
H	-2.605161	-2.867088	-1.733940
H	-6.292659	-3.196021	-2.081851
H	-6.068260	-3.699493	-0.399842
H	-6.788006	-2.102295	-0.776429

M2-□

scf done: -1690.579495

C	-1.480166	0.881278	-1.896816
C	-2.589151	0.300091	-2.320676
C	-0.527990	0.908805	-0.922070
N	0.721771	0.384334	-0.949998
C	1.354008	-0.086131	-2.107290
O	2.613030	-0.402524	-1.797747
O	0.873397	-0.154800	-3.206405
H	-3.163055	0.659085	-3.173148
H	-2.972535	-0.588673	-1.815541
H	-0.747859	1.454199	0.002088
Au	-0.849975	2.636063	-3.095343
P	-0.895192	3.811670	-5.167573
C	0.224669	5.255130	-5.326805
C	0.118235	6.057382	-6.474964
C	1.003417	7.094817	-6.731334
C	2.040807	7.343735	-5.841081
C	2.161835	6.567254	-4.698089
C	1.263480	5.531924	-4.407104
H	-0.673922	5.869526	-7.194146
H	0.887265	7.697829	-7.629111
H	2.753707	8.143293	-6.032944
H	2.963860	6.767623	-3.988952
C	1.512966	4.824512	-3.122604
C	1.592536	0.295535	0.214263
H	1.233348	-0.492233	0.884612
H	1.619146	1.240256	0.766098
C	2.927480	-0.062493	-0.440947
H	3.410908	-0.922590	0.025335
C	2.691204	4.092843	-2.947284
C	3.002928	3.530646	-1.710892
C	2.137269	3.689387	-0.632625
C	0.951594	4.404792	-0.797647
C	0.644613	4.974890	-2.032130
H	3.381036	3.979777	-3.783844
H	3.939827	2.987406	-1.593044

H	2.398465	3.296293	0.348071
H	0.269751	4.538174	0.040357
H	-0.261380	5.571436	-2.144119
H	3.633763	0.776079	-0.458719
C	-0.263490	2.585642	-6.452096
C	1.152897	2.184281	-5.979159
C	-1.160511	1.335360	-6.458493
C	-0.136672	3.136153	-7.886393
H	1.826060	3.052851	-5.939581
H	1.128890	1.705708	-4.990567
H	1.564417	1.464627	-6.702517
H	-2.162272	1.549689	-6.850964
H	-0.693453	0.582705	-7.111063
H	-1.251141	0.903164	-5.450351
H	0.287409	2.335048	-8.510018
H	-1.101152	3.422873	-8.317934
H	0.549581	3.991496	-7.928420
C	-2.670344	4.381225	-5.461073
C	-3.627803	3.347405	-4.828264
C	-2.853848	5.714707	-4.707811
C	-3.083538	4.559259	-6.935565
H	-3.521807	2.351478	-5.275927
H	-3.460870	3.269382	-3.744866
H	-4.658893	3.692471	-4.994498
H	-2.246891	6.519353	-5.140680
H	-3.913055	6.002472	-4.775533
H	-2.598651	5.605750	-3.643692
H	-4.123206	4.919525	-6.946544
H	-2.474893	5.299067	-7.466225
H	-3.053335	3.608781	-7.481352

M3-π

scf done: -1690.584754

C	-0.772507	1.536343	-0.629095
C	-2.014309	1.926830	-0.437784
C	0.404274	1.519624	-1.316212
N	0.834801	0.597969	-2.231327
C	0.205492	-0.634288	-2.444184
O	1.007110	-1.392814	-3.200332
O	-0.855919	-0.979704	-1.997142
H	-2.573803	1.674011	0.460810
H	-2.532965	2.514368	-1.196543
H	1.132112	2.313260	-1.120959
Au	0.323202	0.420065	0.953874
P	0.937119	-1.102803	2.672302
C	2.419086	-0.621616	3.640663
C	2.792931	-1.435015	4.722177
C	3.946619	-1.197462	5.455345
C	4.771886	-0.135748	5.105539
C	4.418145	0.681945	4.042334
C	3.243960	0.473573	3.305856
H	2.175677	-2.284060	4.999334
H	4.199951	-1.846254	6.290827
H	5.685661	0.061680	5.662212
H	5.050533	1.527461	3.774094

C	2.980653	1.485305	2.244777
C	2.226221	0.532834	-2.673232
H	2.883265	0.325148	-1.814683
H	2.536663	1.469156	-3.147302
C	2.141443	-0.629763	-3.651484
H	3.015315	-1.282652	-3.638141
C	2.040392	2.503508	2.450303
C	1.912732	3.546243	1.535199
C	2.727985	3.587637	0.405442
C	3.658263	2.573324	0.186566
C	3.784412	1.529492	1.101327
H	1.429578	2.489833	3.353566
H	1.189343	4.339022	1.717486
H	2.648167	4.417346	-0.295396
H	4.307166	2.606149	-0.687753
H	4.533400	0.752240	0.946010
H	1.940598	-0.298100	-4.675996
C	-0.536227	-1.219861	3.842176
C	-0.528756	0.079881	4.678184
C	-1.842483	-1.244322	3.014019
C	-0.557976	-2.434997	4.787674
H	0.363350	0.153397	5.312671
H	-0.586384	0.968693	4.032151
H	-1.416250	0.076345	5.327034
H	-1.940038	-2.157894	2.416868
H	-2.687517	-1.201291	3.716112
H	-1.910852	-0.377150	2.341517
H	-1.472074	-2.367805	5.395629
H	-0.594446	-3.381627	4.234929
H	0.291654	-2.447012	5.478893
C	1.396289	-2.720154	1.827634
C	0.180841	-3.250260	1.039569
C	2.520335	-2.367040	0.825615
C	1.924382	-3.830700	2.755162
H	-0.605335	-3.623103	1.707763
H	-0.242551	-2.482338	0.375149
H	0.518668	-4.090625	0.415966
H	3.399779	-1.945720	1.333906
H	2.827267	-3.289379	0.311437
H	2.165902	-1.653831	0.067138
H	2.143297	-4.708444	2.130022
H	2.854419	-3.532079	3.253937
H	1.188154	-4.130935	3.509377

Reactants

scf done: -2477.500251

C	4.929481	2.061481	6.637197
C	4.429858	2.982033	5.713347
C	5.009425	3.095178	4.434040
C	6.088757	2.292089	4.064521
C	6.571040	1.381470	4.999025
C	6.002910	1.262467	6.272747
C	3.347831	3.925894	5.804000
C	3.275463	4.588273	4.616103

