Electronic Supplementary Material (ESI) for Chemical Communications.

Multi-site Cyclization via Initial C-H Activation Using Rhodium(III) Catalyst: Rapid Assembly of Frameworks Containing Indoles and Indolins

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Supporting Information

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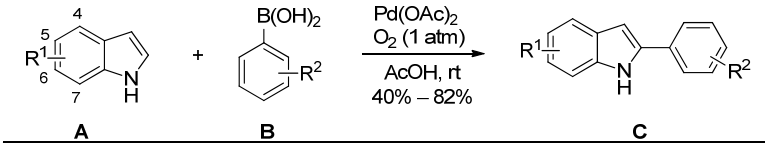
1. General Methods

NMR data were obtained for ^{1}H at 300 MHz or 400 MHz and for ^{13}C at 75 MHz or 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ or DMSO-d_6 solution. ESI HRMS was recorded on a Waters SYNAPT G_2 and Water XEVO G_2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether. All 2-aryl-*3H*-indol-3-ones **1** were synthesized as the experimental operation descripted by Ke-Qing Ling[1] from the corresponding 2-aryl-indoles **C**. 2-Phenyl-indole was purchased from aladdin^{TM}, while other substituted 2-aryl-indoles were prepared from three different methods (A, B, C) according to the literature procedures.[2] Alkynes **2b-2d**,[3] **2i**,[4] **2j-2k**[5] and **2l**[6] were obtained on the basis of previous reports.

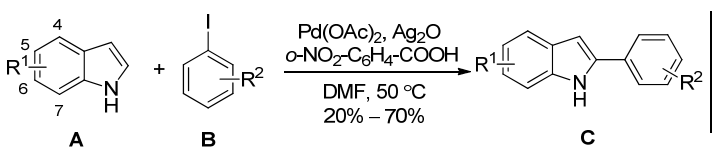
2. Synthesis and Characterization of 2-Aryl-*3H*-indol-3-ones

2.1. General procedure for the preparation of 2-aryl-indoles C (the corresponding precursors for the synthesis of 2-aryl-*3H*-indol-3-ones).



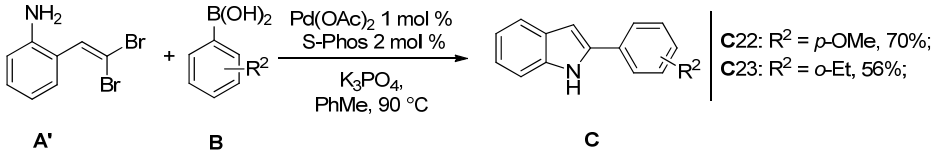
C1: R^1 = H, R^2 = *p*-Me; **C**2: R^1 = H, R^2 = *p*-CF_3; **C**3: R^1 = H, R^2 = *p*-F; **C**4: R^1 = H, R^2 = *p*-Br; **C**5: R^1 = H, R^2 = *p*-Cl; **C**6: R^1 = H, R^2 = *m*-Me; **C**7: R^1 = H, R^2 = *m*-Cl; **C**8: R^1 = H, R^2 = *m*-Br; **C**9: R^1 = H, R^2 = 2,4-2Me; **C**10: R^1 = H, R^2 = 3,4,5-3F; **C**11: R^1 = H, R^2 = 3-F,4-OMe; **C**12: R^1 = H, R^2 = 1-naphthalene; **C**13: R^1 = 4-OMe, R^2 = H; **C**14: R^1 = 5-Br, R^2 = H; **C**15: R^1 = 5-Cl, R^2 = H; **C**16: R^1 = 5-OMe, R^2 = H; **C**17: R^1 = 6-OMe, R^2 = H;

General Procedure of Method A: Indole (**A**1, R^1 = H) (351 mg, 3.0 mmol, 1.0 equiv), phenyl boronic acid (**B**5, R^2 = *p*-Cl) (608 mg, 3.9 mmol, 1.3 equiv) and $Pd(OAc)_2$ (67.4 mg, 0.3 mmol, 0.1 equiv) were added to a Schlenck flask. AcOH (30 mL) was added by syringe and resulting solution was degassed twice and refilled with O_2 (1 atm). The reaction mixture was stirred for 8 h at room temperature. AcOH was recovered by distillation under reduced pressure, and the residue was dissolved in CH_2Cl_2 (150 mL), washed with aqueous $NaHCO_3$ (2×60 mL). The organic layer was dried over Na_2SO_4. After removal of the solvent, the product **C**5 was purified by flash chromatography on silica gel eluting with ethyl acetate and petroleum ether (1:20) to afford 2-(4-chlorophenyl)-1*H*-indole as a white solid (498 mg, 73%).



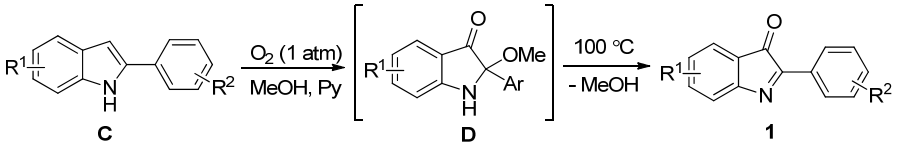
C18: R^1 = H, R^2 = *m*-CN; **C**19: R^1 = H, R^2 = *m*-CO_2Me; **C**20: R^1 = 6-Cl, R^2 = H; **C**21: R^1 = 7-Me, R^2 = H;

General Procedure of Method B: $Pd(OAc)_2$ (11.2 mg, 5 mol %), Ag_2O (174 mg, 0.75 mmol), 2-nitrobenzoic acid (251 mg, 1.5 mmol), 7-methyl-indole (**A**7, R^1 = 7-methyl, 131 mg, 1.0 mmol) and iodobenzene (**B**16, R^2 = H, 406 mg, 2.0 mmol) in dry DMF (0.5 M) were stirred at room temperature for 15 h. The reaction mixture was filtered through a plug of silica gel and then evaporated to dryness under reduced pressure. The crude product was purified by column chromatography (ethyl acetate: petroleum ether = 1:30) to afford 7-methyl-2-phenyl-*1H*-indole **C**21 as a white solid (245 mg, 70%).



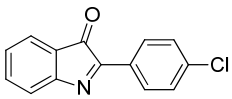
General Procedure of Method C: A 10-mL round-bottomed flask was charged with **A'** (554 mg, 1 mmol), 2-ethylbenzeneboronic acid **B**18 (450 mg, 1.5 mmol), and powdered $K_3PO_4{\cdot}3H_2O$ (2.66 g, 5 mmol). The reaction mixture was purged with argon for at least 10 mins. A separate 10-mL round-bottomed flask was charged with $Pd(OAc)_2$ (9.2 mg, 2 mol %) and S-phos (32.8 mg, 4 mol %), then the flask was purged with argon for 10 mins. Toluene (5 mL) was added to the catalyst flask, and the mixture was stirred at room temperature for 3 mins. The homogeneous catalyst solution was cannulated to the reactant flask, and the heterogeneous mixture was stirred at room temperature for 2 mins and heated to 90 °C for another 6 hours. Then the mixture was cooled to room temperature and diluted with Et_2O (15 mL). After aqueous workup, the product was purified by flash chromatography (ethyl acetate: petroleum ether = 1:30) to afford 2-(3-methoxyphenyl)-1*H*-indole **C**23 as a white crystalline solid (135 mg, 56%).

2.2. General Procedure for Preparation of 2-Aryl-*3H*-indol-3-ones.

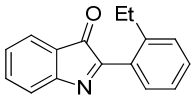


Typical Procedure: Irradiation of a methanol solution (250 mL) of 2-aryl-indoles (**C**, 5 mmol) in the presence of methylene blue (MB, 0.5 mmol) and pyridine (4 mL) was carried out with a tungsten halogen lamp in a typical immersion apparatus through a cutoff filter solution (1% aqueous of $K_2Cr_2O_7$) at ambient temperature under oxygen bubbling. After complete disappearance of the 2-aryl-indoles **C**, the reaction mixture was concentrated. Then the residuum was diluted with ether and washed with water. The ether layer was dried over Na_2SO_4, evaporated to dryness and heated at 100 ^oC under reduced pressure for 30 mins to afford a red solid which was chromatographed over silica gel column elution with ethyl acetate:petroleum to

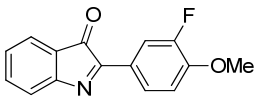
give the 2-aryl-*3H*-indol-3-ones **1**. The Spectral data of representative 2-aryl-*3H*-indol-3-ones **1** are given.



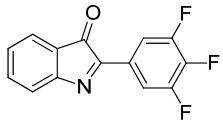
2-(4-chlorophenyl)-*3H*-indol-3-one. Red solid; m.p. 162-164 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.57-7.40 (m, 5H), 7.30-7.26 (m, 1H) ppm.



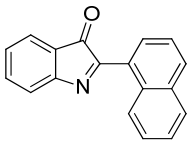
2-(2-ethylphenyl)-*3H*-indol-3-one. Red oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.58-7.54 (m, 2H), 7.45-7.26 (m, 5H), 2.99 (q, *J* = 15.2 Hz, 2H), 1.26 (t, *J* = 9.6 Hz, 3H) ppm.



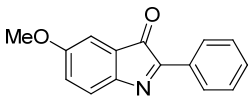
2-(3-fluoro-4-methoxyphenyl)-*3H*-indol-3-one. Deep red solid; m.p. 171-173 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.17 (dd, *J* = 12.4 Hz, 1.6 Hz, 1H), 7.55-7.52 (m, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.24 (m, 1H), 7.05 (t, *J* = 8.6 Hz, 1H), 3.99 (s, 3H) ppm.



2-(3,4,5-trifluorophenyl)-*3H*-indol-3-one. Red solid; m.p. 146-147 ^{o}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (t, *J* = 7.6 Hz, 2H), 7.57 (m, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H) ppm.



2-(naphthalen-1-yl)-3*H*-indol-3-one. Deep red solid; m.p. 78-79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 7.2 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.65-7.50 (m, 7H) ppm.



5-methoxy-2-phenyl-*3H*-indol-3-one. Red solid; m.p. 128-129 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 2H), 754-7.45 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 3.85 (s, 3H) ppm.

(1) Ling, K.-Q. *Synth.Comm.* **1995**, *25*, 3831.

(2) (a) Yang, S.-D.; Sun, C.-L.; Fang, Z.; Li, B.-J.; Li, Y.-Z.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1473. (b) Larrosa, L.; Lebrasseur, N. *J. Am. Chem. Soc.* **2008**, *130*, 2926. (c) Fang, Y.-Q.; Lautens, M. *J. Org. Chem.* **2008**, *73*, 538.

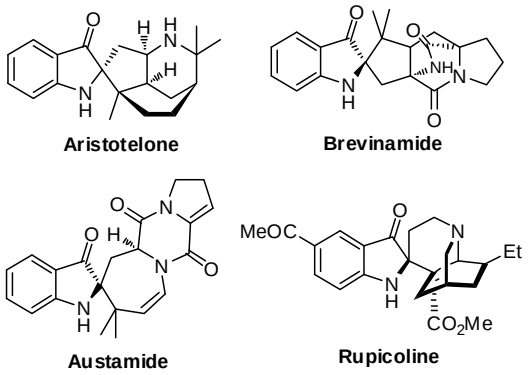
(3) Novák, Z.; Nemes, P.; Kotschy, A. *Org. Lett.* **2004**, *6*, 4917.

(4) Gao, Y.; Wang, G.; Chen, L.; Xu, P.; Zhao, Y.; Zhou, Y.; Han, L.-B. *J. Am. Chem. Soc.* **2009**, *131*, 7956.

(5) Curry. J. W. *J. Am. Chem. Soc.* **1956**, *78*, 1686.

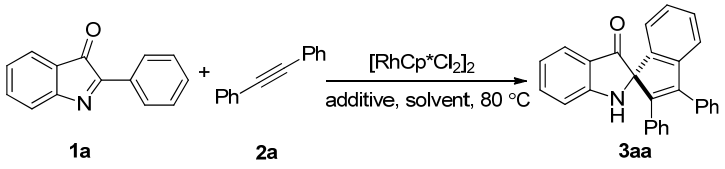
(6) Zou, H.; Zhou, L.; Li, Y.; Cui, Y.; Zhong, H.; Pan, Z.; Yang, Z, Quan, J. *J. Med. Chem*. **2010**, *53*, 994.

3. Figure S1: Natural Products with Spiro indolin-3-ones Structural Unit.



4. The Study of $[RhCp^*Cl_2]_2$ in the Tandem C–H Activation-Grignard-Like Addition Reactions

4.1. Table S1: Optimization of the reaction conditions for synthesis of **3aa** under the catalyst of $[RhCp^*Cl_2]_2$.



Screening of additives[a]

Entry	Additive	Solvent	Time	Yield (%)
1	**$AgSbF_6$**	**DCE**	**8 h**	**48**
2	$AgBF_4$	DCE	8 h	23
3	Ag_2CO_3	DCE	8 h	7
4	$AgCO_2CF_3$	DCE	8 h	12
5	$AgNO_3$	DCE	8 h	29
6	Ag_2O	DCE	8 h	trace
7	$Cu(OAc)_2$	DCE	4 h	43(33)[b]
8	$Cu(acac)_2$	DCE	7 h	trace
9	$Cu(OTf)_2$	DCE	7 h	–
10	CuI	DCE	7 h	–
11	CuCl	DCE	7 h	trace
12	$Cu(OAc)_2$+ $AgSbF_6$	DCE	4 h	36[b]

[a] General procedure: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol % $[RhCp^*Cl_2]_2$, additive (AgX 20 mol % or CuX 100 mol %),

2.0 mL of solvent, Ar atmosphere. Yields are reported for the isolated products. [b] 20 mol % of $Cu(OAc)_2$ was added.

Screening of solvents[a]

Entry	Additive	Solvent	Time	Yield (%)
1	$AgSbF_6$	DCM	8 h	29
2	$AgSbF_6$	$CHCl_3$	8 h	mess
3	$AgSbF_6$	THF	8 h	19
4	$AgSbF_6$	EtOH	8 h	–
5	$AgSbF_6$	Toluene	8 h	19
6	$AgSbF_6$	DMF	4 h	–
7	$AgSbF_6$	DMSO	7 h	trace
8	$AgSbF_6$	dioxane	7 h	–
9	**$AgSbF_6$**	**MeCN**	**7 h**	**43**
10	$AgSbF_6$	AcOH	4 h	18

[a] General procedure: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol % $[RhCp^*Cl_2]_2$, 20 mol % of $AgSbF_6$, 2.0 mL of solvent, Ar atmosphere. Yields are reported for the isolated products.

Screening of acids[a]

Entry	Additive	Acid	Solvent	Time	Yield (%)
1	**$AgSbF_6$**	**AcOH**	**DCE**	**4 h**	**60**
2	$AgSbF_6$	PivOH	DCE	4 h	44
3	$AgSbF_6$	CF_3CO_2H	DCE	6 h	17
4	$AgSbF_6$	CF_3CH_2OH	DCE	6 h	44
5	$AgSbF_6$	*t*-AmOH	DCE	6 h	5
6	$AgSbF_6$	LiOAc	DCE	4 h	12

[a] General procedure: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol % $[RhCp^*Cl_2]_2$, 20 mol % of $AgSbF_6$, 0.1 mmol of acid, 2.0 mL of solvent, Ar atmosphere. Yields are reported for the isolated products.

Screening of co-solvents[a]

Entry	Additive	Acid	Co-solvent	Time	Yield (%)
1	$AgSbF_6$	AcOH	MeCN	18 h	68
2	**$AgSbF_6$**	**AcOH**	**DCE/MeCN = 1/1**	**6 h**	**68**
3	$AgSbF_6$	AcOH	DCE/MeCN = 2/1	6 h	49

4	$AgSbF_6$	AcOH	DCE/MeCN = 1/2	6 h	55
5	$AgSbF_6$	–	DCE/MeCN/AcOH = 1/1/1	6 h	57

[a] General procedure: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol % $[RhCp^*Cl_2]_2$, 20 mol % of $AgSbF_6$, 0.1 mmol of acetic acid or acetic acid was used as co-solvent, 2.0 mL of co-solvent mixture, Ar atmosphere. Yields are reported for the isolated products.

Screening of base[a]

Entry	Additive	Co-solvent (1/1)	Base	Time	Yield (%)
1	$AgSbF_6$	DCE/MeCN	Cs_2CO_3	28 h	mess
2	$AgSbF_6$	DCE/MeCN	CsOAc	28 h	26
3	$AgSbF_6$	DCE/MeCN	KOH	28 h	mess
4	$AgSbF_6$	DCE/MeCN	$NaHCO_3$	28 h	16
5	$AgSbF_6$	DCE/MeCN	DABCO	28 h	–
6	$AgSbF_6$	DCE/MeCN	TEA	28 h	mess

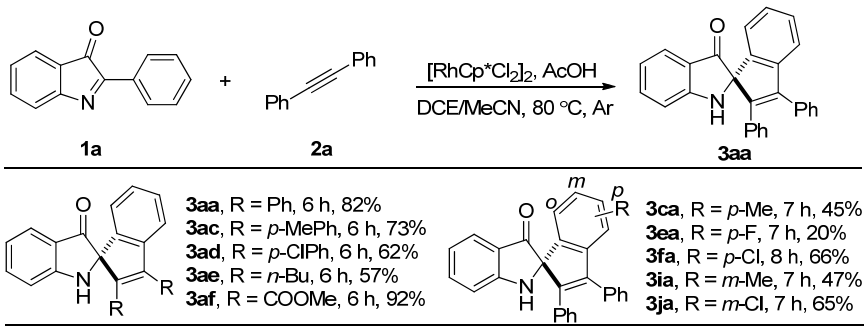
[a] General procedure: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol % $[RhCp^*Cl_2]_2$, 20 mol % of $AgSbF_6$, 0.1 mmol of base, 2.0 mL of co-solvent mixture, Ar atmosphere. Yields are reported for the isolated products.

Screening of the ratio of **1a**/**2a**[a]

Entry	Additive	Co-solvent (1/1)	Acid	**1a**/**2a**	Time	Yield (%)
1	$AgSbF_6$	DCE/MeCN	AcOH	1/2	6 h	68
2	$AgSbF_6$	DCE/MeCN	AcOH	1/1.5	7 h	64
3	$AgSbF_6$	DCE/MeCN	AcOH	1/1.2	7 h	56
4	$AgSbF_6$	DCE/MeCN	AcOH	1.2/1	7 h	78
5	**$AgSbF_6$**	**DCE/MeCN**	**AcOH**	**1.5/1**	**6 h**	**82**
6	$AgSbF_6$	DCE/MeCN	AcOH	2/1	6 h	82

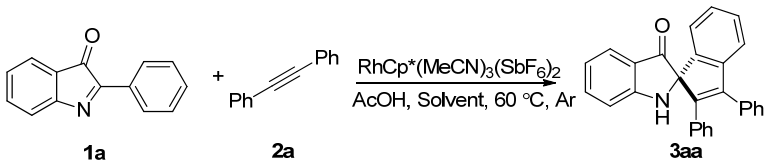
[a] General procedure: 5 mol % $[RhCp^*Cl_2]_2$, 20 mol % of $AgSbF_6$, 1.0 equiv of acid, 2.0 mL of co-solvent mixture, Ar atmosphere. Yields are reported for the isolated products.

4.2. Table S2: $[RhCp^*Cl_2]_2$ catalyzed [3+2] annulation with 2-aryl-*3H*-indol-3-ones **1** and alkynes **2**. [a]



[a] General procedure: 0.15 mmol of **1a**, 0.1 mmol of **2a**, 5 mol % $[RhCp^*Cl_2]_2$, 20 mol % of $AgSbF_6$, 0.1 mmol of acetic acid, 2.0 mL of co-solvent mixture (MeCN/DCE = 1/1), Ar atmosphere. Yields are reported for the isolated products.

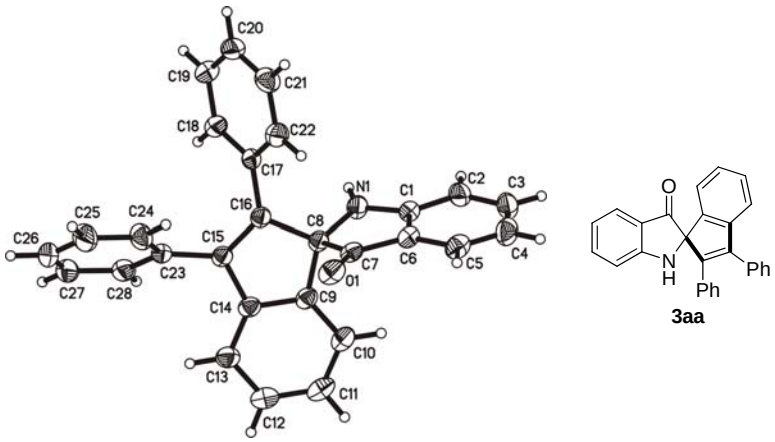
5. Table S3: Examination of Reaction Solvents under the Catalyst of $RhCp^*(MeCN)_3(SbF_6)_2$.[a]



Solvent	DCM	$CHCl_3$	THF	Dioxane	MeCN	Toluene	DMF	*t*-AmOH	Acetone	Ethyl acetate
Time (min)	10	5	5	5	120	20	120	120	5	10
Yield (%)	75	81	85	83	82	70	48	82	73	79

[a] General procedure: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol % of $RhCp^*(MeCN)_3(SbF_6)_2$, 0.1 mmol of AcOH, 2.0 mL of solvent, 60 °C, Ar atmosphere. Yields are reported for the isolated products.

6. The Crystal Data of C2-Cyclization Product 3aa.



Bond precision: C-C = 0.0027 A Wavelength=0.71073

Cell: a=9.9451(6) b=10.9422(5) c=18.8339(11)

alpha=90 beta=90.772(6) gamma=90

Temperature: 293 K

Calculated Reported

Volume	2049.3(2)	2049.3(2)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C28 H19 N O	C28 H19 N O
Sum formula	C28 H19 N O	C28 H19 N O
Mr	385.44	385.44
Dx, g cm^{-3}	1.249	1.249
Z	4	4
Mu (mm-1)	0.075	0.075
F000	808.0	808.0
F000’	808.32	
h,k,lmax	11,13,22	11,13,22
Nref	3745	3738
Tmin,Tmax	0.974,0.985	0.974,0.985
Tmin’	0.974	

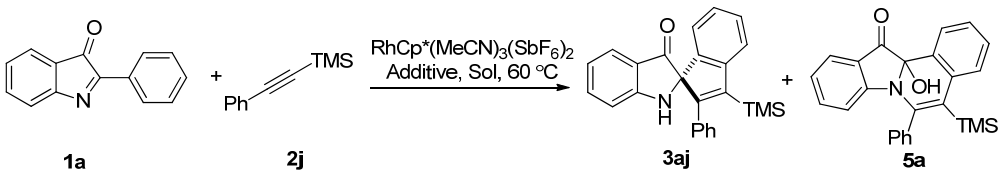
Correction method = MULTI-SCAN

Data completeness = 0.998 Theta(max)= 25.340

R(reflections)= 0.0453(2649) wR2(reflections)= 0.1227(3738)

S = 1.022 Npar= 271

7. Table S4: Condition Sreening of the Reaction of 1a with 2j.[a]

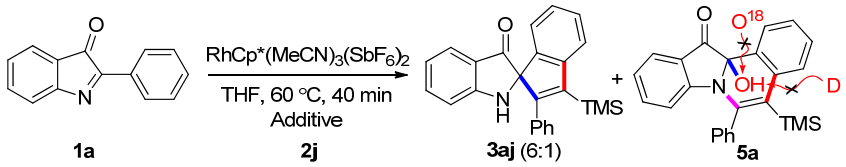


1a **2j** **3aj** **5a**

Entry	Additive	Solvent	Time	Yield (**3aj**)[b]	Yield (**5a**)[b]
1	AcOH	THF	40 min	34%	32%
2[c]	AcOH	THF	40 min	33%	32%
3[d]	AcOH	THF	40 min	30%	30%
4	PivOH	THF	90 min	29%	30%
5	AcONa	THF	40 min	–	–
6	AcOH	DCE	4 h	20%	20%
7	AcOH	MeCN	4 h	20%	20%
8[e]	AcOH/H_2O^{18} (0.5 equiv)	THF	40 min	34%	32%

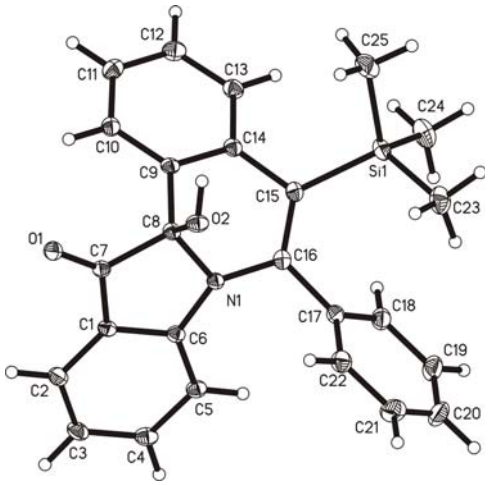
9[e]	AcOD	THF	40 min	32%	32%
10[e]	CD_3CO_2D	THF	40 min	34%	31%

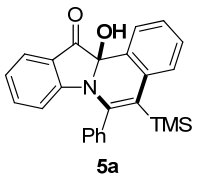
[a] Under the optimal conditions in Table 1 with 1.0 equiv of additive. [b] Yields are reported for the isolated products. [c] Ar atmosphere. [d] 5.0 Equiv of AcOH. [e] No deuterated products were detected.



To get more information about mechanism of the unprecedented [4+2] annulation, isotope-labeling experiments were designed (Table S4, entries 10–12). Both D_2O and H_2O^{18} were failed to affect the isotope of hydroxy group, which might imply the tertiary alcohol of **5a** did not come from water existed in the solvent. Similarly no deuterium was obtained when the reaction was conducted in AcOD or CD_3CO_2D, which indicates that the proton of the hydroxy might be derived from the first C–H bond metalation step. The real reaction mechanism and the role of the silicon in such annulation still need further study.

8. The Crystal Data of N1-Cyclization Product 5a.





Bond precision: C-C = 0.0042 A Wavelength=0.71073

Cell: a=9.6847(7) b=10.6101(8) c=12.7428(10)

alpha=82.268(6) beta=87.114(6) gamma=75.081(7)

Temperature: 170 K

Calculated Reported

Volume	1253.58(17)	1253.59(17)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C25 H23 N O2 Si, C H Cl3	C25 H23 N O2 Si, C H Cl3
Sum formula	C26 H24 Cl3 N O2 Si	C26 H24 Cl3 N O2 Si
Mr	516.90	516.90
Dx,g cm^{-3}	1.369	1.369
Z	2	2
Mu (mm-1)	0.438	0.438
F000	536.0	536.0
F000’	537.22	
h,k,lmax	11,12,15	11,12,15
Nref	4600	4585
Tmin,Tmax	0.886,0.916	0.838,0.918
Tmin’	0.832	

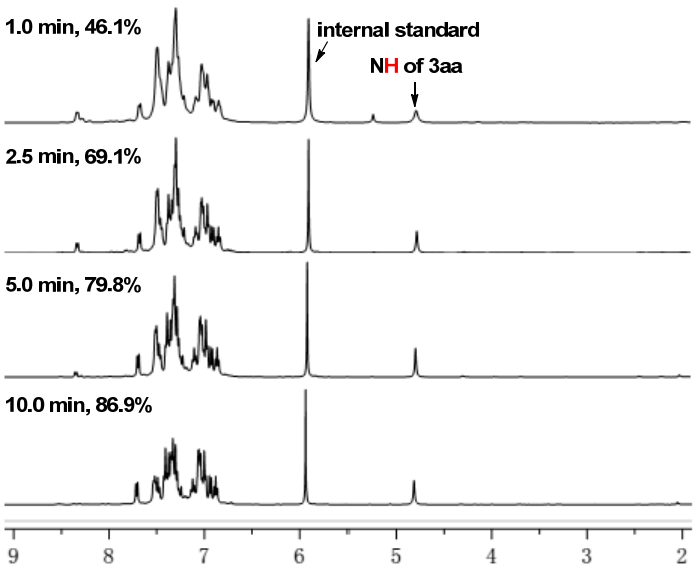
Correction method = MULTI-SCAN

Data completeness = 0.997 Theta(max)= 25.350

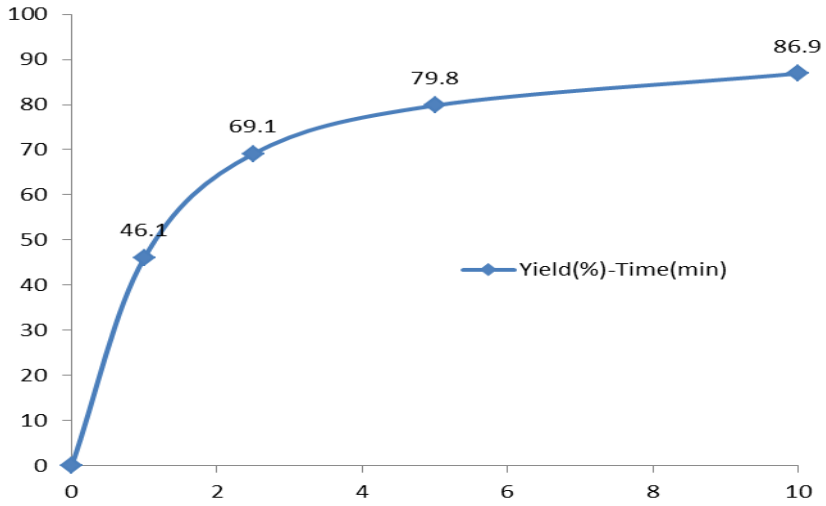
R(reflections)= 0.0556(3483) wR2(reflections)= 0.1426(4585)

S = 1.022 Npar= Npar = 306

9. Figure S2. NMR Experiments and Yield-Time Scheme for C2-Cyclization



a. NMR experiments

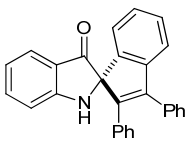


b. Yield-Time scheme

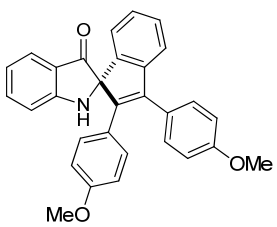
NMR experiments were carried out to study the reaction rate of the [3+2] annulation. Under the optimal conditions, the reaction process was monitored by employing **1a** (0.05 mmol) and **2a** (0.05 mmol) (Figure S2a). Besides, Yield-Time scheme was also depicted to exhibit the high efficiency of this transformation directly (Figure S2b).

10. General Procedure for Synthesis of Spiro Indolin-3-one Derivatives and Characterization Data

2-Phenyl-3*H*-indol-3-one **1a** (20.7 mg, 0.1 mmol), diphenylacetylene **2a** (21.4 mg, 0.12 mmol), $RhCp^*(MeCN)_3(SbF_6)_2$ (1.7 mg, 2 mol %), and AcOH (6 μL, 0.1 mmol) were stirred in THF (2.0 mL) in air at 60 °C for 10 min. After completion, the reaction mixture was cooled down to room temperature. The reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:20) to give the product **3aa** as a bright yellow solid (32.6 mg, 85%).

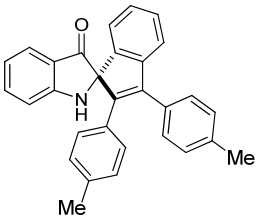


2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3aa). 10 min, 85% yield; Yellow solid; m.p. 222-223 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.43-7.26 (m, 7H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.08-6.99 (m, 6H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 4.82 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 161.4, 145.2, 144.0, 143.2,141.6, 137.5, 134.4, 133.6, 129.4, 128.8, 128.7, 128.6, 128.0, 127.8, 127.3, 126.5, 125.7, 122.2, 121.5, 120.5, 119.1, 113.0, 81.4 ppm. ESI HRMS: calcd. for $C_{28}H_{20}NO$+H 386.1545, found 386.1544.

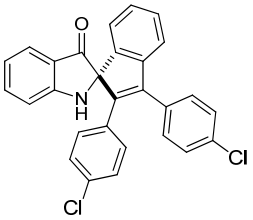


2,3-dimethoxyspiro[indene-1,2'-indolin]-3'-one (3ab). 16 h, 60% yield; Yellow solid; m.p. 106-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.31-7.25 (m, 2H), 7.09 (t, *J* = 7.2

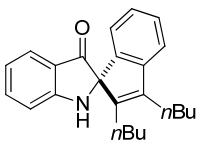
Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.96-6.86 (m, 6H), 6.59 (d, *J* = 8.8 Hz, 2H), 4.82 (s,1H), 3.83 (s, 3H), 3.67 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 161.4, 159.0, 158.6, 145.5, 143.0, 142.3, 140.5, 137.4, 130.7, 130.0, 128.7, 126.8, 126.2, 126.1, 125.6, 122.1, 121.2, 120.4, 119.0, 114.0, 113.5, 113.0, 81.3, 55.2, 55.0 ppm. ESI HRMS: calcd. for $C_{30}H_{23}NO_3$+H 446.1756, found 446.1763 .



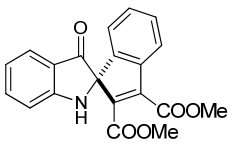
2,3-di-p-tolylspiro[indene-1,2'-indolin]-3'-one (3ac). 5 min, 66% yield; Yellow solid; m.p. 103-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.50-7.47 (m, 1H), 7.32-7.24 (m, 4H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.12-7.08 (m, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.93-6.83 (m, 6H), 4.75 (s, 1H), 2.39 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 161.4, 145.4, 143.3, 143.1, 141.2, 137.5, 137.4, 137.0, 131.5, 130.7, 129.3, 129.3, 128.8, 128.7, 128.6, 126.2, 125.7, 122.2, 121.4, 120.4, 118.9, 113.0, 81.3, 21.4, 21.1 ppm. ESI HRMS: calcd. for $C_{30}H_{23}NO$+H 414.1858, found 414.1855.



2,3-bis(4-chlorophenyl)spiro[indene-1,2'-indolin]-3'-one (3ad). 10 min, 90% yield; Bright yellow solid; m.p. 235-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.38-7.24 (m, 6H), 7.15-7.11 (m, 1H), 7.06-7.02 (m, 3H), 6.96-6.87 (m, 4H), 4.82 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 161.4, 144.5, 143.3, 142.9, 140.9, 137.7, 134.0, 133.4, 132.4, 131.9, 130.7, 130.0, 129.1, 128.9, 128.5, 126.8, 125.8, 122.0, 121.4, 120.7, 119.4, 113.0, 81.3 ppm. ESI HRMS: calcd. for $C_{28}H_{17}Cl_2NO$+H 454.0765, found $C_{28}H_{18}{}^{35}Cl_2NO$+H 454.0761, $C_{28}H_{18}{}^{37}Cl_2NO$+H 456.0740.

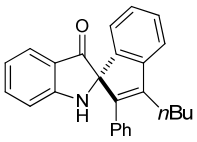


2,3-dibutylspiro[indene-1,2'-indolin]-3'-one (3ae). 20 min, 75% yield; Yellow solid; m.p. 89-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 8.0Hz, 1H), 7.72-7.22 (m, 2H), 7.04-6.93 (m, 3H), 6.85 (t, *J* = 7.6 Hz, 1H), 4.59 (s, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.22-2.14 (m, 1H), 2.12-2.06 (m, 1H), 1.66-1.51 (m, 2H), 1.50-1.40 (m, 2H), 1.38-1.27 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 161.5, 146.0, 142.9, 142.4, 141.9, 137.2, 128.4, 125.4, 125.2, 122.1, 120.4, 119.4, 118.7, 112.6, 81.2, 31.3, 30.8, 25.6, 25.5, 23.0, 22.9, 14.0, 13.7 ppm. ESI HRMS: calcd. for $C_{24}H_{27}NO$+H 346.2171, found 346.2174.

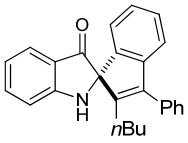


dimethyl 3'-oxospiro[indene-1,2'-indoline]-2,3-dicarboxylate (3af). 10 min, 98% yield; Bright yellow solid; m.p. 158-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.56-7.50 (m, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.07 (d,

J = 7.6 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 4.85 (s, 1H), 3.96 (s, 3H), 3.62 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 164.3, 162.5, 161.3, 144.6, 143.1, 139.3, 137.5, 129.5, 129.3, 125.9, 123.6, 122.0, 121.5, 113.0, 113.0, 78.9, 52.6, 52.2 ppm. ESI HRMS: calcd. for $C_{20}H_{15}NO_5$+H 350.1028, found 350.1030.

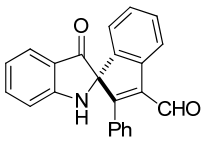


3ag

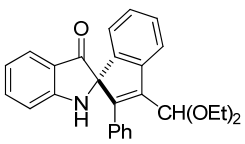


3ag'

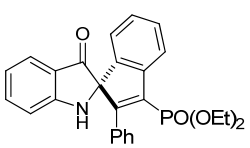
3-butyl-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ag); 2-butyl-3-phenylspiro[indene-1,2'-indolin]-3'-one (3ag'); (3ag:3ag' = 3:1), 10 min, 73% yield; Brown oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.70 (s, 1H, **3ag** and 1H, **3ag'**), 7.57-7.50 (m, 1H, **3ag** and 1H, **3ag'**), 7.47-7.40 (m, 3H, **3ag** and 3H, **3ag'**), 7.35 (t, *J* = 7.6 Hz, 1H, **3ag**), 7.30-7.26 (m, 2H, **3ag** and 1H, **3ag'**), 7.24-7.20 (m, 3H, **3ag'**), 7.16-7.13 (m, 3H, **3ag**), 7.11-7.05 (m, 3H, **3ag'**), 6.97-6.90 (m, 2H, **3ag** and 1H, **3ag'**), 6.78 (t, *J* = 7.6 Hz, 1H, **3ag'**), 6.68 (t, *J* = 7.6 Hz, 1H, **3ag**), 2.60-2.56 (m, 2H, **3ag**), 2.21-2.17 (m, 1H, **3ag'**), 2.11-2.08 (m, 1H, **3ag'**), 1.65-1.53 (m, 2H, **3ag**), 1.39-1.32 (m, 2H, **3ag**), 1.30-1.18 (m, 2H, **3ag'**), 1.15-1.03 (m, 2H, **3ag'**), 0.82 (t, *J* = 7.6 Hz, 3H, **3ag**), 0.60 (t, *J* = 7.2 Hz, 3H, **3ag'**) ppm. ESI HRMS: calcd. for, found $C_{26}H_{23}NO$+Na 388.1677, found 388.1674.



(R)-3'-oxo-2-phenylspiro[indene-1,2'-indoline]-3-carbaldehyde (3ah). 1 h, 50% yield; Bright yellow solid; m.p. 217-218 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.93 (s,1H), 8.11-8.06 (m, 2H), 7.55-7.51 (m, 2H), 7.41-7.23 (m, 7H), 7.04 (t, *J* = 8.0 Hz ,2H), 6.79 (t, *J* = 7.2 Hz ,1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.3, 189.5, 163.0, 162.6, 142.1, 140.1, 138.7, 138.4, 131.0, 130.2, 129.2, 129.0, 128.9, 127.6, 125.5, 123.3, 121.3, 120.0, 118.3, 112.9, 82.2 ppm. ESI HRMS: calcd. for $C_{23}H_{15}NO_2$+H 338.1181, found 338.1180.

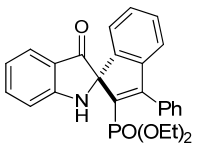


(R)-3-(diethoxymethyl)-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ah'). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.31-7.18 (m, 6H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.89-6.82 (m, 2H), 5.34 (s, 1H), 4.75 (s, 1H), 3.98-3.90 (m, 1H), 3.67-3.57 (m, 2H), 3.51-3.44 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 161.1, 145.1, 142.7, 142.5, 141.0, 137.5, 133.0, 128.7, 128.6, 128.2, 128.0, 126.2, 125.5, 123.8, 121.8, 120.1, 118.9, 112.9, 99.1, 81.9, 63.2, 62.1, 15.3, 15.2 ppm. ESI HRMS: calcd. for $C_{27}H_{25}NO_3$+Na 434.1732, found 434.1732.

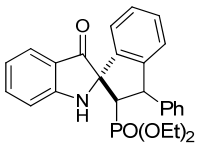


diethyl(3'-oxo-2-phenylspiro[indene-1,2'-indolin]-3-yl)phosphonate (3ai). 20 min,

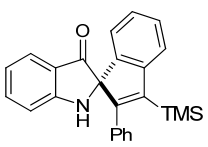
56% yield; Yellow solid; m.p. 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.57 (brs, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.40-7.39 (m, 3H), 7.28-7.23 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.86-6.82 (m, 1H), 5.95 (brs, 1H), 3.87-3.78 (m, 1H), 3.74-3.64 (m, 1H), 3.59-3.47 (m, 2H), 0.77 (t, *J* = 7.2 Hz, 3H), 0.71 (t, *J* = 6.8 Hz, 3H) pm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1，161.8，159.0 (d, J_{CP} = 14.0 Hz), 144.8 (d, J_{CP} = 9.9 Hz)，143.1 (d, J_{CP} = 20.1 Hz), 137.1, 132.6 (d, J_{CP} = 3.8 Hz), 130.2, 129.0, 128.7, 128.7 (d, J_{CP} = 1.9 Hz), 128.6, 128.2, 125.4, 123.0, 122.1, 121.1, 118.2, 112.9, 81.1 (d, J_{CP} = 12.2 Hz), 62.0 (d, J_{CP} = 6.0 Hz), 61.2 (d, J_{CP} = 6.1 Hz), 15.3 (d, J_{CP} = 6.1 Hz), 15.2 (d, J_{CP} = 7.9 Hz) ppm. ESI HRMS: calcd. for $C_{26}H_{24}NO_4P$+H 446.1521, found 446.1522.



diethyl(3'-oxo-3-phenylspiro[indene-1,2'-indolin]-2-yl)phosphonate (3ai'). 20 min, 33% yield; Yellow solid; m.p. 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.23-7.11 (m, 6H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.38 (brs, 1H), 4.13-4.08 (m, 1H), 4.06-4.00 (m, 1H), 3.93-3.87 (m, 1H), 3.78-3.74 (m, 1H), 1.23 (t, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 161.9, 158.9 (d, J_{CP} = 10.7 Hz), 143.0 (d, J_{CP} = 15.6 Hz), 141.9 (d, J_{CP} = 12.2 Hz), 137.7, 133.0, 130.2, 129.0, 128.6, 128.5, 127.6, 126.7, 125.5, 123.6, 121.4, 120.8, 118.9, 112.9, 83.5 (d, J_{CP} = 18.7 Hz), 62.1(d, J_{CP} = 6.1 Hz), 62.1 (d, J_{CP} = 6.0 Hz), 16.1 (d, J_{CP} = 6.8 Hz), 15.8 (d, J_{CP} = 6.8 Hz) ppm. ESI HRMS: calcd. for $C_{26}H_{24}NO_4P$+H 446.1521, found 446.1523.

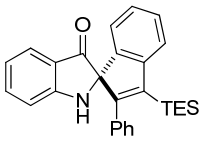


diethyl((1S,2R,3R)-3'-oxo-3-phenyl-2,3-dihydrospiro[indene-1,2'-indolin]-2-yl)phosphonate (reduced-3ai'). Yellow solid; m.p. 106-107°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 6.8 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.31-7.26 (m, 1H), 7.15-7.08 (m, 4H), 6.89 (d, *J* = 6.8 Hz, 1H), 6.83-6.87 (m, 1H), 5.62 (s, 1H), 4.55 (dd, *J* = 25.6 Hz, 6.0 Hz, 1H), 4.01 (brs, 1H), 3.97-3.84 (m, 2H), 3.67-3.64 (m, 1H), 3.50-3.49 (m, 1H), 1.18 (t, *J* = 6.8 Hz, 3H), 1.09 (t, *J* = 6.8 Hz, 3H) ppm.

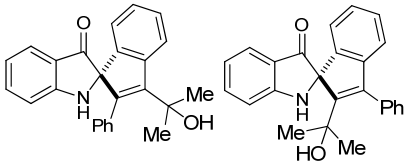


2-phenyl-3-(trimethylsilyl)spiro[indene-1,2'-indolin]-3'-one (3aj). 40 min, 34% yield; Yellow solid; m.p. 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.39-7.35 (m, 1H), 7.31 (td, *J* = 7.6 Hz, 1.6Hz, 1H), 7.20-7.18 (m, 3H), 7.14-7.08 (m, 3H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 4.72 (s, 1H), 0.11 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 161.5, 156.9, 148.8, 144.2, 143.3, 137.2, 136.2, 129.0, 128.6, 127.8, 127.6, 125.6, 125.2, 123.1, 122.2, 121.1, 118.7, 112.6, 84.1, 0.1 ppm. ESI HRMS:

calcd. for $C_{25}H_{23}NOSi$+H 382.1627, found 382.1626.

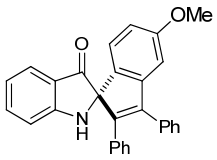


(R)-3-(3-ethylpentan-3-yl)-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ak). 5 h, 41%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.53 (m, 2H), 7.39-7.34 (m, 1H), 7.30 (dt, *J* = 7.6 Hz , 1.2 Hz, 1H), 7.21-7.08 (m, 6H), 7.03 (d, *J* = 7.6 Hz ,1H), 6.81 (d, *J* = 8.4 Hz ,1H), 6.76 (t, *J* = 7.6 Hz ,1H), 4.72 (s, 1H), 0.91 (t, *J* = 8.0 Hz ,9H), 0.63-0.55 (m, 6H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.8, 161.5, 158.5, 149.2, 143.2, 141.7, 137.1, 136.3, 128.9, 128.6, 127.8, 127.5, 125.5, 125.2, 123.1, 122.2, 120.9, 118.7, 112.6, 84.5, 7.5, 3.7 ppm. ESI HRMS: calcd. for $C_{28}H_{30}NOSi$+H 424.2097, found 424.2104.

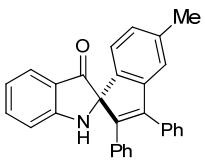


(R)-3-(2-hydroxypropan-2-yl)-2-phenylspiro[indene-1,2'-indolin]-3'-one (3al) ;

(R)-2-(2-hydroxypropan-2-yl)-3-phenylspiro[indene-1,2'-indolin]-3'-one (3al'); (3al:3al' = 3:1), 10 min, 82% yield; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.6 Hz, 1H, **3al'**), 7.75 (d, *J* = 7.2 Hz, 1H, **3al**), 7.57-7.30 (m, 5H, **3al** and 5H, **3al'**), 7.19-7.09 (m, 3H, **3al** and 3H, **3al'**), 7.04-6.96 (m, 2H, **3al** and 2H, **3al'**), 6.89 (d, *J* = 7.2 Hz, 1H, **3al**), 6.80 (d, *J* = 8.4 Hz, 1H, **3al'**), 6.75-6.72 (m, 1H, **3al** and 1H, **3al'**), 4.81 (s, 1H, **3al**), 4.71 (s, 1H, **3al'**), 2.87 (s, 1H, **3al'**), 2.07 (s, 1H, **3al**), 1.52 (s, 3H, **3al'**), 1.46 (s, 3H, **3al'**), 1.39 (s, 3H, **3al**), 1.24 (s, 3H, **3al**) ppm. ESI HRMS: calcd. for $C_{25}H_{21}NO_2$+Na 390.1470, found 390.1460.

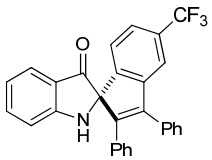


5-methoxy-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ba). 10 min, 72% yield; Bright yellow solid; m.p. 166-167 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.41-7.33 (m, 5H), 7.07-7.02 (m, 3H), 6.98-6.89 (m, 4H), 6.87-6.86 (m, 2H), 6.65 (dd, *J* = 8.0 Hz, 2.0Hz, 1H), 4.78 (s, 1H), 3.75 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ 198.5, 161.4, 160.6, 146.8, 143.7, 142.8, 137.4, 134.9, 134.3, 133.6, 129.4, 128.8, 128.6, 128.0, 127.8, 127.3, 125.6, 122.0, 121.3, 118.9, 112.9, 111.5, 107.9, 80.8, 55.5 ppm. ESI HRMS: calcd. for $C_{29}H_{21}NO_2$+H 416.1651, found 416.1653.

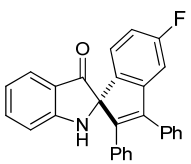


5-methyl-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (**3ca**). 10 min, 91% yield; Bright yellow solid; m.p. 206-207 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.43-7.35 (m, 5H), 7.12 (s, 1H), 7.10-7.02 (m, 3H), 7.00-6.98 (m, 2H), 6.93-6.90 (m, 3H), 6.89 (t, *J* = 7.6 Hz, 1H), 4.79 (s, 1H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz,

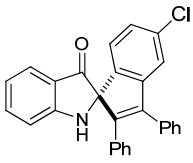
$CDCl_3$): δ 198.4, 161.4, 145.3, 144.0, 141.8, 140.2, 138.7, 137.4, 134.5, 133.7, 129.4, 128.8, 128.6, 128.0, 127.8, 127.2, 127.1, 125.7, 122.3, 122.1, 120.3, 119.0, 112.9, 81.1, 21.6 ppm. ESI HRMS: calcd. for $C_{29}H_{21}NO_5$+H 400.1701, found 400.1703.



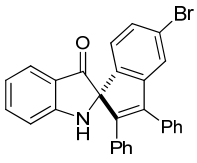
2,3-diphenyl-5-(trifluoromethyl)spiro[indene-1,2'-indolin]-3'-one (3da). 15 min, 77% yield; Yellow solid; m.p. 223-224 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 1H), 7.54-7.51 (m, 2H), 7.41 (brs, 6H), 7.17 (d, J = 7.6 Hz, 1H), 7.13-7.05 (m, 3H), 7.00-6.90 (m, 4H), 4.87 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 161.3, 146.8, 145.9, 143.4, 143.1, 137.9, 133.5, 132.9, 131.0, 129.3, 128.9, 129.1, 128.8, 128.3, 128.2, 127.8, 125.8, 123.5 (q, J_{CF} = 4.0 Hz), 121.9, 120.8, 119.4, 118.1(q, J_{CF} = 3.6 Hz), 113.0, 81.1 ppm. ESI HRMS: calcd. for $C_{29}H_{19}F_3NO$+H 454.1419, found 454.1420.



5-fluoro-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ea). 10 min, 78% yield; Yellow solid; m.p. 215-216 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.39-7.35 (m, 5H), 7.10-6.87 (m, 9H), 6.80 (td, J = 9.2 Hz, 2.4 Hz, 1H), 4.81 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 164.8, 162.4, 161.3, 147.5 (d, J_{CF} = 9.1 Hz), 143.3 (d, J_{CF} = 42.4 Hz), 138.4, 137.7, 133.8, 133.2, 129.3, 128.8, 128.1, 127.6, 125.8, 121.9, 121.7 (d, J_{CF} = 9.1 Hz), 119.2, 113.0, 112.9 (d, J_{CF} = 20.9 Hz), 109.1 (d, J_{CF} = 24.6 Hz), 80.7 ppm. ESI HRMS: calcd. for $C_{28}H_{18}FNO$+H 404.1451, found 404.1450.

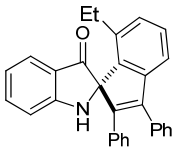


5-chloro-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3fa). 10 min, 71% yield; Bright yellow solid; m.p. 230-231 °C; ^{1}H NMR (400 MHz, CDCl3): δ 7.70 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.38-7.35 (m, 5H), 7.27-7.25 (m, 1H), 7.10-7.03 (m, 4H), 6.98-6.87 (m, 5H), 4.81 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 161.3, 147.0, 143.2, 143.1, 141.3, 137.7, 134.8, 133.7, 133.1, 129.3, 128.8, 128.8, 128.1, 127.6, 126.2, 125.8, 121.9, 121.8, 121.6, 119.2, 113.0, 80.9 ppm. ESI HRMS: calcd. for $C_{28}H_{18}ClNO$+H 420.1155, found $C_{28}H_{19}{}^{35}Cl_2N$+H 420.1154, $C_{28}H_{19}{}^{37}Cl_2N$+H 422.1104.

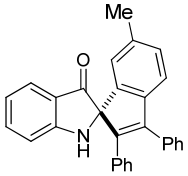


5-bromo-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ga). 10 min, 78% yield; Pale yellow solid; m.p. 231-232 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.42-7.37 (m, 6H), 7.26-7.24 (m, 1H), 7.09-7.03 (m, 3H), 6.98-6.88 (m, 5H), 4.81 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 161.3, 147.3, 143.1, 143.0,

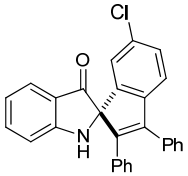
141.9, 137.7, 133.7, 133.1, 129.3, 129.1,128.8, 128.8, 128.1, 127.7, 125.8,124.6, 122.8, 122.0, 121.9, 119.3, 113.0, 80.9 ppm. ESI HRMS: calcd. for $C_{28}H_{18}BrNO+H$ 464.0650, found $C_{28}H_{19}{}^{79}BrNO+H$ 464.0653, $C_{28}H_{19}{}^{81}BrNO+H$ 466.0621.



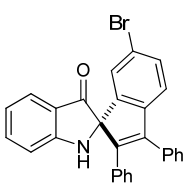
7-ethyl-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ha). 10 min, 90% yield; Yellow solid; m.p. 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.33-7.28 (m, 6H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.07-7.02 (m, 2H), 7.00-6.96 (m, 4H), 6.84-6.80 (m, 2H), 4.80 (s, 1H), 2.36-2.30 (m, 2H), 1.06 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0, 160.6, 145.7, 144.2, 142.5, 140.3, 140.0, 137.5, 134.2, 133.4, 129.5, 129.1, 128.9, 128.3, 127.9, 127.6, 127.3, 127.2, 124.8, 123.7, 119.0, 118.6, 112.6, 81.6, 24.5, 15.1 ppm. ESI HRMS: calcd. for $C_{30}H_{23}NO+H$ 414.1858, found 414.1857.



6-methyl-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ia). 10 min, 72% yield; Yellow solid; m.p. 99-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.43-7.33 (m, 5H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.11-7.02 (m, 4H), 6.99-6.96 (m, 3H), 6.92-6.88 (m, 2H), 4.81 (s, 1H), 2.28 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ 198.4, 161.4, 144.0, 143.4, 142.6, 140.6, 137.5, 136.6, 134.5, 133.7, 129.4, 129.3, 128.8, 128.6, 128.0, 127.8, 127.2, 125.7, 122.2, 121.4, 121.3, 119.0, 113.0, 81.2, 21.4 ppm. ESI HRMS: calcd. for $C_{29}H_{21}NO+H$ 400.1701, found 400.1703.

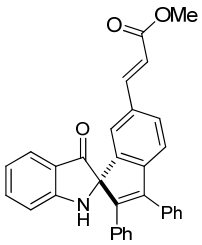


6-chloro-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ja). 20 min, 83% yield; Yellow solid; m.p. 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.38-7.34 (m, 5H), 7.28-7.21 (m, 2H), 7.11-7.03 (m, 4H), 6.98-6.89 (m, 4H), 4.83 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 161.3, 144.8, 143.6, 143.2, 141.9, 137.8, 133.9, 133.2, 132.2, 129.3, 128.7, 128.7, 128.1, 128.1, 127.5, 125.8, 122.3, 121.8, 121.2, 119.3, 113.0, 81.0 ppm. ESI HRMS: calcd. for $C_{28}H_{18}ClNO+H$ 420.1155, found $C_{28}H_{19}{}^{35}ClNO+H$ 420.1156, $C_{28}H_{19}{}^{37}ClNO+H$ 422.1105.

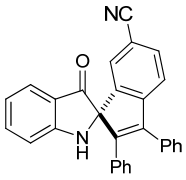


6-bromo-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ka). 20 min, 70% yield; Yellow solid; m.p. 186-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.44-7.35 (m, 6H), 7.19-7.17 (m, 2H), 7.10-7.03 (m, 3H), 6.99-6.90 (m, 4H), 4.84 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 161.2, 145.0, 144.1, 143.2, 141.9,

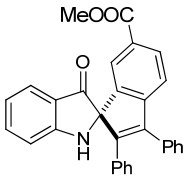
137.8, 133.8, 133.1, 131.6, 129.3, 128.7, 128.1,128.1, 127.5, 125.8, 123.9, 122.7, 121.8, 120.1, 119.3, 113.0, 80.9 ppm. ESI HRMS: calcd. for $C_{28}H_{18}BrNO+H$ 464.0650, found $C_{28}H_{19}{}^{79}BrNO+H$ 464.0646, $C_{28}H_{19}{}^{81}BrNO+H$ 466.0639.



