Supporting Information for

Enantioselective Gold Catalyzed Dearomative [2+2]-Cycloadditions between Indoles and Allenamides

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Table of contents:

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 (deuteron chloroform: 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = duplet, t = triplet, q = quartet, 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 (deuteron chloroform: 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. 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. Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer. 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]Allenamide**2a-e**,[2a-c] **2f-h** [2d-e] were obtained following the known procedure.

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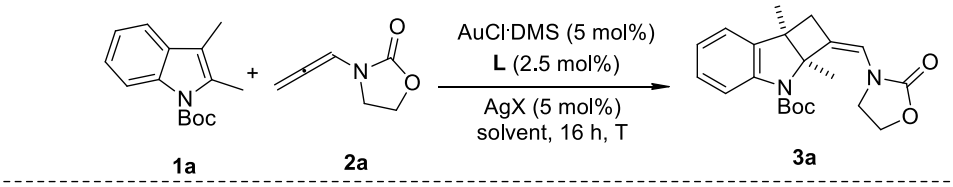
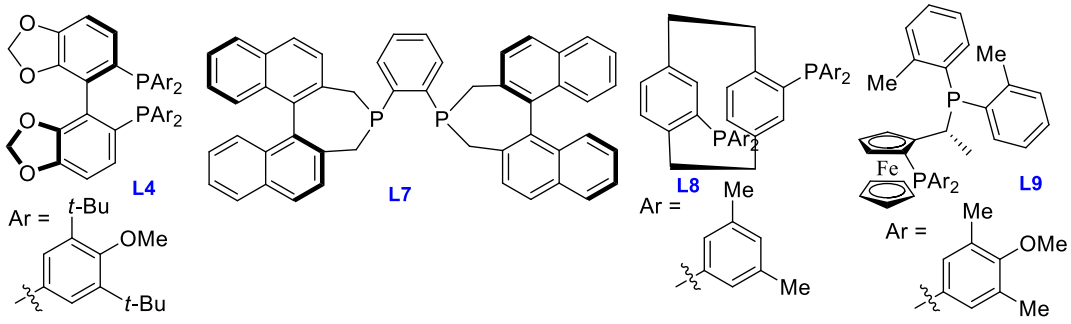
[1] K. S. MacMillan, J. Naidoo,J. Liang, L. Melito, N. S. Williams, L.Morlock, P. J. Huntington,S. Jo Estill, J. Longgood,G. L. Becker, S. L. McKnight, A. A. Pieper,J. K. De Brabander, .J M. Ready, *J. Am. Chem. Soc.,* 2011, **133**, 1428-1437.

[2] a)L.-L. Wei, J. A. Mulder, H. Xiong, C. A. Zificsak, C. J. Douglas, R. P. Hsung, *Tetrahedron*, 2001, **57**, 459-466; b)S.Suárez-Pantiga,C.Hernández-Díaz,M.Piedrafita, E.Rubio, J. M. González,*Adv. Synth. Catal.,*2012, **354**, 1651-1657; c) H.Faustino, F.López,L.Castedo, J. L.Mascareñas,*Chem. Sci.,*2011, **2**, 633-637; d) H. Xiong, R. P. Hsung, L.-L. Wei, C. R. Berry, J. A. Mulder, B. Stockwell, *Org. Lett.,*2000,**2**, 2869-2871; e) T. Lu, R. Hayashi, R. P. Hsung, K. A. DeKorver, A. G. Lohse, Z. Song, T. Tang, *Org. Biomol. Chem.,*2009, **7**, 3331–3337.

Table S1. Optimization of other reaction conditions.[a]

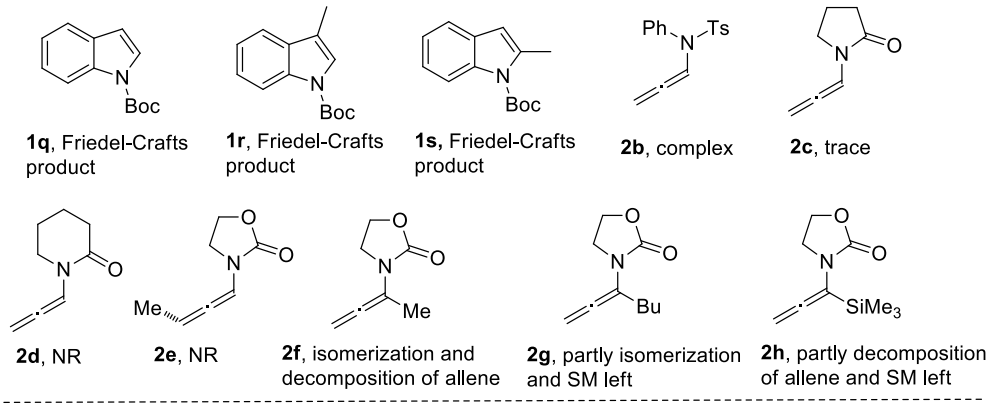




Entry	Ligand	AgX	Solvent	T (^{o}C)	Yield (%)[b]	Ee (%)[c]
1	(*R*,*R*)-**L7**	AgOTf	DCM	rt	trace	--
2	(S_p)-**L8**	AgOTf	DCM	rt	12	-37
3	(*R*,S_p)-**L9**	AgOTf	DCM	rt	52	7
4	(*R*)-**L4**	$AgPF_6$	DCM	rt	complex	--
5	(*R*)-**L4**	AgOTs	DCM	rt	ND	--
6	(*R*)-**L4**	AgOTf	benzene	rt	ND	--
7	(*R*)-**L4**	AgOTf	toluene	rt	complex	--
8	(*R*)-**L4**	AgOTf	THF	rt	trace	--
9	(*R*)-**L4**	AgOTf	DCM	-40	84	89
10	(*R*)-**L4**	AgOTf	DCM	-80	54	94

[a]All reactions were carried out under nitrogen atmosphere in anhydrous solvents (**1a**:**2a**:cat = 1.2:1:0.05). [b] After flash chromatography (*c*Hex:AcOEt:85:15).[c]Determined by HPLC. ND = not determined.

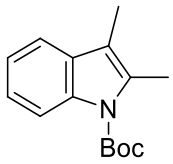
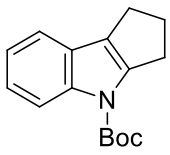
Table S2. List of substrates that were proved unsuccessful under the optimized conditions of the [2+2] reaction:



NR: No reaction. SM: starting material.

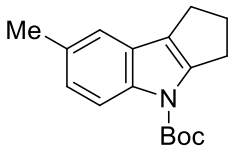
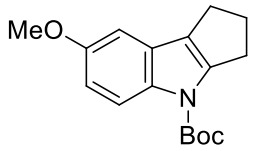
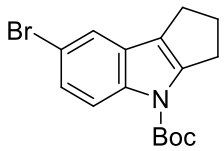
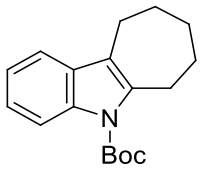
General procedure for the synthesis of *N*-Boc-indoles 1.[3]

Under nitrogen atmosphere, $(Boc)_2O$ (2.2mmol) was added to a solution of indole (2 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (12 mg, 0.1mmol) in dry acetonitrile (1 ml).The solution was stirred at room temperature for 6h, and then was evaporated under reduced pressure. After water was added, the resulting mixture was extracted twice with EtOAc. The combined organic layer was washed with brine, dried with Na_2SO_4, and evaporated under reduced pressure. The residue was purified via flash chromatography (*c*Hex:AcOEt = 98:2) to give the desired product as a white solid or colorless oil.

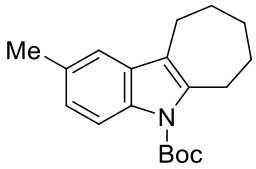
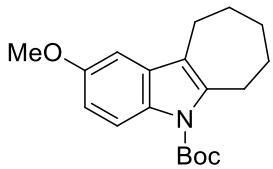
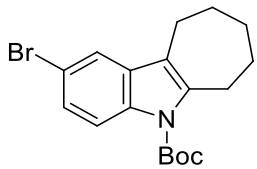
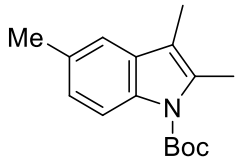
	**1a**.[3,5] White solid. Yield = 95% (*c*Hex:AcOEt = 98:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.11-8.03 (m, 1H), 7.43-7.34 (m, 1H), 7.23-7.15 (m, 2H), 2.51 (d, *J* = 0.8 Hz, 3H), 2.17 (d, *J* = 0.8 Hz, 3H), 1.66 (s, 9H).
	**1b**.[4] White solid. Yield = 92% (*c*Hex:AcOEt = 98:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 1H), 7.42-7.33 (m, 1H), 7.25-7.14 (m, 2H), 3.15-3.02 (m, 2H), 2.82-2.70 (m, 2H), 2.55-2.40 (m, 2H), 1.65 (s, 9H).

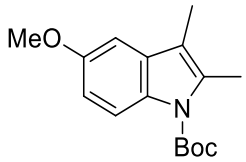
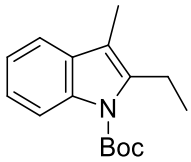
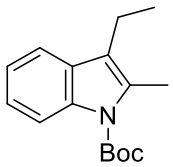
[3] R.Kuwano, M. Kashiwabara, *Org. Lett.,*2006, **8**, 2653-2655.

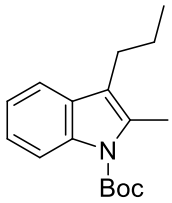
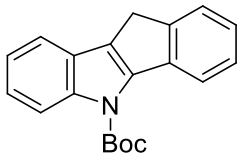
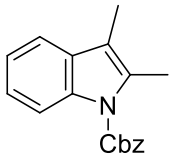
[4] H. Zaimoku, T. Hatta, T. Taniguchi, H. Ishibashi, *Org. Lett.,*2012, **14**, 6088-6091.

	**1c**. White solid. Yield = 96% (*c*Hex:AcOEt = 98:2). ***Mp*** = 129-131°C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.14 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.45 (dd, *J* = 14.4, 7.2 Hz, 2H), 2.40 (s, 3H), 1.62 (s, 9H). ***^{13}C-NMR***(100 MHz, $CDCl_3$) δ 149.9, 144.0, 138.3, 131.9, 126.9, 124.2, 124.0, 118.6, 115.3, 82.7, 29.1, 28.2, 27.3, 24.0, 21.3.***LC-MS*** (m/z): 294 $[M+Na]^+$. ***Anal. calcd*** for ($C_{17}H_{21}NO_2$: 271.16): C, 75.25; H, 7.80, N, 5.16; Found: C, 75.11, H, 7.61, N, 5.15.
	**1d**. White solid. Yield = 90% (*c*Hex:AcOEt = 98:2). ***Mp*** = 112-114°C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 6.90-6.70 (m, 2H), 3.83 (s, 3H), 3.05 (t, *J* = 6.8 Hz, 2H), 2.72 (t, *J* = 6.8 Hz, 2H), 2.56-2.30 (m, 2H), 1.62 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 155.8, 149.8, 144.7, 134.7, 127.5, 124.2, 116.3, 110.7, 101.8, 82.8, 55.6, 29.1, 28.2, 27.3, 24.0.***LC-MS*** (m/z): 288 $[M+H]^+$. ***Anal. calcd*** for ($C_{17}H_{21}NO_3$: 287.15): C, 71.06; H, 7.37, N, 4.87; Found: C, 70.95, H, 7.21, N, 4.75.
	**1e**. White solid. Yield = 95% (*c*Hex:AcOEt= 98:2). ***Mp*** = 135-137°C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.31 (dd, *J* = 8.8, 1.6 Hz, 1H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.55-2.43 (m, 2H), 1.64 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 149.6, 145.3, 138.8, 128.3, 125.4, 123.6, 121.2, 117.0, 115.9, 83.4, 29.1,28.2, 27.3, 23.8. ***LC-MS*** (m/z): 336 $[M+H]^+$. ***Anal. calcd*** for ($C_{16}H_{18}BrNO_2$: 335.05): C, 57.16; H, 5.40, N, 4.17; Found: C, 57.01, H, 5.31, N, 4.13.
	**1f**.[5] White solid. Yield = 92% (*c*Hex:AcOEt = 98:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.07-7.93 (m, 1H), 7.48-7.35 (m, 1H), 7.25-7.14 (m, 2H), 3.30-3.15 (m, 2H), 2.84-2.68 (m, 2H), 2.00-1.75 (m, 6H), 1.68 (s, 9H).

[5] D. Dhanak, C. B. Reese, *J. Chem. Soc., Perkin Trans. 1,* 1986, 2181-2186.

	**1g**. Colorless oil. Yield = 95% (*c*Hex:AcOEt = 98:2).***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.25 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 3.34-3.22 (m, 2H),2.83-2.71 (m, 2H), 2.49 (s, 3H), 1.98-1.78 (m, 6H), 1.72 (s, 9H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 150.9, 139.5, 133.5, 131.5, 130.3, 124.2, 121.1, 117.4, 114.8, 83.1, 30.3, 28.3, 28.0, 26.9, 26.3, 23.0, 21.3.***LC-MS*** (m/z): 300 $[M+H]^+$. ***Anal. calcd*** for ($C_{19}H_{25}NO_2$: 299.19): C, 76.22; H, 8.42, N, 4.68; Found: C, 76.01, H, 8.31, N, 4.75.
	**1h**. Colorless oil. Yield = 89% (*c*Hex:AcOEt = 98:2). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.88-6.82 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.89 (s, 3H), 3.36-3.16 (m, 2H), 2.85-2.62 (m, 2H), 2.00-1.76 (m, 6H), 1.70 (s, 9H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 155.6, 150.8, 140.3, 130.9, 130.0, 121.1, 115.8, 111.2, 100.4, 83.1, 55.6, 30.3, 28.2, 28.0, 26.8, 26.2, 23.1. ***LC-MS*** (m/z): 316 $[M+H]^+$. ***Anal. calcd*** for ($C_{19}H_{25}NO_3$: 315.18): C, 72.35; H, 7.99, N, 4.44; Found: C, 72.43, H, 7.93, N, 4.32.
	**1i**. White solid. Yield = 96% (*c*Hex:AcOEt = 98:2). ***Mp*** = 66-68 °C. ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.29 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.36-3.10 (m, 2H), 2.77-2.59 (m, 2H), 1.71-1.63 (m, 6H), 1.67 (s, 9H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 150.5, 140.8, 134.0, 131.9, 125.6, 120.6, 120.2, 116.5, 115.5, 83.8, 30.1, 28.2, 28.1, 26.7, 26.1, 23.0. ***LC-MS*** (m/z): 402 $[M+K]^+$. ***Anal. calcd*** for ($C_{18}H_{22}BrNO_2$: 363.08): C, 59.35; H, 6.09, N, 3.85; Found: C, 59.21, H, 6.01, N, 3.71.
	**1j**. White solid. Yield = 95% (*c*Hex:AcOEt = 98:2). ***Mp*** = 94-96 °C. ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.20 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 2.52 (s, 3H), 2.45 (s, 3H), 2.17 (s, 3H), 1.68 (s, 9H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 150.9 133.8, 132.9, 131.6, 130.9, 124.5, 117.8, 115.0, 113.5, 83.0, 28.3, 21.3, 13.9, 8.7. ***LC-MS*** (m/z): 260 $[M+H]^+$. ***Anal. calcd*** for

	($C_{16}H_{21}NO_2$: 259.16): C, 74.10; H, 8.16, N, 5.40; Found: C, 74.00, H, 8.21, N, 5.28.
	**1k**. White solid. Yield = 86% (*c*Hex:AcOEt = 98:2). ***Mp*** = 71-73 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 1H), 6.96-6.74 (m, 2H), 3.88 (s, 3H), 2.52 (s, 3H), 2.16 (s, 3H), 1.67 (s, 9H). ***^{13}C-NMR***(100 MHz, $CDCl_3$) δ 155.6, 150.6, 133.5, 131.5, 130.1, 115.9, 113.5, 111.1, 100.8, 82.9, 55.5, 28.2, 13.9, 8.6. ***LC-MS*** (m/z): 276 $[M+H]^+$. ***Anal. calcd*** for ($C_{16}H_{21}NO_3$: 275.15): C, 69.79; H, 7.69, N, 5.09; Found: C, 69.65, H, 7.55, N, 5.00.
	**1l**.[4] White solid. Yield = 94% (*c*Hex:AcOEt = 98:2). ***Mp*** = 54-56 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz,1H), 7.43 (d, *J* = 6.8 Hz, 1H), 7.35-7.15 (m, 2H), 3.04 (q, *J* = 7.2 Hz, 2H), 2.21 (s, 3H), 1.70 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 150.5, 138.6, 135.8, 130.7, 123.3, 122.2, 117.8, 115.4, 113.3, 83.2, 28.2, 20.1, 14.5, 8.5. ***LC-MS*** (m/z): 258 $[M+H]^+$.
	**1m**. Colorless oil. Yield = 94% (*c*Hex:AcOEt = 98:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.15-8.05 (m, 1H), 7.50-7.41 (m, 1H), 7.26-7.18 (m, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.54 (s, 3H), 1.69 (s, 9H), 1.19 (t, *J* = 7.6 Hz, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 150.5, 138.6, 135.8, 130.7, 123.3, 122.2, 117.8, 115.4, 113.3, 83.2, 28.2, 20.1, 14.5, 8.5. ***LC-MS*** (m/z): 260 $[M+H]^+$. ***Anal. calcd*** for ($C_{16}H_{21}NO_2$: 259.16): C, 74.10; H, 8.16, N, 5.40; Found: C, 74.19, H, 8.21, N, 5.43.

	**1n**.[6] Colorless oil. Yield = 95% (*c*Hex:AcOEt = 98:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.15-8.03 (m, 1H), 7.50-7.38 (m, 1H), 7.25-7.14 (m, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.54 (s, 3H), 1.69 (s, 9H), 1.62 (q, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 150.8, 135.7, 132.9, 130.2, 123.0, 122.2, 118.5, 117.9, 115.3, 83.2, 28.3, 25.9, 23.2, 14.0, 13.9. ***LC-MS*** (m/z): 296 $[M+Na]^+$.
	**1p**. White solid. Yield = 90% (*c*Hex:AcOEt = 98:2). ***Mp*** = 168-170 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 8.17-8.06 (m, 1H), 7.61-7.53 (m, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.31-7.17 (m, 3H), 3.69 (s, 2H), 1.77 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 150.4, 147.2, 143.7, 139.9, 135.7, 127.5, 126.7, 126.3, 125.1, 124.9, 123.7, 123.0, 122.6, 118.9, 116.5, 84.3, 29.9, 28.4. ***LC-MS*** (m/z): 306 $[M+H]^+$. ***Anal. calcd*** for ($C_{20}H_{19}NO_2$: 305.14): C, 78.66; H, 6.27, N, 4.59; Found: C, 78.72, H, 6.23, N, 4.52.
	**1q**, synthesized from the known procedure for the protection of Cbz.[7] White solid. Yield = 61% (*c*Hex:AcOEt = 98:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.14-8.04 (m, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.46-7.34 (m, 4H), 7.25-7.16 (m, 2H), 5.47 (s, 2H), 2.54 (s, 3H), 2.19 (s, 3H).

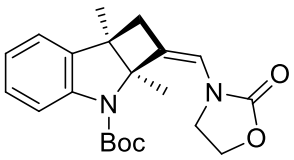
General procedure for the [2+2] cycloaddition reaction.

AuCl·DMS (1.5 mg, 5/10mol%) and (*R*)-DTBM-Segphos (3.0 mg, 2.5/5mol%) 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 aluminum foil. AgOTf

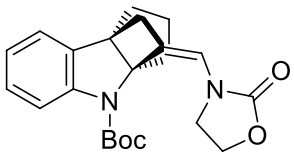
[6] S. Coulton, S. Gilchrist, K. Graham, *Tetrahedron,* 1997, **53**, 791-798.

[7] a) H.-C. Hsu, D.-R. Hou, *Tetrahedron Lett.,* 2009, **50**, 7169-7171; b) I.-K. Park, S.-E. Suh, B.-Y. Lim, C.-G. Cho, *Org. Lett.,* 2009, **11**, 5454-5456.

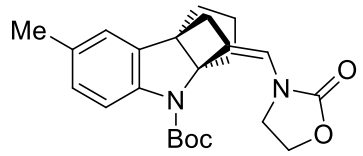
(1.3 mg, 5/10 mol%) was added and the solution was stirred at room temperature for 20 min. Then the mixture was cooled to -60 °C, then substrate **1** (0.12/0.06mmol), and **2a** (0.1/0.05 mmol) were added in sequence and the mixture stirred at the same temperature for16 hours. Removed the solvent under reduced pressure and the crude was purified by flash column chromatography to give the desired product.



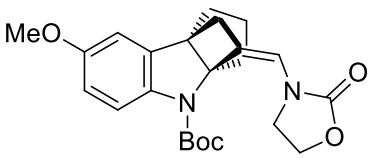
3a. Colorless oil. Yield = 95% (*c*Hex:AcOEt = 85:15). *Ee*= 93%. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (9.8 min), Rt_{major} (10.6 min). $[\alpha]_D$ = 122.2 (*c* = 1.25, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.22-7.08 (m, 2H), 6.99 (t, *J* = 7.0 Hz, 1H), 6.19 (s, 1H), 4.68-4.55 (m, 1H), 4.42-4.32 (m, 2H), 3.87 (dd, *J* = 17.2, 8.8 Hz, 1H), 2.77 (d, *J* = 14.4 Hz, 1H), 2.58 (d, *J* = 14.4 Hz, 1H), 1.70 (s, 3H), 1.58 (s, 9H), 1.38 (s, 3H). ***^{13}C-NMR***(100 MHz, $CDCl_3$) δ 156.9, 151.9, 142.6, 138.0, 127.6, 122.9, 122.8, 119.2, 116.5, 81.6,77.2,75.0, 62.5, 47.6, 45.5, 42.2, 28.5, 18.4, 18.2. ***LC-MS*** (m/z): 371$[M+H]^+$. ***Anal. calcd*** for ($C_{21}H_{26}N_2O_4$: 370.19): C, 68.09; H, 7.07, N, 7.56; Found: C, 68.21, H, 6.59, N, 7.41.



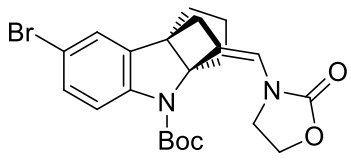
3b.White solid. The Z configuration of alkene was determined by NOE experiment. Yield = 96% (*c*Hex:AcOEt = 85:15). *Ee* = 94%. ***MP*** = 139-141 °C. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (9.4 min), Rt_{major} (13.2 min).$[\alpha]_D$ = 5.2 (*c* = 0.5, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.25-7.07 (m, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.14 (s, 1H), 4.82 (s, 1H), 4.51-4.26 (m, 2H), 3.70 (q, *J* = 8.8 Hz, 1H), 2.85-2.50 (m, 3H), 2.32-1.90 (m, 4H), 1.81-1.64 (m, 1H), 1.59 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.1, 152.4, 144.2, 136.3, 127.7, 123.9, 123.2, 121.0, 116.4, 81.7, 80.1, 77.2, 62.8, 54.8, 45.8, 39.2, 38.1, 36.7, 28.38, 28.36. ***LC-MS*** (m/z): 787 $[2M+Na]^+$. ***Anal. calcd*** for ($C_{22}H_{26}N_2O_4$: 382.19): C, 69.09; H, 6.85, N, 7.32; Found: C, 68.90, H, 6.69, N, 7.44.



3c.White solid. Yield = 96% (*c*Hex:AcOEt = 85:15). *Ee* = 93%. ***MP*** = 116-118 °C. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (11.5 min), Rt_{major} (17.2 min). $[\alpha]_D$ = 25.4 (*c* = 0.85, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.4 Hz, 1H), 7.09-6.85 (m, 2H), 6.14 (s, 1H), 4.84 (s, 1H), 4.46-4.27 (m, 2H), 3.71 (q, *J* = 8.8 Hz, 1H), 2.75 (d, *J* = 16.0 Hz, 1H), 2.67 (dd, *J* = 16.0, 2.0 Hz, 1H),2.65-2.54 (m, 1H), 2.31 (s, 3H), 2.15-1.97 (m, 4H), 1.78-1.68 (m, 1H), 1.58 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.1, 152.5, 142.1, 136.4, 132.8, 128.3, 124.5, 120.9, 116.2, 81.5, 80.2, 77.2, 62.8, 54.9, 45.7, 39.2, 38.1, 36.7, 28.5, 28.4, 20.8.***LC-MS*** (m/z): 435 $[M+K]^+$.***Anal. calcd*** for ($C_{23}H_{28}N_2O_4$: 396.20): C, 69.67; H, 7.12, N, 7.07; Found: C, 69.55, H, 7.01, N, 7.21.

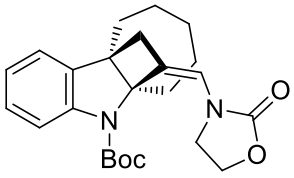


3d.White solid. Yield = 94% (*c*Hex:AcOEt = 85:15). *Ee* = 95%. ***MP*** = 128-130 °C. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (16.7 min), Rt_{major}(21.8 min). $[\alpha]_D$ = 32.7 (*c* = 0. 7, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 6.78-6.63 (m, 2H), 6.16 (s, 1H), 4.87 (s, 1H), 4.49-4.26 (m, 2H), 3.79 (s, 3H), 3.72 (q, *J* = 8.8 Hz, 6H), 2.77 (d, *J* = 15.6 Hz, 1H), 2.68 (dd, *J* = 15.6, 2.0 Hz, 1H), 2.61 (d, *J* = 6.8 Hz, 1H), 2.25-1.96 (m, 4H), 1.80-1.65 (M, 1H), 1.58 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.1, 156.0, 152.3, 138.0, 137.6, 120.9, 117.1, 112.6, 109.7, 81.4, 80.3, 77.2, 62.8, 55.6, 55.0, 45.6, 39.1, 38.1, 36.5, 28.41, 28.37. ***LC-MS*** (m/z): 847 $[2M+Na]^+$. ***Anal. calcd*** for ($C_{23}H_{28}N_2O_5$: 412.20): C, 66.97; H, 6.84, N, 6.79; Found: C, 66.85, H, 6.71, N, 6.55.

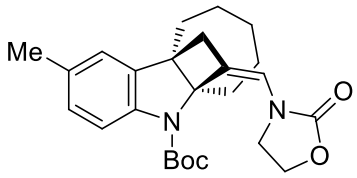


3e. White solid. Yield = 55% (*c*Hex:AcOEt = 85:15). *Ee* = 95%. ***MP*** = 173-175 °C. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (14.3 min), Rt_{major} (25.3 min). $[\alpha]_D$ = 42.2 (*c* = 0.27, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 1H), 7.32-7.29 (m, 1H), 7.24 (s, 1H), 6.16 (s, 1H), 4.80 (s, 1H), 4.50-4.25 (m, 2H), 3.69 (q, *J* = 8.8 Hz, 1H), 2.78 (d, *J* = 16.0 Hz, 2H), 2.69 (d, *J* = 16.0 Hz, 2H), 2.65-2.55 (m, 1H), 2.25-1.96 (m, 4H), 1.80-1.65 (m, 1H), 1.58 (s, 9H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.1, 152.2, 143.5, 138.5, 130.6, 127.0, 121.3, 117.9, 115.4, 82.2, 80.6, 77.2, 62.8, 54.5, 45.8, 39.2, 38.1, 36.6, 28.36,

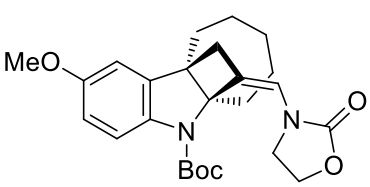
28.30.***LC-MS*** (m/z): 499 $[M+K]^+$. ***Anal. calcd*** for ($C_{22}H_{25}BrN_2O_4$: 460.10): C, 57.27; H, 5.46, N, 6.07; Found: C, 57.15, H, 5.35, N, 6.17.



3f. White solid. The Z configuration of alkene was determined by NOE experiment. Yield = 95% (*c*Hex:AcOEt = 85:15). *Ee* = 98%. ***MP*** = 178-180 °C. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (9.4 min), Rt_{major} (11.6 min). $[\alpha]_D$ = 107.0 (*c* = 0.57, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.04 (s, 1H), 4.61 (s, 1H), 4.46-4.24 (m, 2H), 3.72 (dd, *J* = 17.2, 8.8 Hz, 1H), 3.09 (q, *J* = 7.2 Hz, 1H), 2.71 (d, *J* = 15.2 Hz, 1H), 2.62 (d, *J* = 15.2 Hz, 1H), 2.20 (q, *J* = 7.2 Hz, 1H), 1.94 (t, *J* = 12.8 Hz, 2H), 1.79-1.61 (m, 3H), 1.59 (s, 9H), 1.25-0.95 (m, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.2, 152.0, 144.0, 136.7, 127.6, 122.83, 122.77, 119.7, 116.2, 81.6, 78.7, 77.2, 62.5, 52.1, 46.3, 42.0, 36.1, 32.7, 31.6, 28.4, 25.6, 24.6. ***LC-MS*** (m/z): 843 $[2M+Na]^+$. ***Anal. calcd*** for ($C_{24}H_{30}N_2O_4$: 410.22): C, 70.22; H, 7.37, N, 6.82; Found: C, 70.01, H, 7.21, N, 6.70.

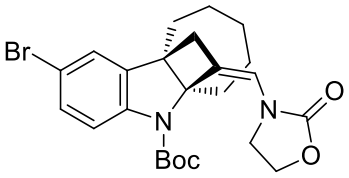


3g. Colorless oil. Yield = 96% (*c*Hex:AcOEt = 85:15). *Ee* = 98%. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (9.0 min), Rt_{major} (14.1 min).$[\alpha]_D$ = 101.7 (*c* = 0.29, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.87 (s, 1H), 6.03 (s, 1H), 4.60 (s, 1H), 4.44-4.26 (m, 2H), 3.72 (q, *J* = 8.8 Hz, 1H), 3.08 (q, *J* = 7.2 Hz, 1H), 2.69 (dd, *J* = 15.2, 1.6 Hz, 1H), 2.61 (dd, *J* = 15.2, 1.6 Hz, 1H), 2.31 (s, 3H), 2.19 (q, *J* = 7.2 Hz, 1H), 2.00-1.85 (m, 2H), 1.78-1.62 (m, 3H), 1.58 (s, 9H), 1.24-0.92 (m, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.2, 152.0, 141.7, 136.8, 132.3, 128.1, 123.3, 119.6, 116.0, 81.3, 78.7, 77.2, 62.5, 52.2, 46.2, 42.0, 36.2, 32.6, 31.6, 28.4, 25.6, 24.7, 20.8. ***LC-MS*** (m/z): 425 $[M+H]^+$. ***Anal. calcd*** for ($C_{25}H_{32}N_2O_4$: 424.24): C, 70.73; H, 7.60, N, 6.60; Found: C, 70.59, H, 7.45, N, 6.41.

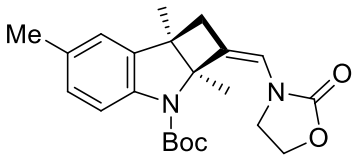


3h. White solid. Yield = 92% (*c*Hex:AcOEt 85:15). *Ee* = 95%. ***MP*** = 124-126 °C. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (8.0 min), Rt_{major} (10.8

min). $[\alpha]_D$ = 59.3 (*c* = 0.29, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 6.72 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 6.04 (s, 1H), 4.63 (s, 1H), 4.44-4.25 (m, 2H), 3.79 (s, 3H), 3.72 (q, *J* = 8.8 Hz, 1H), 3.25-2.96 (m, 1H), 2.71 (d, *J* = 15.2 Hz, 1H), 2.62 (d, *J* = 15.2 Hz, 1H), 2.25-2.11 (m, 1H), 1.99-1.84 (m, 2H), 1.81-1.61 (m, 4H), 1.58 (s, 9H), 1.15-0.92 (m, 2H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.2, 155.8, 151.8, 138.2, 137.8, 119.7, 116.8, 112.2, 108.8, 81.3, 78.9, 77.2, 62.5, 55.6, 52.4, 46.2, 41.9, 36.1, 32.7, 31.6, 28.4, 25.6, 24.7. ***LC-MS*** (m/z): 441 $[M+H]^+$. ***Anal. calcd*** for ($C_{25}H_{32}N_2O_5$: 440.23): C, 68.16; H, 7.32, N, 6.36; Found: C, 68.01, H, 7.16, N, 6.25.

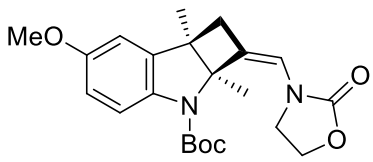


3i. White solid. Yield = 41% (*c*Hex:AcOEt 85:15). *Ee* = 99%. ***MP*** = 148-150 °C. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (11.2 min), Rt_{major} (18.9 min). $[\alpha]_D$ = 133.9 (*c* = 0.28, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 1H), 7.31-7.23 (m, 1H), 7.15 (s, 1H), 6.05 (s, 1H), 4.56 (s, 1H), 4.45-4.26 (m, 2H), 3.70 (q, *J* = 8.8 Hz, 1H), 3.20-2.96 (m, 1H), 2.72 (d, *J* = 15.2 Hz, 1H), 2.62 (d, *J* = 15.2 Hz, 1H), 2.15 (dd, *J* = 7.2 Hz, 1H), 2.00-1.84 (m, 2H), 1.79-1.61 (m, 3H), 1.58 (s, 9H), 1.38-1.24 (m, 1H), 1.21-0.91 (m, 2H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.2, 151.7, 143.2, 139.1, 130.4, 125.8, 120.0, 117.7, 115.0, 82.0, 79.2, 77.2, 62.5, 52.0, 46.2, 42.0, 36.0, 32.7, 31.5, 28.4, 25.6, 24.6. ***LC-MS*** (m/z): 527 $[M+K]^+$. ***Anal. calcd*** for ($C_{24}H_{29}BrN_2O_4$: 488.13): C, 58.90; H, 5.97, N, 5.72; Found: C, 58.72, H, 5.81, N, 5.88.

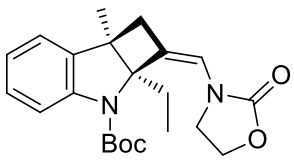


3j. Colorless oil. Yield = 90% (*c*Hex:AcOEt 85:15). *Ee* = 81%. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (8.7 min), Rt_{major} (12.5 min). $[\alpha]_D$ = 117.3 (*c* = 0.48, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.94 (s, 1H), 6.18 (s, 1H), 4.59 (dd, *J* = 14.8, 8.4 Hz, 1H), 4.46-4.30 (m, 2H), 3.88 (dd, *J* = 17.2, 8.4 Hz, 1H), 2.74 (d, *J* = 14.4 Hz, 1H), 2.57 (d, *J* = 14.4 Hz, 1H), 2.31 (s, 3H), 1.70 (s, 3H), 1.57 (s, 9H), 1.36 (s, 3H). ***^{13}C-NMR***(100 MHz, $CDCl_3$) δ 156.8, 151.9, 140.3, 138.1, 132.5, 128.1, 123.4, 119.1, 116.3, 81.4,77.2,75.0, 62.5, 47.7, 45.4,

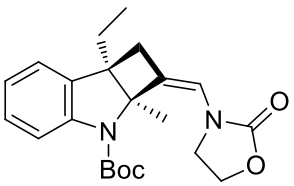
42.0, 28.5, 20.8, 18.4, 18.3.***LC-MS*** (m/z): 385 $[M+H]^+$. ***Anal. calcd*** for ($C_{22}H_{28}N_2O_4$: 384.20): C, 68.73; H, 7.34, N, 7.29; Found: C, 68.58, H, 7.21, N, 7.35.



3k. Colorless oil. Yield = 90% (*c*Hex:AcOEt 85:15). *Ee* = 86%. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (12.7 min), Rt_{major} (17.4 min). $[\alpha]_D$ = 112.8 (*c* = 0.43, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 3H), 6.75-6.67 (m, 2H), 6.19 (t, *J* = 2.0 Hz, 3H), 4.65-4.50 (m, 1H), 4.46-4.30 (m, 2H), 3.88 (q, *J* = 8.8 Hz,1H), 3.79 (s, 3H), 2.76 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.58 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.71 (s, 3H), 1.58 (s, 9H), 1.36 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 156.8, 155.9, 151.9, 139.5, 136.3, 119.1, 117.2, 112.3, 109.0, 81.3, 77.2, 75.0, 62.4, 55.7, 48.0, 45.4, 41.9, 28.5, 18.5, 18.4. ***LC-MS*** (m/z): 401$[M+H]^+$. ***Anal. calcd*** for ($C_{22}H_{28}N_2O_5$: 400.20): C, 65.98; H, 7.05, N, 7.00; Found: C, 65.72, H, 6.90, N, 6.88.

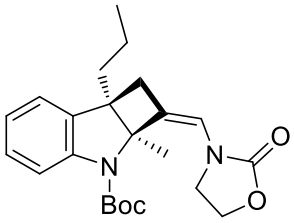


3l. Colorless oil. Yield = 72% (*c*Hex:AcOEt 85:15). *Ee* = 92%. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (7.6 min), Rt_{major} (9.0 min).$[\alpha]_D$ = 110.5 (*c* = 0.21, $CHCl_3$).***^{1}H-NMR*** (400 MHz, $CDCl_3$)δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.14 (s, 1H), 4.57 (dd, *J* = 14.8, 8.8 Hz, 1H), 4.46-4.31 (m, 2H), 3.87 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.82-2.65 (m, 2H), 2.51 (dd, *J* = 14.4, 1.2 Hz, 1H), 1.98-1.82 (m, 1H), 1.60 (s, 9H), 1.50 (s, 3H), 0.74 (t, *J* = 7.2 Hz, 3H).***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.3, 151.9, 143.7, 138.6, 127.5, 122.5, 121.7, 119.5, 115.5, 81.5, 79.2, 77.2, 62.6, 47.1, 46.3, 43.0, 28.4, 24.3, 18.1, 8.2. ***LC-MS*** (m/z): 407 $[M+Na]^+$, 423 $[M+K]^+$. ***Anal. calcd*** for ($C_{22}H_{28}N_2O_4$: 384.20): C, 68.73; H, 7.34, N, 7.29; Found: C, 68.44, H, 7.50, N, 7.21.