N	4.289186	4.095280	3.749092
C	-2.895251	-0.844131	-0.027172
C	-2.793327	-2.130910	-0.261920
Au	-3.866017	-2.957613	-2.075409
P	-5.228840	-2.267720	-3.915647
C	-6.874206	-1.696275	-3.202084
C	2.501676	4.093917	7.017425
C	2.329094	5.666821	4.230985
C	-2.436864	-3.418250	-0.057230
N	-1.229915	-3.987231	-0.448413
C	-0.598495	-3.727959	-1.651421
O	0.428862	-4.575944	-1.791384
C	0.578629	-5.399011	-0.624425
C	-0.679697	-5.158345	0.215121
O	-0.919682	-2.903365	-2.474222
C	-4.251923	-0.933059	-4.824564
C	-5.587102	-3.559987	-5.164424
C	-4.987842	-4.836590	-5.129949
C	-5.219010	-5.719656	-6.193031
C	-6.025031	-5.376138	-7.268365
C	-6.615544	-4.118788	-7.305869
C	-6.388663	-3.225537	-6.268349
C	-4.102609	-5.359797	-4.055367
C	-4.618603	-5.751197	-2.811622
C	-3.809533	-6.412119	-1.888631
C	-2.480472	-6.690037	-2.201000
C	-1.949143	-6.272364	-3.418136
C	-2.757268	-5.615129	-4.340899
H	-3.408820	-0.153716	-0.693431
H	-3.071694	-4.077075	0.543459
H	-4.752997	-6.703482	-6.155915
H	-6.187758	-6.088608	-8.074405
H	-7.244125	-3.825429	-8.143818
H	-6.839696	-2.240344	-6.336950
H	-5.673162	-5.584333	-2.590123
H	-4.229749	-6.738593	-0.938218
H	-1.866196	-7.262794	-1.507510
H	-0.907129	-6.476791	-3.658897
H	-2.352097	-5.308837	-5.305273
C	-7.954903	-1.257243	-4.210774
C	-7.437758	-2.898573	-2.409835
C	-6.616055	-0.535859	-2.220465
C	-5.080124	-0.059657	-5.782363
C	-3.548434	-0.011796	-3.803938
C	-3.151493	-1.667563	-5.624068
H	-1.391743	-5.994414	0.182841
H	-0.444693	-4.940203	1.261958
H	0.688831	-6.435328	-0.955058
H	1.489869	-5.087541	-0.104566
H	-2.450052	-0.424618	0.876521
H	3.108492	4.379337	7.888850
H	1.728175	4.859065	6.891157
H	1.995395	3.153935	7.280853
H	2.848291	6.592473	3.956886
H	1.710484	5.390073	3.369610
H	1.667098	5.881901	5.076557

H	6.546283	2.369071	3.085218
H	7.415028	0.749740	4.726440
H	6.408242	0.539712	6.979084
H	4.479795	1.976518	7.626402
C	4.482062	4.553327	2.443526
O	3.785997	5.399242	1.925761
O	5.514231	3.933639	1.884493
C	5.914295	4.242809	0.496923
C	7.105803	3.309873	0.285087
C	4.784562	3.893068	-0.467965
C	6.353265	5.700253	0.387651
H	6.780709	5.862727	-0.610222
H	5.506106	6.377309	0.528234
H	7.124637	5.914114	1.138354
H	5.159934	3.988204	-1.495184
H	4.465911	2.855000	-0.307196
H	3.931721	4.564701	-0.334583
H	7.501698	3.450465	-0.728178
H	7.895511	3.536961	1.012475
H	6.793532	2.264371	0.403824
H	-8.815538	-0.892242	-3.631339
H	-7.622102	-0.442756	-4.864547
H	-8.301865	-2.098696	-4.820678
H	-7.556366	-0.317828	-1.693885
H	-5.859344	-0.804276	-1.469897
H	-6.301415	0.376781	-2.741387
H	-8.391619	-2.594483	-1.954936
H	-7.631878	-3.757205	-3.068014
H	-6.756310	-3.206048	-1.603616
H	-4.391715	0.635610	-6.284758
H	-5.574112	-0.653738	-6.559828
H	-5.826352	0.540278	-5.246750
H	-2.941127	0.712990	-4.365147
H	-4.259421	0.548637	-3.184658
H	-2.874697	-0.587369	-3.153200
H	-2.506374	-0.907536	-6.087962
H	-2.523066	-2.286660	-4.966674
H	-3.572850	-2.293320	-6.420338

M0

scf done: -2477.522319

C	2.195626	0.001516	5.055646
C	1.730983	0.753275	3.972078
C	2.416874	0.718214	2.742059
C	3.604255	-0.000143	2.595459
C	4.051815	-0.736216	3.686930
C	3.351381	-0.748920	4.901093
C	0.583628	1.604449	3.816792
C	0.591042	2.075948	2.528441
N	1.702753	1.542107	1.851968
C	-0.911141	-0.523355	2.609188
C	-0.419503	-0.801657	1.359221
Au	-1.516481	-0.191566	-0.321790

P	-2.877297	0.704481	-2.073152
C	-4.351404	1.568727	-1.269187
C	-0.394138	1.898798	4.899803
C	-0.423302	2.920527	1.852850
C	0.763745	-1.562147	1.466586
N	1.557036	-2.065416	0.517021
C	1.501030	-1.882467	-0.898648
O	2.321109	-2.774069	-1.456279
C	2.865960	-3.677868	-0.478948
C	2.698911	-2.934703	0.831685
O	0.880329	-1.063689	-1.511234
C	-1.763589	1.851493	-3.085220
C	-3.593334	-0.479984	-3.291115
C	-3.322904	-1.866483	-3.292456
C	-3.817928	-2.650705	-4.345169
C	-4.577426	-2.111673	-5.372063
C	-4.857699	-0.751159	-5.367729
C	-4.363254	0.043257	-4.343017
C	-2.554153	-2.618667	-2.265316
C	-3.046734	-2.805940	-0.968604
C	-2.380881	-3.635853	-0.070542
C	-1.213764	-4.291225	-0.456007
C	-0.715967	-4.112675	-1.744751
C	-1.382235	-3.282120	-2.641303
H	-1.842172	0.028653	2.752018
H	1.103340	-1.861441	2.467459
H	-3.603015	-3.718682	-4.334213
H	-4.950273	-2.752737	-6.168413
H	-5.451910	-0.302421	-6.161056
H	-4.581368	1.105445	-4.373311
H	-3.975494	-2.317327	-0.672737
H	-2.783176	-3.776328	0.931707
H	-0.701892	-4.953170	0.242321
H	0.185820	-4.634960	-2.064106
H	-0.994623	-3.145108	-3.651000
C	-5.412170	2.186476	-2.199794
C	-5.051060	0.481983	-0.418894
C	-3.831160	2.669225	-0.322024
C	-2.459964	2.870914	-4.002220
C	-0.843243	2.631951	-2.119825
C	-0.865924	0.925121	-3.939778
H	2.469256	-3.585976	1.679241
H	3.569015	-2.312124	1.076990
H	2.287825	-4.608552	-0.515494
H	3.906001	-3.873506	-0.745015
H	-0.435922	-0.881562	3.530065
H	0.084179	2.442765	5.726256
H	-1.235953	2.506157	4.548986
H	-0.806888	0.973588	5.329044
H	-0.038963	3.913600	1.594859
H	-0.756720	2.450731	0.915268
H	-1.295320	3.038188	2.506792
H	4.161398	0.012347	1.663408
H	4.971641	-1.311050	3.591963
H	3.729010	-1.340594	5.732702
H	1.660898	0.016873	6.004965

