SUPPORTING INFORMATION

A Silver-Promoted Auto-Tandem Catalysis for the Synthesis of Multiply Substituted Tetrahydrocarbazoles

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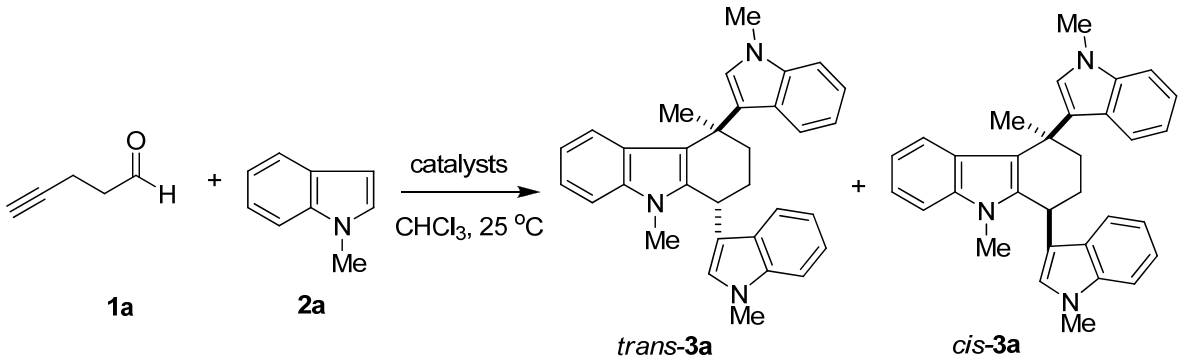
Table S1 Catalyst Screening for Tandem Reaction of Acetylenic Aldehyde **1a** with Indole **2a** [a]



1a **2a** *trans*-**3a** *cis*-**3a**

entry	catalyst	conv.[%] [b]	yield[%] [c]
1	10 mol% AgOTf	100	82% (*trans:cis* = 2.5:1) [d]
2	10 mol% $AgSbF_6$	100	75% (*trans:cis* = 2.4:1) [d]
3	5 mol% $AuCl_3$	100	trace
4	5 mol% PPh_3AuCl/AgOTf	100	trace
5	10 mol% AgOTf	100	75% (*trans:cis* = 2.0:1) [e]
6	10 mol% AgOTf	100	80% (*trans:cis* = 2.3:1) [f]
7	No catalyst	0	0

[a]Reactions were conducted with 2 mmol of **1a**, 7 mmol of **2a** and 5-10 mol % of catalysts in 5 mL of $CHCl_3$ at 25 °C for 6 h. [b]Conversion based on acetylenic aldehyde. [c]Isolated yield. [d]*dr* values (*trans*/*cis*) were determined by ^1H NMR analysis of the crude reaction mixture. [e]Toluene was used as solvent. [f]THF was used as solvent.

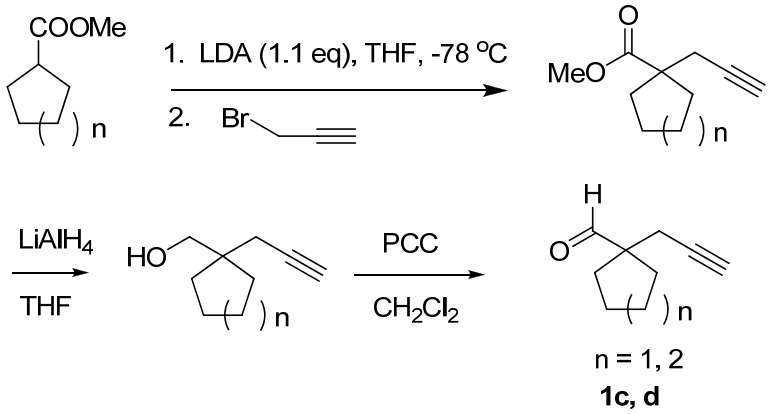
Experimental Section

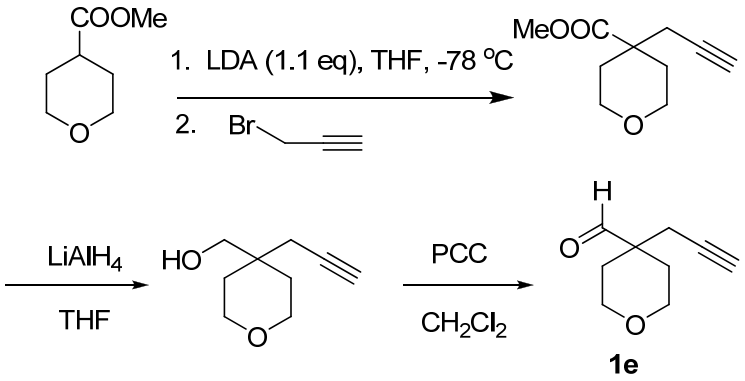
(I) General Methods.

All manipulations with air-sensitive reagents were carried out under a dry nitrogen atmosphere. NMR spectra were recorded on Bruker AMX-300/400 spectrometer for ^{1}H NMR and 75/100 MHz for ^{13}C NMR in $CDCl_3$. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Low resolution mass spectra and high-resolution mass spectra (HRMS) were obtained on a Finnigan GC-MS 4021 or a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV), respectively.

(II) Procedure

General procedure for synthesis of 1-(prop-2-ynyl)cyclopentanecarbaldehyde 1c, 1-(prop-2-ynyl)cyclohexanecarbaldehyde 1d and tetrahydro-4-(prop-2-ynyl)-2*H*-pyran-4-carbaldehyde 1e [1]





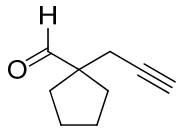
(1) Propargylation*:* To diisopropylamine (2.7 mL, 19.4 mmol) in THF was added dropwise *n*-butyllithium (1.6 M in hexanes, 12.1 mL, 19.4 mmol) at -78 °C with stirring. Subsequently, the reaction mixture was stirred for 15 min. A solution of corresponding methyl ester (17.6 mmol) in dry THF (5 ml) was added dropwise to this solution of LDA in 30 min at -78 °C. After stirring for 1 h, propargyl bromide (80% in toluene, 2.1 mL, 18.5 mmol) was added dropwise to the above solution. The reaction system was kept at -78 °C for 1 h and warmed to 25 °C over 1 h. The resulting reaction mixture was quenched with saturated aqueous NH_4Cl solution, and extracted three times with diethyl ether. The combined organic layers were separated, washed with 2 M aqueous HCl, saturated aqueous $NaHCO_3$ solution and brine; dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford practically pure propargyl substituted methyl ester as an orange liquid.

(2) Reduction: A solution of the above methyl ester in diethyl ether (25 mL) was added to a stirred suspension of lithium aluminium hydride (0.52 g, 13.9 mmol) in diethyl ether (20 mL) at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, treated with 2 M NaOH solution to dissolve the aluminum precipitate, and extracted with diethyl ether. The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine; dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude alcohol product.

(3) Oxidation: A solution of the above crude alcohol (1 equiv.) in dichloromethane was added pyridinium chlorochromate (PCC, 1.6 equiv.) at room temperature. After stirring for 6 h at room temperature, the reaction mixture was filtered and concentrated *in vacuo* to give

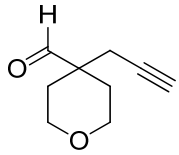
the crude aldehyde. Flash chromatography (5% EtOAc/hexanes) afforded the titled aldehydes **1c**, **1d**, **1e** as a yellow liquid.

1-(Prop-2-ynyl)cyclopentanecarbaldehyde (1d), the yield is 55% for three steps.



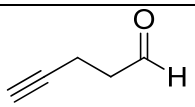
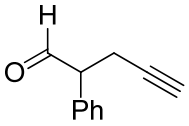
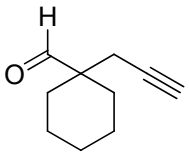
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56-1.75 (m, 6H), 1.94-1.97 (m, 3H), 2.43 (s, 2H), 9.53 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.30, 25.75, 32.56, 37.36, 69.96, 80.92, 203.22; IR (KBr, neat, cm^{-1}) 3302, 2955, 2870, 1705; EIMS *m/z* 136 (M^+); HRMS (EI) for $C_9H_{12}O$, calcd 136.0888, found 136.0885.

Tetrahydro-4-(prop-2-ynyl)-2*H*-pyran-4-carbaldehyde (1e), the yield is 65% for three steps.



^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (t, *J* = 9.0 Hz, 2H), 1.95-2.04 (m, 3H), 2.35 (s, 2H), 3.46 (t, *J* = 9.9 Hz, 2H), 3.72 (t, *J* = 9.8 Hz, 2H), 9.56 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.84, 30.20, 45.82, 64.26, 71.98, 78.34, 204.01; IR (KBr, neat, cm^{-1}) 3287, 2955, 2862, 1720, 1103, 1026, 841; EIMS *m/z* 152 (M^+); HRMS (EI) for $C_9H_{12}O_2$, calcd 152.0837, found 152.0839.

Table S2 Literature references of acetylentic aldehydes

compound	structure	reference
1a		*J. Med. Chem.* **1991***, 34,* 1585-1593
1b		*J. Org. Chem.* **1990**, *55*, 4853-4859
1c		*J. Am. Chem. Soc.* **2006**, *128*, 15598-15599