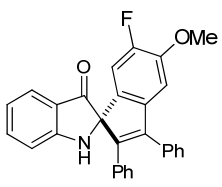
(R,E)-methyl 3-(3'-oxo-2,3-diphenylspiro[indene-1,2'-indolin]-6-yl)acrylate (alkenylation of 3ka).To a stirred solution of **3ka** (7.0 mg, 0.015mmol, 1.0equiv), palladium acetate (0.5 mg, 0.0023 mmol) and triphenyl phosphine (2.0 mg, 0.0075 mmol) in DMF (1.0 mL) was added methyacrylate（3.0 μL, 0.033 mmol）and N,N-Diisopropylethylamine (8.0 μL, 0.045 mmol) under argon atmosphere at 110 °C. The reaction mixture was stirred for 20 h and then washed with water and extacted with DCM. After removal of the solvent by concentration, the residue was purified by flash chromatography on silica gel eluting with ethyl acetate and petroleum ether (1:10) to afford **alkenylation of 3ka** as a yellow solid (3.2 mg, 45%); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 15.6 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.40-7.36 (m, 5H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.23 (s, 1H), 7.11 (t, *J* = 6.6 Hz, 1H), 7.06 (t, *J* = 8.4 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 3H),6.94 (t, *J* = 7.8 Hz, 1H), 6.30 (d, *J* = 15.6 Hz, 1H), 4.84(s,1H), 3.76 (s, 3H) ppm.



3'-oxo-2,3-diphenylspiro[indene-1,2'-indoline]-6-carbonitrile (3la). 6 h, 71% yield; Yellow solid; m.p. 122-124 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.60-7.54 (m, 2H), 7.42-7.32 (m, 7H), 7.15-7.06 (m, 3H), 7.00-6.93 (m, 4H), 4.87 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 161.2, 149.6, 145.6, 143.9, 143.0, 138.1, 133.3, 133.2, 132.5, 129.3, 128.9, 128.7, 128.4, 128.2, 128.1, 126.0, 123.8, 121.8, 121.7, 119.7, 119.0, 113.1, 109.2, 81.0 ppm. ESI HRMS: calcd. for $C_{29}H_{18}N_2O+H$ 411.1497, found 411.1489.

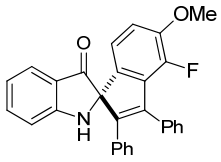


(R)-methyl 3'-oxo-2,3-diphenylspiro[indene-1,2'-indoline]-6-carboxylate (3ma). 10 min, 67% yield; Yellow solid; m.p. 140-141 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.73-7.71 (m, 2H), 7.53 (t, *J* = 8.4 Hz, 1H), 7.40-7.35 (m, 6H), 7.11-7.04 (m, 3H), 7.01-6.96 (m, 3H), 6.91 (t, *J* = 7.6 Hz, 1H), 4.89 (s, 1H), 3.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 166.9, 161.4, 149.8, 145.1, 143.4, 143.2, 137.8, 133.8, 133.1, 130.8, 129.4, 128.8, 128.7, 128.1, 128.1 128.0, 127.8, 125.8, 122.0, 121.6, 121.1, 119.3, 113.1, 81.1, 52.1 ppm. ESI HRMS: calcd. for $C_{30}H_{21}NO_3+H$ 466.1419, found 466.1416.

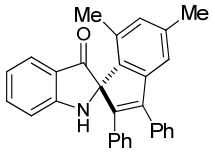


4-fluoro-5-methoxy-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3na). 50 min,

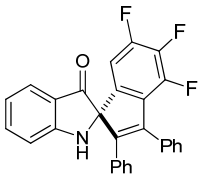
23% yield; Yellow solid; m.p. 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.42-7.37 (m, 5H), 7.09-7.03 (m, 3H), 6.96-6.89 (m, 5H), 6.84 (d, *J* = 10.0 Hz, 1H), 4.84 (s, 1H), 3.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 161.3, 152.7, 150.3, 148.2, 143.2, 142.1, 141.2, 137.7, 134.9, 134.2, 133.3, 129.3, 128.8, 128.7, 128.1, 128.0, 127.4, 125.7, 121.8, 119.2, 112.9, 109.3 (d, J_{CF} = 20.8 Hz), 106.9, 80.8, 56.6 ppm. ESI HRMS: calcd. for $C_{29}H_{20}FNO_2$+Na 456.1376, found 456.1377



6-fluoro-5-methoxy-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3na'). 50 min, 46% yield; Yellow solid; m.p. 220-222 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.40-7.40 (m, 2H), 7.31-7.30 (m, 3H), 7.09-7.00 (m, 3H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.90-6.85 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.68 (t, *J* = 8.0 Hz, 1H), 4.88 (s, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.7, 162.7, 148.5 (d, J_{CF} = 10.1 Hz), 147.2, 144.7, 144.3, 140.6, 138.3, 135.9, 134.8, 133.4, 131.3 (d, J_{CF} = 8.3 Hz), 129.4, 128.8, 128.4, 128.2, 128.1, 127.8, 125.2, 120.2, 117.8, 116.8, 112.7, 111.7, 81.0, 56.7 ppm. ESI HRMS: calcd. for $C_{29}H_{20}FNO_2$+Na 456.1376, found 456.1377.

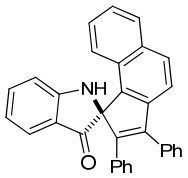


5,7-dimethyl-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3oa). 20 min, 72% yield; Yellow solid; m.p. 283-285 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.88 (s, 1H), 7.47-7.43 (m, 2H), 7.41-7.37 (m, 2H), 7.35-7.33 (m, 1H), 7.27-7.25 (m, 2H), 7.08-7.07 (m, 3H), 7.00-6.97 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 11.2 Hz, 2H), 6.67 (t, *J* = 7.6 Hz, 1H), 2.28 (s, 3H), 1.90 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.5, 162.1, 145.8, 143.1, 143.1, 138.2, 138.2, 138.0, 134.2, 133.9, 133.0, 129.5, 129.2, 129.0, 128.9, 128.1, 128.0, 127.6, 124.1, 122.2, 119.1, 117.2, 112.6, 81.4, 21.2, 17.2 ppm. ESI HRMS: calcd. for $C_{30}H_{23}NO$+Na 436.1677, found 436.1673.

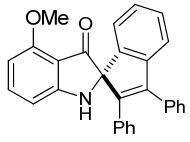


4,5,6-trifluoro-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3pa). 5 h, 80% yield; Yellow solid; m.p. 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* =8.0 Hz, 1H), 7.37-7.36 (m, 2H), 7.32-7.31 (m, 3H), 7.10-7.00 (m, 3H), 6.93-6.88 (m, 4H), 6.74-6.70 (m, 1H), 4.87 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 161.2, 151.2 (d, J_{CF} = 10.2 Hz), 148.7 (d, J_{CF} = 11.9 Hz), 146.8 (dd, J_{CF} = 15.0 Hz, 2.2 Hz), 144.2 (dd, J_{CF} = 9.1 Hz, 3.5 Hz), 143.4 (d, J_{CF} = 3.9 Hz), 141.9 (t, J_{CF} = 15.8 Hz), 140.6 (d, J_{CF} = 2.4 Hz), 139.4 (t, J_{CF} = 15.4 Hz), 138.5 (dd, J_{CF} = 7.5 Hz, 4.0 Hz), 138.1, 133.8, 132.5, 129.5, 129.5, 128.8, 128.1, 128.1, 127.8, 125.9, 121.3, 119.6, 112.9, 105.6 (dd, J_{CF} = 19.7 Hz, 3.6 Hz), 81.1 ppm. ESI HRMS: calcd. for

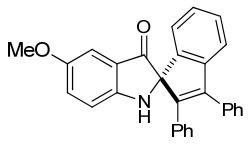
$C_{28}H_{17}F_3NO$+H 440.1262, found 440.1265.



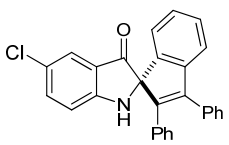
2,3-diphenylspiro[cyclopenta[a]naphthalene-1,2'-indoline] (3qa). 1 d, 20% yield; Yellow solid; m.p. 151-152 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.56-7.50 (m, 2H), 7.43-7.25 (m, 9H), 7.08-7.02 (m, 4H), 6.94-6.88 (m, 2H), 5.02 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2 , 160.9，144.2，143.6，143.2, 137.8，137.5，134.1，133.3, 133.0，129.6，129.6, 129.2，128.5, 128.0，127.8 , 127.4，127.2, 125.5，125.0，123.3，122.8, 119.8, 119.0, 113.0, 82.0 ppm. ESI HRMS: calcd. for $C_{32}H_{21}NO$+H 436.1701, found 436.1702.



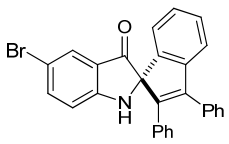
4'-methoxy-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ra). 10 min, 80% yield; Yellow solid; m.p. 209-212 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.25 (m, 8H), 7.11-7.05 (m, 7H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 4.82 (s, 1H), 3.92 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.9, 162.9, 159.5, 145.1, 144.0, 143.4, 141.8, 139.1, 134.4, 133.7, 129.5, 128.9, 128.6, 128.5, 128.0, 127.7, 127.2, 126.3, 121.4, 120.7, 111.0, 104.8, 100.2, 81.6, 55.8 ppm. ESI HRMS: calcd. for $C_{29}H_{21}NO_2$+H 416.1651, found 416.1649.



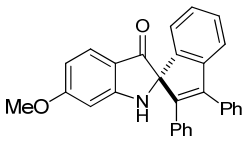
5'-methoxy-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3sa). 10 min, 76% yield; Bright yellow solid; m.p. 221-222 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.25 (m, 7H), 7.21-7.00 (m, 9H), 6.93 (d, *J* = 8.8 Hz, 1H), 4.58 (s, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 157.2, 153.5, 145.2, 143.8, 143.4, 141.7, 134.4, 133.6, 129.4, 128.8, 128.7, 128.6, 128.0, 127.8, 127.3, 126.5, 122.6, 121.5, 120.4, 114.6,105.6, 82.3, 55.8 ppm. ESI HRMS: calcd. for $C_{29}H_{21}NO_2$+H 416.1651., found 416.1649.



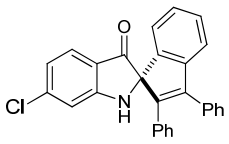
5'-chloro-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ta). 10 min, 70% yield; Brown solid; m.p. 73-75 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 2.0 Hz, 1H), 7.44-7.29 (m, 8H), 7.15-7.11 (m, 1H), 7.09-7.05 (m, 4H), 6.96 (d, *J* = 6.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.84 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 159.6,145.1, 144.2, 142.6, 141.1, 137.4, 134.1, 133.4, 129.4, 128.9, 128.7, 128.6, 128.1, 127.9, 127.5, 126.6, 124.9, 124.4, 123.0, 121.7, 120.5, 114.0, 81.9 ppm. ESI HRMS: calcd. for $C_{28}H_{18}ClNO$+H 420.1155, found $C_{28}H_{19}{}^{35}ClNO$+H 420.1153, $C_{28}H_{19}{}^{37}ClNO$+H 422.1103.



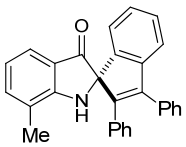
5'-bromo-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3ua). 10 min, 65% yield; Yellow solid; m.p. 85-87 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 1.6 Hz, 1H), 7.55 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.41-7.28 (m, 7H), 7.15-7.03 (m, 5H), 6.97-6.94 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.85 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 159.9, 145.1, 144.3, 142.6, 141.1, 140.0, 134.1, 133.4, 129.4, 129.0, 128.7, 128.6, 128.1, 128.1, 128.0, 127.5, 126.6, 123.5, 121.7, 120.6, 114.4, 111.3, 81.8 ppm. ESI HRMS: calcd. for $C_{28}H_{18}BrNO$+H 464.0650, found $C_{28}H_{19}{}^{79}BrNO$+H 464.0651, $C_{28}H_{19}{}^{81}BrNO$+H 466.0642.



6'-methoxy-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3va). 10 min, 79% yield; Bright yellow solid; m.p. 216-218 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 1H), 7.43-7.26 (m, 8H), 7.15-7.00 (m, 6H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.33 (s, 1H), 4.81 (s, 1H), 3.85 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 167.8, 163.7, 145.0, 143.8, 143,5, 141.8, 134.4, 133.7, 129.5, 128.8, 128.6, 128.6, 128.0, 127.8, 127.2, 127.1, 126.4, 121.4, 120.6, 115.6, 108.7, 95.2, 81.8, 55.6 ppm. ESI HRMS: calcd. for $C_{29}H_{21}NO_2$+H 416.1651, found 416.1649.



6'-chloro-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3wa). 10 min, 79% yield; Yellow solid; m.p. 175-176 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.40-7.27 (m, 7H), 7.15-7.11 (m, 1H), 7.09-7.03 (m, 4H), 6.97-6.95 (m, 2H), 6.90 (s, 1H), 6.83 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 4.88 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 161.6, 145.0, 144.2, 144.0, 142.7, 141.1, 134.1, 133.4, 129.4, 128.9, 128.7, 128.6, 128.1, 127.9, 127.4, 126.6, 126.5, 121.6, 120.6, 120.4, 119.8, 112.7, 81.6 ppm. ESI HRMS: calcd. for $C_{28}H_{18}ClNO$+H 420.1155, found $C_{28}H_{19}{}^{35}ClNO$+H 420.1153, $C_{28}H_{19}{}^{37}ClNO$+H 422.1103.

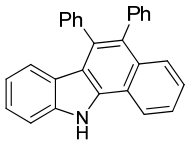


7'-methyl-2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3xa). 19 h, 89% yield; Bright yellow solid; m.p. 199-200 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.43-7.25 (m, 8H), 7.15-7.11 (m, 1H), 7.07-7.00 (m, 6H), 6.83 (t, *J* = 7.6 Hz, 1H), 4.67 (s, 1H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 160.7, 145.2, 144.0, 143.4, 141.7, 137.4, 134.4, 133.6, 129.4, 128.8, 128.7, 128.6, 128.0, 127.8, 127.2, 126.5, 123.1, 122.0, 121.7, 121.5, 120.5, 119.1, 81.6, 15.7 ppm. ESI HRMS: calcd. for $C_{29}H_{21}NO$+H 400.1701, found 400.1690.

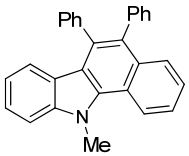
11. General Procedure of Masked [4+2] Annulation for the Synthesis of Benzo[*a*]carbazole Derivatives and Characterization Data

3a (38.5 mg, 0.1 mmol) in dioxane (6.0 mL) was added LiBr (34.8 mg, 0.4 mmol), then $NaBH_4$ (80 mg, 2.1

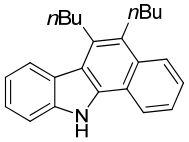
mmol) was added partially to the reaction mixture at room temperature. 0.35 mL of HCl (conc.) was added into the reaction mixture after the consuming of **3a**, and then the reaction was stirred at 50 °C for another 5 minutes. The reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:20) to give the product **4a** as a white solid (29.2 mg, 79%).



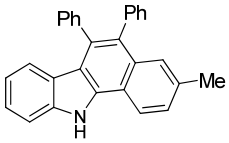
5,6-diphenyl-11*H*-benzo[*a*]carbazole (4a). 14 h, 79% yield; Off white solid; m.p. 202-203 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.58-7.50 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.34-7.19 (m, 11H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 139.2, 138.7. 134.8, 134.3, 131.9, 131.7, 130.9, 130.2, 128.2, 127.9, 127.5, 126.8, 126.3, 125.5, 125.2, 124.6, 124.3, 121.9,120.3, 120.2, 119.7, 117.3, 110.8 ppm. ESI HRMS: calcd. for $C_{29}H_{20}FNO_2$+H 372.1752, found 372.1737.



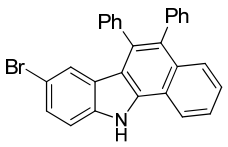
11-methyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole (Methylation of 4a). Off white solid; ^{1}H NMR (400 MHz, CDCl3): δ 8.80 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.58 (dt, J = 7.2 Hz, 1.6 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.44-7.36 (m, 2H), 7.30-7.17 (m, 10H), 6.93 (t, J = 7.2 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 4.43 (s, 3H) ppm.



5,6-dibutyl-11*H*-benzo[*a*]carbazole (4b). 10 h, 56% yield; Off white solid; m.p. 134-135 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.62-7.52 (m, 3H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 3.41 (t, *J* = 8.4 Hz, 2H), 3.22 (t, *J* = 8.0 Hz, 2H), 1.91-1.83 (m, 2H), 1.79-1.60 (m, 6H), 1.13-1.07 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm. 138.6, 134.0, 125.3, 125.3, 124.1, 124.1, 122.1, 120.8, 120.1, 119.8, 111.0, 33.8, 32.3, 30.5, 27.7, 23.4, 23.4, 14.1, 14.1 ppm. ESI HRMS: calcd. For $C_{24}H_{27}N$+H 330.2222, found 330.2211.

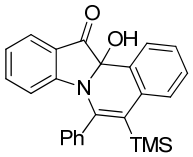


3-methyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole (4c). 16 h, 67% yield; Off white solid; m.p. 242-243 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.31 (s, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.33-7.17 (m, 12H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.3, 139.4, 139.2, 135.0, 134.9, 134.7, 131.8, 131.5, 130.0, 129.1, 128.1, 127.8, 127.3, 127.0, 126.6, 126.4, 126.4, 124.2, 123.5, 122.2, 120.9, 118.9, 115.7, 111.4, 22.0 ppm. ESI HRMS: calcd. for $C_{29}H_{23}N$+H 386.1909, found 386.1927.

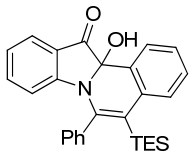


8-bromo-5,6-diphenyl-11*H*-benzo[*a*]carbazole (4d). 16 h, 73% yield; Off white solid; m.p. 231-232 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.63 (s, 1H), 8.63 (d, *J* = 7.2 Hz, 1H), 7.69-7.59 (m, 2H), 7.50-7.18 (m, 13H), 6.52 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 139.7, 139.0, 138.0, 135.6, 134.3, 131.6, 130.0, 129.9, 128.3, 127.8, 127.3, 127.3, 126.8, 126.7, 126.3, 125.7, 125.2, 123.4, 123.3, 122.2, 120.7, 115.5, 113.5, 111.2 ppm. ESI HRMS: calcd. for $C_{28}H_{20}BrN$+H 450.0857, found 450.0857.

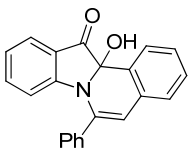
12. Derivatization of Special Indoxyl Core 5a and Characterization Data



12*a*-hydroxy-6-phenyl-5-(trimethylsilyl)indolo[2,1-*a*]isoquinolin-12(12*a*H)-one (5a). 40 min, 32% yield; Yellow solid; m.p. 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.66-7.59 (m, 3H), 7.54-7.50 (m, 3H), 7.45-7.36 (m, 2H), 7.25-7.23 (m, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 5.68 (d, *J* = 8.4 Hz, 1H), 2.98 (s, 1H), 0.03 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 154.4, 143.5, 138.0, 137.8, 137.7, 130.7, 130.4, 130.0, 129.1, 128.5, 128.4, 127.5, 125.7, 125.0, 124.3, 120.9, 119.7, 117.8, 113.2, 83.7, 1.96 ppm. ESI HRMS: calcd. for $C_{25}H_{23}NO_2Si$+Na 420.1396, found 420.1396.

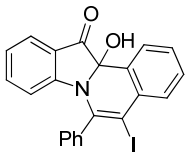


12*a*-hydroxy-6-phenyl-5-(triethylsilyl)indolo[2,1-*a*]isoquinolin-12(12*a*H)-one (5b). 5 h, 16% yield; Yellow solid; m.p. 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.2 Hz, 1H), 7.68-7.61 (m, 3H), 7.56-7.50 (m, 3H), 7.44-7.35 (m, 2H), 7.29-7.23 (m, 1H), 7.09-7.05 (m, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 5.65 (d, *J* = 8.4 Hz, 1H), 2.97 (s, 1H), 0.83 (t, *J* = 8.0 Hz, 9H), 0.58-0.44 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 154.3, 144.5, 138.4, 137.7, 137.6, 130.8, 130.4, 130.2, 129.1, 128.9, 128.4, 128.4, 127.2, 125.8, 124.9, 124.2, 120.9, 119.8, 115.6, 113.2, 84.0, 7.9, 5.8 ppm. ESI HRMS: calcd. for $C_{28}H_{29}NO_2Si$+Na 462.1865, found 462.1872.

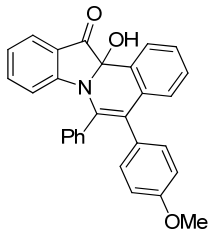


12*a*-hydroxy-6-phenylindolo[2,1-*a*]isoquinolin-12(12*a*H)-one (6). To a stirred solution of **5a** (12.9 mg, 0.03 mol, 1.0 equiv) was added TBAF (1.5 equiv) in THF (1.0 mL) at room temperature and stirred for 3 h. The reaction mixture was then concentrated in vacuum to remove the solvent and the residue was purified by flash chromatography on silica gel eluting with ethyl acetate and petroleum ether (1:20) to afford **6** as a yellow solid (9.4 mg, 90%); m.p. 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.75-7.73 (m, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.50-7.47 (m, 3H), 7.40-7.28 (m, 3H), 7.23-7.18 (m, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 6.10 (d, *J* =

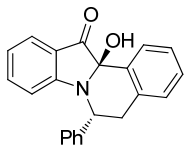
8.4 Hz, 1H), 3.08 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 155.5, 137.7, 137.5, 135.6, 132.5, 129.5, 129.3, 129.0, 128.6, 127.3, 127.1, 126.4, 125.1, 124.9, 120.9, 113.5, 112.4, 85.1 ppm. ESI HRMS: calcd. for $C_{22}H_{15}NO_2$+Na 348.1000, found 348.0995.



12*a*-hydroxy-5-iodo-6-phenylindolo[2,1-*a*]isoquinolin-12(12*aH*)-one (7). To a stirred solution of **5a** (13.1 mg, 0.03 mol, 1.0 equiv) in MeCN (1.0 mL) was added N-Iodosuccinimide (20.1 mg, 0.09 mmol) in darkness. The solution was stirred at room temperature for 2 hours. Then the reaction was quenched with $Na_2S_2O_3$ (aq. 2.0 mL) and the organic phase was dried over magnesium sulfate. Flash chromatography (ethyl acetate : petroleum ether = 1:20 to afford **7** as a yellow oil (10.9 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.79-7.74 (m, 3H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.52-7.46 (m, 4H), 7.35-7.32 (m, 1H), 7.15-7.11 (m, 1H), 6.32 (t, *J* = 7.2 Hz, 1H), 5.76 (d, *J* = 8.4 Hz, 1H), 3.25 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 154.4, 138.7, 138.0, 137.3, 134.9, 132.2, 130.9, 129.9, 129.8, 129.2, 128.6, 128.1, 125.1, 124.3, 121.4, 119.2, 113.1, 83.6, 82.8 ppm. ESI HRMS: calcd. for $C_{22}H_{14}INO_2Si$+H 473.9967, found 473.9968.

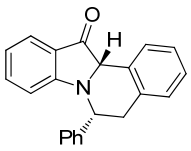


12*a*-hydroxy-5-(4-methoxyphenyl)-6-phenylindolo[2,1-*a*]isoquinolin-12(12*aH*)-one (8). To a 5.0 mL vial was added **7** (7.5 mg, 0.02 mmol, 1.0 equiv), 4-methoxyphenylboronic acid (9.2 mg, 0.06 mmol), Cs_2CO_3 (65.2 mg, 0.2 mmol) and $(Ph_3P)_4PdCl_2$ (0.7 mg, 0.001 mmol) under argon atmosphere. Then 1,4-dioxane (0.4 mL) and water (0.1 mL) were added and the mixture stirred for 1.5 h at 50 °C. Flash chromatography (ethyl acetate : petroleum ether = 1:20) to afford **8** as a yellow solid (5.0 mg, 70%); m.p. 170-171 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.98 (m, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.40-7.38 (m, 2H), 7.31-7.26 (m, 3H), 7.23-7.11 (m, 6H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 5.84 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.20 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 158.5, 155.6, 137.8, 135.5, 134.0, 133.7, 132.7, 130.2, 129.2, 128.3, 128.2, 127.1, 126.0, 126.0, 124.9, 124.8, 123.6, 120.6, 119.2, 113.7, 113.1, 84.0, 55.2 ppm. ESI HRMS: calcd. for $C_{29}H_{21}NO_3$+Na 454.1419, found 454.1413.

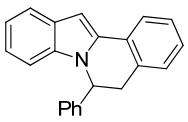


(6S)-12*a*-hydroxy-6-phenyl-5,6-dihydroindolo[2,1-*a*]isoquinolin-12(12*aH*)-one (9). To a stirred solution of **5a** (14.9 mg, 0.04 mmol, 1.0 equiv) in DCM (1.0 mL) was added 10 wt. Pd/C (30%, 4.5 mg) under hydrogenation atmosphere at room temperature. The reaction mixture was stirred for 5 h and then filtered. After removal of the solvent, the residue was purified by flash chromatography on silica gel eluting with ethyl acetate and petroleum ether (1:20) to afford **9** as a

yellow solid (6.4 mg, 52%); m.p. 139-141 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (t, *J* = 8.0 Hz, 3H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.36-7.25 (m, 5H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 4.44 (dd, *J* = 12.4 Hz, 4.8 Hz, 1H), 3.56-3.49 (m, 1H), 3.15 (s, 1H), 3.09 (dd, *J* = 15.2 Hz, 5.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 160.4, 142.9, 138.3, 137.0, 134.3, 129.1, 129.0, 128.1, 127.7, 126.8, 126.4, 125.1, 124.6, 119.5, 119.2, 110.8, 87.0, 60.7, 37.6 ppm. ESI HRMS: calcd. for $C_{22}H_{17}NO_2$+Na 350.1157, found 350.1145.

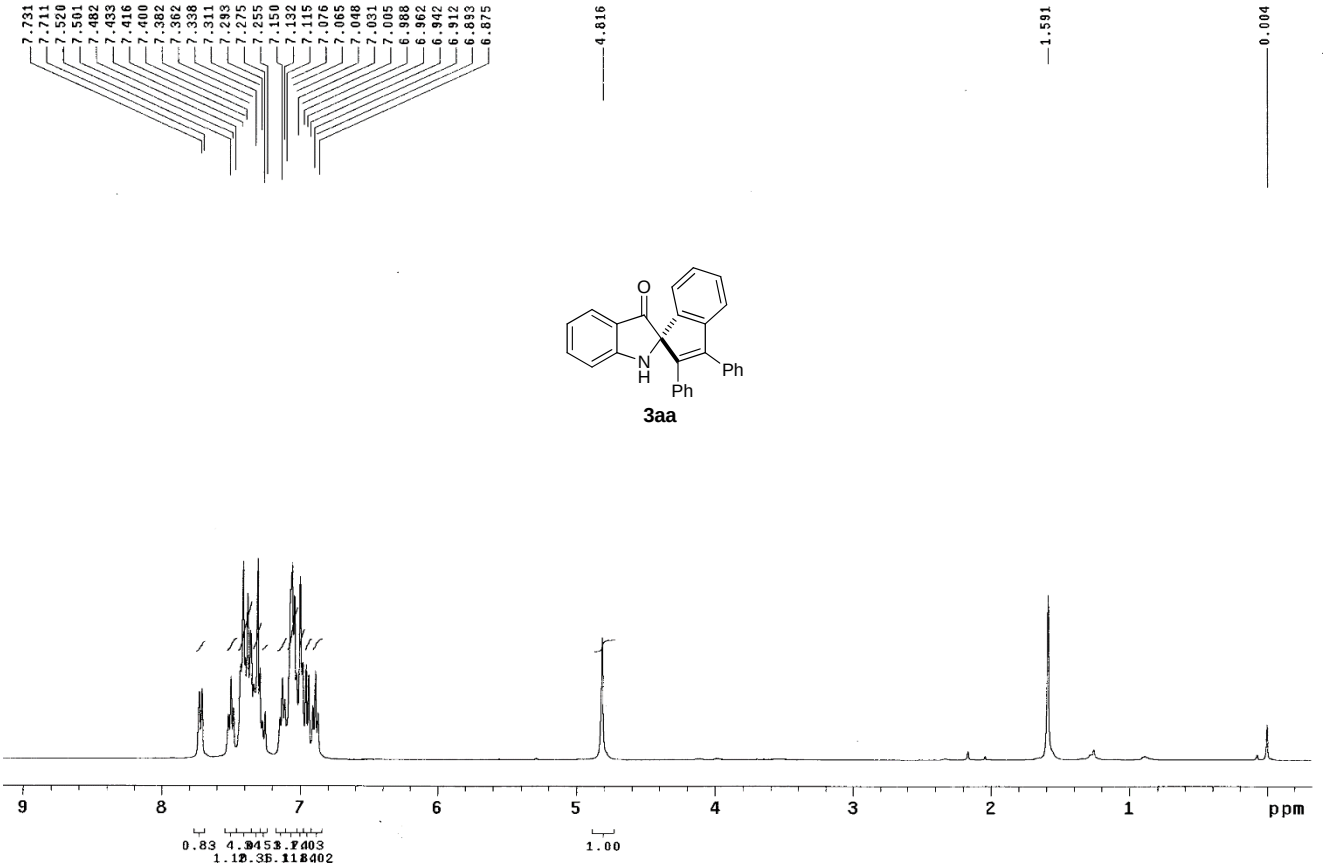


(6S,12*a*R)-6-phenyl-5,6-dihydroindolo[2,1-*a*]isoquinolin-12(12*aH*)-one (10). Under the same conditions, product **10** (39%) was also produced along with **9**. Yellow solid; m.p. 191-192 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.37 (m, 4H), 7.31-7.26 (m, 2H), 7.20-7.13 (m, 4H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.70 (t, *J* = 7.2 Hz, 1H), 4.99 (s, 1H), 4.04-3.93 (m, 2H), 3.23 (dd, *J* = 12.8 Hz, 5.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 160.8, 143.7, 142.4, 137.3, 136.9, 128.6, 128.3, 128.1, 127.1, 126.8, 125.7, 124.9, 121.9, 120.0, 119.2, 111.5, 80.2, 56.6, 34.6 ppm. ESI HRMS: calcd. for $C_{22}H_{17}NO$+Na 334.1208, found 334.1212.

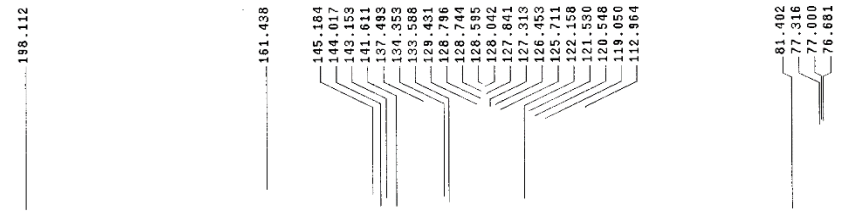


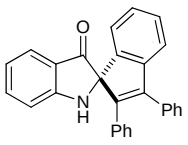
(S)-6-phenyl-5,6-dihydroindolo[2,1-*a*]isoquinoline (11). 0.025 mmol of **10** in dioxane (1.0 mL) was added of 0.1 mmol of LiBr, and then 0.6 mmol of $NaBH_4$ was added partially to the reaction mixture at room temperature. The reaction was stirred for 12 hours and poured into water. The mixture was extracted with ethyl acetate (3×3.0 mL) and the organic layer was dried over Na_2SO_4. After removal of the solvent, the crude intermediate was added $BF_3{\cdot}Et_2O$ (0.05 mmol) and $HSiEt_3$ (0.055 mmol) in DCM at room temperature. The reaction mixture was poured into $NaHCO_3$ (aq. 3.0 mL) and extracted with ethyl acetate (3×3.0 mL). The organic layer was dried over Na_2SO_4 and the residue was purified by flash chromatography on silica gel eluting with ethyl acetate and petroleum ether (1:20) to afford **11** as a white solid (5.8 mg, 78%); m.p. 142-143 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (brs, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.31-7.12 (m, 9H), 6.94-6.93 (m, 2H), 4.49-4.45 (m, 1H), 3.40 (dd, *J* = 15.6 Hz, 6.8 Hz, 1H), 3.23 (dd, *J* = 15.6 Hz, 8.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 137.1, 135.4, 133.4, 128.6, 128.4, 128.4, 128.0, 127.0, 126.8, 126.5, 122.3, 119.8, 119.8, 119.8, 114.9, 111.0 ppm. ESI HRMS: calcd. for $C_{22}H_{17}N$+H 296.1439, found 296.1442.

13. NMR Spectra of the Spirocycle Amines, Benzo[*a*]carbazoles, Special Indoxyl Cores and Other Derivatives

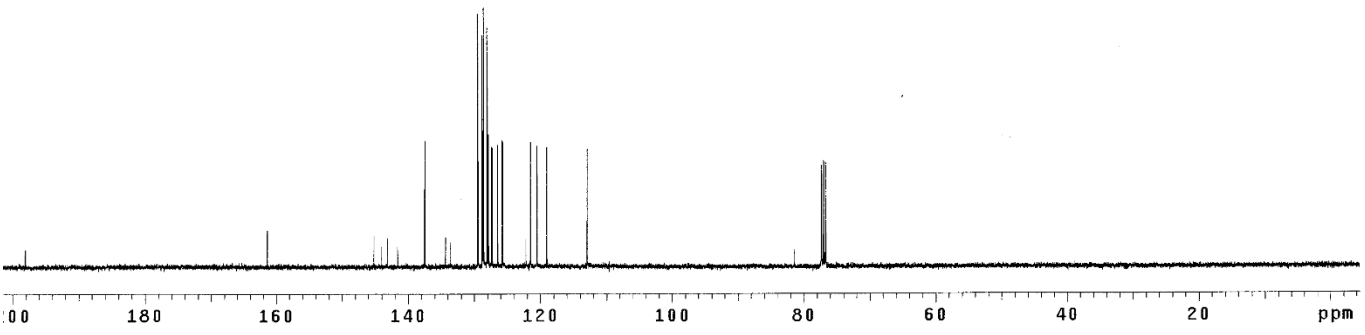


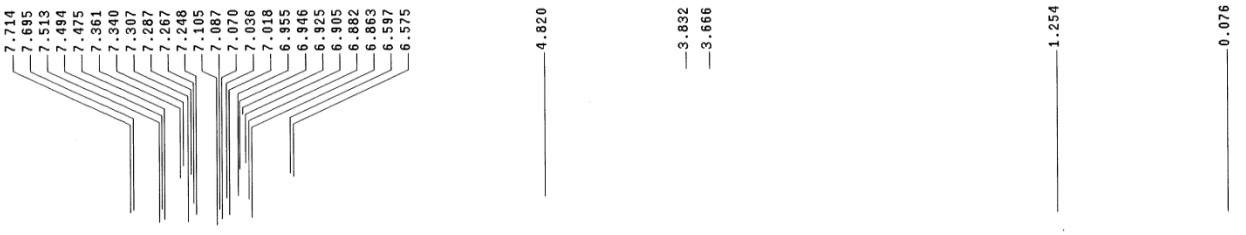
3aa





3aa

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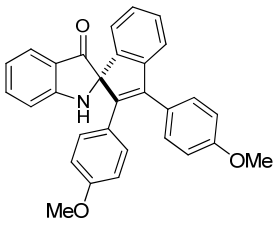
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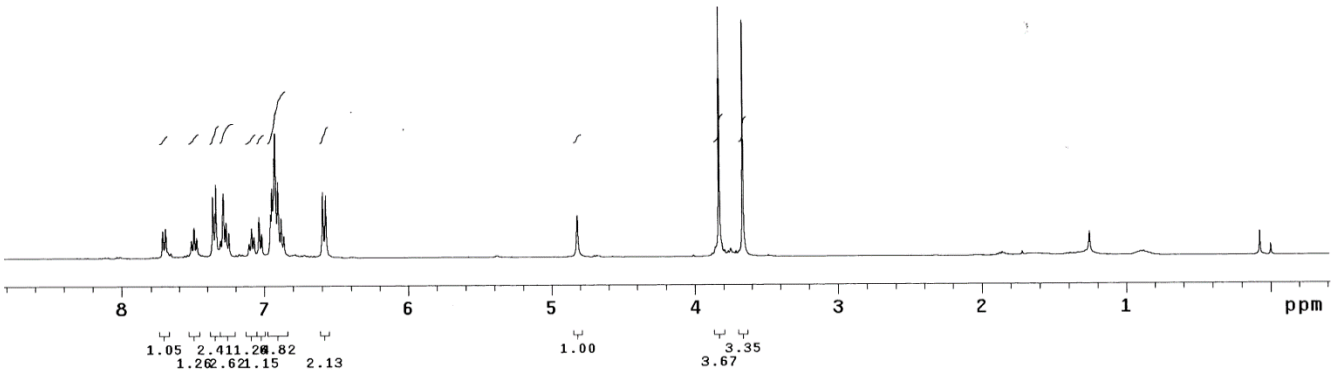
N
H
OMe
MeO

3ab


8
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ppm
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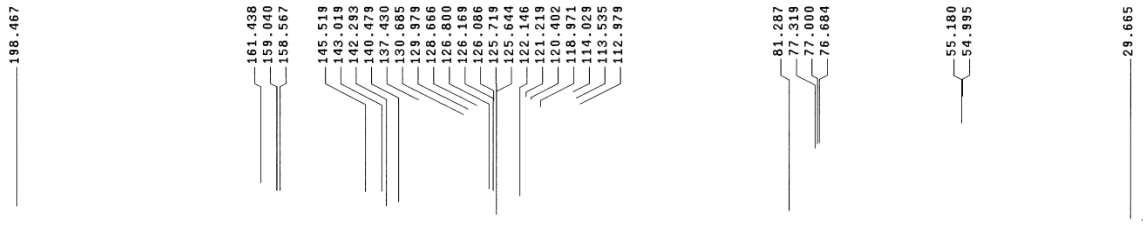
2.13
1.00
3.35
3.67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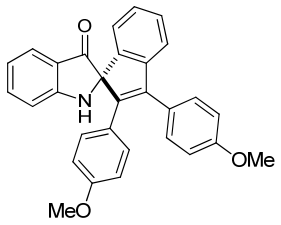
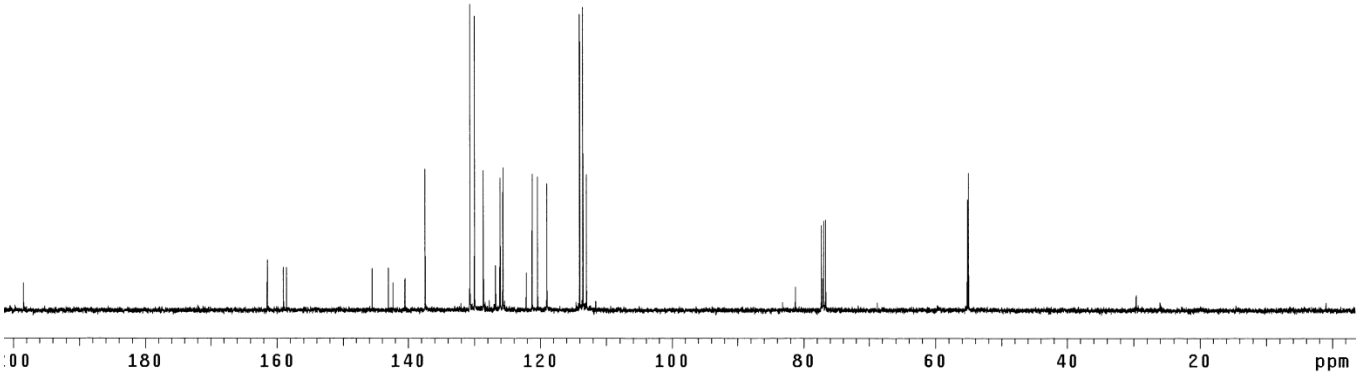
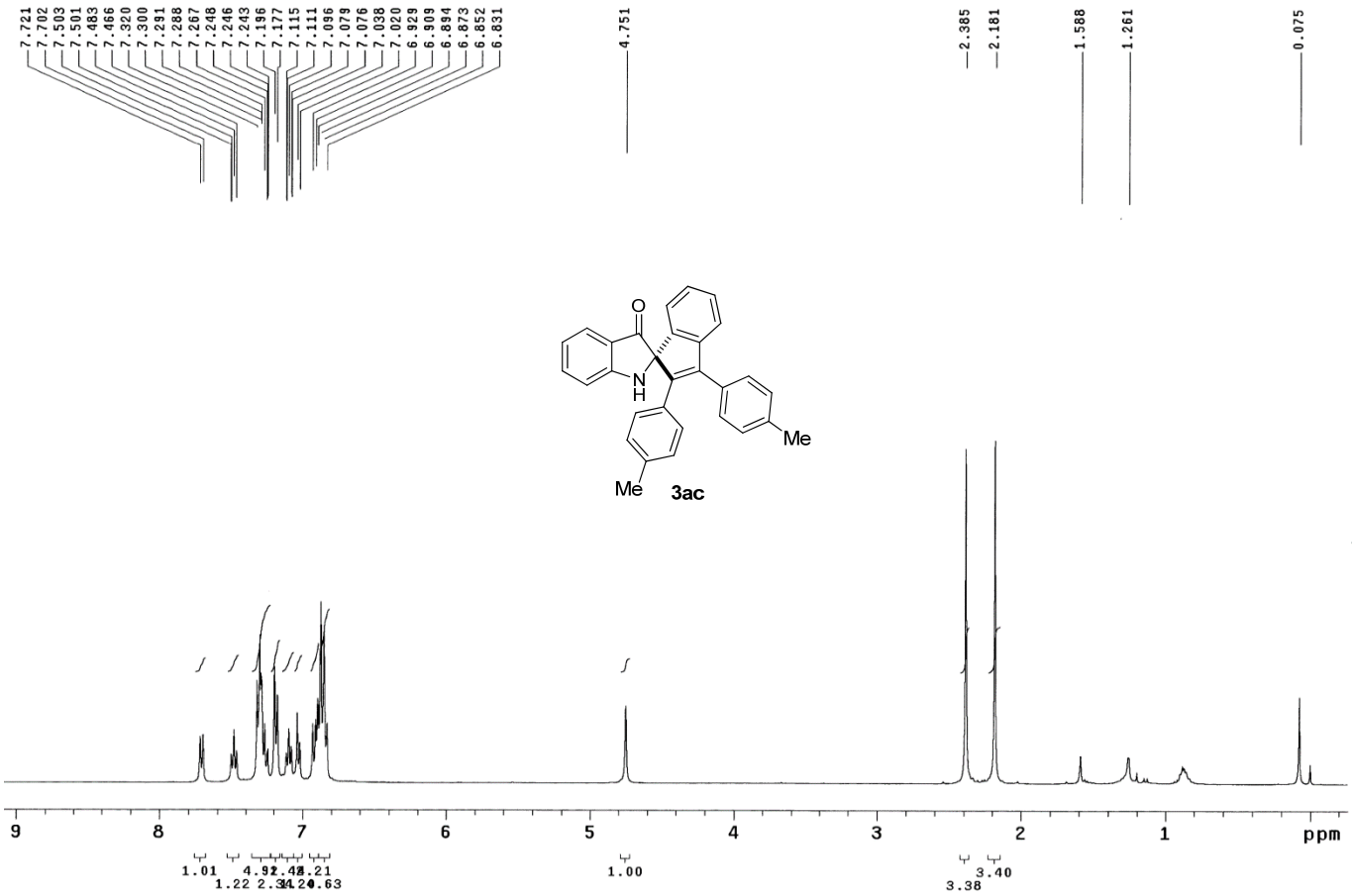
159.040
158.567
145.519
143.019
142.293
140.479
137.430
130.685
129.979
128.666
126.800
126.169
126.086
125.719
125.644
122.146
121.219
120.402
118.971
114.029
113.535
112.979
81.287
77.319
77.000
76.684
55.180
54.995
29.665


O
N
H
OMe
MeO

3ab


180
160
140
120
100
80
60
40
20
ppm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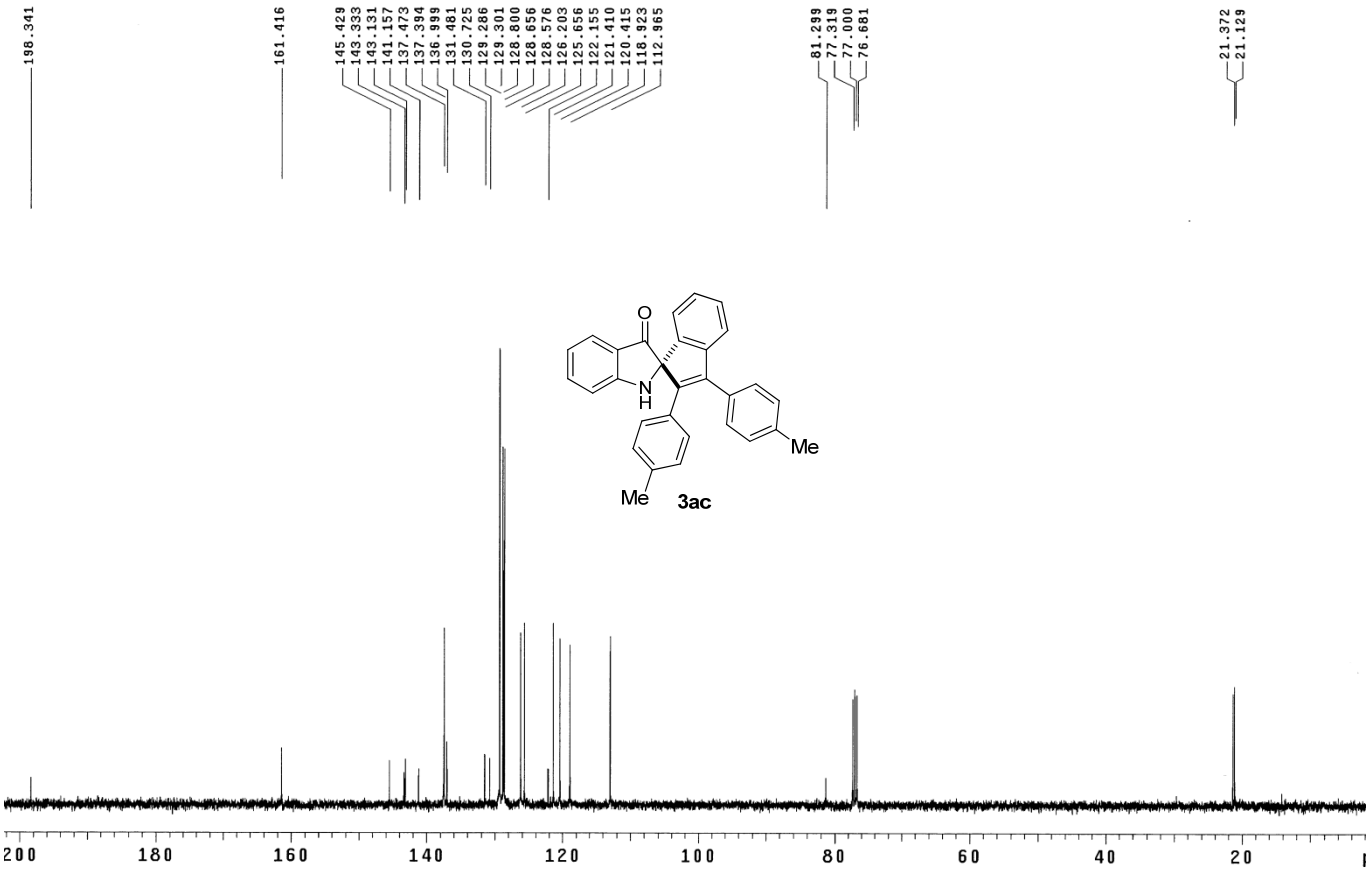
7.702
7.503
7.501
7.483
7.466
7.320
7.300
7.291
7.288
7.267
7.248
7.246
7.243
7.196
7.177
7.115
7.111
7.096
7.079
7.076
7.038
7.020
6.929
6.909
6.894
6.873
6.852
6.831
4.751
2.385
2.181
1.588
1.261
0.075
O
N
H
Me
Me
3ac
9
8
7
6
5
4
3
2
1
ppm
1.01
1.22
1.00
3.38
3.40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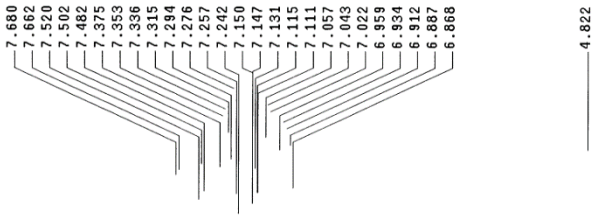
145.429
143.333
143.131
141.157
137.473
137.394
136.999
131.481
130.725
129.286
129.301
128.800
128.656
128.576
126.203
125.656
122.155
121.410
120.415
118.923
112.965
81.299
77.319
77.000
76.681
21.372
21.129
O
N
H
Me
Me
3ac
200
180
160
140
120
100
80
60
40
20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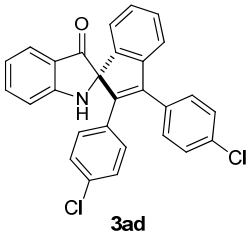
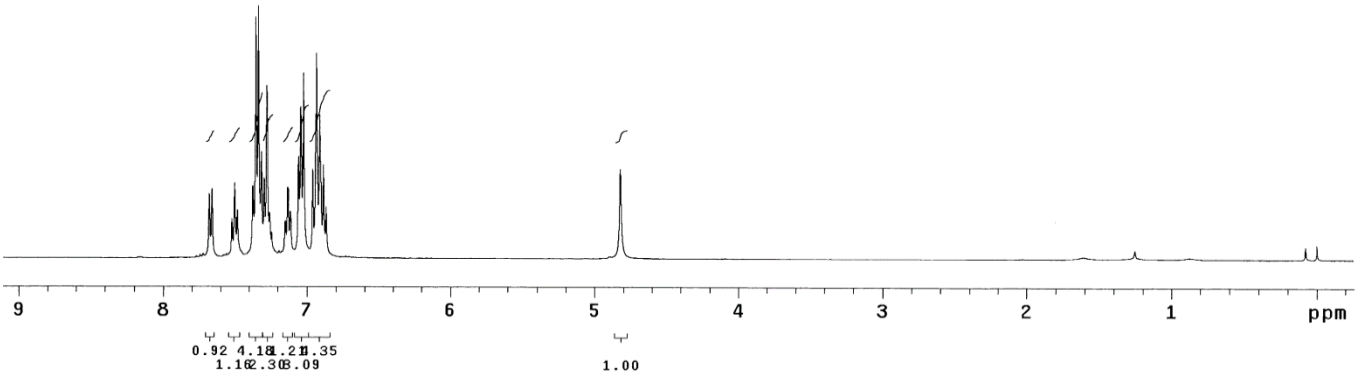
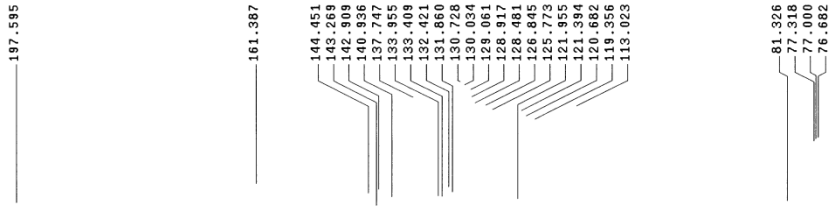
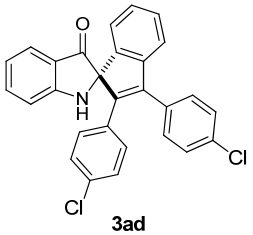
7.662
7.520
7.502
7.482
7.375
7.353
7.336
7.315
7.294
7.276
7.257
7.242
7.150
7.147
7.131
7.115
7.111
7.057
7.043
7.022
6.959
6.934
6.912
6.887
6.868
4.822


O
N
H
Cl
Cl

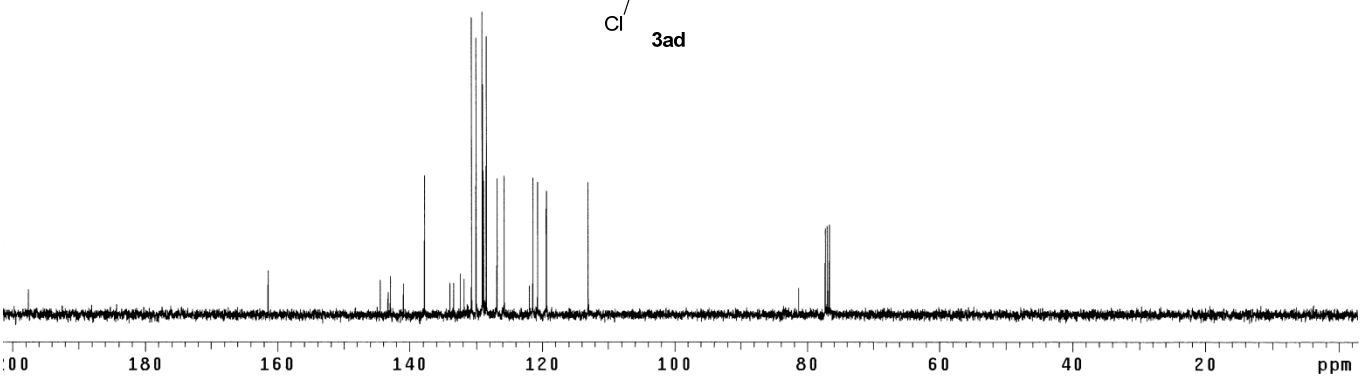
3ad

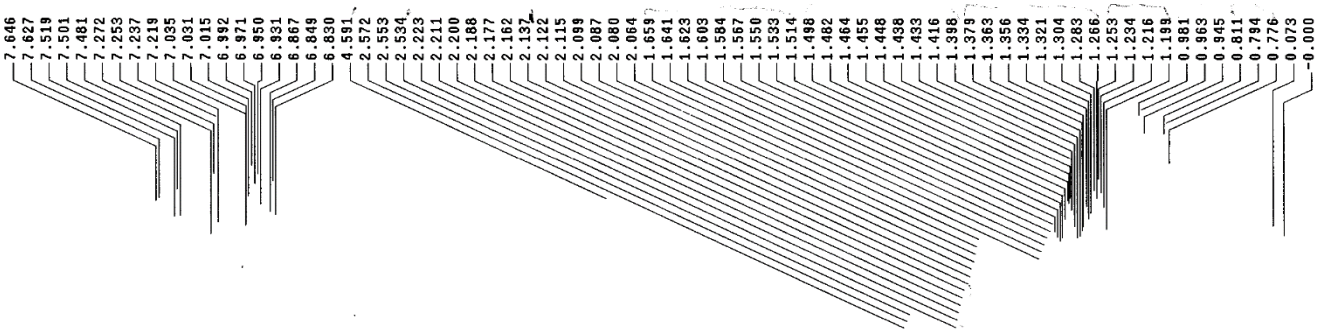

9
8
7
6
5
4
3
2
1
ppm
0.92
4.18
1.21
1.35
1.16
2.30
3.09
1.00

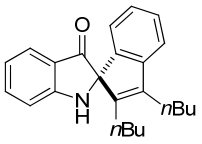

197.595
161.387
144.451
143.268
142.909
140.936
137.747
133.955
133.409
132.421
131.860
130.728
130.034
129.061
128.917
128.481
126.845
125.773
121.955
121.394
120.682
119.356
113.023
81.326
77.318
77.000
76.682