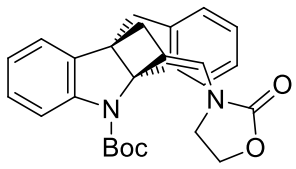


3m. Colorless oil. Yield = 94% (*c*Hex:AcOEt 85:15). *Ee* = 82%. ***HPLC***: Chiralpak-IC: eluent: *n*Hex:IPA = 60:40, flow = 0.7 mL/min, T = 40 °C, Rt_{mino} (16.5 min), Rt_{major} (17.7 min). $[\alpha]_D$ = 27.7 (*c* = 0.47,

$CHCl_3$). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 1H), 7.24-7.11 (m, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.06 (s, 1H), 4.52-4.15 (m, 3H), 3.89 (dd, *J* = 15.6, 8.4 Hz, 1H), 2.67 (d, *J* = 14.4 Hz, 1H), 2.61 (d, *J* = 14.4 Hz, 1H), 1.89 (s, 3H), 1.88-1.77 (m, 2H), 1.57 (s, 9H), 0.82 (t, *J* = 7.2 Hz, 3H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 156.6, 152.0, 143.5, 136.7, 127.5, 123.9, 123.2, 118.6, 117.3, 81.5, 77.2, 74.2, 62.3, 52.5, 45.3, 39.7, 28.4, 26.6, 18.5, 9.3. ***LC-MS*** (m/z): 407 $[M+Na]^+$, 423 $[M+K]^+$. ***Anal. calcd*** for ($C_{22}H_{28}N_2O_4$: 384.20): C, 68.73; H, 7.34, N, 7.29; Found: C, 68.51, H, 7.49, N, 7.36.

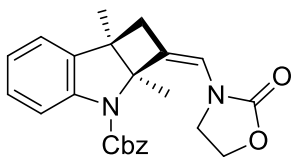


3n. Colorless oil. Yield = 96% (*c*Hex:AcOEt 85:15). *Ee* = 84%. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 90:10, flow = 0.5 mL/min, T = 40 °C, Rt_{minor} (13.7 min), Rt_{major} (14.6 min). $[\alpha]_D$ = 30.0 (*c* = 0.34, $CHCl_3$). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 1H), 7.24-7.12 (m, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.05 (s, 1H), 4.45-4.18 (m, 3H), 3.89 (dd, *J* = 16.0, 8.8 Hz, 1H), 2.67 (d, *J* = 14.4 Hz, 1H),2.60 (d, *J* = 14.4 Hz, 1H), 1.89 (s, 3H), 1.79-1.69 (m, 2H), 1.57 (s, 9H), 1.22-1.01 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 156.6, 152.0, 143.4, 137.1, 127.5, 124.0, 123.3, 118.5, 117.3, 81.5, 77.2, 74.2, 62.3, 52.2, 45.3, 40.0, 36.4, 28.4, 18.6, 18.2, 14.7. ***LC-MS*** (m/z): 399 $[M+H]^+$. ***Anal. calcd*** for ($C_{23}H_{30}N_2O_4$: 398.22): C, 69.32; H, 7.59, N, 7.03; Found: C, 69.20, H, 7.41, N, 6.81.

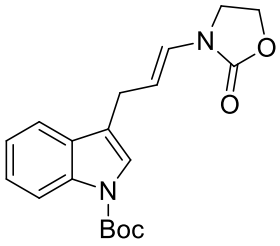


3o. White solid. The Z configuration of alkene was determined by NOE experiment. Yield = 93% (*c*Hex:AcOEt 85:15). *Ee*= 98%. ***MP*** = 183-185 °C. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (12.1 min), Rt_{major} (15.8 min). $[\alpha]_D$ = 109.0 (*c* = 0.42, $CHCl_3$). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.26-7.18 (m, 4H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.31 (s, 1H), 5.07-4.92 (m, 1H), 4.42 (dd, *J* = 17.2, 8.8 Hz, 1H), 4.37-4.25 (m, 1H), 3.51 (dd, *J* = 18.0, 8.8 Hz, 1H), 3.44 (s, 2H), 3.04 (d, *J* = 14.4 Hz, 1H), 2.85 (d, *J* = 14.4 Hz, 1H), 1.63 (s, 9H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 156.9, 152.6, 146.6, 144.0, 142.1, 136.0, 128.6, 128.0, 127.9, 126.8, 125.4, 123.5, 123.0, 120.8, 120.5, 116.3, 84.3, 82.0, 62.7, 53.7, 45.6, 42.4, 40.7, 28.4.***LC-MS*** (m/z):

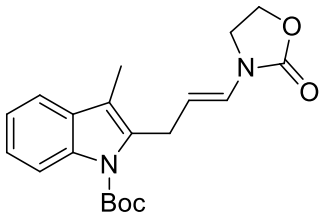
431 $[M+H]^+$.***Anal. calcd*** for ($C_{26}H_{26}N_2O_4$: 430.19): C, 72.54; H, 6.09, N, 6.51; Found: C, 72.41, H, 5.89, N, 6.41.



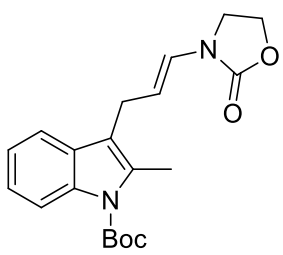
3p. Colorless oil. Yield = 60% (*c*Hex:AcOEt 85:15). *Ee* = 96%. ***HPLC***: Chiralcel-OJ: eluent: *n*Hex:IPA = 70:30, flow = 0.7 mL/min, T = 40 °C, Rt_{minor} (16.4 min), Rt_{major} (18.6 min). $[\alpha]_D$ = 83.8 (*c* = 0.5, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.48-7.33 (m, 5H), 7.21-7.09 (m, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.27 (s, 2H), 5.31 (dd, *J* = 16.0, 12.4 Hz, 2H), 4.60-4.28 (m, 1H), 4.28-4.15 (m, 1H), 4.15-3.86 (m, 1H), 3.85-3.60 (m, 1H), 2.83 (d, *J* = 14.4 Hz, 1H), 2.56 (d, *J* = 14.4 Hz, 1H), 1.66 (s, 3H), 1.41 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 156.7, 152.9, 137.8, 135.9, 128.7, 128.4, 128.2, 127.9, 123.4, 122.6, 121.9, 119.7, 116.6, 77.2, 75.6, 67.4, 62.2, 47.7, 45.4, 42.4, 18.7, 17.6. ***LC-MS*** (m/z): 405 $[M+H]^+$. ***Anal. calcd*** for ($C_{24}H_{24}N_2O_4$: 404.17): C, 71.27; H, 5.98, N, 6.93; Found: C, 71.08, H, 6.07, N, 6.60.



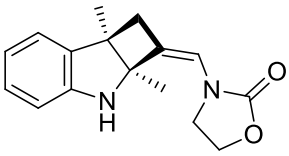
3q. Colorless oil. Yield = 8% (*c*Hex:AcOEt = 85:15).***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.39 (s, 1H), 7.36-7.29 (m, 1H), 7.26-7.20 (m, 1H), 6.86 (d, *J* = 14.4 Hz, 1H), 5.01 (dt, *J* = 14.0, 7.2 Hz, 1H), 4.48-4.39 (m, 2H), 3.70 (t, *J* = 8.0 Hz, 2H), 3.48 (d, *J* = 6.8 Hz, 2H), 1.68 (s, 9H). ***LC-MS*** (m/z): 381 $[M+K]^+$.



3r. Colorless oil. Yield = 5% (*c*Hex:AcOEt= 85:15). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.09-8.00 (m, 1H), 7.47-7.42 (m, 1H), 7.27-7.20 (m, 2H), 6.76 (d, *J* = 14.4 Hz, 1H), 5.04 (dt, *J* = 14.4, 6.8 Hz, 1H), 4.45-4.33 (m, 2H), 3.81 (d, *J* = 6.4 Hz, 2H), 3.67 (t, *J* = 8.0 Hz, 2H), 2.23 (s, 3H), 1.69 (s, 8H). ***LC-MS*** (m/z): 357 $[M+H]^+$.

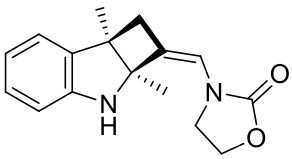


3s.Colorless oil. Yield = 56% (*c*Hex:AcOEt= 85:15). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.51-7.37 (m, 1H), 7.29-7.14 (m, 2H), 6.74 (d, *J* = 14.4 Hz, 1H), 4.90 (dt, *J* = 14.4, 6.4 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 2H), 3.63 (t, *J* = 8.0 Hz, 2H), 3.45 (dd, *J* = 6.4, 0.8 Hz, 2H), 2.55 (s, 3H), 1.69 (s, 9H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 155.3, 150.7, 135.7, 133.5, 129.5, 124.4, 123.4, 122.4, 117.7, 115.9, 115.4, 108.9, 83.5, 62.0, 42.5, 28.3, 24.4, 13.9. ***LC-MS*** (m/z): 357 $[M+H]^+$.

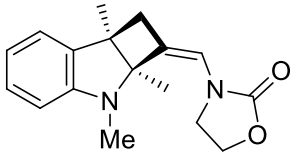


4a.White solid. Yield = 8% (*c*Hex-AcOEt: 70:30), *Ee*= 91%, from [2+2] reaction of 2,3-dimethylindole with allenamide **2a**. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 80:20, flow = 0.8 mL/min, T = 40 °C, Rt_{minor} (9.9 min), Rt_{major} (10.7 min).

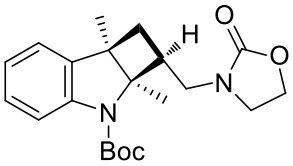
General procedures for the synthetic transformations



Procedure for the deprotection of the Boc group: To a solution of **3a** (37.0 mg, 0.1 mmol) in anhydrous CH_2Cl_2 (0.75 mL) at 0 °C, TFA (0.25 mL) was added, and stirred at this temperature for 2h. Then saturated $NaHCO_3$ (10 mL) was added, extracted with CH_2Cl_2 (3×15 mL), dried over Na_2SO_4 and evaporated. The crude were purified by column chromatography (*c*Hex:AcOEt = 70:30) to provide the desired product **4a** as a white solid. Yield = 91%. E*e* = 93%. ***MP*** = 136-138 °C. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 80:20, flow = 0.8 mL/min, T = 40 °C, Rt_{minor} (9.9 min), Rt_{major} (10.6 min). $[\alpha]_D$ = 193.0 (*c* = 1.0, CH_2Cl_2, 93% ee). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.2 Hz,1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.06 (s, 1H), 4.40 (t, *J* = 8.0 Hz, 2H), 4.28 (q, *J* = 8.0 Hz, 1H), 3.89 (q, *J* = 8.4 Hz, 1H), 2.76 (s, 2H), 1.52 (s, 3H), 1.33 (s, 3H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 156.1, 149.8, 138.7, 128.6, 127.7, 123.8, 120.5, 117.6, 112.1, 70.7, 61.9, 50.3, 45.9, 41.5, 20.7, 20.6. ***LC-MS*** (m/z): 271 $[M+H]^+$. ***Anal. calcd*** for ($C_{16}H_{18}N_2O_2$: 270.14): C, 71.09; H, 6.71, N, 10.36; Found: C, 71.21, H, 6.55, N, 10.26.

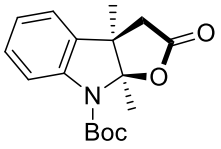


Procedure for the synthesis of *N*-Me-indoline 5a: To a solution of **4a**(16.2 mg, 0.06 mmol) in acetone (1.5 mL), K_2CO_3 (16.8mg, 0.12 mmol) and MeI (19.0 uL, 0.3 mmol) were added. The resulting suspension was stirred at reflux. Upon completion (about 48 h, monitored by TLC), 10 mL of water was added to the reaction mixture. Then the volatiles were removed by evaporation, the aqueous phase was extracted with EtOAc (3×10 mL) and the combined organic phases were washed with brine (20 mL). The organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (*c*Hex:AcOEt = 80:20) on silica gel to afford the product **5a**as a colorless oil. Yield = 90%. *Ee*= 93%.***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 1.0 mL/min, T = 40 °C, Rt_{minor} (18.1 min), Rt_{major} (19.3 min). $[\alpha]_D$ = 211.6° (*c* = 0.5, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.11 (td, *J* = 7.6, 1.2 Hz, 1H), 7.05 (dd, *J* = 7.2, 0.8 Hz, 1H), 6.69 (td, *J* = 7.6, 0.8 Hz, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 5.88 (t, *J* = 2.4 Hz, 1H), 4.40 (t, *J* = 8.0 Hz, 2H), 3.96 (q, *J* = 8.4 Hz, 1H), 3.73 (q, *J* = 8.4 Hz, 1H), 2.86 (s, 3H), 2.72 (dd, *J* = 4.8, 2.0 Hz, 2H), 1.51 (s, 3H), 1.34 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 156.6, 152.1, 136.4, 134.3, 128.0, 122.9, 117.9, 117.4, 107.3, 74.9, 61.9, 48.7, 46.5, 42.0, 31.0, 20.0, 16.6. ***LC-MS*** (m/z): 285 $[M+H]^+$. ***Anal. calcd*** for ($C_{17}H_{20}N_2O_2$: 284.15): C, 71.81; H, 7.09, N, 9.85; Found: C, 71.67, H, 7.01, N, 9.65.



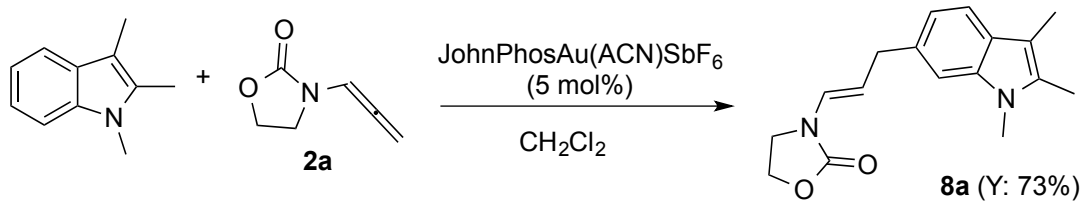
Procedure for the synthesis of indoline 6a: EtOH (1.5mL) was added to a Schlenk tube containing compound **3a** (30.0mg, 0.071 mmol) equipped with a stir bar, then 10% Pd/C (7.5 mg, 25 wt%) was added. The vial was sealed up, and then it was evacuated and filled with hydrogen (three cycles). The reaction was stirred at room temperature for 48h. After the reaction was complete, the reaction mixture was filtrated over a pad of celite and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (*c*Hex:AcOEt = 85:15) to afford compound **6a** as a colorless oil. The absolute configuration of the new stereocenter was determined by NOE experiment. Yield = 93%. *Ee* = 93%, *dr* = 9:1. ***HPLC***: Chiralcel-AD: eluent: *n*Hex:IPA = 95:5, flow = 0.7 mL/min, T = 40 °C, Rt_{minor} (20.3 min), Rt_{major}(23.0 min). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.81 (brs, 1H), 7.22-7.12 (m, 1H), 7.05 (dd, *J* = 7.2, 1.2 Hz, 1H),6.96 (td, *J* = 7.2, 1.2 Hz, 1H), 4.25 (td, *J* = 8.0, 2.0 Hz, 2H), 3.72 (brs, 1H), 3.47 (t, *J* = 8.0 Hz, 2H), 3.15 (brs, 1H), 2.82-2.64 (m, 1H), 2.15 (dd, *J* = 12.0, 9.2 Hz, 1H),1.93 (dd, *J* = 12.0, 8.0 Hz, 1H), 1.61 (s, 9H),1.60 (s, 3H), 1.39 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 158.4,

152.6, 138.3, 127.8, 122.8, 122.0, 115.3, 81.5, 77.2, 70.9, 61.6, 45.8, 44.3, 41.0, 38.2, 28.4, 25.3, 21.8, 20.1. ***LC-MS*** (m/z): 411 $[M+K]^+$.



Procedure for the oxidative cleavage of enamide moiety: To a suspension of **3a** (30.0 mg, 0.08 mmol) dissolved in CCl_4 (0.8 mL) and water (0.8 mL) was added $RuCl_3 \cdot H_2O$ (1.8 mg, 0.024 mmol) and $NaIO_4$ (75.0 mg, 0.35 mmol) at 0 °C. After vigorous stirring for about 12 h, the reaction was quenched with saturated $Na_2S_2O_3$ (5 mL). The solution was extracted with AcOEt (3×10 mL). The combined extracts were dried (Na_2SO_4) and the concentrated residue was purified by flash chromatography to provide the desired product **7a** as a white solid. Yield = 80% (*c*Hex:AcOEt = 85:15). *Ee* = 93%. ***MP*** = 174-176 °C. ***HPLC***: Lux 5u Cellulose-2: eluent: *n*Hex:IPA = 80:20, flow = 0.8 mL/min, T = 40 °C, Rt_{minor} (8.7 min), Rt_{major} (11.8 min). $[\alpha]_D$ = 30.8° (*c* = 0.52, $CHCl_3$). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.27-7.22 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 2.97 (d, *J* = 17.6 Hz, 1H), 2.78 (d, *J* = 17.6 Hz, 1H), 1.99 (s, 3H), 1.63 (s, 9H), 1.42 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 173.2, 151.8, 140.7, 133.5, 129.1, 123.7, 122.8, 115.8, 104.9, 82.9, 51.4, 41.9, 28.3, 22.9, 20.5. ***LC-MS*** (m/z): 323 $[M+Na]^+$. ***Anal. calcd*** for ($C_{17}H_{21}NO_4$: 303.15): C, 67.31; H, 6.98, N, 4.62; Found: C, 67.15, H, 6.80, N, 4.70.

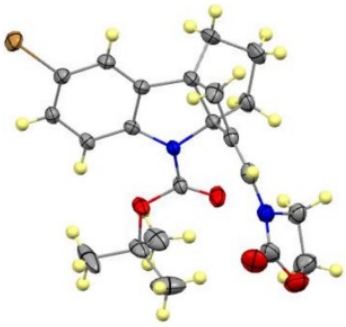
Reaction of 1,2,3-$(Me)_3$-indole and 2a.

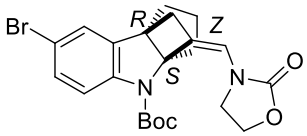


[JohnPhosAu(CH_3CN)]SbF_6 (3.9 mg, 5 mol%) was added at 0 °C, to a solution of 1,2,3-$(Me)_3$-indole (16 mg, 0.1 mmol) and **2a** (12.5 mg, 0.1 mmol) in CH_2Cl_2 (1.0 mL). The solution was allowed to worm at rt and stirred under nitrogen for 20 h. Removal of the solvent under reduced pressure and purification via by flash column chromatography (*c*Hex:AcOEt = 80:20 -- 75:25) afforded compound **8a** in 73% yield. Viscous oil. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.31 (s, 3H), 3.47 (d, *J* = 7.6 Hz, 2H), 3.60 (s, 3H), 3.65 (t, *J* = 8.0 Hz, 2H), 4.38 (t, *J* = 8.0, Hz, 2H), 4.90-5.04 (m, 1H), 6.76 (d, *J* = 14.4 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 4.4 Hz, 1H), 7.26 (s, 1H).

X-ray crystallography: The X-ray intensity data for **3e** were measured on a Bruker Apex II CCD diffractometer. 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 determining the lattice parameters. The collected frames were then processed for integration by the SAINT[8] program, and an empirical absorption correction was applied by using SADABS.[9] The structure was solved by direct methods (SIR97)[10] and subsequent Fourier syntheses, and was refined by full-matrix least-squares calculations on F^2 (SHELXTL), [11] using anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were located in difference Fourier maps. Those bonded to aromatic carbons were treated as riding atoms in geometrically idealized positions. The absolute configuration has been established by anomalous dispersion effects in diffraction measurements on the crystal (Flack parameter= 0.060(11)). The molecular graphics were generated by using ORTEP[11]. Color codes for the molecular graphics: blue (N), red (O), grey (C), white (H), olive green (Br). Crystal data and other experimental details for **3e**are reported in **Table S3**, whereas bond lengths [Å] and angles (deg) are shown in **Table S4**.

X-ray crystal structure of 3e





(*2aS,7bR,Z*)

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

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

[10] A. Altomare, M. C. Burla, M.Cavalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.,*1999, **32**, 115-118.

[11] L. J. Farrugia, ORTEP-3, *J. Appl. Cryst.,* 2012, **45**, 849-854.

Table S3. Crystal data and structure refinement for **3e**

Empirical formula	C22 H25 Br N2 O4
Formula weight	461.35
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 10.417(5) Å α= 90°.
b = 10.000(5) Å	β= 106.396(5)°.
c = 11.057(5) Å	γ = 90°.
Volume	1105.0(9) $Å^3$
Z	2
Density (calculated)	1.387 Mg/m^3
Absorption coefficient	1.889 mm^{-1}
F(000)	476
Crystal size	0.28 x 0.25 x 0.25 mm^3
Theta range for data collection	2.37 to 25.98°.
Index ranges	-12<=h<=12, -11<=k<=12, -13<=l<=13
Reflections collected	9268
Independent reflections	4186 [R(int) = 0.0426]
Completeness to theta = 25.98°	99.1 %
Absorption correction	Empirical
Max. and min. transmission	0.689 and 0.621
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4186 / 1 / 263
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1308
R indices (all data)	R1 = 0.0595, wR2 = 0.1369
Absolute structure parameter	0.060(11)
Extinction coefficient	0.056(5)
Largest diff. peak and hole	1.024 and -0.512 $e.Å^{-3}$

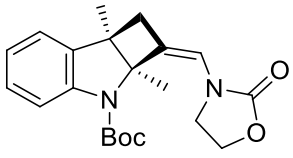
Table S4. Selected bond lengths (Å) and angles (deg) for **3e**.

Br-C(10)	1.904(4)	C(4)-C(5)-C(6)	128.6(4)
N(1)-C(1)	1.355(6)	C(4)-C(5)-C(14)	139.1(4)
N(1)-C(4)	1.410(5)	C(6)-C(5)-C(14)	92.0(3)
N(1)-C(3)	1.468(6)	C(7)-C(6)-C(5)	90.2(3)
N(2)-C(18)	1.375(4)	C(7)-C(6)-H(6A)	113.6
N(2)-C(13)	1.418(5)	C(5)-C(6)-H(6A)	113.6
N(2)-C(14)	1.477(4)	C(7)-C(6)-H(6B)	113.6
O(2)-C(1)	1.356(7)	C(5)-C(6)-H(6B)	113.6
O(2)-C(2)	1.428(8)	H(6A)-C(6)-H(6B)	110.9
O(1)-C(1)	1.209(7)	C(8)-C(7)-C(6)	116.8(5)
O(3)-C(18)	1.201(5)	C(8)-C(7)-C(17)	117.1(4)
O(4)-C(18)	1.325(5)	C(6)-C(7)-C(17)	117.7(4)
O(4)-C(19)	1.483(4)	C(8)-C(7)-C(14)	103.2(4)
C(2)-C(3)	1.496(8)	C(6)-C(7)-C(14)	90.4(3)
C(2)-H(2A)	0.9700	C(17)-C(7)-C(14)	105.6(4)
C(2)-H(2B)	0.9700	C(9)-C(8)-C(13)	120.0(4)
C(3)-H(3A)	0.9700	C(9)-C(8)-C(7)	128.6(4)
C(3)-H(3B)	0.9700	C(13)-C(8)-C(7)	111.4(4)
C(4)-C(5)	1.314(6)	C(8)-C(9)-C(10)	119.3(3)
C(4)-H(4)	0.9300	C(8)-C(9)-H(9)	120.4
C(5)-C(6)	1.522(6)	C(10)-C(9)-H(9)	120.4
C(5)-C(14)	1.537(5)	C(9)-C(10)-C(11)	121.0(4)
C(6)-C(7)	1.511(9)	C(9)-C(10)-Br	118.6(3)
C(6)-H(6A)	0.9700	C(11)-C(10)-Br	120.4(3)
C(6)-H(6B)	0.9700	C(10)-C(11)-C(12)	120.9(4)
C(7)-C(8)	1.488(6)	C(10)-C(11)-H(11)	119.5
C(7)-C(17)	1.542(5)	C(12)-C(11)-H(11)	119.5

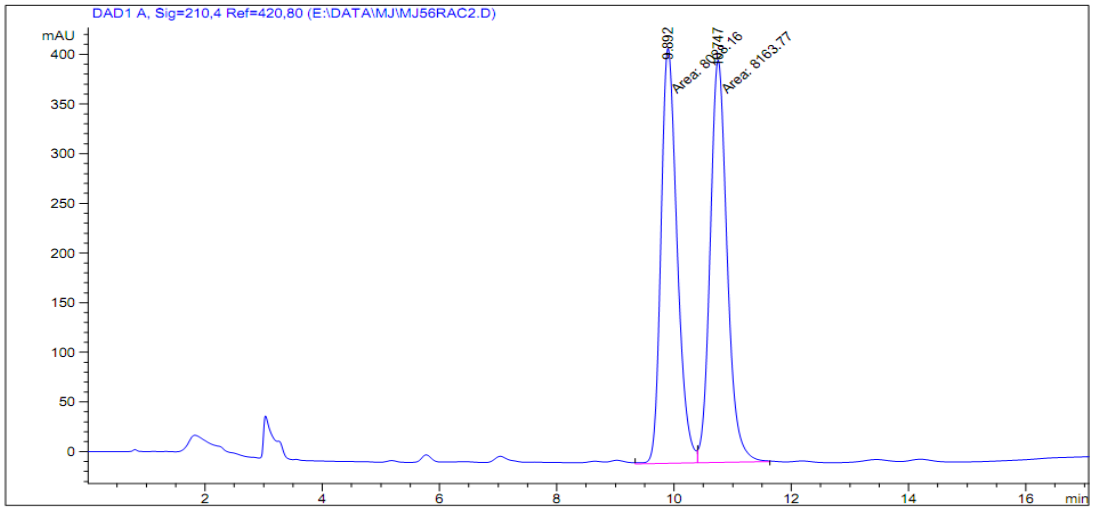
C(7)-C(14)	1.587(6)	C(11)-C(12)-C(13)	118.6(3)
C(8)-C(9)	1.373(6)	C(11)-C(12)-H(12)	120.7
C(8)-C(13)	1.411(5)	C(13)-C(12)-H(12)	120.7
C(9)-C(10)	1.375(6)	C(12)-C(13)-C(8)	120.1(3)
C(9)-H(9)	0.9300	C(12)-C(13)-N(2)	130.0(3)
C(10)-C(11)	1.377(5)	C(8)-C(13)-N(2)	109.9(3)
C(11)-C(12)	1.379(5)	N(2)-C(14)-C(15)	117.5(3)
C(11)-H(11)	0.9300	N(2)-C(14)-C(5)	115.3(3)
C(12)-C(13)	1.388(5)	C(15)-C(14)-C(5)	118.9(3)
C(12)-H(12)	0.9300	N(2)-C(14)-C(7)	105.2(3)
C(14)-C(15)	1.532(6)	C(15)-C(14)-C(7)	106.3(3)
C(15)-C(16)	1.534(6)	C(5)-C(14)-C(7)	86.9(4)
C(15)-H(15A)	0.9700	C(14)-C(15)-C(16)	104.9(3)
C(15)-H(15B)	0.9700	C(14)-C(15)-H(15A)	110.8
C(16)-C(17)	1.5391	C(16)-C(15)-H(15A)	110.8
C(16)-H(16A)	0.9700	C(14)-C(15)-H(15B)	110.8
C(16)-H(16B)	0.9700	C(16)-C(15)-H(15B)	110.8
C(17)-H(17A)	0.9700	H(15A)-C(15)-H(15B)	108.8
C(17)-H(17B)	0.9700	C(15)-C(16)-C(17)	104.8(2)
C(19)-C(21)	1.501(8)	C(15)-C(16)-H(16A)	110.8
C(19)-C(20)	1.501(7)	C(17)-C(16)-H(16A)	110.8
C(19)-C(22)	1.526(9)	C(15)-C(16)-H(16B)	110.8
C(20)-H(20A)	0.9600	C(17)-C(16)-H(16B)	110.8
C(20)-H(20B)	0.9600	H(16A)-C(16)-H(16B)	108.9
C(20)-H(20C)	0.9600	C(16)-C(17)-C(7)	103.6(2)
C(21)-H(21A)	0.9600	C(16)-C(17)-H(17A)	111.0
C(21)-H(21B)	0.9600	C(7)-C(17)-H(17A)	111.1
C(21)-H(21C)	0.9600	C(16)-C(17)-H(17B)	111.0
C(22)-H(22A)	0.9600	C(7)-C(17)-H(17B)	111.0

C(22)-H(22B)	0.9600	H(17A)-C(17)-H(17B)	109.0
C(22)-H(22C)	0.9600	O(3)-C(18)-O(4)	126.4(3)
C(1)-N(1)-C(4)	119.5(4)	O(3)-C(18)-N(2)	122.8(3)
C(1)-N(1)-C(3)	110.2(4)	O(4)-C(18)-N(2)	110.9(3)
C(4)-N(1)-C(3)	124.6(3)	O(4)-C(19)-C(21)	101.4(4)
C(18)-N(2)-C(13)	129.6(3)	O(4)-C(19)-C(20)	110.3(4)
C(18)-N(2)-C(14)	120.1(3)	C(21)-C(19)-C(20)	111.2(6)
C(13)-N(2)-C(14)	110.2(3)	O(4)-C(19)-C(22)	109.3(4)
C(1)-O(2)-C(2)	108.3(4)	C(21)-C(19)-C(22)	113.8(6)
C(18)-O(4)-C(19)	121.4(3)	C(20)-C(19)-C(22)	110.5(5)
O(1)-C(1)-N(1)	127.7(5)	C(19)-C(20)-H(20A)	109.5
O(1)-C(1)-O(2)	122.8(5)	C(19)-C(20)-H(20B)	109.5
N(1)-C(1)-O(2)	109.5(4)	H(20A)-C(20)-H(20B)	109.5
O(2)-C(2)-C(3)	105.5(5)	C(19)-C(20)-H(20C)	109.5
O(2)-C(2)-H(2A)	110.6	H(20A)-C(20)-H(20C)	109.5
C(3)-C(2)-H(2A)	110.6	H(20B)-C(20)-H(20C)	109.5
O(2)-C(2)-H(2B)	110.6	C(19)-C(21)-H(21A)	109.5
C(3)-C(2)-H(2B)	110.6	C(19)-C(21)-H(21B)	109.5
H(2A)-C(2)-H(2B)	108.8	H(21A)-C(21)-H(21B)	109.5
N(1)-C(3)-C(2)	99.7(4)	C(19)-C(21)-H(21C)	109.5
N(1)-C(3)-H(3A)	111.8	H(21A)-C(21)-H(21C)	109.5
C(2)-C(3)-H(3A)	111.8	H(21B)-C(21)-H(21C)	109.5
N(1)-C(3)-H(3B)	111.8	C(19)-C(22)-H(22A)	109.5
C(2)-C(3)-H(3B)	111.8	C(19)-C(22)-H(22B)	109.5
H(3A)-C(3)-H(3B)	109.6	H(22A)-C(22)-H(22B)	109.5
C(5)-C(4)-N(1)	127.8(4)	C(19)-C(22)-H(22C)	109.5
C(5)-C(4)-H(4)	116.1	H(22A)-C(22)-H(22C)	109.5
N(1)-C(4)-H(4)	116.1	H(22B)-C(22)-H(22C)	109.5

HPLC spectra



3a



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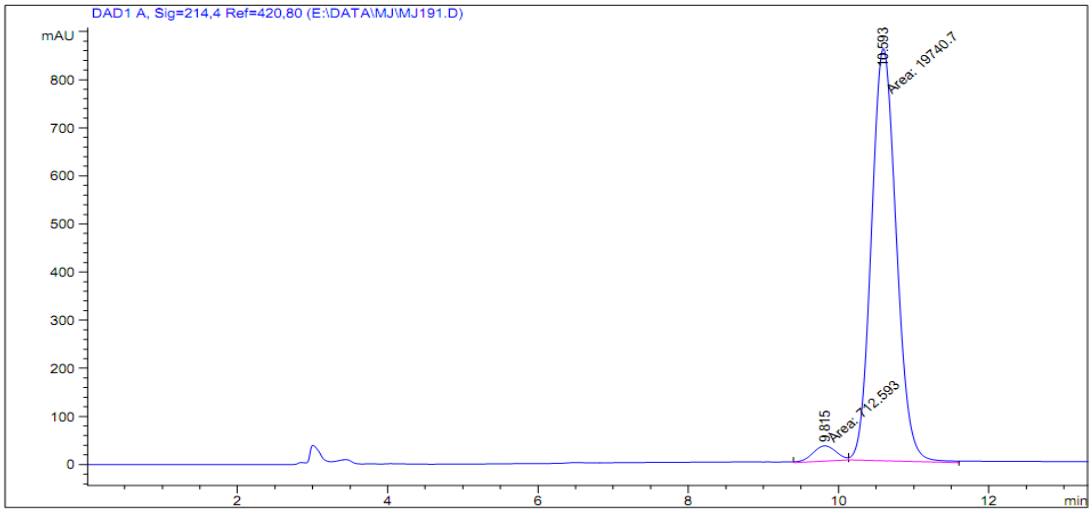

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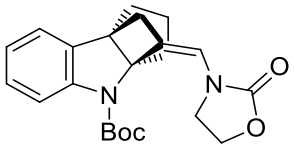
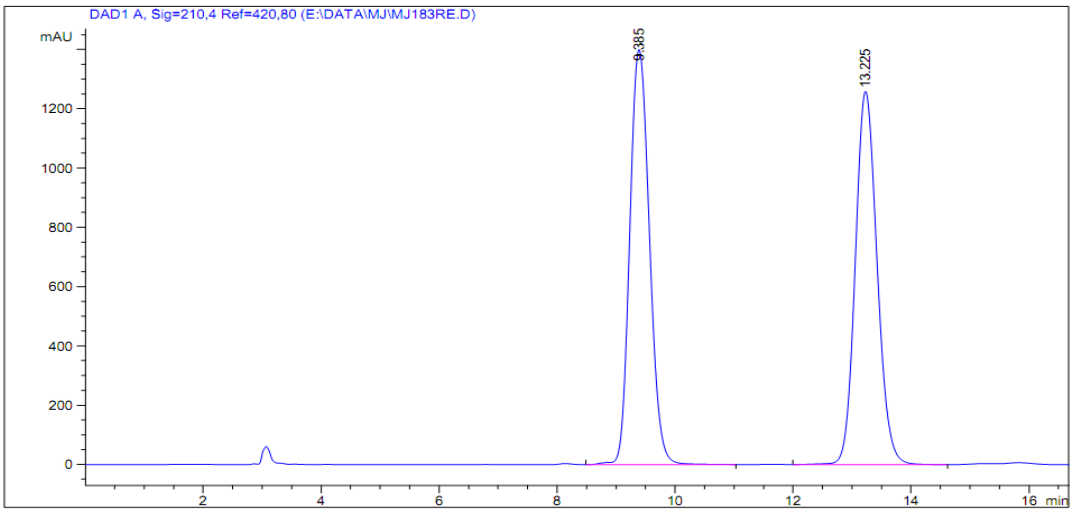


3b



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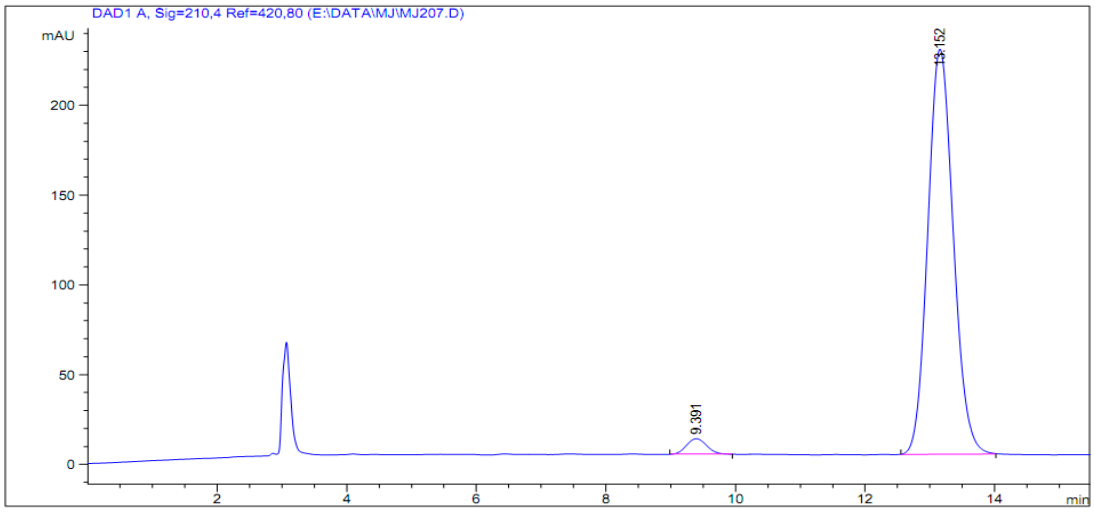

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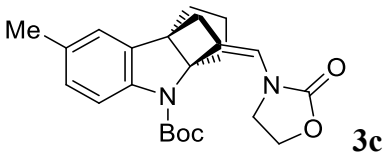
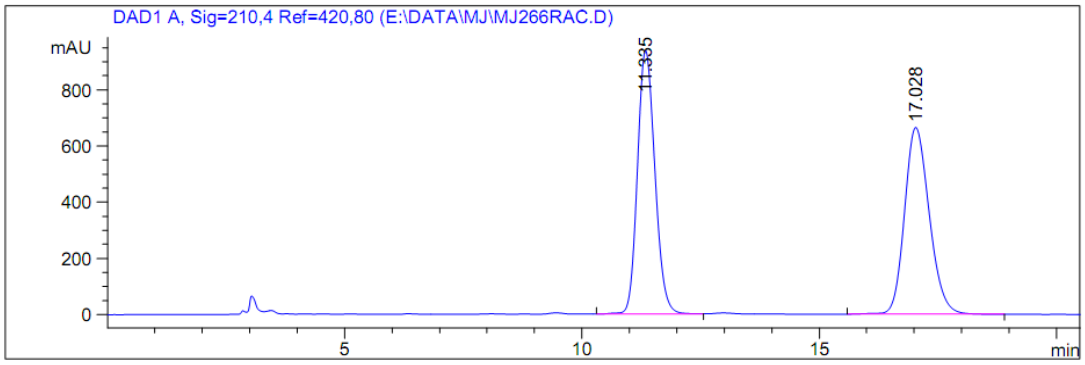