C	2.068839	1.894169	0.541558
O	1.692058	2.913590	0.012839
O	2.859057	0.963796	0.018570
C	3.662375	1.282026	-1.192038
C	4.491377	0.013491	-1.386433
C	2.758247	1.523572	-2.397977
C	4.573735	2.467604	-0.887396
H	5.267180	2.601768	-1.727320
H	3.996093	3.388216	-0.758477
H	5.157673	2.267083	0.021269
H	3.383331	1.549758	-3.300259
H	2.036543	0.702760	-2.486534
H	2.219479	2.470205	-2.303921
H	5.131570	0.133573	-2.268528
H	5.130659	-0.166619	-0.512131
H	3.836793	-0.852116	-1.548161
H	-6.160748	2.685231	-1.566170
H	-4.990704	2.939407	-2.876341
H	-5.932608	1.420027	-2.785925
H	-4.681523	3.050311	0.261957
H	-3.082114	2.274299	0.379681
H	-3.397945	3.510460	-0.877769
H	-5.900075	0.943175	0.106986
H	-5.440551	-0.330420	-1.049697
H	-4.365267	0.059901	0.330081
H	-1.678762	3.457264	-4.508871
H	-3.064188	2.389682	-4.778850
H	-3.085282	3.570189	-3.432927
H	-0.132557	3.218779	-2.721218
H	-1.402265	3.327760	-1.482138
H	-0.261921	1.954968	-1.479173
H	-0.107938	1.548088	-4.438469
H	-0.341213	0.187508	-3.314584
H	-1.445112	0.399027	-4.709585

TS1(K)

scf done: -2477.513228

C	2.855907	-0.831484	3.773249
C	2.195901	0.114973	2.989394
C	2.707334	0.486446	1.738590
C	3.882097	-0.073625	1.238635
C	4.530958	-1.009258	2.035889
C	4.031235	-1.387118	3.288749
C	0.924694	0.779400	3.165311
C	0.764555	1.631543	2.059027
N	1.803151	1.431129	1.183693
C	-0.376814	-0.633620	2.158873
C	-0.023611	-0.919042	0.815172
Au	-1.173654	-0.155442	-0.756746
P	-2.649458	0.698081	-2.452574
C	-3.472757	2.245601	-1.752243
C	0.224791	0.889631	4.479676
C	-0.357341	2.565361	1.831875
C	0.946184	-1.883695	0.744198

N	1.578683	-2.386842	-0.367925
C	1.935132	-1.685814	-1.518000
O	2.630207	-2.511854	-2.320969
C	2.634016	-3.843694	-1.789516
C	2.289966	-3.660407	-0.320005
O	1.729528	-0.528569	-1.782781
C	-1.649704	1.010578	-4.018067
C	-4.052116	-0.398056	-2.936918
C	-4.294726	-1.652657	-2.338415
C	-5.451362	-2.361988	-2.691306
C	-6.347047	-1.881437	-3.634869
C	-6.093302	-0.664796	-4.256098
C	-4.964349	0.060986	-3.902104
C	-3.401240	-2.349118	-1.373294
C	-3.775262	-2.480293	-0.032477
C	-3.015800	-3.253517	0.841214
C	-1.883578	-3.919453	0.380004
C	-1.511885	-3.805947	-0.956933
C	-2.264858	-3.025867	-1.828993
H	-1.296729	-0.086311	2.377437
H	1.277661	-2.404059	1.654783
H	-5.628357	-3.326425	-2.215672
H	-7.232657	-2.460053	-3.890596
H	-6.774418	-0.272753	-5.008708
H	-4.801893	1.017925	-4.388329
H	-4.676590	-1.977540	0.319849
H	-3.318676	-3.346598	1.883069
H	-1.293482	-4.533365	1.060077
H	-0.631879	-4.331547	-1.326948
H	-1.987569	-2.955271	-2.881292
C	-4.580212	2.915207	-2.585225
C	-4.106652	1.797188	-0.413504
C	-2.378278	3.293892	-1.465732
C	-2.318053	1.856304	-5.115605
C	-0.316526	1.687879	-3.631004
C	-1.313868	-0.385055	-4.593256
H	1.643878	-4.455945	0.066074
H	3.180222	-3.580379	0.319860
H	1.877254	-4.429657	-2.324781
H	3.620038	-4.279545	-1.961176
H	-0.073438	-1.321353	2.957617
H	0.790961	1.535033	5.163732
H	-0.786577	1.300645	4.387942
H	0.138125	-0.094967	4.957252
H	-0.005132	3.562385	1.548501
H	-0.988975	2.208297	1.004232
H	-0.965194	2.643380	2.738123
H	4.279924	0.206443	0.269566
H	5.454276	-1.455854	1.671533
H	4.571068	-2.120488	3.884159
H	2.455566	-1.125393	4.743090
C	1.953311	2.146632	-0.043572
O	1.047801	2.770051	-0.538572
O	3.194842	2.036061	-0.454018
C	3.694680	2.798022	-1.629636
C	5.139705	2.315654	-1.729244

C	2.917142	2.429060	-2.885709
C	3.635275	4.287273	-1.311070
H	4.102814	4.839845	-2.135834
H	2.598178	4.622480	-1.205378
H	4.189287	4.498831	-0.387780
H	3.459684	2.826836	-3.753483
H	2.846850	1.338608	-2.972078
H	1.909376	2.852648	-2.869721
H	5.645736	2.856314	-2.538092
H	5.668942	2.504562	-0.786733
H	5.163798	1.240776	-1.951184
H	-4.910067	3.811480	-2.038628
H	-4.227419	3.236037	-3.572907
H	-5.448907	2.257803	-2.704614
H	-2.804646	4.072079	-0.814809
H	-1.507005	2.854177	-0.962158
H	-2.040621	3.776447	-2.392286
H	-4.558193	2.676191	0.070106
H	-4.896985	1.050647	-0.578866
H	-3.353205	1.370550	0.264460
H	-1.593387	1.977730	-5.934868
H	-3.206301	1.368798	-5.533474
H	-2.584698	2.857748	-4.754881
H	0.326994	1.704575	-4.524380
H	-0.463152	2.722646	-3.298141
H	0.207640	1.134469	-2.839952
H	-0.668190	-0.248093	-5.472979
H	-0.762403	-0.992685	-3.860142
H	-2.217231	-0.925551	-4.906505

M1(K)

scf done: -2477.525277

C	2.290159	-0.095100	4.527395
C	1.825323	0.480145	3.355837
C	2.663909	0.585042	2.253627
C	3.975619	0.134311	2.259451
C	4.429054	-0.447851	3.441341
C	3.602975	-0.561289	4.560278
C	0.470198	1.019942	3.011484
C	0.684529	1.500853	1.602629
N	1.916658	1.235207	1.211613
C	-0.606358	-0.119230	2.987192
C	-0.522935	-0.941402	1.717912
Au	-2.100753	-0.883655	0.352644
P	-3.924836	-0.688225	-1.206774
C	-5.089204	0.651532	-0.551799
C	0.040908	2.162524	3.937692
C	-0.313395	2.240384	0.817382
C	0.567936	-1.700114	1.543414
N	0.939515	-2.313962	0.323170
C	1.028066	-1.641725	-0.870247
O	1.664956	-2.428802	-1.774208
C	1.937479	-3.708005	-1.187403
C	1.837195	-3.455145	0.307209
O	0.648376	-0.525816	-1.154318