O
N
H
Cl
Cl

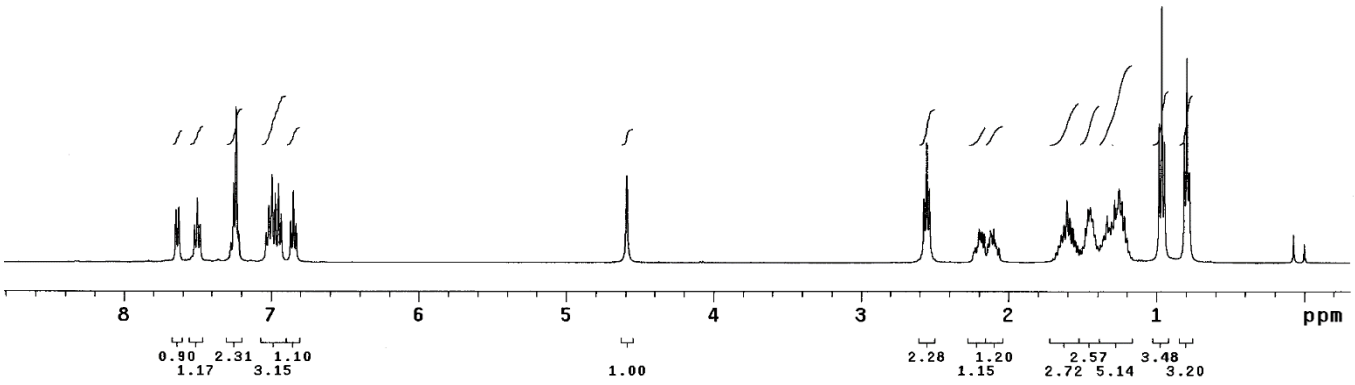
3ad

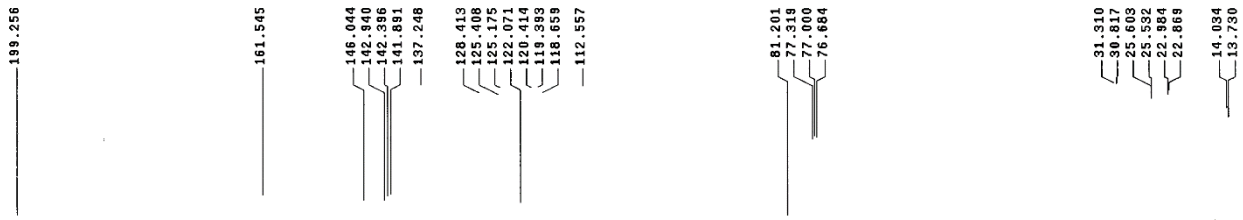

200
180
160
140
120
100
80
60
40
20
ppm

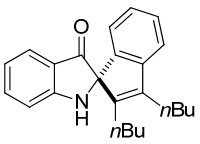

7.646
7.627
7.519
7.501
7.481
7.272
7.253
7.237
7.219
7.035
7.031
7.015
6.992
6.971
6.950
6.931
6.867
6.849
6.830
4.591
2.572
2.553
2.534
2.223
2.211
2.200
2.188
2.177
2.162
2.137
2.122
2.115
2.099
2.087
2.080
2.064
1.659
1.641
1.623
1.603
1.584
1.567
1.550
1.533
1.514
1.498
1.482
1.464
1.455
1.448
1.438
1.433
1.416
1.398
1.379
1.363
1.356
1.334
1.321
1.304
1.283
1.266
1.253
1.234
1.216
1.198
0.981
0.963
0.945
0.811
0.794
0.776
0.073
-0.000


O
N
H
nBu
nBu

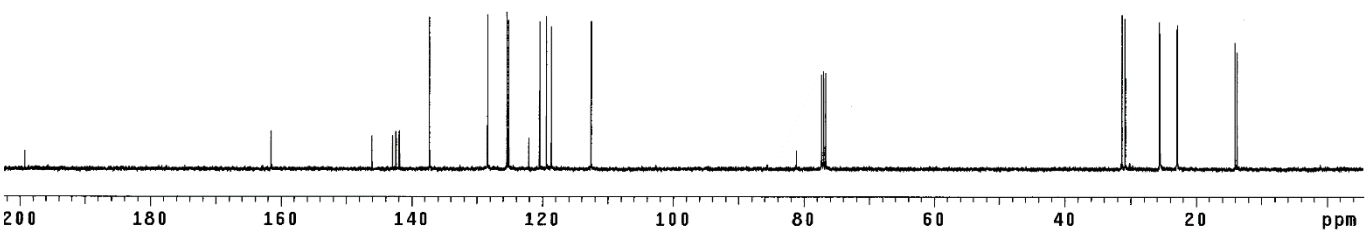
3ae

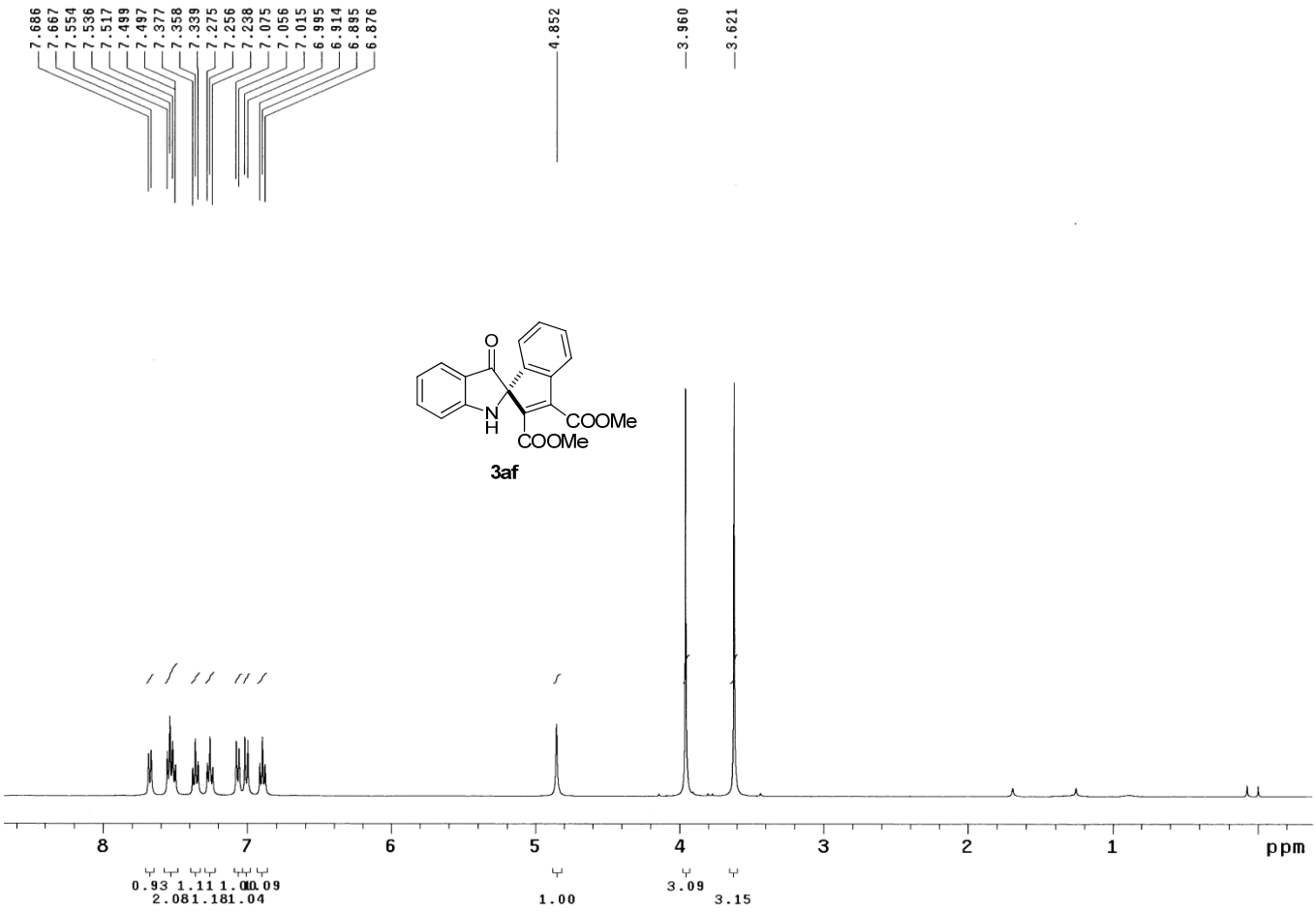

8
7
6
5
4
3
2
1
ppm
0.90
1.17
2.31
3.15
1.10
1.00
2.28
1.15
1.20
2.57
2.72
5.14
3.48
3.20

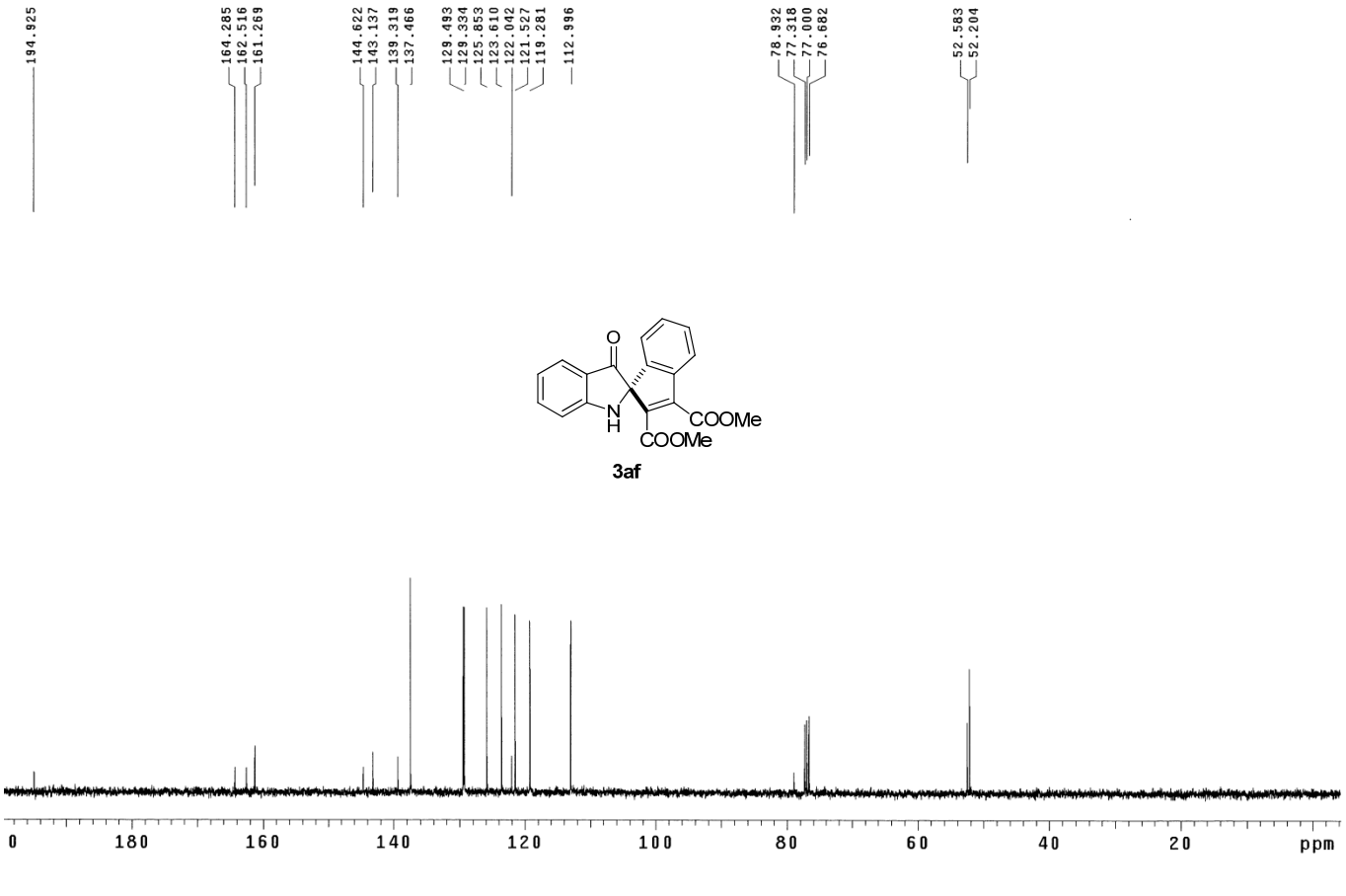

199.256
161.545
146.044
142.940
142.396
141.891
137.248
128.413
125.408
125.175
122.071
120.414
119.393
118.659
112.557
81.201
77.319
77.000
76.684
31.310
30.817
25.603
25.532
22.984
22.869
14.034
13.730

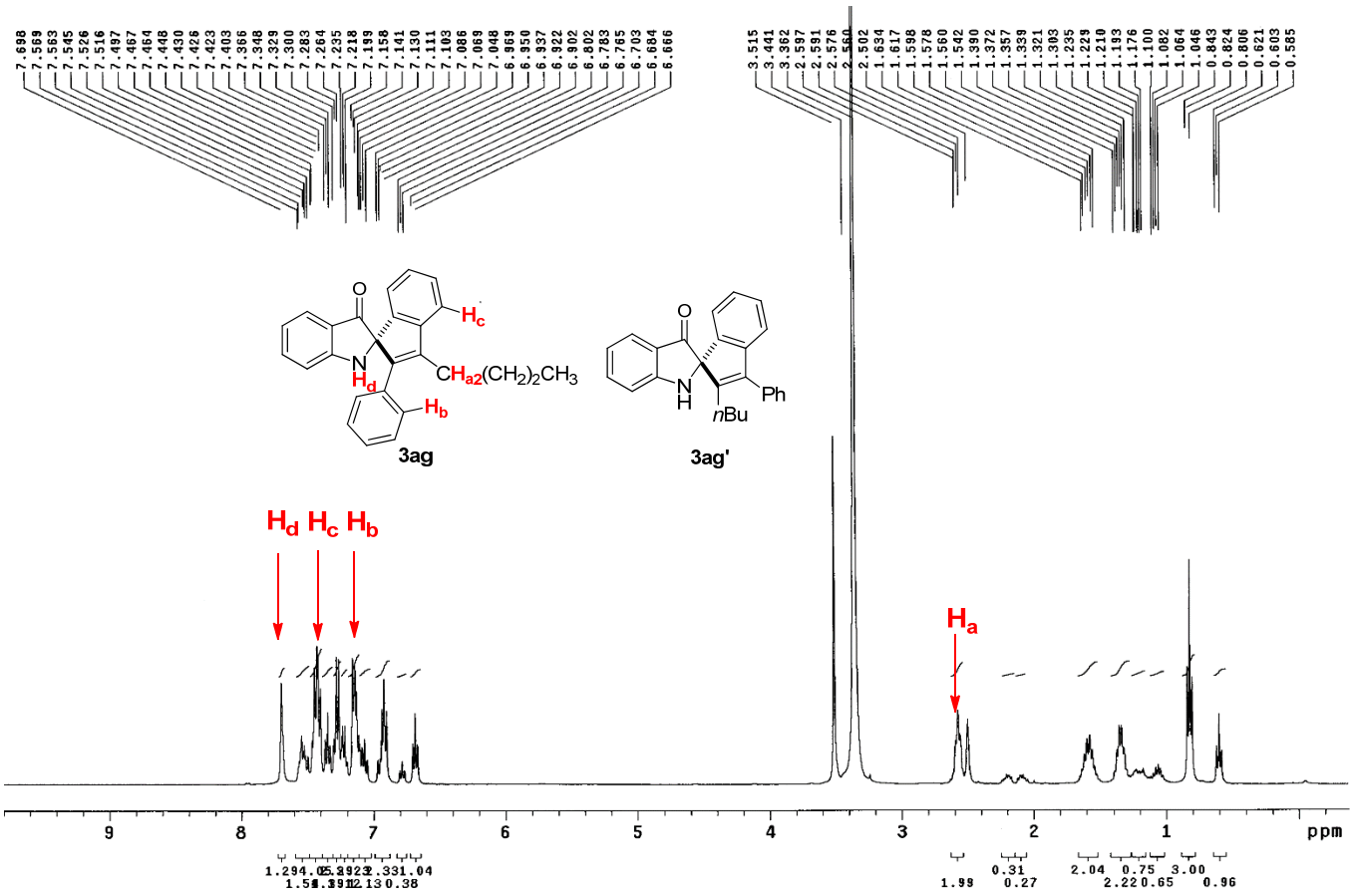

O
N
H
nBu
nBu

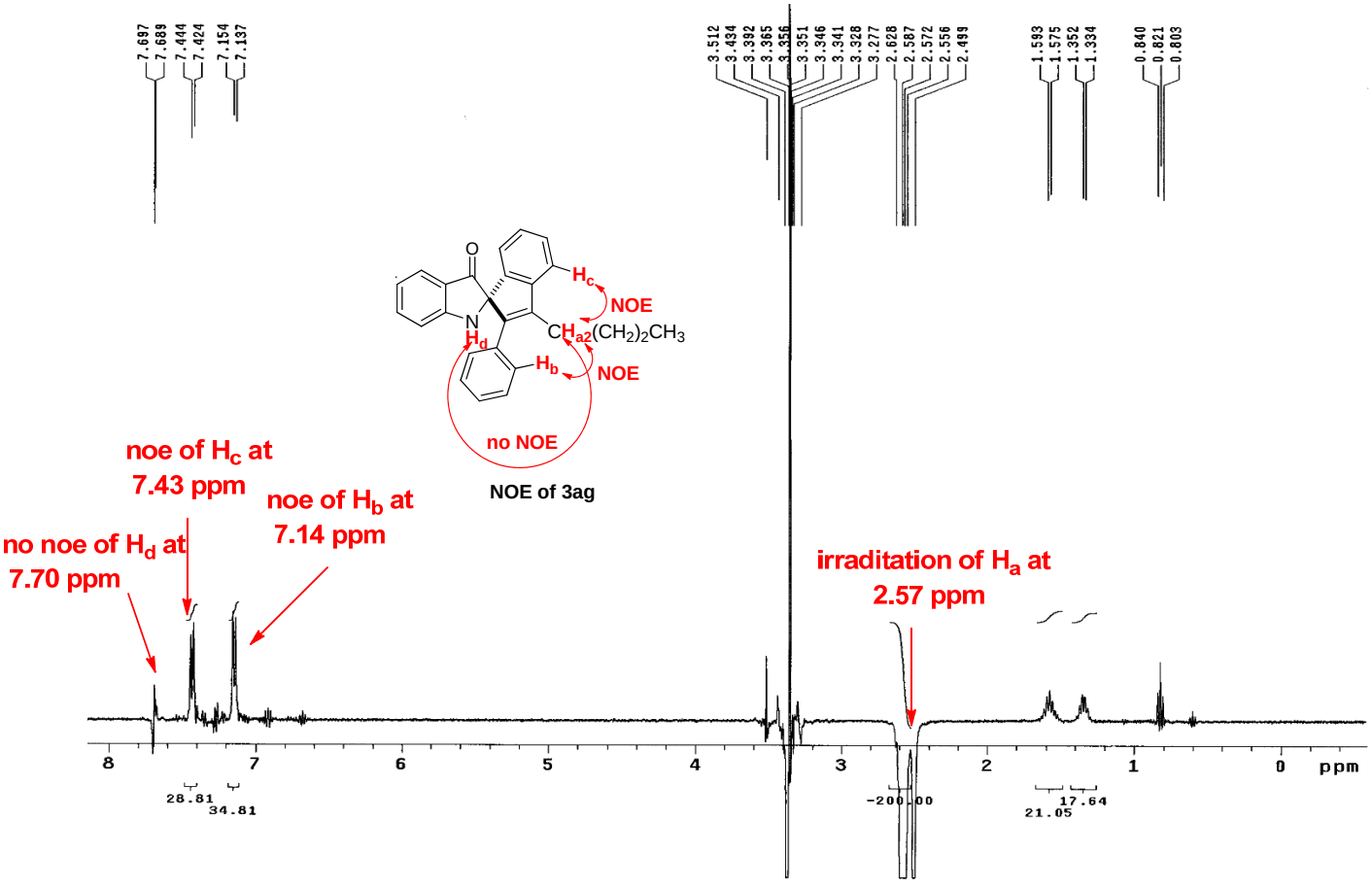
3ae

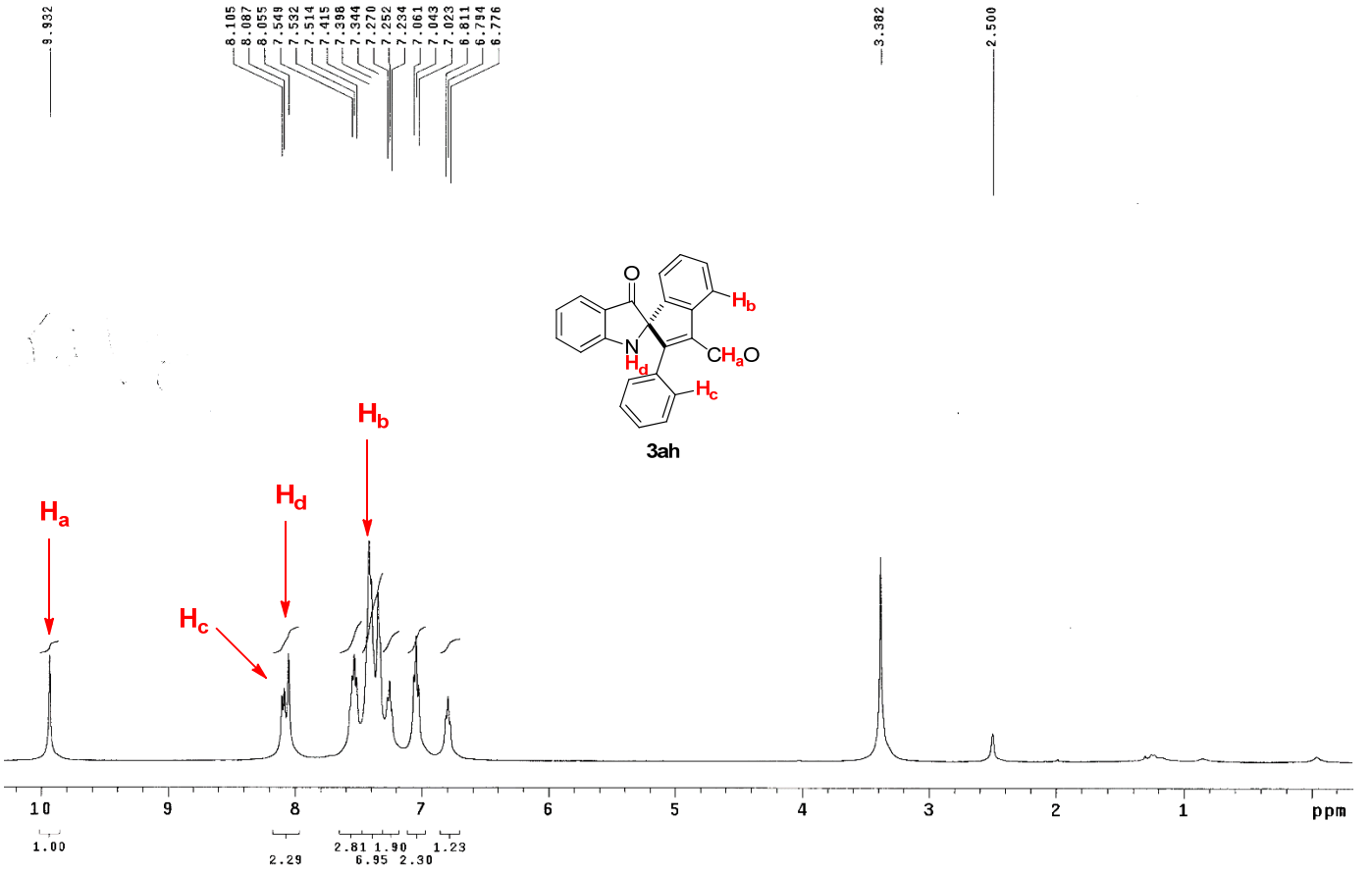

200
180
160
140
120
100
80
60
40
20
ppm

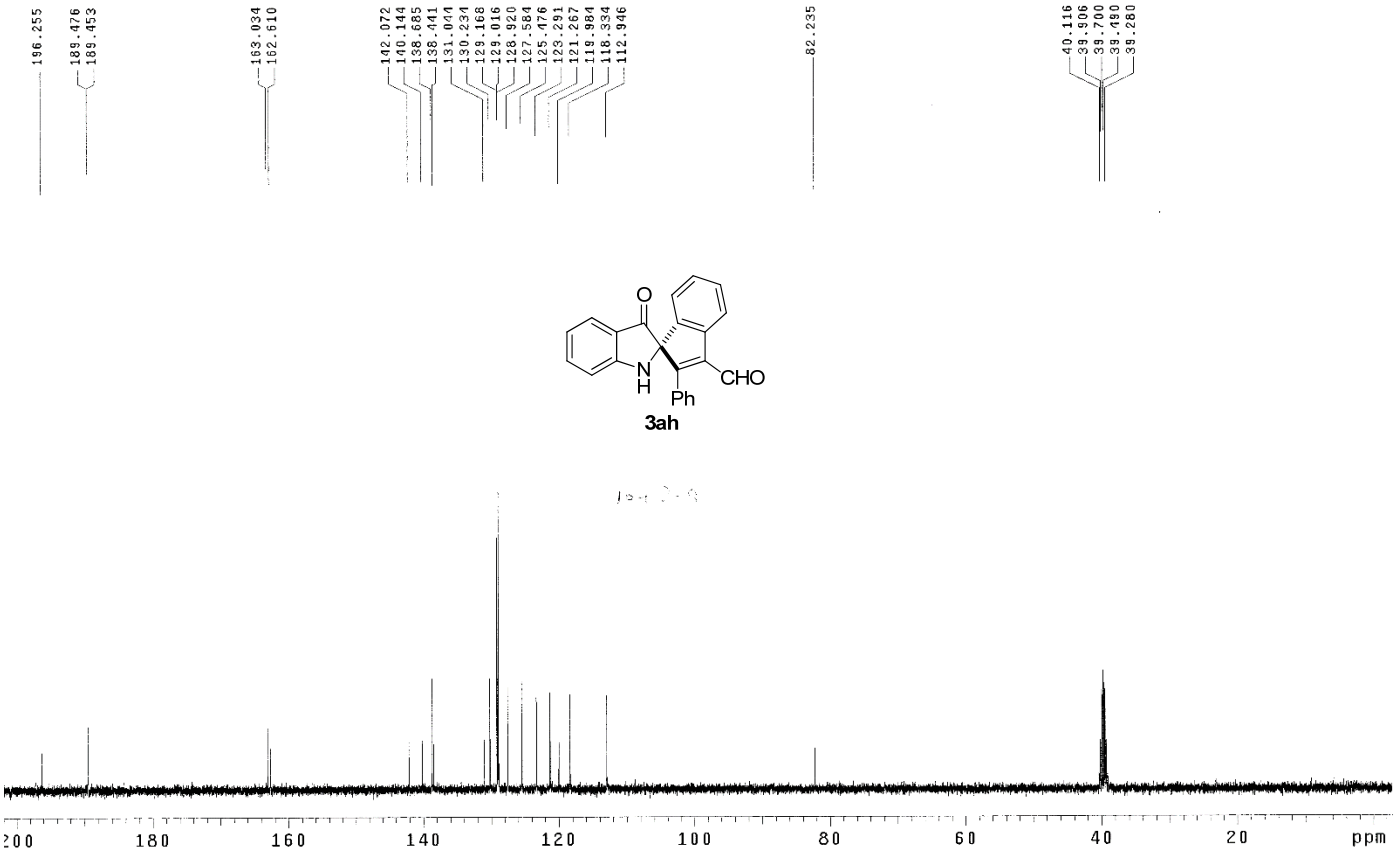

7.686
7.667
7.554
7.536
7.517
7.499
7.497
7.377
7.358
7.339
7.275
7.256
7.238
7.075
7.056
7.015
6.995
6.914
6.895
6.876
4.852
3.960
3.621
O
N
H
COOMe
COOMe
3af
8
7
6
5
4
3
2
1
ppm
0.93 1.11 1.00 0.09
2.08 1.18 1.04
1.00
3.09
3.15

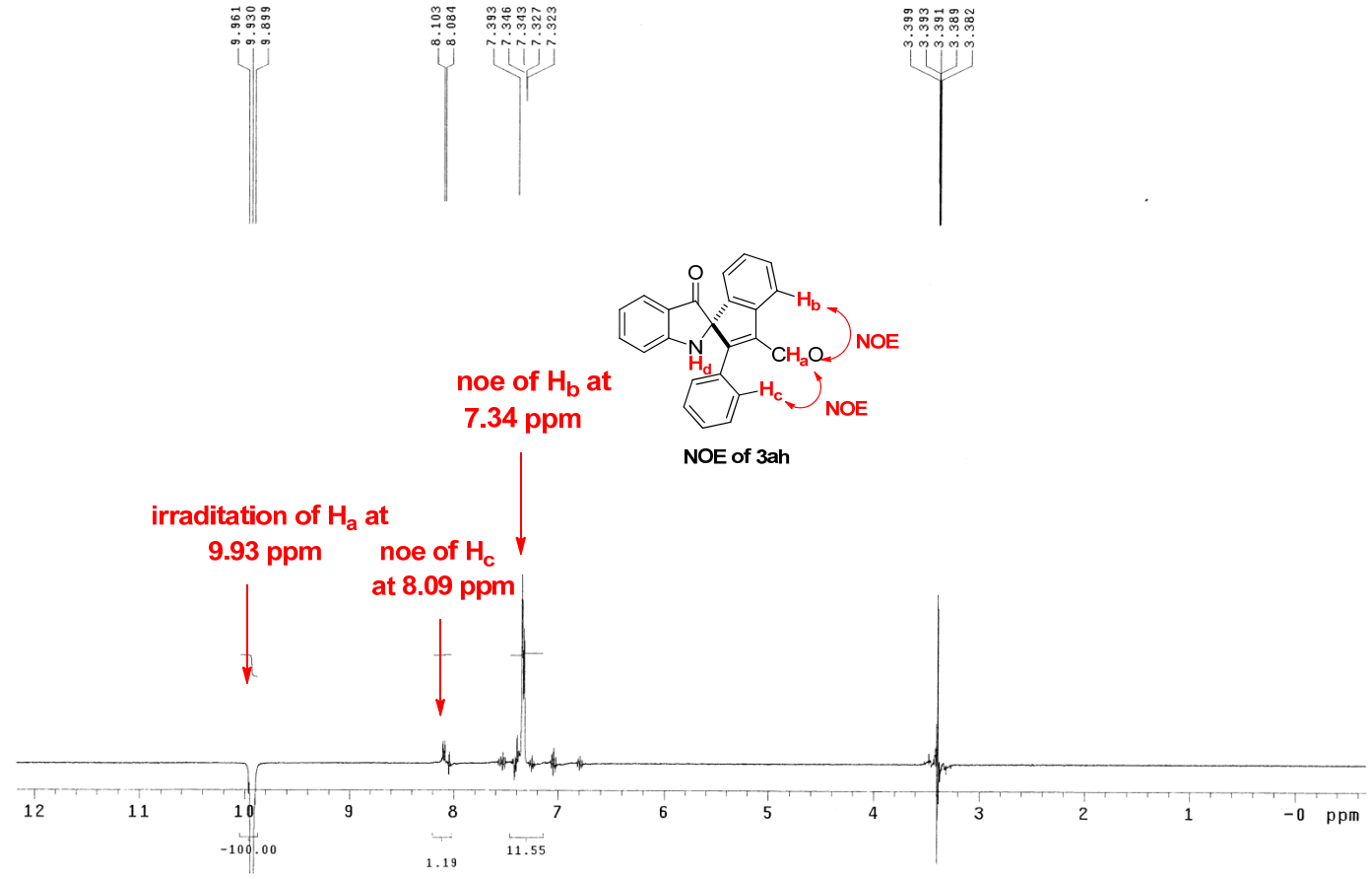

194.825
164.285
162.516
161.269
144.622
143.137
139.319
137.466
129.493
129.334
125.853
123.610
122.042
121.527
119.281
112.996
78.932
77.318
77.000
76.682
52.583
52.204
O
N
H
COOMe
COOMe
3af
0
180
160
140
120
100
80
60
40
20
ppm


3ag
3ag'
Hd Hc Hb
Ha
ppm

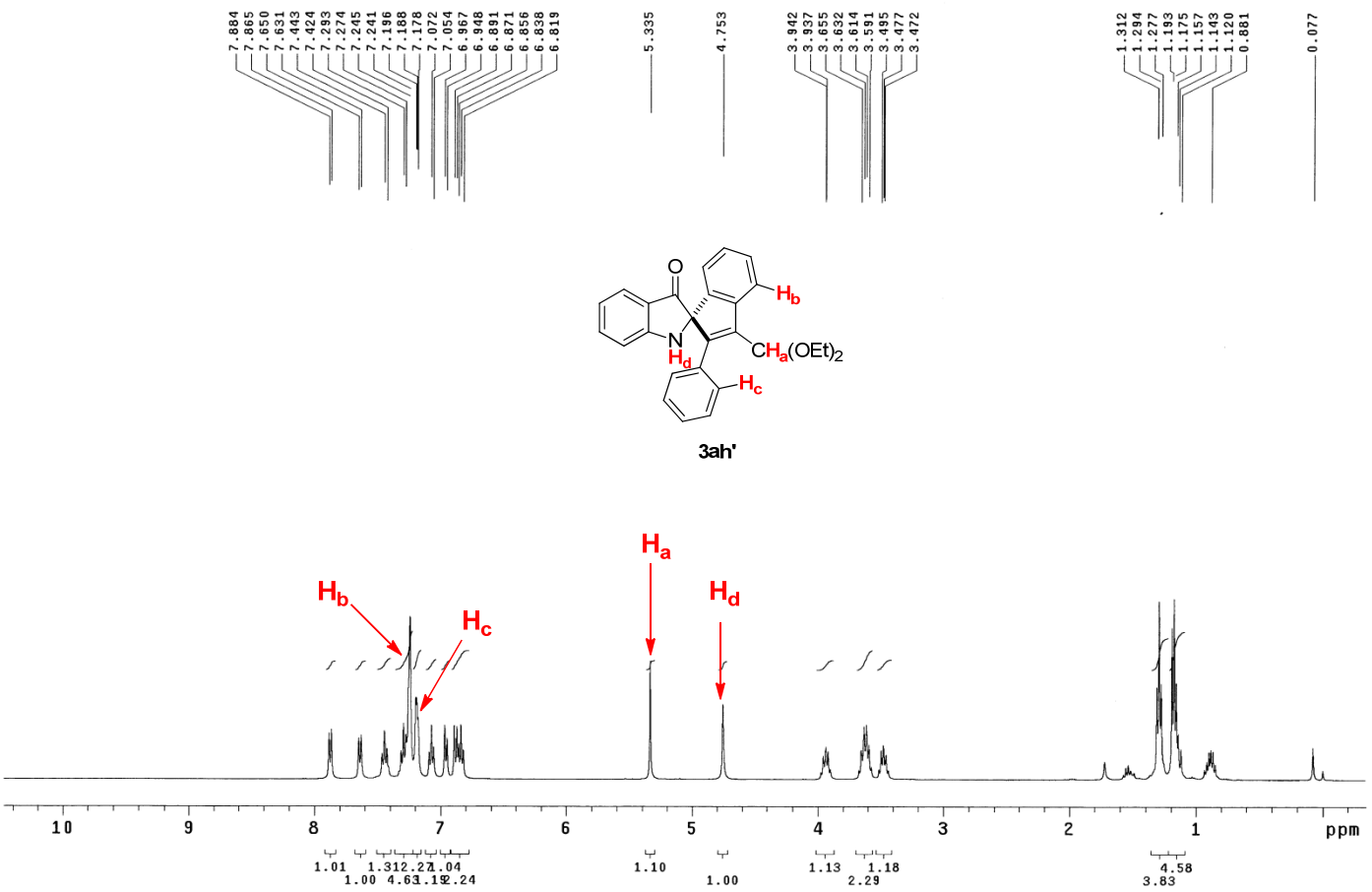

NOE
NOE
no NOE
NOE of 3ag
noe of Hc at 7.43 ppm
noe of Hb at 7.14 ppm
no noe of Hd at 7.70 ppm
irraditation of Ha at 2.57 ppm
ppm


9.932
8.105
8.087
8.055
7.549
7.532
7.514
7.415
7.398
7.344
7.270
7.252
7.234
7.061
7.043
7.023
6.811
6.794
6.776
3.382
2.500
O
N
H
H_b
CH_aO
H_d
H_c
3ah
H_a
H_d
H_b
H_c
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.29
2.81
1.90
1.23
6.95
2.30

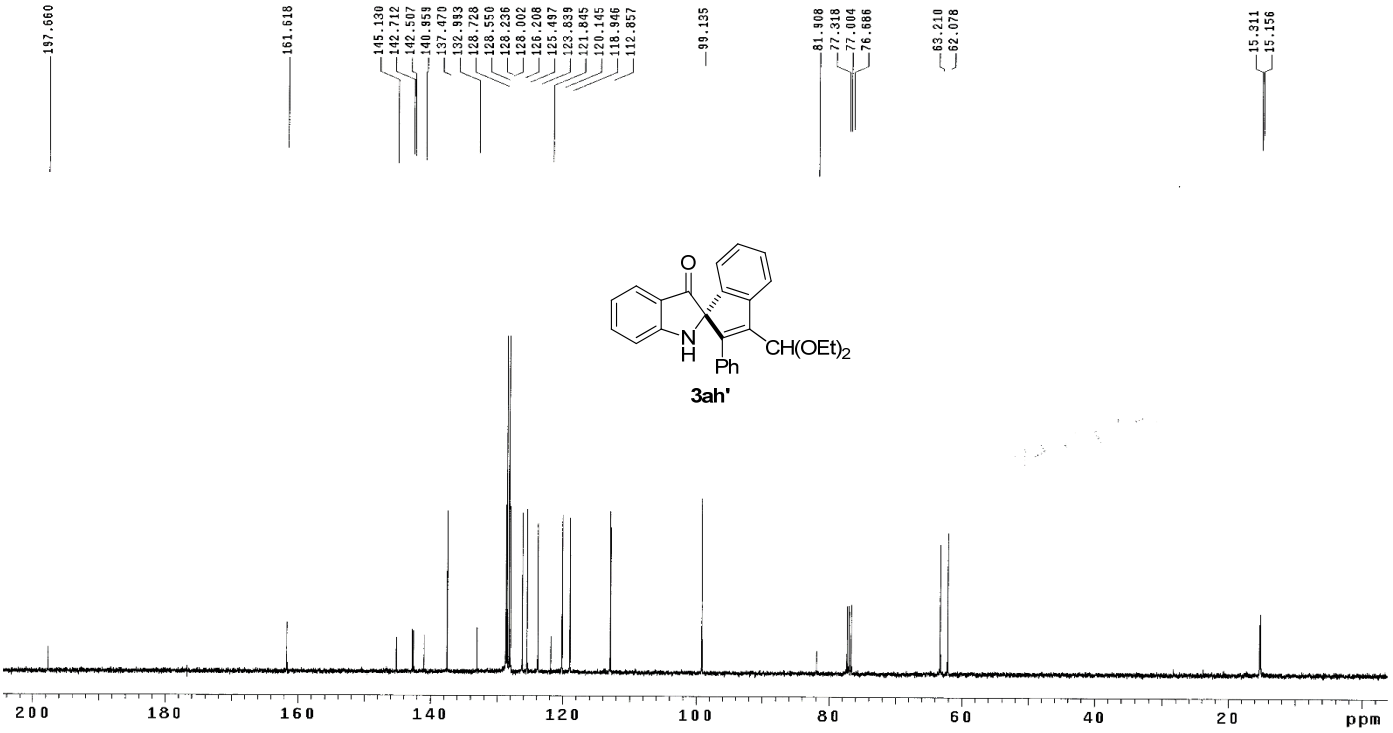

196.255
189.476
189.453
163.034
162.610
142.072
140.144
138.685
138.441
131.044
130.234
129.168
128.016
126.920
127.584
125.476
123.291
121.267
119.984
118.334
112.946
82.235
40.116
39.906
39.700
39.490
39.280
O
N
H
CHO
Ph
3ah
200
180
160
140
120
100
80
60
40
20
ppm

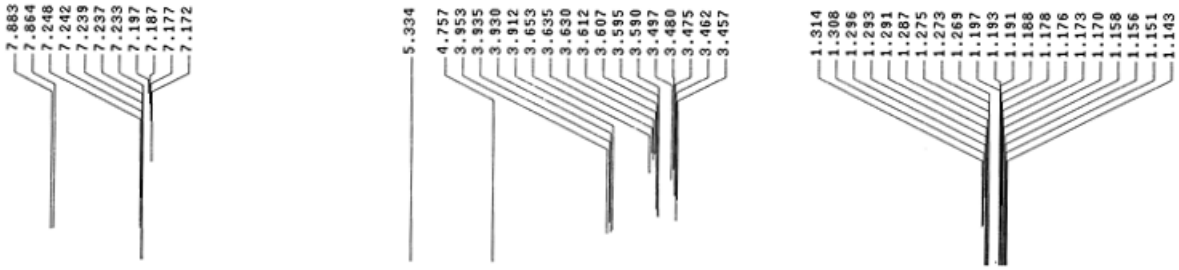


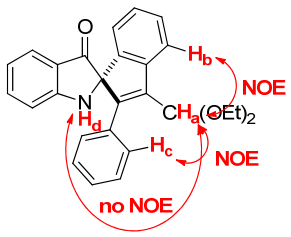
NOE of 3ah



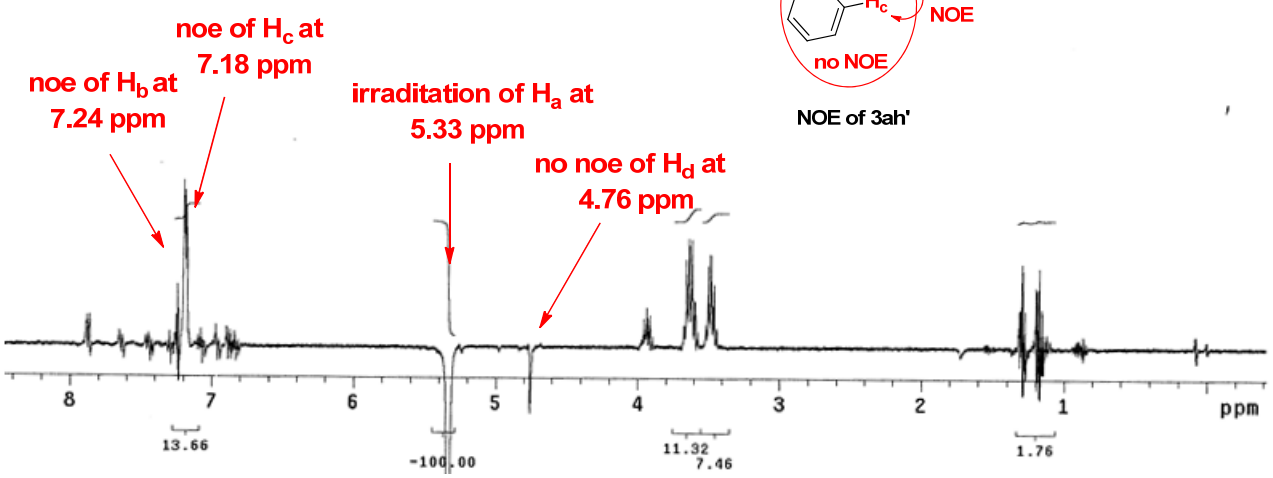
3ah'

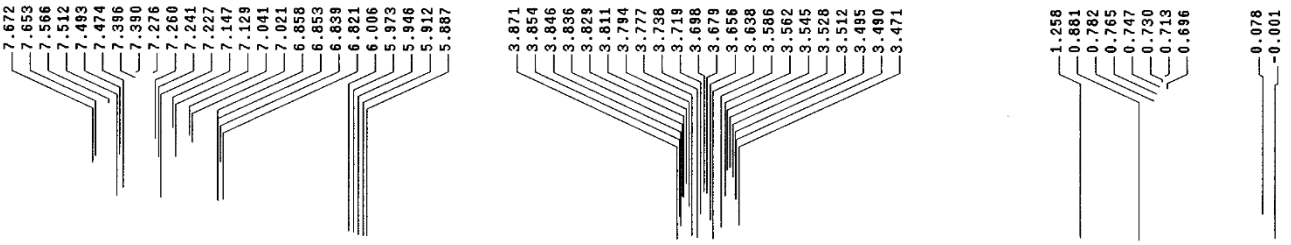

197.660
161.618
145.130
142.712
142.507
140.853
137.470
132.993
128.728
128.550
128.236
128.002
126.208
125.497
123.839
121.845
120.145
118.946
112.857
99.135
81.908
77.318
77.004
76.686
63.210
62.078
15.311
15.156
O
N
H
Ph
CH(OEt)2
3ah'
200
180
160
140
120
100
80
60
40
20
ppm

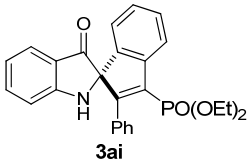

7.883
7.864
7.248
7.242
7.239
7.237
7.233
7.197
7.187
7.177
7.172
5.334
4.757
3.953
3.935
3.830
3.912
3.653
3.635
3.630
3.612
3.607
3.595
3.590
3.497
3.480
3.475
3.462
3.457
1.314
1.308
1.296
1.293
1.291
1.287
1.275
1.273
1.269
1.197
1.193
1.191
1.188
1.178
1.176
1.173
1.170
1.158
1.156
1.151
1.143


O
N
Hd
Hb
CHa(OEt)2
Hc
NOE
NOE
no NOE

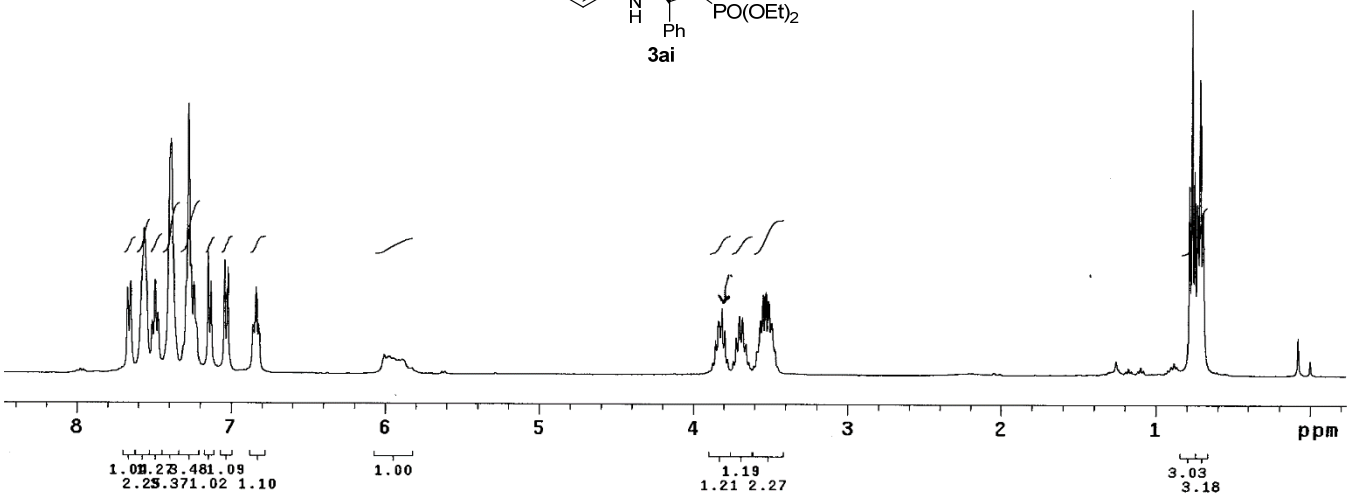
NOE of 3ah'

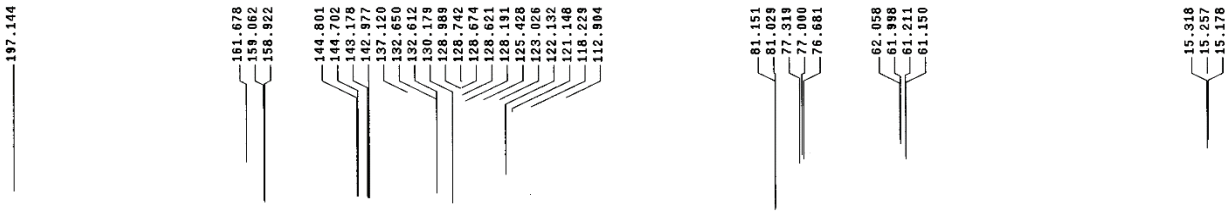

noe of Hb at 7.24 ppm
noe of Hc at 7.18 ppm
irraditation of Ha at 5.33 ppm
no noe of Hd at 4.76 ppm
8
7
6
5
4
3
2
1
ppm
13.66
-100.00
11.32
7.46
1.76

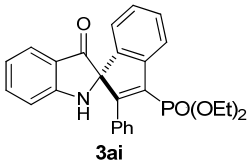

7.672
7.653
7.566
7.512
7.493
7.474
7.396
7.390
7.276
7.260
7.241
7.227
7.147
7.129
7.041
7.021
6.858
6.853
6.839
6.821
6.006
5.973
5.946
5.912
5.887
3.871
3.854
3.846
3.836
3.829
3.811
3.794
3.777
3.738
3.719
3.698
3.679
3.656
3.638
3.586
3.562
3.545
3.528
3.512
3.495
3.490
3.471
1.258
0.881
0.782
0.765
0.747
0.730
0.713
0.696
0.078
-0.001


O
N
H
Ph
PO(OEt)2

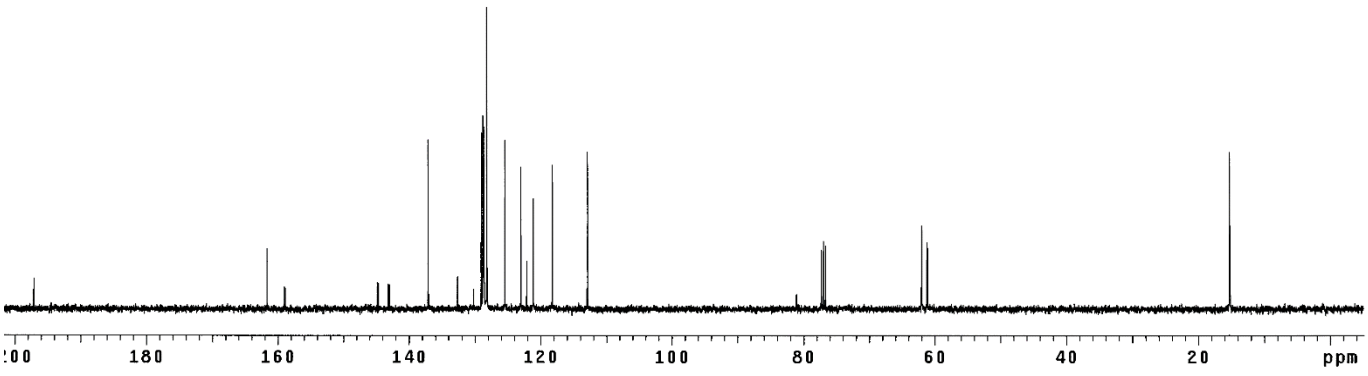
3ai

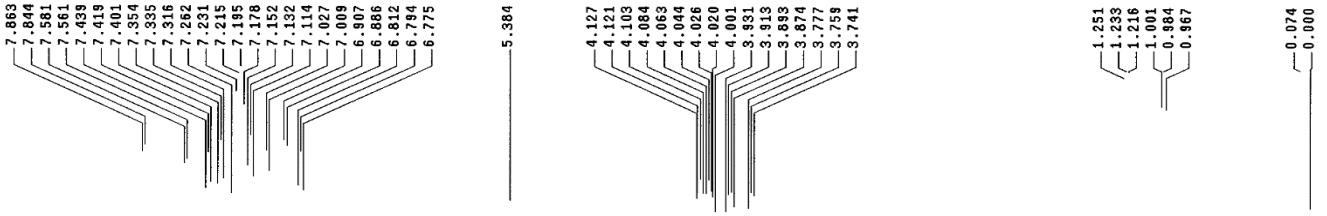

8
7
6
5
4
3
2
1
ppm
1.00
1.19
1.21 2.27
3.03
3.18

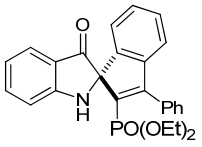

197.144
161.678
159.062
158.922
144.801
144.702
143.178
142.977
137.120
132.650
132.612
130.179
128.989
128.742
128.674
128.621
128.191
125.426
123.026
122.132
121.148
118.229
112.904
81.151
81.029
77.319
77.000
76.681
62.058
61.998
61.211
61.150
15.318
15.257
15.178


O
N
H
Ph
PO(OEt)2

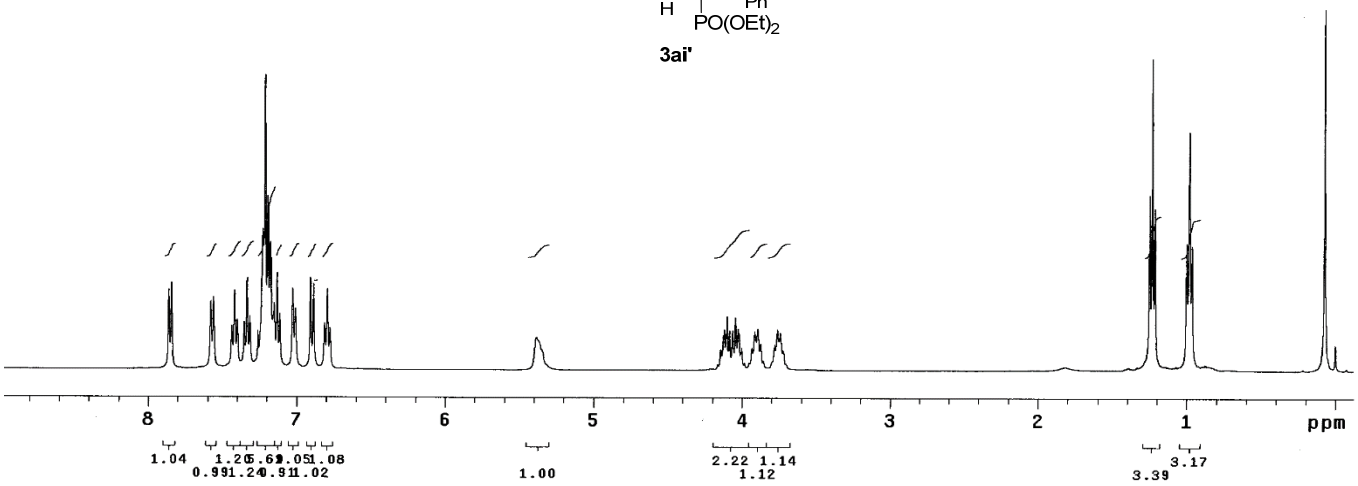
3ai

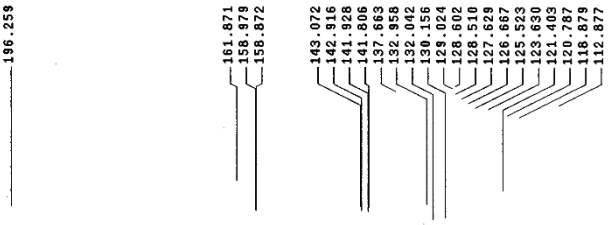

200
180
160
140
120
100
80
60
40
20
ppm


7.863
7.844
7.581
7.561
7.439
7.419
7.401
7.354
7.335
7.316
7.262
7.231
7.215
7.195
7.178
7.152
7.132
7.114
7.027
7.009
6.907
6.886
6.812
6.794
6.775
5.384
4.127
4.121
4.103
4.084
4.063
4.044
4.026
4.020
4.001
3.931
3.913
3.893
3.874
3.777
3.759
3.741
1.251
1.233
1.216
1.001
0.984
0.967
0.074
0.000


O
N
H
Ph
PO(OEt)2

3ai'


8
7
6
5
4
3
2
1
ppm
1.04
1.26
5.62
2.05
1.08
0.99
1.24
0.91
1.02
1.00
2.22
1.14
1.12
3.39
3.17