3c



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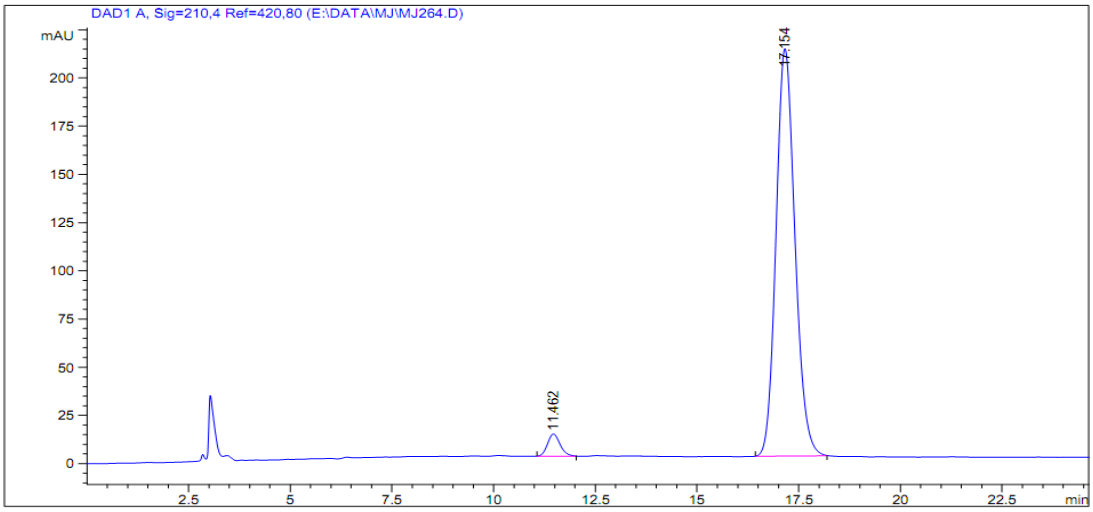

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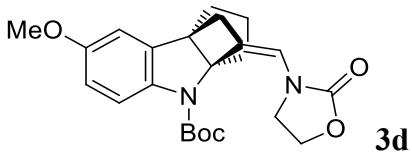
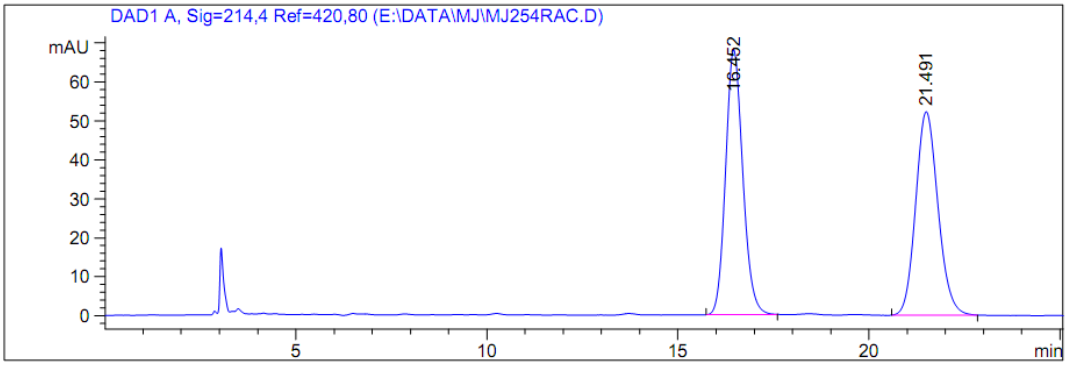
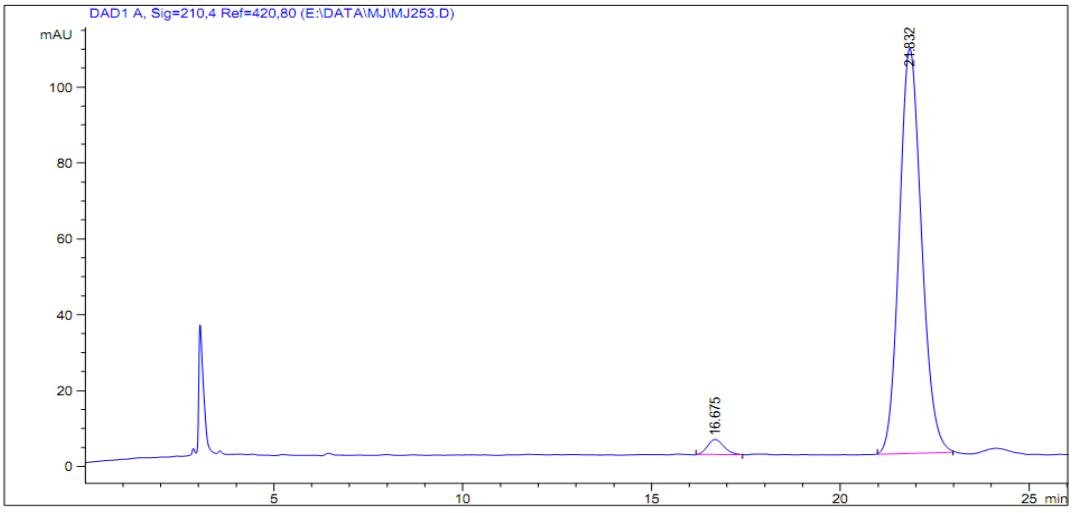


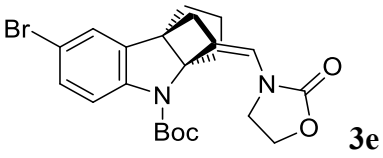
3d



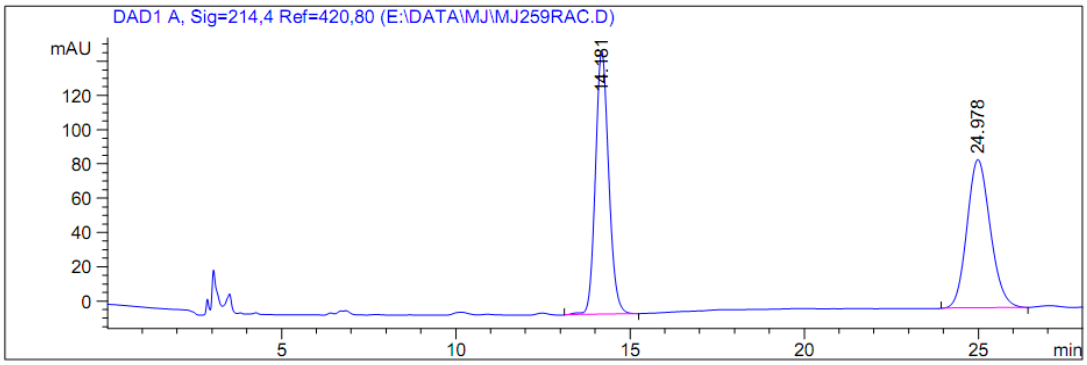
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.452	BB	0.4821	2132.49023	67.96579	50.0658
2	21.491	BB	0.6309	2126.88184	52.24894	49.9342



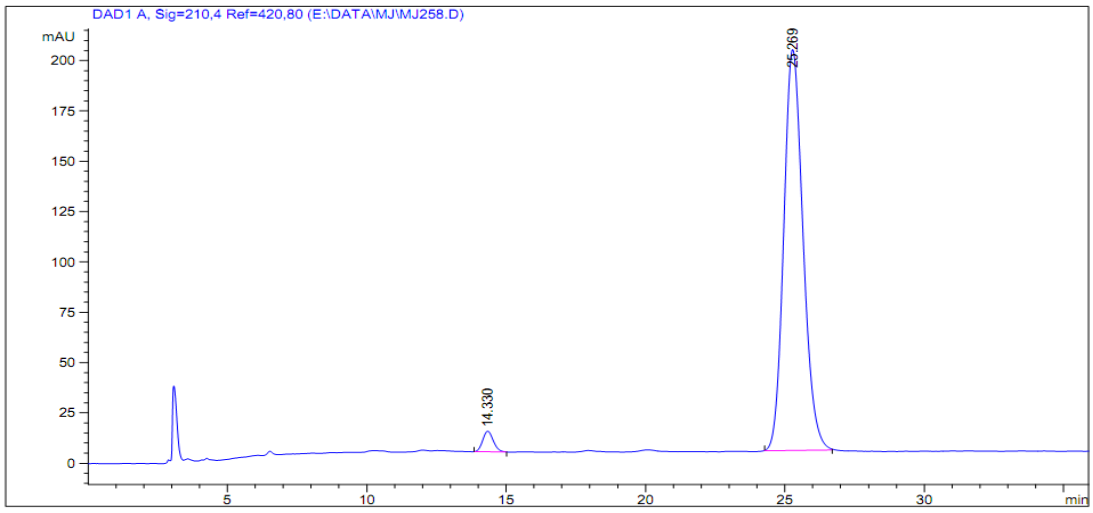
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.675	BB	0.4373	121.78708	3.99850	2.7056
2	21.832	BB	0.6323	4379.45459	106.83022	97.2944



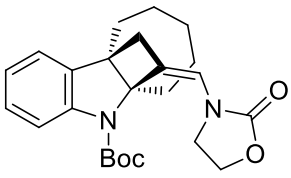
3e



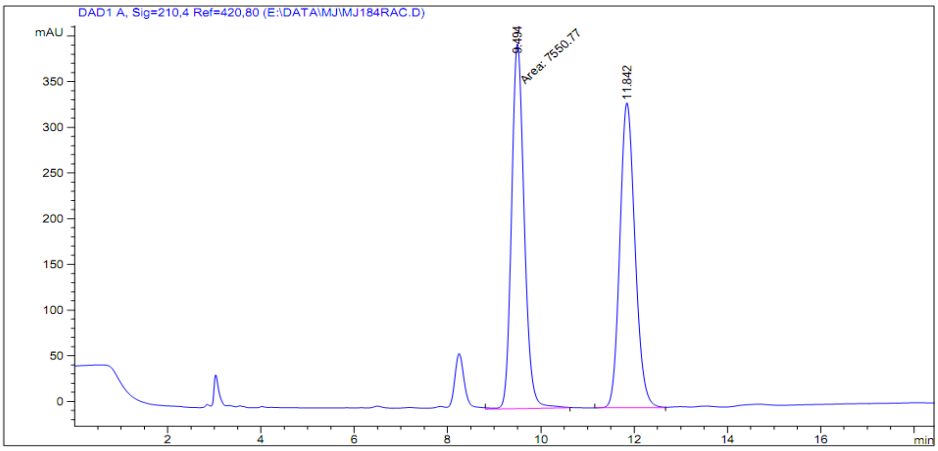
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.181	BB	0.4096	4077.33008	153.65942	50.1443
2	24.978	BV	0.7251	4053.85669	86.76254	49.8557



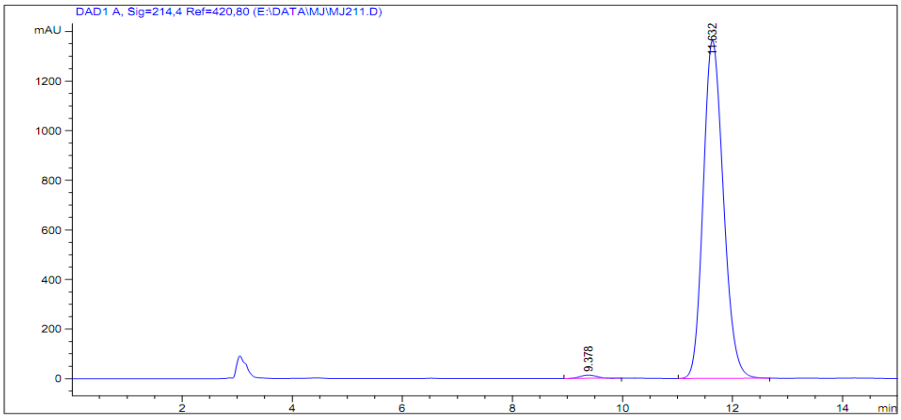
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.330	BB	0.4089	272.80075	10.30353	2.7628
2	25.269	BB	0.7418	9601.16309	199.36646	97.2372



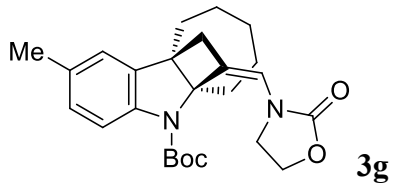
3f



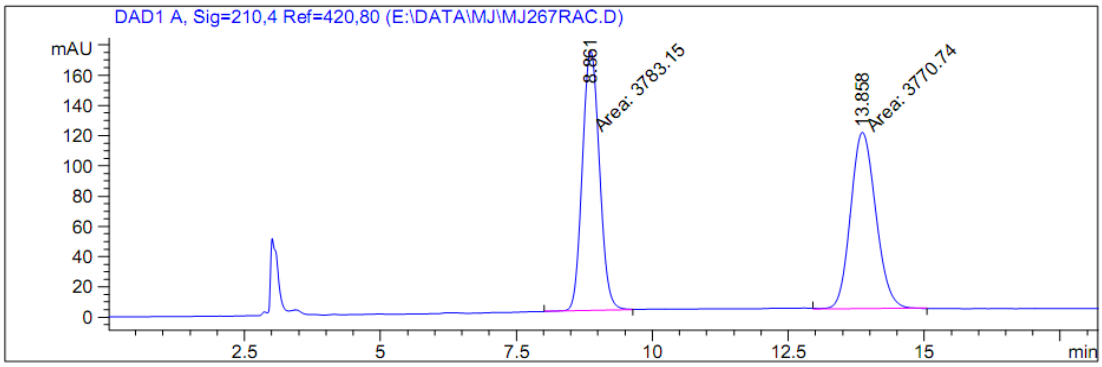
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.494	MM	0.3150	7550.76660	399.51056	49.9666
2	11.842	BV	0.3482	7560.84912	333.81473	50.0334



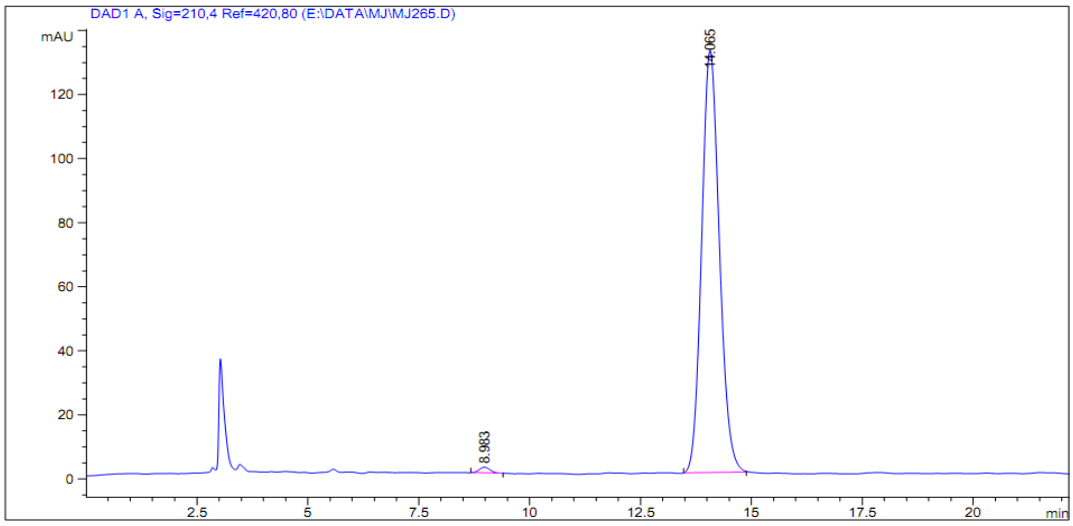
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.378	BB	0.3319	274.83286	13.25626	0.7863
2	11.632	BB	0.3968	3.46774e4	1362.87878	99.2137



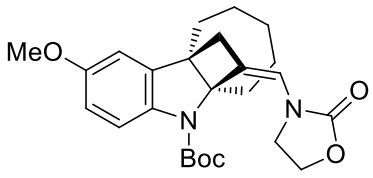
3g



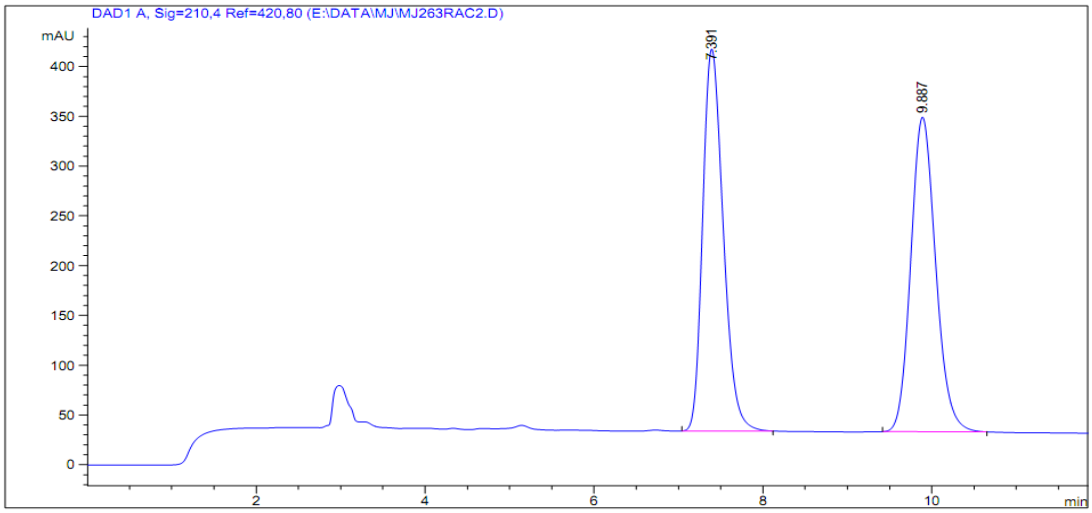
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.861	MM	0.3673	3783.15356	171.65649	50.0822
2	13.858	MM	0.5386	3770.73975	116.68171	49.9178



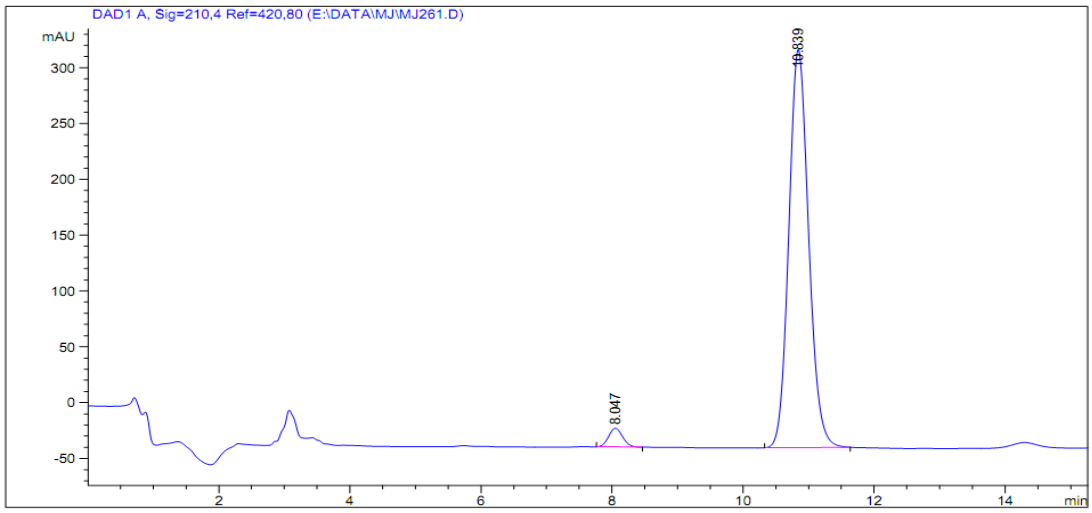
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.983	BB	0.2620	31.31799	1.80890	0.8453
2	14.065	BB	0.4292	3673.44873	131.80640	99.1547



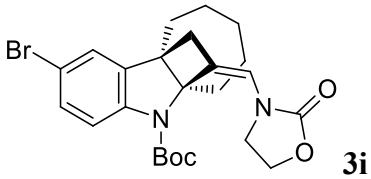
3h



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.391	BB	0.2633	6494.52686	384.02740	50.0126
2	9.887	BB	0.3173	6491.25098	316.41537	49.9874



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.047	BB	0.2296	250.82452	16.85236	3.2349
2	10.839	BB	0.3254	7502.87842	356.71167	96.7651



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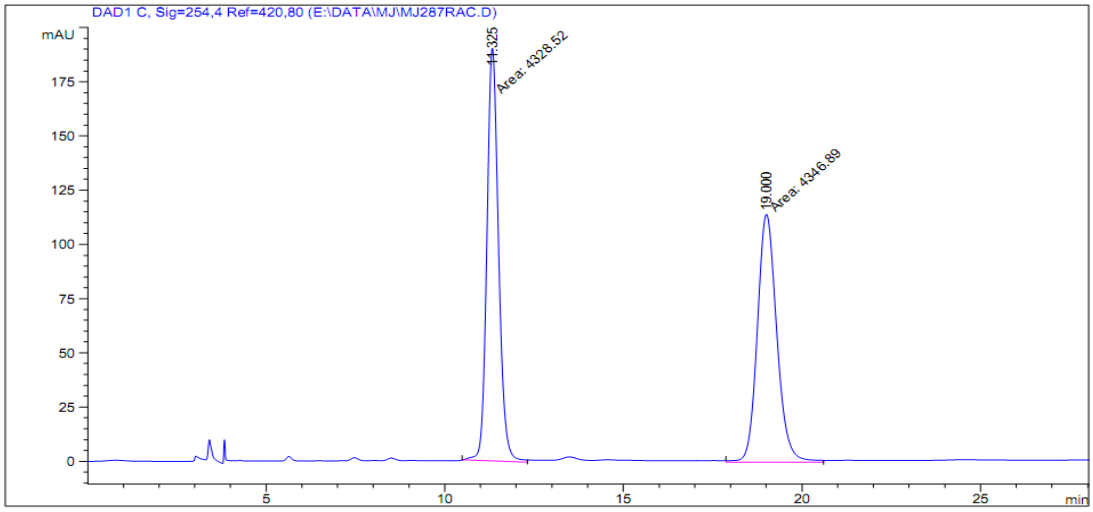
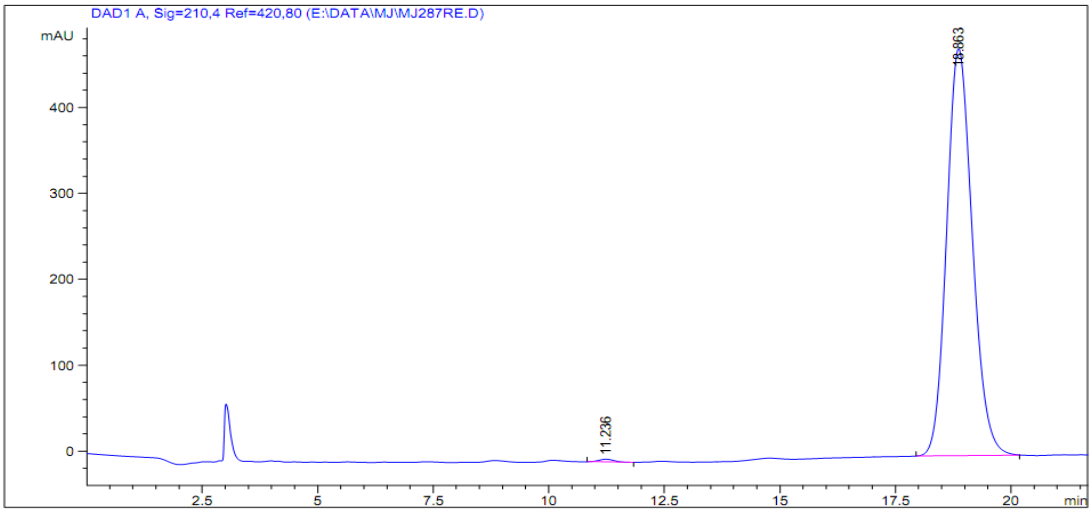
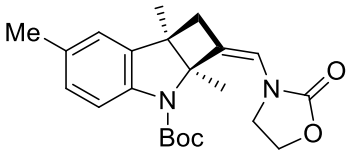


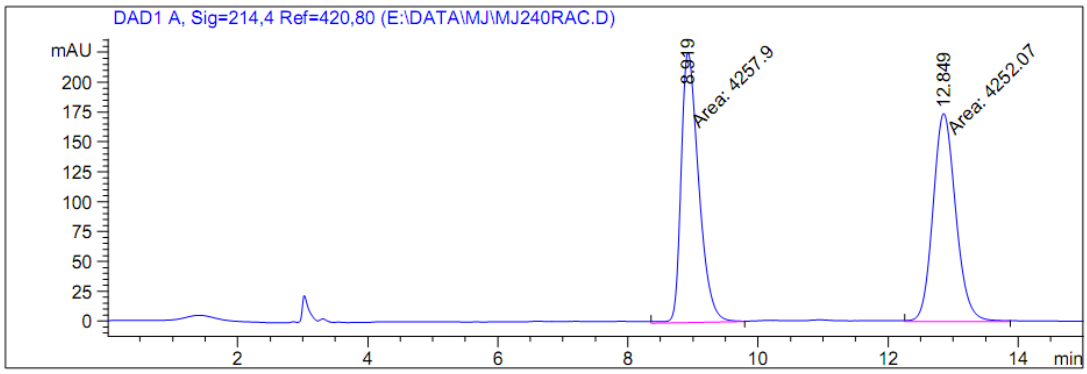
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.325	MM	0.3788	4328.52051	190.42987	49.8941
2	19.000	MM	0.6333	4346.89209	114.40393	50.1059



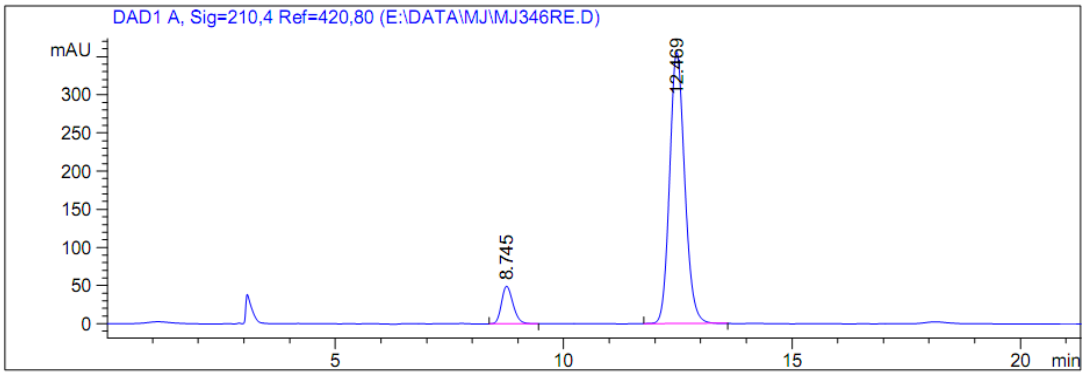
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.236	BB	0.3556	73.48380	3.22730	0.3986
2	18.863	BB	0.6020	1.83602e4	473.87088	99.6014



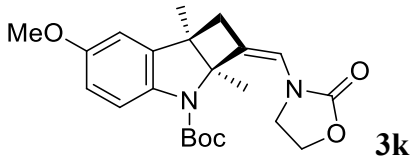
3j



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.919	MM	0.3136	4257.89941	226.25725	50.0342
2	12.849	MM	0.4069	4252.07422	174.16379	49.9658



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.745	BB	0.2688	864.25604	49.22360	9.5512
2	12.469	BB	0.3564	8184.41943	355.77036	90.4488



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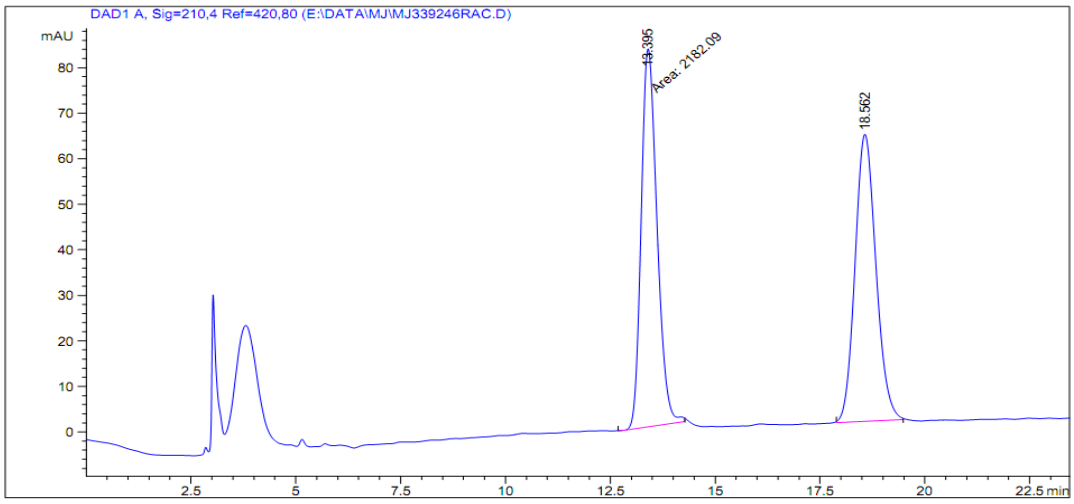
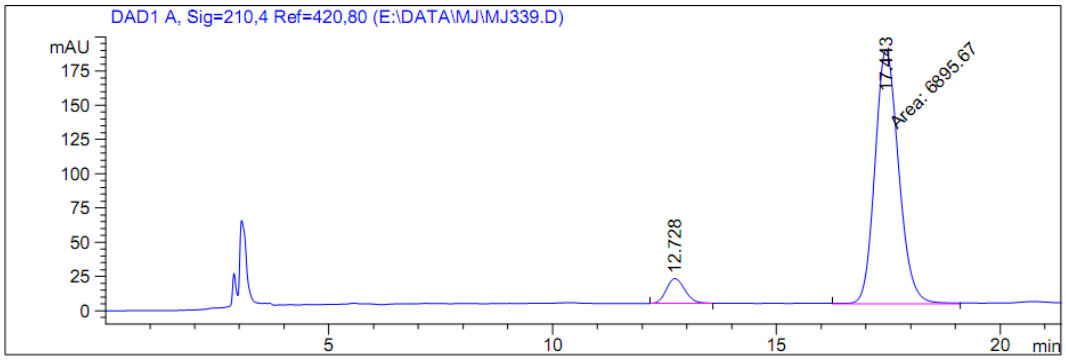
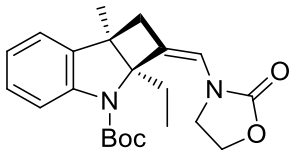


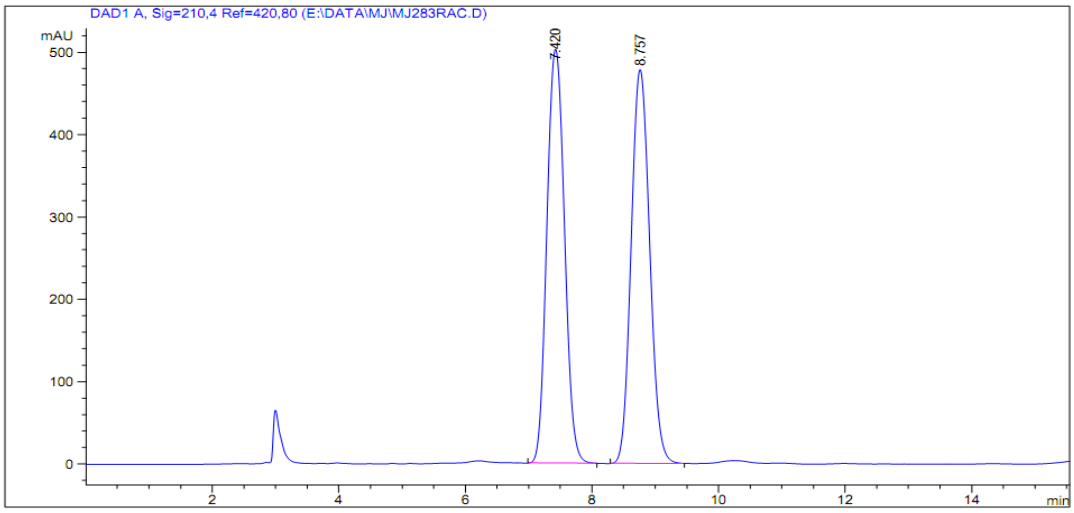
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.395	MM	0.4380	2182.09058	83.04156	49.9354
2	18.562	BB	0.5368	2187.73462	63.05071	50.0646



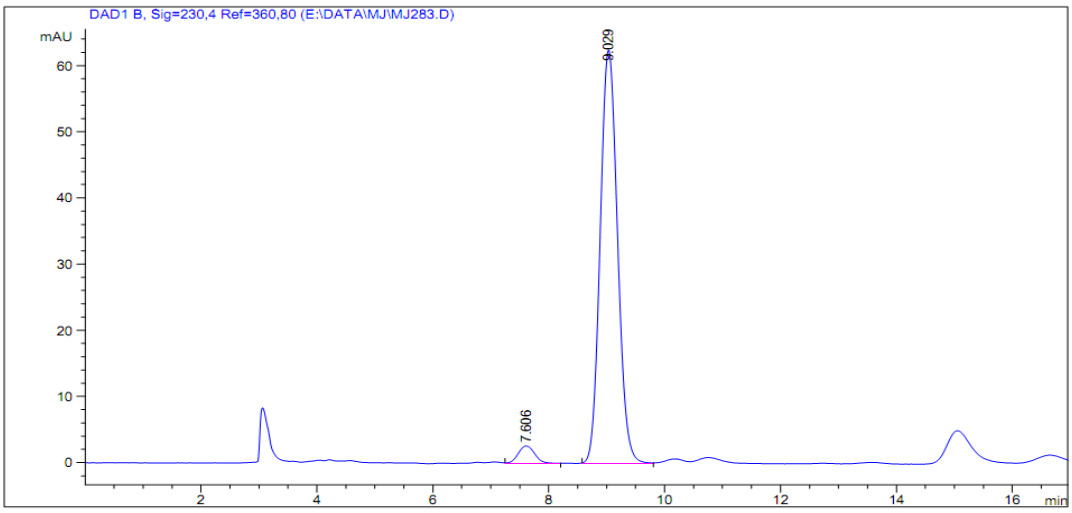
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.728	BB	0.4577	525.40118	18.15183	7.0799
2	17.443	MM	0.6188	6895.67041	185.72357	92.9201



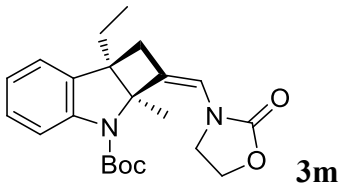
3l



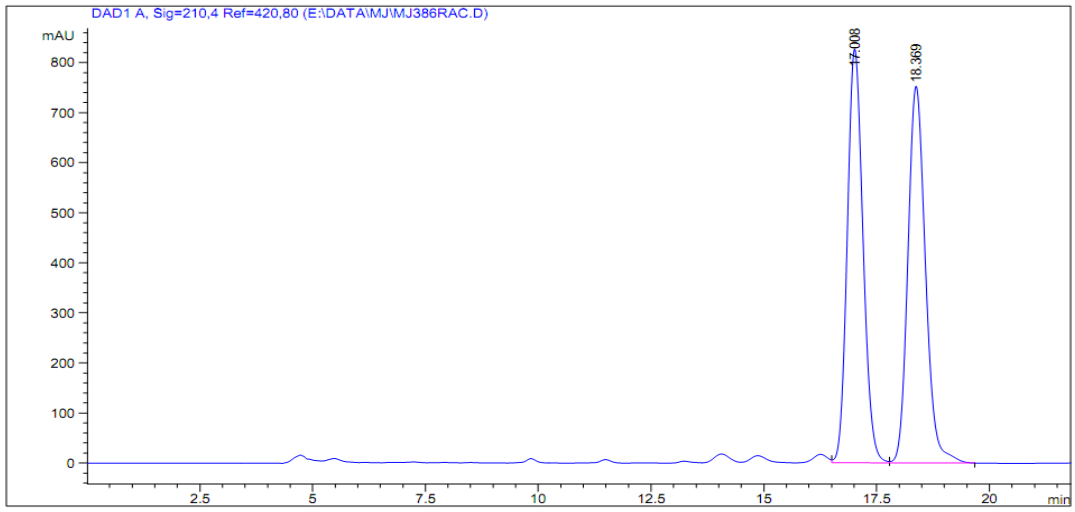
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.420	BB	0.3094	9712.37207	502.79468	50.0065
2	8.757	BB	0.3208	9709.86328	478.47415	49.9935