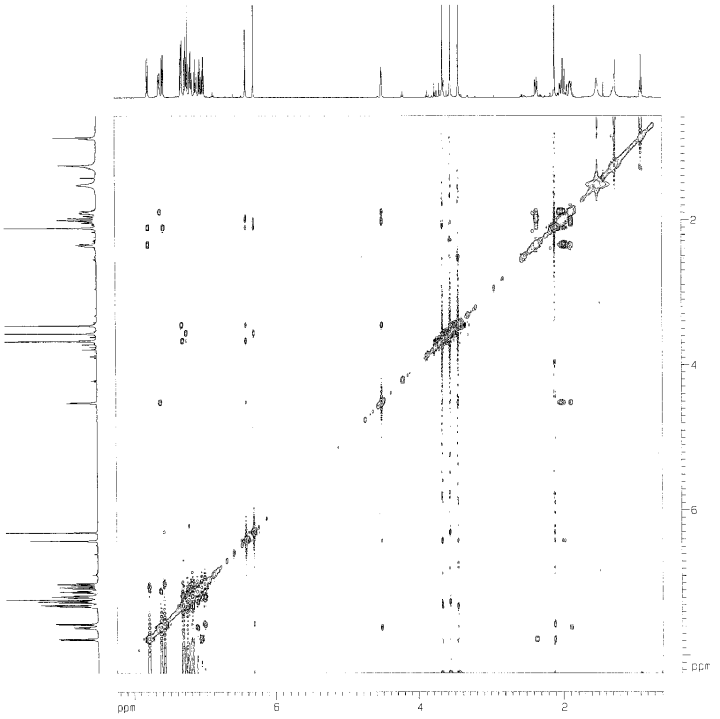


Figure S1 ^{1}H-^{1}H NOESY spectrum of *trans*-**3a**

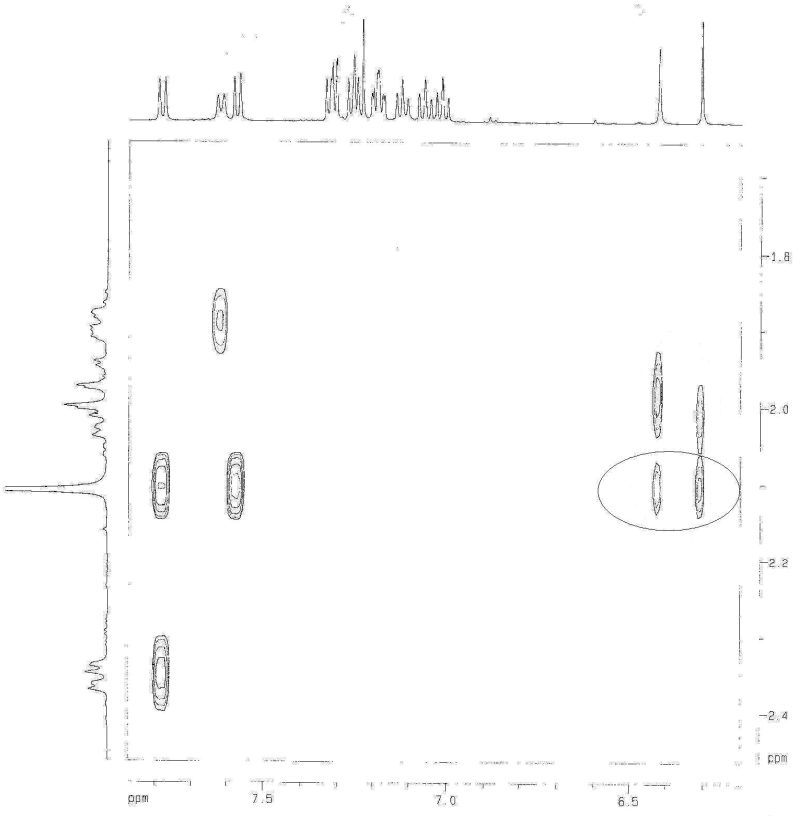


Figure S2 ^{1}H-^{1}H NOESY spectrum of *trans*-**3a**

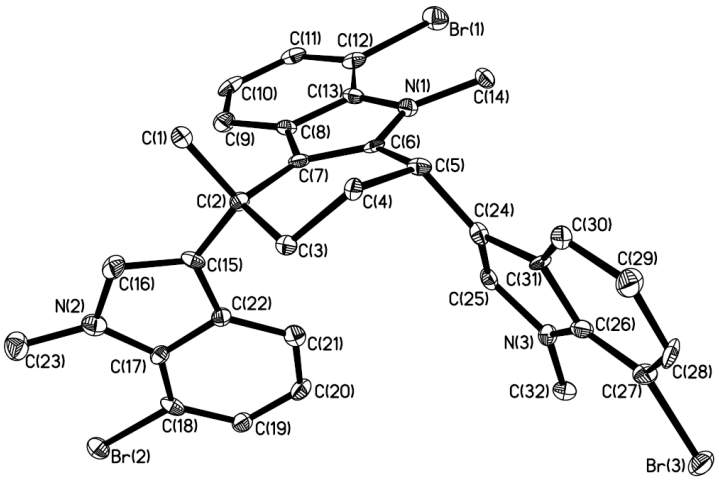


Figure S3 ORTEP plot of *cis*-**3e** (ellipsoids at 30% probability)

Table S3 Crystal data and structure refinement for compound *trans*-**3a**.

Compound code	*trans*-**3a**
Empirical formula	$C_{32.50}\ H_{32}\ Cl\ N_3$
Formula weight	500.06
Temperature	301(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1(#2)
Unit cell dimensions	a = 9.4790(6) Å □= 72.34(2)° b = 12.1347(8) Å □= 80.30(2)° c = 12.4926(8) Å □= 84.57(2)°
Volume	1348.24(15) $Å^3$
Z	2
Density (calculated)	1.232 Mg/m^3
Absorption coefficient	0.168 mm^{-1}
F(000)	530
Crystal size	0.44 x 0.13 x 0.09 mm^3
Theta range for data collection	1.73 to 25.68°
Index ranges	-11<=h<=11, -14<=k<=14, -15<=l<=15
Reflections collected	14078
Independent reflections	5118 [R(int) = 0.0167]
Completeness to theta = 25.68°	99.7 %
Absorption correction	Empirical
Max. and min. transmission	1.000000 and 0.888932
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5118 / 2 / 338
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1742
R indices (all data)	R1 = 0.0805, wR2 = 0.1913
Largest diff. peak and hole	0.542 and -0.633 $e.Å^{-3}$

Table S4 Crystal data and structure refinement for compound *cis*-**3e**

Compound code	***cis*-3e**
Empirical formula	$C_{32}H_{28}Br_3N_3$
Formula weight	694.30
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 10.4882(7) Å □= 90° b = 15.1646(10) Å □= 90.89(2)° c = 17.8633(10) Å □ = 90°
Volume	2841.1(3) $Å^3$
Z	4
Density (calculated)	1.623 Mg/m^3
Absorption coefficient	5.465 mm^{-1}
F(000)	1384
Crystal size	0.04 x 0.01 x 0.01 mm^3
Theta range for data collection	3.82 to 65.96°
Index ranges	-12<=h<=11, -17<=k<=17, -16<=l<=21
Reflections collected	13199
Independent reflections	4362 [R(int) = 0.0735]
Completeness to theta = 65.96°	95.0 %
Absorption correction	Empirical
Max. and min. transmission	0.95 and 0.93
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4362 / 0 / 347
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0709, wR2 = 0.1924
R indices (all data)	R1 = 0.0779, wR2 = 0.1971
Largest diff. peak and hole	1.539 and -0.870 $e.Å^{-3}$

Table S5 Crystal data and structure refinement for compound *cis*-**3j**

Compound code	**3j**
Empirical formula	C_{75} H_{74} N_6
Formula weight	1059.40
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 2_1/c
Unit cell dimensions	a = 12.6510 Å □ = 72° b = 13.2655 Å □ = 82° c = 19.6439 Å = 78°
Volume	3067.1(2) $Å^3$
Z	2
Density (calculated)	1.147 Mg/m^3
Absorption coefficient	0.511 mm^{-1}
F(000)	1132
Crystal size	0.42 x 0.30 x 0.25 mm^3
Theta range for data collection	2.37 to 66.22°
Index ranges	-14<=h<=14, -14<=k<=15, -23<=l<=23
Reflections collected	66128
Independent reflections	10240 [R(int) = 0.0409]
Completeness to theta = 66.22°	95.4 %
Absorption correction	Empirical
Max. and min. transmission	1.000000 and 0.87682
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10240 / 0 / 737
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0800, wR2 = 0.2570
R indices (all data)	R1 = 0.0912, wR2 = 0.2752
Largest diff. peak and hole	1.242 and -0.201 $e.Å^{-3}$

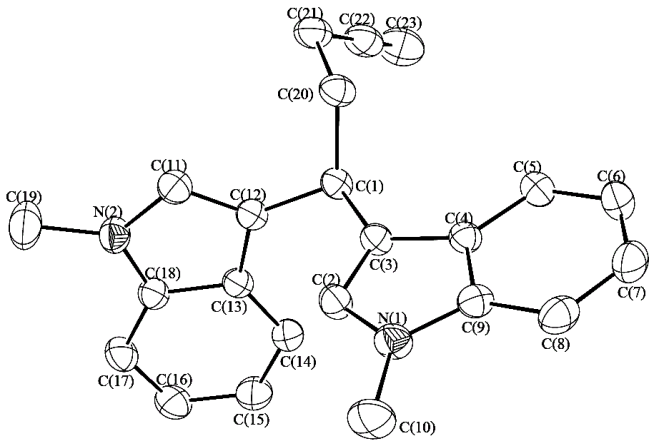
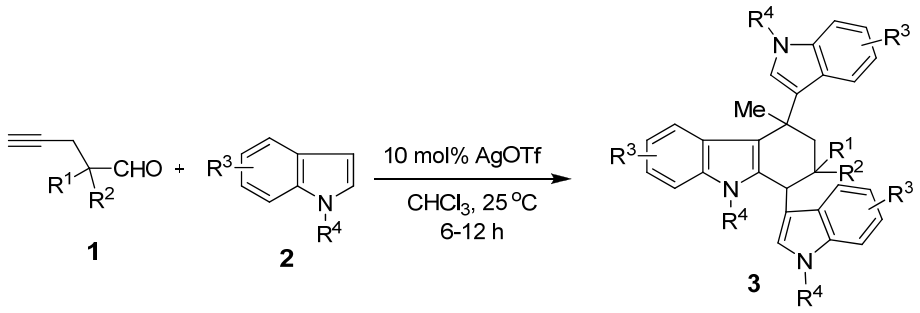


Figure S4 ORTEP plot of **4a** (ellipsoids at 30% probability)

Table S6 Crystal data and structure refinement for compound **4a**

Compound code	**4a**
Empirical formula	$C_{23}H_{22}N_2$
Formula weight	326.43
Temperature	301(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2_1/c
Unit cell dimensions	a = 8.1814(9) Å □= 90° b = 8.5337(9) Å □= 90.89(2)° c = 26.531(3) Å □ = 90°
Volume	1852.1(3) Å^3
Z	4
Density (calculated)	1.171 Mg/m^3
Absorption coefficient	0.069 mm^{-1}
F(000)	696
Crystal size	0.43 x 0.32 x 0.28 mm^3
Theta range for data collection	2.49 to 25.68°
Index ranges	-9<=h<=9, -10<=k<=10, -32<=l<=29
Reflections collected	10612
Independent reflections	3495 [R(int) = 0.0173]
Completeness to theta = 25.68°	99.5 %
Absorption correction	Empirical
Max. and min. transmission	1.000000 and 0.811581
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3495 / 0 / 228
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1104
R indices (all data)	R1 = 0.0518, wR2 = 0.1173
Largest diff. peak and hole	0.188 and -0.225 e.Å^{-3}

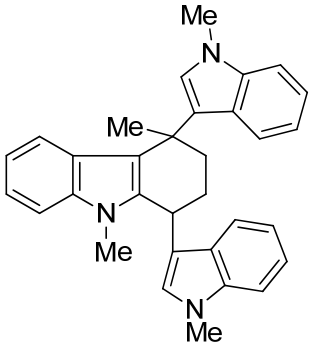
General procedure for silver-catalyzed tandem reaction of acetylenic aldehydes and indoles (Table 2):



To a mixture of acetylenic aldehyde **1** (2 mmol) and indole **2** (7 mmol) in $CHCl_3$ (5 mL) was added silver triflate (51 mg, 0.2 mmol). The reaction mixture was stirred at room temperature for 6–12 h. When the reaction was complete, the reaction mixture was concentrated and the residue was loaded directly onto a silica gel column; elution with ethyl acetate/hexane afforded the products.

(III) Characterization Data of Compound 3

4,9-Dimethyl-1,4-bis(1-methyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (3a)

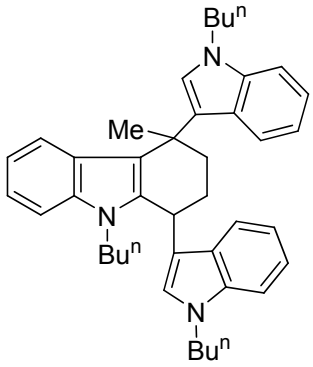


trans-Diastereomer (major): Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95-1.99 (m, 1H), 2.01-2.13 (m, 2H), 2.22 (s, 3H), 2.41-2.45 (m, 1H), 3.51 (s, 3H), 3.62 (s, 3H), 3.73 (s, 3H), 4.51-4.53 (m, 1H), 6.30 (s, 1H), 6.42 (s, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.17-7.23 (m, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.30-7.33 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.42, 29.41, 29.71, 29.97, 32.51, 32.69, 34.72, 36.67, 108.72, 109.41, 109.44, 117.18, 117.81, 118.21, 118.38, 118.62, 118.82, 118.95, 120.39, 120.83, 121.20,

121.41, 121.69, 122.46, 125.98, 126.53, 126.75, 128.14, 129.09, 137.21, 137.42, 138.11; IR (KBr, neat, cm^{-1}) 3441, 2930, 1720, 1643, 1556, 1458, 1320, 1096, 741; EIMS *m/z* 457 (M^+); HRMS (EI) for $C_{33}H_{31}N_3$, calcd 457.2518, found 457.2510.

cis-Diastereomer (minor): Yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 1.93-1.97 (m, 4H), 1.99-2.02 (m, 1H), 2.39 (d, *J* = 7.1 Hz, 2H), 3.46 (s, 3H), 3.66 (s, 3H), 3.72 (s, 3H), 4.57 (m, 1H), 6.60 (s, 1H), 6.86-6.90 (m, 3H), 7.05-7.12 (m, 4H), 7.25-7.29 (m, 4H), 7.55 (d, *J* = 6.8 Hz, 1H), 7.60 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.51, 29.58, 29.68, 30.27, 32.60, 32.64, 35.95, 36.48, 108.49, 109.11, 109.33, 117.33, 117.82, 118.15, 118.20, 118.40, 120.32, 120.65, 120.77, 120.84, 121.15, 121.36, 121.58, 123.90, 126.29, 126.35, 126.69, 127.00, 127.87, 136.87, 137.31, 137.81; IR (KBr, neat, cm^{-1}) 3450, 2931, 1716, 1624, 1558, 1506, 1456, 1323, 1097, 1010, 739; EIMS *m/z* 457 (M^+); HRMS (EI) for $C_{33}H_{31}N_3$, calcd 457.2518, found 457.2512.