196.259
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158.878
158.872
143.072
142.916
141.928
141.806
137.663
132.958
132.042
130.156
129.024
128.602
128.510
127.629
126.687
125.523
123.630
121.403
120.787
118.879
112.877
83.595
83.408
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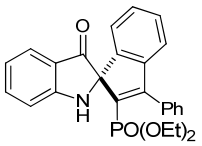
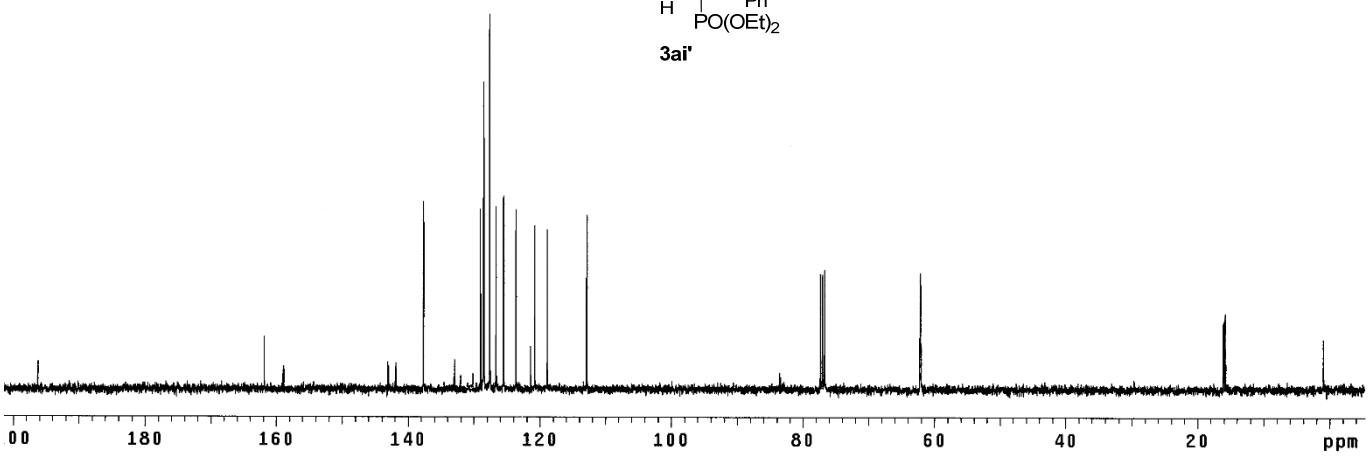
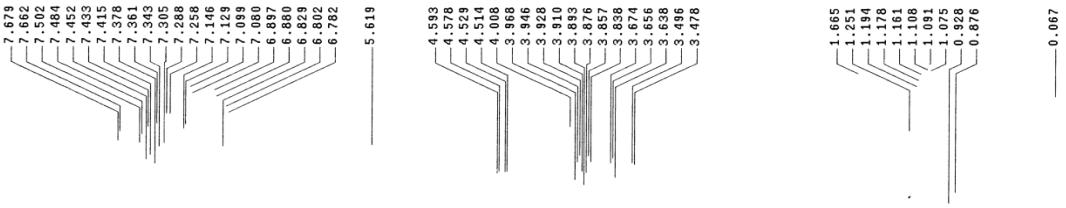
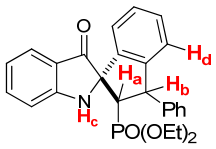
16.105
16.037
15.854
15.782
0.977


O
N
H
Ph
PO(OEt)2

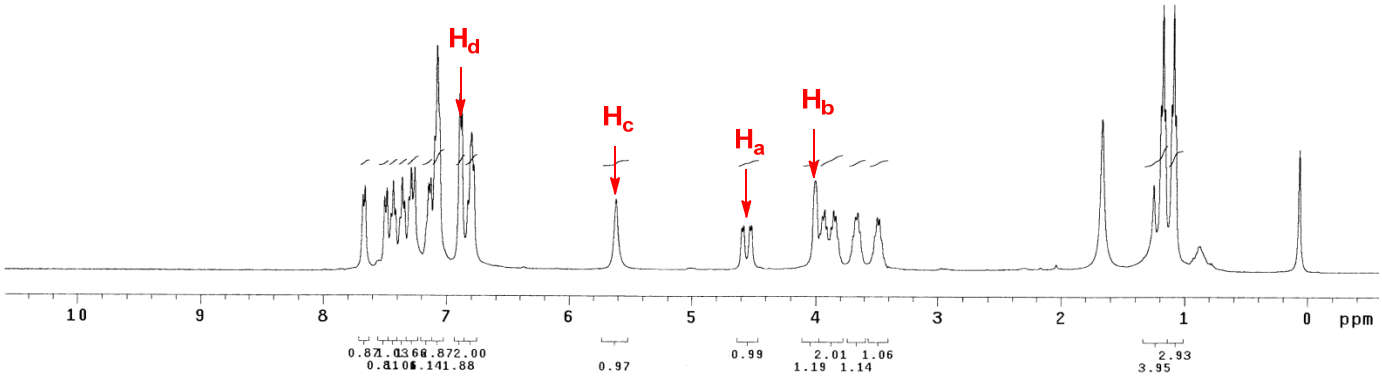
3ai'

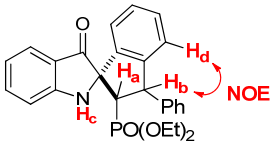

00
180
160
140
120
100
80
60
40
20
ppm



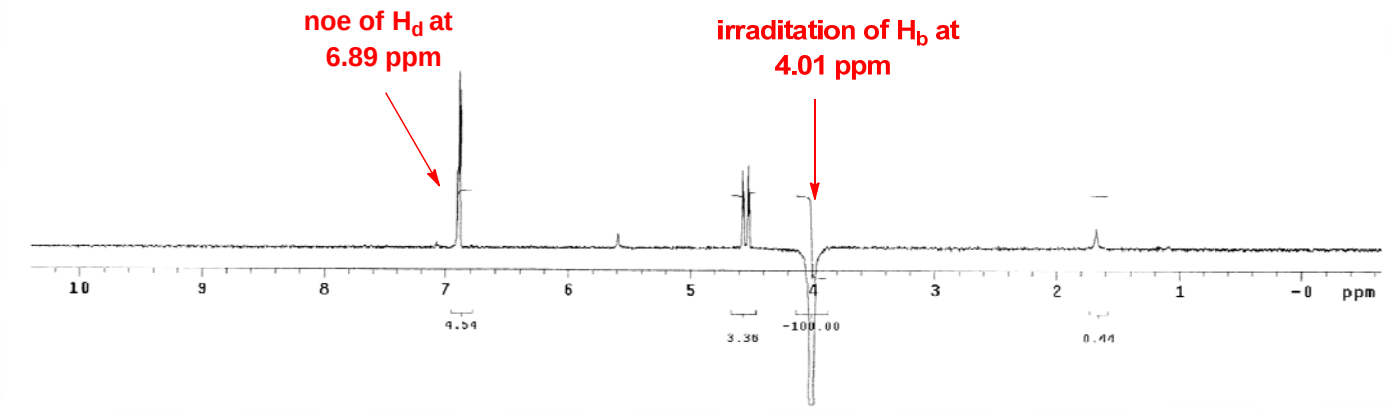


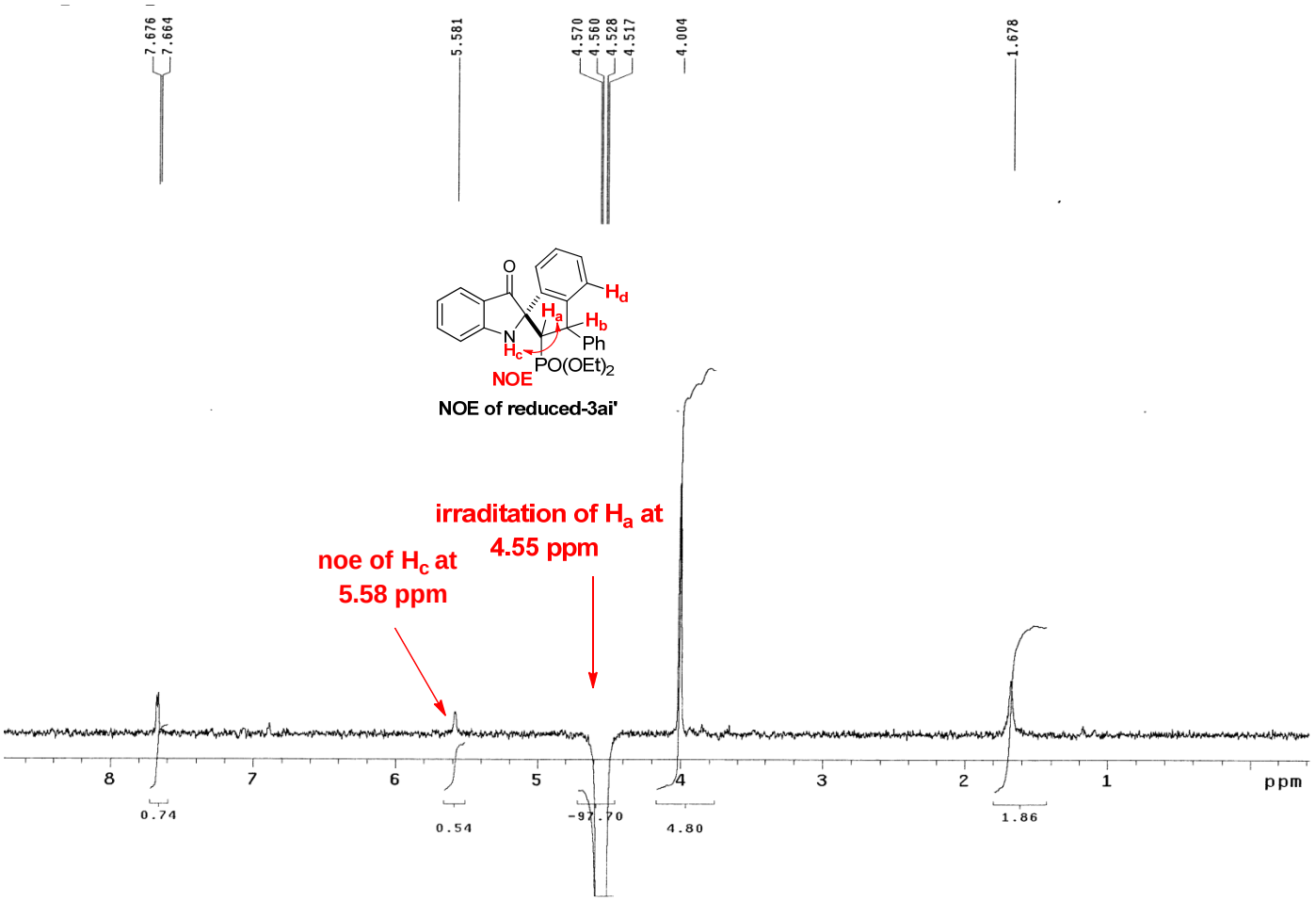
reduced-3ai'



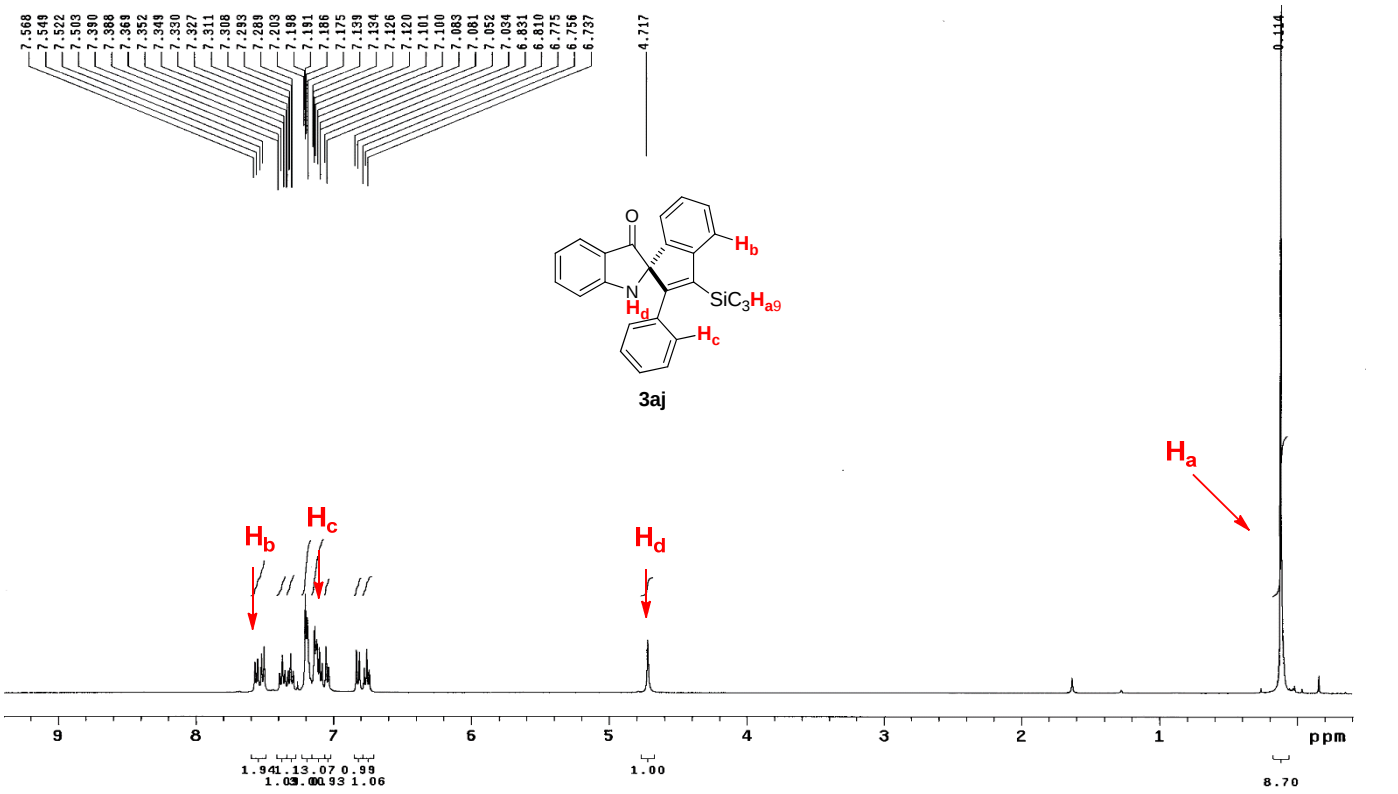


NOE of reduced-3ai'

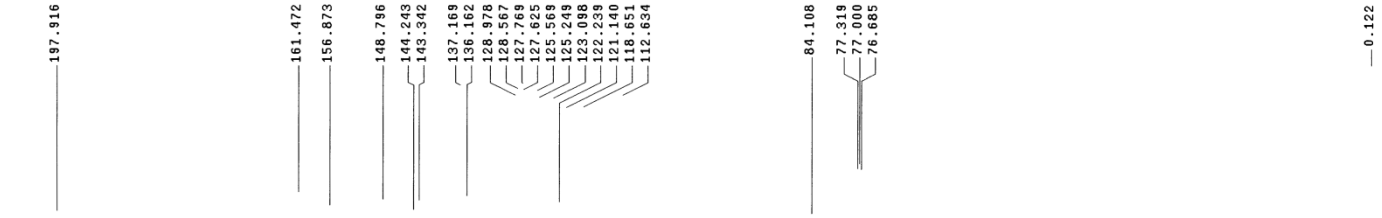


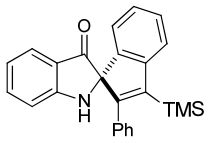


NOE of reduced-3ai'

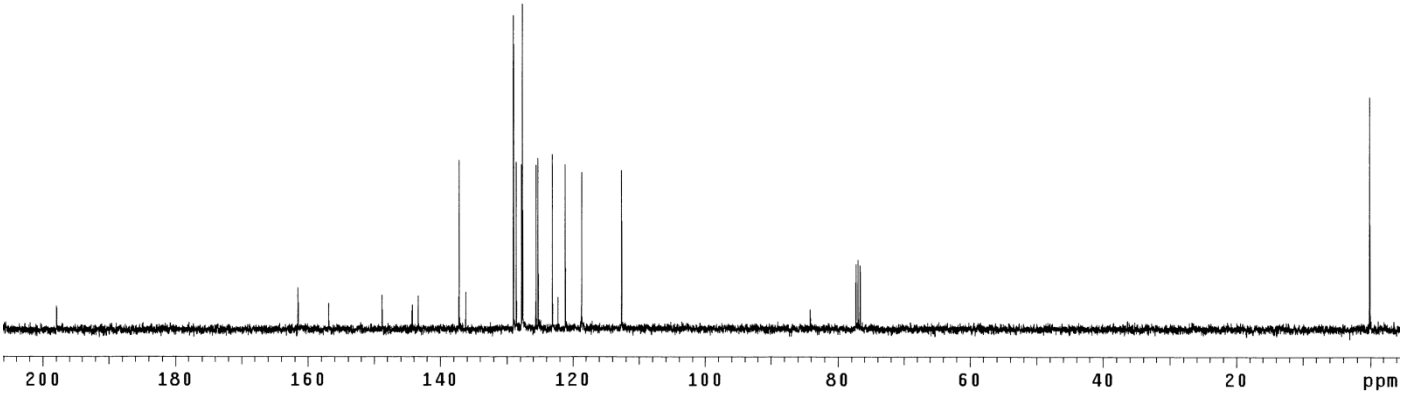


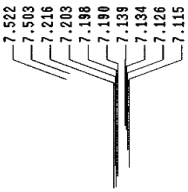
3aj

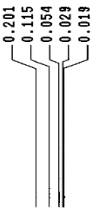


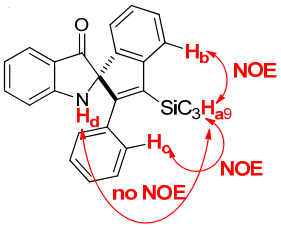


3aj









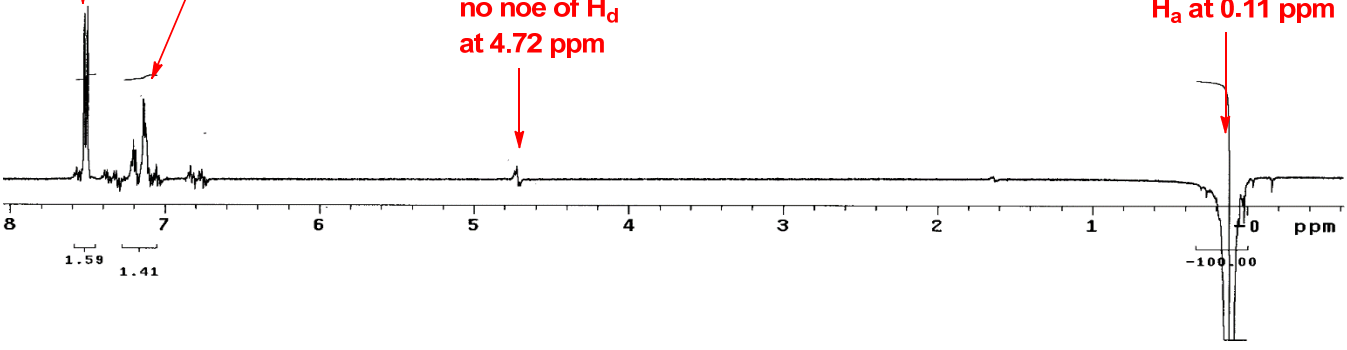
NOE of 3aj

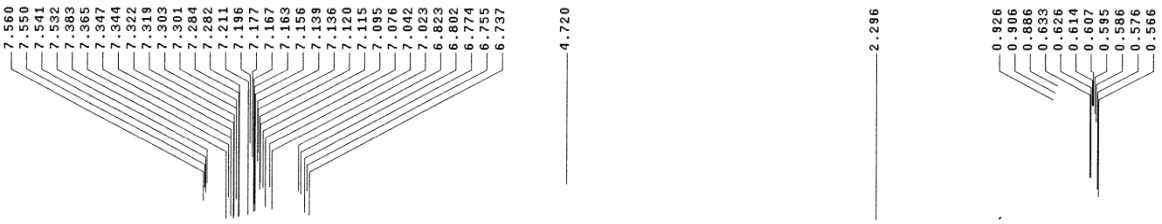
noe of H_b at 7.51 ppm

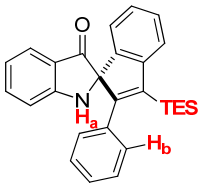
noe of H_c at 7.13 ppm

no noe of H_d at 4.72 ppm

irraditation of H_a at 0.11 ppm

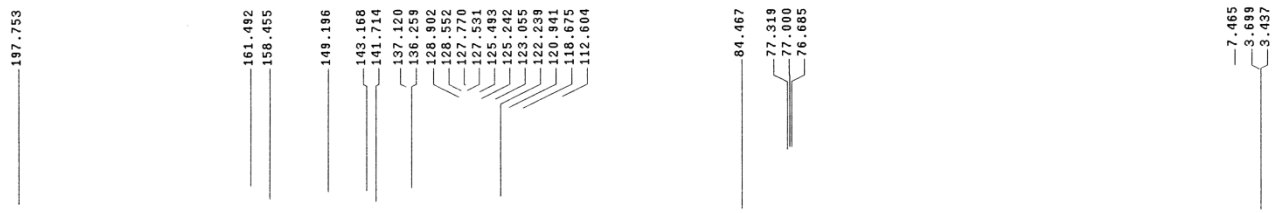


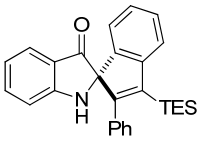

7.560
7.550
7.541
7.532
7.383
7.365
7.347
7.344
7.322
7.319
7.303
7.301
7.284
7.282
7.211
7.196
7.177
7.167
7.163
7.156
7.139
7.136
7.120
7.115
7.095
7.076
7.042
7.023
6.823
6.802
6.774
6.755
6.737
4.720
2.296
0.926
0.906
0.886
0.633
0.626
0.614
0.607
0.595
0.586
0.576
0.566


O
N
H
a
TES
H
b

3ak

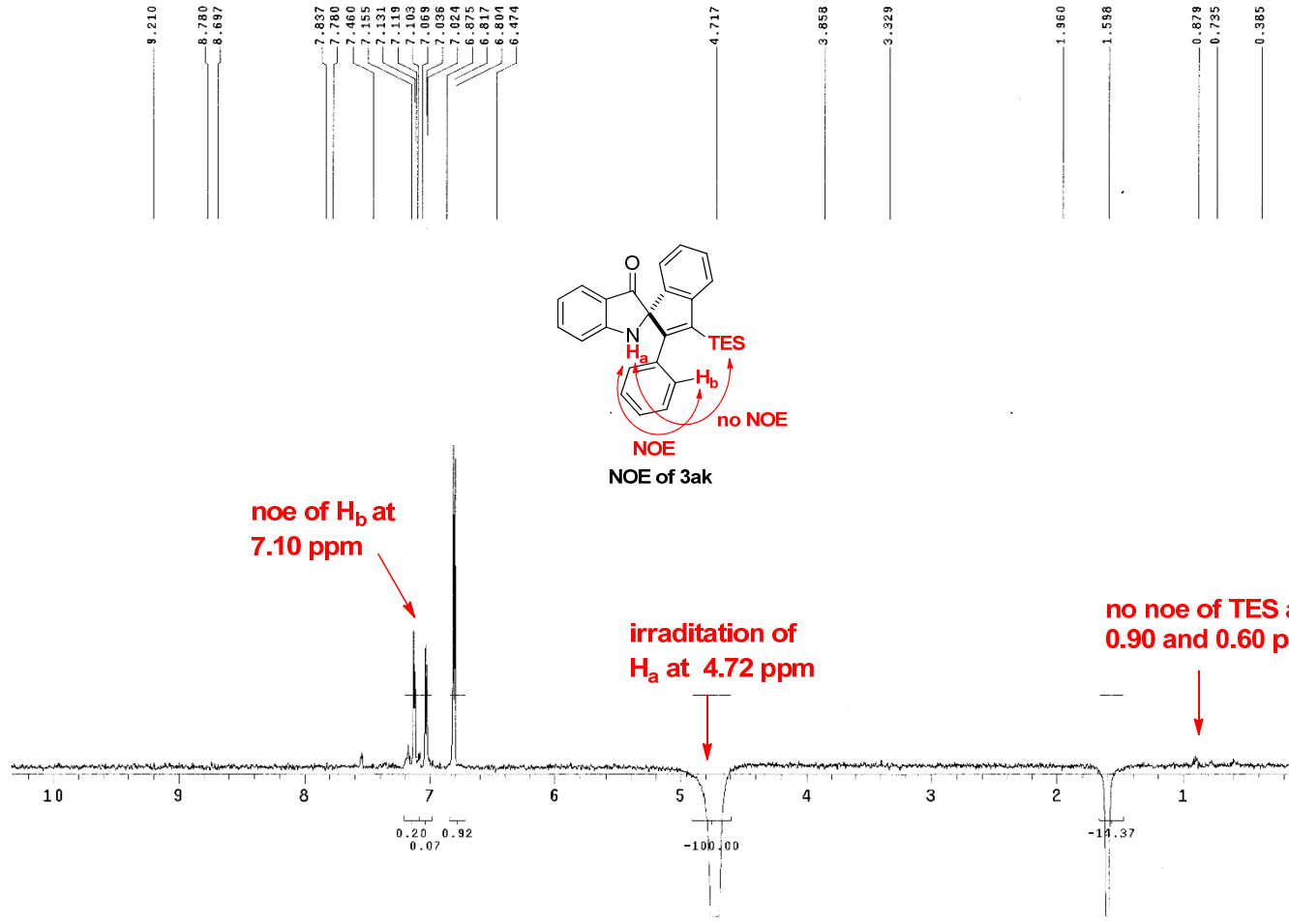
H
b
H
a
TES
10
9
8
7
6
5
4
3
2
1
ppm
1.96
1.02
2.15
1.05
1.03
3.06
6.14
1.00
1.00
9.29
6.58

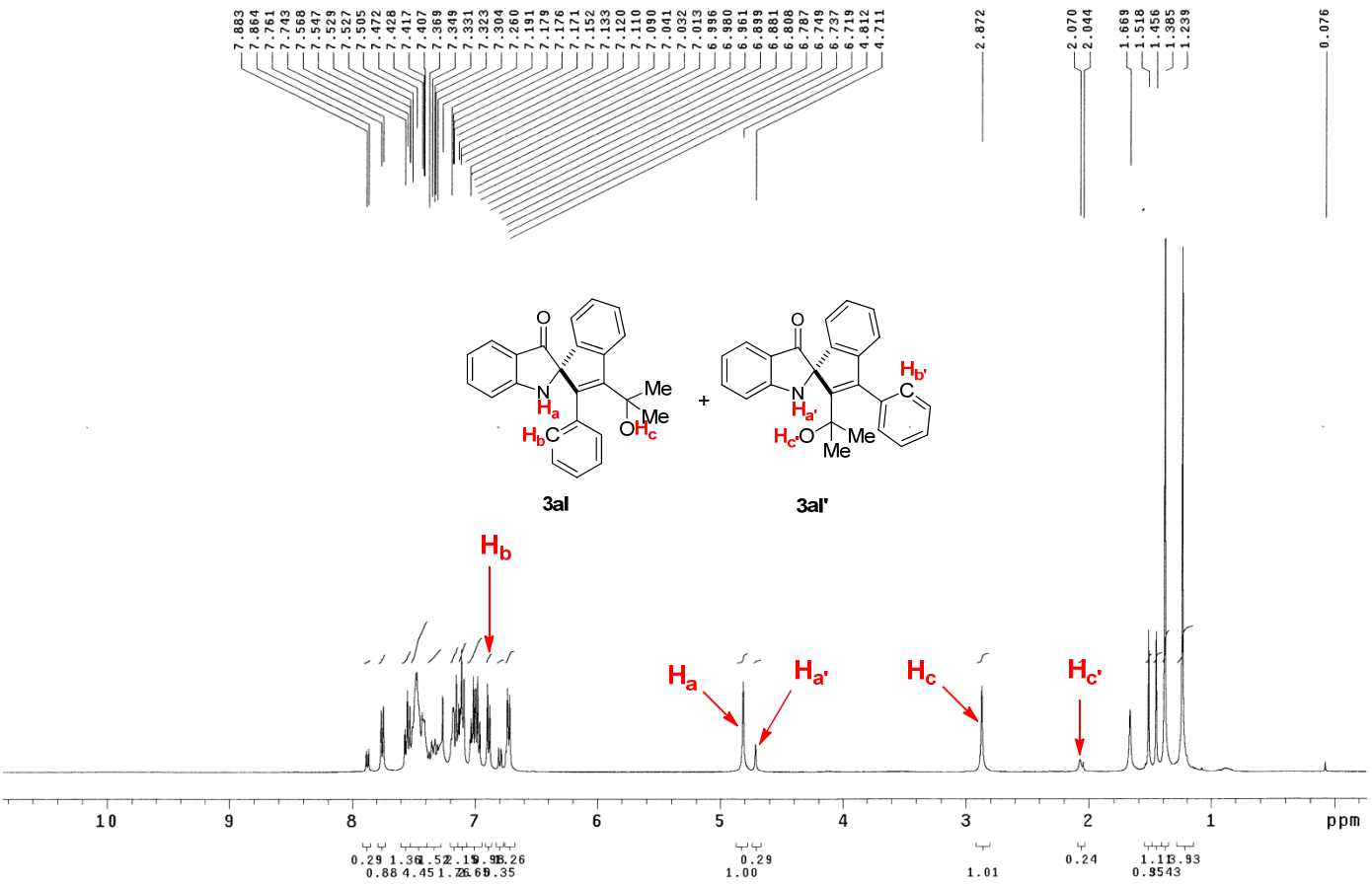

197.753
161.492
158.455
149.196
143.168
141.714
137.120
136.259
128.902
128.552
127.770
127.531
125.493
125.242
123.055
122.239
120.941
118.675
112.604
84.467
77.319
77.000
76.685
7.465
3.699
3.437


O
N
H
TES
Ph

3ak

200
180
160
140
120
100
80
60
40
20
ppm


9.210
8.780
8.697
7.837
7.780
7.460
7.155
7.131
7.119
7.103
7.069
7.036
7.024
6.875
6.817
6.804
6.474
4.717
3.858
3.329
1.960
1.588
0.879
0.735
0.385
O
N
Ha
TES
Hb
no NOE
NOE
NOE of 3ak
noe of Hb at
7.10 ppm
irraditation of
Ha at 4.72 ppm
no noe of TES at
0.90 and 0.60 ppm
10
9
8
7
6
5
4
3
2
1
ppm
0.20
0.07
0.92
-100.00
-14.37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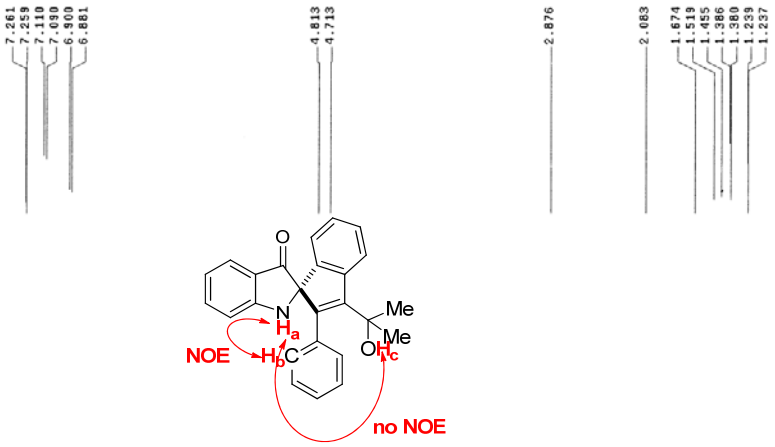
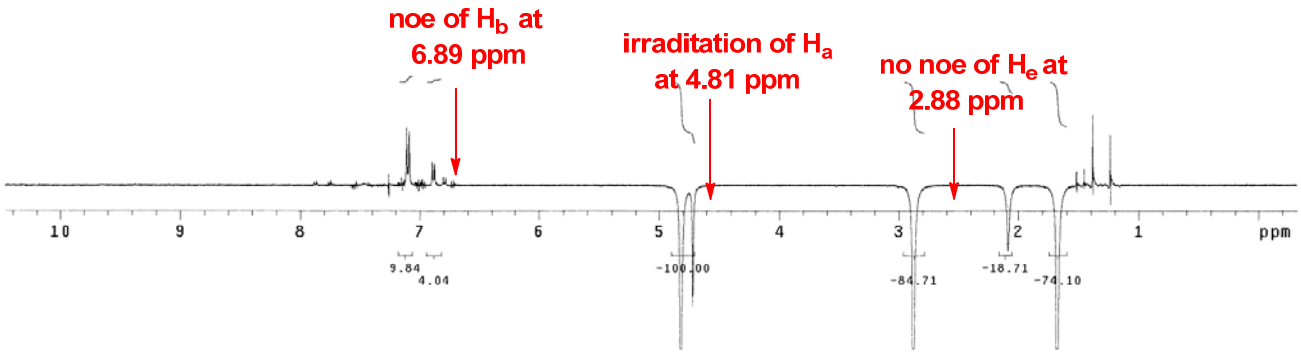
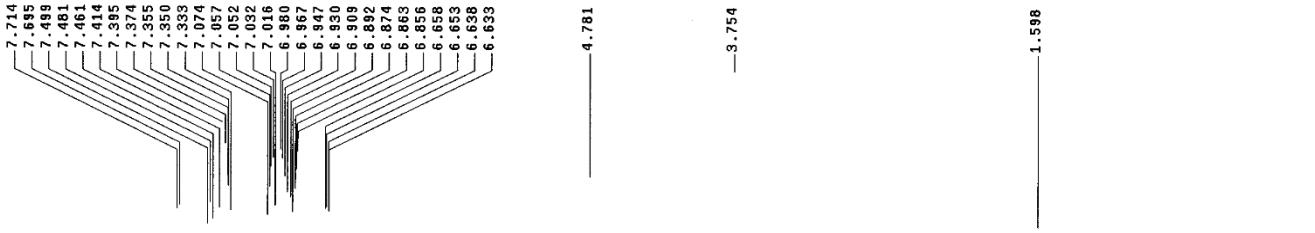
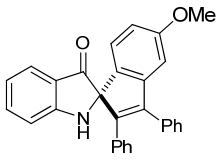
7.864
7.761
7.743
7.568
7.547
7.529
7.527
7.505
7.472
7.428
7.417
7.407
7.369
7.349
7.331
7.323
7.304
7.260
7.191
7.179
7.176
7.171
7.152
7.133
7.120
7.110
7.090
7.041
7.032
7.013
6.996
6.980
6.961
6.899
6.881
6.808
6.787
6.749
6.737
6.719
4.812
4.711
2.872
2.070
2.044
1.669
1.518
1.456
1.385
1.239
0.076
O
N
Ha
Me
Me
OHc
HbC
3al
+
O
N
Ha'
Hb'
C
Hc'O
Me
Me
3al'
Hb
Ha
Ha'
Hc
Hc'
10
9
8
7
6
5
4
3
2
1
ppm
0.29
0.88
1.36
4.45
1.52
1.26
2.15
6.69
9.35
8.26
0.29
1.00
1.01
0.24
1.15
0.95
3.93
43



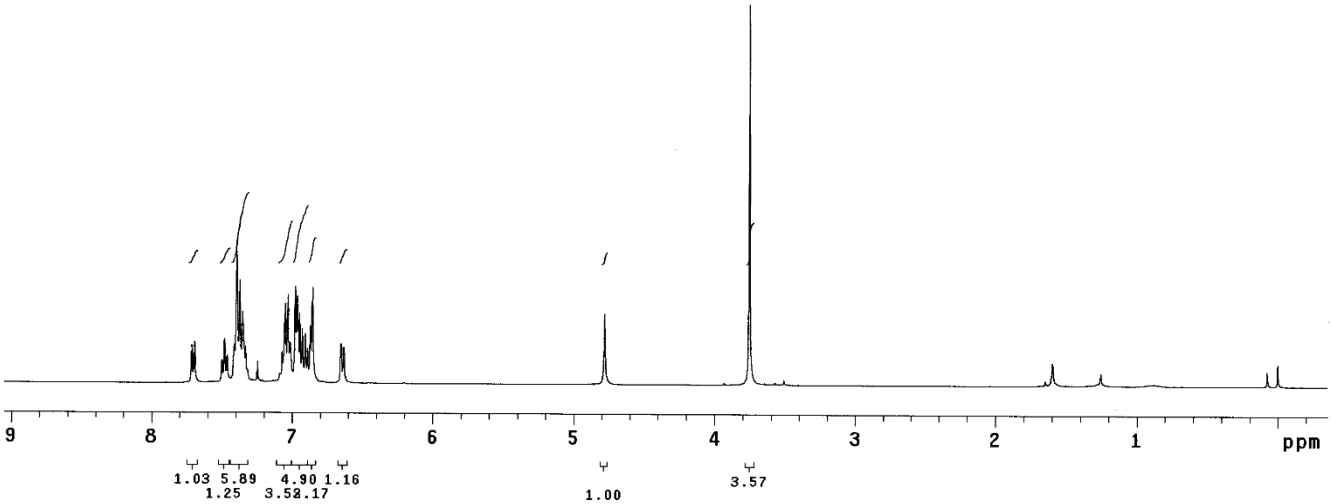
NOE of 3al

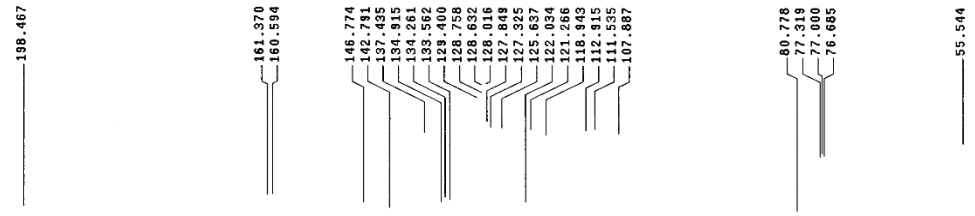


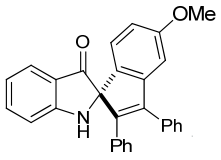




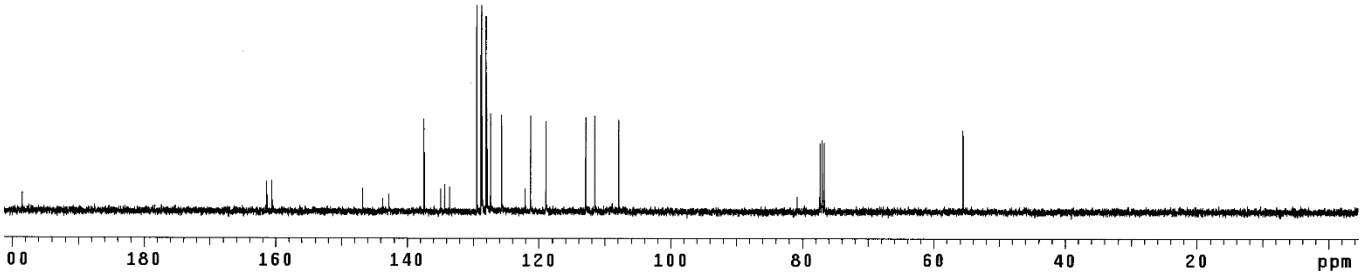
3ba

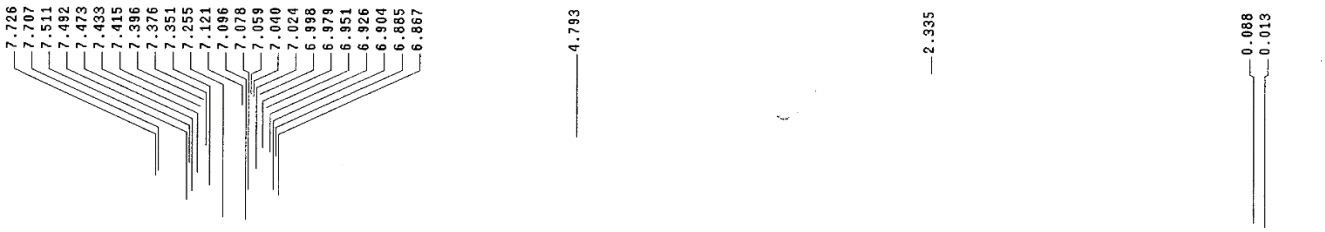


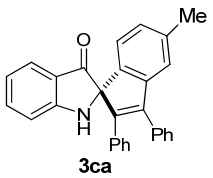

198.467
161.370
160.594
146.774
142.791
137.435
134.915
134.261
133.562
129.400
128.758
128.632
128.016
127.849
127.325
125.637
122.034
121.266
118.343
112.915
111.535
107.887
80.778
77.319
77.000
76.685
55.544


OMe
O
N
H
Ph
Ph

3ba

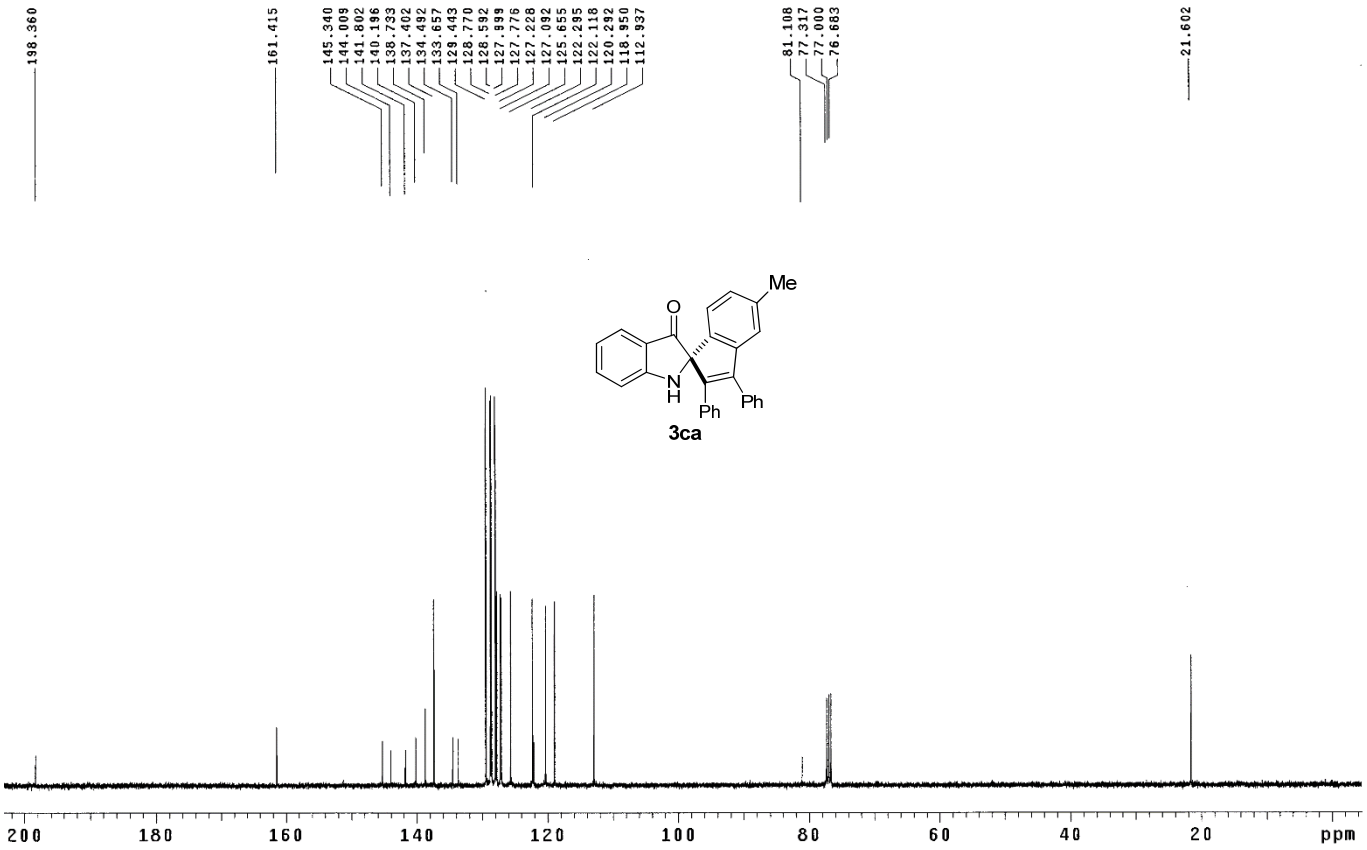

00
180
160
140
120
100
80
60
40
20
ppm


7.726
7.707
7.511
7.492
7.473
7.433
7.415
7.396
7.376
7.351
7.255
7.121
7.096
7.078
7.059
7.040
7.024
6.998
6.979
6.951
6.926
6.904
6.885
6.867
4.793
2.335
0.088
0.013


Me
O
N
H
Ph
Ph

3ca

8
7
6
5
4
3
2
1
ppm
0.89
5.23
1.20
0.99
3.10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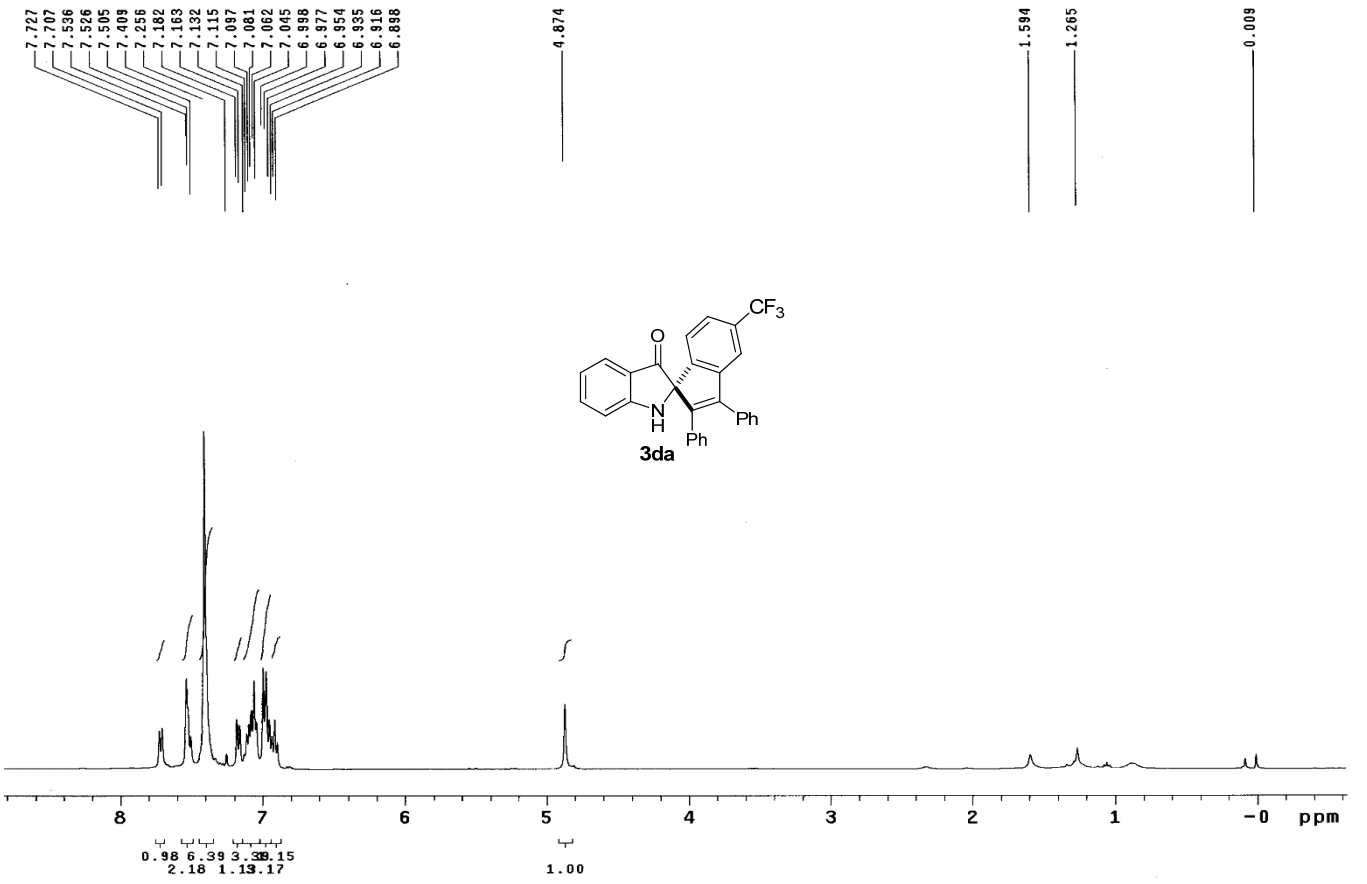
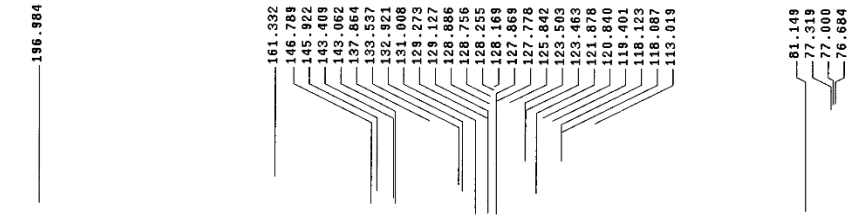
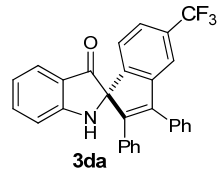
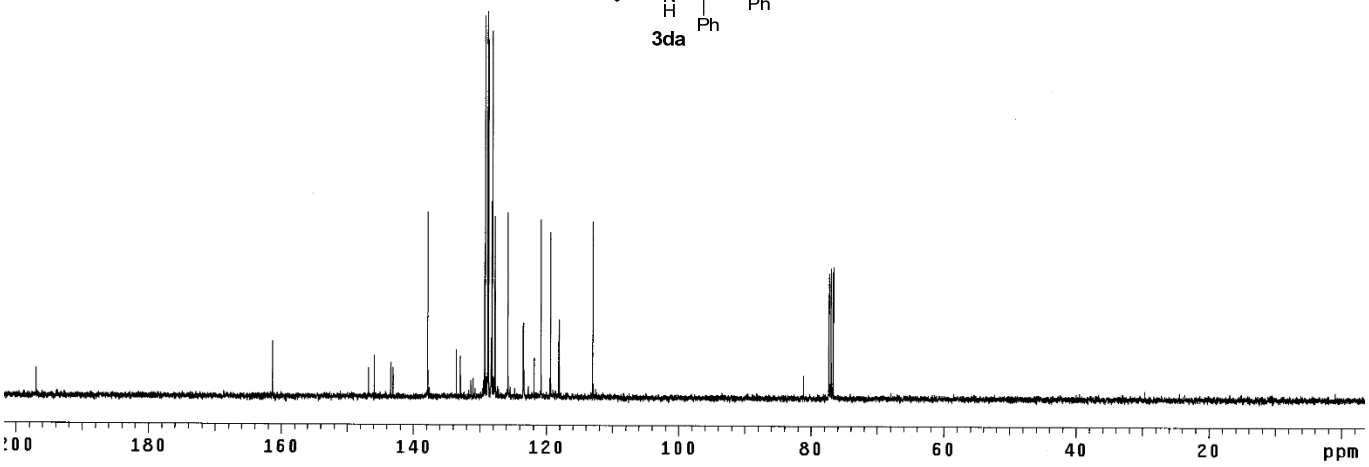
145.340
144.009
141.802
140.196
138.733
137.402
134.492
133.657
129.443
128.770
128.592
127.999
127.776
127.228
127.092
125.655
122.295
122.118
120.292
118.950
112.937
81.108
77.317
77.000
76.683
21.602
Me
O
N
H
Ph
Ph
3ca
200
180
160
140
120
100
80
60
40
20
ppm

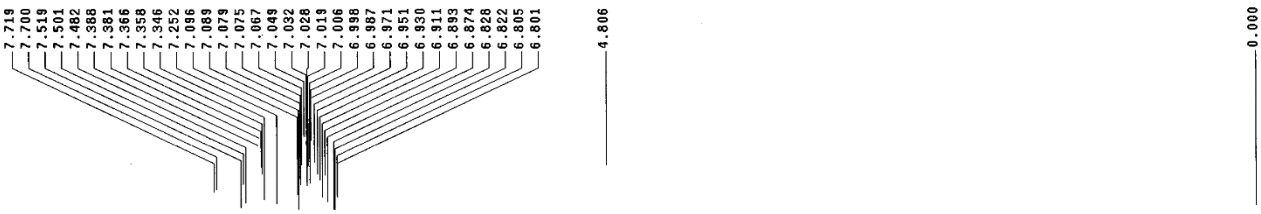

7.727
7.707
7.536
7.526
7.505
7.409
7.256
7.182
7.163
7.132
7.115
7.097
7.081
7.062
7.045
6.998
6.977
6.954
6.935
6.916
6.898
4.874
1.594
1.265
0.009
CF3
O
N
H
Ph
Ph
3da
8
7
6
5
4
3
2
1
-0
ppm
0.98
6.39
3.33
3.15
2.18
1.13
3.17
1.00


196.984
161.332
146.788
145.922
143.409
143.062
137.864
133.537
132.921
131.008
129.273
129.127
128.886
128.756
128.255
128.169
127.869
127.778
125.842
123.503
123.463
121.878
120.840
118.401
118.123
118.087
113.019
81.149
77.319
77.000
76.684


CF3
O
N
H
Ph
Ph

3da


200
180
160
140
120
100
80
60
40
20
ppm


7.719
7.700
7.519
7.501
7.482
7.388
7.381
7.366
7.358
7.346
7.252
7.096
7.089
7.079
7.075
7.067
7.049
7.032
7.028
7.018
7.006
6.998
6.987
6.971
6.951
6.930
6.911
6.893
6.874
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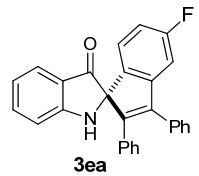
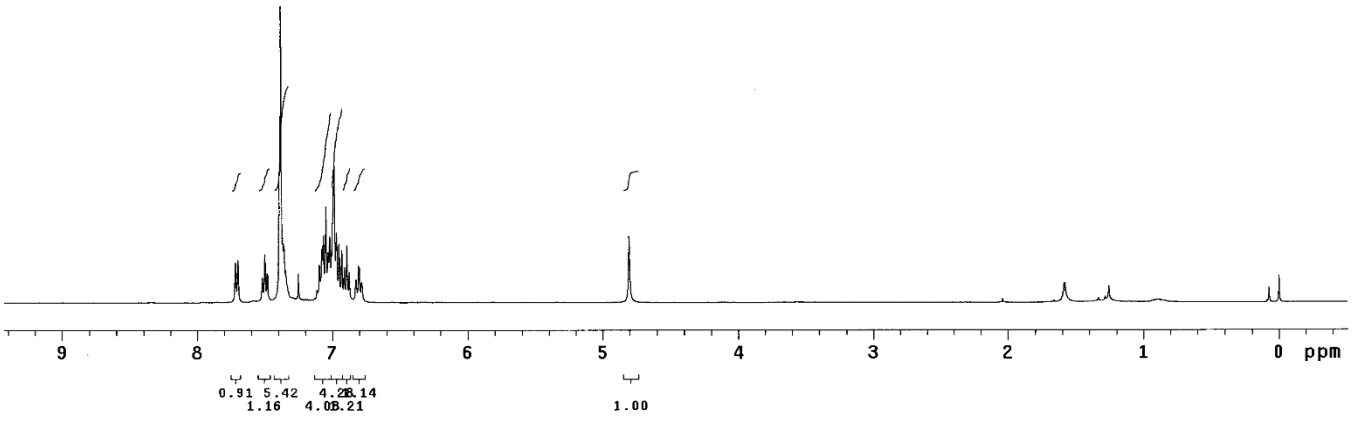
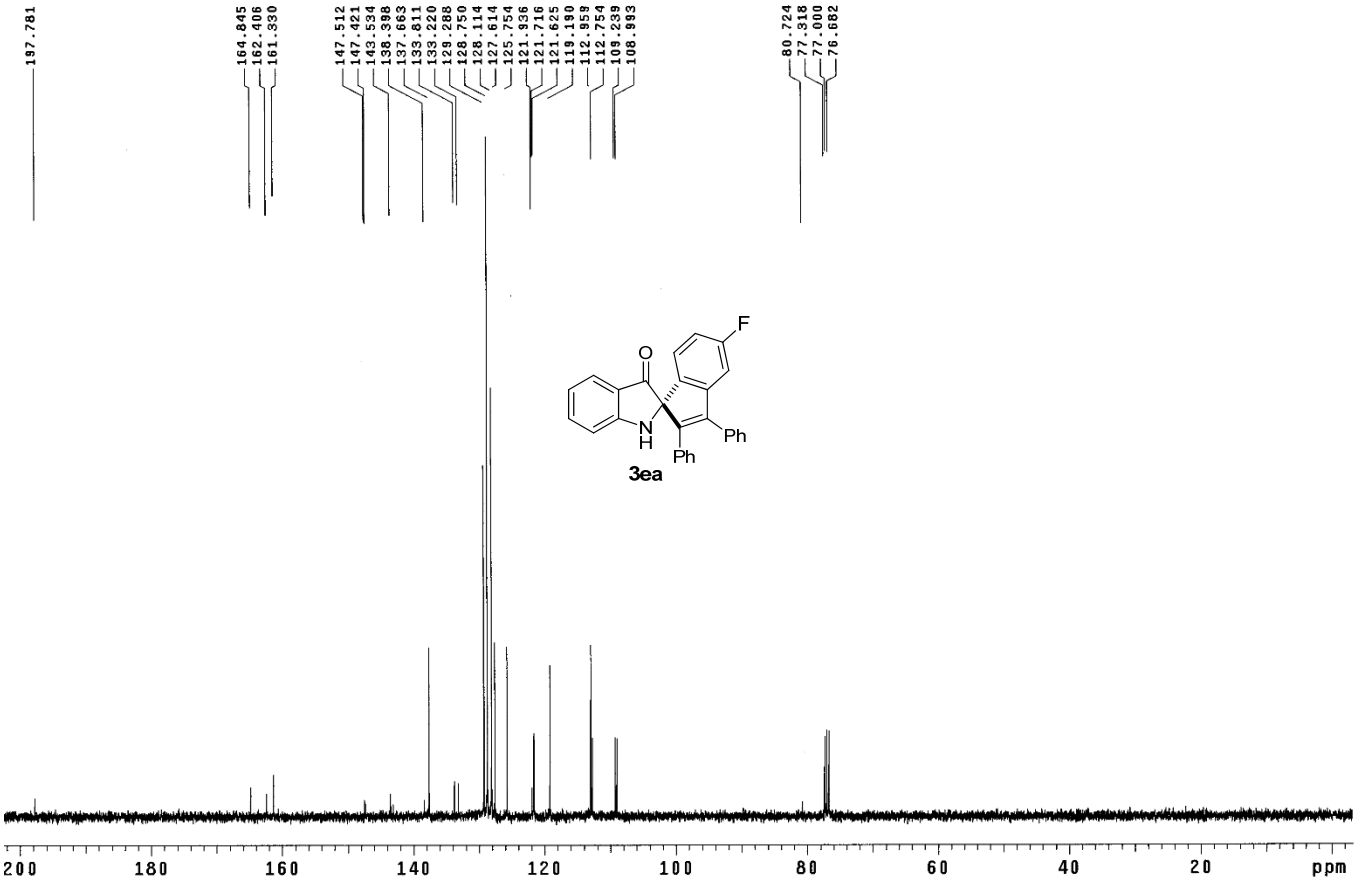
6.822
6.805
6.801
4.806
0.000