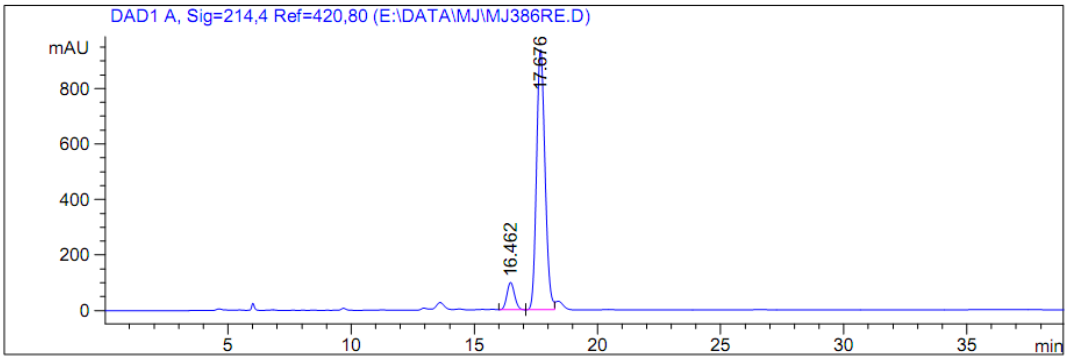
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.606	VB	0.3208	52.58137	2.63498	3.8964
2	9.029	BB	0.3262	1296.91614	62.47847	96.1036



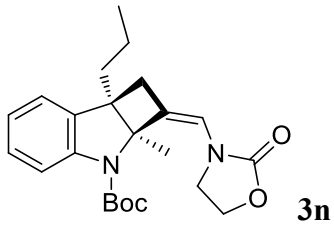
3m



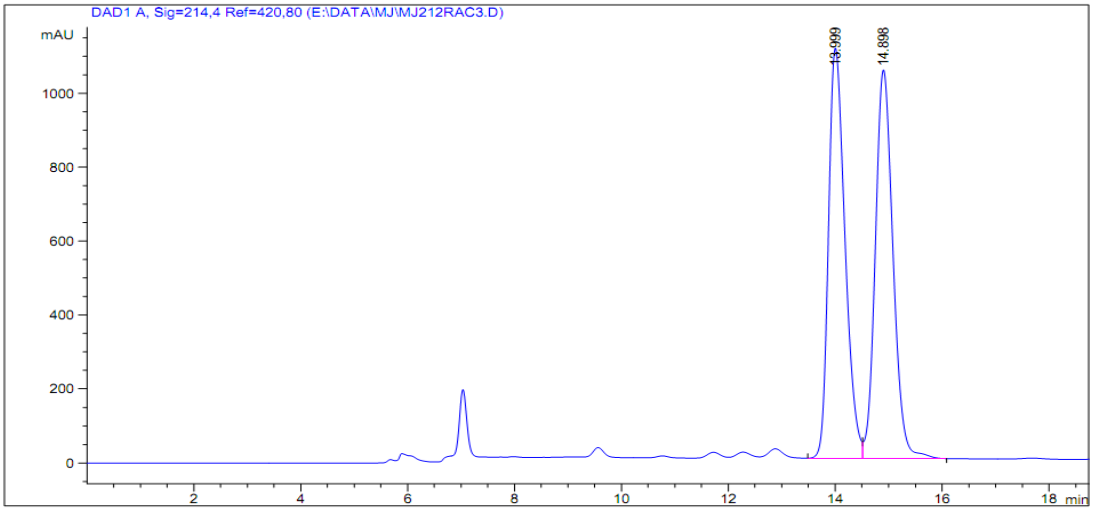
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.914	BV	0.3130	5455.87598	270.85373	50.8495
2	17.002	VV	0.3334	5273.57520	246.64899	49.1505



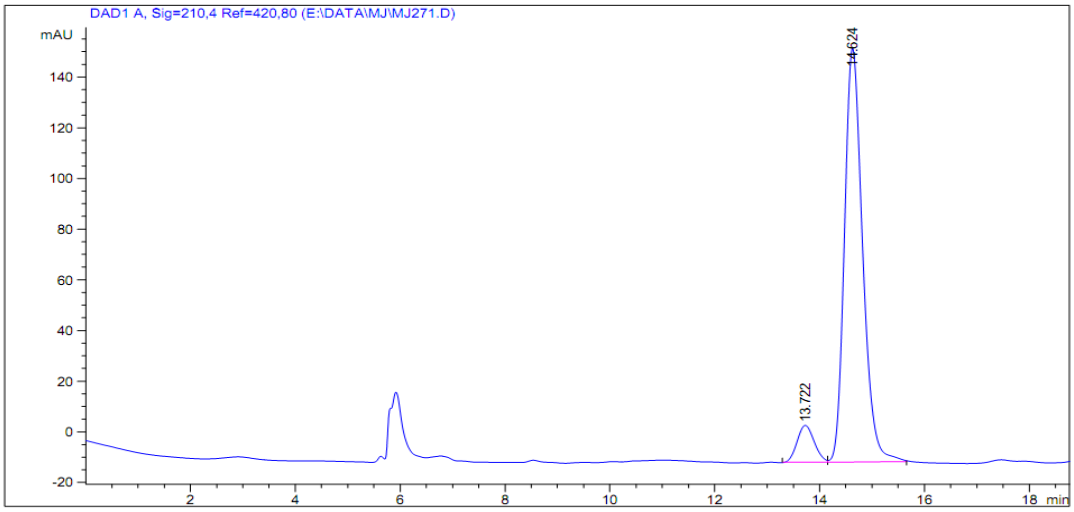
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.462	VV	0.3419	2202.20264	99.62859	8.8702
2	17.676	VV	0.3732	2.26249e4	938.71509	91.1298



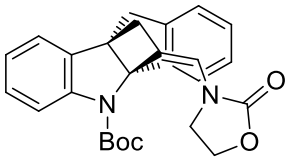
3n



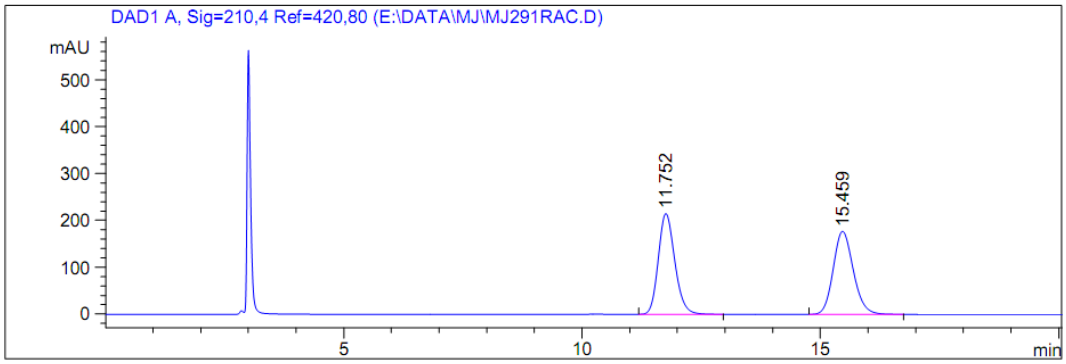
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.999	BV	0.3306	2.38433e4	1110.05676	49.7225
2	14.898	VB	0.3536	2.41094e4	1051.26038	50.2775



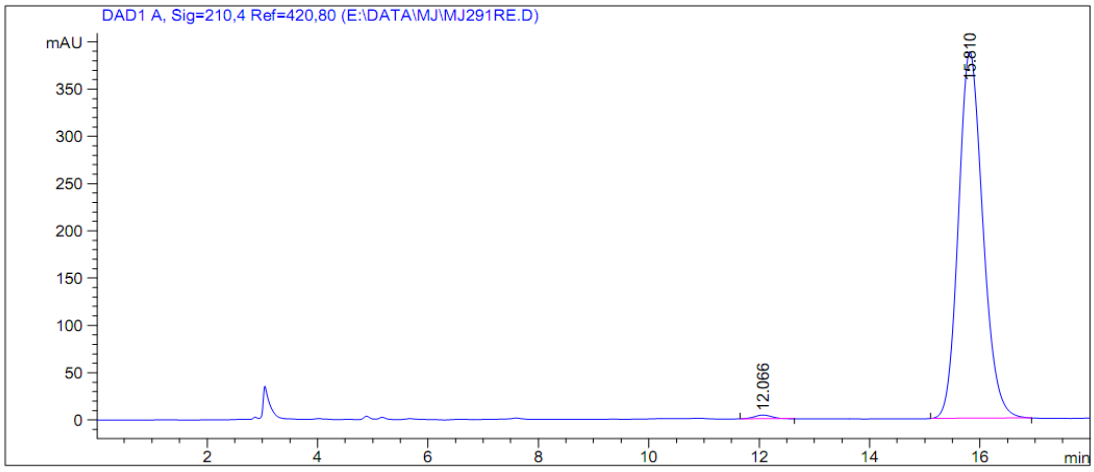
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.722	BV	0.3527	334.98462	14.65649	7.8616
2	14.624	VB	0.3664	3926.02100	163.33183	92.1384



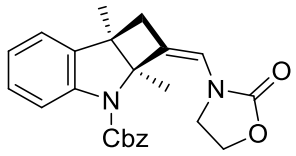
3o



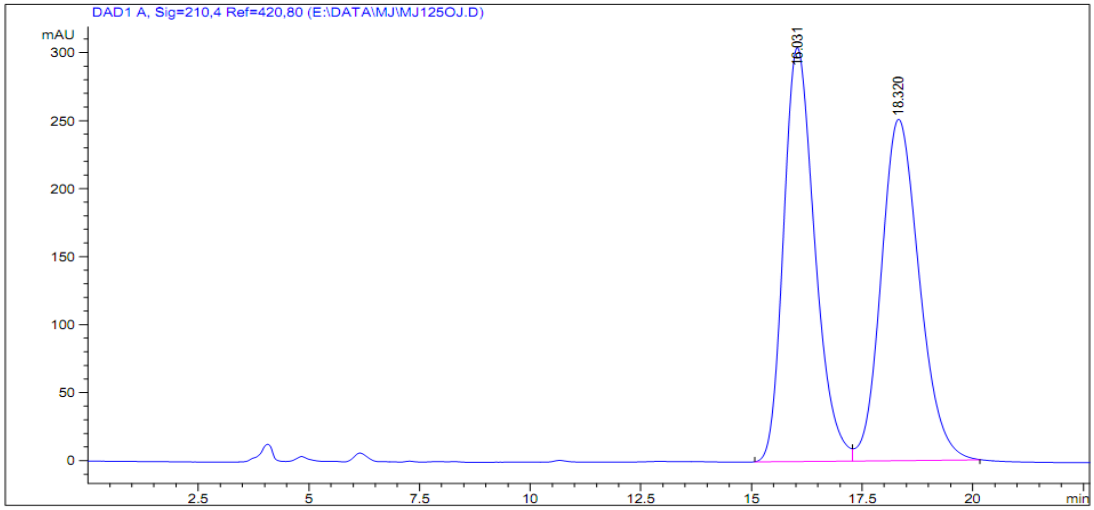
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.752	BB	0.3742	5204.89648	215.15010	49.9378
2	15.459	BB	0.4552	5217.86328	177.35817	50.0622



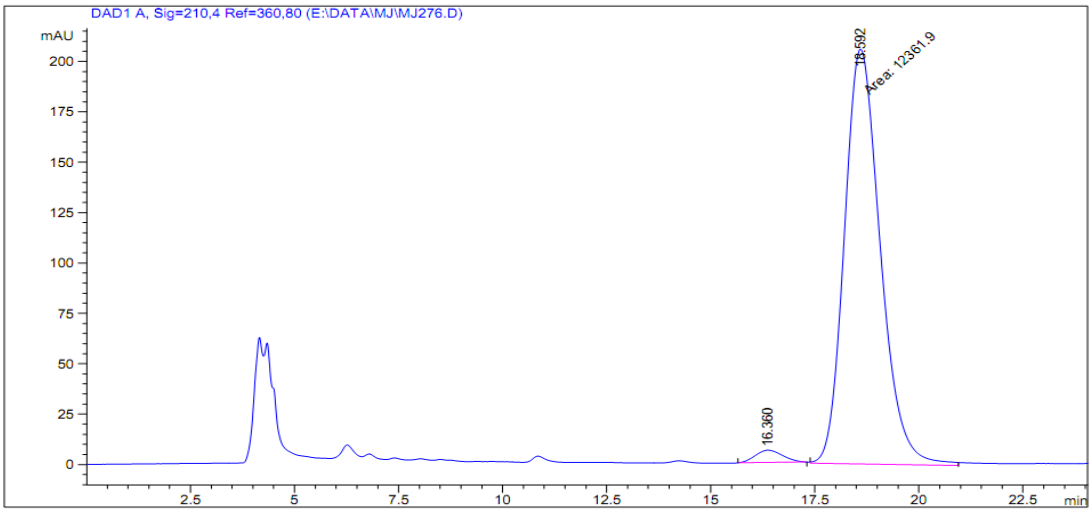
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.066	BB	0.3506	92.33147	4.04050	0.7682
2	15.810	BB	0.4745	1.19265e4	388.08340	99.2318



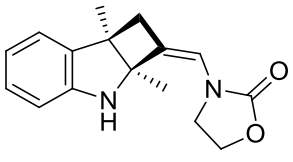
3p



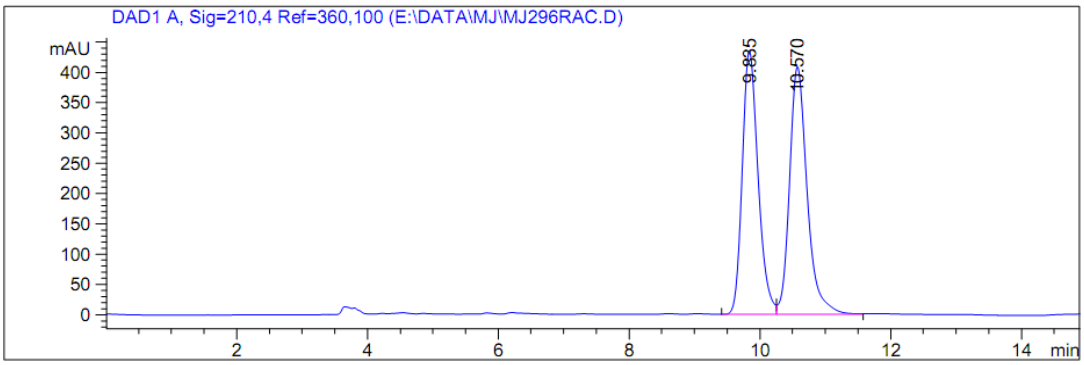
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.031	BV	0.7601	1.49271e4	304.42053	49.7436
2	18.320	VB	0.9265	1.50810e4	251.17874	50.2564



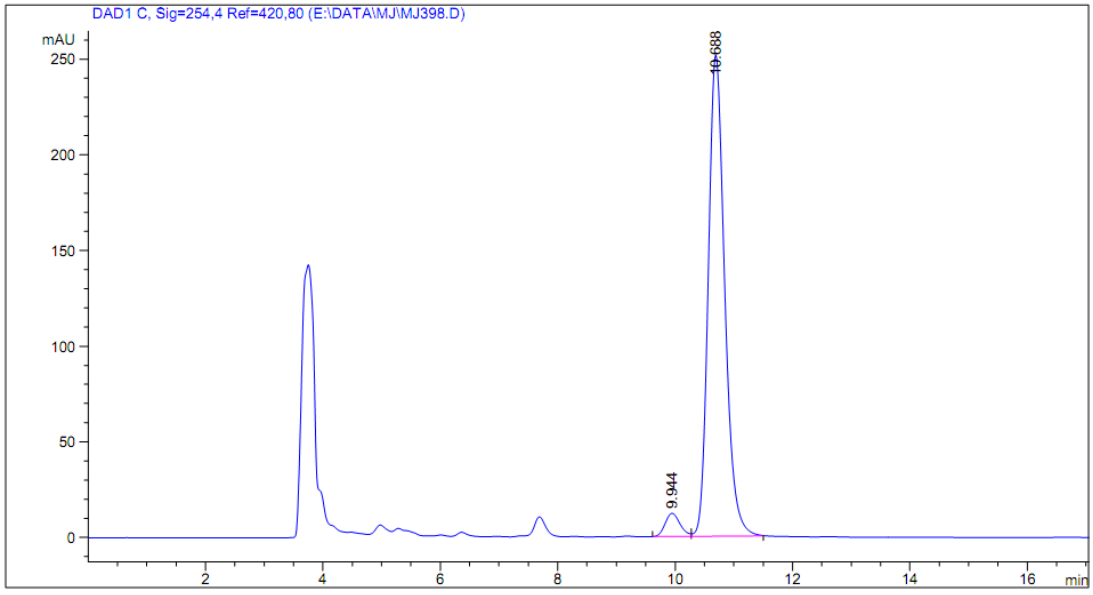
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.360	BV	0.5512	281.35953	6.13373	2.2254
2	18.592	MM	1.0005	1.23619e4	205.93063	97.7746



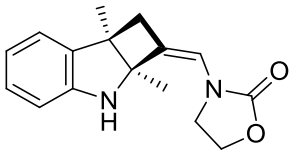
4a from [2+2] cycloaddition



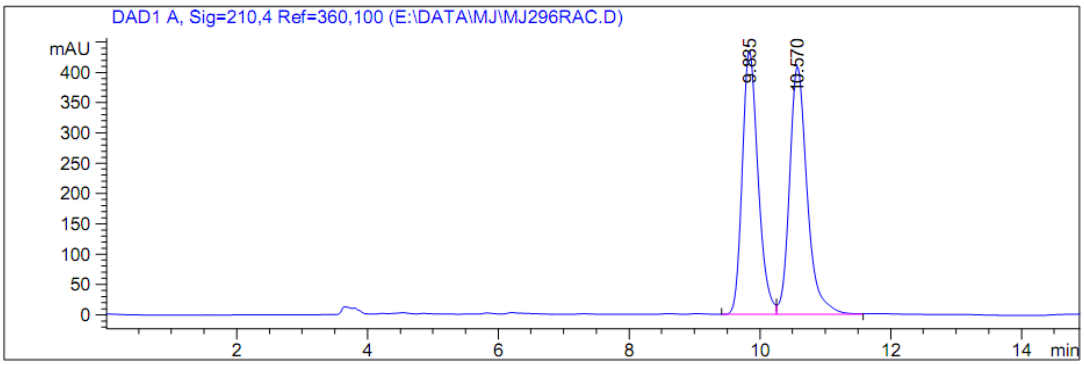
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.835	VV	0.2570	7333.54443	434.30151	48.8227
2	10.570	VV	0.2875	7687.23047	408.64740	51.1773



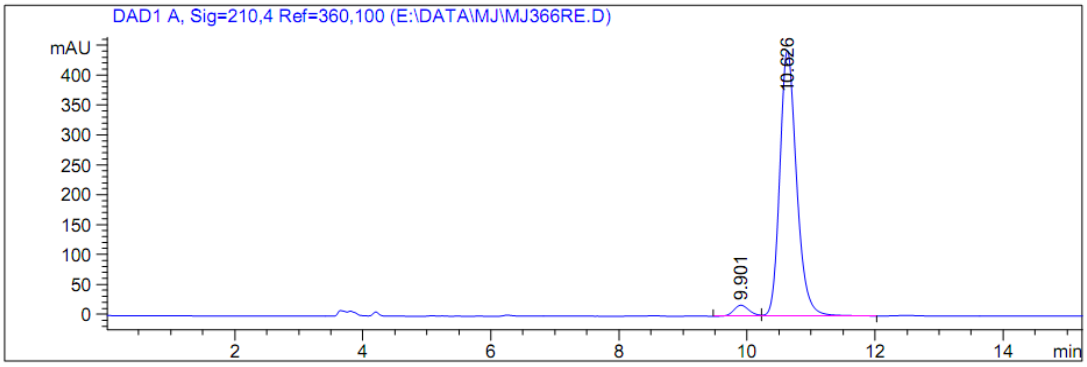
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.944	BV	0.2759	217.50160	12.20770	4.2572
2	10.688	VB	0.2988	4891.54346	251.59767	95.7428



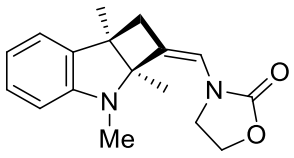
4a from deprotection of Boc



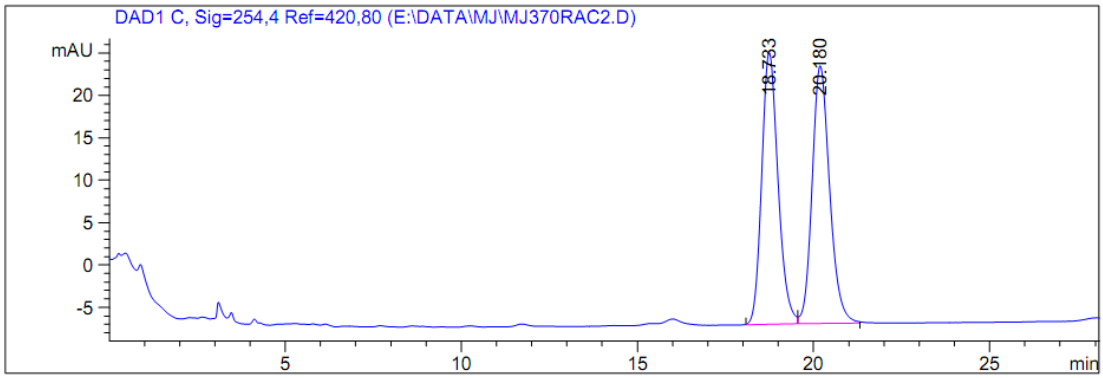
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.835	VV	0.2570	7333.54443	434.30151	48.8227
2	10.570	VV	0.2875	7687.23047	408.64740	51.1773



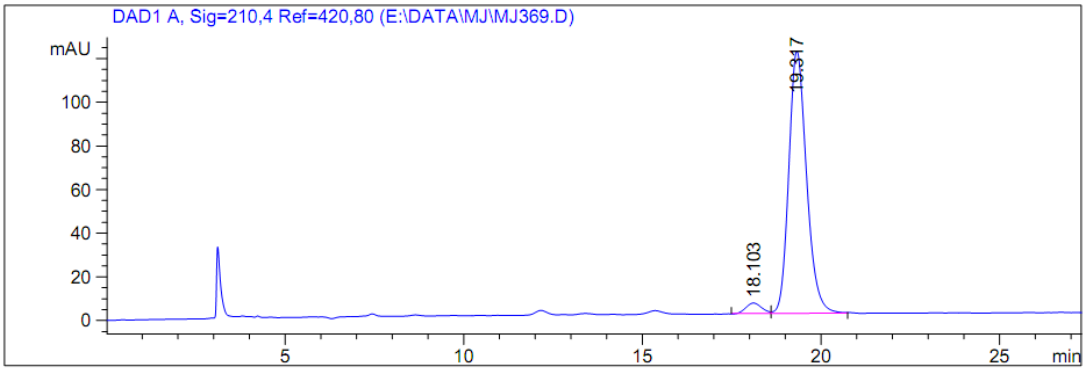
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.901	VV	0.2618	311.87476	18.39416	3.6985
2	10.626	VB	0.2773	8120.53125	444.10443	96.3015



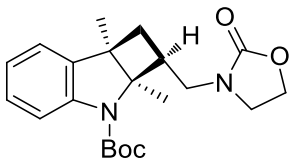
5a



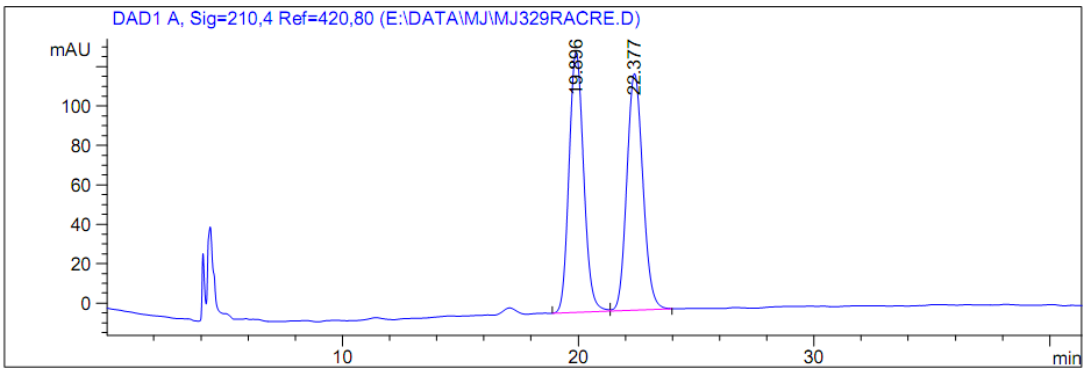
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.733	BV	0.4966	1035.25757	32.07269	49.5378
2	20.180	VB	0.5325	1054.57544	30.41357	50.4622



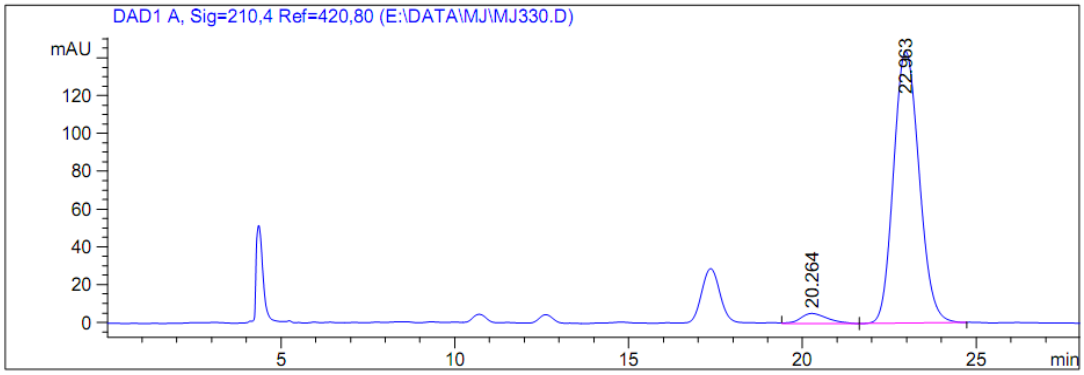
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.103	BV	0.4876	156.83577	4.97823	3.6236
2	19.317	VB	0.5327	4171.36377	120.25941	96.3764



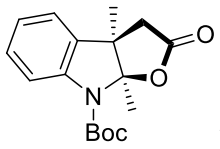
6a



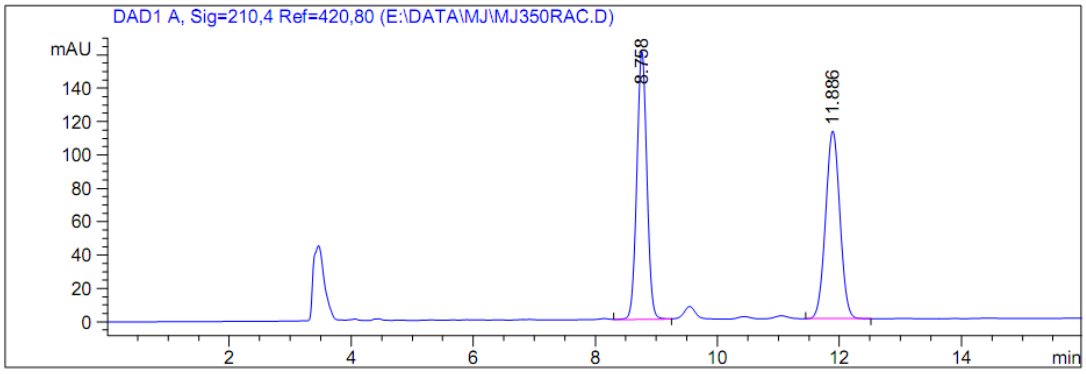
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.896	BV	0.6769	5710.79639	131.94768	100.0362
2	22.377	VB	0.7460	5706.66504	120.17332	99.9638



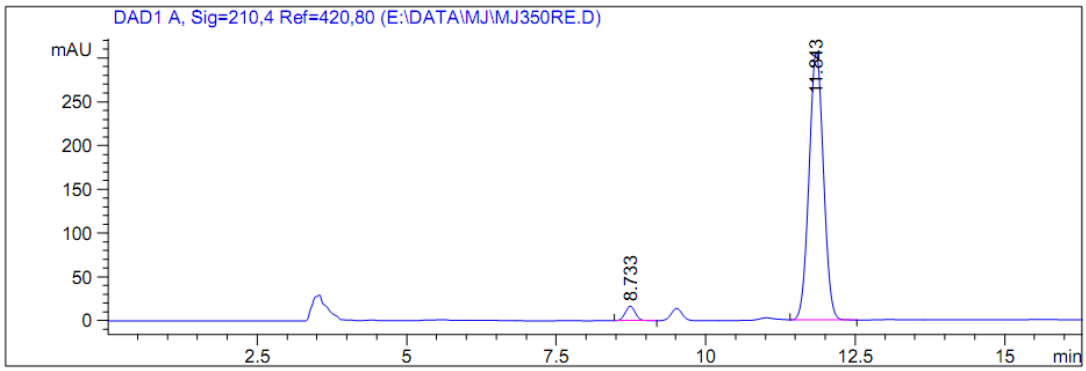
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.264	BV	0.8407	291.32855	5.37224	7.6001
2	22.963	VB	0.8102	7375.09619	143.83521	192.3999



7a

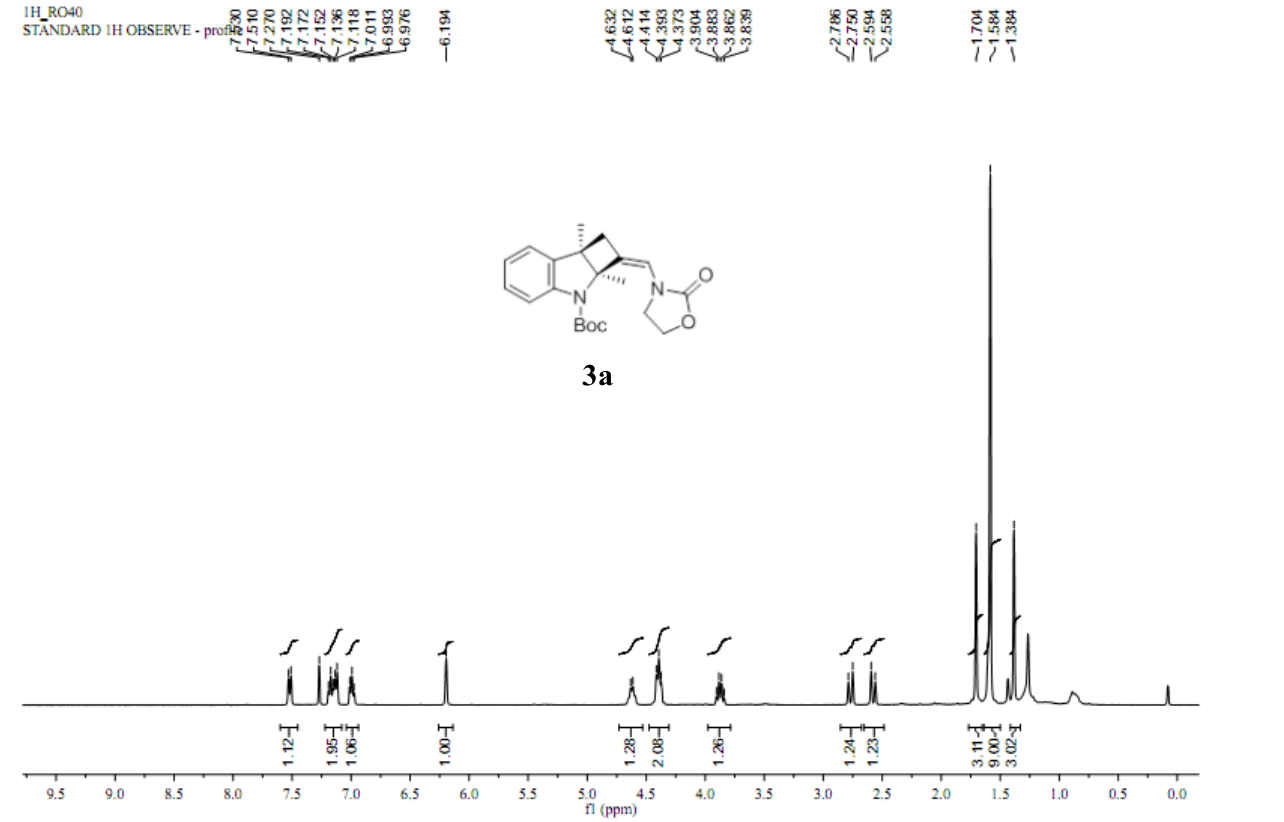


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.758	VB	0.1782	1845.92090	160.52551	50.0586
2	11.886	VB	0.2549	1841.59766	112.56579	49.9414

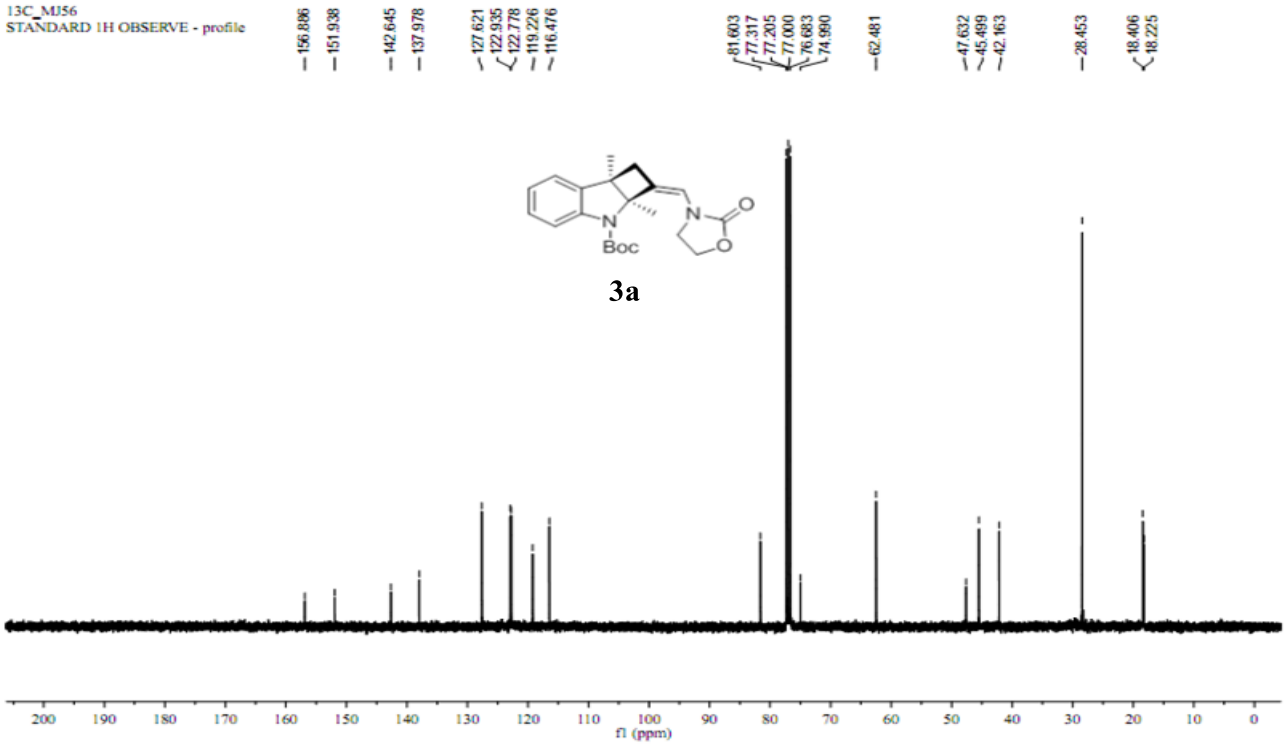


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.733	BV	0.1866	196.11549	16.51329	3.6706
2	11.843	VB	0.2643	5146.79883	305.96567	96.3294