C	-3.185918	-0.290392	-2.896409
C	-4.946316	-2.187832	-1.524090
C	-4.582554	-3.466651	-1.053126
C	-5.322098	-4.580971	-1.473466
C	-6.422664	-4.457851	-2.308692
C	-6.813523	-3.195052	-2.737761
C	-6.075124	-2.084448	-2.353268
C	-3.496089	-3.763089	-0.079720
C	-3.703315	-3.538980	1.286195
C	-2.766440	-3.961729	2.223478
C	-1.611361	-4.619568	1.808387
C	-1.399498	-4.850145	0.452391
C	-2.335008	-4.425551	-0.487382
H	-1.590495	0.359951	3.084357
H	1.319208	-1.874912	2.328124
H	-5.023519	-5.563427	-1.108704
H	-6.980138	-5.342463	-2.610641
H	-7.684202	-3.070675	-3.378321
H	-6.390729	-1.110899	-2.717165
H	-4.620216	-3.044460	1.610276
H	-2.943793	-3.783301	3.283029
H	-0.881172	-4.960608	2.541308
H	-0.511688	-5.390301	0.124022
H	-2.177611	-4.624691	-1.548418
C	-6.035594	1.331559	-1.558488
C	-5.923137	-0.016581	0.564185
C	-4.238350	1.764820	0.103231
C	-4.166828	-0.113085	-4.068183
C	-2.315602	0.976472	-2.768347
C	-2.262447	-1.485981	-3.231860
H	1.416231	-4.304065	0.857693
H	2.808138	-3.187307	0.759130
H	1.176595	-4.417541	-1.539180
H	2.924630	-4.037899	-1.520836
H	-0.454695	-0.711872	3.905823
H	0.795907	2.956592	3.978921
H	-0.914606	2.594594	3.617388
H	-0.090578	1.761379	4.950295
H	-0.045602	3.307784	0.822276
H	-0.325123	1.913353	-0.227388
H	-1.306695	2.122328	1.259989
H	4.622065	0.222450	1.392732
H	5.451156	-0.816499	3.488087
H	3.990080	-1.017112	5.468898
H	1.642631	-0.186756	5.398855
C	2.414267	1.515077	-0.135615
O	2.042364	2.485322	-0.733839
O	3.257667	0.577879	-0.455247
C	4.061898	0.662708	-1.720909
C	4.813163	-0.663702	-1.700267
C	3.143007	0.755160	-2.931688
C	5.011828	1.846483	-1.594602
H	5.692590	1.837787	-2.455178
H	4.466365	2.796616	-1.590473
H	5.609293	1.758306	-0.677683
H	3.758267	0.629210	-3.831777

H	2.393561	-0.042840	-2.891554
H	2.639024	1.724840	-2.977227
H	5.454653	-0.727494	-2.587119
H	5.440699	-0.737527	-0.803089
H	4.096530	-1.494172	-1.715520
H	-6.647899	2.059790	-1.005014
H	-5.479568	1.880014	-2.328353
H	-6.722510	0.628404	-2.041576
H	-4.921336	2.505089	0.545861
H	-3.602759	1.354348	0.900657
H	-3.599257	2.277861	-0.626251
H	-6.525339	0.757791	1.061436
H	-6.600488	-0.780228	0.161820
H	-5.271634	-0.481260	1.319830
H	-3.573759	0.092189	-4.972119
H	-4.745985	-1.026378	-4.249850
H	-4.853947	0.726821	-3.918163
H	-1.764776	1.114433	-3.710688
H	-2.925325	1.873327	-2.596392
H	-1.581707	0.868826	-1.956636
H	-1.762066	-1.276414	-4.189163
H	-1.489973	-1.622536	-2.463385
H	-2.835926	-2.417929	-3.338221

TS2(K)

scf done: -2477.520167

C	2.186199	-0.871598	4.031920
C	1.847505	0.070322	3.072750
C	2.784592	0.478773	2.126102
C	4.077361	-0.032693	2.102108
C	4.402462	-0.982549	3.068188
C	3.474394	-1.400667	4.022851
C	0.541411	0.779336	2.852087
C	0.848275	1.557934	1.575893
N	2.167769	1.458395	1.291638
C	-0.555709	-0.198269	2.393735
C	-0.199112	-0.337716	0.925378
Au	-1.608385	0.173259	-0.558244
P	-3.265125	0.758903	-2.171903
C	-4.461899	1.973900	-1.359815
C	0.168288	1.677994	4.029229
C	0.003523	2.679073	1.106087
C	0.793172	-1.224719	0.656173
N	1.520135	-1.367320	-0.521852
C	1.625421	-0.471098	-1.564138
O	2.438819	-0.996005	-2.507861
C	2.779310	-2.346941	-2.162090
C	2.520557	-2.415682	-0.668077
O	1.125084	0.624911	-1.676680
C	-2.366083	1.461563	-3.672600
C	-4.265091	-0.625874	-2.857934
C	-3.977386	-1.984284	-2.603060
C	-4.690919	-2.969508	-3.300142
C	-5.693124	-2.650331	-4.204294

C	-6.009787	-1.315645	-4.425991
C	-5.295955	-0.326142	-3.764305
C	-2.998432	-2.507107	-1.609773
C	-3.313690	-2.510901	-0.245436
C	-2.480515	-3.141870	0.672448
C	-1.317080	-3.773807	0.240406
C	-0.998027	-3.781670	-1.114842
C	-1.836493	-3.157797	-2.035598
H	-1.544748	0.259476	2.537277
H	1.148663	-1.937844	1.412352
H	-4.453318	-4.014062	-3.100467
H	-6.230236	-3.441486	-4.723860
H	-6.803203	-1.039714	-5.117465
H	-5.549932	0.709510	-3.972401
H	-4.235989	-2.033830	0.088641
H	-2.743340	-3.141553	1.729370
H	-0.664826	-4.270386	0.958178
H	-0.101880	-4.296258	-1.461690
H	-1.599392	-3.182615	-3.100025
C	-5.312351	2.858860	-2.288070
C	-5.398915	1.128626	-0.467848
C	-3.655857	2.912991	-0.431422
C	-3.228323	1.877381	-4.877228
C	-1.519399	2.669065	-3.219697
C	-1.408560	0.339592	-4.139732
H	2.128537	-3.386347	-0.344552
H	3.414013	-2.170611	-0.069447
H	2.126744	-3.021361	-2.730713
H	3.821016	-2.521759	-2.441627
H	-0.535671	-1.136513	2.974732
H	0.963432	2.400983	4.252617
H	-0.761469	2.225650	3.830847
H	0.011624	1.058104	4.921058
H	0.346722	3.603680	1.596432
H	0.074524	2.834526	0.026784
H	-1.040025	2.498413	1.381433
H	4.809313	0.289494	1.368447
H	5.406420	-1.401583	3.075005
H	3.760851	-2.143483	4.764034
H	1.453898	-1.196074	4.771202
C	2.788613	2.129683	0.181155
O	2.488793	3.254643	-0.119963
O	3.667282	1.324580	-0.365850
C	4.608830	1.823075	-1.414409
C	5.386513	0.559950	-1.771692
C	3.842351	2.351698	-2.622506
C	5.517735	2.870318	-0.782133
H	6.280315	3.158354	-1.516391
H	4.951655	3.763144	-0.495207
H	6.020927	2.452223	0.099913
H	4.558801	2.498527	-3.441223
H	3.084474	1.623548	-2.934274
H	3.354730	3.304663	-2.398480
H	6.152427	0.808853	-2.515839
H	5.878046	0.146388	-0.881494
H	4.705336	-0.187591	-2.196185