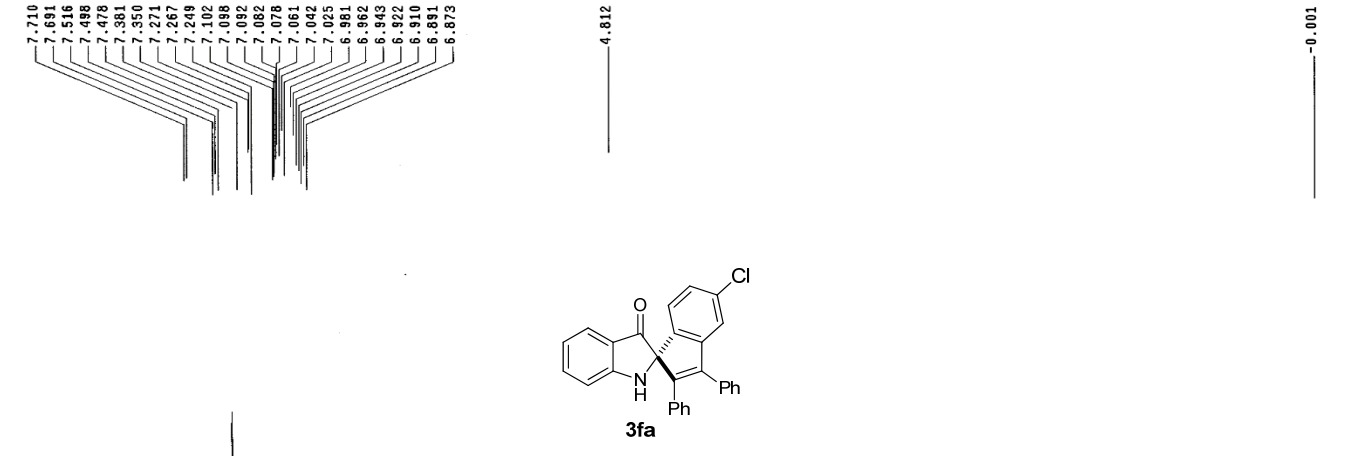

F
O
N
H
Ph
Ph

3ea

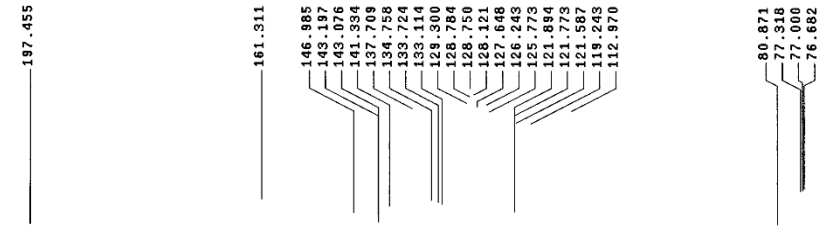

9
8
7
6
5
4
3
2
1
0
ppm
0.91
5.42
4.28
8.14
1.16
4.03
3.21
1.00

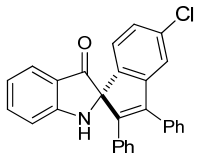

197.781
164.845
162.406
161.390
147.512
147.421
143.534
138.398
137.663
133.811
133.220
129.288
128.750
128.114
127.614
125.754
121.936
121.716
121.625
119.190
112.959
112.754
109.239
108.993
80.724
77.318
77.000
76.682
F
O
N
H
Ph
Ph
200
180
160
140
120
100
80
60
40
20
ppm

3ea

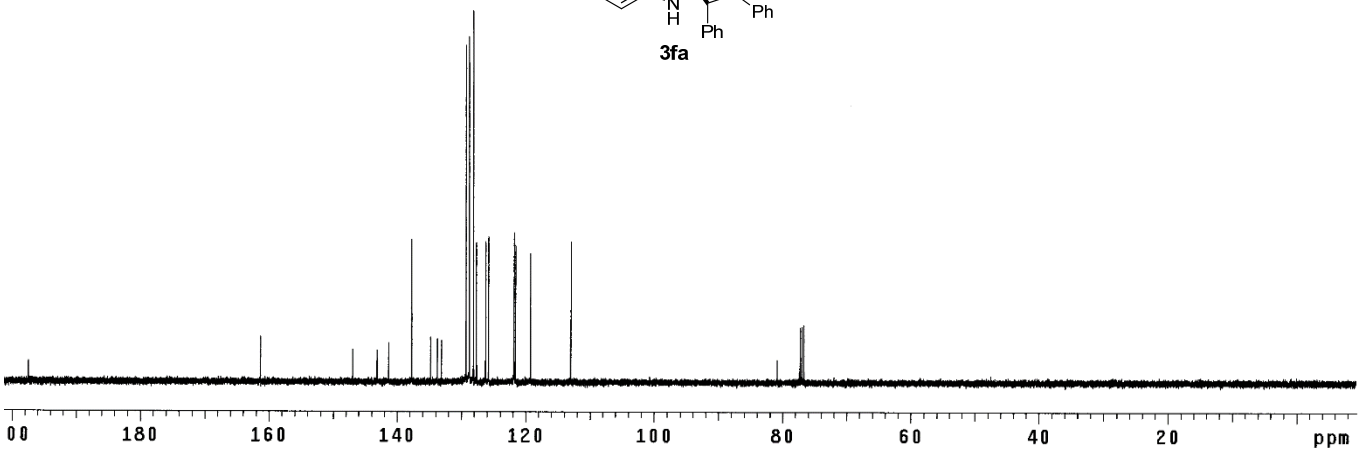

7.710
7.691
7.516
7.498
7.478
7.381
7.350
7.271
7.267
7.249
7.102
7.098
7.092
7.082
7.078
7.061
7.042
7.025
6.981
6.962
6.943
6.922
6.910
6.891
6.873
4.812
-0.001
Cl
O
N
H
Ph
Ph
8
7
6
5
4
3
2
1
ppm
0.91
5.26
1.96
48
1.09
0.92
2.33
76
1.00

3fa

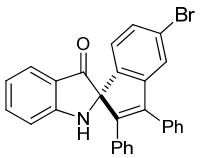

197.455
161.311
146.885
143.197
143.076
141.334
137.709
134.758
133.724
133.114
129.300
128.784
128.750
128.121
127.648
126.243
125.773
121.894
121.773
121.587
119.243
112.970
80.871
77.318
77.000
76.682


Cl
O
N
H
Ph
Ph

3fa

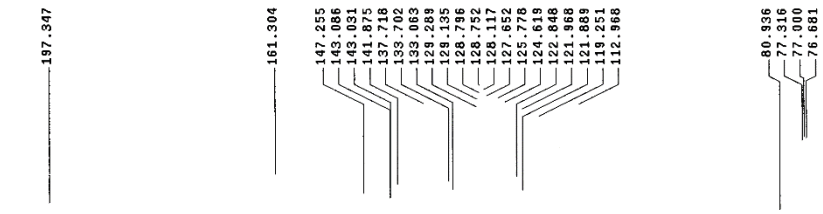

00
180
160
140
120
100
80
60
40
20
ppm

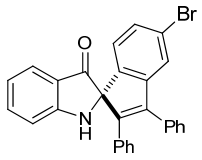

7.713
7.694
7.521
7.502
7.482
7.419
7.416
7.382
7.374
7.257
7.252
7.241
7.237
7.094
7.077
7.064
7.045
7.027
6.976
6.958
6.954
6.950
6.937
6.929
6.917
6.895
6.876
5.288
4.812
1.580
0.000


Br
O
N
H
Ph
Ph

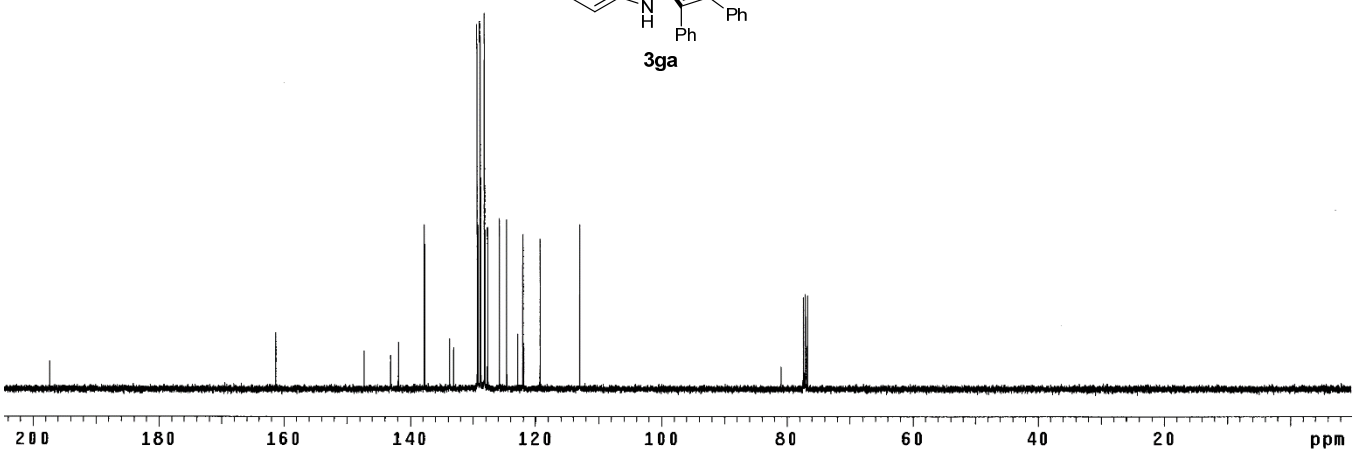
3ga

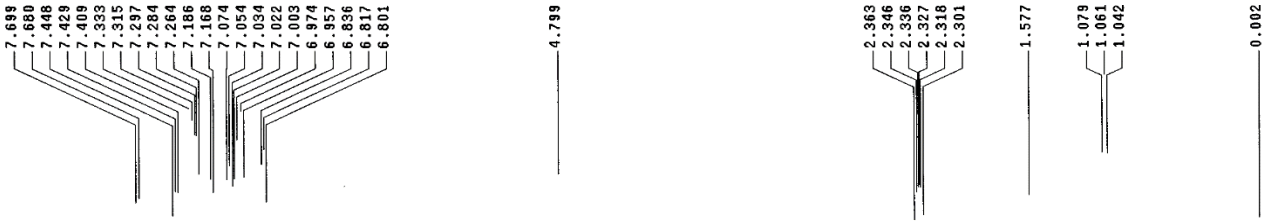
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.11
1.36
5.71
1.13

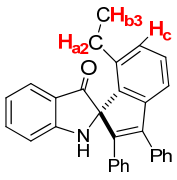

197.347
161.304
147.255
143.086
143.031
141.875
137.718
133.702
133.063
128.289
128.135
128.796
128.752
128.117
127.652
125.778
124.619
122.848
121.968
121.889
119.251
112.968
80.936
77.316
77.000
76.681


Br
O
N
H
Ph
Ph

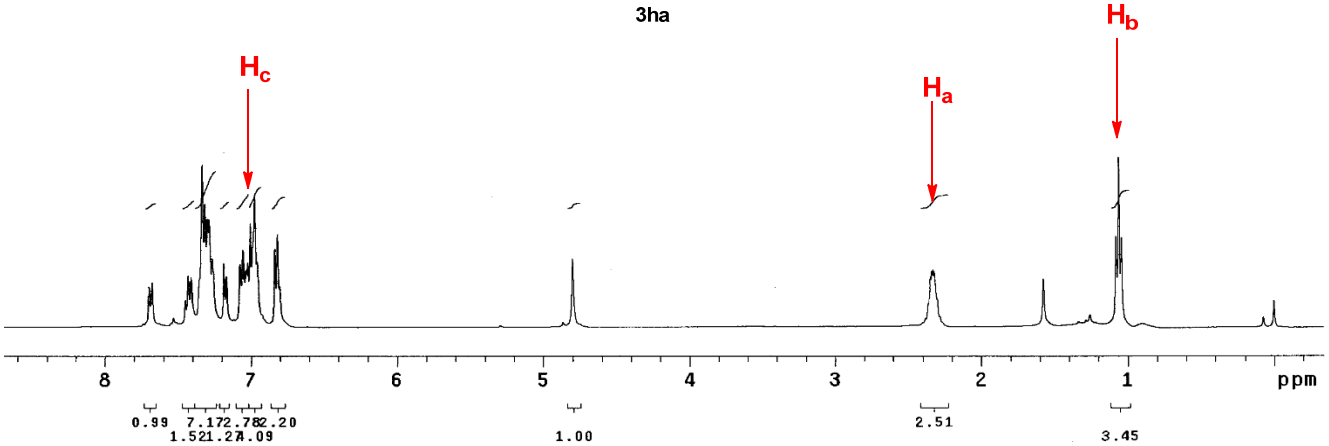
3ga

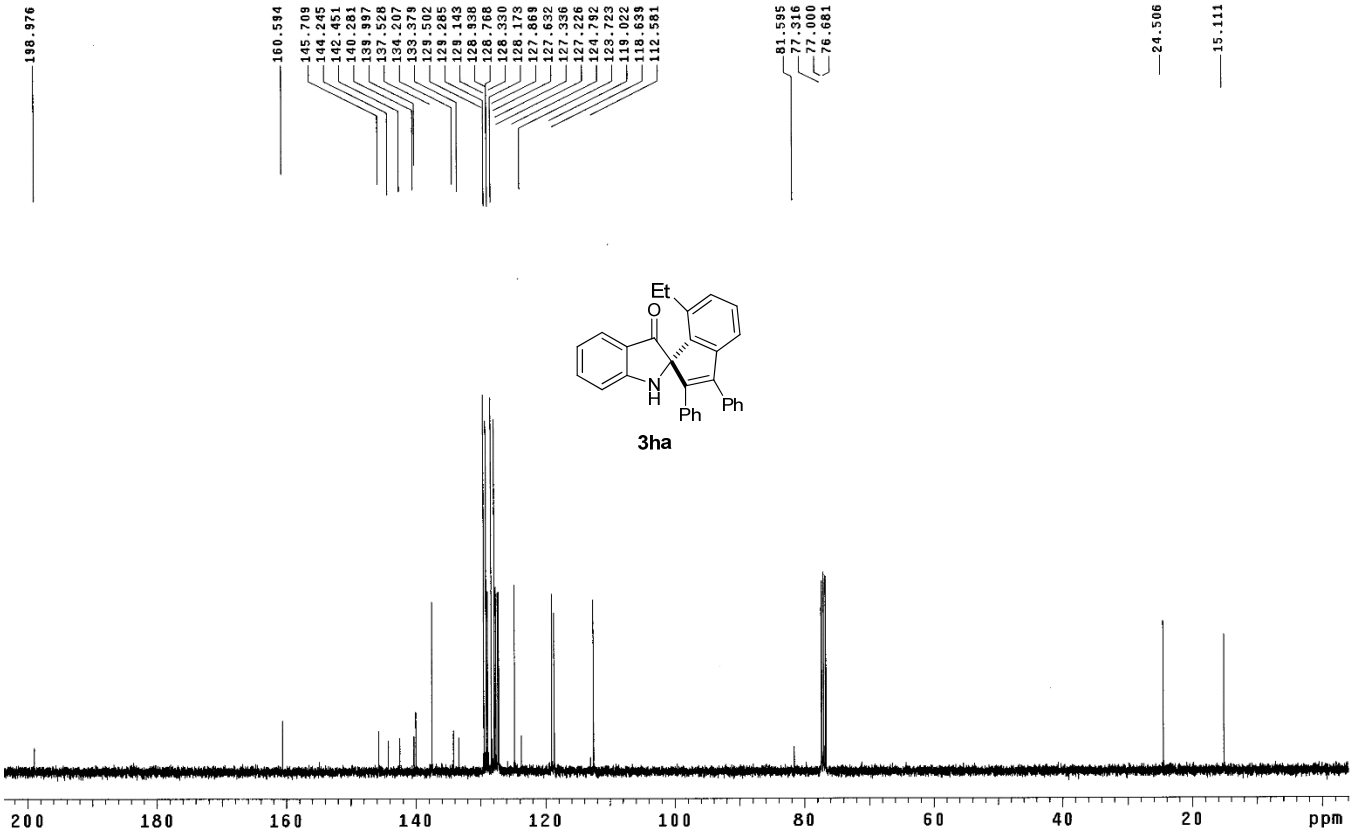

200
180
160
140
120
100
80
60
40
20
ppm

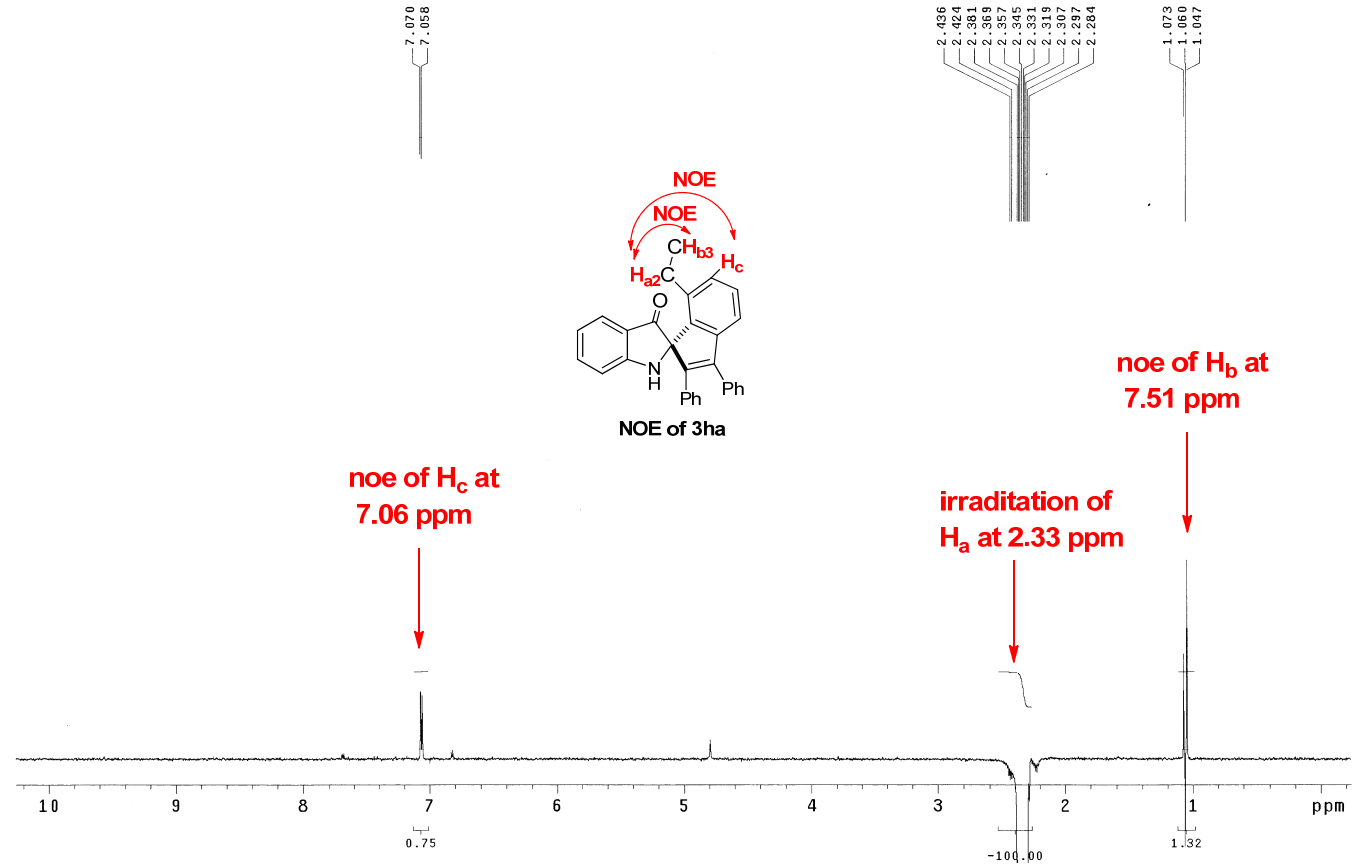

7.699
7.680
7.448
7.429
7.409
7.333
7.315
7.297
7.284
7.264
7.186
7.168
7.074
7.054
7.034
7.022
7.003
6.974
6.957
6.836
6.817
6.801
4.799
2.363
2.346
2.336
2.327
2.318
2.301
1.577
1.079
1.061
1.042
0.002

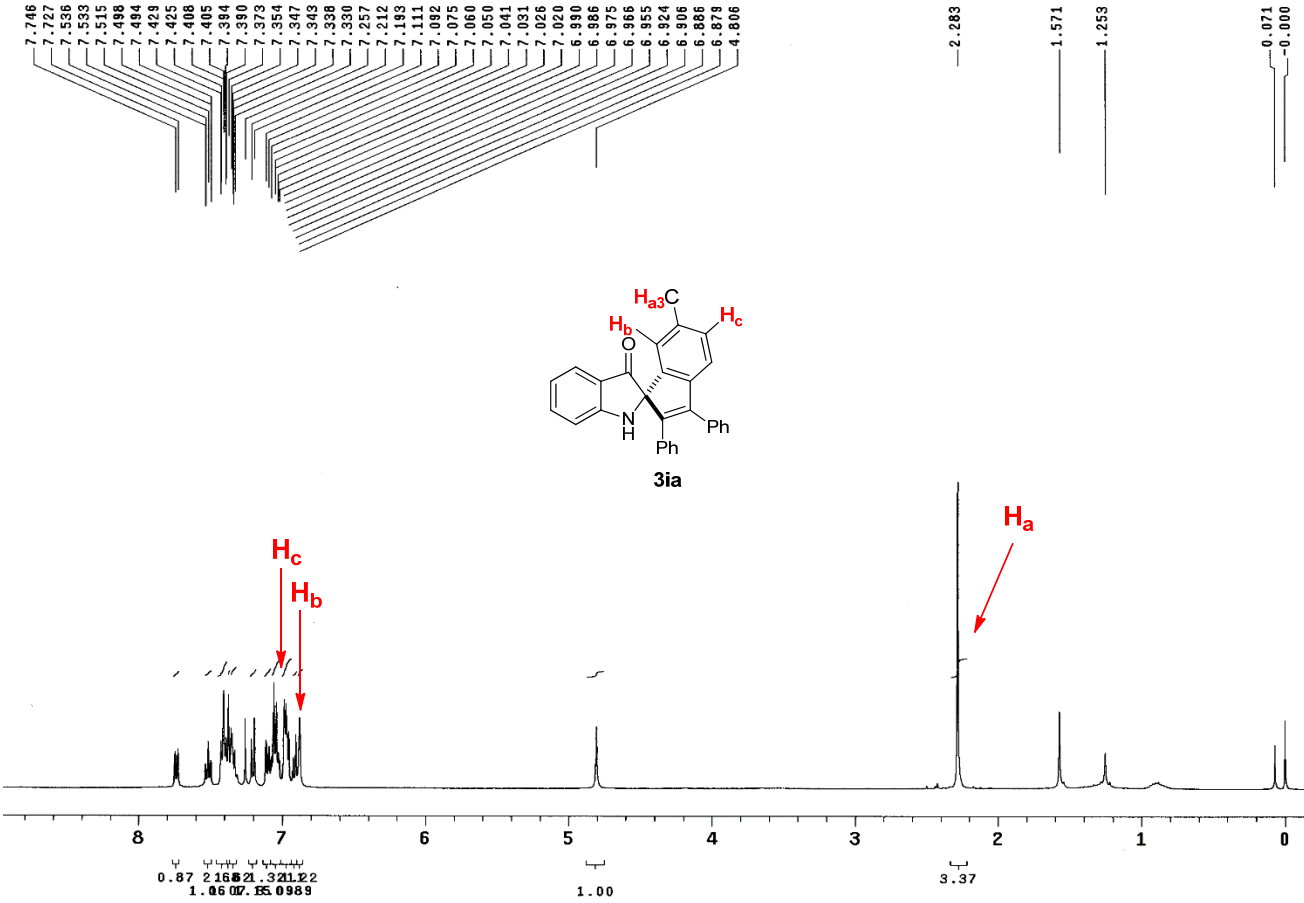

CHb3
Hc
Ha2
C
O
N
H
Ph
Ph

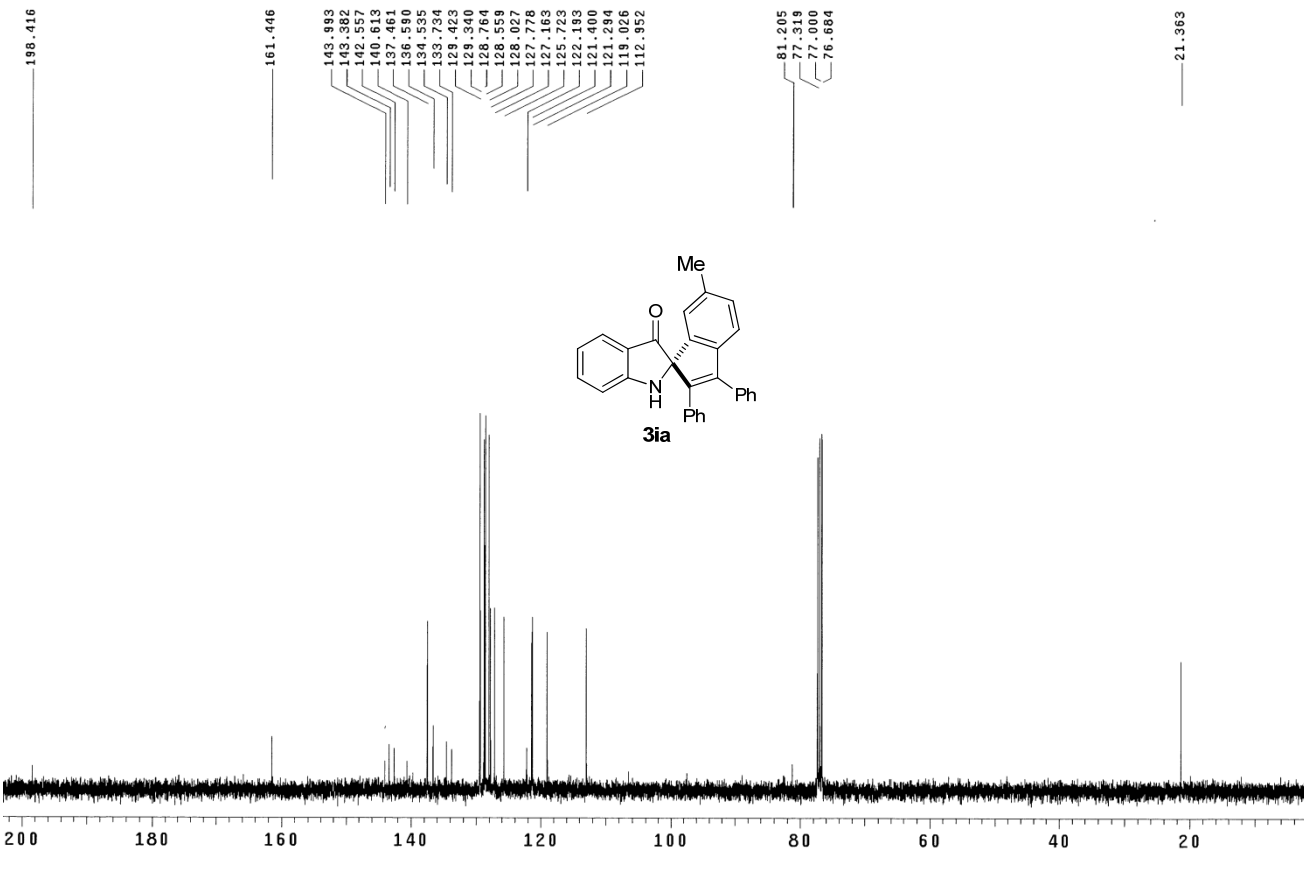
3ha

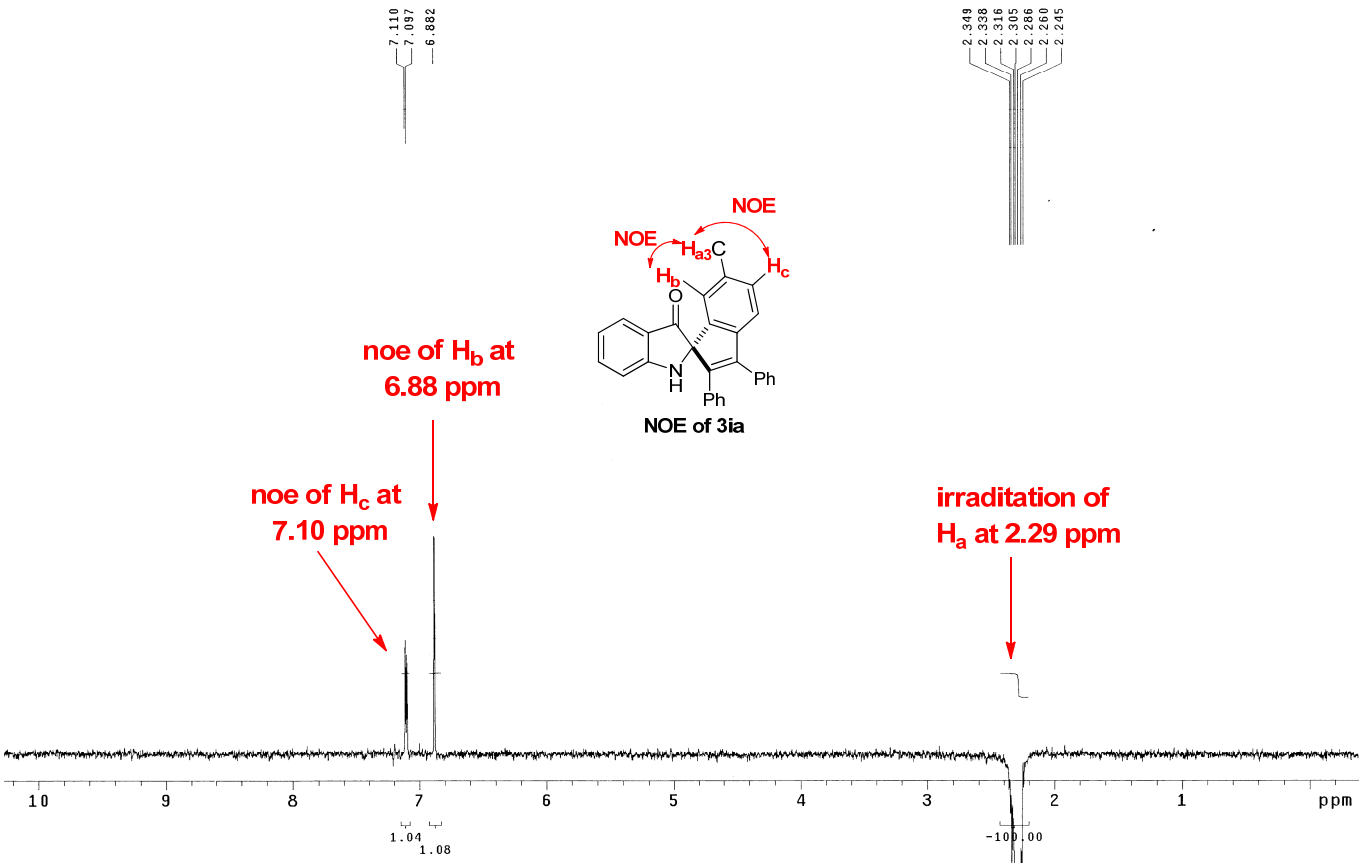

Hc
Ha
Hb
8
7
6
5
4
3
2
1
ppm
0.99
7.17
2.78
2.20
1.52
1.27
4.09
1.00
2.51
3.45

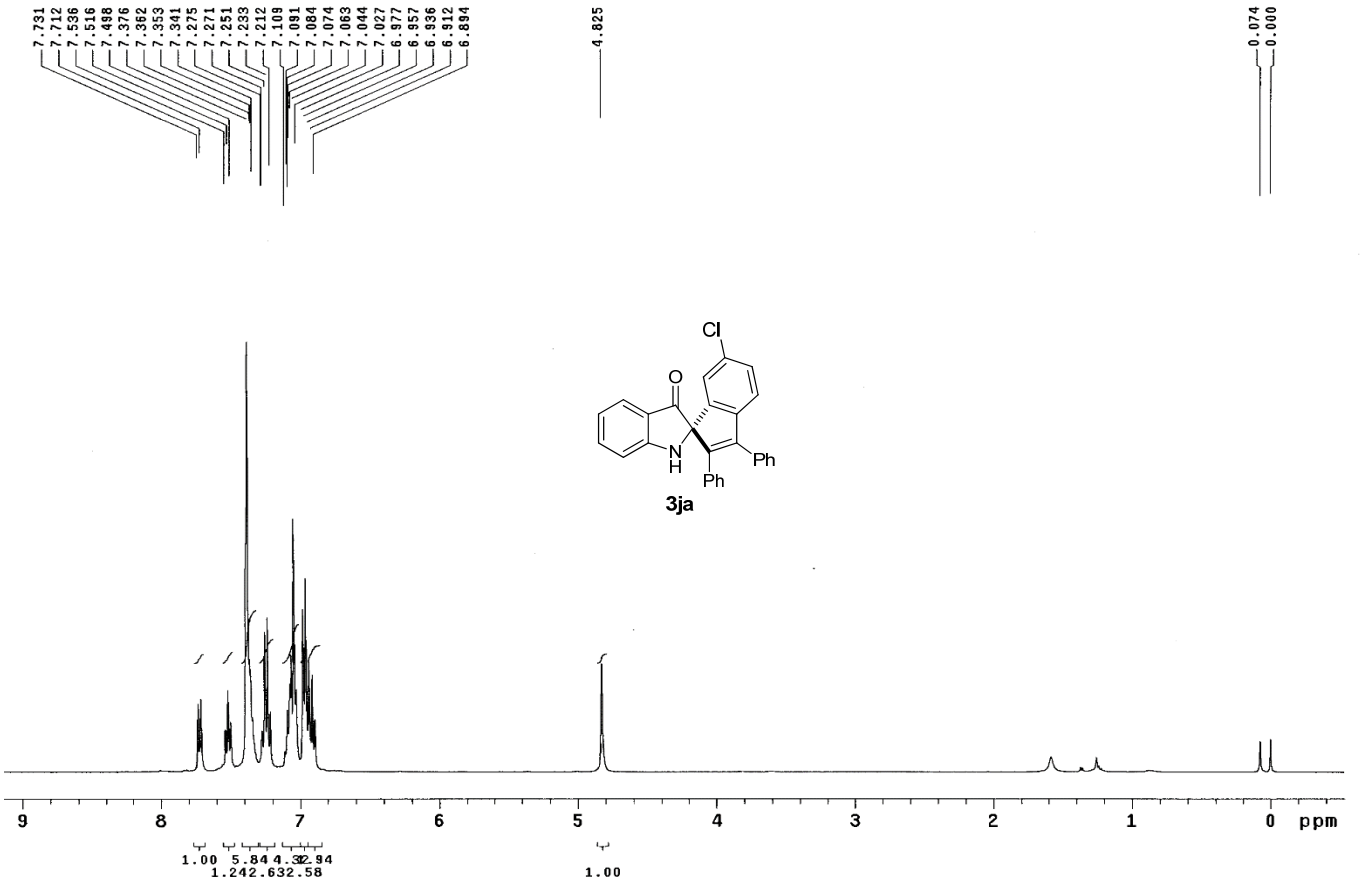

198.976
160.594
145.709
144.245
142.451
140.281
139.997
137.528
134.207
133.379
129.502
129.285
129.143
128.938
128.768
128.330
128.173
127.869
127.632
127.336
127.226
124.782
123.723
119.022
118.639
112.581
81.595
77.316
77.000
76.681
24.506
15.111
Et
O
N
H
Ph
Ph
3ha
200
180
160
140
120
100
80
60
40
20
ppm

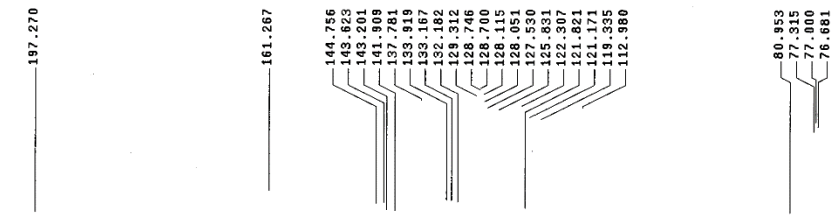

7.070
7.058
2.436
2.424
2.381
2.369
2.357
2.345
2.331
2.319
2.307
2.297
2.284
1.073
1.060
1.047
NOE
NOE
CHb3
Hc
Ha2
C
O
N
H
Ph
Ph
NOE of 3ha
noe of Hb at
7.51 ppm
noe of Hc at
7.06 ppm
irraditation of
Ha at 2.33 ppm
10
9
8
7
6
5
4
3
2
1
ppm
0.75
-100.00
1.32

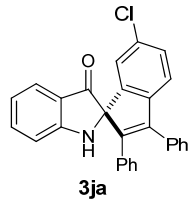

7.746
7.727
7.536
7.533
7.515
7.498
7.494
7.429
7.425
7.408
7.405
7.394
7.390
7.373
7.354
7.347
7.343
7.338
7.330
7.257
7.212
7.193
7.111
7.092
7.075
7.060
7.050
7.041
7.031
7.026
7.020
6.990
6.986
6.975
6.966
6.955
6.924
6.906
6.886
6.879
4.806
2.283
1.571
1.253
0.071
-0.000
Ha3C
Hb
Hc
O
N
H
Ph
Ph
3ia
Hc
Hb
Ha
8
7
6
5
4
3
2
1
0
ppm
0.87
1.00
3.37


198.416
161.446
143.993
143.382
142.557
140.613
137.461
136.590
134.535
133.734
129.423
129.340
128.764
128.559
128.027
127.778
127.163
125.723
122.193
121.400
121.294
119.026
112.952
81.205
77.319
77.000
76.684
21.363
Me
O
N
H
Ph
Ph
3ia
200
180
160
140
120
100
80
60
40
20
ppm


7.110
7.097
6.882
2.349
2.338
2.316
2.305
2.286
2.260
2.245
NOE
NOE
$H_{a3}C$
H_b
H_c
O
N
H
Ph
Ph
NOE of 3ia
noe of H_b at 6.88 ppm
noe of H_c at 7.10 ppm
irraditation of H_a at 2.29 ppm
10
9
8
7
6
5
4
3
2
1
ppm
1.04
1.08
-100.00

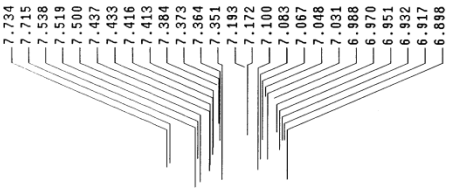

7.731
7.712
7.536
7.516
7.498
7.376
7.362
7.353
7.341
7.275
7.271
7.251
7.233
7.212
7.109
7.091
7.084
7.074
7.063
7.044
7.027
6.977
6.957
6.936
6.912
6.894
4.825
0.074
0.000
Cl
O
N
H
Ph
Ph
3ja
9
8
7
6
5
4
3
2
1
0
ppm
1.00
5.84
4.32
2.94
1.24
2.63
2.58
1.00


197.270
161.267
144.756
143.623
143.201
141.908
137.781
133.919
133.167
132.182
129.312
128.746
128.700
128.115
128.051
127.530
125.831
122.307
121.821
121.171
119.335
112.980
80.953
77.315
77.000
76.681


Cl
O
N
H
Ph
Ph

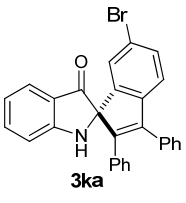
3ja

200
180
160
140
120
100
80
60
40
20
ppm


7.734
7.715
7.538
7.519
7.500
7.437
7.433
7.416
7.413
7.384
7.373
7.364
7.351
7.193
7.172
7.100
7.083
7.067
7.048
7.031
6.988
6.970
6.951
6.932
6.917
6.888

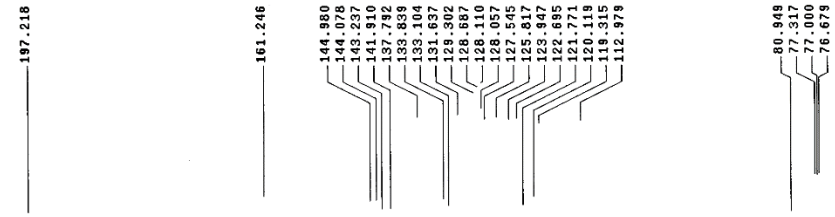

4.837

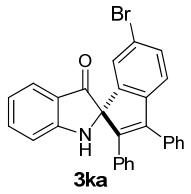
0.095


Br
O
N
H
Ph
Ph

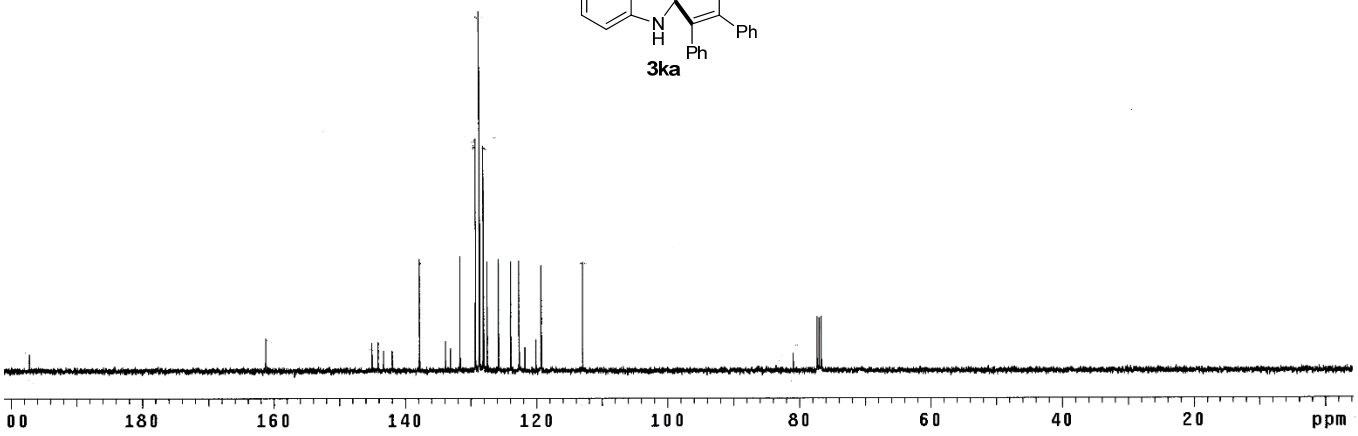
3ka

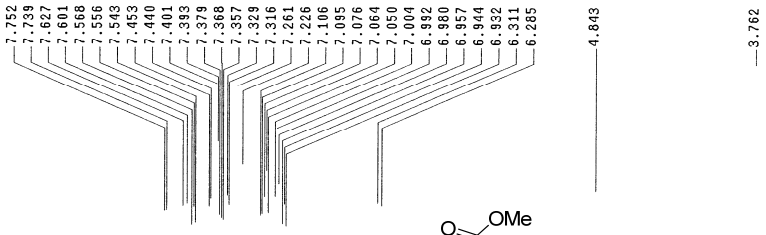
9
8
7
6
5
4
3
2
1
ppm
1.00
1.15
1.05

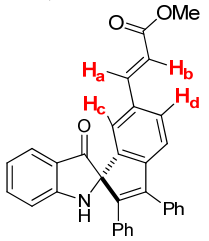




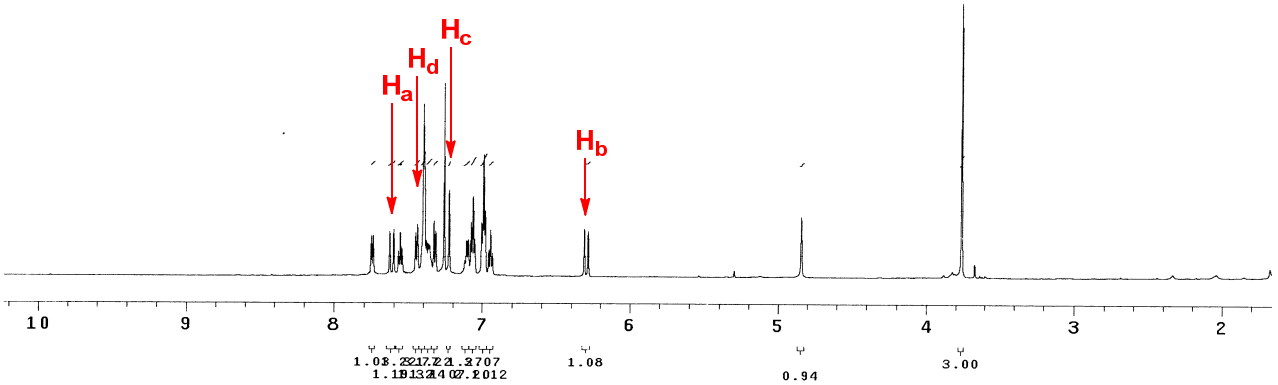
3ka

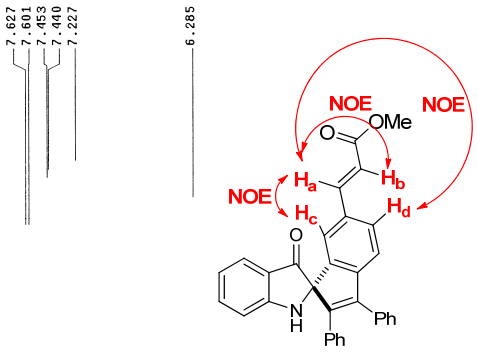




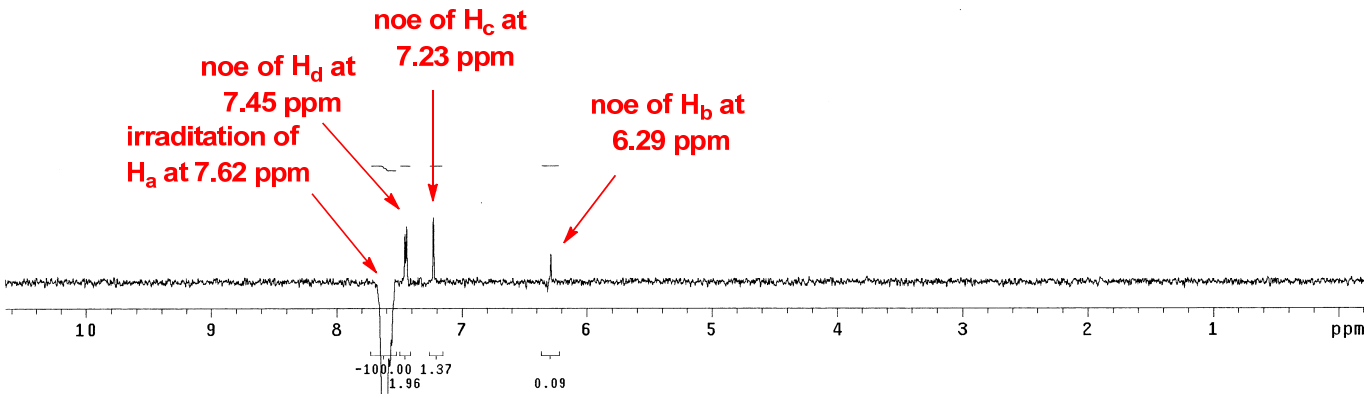


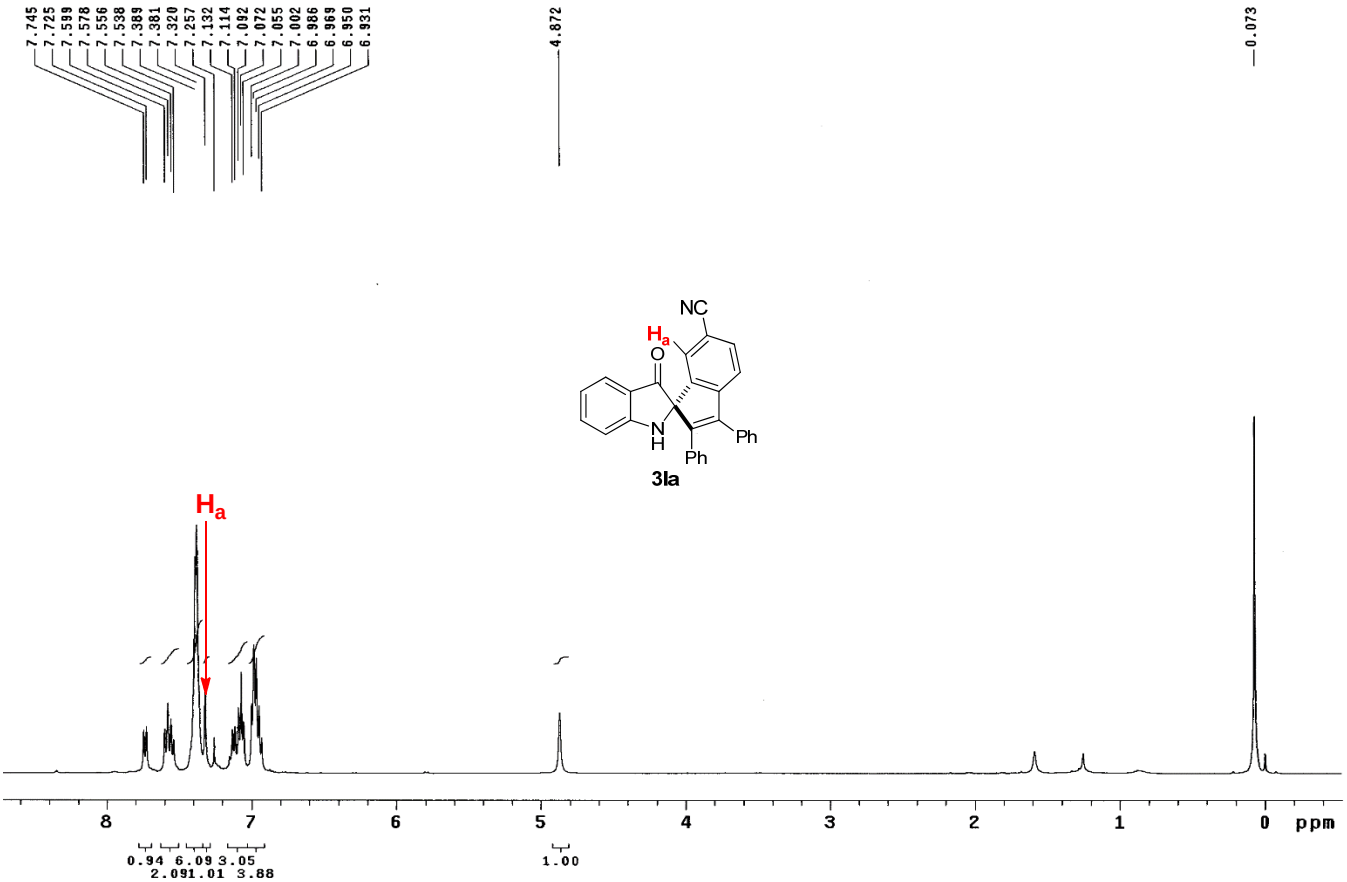
alkenylation of 3ka



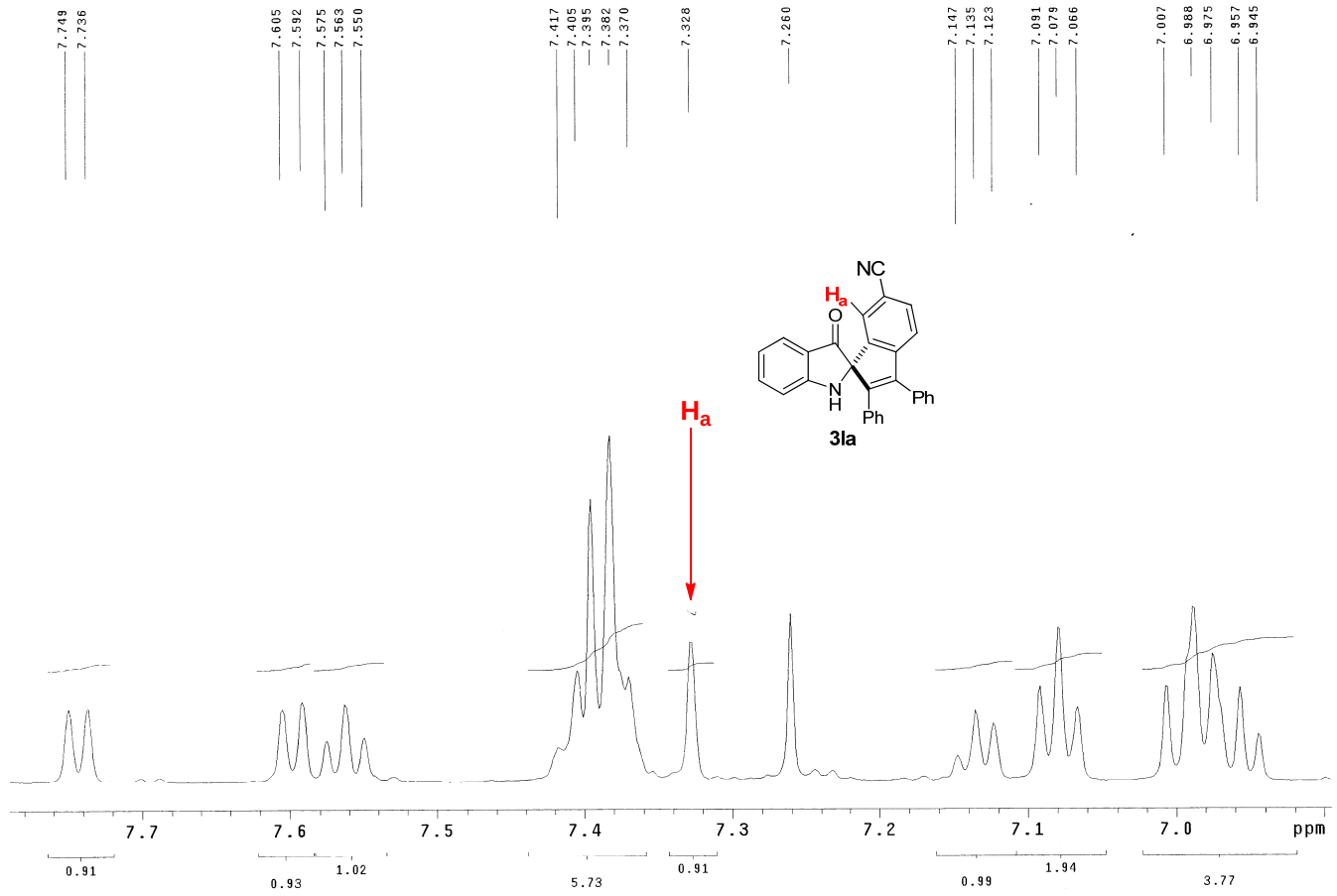


NOE of alkenylation of 3ka





3la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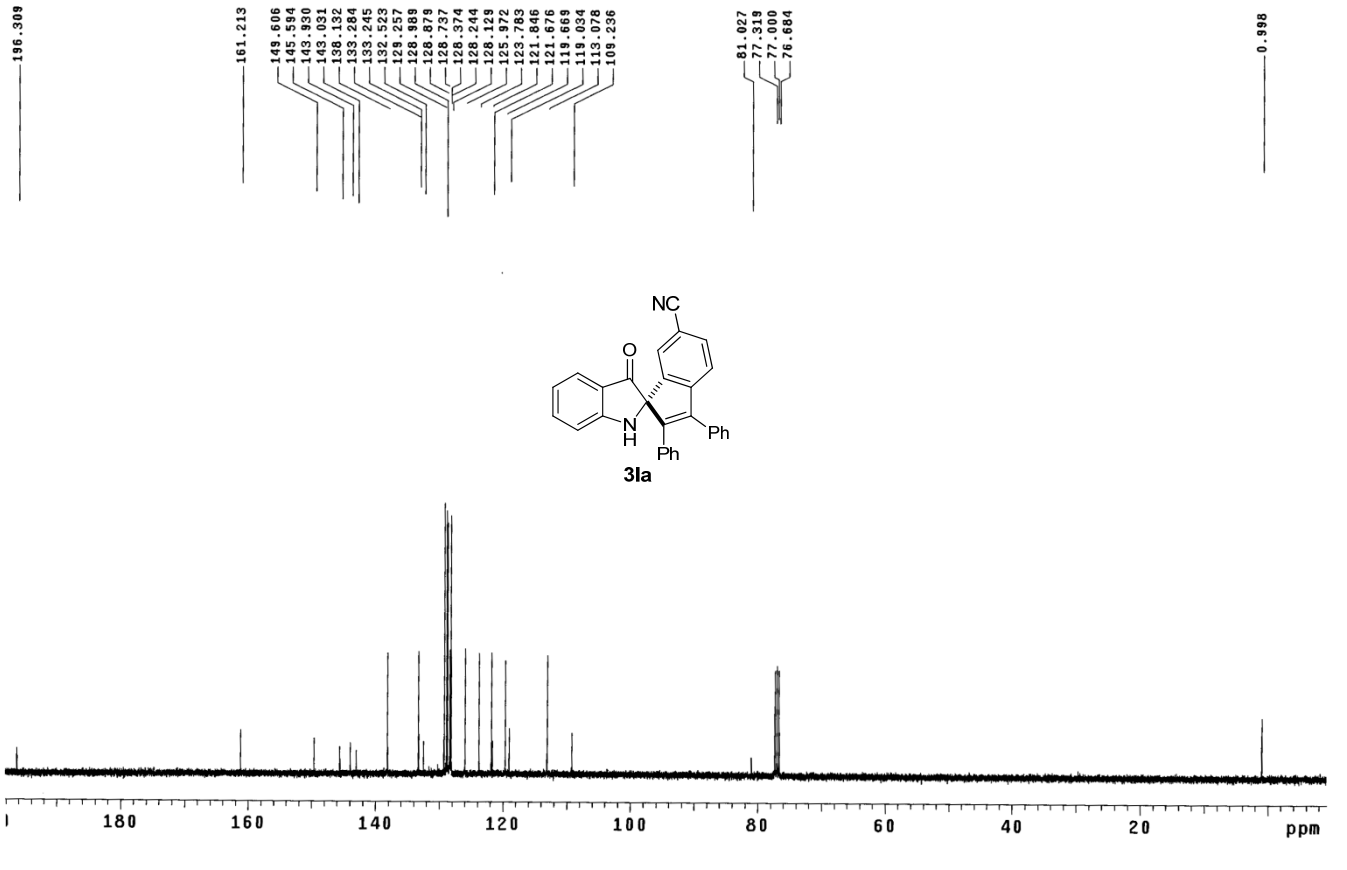
7.417
7.405
7.395
7.382
7.370
7.328
7.260
7.147
7.135
7.123
7.091
7.079
7.066
7.007
6.988
6.975
6.957
6.945
NC
Ha
O
N
H
Ph
Ph
3la
Ha
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
ppm
0.91
0.93
1.02
5.73
0.91
0.99
1.94
3.77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132.523
129.257
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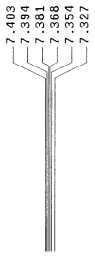
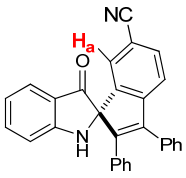
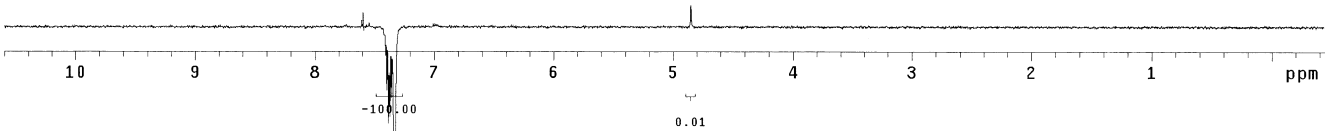
128.879
128.737
128.374
128.244
128.129
125.972
123.783
121.846
121.676
119.669
119.034
113.078
109.236
81.027
77.319
77.000
76.684
0.998
NC
O
N
H
Ph
Ph
3la
180
160
140
120
100
80
60
40
20
ppm