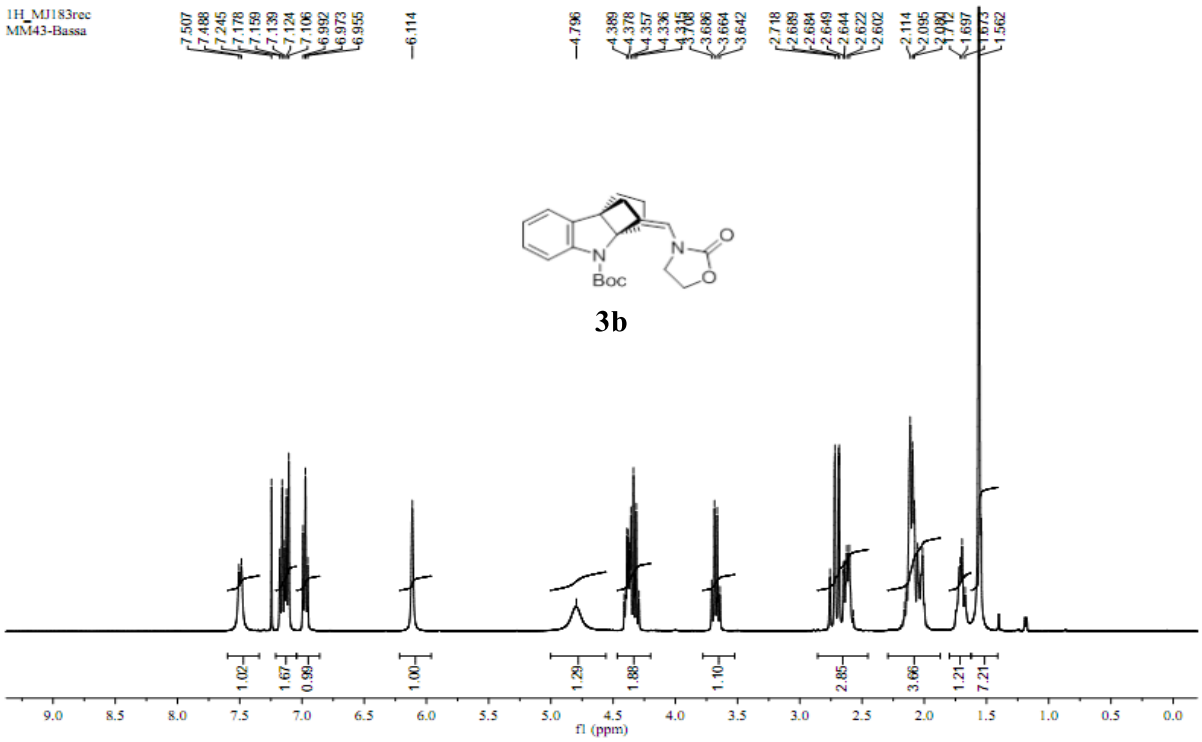
NMR spectra



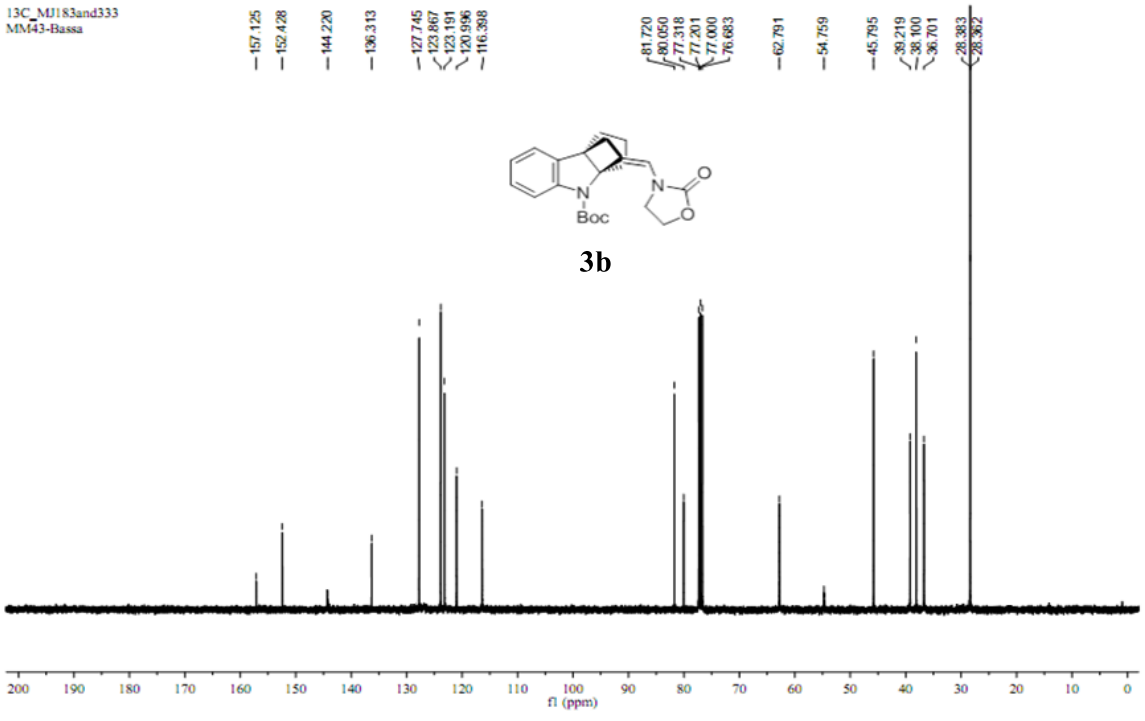
3a



3a


1H_MJ183rec
MM43-Bassa
7.507
7.488
7.245
7.178
7.159
7.139
7.124
7.106
6.992
6.973
6.955
6.114
4.796
4.389
4.378
4.357
4.336
3.686
3.664
3.642
2.718
2.689
2.684
2.649
2.644
2.622
2.602
2.114
2.095
1.697
1.562
Boc
1.02
1.67
0.99
1.00
1.29
1.88
1.10
2.85
3.66
1.21
7.21
f1 (ppm)

3b


13C_MJ183and333
MM43-Bassa
157.125
152.428
144.220
136.313
127.745
123.867
123.191
120.996
116.398
81.720
80.050
77.318
77.201
77.000
76.683
62.791
54.759
45.795
39.219
38.100
36.701
28.383
28.362
Boc
f1 (ppm)

3b

1H_NOE_

MJ189
Selective band center: 6.11 (ppm); width: 49.8 (Hz)

Sample Name:

Data Collected on:
agilent400-vnmrs400
Archive directory:

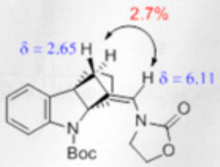
Sample directory:

FidFile: 1H_NOE_MJ183

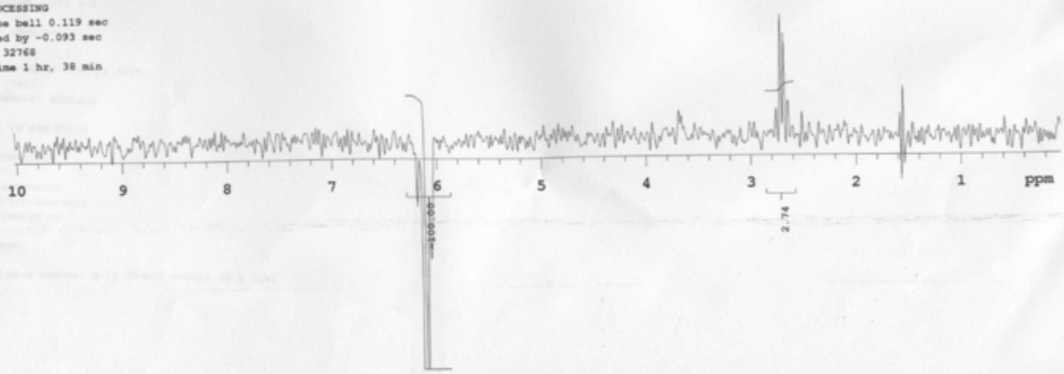
Pulse Sequence: NOESY1D
Solvent: cdcl3
Data collected on: Nov 26 2014

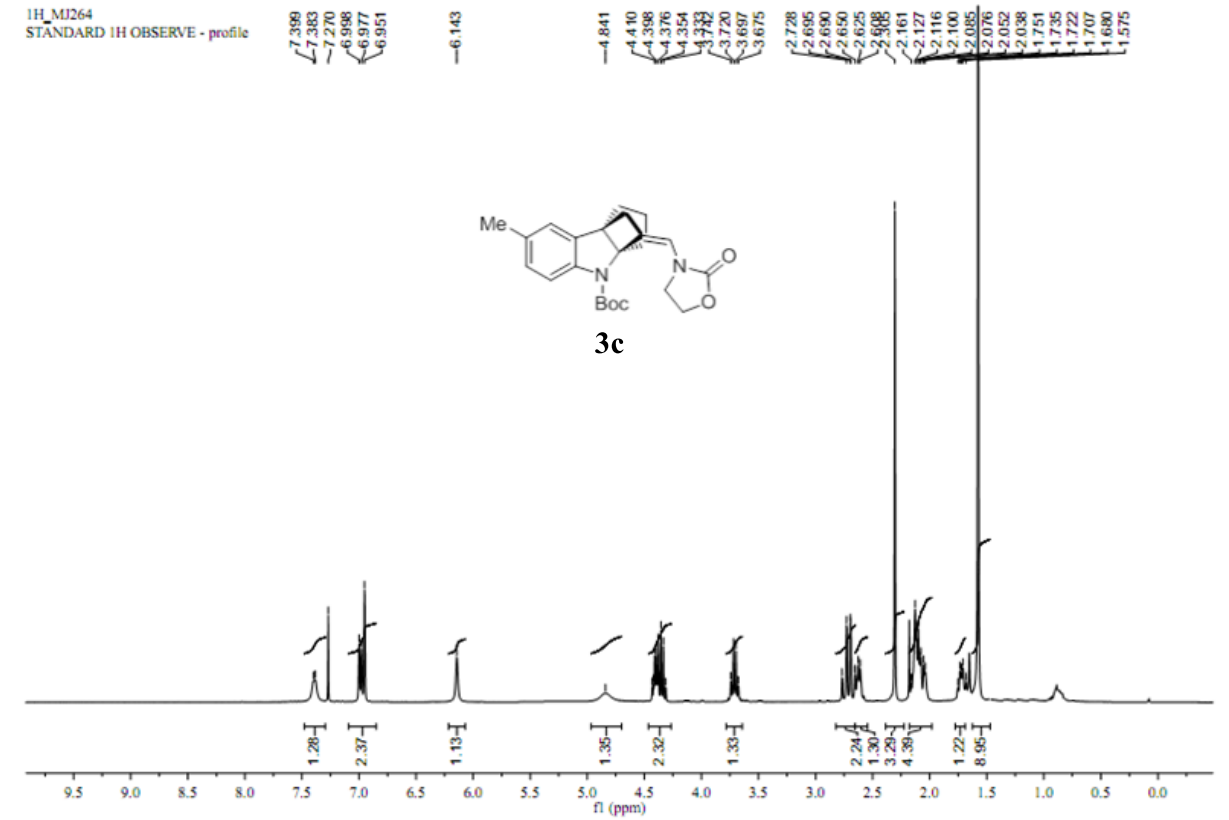
Operator: bandini

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
128 repetitions
OBSERVE H1, 400.7199780 MHz
DATA PROCESSING
Sq. sine bell 0.119 sec
Shifted by -0.093 sec
FT size 32768
Total time 1 hr, 38 min

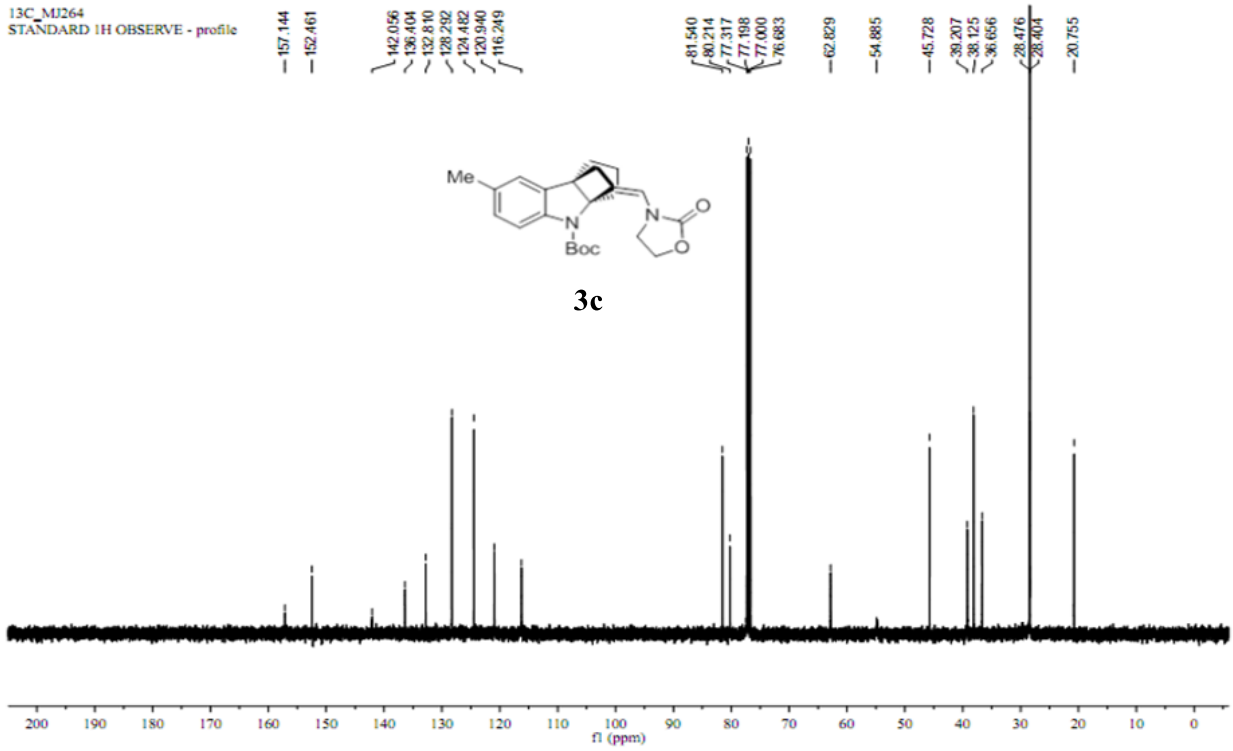


3b-NOE

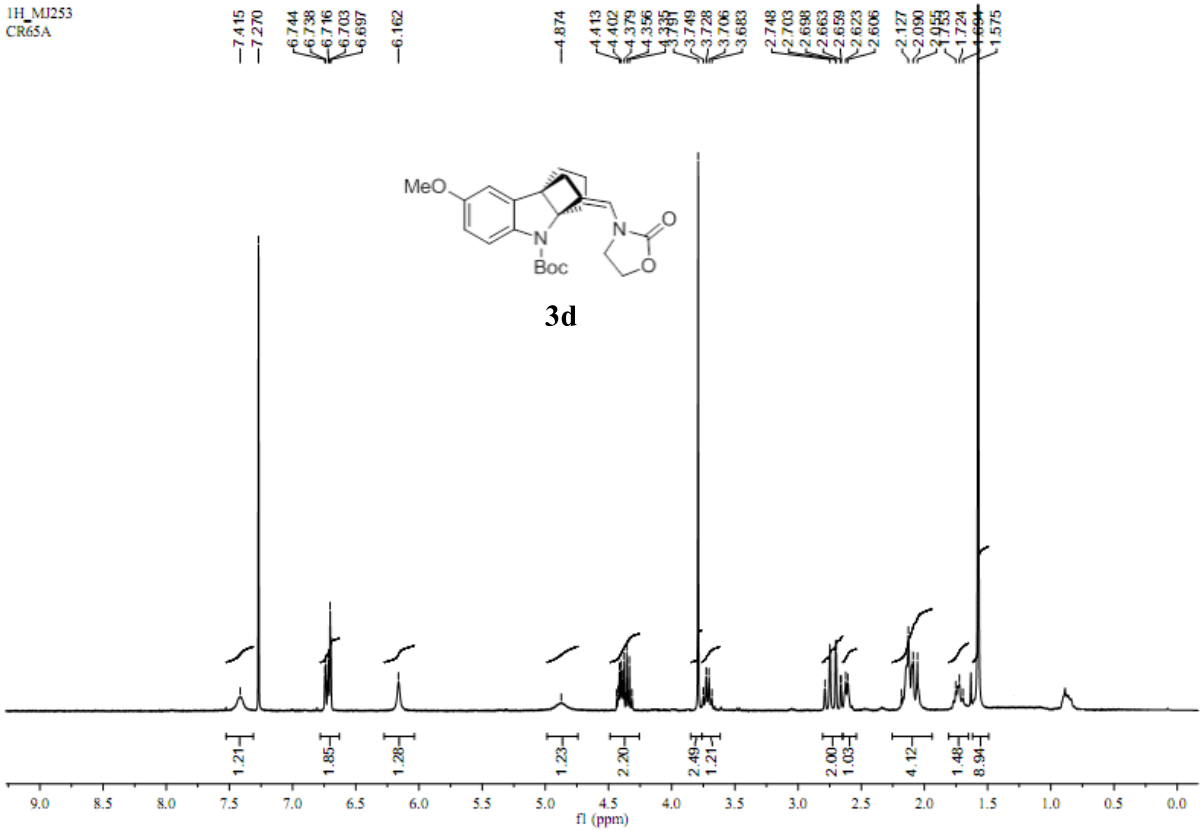


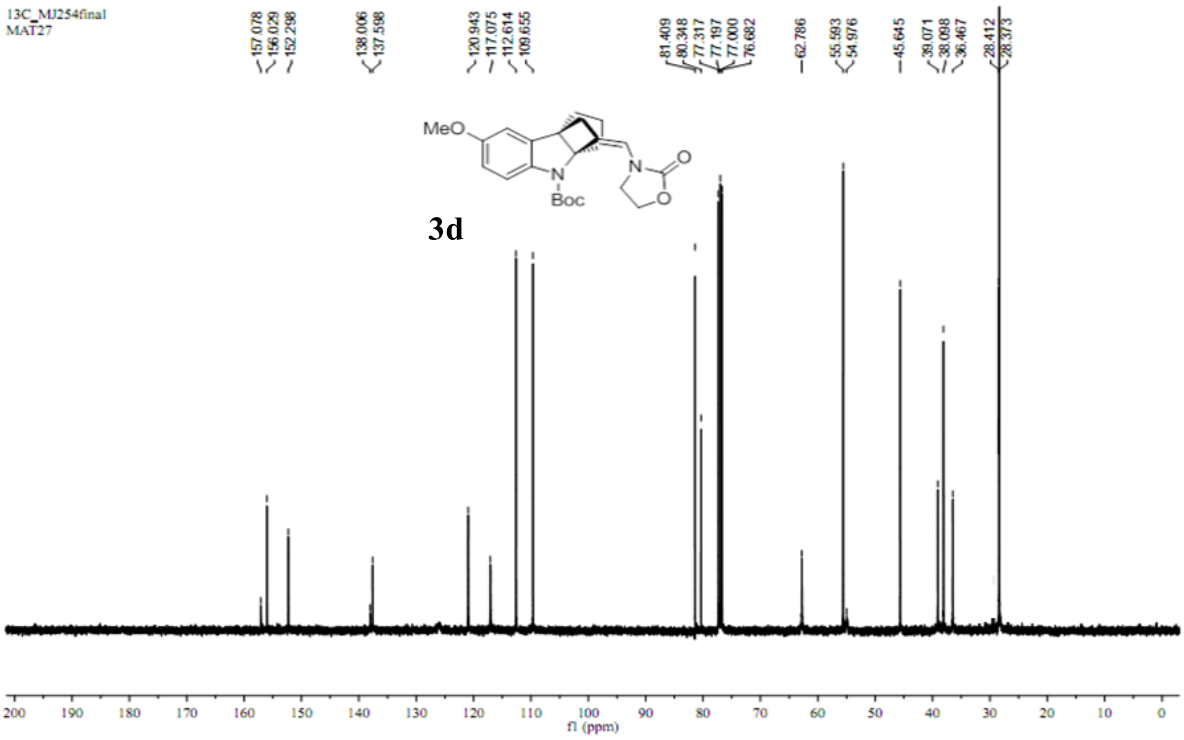

1H_MJ264
STANDARD 1H OBSERVE - profile
7.399
7.383
7.270
6.998
6.977
6.951
6.143
4.841
4.410
4.398
4.376
4.354
3.742
3.720
3.697
3.675
2.728
2.695
2.690
2.650
2.625
2.608
2.588
2.161
2.127
2.116
2.100
2.085
2.076
2.052
2.038
1.751
1.735
1.722
1.707
1.680
1.575
Me
N
Boc
N
O
O
1.28
2.37
1.13
1.35
2.32
1.33
2.24
1.30
3.29
4.39
1.22
8.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

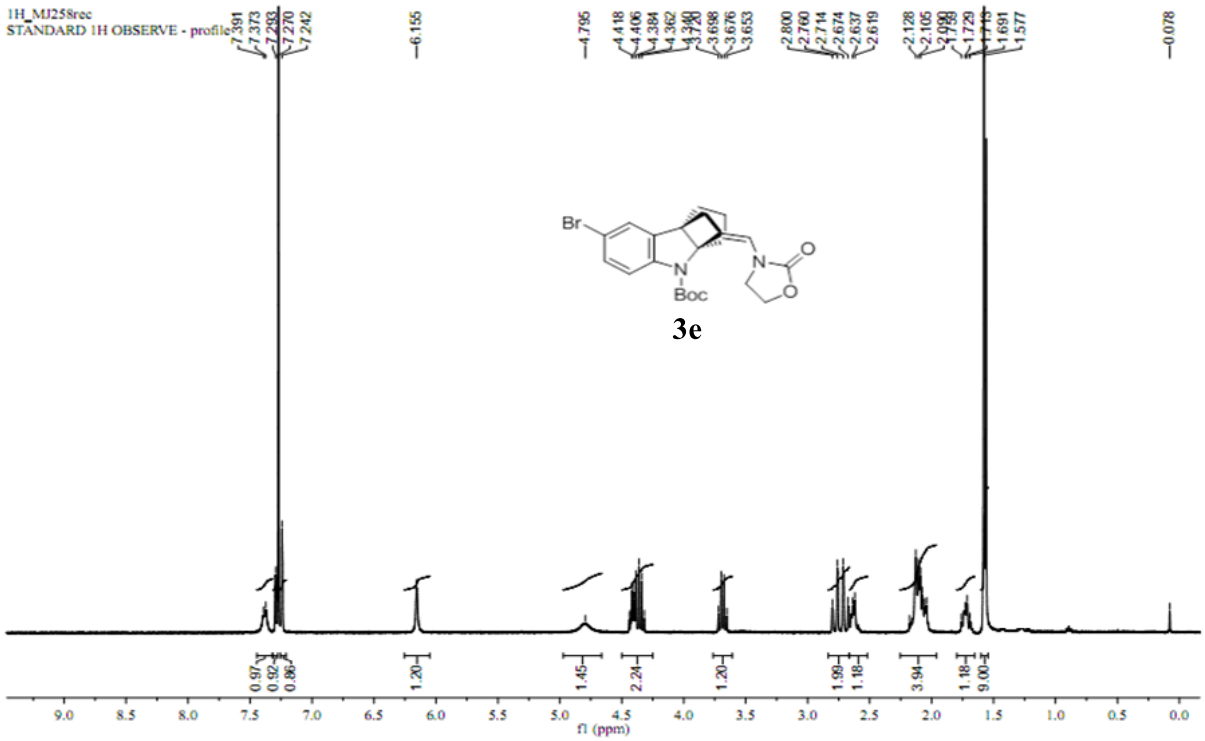
3c


13C_MJ264
STANDARD 1H OBSERVE - profile
157.144
152.461
142.056
136.404
132.810
128.292
124.482
120.940
116.249
81.540
80.214
77.317
77.198
77.000
76.683
62.829
54.885
45.728
39.207
38.125
36.656
28.476
28.404
20.755
Me
N
Boc
N
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

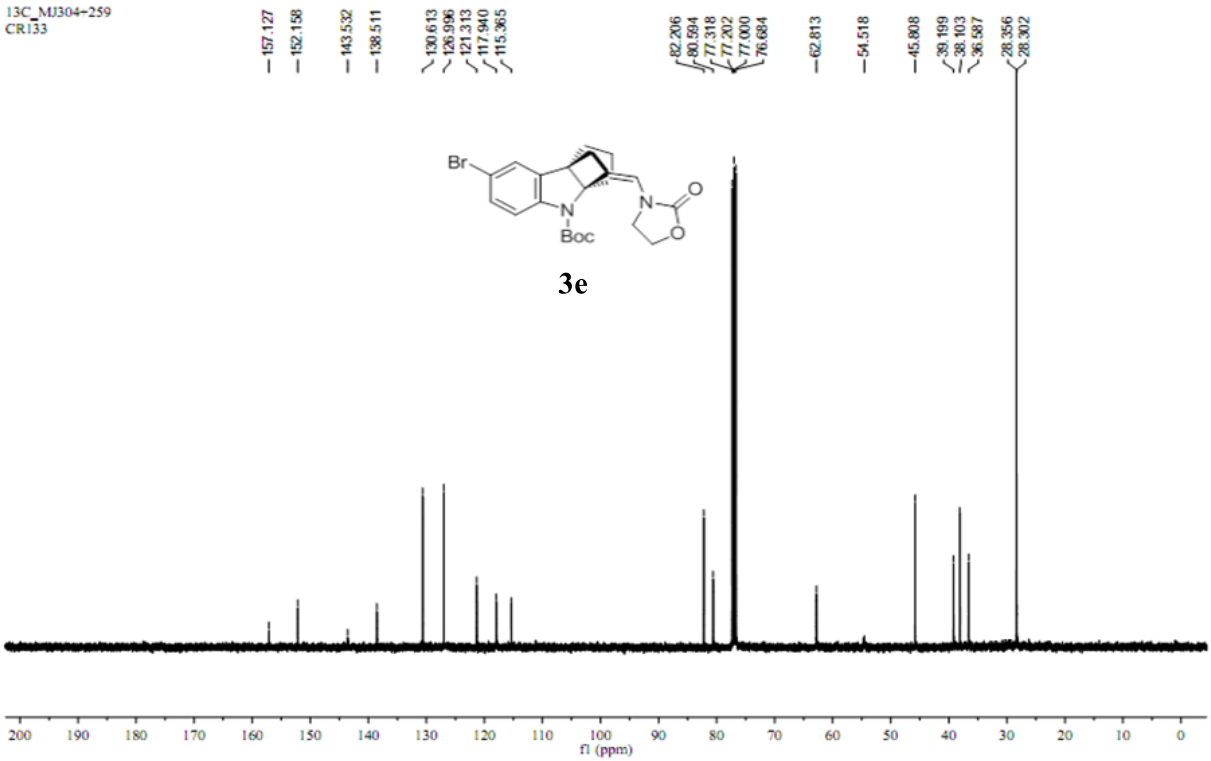
3c


1H_MJ253
CR65A
MeO
N
Boc
O
N
O
3d
fl (ppm)

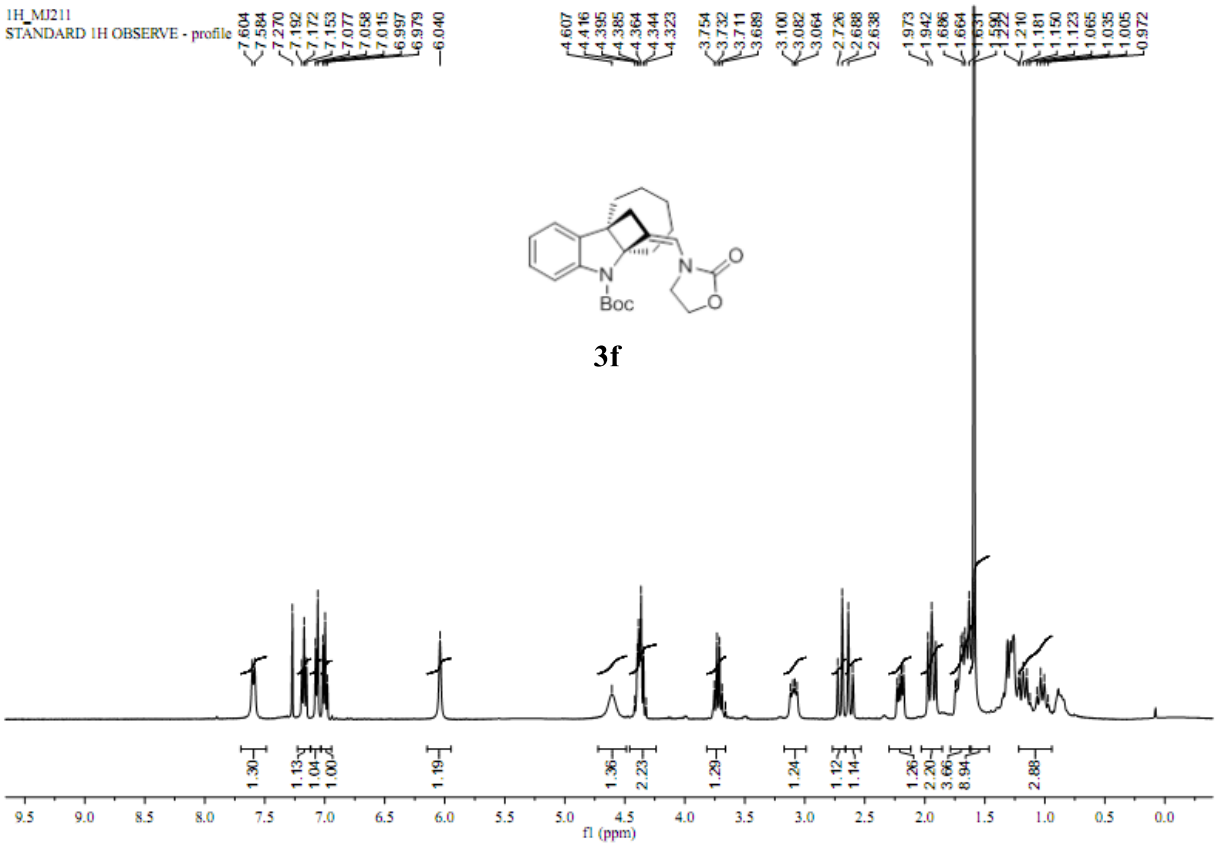

13C_MJ254final
MAT27
MeO
N
Boc
O
N
O
3d
fl (ppm)


1H_MJ258rec
STANDARD 1H OBSERVE - profile
Br
N
Boc
O
N
O
f1 (ppm)

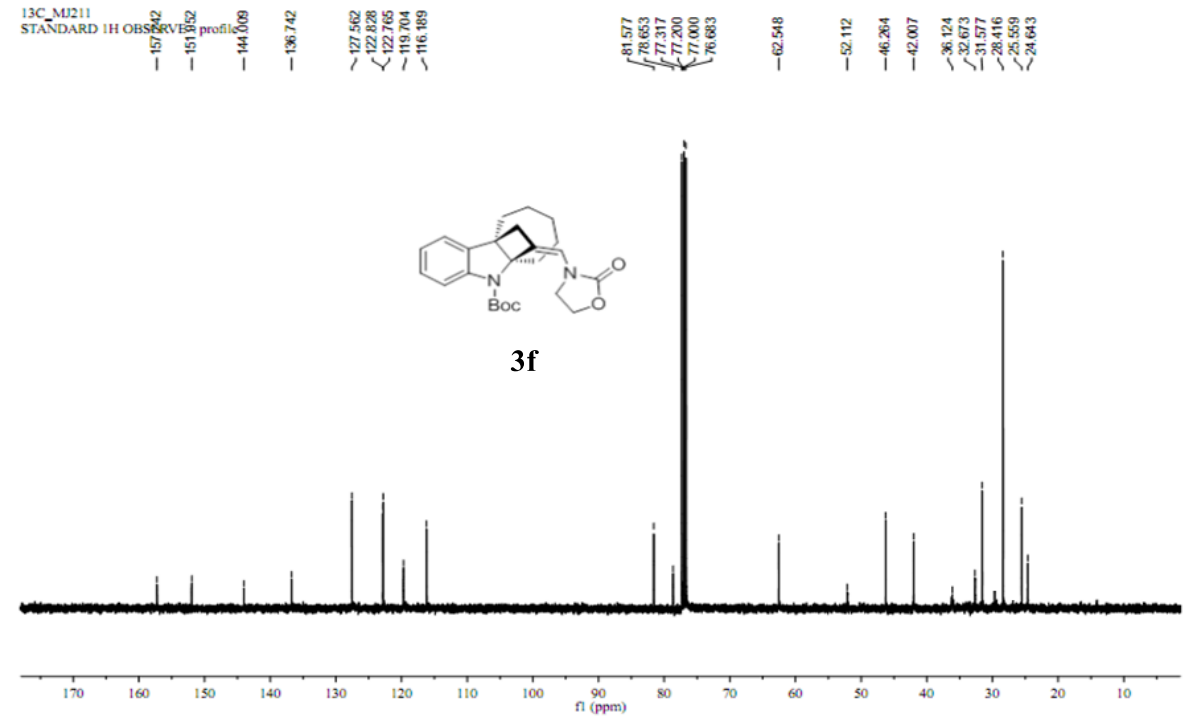
3e


13C_MJ304-259
CR133
Br
N
Boc
O
N
O
f1 (ppm)

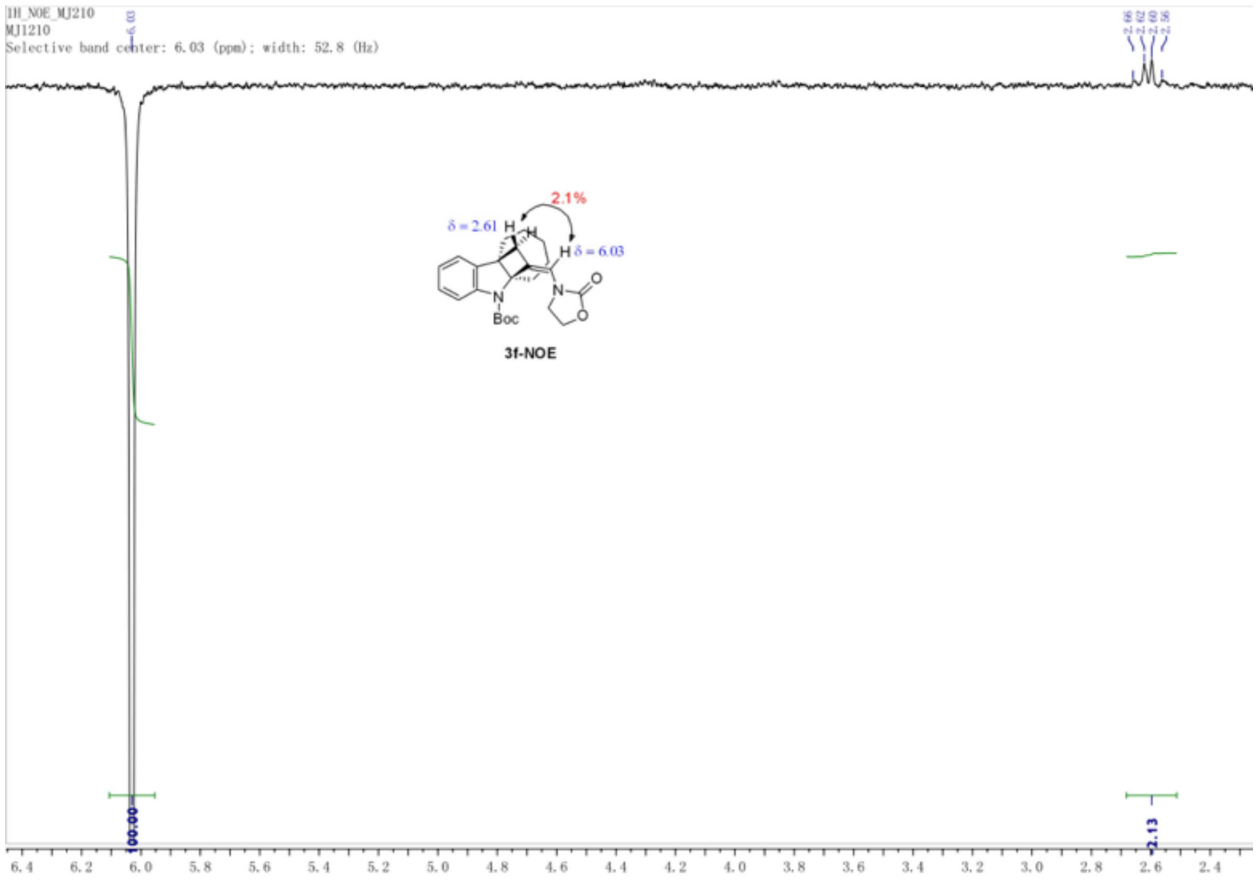
3e

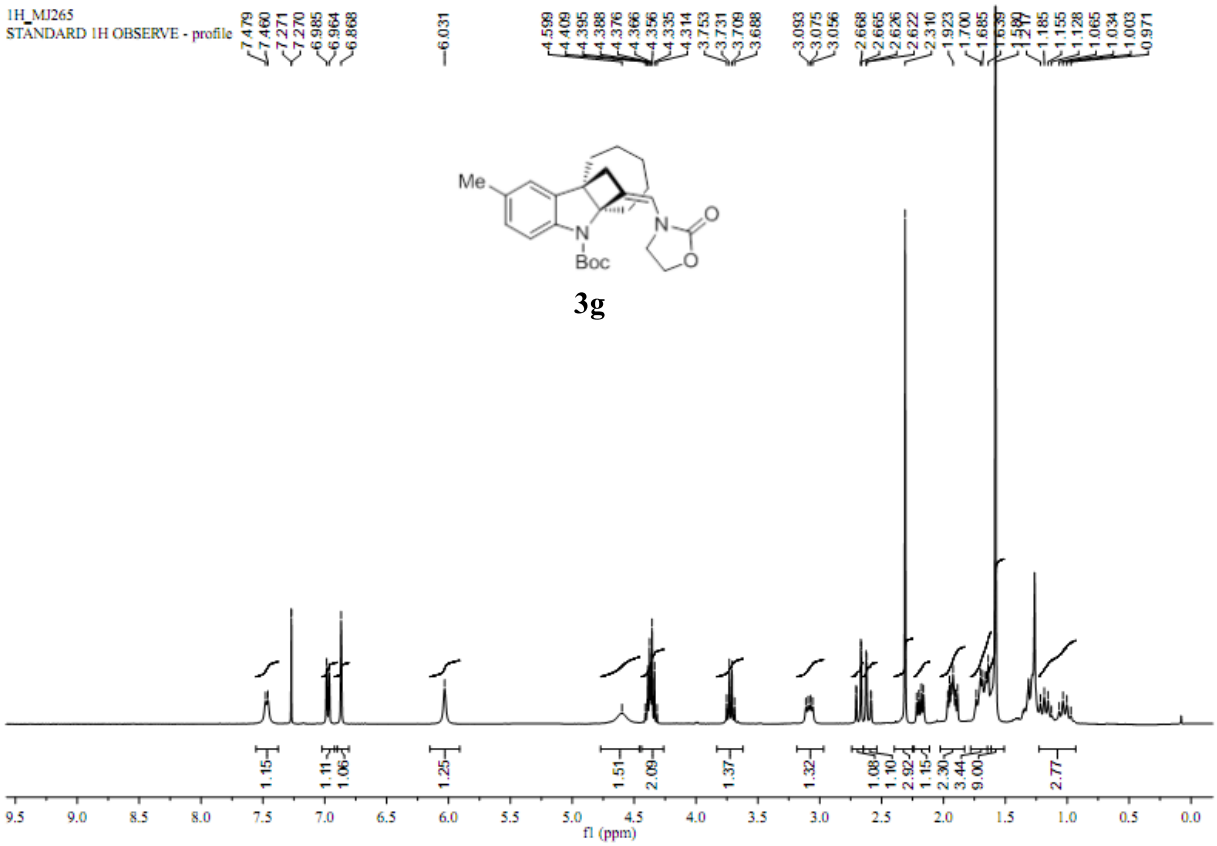

1H_MJ211
STANDARD 1H OBSERVE - profile
7.604
7.584
7.270
7.192
7.172
7.153
7.077
7.058
7.015
6.997
6.979
6.040
4.607
4.416
4.395
4.385
4.364
4.344
4.323
3.754
3.732
3.711
3.689
3.100
3.082
3.064
2.726
2.688
2.638
1.973
1.942
1.686
1.664
1.631
1.222
1.210
1.181
1.150
1.123
1.065
1.035
1.005
0.972
Boc
1.30
1.13
1.04
1.00
1.19
1.36
2.23
1.29
1.24
1.12
1.14
1.26
2.20
3.66
8.94
2.88
f1 (ppm)