H	-5.961653	3.480465	-1.653512
H	-4.693708	3.534591	-2.890864
H	-5.963937	2.277771	-2.949180
H	-4.363557	3.583845	0.077679
H	-3.111869	2.337712	0.330502
H	-2.934783	3.527122	-0.985625
H	-6.033500	1.812692	0.114246
H	-6.047876	0.474942	-1.064588
H	-4.823499	0.513061	0.239815
H	-2.549924	2.255518	-5.656719
H	-3.774987	1.024491	-5.296919
H	-3.935659	2.677875	-4.633496
H	-0.872154	2.969804	-4.056935
H	-2.147624	3.528744	-2.951581
H	-0.875186	2.405341	-2.368862
H	-0.847797	0.707780	-5.011766
H	-0.688015	0.083523	-3.352149
H	-1.961215	-0.562384	-4.440917

M2(K)

scf done: -2477.554161

C	0.885126	-0.294173	3.631312
C	1.346955	0.652247	2.730688
C	2.696571	0.699835	2.370682
C	3.602006	-0.217893	2.898451
C	3.124435	-1.166035	3.802810
C	1.782897	-1.212306	4.173203
C	0.563867	1.730311	2.038566
C	1.599339	2.229833	0.956613
N	2.904526	1.718285	1.403982
C	-0.349205	1.196019	0.902910
C	0.851270	1.305744	-0.003706
Au	0.042089	2.003408	-2.189421
P	-1.437871	3.426594	-3.382772
C	-2.911432	3.789810	-2.269411
C	-0.040911	2.730152	3.002228
C	1.545989	3.701056	0.625998
C	1.321686	0.437255	-0.946059
N	2.668296	0.443717	-1.360770
C	3.230163	1.336136	-2.241113
O	4.482859	0.940636	-2.522476
C	4.842367	-0.161883	-1.677586
C	3.515309	-0.725950	-1.186481
O	2.708219	2.307624	-2.745963
C	-0.468027	4.953698	-3.912348
C	-2.155821	2.650314	-4.882082
C	-2.001941	1.282982	-5.194731
C	-2.698277	0.761258	-6.293942
C	-3.502957	1.555338	-7.097335
C	-3.627886	2.909706	-6.812730
C	-2.967238	3.439254	-5.713494
C	-1.129700	0.301927	-4.490558
C	-1.705424	-0.752616	-3.773224
C	-0.915831	-1.784165	-3.273213

C	0.459421	-1.785424	-3.499874
C	1.045438	-0.737386	-4.205942
C	0.257976	0.304778	-4.693000
H	-1.153307	1.908498	0.676582
H	0.743486	-0.454904	-1.221469
H	-2.578078	-0.296792	-6.523887
H	-4.022099	1.117579	-7.947463
H	-4.243338	3.554537	-7.436275
H	-3.098622	4.496139	-5.499242
H	-2.785715	-0.766886	-3.626827
H	-1.380716	-2.603692	-2.728122
H	1.069991	-2.612633	-3.139698
H	2.117860	-0.736517	-4.399656
H	0.712997	1.107019	-5.275116
C	-4.037784	4.632167	-2.898971
C	-3.510221	2.415188	-1.891608
C	-2.419429	4.494536	-0.989326
C	-1.301524	6.196717	-4.275264
C	0.496244	5.345081	-2.770708
C	0.390482	4.531043	-5.125350
H	3.151692	-1.571345	-1.790496
H	3.552681	-1.033713	-0.134524
H	5.437200	-0.863530	-2.265366
H	5.442859	0.228067	-0.847161
H	-0.780504	0.192633	1.013445
H	0.735594	3.183286	3.632552
H	-0.577451	3.532898	2.479447
H	-0.756833	2.225069	3.664228
H	1.949132	4.293905	1.457149
H	2.114843	3.924141	-0.280346
H	0.502286	4.000672	0.464440
H	4.651747	-0.195571	2.624099
H	3.824993	-1.885158	4.223803
H	1.436726	-1.963050	4.880485
H	-0.170612	-0.317993	3.903922
C	4.112101	2.228241	0.963817
O	4.222152	2.916255	-0.033435
O	5.105032	1.848717	1.767721
C	6.448504	2.451455	1.653416
C	7.187405	1.819514	2.832645
C	7.117430	2.062025	0.338551
C	6.357014	3.965192	1.831439
H	7.374435	4.370004	1.905901
H	5.848378	4.432071	0.982727
H	5.819275	4.198785	2.759583
H	8.134752	2.474440	0.330043
H	7.191795	0.968893	0.267536
H	6.564906	2.457850	-0.519648
H	8.215201	2.201364	2.864623
H	6.681120	2.070703	3.772801
H	7.216342	0.728045	2.719644
H	-4.823484	4.757306	-2.139304
H	-3.698945	5.630060	-3.199513
H	-4.485802	4.124368	-3.761071
H	-3.259336	4.552834	-0.282042
H	-1.604709	3.933966	-0.507913

H	-2.075438	5.516904	-1.192538
H	-4.339587	2.580700	-1.188638
H	-3.908521	1.897607	-2.775344
H	-2.766800	1.766789	-1.406444
H	-0.601707	6.987348	-4.583395
H	-1.987022	6.020614	-5.111642
H	-1.868500	6.571415	-3.414226
H	1.102999	6.194864	-3.115631
H	-0.038489	5.652591	-1.864013
H	1.173680	4.517312	-2.523920
H	1.047442	5.372214	-5.389232
H	1.030821	3.670884	-4.878895
H	-0.227685	4.284360	-5.997447

TS1(T)

scf done: -2477.510064

O	5.562710	2.296546	2.799977
N	6.588799	4.404512	2.858951
C	4.232394	5.182808	2.536429
O	7.780058	2.531275	3.000730
C	7.940729	4.851041	3.180149
H	8.240039	5.683140	2.532084
C	5.559047	5.308925	2.873343
H	5.936392	6.295646	3.178383
C	3.531679	6.386377	2.798328
H	2.521480	6.532360	2.409124
H	4.091401	7.319960	2.931573
C	6.529397	3.007827	2.870736
C	8.744211	3.587288	2.920059
H	9.186847	3.572838	1.917419
C	2.302438	5.395712	4.869574
C	3.006494	6.611736	4.858188
C	3.177087	4.390294	5.338788
C	4.407017	4.998858	5.683399
C	3.011014	2.998202	5.443702
H	2.063371	2.534971	5.170906
N	4.271796	6.374160	5.464467
C	5.480327	4.226265	6.144538
H	6.425365	4.674255	6.431891
C	5.288119	2.856886	6.234534
H	6.111102	2.239265	6.589701
C	4.070612	2.239908	5.890261
H	3.973081	1.159581	5.973700
O	6.343023	6.890946	6.147547
O	5.093902	8.485989	5.125691
C	7.492260	7.786619	6.447481
C	5.260790	7.367830	5.557548
C	8.464375	6.843102	7.151647
H	8.764555	6.027912	6.479605
H	7.996467	6.418035	8.048497
H	9.360329	7.402170	7.446904
C	8.097365	8.322723	5.154149
H	7.406279	8.996810	4.640287
H	8.367280	7.492786	4.487326

