銀触媒の特性を活用した、
非典型的脱芳香族化反応の開発

2021 年

本間　榛花

目次

略語表

便宜上、本論文全般において以下に示す略語、および略称を用いた。

Ac	acetyl
aq.	aqueous
Ar	aryl
p-ABSA	4-acetamidobenzenesulfonyl azide
BINAP	2,2’-bis(diphenylphosphino)-1,1’-binaphthyl
Bn	benzyl
BTEA	benzyltriethylammonium
^{t}Bu	tertiary butyl
Bz	benzoyl
calcd	calculated
cat.	catalyst
CP	compound
dba	dibenzylideneacetone
DDQ	2,3-dichloro-5,6-dicyano-*p*-benzoquinone
DFT	density functional theory
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
dr	diastereomeric ratio
ee	enantiomeric excess
eq.	equation
equiv.	equivalent
h	hour(s)
HDAC	histone deacetylase
HFIP	hexafluoroisopropanol
HOMO	highest occupied molecular orbital
HRMS	high resolution mass spectrometry
IC_{50}	half maximal inhibitory concentration
ICT	intramolecular charge-transfer
INT	intermediate
IR	infrared
J	coupling constant (in NMR)
Ki	inhibitory constant

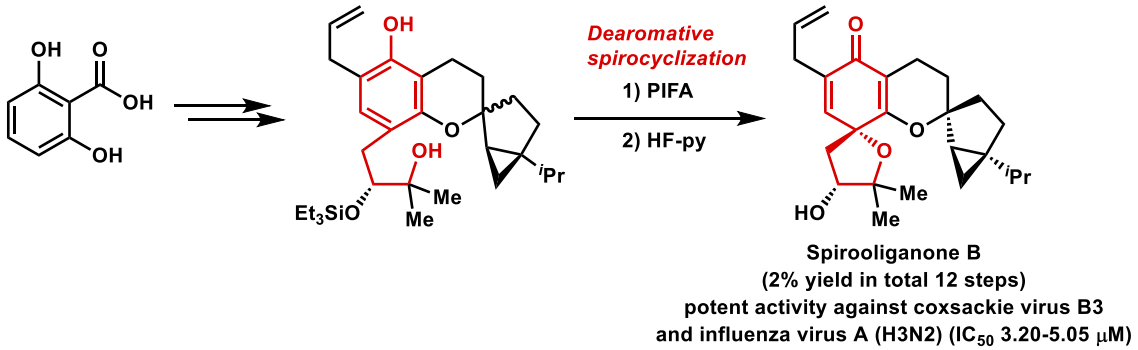
LUMO	lowest unoccupied molecular orbital
M	mol/L
Me	methyl
m.p.	melting point
MS	molecular sieve
n	normal
N	normality
NBS	*N*-bromosuccinimide
NMR	nuclear magnetic resonance
NOESY	nuclear Overhauser effect and exchange spectroscopy
Ph	phenyl
PIFA	bis(trifluoroacetoxy)iodo)benzene
PMB	*para*-methoxybenzyl
^{i}Pr	isopropyl
PRO	product
py	pyridine
quant.	quantitative yield
R_f	rate of flow
rt	room temperature
TBA	tetrabutylammonium
TBS	*tert*-butyldimethylsilyl
TEA	triethylamine
temp.	temperature
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIPS	triisopropylsilyl
tol	tolyl
TRIP	3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate
Ts	tosyl
TS	transition state
UV	ultraviolet

第 1 部　研究背景

第 1 章　脱芳香族的スピロ環化反応

脱芳香族化反応[1]は、入手容易な平面構造を有する芳香族化合物から立体構造を持つ化合物を合成可能な反応であり、多くの研究グループから注目を集めている。You ら、Luan ら、Johnson ら、そして当研究室は、フェノール[2]やナフトール[3,4]、インドール[5]など様々な芳香族化合物の脱芳香族化反応を開発してきた。[6] その中でも、様々な生物活性物質や既知医薬分子に含まれるスピロ骨格を合成可能な脱芳香族的スピロ環化反応は、創薬研究において有用な手法である。2014 年の Tong らによる、抗インフルエンザウイルス活性を有する Spirooliganone B[7]の全合成研究では、合成の終盤に当該反応を適用しスピロシクロヘキサジエノン骨格を構築した（Scheme 1）。[8]

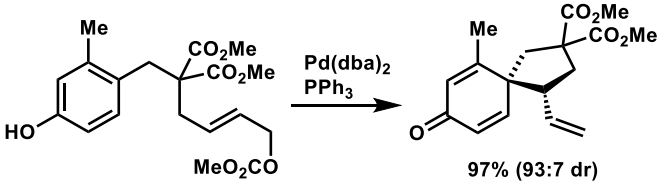
Scheme 1



Spirooliganone B
(2% yield in total 12 steps)
potent activity against coxsackie virus B3
and influenza virus A (H3N2) (IC_{50} 3.20-5.05 μM)

先述のように、当研究室では脱芳香族的スピロ環化反応の開発研究に取り組んできた。[9] 2010 年にパラジウム触媒を用いた *ipso*-Friedel-Crafts アルキル化反応による、フェノール類の脱芳香族的スピロ環化反応を開発した（Scheme 2）。[9a]

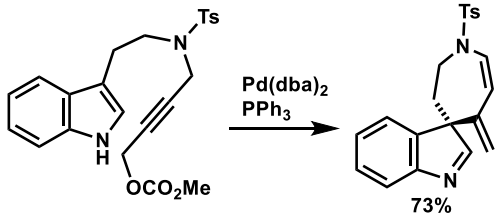
Scheme 2



97% (93:7 dr)

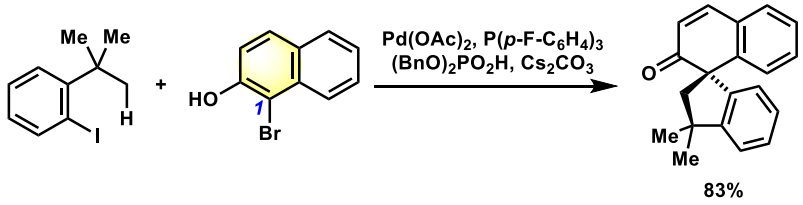
さらに、同様の触媒系をインドール類の脱芳香族的スピロ環化反応へと応用した（Scheme 3）。[9e]

Scheme 3



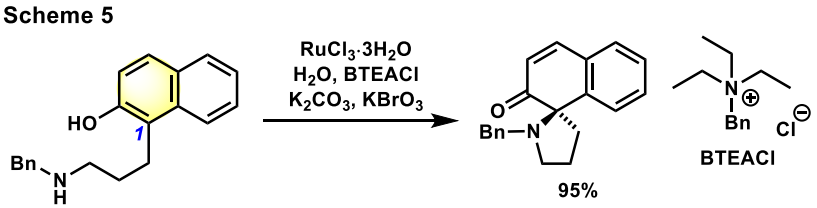
近年、平面化合物から一挙に縮環型スピロ環化合物を合成可能なことから、β−ナフトール類の脱芳香族的スピロ環化反応が注目を集めている。[4b,q,10,11,12] 2019 年に Luan らはパラジウム触媒を用いたカップリング反応による、β−ナフトールの脱芳香族的スピロ環化反応を開発した（Scheme 4）。[4q]

Scheme 4



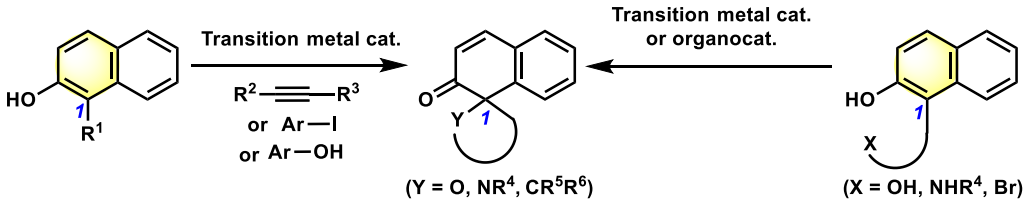
同時期に Sarkar らはルテニウム触媒を用いたアミノ化反応により、ヘテロ原子を含むスピロ環骨格を合成した（Scheme 5）。[10a]

Scheme 5



既知のβ−ナフトール類の脱芳香族的スピロ環化反応の反応形式は、分子内および分子間反応のいずれも、遷移金属触媒 [7] や有機分子触媒 [8] を用いたカップリング反応 [4g,j,n,o,q]、アミノ化反応、エーテル化反応、ラクトン化反応が主流である。水素添加による還元反応[13]を除けば、既知反応はいずれもフェノール環を脱芳香族化しており、反応点は C1 位に限られる（Scheme 6）。

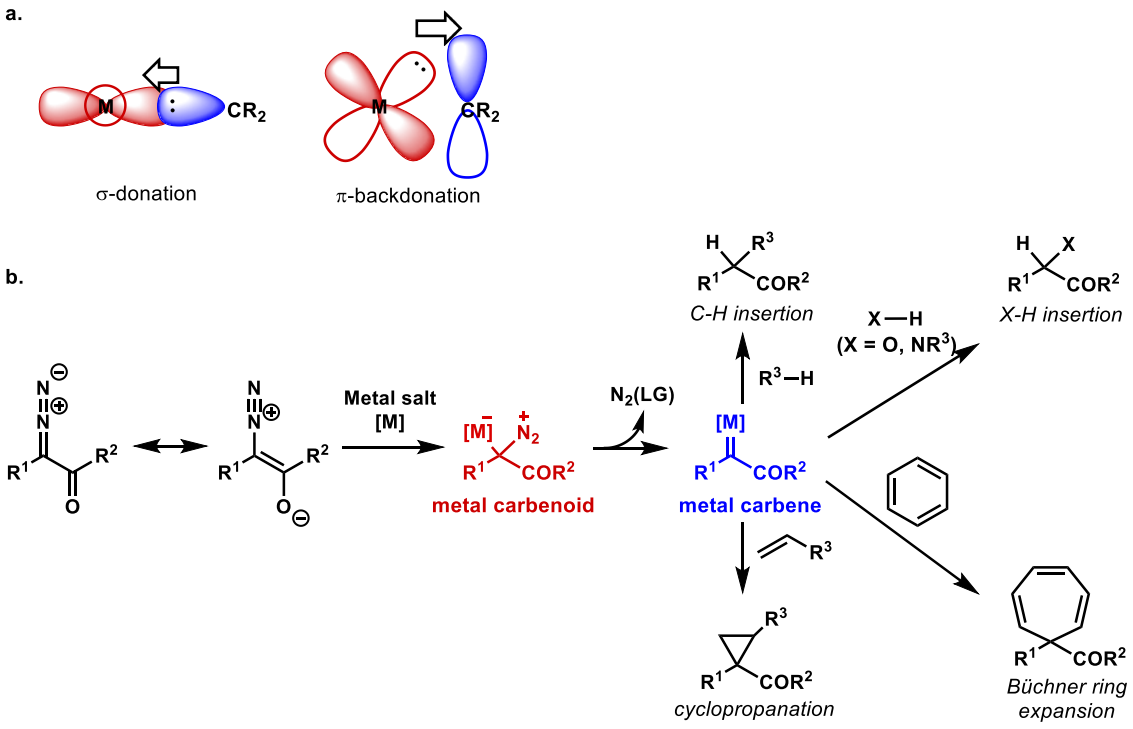
Scheme 6


Transition metal cat.
R2—≡—R3
or Ar—I
or Ar—OH
Transition metal cat.
or organocat.
HO
1
R1
O
Y
1
(Y = O, NR4, CR5R6)
HO
1
X
(X = OH, NHR4, Br)

第 2 章　金属カルベン反応

当研究室では、前章で述べた遷移金属触媒を用いた脱芳香族的スピロ環化反応の開発に加えて、金属カルベン反応[14]の開発にも取り組んできた。カルベンは電荷を持たない中性の化学種であり、オクテット則を満たさないことから高活性種として知られる。カルベン発生法の一つにジアゾ化合物を用いた手法が知られており、金属を用いて窒素脱離を促進した場合、金属カルベン錯体が生成する。金属カルベン錯体は、カルベン炭素から金属原子の d 軌道への σ 供与と金属原子からカルベン炭素の p 軌道への π 逆供与により結合が形成された、カルベン等価体である（Figure 1a）。特に、化合物の安定性から、金属カルベン反応の基質としてジアゾカルボニル化合物が一般的に用いられる。多くの場合、“金属カルベン”と“金属カルベノイド”は同義で用いられてきたが、Pérez らはそれぞれを Figure 1b のように定義した。[15] すなわち、金属カルベンは前述のように金属とカルベン炭素が二重結合様の性質を示す化学種であり、金属カルベノイドは、金属原子と炭素原子が単結合を有しており、かつカルベノイド炭素が脱離基を有する化学種である。よって、本論文中においてもその定義に従って説明する。金属カルベンはその高い反応性故に、不活性な結合とも反応し得る。代表例として C－H 挿入反応や X－H 挿入反応、Büchner 環拡大反応、シクロプロパン化反応が挙げられる。

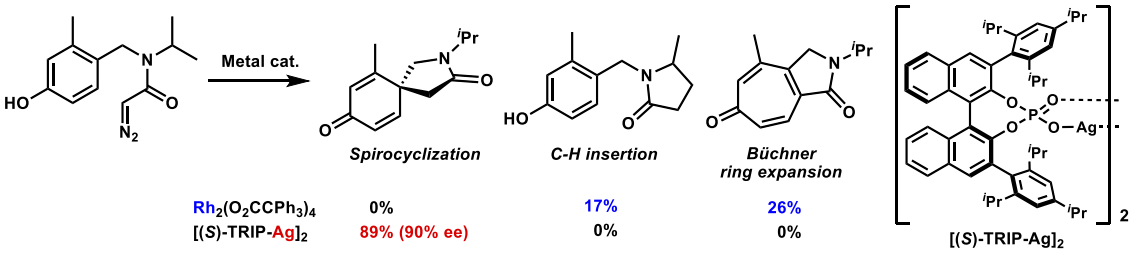
Figure 1



金属カルベン反応ではロジウム触媒が一般的に用いられるが、[16]当研究室では銀カルベン

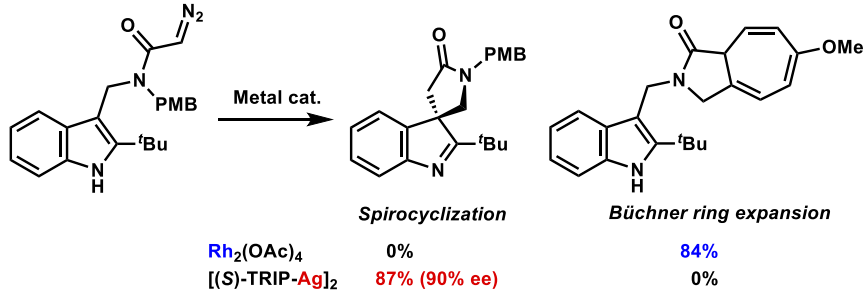
の特異な性質[17]に着目し研究を進めてきた。2017 年に銀触媒を用いた化学選択的なフェノール類の不斉脱芳香族的スピロ環化反応を開発した（Scheme 7）。[18] ロジウム触媒を用いると、C－H 挿入反応や Büchner 環拡大反応が進行するのに対し、銀触媒を用いるとスピロ環化反応が選択的に進行することを見出した。理論解析により、銀カルベンの方がロジウムカルベンに比べて求電子性であることが化学選択性の発現に寄与していると明らかになった。

Scheme 7



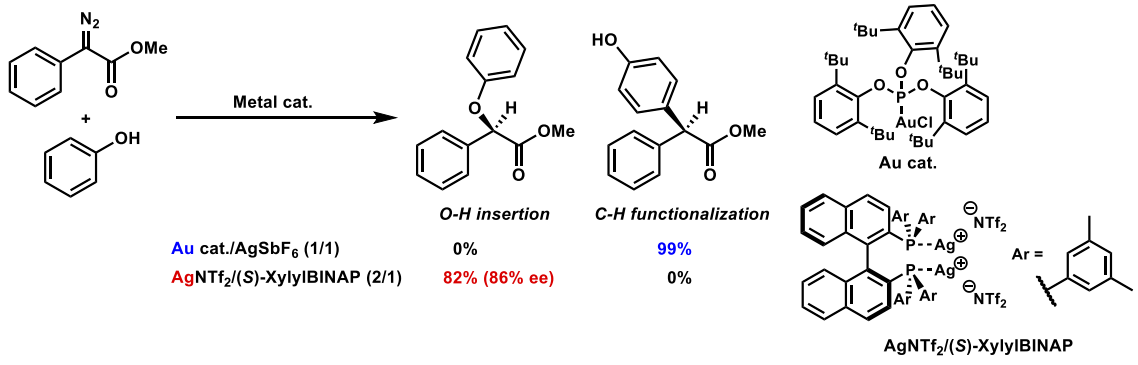
さらに、2020 年には銀触媒の特性をインドール類の不斉脱芳香族的スピロ環化反応へと応用した（Scheme 8）。[19]

Scheme 8



また、銀カルベンを用いた分子間反応にも挑戦し、エナンチオ選択的な分子間 O－H 挿入反応を開発した（Scheme 9）。[20] 本反応系では銀触媒を用いると金触媒[21]とは異なる化学選択性を示すことを見出し、不斉二核銀錯体を作用させることでエナンチオ選択性の発現に成功した。

Scheme 9

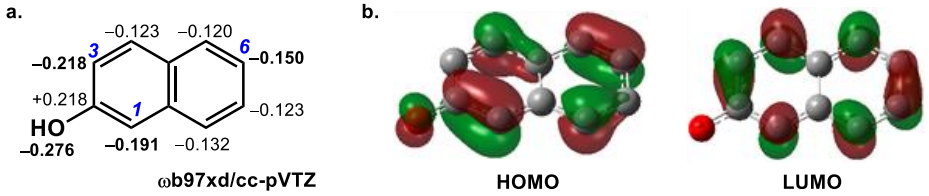


第 2 部　銀触媒の特性を活用したβ−ナフトール類の非典型的脱芳香族化反応の開発

第 1 章　研究背景

第 1 部で述べたように、当研究室では遷移金属触媒を用いて様々な反応形式の脱芳香族的スピロ環化反応を開発してきた。私は銀カルベンの特異な性質に最も興味を持ち、それをさらに他の芳香族化合物の脱芳香族的スピロ環化反応へと応用展開することを考えた。そこで、先述のように、効率的に縮環スピロ環化合物が合成可能であることから、β−ナフトール類に着目した。既知のβ−ナフトール類の脱芳香族的スピロ環化反応は C1 位での反応に限定されている。もし他の反応点からのスピロ環化反応が進行すれば、これまで合成困難であった縮環型化合物を直接的に合成可能である。私はβ−ナフトール類の隠れた反応性を調べるために、マリケン電子密度解析[22]を行った（Figure 2a）。電子密度解析の結果より、炭素原子の中では C1 位、C3 位ほどではないものの、C6 位に電子が比較的、局在化していると算出された。また、分子軌道の解析結果より、C6 位にも HOMO の軌道が広がっており、潜在的な求核性を有することが予測された（Figure 2b）。

Figure 2



予備計算データを踏まえて、今回私は、反応形式と反応部位において新規性の高い、脱芳香族化反応を考案した（Scheme 10）。基質 **1** を銀触媒と反応させることで、ナフトールの 6 位炭素がジアゾ基を有する炭素へ求核攻撃し、脱芳香族的スピロ環化反応が進行する。生じた中間体に対し求核剤を作用させることで、低反応性のベンゼノイド部位が脱芳香族化された **2** を得られると予想した。さらに、本反応の反応機構を計算化学により解析し、銀カルベンおよび銀カルベノイドに関する知見を得ることを目的とした。**2** が持つスピロ骨格は、ヒスタミン H_3 受容体アゴニスト[23]や HDAC6 阻害剤[24]、コネシン前駆体[25]に含まれることから、生成物の有用性も期待できる（Figure 3）。

Scheme 10

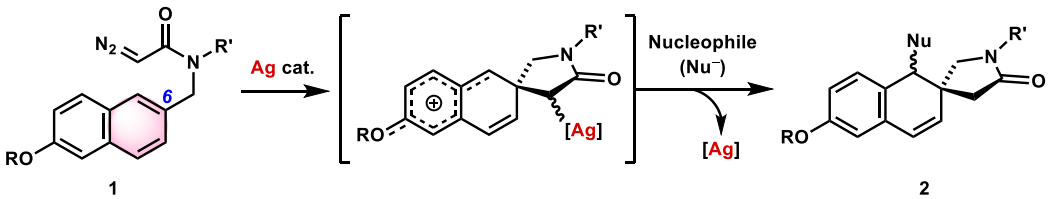
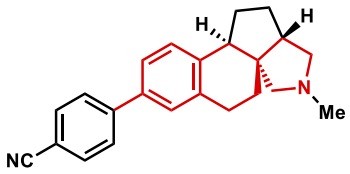
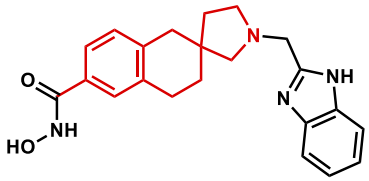


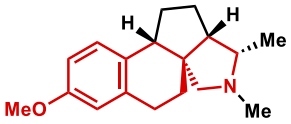
Figure 3



Histamine H_3 receptor agonist (human H_3 *Ki* 14.5 nM)



Histone deacetylase 6 (HDAC6) inhibitor (IC_{50} ≤0.1 μM)

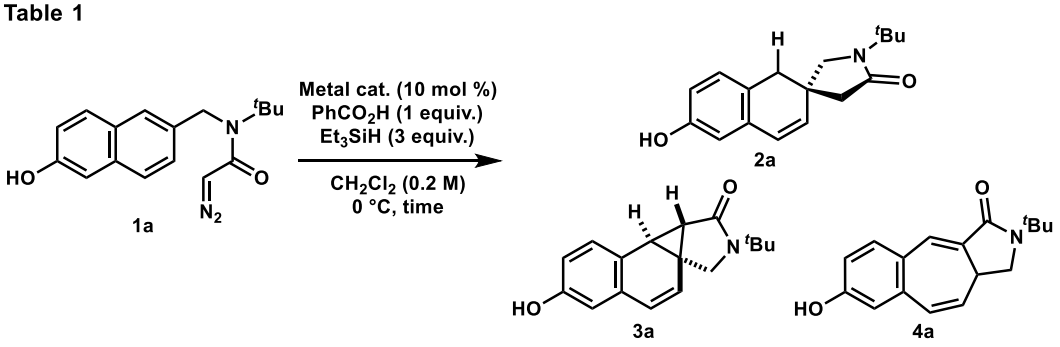


(+)-Conessine precursor

第 2 章　反応条件の最適化

まず初めに、求核剤としてトリエチルシラン存在下、**1a** の脱芳香族的スピロ環化反応の条件を最適化した（Table 1）。entry 1 から 4 では種々の金属塩を用いて脱芳香族化反応を検討した。ロジウム触媒存在下では、シクロプロパン化体 **3a** と七員環化合物 **4a** が生成した（entry 1）。金触媒では、所望のスピロ環化体 **2a** は一切得られず、銅触媒では **2a** が得られたものの化学選択性は低かった（entries 2 and 3）。一方で、銀触媒では予想通り高い化学選択性で **2a** が得られたため、続いて銀塩のカウンターアニオンを検討した（entry 4）。その結果、$AgNTf_2$ を用いた際に収率 80%で **2a** が得られた（entry 6）。さらなる検討にて、プロトン化剤である安息香酸および求核剤であるトリエチルシランは、高い化学選択性で反応が進行するために必須であることが判明した（entries 7 and 8）。ジアゾ化合物の重合化をはじめとした副反応を懸念しシリンジポンプを用いたところ、反応濃度を薄くすることで entry 6 と同等の結果が得られた。しかしながら、**1a** の溶解性の低さより、再現性に乏しかった（entry 10）。

Table 1



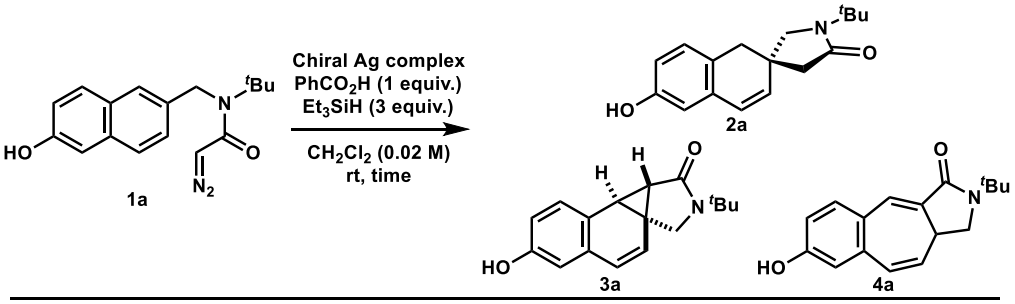
entry	Metal cat.	time (h)	2a (%)	3a (%)	4a (%)
1	$Rh_2(OAc)_4$	0.5	0	88	9
2[a]	$Ph_3PAuCl/AgSbF_6$ (1/1)	24	0	0	0
3[a]	CuOTf•1/2toluene	3	32	12	10
4	AgOTf	0.5	70	0	0
5	$AgClO_4$	0.5	55	0	0
6	$AgNTf_2$	0.5	80	0	0
7[b]	$AgNTf_2$	0.5	64	7	0
8[c]	$AgNTf_2$	1	0	0	0
9[d]	$AgNTf_2$	0.5	30	0	0
10[d,e]	$AgNTf_2$	0.5	63-80	0	0

[a] Run at rt. [b] without $PhCO_2H$. [c] without Et_3SiH.
[d] 1a was added *via* a syringe pump over 0.5 h. [e] CH_2Cl_2: 0.02 M.

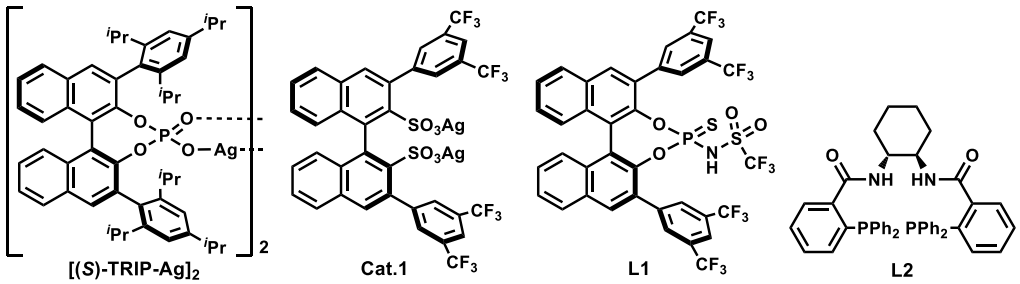
次に、不斉脱芳香族的スピロ環化反応を検討した（Table 2）。不斉配位子の溶解性を考慮し、反応濃度を 0.02 M に薄めた。フェノールやインドールの不斉脱芳香族的スピロ環化反応において最適であった$[(S)$-TRIP-Ag$]_2$ を用いたが、反応が複雑化し、**2a** が痕跡量得られる

のみであった（entry 1）。**Cat. 1** でも同様に脱芳香族化反応の進行は確認されなかった（entry 2）。炭酸銀と不斉配位子 **L1** を混合し、不斉銀錯体を用時調製し反応に用いたところ、**2a** は得られず、**3a** が 61%、**4a** が 28%得られた（entry 3）。$AgNTf_2$ と(*S*)-BINAP および **L2** から調製した不斉銀錯体をそれぞれ用いた際には、所望の **2a** が選択的に得られたもののエナンチオ選択性は発現しなかった（entries 4 to 6）。これらの検討結果より、本反応の不斉化は困難であると判断した。

Table 2



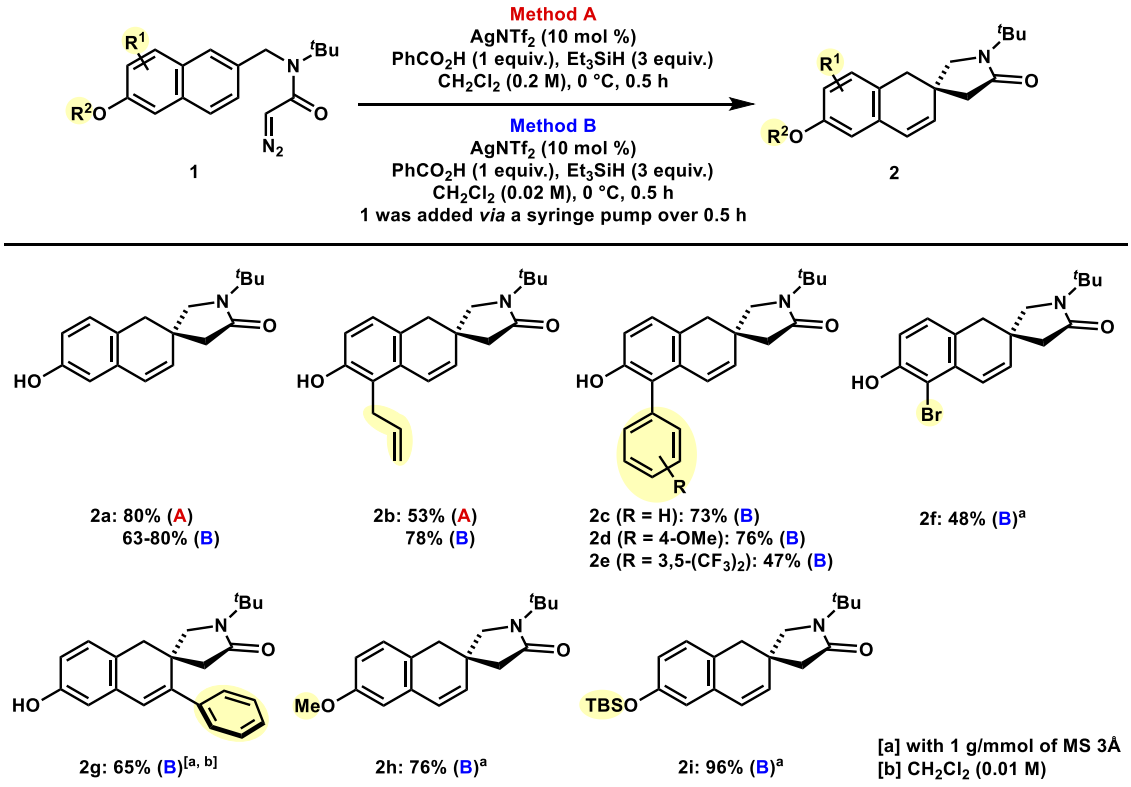
entry	Chiral Ag complex	time (h)	2a (%)	ee of 2a (%)	3a (%)	4a (%)	1a (%)
1	[(*S*)-TRIP-Ag]$_2$ (5 mol %)	24	0	-	trace	0	0
2	Cat.1 (10 mol %)	24	0	-	0	0	12
3	Ag_2CO_3/L1 (2/1, 10 mol %)	24	0	-	61	28	0
4	$AgNTf_2$/(*S*)-BINAP (2/1, 10 mol %)	4	77	0	0	0	0
5	$AgNTf_2$/L2 (2/1, 10 mol %)	24	56	3	0	0	0



第 3 章　還元的脱芳香族化反応の基質一般性の検討

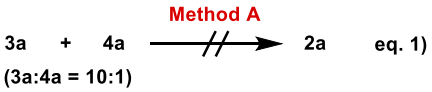
モデル基質 **1a** における最適条件（Method A: entry 6, Table 1 の条件）を用いて、1 位にアリル基を有する基質の脱芳香族的スピロ環化反応を検討したところ、収率は 53%に留まった。本基質はジクロロメタンに溶解したため、基質をシリンジポンプで滴下する Method B（entry 10, Table 1 の条件）を検討した。その結果、**2b** の収率が 78%に改善した。その他の基質もジクロロメタンに溶解したため、Method B で検討を行った。1 位にアリール基を有する基質では、置換基の電子密度が高いほど **2** の収率は高かった。ブロモ基も共存可能であり、反応点近傍が嵩高い基質でも **2g** が収率 65%で得られた。アルキル基やシリル基で保護したナフトールも高収率で **2h** および **2i** を生成し、フェノール類の脱芳香族的スピロ環化反応とは異なる結果を示した。[18] 副生成物である **3** や **4** は得られず、銀触媒の高い化学選択性が示唆された。

Scheme 11



第 4 章　反応機構解析

反応機構を実験化学および計算化学を用いて解析した。まず、**3a** と **4a** の混合物を Method A の条件に付した（eq. 1）。しかしながら、**2a** は生成せず出発物質が回収された。シクロプロパン環の開環が観測されなかったことから、**2** は **3** を経由せずに **1** から直接的に得られることが明らかとなった（Scheme 12）。次に、DFT 計算を用いて詳細な反応機構解析を行った（Figure 4）。**1a** と $AgNTf_2$ が反応し、銀カルベノイドが生成する。[15] その後、銀カルベンが生成する反応経路は見つからず、銀カルベノイドから窒素の脱離を伴って直接的に環化が進行する素反応過程のみが求められた。スピロ環形成における遷移状態は **TS2**$_A$ と **TS2**$_C$ の 2 種類が考えられる。カウンターアニオンとナフトール水酸基が水素結合により相互作用した **TS2**$_C$ は、**TS2**$_A$ と比較し 12.5 kcal/mol もエネルギーが高く、本反応における **TS2**$_A$ の経由が示唆された。これは、ナフトール水酸基を保護した基質も適用可能であったことと相関する。シクロプロパン化体 **CP2** が生成する際のエネルギー障壁は 21.8 kcal/mol であり、スピロ環化よりも 1.04 kcal/mol 高かった。このエネルギー差が化学選択性の発現に起因している。



Scheme 12

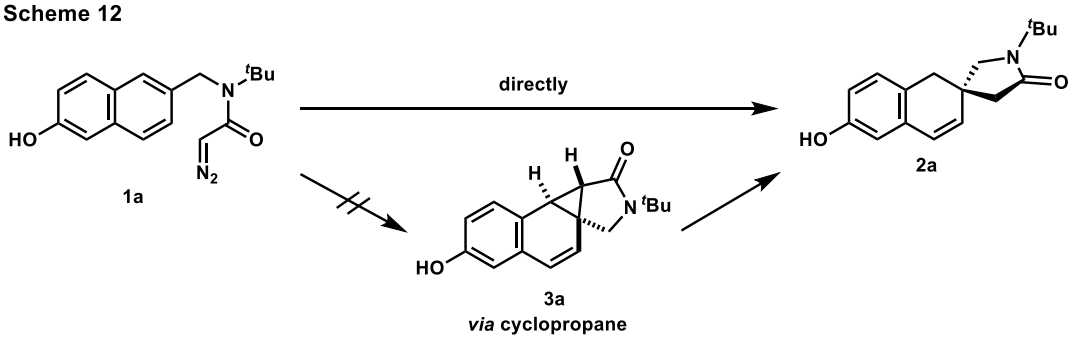
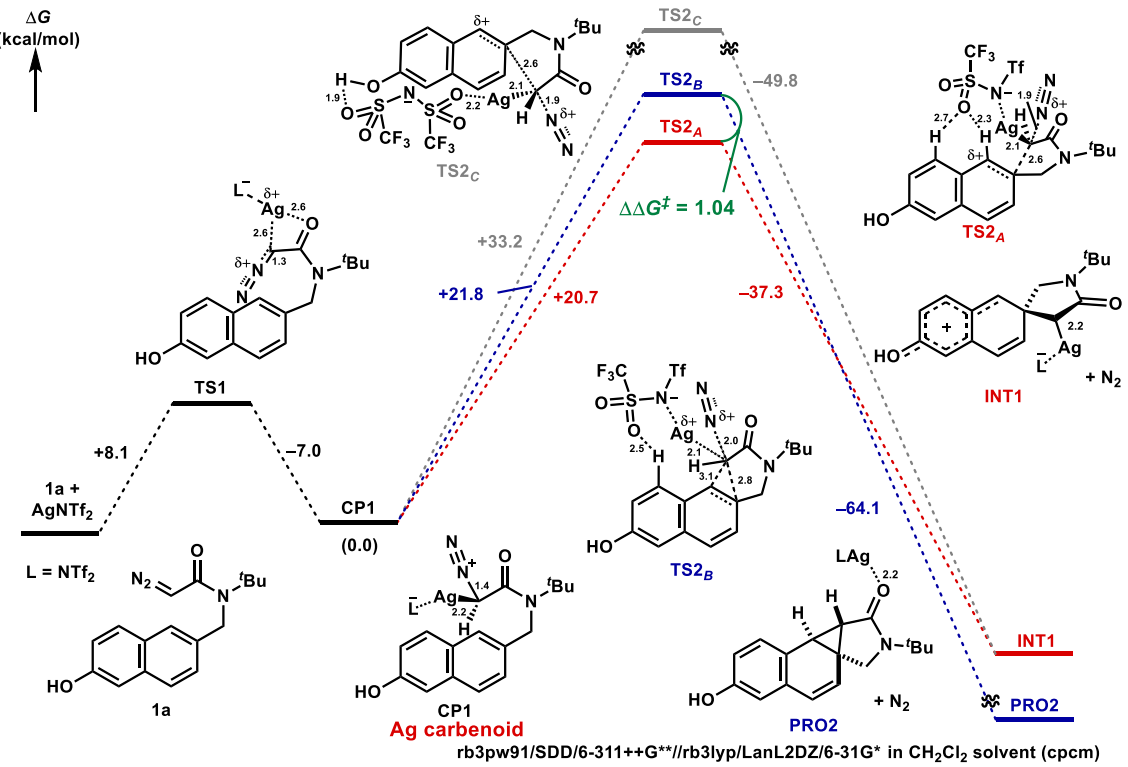


Figure 4

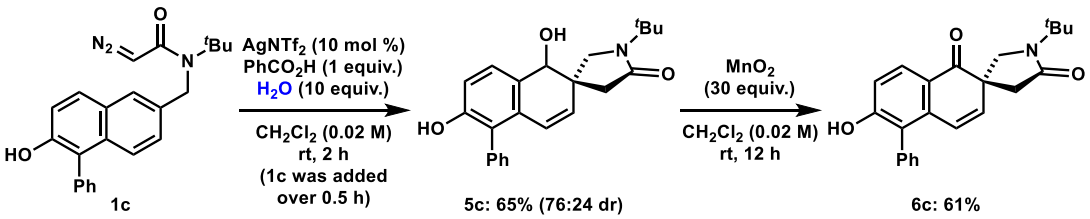


rb3pw91/SDD/6-311++G**//rb3lyp/LanL2DZ/6-31G* in CH_2Cl_2 solvent (cpcm)