3f

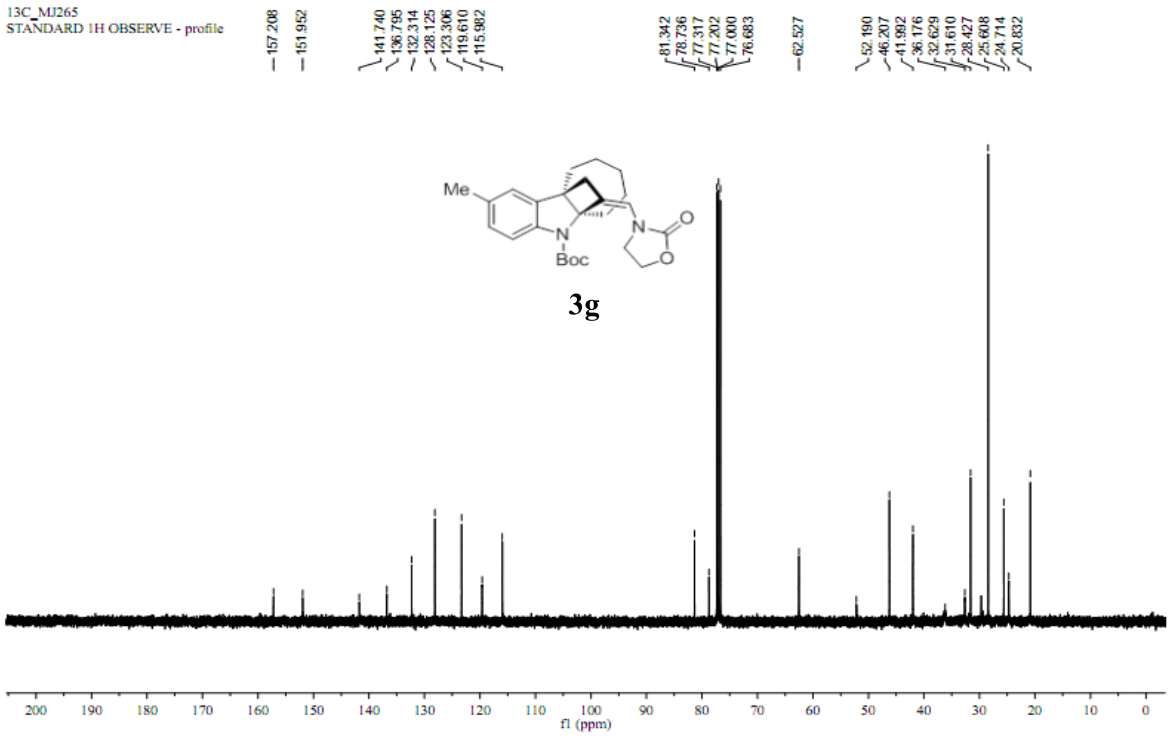

13C_MJ211
STANDARD 1H OBSERVE - profile
157.542
151.052
144.009
136.742
127.562
122.828
122.765
119.704
116.189
81.577
78.653
77.317
77.200
77.000
76.683
62.548
52.112
46.264
42.007
36.124
32.673
31.577
28.416
25.559
24.643
Boc
f1 (ppm)

3f

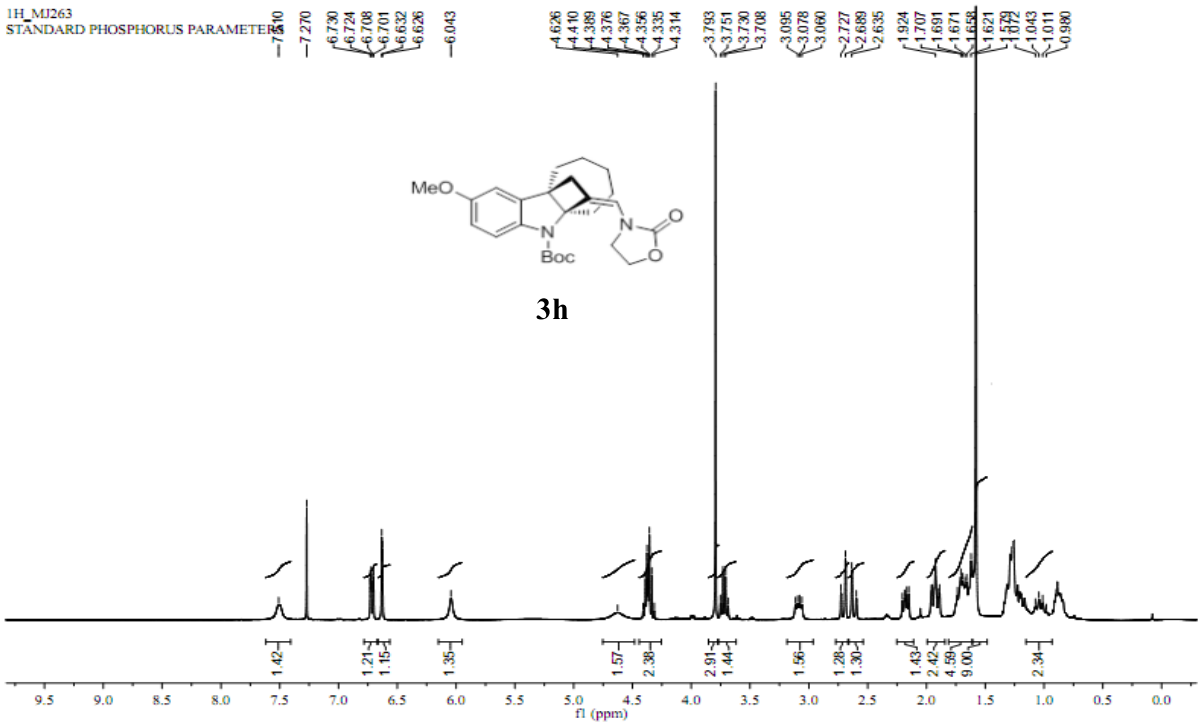

1H_NOE_MJ210
MJ1210
Selective band center: 6.03 (ppm); width: 52.8 (Hz)
6.03
2.66
2.62
2.60
2.56
2.1%
δ = 2.61
H
H
H
δ = 6.03
N
N
O
O
Boc
3f-NOE
100.00
2.13
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4


1H_MJ265
STANDARD 1H OBSERVE - profile
Me
N
Boc
N
O
O
f1 (ppm)

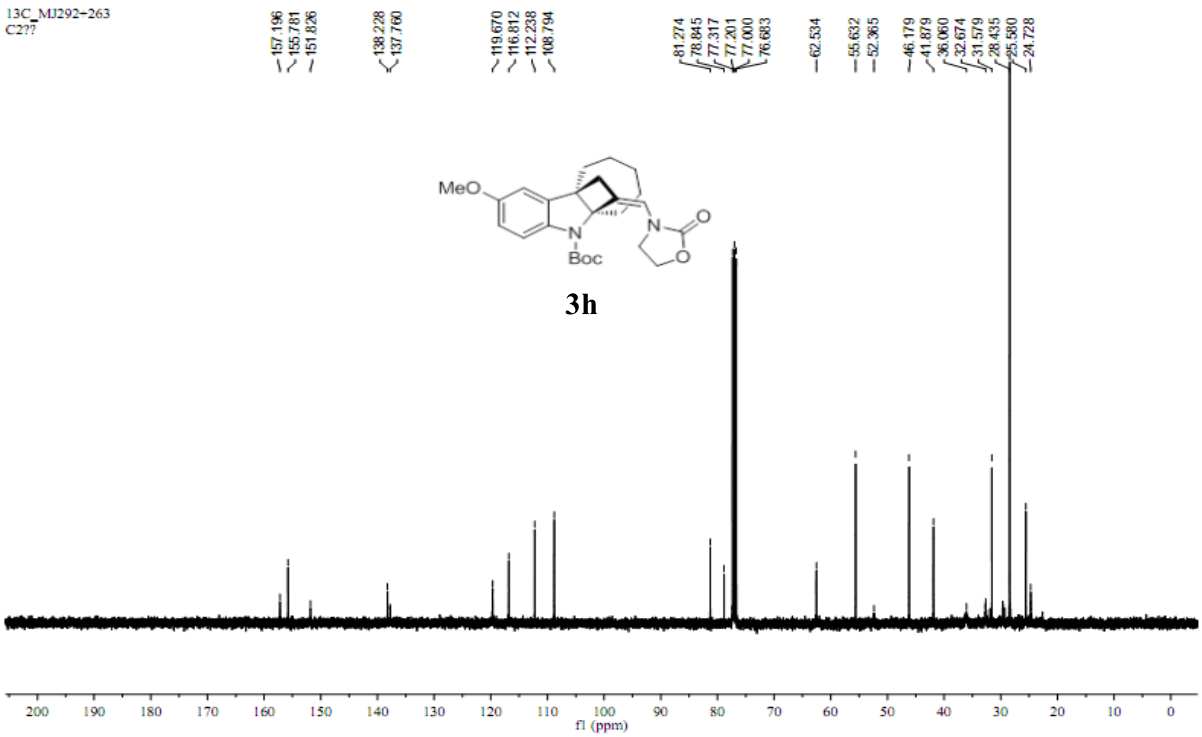
3g


13C_MJ265
STANDARD 1H OBSERVE - profile
Me
N
Boc
N
O
O
f1 (ppm)

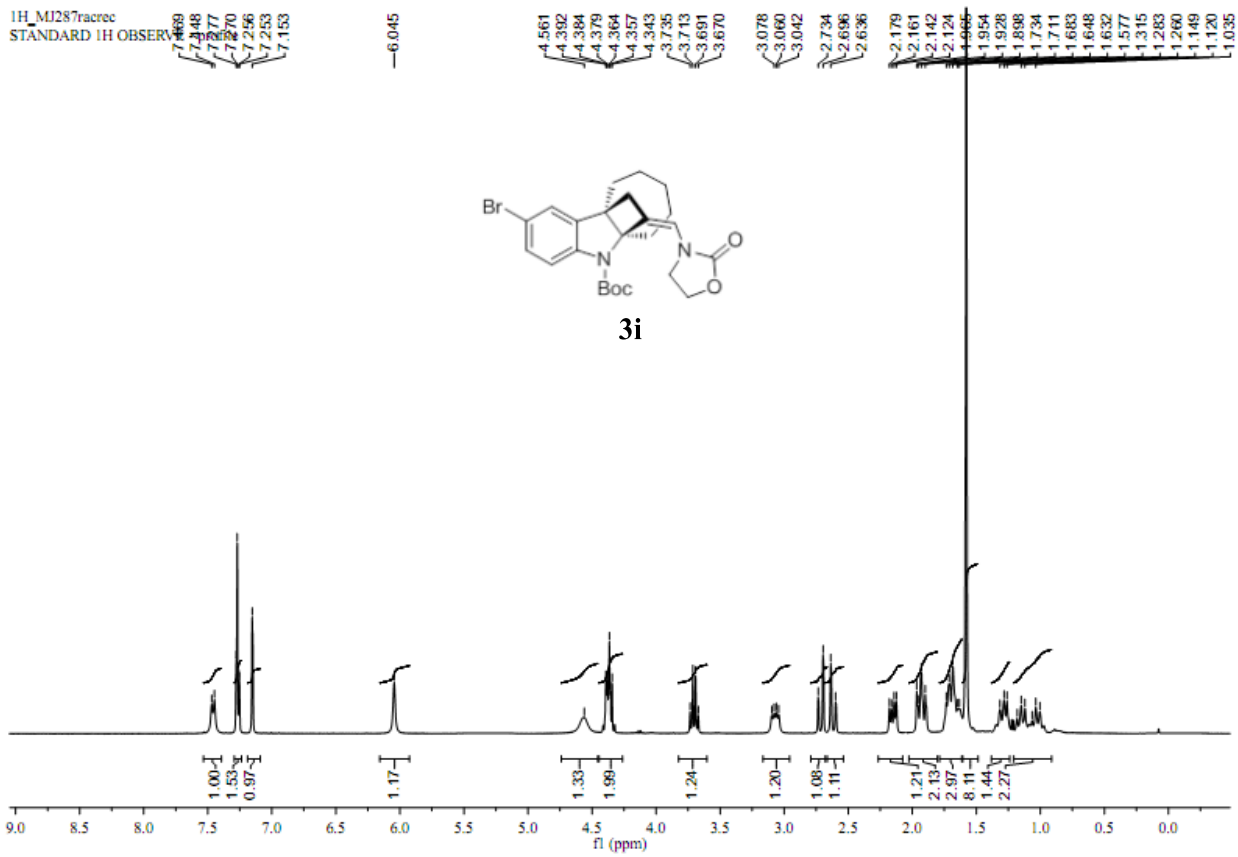
3g


1H_MJ263
STANDARD PHOSPHORUS PARAMETER
MeO
N
Boc
O
f1 (ppm)

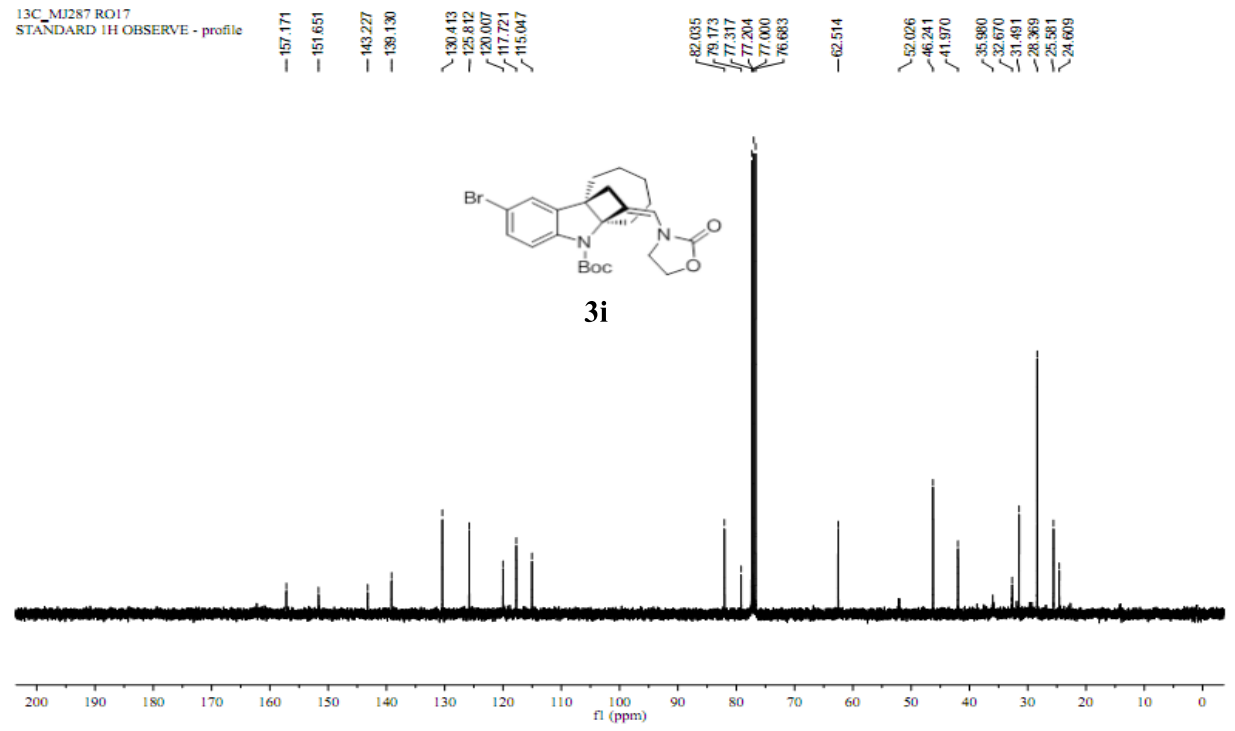
3h


13C_MJ292-263
C27?
MeO
N
Boc
O
f1 (ppm)

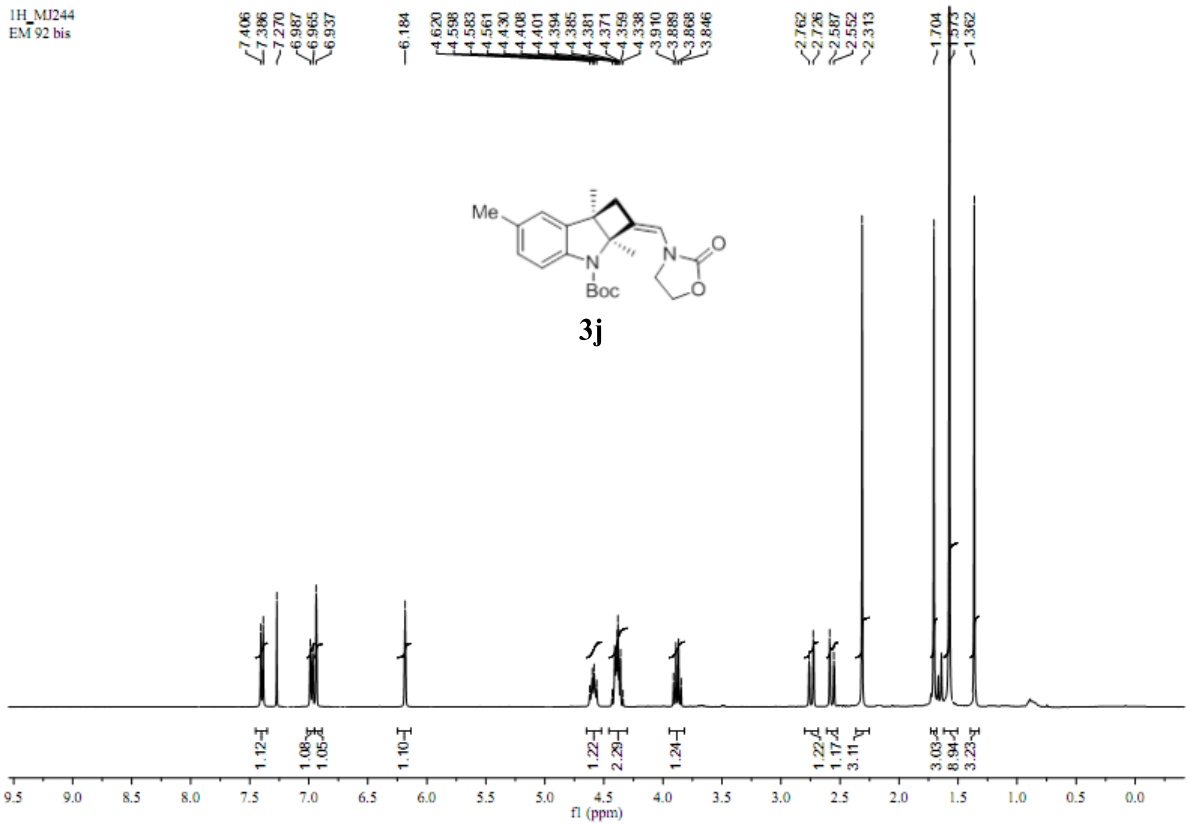
3h


1H_MJ287racrec
STANDARD 1H OBSERVE - profile
Br
N
Boc
O
N
O
f1 (ppm)

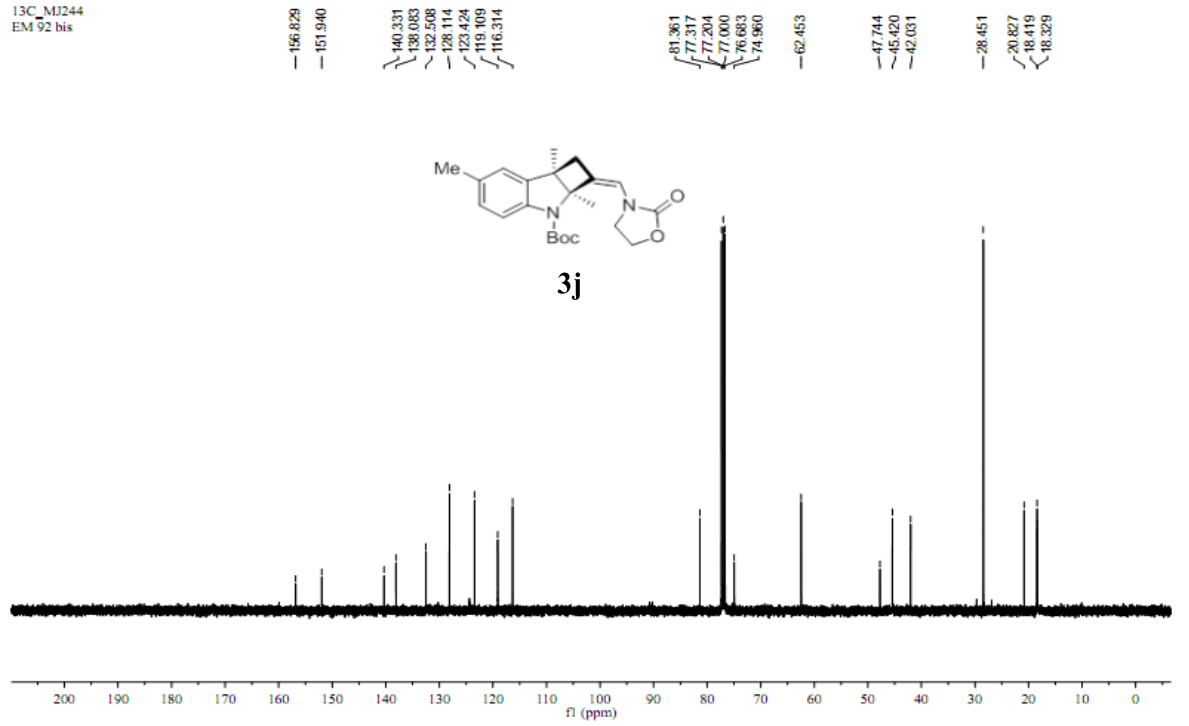
3i


13C_MJ287 RO17
STANDARD 1H OBSERVE - profile
Br
N
Boc
O
N
O
f1 (ppm)

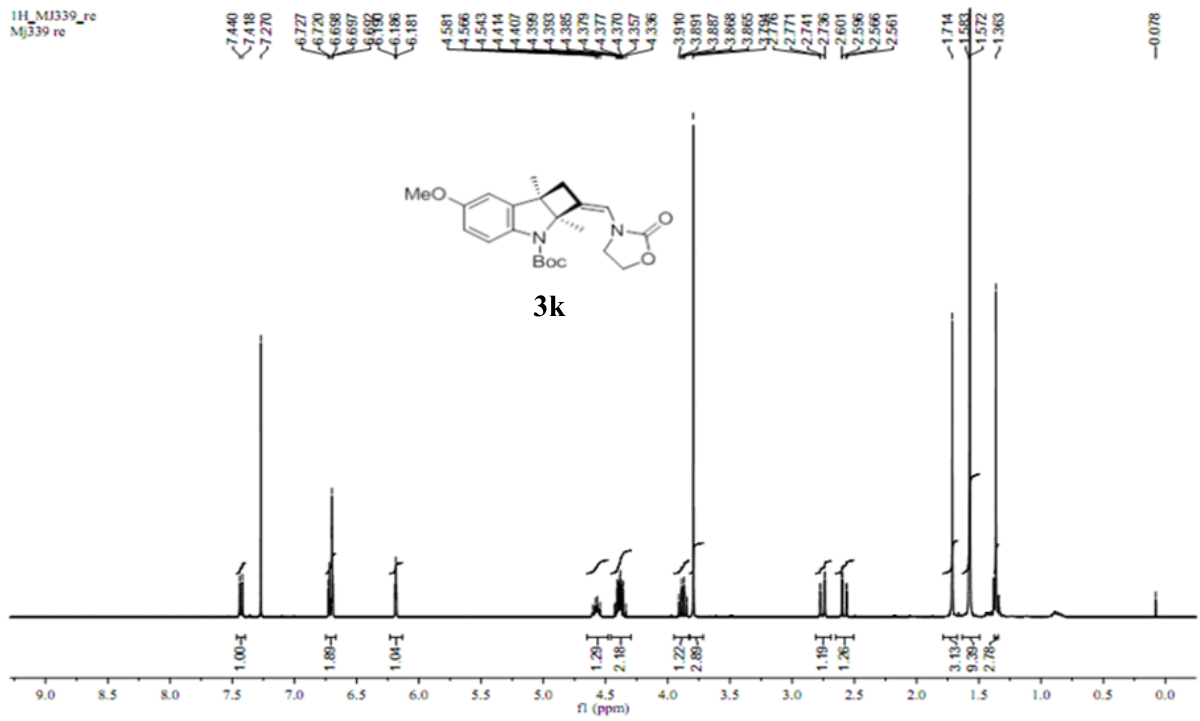
3i

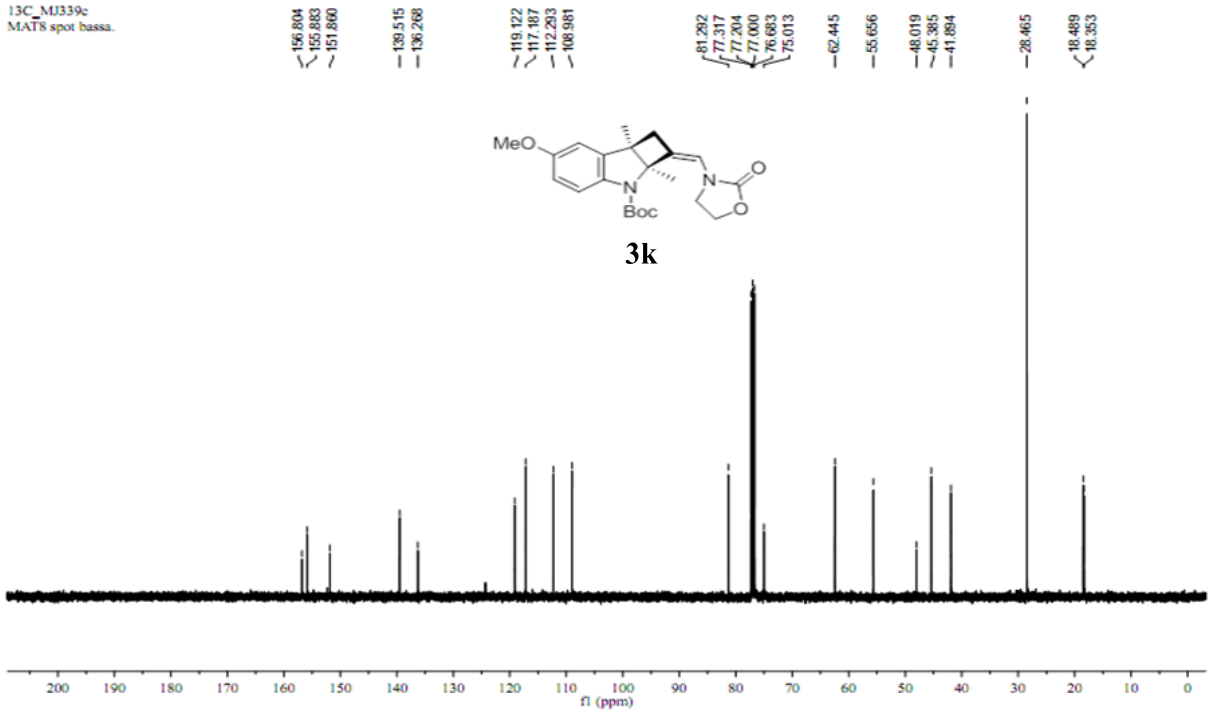

1H_MJ244
EM 92 bis
7.406
7.386
7.270
6.987
6.965
6.937
6.184
4.620
4.598
4.583
4.561
4.430
4.408
4.401
4.394
4.385
4.381
4.371
4.359
4.338
3.910
3.889
3.868
3.846
2.762
2.726
2.587
2.552
2.313
1.704
1.573
1.362
Me
N
O
Boc
1.12
1.08
1.05
1.10
1.22
2.29
1.24
1.22
1.17
3.11
3.03
8.94
3.23
f1 (ppm)

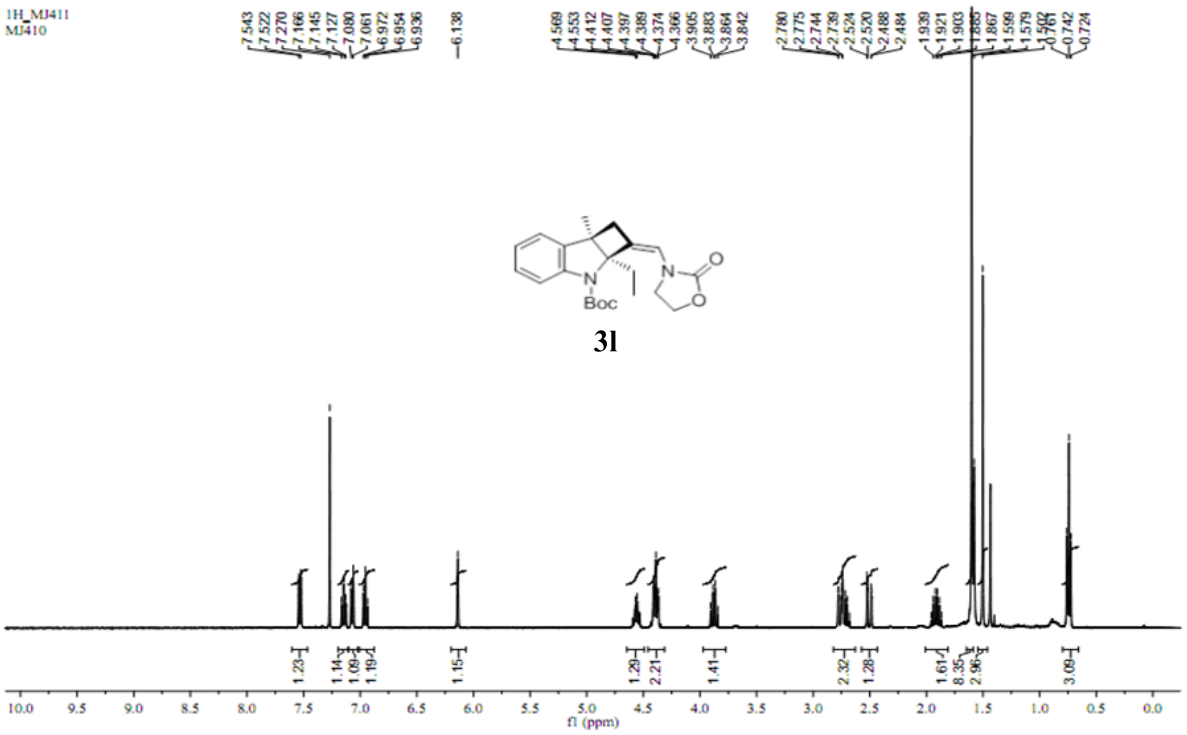
3j


13C_MJ244
EM 92 bis
156.829
151.940
140.331
138.083
132.508
128.114
123.424
119.109
116.314
81.361
77.317
77.204
77.000
76.683
74.960
62.453
47.744
45.420
42.031
28.451
20.827
18.419
18.329
Me
N
O
Boc
f1 (ppm)

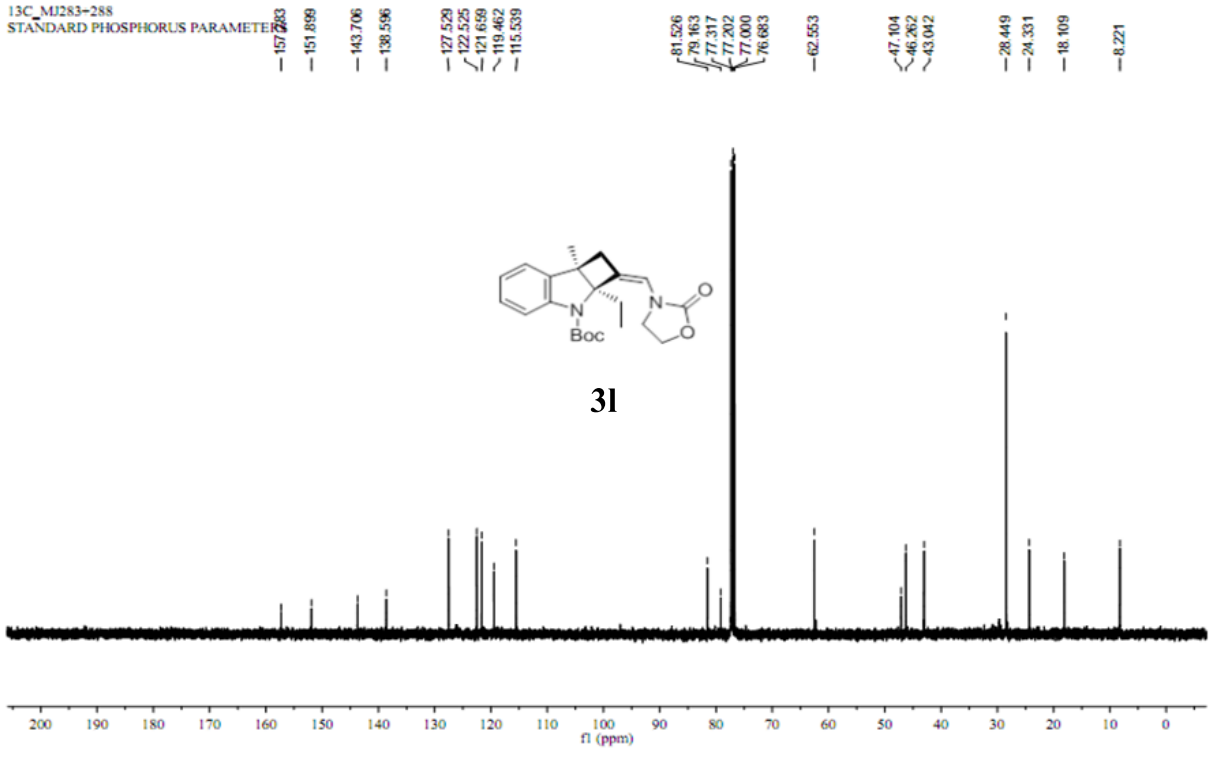
3j


1H_MJ339_re
MJ339 re
MeO
N
Boc
O
3k
f1 (ppm)

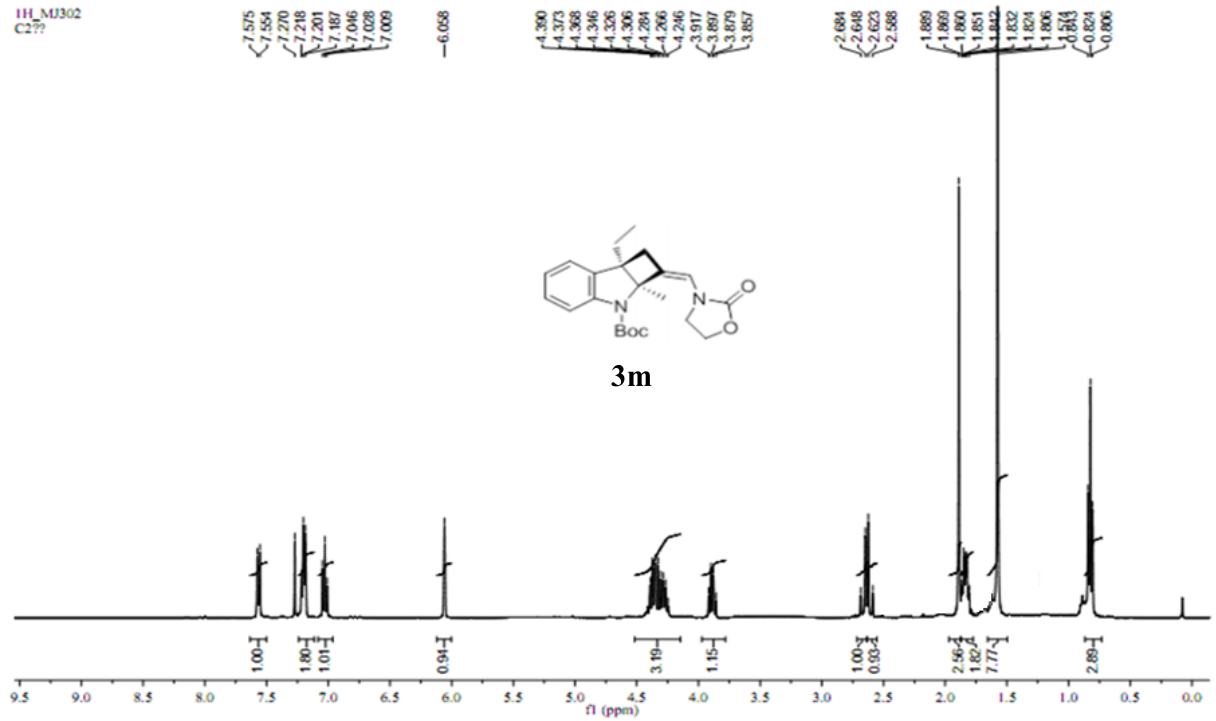

13C_MJ339c
MAT8 spot bassa.
MeO
N
Boc
O
3k
f1 (ppm)