9-Butyl-1,4-bis(1-butyl-1*H*-indol-3-yl)-4-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (3b)

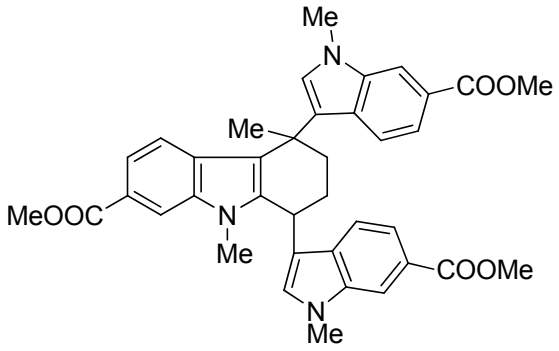


trans-Diastereomer (major): Yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 0.74-0.94 (m, 9H), 1.11-1.32 (m, 6H), 1.60-1.77 (m, 6H), 1.87-2.09 (m, 3H), 2.17 (s, 3H), 2.31-2.35 (m, 1H), 3.84-4.02 (m, 6H), 4.52 (brs, 1H), 6.34 (s, 1H), 6.48 (s, 1H), 6.95-7.13 (m, 2H), 7.15-7.22 (m, 3H), 7.25-7.27 (m, 2H), 7.30-7.35 (m, 2H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.04, 17.35, 17.40, 23.48, 23.95, 24.77, 33.36, 33.68, 34.91, 35.84, 36.00, 36.24, 38.50, 46.56, 47.39, 49.63, 49.78, 112.62, 113.07, 113.21, 120.76, 121.16, 121.64, 121.73, 122.43, 122.79, 123.19, 123.74,

123.93, 124.08, 124.58, 124.93, 125.04, 125.47, 126.29, 128.45, 130.24, 130.96, 131.43, 131.79, 136.08; IR (KBr, neat, cm^{-1}) 3057, 2951, 2856, 2353, 1606, 1555, 1456, 1362, 1208, 739; EIMS *m/z* 583 (M^+); HRMS (EI) for $C_{41}H_{49}N_3$, calcd 583.3926, found 583.3922.

cis-Diastereomer (minor): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H), 1.06-1.33 (m, 6H), 1.58-1.82 (m, 6H), 1.91-2.01 (m, 4H), 2.09-2.11 (m, 1H), 2.38-2.41 (m, 2H), 3.84-4.06 (m, 6H), 4.56 (brs, 1H), 6.64 (s, 1H), 6.77-6.95 (m, 3H), 7.03-7.12 (m, 3H), 7.16-7.34 (m, 5H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.58, 13.71, 20.13, 20.23, 27.66, 28.45, 29.66, 31.20, 32.28, 32.43, 32.54, 36.03, 36.48, 43.09, 45.84, 45.92, 46.07, 108.95, 109.27, 109.45, 117.30, 117.48, 117.74, 117.90, 118.62, 118.72, 120.03, 120.38, 120.52, 120.98, 121.32, 123.10, 123.65, 126.15, 126.43, 126.54, 126.81, 128.52, 136.71, 137.05, 137.28; IR (KBr, neat, cm^{-1}) 3057, 2961, 2866, 2361, 1606, 1560, 1463, 1365, 1196, 739; EIMS *m/z* 583 (M^+); HRMS (EI) for $C_{41}H_{49}N_3$, calcd 583.3926, found 583.3918.

Dimethyl 3,3'-(7-(methoxycarbonyl)-4,9-dimethyl-2,3,4,9-tetrahydro-*1H*-carbazole-1,4-diyl)bis(1-methyl-1*H*-indole-6-carboxylate) (3c)

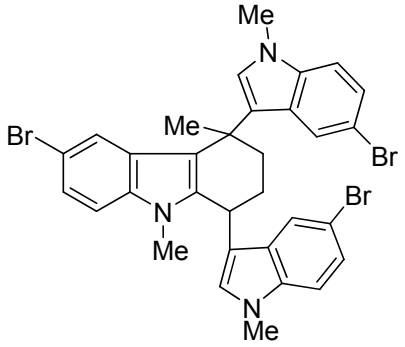


trans-Diastereomer (major): Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.89-2.04 (m, 3H), 2.17 (s, 3H), 2.32-2.36 (m, 1H), 3.48 (s, 3H), 3.65 (s, 3H), 3.77 (s, 3H), 3.81-3.93 (m, 9H), 4.57 (brs, 1H), 6.45 (s, 1H), 6.61 (s, 1H), 7.51-7.66 (m, 2H), 7.69-7.72 (m, 3H), 7.79 (d, *J* = 8.3 Hz, 1H), 8.04 (s, 1H), 8.09 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.52, 29.46, 29.64, 29.97, 30.09, 32.73, 32.96, 34.87, 36.39, 51.88, 51.98, 111.17, 111.88, 112.01,

117.01, 118.20, 119.40, 119.83, 120.24, 120.38, 120.45, 122.30, 122.56, 122.68, 123.57, 129.22, 129.80, 129.89, 130.75, 130.88, 131.90, 136.73, 136.79, 137.41, 140.54, 168.06, 168.18, 168.31; IR (KBr, neat, cm^{-1}) 3456, 2947, 1712, 1653, 1616, 1558, 1473, 1377, 1263, 1085, 987, 827, 771, 737, 702; EIMS *m/z* 631 (M^+); HRMS (EI) for $C_{38}H_{37}N_3O_6$, calcd 631.2682, found 631.2665.

Only *trans*-diastereomer was obtained as a pure product by chromatography. *cis*-Diastereomer contains inseparable *trans*-diastereomer**.**

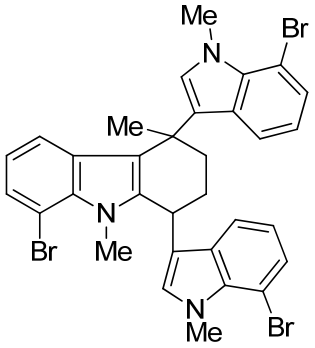
6-Bromo-1,4-bis(5-bromo-1-methyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-4,9-dimethyl-1*H*-carbazole (3d)



The inseparable mixture of two diastereomers: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81-1.88 (m, 3H), 1.95-1.97 (m, 2H), 2.04 (s, 3H), 2.19-2.27 (m, 1.8H), 2.38-2.41 (m, 1.4H), 3.42 (s, 3H), 3.44 (s, 2H), 3.58 (s, 3H), 3.68 (s, 3H), 3.75 (s, 2H), 3.78 (s, 2H), 4.42-4.45 (m, 1H), 4.48-4.50 (m, 0.6H), 6.24 (s, 1H), 6.36 (s, 1H), 6.71 (s, 0.6H), 6.99 (s, 1H), 7.12-7.20 (m, 6.8H), 7.28-7.34 (m, 3H), 7.50 (s, 0.6H), 7.64 (s, 1H), 7.73 (s, 1H), 7.50 (s, 0.6H), 7.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.00, 27.19, 27.89, 29.48, 29.52, 29.66, 29.77, 30.19, 32.74, 32.90, 32.97, 33.19, 34.49, 35.37, 35.89, 36.30, 110.16, 110.22, 110.83, 110.90, 111.01, 111.05, 111.42, 111.82, 111.95, 112.38, 112.51, 116.31, 116.44, 117.29, 121.18, 121.54, 121.66, 122.34, 122.98, 123.19, 123.38, 123.48, 123.76, 124.64, 127.31, 127.80, 128.14, 128.68, 128.95, 129.96, 136.05, 136.56, 136.72, 138.07; IR (KBr, neat, cm^{-}

[1]) 3056, 2923, 2852, 1635, 1559, 1485, 1451, 1215, 778, 735; EIMS *m/z* 690 (M^+); HRMS (EI) for $C_{32}H_{28}Br_3N_3$, calcd 690.9833, found 690.9826.

8-Bromo-1,4-bis(7-bromo-1-methyl-1*H*-indol-3-yl)-4,9-dimethyl-2,3,4,9-tetrahydro-1*H*-carbazole (3e)

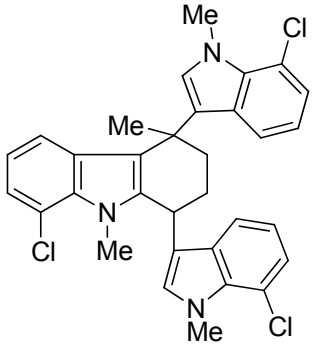


trans-Diastereomer (major): Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.83-1.97 (m, 3H), 2.04 (s, 3H), 2.26-2.30 (m, 1H), 3.80 (s, 3H), 3.95 (s, 3H), 4.06 (s, 3H), 4.44 (m, 1H), 6.19 (s, 1H), 6.35 (s, 1H), 6.78-6.93 (m, 2H), 6.95 (t, *J* = 7.7 Hz, 1H), 7.29-7.36 (m, 2H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.10, 29.30, 29.68, 29.99, 32.53, 34.76, 36.26, 36.70, 103.61, 104.12, 104.20, 116.45, 117.35, 117.93, 119.60, 119.72, 120.28, 120.32, 120.52, 121.50, 126.08, 126.22, 126.86, 129.04, 129.45, 129.56, 130.98, 132.04, 133.73, 133.77, 134.28, 138.56; IR (KBr, neat, cm^{-1}) 3057, 2941, 2856, 2360, 1606, 1558, 1485, 1456, 1208, 1089, 777, 735; EIMS *m/z* 690 (M^+); HRMS (EI) for $C_{32}H_{28}Br_3N_3$ calcd 690.9833, found 690.9845.

cis-Diastereomer (minor): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75-1.78 (m, 1H), 1.85 (s, 3H), 2.13-2.16 (m, 1H), 2.24-2.31 (m, 1H), 2.41-2.47 (m, 1H), 3.84 (s, 3H), 4.05 (s, 3H), 4.13 (s, 3H), 4.49 (m, 1H), 6.55 (s, 1H), 6.62-6.67 (m, 2H), 6.81 (s, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.38, 28.04, 30.18, 30.35, 33.08, 35.92, 36.57, 37.23, 37.30, 103.87, 104.38, 104.71, 117.09,

118.40, 118.59, 119.53, 120.05, 120.19, 120.69, 120.85, 123.75, 126.62, 126.75, 127.37, 129.78, 129.91, 130.07, 130.24, 131.44, 134.09, 134.20, 134.52, 138.53; IR (KBr, neat, cm^{-1}) 3056, 2940, 2852, 2365, 1605, 1558, 1482, 1455, 1206, 1092, 778, 735; EIMS *m/z* 690 (M^+); HRMS (EI) for $C_{32}H_{28}Br_3N_3$ calcd 690.9833, found 690.9842.