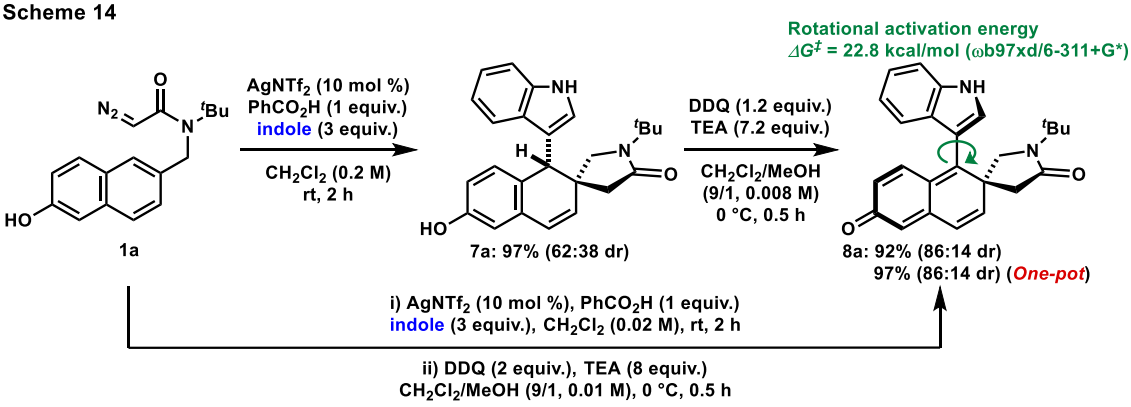
第 5 章　求核剤の検討

他の求核剤を用いた中間体 **INT1** の捕捉を検討した。**1c** の脱芳香族的スピロ環化反応において、トリエチルシランの代わりに水を 10 当量添加したところ、第二級アルコール **5c** がジアステレオマー混合体で収率 65%にて得られた（Scheme 13）。さらに、二酸化マンガンによる酸化反応に付した結果、ケトン **6c** が収率 61%で得られ、ナフトール 5 位へのカルボニル基の導入に成功した。続いて、インドールを求核剤に用いた（Scheme 14）。高収率で **7a** が得られたため、DDQ 酸化を検討したところ、*β*−ナフトールの 2 つのベンゼン環が両方とも脱芳香族化した、ナフタレノン **8a** が収率 92%で得られた。[26] さらに、ワンポットでの **1a** の酸化的タンデム型脱芳香族化反応に挑戦した結果、**8a** が収率 97%で得られた。なお、^{1}H NMR において **8a** はジアステレオマー混合物として観測された。その他の反応条件で合成した **8a** のサンプルでもジアステレオマー混合比が一定であること、および量子計算化学により算出された結合回転障壁が 22.8 kcal/mol であったことから、嵩高いスピロ環とインドール部位との立体障害により、生成する σ 結合の室温での回転が困難であるため、混合物として観測されたと予測した。[27] **8a** の構造は、**8a** のインドール 1 位に *p* −ブロモベンゾイル基を導入した **9a** の X 線結晶構造解析、およびメジャージアステレオマーの相対立体化学は NOESY 相関解析にて決定した（Scheme 15）。これまでに、アトロプ異性体の合成法は報告例があるものの、[28,29,30] 脱芳香族的スピロ環化において区別可能なロータマーを合成した例は報告がない。**8a** の興味深い構造と有用性[31,32]を調査するため、さらに検討を続けることとした。

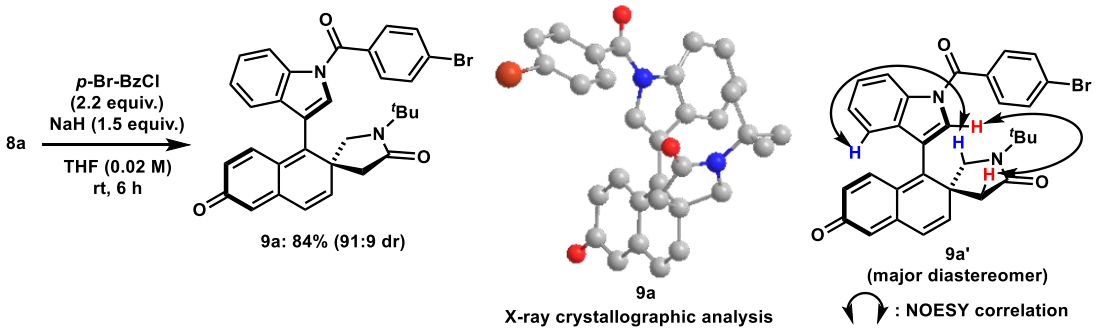
Scheme 13



Scheme 14

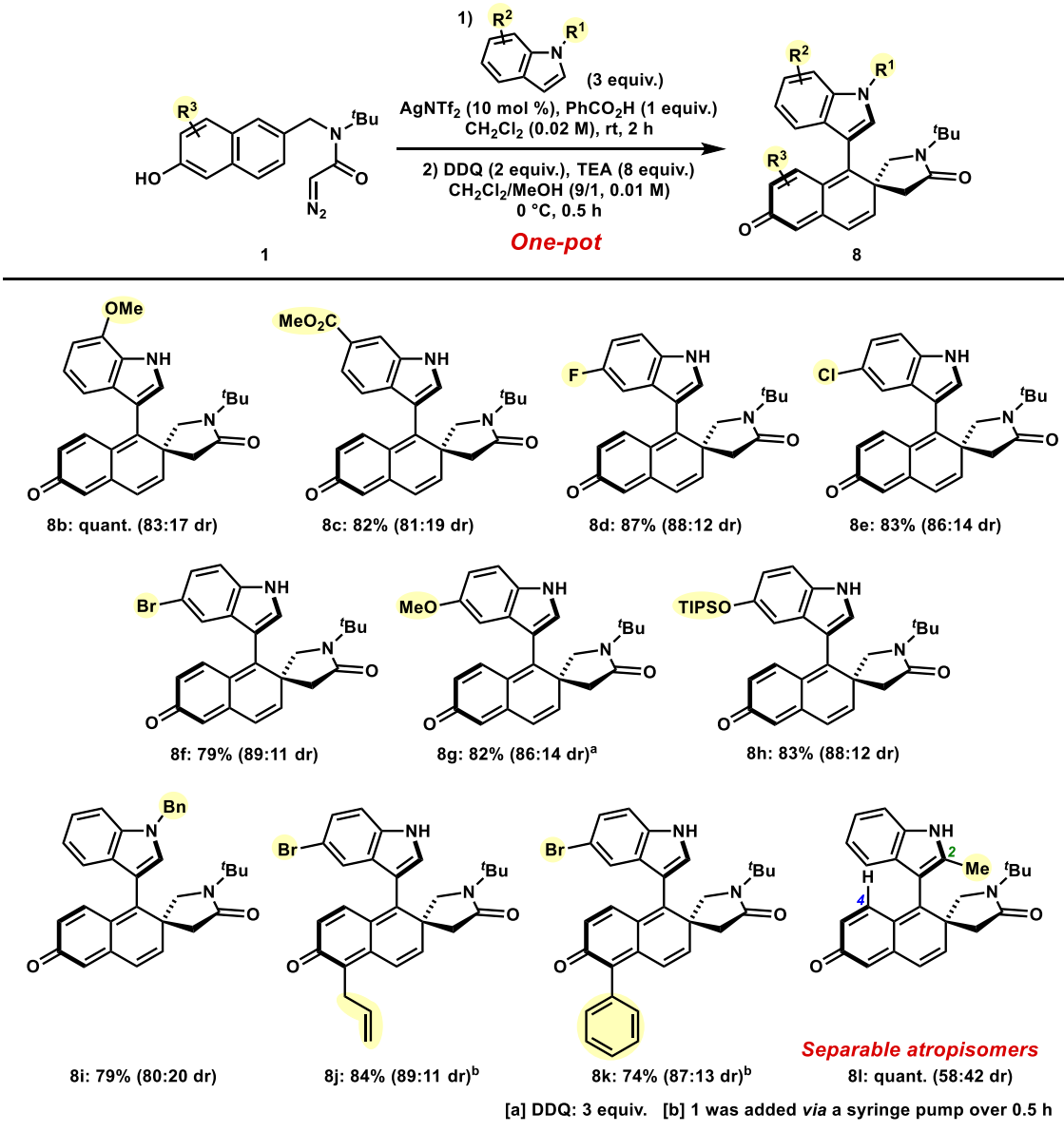


Scheme 15


8a
p-Br-BzCl
(2.2 equiv.)
NaH (1.5 equiv.)
THF (0.02 M)
rt, 6 h
Br
tBu
9a: 84% (91:9 dr)
9a
X-ray crystallographic analysis
H
9a'
(major diastereomer)
: NOESY correlation

酸化的タンデム型脱芳香族化反応の基質一般性を検討した（Scheme 16）。まず様々な置換インドールを用いた。電子供与性基および電子求引性基共に適用可能であり、5、6、7 位のいずれに置換基を有していても収率に大きな影響を及ぼさなかった（**8b-8h**）。インドールの窒素原子がベンジル基で保護された基質や、ナフトール 1 位に置換基を持つ基質を用いた際も、高収率で **8i-8k** が得られた。インドール 2 位にメチル基を持つ **8l** を用いた時、生成物の回転異性体は分離可能であった。これは、ナフタレノン 4 位の水素原子とメチル基間の立体障害により、インドール－ナフタレノン結合の回転速度が更に小さくなったためと考察した。

Scheme 16

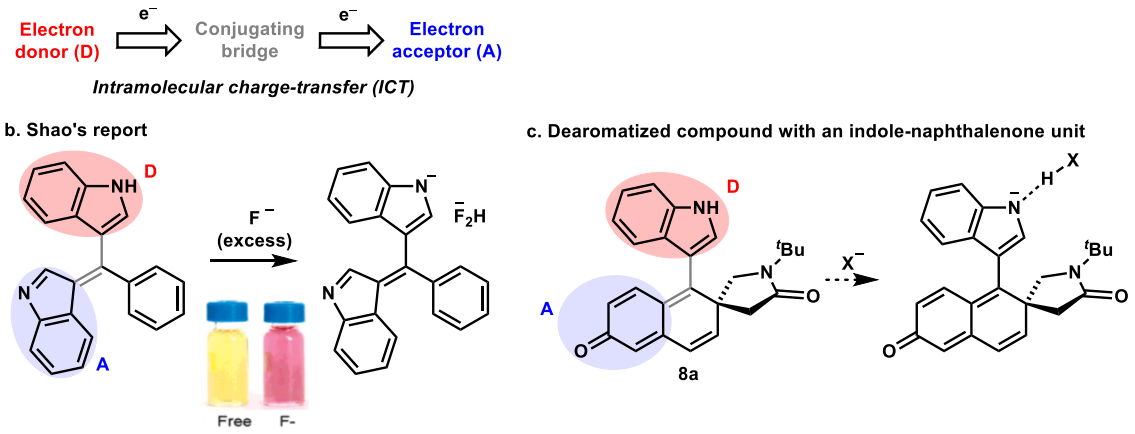


[a] DDQ: 3 equiv.　[b] 1 was added *via* a syringe pump over 0.5 h

第 7 章　フッ素アニオンセンサーとしての有用性検証

化学センサー[33]の一種であるアニオンセンサー[34]はアニオンの含有量を定性的かつ定量的に測定可能であり、生物学・化学および環境などの研究分野において需要が高まっている。特に、発色アニオンセンサーはその可視性の高さから注目を集めている。[35] それらの化合物は、特定のアニオンとの相互作用により分子内電荷移動（ICT: Intramolecular Charge-Transfer）を引き起こすことで色が変化する（Figure 5a）。2006 年に Shao らは酸化ビスイミダリルメタン化合物がフッ素アニオンセンサーとして利用可能であることを見出した（Figure 5b）。インドール部位が電子供与部位として、インドレニン部位が電子受容部位として働くことで ICT が起こったと考えられる。私が合成した **8a** も ICT を引き起こし得る構造、すなわち、電子供与部位であるインドール構造と電子受容部位であるシクロヘキサジエノン構造、そしてそれらを繋ぐ共役結合を有する（Figure 5c）。よって、アニオンセンサーとしての機能を期待できたため、検討を開始した。

Figure 5



8a の 0.05 mM のアセトニトリル溶液を調製し、アニオン源として F^-、Cl^-、Br^-、I^-のテトラブチルアンモニウム塩、および有機塩基のトリエチルアミンをそれぞれ 10 当量添加した（Figure 6a）。コントロール溶液と比較したところ、TBAF を添加した溶液のみ薄黄色から紫色に変化した。さらに、コントロール溶液と TBAF を添加した溶液の吸収波長をそれぞれ測定した結果、320 nm から 564 nm への大きな長波長シフトが観測された（Figure 6b）。この色の変化の原因を明らかにするべく、**8a'**と **10a** の最安定構造を計算により求めた（Figure 6c）。計算結果より、フッ素アニオンと **8a** のインドール NH との相互作用により、ナフタレノン平面とインドール平面の二面角が 78.5°から 39.5°へと小さくなっていることが明らかとなった。また、結合回転障壁は 16.4 kcal/mol と **8a** の結合回転障壁より低く見積もられ、インドールーナフタレノン結合が室温で回転できると示唆された。さらに **10a** の

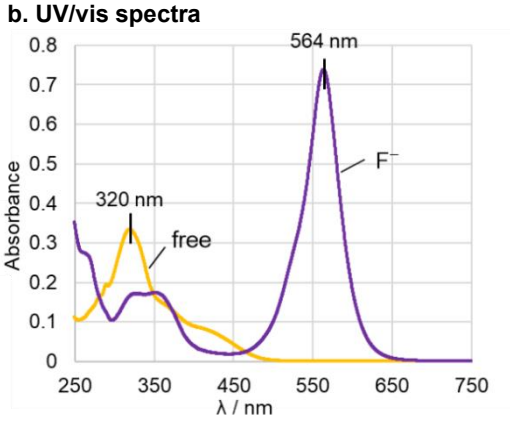
^{1}H NMR 測定にて単一の化合物として観測されたことも、インドール－ナフタレノン結合の回転が速くなったことを支持している（Figure 6d）。よって、フッ素アニオンが相互作用することで再芳香化し共役系が広がった結果、色が変化したと考えられる。

Figure 6

a. Colorimetric tests

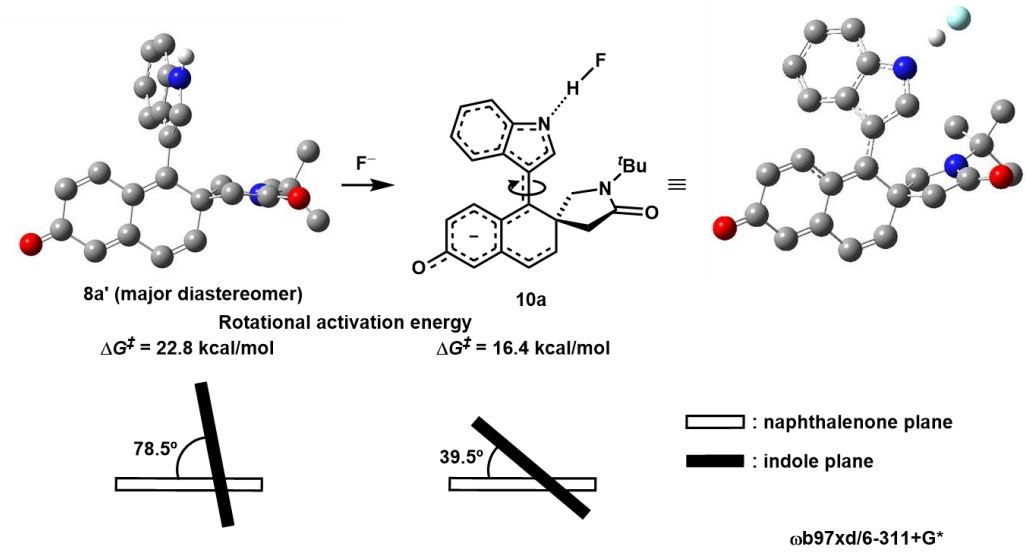
Conditions[1]: **8a** (0.5 μmol)
TBAX (X = F, Cl, Br, I) or TEA (10 equiv.), MeCN (0.05 mM)

b. UV/vis spectra



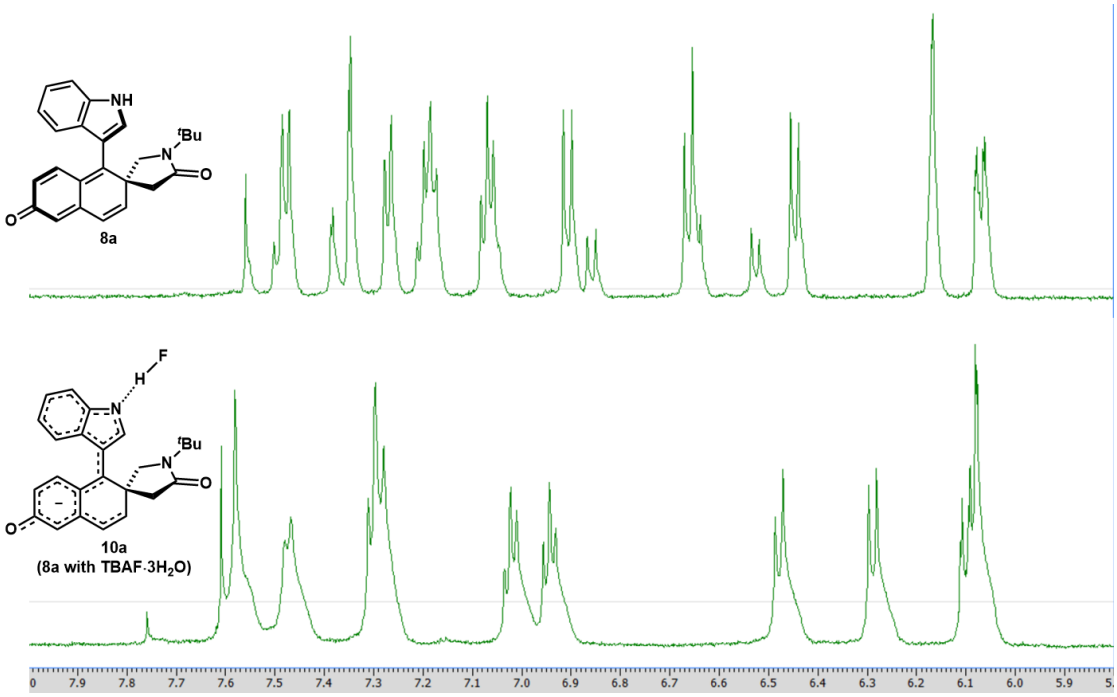
Conditions: MeCN (0.017 mM)

c. Computational study



d. ^{1}H NMR experiments (in CD_3CN)

Samples (1.9 mg, 0.005 mmol) were dissolved in acetonitrile-d6 (1 mL, 5 mM). TBAF•$3H_2O$ (15.8 mg, 10 equiv.) was used as F anion.

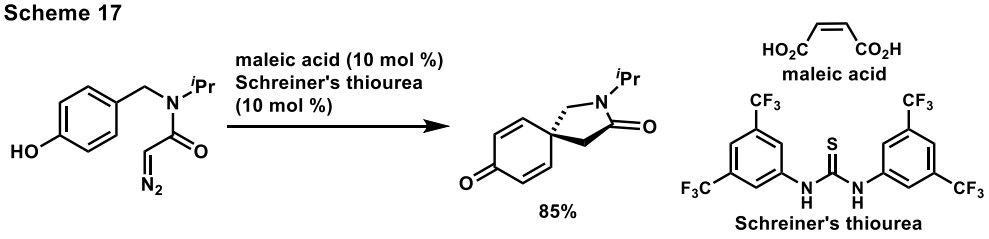


第 3 部　ホウ素触媒を用いた脱芳香族的スピロ環化反応の開発

第 1 章　研究背景

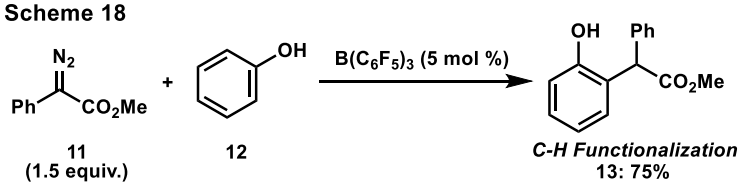
第 2 部で述べた反応を始めとし、カルベン反応はジアゾ化合物に対して遷移金属触媒を作用させ、金属カルベンおよび金属カルベノイドを発生させる手法が主流である。しかし近年、新規法として遷移金属触媒不使用の反応が盛んに開発されている。これまでにジアゾ化合物に対して Brønsted 酸[36]や有機ケイ素試薬[37]、熱[38]、青色光[39]など[40,41]を作用させる反応が報告されている。当研究室では、2018 年にマレイン酸と Schreiner's thiourea を触媒量用いた、フェノール類の脱芳香族的スピロ環化反応を報告した（Scheme 17）。[42]

Scheme 17



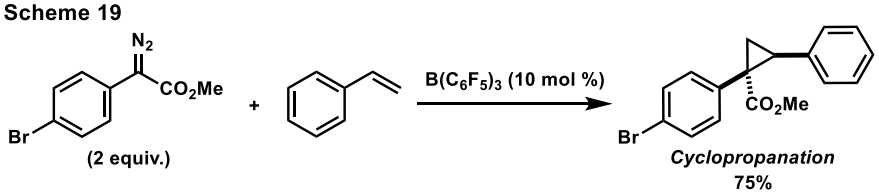
また、Wang や Battilocchio らが筆頭となり、ボラン化合物を用いる手法も開発されてきた。[43]特に近年、Lewis 酸[44]としてジアゾ基の活性化が可能な $B(C_6F_5)_3$[45]が注目を集めている。[46] 2016 年に Zhang らは、$B(C_6F_5)_3$ 触媒を活用し他の金属カルベン反応では困難であった、フェノールのオルト位選択的な C－H 官能基化反応を開発した（Scheme 18）。[46a]

Scheme 18



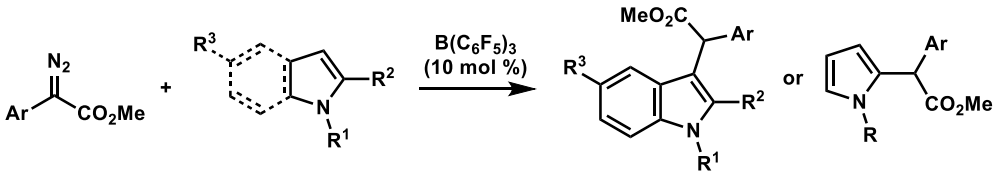
2020 年に Wilkerson-Hill らは、カルベン反応によく見られるシクロプロパン化反応の開発を、$B(C_6F_5)_3$ 触媒系を用いて達成した（Scheme 19）。[46e]

Scheme 19

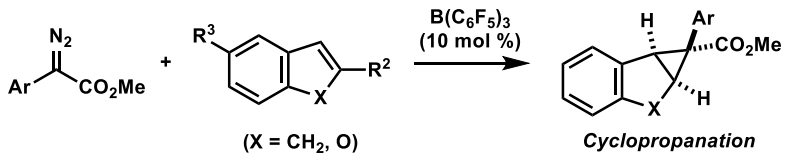


同時期に Dasgupta らは、$B(C_6F_5)_3$ 触媒存在下、ジアゾエステルをヘテロ五員環と網羅的に反応させた。[46f] インドールやピロールでは C－H 官能基化反応（Scheme 20）、インデンやベンゾフランではシクロプロパン化反応（Scheme 21）がそれぞれ進行することを示した。

Scheme 20

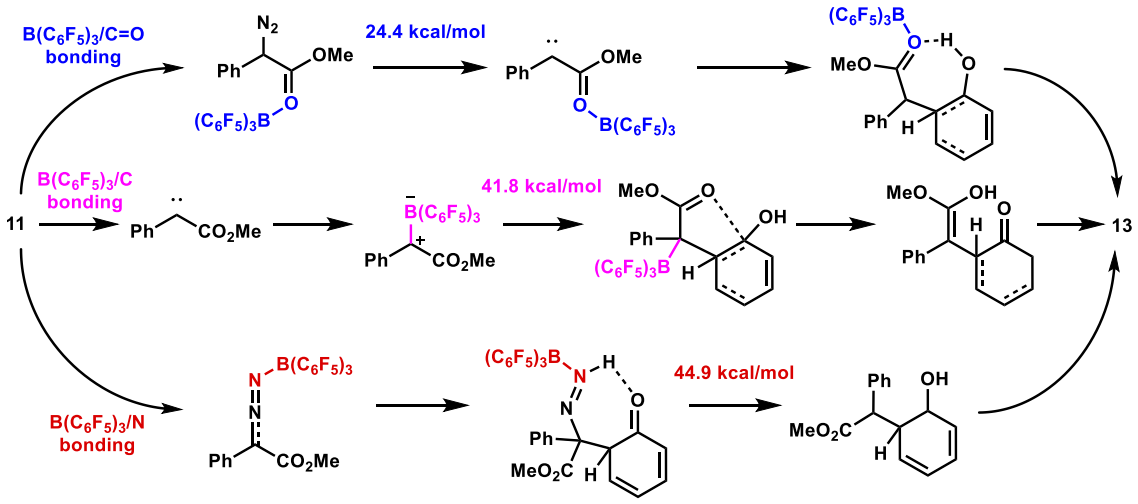


Scheme 21



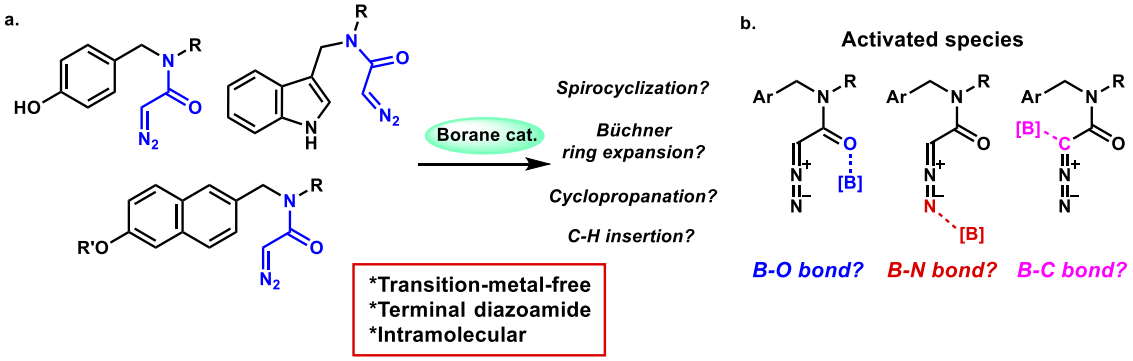
これらを始めとした $B(C_6F_5)_3$ 触媒とジアゾ化合物の反応について、様々な反応メカニズムが提唱されている。そんな中、Liu、Jiang、Wu らは、量子化学計算によりフェノールの C－H 官能基化反応のメカニズムを明らかにした（Scheme 22）。[47,48] ホウ素触媒がジアゾエステルを活性化する際の結合パターンは大別すると 3 種類ある。すなわち、ホウ素－酸素結合、ホウ素－炭素結合、そしてホウ素－窒素結合を生成する 3 つのパターンが考えられる。彼らは各反応経路の活性化エネルギーを算出した結果、ホウ素－酸素結合により基質が活性化し、フリーカルベン生成後に C－H 官能基化反応が進行する経路が最も有利であると結論付けた。

Scheme 22. Computational studies based on M06-2X/6-311++G**//rb3lyp/6-31G* in CH_2Cl_2 solvent (smd)



しかしながら、これまで報告された反応はいずれも基質がジアゾエステル構造を有する二置換ジアゾ化合物の分子間反応に限られており、ホウ素触媒の特性の解明は未だ不十分である。以上の研究背景を踏まえて、今回私は、第 2 部で用いた様な分子内にジアゾアミド構造を有する芳香族化合物にホウ素触媒を作用させることで、Lewis 酸触媒を用いた遷移金属フリーな脱芳香族的スピロ環化反応の開発が可能であると予想した（Figure 7a）。新たな触媒系の活用により、脱芳香族化反応における基質適応性の改善や新しい化学選択性の発現の可能性が見出せる。本反応は、基質が末端ジアゾアミド構造を有する点や分子内反応である点が既知の報告例と異なり、ホウ素触媒の汎用性拡大への貢献も期待できる。また、本反応のメカニズムを量子化学計算により解析することで、新たな活性種の発見を期待し研究に着手した（Figure 7b）。

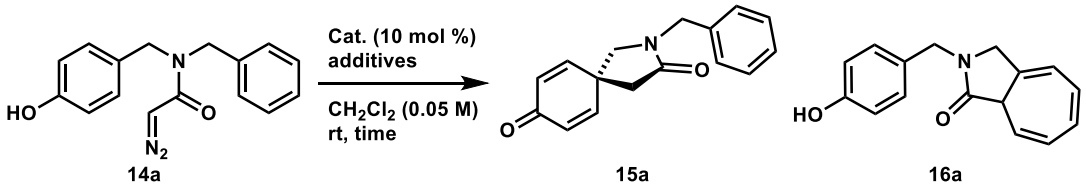
Figure 7



第 2 章　反応条件の最適化

モデル基質として、窒素原子上にベンジル基を有するフェノール **14a** を設計した（Table 2)。本基質は、電子的・立体的環境の似た芳香環を反応点近傍に有するため、金属カルベンでは認識が困難であり、挑戦的な基質である。実際に、銀触媒存在下では、フェノール部位からスピロ環化が進行した **15a** とベンジル基と Büchner 環拡大が進行した **16a** が生成し、ロジウム触媒存在下では **16a** が選択的に生成した（entries 1 and 2)。一方で、$B(C_6F_5)_3$ と作用させたところ **15a** のみが収率 79%で得られた（entry 3)。他のボラン触媒や Lewis 酸触媒を検討したものの、entry 3 を超える結果は得られなかった（entries 4 to 7)。また、脱水剤としてモレキュラーシーブス 3Å を添加したが、原料の残存が観測された（entry 8)。しかし、プロトン捕捉剤である 2,6-di-*tert*-butylpyridine を触媒量添加したところ、わずかに収率が向上した（entry 9)。$B(C_6F_5)_3$ と水との反応により発生する Brønsted 酸の捕捉により、副反応を抑制したためと考察した（Scheme 23)。[49] よって、entry 9 の条件を最適条件に決定した。

Table 2

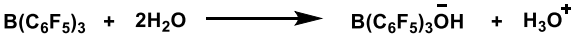


entry	Cat.	additives	time (h)	15a (%)	16a (%)	14a (%)
1	$AgSbF_6$	-	3	39	6	0
2	$Rh_2(OAc)_4$[a]	-	3	0	38	0
3	$B(C_6F_5)_3$	-	3	79	0	0
4	BPh_3	-	72	0	0	81
5	$BF(mesityl)_2$	-	72	26	0	25
6	$BF_3{\bullet}Et_2O$	-	72	63	0	7
7	$Sc(OTf)_3$	-	72	49	0	trace
8	$B(C_6F_5)_3$	MS 3Å (1 g/mmol)	72	35	0	35
9	$B(C_6F_5)_3$	2,6-^{t}Bu$_2$py (10 mol %)	48	86	0	0

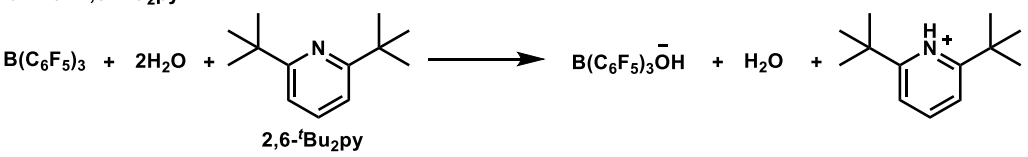
[a] cat.: 5 mol %

Scheme 23

a. without 2,6-^{t}Bu$_2$py



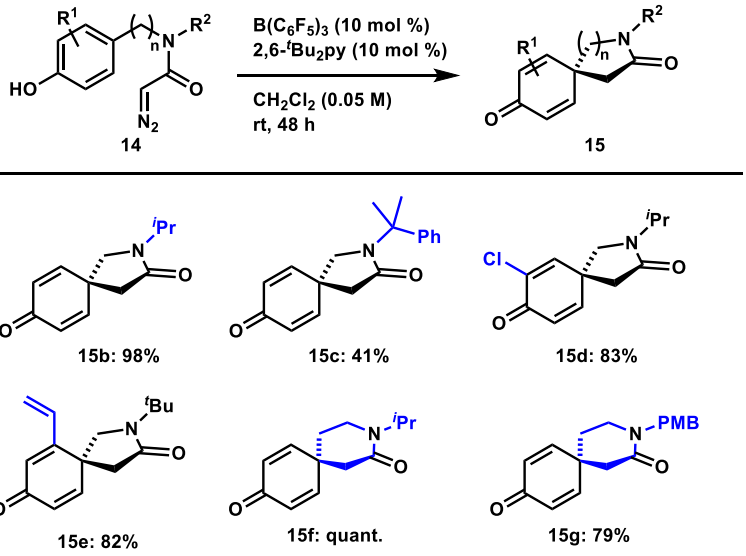
b. with 2,6-^{t}Bu$_2$py



第 3 章　基質一般性の検討

最適条件下にてホウ素触媒を用いたフェノール類の脱芳香族的スピロ環化反応の基質一般性を調査した（Scheme 24）。窒素上の保護基について ^{i}Pr 基も適用可能であったが（**15b**）、嵩高い置換基では収率が中程度に留まった（**15c**）。フェノール 2 位にクロロ基、3 位にビニル基を持つ基質でも反応は進行し、高収率で **15d** および **15e** を得た。一炭素増炭した基質では、六員環スピロ化合物 **15f** が定量的に、**15g** が収率 79%で得られた。

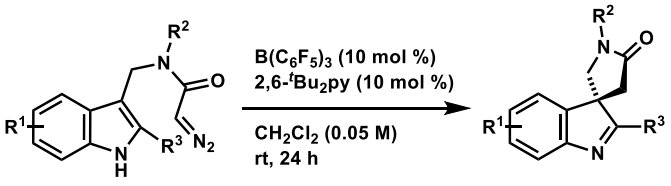
Scheme 24



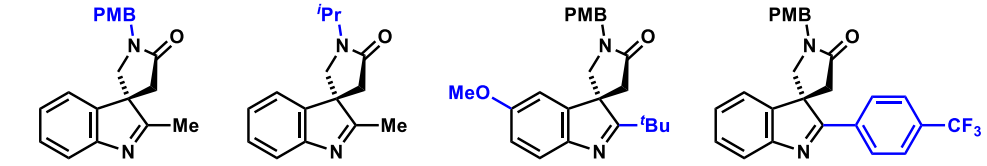
次に、インドール類に対して $B(C_6F_5)_3$ を作用させた（Scheme 25）。2 位に Me 基、窒素原子上に PMB 基を有するインドール誘導体にフェノール類の最適条件を用いた。予想通り **18a** が得られ、[(*S*)-TRIP-Ag]$_2$ を作用させた際より高い化学選択性でスピロ環化が進行した。[19] 続けて基質一般性を検討した。窒素原子上の保護基が ^{i}Pr 基の基質では高収率で **18b** が得られた。さらに、5 位置換インドールや、2 位の置換基が嵩高い基質も適用可能であった。

β−ナフトールの還元的脱芳香族化反応も検討したところ、所望の **2a** が収率 82%で得られた。よって、$B(C_6F_5)_3$ 触媒を活用した脱芳香族化反応は、*β*−ナフトール類にも適用可能であることが示唆された（Scheme 26）。

Scheme 25



17 18



18a: 84%
(with [(*S*)-TRIP-Ag]$_2$ 60%, 16% ee)

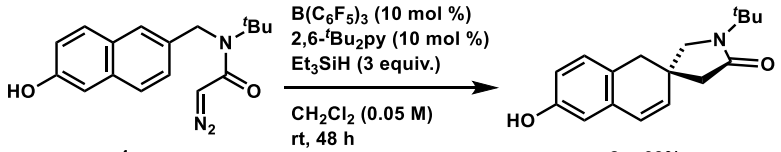
18b: 97%[a]

18c: 87%

18d: 83%[a]

[a] Reaction was carried out for 48 h.