H	9.014294	8.872604	5.402890
C	7.043131	8.897895	7.390466
H	7.930285	9.455061	7.716961
H	6.557220	8.464863	8.274029
H	6.355032	9.586766	6.891433
C	2.365549	7.963745	4.860727
H	2.361503	8.377386	5.876815
H	1.326994	7.873732	4.526459
H	2.876794	8.684495	4.219014
C	0.938732	5.164929	4.343379
H	0.414053	4.400694	4.929230
H	1.002495	4.787491	3.307456
H	0.323447	6.070225	4.330384
H	9.523058	3.401294	3.662158
H	7.981992	5.178115	4.231516
Au	3.277179	3.571371	1.603497
P	2.101581	1.823895	0.454975
C	2.588592	1.566251	-1.303893
C	1.977720	0.532280	-2.033990
C	3.584941	2.331124	-1.946129
C	2.317704	0.255277	-3.350359
H	1.214756	-0.082191	-1.567154
C	3.914837	2.038983	-3.276939
C	3.294480	1.017079	-3.980034
H	1.819466	-0.555936	-3.877456
H	4.685931	2.639086	-3.759205
H	3.574927	0.815262	-5.012024
C	4.367883	3.449869	-1.348140
C	3.928656	4.771800	-1.469488
C	5.642762	3.204068	-0.827475
C	4.740887	5.826337	-1.062732
H	2.946954	4.969832	-1.900987
C	6.454175	4.259941	-0.423345
H	5.999162	2.175787	-0.753680
C	6.006789	5.572729	-0.541034
H	4.386931	6.851032	-1.165762
H	7.450477	4.056630	-0.029013
H	6.647560	6.398161	-0.231927
C	0.264698	2.253389	0.413671
C	-0.276495	2.245338	1.858079
C	0.180539	3.693312	-0.143680
C	-0.650703	1.369165	-0.454105
H	-0.369626	1.222221	2.244717
H	0.367562	2.824137	2.534790
H	-1.276899	2.702421	1.857313
H	0.558167	3.741338	-1.175343
H	-0.874800	4.003308	-0.149860
H	0.752507	4.397976	0.477127
H	-1.680312	1.740062	-0.337930
H	-0.389072	1.439396	-1.516316
H	-0.637066	0.317316	-0.145129
C	2.456402	0.187115	1.332714
C	3.901364	-0.204538	0.945270
C	2.441496	0.426758	2.860216
C	1.506268	-0.981117	1.020558
H	3.993826	-0.419093	-0.127121

H	4.610854	0.587977	1.224218
H	4.170243	-1.113071	1.504719
H	1.439658	0.677873	3.230572
H	2.766314	-0.502002	3.353549
H	3.138307	1.228516	3.137401
H	1.830119	-1.847191	1.617299
H	0.471308	-0.748839	1.301067
H	1.539171	-1.277916	-0.033973

M1(T)

scf done: -2477.524110

O	5.245328	2.520555	3.388424
N	6.413610	4.389485	2.608016
C	4.159325	5.399465	2.598684
O	7.426767	2.431520	2.867829
C	7.834013	4.699201	2.541664
H	8.059730	5.399885	1.730555
C	5.479385	5.422182	2.836905
H	5.971197	6.297141	3.288316
C	3.387194	6.553499	3.186434
H	2.423207	6.714554	2.686584
H	3.940984	7.503564	3.138514
C	6.241843	3.085536	2.989451
C	8.414445	3.316542	2.313482
H	8.525965	3.082534	1.247227
C	2.386229	5.037489	4.888917
C	3.052084	6.352685	4.708185
C	3.232683	4.176080	5.551728
C	4.440197	4.877345	5.872460
C	3.051296	2.811782	5.899090
H	2.114790	2.309835	5.667269
N	4.312754	6.182514	5.469811
C	5.476729	4.199340	6.529543
H	6.405992	4.686379	6.793736
C	5.264321	2.871275	6.846134
H	6.060269	2.338714	7.362541
C	4.069774	2.168842	6.543167
H	3.975041	1.125773	6.831241
O	6.395056	6.779482	6.041071
O	4.984181	8.358340	5.229942
C	7.534687	7.700549	6.296232
C	5.253440	7.221482	5.556942
C	8.608546	6.746184	6.810140
H	8.845199	5.998597	6.042490
H	8.258487	6.236511	7.716823
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C	7.990226	8.373704	5.005954
H	7.243311	9.079869	4.634752
H	8.195670	7.619039	4.236644
H	8.921890	8.914101	5.217590
C	7.136956	8.701368	7.373227
H	8.030162	9.273670	7.654855
H	6.762772	8.167959	8.256014
H	6.371647	9.392120	7.006701

C	2.179183	7.485925	5.243485
H	1.955858	7.326611	6.304580
H	1.236771	7.512305	4.685502
H	2.693547	8.441335	5.120243
C	1.009653	4.779927	4.450319
H	0.771965	3.712059	4.439860
H	0.806297	5.220655	3.465262
H	0.321861	5.264545	5.159831
H	9.363647	3.146439	2.824629
H	8.170700	5.140249	3.493406
Au	3.212126	3.851656	1.569116
P	2.103641	2.045634	0.394328
C	2.745323	1.593964	-1.280000
C	2.191291	0.482963	-1.938802
C	3.851775	2.233108	-1.877750
C	2.714018	-0.013207	-3.125652
H	1.330315	-0.022921	-1.515939
C	4.380560	1.706856	-3.066698
C	3.830381	0.595267	-3.688258
H	2.252776	-0.877963	-3.598383
H	5.241338	2.204595	-3.512691
H	4.264810	0.215031	-4.611024
C	4.518040	3.469931	-1.391231
C	3.872482	4.708842	-1.465620
C	5.863288	3.428917	-1.008127
C	4.558196	5.882075	-1.162967
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H	4.042748	6.839466	-1.226285
H	7.595794	4.555720	-0.416125
H	6.436858	6.747355	-0.540893
C	0.284991	2.465884	0.138304
C	-0.366414	2.695356	1.515832
C	0.279371	3.803988	-0.637440
C	-0.575309	1.464398	-0.653487
H	-0.483892	1.758254	2.074976
H	0.217252	3.401857	2.119878
H	-1.366716	3.123912	1.355761
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H	-0.765358	4.122387	-0.767704
H	0.815797	4.589337	-0.086013
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H	-0.232408	1.367763	-1.690662
H	-0.604091	0.473628	-0.185087
C	2.382360	0.490979	1.444961
C	3.865868	0.100055	1.248202
C	2.196981	0.860579	2.935445
C	1.493414	-0.729233	1.152147
H	4.068244	-0.234208	0.222505
H	4.529685	0.942618	1.496546
H	4.089962	-0.729090	1.936725
H	1.164106	1.146527	3.162823
H	2.444555	-0.026008	3.540207
H	2.868893	1.677162	3.232991