8-Chloro-1,4-bis(7-chloro-1-methyl-*1H*-indol-3-yl)-4,9-dimethyl-2,3,4,9-tetrahydro-*1H*-carbazole (3f)

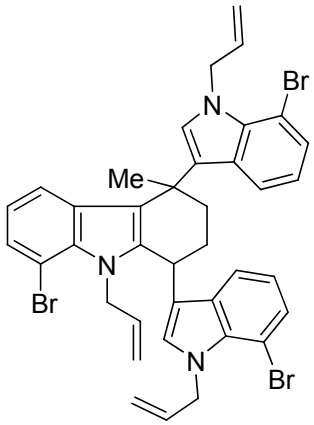


trans-Diastereomer (major): Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88-1.98 (m, 3H), 2.04 (s, 3H), 2.26-2.29 (m, 1H), 3.77 (s, 3H), 3.94 (s, 3H), 4.05 (s, 3H), 4.44 (m, 1H), 6.23 (s, 1H), 6.39 (s, 1H), 6.85-6.94 (m, 2H), 6.97 (t, *J* = 7.8 Hz, 1H), 7.09-7.12 (m, 2H), 7.16 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.12, 29.31, 29.68, 29.95, 32.49, 34.70, 36.28, 36.55, 116.62, 116.69, 117.13, 117.36, 117.94, 119.58, 119.73, 119.88, 119.93, 121.79, 122.53, 122.64, 123.33, 129.02, 129.34, 129.58, 130.69, 130.96, 131.74, 132.02, 132.66, 132.73, 133.25, 138.44; IR (KBr, neat, cm^{-1}) 3057, 2931, 2846, 1635, 1558, 1488, 1456, 1209, 1091, 779, 733; EIMS *m/z* 559 (M^+); HRMS (EI) for $C_{32}H_{28}Cl_3N_3$ calcd 559.1349, found 559.1343.

cis-Diastereomer (minor): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74-1.77 (m, 1H), 1.85 (s, 3H), 2.14-2.16 (m, 1H), 2.24-2.30 (m, 1H), 2.41-2.44 (m, 1H), 3.85 (s, 3H), 4.11 (s, 3H), 4.14 (s, 3H), 4.50 (m, 1H), 6.55 (s, 1H), 6.68-6.73 (m, 2H), 6.86 (s, 1H), 7.00-7.04 (m, 4H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 27.41, 28.06, 30.32, 33.05, 35.96, 36.51, 37.09, 37.17, 116.83, 117.33, 117.37, 117.77, 118.02, 118.54, 119.12, 119.57, 119.63, 120.29, 122.35, 123.07, 123.18, 123.85, 124.01, 128.92, 129.67, 129.97, 130.08, 131.16, 132.99, 133.13, 133.48, 137.96; IR (KBr, neat, cm^{-1}) 3066, 2931, 2847, 1652, 1558, 1488, 1456, 1362, 1209, 1101, 779, 733; EIMS *m/z* 559 (M^+); HRMS (EI) for $C_{32}H_{28}Cl_3N_3$ calcd 559.1349, found 559.1343.

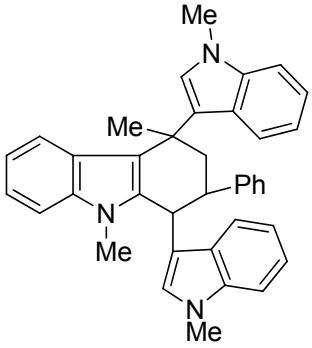
9-Allyl-1,4-bis(1-allyl-7-bromo-1*H*-indol-3-yl)-8-bromo-2,3,4,9-tetrahydro-4-methyl-1*H*-carbazole (3g)



trans-Diastereomer **(**major**)**: Yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 1.83-1.99 (m, 3H), 2.16 (s, 3H), 2.27-2.30 (m, 1H), 4.34-4.39 (m, 2H), 4.49 (d, *J* = 17 Hz, 1H), 4.67-4.83 (m, 2H), 4.87-4.96 (m, 1H), 5.01-5.16 (m, 6H), 5.45-5.50 (m, 1H), 5.90-6.07 (m, 3H), 6.32 (s, 1H), 6.51 (s, 1H), 6.78-6.88 (m, 2H), 6.97 (t, *J* = 13.7 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.1 Hz, 2H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.35, 29.32, 29.82, 35.12, 36.32, 46.05, 50.06, 50.16, 103.70, 104.06, 104.15, 114.64, 115.88, 116.15, 117.48, 118.18, 119.80, 119.97, 120.52, 120.61, 126.68, 126.81, 127.44, 129.53, 129.81, 129.98, 130.21, 131.05, 133.26, 133.33, 133.79, 135.25, 135.34, 136.02, 138.77; IR (KBr, neat, cm^{-1}) 3055, 2936, 2852, 2358, 1655, 1552, 1485, 1452, 1205, 985, 915, 775, 738; EIMS *m/z* 769 (M^+); HRMS (EI) for $C_{38}H_{34}Br_3N_3$ calcd 769.0303, found 769.0325.

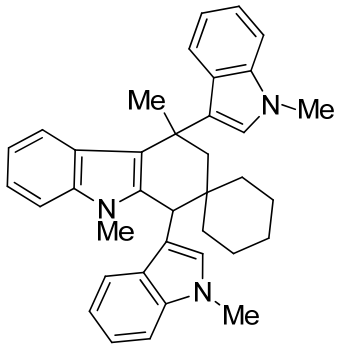
Only *trans*-diastereomer was obtained as a pure product by chromatography. *cis*-Diastereomer contains inseparable *trans*-diastereomer.

4,9-Dimethyl-1,4-bis(1-methyl-1*H*-indol-3-yl)-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazole (3h)



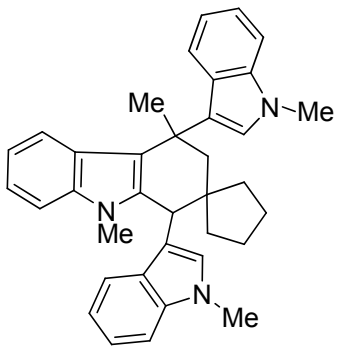
The inseparable mixture of two diastereomers: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12-2.17 (m, 5H), 2.49 (t, *J* = 12.8 Hz, 1H), 2.93-2.98 (m, 1.5H), 3.09 (t, *J* = 10.4 Hz, 1H), 3.22 (s, 3H), 3.24 (s, 1.3H), 3.56 (s, 3.6H), 3.64 (s, 1.8H), 3.66 (s, 1H), 4.46 (d, *J* = 10.0 Hz, 1H), 4.62 (brs, 0.42H), 6.29 (s, 1H), 6.32 (brs, 0.42H), 6.74-6.77 (m, 2.8H), 6.78-6.85 (m, 4.4H), 6.93-6.95 (m, 1.3H), 6.98-7.05 (m, 2H), 7.06-7.12 (m, 7.2H), 7.13-7.20 (m, 5.8H), 7.24-7.28 (m, 4H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.72, 30.11, 30.63, 32.55, 32.58, 35.98, 37.74, 40.64, 46.44, 46.99, 47.11, 108.53, 108.89, 108.95, 108.97, 109.29, 118.11, 118.26, 118.40, 118.52, 118.95, 119.64, 120.27, 120.47, 120.75, 120.88, 121.15, 121.23, 121.26, 121.31, 122.34, 125.66, 125.80, 125.94, 126.12, 126.54, 126.74, 127.42, 127.63, 127.78, 128.05, 128.09, 129.31, 136.91, 137.73, 137.76, 137.91, 138.17, 145.46; IR (KBr, neat, cm^{-1}) 3457, 2926, 1715, 1640, 1552, 1458, 1321, 1102, 739; EIMS *m/z* 533 (M^+); HRMS (EI) for $C_{38}H_{35}N_3$, calcd 533.2831, found 533.2825.

4,9-Dimethyl-1,4-bis(1-methyl-1*H*-indol-3-yl)-1,3,4,9-tetrahydrospiro[carbazole-2,1'-cyclohexane] (**3i**)



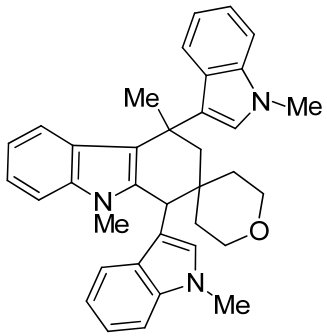
cis-Diastereomer (major): Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.47 (m, 4H), 1.52-1.73 (m, 6H), 2.00-2.16 (m, 4H), 2.74 (d, *J* = 14.8 Hz, 1H) 3.42 (s, 6H), 3.67 (s, 3H), 4.17 (s, 1H), 6.40 (s, 1H), 6.63 (s, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 7.10-7.21 (m, 7H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.09, 22.59, 26.64, 28.31, 29.05, 29.68, 32.47, 32.68, 36.13, 37.15, 37.31, 39.00, 42.96, 108.58, 109.19, 109.34, 113.02, 113.95, 118.14, 118.20, 118.77, 118.83, 119.99, 121.06, 121.14, 121.67, 121.97, 125.89, 126.35, 126.83, 127.85, 128.63, 129.22, 136.45, 137.57, 138.10, 139.89; IR (KBr, neat, cm^{-1}) 3046, 2925, 2865, 1699, 1610, 1538, 1470, 1369, 1260, 1008, 806, 738, 702; EIMS *m/z* 525 (M^+); HRMS (EI) for $C_{37}H_{39}N_3$ calcd 525.3144, found 525.3139.

4,9-Dimethyl-1,4-bis(1-methyl-1*H*-indol-3-yl)-1,3,4,9-tetrahydrospiro[carbazole-2,1'-cyclopentane] (**3j**)



cis-Diastereomer (major): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45-1.67 (m, 3H), 1.75-1.84 (m, 2H), 1.87-1.94 (m, 3H), 2.10 (s, 3H), 2.26 (d, *J* = 14.4 Hz, 1H), 2.57 (d, *J* = 14.2 Hz, 1H), 3.40 (s, 3H), 3.46 (s, 3H), 3.72 (s, 3H), 4.21 (s, 1H), 6.45 (s, 1H), 6.67 (s, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 7.06-7.15 (m, 3H), 7.18-7.25 (m, 4H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.39, 25.16, 28.90, 29.24, 32.67, 32.86, 36.60, 37.52, 37.67, 39.12, 48.66, 48.78, 108.73, 109.40, 109.47, 115.17, 118.26, 118.31, 118.41, 119.07, 120.28, 121.20, 121.39, 121.89, 122.03, 126.06, 126.45, 126.51, 128.88, 129.22, 136.52, 137.71, 138.17, 140.10; IR (KBr, neat, cm^{-1}) 3047, 2923, 2866, 1697, 1612, 1539, 1471, 1371, 1261, 1010, 808, 739, 701; EIMS *m/z* 511 (M^+); HRMS (EI) for $C_{36}H_{37}N_3$ calcd 511.2987, found 511.2968.

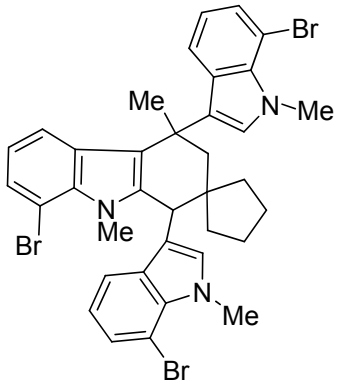
4,9-Dimethyl-1,4-bis(1-methyl-1*H*-indol-3-yl)-1,2',3,3',4,5',6',9-octahydrospiro[carbazole-2,4'-pyran] (3k)



cis-Diastereomer (major)**:** Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56-1.69 (m, 3H), 2.02 (t, *J* = 13.5 Hz, 2H), 2.12 (s, 3H), 2.55 (t, *J* = 10.7 Hz, 1H), 3.04-3.07 (m, 1H), 3.22 (d, *J* = 14.2 Hz, 1H), 3.32 (s, 3H), 3.42 (t, *J* = 11.9 Hz, 1H), 3.52-3.57 (m, 4H), 3.67 (s, 3H), 4.14 (s, 1H), 6.41 (s, 1H), 6.43 (s, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 7.10-7.32 (m, 8H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.09, 29.69, 32.33, 32.53, 32.82, 35.64, 36.15, 37.08, 37.40, 42.03, 63.89, 63.94, 108.73, 109.36, 109.54, 115.10, 118.32, 118.60, 119.13, 120.38, 120.66, 120.95, 121.35, 121.55, 122.06, 123.18, 126.09, 128.33, 129.05, 130.06, 132.17, 133.15, 134.56, 136.79,

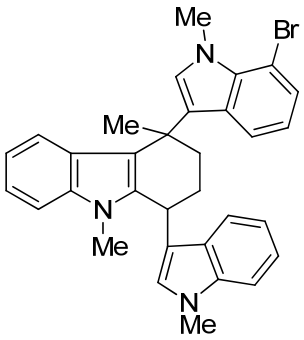
137.76, 137.98; IR (KBr, neat, cm^{-1}) 3046, 2928, 2867, 1695, 1610, 1534, 1459, 1365, 1262, 1010, 739, 702; EIMS *m/z* 527 (M^+); HRMS (EI) for $C_{36}H_{337}N_3O$, calcd 527.2937, found 527.2932.