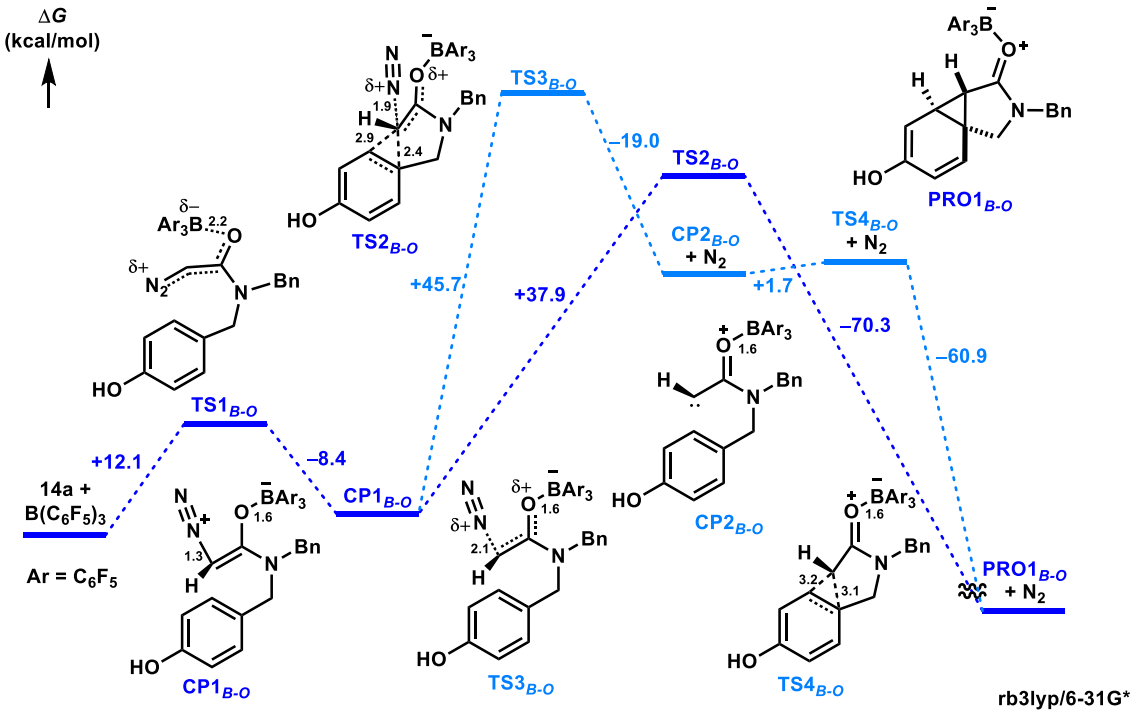
Scheme 26



1a 2a: 63%

量子化学計算を用いて、**14a** の脱芳香族的スピロ環化反応のメカニズム解析を行った。最初に、報告例のあるホウ素－酸素結合を形成するメカニズムについて計算したところ、2 つの反応経路が算出された（Figure 9）。1 つは、窒素が脱離しながらシクロプロパン環が形成する経路（**CP1**$_{B\text{-}O}$**→TS2**$_{B\text{-}O}$**→PRO1**$_{B\text{-}O}$）、もう一方は窒素が脱離しフリーカルベンが生成した後に、シクロプロパン環が形成する経路（**CP1**$_{B\text{-}O}$**→TS3**$_{B\text{-}O}$**→CP2**$_{B\text{-}O}$**→TS4**$_{B\text{-}O}$**→PRO1**$_{B\text{-}O}$）である。しかしながら、どちらの反応経路も全体の活性化エネルギーが 35.0 kcal/mol 以上であり、尚且つ最終生成物がスピロ環化体でないことから、いずれも本反応の反応経路ではないことが示唆された。

Figure 9



次に、ホウ素－炭素結合を形成するメカニズムを計算した（Figure 10）。カルベン－ホウ素付加体が発生する経路が 2 パターン算出された。一つはホウ素－炭素結合が生成した後に窒素が脱離する段階的な経路（**14a** + B(C_6F_5)$_3$**→TS1**$_{B\text{-}C}$**→CP1**$_{B\text{-}C}$**→TS2**$_{B\text{-}C}$**→CP2**$_{B\text{-}C}$）、もう一方はホウ素－炭素結合の生成と同時に窒素が脱離する協奏的な経路（**14a** + B(C_6F_5)$_3$**→TS3**$_{B\text{-}C}$**→CP2**$_{B\text{-}C}$）である。2017 年に Stephan らはジフェニルジアゾメタンと B(C_6F_5)$_3$ を作用させると、窒素脱離と協奏的にホウ素－炭素結合が生成し得ることを量子化学計算により示した（Figure 11）。[50] 彼らはその活性種をカルベン－ホウ素付加体（carbene-borane adduct）と称している。本反応では彼らの報告例とは異なり、段階的な経路の方が協奏的な経路よりも

活性化エネルギーが低いため、段階的なホウ素－炭素結合の生成が有利であると考えられる。その後、コンフォメーションが変化した後にスピロ環化反応が進行するが（**CP2**$_{B\text{-}C}$→**TS4**$_{B\text{-}C}$→**INT1**$_{B\text{-}C}$）、その際の活性化エネルギーは 3.3 kcal/mol と低く、容易に進行することが示唆された。また、反応全体の活性化エネルギーは 27.6 kcal/mol であった。ホウ素－酸素結合が形成される場合の反応経路よりも全体の活性化エネルギーが低いことから、現段階ではこのメカニズムが有利であると考察した。

Figure 10

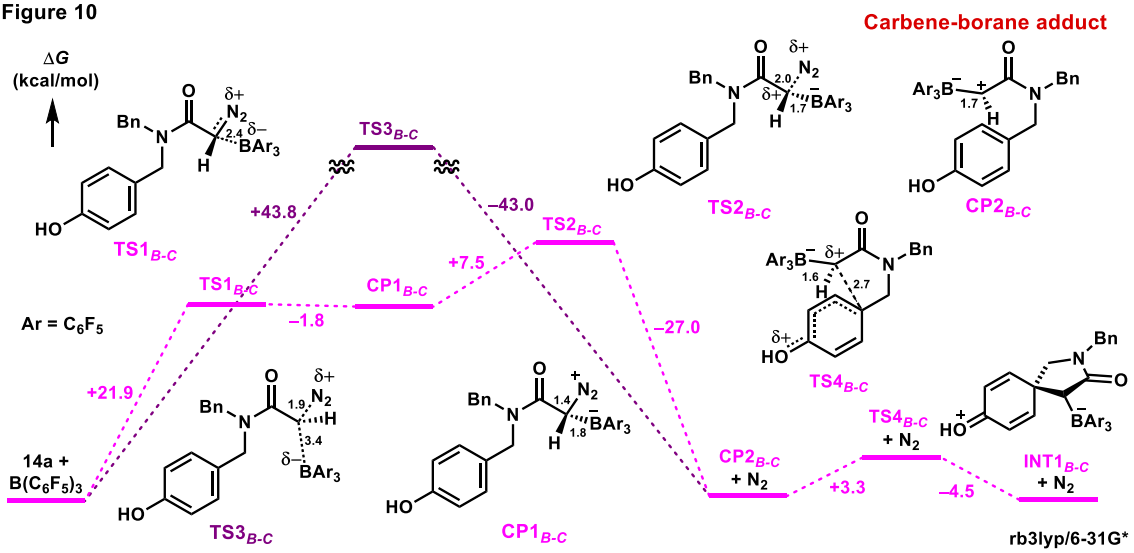
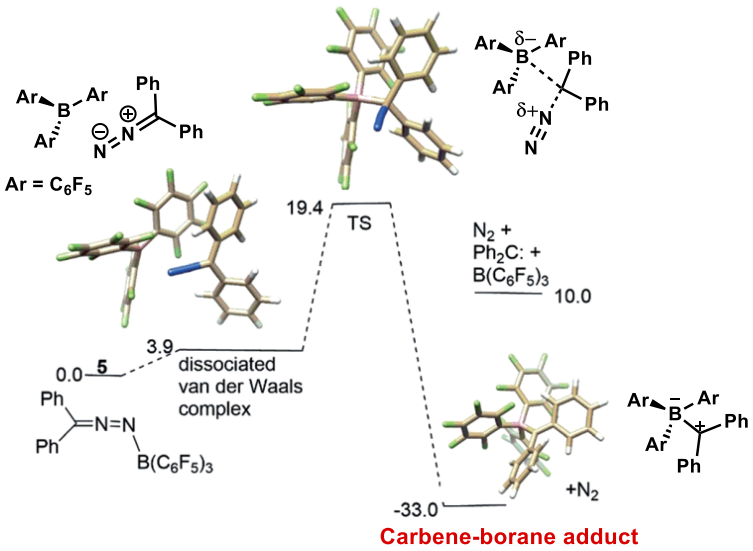


Figure 11



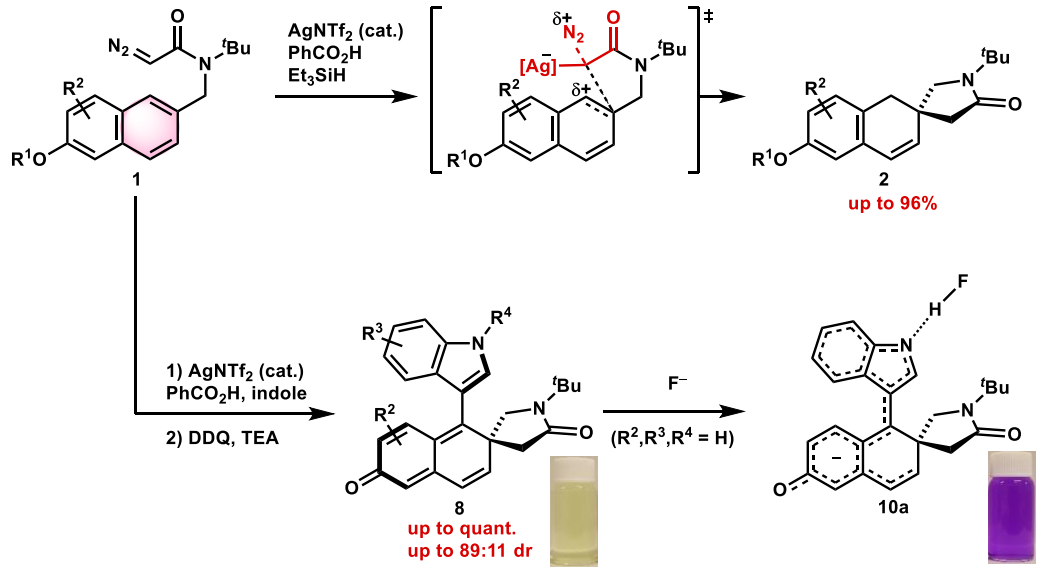
結語

私は本論文中にて、以下のことを纏めた。

第 1 部にて、これまで当研究室にて取り組んできた、脱芳香族的スピロ環化反応および金属カルベン反応について述べ、創薬研究におけるそれらの重要性を示した。

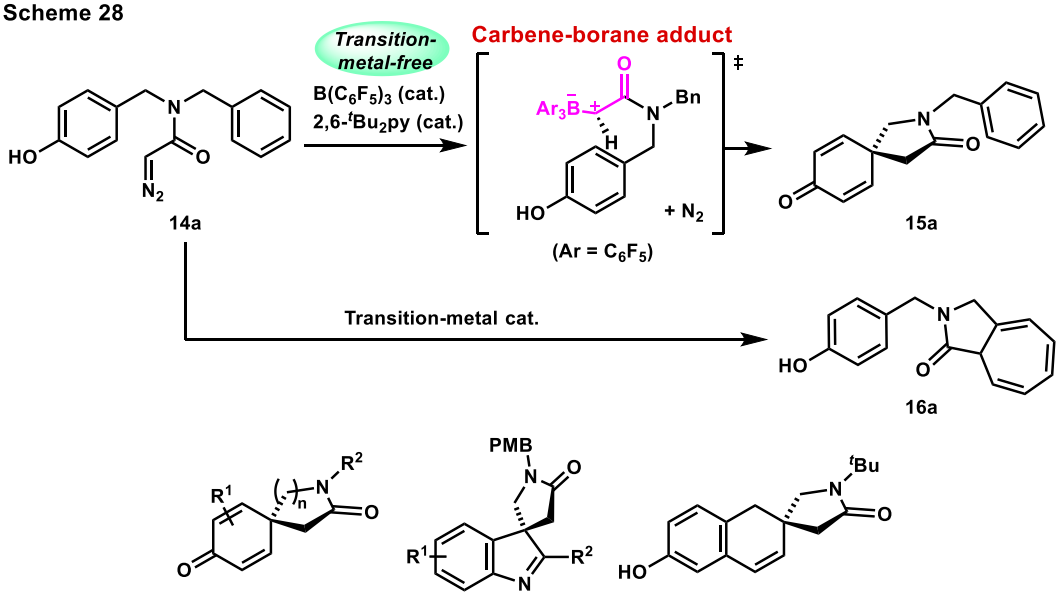
第 2 部にて、銀触媒を活用したβ−ナフトール類の非典型的脱芳香族化反応の開発研究について述べた（Scheme 27）。世界初のβ−ナフトール類が持つベンゼノイド環の脱芳香族化に成功し、スピロ環化体 **2** を最高収率 96%で合成した。さらに量子化学計算を用いて、本環化反応が銀カルベノイドから直接進行していることを明らかにした。また、インドール付加反応に続く酸化反応よりナフタレノン **8** を合成した。合成した **8** のねじれ構造および連続した不飽和結合を活用し、**8** のフッ素アニオンセンサーとしての有用性を見出した。

Scheme 27



第 3 部にて、ボラン触媒を用いた遷移金属フリーな脱芳香族的スピロ環化反応の開発研究について述べた（Scheme 28）。遷移金属触媒存在下では Büchner 環拡大反応が進行する基質に対しても、$B(C_6F_5)_3$ を作用させることで、脱芳香族的スピロ環化反応が化学選択的に進行することを見出した。またメカニズム解析によって、本反応は既知の報告例とは異なり、ホウ素−炭素結合を有する活性種の段階的な生成が示唆された。本触媒系は置換基を持つフェノールやインドール、β−ナフトールと様々な芳香族化合物に有用であることも確認した。

Scheme 28


Transition-metal-free
B(C6F5)3 (cat.)
2,6-tBu2py (cat.)
Carbene-borane adduct
Ar3B
Bn
H
HO
+ N2
(Ar = C6F5)
14a
15a
Transition-metal cat.
16a
R1
R2
n
PMB
tBu

実験の部

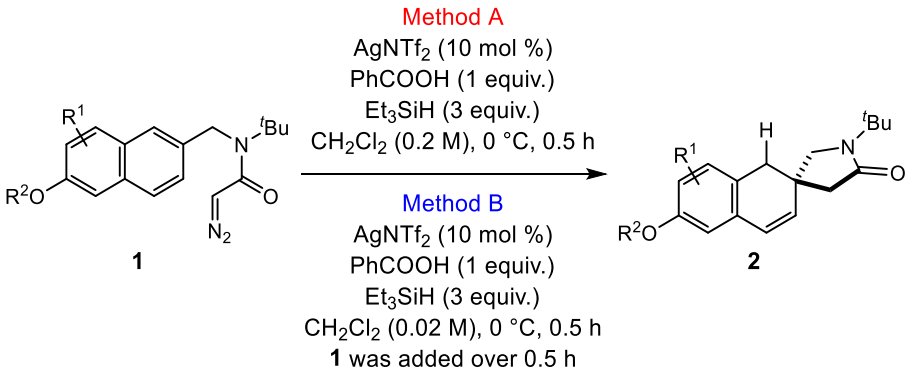
目次

1. General Information

NMR spectra were recorded at 400 MHz or 600 MHz for ^{1}H NMR, 100 MHz or 150 MHz for ^{13}C NMR, and 564 MHz for ^{19}F NMR Chemical shifts in $CDCl_3$, CD_3OD, or DMSO-d6, were reported downfield from TMS (= 0 ppm) or solvent signals [CH_3OH (3.31 ppm), DMSO (2.50 ppm)] for ^{1}H NMR. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, sep = septet, m = multiplet, and br = broad), integration and coupling constants in Hz. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent signal [$CHCl_3$ (77.16 ppm), CH_3OH (49.00 ppm), DMSO (39.52 ppm)] as an internal reference. ESI mass spectra were measured on JEOL AccuTOF LC-plus JMS-T100LP. Optical rotations were measured on a JASCO P-1020 polarimeter. Melting points were measured with a SIBATA NEL-270 melting point apparatus. The UV-Vis spectrometer was a JASCO V-730 spectrometer. Analytical thin layer chromatography was performed on Kieselgel 60F254, 0.25 mm-thick plates. Column chromatography was performed with silica gel 60 N (spherical, neutral 63-210 mesh). Reactions were conducted in dry solvent. Other reagents were purified by the usual methods.

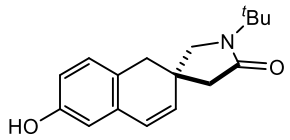
2. Characterization of Dearomatized Cyclic Products 4a–4i, 5a, 6a, 7c, 8c, 9a-9l, 10a

General Procedure A for Reductive Dearomatization



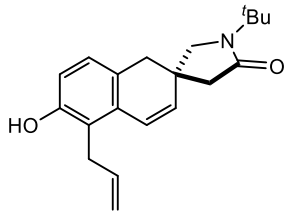
Method A: A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with $AgNTf_2$ (3.9 mg, 0.01 mmol, 10 mol%), benzoic acid (12.2 mg, 0.1 mmol, 1 equiv.), and triethylsilane (47.9 μL, 0.3 mmol, 3 equiv.), which were subsequently dissolved partially in CH_2Cl_2 (0.5 mL) under an argon gas atmosphere. Diazo compound **1** (0.1 mmol) was added to the suspension at 0 °C in an ice bath, and the reaction mixture was stirred for 0.5 h at the same temperature. The reaction was quenched with the addition of water and 1 M TBAF in THF (0.1 mL), and stirred for 15 min at room temperature. The aqueous solution was extracted with CH_2Cl_2×2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; gradient elution: *n*-hexane/EtOAc, 3/1 → 1/1) to afford spirocyclic compound **2**.

Method B: A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with $AgNTf_2$ (3.9 mg, 0.01 mmol, 10 mol%), benzoic acid (12.2 mg, 0.1 mmol, 1 equiv.), and triethylsilane (47.9 μL, 0.3 mmol, 3 equiv.), which were subsequently dissolved partially in CH_2Cl_2 (1 mL) under an argon gas atmosphere. Diazo compound **1** (0.1 mmol) in CH_2Cl_2 (4 mL) was added slowly over 0.5 h *via* a syringe pump to the suspension at 0 °C in an ice bath, and the reaction mixture was stirred for 0.5 h at the same temperature. The reaction was quenched with the addition of water and 1 M TBAF in THF (0.1 mL), and stirred for 15 min at room temperature. The aqueous solution was extracted with CH_2Cl_2×2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; gradient elution: *n*-hexane/EtOAc, 3/1 → 1/1) to afford spirocyclic compound **2**.



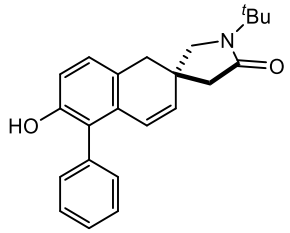
1'-(*tert*-Butyl)-6-hydroxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (2a)

Prepared according to the general procedure A (Method A) using **1a** (29.7 mg), and isolated as white solid (21.6 mg, 80% yield).: m.p. 220−221 °C; R_f = 0.4 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (d, *J* = 9.6 Hz, 1H), 6.63 (d, *J* = 9.6 Hz, 1H), 6.58 (s, 1H), 6.39 (d, *J* = 9.6 Hz, 1H), 5.86 (d, *J* = 9.6 Hz, 1H), 5.67 (br s, 1H), 3.37 (d, *J* = 10.8 Hz, 1H), 3.30 (d, *J* = 10.8 Hz, 1H), 2.81 (d, *J* = 15.6 Hz, 1H), 2.77 (d, *J* = 15.6 Hz, 1H), 2.38 (d, *J* = 18.6 Hz, 1H), 2.35 (d, *J* = 18.6 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.1, 155.1, 134.9, 134.3, 129.4, 128.5, 124.9, 114.2, 113.5, 55.8, 54.2, 45.5, 38.6, 36.8, 27.9 (3C); IR (ATR) 3113, 2970, 2928, 1730, 1650, 1601, 1445, 1421, 1365, 1284, 1218 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{17}H_{21}NNaO_2^+$ *m*/*z* 294.1465, found *m*/*z* 294.1465.



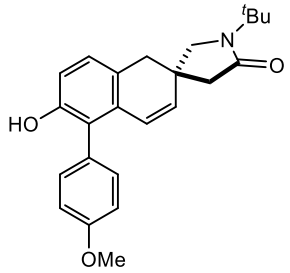
5-Allyl-1'-(*tert*-butyl)-6-hydroxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (2b)

Prepared according to the general procedure A (Method B) using **1b** (33.7 mg), and isolated as yellow solid (24.3 mg, 78% yield).: m.p. 69-71 °C; R_f = 0.5 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.6 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 5.95 (ddt, *J* = 16.8, 9.6, 6.0 Hz, 1H), 5.88 (d, *J* = 9.6 Hz, 1H), 5.01 (dd, *J* = 9.6, 1.8 Hz, 1H), 4.92 (dd, *J* = 16.8, 1.8 Hz, 1H), 3.47 (d, *J* = 6.0 Hz, 2H), 3.37 (d, *J* = 10.2 Hz, 1H), 3.31 (d, *J* = 10.2 Hz, 1H), 2.79 (d, *J* = 15.6 Hz, 1H), 2.75 (d, *J* = 15.6 Hz, 1H), 2.36 (d, *J* = 16.8 Hz, 1H), 2.33 (d, *J* = 16.8 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.4, 153.6, 136.4, 134.8, 132.3, 127.3, 125.6, 125.0, 122.0, 115.3, 114.2, 55.9, 54.3, 44.9, 39.6, 36.1, 29.6, 27.9 (3C); IR (ATR) 3275, 2971, 2926, 2876, 1739, 1649, 1365, 1217 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{20}H_{25}NNaO_2^+$ *m*/*z* 334.1778, found *m*/*z* 334.1770.



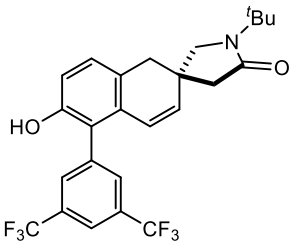
1'-(*tert*-Butyl)-6-hydroxy-5-phenyl-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (2c)

Prepared according to the general procedure A (Method B) using **1c** (37.3 mg), and isolated as yellow solid (25.4 mg, 73% yield).: m.p. 225−227 °C; R_f = 0.4 (*n*-hexane/EtOAc, 2/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.4, 8.4 Hz, 2H), 7.43 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 9.6 Hz, 1H), 6.83 (d, *J* = 9.6 Hz, 1H), 6.16 (d, *J* = 10.8 Hz, 1H), 5.76 (d, *J* = 10.8 Hz, 1H), 5.26 (br s, 1H), 3.41 (d, *J* = 10.8 Hz, 1H), 3.28 (d, *J* = 10.8 Hz, 1H), 2.87 (d, *J* = 15.6 Hz, 1H), 2.84 (d, *J* = 15.6 Hz, 1H), 2.39 (s, 2H), 1.39 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.0, 152.1, 135.0, 134.3, 131.7, 130.9, 130.8, 129.4, 129.3, 128.8, 128.4, 126.3, 125.6, 125.1, 114.0, 55.5, 54.1, 45.6, 39.3, 36.1, 27.9 (3C); IR (ATR) 3030, 2970, 2934, 2710, 1745, 1644, 1568, 1432, 1364, 1279, 1215 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{23}H_{25}NNaO_2^+$ *m*/*z* 370.1778, found *m*/*z* 370.1778.



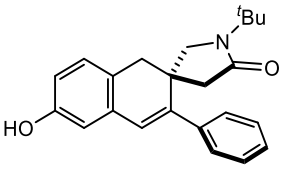
1'-(*tert*-Butyl)-6-hydroxy-5-(4-methoxyphenyl)-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (2d)

Prepared according to the general procedure A (Method B) using **1d** (40.3 mg), and isolated as yellow solid (28.5 mg, 76% yield).: m.p. 199-201 °C; R_f = 0.4 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.18 (d, *J* = 9.6 Hz, 1H), 5.77 (d, *J* = 9.6 Hz, 1H), 5.04 (br s, 1H), 3.87 (s, 3H), 3.40 (d, *J* = 10.8 Hz, 1H), 3.27 (d, *J* = 10.8 Hz, 1H), 2.86 (d, *J* = 15.6 Hz, 1H), 2.83 (d, *J* = 15.6 Hz, 1H), 2.37 (s, 2H), 1.38 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 159.7, 152.3, 135.0, 135.0, 132.1, 132.0, 128.6, 126.4, 125.9, 125.2, 125.1, 114.9, 114.8, 113.8, 55.5, 55.5, 54.1, 45.7, 39.4, 36.1, 27.9 (3C); IR (ATR) 2956, 2829, 1749, 1648, 1601, 1514, 1444, 1430, 1364, 1281, 1243, 1218 cm^{-1}; HRMS (ESI-TOF) $[M + H]^+$ calcd for $C_{24}H_{28}NO_3^+$ *m*/*z* 378.2064, found *m*/*z* 378.2065



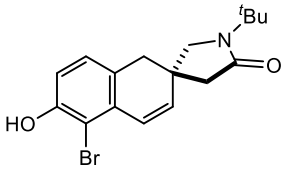
5-(3,5-Bis(trifluoromethyl)phenyl)-1'-(*tert*-butyl)-6-hydroxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (2e)

Prepared according to the general procedure A (Method B) using **1e** (30.0 mg), and isolated as colorless oil (13.4 mg, 47% yield, 0.059 mmol scale).; R_f = 0.5 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.77 (s, 1H), 7.74 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.32 (br s, 1H), 6.08 (d, *J* = 9.6 Hz, 1H), 5.84 (d, *J* = 9.6 Hz, 1H), 3.41 (d, *J* = 10.2 Hz, 1H), 3.35 (d, *J* = 10.2 Hz, 1H), 2.88 (d, *J* = 15.0 Hz, 1H), 2.82 (d, *J* = 15.0 Hz, 1H), 2.38 (d, *J* = 17.4 Hz, 1H), 2.35 (d, *J* = 17.4 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.1, 152.4, 137.9, 136.0, 131.9, 131.8 (*J* = 27.3 Hz, 2C), 131.3, 129.8, 125.5, 125.3, 123.5 (*J* = 270.0 Hz, 2C), 123.2, 121.5 (*J* = 3.0 Hz, 2C), 114.5, 55.9, 54.4, 44.7, 39.3, 36.2, 27.9 (3C); ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.6; IR (ATR) 3331, 1659, 1577, 1456, 1424, 1369, 1279, 1218, 1176 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{25}H_{23}F_6NNaO_2^+$ *m*/*z* 506.1525, found *m*/*z* 506.1536



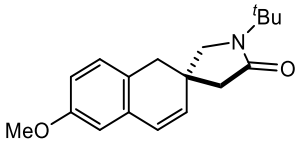
1'-(*tert*-Butyl)-6-hydroxy-3-phenyl-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (2f)

Prepared according to the general procedure A (Method B) using **1f** (37.3 mg), CH_2Cl_2 (0.01 M), and MS 3Å (100 mg) and isolated as white solid (22.5 mg, 65% yield).: m.p. 230-232 °C; R_f = 0.3 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.62 (s, 1H), 6.42 (s, 1H), 5.00 (br s, 1H), 3.51 (d, *J* = 9.0 Hz, 1H), 3.38 (d, *J* = 9.0 Hz, 1H), 2.97 (d, *J* = 15.0 Hz, 1H), 2.90 (d, *J* = 15.0 Hz, 1H), 2.74 (d, *J* = 15.6 Hz, 1H), 2.32 (d, *J* = 15.6 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d6) δ 172.4, 156.4, 145.4, 140.1, 134.3, 128.9, 128.4 (2C), 127.9, 127.8 (2C), 127.5, 123.2, 114.3, 113.5, 53.3, 53.0, 43.8, 40.6, 38.1, 27.2 (3C); IR (ATR) 2956, 2829, 1749, 1648, 1601, 1514, 1444, 1430, 1364, 1281, 1243, 1218 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{23}H_{25}NNaO_2^+$ *m*/*z* 370.1778, found *m*/*z* 370.1762



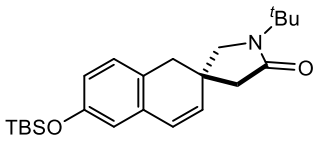
5-Bromo-1'-(*tert*-butyl)-6-hydroxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (2g)

Prepared according to the general procedure A (Method B) using **1g** (37.6 mg) and MS 3Å (100 mg) and isolated as white solid (16.7 mg, 48% yield).: m.p. 205-207 °C; R_f = 0.5 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, CD_3OD) δ 6.96 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 9.6 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.06 (d, *J* = 9.6 Hz, 1H), 3.45 (d, *J* = 10.2 Hz, 1H), 3.41 (d, *J* = 10.2 Hz, 1H), 2.85 (d, *J* = 16.2 Hz, 1H), 2.78 (d, *J* = 16.2 Hz, 1H), 2.37 (d, *J* = 16.2 Hz, 1H), 2.31 (d, *J* = 16.2 Hz, 1H),1.39 (s, 9H); ^{13}C NMR (150 MHz, CD_3OD) δ 176.0, 154.5, 137.4, 134.1, 129.0, 128.2, 127.0, 115.5, 111.1, 56.4, 55.4, 45.9, 39.7, 37.4, 27.9 (3C); IR (ATR) 3373, 2973, 2925, 2485, 2077, 1651, 1471, 1418, 1295, 1217, 1117 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{17}H_{20}BrNNaO_2^+$ *m*/*z* 372.0570, found *m*/*z* 372.0572



1'-(*tert*-Butyl)-6-methoxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (2h)

Prepared according to the general procedure A (Method B) using **1h** (31.1 mg) and MS 3Å (100 mg), and isolated as colorless oil (21.6 mg, 76% yield).; R_f = 0.6 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 2.4 Hz, 1H), 6.44 (d, *J* = 9.6 Hz, 1H), 5.88 (d, *J* = 9.6 Hz, 1H), 5.71 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.80 (s, 3H), 3.37 (d, *J* = 8.4 Hz, 1H), 3.27 (d, *J* = 8.4 Hz, 1H), 2.83 (d, *J* = 16.2 Hz, 1H), 2.81 (d, *J* = 16.2 Hz, 1H), 2.41 (d, *J* = 16.8 Hz, 1H), 2.35 (d, *J* = 16.8 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 158.9, 135.1, 134.1, 129.2, 128.5, 125.2, 112.6, 112.2, 55.5, 55.5, 54.1, 45.8, 38.6, 36.7, 27.9 (3C); IR (ATR) 3352, 2971, 2871, 1682, 1604, 1573, 1494, 1404, 1364, 1300, 1261, 1222 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{18}H_{23}NNaO_2^+$ m/z 308.1621, found m/z 308.1635

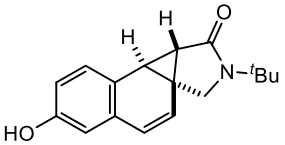


1'-(*tert*-Butyl)-6-((*tert*-butyldimethylsilyl)oxy)-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (2i)

Prepared according to the general procedure A using **1i** (41.2 mg) and MS 3Å (100 mg), and isolated

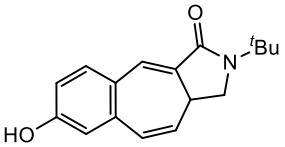
as colorless oil (37.2 mg, 96% yield).; R_f = 0.8 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.4 Hz, 1H), 6.63 (dd, *J* = 8.4, 3.0 Hz, 1H), 6.56 (d, *J* = 3.0 Hz, 1H), 6.39 (d, *J* = 9.6 Hz, 1H), 5.84 (d, *J* = 9.6 Hz, 1H), 3.36 (d, *J* = 9.6 Hz, 1H), 3.27 (d, *J* = 9.6 Hz, 1H), 2.81 (d, *J* = 15.6 Hz, 1H), 2.78 (d, *J* = 15.6 Hz, 1H), 2.39 (d, *J* = 16.2 Hz, 1H), 2.34 (d, *J* = 16.2 Hz, 1H), 1.38 (s, 9H), 0.98 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 154.8, 134.7, 134.1, 129.2, 128.5, 125.8, 118.8, 118.1, 55.6, 54.1, 45.8, 38.7, 36.7, 27.9 (3C), 25.8 (3C), 18.3, -4.3 (2C); IR (ATR) 2957, 2929, 2858, 1747, 1688, 1604, 1568, 1492, 1401, 1363, 1277 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{23}H_{35}NNaO_2Si^+$ *m*/*z* 408.2329, found *m*/*z* 408.2343

Characterization of 3a and 4a



2-(*tert*-Butyl)-7-hydroxy-2,3,9b,9c-tetrahydro-1*H*-naphtho[2',1':1,3]cyclopropa[1,2-*c*]pyrrol-1-one (3a)

Prepared according to general procedure A using $Rh_2(OAc)_4$ (4.4 mg) instead of $AgNTf_2$, and isolated yellow solid (23.7 mg, 88% yield) (preparative thin layer chromatography condition: toluene/EtOAc 2/1).: m.p. 206−208 °C; R_f = 0.4 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 1H), 6.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 6.29 (d, *J* = 9.6 Hz, 1H), 6.08 (br s, 1H), 6.08 (d, *J* = 9.6 Hz, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 3.59 (d, *J* = 10.8 Hz, 1H), 2.56 (d, *J* = 1.8 Hz, 1H), 1.41 (s, 9H), 0.72 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.7, 154.9, 132.4, 130.0, 126.1, 125.4, 124.1, 115.5, 114.7, 54.0, 52.1, 33.4, 28.0, 27.8 (3C), 26.3; IR (ATR) 3250, 2967, 2927, 1708, 1636, 1562, 1486, 1417, 1365, 1277, 1216 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{17}H_{19}NNaO_2^+$ *m*/*z* 292.1308, found *m*/*z* 292.1310.

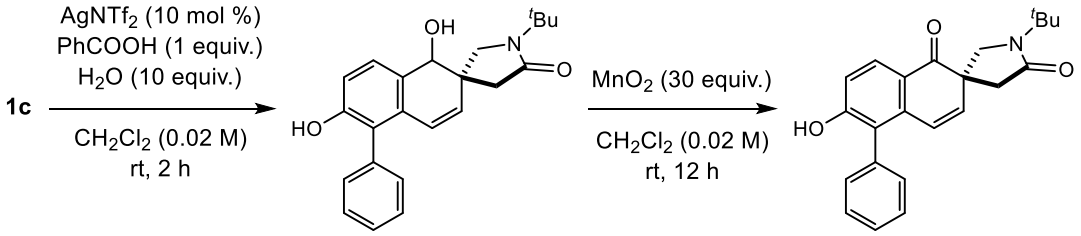


2-(*tert*-Butyl)-7-hydroxy-1,10a-dihydrobenzo[4,5]cyclohepta[1,2-*c*]pyrrol-3(2*H*)-one (4a)

Prepared according to general procedure A using $Rh_2(OAc)_4$ (4.4 mg) instead of $AgNTf_2$, and isolated yellow solid (2.4 mg, 9% yield) (preparative thin layer chromatography condition: toluene/EtOAc 2/1).: m.p. 216−218 °C; R_f = 0.4 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* =

7.6 Hz, 1H), 7.71 (br s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.16 (s, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 5.21 (s, 1H), 4.70 (dd, *J* = 5.2, 2.4 Hz, 1H), 3.28 (dd, *J* = 14.8, 5.2 Hz, 1H), 2.74 (dd, *J* = 14.8, 2.4 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 154.0, 136.2, 134.6, 129.8, 128.8, 127.5, 126.0, 124.3, 118.5, 109.7, 54.9, 53.5, 45.9, 28.3 (3C); IR (ATR) 3287, 2973, 2929, 1711, 1635, 1607, 1446, 1366, 1287, 1226 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{17}H_{19}NNaO_2^+$ *m*/*z* 292.1308, found *m*/*z* 292.1315.

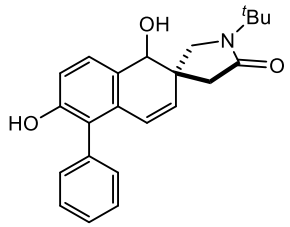
Procedure for Dearomatizative Spirocyclization with Water and Oxidation



5c: 65% (76:24 dr) **6c**: 61%

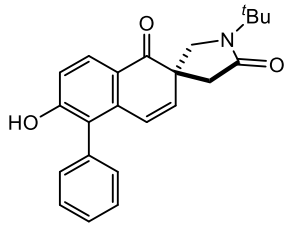
A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with $AgNTf_2$ (5.8 mg, 0.015 mmol, 10 mol%), benzoic acid (18.3 mg, 0.15 mmol, 1 equiv.), and H_2O (27 μL, 1.5 mmol, 10 equiv.), which were subsequently dissolved partially in CH_2Cl_2 (1.5 mL) under an argon gas atmosphere. Diazo compound **1c** (56.0 mg, 0.15 mmol) in CH_2Cl_2 (6 mL) was added slowly over 0.5 h *via* a syringe pump to the suspension at room temperature, and the reaction mixture was stirred for 0.5 h at the same temperature. The reaction was quenched with the addition of water. The aqueous solution was extracted with CH_2Cl_2×2. The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; gradient elution: *n*-hexane/EtOAc, 1/1 → 1/3) to afford spirocyclic compound **5c** as colorless oil (35.5 mg, 65% yield, 76:24 dr)**.**

A pre-dried 30 mL eggplant-shaped flask were equipped with a magnetic stir bar was charged with **7c** (35.3 mg, 0.098 mmol), which was subsequently dissolved in CH_2Cl_2 (4.9 mL) under an argon gas atmosphere. To a stirred solution was added MnO_2 (252.1 mg, 2.9 mmol, 30 equiv.), and the reaction mixture was stirred for 12 h at room temperature. The reaction was diluted with CH_2Cl_2, filtrated through Celite®. The filtrate was concentrated under reduced pressure, and purified by flash column chromatography (*n*-hexane/EtOAc, 1/2) to afford spirocyclic compound **6c** as pale yellow solid (21.8 mg, 61% yield)**.**



1'-(*tert*-Butyl)-1,6-dihydroxy-5-phenyl-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (5c)

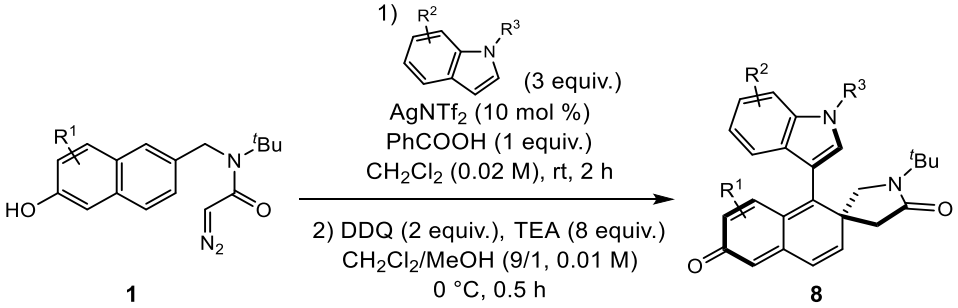
R_f = 0.2 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (600 MHz, CD_3OD) δ 7.40 (br s, 1H), 7.40 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 9.6 Hz, 1H), 7.26-7.19 (m, 1H), 7.16 (d, *J* = 9.6 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.19 (d, *J* = 9.6 Hz, 1H), 5.81 (d, *J* = 9.6 Hz, 1H), 4.44 (s, 1H), 3.97 (d, *J* = 10.2 Hz, 1H), 3.39 (d, *J* = 10.2 Hz, 1H), 2.51 (d, *J* = 16.2 Hz, 1H), 2.12 (d, *J* = 16.2 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (150 MHz, CD_3OD) δ 176.1, 155.9, 137.5, 134.8, 132.6, 132.0, 131.9, 131.8, 129.4, 129.3, 129.0, 128.1, 128.0, 126.6, 115.2, 74.7, 55.5, 53.1, 44.1, 42.3, 27.9 (3C) (NMR data of major diastereomer of **7c** were shown.); IR (ATR) 2970, 2950, 1746, 1714, 1666, 1646, 1369, 1316, 1284 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{23}H_{25}NNaO_3^+$ *m*/*z* 386.1727, found *m*/*z* 386.1727.