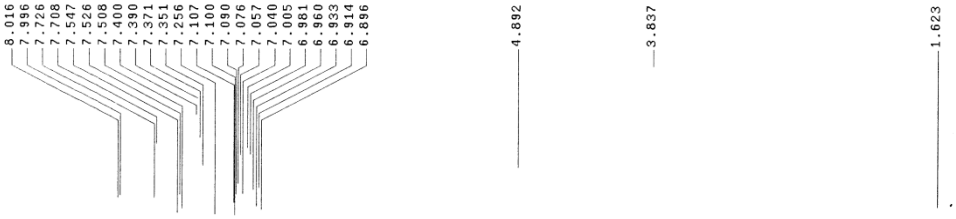


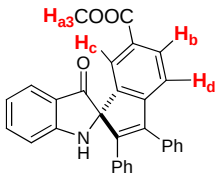


3la

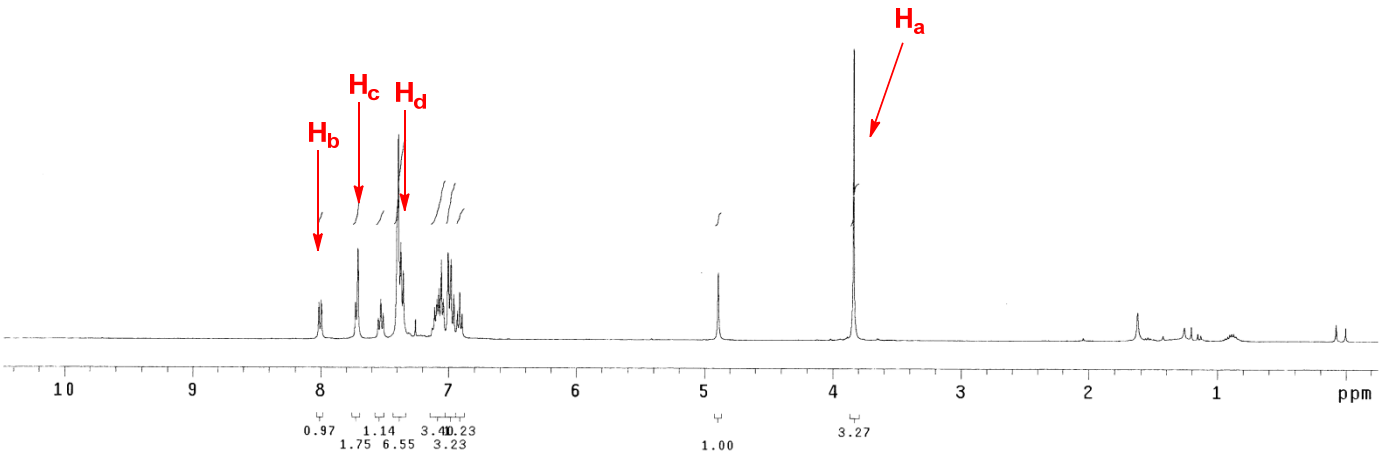
irraditation of H_a at 7.32 ppm

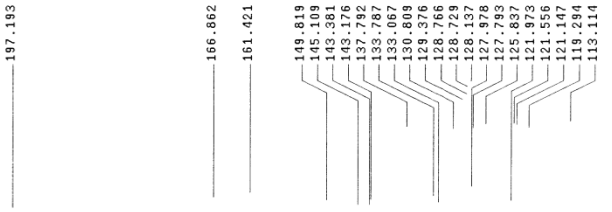


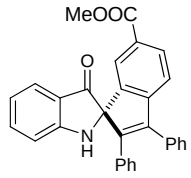




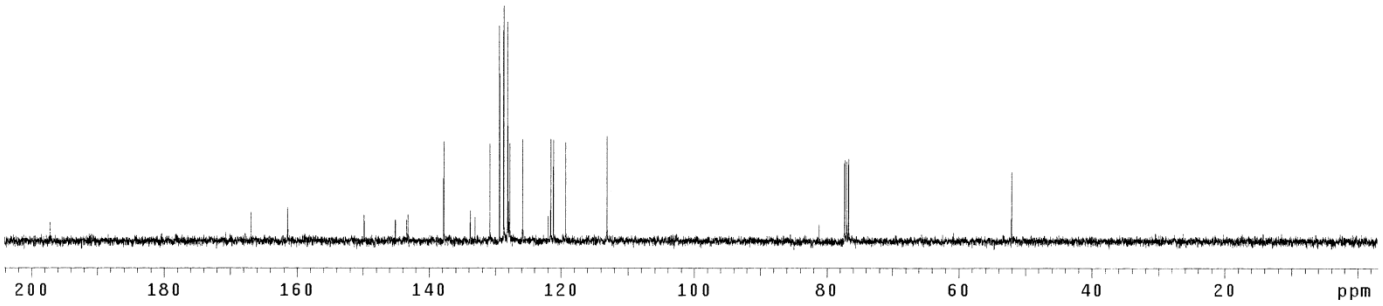
3ma

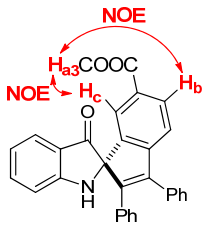




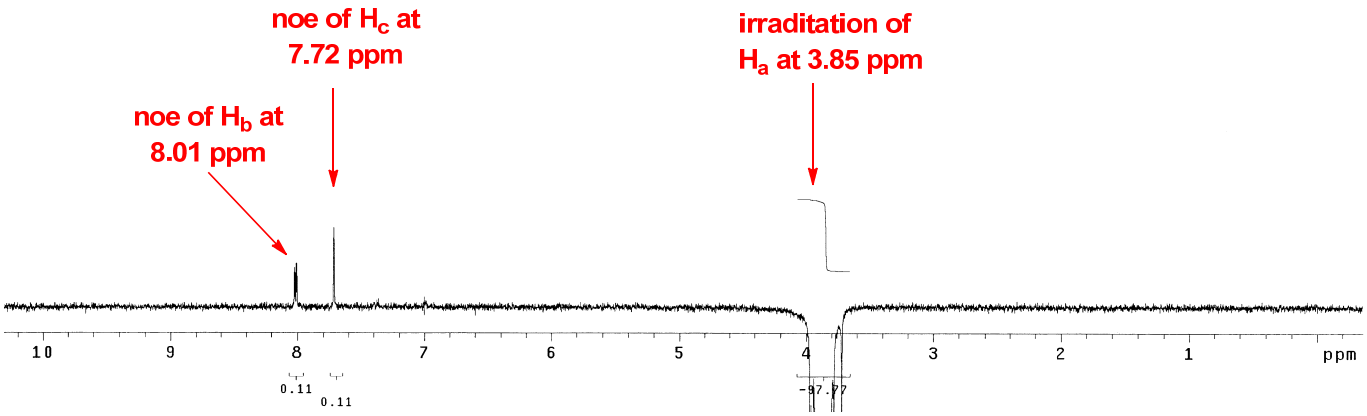


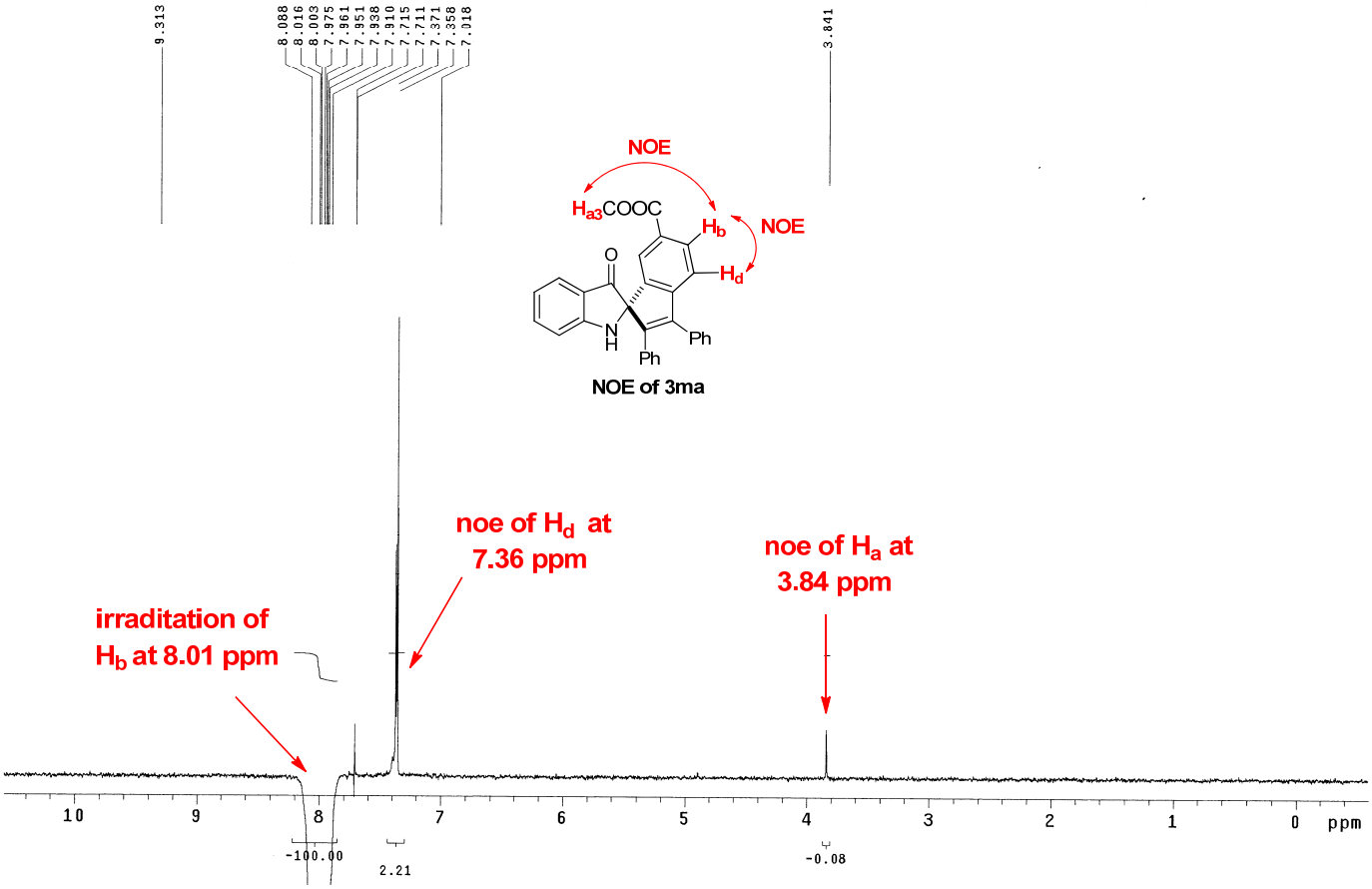
3ma





NOE of 3ma

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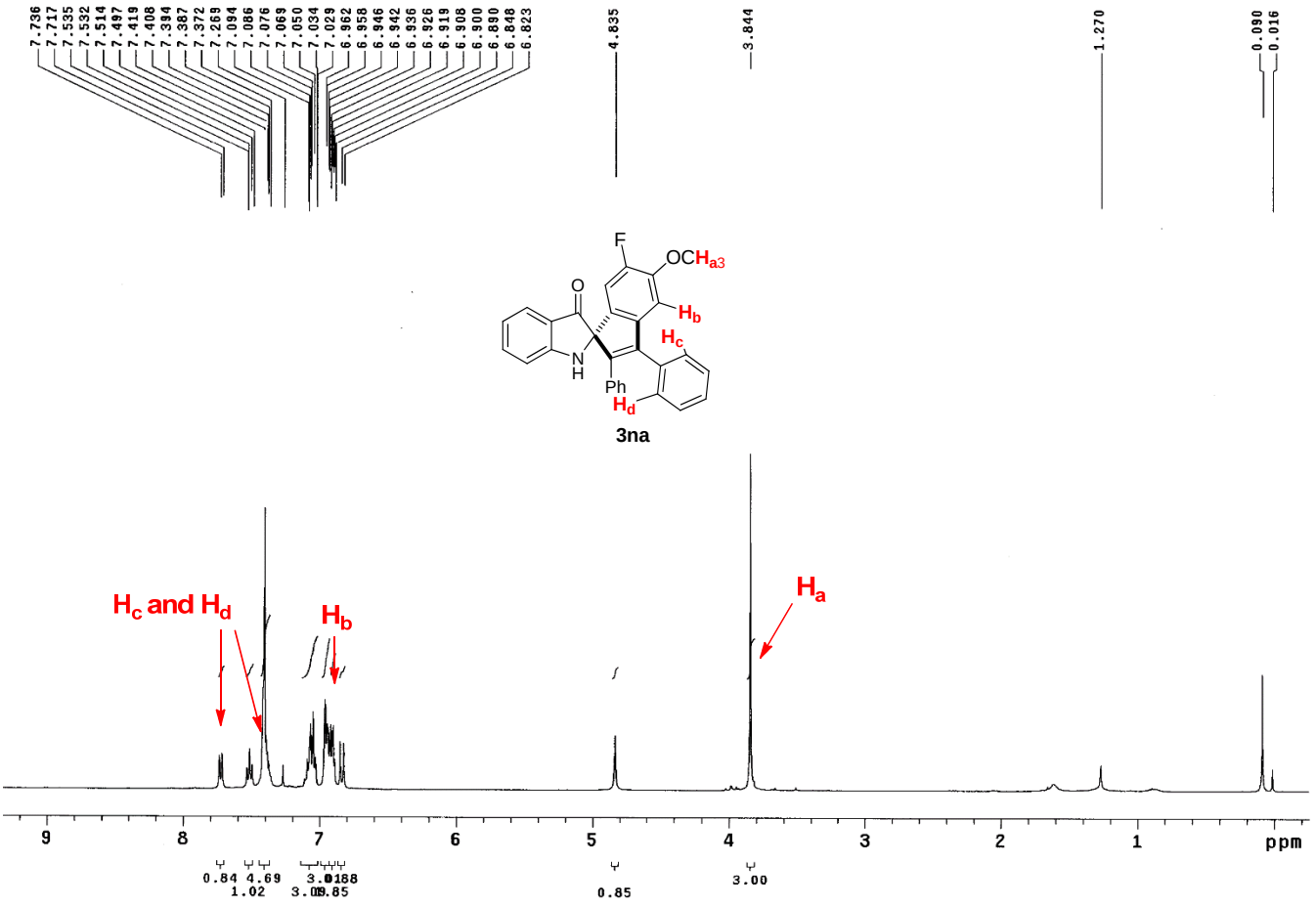
8.088
8.016
8.003
7.975
7.961
7.951
7.938
7.910
7.715
7.711
7.371
7.358
7.018
3.841
NOE
Ha3COOC
Hb
NOE
Hd
O
N
H
Ph
Ph
NOE of 3ma
noe of Hd at 7.36 ppm
noe of Ha at 3.84 ppm
irraditation of Hb at 8.01 ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
-100.00
2.21
-0.08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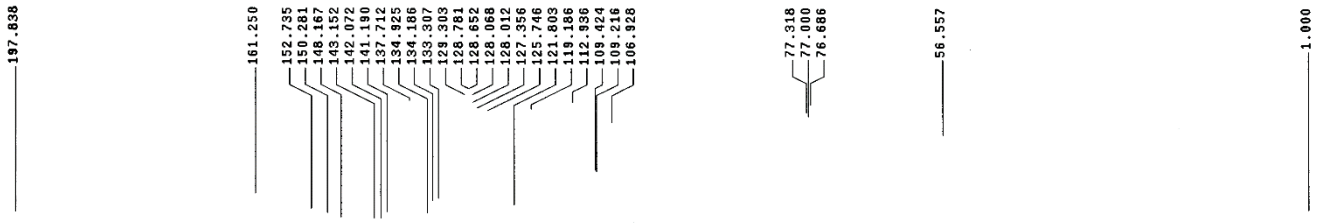
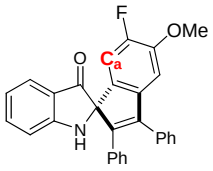
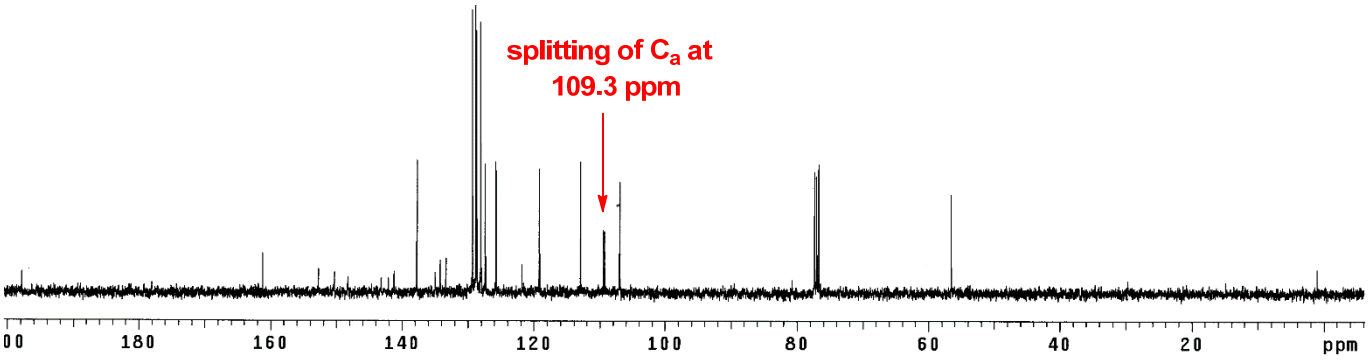
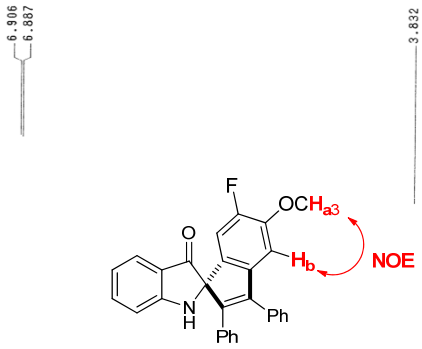
7.717
7.535
7.532
7.514
7.497
7.419
7.408
7.394
7.387
7.372
7.269
7.094
7.086
7.076
7.069
7.050
7.034
7.029
6.962
6.958
6.946
6.942
6.936
6.926
6.919
6.908
6.900
6.880
6.848
6.823
4.835
3.844
1.270
0.090
0.016
F
OCHa3
O
Hb
Hc
N
H
Ph
Hd
3na
Hc and Hd
Hb
Ha
9
8
7
6
5
4
3
2
1
ppm
0.84
4.69
3.00
1.02
0.85
3.00



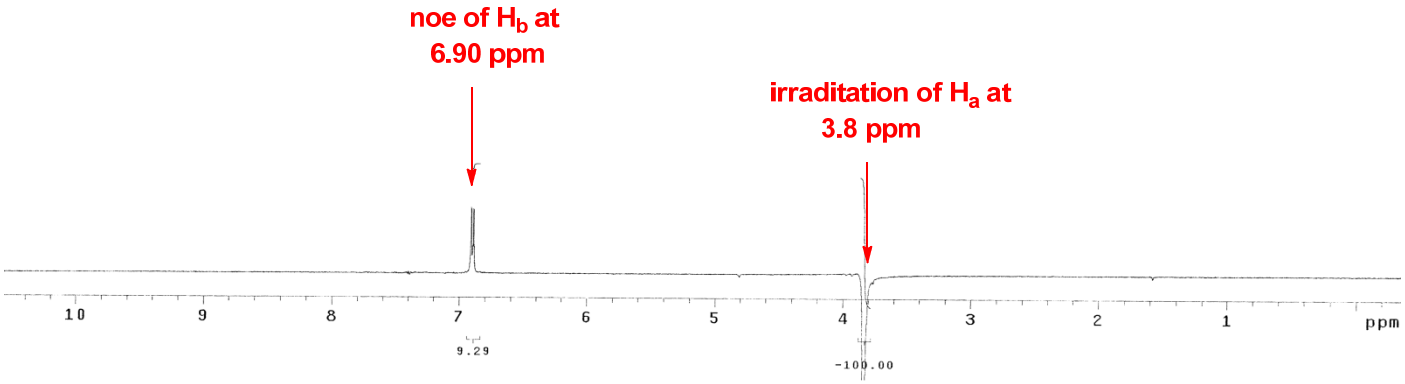


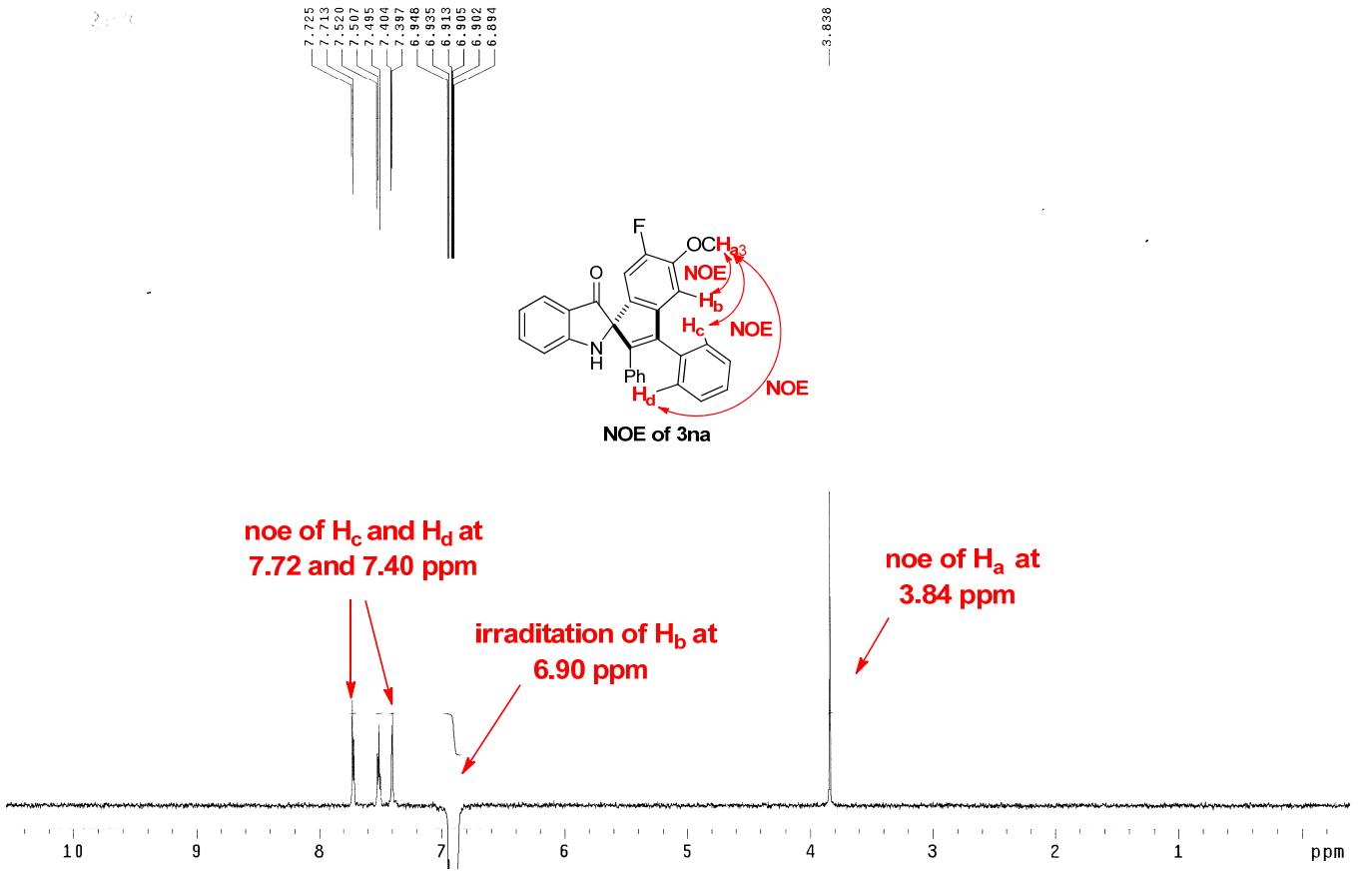
3na





NOE of 3na

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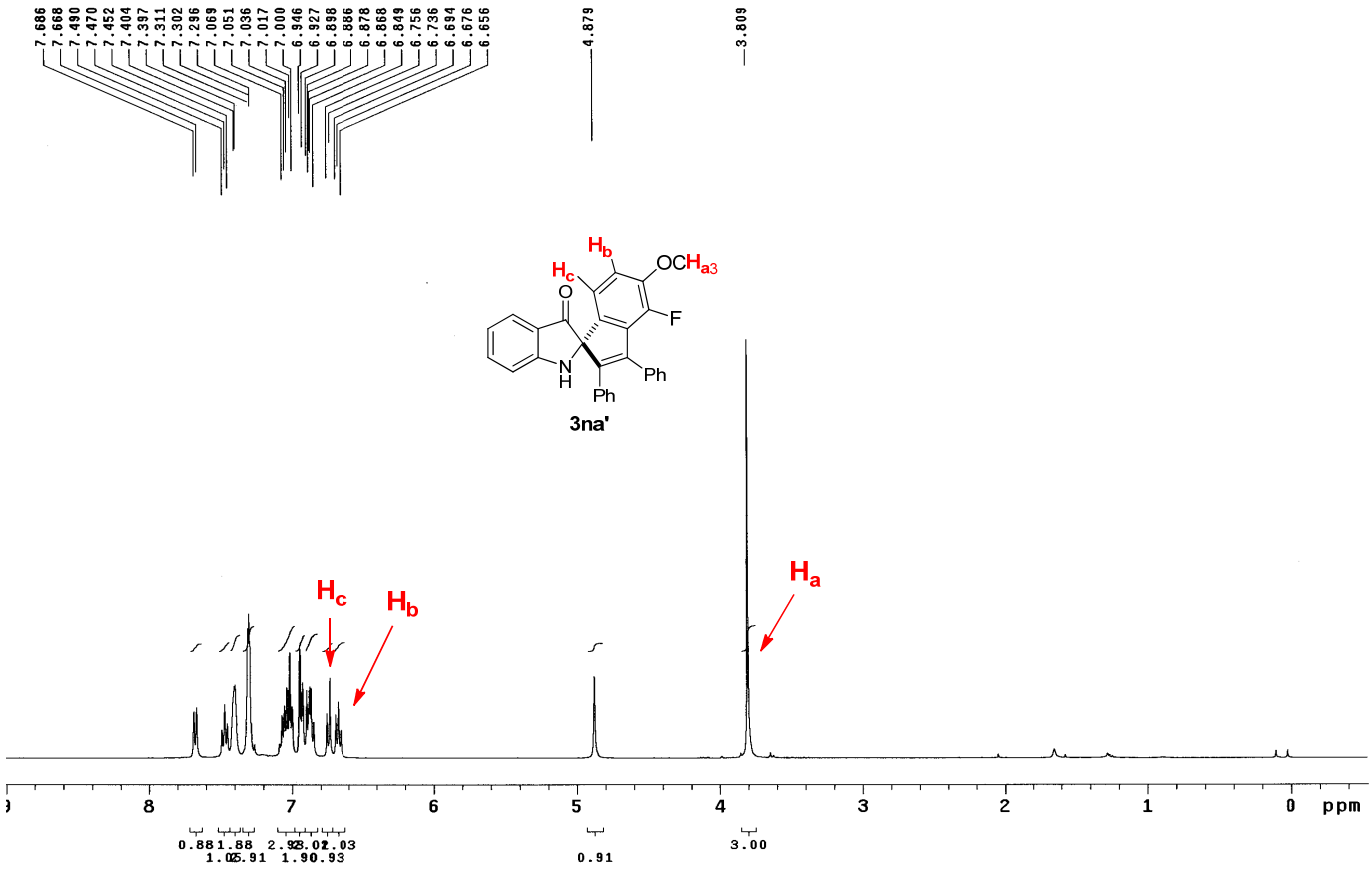
7.507
7.495
7.404
7.397
6.948
6.935
6.913
6.905
6.902
6.894
3.838
F
OCH$_{a3}$
O
NOE
H$_b$
H$_c$
NOE
N
H
Ph
H$_d$
NOE
NOE of 3na
noe of H$_c$ and H$_d$ at
7.72 and 7.40 ppm
irraditation of H$_b$ at
6.90 ppm
noe of H$_a$ at
3.84 ppm
10
9
8
7
6
5
4
3
2
1
ppm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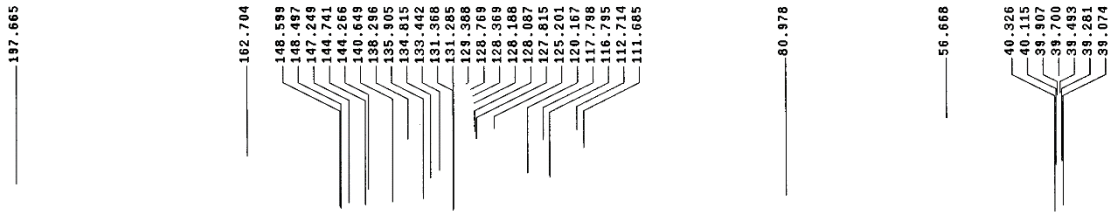
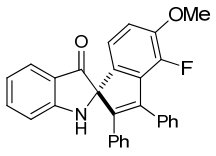
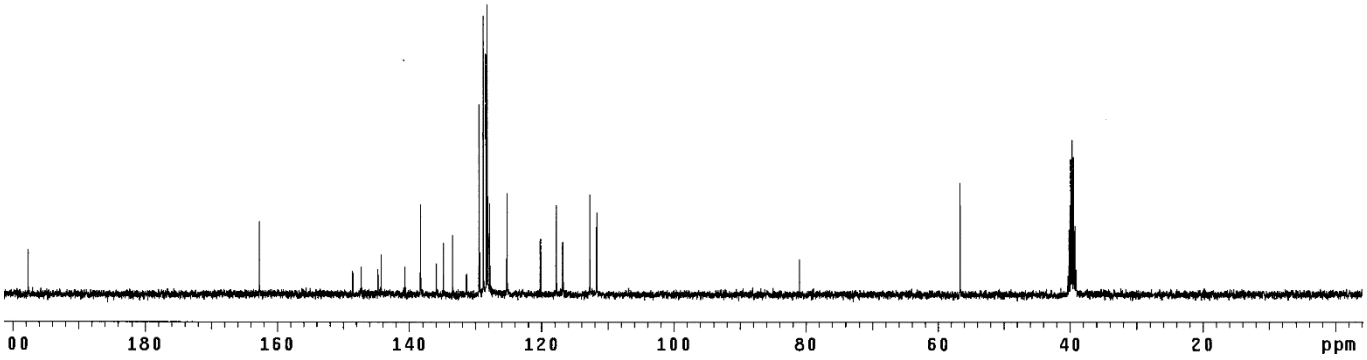
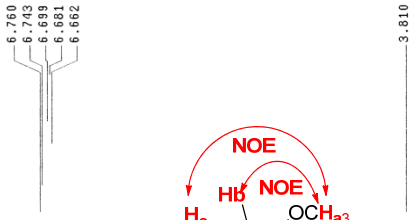
7.470
7.452
7.404
7.397
7.311
7.302
7.296
7.069
7.051
7.036
7.017
7.000
6.946
6.927
6.898
6.886
6.878
6.868
6.849
6.756
6.736
6.694
6.676
6.656
4.879
3.809
H$_b$
H$_c$
OCH$_{a3}$
O
F
N
H
Ph
Ph
3na'
H$_c$
H$_b$
H$_a$
8
7
6
5
4
3
2
1
0
ppm
0.88
1.88
2.92
2.01
2.03
1.00
5.91
1.90
0.93
0.91
3.00

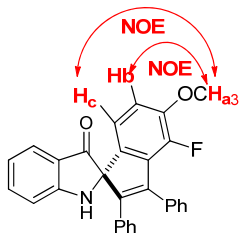




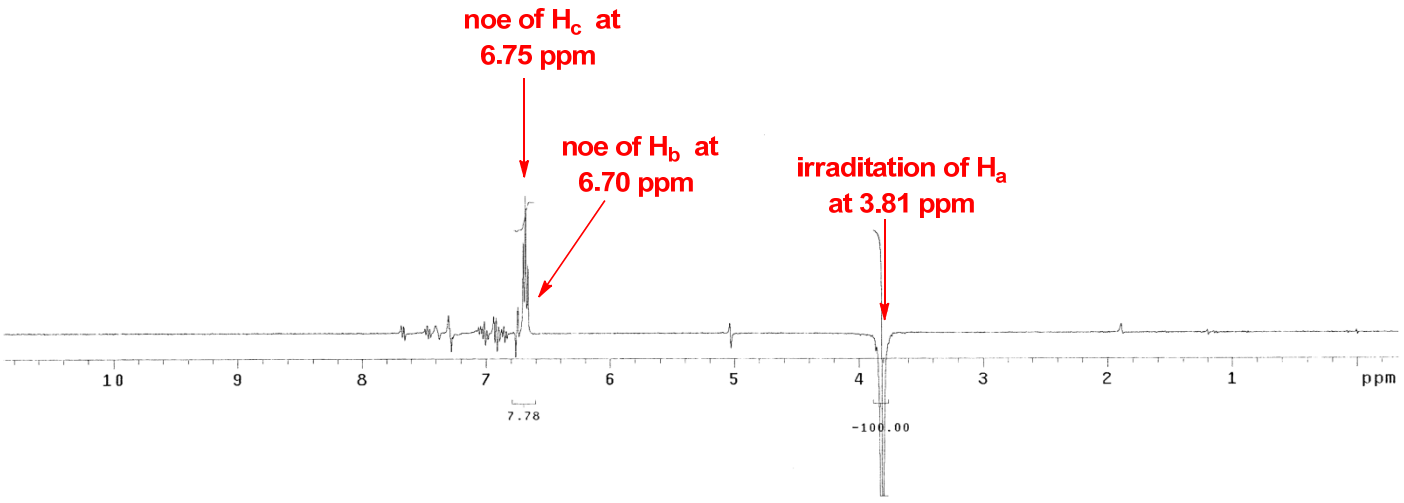
3na'

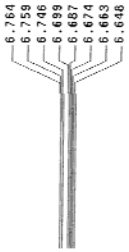


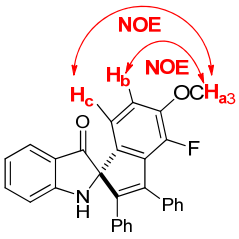




NOE of 3na'







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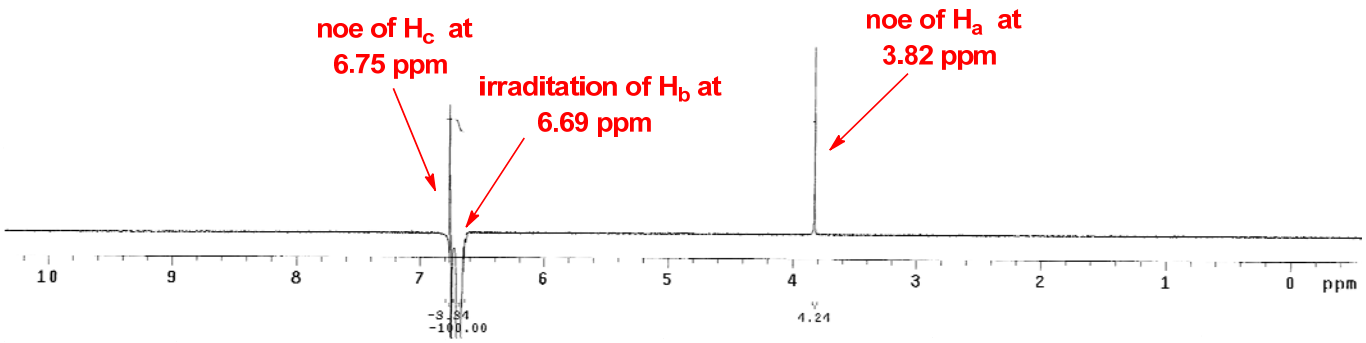
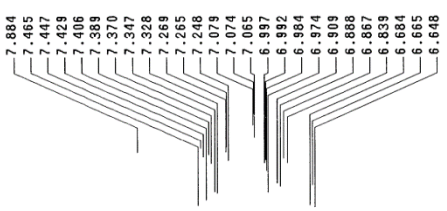
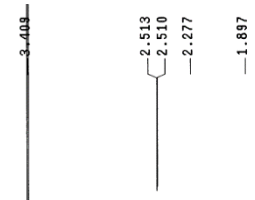
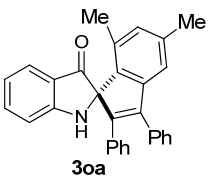
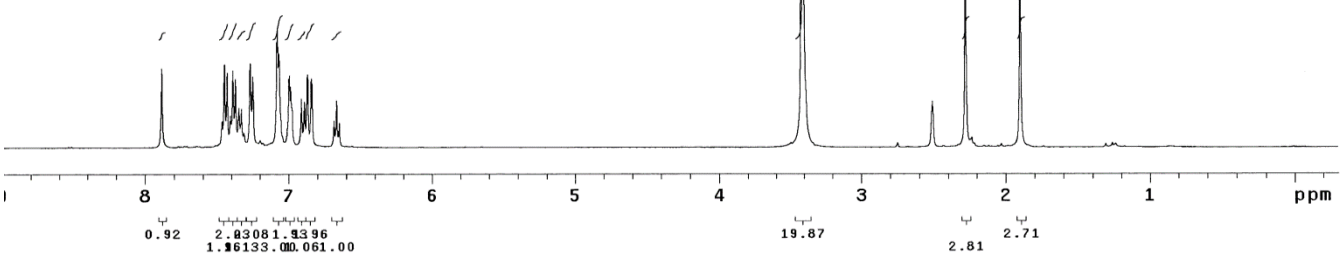


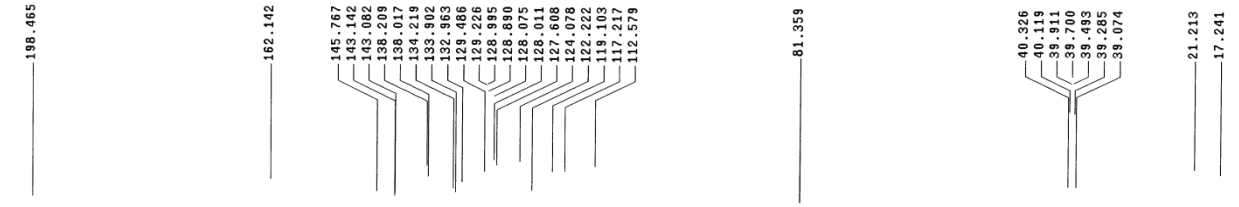






3oa

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143.142
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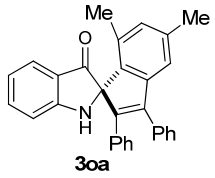
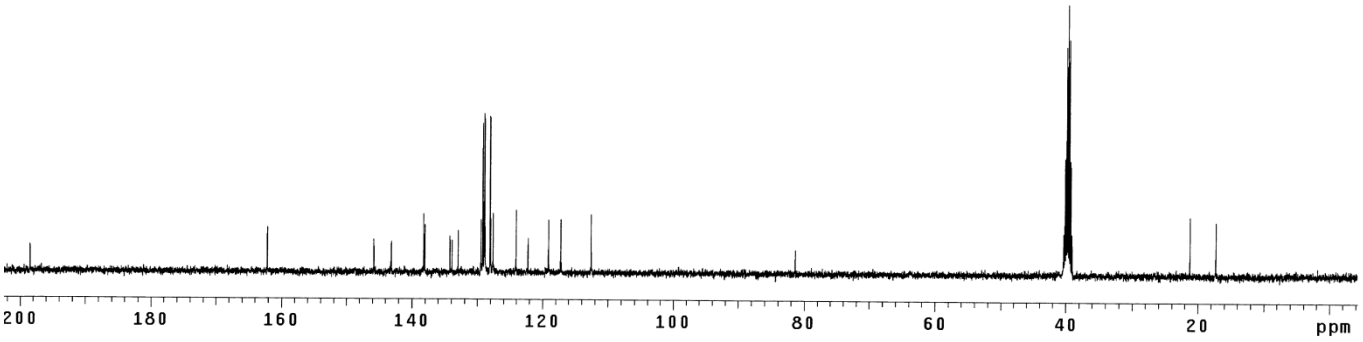
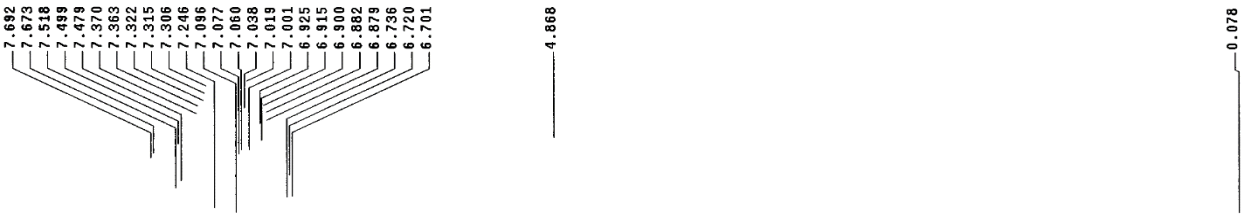
138.017
134.219
133.902
132.963
129.486
129.226
128.995
128.880
128.075
128.011
127.608
124.078
122.222
119.103
117.217
112.579
81.359
40.326
40.119
39.911
39.700
39.493
39.285
39.074
21.213
17.241


Me
Me
O
N
H
Ph
Ph

3oa


200
180
160
140
120
100
80
60
40
20
ppm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7.077
7.060
7.038
7.019
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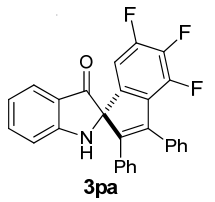
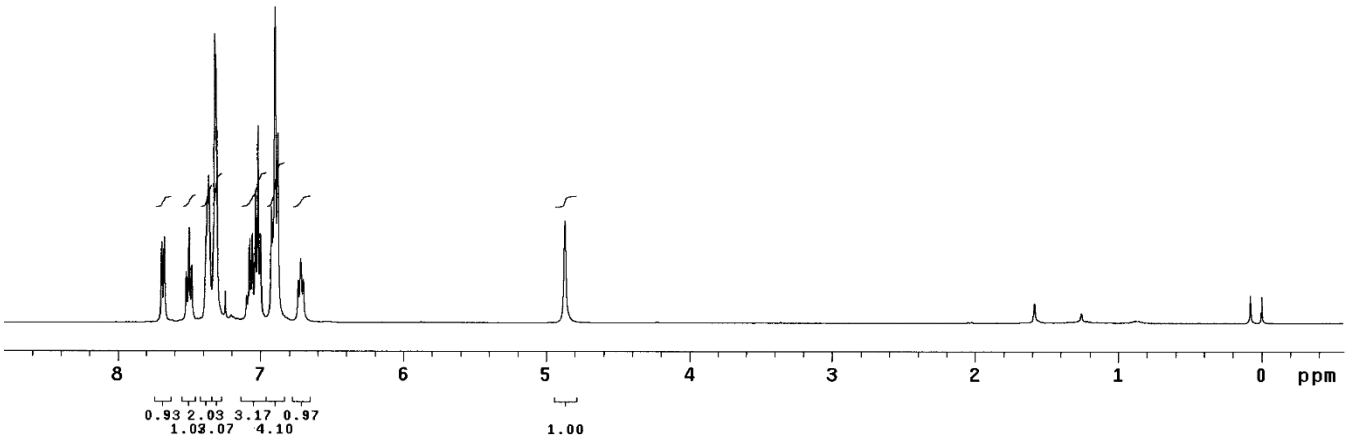
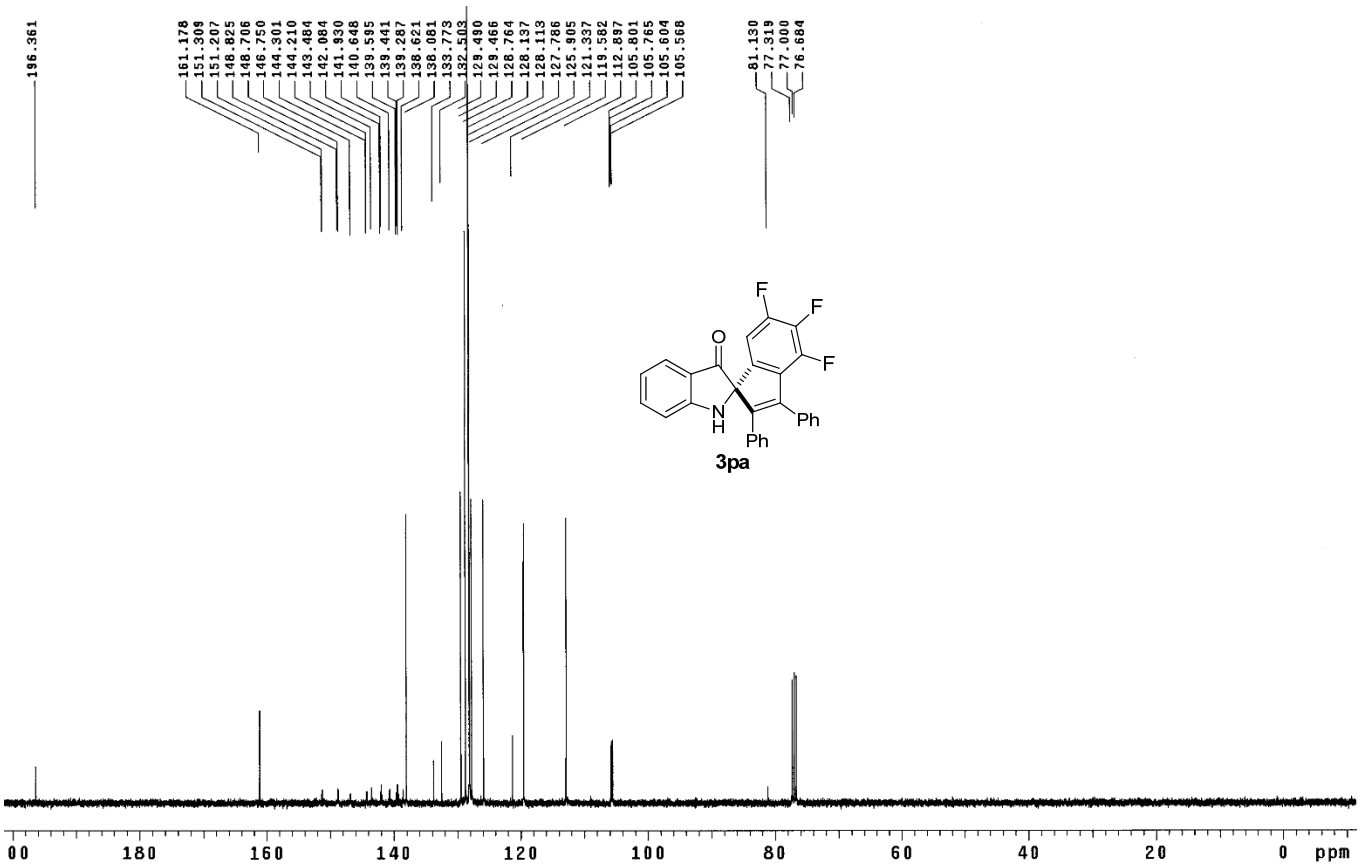
-0.000


F
F
F
O
N
H
Ph
Ph

3pa


8
7
6
5
4
3
2
1
0
ppm
0.93
2.03
3.17
0.97
1.03
1.07
4.10
1.00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151.309
151.207
148.825
148.706
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144.301
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143.484
142.084
141.830
140.648
139.595
139.441
139.287
138.621
138.081
133.773
132.503
129.490
129.466
128.764
128.137
128.113
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125.905
121.337
119.582
112.897
105.801
105.765
105.604
105.568
81.130
77.319
77.000
76.684
F
F
F
O
N
H
Ph
Ph
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00
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140
120
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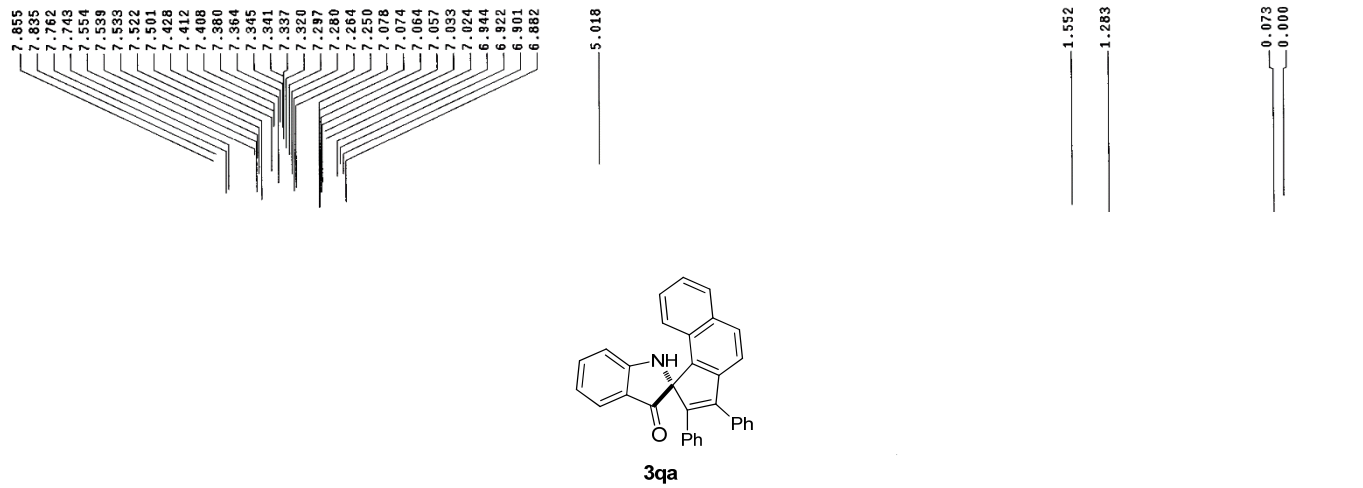
40
20
0
ppm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7.412
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7.380
7.364
7.345
7.341
7.337
7.320
7.297
7.280
7.264
7.250
7.078
7.074
7.064
7.057
7.033
7.024
6.944
6.922
6.901
6.882
5.018
1.552
1.283
0.073
0.000
NH
O
Ph
Ph
3qa
9
8
7
6
5
4
3
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6.33
1.06
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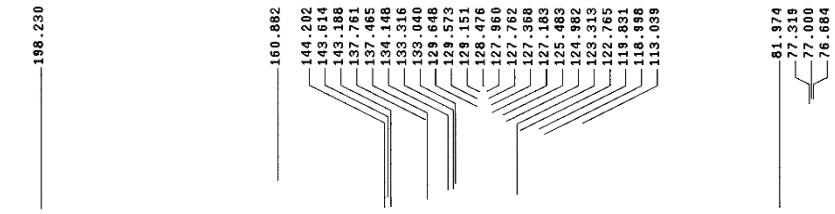
3.99
1.00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134.148
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133.040
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129.573
129.151
128.476
127.960
127.762
127.368
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122.765
119.831
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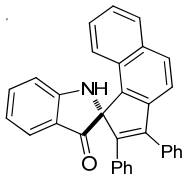
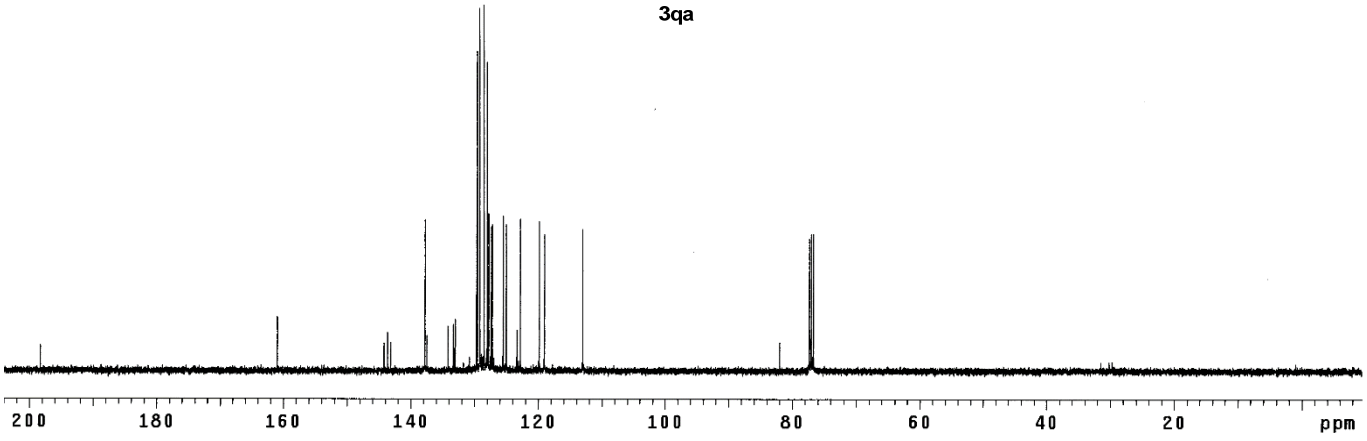
81.974
77.319
77.000
76.684