8-Bromo-4,9-dimethyl-1,4-bis(7-bromo-1-methyl-1*H*-indol-3-yl)-1,3,4,9-tetrahydrospiro[carbazole-2,1'-cyclopentane] (**3l**)



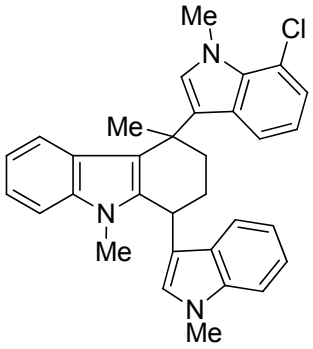
cis-Diastereomer (major): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23-1.38 (m, 3H), 1.68-1.72 (m, 2H), 1.79-1.89 (m, 3H), 2.03 (s, 3H), 2.16 (d, *J* = 13.8 Hz, 1H), 2.57 (d, *J* = 14.2 Hz, 1H), 3.70 (s, 3H), 3.79 (s, 3H), 4.08 (s, 3H), 4.15 (s, 1H), 6.40 (s, 1H), 6.59 (s, 1H), 6.77 (t, *J* = 7.8 Hz, 1H), 6.85 (t, *J* = 7.8 Hz, 2H), 6.95 (t, *J* = 7.8 Hz, 1H), 7.31-7.34 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.12, 24.98, 28.37, 32.00, 36.09, 36.68, 36.88, 37.30, 37.42, 38.88, 48.53, 48.68, 103.43, 104.13, 114.52, 117.42, 119.36, 119.44, 120.32, 120.37, 120.85, 121.04, 124.85, 126.07, 126.11, 126.33, 126.54, 129.08, 129.28, 129.32, 131.52, 131.95, 132.15, 133.85, 134.20, 141.31; IR (KBr, neat, cm^{-1}) 3051, 2938, 2852, 2321, 1595, 1556, 1482, 1211, 1092, 775, 736; EIMS *m/z* 745 (M^+); HRMS (EI) for $C_{36}H_{34}Br_3N_3$ calcd 745.0303, found 745.0285.

4-(7-Bromo-1-methyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-4,9-dimethyl-1-(1-methyl-1*H*-indol-3-yl)-1*H*-carbazole (3m)



The inseparable mixture of two diastereomers: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91-1.99 (m, 4H), 2.08 (s, 3H), 2.16-2.19 (m, 0.3H), 2.26-2.35 (m, 1.7H), 3.47 (s, 3H), 3.48 (s, 1H), 3.68 (s, 4H), 3.95 (s, 3H), 4.12 (s, 1H), 4.54-4.55 (m, 1H), 4.56-4.57 (m, 0.3H), 6.28 (s, 1H), 6.43 (s, 1H), 6.59 (s, 0.3H), 6.67 (t, *J* = 7.8 Hz, 0.3H), 6.84-6.91 (m, 1.3H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.14-7.35 (m, 9H), 7.45 (d, *J* = 7.2 Hz, 0.2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.35, 28.09, 29.43, 29.59, 29.70, 29.90, 30.11, 30.73, 32.68, 34.48, 35.72, 36.07, 36.43, 36.69, 36.77, 108.57, 108.73, 109.39, 112.24, 112.69, 116.98, 117.21, 117.40, 118.36, 118.43, 118.75, 118.83, 118.92, 119.34, 120.43, 120.54, 120.66, 121.18, 121.66, 122.13, 122.38, 123.66, 125.92, 126.28, 126.64, 127.81, 128.04, 129.14, 129.58, 130.13, 132.22, 134.28, 136.77, 137.15, 137.36; IR (KBr, neat, cm^{-1}) 3052, 2930, 2851, 1629, 1557, 1482, 1459, 1211, 1092, 736; EIMS *m/z* 536 (M^+); HRMS (EI) for $C_{33}H_{30}BrN_3$, calcd 535.1623, found 535.1619.

4-(7-Chloro-1-methyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-4,9-dimethyl-1-(1-methyl-1*H*-indol-3-yl)-1*H*-carbazole (3n)



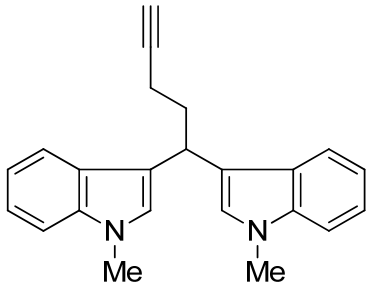
trans-Diastereomer (major): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90-1.98 (m, 3H), 2.07 (s, 3H), 2.29-2.31 (m, 1H), 3.46 (s, 3H), 3.67 (s, 3H), 3.93 (s, 3H), 4.52-4.53 (m, 1H), 6.26 (s, 1H), 6.41 (s, 1H), 6.91 (t, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 7.08-7.14 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.13-7.27 (m, 1H), 7.31-7.34 (m, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.60-7.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.50, 29.55, 29.59, 30.05, 32.82, 34.66, 36.58, 36.69, 108.87, 109.55, 117.14, 117.16, 117.51, 118.57, 118.89, 119.07, 119.09, 120.01, 120.56, 121.32, 121.51, 121.81, 122.53, 125.78, 126.78, 126.91, 128.19, 130.02, 132.08, 133.50, 137.30, 137.51; IR (KBr, neat, cm^{-1}) 3055, 2931, 2850, 1632, 1553, 1480, 1458, 1210, 1091, 736; EIMS *m/z* 491 (M^+); HRMS (EI) for $C_{33}H_{30}ClN_3$, calcd 491.2128, found 491.2126.

Only *trans*-diastereomer was obtained as a pure product by chromatography. *cis*-Diastereomer contains inseparable *trans*-diastereomer.

General procedure for the synthesis of 4a

To a mixture of acetylenic aldehyde **1a** (205 mg, 2.5 mmol) and *N*-methyl indole **2a** (820 mg, 6.25 mmol) in $CHCl_3$ (10 mL) was added 10 mol% of BF_3·OEt (0.25 mmol). The reaction mixture was stirred at room temperature for 6 h and was concentrated and loaded directly onto a silica gel column; elution with ethyl acetate/hexane (50:1) afforded the product **4a** (610 mg) as a white solid in 75% yield.

1-Methyl-3-(1-(1-methyl-1*H*-indol-3-yl)pent-4-ynyl)-1*H*-indole (4a)

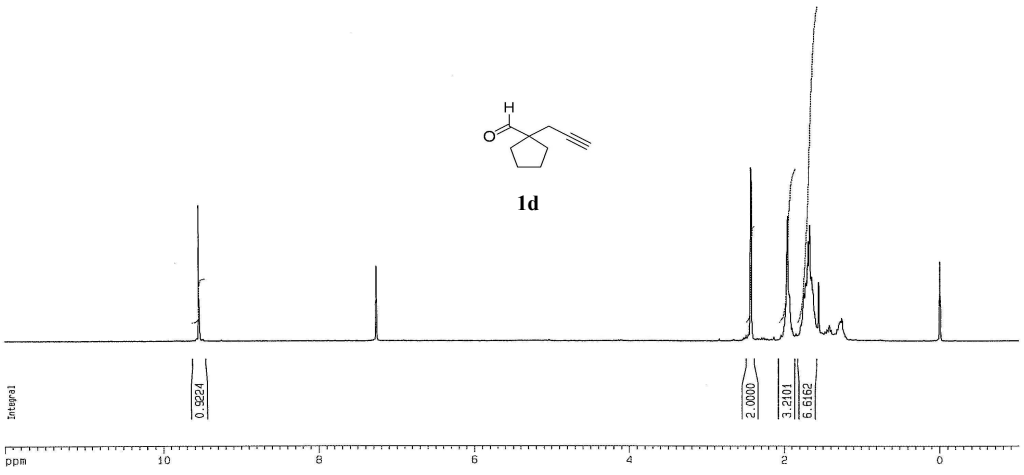


^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97-2.01 (m, 1H), 2.22-2.30 (m, 2H), 2.39-2.46 (m, 2H), 3.71 (s, 6H), 4.65 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 2H), 7.04 (t, *J* = 6.8 Hz, 2H), 7.16 (t, *J* = 8.2 Hz, 2H), 7.21-7.38 (m, 2H), 7.62 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.78, 33.16, 33.37, 35.34, 69.07, 85.32, 109.64, 118.45, 119.06, 120.26, 121.90, 126.87, 127.91, 137.82; IR (KBr, neat, cm^{-1}) 3441, 1643, 1471, 741; EIMS *m/z* 326 (M^+); HRMS (EI) for $C_{23}H_{22}N_2$, calcd 326.1783, found 326.1781.

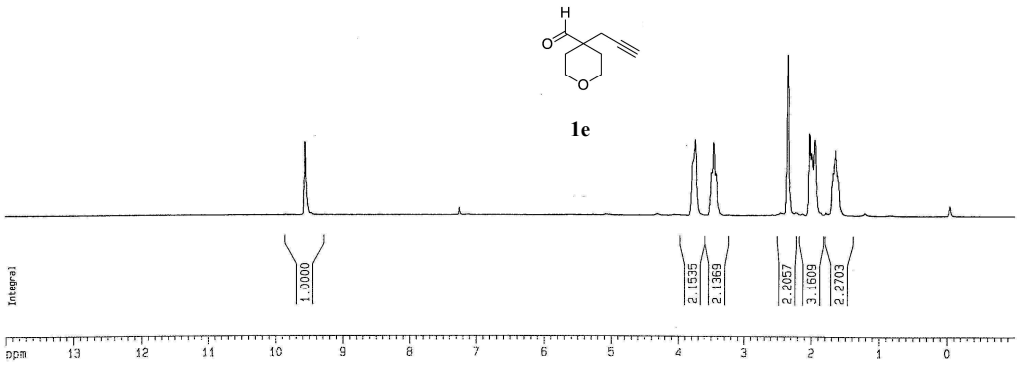
Reference:

1. Y. Chen and C. Lee, *J. Am. Chem. Soc.,* **2006**, *128*, 15598.

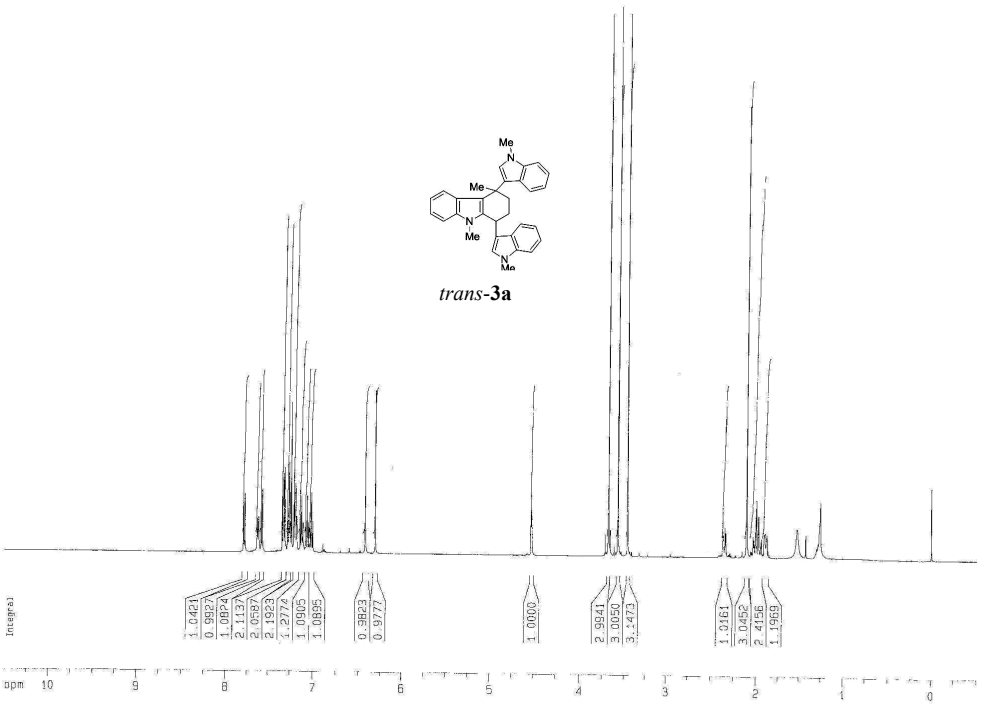
^{1}H NMR Spectrum



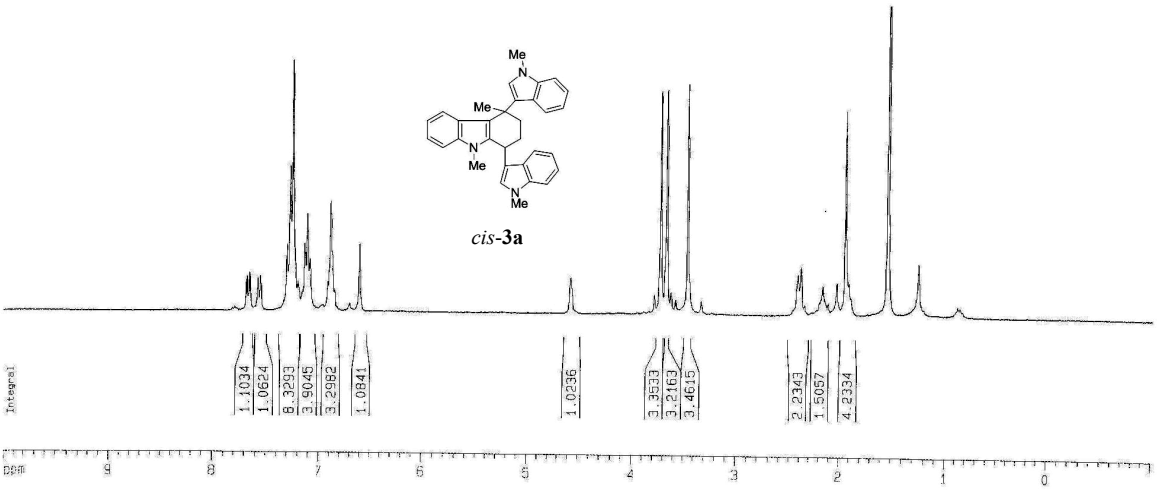
1d



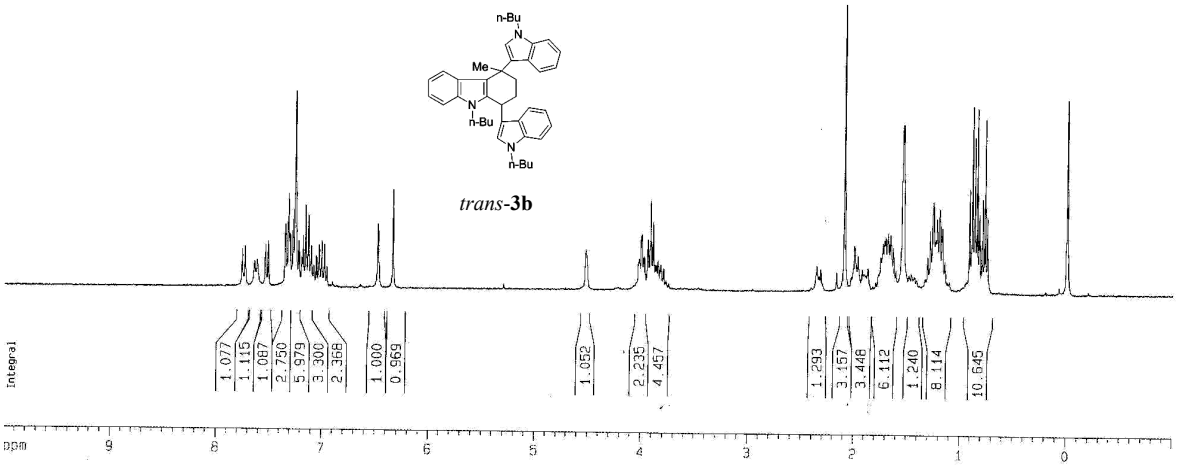
1e



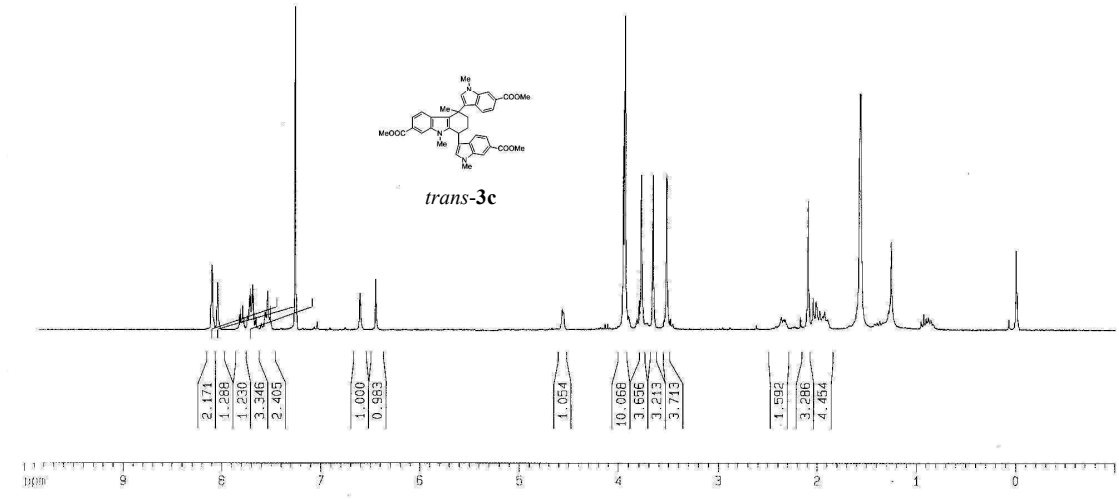
trans-**3a**



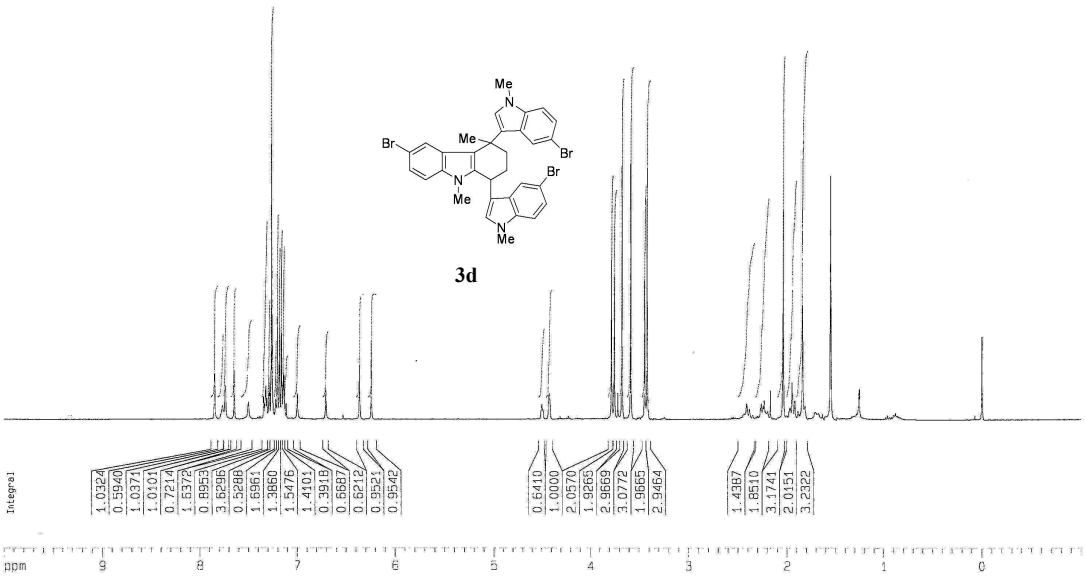
cis-**3a**



trans-**3b**



trans-**3c**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Br
N
Me
Br
N
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3.8236
0.5268
1.6961
1.3860
1.5476
1.4101
0.3918
0.6687
0.6212
0.9521
0.9542
0.6410
1.0000
2.0570
1.9265
2.9669
3.0772
1.9665
2.9464
1.4367
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3.2322
ppm
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6
5
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2
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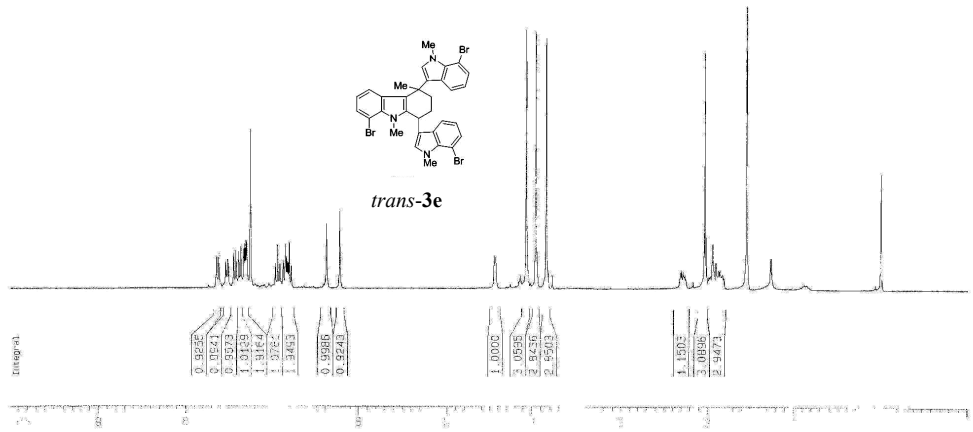
3d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Br
N
Me
Br
N
Me
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1.3453
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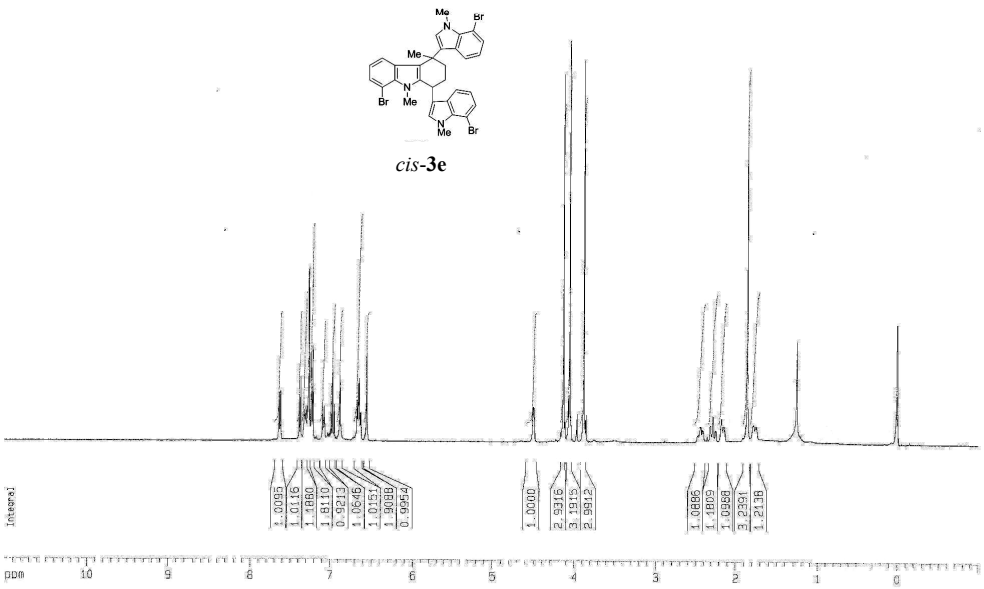
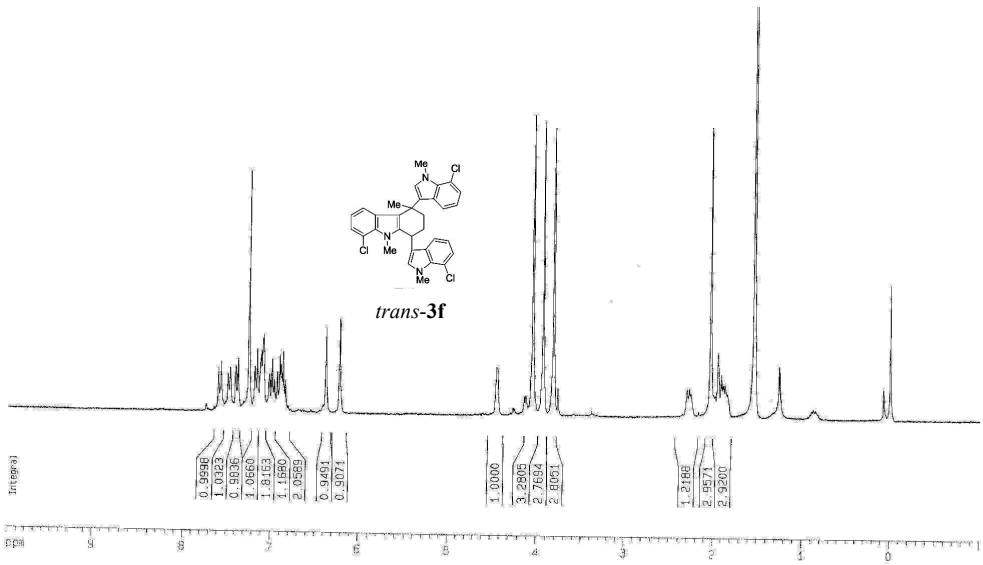
1.0000
3.0595
2.8436
2.9503
1.1502
3.0896
2.9473