1'-(*tert*-Butyl)-6-hydroxy-5-phenyl-1*H*-spiro[naphthalene-2,3'-pyrrolidine]-1,5'-dione (6c)

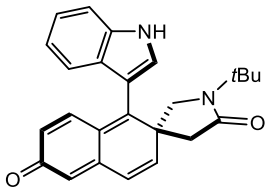
m.p. 235−237 °C; R_f = 0.4 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 6.0 Hz, 1H), 7.53 (d, *J* = 6.0 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.69 (br s, 1H), 6.32 (d, *J* = 10.2 Hz, 1H), 6.18 (d, *J* = 10.2 Hz, 1H), 3.86 (d, *J* = 9.6 Hz, 1H), 3.33 (d, *J* = 9.6 Hz, 1H), 2.94 (d, *J* = 16.2 Hz, 1H), 2.30 (d, *J* = 16.2 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.7, 172.4, 159.6, 137.6, 136.8, 133.2, 131.0, 130.8, 129.6, 129.5 (2C), 128.9, 125.8, 122.4, 122.2, 115.7, 55.3, 54.7, 47.0, 44.4, 27.8 (3C); IR (ATR) 2971, 2751, 2702, 2665, 1745, 1656, 1565, 1434, 1409, 1304, 1262, 1207, 1088 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{23}H_{23}NNaO_3^+$ *m*/*z* 384.1570, found *m*/*z* 384.1572.

General Procedure B for One-pot Tandem Oxidative Dearomatizing Spirocyclization



A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with $AgNTf_2$ (3.9 mg, 0.01 mmol, 10 mol%), an indole derivative (0.3 mmol, 3 equiv.), benzoic acid (12.2 mg, 0.1 mmol, 1 equiv.), and **1** (0.1 mmol), which were subsequently dissolved partially in CH_2Cl_2 (5 mL) under an argon gas atmosphere. The reaction mixture was stirred for 2 h at room temperature, and then cooled to 0 °C in an ice bath. TEA (111.5 μL, 0.8 mmol, 8 equiv.), MeOH (1 mL), and DDQ (45.4 mg, 0.2 mmol, 2 equiv.) in CH_2Cl_2 (4 mL) was added dropwise to the reaction mixture, and stirring was continued for 0.5 h at the same temperature. The reaction was quenched with the addition of 1 N aqueous NaOH. The aqueous solution was extracted with CH_2Cl_2×3, and the combined organic layers were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; diol SiO_2, gradient elution: *n*-hexane/EtOAc, 2/1 → 1/4) to afford **8**.

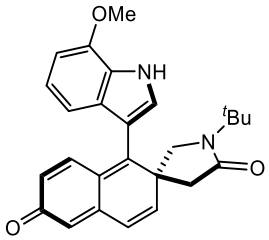
NMR data of major diastereomers of **8a-i**, **k**, **l** and **9a** were shown.



1'-(*tert*-Butyl)-1-(1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8a)

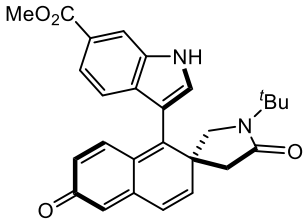
Prepared according to the general procedure B using **1a** and indole, and isolated as orange solid (37.4 mg, 97% yield).: m.p. 159-161 °C; R_f = 0.2 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.32 (br s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.27 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.16 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.01 (d, *J* = 9.6 Hz, 1H), 6.66 (d, *J* = 9.6 Hz, 1H), 6.35 (d, *J* = 9.6 Hz, 1H), 6.29 (d, *J* = 1.8 Hz, 1H), 6.24 (d, *J* = 9.6, 1.8 Hz, 1H), 3.51 (d, *J* = 10.8 Hz, 1H), 3.45 (d, *J* = 10.8 Hz, 1H), 2.91 (d, *J* = 18.0 Hz, 1H), 2.80 (d, *J* = 18.0 Hz, 1H), 0.84 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 172.3, 153.8, 140.2, 139.6, 137.4, 135.6, 129.5, 128.7, 128.1, 126.1,

124.0, 123.4, 123.3, 121.3, 118.9, 111.9, 110.5, 54.8, 54.2, 44.5, 43.1, 27.0 (3C); IR (ATR) 3134, 2971, 2923, 1748, 1672, 1621, 1549, 1509, 1453, 1410, 1217 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{25}H_{24}N_2NaO_2^+$ *m*/*z* 407.1730, found *m*/*z* 407.1739.



1'-(*tert*-Butyl)-1-(7-methoxy-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8b)

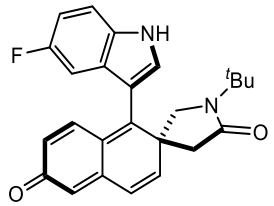
Prepared according to the general procedure B using **1a** and 7-methoxyindole, and isolated as orange solid (39.6 mg, 95% yield).: m.p. 155-156 °C; R_f = 0.2 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (br s, 1H), 7.29 (d, *J* = 1.8 Hz, 1H), 7.08 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.00 (d, *J* = 10.2 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 9.0 Hz, 1H), 6.35 (d, *J* = 9.0 Hz, 1H), 6.28 (d, *J* = 1.8 Hz, 1H), 6.23 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.99 (s, 3H), 3.47 (d, *J* = 10.2 Hz, 1H), 3.44 (d, *J* = 10.2 Hz, 1H), 2.91 (d, *J* = 17.4 Hz, 1H), 2.73 (d, *J* = 17.4 Hz, 1H), 0.88 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 172.1, 153.5, 146.5, 140.5, 139.6, 137.4, 129.9, 129.4, 128.2, 126.2, 125.9, 124.0, 122.8, 121.1, 111.5, 111.1, 102.9, 55.7, 54.7, 54.2, 44.5, 43.0, 27.1 (3C); IR (ATR) 3204, 2925, 2853, 1746, 1668, 1620, 1544, 1420, 1366, 1217 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{26}H_{26}N_2NaO_3^+$ *m*/*z* 437.1836, found *m*/*z* 437.1843.



Methyl 3-(1'-(*tert*-butyl)-5',6-dioxo-6*H*-spiro[naphthalene-2,3'-pyrrolidin]-1-yl)-1*H*-indole-6-carboxylate (8c)

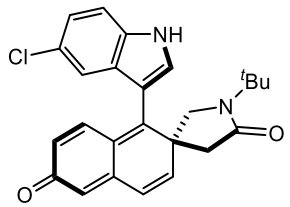
Prepared according to the general procedure B using **1a** and methyl indole-6-carboxylate, and isolated as orange solid (36.1 mg, 82% yield).: m.p. 155-156 °C; R_f = 0.1 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.21 (br s, 1H), 8.28 (d, *J* = 1.8 Hz, 1H), 7.86 (dd, *J* = 10.2, 1.8 Hz, 1H), 7.50 (d, *J* = 3.0 Hz, 1H), 7.34 (d, *J* = 10.2 Hz, 1H), 6.93 (d, *J* = 10.2 Hz, 1H), 6.67 (d, *J* = 9.6 Hz, 1H), 6.35 (d, *J* = 9.6 Hz, 1H), 6.30 (d, *J* = 1.8 Hz, 1H), 6.24 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.97 (s, 3H), 3.55 (d, *J* = 11.4 Hz, 1H), 3.43 (d, *J* = 11.4 Hz, 1H), 2.90 (d, *J* = 17.4 Hz, 1H), 2.85 (d, *J* = 17.4 Hz, 1H), 0.82

(s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 172.4, 168.0, 152.6, 140.0, 139.5, 137.0, 135.1, 132.0, 129.7, 128.3, 126.8, 126.3, 124.9, 124.2, 122.2, 118.5, 114.6, 110.6, 54.8, 54.3, 52.4, 44.4, 43.2, 27.0 (3C); IR (ATR) 3208, 2972, 2918, 1709, 1661, 1618, 1544, 1434, 1311, 1274, 1214 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{27}H_{26}N_2NaO_4^+$ *m*/*z* 465.1785, found *m*/*z* 465.1774.



1'-(*tert*-Butyl)-1-(5-fluoro-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8d)

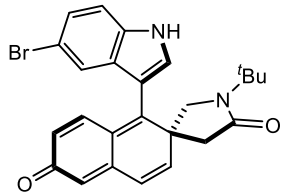
Prepared according to the general procedure B using **1a** and 5-fluoroindole, and isolated as pale orange solid (34.9 mg, 87% yield).: m.p. 206-208 °C; R_f = 0.2 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.56 (br s, 1H), 7.42 (dd, *J* = 9.0, 5.4 Hz, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.02 (ddd, *J* = 9.0, 9.0, 1.8 Hz, 1H), 6.98 (d, *J* = 10.2 Hz, 1H), 6.95 (dd, *J* = 9.0, 1.8 Hz, 1H), 6.66 (d, *J* = 9.6 Hz, 1H), 6.34 (d, *J* = 9.6 Hz, 1H), 6.29 (d, *J* = 1.8 Hz, 1H), 6.26 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.53 (d, *J* = 10.8 Hz, 1H), 3.41 (d, *J* = 10.8 Hz, 1H), 2.89 (d, *J* = 17.4 Hz, 1H), 2.82 (d, *J* = 17.4 Hz, 1H), 0.86 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 172.4, 158.1, 152.9, 140.0, 139.5, 137.1, 132.1, 129.7, 129.0 (dd, *J* = 10.1 Hz), 128.1, 126.2, 125.2, 124.2, 112.9 (d, *J* = 10.1 Hz), 111.9 (d, *J* = 25.8 Hz), 110.5 (d, *J* = 4.4 Hz), 103.7 (d, *J* = 24.5 Hz), 54.8, 54.3, 44.4, 43.2, 27.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -121.9; IR (ATR) 3167, 3111, 2971, 2926, 1739, 1669, 1615, 1542, 1417, 1231 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{25}H_{23}FN_2NaO_2^+$ *m*/*z* 425.1636, found *m*/*z* 425.1632.



1'-(*tert*-Butyl)-1-(5-chloro-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8e)

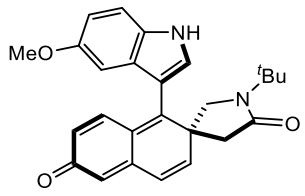
Prepared according to the general procedure B using **1a** and 5-chloroindole, and isolated as pale orange solid (34.6 mg, 83% yield).: m.p. 235-237 °C; R_f = 0.1 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.79 (br s, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.27 (s, 1H), 7.22 (d, *J* = 9.0 Hz, 1H), 6.95 (d, *J* = 10.2 Hz, 1H), 6.67 (d, *J* = 9.6 Hz, 1H), 6.34 (d, *J* = 9.6 Hz, 1H), 6.30 (s, 1H), 6.27 (d, *J* = 10.2 Hz, 1H), 3.55 (d, *J* = 10.2 Hz, 1H), 3.43 (d, *J* = 10.2 Hz, 1H), 2.87 (d, *J* = 17.4 Hz,

1H), 2.83 (d, J = 17.4 Hz, 1H), 0.86 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 172.4, 152.6, 140.0, 139.5, 137.0, 134.0, 129.8, 129.6, 128.3, 127.1, 126.3, 124.8, 124.2, 123.7, 118.1, 113.2, 110.0, 54.9, 54.3, 44.3, 43.3, 27.0 (3C); IR (ATR) 3104, 2971, 2924, 2877, 1739, 1668, 1612, 1541, 1508, 1416, 1217 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{25}H_{23}ClN_2NaO_2^+$ *m*/*z* 441.1340, found *m*/*z* 441.1336.



1-(5-Bromo-1*H*-indol-3-yl)-1'-(*tert*-butyl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8f)

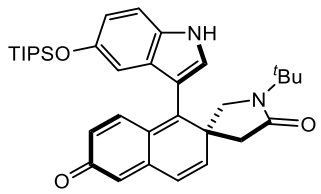
Prepared according to the general procedure B using **1a** and 5-bromoindole, and isolated as pale orange solid (36.6 mg, 79% yield).: m.p. 238-240 °C; R_f = 0.2 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.54 (br s, 1H), 7.43 (s, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.38-7.35 (m, 1H), 7.32 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 10.2 Hz, 1H), 6.66 (d, J = 9.6 Hz, 1H), 6.33 (d, J = 9.6 Hz, 1H), 6.30 (d, J = 1.8 Hz, 1H), 6.27 (dd, J = 10.2, 1.8 Hz, 1H), 3.54 (d, J = 10.2 Hz, 1H), 3.43 (d, J = 10.2 Hz, 1H), 2.86 (d, J = 17.4 Hz, 1H), 2.81 (d, J = 17.4 Hz, 1H), 0.85 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 172.3, 152.4, 140.0, 139.4, 136.9, 134.3, 130.2, 129.9, 128.4, 126.3, 126.3, 124.7, 124.3, 121.2, 114.5, 113.5, 110.0, 54.9, 54.3, 44.3, 43.3, 27.0 (3C); IR (ATR) 3213, 2971, 2924, 1746, 1673, 1610, 1541, 1507, 1413, 1218 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{25}H_{23}BrN_2NaO_2^+$ *m*/*z* 485.0835, found *m*/*z* 485.0842.



1'-(*tert*-Butyl)-1-(5-methoxy-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8g)

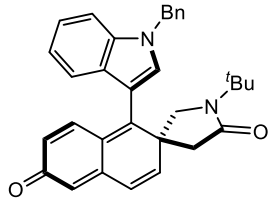
Prepared according to the general procedure B using **1a**, 5-methoxyindole, and 3 equiv. of DDQ and isolated as orange solid (34.2 mg, 82% yield).: m.p. 173-175 °C; R_f = 0.2 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.06 (br s, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.28 (s, 1H), 7.04 (d, J = 10.2 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.65 (s, 1H), 6.65 (d, J = 9.6 Hz, 1H), 6.35 (d, J = 9.6 Hz, 1H), 6.29 (s, 1H), 6.26 (d, J = 10.2 Hz, 1H), 3.76 (s, 3H), 3.50 (d, J = 10.8 Hz, 1H), 3.42 (d, J = 10.8 Hz, 1H), 2.90

(d, J = 16.8 Hz, 1H), 2.78 (d, J = 16.8 Hz, 1H), 0.88 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 172.3, 157.0, 155.5, 140.3, 139.7, 137.5, 130.7, 129.4, 129.1, 127.8, 126.1, 124.1, 124.0, 113.5, 112.7, 110.3, 100.4, 56.1, 54.9, 54.3, 44.5, 43.1, 27.1 (3C); IR (ATR) 3647, 3469, 3229, 2939, 1739, 1658, 1616, 1544, 1486, 1422, 1288, 1217 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{26}H_{26}N_2NaO_3^+$ m/z 437.1836, found m/z 437.1849.



1'-(*tert*-Butyl)-1-(5-((triisopropylsilyl)oxy)-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8h)

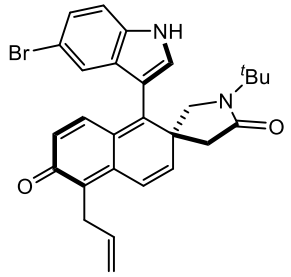
Prepared according to the general procedure B using **1a** and 5-((triisopropylsilyl)oxy)-indole, and isolated as orange solid (47.1 mg, 83% yield).: m.p. 156-158 °C; R_f = 0.3 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.98 (br s, 1H), 7.30 (d, J = 1.2 Hz, 1H), 7.30 (d, J = 9.0 Hz, 1H), 7.03 (d, J = 9.6 Hz, 1H), 6.88 (dd, J = 9.0, 1.8 Hz, 1H), 6.68 (d, J = 1.8 Hz, 1H), 6.65 (d, J = 9.6 Hz, 1H), 6.35 (d, J = 9.6 Hz, 1H), 6.29 (d, J = 1.8 Hz, 1H), 6.23 (dd, J = 9.6, 1.8 Hz, 1H), 3.48 (d, J = 10.2 Hz, 1H), 3.35 (d, J = 10.2 Hz, 1H), 2.93 (d, J = 18.0 Hz, 1H), 2.78 (d, J = 18.0 Hz, 1H), 1.20 (sep, J = 7.8 Hz, 3H), 1.05 (d, J = 7.8 Hz, 18H), 0.91 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 172.3, 153.7, 151.3, 140.2, 139.6, 137.6, 130.7, 129.6, 129.4, 127.7, 126.0, 124.2, 123.9, 117.5, 112.2, 110.2, 107.7, 54.8, 54.3, 44.4, 43.0, 27.1 (3C), 18.1 (6C), 12.7 (3C); IR (ATR) 2942, 2865, 1746, 1672, 1621, 1543, 1469, 1419, 1365, 1217 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{34}H_{44}N_2NaO_3Si^+$ m/z 579.3013, found m/z 579.3002.



1-(1-Benzyl-1*H*-indol-3-yl)-1'-(*tert*-butyl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8i)

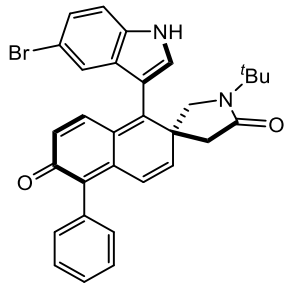
Prepared according to the general procedure B using **1a** and *N*-benzylindole, and isolated as pale orange solid (37.4 mg, 79% yield).: m.p. 90-91 °C; R_f = 0.2 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.34 (m, 3H), 7.30 (dd, J = 7.2, 7.2 Hz, 2H), 7.29 (s, 1H), 7.24 (d, J = 7.2 Hz, 2H), 7.16 (d, J = 6.6 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 9.6 Hz, 1H), 6.63 (d, J = 9.6 Hz,

1H), 6.35 (d, *J* = 9.6 Hz, 1H), 6.27 (d, *J* = 2.4 Hz, 1H), 6.25 (dd, *J* = 9.6, 2.4 Hz, 1H), 5.39 (d, *J* = 15.0 Hz, 1H), 5.32 (d, *J* = 15.0 Hz, 1H), 3.47 (d, *J* = 10.4 Hz, 1H), 3.43 (d, *J* = 10.4 Hz, 1H), 2.91 (d, *J* = 17.4 Hz, 1H), 2.72 (d, *J* = 17.4 Hz, 1H), 0.86 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 172.0, 153.5, 140.2, 139.6, 137.4, 136.4, 135.9, 129.4, 129.4, 129.1 (2C), 128.2, 128.1, 127.4, 127.3 (2C), 125.8, 123.9, 123.1, 121.2, 119.3, 110.5, 109.8, 54.7, 54.1, 50.7, 44.4, 42.9, 27.0 (3C); IR (ATR) 3029, 2970, 2927, 1746, 1680, 1625, 1550, 1455, 1415, 1218 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{32}H_{30}N_2NaO_2^+$ *m*/*z* 497.2199, found *m*/*z* 497.2210.



5-Allyl-1-(5-bromo-1*H*-indol-3-yl)-1'-(*tert*-butyl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8j)

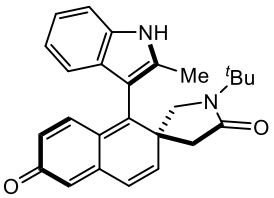
Prepared according to the general procedure B using 5-bromoindole and **1b** which was added slowly over 0.5 h *via* a syringe pump at room temperature, and isolated as yellow solid (42.2 mg, 84% yield).: m.p. 187-189 °C; R_f = 0.4 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (br s, 1H), 7.43 (s, 1H), 7.35 (d, *J* = 4.0 Hz, 1H), 7.35 (d, *J* = 2.8 Hz, 1H), 7.29 (d, *J* = 2.8 Hz, 1H), 6.98 (d, *J* = 10.4 Hz, 1H), 6.93 (d, *J* = 10.0 Hz, 1H), 6.34 (d, *J* = 10.0 Hz, 1H), 6.28 (d, *J* = 10.4 Hz, 1H), 5.90 (ddt, *J* = 17.2, 10.0, 6.4 Hz, 1H), 5.09 (dd, *J* = 17.2, 2.4 Hz, 1H), 5.05 (dd, *J* = 10.0, 2.4 Hz, 1H), 3.53 (d, *J* = 10.8 Hz, 1H), 3.46 (d, *J* = 6.4 Hz, 2H), 3.44 (d, *J* = 10.8 Hz, 1H), 2.84 (d, *J* = 18.4 Hz, 1H), 2.80 (d, *J* = 18.4 Hz, 1H), 0.84 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 172.5, 151.1, 139.4, 136.5, 135.7, 134.8, 134.4, 131.7, 130.4, 129.0, 128.7, 126.1, 124.6, 123.3, 121.3, 115.6, 114.3, 113.5, 110.3, 55.0, 54.2, 43.6, 28.8, 27.8, 27.0 (3C); IR (ATR) 3214, 2979, 2922, 1667, 1617, 1548, 1419, 1361, 1210 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{28}H_{27}BrN_2NaO_2^+$ *m*/*z* 525.1148, found *m*/*z* 525.1172.



1-(5-Bromo-1*H*-indol-3-yl)-1'-(*tert*-butyl)-5-phenyl-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-

5',6-dione (8k)

Prepared according to the general procedure B using 5-bromoindole and **1c** which was added slowly over 0.5 h *via* a syringe pump at room temperature, and isolated as pale orange solid (40.2 mg, 74% yield).: m.p. 185-186 °C; R_f = 0.4 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.07 (br s, 1H), 7.49 (s, 1H), 7.46 (dd, *J* = 6.0, 7.2 Hz, 2H), 7.40-7.32 (m, 4H), 7.26 (s, 2H),0.85 (s, 9H), 7.03 (d, *J* = 9.6 Hz, 1H), 6.65 (d, *J* = 9.6 Hz, 1H), 6.37 (d, *J* = 9.6 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 3.51 (d, *J* = 10.8 Hz, 1H), 3.46 (d, *J* = 10.8 Hz, 1H), 2.89 (d, *J* = 17.4 Hz, 1H), 2.88 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.3, 172.4, 152.8, 139.5, 136.8, 135.0, 135.0, 134.5, 134.4, 130.7, 130.6, 130.3, 129.4, 128.6, 128.4, 128.3, 128.0, 126.0, 124.8, 124.6, 121.2, 114.3, 113.7, 110.0, 55.0, 54.3, 43.9, 43.4, 27.0 (3C); IR (ATR) 3238, 2972, 2923, 2864, 1745, 1669, 1622, 1541, 1456, 1415, 1362, 1215 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{31}H_{27}BrN_2NaO_2^+$ *m*/*z* 561.1148, found *m*/*z* 561.1135.



1-(1-Benzyl-1*H*-indol-3-yl)-1'-(*tert*-butyl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (8l)

Prepared according to the general procedure B using **1a** and 2-methylindole.

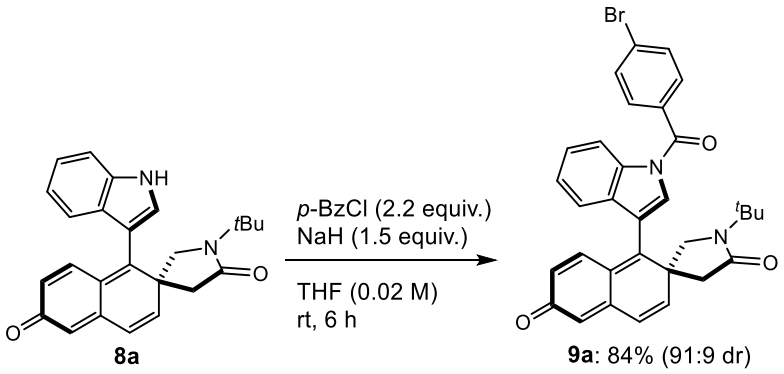
Major atropisomer: Orange solid (22.6 mg, 58% yield): m.p. 174-176 °C; R_f = 0.2 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (br s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.20 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.10 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.82 (d, *J* = 9.6 Hz, 1H), 6.67 (d, *J* = 10.8 Hz, 1H), 6.50 (d, *J* = 9.6 Hz, 1H), 6.29 (d, *J* = 2.4 Hz, 1H), 6.22 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.87 (d, *J* = 9.6 Hz, 1H), 3.42 (d, *J* = 9.6 Hz, 1H), 2.83 (d, *J* = 16.8 Hz, 1H), 2.45 (d, *J* = 16.8 Hz, 1H), 2.33 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 172.0, 153.5, 140.0, 139.7, 136.6, 135.6, 133.5, 131.3, 129.9, 129.5, 125.8, 124.0, 122.4, 120.8, 118.5, 111.1, 108.0, 54.3, 54.2, 47.4, 43.4, 27.3 (3C), 13.4; IR (ATR) 3272, 2973, 2925, 1747, 1670, 1621, 1524, 1456, 1228 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{26}H_{26}N_2NaO_2^+$ *m*/*z* 421.1886, found *m*/*z* 421.1893.

Minor atropisomer: Orange solid (16.7 mg, 42% yield): m.p. 183-184 °C; R_f = 0.3 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (br s, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.21 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.78 (d, *J* = 9.6 Hz, 1H), 6.67 (d, *J* = 10.8 Hz, 1H), 6.61 (d, *J* = 10.2 Hz, 1H), 6.30 (s, 1H), 6.23 (d, *J* = 9.6 Hz, 1H), 3.70 (d, *J* = 9.0 Hz, 1H), 3.29 (d, *J* = 9.0 Hz, 1H), 3.14 (d, *J* = 15.6 Hz, 1H), 2.33 (d, *J* = 15.6 Hz, 1H), 2.26 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 171.9, 153.1, 139.8, 139.6, 136.6, 135.5, 132.9, 132.4,

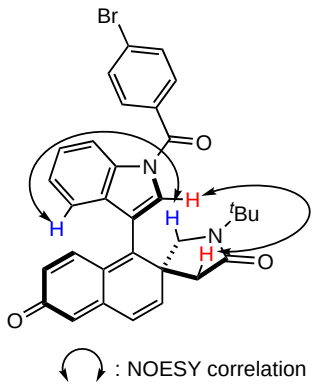
130.0, 129.4, 125.4, 123.9, 122.7, 121.2, 119.4, 110.9, 108.4, 54.5, 53.7, 48.0, 43.7, 27.8 (3C), 13.0; IR (ATR) 3272, 2972, 2924, 1746, 1671, 1621, 1523, 1456, 1228 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{26}H_{26}N_2NaO_2^+$ *m*/*z* 421.1886, found *m*/*z* 421.1882.

The relative configurations of **8l** were determined by NOESY experiments.

Preparation of 9a



A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with **8a** (19.2 mg, 0.05 mmol), which was subsequently dissolved in THF (2.5 mL) under an argon gas atmosphere. NaH (5 mg, 0.125 mmol, 1.5 equiv.) was added to the solution at 0 °C in an ice bath, and the reaction mixture was stirred for 0.5 h at room temperature. The resulting solution was cooled to 0 °C in an ice bath, *para*-bromo-benzoyl chloride (24.2 mg, 0.11 mmol, 2.2 equiv.) was then added, and stirring was continued for 6 h at room temperature. The reaction was quenched with the addition of water. The aqueous solution was extracted with EtOAc×2. The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; diol SiO_2, gradient elution: *n*-hexane/EtOAc = 3/1 → 2/1) to give **9a** as yellow solid (23.8 mg, 84% yield).

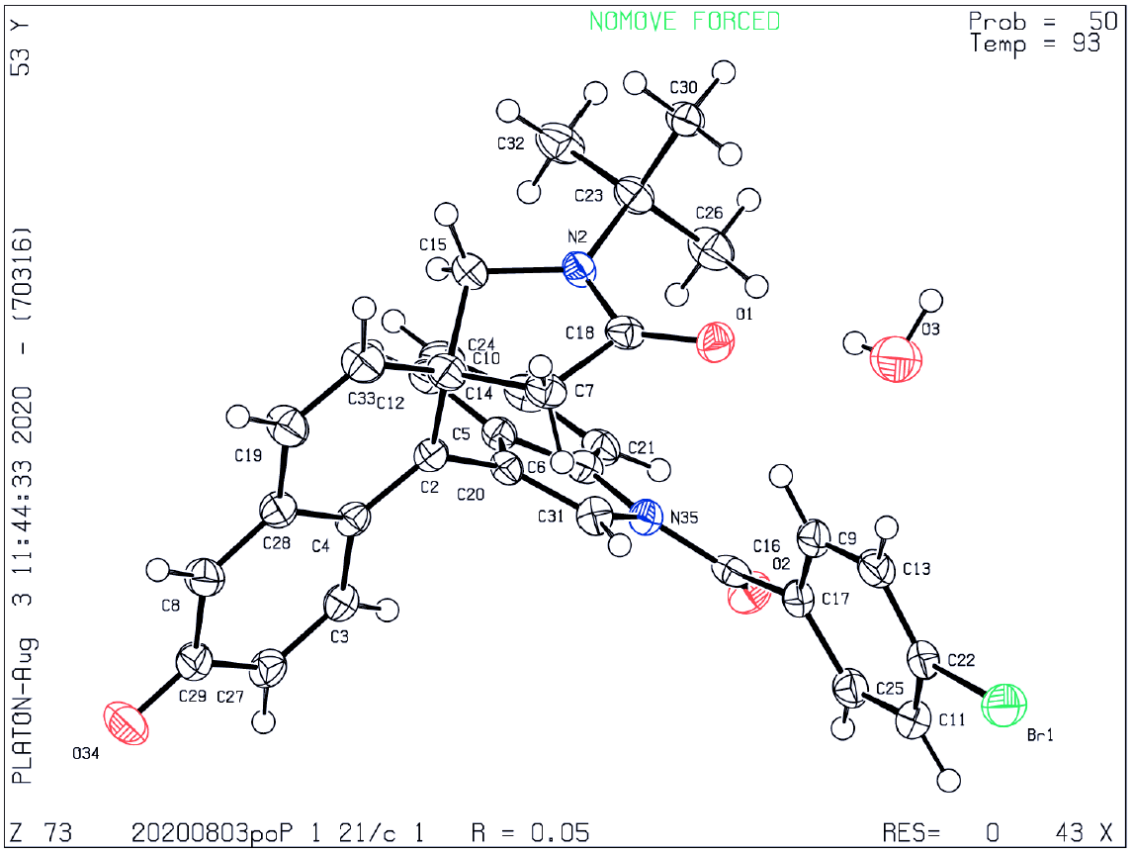


1-(1-(4-Bromobenzoyl)-1*H*-indol-3-yl)-1'-(*tert*-butyl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (9a)

m.p. 157-159 °C; R_f = 0.4 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 9.0 Hz, 2H), 7.51 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.39 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.35 (s, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 9.6 Hz, 1H), 6.65 (d, *J* = 9.6 Hz, 1H), 6.30 (d, *J* = 9.6 Hz, 1H), 6.27 (d, *J* = 1.2 Hz, 1H), 6.23 (dd, *J* = 9.6, 1.2 Hz, 1H), 3.56 (d, *J* = 10.4 Hz, 1H), 3.53 (d, *J* = 10.4 Hz, 1H), 2.80 (d, *J* = 17.4 Hz, 1H), 2.64 (d, *J* = 17.4 Hz, 1H), 0.84 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.5, 172.0, 167.9, 149.6, 139.6, 138.9, 136.0, 135.7, 132.4 (2C), 132.4, 131.5, 131.3 (2C), 130.2, 128.7, 127.7, 126.6, 126.5, 125.5, 125.4, 124.5, 119.2, 117.3, 116.5, 54.5, 54.1, 44.3, 43.3, 27.0 (3C); IR (ATR) 2976, 1690, 1670, 1626, 1585, 1450, 1362, 1332, 1261, 1224 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{32}H_{27}BrN_2NaO_3^+$ *m*/*z* 589.1097, found *m*/*z* 589.1105.

3. X-ray Crystallographic Data

ORTEP of **9a**, CCDC No. 2031608



The ellipsoid contour probability level in the ORTEP is 50%. Experimental

Data Collection

A colorless block crystal of C32H29BrN2O4 having approximate dimensions of 0.200 x 0.200 x 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated Cu-Ka radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 7.77343(14) Å

b = 13.7756(3) Å b = 90.465(6)°

c = 24.8433(5) Å

V = 2660.22(8) Å^3

For Z = 4 and F.W. = 585.50, the calculated density is 1.462 g/cm^3. The reflection conditions of:

h0l: l = 2n

0k0: k = 2n

uniquely determine the space group to be:

$P2_1/c$ (#14)

The data were collected at a temperature of -180 ± 1°C to a maximum 2q value of 136.4°. A total of 45 oscillation images were collected. A sweep of data was done using w scans from 80.0 to 260.0° in 20.00° step, at c=54.0° and f = 0.0°. The exposure rate was 6.0 [sec./°]. A second sweep was performed using w scans from 80.0 to 260.0° in 20.00° step, at c=54.0° and f = 90.0°. The exposure rate was 6.0 [sec./°]. Another sweep was performed using w scans from 80.0 to 260.0° in 20.00° step, at c=54.0° and f = 180.0°. The exposure rate was 6.0 [sec./°]. Another sweep was performed using w scans from 80.0 to 260.0° in 20.00° step, at c=54.0° and f = 270.0°. The exposure rate was 6.0 [sec./°]. Another sweep was performed using w scans from 80.0 to 260.0° in 20.00° step, at c=0.0° and f = 0.0°. The exposure rate was 6.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

EXPERIMENTAL DETAILS

The sample for X-ray crystal structure analysis was prepared by condensation method. A pre-dried 1 mL sample tube was charged with **9a**, which was dissolved in CH_2Cl_2. The sample tube was left to stand in a 5 mL sample tube charged with argon gas until a single crystal forms.

A. Crystal Data

Empirical Formula	$C_{32}H_{29}BrN_2O_4$
Formula Weight	585.50
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.200 X 0.200 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 7.77343(14) Å b = 13.7756(3) Å c = 24.8433(5) Å b = 90.465(6) ° V = 2660.22(8) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.462 g/cm^3
F_{000}	1208.00
m(CuKa)	24.469 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID

Radiation	CuKa (l = 1.54187 Å) multi-layer mirror monochromated
Voltage, Current	40kV, 30mA
Temperature	-180.0°C
Detector Aperture	460.0 x 256.0 mm
Data Images	45 exposures
w oscillation Range (c=54.0, f=0.0)	80.0 - 260.0°
Exposure Rate	6.0 sec./°
w oscillation Range (c=54.0, f=90.0)	80.0 - 260.0°
Exposure Rate	6.0 sec./°
w oscillation Range (c=54.0, f=180.0)	80.0 - 260.0°
Exposure Rate	6.0 sec./°
w oscillation Range (c=54.0, f=270.0)	80.0 - 260.0°
Exposure Rate	6.0 sec./°
w oscillation Range (c=0.0, f=0.0)	80.0 - 260.0°
Exposure Rate	6.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2q_{max}$	136.4°

No. of Reflections Measured	Total: 29736 Unique: 4860 (R_{int} = 0.0614)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.582 - 0.783)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	S w $(Fo^2 - Fc^2)^2$
Least Squares Weights	w = 1/ [$s^2(Fo^2)$ + $(0.0461 \cdot P)^2$ + 2.4256 · P] where P = $(Max(Fo^2,0) + 2Fc^2)/3$
$2q_{max}$ cutoff	136.4°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	4860
No. Variables	360
Reflection/Parameter Ratio	13.50
Residuals: R1 (I>2.00s(I))	0.0501
Residuals: R (All reflections)	0.0801

Residuals: wR2 (All reflections)	0.1172
Goodness of Fit Indicator	1.047
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.82 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.57 $e^-/Å^3$

4. Additional Studies on F^- Anion Sensor

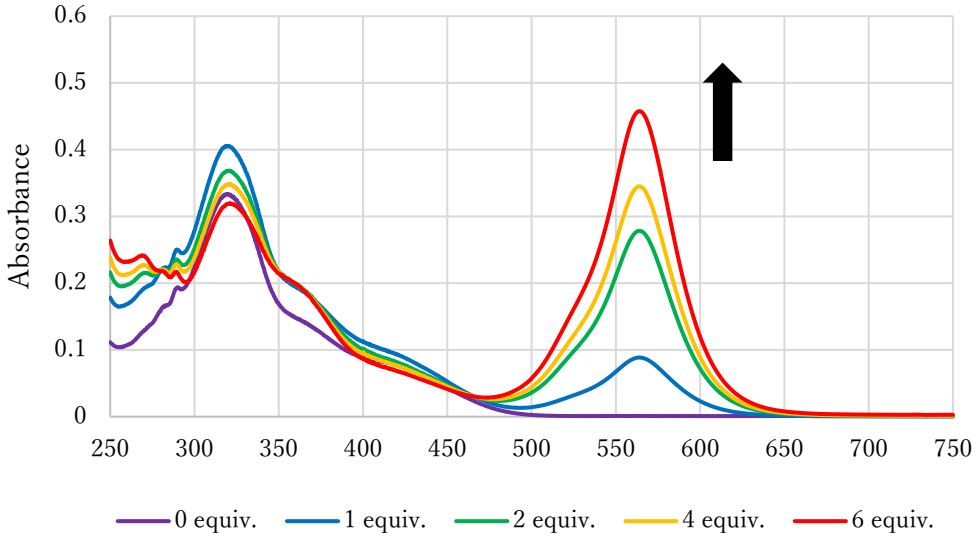
Figure S1. Additional Colorimetric Experiments

free (8a only) **F^- (1 eq.)** **F^- (10 eq.)**

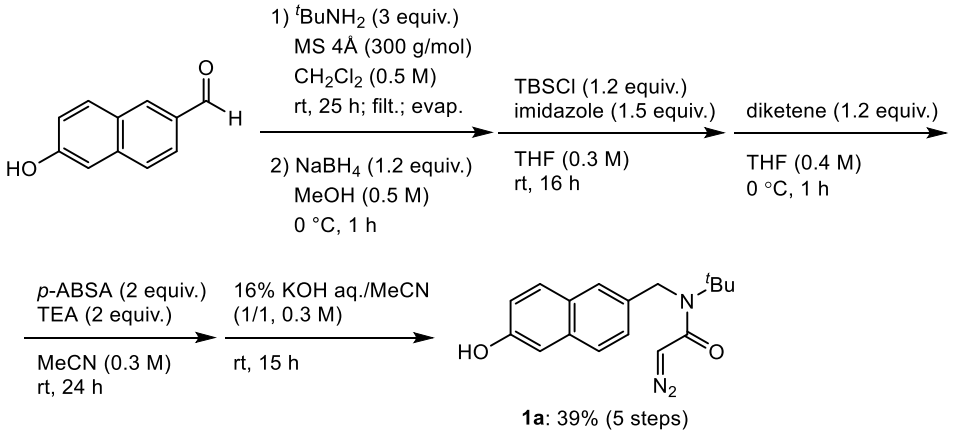
conditions: **8a** (0.19 mg, 0.5 μmol), TBAF (1 M in THF) (0.5 μL, 0.5 μmol, 1 equiv. or 5 μL, 5 μmol, 10 equiv.), MeCN (10 mL, 0.05 mM)

Figure S2. Additional UV/vis Spectra Experiments

UV/vis spectra of **8a** recorded in MeCN (0.017 mM) after addition of TBAF (1 M in THF, 0-6 equiv.).