NH
O
Ph
Ph

3qa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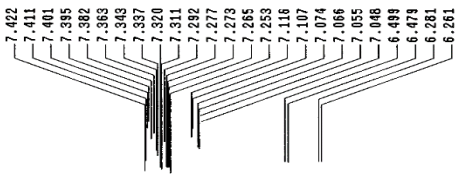
180
160
140
120
100
80
60
40
20
ppm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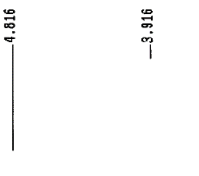
7.411
7.401
7.385
7.382
7.363
7.343
7.337
7.320
7.311
7.282
7.277
7.273
7.265
7.253
7.116
7.107
7.074
7.066
7.055
7.048
6.499
6.473
6.281
6.261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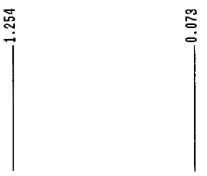
3.916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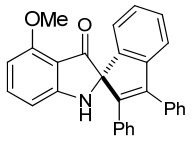
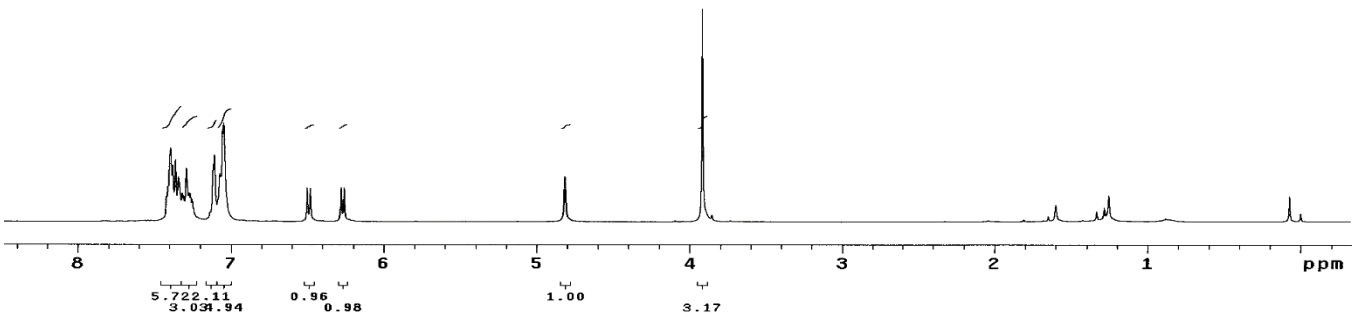
0.073


OMe
O
N
H
Ph
Ph

3ra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7
6
5
4
3
2
1
ppm
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3.03
1.94
0.96
0.98
1.00
3.17

194.917
162.922
159.500
145.074
143.963
143.405
141.845
139.102
134.449
133.733
129.479
128.902
128.606
128.536
128.006
127.746
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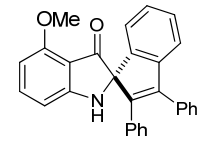
77.000
76.576
55.766



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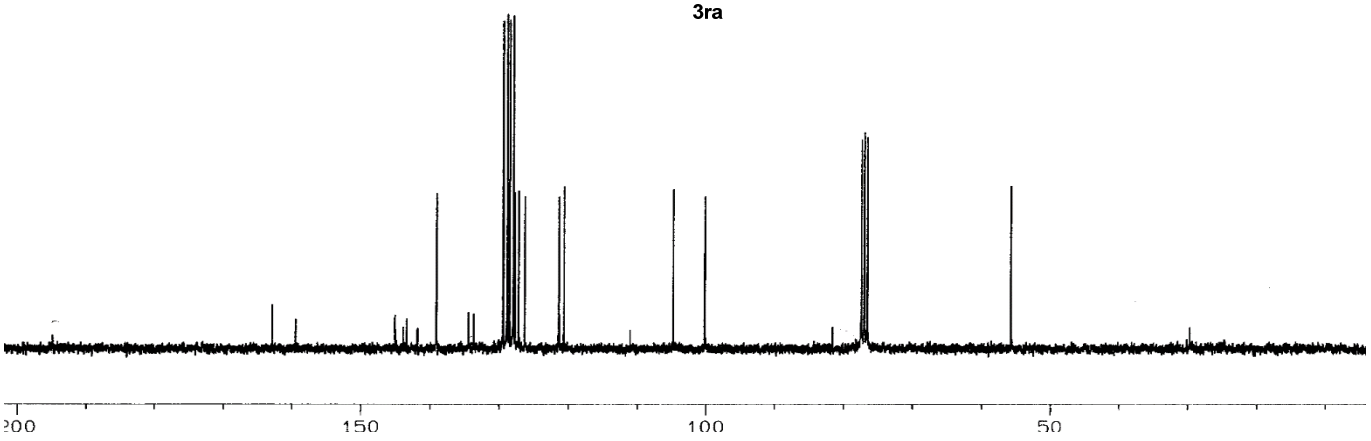

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7.337
7.320
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7.284
7.251
7.210
7.203
7.188
7.181
7.169
7.164
7.146
7.142
7.127
7.124
7.111
7.107
7.088
7.067
7.065
7.050
7.036
7.030
7.010
7.007
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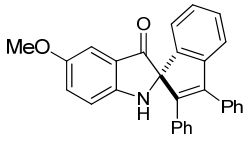
6.923
4.577
3.813
1.584



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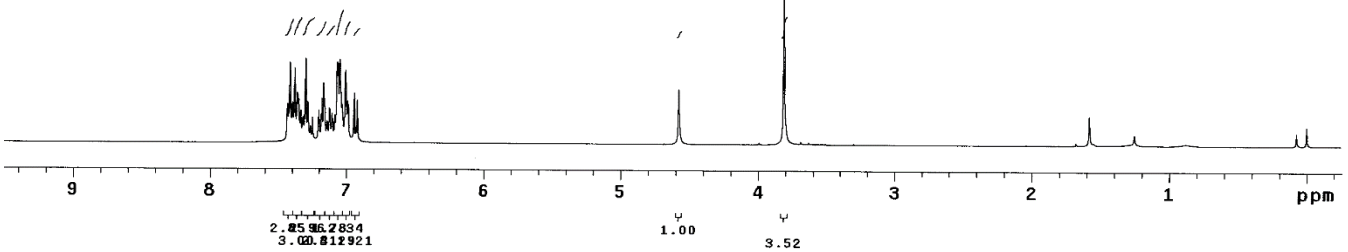

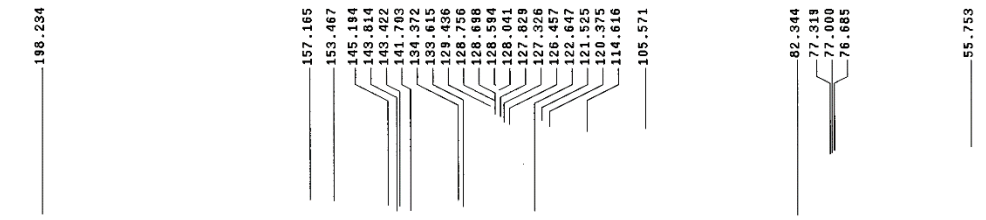
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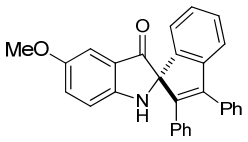
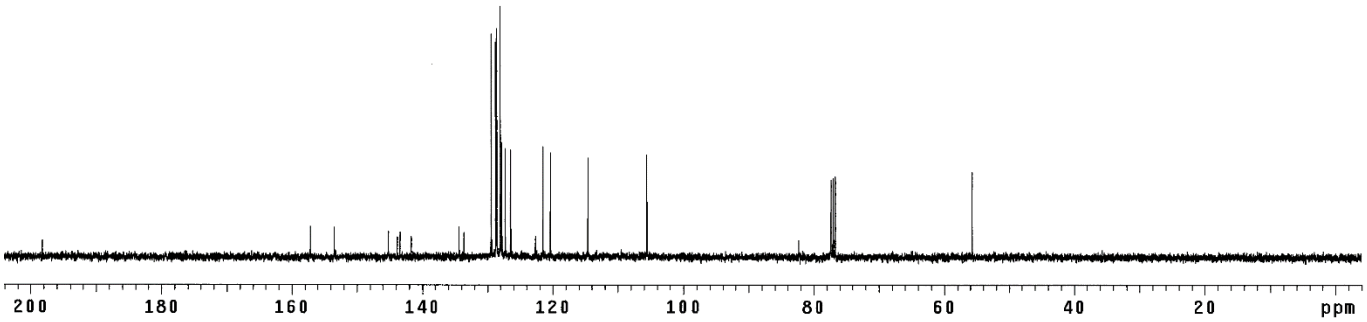
143.814
143.422
141.703
134.372
133.615
129.436
128.756
128.698
128.594
128.041
127.829
127.326
126.457
122.647
121.525
120.375
114.616
105.571
82.344
77.319
77.000
76.685
55.753


MeO
O
N
H
Ph
Ph

3sa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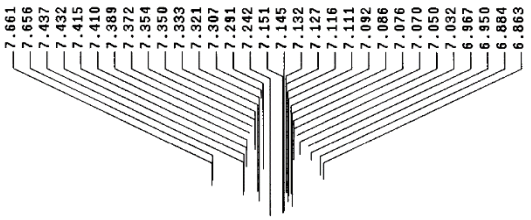
160
140
120
100
80
60
40
20
ppm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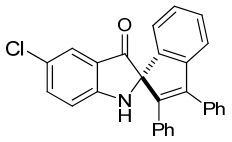
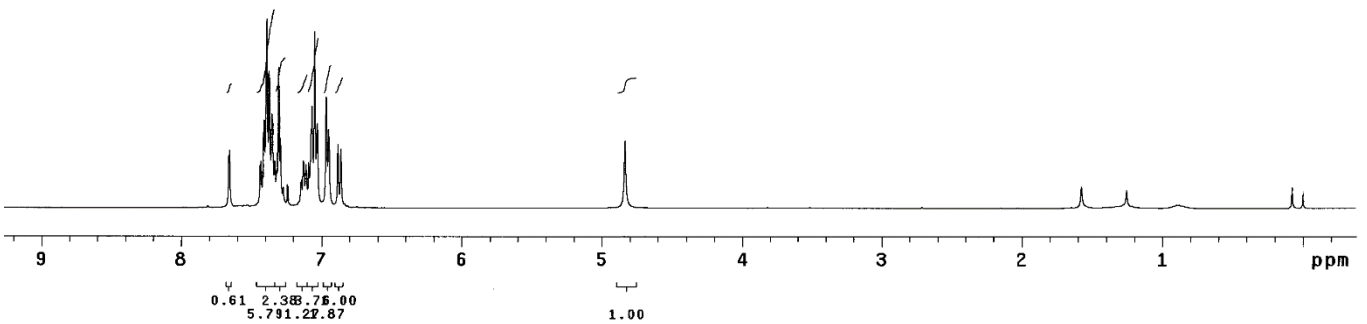
7.415
7.410
7.389
7.372
7.354
7.350
7.333
7.321
7.307
7.291
7.242
7.151
7.145
7.132
7.127
7.116
7.111
7.092
7.086
7.076
7.070
7.050
7.032
6.967
6.950
6.884
6.863


4.835

1.575


Cl
O
N
H
Ph
Ph

3ta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7
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5
4
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1
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5.00
5.79
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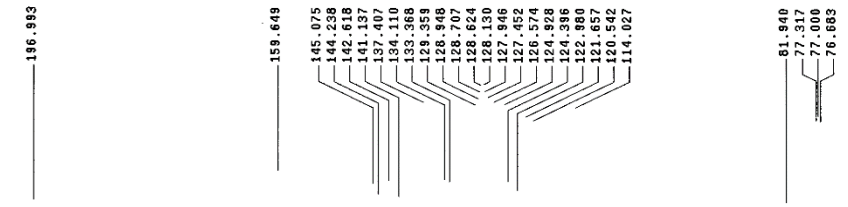
2.87
1.00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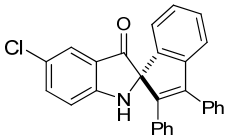
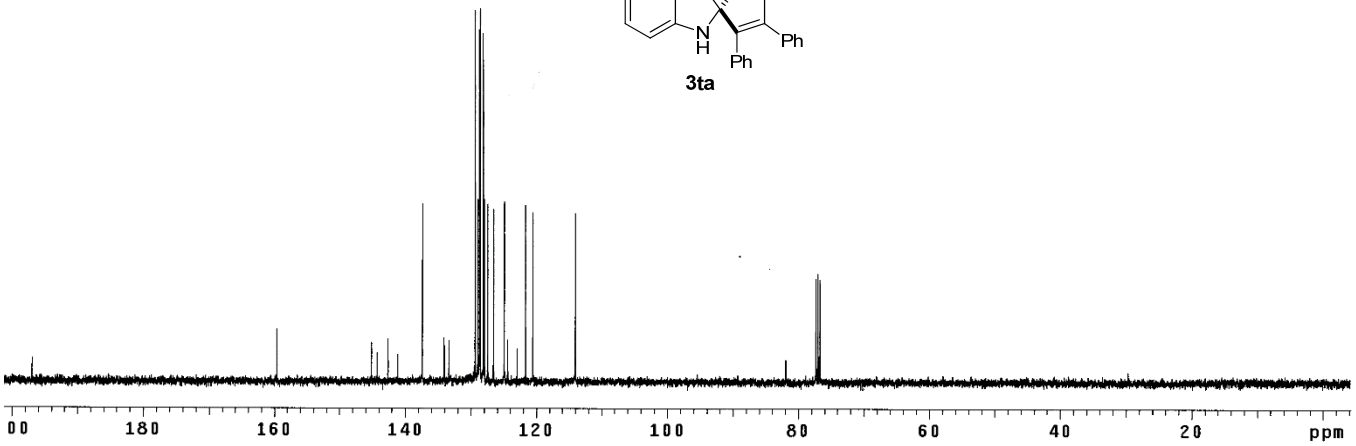
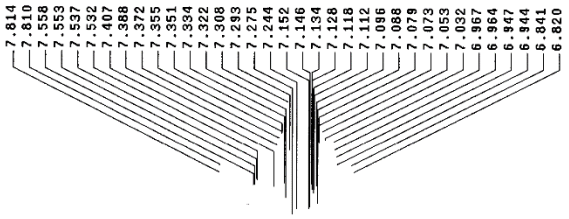
144.238
142.618
141.137
137.407
134.110
133.368
129.359
128.948
128.707
128.624
128.130
127.946
127.452
126.574
124.828
124.396
122.880
121.657
120.542
114.027
81.940
77.317
77.000
76.683


O
Cl
N
H
Ph
Ph

3ta


00
180
160
140
120
100
80
60
40
20
ppm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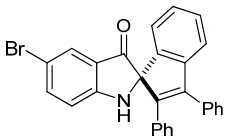
7.553
7.537
7.532
7.407
7.388
7.372
7.355
7.351
7.334
7.322
7.308
7.293
7.275
7.244
7.152
7.146
7.134
7.128
7.118
7.112
7.096
7.088
7.079
7.073
7.053
7.032
6.967
6.964
6.947
6.944
6.841
6.820

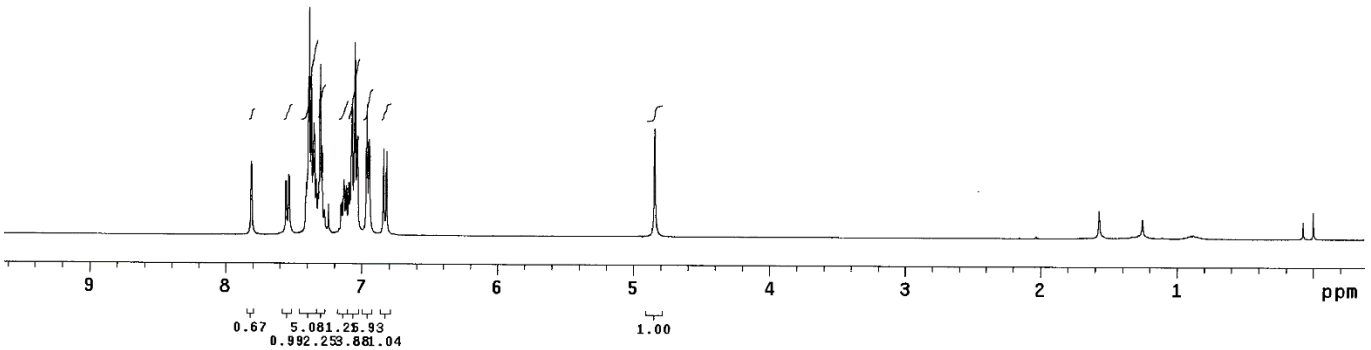

4.845

1.572

-0.000


O
Br
N
H
Ph
Ph

3ua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7
6
5
4
3
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0.99
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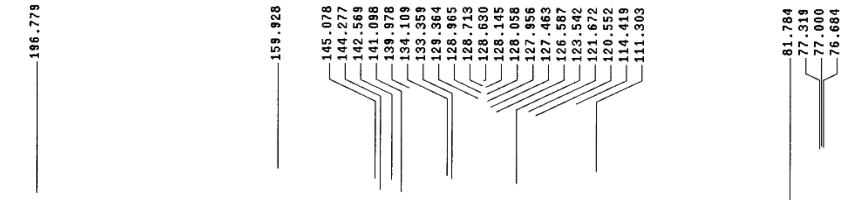
1.00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139.978
134.109
133.359
129.364
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128.713
128.630
128.145
128.058
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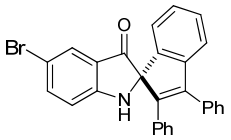
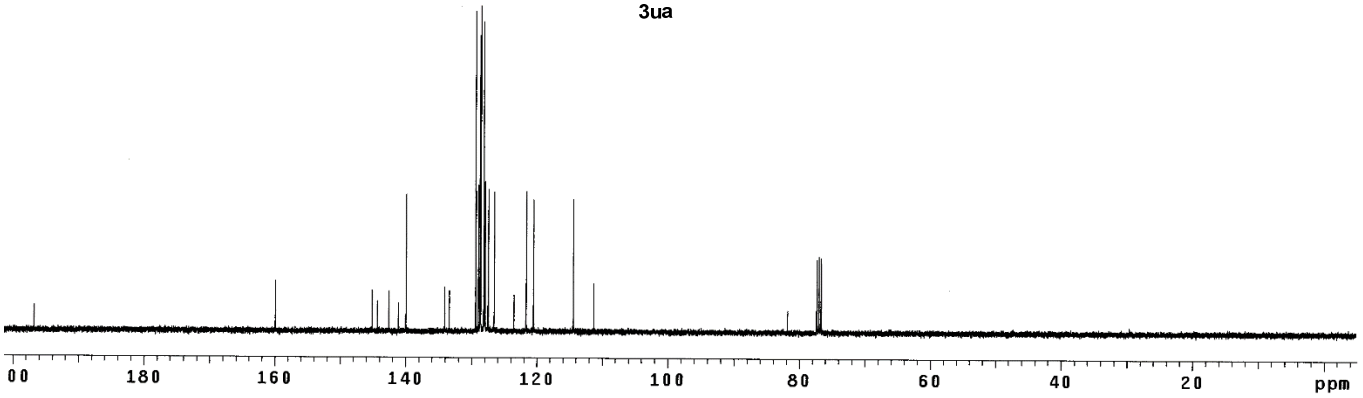
123.542
121.672
120.552
114.419
111.303
81.784
77.319
77.000
76.684


Br
O
N
H
Ph
Ph

3ua


00
180
160
140
120
100
80
60
40
20
ppm


7.643
7.622
7.427
7.410
7.393
7.375
7.355
7.332
7.324
7.305
7.286
7.268
7.256
7.154
7.136
7.119
7.100
7.073
7.053
7.035
7.021
7.003
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6.451
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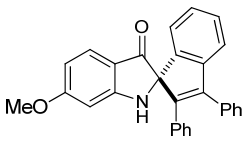
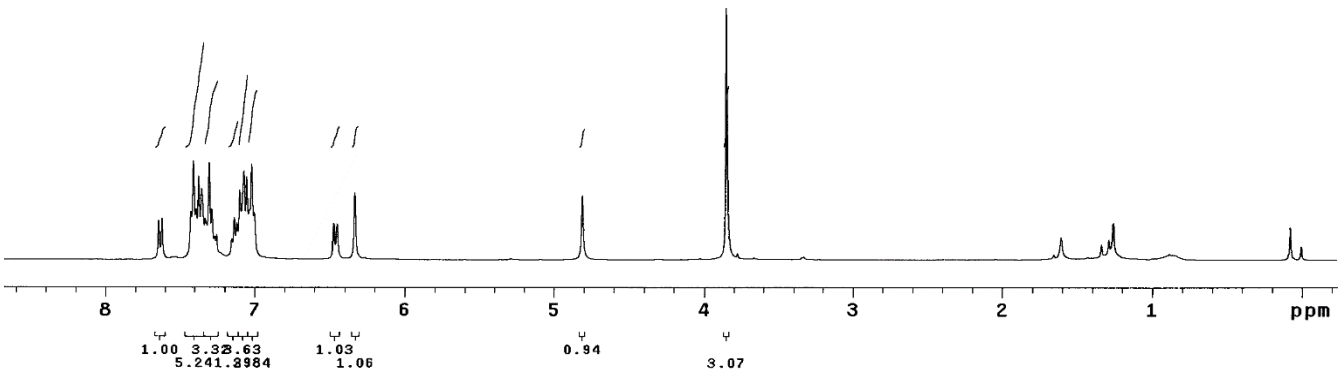
3.848
1.608
1.338
1.288
1.260
0.079
0.005


MeO
O
N
H
Ph
Ph

3va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7
6
5
4
3
2
1
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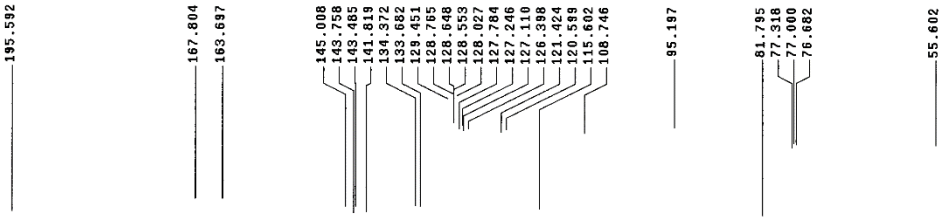
3.63
5.24
1.39
84
1.03
1.06
0.94
3.07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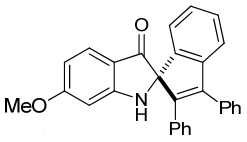
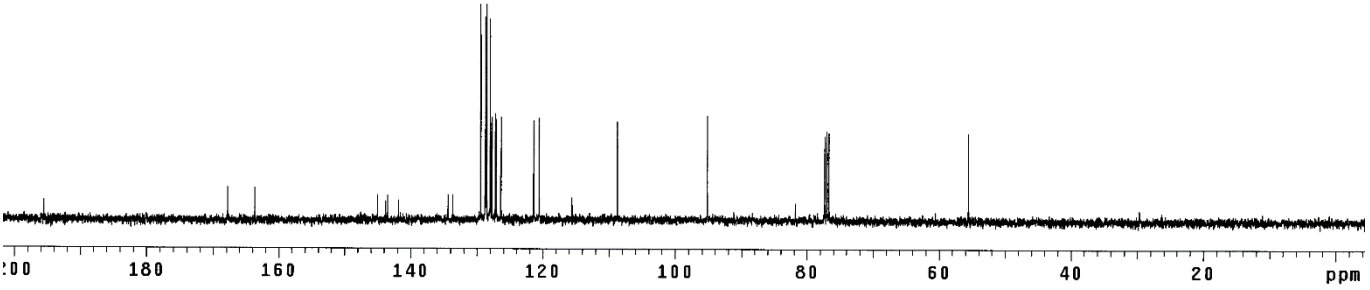
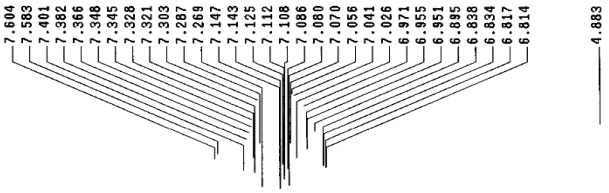
134.372
133.682
129.451
128.765
128.648
128.553
128.027
127.784
127.246
127.110
126.398
121.424
120.589
115.602
108.746
95.197
81.795
77.318
77.000
76.682
55.602


O
MeO
N
H
Ph
Ph

3va


200
180
160
140
120
100
80
60
40
20
ppm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7.382
7.366
7.348
7.345
7.328
7.321
7.303
7.287
7.269
7.147
7.143
7.125
7.112
7.108
7.086
7.080
7.070
7.056
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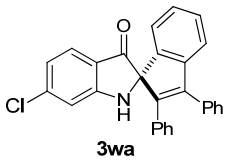
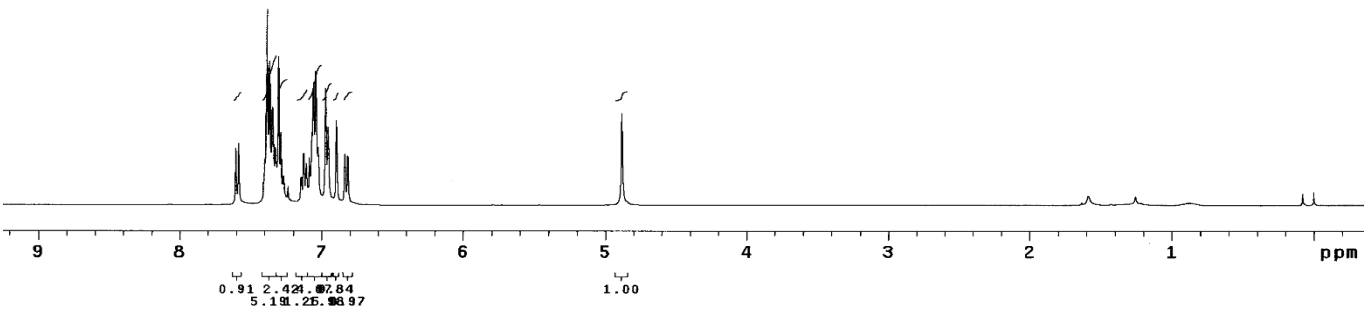
6.955
6.951
6.895
6.838
6.834
6.817
6.814
4.883


O
Cl
N
H
Ph
Ph

3wa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8
7
6
5
4
3
2
1
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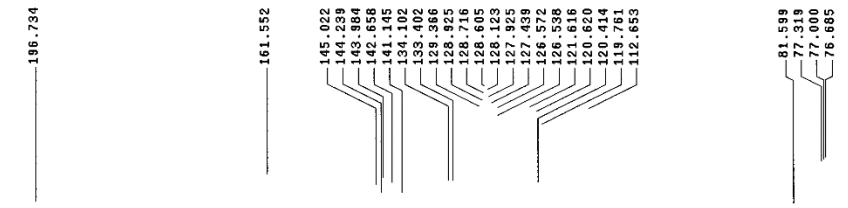
1.00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144.239
143.984
142.658
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134.102
133.402
129.366
128.925
128.716
128.605
128.123
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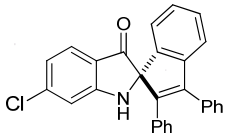
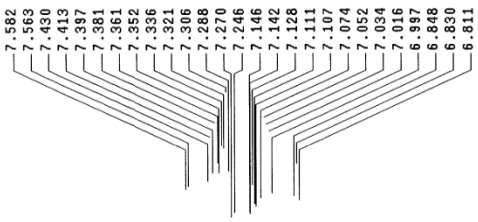
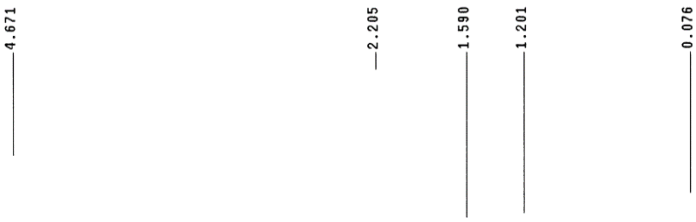
126.538
121.616
120.620
120.414
119.761
112.653
81.599
77.319
77.000
76.685


O
Cl
N
H
Ph
Ph

3wa

00
180
160
140
120
100
80
60
40
20
ppm


7.582
7.563
7.430
7.413
7.397
7.381
7.361
7.352
7.336
7.321
7.306
7.288
7.270
7.246
7.146
7.142
7.128
7.111
7.107
7.074
7.052
7.034
7.016
6.997
6.848
6.830
6.811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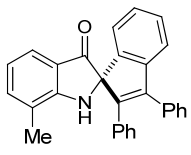
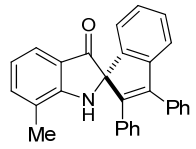
2.205
1.590
1.201
0.076


O
N
H
Me
Ph
Ph

3xa

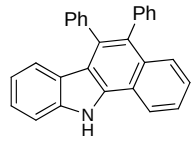
8
7
6
5
4
3
2
1
ppm
0.965.056.19
3.84 1.39 1.15
1.00
3.37

198.388
160.661
145.216
144.001
143.437
141.674
137.434
134.416
133.604
129.411
128.788
128.713
128.595
127.981
127.810
127.246
126.468
123.077
121.976
121.712
121.491
120.505
119.109
81.556
77.319
77.004
76.684
15.742

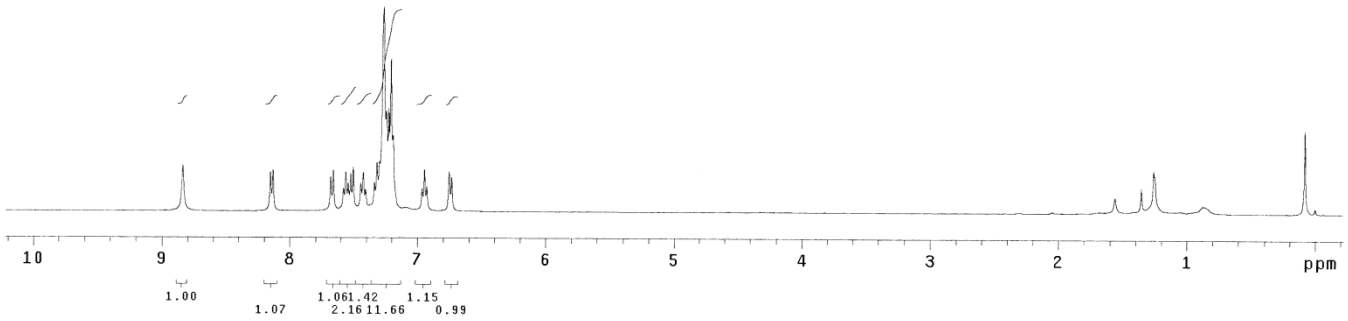


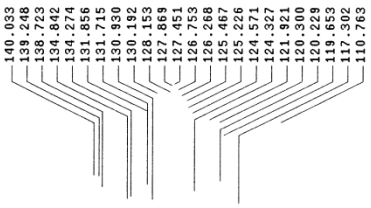
3xa

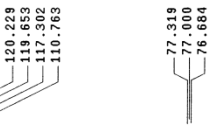
8.841
8.153
8.133
7.682
7.661
7.581
7.562
7.543
7.524
7.504
7.443
7.424
7.406
7.336
7.317
7.296
7.264
7.242
7.224
7.208
7.192
6.965
6.946
6.927
6.756
6.736
1.561
1.356
1.261
1.253
0.082

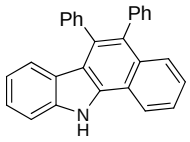


4a

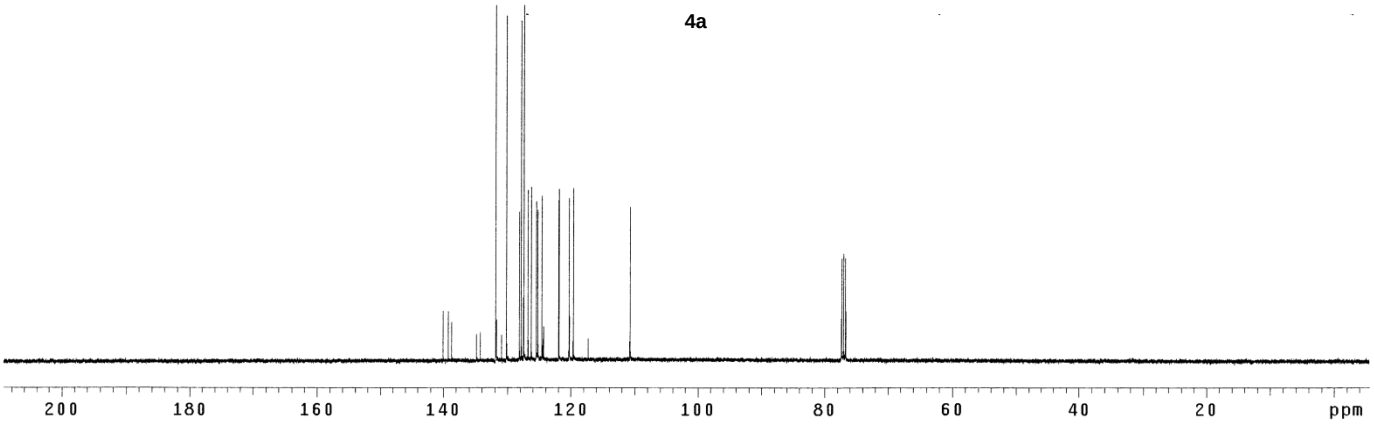


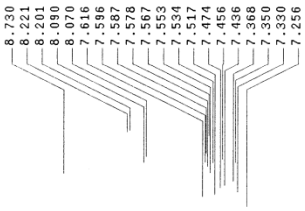

140.033
139.248
138.723
134.842
134.274
131.856
131.715
130.930
130.192
128.153
127.869
127.451
126.753
126.268
125.467
125.226
124.571
124.327
121.921
120.300
120.229
119.653
117.302
110.763

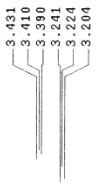

77.319
77.000
76.684

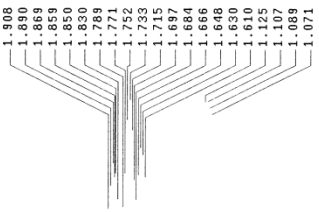

Ph
Ph
N
H

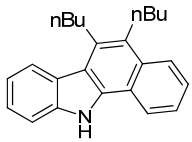
4a


200
180
160
140
120
100
80
60
40
20
ppm

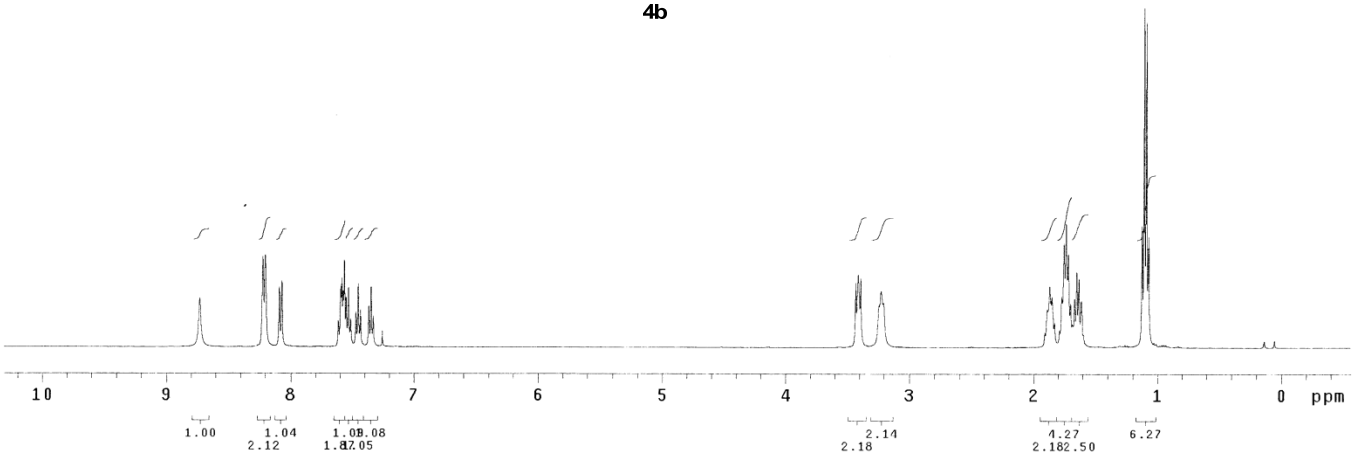

8.730
8.221
8.201
8.090
8.070
7.616
7.596
7.587
7.578
7.567
7.553
7.534
7.517
7.474
7.456
7.436
7.368
7.350
7.330
7.256

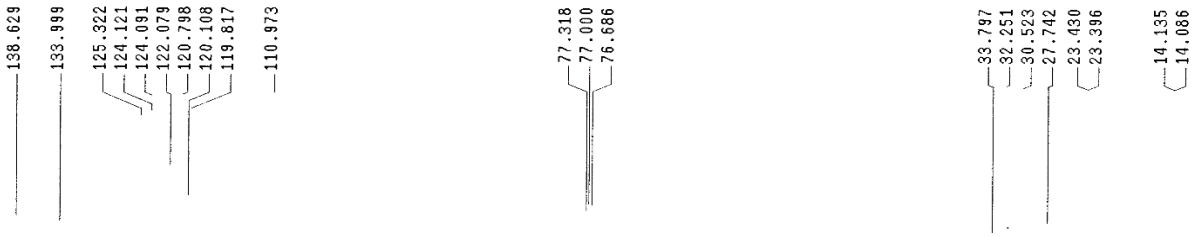

3.431
3.410
3.390
3.241
3.224
3.204

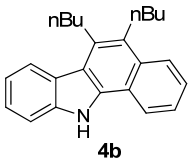

1.908
1.890
1.869
1.859
1.850
1.830
1.789
1.771
1.752
1.733
1.715
1.697
1.684
1.666
1.648
1.630
1.610
1.125
1.107
1.089
1.071


nBu
nBu
N
H

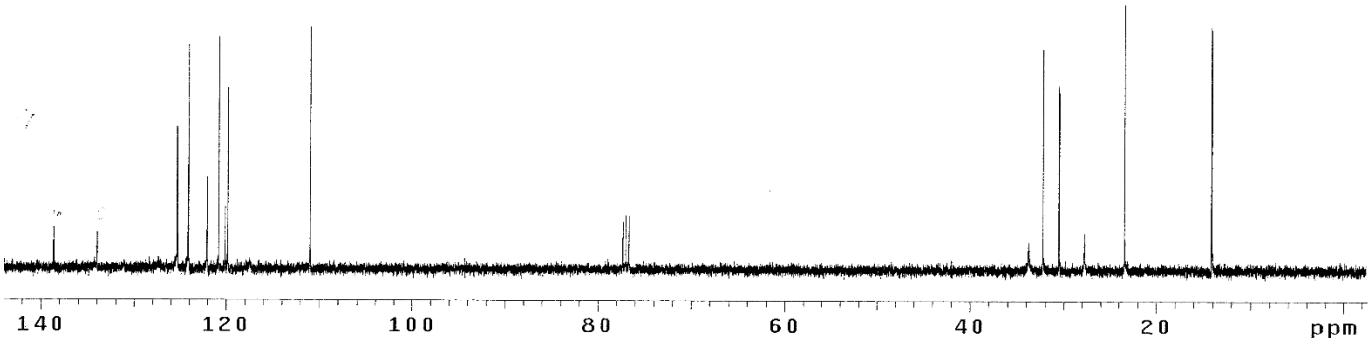
4b

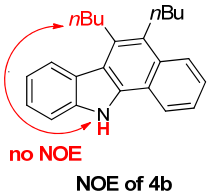

10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
2.12
1.08
1.05
2.14
2.18
4.27
2.18
2.50
6.27





4b

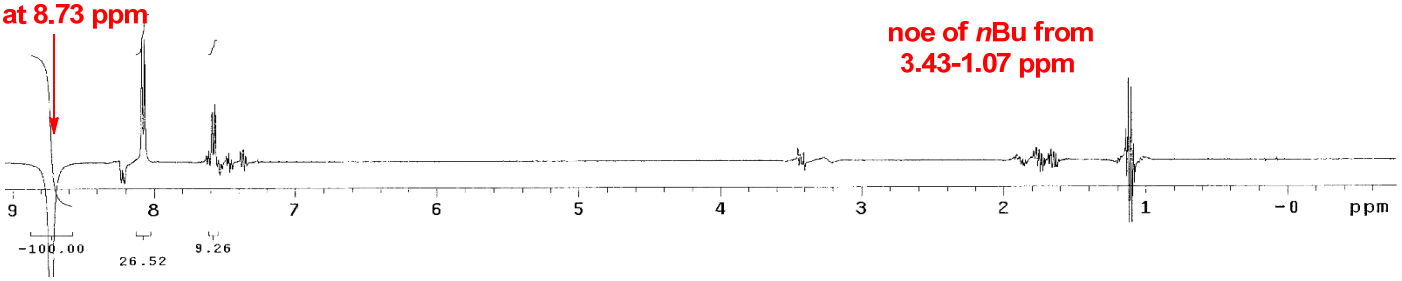


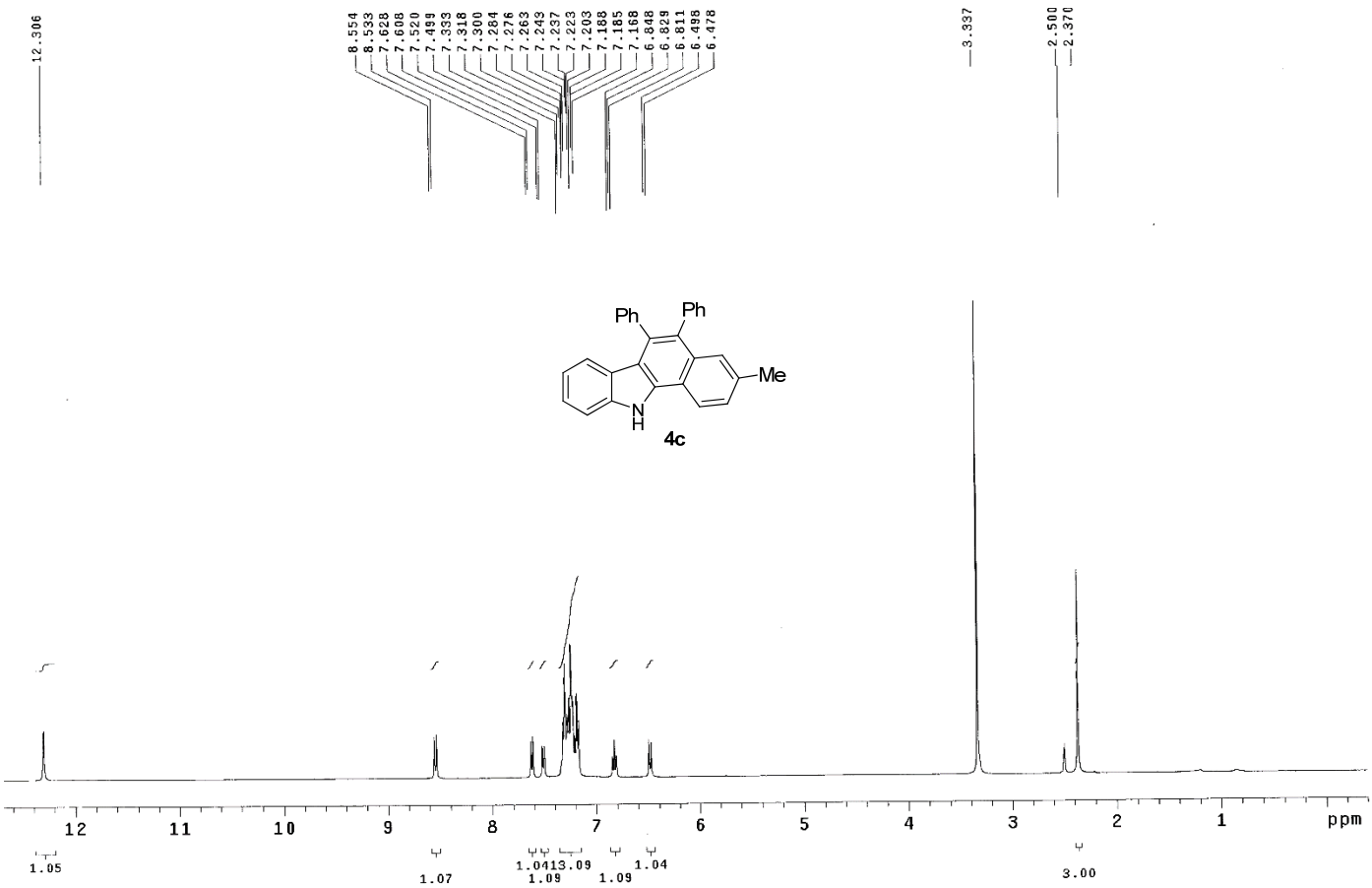


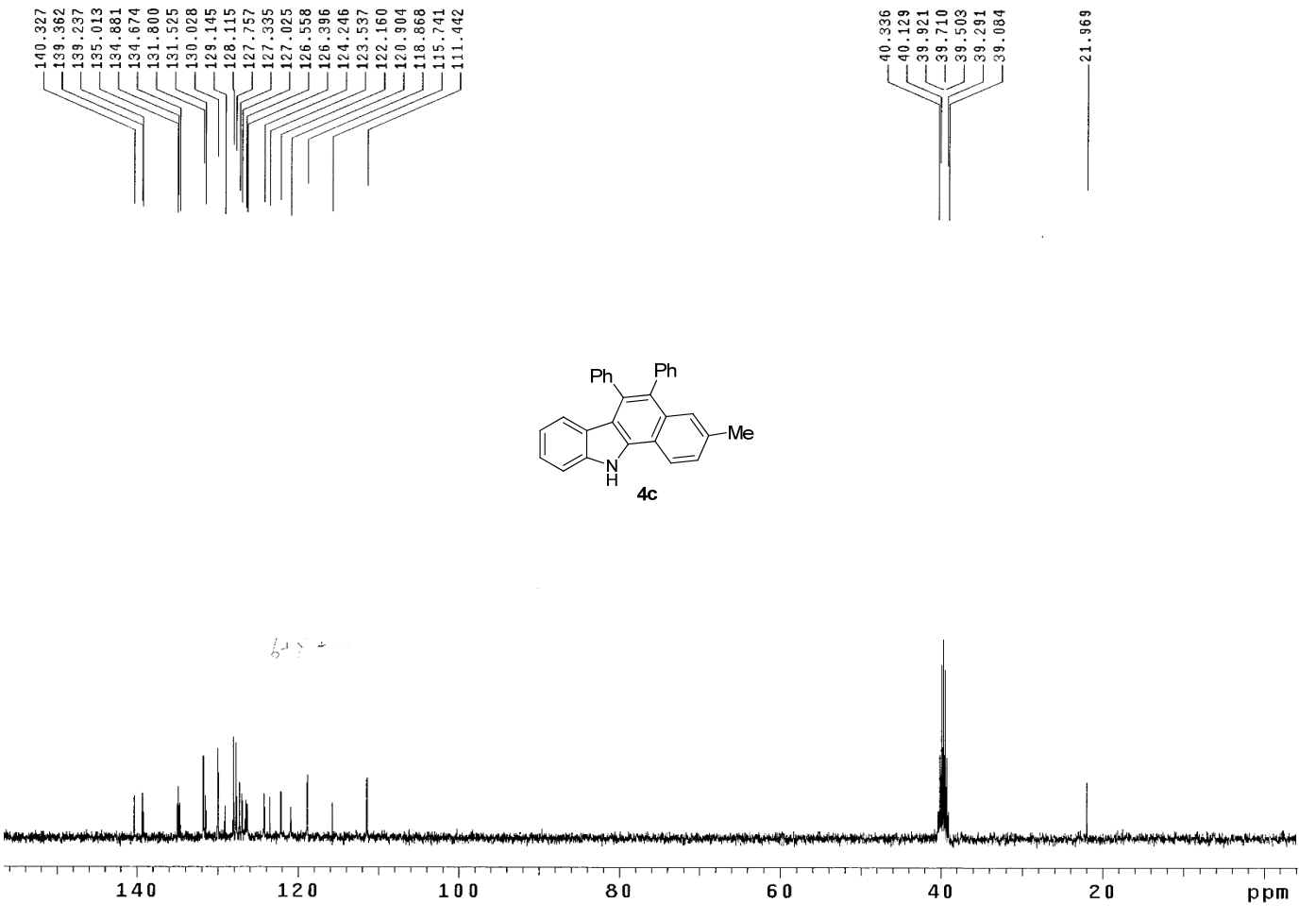
NOE of 4b

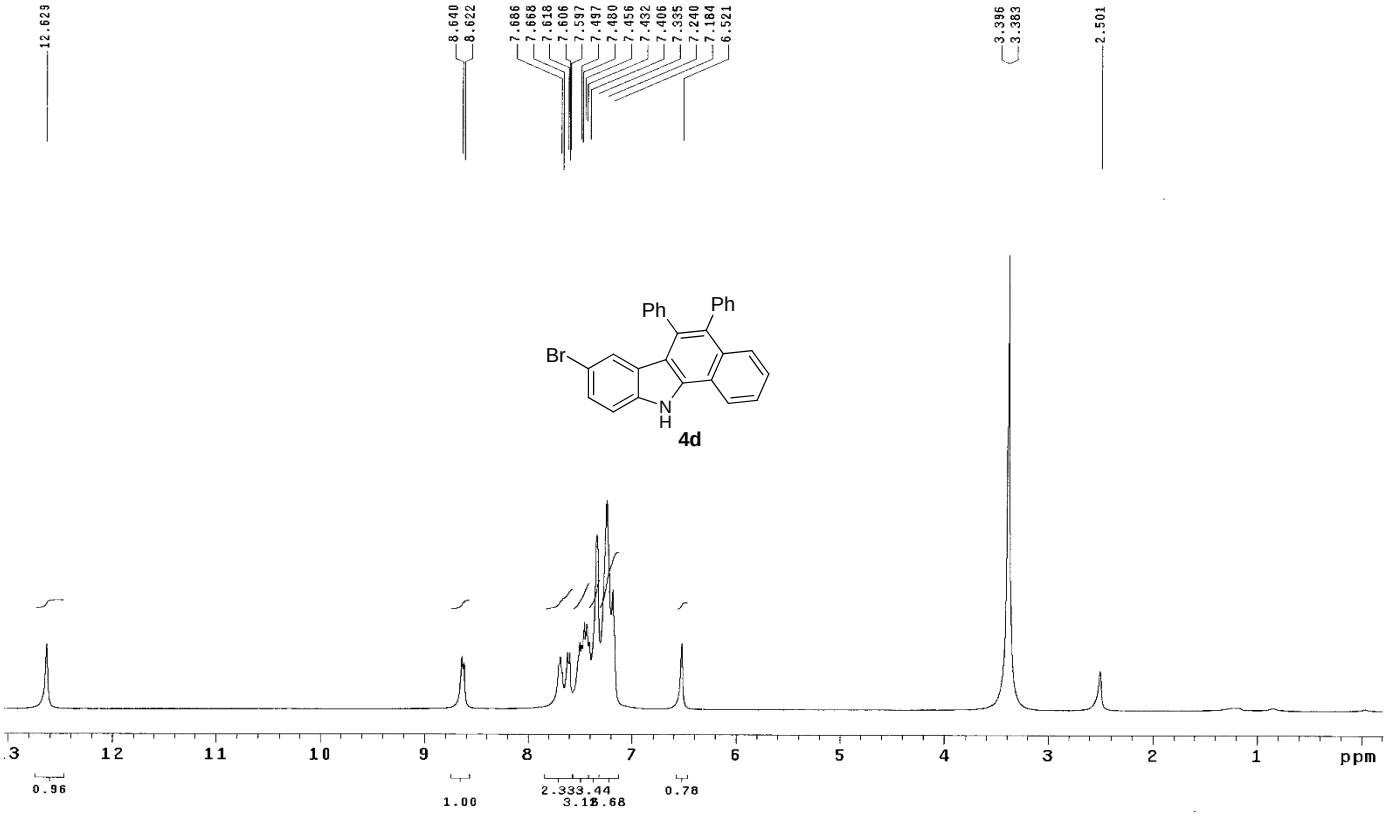
irraditation of NH at 8.73 ppm

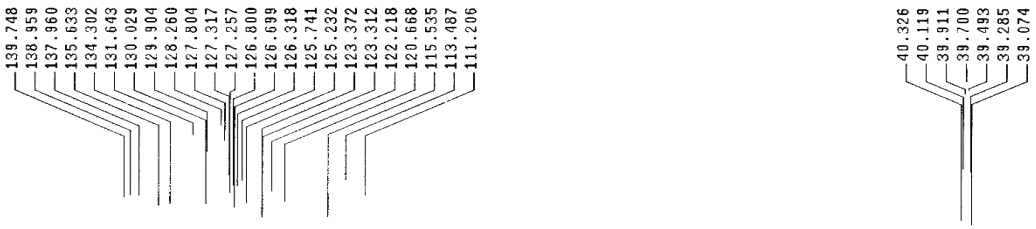
noe of *n*Bu from 3.43-1.07 ppm

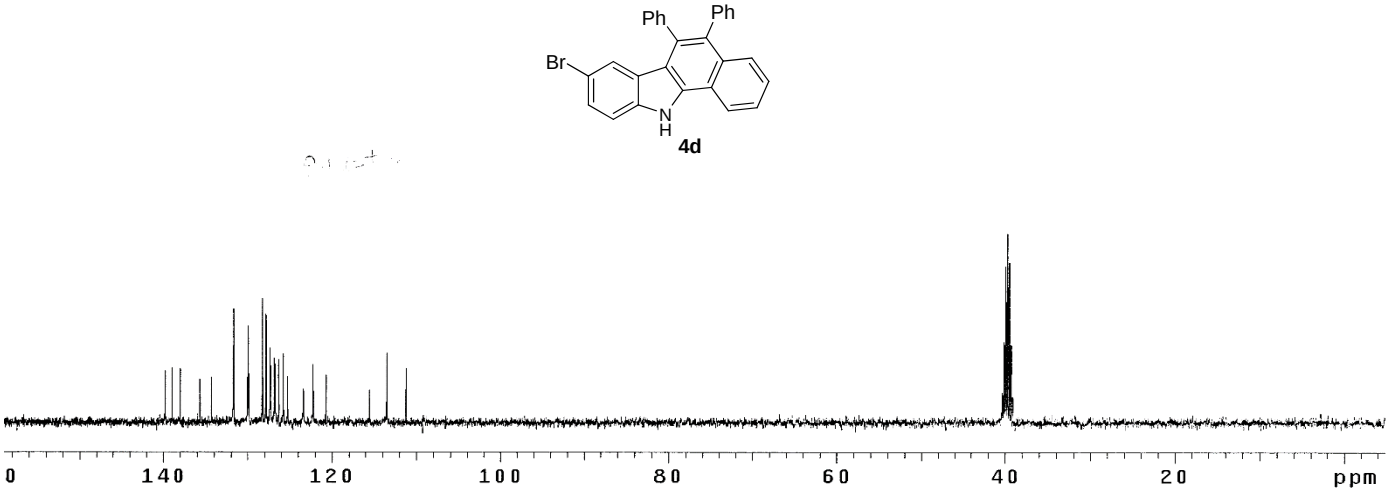


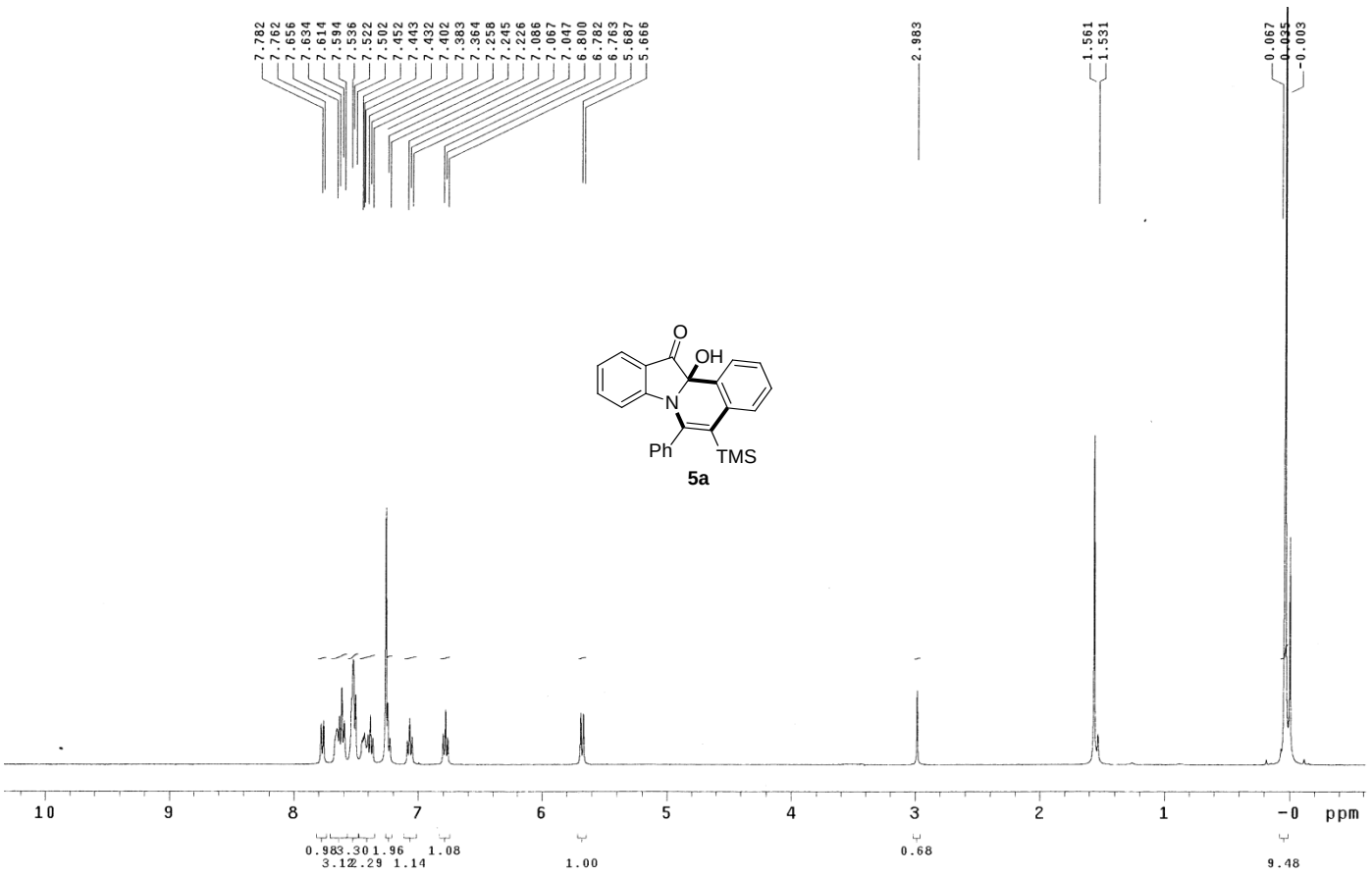

12.306
8.554
8.533
7.628
7.608
7.520
7.499
7.333
7.318
7.300
7.284
7.276
7.263
7.249
7.237
7.223
7.203
7.188
7.185
7.168
6.848
6.829
6.811
6.498
6.478
3.337
2.500
2.370
Ph
Ph
Me
N
H
4c
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.05
1.07
1.04
13.09
1.09
1.09
1.04
3.00