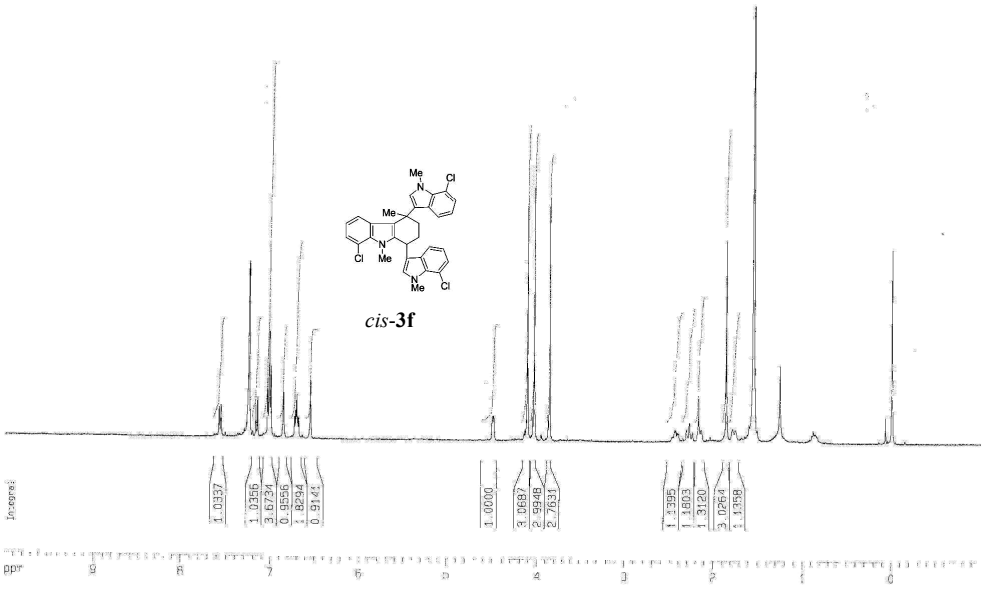
trans-**3e**



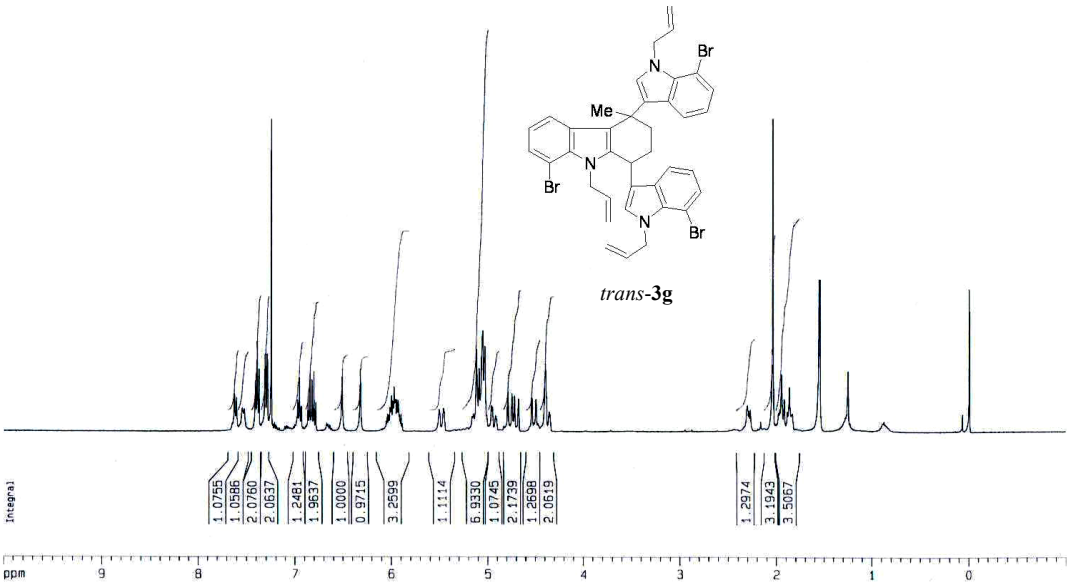
cis-**3e**



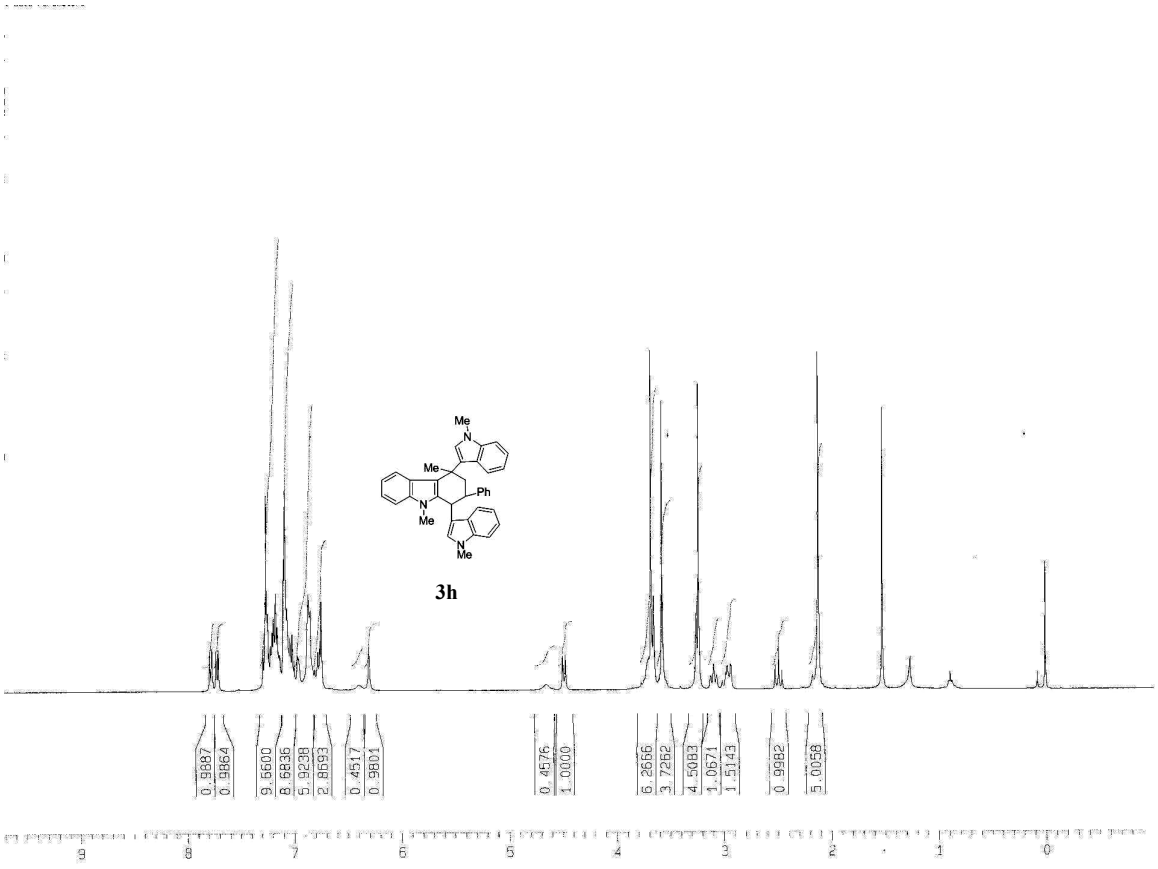
trans-**3f**



cis-**3f**



trans-**3g**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Ph
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0.9801
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3.7262
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1.0671
1.5143
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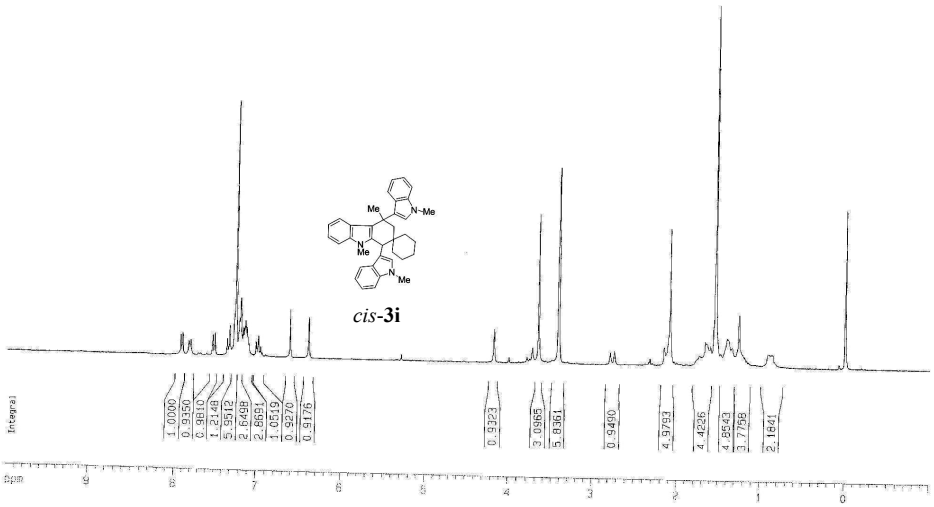
5.0058