H	1.777379	-1.523559	1.859370
H	0.431674	-0.504179	1.309888
H	1.633563	-1.122099	0.138812

TS2(T)
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N	6.321145	4.035977	3.188473
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O	7.260292	2.049000	3.509129
C	7.729179	4.344291	3.349109
H	8.161183	4.706542	2.404001
C	5.387547	5.058304	3.042281
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H	2.290210	6.280805	2.851116
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C	8.292283	2.992847	3.787328
H	9.190050	2.695145	3.238417
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C	3.197496	6.011783	4.776642
C	3.929585	3.986216	5.778275
C	4.882183	4.994997	6.087364
C	4.071194	2.671034	6.265253
H	3.350069	1.905482	5.984811
N	4.513082	6.167415	5.461694
C	5.978527	4.688545	6.903284
H	6.718242	5.437121	7.161479
C	6.082180	3.390210	7.377440
H	6.926407	3.141116	8.018739
C	5.150134	2.378839	7.063904
H	5.293956	1.374921	7.454585
O	6.437100	7.249849	5.865323
O	4.703949	8.376014	4.916599
C	7.361020	8.415490	5.880913
C	5.207102	7.385000	5.390521
C	8.605447	7.835795	6.549264
H	8.986218	6.982056	5.973730
H	8.373788	7.511224	7.571851
H	9.385251	8.605218	6.593971
C	7.661523	8.838767	4.446841
H	6.770495	9.245925	3.959450
H	8.039188	7.982021	3.871811
H	8.440165	9.611716	4.464018
C	6.776177	9.545121	6.722708
H	7.542221	10.322254	6.841674
H	6.506985	9.171426	7.719053
H	5.896810	9.985718	6.244578
C	2.129149	6.844373	5.483832
H	2.076730	6.592292	6.551154
H	1.147940	6.659202	5.030478

H	2.365224	7.907506	5.381091
C	1.641368	3.914598	4.651973
H	1.738605	2.846299	4.431251
H	1.117362	4.398418	3.822034
H	1.008782	4.010525	5.551325
H	8.505205	2.961598	4.863103
H	7.861980	5.126968	4.111090
Au	3.180771	3.533681	1.567730
P	1.956826	1.983562	0.201288
C	2.516213	1.781414	-1.538715
C	1.751709	0.987847	-2.410209
C	3.627481	2.469965	-2.067463
C	2.048488	0.878325	-3.760783
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C	3.130538	1.577269	-4.281517
H	1.430447	0.253125	-4.402076
H	4.765629	2.896060	-3.832389
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C	4.590600	3.311420	-1.306173
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H	5.675886	6.538573	-1.186219
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C	-0.208475	3.275055	1.442180
C	0.229810	3.805215	-0.952053
C	-0.921706	1.663379	-0.311370
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H	-1.219840	3.697586	1.348868
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H	-0.741371	1.191287	-1.283265
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C	2.063086	0.266500	0.972030
C	3.567278	-0.092665	0.986083
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H	3.680016	-1.082201	1.453996
H	0.500126	0.563059	2.495114
H	1.754734	-0.625778	2.911927
H	2.141858	1.110230	2.985893
H	1.472293	-1.793174	0.830711
H	0.234452	-0.695455	0.191037
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O	7.037369	1.100823	3.847632
C	7.656634	3.348870	3.449754
H	8.194177	3.608699	2.527058
C	5.375811	4.040981	2.699410
H	5.781719	4.673828	1.901033
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H	3.998653	6.562982	2.816795
C	5.947396	1.744752	3.406378
C	8.116993	2.022670	4.065069
H	9.013007	1.611289	3.594426
C	3.770653	4.127329	4.792260
C	3.432612	5.661695	4.832074
C	4.885853	3.963988	5.781540
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C	6.482820	5.340830	6.979329
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C	7.011247	4.171178	7.529371
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C	6.478806	2.918635	7.237217
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C	6.504217	9.320079	5.916286
C	4.904207	7.577681	5.319769
C	7.800440	9.241316	6.721588
H	8.499934	8.544337	6.242959
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H	5.936426	11.226955	6.717847
H	5.280965	9.836778	7.621061
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H	2.230661	5.826030	6.605578
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H	2.066062	7.192904	5.471731
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H	2.961613	2.139671	4.717394
H	1.799393	3.390458	4.240309
H	2.220889	3.184392	5.959187

H	8.273873	2.105702	5.146159
H	7.743202	4.184720	4.155846
Au	3.604855	3.030321	1.493890
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C	1.460028	1.390671	-2.536747
C	3.654455	2.331796	-2.143342
C	1.704535	1.320121	-3.900624
H	0.498294	1.043447	-2.171249
C	3.874755	2.268351	-3.526129
C	2.919496	1.772090	-4.400775
H	0.943877	0.919454	-4.567019
H	4.835402	2.609146	-3.910697
H	3.127743	1.733734	-5.467992
C	4.807922	2.844272	-1.353656
C	5.218311	4.172185	-1.520649
C	5.608340	1.979659	-0.593143
C	6.406813	4.624077	-0.955160
H	4.604626	4.843511	-2.121946
C	6.802805	2.430926	-0.034791
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C	7.208768	3.750137	-0.223777
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H	7.430575	1.737773	0.525697
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C	0.462263	3.266427	0.146696
C	0.135340	3.666991	1.601455
C	0.946029	4.534390	-0.596776
C	-0.836296	2.765942	-0.510503
H	-0.284489	2.835738	2.179621
H	1.027299	4.045026	2.119558
H	-0.610877	4.473798	1.571198
H	1.175265	4.328456	-1.650524
H	0.140409	5.281649	-0.558918
H	1.835295	4.967109	-0.112567
H	-1.593156	3.556390	-0.398981
H	-0.711912	2.580876	-1.582799
H	-1.222443	1.862973	-0.021720
C	1.568043	0.339102	0.765333
C	2.917735	-0.414176	0.703087
C	1.126522	0.430323	2.239407
C	0.527556	-0.484015	-0.015905
H	3.287804	-0.488879	-0.329689
H	3.677801	0.063859	1.336743
H	2.753656	-1.434969	1.079042
H	0.117404	0.850146	2.335547
H	1.110397	-0.587874	2.654141
H	1.830349	1.030042	2.833223
H	0.411738	-1.446608	0.503715
H	-0.454971	0.000492	-0.044102
H	0.862088	-0.696568	-1.037851

Crystallographic Data Collection and Structure Determination for 4b', 4r and 7hd.

The X-ray intensity data of **4b'** and **7hd** were measured on a Bruker SMART Apex II CCD area detector diffractometer. X-ray diffraction study on compound **4r** was carried out using a four-circle Bruker X8APEX diffractometer equipped with a Mo-Kα generator (λ = 0.71073 Å) and an area detector and controlled by the Bruker-Nonius X8APEX software, that was used also for data reduction. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.3° ω steps. The software SMART[8] was used for collecting frames of data, indexing reflections, and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program and an empirical absorption correction was applied using SADABS.[9] The structures were solved by direct methods (SIR 2004)[10] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL)[11], using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters, U(H) = 1.2 U_{eq}(C) [U(H) = 1.5 U_{eq}(C-Me)], and allowed to ride on their carrier carbons. Crystal data and details of the data collection for **4b', 4r** and **7hd** are reported in Table S3.