5. Synthesis and Characterization of Substrates 1a-1i



1a: 39% (5 steps)

To a stirred suspension of 6-hydroxy-2-naphthaldehyde (860.9 mg, 5 mmol) and activated MS 4Å (1500 mg, 300 g/mol) in CH_2Cl_2 (10 mL) was added $^tBuNH_2$ (1.6 mL, 15 mmol, 3 equiv.), and the reaction mixture was stirred for 25 h at room temperature. The mixture was then filtered through Celite® and concentrated under reduced pressure to remove CH_2Cl_2. MeOH (10 mL) was added to the residue. The resulting solution was cooled to 0 °C in an ice bath, $NaBH_4$ (227 mg, 6 mmol, 1.2 equiv.) was then added, and stirring was continued for 1 h at 0 °C. The reaction was quenched with the addition of water and concentrated under reduced pressure to remove most of the MeOH. The aqueous solution was extracted with EtOAc×3, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford crude secondary amine (750.4 mg), which was used for the next step without further purification.

To a stirred solution of crude secondary amine and imidazole (333.6 mg, 4.9 mmol, 1.5 equiv.) in THF (11 mL) was added TBSCl (587.8 mg, 3.9 mmol, 1.2 equiv.) at 0 °C in an ice bath. After being stirred for 16 h at room temperature, saturated aqueous NH_4Cl was added. The reaction mixture was extracted with EtOAc×3, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude mixture, which was used for the next step without further purification.

To a stirred solution of the crude residue obtained above in THF (8.3 mL) was added diketene (0.31 mL, 4.0 mmol, 1.2 equiv.) at 0 °C in an ice bath, and the reaction mixture was stirred for 1 h at 0 °C. The reaction was quenched with the addition of 1 N aqueous $KHSO_4$ and the aqueous layer was extracted with EtOAc×2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was passed through a short pad of silica to remove polar compounds (*n*-hexane/EtOAc = 3/1). The filtrate was concentrated to give crude mixture, which was used for the next step without further purification.

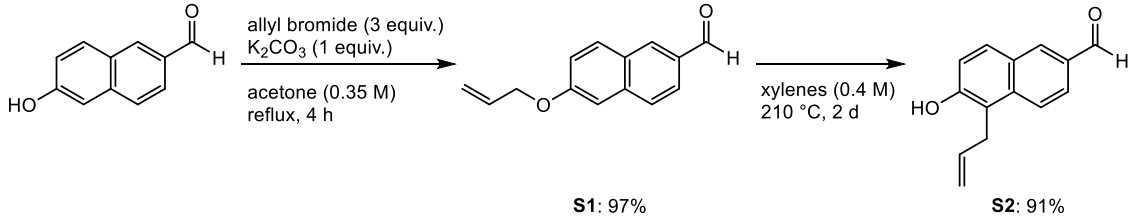
The crude residue obtained above was dissolved in MeCN (11 mL), and *para*-acetamidobenzenesulfonyl azide (1585.6 mg, 6.6 mmol, 2 equiv.) and Et_3N (0.92 mL, 6.6 mmol, 2

equiv.) were added at 0 °C in an ice bath. After being stirred for 24 h at room temperature, the reaction mixture was quenched with the addition of saturated aqueous NH_4Cl and the aqueous layer was extracted with EtOAc×2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was passed through a short pad of silica to remove polar compounds (*n*-hexane/EtOAc = 2/1) and concentrated to give crude mixture (987.0 mg), which was used for the next step without further purification.

A solution of the crude residue obtained above in 16% aqueous KOH/CH_3CN (1/1, 7.4 mL) was stirred for 15 h at room temperature. The reaction was quenched with the addition of saturated aqueous NH_4Cl and diluted with EtOAc. The aqueous layer was extracted with EtOAc×3, and the combined organic layers were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by recrystallization (*n*-hexane/ CH_2Cl_2) to afford diazocarbonyl compound **1a** as yellow solid (585.8 mg, 39% yield (5 steps)).

***N*-(*tert*-Butyl)-2-diazo-*N*-((6-hydroxynaphthalen-2-yl)methyl)acetamide (1a)**

m.p. 147-149 °C; R_f = 0.4 (*n*-hexane/EtOAc, 1/3); ^{1}H NMR (400 MHz, DMSO-d6) δ 9.71 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.55 (s, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.10 (s, 1H), 7.06 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.62 (s, 1H), 4.54 (s, 2H), 1.39 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d6) δ 167.0, 155.2, 134.0, 133.7, 129.2, 127.7, 126.5, 124.6, 123.9, 118.9, 108.6, 57.7, 48.4, 48.2, 28.6 (3C); IR (ATR) 3157, 3095, 2960, 2098, 1632, 1575, 1415, 1393, 1365, 1220, 1189, 1172 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{17}H_{19}N_3NaO_2^+$ *m*/*z* 320.1369, found *m*/*z* 320.1363.



S1: 97% **S2**: 91%

A pre-dried 100 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with 6-hydroxy-2-naphthaldehyde (1721.8 mg, 10 mmol) and K_2CO_3 (1382.1 mg, 10 mmol, 1 equiv.), which were subsequently dissolved partially in acetone (28.6 mL) under an argon gas atmosphere. To the stirred suspension was added allyl bromide (2.6 mL, 30 mmol, 3 equiv.) at room temperature. The reaction mixture was refluxed for 4 h in an oil bath. The reaction mixture was then cooled to room temperature, diluted with Et_2O, and quenched with the addition of water. The aqueous layer was extracted with Et_2O×2 and the combined organic layers were dried over Na_2SO_4, filtered through a plug of cotton, and concentrated under reduced pressure. The resulting residue was purified by flash

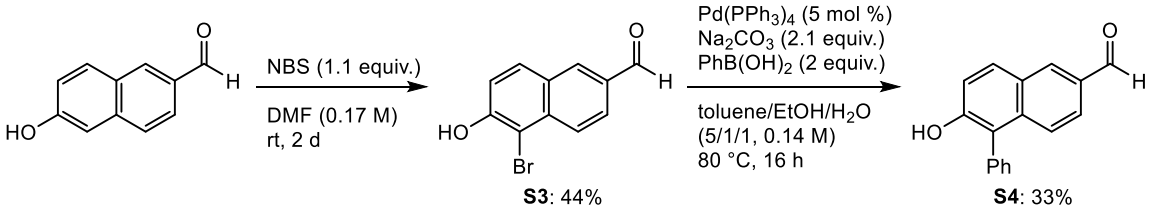
chromatography on silica gel (*n*-hexane/EtOAc = 6/1) to afford **S1** as beige solid (2.1 g, 97% yield). A pre-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged with **S1** (2.1 g, 9.7 mmol), which was subsequently dissolved in xylenes (24.3 mL) under an argon gas atmosphere. After being stirred for 2 days at 210 °C, the reaction mixture was then cooled to room temperature, and concentrated under reduced pressure. The aqueous layer was extracted with Et_2O×2 and the combined organic layers were dried over Na_2SO_4, filtered through a plug of cotton, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (*n*-hexane/EtOAc = 3/1) to afford **S2** as green solid (1.9 g, 91% yield).

6-(Allyloxy)-2-naphthaldehyde (S1)

m.p. 56−58 °C; R_f = 0.6 (*n*-hexane/EtOAc, 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.24 (d, *J* = 1.6 Hz, 1H), 7.91 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.26 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 6.12 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.49 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.36 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.69 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 159.3, 138.3, 134.4, 132.7, 132.5, 131.3, 128.1, 127.9, 123.7, 120.3, 118.4, 107.3, 69.1; IR (ATR) 2915, 2831, 2725, 2119, 1907, 1678, 1620, 1474, 1420, 1383, 1360, 1333, 1264, 1240, 1178, 1150 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{14}H_{12}NaO_2^+$ *m*/*z* 235.0730, found *m*/*z* 235.0735.

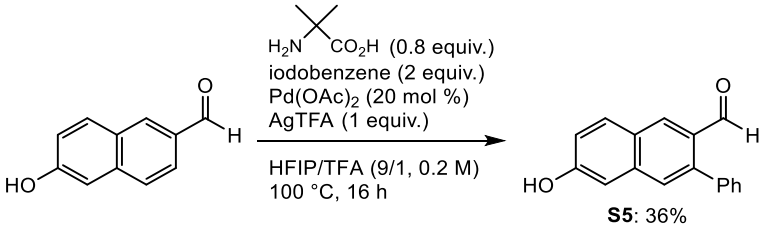
5-Allyl-6-hydroxy-2-naphthaldehyde (S2)

m.p. 122−124 °C; R_f = 0.3 (*n*-hexane/EtOAc, 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.28 (d, *J* = 1.6 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.95 (dd, *J* = 9.2, 1.6 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.22 (d, *J* = 9.2 Hz, 1H), 6.07 (ddt, *J* = 17.2, 10.0, 4.0 Hz, 1H), 5.60 (s, 1H), 5.14 (dd, *J* = 10.0, 1.6 Hz, 1H), 5.06 (dd, *J* = 17.2, 1.6 Hz, 1H), 3.85 (dd, *J* = 4.0, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 154.4, 137.0, 135.4, 135.3, 131.9, 130.4, 128.6, 124.3, 123.7, 119.2, 117.8, 116.5, 29.4; IR (ATR) 2970, 1747, 1670, 1488, 1426, 1365, 1285, 1230 cm^{-1}; $[M + Na + 2H_2O]^+$ calcd for $C_{14}H_{16}NaO_4^+$ *m*/*z* 271.0941, found *m*/*z* 271.0946.



S3 was synthesized with reported procedure.[51]

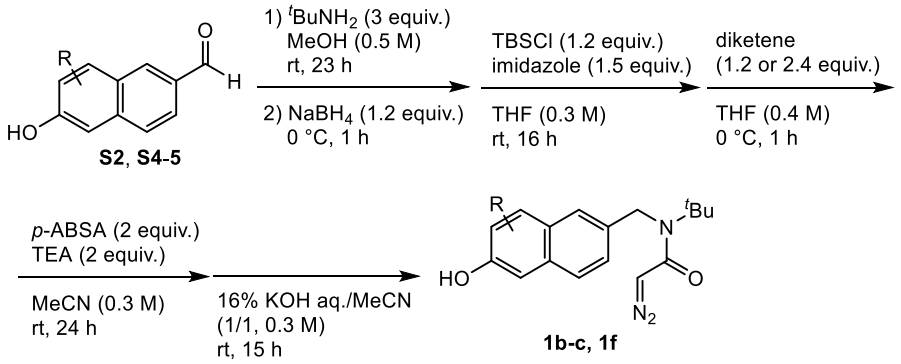
A pre-dried 50 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with toluene/EtOH/H_2O (5/1/1, 14.3 mL) and the solvents were degassed by bubbling with argon gas over 0.5 h. To the stirred solution were added $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol, 5 mol%), Na_2CO_3 (22.3 mg, 0.21 mmol, 2.1 equiv.), **S3** (502.2 mg, 2 mmol), and $PhB(OH)_2$ (607.8 mg, 4 mmol, 2 equiv.) at room temperature. After being stirred for 16 h at 80 °C, the reaction mixture was then cooled and diluted with water. The aqueous layer was extracted with EtOAc×3 and the combined organic layers were dried over Na_2SO_4, filtered through a plug of cotton, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (gradient elution: toluene/ EtOAc = 15/1 → 5/1) and recrystallization (*n*-hexane/EtOAc) to afford as white solid **S4** (162.3 mg, 33% yield). ^1H and ^{13} C NMR, and other data are identical to those reported.[52]



A 100mL Schlenk tube equipped with a magnetic stir bar was charged with 6-hydroxy-2-naphthaldehyde (516.5 mg, 3 mmol), iodobenzene (0.67 mL, 6 mmol, 2 equiv.), $Pd(OAc)_2$ (134.7 mg, 0.6 mmol, 20 mol%), 2-aminoisobutyric acid (247.5 mg, 2.4 mmol, 0.8 equiv.), and AgTFA (662.6 mg, 3 mmol, 1 equiv.), which were subsequently dissolved in HFIP/TFA (9/1, 15 mL) under an argon gas atmosphere. After being stirred for 16 h at 100 °C, the reaction mixture was then cooled, diluted with EtOAc, filtrated through Celite®, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (*n*-hexane/EtOAc = 6/1) to afford **S5** as white solid (270.6 mg, 36% yield).

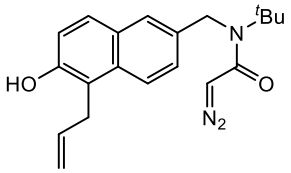
6-Hydroxy-3-phenyl-2-naphthaldehyde (S5)

m.p. 147-149 °C; R_f = 0.1 (*n*-hexane/EtOAc, 5/1); ^1H NMR (600 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.51 (s, 1H), 7.95 (d, *J* = 9.6 Hz, 1H), 7.68 (s, 1H), 7.51-7.48 (m, 1H), 7.49 (d, *J* = 6.0 Hz, 1H), 7.46 (s, 1H), 7.45-7.46 (m, 1H), 7.46 (d, *J* = 6.0 Hz, 1H), 7.20-7.18 (m, 2H), 5.51 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 156.7, 141.8, 138.5, 137.5, 132.2, 130.2 (2C), 130.2, 130.0, 128.6 (2C), 128.2, 128.0, 127.4, 119.5, 109.6; IR (ATR) 2970, 1746, 1661, 1610, 1430, 1396, 1366, 1282, 1229, 1145 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{17}H_{12}NaO_2^+$ *m/z* 271.0730, found *m/z* 271.0735.



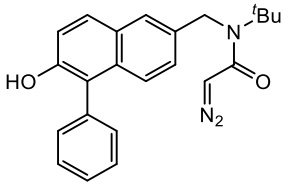
To a stirred solution of **S2** or **S4-5** in MeOH was added ^{t}BuNH$_2$ (3 equiv.), and the reaction mixture was stirred for 23 h at room temperature. The reaction mixture was cooled to 0 °C in an ice bath, $NaBH_4$ (1.2 equiv.) was then added, and stirring was continued for 1 h at 0 °C. The reaction was quenched with the addition of water and concentrated under reduced pressure to remove most of the MeOH. The aqueous solution was extracted with EtOAc×3, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford crude secondary amine, which was used for the next step without further purification.

1b-c and **1f** were synthesized from secondary amine under the same conditions as synthesis of **1a**.



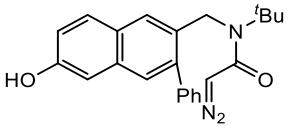
***N*-((5-Allyl-6-hydroxynaphthalen-2-yl)methyl)-*N*-(*tert*-butyl)-2-diazoacetamide (1b)**

5 mmol of **S2** and 2.4 equiv. of diketene were used and **1b** was afforded as pale yellow solid (197.2 mg, 12% yield (5 steps)).: m.p. 133-135 °C; R_f = 0.6 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.60 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.07 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.37-5.51 (m, 1H), 5.11 (d, *J* = 10.4 Hz, 1H), 5.08 (d, *J* = 17.2 Hz, 1H), 4.81 (s, 1H), 4.57 (s, 2H), 3.83 (d, *J* = 5.6 Hz, 2H), 1.53 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 151.7, 135.9, 133.3, 132.7, 129.5, 128.1, 125.1, 124.4, 124.1, 118.8, 117.3, 116.0, 58.6, 49.2, 49.0, 29.5, 29.2 (3C); IR (ATR) 3155, 2971, 2926, 2098, 1745, 1574, 1413, 1379, 1218, 1193 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{20}H_{23}N_3NaO_2^+$ *m*/*z* 360.1682, found *m*/*z* 360.1686.



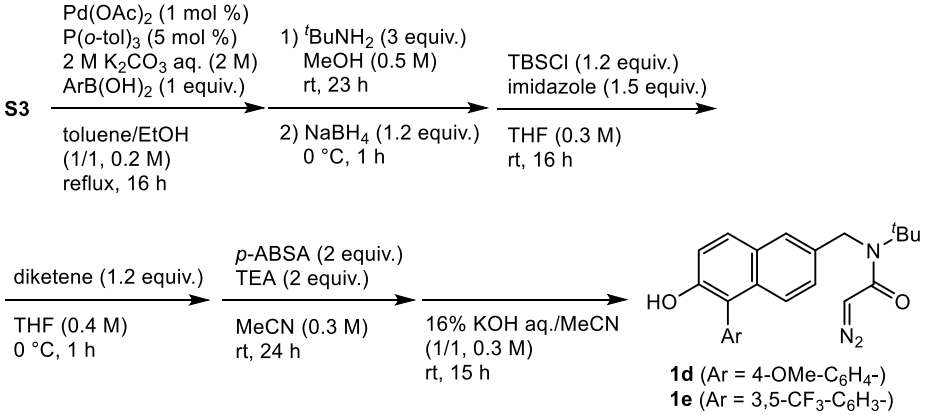
***N*-(*tert*-Butyl)-2-diazo-*N*-((6-hydroxy-5-phenylnaphthalen-2-yl)methyl)acetamide (1c)**

1.8 mmol of **S4** was used and **1c** was afforded as pale yellow solid (146.6 mg, 33% yield (5 steps)).: m.p. 225-227 °C; R_f = 0.5 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.60 (dd, *J* = 6.8, 6.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.53 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.43 (s, 1H), 7.42 (d, *J* = 6.8 Hz, 1H), 7.40 (d, *J* = 6.0 Hz, 1H), 7.29 (d, *J* = 9.2 Hz, 1H), 7.18 (dd, *J* = 9.2, 1.6 Hz, 1H), 5.15 (a, 1H), 4.79 (s, 1H), 4.55 (s, 2H), 1.56 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 150.4, 134.0, 133.8, 132.6, 131.2 (2C), 129.9 (2C), 129.4, 129.0, 128.8, 125.7, 124.6, 124.5, 121.2, 118.2, 58.5, 49.0, 48.9, 29.1 (3C); IR (ATR) 3372, 3113, 2955, 2112, 1739, 1613, 1598, 1405, 1380, 1217, 1191, 1159, 1138 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{23}H_{23}N_3NaO_2^+$ *m*/*z* 396.1682, found *m*/*z* 396.1686.



***N*-(*tert*-Butyl)-2-diazo-*N*-((6-hydroxy-3-phenylnaphthalen-2-yl)methyl)acetamide (1f)**

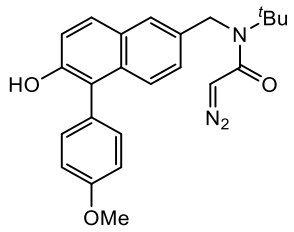
1.1 mmol of **S5** was used and **1f** was afforded as pale pink solid (60.1 mg, 15% yield (5 steps)).: m.p. 161−163 °C; R_f = 0.3 (*n*-hexane/EtOAc, 3/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 9.0 Hz, 1H), 7.71 (s, 1H), 7.54 (s, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 7.8, 9.0 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.18 (s, 1H), 7.17 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.03 (br s, 1H), 4.80 (s, 1H), 4.31 (s, 2H), 1.46 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 154.5, 140.4, 139.2, 133.7, 131.6, 129.7, 128.9 (2C), 128.8 (2C), 128.2, 127.9, 127.8, 125.1, 118.7, 109.4, 58.5, 49.1, 48.4, 29.0 (3C); IR (ATR) 3220, 3099, 2956, 2925, 2109, 1746, 1588, 1415, 1372, 1212 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{23}H_{23}N_3NaO_2^+$ *m*/*z* 396.1682, found *m*/*z* 396.1684.



A 50 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with **S3** (749.9 mg, 3 mmol), $ArB(OH)_2$ (3 mmol, 1 equiv.), P(*o*-tol)$_3$ (45.7 mg, 0.15 mmol, 5 mol%), and 2 M aqueous

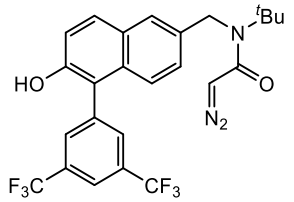
K_2CO_3 (1.5 mL), which were subsequently dissolved partially in toluene/EtOH (1/1, 15 mL) under an argon gas atmosphere. After being refluxed for 16 h, the reaction mixture was then cooled, diluted with EtOAc and water. The aqueous layer was extracted with EtOAc×3 and the combined organic layers were dried over Na_2SO_4, filtered through a plug of cotton, concentrated under reduced pressure, and passed through a short pad of silica to remove borane reagents (*n*-hexane/EtOAc) to give the crude mixture.

1d and **1e** were synthesized from the crude aldehyde with the same conditions as synthesis of **1c**.



***N*-(*tert*-Butyl)-2-diazo-*N*-((6-hydroxy-5-(4-methoxyphenyl)naphthalen-2-yl)methyl)acetamide (1d)**

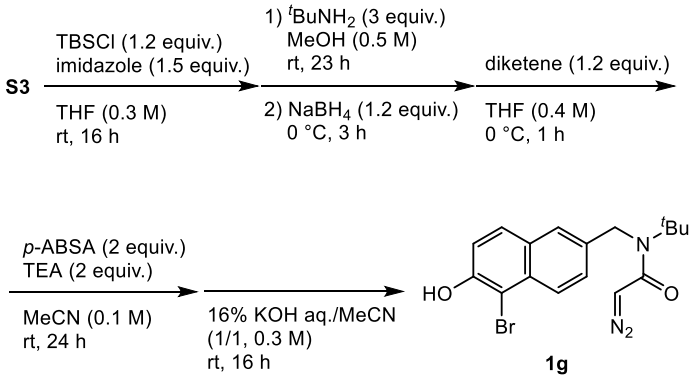
3 mmol of **S3** was used and **1d** was afforded as pale yellow solid (77.3 mg, 6% yield (6 steps)).: m.p. 199-201 °C; R_f = 0.6 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 1H), 7.63 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 5.21 (br s, 1H), 4.79 (s, 1H), 4.55 (s, 2H), 3.92 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 160.0, 150.7, 133.7, 133.0, 132.4 (2C), 129.2, 129.1, 125.7 (2C), 124.6, 124.4, 120.9, 118.1, 115.3 (2C), 58.5, 55.6, 49.0, 49.0, 29.1 (3C); IR (ATR) 3296, 2970, 2107, 1739, 1596, 1515, 1406, 1379, 1217 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{24}H_{25}N_3NaO_3^+$ *m*/*z* 426.1788, found *m*/*z* 426.1798.



***N*-((5-(3,5-Bis(trifluoromethyl)phenyl)-6-hydroxynaphthalen-2-yl)methyl)-*N*-(*tert*-butyl)-2-diazoacetamide (1e)**

3 mmol of **S3** was used and **1e** was afforded as pale yellow solid (79.0 mg, 6% yield (6 steps)).: m.p. 136-138 °C; R_f = 0.6 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.80 (s 1H), 7.66 (s, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 6.10 (br s, 1H), 4.80 (s, 1H), 4.57 (s, 2H), 1.53 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ

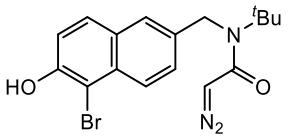
168.5, 151.0, 137.8, 134.1, 132.4 (J = 34.5 Hz, 2C), 132.3, 131.7 (2C), 130.5, 129.1, 127.8, 125.3, 124.9, 124.4, 122.6, 122.0, 118.8, 118.6, 58.7, 49.3, 49.0, 29.2 (3C); ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.6; IR (ATR) 3296, 2970, 2107, 1739, 1596, 1515, 1406, 1379, 1217 cm^{-1}; HRMS (ESI-TOF) [M + Na]$^+$ calcd for $C_{25}H_{21}F_6N_3NaO_2^+$ m/z 532.1430, found m/z 532.1437.



To a stirred solution of **S3** (2510.8 mg, 10 mmol) and imidazole (1021.2 mg, 15 mmol, 1.5 equiv.) in THF (33.3 mL) was added TBSCl (1808.6 mg, 12 mmol, 1.2 equiv.) at 0 °C in an ice bath. After being stirred for 16 h at room temperature, saturated aqueous NH_4Cl was added. The reaction mixture was extracted with EtOAc×3, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was passed through a short pad of silica to remove excessive imidazole (*n*-hexane/EtOAc = 5/1) and azeotropically distilled with toluene to remove *tert*-butyldimethylsilanol and give crude silylated product (913.4 mg), which was used for the next step without further purification.

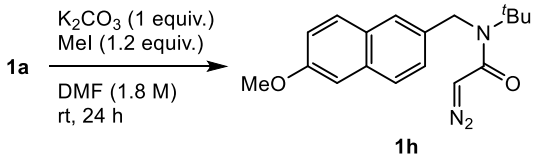
To a stirred solution of the silylated product in MeOH was added ^{t}BuNH$_2$ (0.79 mL, 7.5 mmol, 3 equiv.), and the reaction mixture was stirred for 23 h at room temperature. The reaction mixture was cooled to 0 °C in an ice bath, $NaBH_4$ (113.5 mg, 3 mmol, 1.2 equiv.) was then added, and stirring was continued for 1 h at 0 °C. The reaction was quenched with the addition of water and concentrated under reduced pressure to remove most of the MeOH. The aqueous solution was extracted with EtOAc×3, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford crude secondary amine, which was used for the next step without further purification.

1g was synthesized from silylated product under the same conditions as synthesis of **1a**.



***N*-((5-Bromo-6-hydroxynaphthalen-2-yl)methyl)-*N*-(*tert*-butyl)-2-diazoacetamide (1g)**

1g was afforded as beige solid (69.8 mg, 3% yield (5 steps)).: m.p. 112-114 °C; R_f = 0.7 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.61 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 4.78 (s, 1H), 4.59 (s, 2H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 150.8, 134.8, 131.7, 129.8, 129.2, 127.8, 126.4, 125.8, 118.0, 106.1, 58.5, 49.0, 48.8, 29.1 (3C); IR (ATR) 3095, 2969, 2925, 2105, 1714, 1584, 1416, 1362, 1329, 1296 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{17}H_{18}BrN_3NaO_2^+$ *m*/*z* 398.0475, found *m*/*z* 398.0495.

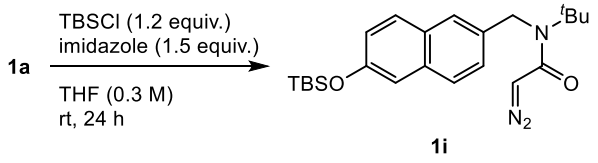


1h

A 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with **1a** (61.5 mg, 0.21 mmol) and K_2CO_3 (34.6 mg, 0.25 mmol, 1.2 equiv.), which were subsequently dissolved in DMF (0.12 mL) under an argon gas atmosphere. To the stirred solution was added dropwise MeI (15.6 μL, 0.25 mmol, 1.2 equiv.) at room temperature. After being stirred for 24 h, the reaction mixture was quenched with the addition of water. The aqueous layer was extracted with Et_2O×3 and the combined organic layers were dried over Na_2SO_4, filtered through a plug of cotton, concentrated under reduced pressure, and purified by flash column chromatography (*n*-hexane/EtOAc = 6/1) to afford **1h** as yellow oil (64.7 mg, 99% yield).

***N*-(*tert*-Butyl)-2-diazo-*N*-((6-methoxynaphthalen-2-yl)methyl)acetamide (1h)**

R_f = 0.6 (*n*-hexane/EtOAc, 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.59 (s, 1H), 7.28 (d, *J* = 9.2 Hz, 1H), 7.18 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 4.81 (s, 1H), 4.56 (s, 2H), 3.93 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 157.9, 134.1, 133.9, 129.3, 129.1, 127.7, 124.4, 124.3, 119.4, 105.9, 58.5, 55.5, 49.0, 49.0, 29.1 (3C); IR (ATR) 2963, 2101, 1739, 1607, 1484, 1400, 1360, 1264, 1210, 1194, 1171 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{18}H_{21}N_3NaO_2^+$ *m*/*z* 334.1526, found *m*/*z* 334.1541.



1i

A 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with **1a** (89.2 mg, 0.3

mmol) and imidazole (30.6 mg, 0.45 mmol, 1.5 equiv.), which were subsequently dissolved in THF (1 mL) under an argon gas atmosphere. To the stirred solution was added TBSCl (54.3 mg, 0.36 mmol, 1.2 equiv.) at 0 °C in an ice bath. After being stirred for 24 h at room temperature, the reaction mixture was quenched with the addition of water. The aqueous layer was extracted with Et_2O×3 and the combined organic layers were dried over Na_2SO_4, filtered through a plug of cotton, concentrated under reduced pressure, and purified by flash column chromatography (*n*-hexane/EtOAc = 8/1) to afford **1g** as yellow oil (99.4 mg, 80% yield).

***N*-(*tert*-Butyl)-*N*-((6-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-yl)methyl)-2-diazoacetamide (1i)**

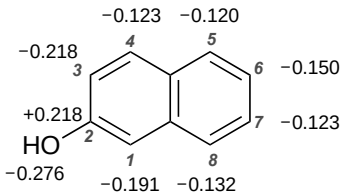
R_f = 0.7 (*n*-hexane/EtOAc, 2/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.59 (s, 1H), 7.25 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.19 (d, *J* = 3.0 Hz, 1H), 7.10 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.81 (s, 1H), 4.55 (s, 2H), 1.52 (s, 9H), 1.02 (s, 9H), 0.25 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 153.8, 134.3, 133.9, 129.4, 129.2, 127.6, 124.2, 124.1, 122.9, 115.0, 58.5, 49.1, 49.0, 29.2 (3C), 25.9 (3C), 18.4, -4.2 (2C); IR (ATR) 2952, 2929, 2858, 2098, 1602, 1482, 1399, 1380, 1264, 1232, 1216 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{23}H_{33}N_3NaO_2Si^+$ *m*/*z* 434.2234, found *m*/*z* 434.2241.

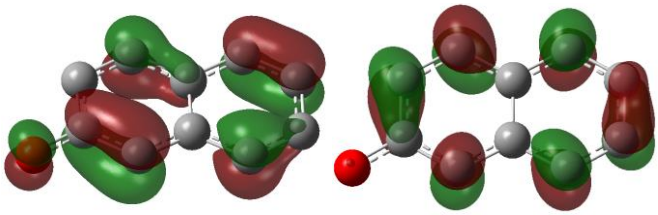
6. Computational Details of Part2

All the calculations were performed with Gaussian 16 program.[53]

Mulliken Charge Distribution and Frontier Molecular Orbital of *b*-Naphthol

The molecular structure optimizations were carried out using the hybrid density functional method based on wB97XD functional and the cc-pVTZ basis set for H, C, and O. The vibrational frequencies were computed at the same level to check whether each optimized structure is at an energy minimum on the potential energy surfaces (no imaginary frequency), and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298.15 K.





Energy (RwB97XD): -461.107554 A.U.

Zero-point correction=	0.153124 (Hartree/Particle)
Thermal correction to Energy=	0.161079
Thermal correction to Enthalpy=	0.162023
Thermal correction to Gibbs Free Energy=	0.120520
Sum of electronic and zero-point Energies=	-460.954430
Sum of electronic and thermal Energies=	-460.946475
Sum of electronic and thermal Enthalpies=	-460.945531
Sum of electronic and thermal Free Energies=	-460.987033

Cartesian Coordinates

Atom	X	Y	Z
C	1.852093	1.260232	-0.000084
C	2.678805	-0.99614	0.000102
C	0.522034	0.779055	0.000090
H	2.018765	2.330236	0.000089
C	1.407348	-1.490583	0.000109
H	3.521431	-1.674438	0.000723
C	0.290043	-0.619732	-0.000080
C	-0.592807	1.646779	0.000130
H	1.234947	-2.559283	0.000307

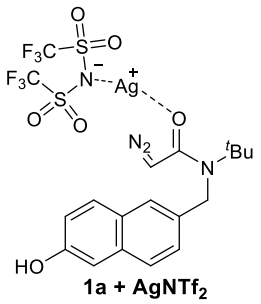
C	-1.034759	-1.105582	-0.000168
C	-1.865408	1.157536	0.000025
H	-0.425732	2.716379	0.000182
C	-2.090174	-0.236866	-0.000051
H	-1.223861	-2.170492	-0.000166
H	-2.711026	1.835595	-0.000075
O	-3.349814	-0.745755	-0.000137
H	-3.984483	-0.028991	0.001163
C	2.907404	0.396008	-0.000154
H	3.921000	0.772798	-0.000639

Mechanistic Studies on Dearomative Spirocyclization of *β*-Naphthols

The molecular structure optimizations were carried out using the hybrid density functional method based on Becke's three-parameter exchange function and the Lee-YangParr nonlocal correlation functional (B3LYP)[54] and the LANL2DZ basis set for Ag, and the 6-31G* basis set for H, C, N, O, F and S. The vibrational frequencies were computed at the same level to check whether each optimized structure is at an energy minimum on the potential energy surfaces (no imaginary frequency) or a transition state (one imaginary frequency) and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298.15 K. The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.[55] Single point energies were calculated at the RB3PW91 level using SDD basis set[56] for Ag and 6-311++G** basis set for H, C, N, O, F and S in CH_2Cl_2 solvent using CPCM model.