3h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0.9270
0.9176
0.9323
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0.9490
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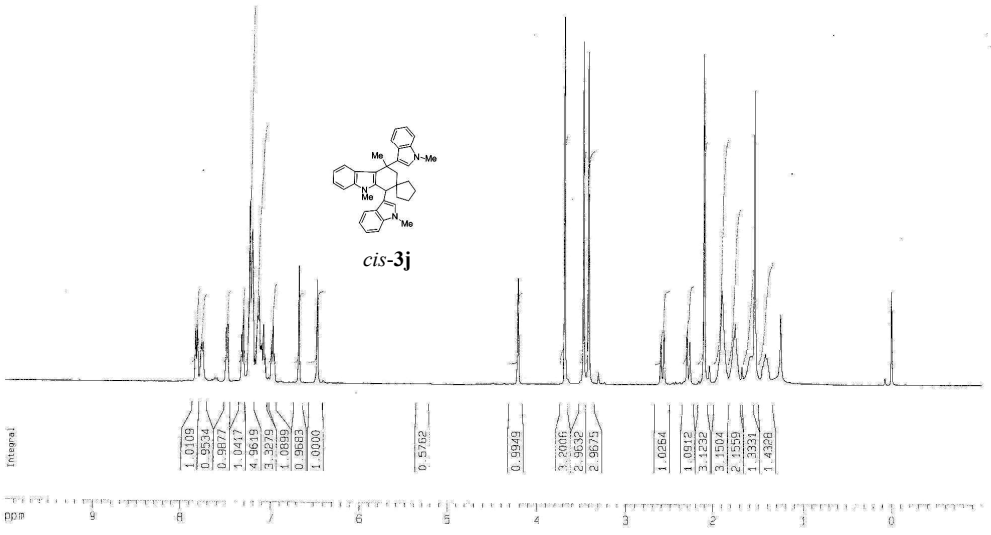
4.8643
3.7758
2.1841

cis-**3i**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N
Me
N
Me
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0.9683
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0.5762
0.9949
3.2006
2.9632
2.9675
1.0264
1.0912
3.1232
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4
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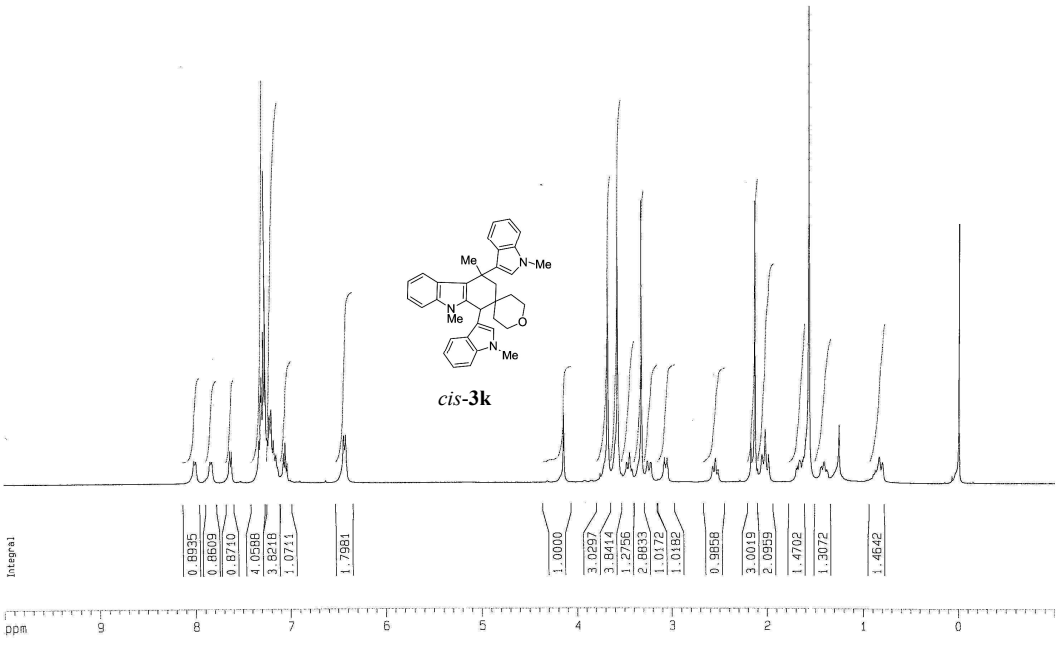
1
0

cis-**3j**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Me
O
N
Me
Integral
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1.7981
1.0000
3.0297
3.8414
1.2756
2.8833
1.0172
1.0182
0.9858
3.0019
2.0959
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1.4642
ppm
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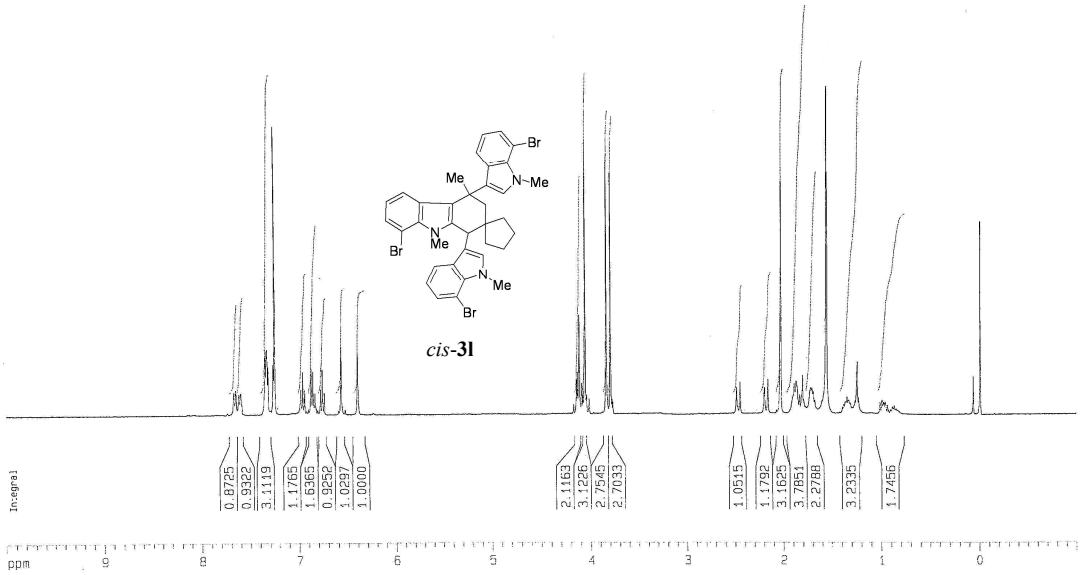
8
7
6
5
4
3
2
1
0

cis-**3k**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Me
N
Me
Br
N
Me
Br
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0.9252
1.0297
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3.1226
2.7545
2.7033
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3.1625
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ppm
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5
4
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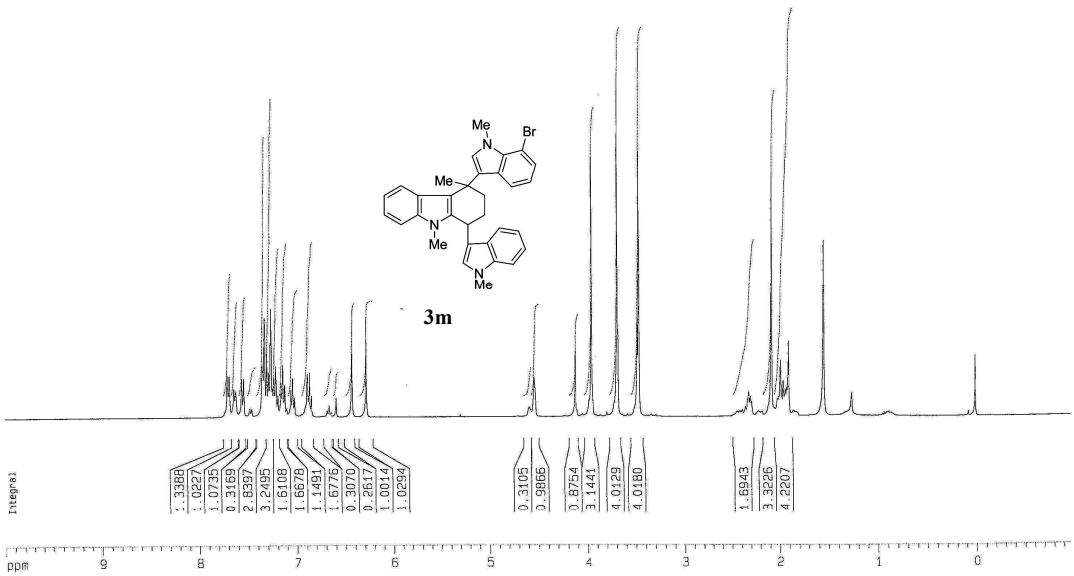
2
1
0

cis-**3l**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0.3105
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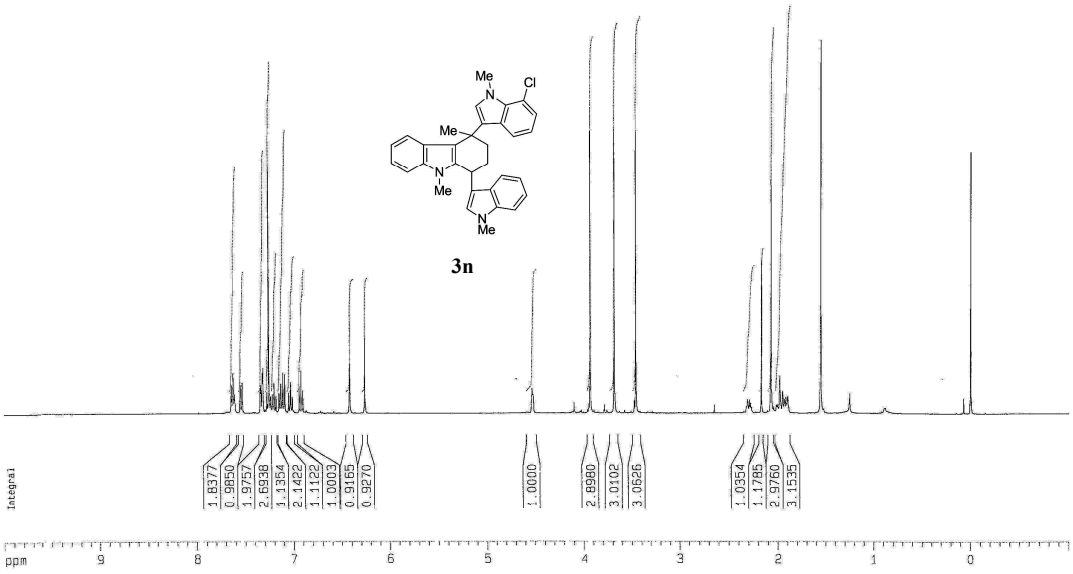
6
5
4
3
2
1
0

3m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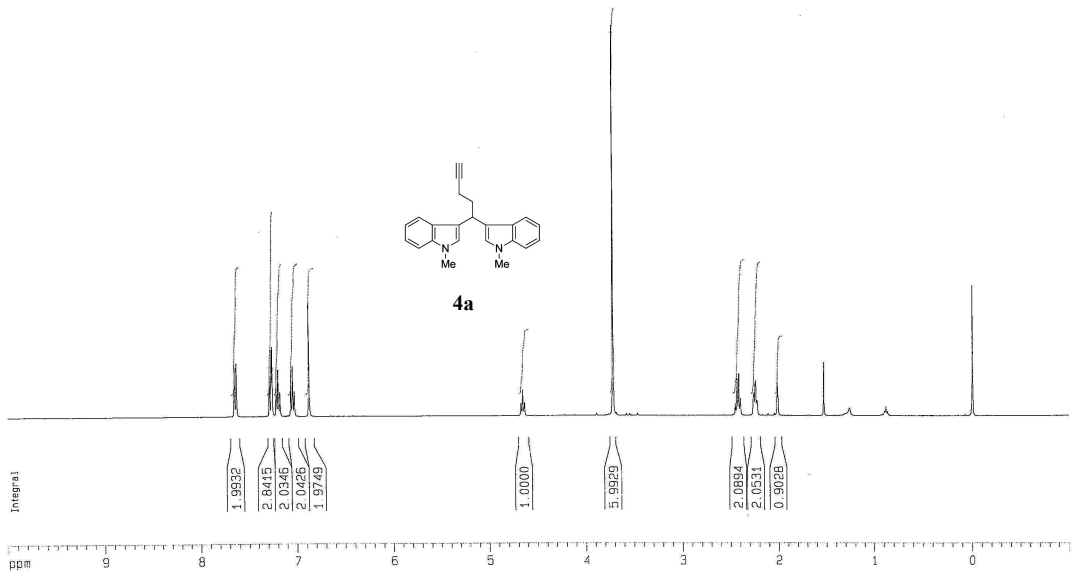
3n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Me
Integral
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5.9929
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2.0531
0.9028
ppm
9
8
7
6
5
4
3
2
1
0

4a