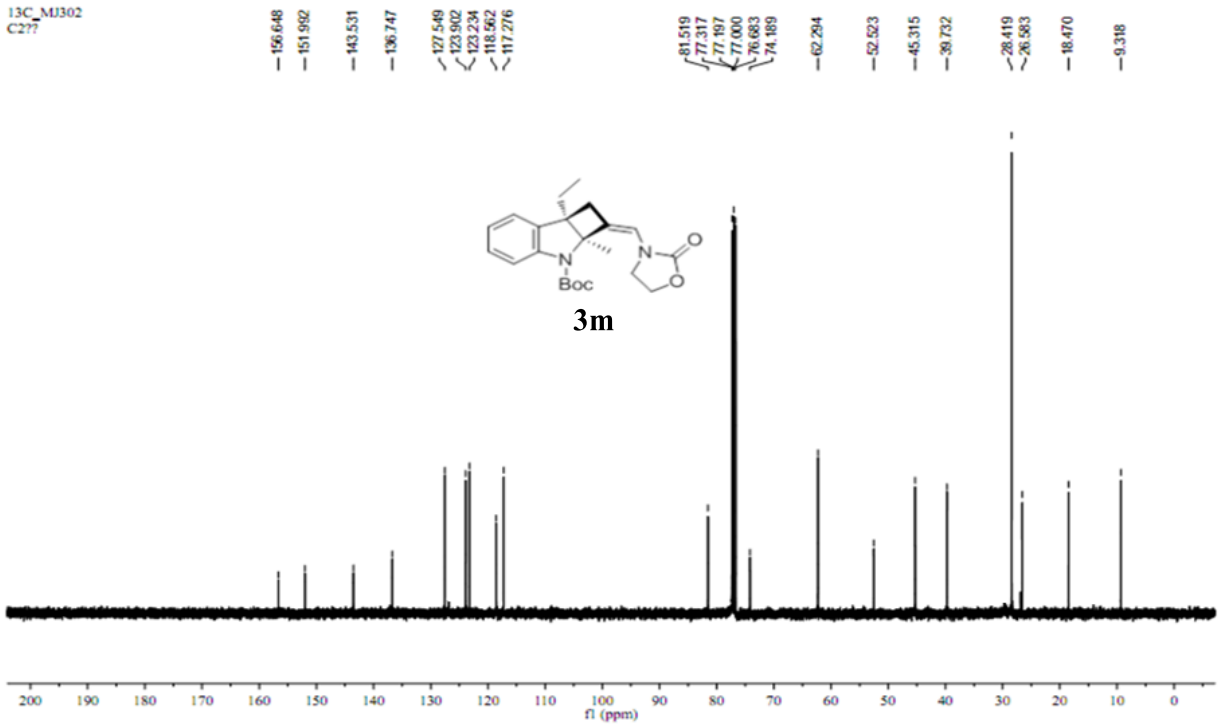

1H_MJ411
MJ410
7.543
7.522
7.270
7.166
7.145
7.127
7.080
7.061
6.972
6.954
6.936
6.138
4.569
4.553
4.412
4.407
4.397
4.389
4.374
4.366
3.905
3.883
3.864
3.842
2.780
2.775
2.744
2.739
2.524
2.520
2.488
2.484
1.939
1.921
1.903
1.885
1.867
1.599
1.579
0.765
0.742
0.724
Boc
1.23
1.14
1.09
1.19
1.15
1.29
2.21
1.41
2.32
1.28
1.61
8.35
2.96
3.09
f1 (ppm)

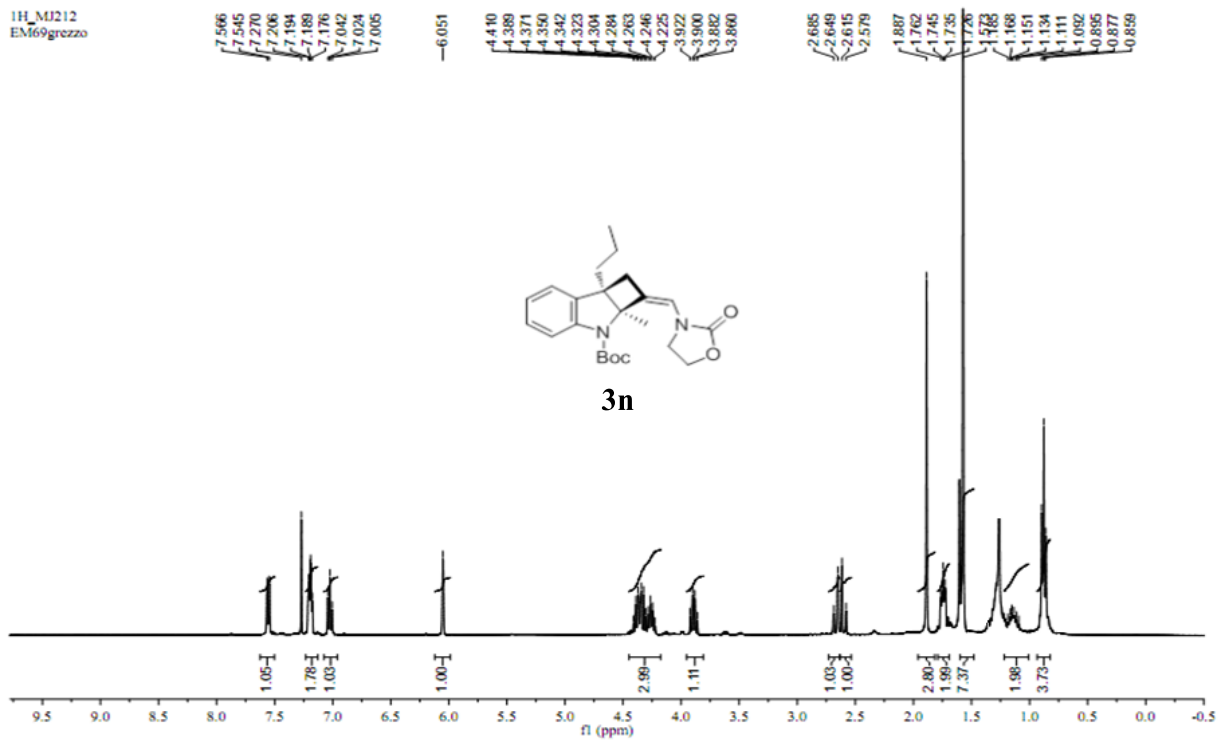
3l

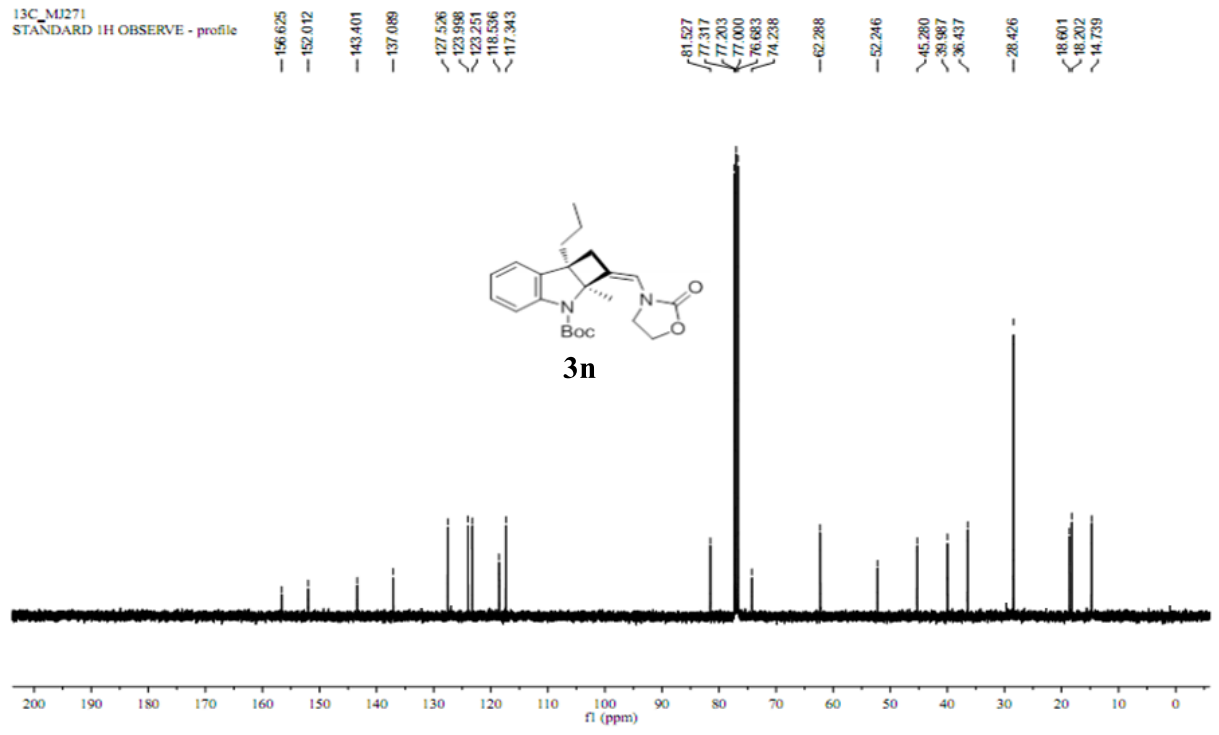

13C_MJ283~288
STANDARD PHOSPHORUS PARAMETER
157.263
151.899
143.706
138.596
127.529
122.525
121.659
119.462
115.539
81.526
79.163
77.317
77.202
77.000
76.683
62.553
47.104
46.262
43.042
28.449
24.331
18.109
8.221
Boc
f1 (ppm)

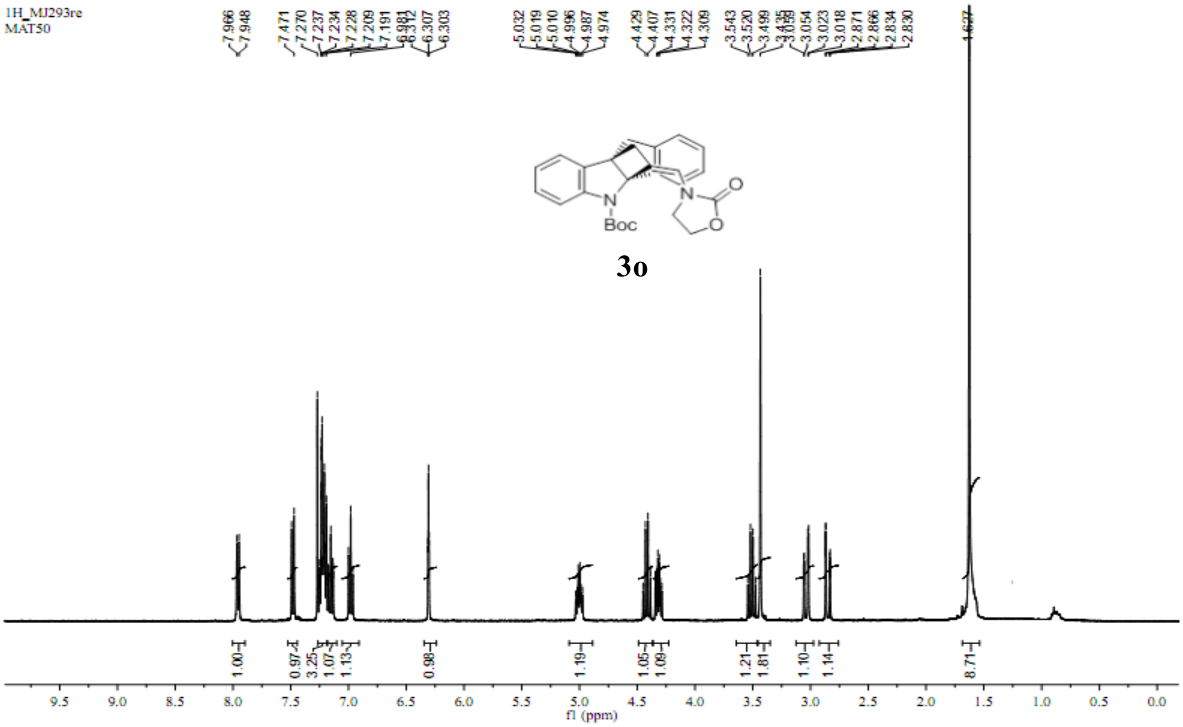
3l

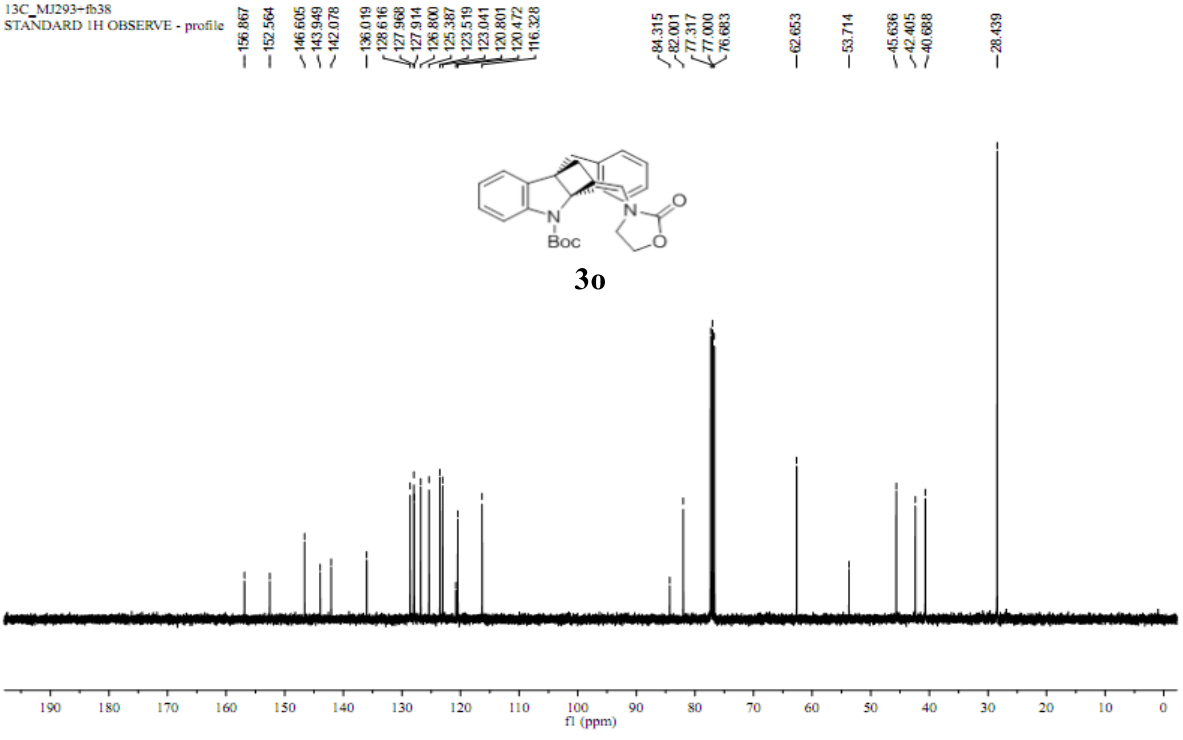

1H_MJ302
C27?
Boc
3m
f1 (ppm)

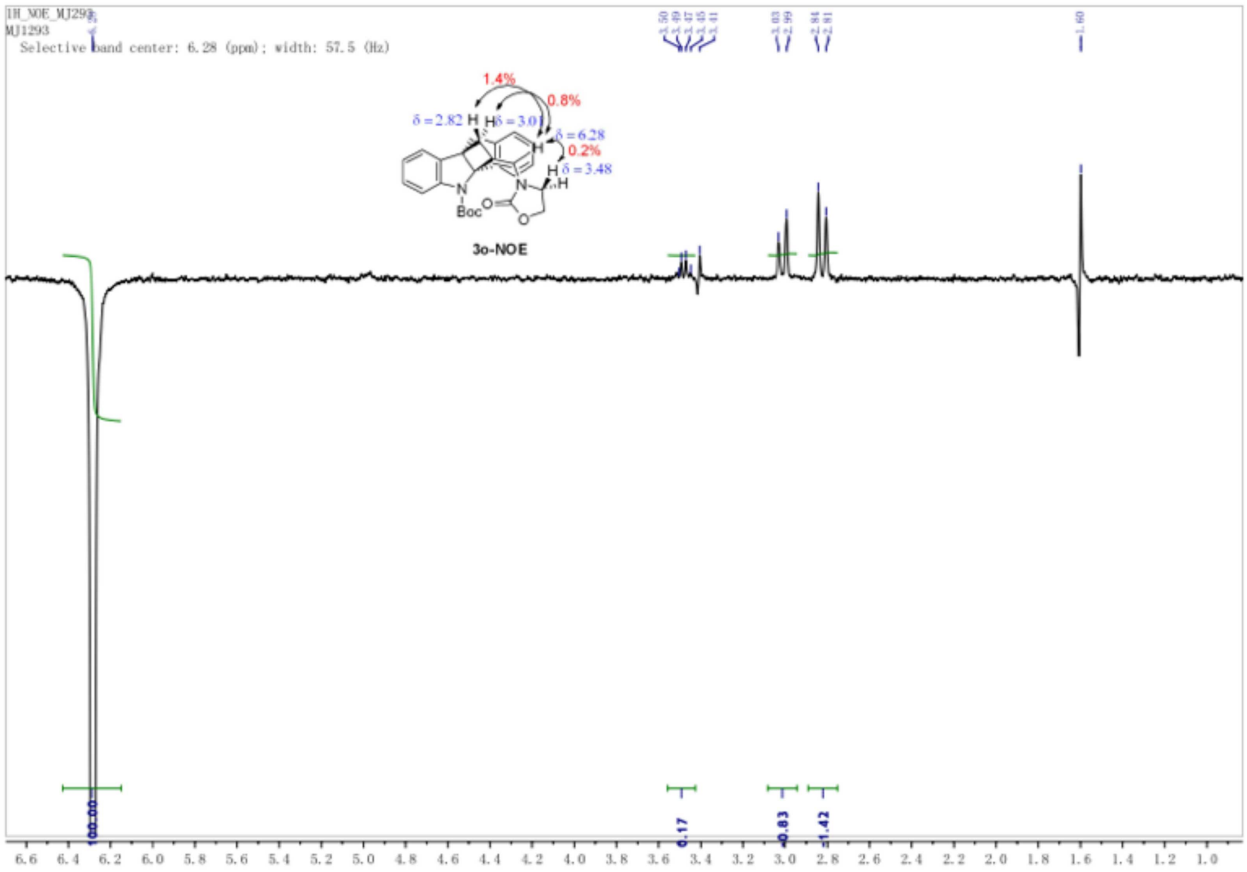

13C_MJ302
C27?
Boc
3m
f1 (ppm)

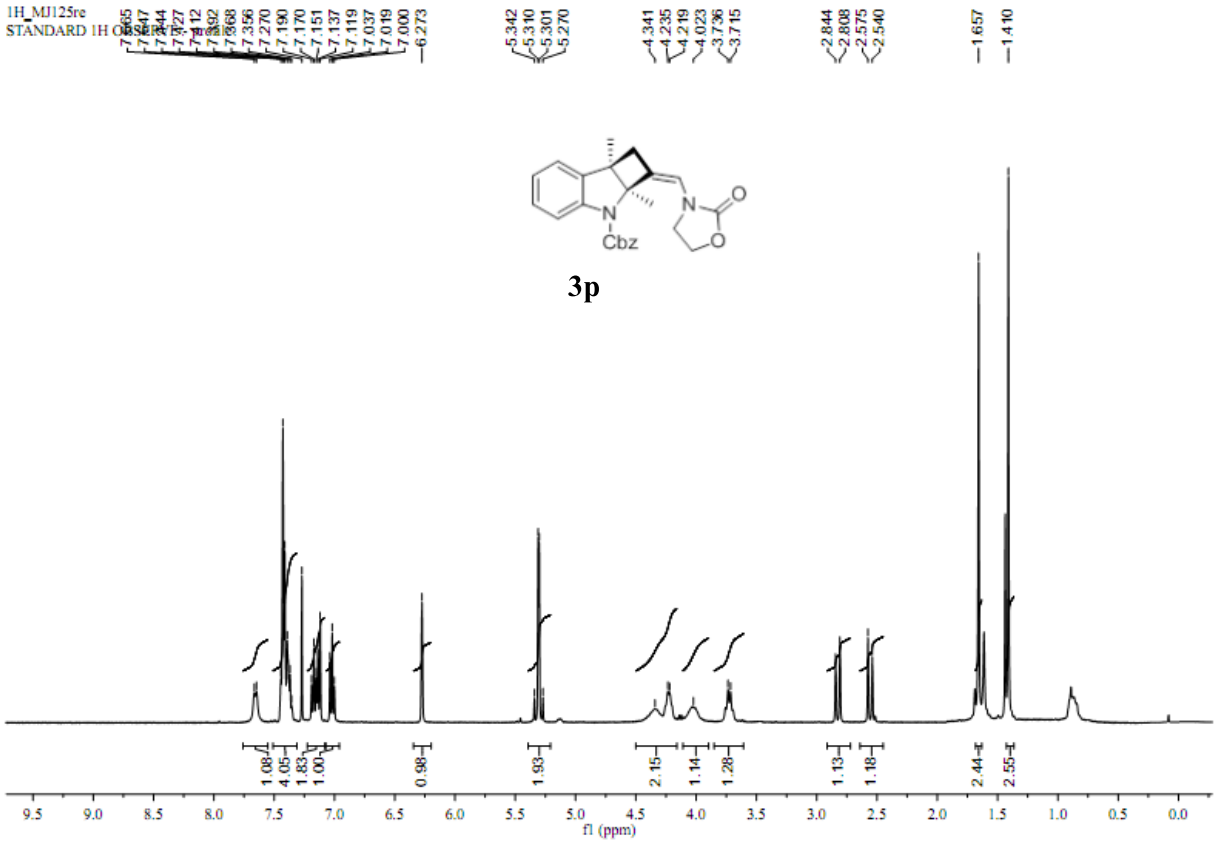

1H_MJ212
EM69grezzo
Boc
3n
fl (ppm)


13C_MJ271
STANDARD 1H OBSERVE - profile
Boc
3n
fl (ppm)

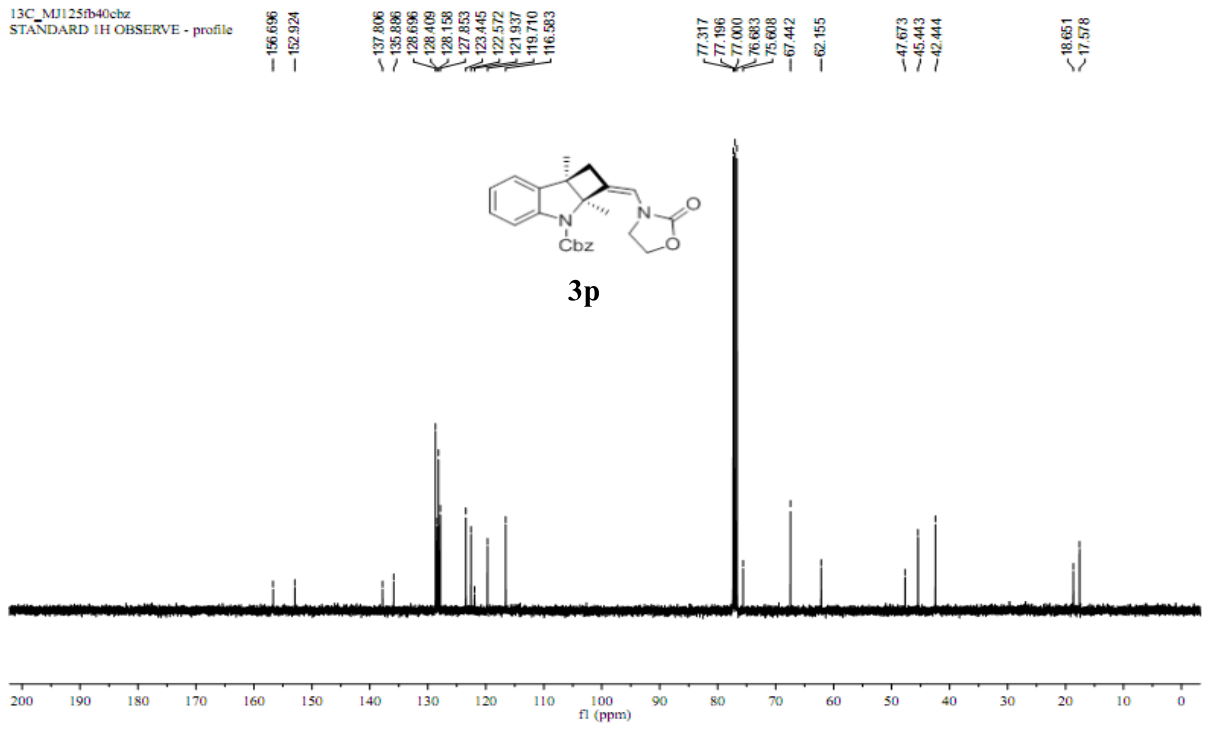

1H_MJ293re
MAT50
Boc
3o
f1 (ppm)


13C_MJ293-fh38
STANDARD 1H OBSERVE - profile
Boc
3o
f1 (ppm)

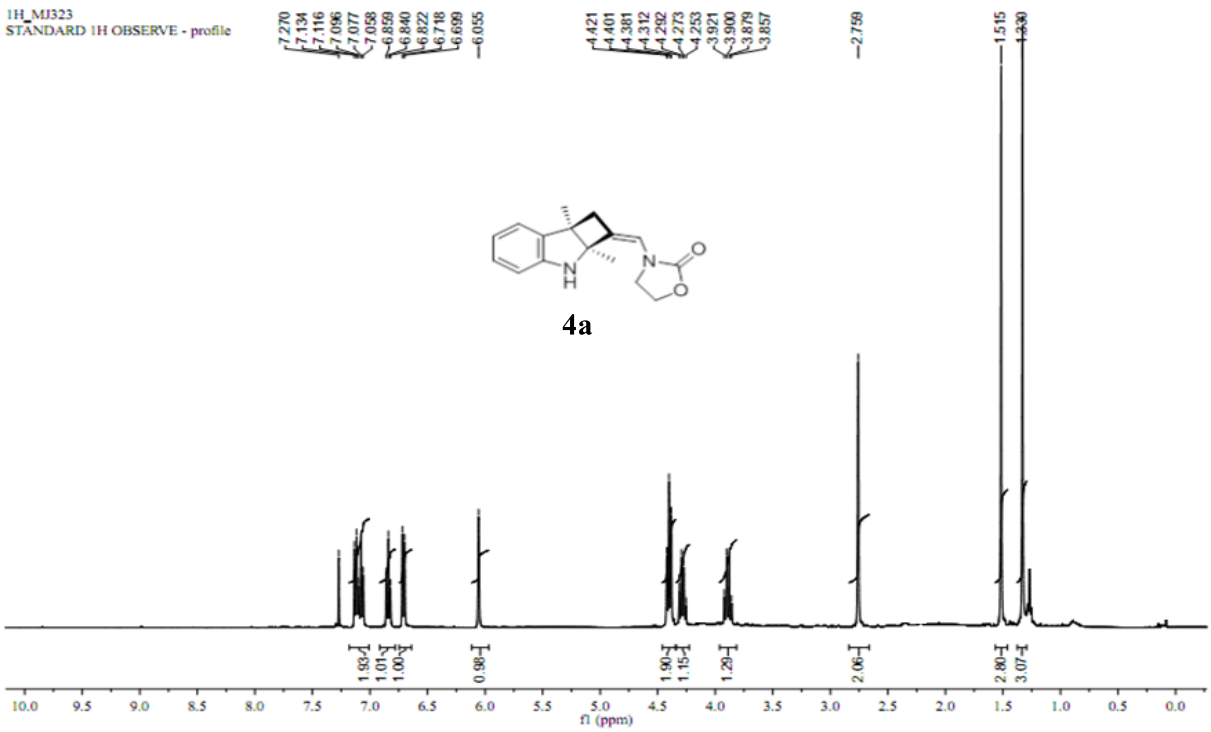

1H_NOE_MJ1293
MJ1293
Selective band center: 6.28 (ppm); width: 57.5 (Hz)
1.4%
0.8%
δ = 2.82 H
H δ = 3.01
δ = 6.28
0.2%
H δ = 3.48
Boc
3o-NOE
3.50
3.49
3.47
3.45
3.41
3.03
2.99
2.84
2.81
1.60
1.00
0.17
0.83
1.42
6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0


1H_MJ125re
STANDARD 1H OBSERVE - proton
7.365
7.347
7.344
7.327
7.312
7.292
7.268
7.256
7.270
7.190
7.170
7.151
7.137
7.119
7.037
7.019
7.000
6.273
5.342
5.310
5.301
5.270
4.341
4.235
4.219
4.023
3.736
3.715
2.844
2.808
2.575
2.540
1.657
1.410
N
O
N
O
Cbz
1.08
4.05
1.83
1.00
0.98
1.93
2.15
1.14
1.28
1.13
1.18
2.44
2.55
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

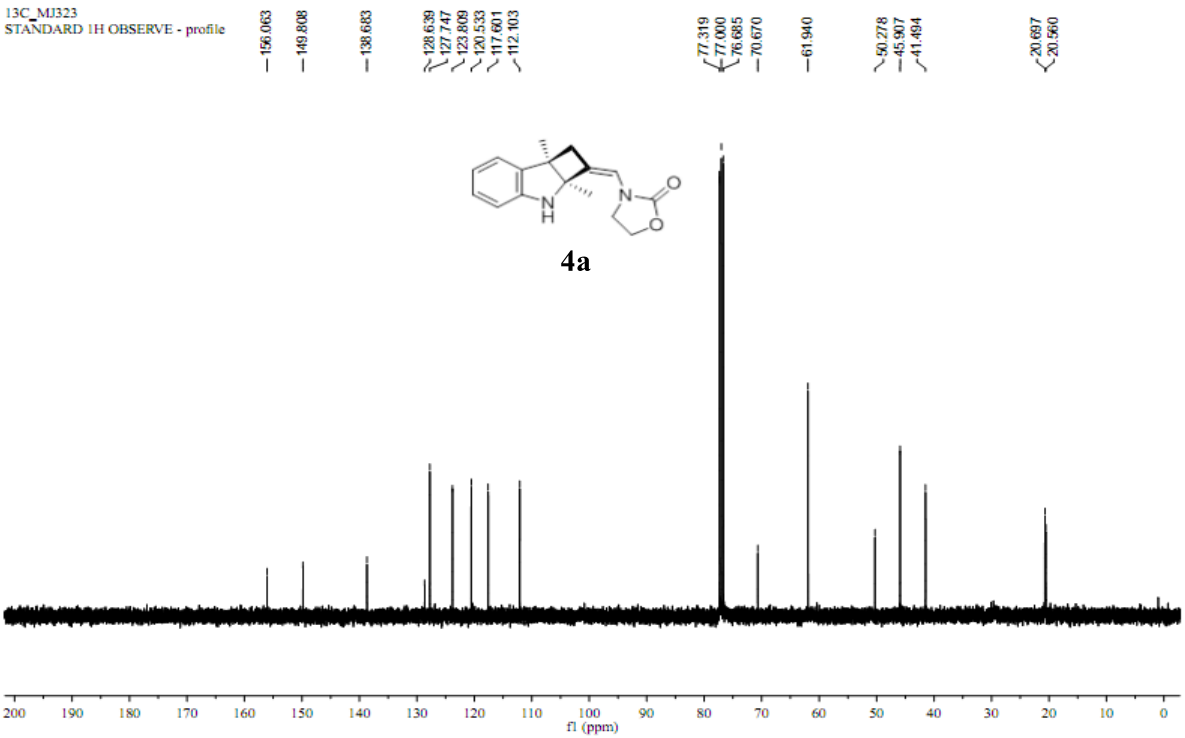
3p


13C_MJ125fb40cbz
STANDARD 1H OBSERVE - profile
156.696
152.924
137.806
135.886
128.696
128.409
128.158
127.853
123.445
122.572
121.937
119.710
116.583
77.317
77.196
77.000
76.683
75.608
67.442
62.155
47.673
45.443
42.444
18.651
17.578
N
O
N
O
Cbz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

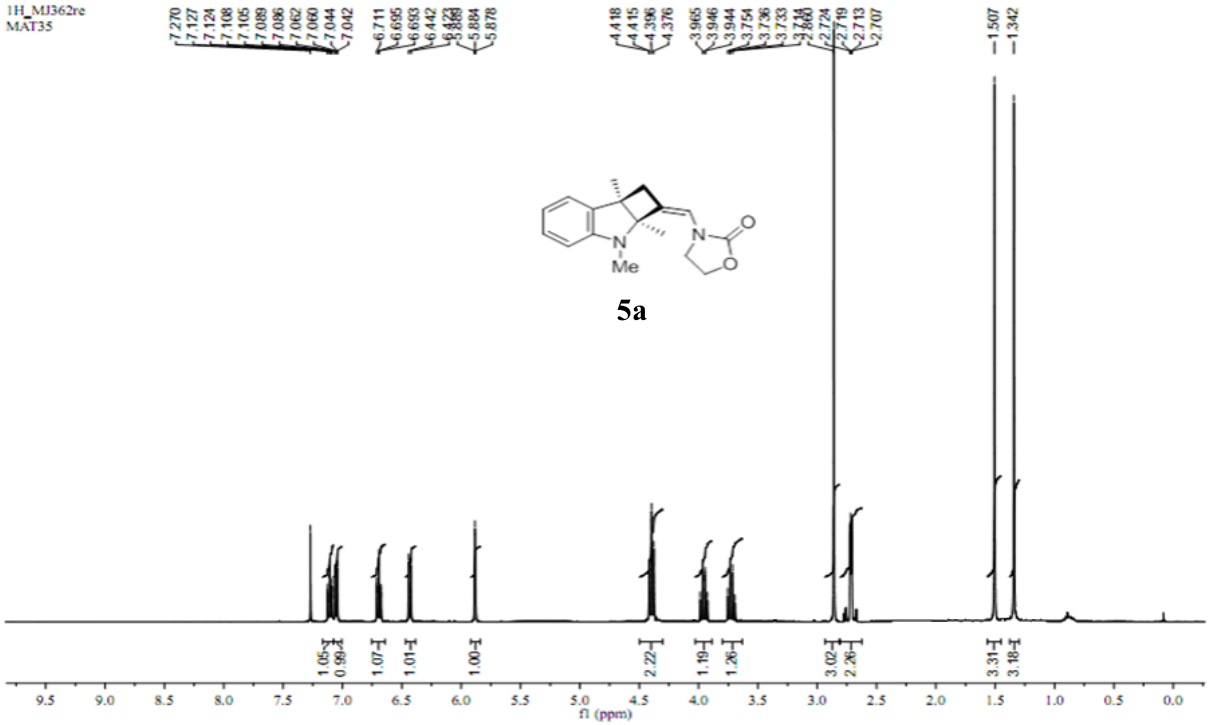
3p


1H_MJ323
STANDARD 1H OBSERVE - profile
7.270
7.134
7.116
7.096
7.077
7.058
6.859
6.840
6.822
6.718
6.699
6.055
4.421
4.401
4.381
4.312
4.292
4.273
4.253
3.921
3.900
3.879
3.857
2.759
1.515
1.330
1.93
1.01
1.00
0.98
1.90
1.15
1.29
2.06
2.80
3.07
f1 (ppm)

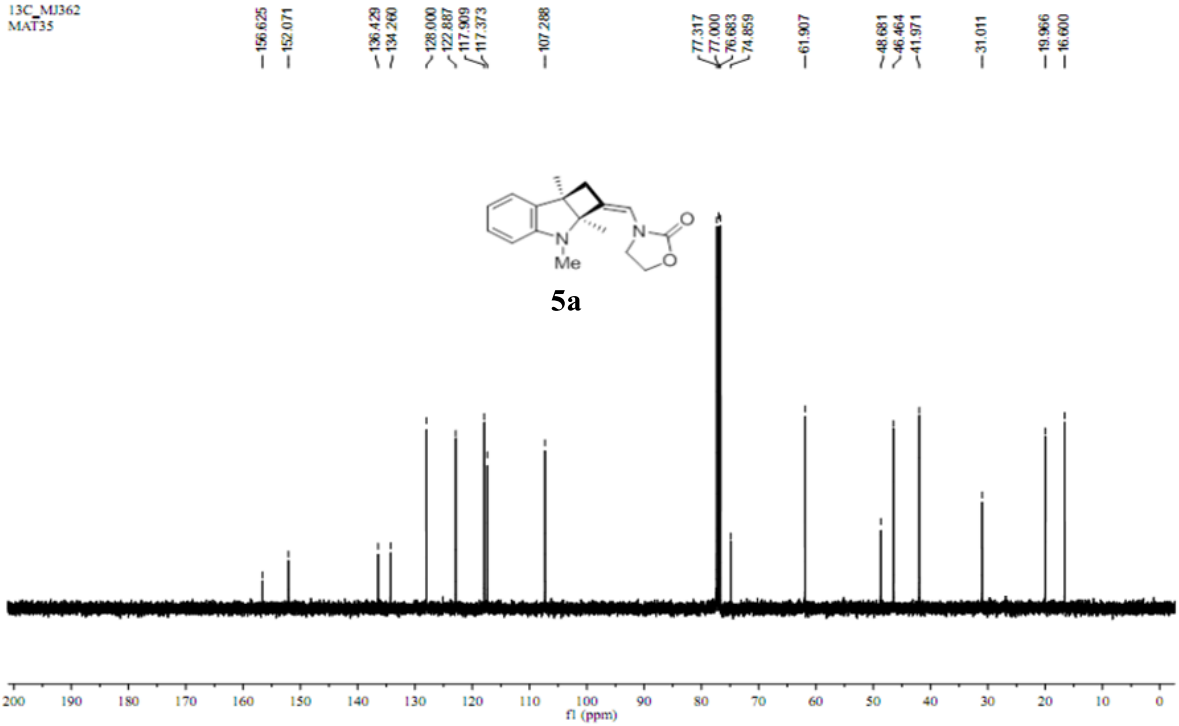
4a


13C_MJ323
STANDARD 1H OBSERVE - profile
156.063
149.808
138.683
128.639
127.747
123.809
120.533
117.601
112.103
77.319
77.000
76.685
70.670
61.940
50.278
45.907
41.494
20.697
20.560
f1 (ppm)