	E(RB3LYP/6-31G*) (A.U.)	Thermal Correction to Free Energy (A.U.)	Sum of Electronic and Thermal Free Energies (A.U.)
1a+$AgNTf_2$	-2946.817203	0.310667	-1848962.316
TS1	-2946.802981	0.311878	-1848952.632
CP1	-2946.809715	0.311874	-1848956.86
TS2A	-2946.780869	0.309385	-1848940.321
TS2B	-2946.779106	0.309294	-1848939.272
TS2C	-2946.764332	0.312167	-1848928.198
INT1	-2946.829151	0.303944	-1848974.033
CP2	-2946.874147	0.304287	-1849002.053

	E(RB3PW91/ 6-311++G**) (A.U.)	Thermal Correction to Free Energy (A.U.)	Sum of Electronic and Thermal Free Energies (A.U.)
1a+AgNTf$_2$	-2947.926064	0.310667	-1849658.138
TS1	-2947.91443	0.311878	-1849650.077
CP1	-2947.925639	0.311874	-1849657.114
TS2A	-2947.890114	0.309385	-1849636.383
TS2B	-2947.888362	0.309294	-1849635.341
TS2C	-2947.872962	0.312167	-1849623.874
INT1	-2947.944093	0.303944	-1849673.67
CP2	-2947.985516	0.304287	-1849699.448



1a + AgNTf$_2$ (Figure 4)

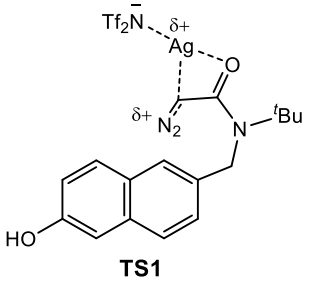
Zero-point correction= 0.390951 (Hartree/Particle)
Thermal correction to Energy= 0.430293
Thermal correction to Enthalpy= 0.431237
Thermal correction to Gibbs Free Energy= 0.310667
Sum of electronic and zero-point Energies= -2946.426252
Sum of electronic and thermal Energies= -2946.386910
Sum of electronic and thermal Enthalpies= -2946.385966
Sum of electronic and thermal Free Energies= -2946.506536

Cartesian Coordinates

Atom	X	Y	Z
Ag	1.49104	-1.46036	-0.18948
C	-1.48621	-2.16885	-2.06415
H	-2.33682	-1.61238	-2.42909
C	-1.26056	-2.6282	-0.69343
O	-0.09204	-2.97063	-0.33981

N	-2.32359	-2.68468	0.14594
C	-2.13828	-3.03901	1.61876
C	-3.67166	-2.47467	-0.40926
H	-3.69404	-2.92182	-1.40985
H	-4.37478	-3.06816	0.17487
N	0.39987	-2.39546	-3.60577
N	-0.47955	-2.28128	-2.89649
C	-4.15307	-1.03097	-0.46931
C	-3.33363	0.0547	-0.2389
C	-5.51744	-0.80367	-0.80928
C	-3.8237	1.38561	-0.33546
H	-2.28855	-0.08141	0.02419
C	-6.02221	0.4704	-0.90934
H	-6.16995	-1.65614	-0.98923
C	-5.19708	1.60786	-0.67761
H	-7.06731	0.62447	-1.16651
C	-5.68771	2.93164	-0.77477
H	-6.72633	3.11632	-1.03223
C	-4.84692	4.00329	-0.54403
C	-2.98598	2.50936	-0.10578
C	-3.48503	3.78744	-0.20804
H	-2.8342	4.64231	-0.03228
H	-1.94142	2.34832	0.14771
O	-5.36378	5.26252	-0.65018
H	-4.66519	5.90968	-0.46622
N	2.56893	0.3732	0.18311
S	4.20053	0.40551	-0.12816
S	1.6897	1.62512	0.80429
O	4.93914	1.37145	0.67531
O	4.60206	-1.0008	-0.2126
O	2.22896	2.94953	0.5228
O	0.28339	1.30252	0.51386
C	1.84451	1.35738	2.65017
C	4.24268	1.02203	-1.89452
F	3.69579	2.23183	-1.98486
F	5.51046	1.07095	-2.30411

F	3.5609	0.17222	-2.67592
F	1.3543	0.14716	2.96501
F	3.11404	1.4268	3.0348
F	1.13049	2.29092	3.28244
C	-3.46846	-2.86325	2.37811
H	-4.21872	-3.61105	2.10256
H	-3.26469	-3.00005	3.44396
H	-3.89315	-1.86377	2.24484
C	-1.10849	-2.09664	2.27511
H	-0.09872	-2.27029	1.9041
H	-1.36803	-1.04563	2.1153
H	-1.09693	-2.2799	3.35455
C	-1.69324	-4.50975	1.72707
H	-1.59412	-4.78681	2.78265
H	-2.43756	-5.17402	1.27297
H	-0.73259	-4.66933	1.23442



TS1

(Figure 4)

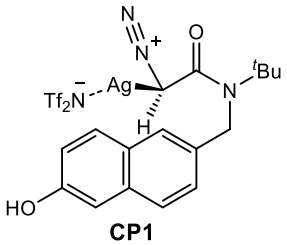
Zero-point correction=	0.390225 (Hartree/Particle)
Thermal correction to Energy=	0.428914
Thermal correction to Enthalpy=	0.429858
Thermal correction to Gibbs Free Energy=	0.311878
Sum of electronic and zero-point Energies=	-2946.412756
Sum of electronic and thermal Energies=	-2946.374067
Sum of electronic and thermal Enthalpies=	-2946.373122
Sum of electronic and thermal Free Energies=	-2946.491102

Cartesian Coordinates

Atom	X	Y	Z

Ag	0.87109	-1.1831	-0.96533
C	-1.3719	-1.63938	-2.09569
H	-1.92279	-0.71592	-2.23308
C	-1.49866	-2.55054	-0.89968
O	-0.55046	-3.32707	-0.67078
N	-2.59754	-2.40805	-0.1201
C	-2.6568	-3.10594	1.23695
C	-3.7849	-1.72816	-0.6695
H	-3.83984	-1.95574	-1.74008
H	-4.66813	-2.20123	-0.23682
N	-0.57946	-2.70138	-4.16749
N	-0.95573	-2.20993	-3.21921
C	-3.86151	-0.22142	-0.46693
C	-2.88764	0.5151	0.17476
C	-5.00432	0.45133	-0.98764
C	-3.00613	1.92482	0.32608
H	-2.00607	0.03142	0.58653
C	-5.14828	1.81126	-0.85782
H	-5.77614	-0.12534	-1.49434
C	-4.15821	2.59539	-0.19909
H	-6.02796	2.30774	-1.26005
C	-4.27904	3.99744	-0.05226
H	-5.14637	4.51935	-0.44526
C	-3.2918	4.71647	0.59383
C	-2.01053	2.69347	0.98569
C	-2.14964	4.05623	1.11629
H	-1.37999	4.63595	1.62304
H	-1.13497	2.19107	1.38747
O	-3.45067	6.06713	0.7113
H	-2.68623	6.43799	1.17911
N	2.27953	0.14215	0.05343
S	3.6623	0.46808	-0.7984
S	1.9849	0.57253	1.61704
O	4.85565	0.64095	0.02035
O	3.63009	-0.46826	-1.92913

O	2.70544	1.75742	2.06677
O	0.52833	0.46073	1.79183
C	2.66923	-0.88117	2.57708
C	3.2766	2.136	-1.55409
F	3.05256	3.04251	-0.60603
F	4.30988	2.51829	-2.30505
F	2.18699	2.03041	-2.32776
F	2.04535	-2.00377	2.18377
F	3.97465	-1.01147	2.36592
F	2.43953	-0.68968	3.87679
C	-3.87908	-2.60913	2.03322
H	-4.83017	-2.96789	1.62698
H	-3.80062	-3.00635	3.04941
H	-3.91066	-1.51785	2.10279
C	-1.39565	-2.76851	2.05811
H	-0.48862	-3.15385	1.59477
H	-1.28712	-1.68837	2.19981
H	-1.49106	-3.22783	3.04771
C	-2.77976	-4.6237	1.00832
H	-2.86699	-5.13622	1.97292
H	-3.67598	-4.8581	0.42151
H	-1.90372	-5.01362	0.48639



CP1

(Figure 4)

Zero-point correction= 0.390225 (Hartree/Particle)

Thermal correction to Energy= 0.428914

Thermal correction to Enthalpy= 0.429858

Thermal correction to Gibbs Free Energy= 0.311878

Sum of electronic and zero-point Energies= -2946.412756

Sum of electronic and thermal Energies= -2946.374067

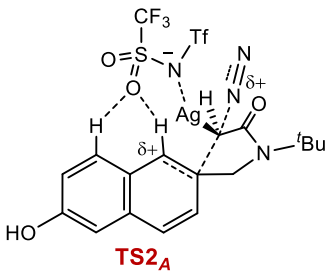
Sum of electronic and thermal Enthalpies= -2946.373122

Sum of electronic and thermal Free Energies= -2946.491102

Cartesian Coordinates

Atom	X	Y	Z
Ag	-0.90295	-0.21523	1.07009
C	1.05377	-0.94454	1.85897
H	1.72566	-0.16636	1.48874
C	1.27523	-2.40101	1.40964
O	1.04409	-3.29049	2.22285
N	1.71601	-2.57576	0.12843
C	1.88021	-4.00523	-0.37949
C	1.79594	-1.41841	-0.78752
H	1.88527	-1.81098	-1.7975
H	0.84508	-0.87296	-0.78936
N	0.96341	-0.91219	4.33792
N	1.02077	-0.90234	3.21843
C	2.93593	-0.44208	-0.53737
C	2.74282	0.90229	-0.80565
C	4.21257	-0.8796	-0.09398
C	3.793	1.84415	-0.65685
H	1.77113	1.25116	-1.15263
C	5.24998	0.0121	0.06395
H	4.36584	-1.931	0.13217
C	5.07901	1.39601	-0.21189
H	6.22109	-0.33885	0.40525
C	6.12839	2.33858	-0.05719
H	7.1049	1.99547	0.28124
C	5.91476	3.6738	-0.33467
C	3.61226	3.22901	-0.9311
C	4.64174	4.12368	-0.77656
H	4.5136	5.1808	-0.98597
H	2.63918	3.57302	-1.27222
O	6.87664	4.6327	-0.20977
H	7.70218	4.21947	0.08923

N	-2.5336	0.53423	-0.13531
S	-2.24376	0.73353	-1.74853
S	-4.01698	0.64243	0.60239
O	-3.21091	1.57575	-2.43869
O	-0.79859	0.97118	-1.86596
O	-5.14698	0.3573	-0.27248
O	-3.84292	-0.04068	1.88906
C	-4.10436	2.46211	1.03044
C	-2.46617	-1.00437	-2.41056
F	-3.69565	-1.45011	-2.18254
F	-2.21803	-1.01034	-3.71997
F	-1.58406	-1.82453	-1.80039
F	-3.08431	2.77439	1.84114
F	-4.03342	3.20663	-0.06948
F	-5.25411	2.70005	1.66167
C	2.43562	-4.01813	-1.81533
H	3.37088	-3.45537	-1.90912
H	2.65248	-5.05834	-2.07686
H	1.71924	-3.6483	-2.55613
C	0.50442	-4.70101	-0.37967
H	0.10032	-4.78008	0.63078
H	-0.20548	-4.14591	-1.00379
H	0.6007	-5.71113	-0.79345
C	2.89004	-4.75929	0.51102
H	2.99906	-5.78428	0.1401
H	3.87637	-4.28248	0.46768
H	2.56123	-4.80034	1.54828



TS2*A*

(Figure 4)

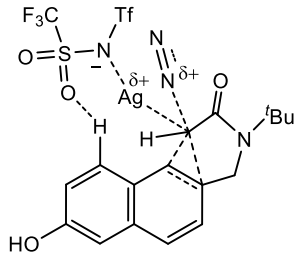
Zero-point correction= 0.388381 (Hartree/Particle)

Thermal correction to Energy=	0.427673
Thermal correction to Enthalpy=	0.428618
Thermal correction to Gibbs Free Energy=	0.309385
Sum of electronic and zero-point Energies=	-2946.392488
Sum of electronic and thermal Energies=	-2946.353195
Sum of electronic and thermal Enthalpies=	-2946.352251
Sum of electronic and thermal Free Energies=	-2946.471484

Cartesian Coordinates

Atom	X	Y	Z
Ag	-0.30376	-0.42018	0.72663
C	1.69885	-0.59646	1.4147
H	2.24657	0.31133	1.6559
C	2.53344	-1.85482	1.2085
O	2.64728	-2.65166	2.14204
N	3.06145	-2.0547	-0.04105
C	3.70056	-3.40497	-0.34215
C	2.71984	-1.11631	-1.12892
H	3.3826	-1.3315	-1.96454
H	1.69438	-1.28662	-1.48612
N	0.91598	-0.9946	4.31753
N	1.36259	-0.89019	3.31116
C	2.89047	0.34139	-0.75415
C	1.9051	1.26398	-1.0763
C	4.10832	0.80771	-0.17683
C	2.07015	2.64588	-0.81178
H	0.98233	0.93964	-1.55095
C	4.29588	2.14279	0.0904
H	4.88808	0.09002	0.0648
C	3.28816	3.10496	-0.21317
H	5.22818	2.48347	0.53454
C	3.45012	4.48575	0.05273
H	4.37567	4.83734	0.50586
C	2.44251	5.37954	-0.26293
C	1.05292	3.59349	-1.1199

C	1.23194	4.9283	-0.85298
H	0.46588	5.66203	-1.08162
H	0.12818	3.23866	-1.56686
O	2.53308	6.71866	-0.03651
H	3.39405	6.92009	0.36372
N	-2.28691	-0.1821	-0.11768
S	-2.46474	0.18891	-1.71641
S	-3.52679	-0.64453	0.88653
O	-3.8024	0.62717	-2.0905
O	-1.27858	0.97023	-2.09111
O	-4.65901	-1.26211	0.20807
O	-2.86601	-1.2928	2.02535
C	-4.12086	1.00083	1.55188
C	-2.18656	-1.46906	-2.53933
F	-3.08561	-2.35869	-2.13259
F	-2.26365	-1.3215	-3.86178
F	-0.95494	-1.92032	-2.22573
F	-3.11757	1.60176	2.20539
F	-4.53194	1.78863	0.56172
F	-5.1268	0.78293	2.39967
C	4.21376	-3.45825	-1.79256
H	4.97361	-2.69606	-1.99896
H	4.68825	-4.43356	-1.9387
H	3.41233	-3.37635	-2.53394
C	2.65314	-4.52275	-0.16241
H	2.28674	-4.56327	0.86381
H	1.80326	-4.36744	-0.83746
H	3.10295	-5.49144	-0.40726
C	4.91493	-3.6152	0.58584
H	5.39863	-4.56694	0.33907
H	5.6511	-2.81603	0.43887
H	4.62041	-3.6359	1.634



TS2$_B$

(Figure 4)

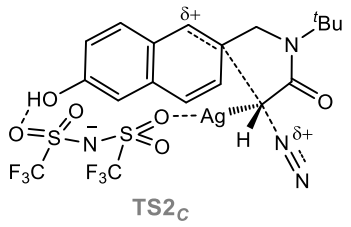
Zero-point correction=	0.388891 (Hartree/Particle)
Thermal correction to Energy=	0.427726
Thermal correction to Enthalpy=	0.428670
Thermal correction to Gibbs Free Energy=	0.312167
Sum of electronic and zero-point Energies=	-2946.375441
Sum of electronic and thermal Energies=	-2946.336606
Sum of electronic and thermal Enthalpies=	-2946.335662
Sum of electronic and thermal Free Energies=	-2946.452165

Cartesian Coordinates

Atom	X	Y	Z
Ag	0.24449	-0.64637	0.85368
C	2.22494	-0.27896	1.50736
H	2.43947	0.56977	2.15521
C	3.36904	-0.9192	0.74828
O	3.50577	-2.14003	0.8119
N	4.10735	-0.07925	-0.04679
C	5.05085	-0.67532	-1.07717
C	4.15527	1.34697	0.32136
H	4.50345	1.44982	1.35943
H	4.92086	1.82277	-0.28935
N	2.06093	-2.20953	3.86389
N	2.29882	-1.48157	3.06604
C	2.84421	2.09582	0.15734
C	1.89699	1.74154	-0.79058
C	2.61431	3.24956	0.96079
C	0.70505	2.49479	-0.96237
H	2.05709	0.87222	-1.42285

C	1.47419	4.00166	0.81314
H	3.35735	3.53636	1.70231
C	0.47828	3.65053	-0.14435
H	1.31266	4.87578	1.43895
C	-0.7182	4.38701	-0.29256
H	-0.91022	5.25723	0.32757
C	-1.67148	3.98755	-1.21187
C	-0.28553	2.12602	-1.91089
C	-1.4466	2.85219	-2.03248
H	-2.20935	2.54226	-2.74361
H	-0.13711	1.23789	-2.51655
O	-2.82016	4.71241	-1.30065
H	-3.42219	4.28414	-1.92966
N	-1.77156	-0.98033	0.14748
S	-3.00273	-0.71111	1.22479
S	-1.9788	-1.41356	-1.43533
O	-4.24868	-1.38973	0.89045
O	-2.39386	-0.82543	2.55282
O	-3.2189	-0.93202	-2.03568
O	-0.68277	-1.16721	-2.0829
C	-2.10054	-3.28006	-1.3464
C	-3.32444	1.12223	1.02188
F	-3.70791	1.40619	-0.22437
F	-4.28423	1.48773	1.87298
F	-2.20698	1.8071	1.302
F	-0.98374	-3.76845	-0.79347
F	-3.14981	-3.65309	-0.62042
F	-2.22074	-3.75766	-2.58693
C	5.59687	0.42572	-2.00509
H	6.31816	1.08601	-1.51186
H	6.12723	-0.05983	-2.82981
H	4.79577	1.03316	-2.44091
C	4.27439	-1.67624	-1.95863
H	3.8703	-2.50415	-1.37755
H	3.45073	-1.17547	-2.48016
H	4.9526	-2.08469	-2.71535

C	6.22755	-1.36434	-0.35915
H	6.92965	-1.76827	-1.0975
H	6.77395	-0.64799	0.2662
H	5.87261	-2.18297	0.26914



$TS2_C$ (Figure 4)

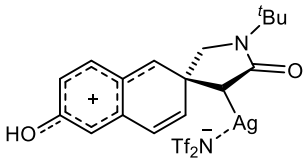
Zero-point correction=	0.387681 (Hartree/Particle)
Thermal correction to Energy=	0.427160
Thermal correction to Enthalpy=	0.428104
Thermal correction to Gibbs Free Energy=	0.309294
Sum of electronic and zero-point Energies=	-2946.391425
Sum of electronic and thermal Energies=	-2946.351946
Sum of electronic and thermal Enthalpies=	-2946.351002
Sum of electronic and thermal Free Energies=	-2946.469812

Cartesian Coordinates

Atom	X	Y	Z
Ag	0.86997	-0.8617	-0.21971
C	2.77702	-0.41864	0.65883
H	2.76124	0.30644	1.46751
C	4.12937	-0.77904	0.05433
O	4.43708	-1.97446	0.07229
N	4.94333	0.19849	-0.45818
C	6.26284	-0.24551	-1.08787
C	4.47416	1.5659	-0.8011
H	5.28893	2.25447	-0.57273
H	4.3094	1.61049	-1.88563
N	2.52431	-2.65175	2.60972
N	2.77308	-1.8331	1.90734

C	3.23384	2.05513	-0.10153
C	2.01723	2.07473	-0.76923
C	3.29582	2.59858	1.21826
C	0.82779	2.51511	-0.1432
H	1.96498	1.72978	-1.80092
C	2.15677	3.02595	1.85776
H	4.25678	2.64616	1.72574
C	0.87814	2.95865	1.22249
H	2.21389	3.41469	2.87145
C	-0.32311	3.26349	1.8958
H	-0.30994	3.55945	2.94045
C	-1.54615	3.10821	1.25547
C	-0.43046	2.46703	-0.79998
C	-1.5875	2.75649	-0.12384
H	-2.54733	2.6795	-0.61944
H	-0.47373	2.16288	-1.84293
O	-2.67863	3.30271	1.95721
H	-3.41533	2.82188	1.52041
N	-2.91194	-0.18493	-0.13607
S	-4.4849	0.20919	0.07929
S	-2.41336	-1.67083	-0.45426
O	-5.35447	-0.86133	0.5575
O	-4.50144	1.51665	0.75834
O	-3.30875	-2.59387	-1.14073
O	-1.03441	-1.54312	-1.03857
C	-2.07462	-2.43545	1.2234
C	-5.05023	0.61968	-1.65662
F	-4.88532	-0.42697	-2.4633
F	-6.33926	0.95941	-1.62343
F	-4.3397	1.65324	-2.13361
F	-1.13456	-1.71484	1.87397
F	-3.17898	-2.4603	1.95695
F	-1.61042	-3.67607	1.05801
C	7.09038	0.97658	-1.5377
H	7.3485	1.63581	-0.70173
H	8.02952	0.60095	-1.95491

H	6.6054	1.56702	-2.32015
C	5.97275	-1.11982	-2.32393
H	5.42989	-2.02484	-2.04895
H	5.38503	-0.56348	-3.06441
H	6.91571	-1.41158	-2.79964
C	7.11528	-0.99788	-0.04445
H	8.09511	-1.22264	-0.48006
H	7.27723	-0.36886	0.83861
H	6.65027	-1.93083	0.26699



INT1 + N_2 (Figure 4)

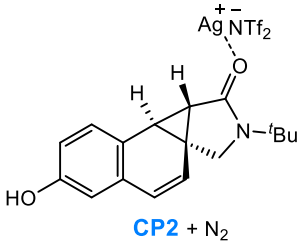
Zero-point correction=	0.388117 (Hartree/Particle)
Thermal correction to Energy=	0.428748
Thermal correction to Enthalpy=	0.429692
Thermal correction to Gibbs Free Energy=	0.303944
Sum of electronic and zero-point Energies=	-2946.441034
Sum of electronic and thermal Energies=	-2946.400403
Sum of electronic and thermal Enthalpies=	-2946.399459
Sum of electronic and thermal Free Energies=	-2946.525207

Cartesian Coordinates

Atom	X	Y	Z
Ag	-0.18357	-0.36575	0.66453
C	1.95797	-0.52876	1.04082
H	2.12329	-0.00011	1.97841
C	2.2978	-1.98607	1.08987
O	2.02349	-2.72908	2.02572
N	2.98456	-2.34597	-0.06365
C	3.1343	-3.77465	-0.48418
C	2.97436	-1.25001	-1.01885

H	3.87284	-1.24055	-1.63941
H	2.09613	-1.28083	-1.68307
N	-0.77907	-2.30992	4.25465
N	-0.51511	-1.30219	3.88681
C	2.89704	0.02371	-0.12849
C	2.06585	1.10541	-0.6535
C	4.20479	0.46631	0.42556
C	2.33366	2.45291	-0.40014
H	1.19239	0.85124	-1.24731
C	4.50221	1.76847	0.6197
H	4.89488	-0.31504	0.73274
C	3.57134	2.81459	0.24189
H	5.44408	2.06237	1.07536
C	3.84429	4.16336	0.45757
H	4.775	4.45833	0.93826
C	2.92591	5.14424	0.05582
C	1.42291	3.47385	-0.80659
C	1.70993	4.79792	-0.58235
H	1.0308	5.59133	-0.87411
H	0.49191	3.17629	-1.28133
O	3.14634	6.45714	0.24747
H	3.99654	6.59546	0.69776
N	-2.16104	0.05774	-0.22385
S	-2.18692	0.65972	-1.75182
S	-3.50632	-0.48208	0.58756
O	-3.45674	1.23594	-2.17429
O	-0.93521	1.41959	-1.92582
O	-4.61475	-0.87635	-0.27401
O	-2.99659	-1.36848	1.63593
C	-4.04649	1.0688	1.48351
C	-1.90944	-0.86677	-2.80039
F	-2.84826	-1.77824	-2.57122
F	-1.92093	-0.52221	-4.08914
F	-0.70496	-1.39787	-2.50803
F	-3.07155	1.47182	2.30837
F	-4.31285	2.04383	0.61493

F	-5.1396	0.79728	2.19822
C	3.9093	-3.83837	-1.81147
H	4.89863	-3.37425	-1.72449
H	4.05879	-4.88847	-2.08164
H	3.36847	-3.36245	-2.6369
C	1.73746	-4.40208	-0.66627
H	1.1815	-4.38337	0.2747
H	1.15898	-3.8612	-1.42525
H	1.82814	-5.44442	-0.99222
C	3.93814	-4.53347	0.58869
H	4.06374	-5.57852	0.28311
H	4.93341	-4.08905	0.70598
H	3.42759	-4.50413	1.55162



CP2 + N_2

(Figure 4)

Zero-point correction=	0.389350 (Hartree/Particle)
Thermal correction to Energy=	0.429881
Thermal correction to Enthalpy=	0.430825
Thermal correction to Gibbs Free Energy=	0.304287
Sum of electronic and zero-point Energies=	-2946.484797
Sum of electronic and thermal Energies=	-2946.444267
Sum of electronic and thermal Enthalpies=	-2946.443323
Sum of electronic and thermal Free Energies=	-2946.569861

Cartesian Coordinates

Atom	X	Y	Z
Ag	-0.44564	-1.24761	0.62415
C	2.66284	0.13886	0.69992
H	2.1638	0.59769	1.54676

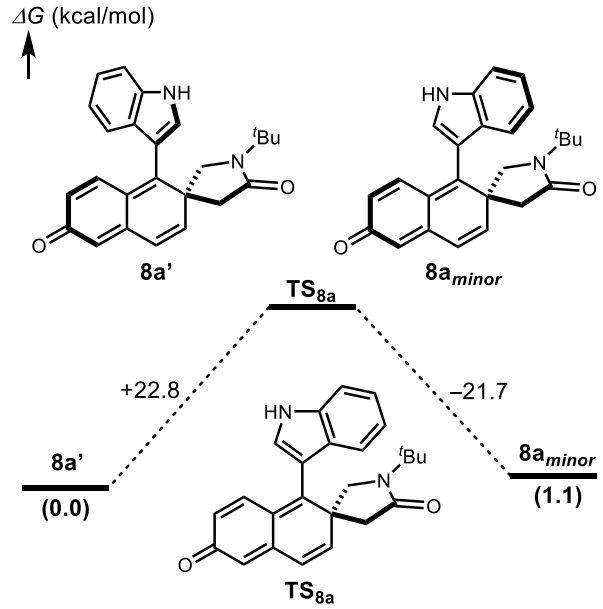
C	2.56962	-1.3293	0.52109
O	1.58968	-2.03996	0.85927
N	3.69578	-1.80488	-0.05978
C	3.91375	-3.24889	-0.41276
C	4.74559	-0.77336	-0.16033
H	5.5674	-0.99514	0.53463
H	5.15976	-0.73675	-1.17183
N	-1.04643	-1.73659	4.62437
N	-0.63866	-1.29289	3.69863
C	4.05896	0.53409	0.22208
C	2.84534	0.92966	-0.59889
C	4.83764	1.61438	0.85837
C	2.47337	2.36841	-0.6308
H	2.63514	0.3702	-1.50957
C	4.42718	2.89569	0.81955
H	5.7594	1.34114	1.36717
C	3.22962	3.31893	0.09763
H	5.01052	3.66643	1.31742
C	2.85153	4.66783	0.07705
H	3.41866	5.40973	0.63159
C	1.74156	5.08118	-0.66112
C	1.37545	2.8007	-1.38022
C	1.00449	4.14381	-1.3963
H	0.13575	4.45864	-1.97094
H	0.78191	2.07689	-1.93199
O	1.42648	6.40915	-0.63225
H	0.63182	6.55808	-1.16848
N	-2.29338	-0.40421	-0.13247
S	-3.59178	-0.27187	0.89108
S	-2.26209	0.14128	-1.69324
O	-4.87628	-0.15341	0.21262
O	-3.36524	-1.26227	1.94633
O	-3.16091	1.25642	-1.96767
O	-0.83949	0.21084	-2.0602
C	-2.91159	-1.33042	-2.64964
C	-3.26395	1.37512	1.71659

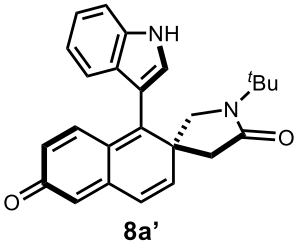
F	-3.23974	2.3595	0.82113
F	-4.22203	1.60998	2.61418
F	-2.07842	1.32825	2.34641
F	-2.10728	-2.3825	-2.44331
F	-4.14473	-1.63907	-2.26082
F	-2.91249	-1.03118	-3.95035
C	5.2506	-3.39919	-1.15917
H	6.10524	-3.0733	-0.55748
H	5.39863	-4.45821	-1.39107
H	5.25605	-2.85054	-2.10687
C	2.77887	-3.72988	-1.33728
H	1.80987	-3.68751	-0.83817
H	2.73364	-3.11807	-2.24516
H	2.96838	-4.76664	-1.63553
C	3.95653	-4.07535	0.88755
H	4.12195	-5.13234	0.65192
H	4.77528	-3.74081	1.53514
H	3.01653	-3.98679	1.43684

Calculation of Axial Rotation of 8a and 10a

The molecular structure optimizations were carried out using the hybrid density functional method based on wB97XD functional and the 6-311+G* basis set for H, C, N, O, and F. The vibrational frequencies were computed at the same level to check whether each optimized structure is at an energy minimum on the potential energy surfaces (no imaginary frequency) or a transition state (one imaginary frequency) and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298.15 K. The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.

Figure S3





(Figure S3)

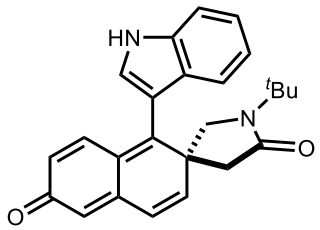
Zero-point correction=	0.440038 (Hartree/Particle)
Thermal correction to Energy=	0.464539
Thermal correction to Enthalpy=	0.465484
Thermal correction to Gibbs Free Energy=	0.385051
Sum of electronic and zero-point Energies=	-1226.506488
Sum of electronic and thermal Energies=	-1226.481987
Sum of electronic and thermal Enthalpies=	-1226.481043
Sum of electronic and thermal Free Energies=	-1226.561476

Cartesian Coordinates

Atom	X	Y	Z
O	-3.59463	-1.59654	1.96351
O	5.84025	-2.33083	-0.69463
N	-2.69622	-1.00913	-0.09089

C	3.31718	-0.00991	0.31161
H	3.1976	1.01846	0.63646
C	0.68505	2.19813	-0.02922
C	0.51451	3.37165	0.73533
C	3.51483	-2.70467	-0.5257
H	3.65165	-3.73134	-0.85403
C	-1.41023	-0.52138	-0.57153
H	-1.36018	0.57408	-0.53062
H	-1.21538	-0.83706	-1.5986
C	2.11184	-0.83088	0.20951
C	0.69852	3.54058	-2.01377
H	0.77464	3.63363	-3.0926
C	0.78236	2.29228	-1.42523
H	0.93073	1.39793	-2.02426
C	-1.20385	-1.22526	1.70439
H	-0.93817	-2.05913	2.35691
H	-1.11463	-0.29623	2.27628
C	0.52138	4.70044	-1.23395
H	0.46021	5.66646	-1.72558
C	1.09271	-3.04962	-0.34748
H	1.22228	-4.07641	-0.6789
C	-4.86923	-1.97583	-0.72302
H	-5.79758	-1.78996	-1.27379
H	-5.11262	-2.21449	0.31256
H	-4.36763	-2.83837	-1.17499
C	-0.37778	-1.16785	0.39948
C	0.42862	4.6359	0.14521
H	0.2962	5.53231	0.74361
C	0.72479	1.08868	0.89242
C	-2.65147	-1.32199	1.24242
C	-4.65236	0.48025	-0.16341
H	-4.00313	1.36163	-0.22131
H	-4.88304	0.27917	0.88543
H	-5.58585	0.71012	-0.68809
C	4.53441	-0.49171	0.01688
H	5.42679	0.1215	0.09304

C	-3.96761	-0.73638	-0.80389
C	-3.67444	-0.44159	-2.27936
H	-3.0613	0.45617	-2.41015
H	-4.62299	-0.27182	-2.79745
H	-3.17424	-1.28561	-2.76629
C	4.73131	-1.88656	-0.42653
C	2.28683	-2.22317	-0.23197
C	0.59254	1.62671	2.14423
H	0.60304	1.13681	3.10784
C	-0.11986	-2.57415	-0.06422
H	-0.99819	-3.20783	-0.16566
C	0.88453	-0.33414	0.51033
N	0.46488	2.99297	2.05705
H	0.35883	3.61492	2.84081



TS_{8a} (Figure S3)

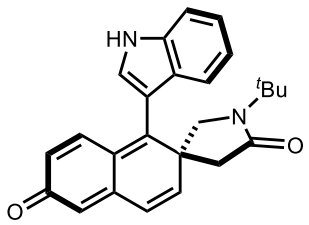
Zero-point correction=	0.441555 (Hartree/Particle)
Thermal correction to Energy=	0.464633
Thermal correction to Enthalpy=	0.465578
Thermal correction to Gibbs Free Energy=	0.390535
Sum of electronic and zero-point Energies=	-1226.474182
Sum of electronic and thermal Energies=	-1226.451104
Sum of electronic and thermal Enthalpies=	-1226.450160
Sum of electronic and thermal Free Energies=	-1226.525202

Cartesian Coordinates

Atom	X	Y	Z
O	-3.00083	-1.5689	2.02116
O	6.36581	-1.05285	-1.02103

N	-1.90419	-1.65804	-0.01521
C	3.65185	0.98479	0.11
H	3.52199	2.0094	0.40055
C	-0.79755	2.17487	0.01831
C	-0.76382	3.58474	-0.10382
C	4.26112	-1.71817	-0.16399
H	4.55817	-2.763	-0.18599
C	-0.69206	-1.12085	-0.61832
H	-0.88984	-0.23438	-1.23183
H	-0.20004	-1.85826	-1.2551
C	2.54671	0.03449	0.25925
C	-3.20762	2.40791	-0.24899
H	-4.17981	1.92703	-0.29825
C	-2.08989	1.61385	-0.06563
H	-2.26798	0.55744	0.0133
C	-0.79368	-0.57249	1.75988
H	-0.43668	-0.97159	2.71193
H	-1.05092	0.47512	1.92474
C	-3.11457	3.80192	-0.36249
H	-4.00833	4.40076	-0.50426
C	2.12092	-2.41418	0.70411
H	2.52827	-3.40792	0.86519
C	-3.40901	-3.60415	-0.13754
H	-4.18277	-4.09245	-0.73963
H	-3.79681	-3.43364	0.86711
H	-2.54755	-4.27796	-0.07397
C	0.2161	-0.80847	0.6143
C	-1.877	4.40553	-0.29018
H	-1.76008	5.48203	-0.37453
C	0.60715	1.71196	0.19259
C	-2.03953	-1.32829	1.31233
C	-4.1886	-1.31292	-0.86911
H	-3.9093	-0.39707	-1.40278
H	-4.52721	-1.05289	0.13688
H	-5.0217	-1.77714	-1.40745
C	4.89169	0.64814	-0.28428

H	5.67513	1.39542	-0.36635
C	-2.99807	-2.28199	-0.80095
C	-2.50771	-2.58	-2.22223
H	-2.18914	-1.67485	-2.74938
H	-3.33313	-3.01957	-2.79006
H	-1.68257	-3.29967	-2.22483
C	5.27138	-0.74456	-0.56435
C	3.01785	-1.3708	0.24803
C	1.33388	2.89353	0.14895
H	2.38416	3.08398	0.21626
C	0.84316	-2.14209	0.9203
H	0.1566	-2.91503	1.25676
C	1.19859	0.34439	0.35739
N	0.54362	3.97915	-0.01285
H	0.87603	4.92738	-0.07429



8a*minor* (Figure S3)

Zero-point correction=	0.440237 (Hartree/Particle)
Thermal correction to Energy=	0.464653
Thermal correction to Enthalpy=	0.465597
Thermal correction to Gibbs Free Energy=	0.385441
Sum of electronic and zero-point Energies=	-1226.504993
Sum of electronic and thermal Energies=	-1226.480577
Sum of electronic and thermal Enthalpies=	-1226.479632
Sum of electronic and thermal Free Energies=	-1226.559789

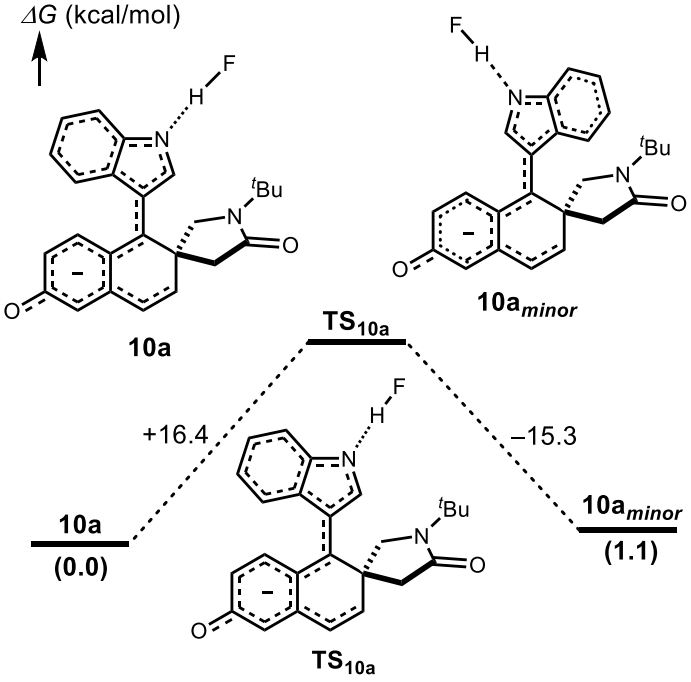
Cartesian Coordinates

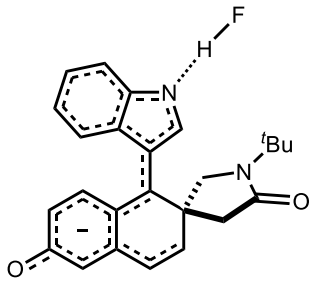
Atom	X	Y	Z
O	3.48166	0.41467	-2.10443

O	-5.18087	-3.56154	0.20367
N	2.96022	-0.59571	-0.08542
C	-3.11062	-0.69634	0.72386
H	-3.15345	0.31587	1.11215
C	-1.30509	2.13002	-0.06628
C	-1.22745	3.27504	0.75396
C	-2.89135	-3.31627	-0.31975
H	-2.86811	-4.32909	-0.71249
C	1.75951	-0.76766	0.72097
H	1.61484	0.08498	1.39657
H	1.79783	-1.68191	1.31655
C	-1.82617	-1.17033	0.21091
C	-2.22113	3.49128	-1.81156
H	-2.61923	3.6013	-2.81531
C	-1.81509	2.2467	-1.36765
H	-1.89219	1.37046	-2.00521
C	1.16556	0.08095	-1.43511
H	0.84799	-0.20057	-2.44105
H	0.87602	1.12388	-1.26697
C	-2.12972	4.62471	-0.9797
H	-2.45674	5.58833	-1.35792
C	-0.51446	-3.02225	-0.84828
H	-0.48441	-4.035	-1.24116
C	5.28085	-1.32233	-0.46427
H	6.28295	-1.35931	-0.02358
H	5.3329	-0.80395	-1.42181
H	4.94278	-2.34971	-0.63765
C	0.61364	-0.84978	-0.32822
C	-1.63549	4.536	0.30954
H	-1.56959	5.41078	0.94954
C	-0.80496	1.01681	0.70381
C	2.67754	-0.00465	-1.29129
C	4.77799	0.84191	0.7407
H	4.08982	1.35179	1.4252
H	4.81122	1.39447	-0.2011
H	5.77705	0.856	1.18935

C	-4.20756	-1.46923	0.72242
H	-5.15903	-1.11332	1.10475
C	4.32322	-0.6049	0.49732
C	4.3082	-1.36865	1.82632
H	3.67151	-0.88703	2.57601
H	5.32599	-1.3954	2.22672
H	3.97445	-2.40312	1.69197
C	-4.18389	-2.85084	0.20145
C	-1.78447	-2.54109	-0.32155
C	-0.46556	1.52211	1.92994
H	-0.08381	1.01131	2.80291
C	0.57712	-2.25752	-0.85425
H	1.51625	-2.63943	-1.24859
C	-0.71967	-0.38312	0.22403
N	-0.7136	2.87412	1.96592
H	-0.55328	3.47119	2.75965

Figure S4





10a

(Figure S4)

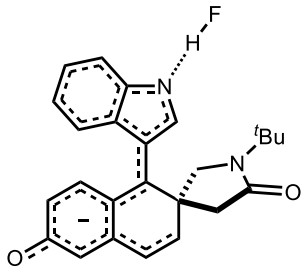
Zero-point correction=	0.438313 (Hartree/Particle)
Thermal correction to Energy=	0.464260
Thermal correction to Enthalpy=	0.465204
Thermal correction to Gibbs Free Energy=	0.381072
Sum of electronic and zero-point Energies=	-1326.457501
Sum of electronic and thermal Energies=	-1326.431554
Sum of electronic and thermal Enthalpies=	-1326.430609
Sum of electronic and thermal Free Energies=	-1326.514741