140.327
139.362
139.237
135.013
134.881
134.674
131.800
131.525
130.028
129.145
128.115
127.757
127.335
127.025
126.558
126.396
124.246
123.537
122.160
120.904
118.868
115.741
111.442
40.336
40.129
39.921
39.710
39.503
39.291
39.084
21.969
Ph
Ph
Me
N
H
4c
140
120
100
80
60
40
20
ppm

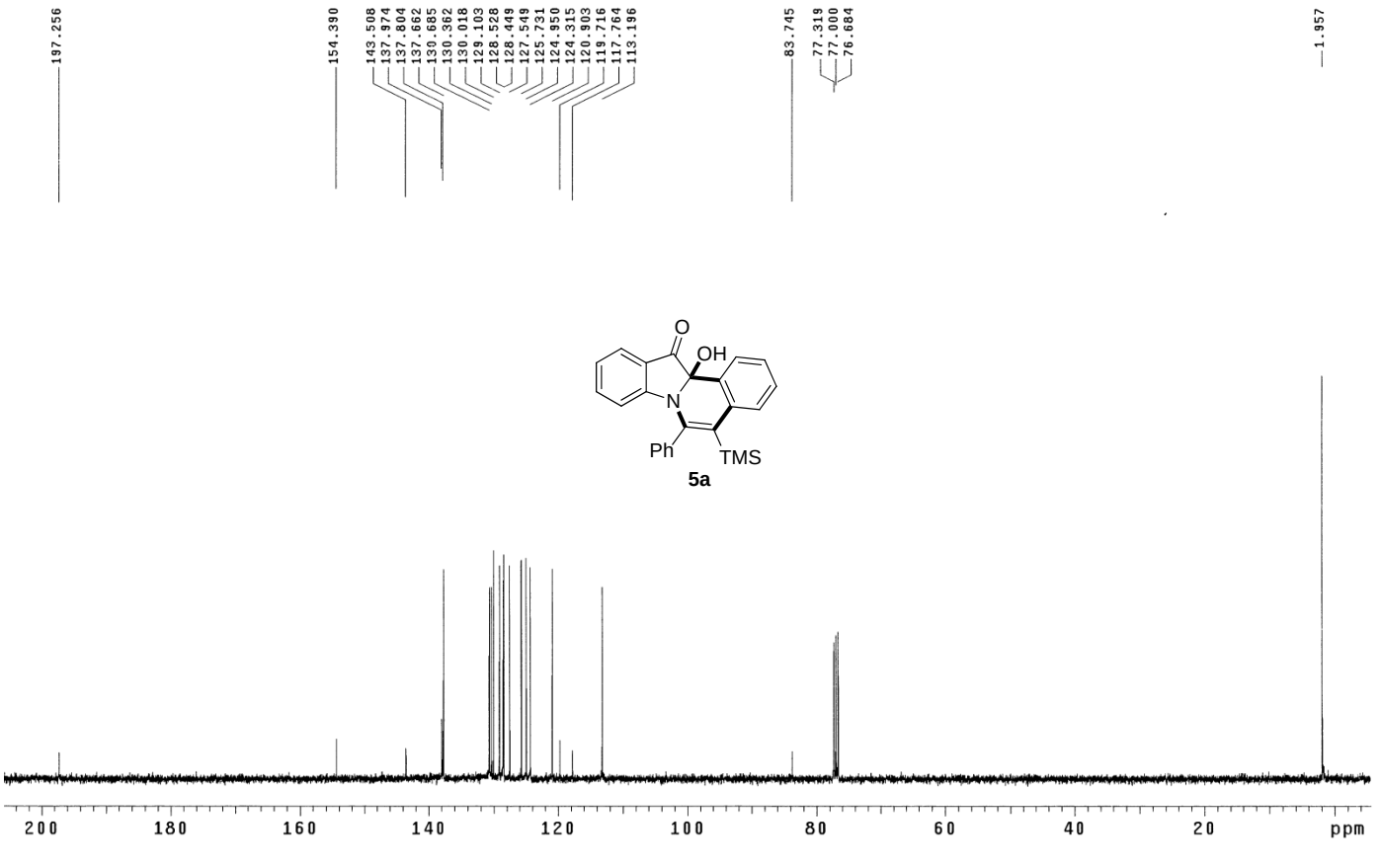

12.629
8.640
8.622
7.686
7.668
7.618
7.606
7.597
7.497
7.480
7.456
7.432
7.406
7.335
7.240
7.184
6.521
3.396
3.383
2.501
Ph
Ph
Br
N
H
4d
ppm
0.96
1.00
2.33
3.44
3.68
0.78


139.748
138.959
137.960
135.633
134.302
131.643
130.029
129.904
128.260
127.804
127.317
127.257
126.800
126.699
126.318
125.741
125.232
123.372
123.312
122.218
120.668
115.535
113.487
111.206
40.326
40.119
39.911
39.700
39.493
39.285
39.074

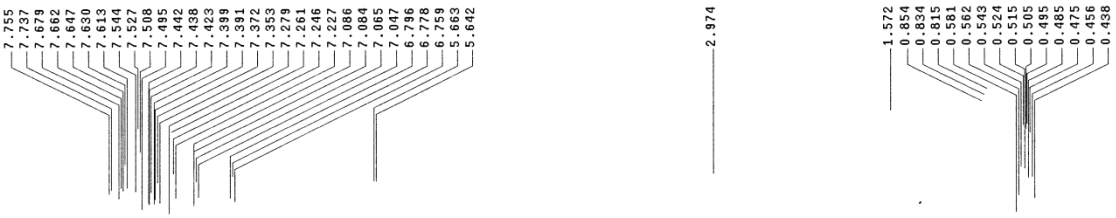

Ph
Ph
Br
N
H
4d
0
140
120
100
80
60
40
20
ppm

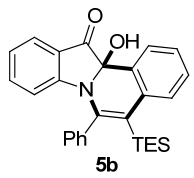

7.782
7.762
7.656
7.634
7.614
7.594
7.536
7.522
7.502
7.452
7.443
7.432
7.402
7.383
7.364
7.258
7.245
7.226
7.086
7.067
7.047
6.800
6.782
6.763
5.687
5.666
2.983
1.561
1.531
0.067
0.035
-0.003
O
OH
N
Ph
TMS
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.98
3.30
1.96
1.08
3.12
2.29
1.14
1.00
0.68
9.48

5a


197.256
154.390
143.508
137.974
137.804
137.662
130.685
130.362
130.018
129.103
128.528
128.449
127.549
125.731
124.950
124.315
120.903
119.716
117.764
113.196
83.745
77.319
77.000
76.684
1.957
O
OH
N
Ph
TMS
200
180
160
140
120
100
80
60
40
20
ppm

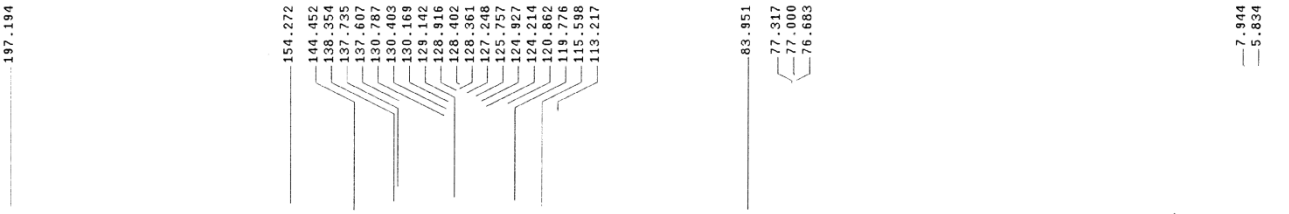
5a

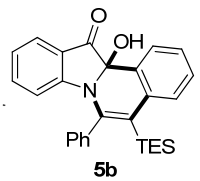

7.755
7.737
7.679
7.662
7.647
7.630
7.613
7.544
7.527
7.508
7.495
7.442
7.438
7.423
7.399
7.391
7.372
7.353
7.279
7.261
7.246
7.227
7.086
7.084
7.065
7.047
6.796
6.778
6.759
5.663
5.642
2.974
1.572
0.854
0.834
0.815
0.581
0.562
0.543
0.524
0.515
0.505
0.495
0.485
0.475
0.456
0.438


O
OH
N
Ph
TES

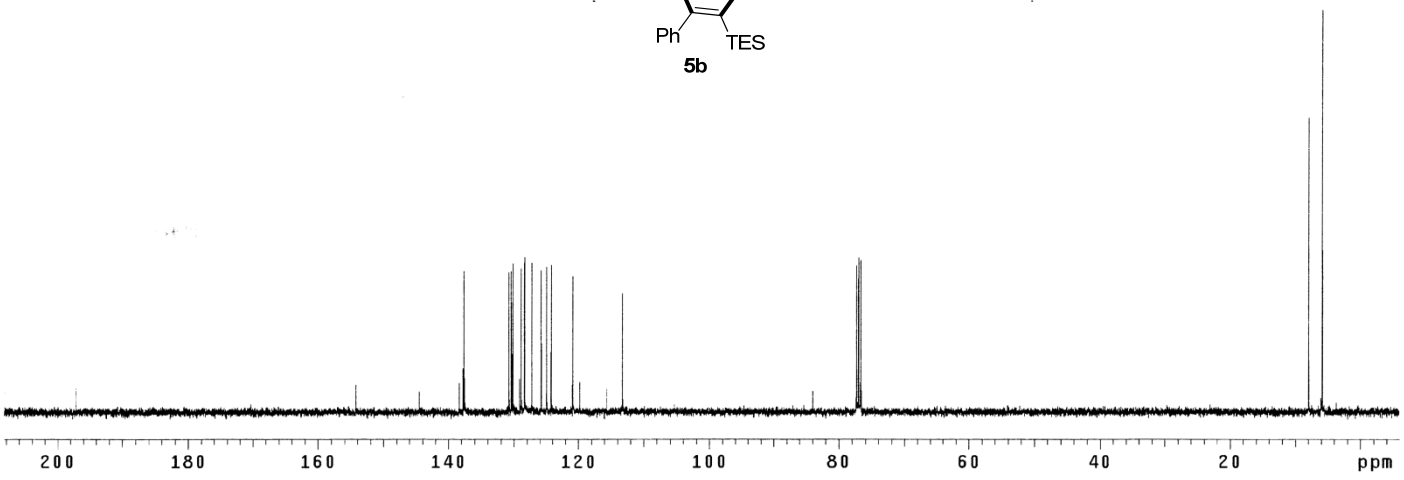
5b

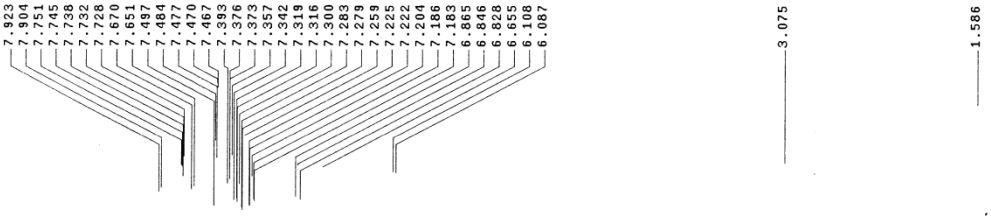
10
9
8
7
6
5
4
3
2
1
ppm
1.05
3.16
3.49
2.77
2.57
1.45
1.14
1.00
0.78
9.81
6.88

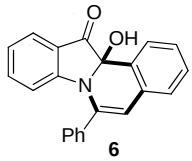

197.194
154.272
144.452
138.354
137.735
137.607
130.787
130.403
130.169
129.142
128.916
128.402
128.361
127.248
125.757
124.927
124.214
120.862
119.776
115.598
113.217
83.951
77.317
77.000
76.683
7.944
5.834


O
OH
N
Ph
TES

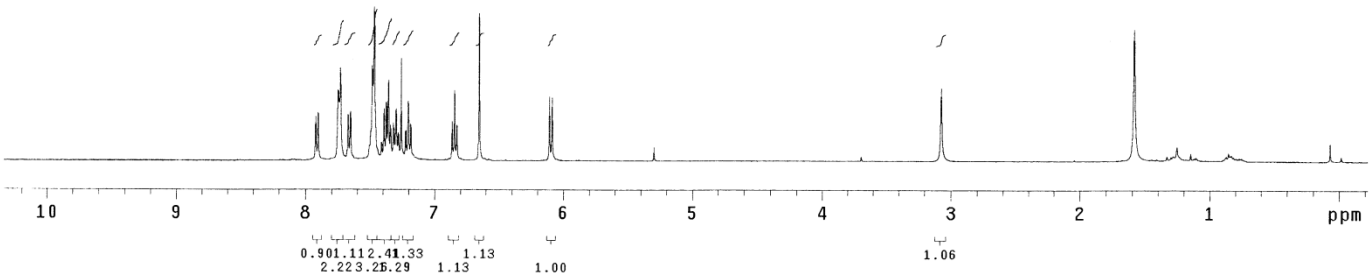
5b

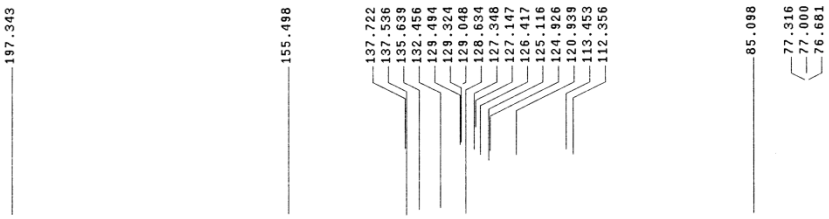

200
180
160
140
120
100
80
60
40
20
ppm

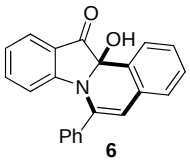

7.923
7.904
7.751
7.745
7.738
7.732
7.728
7.670
7.651
7.497
7.484
7.477
7.470
7.467
7.393
7.376
7.373
7.357
7.342
7.319
7.316
7.300
7.283
7.279
7.259
7.225
7.222
7.204
7.186
7.183
6.865
6.846
6.828
6.655
6.108
6.087
3.075
1.586


O
OH
N
Ph

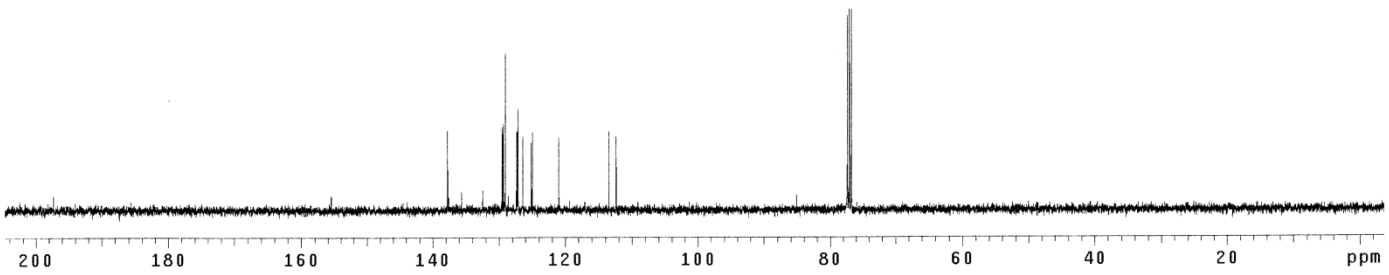
6

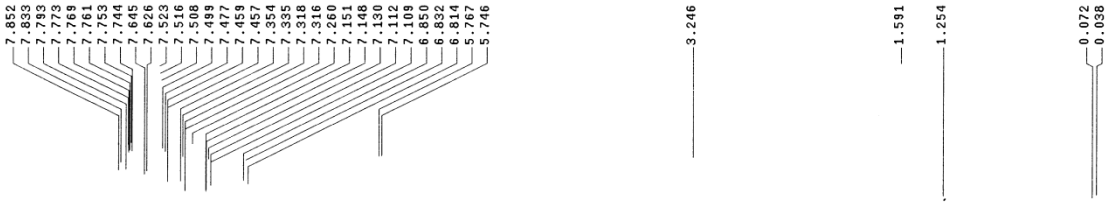

10
9
8
7
6
5
4
3
2
1
ppm
0.90
1.11
2.41
1.33
1.13
2.22
3.25
5.29
1.13
1.00
1.06

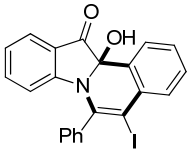

197.343
155.498
137.722
137.536
135.639
132.456
129.494
129.324
129.048
128.634
127.348
127.147
126.417
125.116
124.926
120.939
113.453
112.356
85.098
77.316
77.000
76.681


O
OH
N
Ph

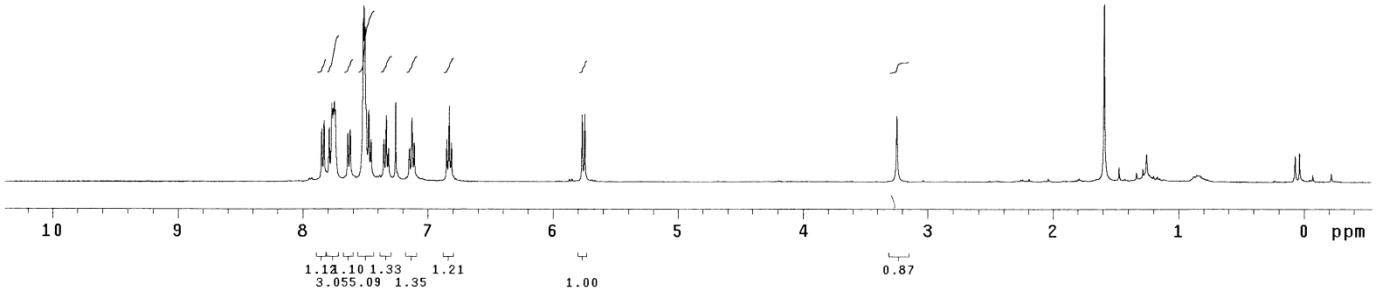
6

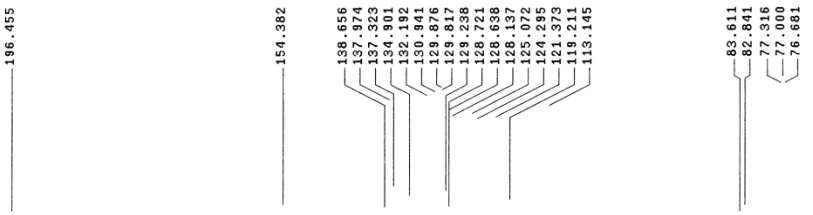

200
180
160
140
120
100
80
60
40
20
ppm

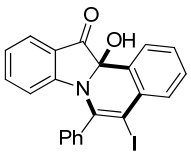

7.852
7.833
7.793
7.773
7.769
7.761
7.753
7.744
7.645
7.626
7.523
7.516
7.508
7.499
7.477
7.459
7.457
7.354
7.335
7.318
7.316
7.260
7.151
7.148
7.130
7.112
7.109
6.850
6.832
6.814
5.767
5.746
3.246
1.591
1.254
0.072
0.038


O
OH
N
Ph
I

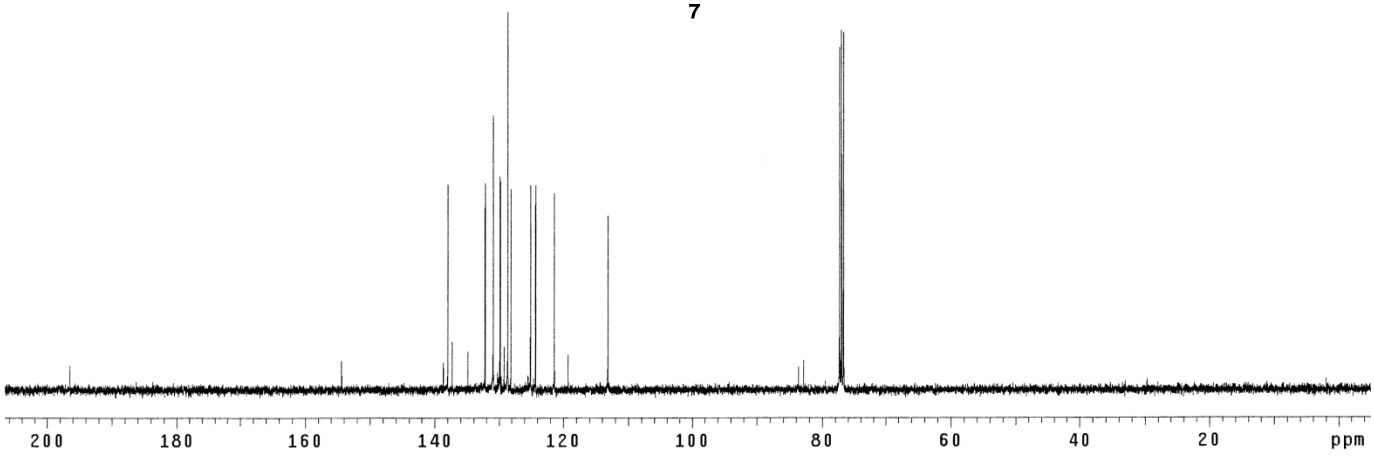
7

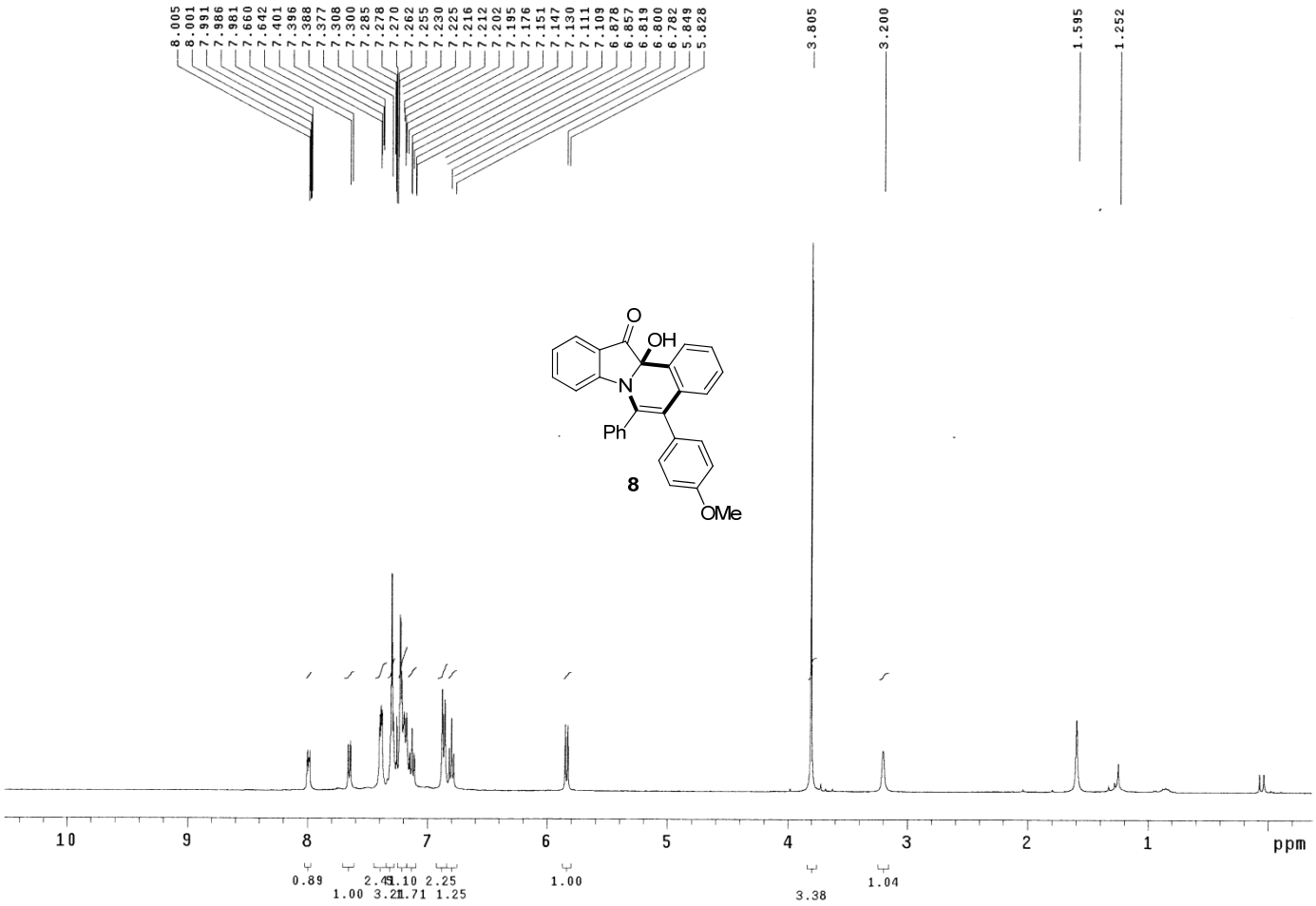

10
9
8
7
6
5
4
3
2
1
0
ppm
1.12
1.10
1.33
1.21
3.05
5.09
1.35
1.00
0.87

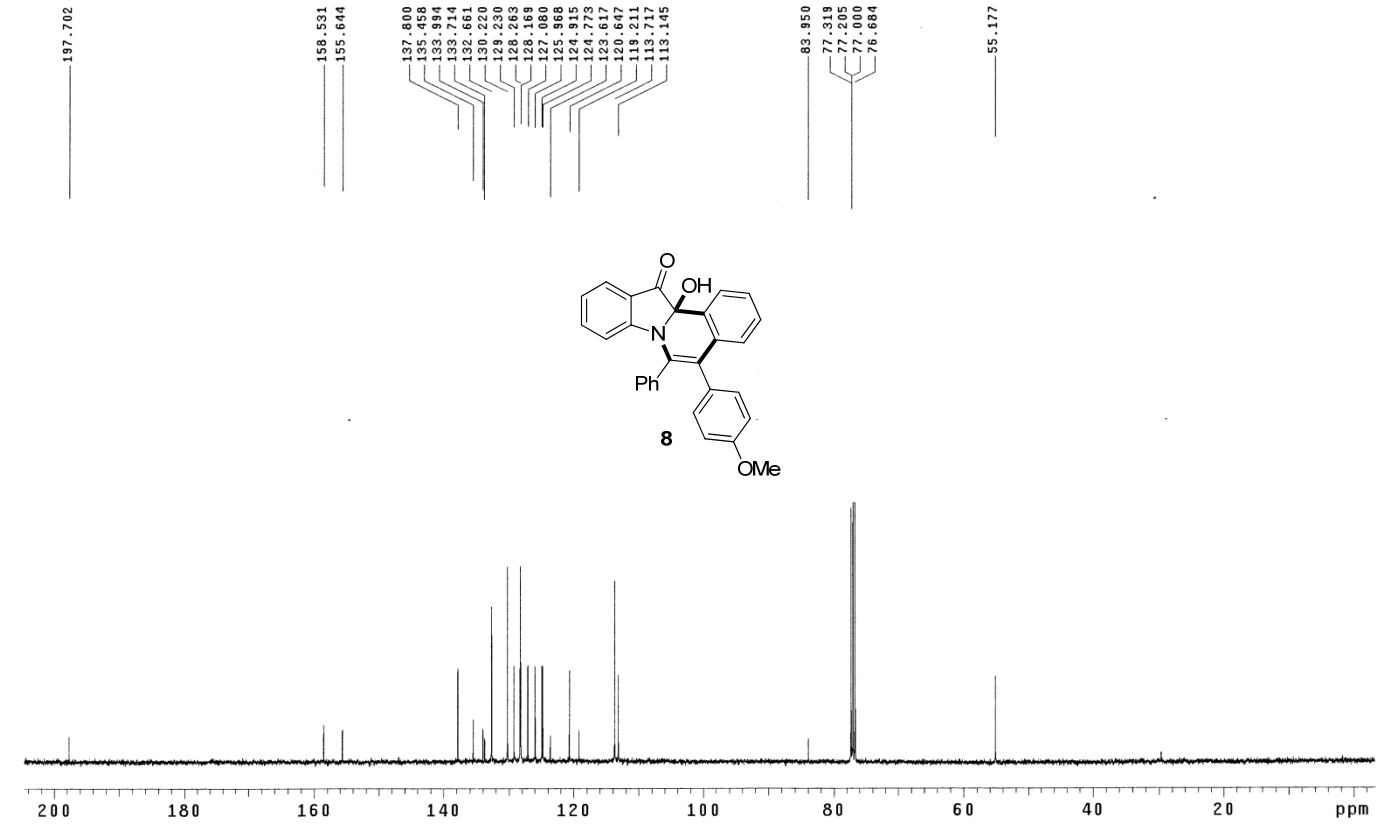

196.455
154.382
138.656
137.974
137.323
134.901
132.192
130.941
129.876
129.817
129.238
128.721
128.638
128.137
125.072
124.295
121.373
119.211
113.145
83.611
82.841
77.316
77.000
76.681

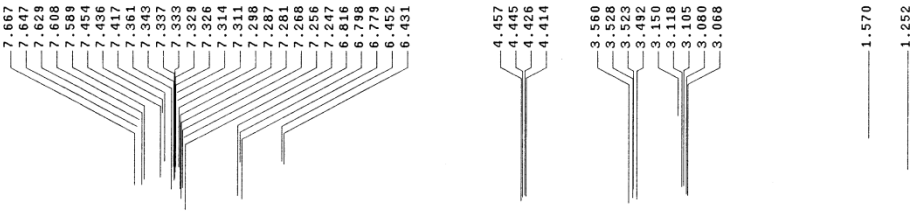

O
OH
N
Ph
I

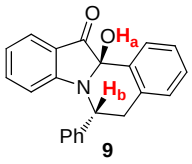
7


200
180
160
140
120
100
80
60
40
20
ppm

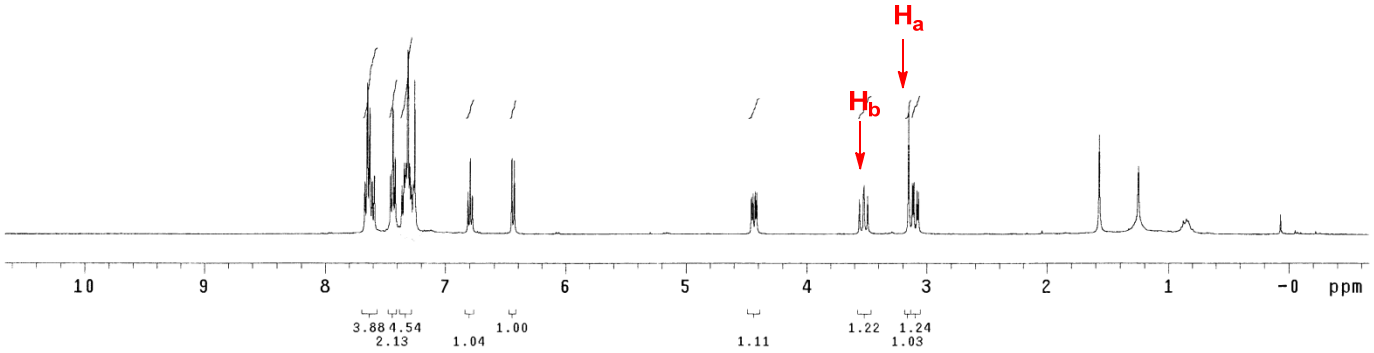

8.005
8.001
7.991
7.986
7.981
7.660
7.642
7.401
7.396
7.388
7.377
7.308
7.300
7.285
7.278
7.270
7.262
7.255
7.230
7.225
7.216
7.212
7.202
7.195
7.176
7.151
7.147
7.130
7.111
7.109
6.878
6.857
6.819
6.800
6.782
5.849
5.828
3.805
3.200
1.595
1.252
O
OH
N
Ph
OMe
8
10
9
8
7
6
5
4
3
2
1
ppm
0.89
1.00
2.45
3.21
1.10
1.71
2.25
1.25
1.00
3.38
1.04

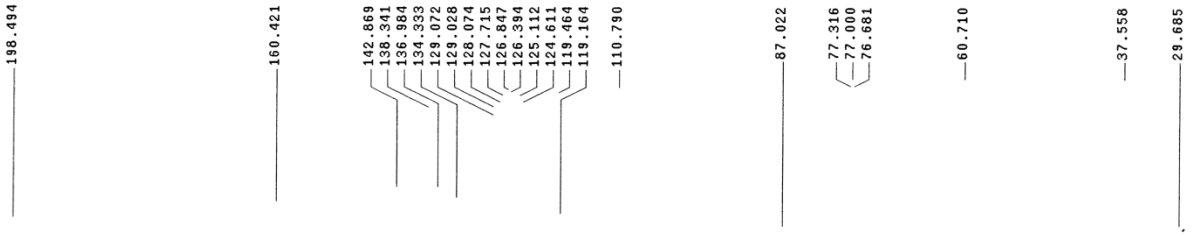

197.702
158.531
155.644
137.800
135.458
133.994
133.714
132.661
130.220
129.230
128.263
128.169
127.080
125.968
124.915
124.773
123.617
120.647
119.211
113.717
113.145
83.950
77.319
77.205
77.000
76.684
55.177
O
OH
N
Ph
OMe
8
200
180
160
140
120
100
80
60
40
20
ppm

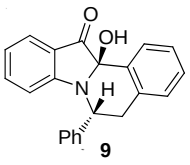

7.667
7.647
7.629
7.608
7.589
7.454
7.436
7.417
7.361
7.343
7.337
7.333
7.329
7.326
7.314
7.311
7.298
7.287
7.281
7.268
7.256
7.247
6.816
6.798
6.779
6.452
6.431
4.457
4.445
4.426
4.414
3.560
3.528
3.523
3.492
3.150
3.118
3.105
3.080
3.068
1.570
1.252


O
OH$_a$
N
H$_b$
Ph

9

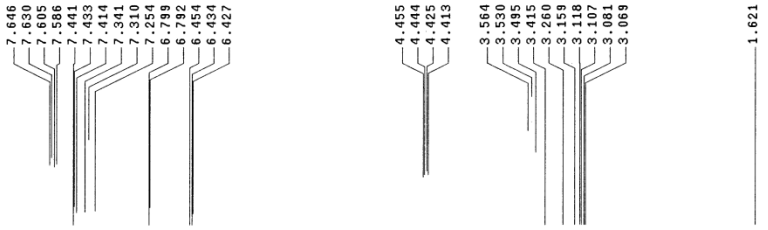

H$_a$
H$_b$
10
9
8
7
6
5
4
3
2
1
-0
ppm
3.88
4.54
2.13
1.04
1.00
1.11
1.22
1.24
1.03

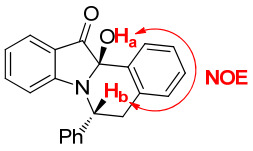

198.494
160.421
142.869
138.341
136.984
134.333
129.072
129.028
128.074
127.715
126.847
126.394
125.112
124.611
119.464
119.164
110.790
87.022
77.316
77.000
76.681
60.710
37.558
29.685


O
OH
N
H
Ph

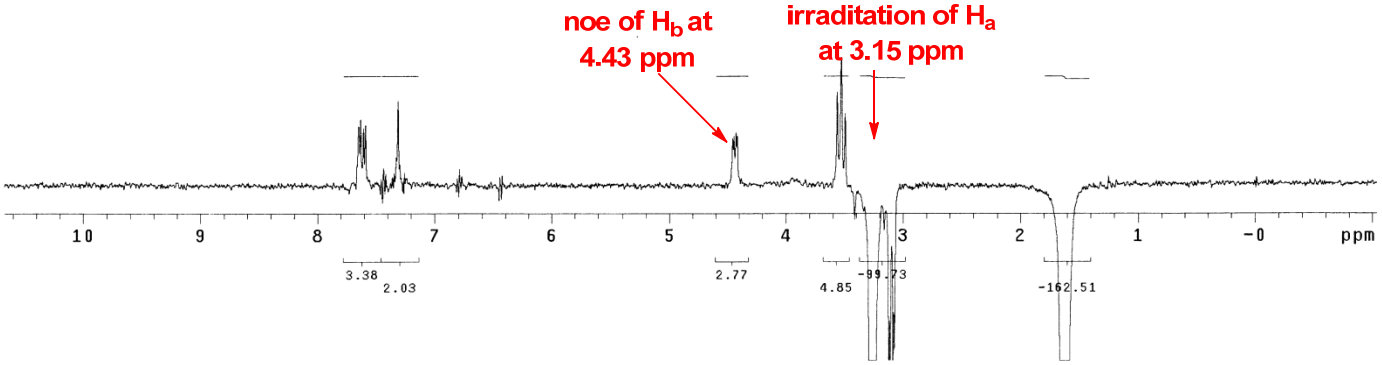
9

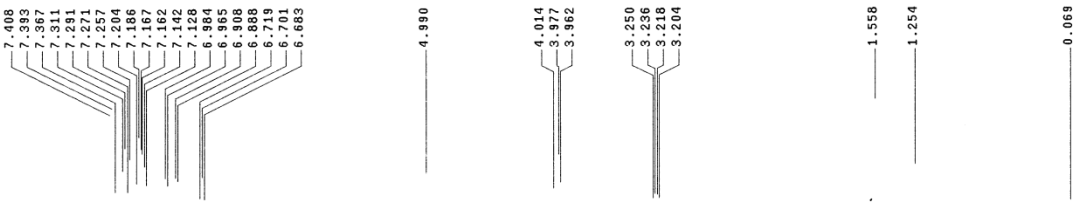
200
180
160
140
120
100
80
60
40
20

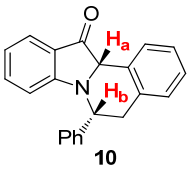

7.646
7.630
7.605
7.586
7.441
7.433
7.414
7.341
7.310
7.254
6.799
6.792
6.454
6.434
6.427
4.455
4.444
4.425
4.413
3.564
3.530
3.495
3.415
3.260
3.159
3.118
3.107
3.081
3.069
1.621


O
OHa
N
Hb
Ph
NOE

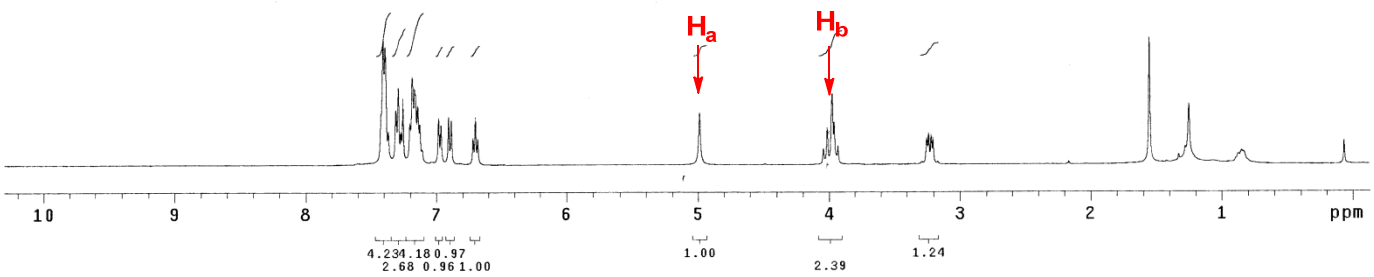
NOE of 9

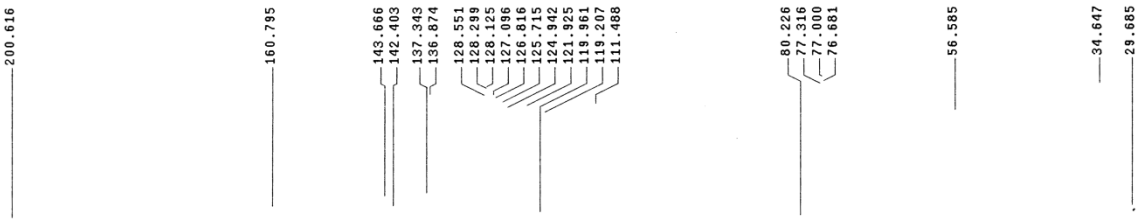

noe of Hb at 4.43 ppm
irraditation of Ha at 3.15 ppm
10
9
8
7
6
5
4
3
2
1
-0
ppm
3.38
2.03
2.77
4.85
-99.73
-162.51

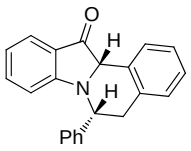

7.408
7.393
7.367
7.311
7.291
7.271
7.257
7.204
7.186
7.167
7.162
7.142
7.128
6.984
6.965
6.908
6.888
6.719
6.701
6.683
4.990
4.014
3.977
3.962
3.250
3.236
3.218
3.204
1.558
1.254
0.069


O
Ha
N
Hb
Ph

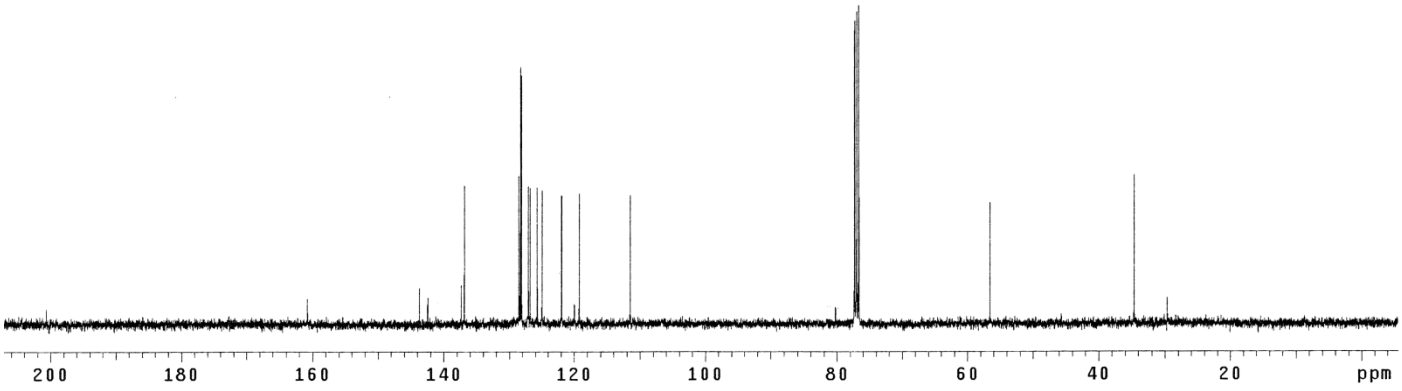
10

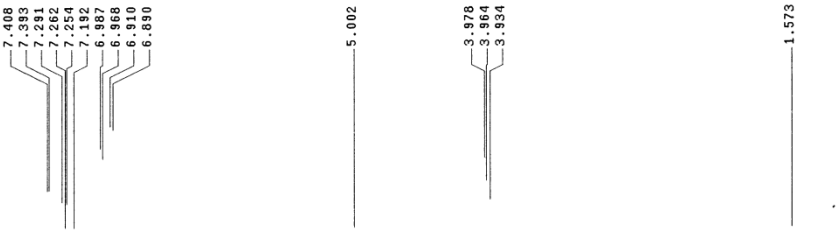

Ha
Hb
10
9
8
7
6
5
4
3
2
1
ppm
4.23
4.18
0.97
2.68
0.96
1.00
1.00
2.39
1.24

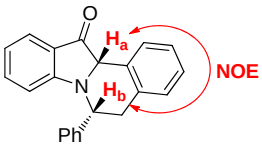

200.616
160.795
143.666
142.403
137.343
136.874
128.551
128.239
128.125
127.096
126.816
125.715
124.942
121.925
119.961
119.207
111.488
80.226
77.316
77.000
76.681
56.585
34.647
29.685


O
H
N
H
Ph

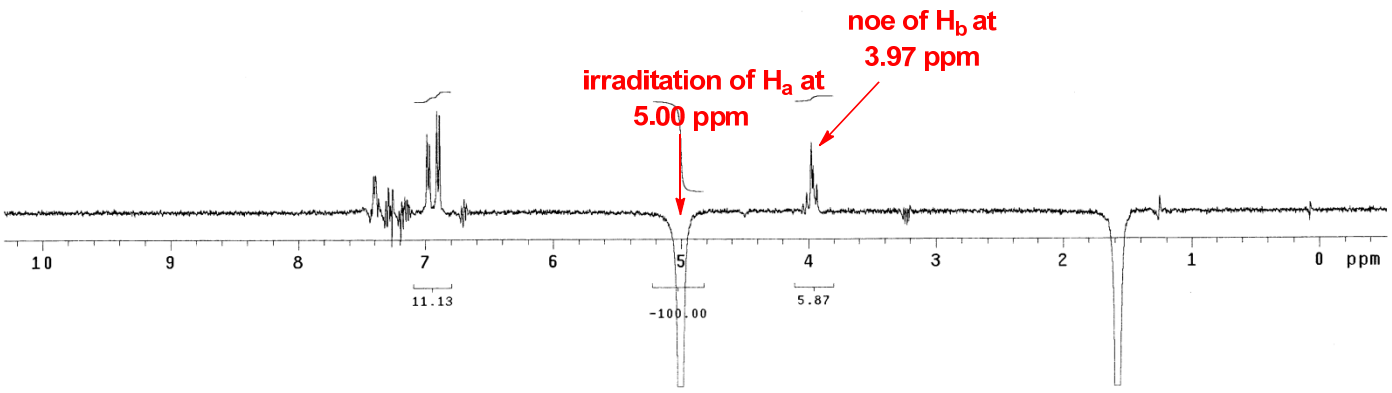
10

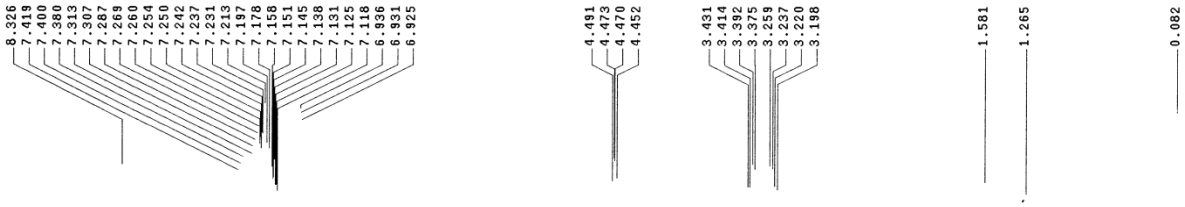

200
180
160
140
120
100
80
60
40
20
ppm

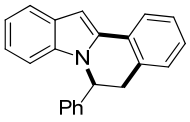

7.408
7.393
7.291
7.262
7.254
7.182
6.987
6.968
6.910
6.890
5.002
3.978
3.964
3.934
1.573


O
Ha
NOE
N
Hb
Ph

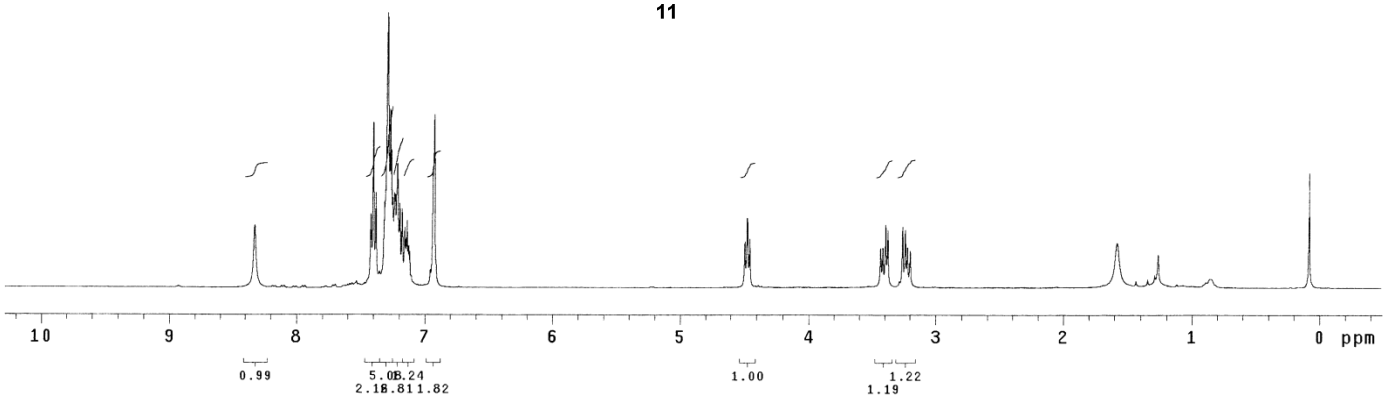
NOE of 10

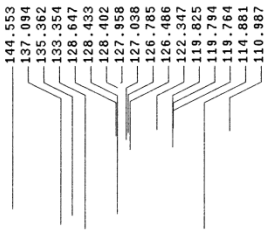

noe of Hb at
3.97 ppm
irraditation of Ha at
5.00 ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
11.13
-100.00
5.87

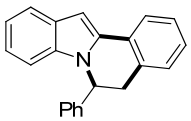

8.326
7.419
7.400
7.380
7.313
7.307
7.287
7.269
7.260
7.254
7.250
7.242
7.237
7.231
7.213
7.197
7.178
7.158
7.151
7.145
7.138
7.131
7.125
7.118
6.936
6.931
6.925
4.491
4.473
4.470
4.452
3.431
3.414
3.392
3.375
3.259
3.237
3.220
3.198
1.581
1.265
0.082


N
Ph

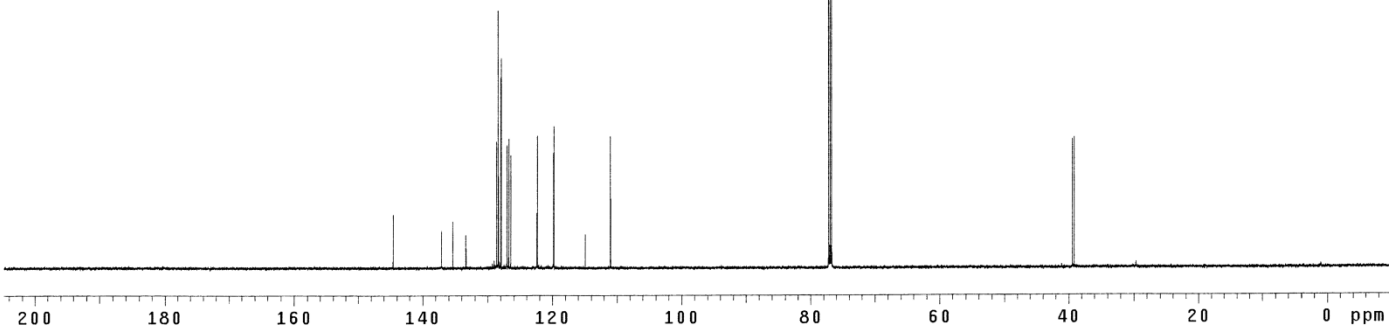
11


10
9
8
7
6
5
4
3
2
1
0 ppm
0.99
5.08
3.24
2.18
8.81
1.82
1.00
1.22
1.19


144.553
137.094
135.362
133.354
128.647
128.433
128.402
127.958
127.038
126.785
126.486
122.347
119.825
119.794
119.764
114.881
110.987
77.215
77.000
76.793
39.410
39.127


N
Ph

11


200
180
160
140
120
100
80
60
40
20
0 ppm