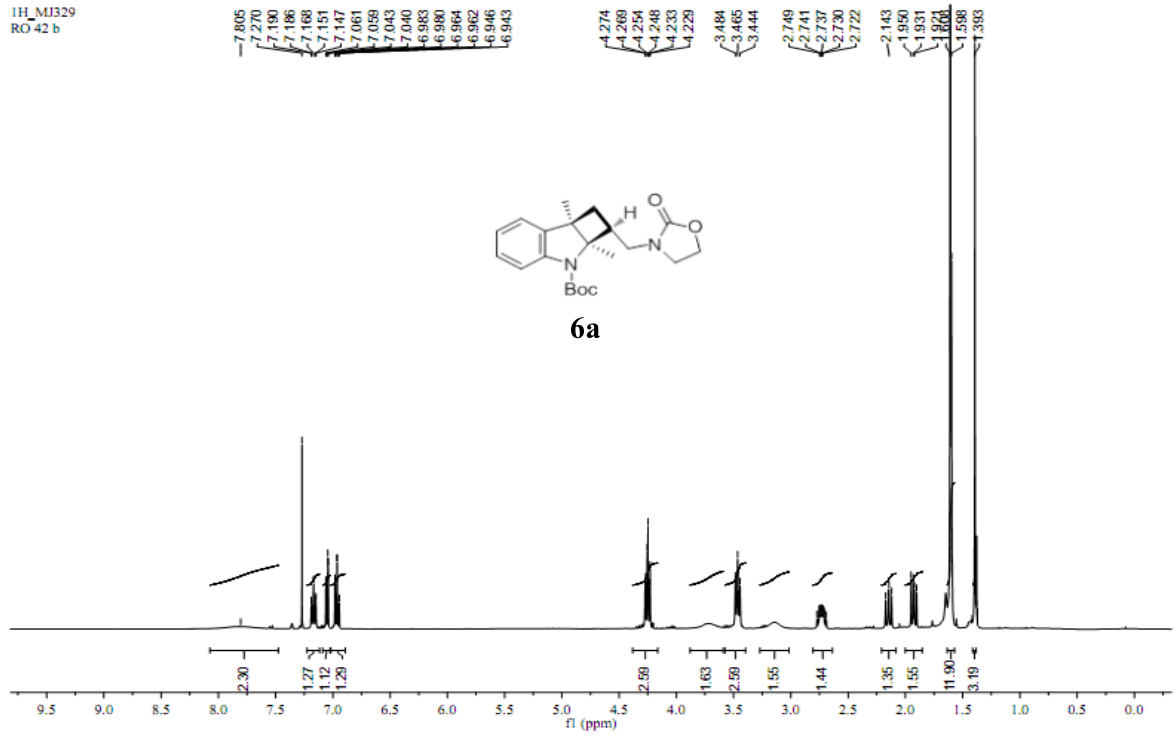
4a


1H_MJ362re
MAT35
7.270
7.127
7.124
7.108
7.105
7.089
7.086
7.062
7.060
7.044
7.042
6.711
6.695
6.693
6.442
6.423
5.888
5.884
5.878
4.418
4.415
4.396
4.376
3.965
3.946
3.944
3.754
3.736
3.733
3.724
2.860
2.724
2.719
2.713
2.707
1.507
1.342
Me
1.05
0.99
1.07
1.01
1.00
2.22
1.19
1.26
3.02
2.26
3.31
3.18
f1 (ppm)

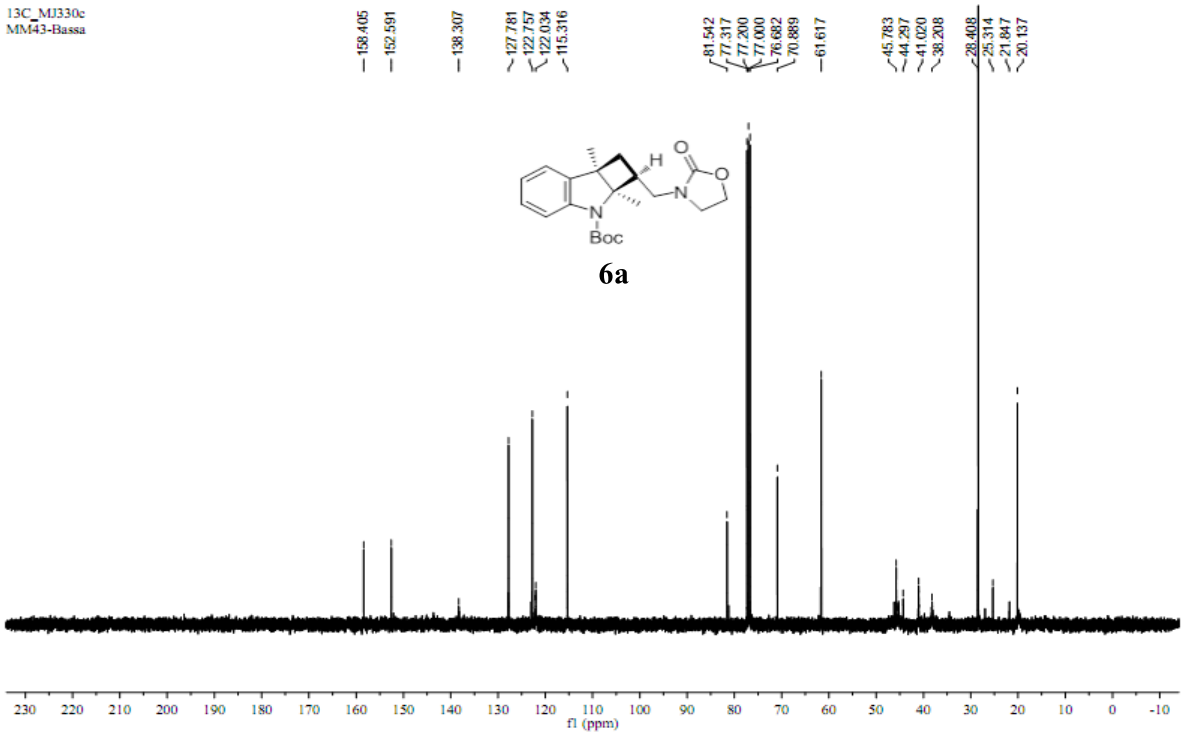
5a


13C_MJ362
MAT35
156.625
152.071
136.429
134.260
128.000
122.887
117.909
117.373
107.288
77.317
77.000
76.683
74.859
61.907
48.681
46.464
41.971
31.011
19.966
16.600
Me
f1 (ppm)

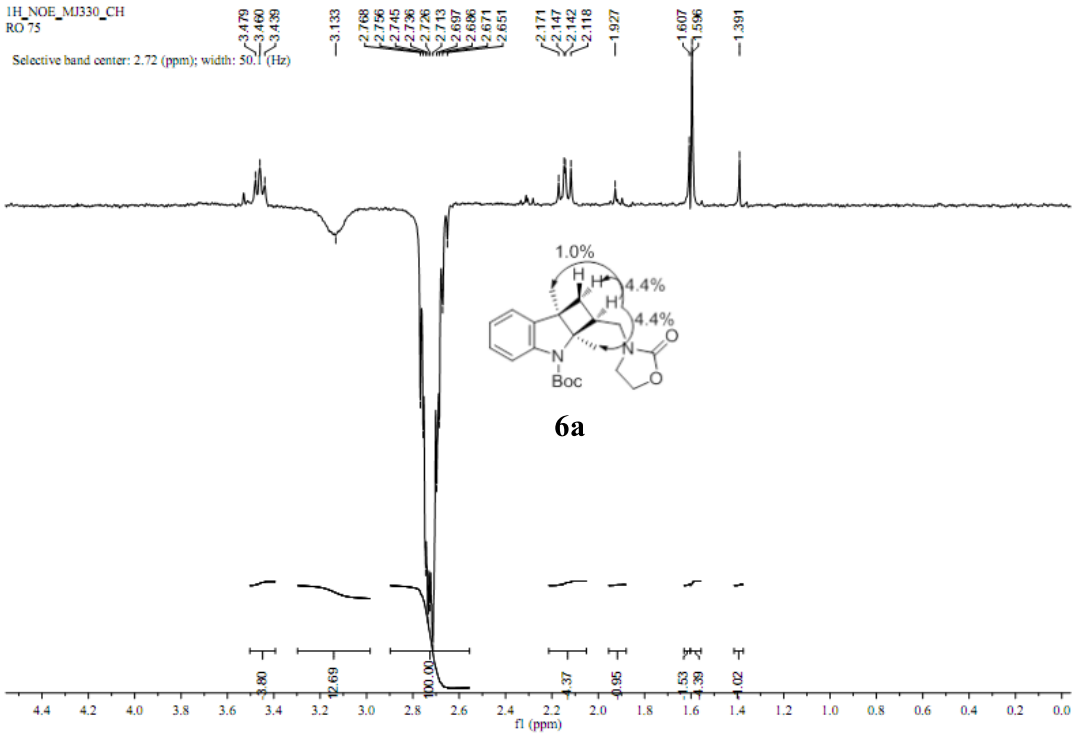
5a


1H_MJ329
RO 42 b
7.805
7.270
7.190
7.186
7.168
7.151
7.147
7.061
7.059
7.043
7.040
6.983
6.980
6.964
6.962
6.946
6.943
4.274
4.269
4.254
4.248
4.233
4.229
3.484
3.465
3.444
2.749
2.741
2.737
2.730
2.722
2.143
1.950
1.931
1.598
1.393
H
O
O
N
N
Boc
2.30
1.27
1.12
1.29
2.59
1.63
2.59
1.55
1.44
1.35
1.55
11.90
3.19
f1 (ppm)

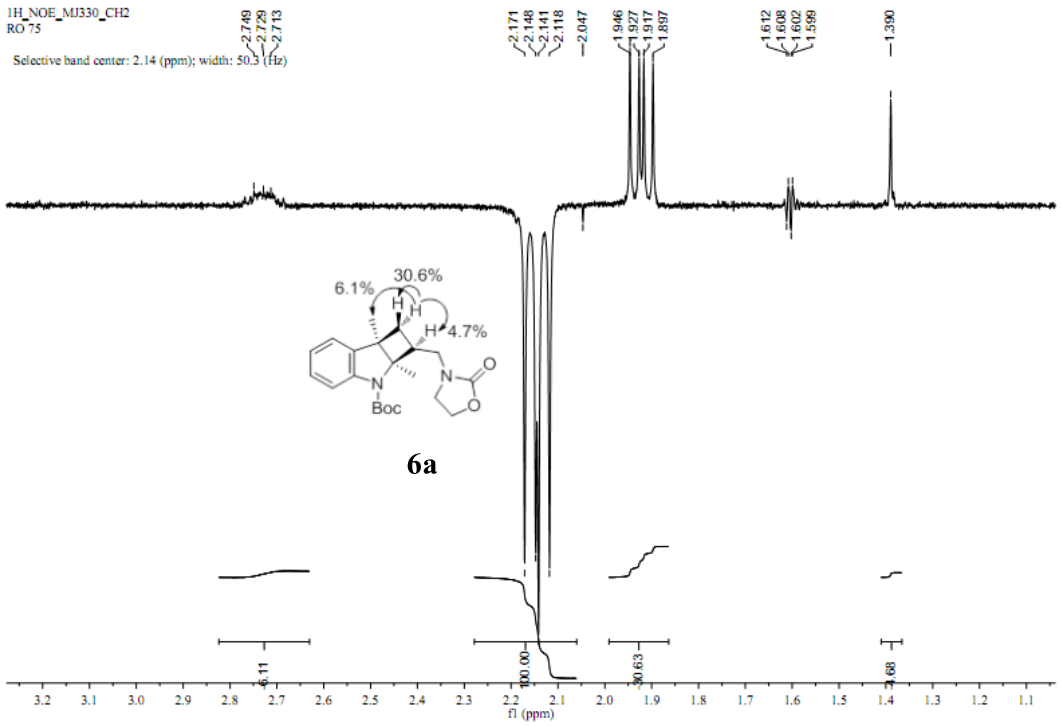
6a


13C_MJ330c
MM43-Bassa
158.405
152.591
138.307
127.781
122.757
122.034
115.316
81.542
77.317
77.200
77.000
76.682
70.889
61.617
45.783
44.297
41.020
38.208
28.408
25.314
21.847
20.137
H
O
O
N
N
Boc
f1 (ppm)

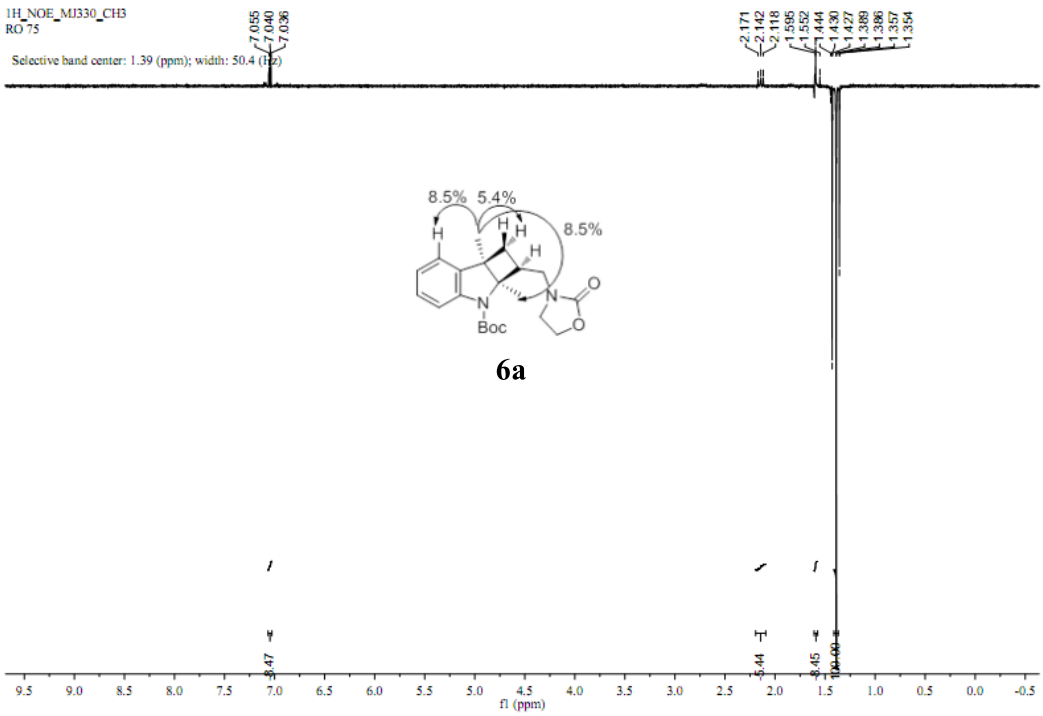
6a


1H_NOE_MJ330_CH
RO 75
Selective band center: 2.72 (ppm); width: 50.1 (Hz)
1.0%
4.4%
4.4%
Boc
fl (ppm)

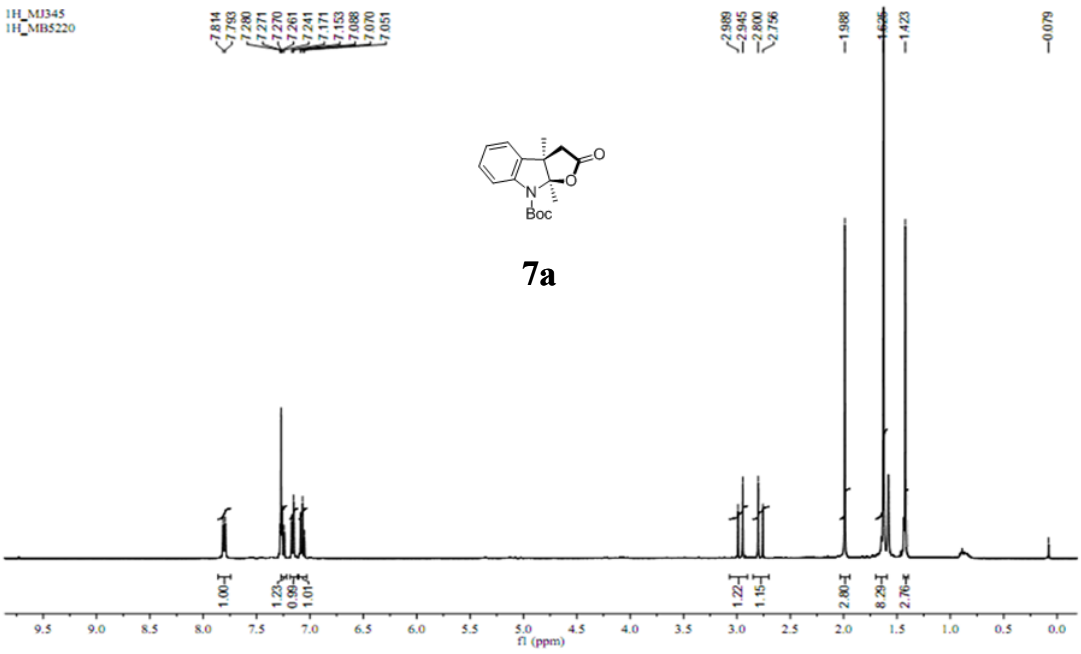
6a


1H_NOE_MJ330_CH2
RO 75
Selective band center: 2.14 (ppm); width: 50.3 (Hz)
6.1%
30.6%
4.7%
Boc
fl (ppm)

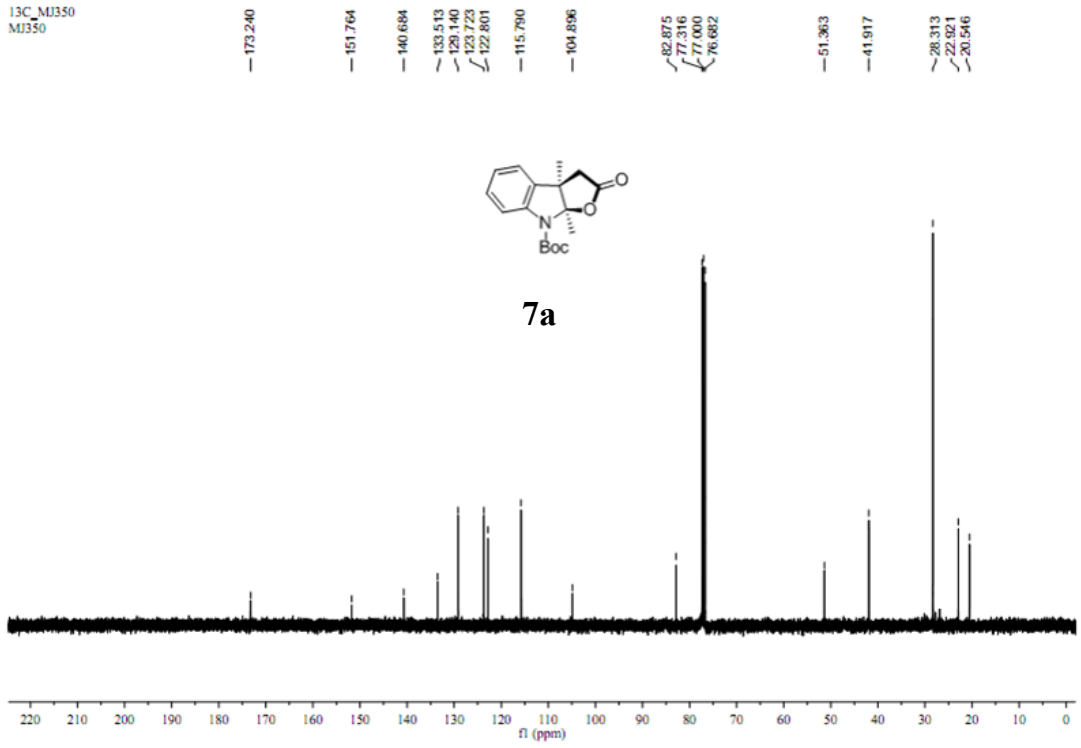
6a


1H_NOE_MJ330_CH3
RO 75
Selective band center: 1.39 (ppm); width: 50.4 (Hz)
7.055
7.040
7.036
2.171
2.142
2.118
1.595
1.552
1.444
1.430
1.427
1.389
1.386
1.357
1.354
8.5%
5.4%
8.5%
H
H
H
H
N
Boc
N
O
O
3.47
5.44
8.45
10.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

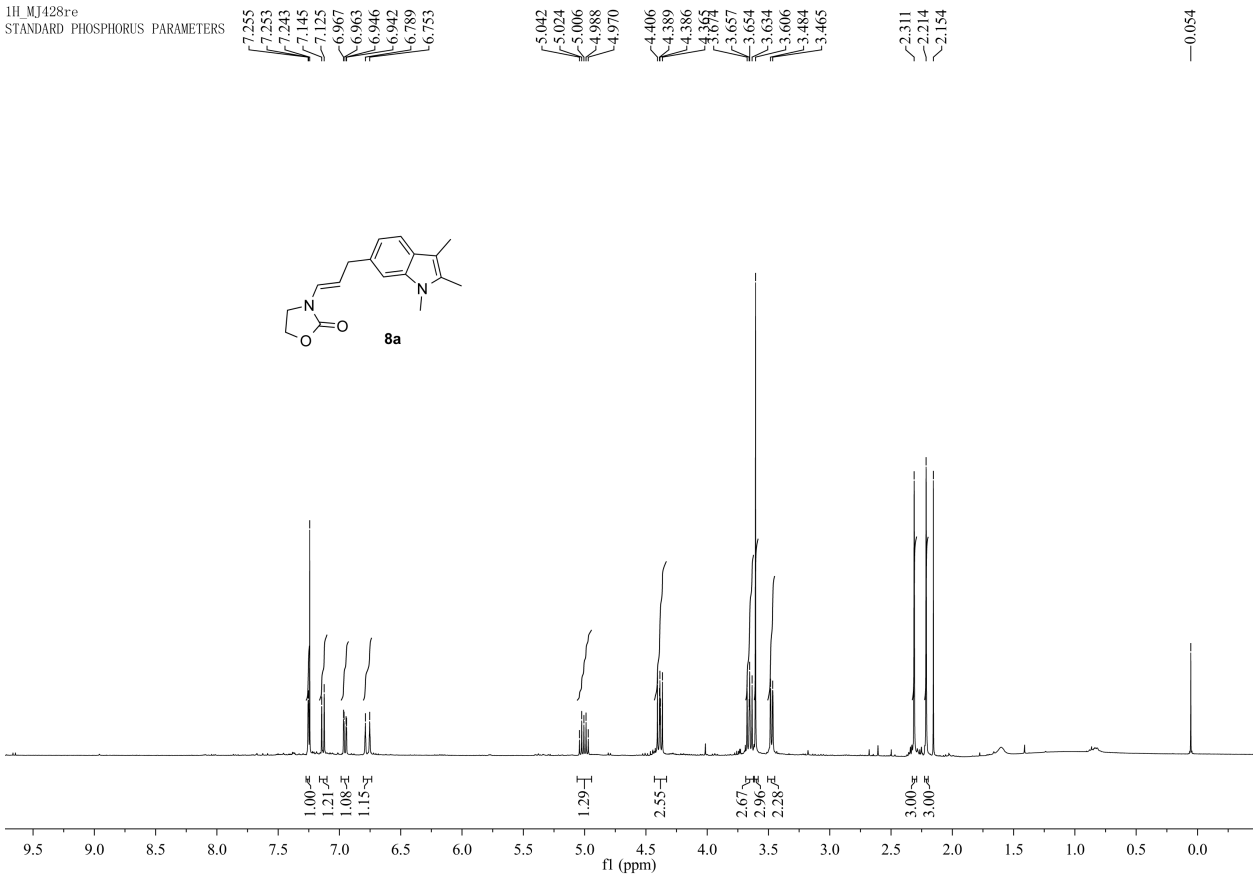
6a

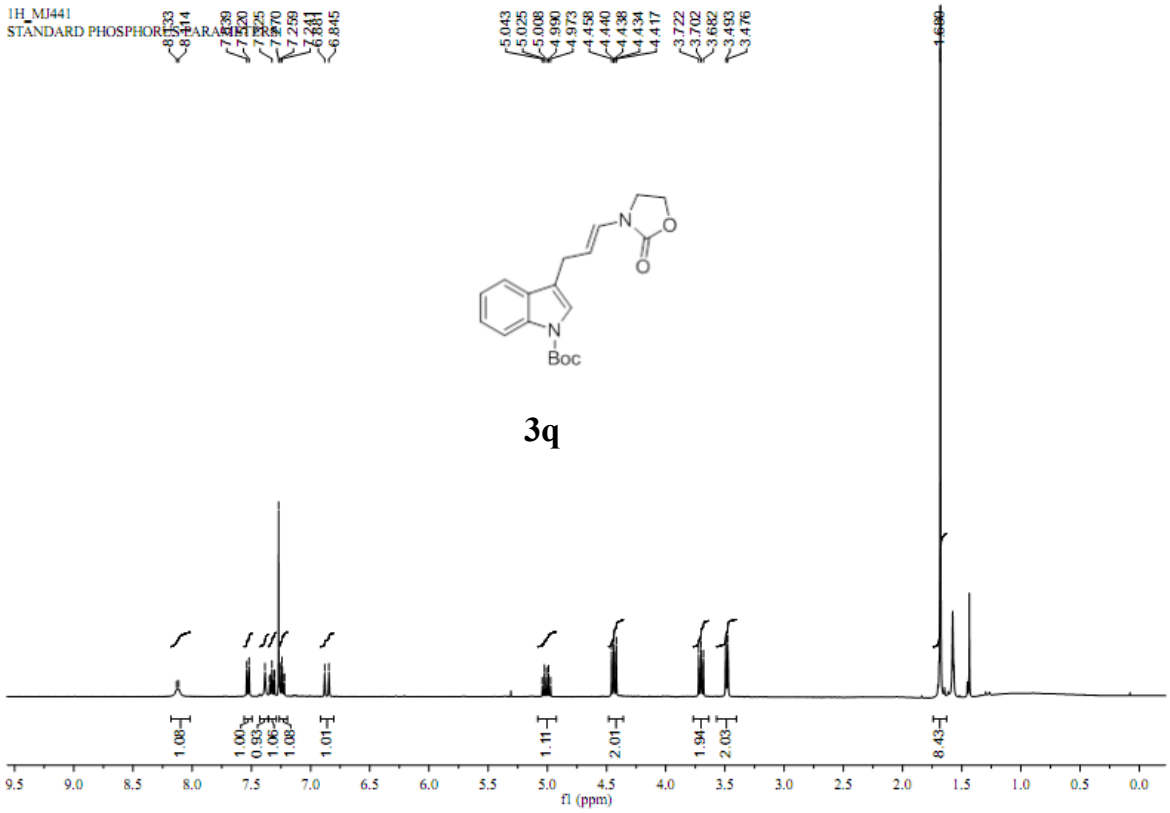

1H_MJ345
1H_MB5220
7.814
7.793
7.280
7.271
7.270
7.261
7.241
7.171
7.153
7.088
7.070
7.051
2.989
2.945
2.800
2.796
1.988
1.626
1.423
0.079
Boc
1.00
1.23
0.99
1.01
1.22
1.15
2.80
8.29
2.76
f1 (ppm)

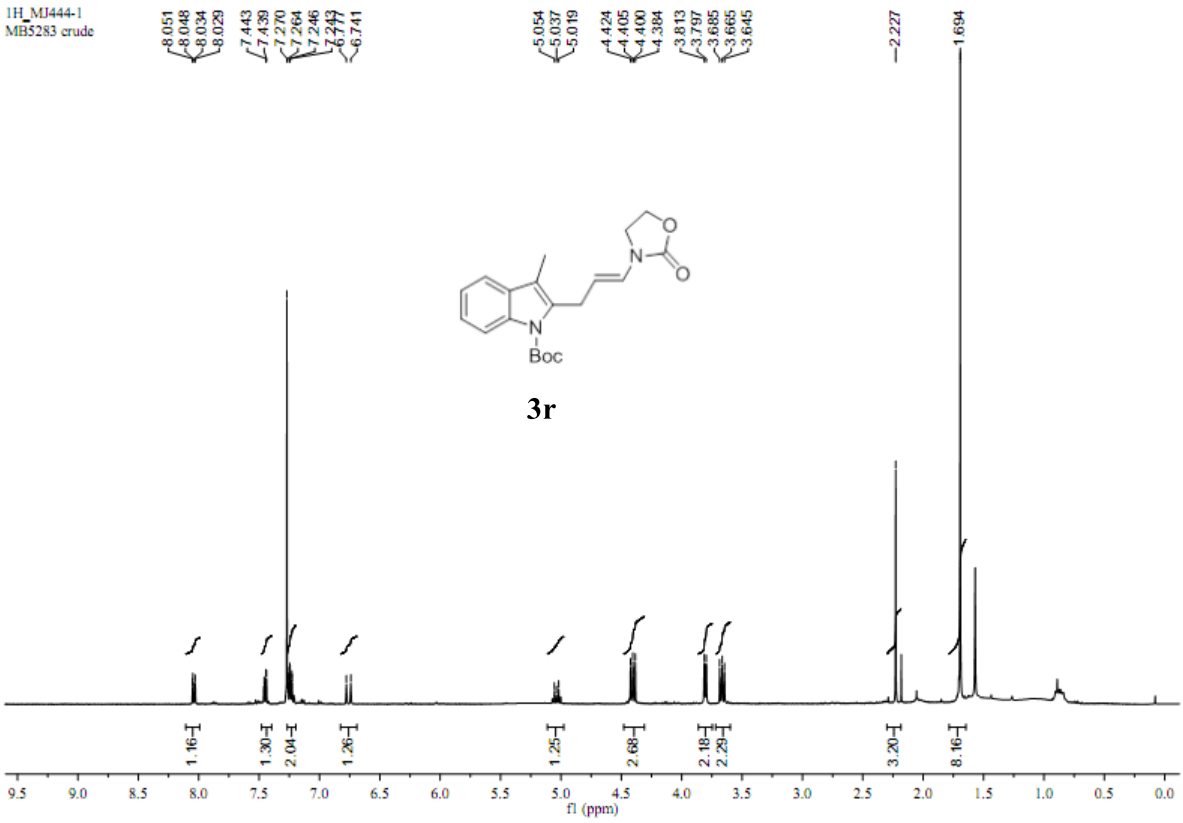
7a


13C_MJ350
MJ350
173.240
151.764
140.684
133.513
129.140
123.723
122.801
115.790
104.896
82.875
77.316
77.000
76.682
51.363
41.917
28.313
22.921
20.546
Boc
f1 (ppm)

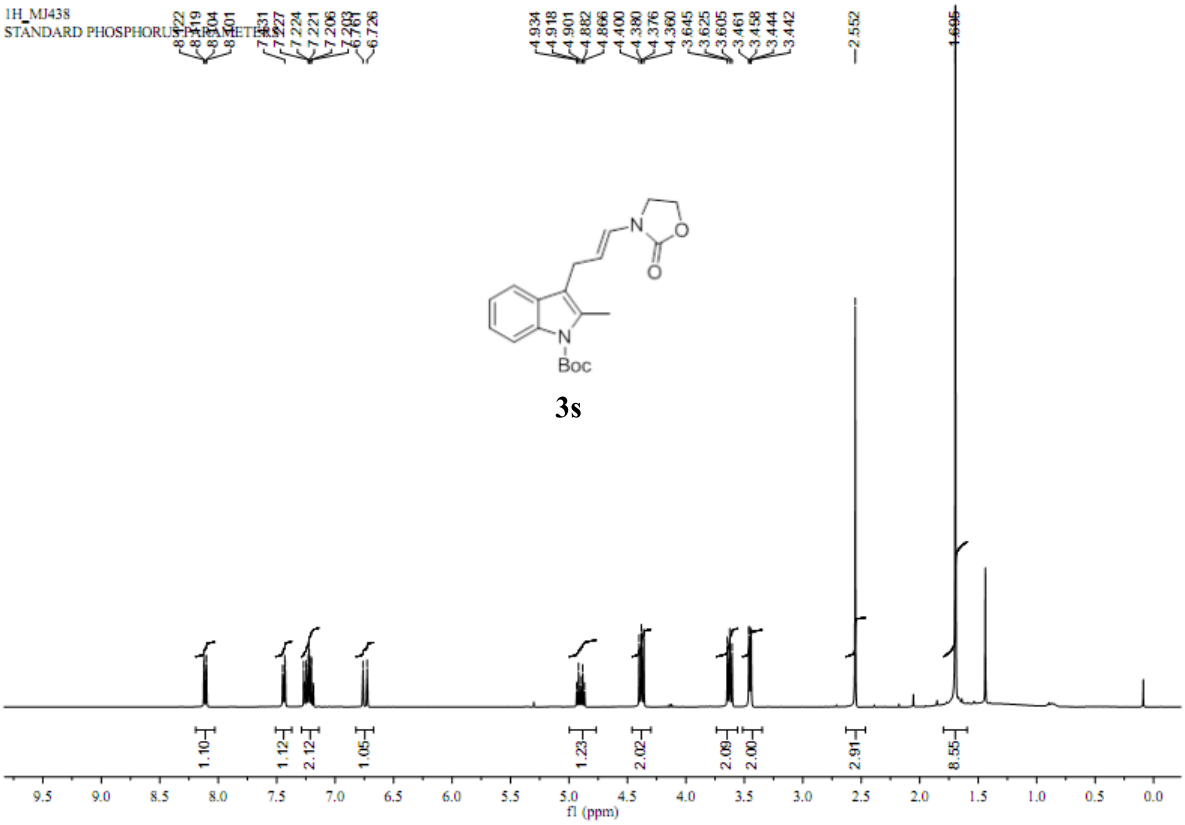
7a


1H_MJ428re
STANDARD PHOSPHORUS PARAMETERS
7.255
7.253
7.243
7.145
7.125
6.967
6.963
6.946
6.942
6.789
6.753
5.042
5.024
5.006
4.988
4.970
4.406
4.389
4.386
4.365
3.674
3.657
3.654
3.634
3.606
3.484
3.465
2.311
2.214
2.154
0.054
8a
1.00
1.21
1.08
1.15
1.29
2.55
2.67
2.96
2.28
3.00
3.00
fl (ppm)

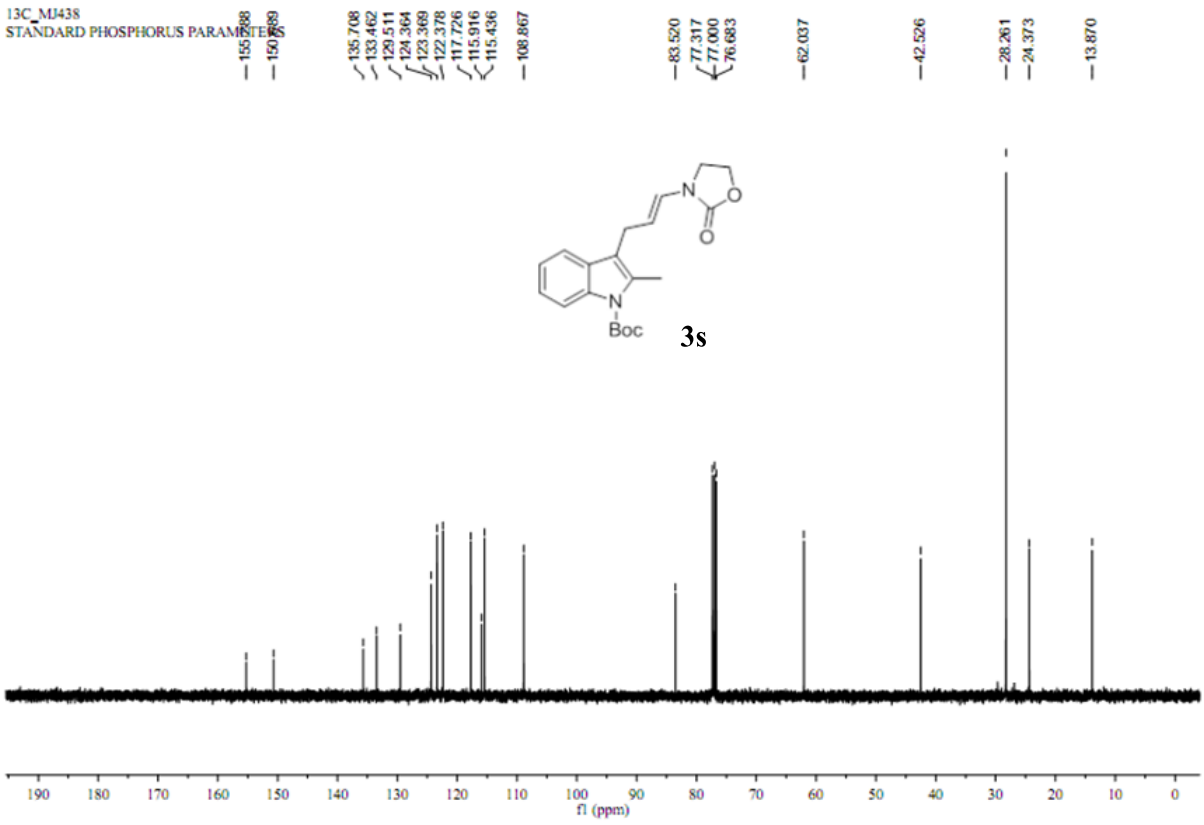

1H_MJ441
STANDARD PHOSPHORUS PARAMETERS
8.153
8.134
7.259
6.845
5.043
5.025
5.008
4.990
4.973
4.458
4.440
4.438
4.434
4.417
3.722
3.702
3.682
3.493
3.476
1.680
Boc
3q
1.08
1.00
0.93
1.06
1.08
1.01
1.11
2.01
1.94
2.03
8.43
fl (ppm)


1H_MJ444-1
MB5283 crude
8.051
8.048
8.034
8.029
7.443
7.439
7.270
7.264
7.246
7.243
6.777
6.741
5.054
5.037
5.019
4.424
4.405
4.400
4.384
3.813
3.797
3.685
3.665
3.645
2.227
1.694
O
N
O
N
Boc
1.16
1.30
2.04
1.26
1.25
2.68
2.18
2.29
3.20
8.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3r


1H_MJ438
STANDARD PHOSPHORUS PARAMETERS
8.422
8.419
8.404
8.401
7.431
7.427
7.224
7.221
7.206
7.203
6.761
6.726
4.934
4.918
4.901
4.882
4.866
4.400
4.380
4.376
4.360
3.645
3.625
3.605
3.461
3.458
3.444
3.442
2.552
1.695
N
O
O
N
Boc
1.10
1.12
2.12
1.05
1.23
2.02
2.09
2.00
2.91
8.55
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3s


13C_MJ438
STANDARD PHOSPHORUS PARAMETERS
155.288
150.869
135.708
133.462
129.511
124.364
123.369
122.378
117.726
115.916
115.436
108.867
83.520
77.317
77.000
76.683
62.037
42.526
28.261
24.373
13.870
N
O
O
N
Boc
3s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)