Cartesian Coordinates

Atom	X	Y	Z
O	3.13664	-2.53287	-1.70496
O	-6.24052	-1.86716	-0.13849
N	2.57182	-1.22476	0.12246
C	-3.23497	-0.01827	-0.81756
H	-2.90314	0.87037	-1.34509
C	-1.04406	2.14813	-0.00512
C	-0.0668	3.1395	-0.29036
C	-4.00699	-2.39863	0.43451
H	-4.34037	-3.32426	0.89841
C	1.39593	-0.99548	0.95066
H	1.28053	0.06139	1.18901
H	1.48711	-1.54488	1.89802
C	-2.22797	-0.82523	-0.1742
C	-2.42122	3.86931	0.96331
H	-3.33846	4.16717	1.4653
C	-2.22262	2.53229	0.65287
H	-2.97758	1.79847	0.91708

C	0.81577	-2.02425	-1.19615
H	0.48844	-3.03005	-1.46757
H	0.57686	-1.36533	-2.03672
C	-1.46146	4.84454	0.64147
H	-1.64805	5.88574	0.89288
C	-1.688	-2.96916	0.9839
H	-2.03971	-3.86885	1.4834
C	4.59236	-2.10507	1.18402
H	5.59949	-1.86872	1.54603
H	4.66592	-2.89408	0.43012
H	4.00452	-2.47961	2.03114
C	0.17399	-1.52432	0.1344
C	-0.27618	4.48585	0.02025
H	0.49012	5.22014	-0.21297
C	-0.44022	0.88487	-0.4005
C	2.31803	-1.98939	-0.97744
C	4.75516	-0.31698	-0.60494
H	4.31092	0.61469	-0.96932
H	4.82306	-1.0463	-1.412
H	5.76632	-0.08524	-0.25012
C	-4.54697	-0.35274	-0.82511
H	-5.28018	0.25691	-1.34535
C	3.93401	-0.85881	0.57556
C	3.84111	0.27071	1.61032
H	3.42036	1.17339	1.15523
H	4.85551	0.5141	1.94332
H	3.26104	-0.01057	2.4956
C	-5.04312	-1.5614	-0.16525
C	-2.68593	-2.06931	0.41504
C	0.838	1.26792	-0.87873
H	1.61588	0.61468	-1.25618
C	-0.38589	-2.72855	0.84699
H	0.3526	-3.44202	1.21063
C	-0.88663	-0.45126	-0.15437
N	1.06726	2.57406	-0.84137
H	2.58759	2.85762	-0.80407

F	3.57186	2.79499	-0.69091



TS_{10a} (Figure S4)

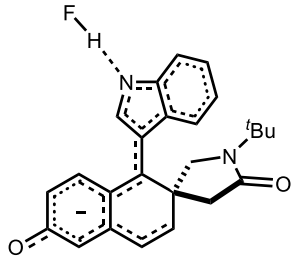
Zero-point correction=	0.439236 (Hartree/Particle)
Thermal correction to Energy=	0.464418
Thermal correction to Enthalpy=	0.465363
Thermal correction to Gibbs Free Energy=	0.383143
Sum of electronic and zero-point Energies=	-1326.432471
Sum of electronic and thermal Energies=	-1326.407289
Sum of electronic and thermal Enthalpies=	-1326.406344
Sum of electronic and thermal Free Energies=	-1326.488564

Cartesian Coordinates

Atom	X	Y	Z
O	-3.37508	-1.69624	2.12647
O	6.0245	-2.72506	-0.505
N	-2.65725	-1.11467	-0.00956
C	3.45104	-0.2402	-0.01812
H	3.36755	0.81744	0.09422
C	1.32258	2.36101	0.15493
C	0.26054	3.33201	0.11907
C	3.67275	-2.98368	-0.282
H	3.77448	-4.06265	-0.38233
C	-1.40215	-1.10994	-0.76589
H	-1.2569	-0.17505	-1.30749
H	-1.39897	-1.92071	-1.50632
C	2.2308	-0.99191	0.03329
C	2.82482	4.29632	0.00117

H	3.84764	4.66582	-0.0243
C	2.62118	2.92058	0.11604
H	3.52579	2.33815	0.19853
C	-1.01368	-1.2746	1.66844
H	-0.71447	-2.0693	2.35653
H	-0.84923	-0.32154	2.17888
C	1.75704	5.19899	-0.07147
H	1.94274	6.26658	-0.16456
C	1.28105	-3.31626	-0.04707
H	1.45043	-4.38579	-0.15287
C	-4.55749	-2.42	-0.88051
H	-5.53603	-2.37509	-1.37403
H	-4.6776	-2.91833	0.08604
H	-3.89085	-3.0261	-1.50697
C	-0.26198	-1.36164	0.30158
C	0.46037	4.7091	-0.00328
H	-0.40578	5.36528	-0.03105
C	0.6365	1.03383	0.26606
C	-2.49363	-1.40646	1.32453
C	-4.94222	-0.14168	0.17911
H	-4.53292	0.86793	0.28551
H	-5.10405	-0.58208	1.1626
H	-5.90611	-0.06464	-0.33955
C	4.69114	-0.77507	-0.18895
H	5.5729	-0.13865	-0.21366
C	-3.98984	-1.00223	-0.67747
C	-3.81986	-0.2763	-2.02552
H	-3.45554	0.7436	-1.86297
H	-4.80112	-0.20787	-2.50847
H	-3.15166	-0.80573	-2.71351
C	4.90156	-2.20926	-0.34265
C	2.42757	-2.43289	-0.10443
C	-0.74057	1.4405	0.34676
H	-1.60549	0.81366	0.46937
C	0.0582	-2.82675	0.1438
H	-0.80598	-3.48767	0.20525

C	0.9593	-0.38432	0.194
N	-0.97703	2.73533	0.24209
H	-2.47176	2.93291	-0.15071
F	-3.40918	2.76898	-0.44958



10a*minor* (Figure S4)

Zero-point correction= 0.438603 (Hartree/Particle)
Thermal correction to Energy= 0.464628
Thermal correction to Enthalpy= 0.465573
Thermal correction to Gibbs Free Energy= 0.381001
Sum of electronic and zero-point Energies= -1326.455404
Sum of electronic and thermal Energies= -1326.429378
Sum of electronic and thermal Enthalpies= -1326.428434
Sum of electronic and thermal Free Energies= -1326.513006

Cartesian Coordinates

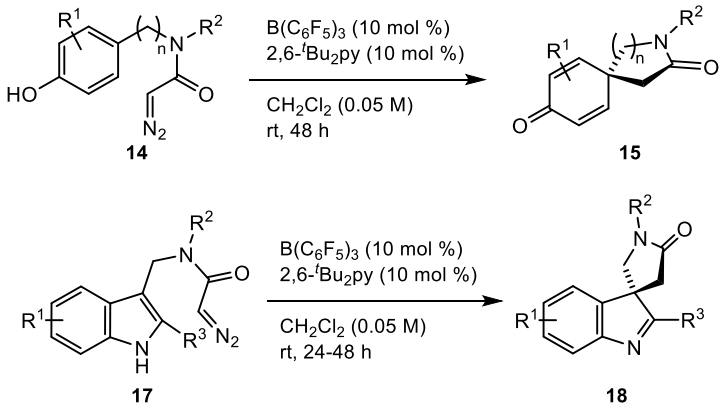
Atom	X	Y	Z
O	-3.53885	-0.65644	2.20213
O	5.7776	-2.64158	-0.89876
N	-2.69315	-1.06244	0.08858
C	3.03259	-0.3229	-0.91247
H	2.76728	0.64958	-1.31253
C	1.34491	2.09346	0.22187
C	0.51631	3.22096	-0.032
C	3.60318	-2.90554	-0.00358
H	3.84705	-3.9195	0.30567
C	-1.44528	-1.51491	-0.50213
H	-1.17594	-0.92959	-1.38384

H	-1.51867	-2.56435	-0.817
C	2.02796	-1.02967	-0.15385
C	3.10289	3.60131	0.87915
H	4.11289	3.76459	1.24704
C	2.64498	2.3041	0.70687
H	3.29265	1.46412	0.94017
C	-1.14075	-0.78015	1.81883
H	-0.97816	-1.33161	2.74808
H	-0.8748	0.26507	1.99898
C	2.2864	4.70796	0.58578
H	2.67535	5.71377	0.72469
C	1.33514	-3.20464	0.86295
H	1.60253	-4.21356	1.16849
C	-4.81724	-2.24129	-0.24292
H	-5.7713	-2.24564	-0.78264
H	-5.01947	-2.20316	0.83044
H	-4.28944	-3.17541	-0.47096
C	-0.3534	-1.36991	0.62319
C	0.98879	4.52594	0.13586
H	0.33448	5.36837	-0.07137
C	0.50255	0.93189	-0.00654
C	-2.60573	-0.8287	1.43288
C	-4.71444	0.28561	-0.36087
H	-4.11548	1.15844	-0.64474
H	-4.96473	0.3595	0.69773
H	-5.64311	0.30665	-0.94361
C	4.25598	-0.84029	-1.17152
H	4.98199	-0.29472	-1.76757
C	-3.97221	-1.02786	-0.65732
C	-3.68713	-1.07783	-2.16368
H	-3.10109	-0.21058	-2.48498
H	-4.64151	-1.04914	-2.69882
H	-3.16512	-1.99304	-2.46283
C	4.65446	-2.16661	-0.69757
C	2.36693	-2.38733	0.23532
C	-0.75092	1.50198	-0.34773

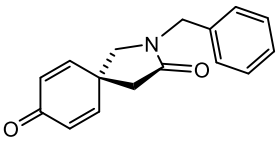
H	-1.66709	0.97951	-0.58857
C	0.09118	-2.7546	1.00719
H	-0.68768	-3.39299	1.42332
C	0.78926	-0.46477	0.13735
N	-0.754	2.82678	-0.40108
H	-2.18247	3.24683	-0.91535
F	-3.10405	3.19371	-1.26108

7. Characterization of Dearomatized Products 15a-15g, 18a-18d

Procedure A for Dearomative Spirocyclization of Phenols and Indoles

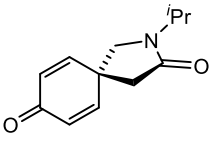


A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol%), diazo compound **14** or **17** (0.2 mmol), and 2,6-*tert*-butylpyridine (4.5 μL, 0.02 mmol, 10 mol%), which were subsequently dissolved partially in CH_2Cl_2 (4 mL) under an argon gas atmosphere. After being stirred for 24-48 h at room temperature, the reaction mixture was concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; gradient elution: *n*-hexane/EtOAc, 1/1 → 1/3) to afford spirocyclic compound **15**.



2-benzyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (15a)

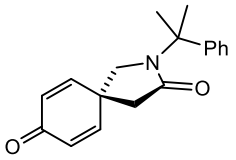
Prepared according to the general procedure A using **14a** (56.3 mg), and isolated as pale brown solid (43.4 mg, 86% yield).; R_f = 0.2 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 10.0 Hz, 2H), 6.27 (d, *J* = 10.0 Hz, 2H), 4.52 (s, 2H), 3.30 (s, 2H), 2.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 171.3, 149.7 (2C), 135.4, 129.2 (2C), 128.9 (2C), 128.2 (2C), 128.0, 53.6, 46.7, 41.0, 40.9; IR (ATR) 3030, 2921, 1681, 1658, 1622, 1486, 1443, 1431, 1274, 1258 cm$^{-1;}$ HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{16}H_{15}NNaO_2^+$ *m*/*z* 276.0995, found *m*/*z* 276.1006.



2-isopropyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (15b)

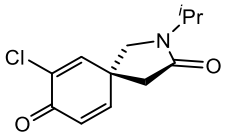
Prepared according to the general procedure A using **14b** (46.7 mg), and isolated as orange solid (40.3 mg, 98% yield).

^{1}H and ^{13}C NMR, IR, and MS were identical to those reported.[42]



2-(2-phenylpropan-2-yl)-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (15c)

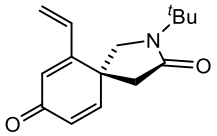
Prepared according to the general procedure A using **14c** (61.9 mg), and isolated as beige oil (23.3 mg, 41% yield).; R_f = 0.3 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 4.8 Hz, 4H), 7.30-7.25 (m, 1H), 6.93 (d, *J* = 10.0 Hz, 2H), 6.30 (d, *J* = 10.0 Hz, 2H), 3.35 (s, 2H), 2.57 (s, 2H), 1.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 171.6, 149.9 (2C), 145.4, 129.4 (2C), 128.6 (2C), 127.2, 125.0 (2C), 59.6, 53.8, 42.6, 41.0, 27.4 (2C); IR (ATR) 2978, 2932, 1687, 1660, 1626, 1403, 1387, 1270, 1254, 1179 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{18}H_{19}NNaO_2^+$ *m*/*z* 304.1308, found *m*/*z* 304.1310.



7-chloro-2-isopropyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (15d)

Prepared according to the general procedure A using **14d** (53.5 mg), and isolated as beige solid (39.9 mg, 83% yield).

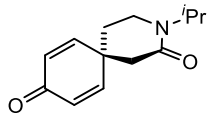
^{1}H and ^{13}C NMR, IR, and MS were identical to those reported.[18]



2-(*tert*-butyl)-6-vinyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (15e)

Prepared according to the general procedure A using **14e** (54.7 mg), and isolated as yellow oil (40.0 mg, 82% yield).

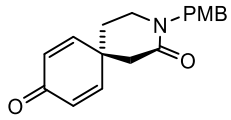
^{1}H and ^{13}C NMR, IR, and MS were identical to those reported.[42]



3-isopropyl-3-azaspiro[5.5]undeca-7,10-diene-2,9-dione (15f)

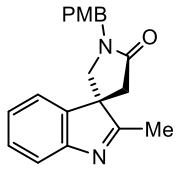
Prepared according to the general procedure A using **14f** (49.5 mg), and isolated as pale yellow solid (43.8 mg, quant.).

^{1}H and ^{13}C NMR, IR, and MS were identical to those reported.[42]



3-(4-methoxybenzyl)-3-azaspiro[5.5]undeca-7,10-diene-2,9-dione (15g)

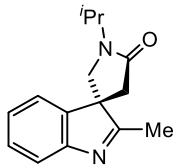
Prepared according to the general procedure A using **14g** (65.1 mg), and isolated as white solid (46.7 mg, 79% yield).; R_f = 0.2 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 10.0 Hz, 2H), 6.31 (d, *J* = 10.0 Hz, 2H), 4.62 (s, 2H), 3.82 (s, 3H), 3.38 (t, *J* = 6.8 Hz, 2H), 2.50 (s, 2H), 1.91 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 166.2, 159.2, 150.6 (2C), 129.6 (2C), 129.5 (2C), 128.6, 114.1 (2C), 55.2, 49.5, 43.6, 40.2, 39.7, 32.1; IR (ATR) 2962, 2925, 1658, 1620, 1510, 1467, 1243, 1172, 1033, 959 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{18}H_{19}NNaO_3^+$ *m*/*z* 320.1257, found *m*/*z* 320.1267.



1'-(4-methoxybenzyl)-2-methylspiro[indole-3,3'-pyrrolidin]-5'-one (18a)

Prepared according to the general procedure A using **17a** (35.0 mg), and isolated as yellow oil (28.6 mg, 87% yield, 0.083mmol scale).

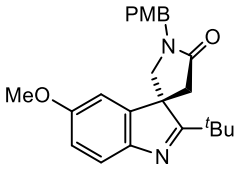
^{1}H and ^{13}C NMR, IR, and MS were identical to those reported. [19]



1'-isopropyl-2-methylspiro[indole-3,3'-pyrrolidin]-5'-one (18b)

Prepared according to the general procedure A using **17b** (27.0 mg), and isolated as yellow solid (24.9 mg, quant., 0.1 mmol scale): R_f = 0.2 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 8.0, 0.8

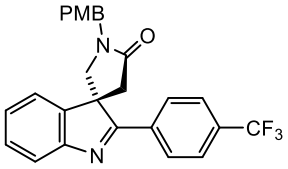
Hz, 1H), 7.39-7.35 (m, 2H), 7.24 (dt, *J* = 8.0, 0.8 Hz, 1H), 4.55 (sept, *J* = 6.8 Hz, 1H), 3.50 (d, *J* = 10.0 Hz, 1H), 3.46 (d, *J* = 10.0 Hz, 1H), 2.71 (d, *J* = 16.8 Hz, 1H), 2.65 (d, *J* = 16.8 Hz, 1H), 2.33 (s, 3H), 1.23 (dd, *J* = 6.8, 2.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 171.3, 154.0, 141.8, 128.7, 126.1, 121.0, 120.3, 55.4, 47.8, 43.0, 38.9, 19.7, 19.6, 15.8 ; IR (ATR) 2972, 2932, 2875, 2359, 1682, 1612, 1578, 1486, 1458, 1424, 1379 cm^{-1}; HRMS (ESI-TOF) $[M + H]^+$ calcd for $C_{15}H_{19}N_2O^+$ *m*/*z* 243.1419, found *m*/*z* 243.1493.



2-(*tert*-Butyl)-5-methoxy-1'-(4-methoxybenzyl)spiro[indole-3,3'-pyrrolidin]-5'-one (18c)

Prepared according to the general procedure A using **17c** (35.0 mg), and isolated as yellow oil (28.6 mg, 87% yield, 0.083mmol scale).

^{1}H and ^{13}C NMR, IR, and MS were identical to those reported. [19]

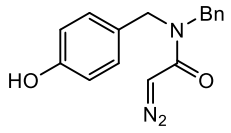


1'-(4-methoxybenzyl)-2-(4-(trifluoromethyl)phenyl)spiro[indole-3,3'-pyrrolidin]-5'-one (18d)

Prepared according to the general procedure A using **17d** (17.0 mg), and isolated as pale pink solid (13.3 mg, 83% yield, 0.036 mmol scale): R_f = 0.4 (*n*-hexane/EtOAc, 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.43-7.39 (m, 1H), 7.35-7.31 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.81 (d, *J* = 14.0 Hz, 1H), 4.41 (d, *J* = 14.0 Hz, 1H), 3.80 (s, 3H), 3.76 (d, *J* = 10.8 Hz, 1H), 3.55 (d, *J* = 10.8 Hz, 1H), 3.11 (d, *J* = 18.0 Hz, 1H), 2.85 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 171.6, 159.5, 152.9, 146.0, 134.1, 132.5 (d, *J* = 32.4 Hz), 130.0 (2C), 128.9, 127.9 (2C), 127.7, 127.3, 125.9 (d, *J* = 2.9 Hz, 2C) 123.6 (d, *J* = 271.8 Hz), 121.6, 120.5, 114.3 (2C), 55.2, 53.3, 53.0, 46.6, 40.2; ^{19}F NMR (376 MHz, $CDCl_3$) -62.9; IR (ATR) 2938, 1688, 1615, 1585, 1513, 1495, 1444, 1420, 1409, 1325, 1248 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{26}H_{21}F_3N_2NaO_2^+$ *m*/*z* 473.1447, found *m*/*z* 473.1469.

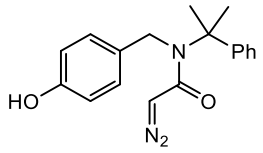
8. Synthesis and Characterization of Substrates 14a-14g, 17a-17g

14a-14g were synthesized with reported procedure and ^{1}H and ^{13}C NMR, IR, and MS of **14b**,[42] **14d**,[18] **14e**,[xx] and **14f**[18] were identical to those reported.



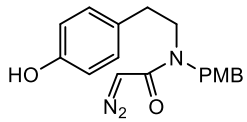
***N*-benzyl-2-diazo-*N*-(4-hydroxybenzyl)acetamide (14a)**

Pale yellow solid (816.5 mg, 62% yield).; R_f = 0.5 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 3H), 7.20 (br s, 2H), 7.02 (br s, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.01 (s, 1H), 4.41 (br s, 4H), OH peak was not detected.; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 156.0 128.8 (4C), 127.6 (3C), 115.8 (4C), 49.1 (2C), 47.4; IR (ATR) 3182, 3114, 2105, 1587, 1577, 1514, 1469, 1438, 1428, 1351, 1216 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{16}H_{15}N_3NaO_2^+$ *m*/*z* 304.1056, found *m*/*z* 304.1053.



2-diazo-*N*-(4-hydroxybenzyl)-*N*-(2-phenylpropan-2-yl)acetamide (14c)

Yellow solid (179.2 mg, 16% yield).; R_f = 0.5 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 4H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.75 (s, 2H), 4.64 (s, 3H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, acetonitrile-d3) δ 167.9, 156.9, 150.3, 131.8, 129.1 (2C), 128.8 (2C), 126.8, 125.3 (2C), 116.2 (2C), 63.0, 49.8, 48.9, 29.6 (2C); IR (ATR) 3163, 3105, 2102, 1572, 1513, 1416, 1361, 1276, 1204, 1161 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{18}H_{19}N_3NaO_2^+$ *m*/*z* 332.1369, found *m*/*z* 332.1375.

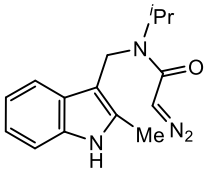


2-diazo-*N*-(4-hydroxyphenethyl)-*N*-(4-methoxybenzyl)acetamide (14g)

Yellow solid (46.7 mg, 79% yield).; R_f = 0.2 (*n*-hexane/EtOAc, 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.00 (m, 3H), 7.04 (d, *J* = 5.2 Hz, 1H), 6.85 (d, *J* = 5.2 Hz, 2H), 6.75 (d, *J* = 6.4 Hz, 1H), 4.87 (s, 1H), 3.78 (s, 3H), 3.52 (br s, 2H), 2.81 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 166.2, 159.2, 150.6 (2C), 129.6 (2C), 129.5 (2C), 128.6, 114.1 (2C), 55.2, 49.5, 43.6, 40.2, 39.7, 32.1; IR (ATR)

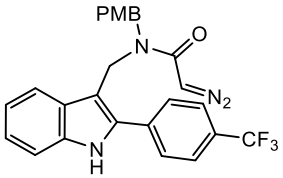
3158, 2109, 1562, 1513, 1456, 1416, 1363, 1350, 1242, 1197 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{18}H_{19}N_3NaO_3^+$ *m*/*z* 348.1319, found *m*/*z* 348.1318.

17a-17d were synthesized with reported procedure and ^1H and ^{13}C NMR, IR, and MS of **17a** and **17c** were identical to those reported.[19]



2-Diazo-*N*-isopropyl-*N*-((2-methyl-1*H*-indol-3-yl)methyl)acetamide (17b)

yellow solid (25.4 mg, 73% yield).: R_f = 0.5 (EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (br s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.11 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.06 (dt, *J* = 8.0, 1.2 Hz, 1H), 5.06 (s, 1H), 4.58 (br s, 2H), 4.25 (br s, 1H), 2.39 (s, 3H), 1.12 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 135.1, 131.8, 127.5, 121.1, 119.4, 118.3, 110.3, 107.6, 47.7, 47.5 (2C), 20.4, 12.0 (2C); IR (ATR) 3270, 3107, 2975, 2931, 2366, 2099, 1576, 1460, 1425, 1368, 1302 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{15}H_{18}N_4NaO_1^+$ *m*/*z* 293.1373, found *m*/*z* 293.1378.



2-Diazo-*N*-(4-methoxybenzyl)-*N*-((2-(4-(trifluoromethyl)phenyl)-1*H*-indol-3-yl)methyl)acetamide (17d)

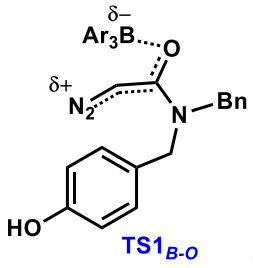
yellow solid (25.4 mg, 73% yield).: R_f = 0.4 (*n*-hexane/EtOAc, 2/1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (br s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.28 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.17 (dt, *J* = 8.0, 0.8 Hz, 1H), 6.68-6.61 (m, 4H), 5.03 (br s, 1H), 4.89 (br s, 2H), 3.97 (br s, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 158.8, 136.2, 135.7 (d, *J* = 9.5 Hz), 130.0, 129.7, 128.6 (2C), 128.2, 128.0, 127.8, 127.7, 121.7, 125.7 (d, *J* = 3.8 Hz, 2C), 123.9 (d, *J* = 270.8), 122.0 (d, *J* = 277.5 Hz, 2C), 120.2, 113.8 (2C), 111.0, 55.1 (2C), 47.6, 47.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4; IR (ATR) 3257, 2935, 2838, 2105, 1614, 1579, 1511, 1434, 1418, 1353, 1320 cm^{-1}; HRMS (ESI-TOF) $[M + Na]^+$ calcd for $C_{26}H_{21}N_4NaO_2^+$ *m*/*z* 501.1509, found *m*/*z* 501.1542.

9. Computational Details of Part 3

Mechanistic Studies on Dearomative Spirocyclization of Phenol with $B(C_6F_5)_3$

The molecular structure optimizations were carried out using the hybrid density functional method based on Becke's three-parameter exchange function and the Lee-YangParr nonlocal correlation functional (B3LYP), and the 6-31G* basis set for H, B, C, N, O, and F. The vibrational frequencies were computed at the same level to check whether each optimized structure is at an energy minimum on the potential energy surfaces (no imaginary frequency) or a transition state (one imaginary frequency) and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298.15 K. The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.

	E(RB3LYP/6-31G*) (A.U.)	Thermal Correction to Free Energy (A.U.)	Sum of Electronic and Thermal Free Energies (A.U.)
14a+$B(C_6F_5)_3$	-3141.547067859	0.326483	-3141.289561
TS1$_{B\text{-}O}$	-3141.61831801	0.353702	-3141.254664
CP1$_{B\text{-}O}$	-3141.62254440	0.355313	-3141.281448
TS2$_{B\text{-}O}$	-3141.56969410	0.309385	-3141.223391
PRO1$_{B\text{-}O}$	-3032.04884517	0.350878	-3031.798504
TS3$_{B\text{-}O}$	-3141.55699726	0.350952	-3141.210921
CP2$_{B\text{-}O}$	-3032.04884517	0.344841	-3031.704224
TS4$_{B\text{-}O}$	-3032.04886142	0.347328	-3031.701518
TS1$_{B\text{-}C}$	-3141.60824706	0.353702	-3141.254664
CP1$_{B\text{-}C}$	-3141.60683022	0.355601	-3141.257575
TS2$_{B\text{-}C}$	-3141.59352372	0.352214	-3141.245647
TS3$_{B\text{-}C}$	-3141.56149691	0.341656	-3141.219841
CP2$_{B\text{-}C}$	-3032.09413429	0.345884	-3031.751719
TS3$_{B\text{-}C}$	-3032.09415907	0.347711	-3031.746448
INT1$_{B\text{-}C}$	-3032.09413035	0.351938	-3031.753646



(Figure 9)

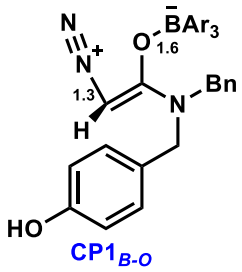
Zero-point correction=	0.439260 (Hartree/Particle)
Thermal correction to Energy=	0.487890
Thermal correction to Enthalpy=	0.488834
Thermal correction to Gibbs Free Energy=	0.352141
Sum of electronic and zero-point Energies=	-3141.183262
Sum of electronic and thermal Energies=	-3141.134632
Sum of electronic and thermal Enthalpies=	-3141.133688
Sum of electronic and thermal Free Energies=	-3141.270380

Cartesian Coordinates

Atom	X	Y	Z
C	0.93596	-2.01069	-1.39415
H	1.94463	-2.39497	-1.44202
C	0.59935	-0.59301	-1.39651
O	-0.54482	-0.14872	-1.16213
N	1.6363	0.25361	-1.71044
C	1.35272	1.69011	-1.88853
C	2.93351	-0.21973	-2.21029
H	2.77791	-0.87263	-3.08088
H	3.44739	0.67167	-2.58427
N	-0.71958	-3.79171	-1.16645
N	0.01901	-2.93613	-1.25937
C	3.84628	-0.92	-1.21132
C	3.77454	-0.70052	0.17089
C	4.83713	-1.78277	-1.69419
C	4.6693	-1.31437	1.04217
H	3.00032	-0.05688	0.57259
C	5.74406	-2.39924	-0.83259
H	4.91012	-1.97786	-2.76253

C	5.66305	-2.16325	0.54329
H	6.50682	-3.06695	-1.22944
H	7.15091	-3.29424	0.97069
B	-2.07856	-0.07645	0.29789
C	-1.73012	1.36786	0.88887
C	-1.69928	2.5219	0.09189
C	-1.53022	1.63966	2.25023
C	-1.46059	3.80941	0.55364
C	-1.29378	2.9043	2.78187
C	-1.25602	3.99715	1.9198
C	-3.33827	-0.14578	-0.68406
C	-4.46926	0.66099	-0.49518
C	-3.46679	-1.01952	-1.77055
C	-5.60097	0.65101	-1.30325
C	-4.56006	-1.07268	-2.62653
C	-5.63798	-0.22248	-2.38707
C	-1.66894	-1.36664	1.13756
C	-2.53741	-2.43392	1.40686
C	-0.39958	-1.53102	1.71108
C	-2.19702	-3.56239	2.1481
C	0.01102	-2.63342	2.44624
C	-0.90786	-3.66109	2.66395
F	-1.90292	2.39049	-1.24297
F	-1.59546	0.62534	3.14424
F	-2.46545	-1.89444	-2.03032
F	-4.49943	1.50588	0.56499
F	-3.8065	-2.38347	0.94567
F	0.52216	-0.54562	1.53242
C	2.20384	2.58998	-1.01426
C	3.13548	3.46302	-1.58646
C	2.05661	2.5786	0.3809
C	3.91175	4.30665	-0.78757
H	3.24971	3.49036	-2.66854
C	2.83141	3.41766	1.17982
H	1.32877	1.91424	0.83842
C	3.76227	4.28354	0.59846

H	4.63054	4.97852	-1.24935
H	2.70208	3.40136	2.25869
H	4.36414	4.93768	1.22375
O	6.51373	-2.73837	1.44563
H	0.2922	1.82711	-1.68534
H	1.51828	1.94321	-2.94462
H	4.61148	-1.14655	2.11301
F	-1.44333	4.83486	-0.32424
F	-1.02769	5.23582	2.40567
F	-1.12444	3.03363	4.11495
F	-6.62589	1.47919	-1.00974
F	-6.71906	-0.2552	-3.19497
F	-4.5516	-1.95247	-3.65044
F	-3.12392	-4.52439	2.34282
F	-0.54797	-4.74702	3.3807
F	1.2693	-2.67662	2.93343



$CP1_{B\text{-}O}$ (Figure 9)

Zero-point correction= 0.440722 (Hartree/Particle)

Thermal correction to Energy= 0.489287

Thermal correction to Enthalpy= 0.490231

Thermal correction to Gibbs Free Energy= 0.355313

Sum of electronic and zero-point Energies= -3141.196040

Sum of electronic and thermal Energies= -3141.147474

Sum of electronic and thermal Enthalpies= -3141.146530

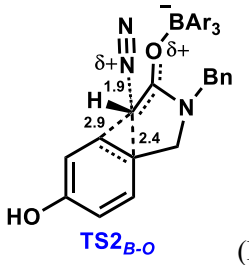
Sum of electronic and thermal Free Energies= -3141.281448

Cartesian Coordinates

Atom	X	Y	Z

C	1.43625	-1.93235	-1.78969
H	2.43583	-2.28308	-2.00304
C	1.05664	-0.52791	-1.70125
O	-0.07472	-0.1451	-1.32401
N	2.0211	0.36802	-2.08905
C	1.66476	1.79484	-2.19718
C	3.28188	-0.02972	-2.73793
H	3.06172	-0.60804	-3.64647
H	3.74109	0.90583	-3.07269
N	-0.1172	-3.76278	-1.33938
N	0.57619	-2.88613	-1.53726
C	4.29136	-0.78913	-1.88837
C	4.40296	-0.61504	-0.50178
C	5.1876	-1.65891	-2.5204
C	5.37971	-1.28222	0.2295
H	3.70861	0.03793	0.01499
C	6.17793	-2.32728	-1.80051
H	5.11985	-1.81817	-3.59491
C	6.27741	-2.13868	-0.41857
H	6.86474	-2.999	-2.31221
H	7.76901	-3.32625	-0.21516
B	-1.48808	-0.09342	0.3346
C	-1.0658	1.3301	0.91595
C	-1.1184	2.49168	0.13292
C	-0.69704	1.54556	2.25047
C	-0.79506	3.75853	0.60325
C	-0.37645	2.80057	2.76501
C	-0.42304	3.91523	1.9355
C	-2.82345	-0.1448	-0.53663
C	-3.90179	0.71659	-0.29424
C	-3.03371	-1.06184	-1.57291
C	-5.08191	0.70069	-1.03349
C	-4.19026	-1.10109	-2.34448
C	-5.22478	-0.21086	-2.07334
C	-0.98515	-1.4085	1.07393
C	-1.82592	-2.4866	1.37818

C	0.34552	-1.56793	1.48445
C	-1.3854	-3.64197	2.02212
C	0.82758	-2.70706	2.11592
C	-0.04864	-3.75604	2.38664
F	-1.4844	2.41951	-1.16223
F	-0.6603	0.52929	3.13229
F	-2.09868	-1.98056	-1.87236
F	-3.8557	1.61166	0.71218
F	-3.13513	-2.44789	1.07596
F	1.24649	-0.58578	1.26353
C	2.55139	2.70927	-1.37414
C	3.3057	3.71106	-1.99403
C	2.60904	2.58761	0.02247
C	4.10265	4.57675	-1.24045
H	3.26335	3.82202	-3.0757
C	3.40651	3.4474	0.77621
H	2.02545	1.8162	0.51776
C	4.15572	4.44545	0.14644
H	4.6805	5.35039	-1.73884
H	3.44059	3.34238	1.85734
H	4.77471	5.11628	0.73577
O	7.21564	-2.76517	0.35024
H	0.62176	1.88121	-1.89899
H	1.72381	2.08352	-3.25505
H	5.45917	-1.15461	1.30426
F	-0.84724	4.82289	-0.20641
F	-0.11299	5.12303	2.41109
F	-0.03221	2.9401	4.05194
F	-6.07607	1.55145	-0.74801
F	-6.34615	-0.23929	-2.79809
F	-4.32039	-1.99484	-3.33394
F	-2.23699	-4.63784	2.29106
F	0.39294	-4.85796	2.9965
F	2.11611	-2.80398	2.46813



$TS2_{B\text{-}O}$ (Figure 9)

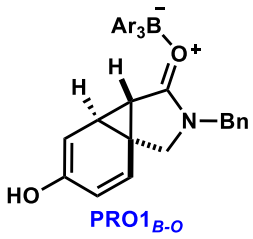
Zero-point correction=	0.436586 (Hartree/Particle)
Thermal correction to Energy=	0.485526
Thermal correction to Enthalpy=	0.486470
Thermal correction to Gibbs Free Energy=	0.350952
Sum of electronic and zero-point Energies=	-3141.137756
Sum of electronic and thermal Energies=	-3141.088816
Sum of electronic and thermal Enthalpies=	-3141.087872
Sum of electronic and thermal Free Energies=	-3141.223391

Cartesian Coordinates

Atom	X	Y	Z
C	1.20006	-1.63507	-1.19915
H	1.31188	-2.13633	-0.23792
C	0.81148	-0.21356	-1.13543
O	-0.34473	0.25297	-0.88703
N	1.75996	0.66076	-1.54564
C	1.46955	2.08749	-1.77521
C	3.05231	0.13861	-1.99231
H	2.98104	-0.19724	-3.03649
H	3.75774	0.97578	-1.95523
N	-0.88109	-3.44922	-2.1345
N	-0.46533	-2.58202	-1.57944
C	3.53392	-0.99692	-1.11672
C	3.57648	-0.85877	0.28802
C	4.11691	-2.14521	-1.68893
C	4.1408	-1.84396	1.08835
H	3.1398	0.0197	0.75344
C	4.69346	-3.12744	-0.89947
H	4.09538	-2.27027	-2.76787

C	4.70521	-2.98122	0.49767
H	5.12549	-4.01493	-1.35743
H	5.59245	-4.65175	0.80152
B	-1.56759	-0.09537	0.06826
C	-1.92887	1.36802	0.74064
C	-2.05964	2.52015	-0.04573
C	-2.24041	1.60117	2.08627
C	-2.40561	3.78437	0.41795
C	-2.599	2.83627	2.62115
C	-2.67788	3.93969	1.77574
C	-2.83819	-0.50422	-0.874
C	-4.09716	-0.67167	-0.28374
C	-2.8765	-0.59414	-2.26734
C	-5.28277	-0.90918	-0.96507
C	-4.026	-0.82888	-3.01921
C	-5.24086	-0.98505	-2.35759
C	-1.04599	-1.207	1.155
C	-1.58721	-2.47716	1.38503
C	0.03565	-0.93005	1.99947
C	-1.13921	-3.37332	2.35505
C	0.54276	-1.76869	2.98195
C	-0.0676	-3.01017	3.1647
F	-1.83376	2.42299	-1.38833
F	-2.20748	0.56994	2.96458
F	-1.721	-0.47402	-2.98164
F	-4.16826	-0.60257	1.07059
F	-2.60237	-2.91991	0.60582
F	0.68332	0.26608	1.83947
C	2.28944	3.00963	-0.89415
C	3.27215	3.83778	-1.44789
C	2.06328	3.05461	0.48985
C	4.02233	4.69532	-0.63904
H	3.44568	3.81998	-2.52216
C	2.81362	3.90774	1.2978
H	1.29606	2.42506	0.93088
C	3.79525	4.72964	0.73633

H	4.78022	5.3341	-1.08477
H	2.62532	3.93771	2.36764
H	4.37573	5.39602	1.36876
O	5.2451	-3.91297	1.32618
H	0.40095	2.22716	-1.61729
H	1.67554	2.29911	-2.83266
H	4.15629	-1.7509	2.16902
F	-2.486	4.81024	-0.4559
F	-3.02358	5.14908	2.266
F	-2.87081	2.92201	3.94072
F	1.58687	-1.36136	3.73455
F	0.38492	-3.85592	4.11467
F	-1.75859	-4.56659	2.47747
F	-3.92721	-0.89798	-4.36381
F	-6.37133	-1.21306	-3.0594
F	-6.42994	-1.05686	-0.26888



PRO1$_{B\text{-}O}$ (Figure 9)