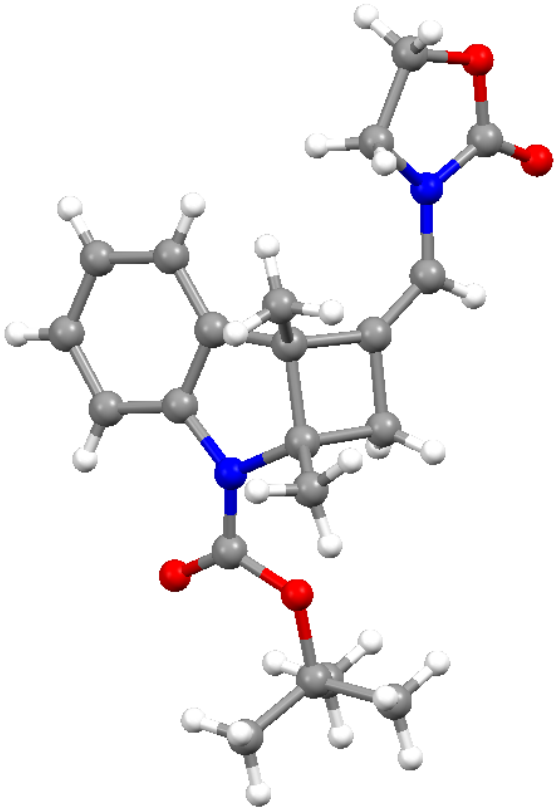
[8] *SMART & SAINT Software Reference Manuals*, version 5.051 (Windows NT Version), Bruker Analytical X-ray Instruments Inc.: Madison, WI, **1998**.

[9] Sheldrick, G.M. *SADABS, program for empirical absorption correction*, University of Göttingen, Germany, **1996**.

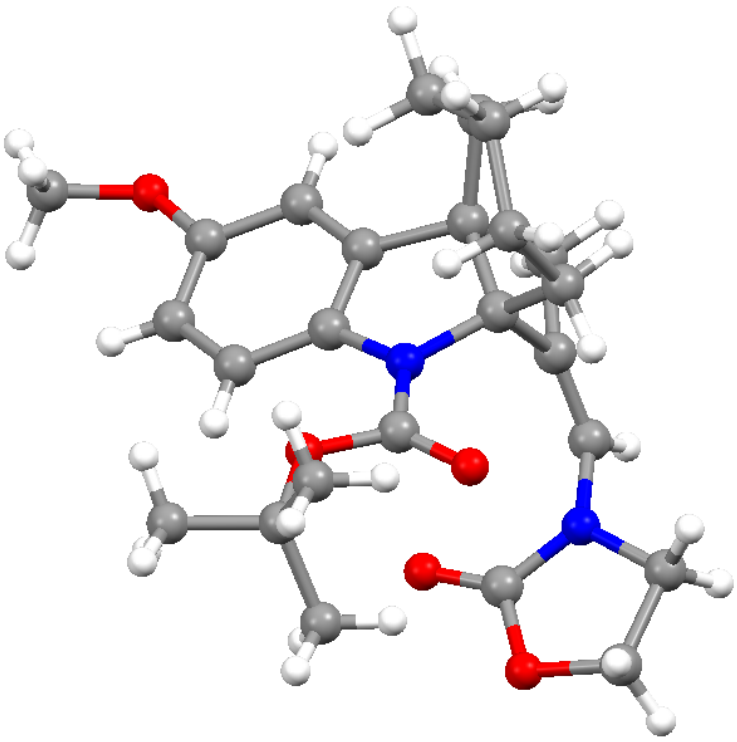
[10] Burla, M.C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; De Caro, G.L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr*. **2005**, *38*, 381-388.

[11] G. M. Sheldrick, SHELXTL*plus (Windows NT Version) Structure Determination Package,* Version 5.1. Bruker Analytical X-ray Instruments Inc.: Madison, WI, USA, 1998.

X-ray crystal structure of 4b', 4r and 7hd.



a)



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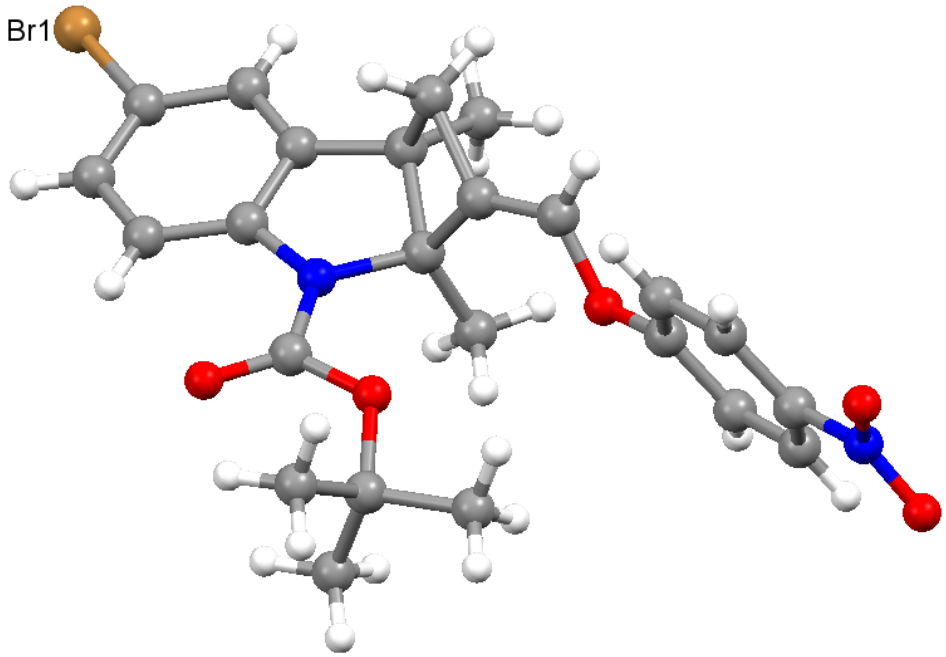

c)

Figure S10. a) Molecular structure of **4b'**; b) Molecular structure of **4r**; c) Molecular structure of **7hd.**

Table S3. Crystal data and structure refinement for **3b'** and **4r and 7hd**.

	4b'	**4r**	**7hd**
Formula	$C_{21}H_{26}N_2O_4$	$C_{25}H_{32}N_2O_5$	$C_{24}H_{25}BrN_2O_5$
Fw	370.44	440.53	501.36
T, K	296 (2)	293(2)	296 (2)
Crystal symmetry	orthorhombic	triclinic	monoclinic
Space group	*P ca2₁*	*P -1*	*P 2₁/n*
a, Å	9.887(1)	9.9946(9)	10.315(3)
b, Å	22.511(3)	11.648(1)	16.082(5)
c, Å	8.827(1)	20.470(2)	14.351(5)
α, °	90	87.347(4)	90
β, °	90	81.681(4)	102.518(4)
γ, °	90	89.034(4)	90
Cell volume, $Å^3$	1965(5)	2355.3(4)	2324(13)
Z	4	4	4
D_c, g cm^{-3}	1.252	1.242	1.433
μ(Mo-K_α), mm^{-1}	0.087	0.086	1.806
F(000)	792	944	1032
Crystal size mm	0.35x0.20x0.10	0.35x0.15x0.10	0.30x0.15x0.10
θ limits, °	1.81, 28.73	1.75, 27.98	1.93, 24.74
Refl. collected, unique (R_{int})	12932, 4363 (0.0194)	46979, 11227 (0.0369)	19491, 3861 (0.0568)
Goodness-of-fit-on F^2	1.242	1.020	1.064
$R_1(F)$[a], wR_2 (F^2) [$I > 2\sigma(I)$][b]	0.0507, 0.0940	0.0634, 0.2105	0.0862, 0.2368
Largest diff. peak and hole, e. $Å^{-3}$	0.134, -0.157	0.303, -0.389	1.529, -0.446

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.