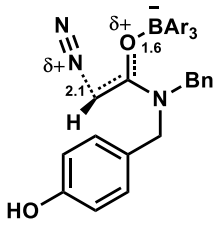
Zero-point correction=	0.432694 (Hartree/Particle)
Thermal correction to Energy=	0.478382
Thermal correction to Enthalpy=	0.479326
Thermal correction to Gibbs Free Energy=	0.350878
Sum of electronic and zero-point Energies=	-3031.716688
Sum of electronic and thermal Energies=	-3031.671000
Sum of electronic and thermal Enthalpies=	-3031.670056
Sum of electronic and thermal Free Energies=	-3031.798504

Cartesian Coordinates

Atom	X	Y	Z
C	1.69708	-0.7309	1.39314

C	1.16411	0.44462	0.81754
O	-0.00689	0.56267	0.28931
C	1.86337	2.40236	-0.51884
H	2.7647	2.33389	-1.13805
H	1.02109	2.03647	-1.10421
B	-1.12085	-0.48648	-0.08131
C	-2.05214	0.38112	-1.10825
C	-2.51522	1.6469	-0.7332
C	-3.25739	2.48449	-1.55617
C	-3.59222	2.05115	-2.83642
C	-3.17594	0.79417	-3.25615
C	-2.42511	-0.00995	-2.3962
C	-1.85387	-0.82632	1.35524
C	-1.09155	-1.28387	2.41781
C	-1.52527	-1.51335	3.71532
C	-2.87202	-1.29493	3.99117
C	-3.70953	-0.86377	2.96682
C	-3.19921	-0.64434	1.68522
C	-0.42504	-1.79946	-0.76226
C	-0.90697	-3.09867	-0.59063
C	-0.3149	-4.22422	-1.16087
C	0.81676	-4.07525	-1.95544
C	1.32723	-2.79949	-2.17284
C	0.68874	-1.70746	-1.59822
F	-2.26061	2.11232	0.5144
F	-2.07528	-1.21381	-2.89181
F	0.24786	-1.63421	2.19196
F	-4.09291	-0.2476	0.76482
F	1.23171	-0.49378	-1.88372
F	-2.00941	-3.32478	0.15569
F	-4.30889	2.83529	-3.64898
F	-3.66305	3.68882	-1.12767
F	-3.49445	0.36174	-4.48408
F	-0.82651	-5.4448	-0.95048
F	1.40655	-5.14333	-2.50297
F	2.42321	-2.6302	-2.92913

F	-0.69204	-1.9508	4.66643
F	-3.35217	-1.50552	5.21957
F	-5.00615	-0.66093	3.21974
H	2.20711	-0.71858	2.35146
N	2.03531	1.46905	0.62278
C	3.28828	1.56691	1.37378
H	3.5725	2.62462	1.34579
H	3.07374	1.3429	2.42657
C	1.64483	3.83255	-0.06857
C	0.43944	4.21203	0.53966
C	2.64261	4.79498	-0.26349
C	0.24308	5.53098	0.94508
H	-0.3483	3.47808	0.68085
C	2.44521	6.11703	0.14255
H	3.57506	4.51207	-0.74791
C	1.24532	6.48587	0.74987
H	-0.69796	5.81652	1.40716
H	3.22655	6.85467	-0.01909
H	1.0871	7.51375	1.06478
C	4.43208	0.6942	0.86757
C	5.64095	0.69997	1.57503
C	4.33824	-0.10386	-0.28091
C	6.72456	-0.06682	1.15626
H	5.74284	1.31193	2.46933
C	5.41519	-0.87744	-0.70867
H	3.41755	-0.14483	-0.85218
C	6.6144	-0.86183	0.00769
H	7.65484	-0.0502	1.72116
H	5.33179	-1.502	-1.59217
O	7.63739	-1.63758	-0.45419
H	8.40334	-1.54108	0.13291



$TS3_{B\text{-}O}$ (Figure 9)

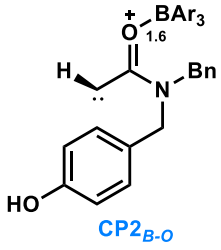
Zero-point correction=	0.435328 (Hartree/Particle)
Thermal correction to Energy=	0.485085
Thermal correction to Enthalpy=	0.486029
Thermal correction to Gibbs Free Energy=	0.346108
Sum of electronic and zero-point Energies=	-3141.121701
Sum of electronic and thermal Energies=	-3141.071944
Sum of electronic and thermal Enthalpies=	-3141.071000
Sum of electronic and thermal Free Energies=	-3141.210921

Cartesian Coordinates

Atom	X	Y	Z
C	-0.86323	-1.15742	-2.72196
C	-1.04101	-0.19647	-1.65892
O	0.15186	-0.19089	-1.19788
C	-2.07666	1.0646	0.18752
H	-2.75205	0.49922	0.83724
H	-1.07426	0.96323	0.59644
B	1.27424	-0.13769	-0.02378
C	1.51933	1.47567	0.0755
C	2.01667	2.16982	-1.03588
C	2.2625	3.53861	-1.04908
C	1.99764	4.28972	0.09348
C	1.48176	3.65653	1.21708
C	1.24614	2.28183	1.183
C	2.51937	-0.99923	-0.64086
C	2.2994	-2.28797	-1.13802
C	3.30662	-3.1124	-1.63084
C	4.62274	-2.66155	-1.6119
C	4.9001	-1.39879	-1.10084

C	3.85911	-0.60273	-0.62446
C	0.79817	-0.90892	1.33505
C	1.67754	-0.89764	2.42416
C	1.46463	-1.60262	3.60256
C	0.32116	-2.38855	3.72729
C	-0.57967	-2.44485	2.67151
C	-0.32061	-1.71958	1.50849
F	2.29488	1.50471	-2.17573
F	0.68268	1.76406	2.29549
F	1.04943	-2.80097	-1.14778
F	4.2213	0.59752	-0.13168
F	-1.25581	-1.83245	0.53218
F	2.80698	-0.16422	2.34865
H	-0.17714	-0.78426	-3.48534
N	-2.10532	0.41148	-1.14014
C	-3.43029	0.3575	-1.79006
H	-3.83185	1.37462	-1.763
H	-3.27104	0.11674	-2.84112
C	-2.49112	2.52162	0.13423
C	-1.78047	3.44433	-0.64619
C	-3.57826	2.97035	0.89223
C	-2.15202	4.78782	-0.66665
H	-0.9296	3.11082	-1.23481
C	-3.94766	4.3173	0.87837
H	-4.13516	2.2624	1.5017
C	-3.23626	5.22784	0.09738
H	-1.59021	5.49358	-1.27225
H	-4.79059	4.65201	1.47668
H	-3.52139	6.27611	0.0848
C	-4.40649	-0.59767	-1.13362
C	-5.67394	-0.14473	-0.755
C	-4.08831	-1.94952	-0.92216
C	-6.61133	-1.01071	-0.19184
H	-5.93992	0.89962	-0.90196
C	-5.00981	-2.82017	-0.35423
H	-3.10492	-2.32587	-1.18854

C	-6.28014	-2.35389	0.00988
H	-7.59359	-0.64032	0.09535
H	-4.7646	-3.86314	-0.1825
O	-7.1434	-3.25607	0.55747
H	-7.97909	-2.81225	0.77093
N	-2.30464	-1.39514	-4.14712
N	-2.87186	-2.13958	-4.7443
F	2.75105	4.1383	-2.1441
F	2.22118	5.60793	0.10062
F	1.19532	4.36926	2.31414
F	6.165	-0.95654	-1.06736
F	5.60972	-3.43658	-2.07575
F	3.02282	-4.33381	-2.10673
F	2.3447	-1.53924	4.61014
F	0.09244	-3.07655	4.85127
F	-1.68661	-3.19527	2.77198



$CP2_{B\text{-}O}$ (Figure 9)

Zero-point correction= 0.429429 (Hartree/Particle)

Thermal correction to Energy= 0.475984

Thermal correction to Enthalpy= 0.476928

Thermal correction to Gibbs Free Energy= 0.344841

Sum of electronic and zero-point Energies= -3031.619635

Sum of electronic and thermal Energies= -3031.573081

Sum of electronic and thermal Enthalpies= -3031.572136

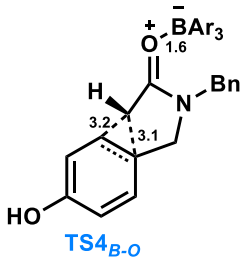
Sum of electronic and thermal Free Energies= -3031.704224

Cartesian Coordinates

Atom	X	Y	Z

C	1.69708	-0.7309	1.39314
C	1.16411	0.44462	0.81754
O	-0.00689	0.56267	0.28931
C	1.86337	2.40236	-0.51884
H	2.7647	2.33389	-1.13805
H	1.02109	2.03647	-1.10421
B	-1.12085	-0.48648	-0.08131
C	-2.05214	0.38112	-1.10825
C	-2.51522	1.6469	-0.7332
C	-3.25739	2.48449	-1.55617
C	-3.59222	2.05115	-2.83642
C	-3.17594	0.79417	-3.25615
C	-2.42511	-0.00995	-2.3962
C	-1.85387	-0.82632	1.35524
C	-1.09155	-1.28387	2.41781
C	-1.52527	-1.51335	3.71532
C	-2.87202	-1.29493	3.99117
C	-3.70953	-0.86377	2.96682
C	-3.19921	-0.64434	1.68522
C	-0.42504	-1.79946	-0.76226
C	-0.90697	-3.09867	-0.59063
C	-0.3149	-4.22422	-1.16087
C	0.81676	-4.07525	-1.95544
C	1.32723	-2.79949	-2.17284
C	0.68874	-1.70746	-1.59822
F	-2.26061	2.11232	0.5144
F	-2.07528	-1.21381	-2.89181
F	0.24786	-1.63421	2.19196
F	-4.09291	-0.2476	0.76482
F	1.23171	-0.49378	-1.88372
F	-2.00941	-3.32478	0.15569
F	-4.30889	2.83529	-3.64898
F	-3.66305	3.68882	-1.12767
F	-3.49445	0.36174	-4.48408
F	-0.82651	-5.4448	-0.95048
F	1.40655	-5.14333	-2.50297

F	2.42321	-2.6302	-2.92913
F	-0.69204	-1.9508	4.66643
F	-3.35217	-1.50552	5.21957
F	-5.00615	-0.66093	3.21974
H	2.20711	-0.71858	2.35146
N	2.03531	1.46905	0.62278
C	3.28828	1.56691	1.37378
H	3.5725	2.62462	1.34579
H	3.07374	1.3429	2.42657
C	1.64483	3.83255	-0.06857
C	0.43944	4.21203	0.53966
C	2.64261	4.79498	-0.26349
C	0.24308	5.53098	0.94508
H	-0.3483	3.47808	0.68085
C	2.44521	6.11703	0.14255
H	3.57506	4.51207	-0.74791
C	1.24532	6.48587	0.74987
H	-0.69796	5.81652	1.40716
H	3.22655	6.85467	-0.01909
H	1.0871	7.51375	1.06478
C	4.43208	0.6942	0.86757
C	5.64095	0.69997	1.57503
C	4.33824	-0.10386	-0.28091
C	6.72456	-0.06682	1.15626
H	5.74284	1.31193	2.46933
C	5.41519	-0.87744	-0.70867
H	3.41755	-0.14483	-0.85218
C	6.6144	-0.86183	0.00769
H	7.65484	-0.0502	1.72116
H	5.33179	-1.502	-1.59217
O	7.63739	-1.63758	-0.45419
H	8.40334	-1.54108	0.13291



$TS4_{B\text{-}O}$ (Figure 9)

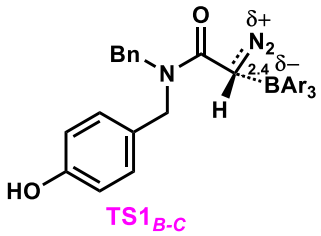
Zero-point correction=	0.429060 (Hartree/Particle)
Thermal correction to Energy=	0.474757
Thermal correction to Enthalpy=	0.475701
Thermal correction to Gibbs Free Energy=	0.347328
Sum of electronic and zero-point Energies=	-3031.619785
Sum of electronic and thermal Energies=	-3031.574089
Sum of electronic and thermal Enthalpies=	-3031.573144
Sum of electronic and thermal Free Energies=	-3031.701518

Cartesian Coordinates

Atom	X	Y	Z
C	1.68414	-0.80478	1.36726
C	1.19274	0.3803	0.78001
O	0.02815	0.54155	0.24761
C	1.97502	2.28667	-0.58453
H	2.87305	2.16509	-1.20047
H	1.11775	1.94759	-1.16435
B	-1.1451	-0.45153	-0.07077
C	-2.06917	0.4483	-1.07639
C	-2.4611	1.73727	-0.69937
C	-3.18838	2.6024	-1.50685
C	-3.58199	2.17541	-2.77244
C	-3.23717	0.89737	-3.19329
C	-2.49842	0.06553	-2.34928
C	-1.84321	-0.74002	1.39614
C	-1.06586	-1.23393	2.43005
C	-1.45273	-1.43128	3.74722
C	-2.77154	-1.13304	4.07795
C	-3.6259	-0.65998	3.08607

C	-3.16038	-0.47816	1.78158
C	-0.5441	-1.80843	-0.75605
C	-1.12103	-3.06769	-0.57923
C	-0.62532	-4.23385	-1.15857
C	0.50229	-4.16893	-1.97025
C	1.10582	-2.93558	-2.19284
C	0.56378	-1.79855	-1.60488
F	-2.14572	2.20028	0.53529
F	-2.21854	-1.15608	-2.84566
F	0.24262	-1.66478	2.14476
F	-4.06828	-0.03562	0.89742
F	1.19492	-0.63045	-1.89711
F	-2.22889	-3.2083	0.18057
F	-4.28607	2.98583	-3.57001
F	-3.52399	3.82768	-1.07715
F	-3.61236	0.47118	-4.40728
F	-1.2256	-5.41236	-0.94256
F	0.99973	-5.27715	-2.52971
F	2.1965	-2.84937	-2.96959
F	-0.60502	-1.91063	4.66432
F	-3.21019	-1.30771	5.32715
F	-4.89612	-0.38072	3.39285
H	2.21752	-0.80938	2.31166
N	2.10236	1.37039	0.57626
C	3.3522	1.43849	1.3346
H	3.65539	2.49127	1.3197
H	3.12668	1.20732	2.38343
C	1.82137	3.73468	-0.16509
C	0.63876	4.17949	0.44362
C	2.85731	4.64887	-0.39059
C	0.50194	5.51488	0.81856
H	-0.17763	3.48318	0.61012
C	2.71957	5.98748	-0.01527
H	3.77306	4.3147	-0.87414
C	1.54172	6.4215	0.5921
H	-0.42191	5.85095	1.28137

H	3.53019	6.68703	-0.20042
H	1.42992	7.46241	0.88324
C	4.48641	0.55523	0.82568
C	5.70951	0.58318	1.50761
C	4.37139	-0.27333	-0.29869
C	6.78662	-0.1929	1.08902
H	5.82797	1.22074	2.38178
C	5.44278	-1.05442	-0.72754
H	3.4391	-0.33073	-0.84996
C	6.65581	-1.01785	-0.03566
H	7.72814	-0.15836	1.63417
H	5.34682	-1.70006	-1.59444
O	7.67179	-1.80283	-0.49831
H	8.44917	-1.68869	0.07028



$TS1_{B\text{-}C}$ (Figure 10)

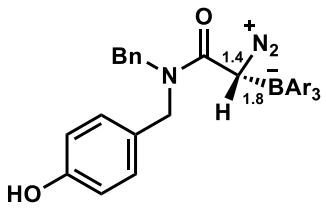
Zero-point correction= 0.439757 (Hartree/Particle)
Thermal correction to Energy= 0.488162
Thermal correction to Enthalpy= 0.489106
Thermal correction to Gibbs Free Energy= 0.353702
Sum of electronic and zero-point Energies= -3141.168609
Sum of electronic and thermal Energies= -3141.120205
Sum of electronic and thermal Enthalpies= -3141.119260
Sum of electronic and thermal Free Energies= -3141.254664

Cartesian Coordinates

Atom	X	Y	Z
C	0.3335	-1.28352	-0.83142
H	0.22781	-0.75583	-1.76814
C	-0.83325	-1.60273	0.08328

O	-0.71186	-2.55161	0.85895
N	-1.97078	-0.84841	0.0063
C	-3.10104	-1.27689	0.85761
C	-2.26971	0.15188	-1.02519
H	-1.34537	0.41251	-1.53979
H	-2.94137	-0.29191	-1.77334
N	1.69805	-3.33008	-1.01848
N	1.05231	-2.4127	-1.0008
C	-2.90818	1.41735	-0.47798
C	-2.38159	2.08107	0.64075
C	-4.02394	1.96986	-1.11216
H	-1.5209	1.66356	1.15444
C	-4.59989	3.15812	-0.65858
H	-4.45463	1.46979	-1.97687
C	-4.06328	3.80575	0.45711
H	-5.4686	3.57316	-1.1669
B	2.00188	-0.01454	0.01549
O	-4.57941	4.96831	0.95963
H	-5.34284	5.23254	0.42302
C	-2.95132	3.25914	1.10964
H	-2.54566	3.77199	1.97583
C	-4.09425	-2.17005	0.13544
C	-3.77644	-3.50759	-0.14735
C	-5.34333	-1.67545	-0.25876
C	-4.68864	-4.3255	-0.8128
H	-2.81245	-3.89884	0.16499
C	-6.2588	-2.49483	-0.92397
H	-5.60224	-0.64201	-0.03886
C	-5.93242	-3.82171	-1.2037
H	-4.43207	-5.36116	-1.02074
H	-7.22571	-2.09614	-1.22033
H	-6.6434	-4.46223	-1.71904
C	3.19244	-0.08063	-1.08675
C	3.20491	-0.47291	-2.42538
C	4.40946	0.49035	-0.68158
C	4.29329	-0.35604	-3.28514

C	5.53351	0.6432	-1.47897
C	5.47034	0.20792	-2.80276
C	2.14801	-0.83931	1.37093
C	3.176	-1.75781	1.64259
C	1.22867	-0.72722	2.42723
C	3.31955	-2.45894	2.83548
C	1.31019	-1.39447	3.639
C	2.37747	-2.26799	3.84239
C	1.39755	1.47776	0.018
C	1.57999	2.3761	1.08333
C	0.86534	2.09485	-1.12117
C	1.23874	3.7248	1.04716
C	0.49399	3.42741	-1.2254
C	0.68653	4.25142	-0.11794
F	2.15273	1.93779	2.22369
F	0.67325	1.32911	-2.23951
F	4.48902	0.94028	0.59587
F	2.08329	-1.03313	-2.97362
F	4.11295	-2.0038	0.69621
F	0.15606	0.08923	2.25979
H	-3.59991	-0.37396	1.21703
H	-2.66498	-1.79507	1.71147
F	1.46891	4.48487	2.13886
F	0.3428	5.55562	-0.17634
F	-0.02981	3.88373	-2.38294
F	4.36298	-3.30369	2.97747
F	2.48899	-2.93856	5.00875
F	0.35602	-1.19191	4.57229
F	4.17176	-0.78898	-4.55805
F	6.54289	0.33641	-3.61246
F	6.64374	1.20569	-0.95598



$CP1_{B\text{-}C}$ (Figure 10)

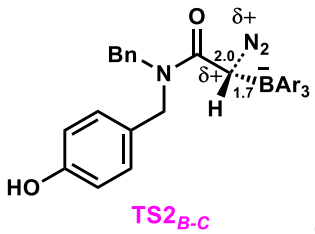
Zero-point correction=	0.440763 (Hartree/Particle)
Thermal correction to Energy=	0.489254
Thermal correction to Enthalpy=	0.490198
Thermal correction to Gibbs Free Energy=	0.355601
Sum of electronic and zero-point Energies=	-3141.172413
Sum of electronic and thermal Energies=	-3141.123922
Sum of electronic and thermal Enthalpies=	-3141.122978
Sum of electronic and thermal Free Energies=	-3141.257575

Cartesian Coordinates

Atom	X	Y	Z
C	-0.07037	-1.01701	-1.20571
H	-0.23741	-0.34954	-2.04732
C	-1.32825	-1.65812	-0.54898
O	-1.19422	-2.79248	-0.09501
N	-2.49286	-0.96276	-0.51387
C	-3.64661	-1.64694	0.12429
C	-2.79965	0.26484	-1.26137
H	-1.87556	0.66993	-1.67141
H	-3.43714	-0.00105	-2.11512
N	1.22197	-3.01076	-2.02391
N	0.61994	-2.11975	-1.72791
C	-3.49858	1.3336	-0.43852
C	-3.12384	1.62281	0.88228
C	-4.51826	2.09263	-1.02018
H	-2.34495	1.03608	1.36003
C	-5.14278	3.12335	-0.31759
H	-4.82999	1.88563	-2.04158
C	-4.75807	3.3991	0.99785

H	-5.93061	3.70684	-0.7902
B	1.18578	-0.21943	-0.12399
O	-5.33154	4.38391	1.74791
H	-6.00022	4.8433	1.21637
C	-3.74702	2.63854	1.59904
H	-3.46548	2.85686	2.62436
C	-4.55325	-2.34889	-0.86818
C	-4.18928	-3.58827	-1.41609
C	-5.77043	-1.77087	-1.25026
C	-5.02428	-4.22832	-2.33102
H	-3.25291	-4.04748	-1.11192
C	-6.60771	-2.4121	-2.16616
H	-6.06504	-0.81359	-0.82592
C	-6.23479	-3.64142	-2.70981
H	-4.73344	-5.19078	-2.74393
H	-7.54727	-1.94932	-2.45667
H	-6.88222	-4.14141	-3.42528
C	2.53443	0.11035	-1.01627
C	2.68799	0.11418	-2.40206
C	3.65899	0.58051	-0.32378
C	3.85069	0.5067	-3.06386
C	4.84038	0.98492	-0.9351
C	4.93993	0.94669	-2.32385
C	1.38558	-1.32703	1.0577
C	2.43882	-2.24684	1.10922
C	0.42675	-1.51049	2.06023
C	2.55702	-3.23855	2.08182
C	0.49614	-2.48557	3.046
C	1.57777	-3.36052	3.05976
C	0.60532	1.25458	0.30589
C	0.71533	1.80153	1.59256
C	0.14291	2.16404	-0.65154
C	0.33107	3.10461	1.90981
C	-0.25659	3.46811	-0.38326
C	-0.16333	3.9454	0.91912
F	1.22636	1.09084	2.61121

F	0.05094	1.78458	-1.95888
F	3.62176	0.65668	1.02148
F	1.67737	-0.29935	-3.22083
F	3.41246	-2.24237	0.17026
F	-0.67745	-0.72692	2.08626
H	-4.20401	-0.8838	0.67131
H	-3.23084	-2.35244	0.84298
F	0.44698	3.55581	3.16476
F	-0.54091	5.19198	1.21283
F	-0.71718	4.25797	-1.36134
F	3.597	-4.08314	2.0666
F	1.66313	-4.31638	3.98927
F	-0.47286	-2.60202	3.96316
F	3.91709	0.46272	-4.40128
F	6.0659	1.32777	-2.93419
F	5.87715	1.41281	-0.20499



$TS2_{B\text{-}C}$ (Figure 10)

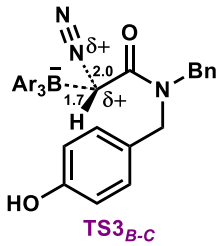
Zero-point correction= 0.438286 (Hartree/Particle)
Thermal correction to Energy= 0.487085
Thermal correction to Enthalpy= 0.488029
Thermal correction to Gibbs Free Energy= 0.352214
Sum of electronic and zero-point Energies= -3141.159575
Sum of electronic and thermal Energies= -3141.110776
Sum of electronic and thermal Enthalpies= -3141.109831
Sum of electronic and thermal Free Energies= -3141.245647

Cartesian Coordinates

Atom	X	Y	Z

C	0.46086	-0.97143	-0.65462
H	0.28831	-0.91109	-1.72398
C	-0.726	-1.46877	0.16921
O	-0.54827	-2.43642	0.90887
N	-1.92375	-0.83588	0.04419
C	-3.02719	-1.31978	0.90174
C	-2.27854	0.13926	-0.99579
H	-1.38143	0.38917	-1.56328
H	-2.97421	-0.34425	-1.69472
N	1.91784	-3.63376	-0.83625
N	1.26986	-2.74035	-0.85553
C	-2.91992	1.40771	-0.46042
C	-2.38904	2.09876	0.63962
C	-4.04877	1.93444	-1.09425
H	-1.51928	1.70386	1.15491
C	-4.63273	3.12524	-0.65956
H	-4.48222	1.41299	-1.94496
C	-4.09091	3.80201	0.43646
H	-5.51128	3.52005	-1.16692
B	1.75286	-0.13123	-0.06501
O	-4.6141	4.96847	0.92015
H	-5.38266	5.21723	0.38344
C	-2.96686	3.28052	1.08878
H	-2.55796	3.81532	1.93997
C	-3.95343	-2.28817	0.18954
C	-3.55212	-3.61051	-0.0543
C	-5.22263	-1.87684	-0.23488
C	-4.40453	-4.49723	-0.71065
H	-2.57106	-3.93528	0.28025
C	-6.07776	-2.76534	-0.89139
H	-5.54532	-0.85557	-0.04418
C	-5.66944	-4.07723	-1.13159
H	-4.08474	-5.52076	-0.88834
H	-7.06164	-2.43222	-1.2114
H	-6.33351	-4.77124	-1.64
C	3.03659	-0.14129	-1.10398

C	3.1005	-0.62046	-2.41343
C	4.2174	0.51213	-0.71931
C	4.19529	-0.51009	-3.26543
C	5.34956	0.66198	-1.50838
C	5.33503	0.14031	-2.80179
C	2.06316	-0.73005	1.4323
C	3.12409	-1.58455	1.74842
C	1.22084	-0.50458	2.52571
C	3.38144	-2.11089	3.01169
C	1.40732	-0.98885	3.81139
C	2.51572	-1.79896	4.05574
C	1.25054	1.46734	-0.1304
C	1.50921	2.42726	0.8636
C	0.74705	2.04064	-1.30398
C	1.25681	3.79048	0.7272
C	0.47169	3.38493	-1.50959
C	0.72875	4.27239	-0.46708
F	2.06716	2.05386	2.03175
F	0.49384	1.21352	-2.37121
F	4.26511	1.05037	0.52353
F	2.01434	-1.27663	-2.94177
F	3.97393	-1.97759	0.76038
F	0.09734	0.24732	2.32133
H	-3.58279	-0.44106	1.23803
H	-2.56353	-1.79113	1.76877
F	1.55475	4.60732	1.75992
F	0.47523	5.5899	-0.61679
F	-0.02345	3.78766	-2.69918
F	6.42275	1.30785	-1.00476
F	6.41696	0.26739	-3.59914
F	4.11804	-1.03127	-4.50837
F	4.45429	-2.91247	3.18182
F	2.73639	-2.29293	5.29259
F	0.51597	-0.67502	4.77549



$TS3_{B\text{-}C}$ (Figure 10)

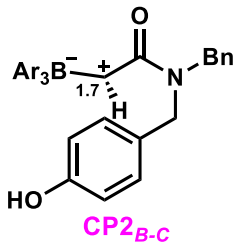
Zero-point correction=	0.435222 (Hartree/Particle)
Thermal correction to Energy=	0.485628
Thermal correction to Enthalpy=	0.486572
Thermal correction to Gibbs Free Energy=	0.341656
Sum of electronic and zero-point Energies=	-3141.126274
Sum of electronic and thermal Energies=	-3141.075869
Sum of electronic and thermal Enthalpies=	-3141.074924
Sum of electronic and thermal Free Energies=	-3141.219841

Cartesian Coordinates

Atom	X	Y	Z
N	-1.03312	2.48502	1.17095
N	-0.68941	2.94489	2.12311
B	2.40566	-0.27268	-0.04601
C	3.03706	1.09839	0.40014
C	2.61449	1.77517	1.55367
C	3.13905	2.99759	1.95668
C	4.16228	3.5789	1.21127
C	4.63472	2.93659	0.06965
C	4.06678	1.72656	-0.31561
C	2.02573	-1.33611	1.05324
C	0.8961	-2.15956	0.94527
C	0.53883	-3.09126	1.91225
C	1.33722	-3.24604	3.04282
C	2.47852	-2.46269	3.19103
C	2.79491	-1.52849	2.20965
C	2.24119	-0.61727	-1.56705
C	2.38044	-1.92301	-2.06444
C	2.21707	-2.25086	-3.40501

C	1.88509	-1.25076	-4.3151
C	1.73349	0.06132	-3.87484
C	1.92429	0.35276	-2.53101
F	1.63468	1.26463	2.31931
F	4.5733	1.15332	-1.41991
F	0.08685	-2.05961	-0.12195
F	3.91594	-0.81277	2.40551
F	1.76535	1.63953	-2.17479
F	2.71558	-2.93268	-1.24181
C	-0.6603	1.22431	-0.26662
C	-1.76024	0.47364	-0.84666
O	-1.21659	-0.03411	-1.85392
C	-3.83102	-0.72604	-1.25112
H	-4.70162	-0.16751	-1.61463
H	-3.2171	-0.99274	-2.11431
H	-0.39461	2.0512	-0.92882
N	-3.01059	0.17754	-0.42621
C	-3.64483	0.75268	0.76108
H	-4.09085	-0.07016	1.33001
H	-2.85876	1.16966	1.39127
C	-4.28916	-1.96691	-0.5077
C	-3.36034	-2.8225	0.10127
C	-5.6502	-2.28374	-0.43469
C	-3.78806	-3.96941	0.76865
H	-2.3008	-2.59153	0.05324
C	-6.07962	-3.43781	0.22508
H	-6.37924	-1.62388	-0.9003
C	-5.14877	-4.28216	0.83019
H	-3.05473	-4.61845	1.23844
H	-7.14011	-3.67185	0.26944
C	-4.70896	1.79218	0.45505
C	-5.98941	1.6783	1.0029
C	-4.43293	2.90192	-0.35852
C	-6.96862	2.64312	0.76129
H	-6.23179	0.82311	1.62965
C	-5.39804	3.86879	-0.61338

H	-3.44762	3.00937	-0.80531
C	-6.67408	3.74289	-0.04895
H	-7.96042	2.53561	1.19688
H	-5.18548	4.72665	-1.24341
H	-5.47999	-5.17835	1.34808
O	-7.58318	4.72234	-0.33109
H	-8.41863	4.5196	0.118
F	-0.56197	-3.84396	1.76629
F	1.01174	-4.14187	3.97524
F	3.2561	-2.61368	4.26908
F	2.37841	-3.51056	-3.82684
F	1.71839	-1.54784	-5.60358
F	1.41301	1.02407	-4.74598
F	5.6242	3.4863	-0.64319
F	4.68627	4.74514	1.58916
F	2.67408	3.61462	3.04947



$CP2_{B\text{-}C}$ (Figure 10)

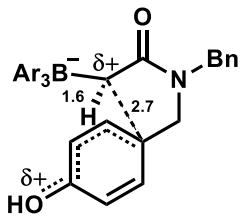
Zero-point correction=	0.430844 (Hartree/Particle)
Thermal correction to Energy=	0.477511
Thermal correction to Enthalpy=	0.478455
Thermal correction to Gibbs Free Energy=	0.345884
Sum of electronic and zero-point Energies=	-3031.666759
Sum of electronic and thermal Energies=	-3031.620093
Sum of electronic and thermal Enthalpies=	-3031.619149
Sum of electronic and thermal Free Energies=	-3031.751719

Cartesian Coordinates

Atom	X	Y	Z

C	-0.64443	0.24313	-0.84234
H	-0.59841	0.9802	-1.63545
C	-1.88694	-0.52732	-0.86633
O	-1.7342	-1.34151	-1.79286
N	-2.93664	-0.38919	-0.05426
C	-3.00117	0.71644	0.91474
H	-4.06641	0.89064	1.10381
H	-2.54447	0.41064	1.86306
C	-2.35474	1.98849	0.40011
C	-1.44128	2.70946	1.19192
C	-2.79255	2.57301	-0.80596
H	-1.09803	2.29511	2.13306
C	-2.31128	3.80641	-1.21986
H	-3.52346	2.05247	-1.42027
C	-1.38904	4.50192	-0.42027
H	-2.65264	4.23931	-2.15788
B	0.70855	-0.1909	-0.04232
C	0.24297	-0.6317	1.48679
C	-0.49105	-1.79931	1.72805
C	0.47994	0.12767	2.63666
C	-0.9398	-2.2037	2.98133
C	0.05478	-0.23704	3.91511
C	-0.65777	-1.41621	4.09349
C	1.87833	0.97308	-0.09564
C	1.8572	2.16844	-0.81321
C	3.09394	0.72194	0.5532
C	2.9287	3.05936	-0.8771
C	4.18826	1.57873	0.52272
C	4.10717	2.76269	-0.20555
C	1.34607	-1.43756	-0.95682
C	1.92856	-2.5966	-0.43498
C	1.45387	-1.3053	-2.34383
C	2.54801	-3.56129	-1.2301
C	2.06277	-2.24135	-3.17141
C	2.61401	-3.3874	-2.60713

F	3.23985	-0.40974	1.27291
F	0.75223	2.55819	-1.50348
F	1.11414	1.3197	2.57014
F	-0.82442	-2.61017	0.69874
F	1.93831	-2.84463	0.88694
F	0.96047	-0.2019	-2.95548
C	-0.96331	3.9505	0.79361
H	-0.24973	4.49833	1.39962
O	-0.88348	5.7108	-0.76642
H	-1.21088	5.96624	-1.6435
C	-5.28355	-0.84124	-0.75553
C	-6.44125	-0.61616	-0.00359
C	-5.29647	-0.55485	-2.12931
C	-7.59457	-0.10931	-0.60844
H	-6.44601	-0.84762	1.0595
C	-6.44546	-0.04682	-2.73301
H	-4.4051	-0.74534	-2.72271
C	-7.59725	0.17834	-1.97282
H	-8.48772	0.0581	-0.01284
H	-6.44683	0.16447	-3.7989
H	-8.49342	0.57066	-2.44549
C	-4.02541	-1.38126	-0.10759
H	-4.22573	-1.7124	0.91735
H	-3.63128	-2.2363	-0.66256
F	2.82604	4.19393	-1.58536
F	5.14743	3.60249	-0.25387
F	5.31598	1.27421	1.17882
F	0.31394	0.55378	4.96601
F	-1.0817	-1.77935	5.30838
F	-1.64265	-3.3368	3.12331
F	3.08498	-4.65415	-0.6705
F	3.20505	-4.30518	-3.37972
F	2.12613	-2.04697	-4.49619



$TS4_{B\text{-}C}$ (Figure 10)

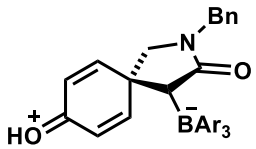
Zero-point correction=	0.429769 (Hartree/Particle)
Thermal correction to Energy=	0.475704
Thermal correction to Enthalpy=	0.476648
Thermal correction to Gibbs Free Energy=	0.347711
Sum of electronic and zero-point Energies=	-3031.664390
Sum of electronic and thermal Energies=	-3031.618456
Sum of electronic and thermal Enthalpies=	-3031.617511
Sum of electronic and thermal Free Energies=	-3031.746448

Cartesian Coordinates

Atom	X	Y	Z
C	-0.1531	0.21751	-0.65363
H	-0.10873	0.95547	-1.44269
C	-1.35826	-0.66294	-0.77863
O	-1.42743	-1.36594	-1.78423
N	-2.26777	-0.63064	0.22693
C	-2.10213	0.36119	1.28081
H	-3.10109	0.64129	1.63714
H	-1.54582	-0.04945	2.13128
C	-1.39475	1.59114	0.72767
C	-0.40356	2.26519	1.48801
C	-2.01612	2.32019	-0.32622
H	0.06912	1.75789	2.31865
C	-1.6156	3.59971	-0.65141
H	-2.82177	1.8515	-0.88558
C	-0.60047	4.22214	0.10021
H	-2.08452	4.13124	-1.47675
B	1.27326	-0.31828	-0.03997
C	0.98396	-1.02232	1.43358

C	0.27097	-2.22262	1.57425
C	1.35465	-0.49413	2.67563
C	-0.04265	-2.85108	2.77369
C	1.08037	-1.06224	3.91821
C	0.37634	-2.26159	3.96533
C	2.47865	0.80695	-0.06316
C	2.4839	2.04844	-0.70382
C	3.73622	0.48647	0.47278
C	3.57005	2.9168	-0.78285
C	4.86322	1.29653	0.43572
C	4.77504	2.53344	-0.20237
C	1.77143	-1.40662	-1.229
C	2.40441	-2.63094	-0.96674
C	1.7559	-1.08914	-2.59265
C	2.93869	-3.4699	-1.94183
C	2.268	-1.87847	-3.61384
C	2.86303	-3.09272	-3.27889
F	3.87895	-0.71695	1.08047
F	1.34156	2.49917	-1.31226
F	2.00521	0.70469	2.7247
F	-0.17775	-2.84237	0.45041
F	2.55032	-3.0567	0.30828
F	1.21799	0.10251	-2.97989
C	-0.00765	3.55273	1.18058
H	0.77493	4.05058	1.74239
O	-0.16458	5.47087	-0.16878
H	-0.62031	5.81856	-0.95259
C	-4.69843	-1.01805	-0.11381
C	-5.72264	-0.86037	0.82529
C	-4.9226	-0.61131	-1.43848
C	-6.95031	-0.30416	0.45491
H	-5.56318	-1.18212	1.85251
C	-6.14574	-0.05491	-1.809
H	-4.13357	-0.74765	-2.17436
C	-7.16298	0.10126	-0.86219
H	-7.73744	-0.1899	1.19554

H	-6.31062	0.24893	-2.83948
H	-8.11732	0.53197	-1.15321
C	-3.35641	-1.60699	0.27651
H	-3.39776	-2.02442	1.28963
H	-3.06991	-2.41052	-0.40681
F	3.42368	4.09392	-1.42742
F	5.85019	3.34761	-0.26294
F	6.00618	0.86009	1.00638
F	1.51351	-0.43688	5.03348
F	0.09873	-2.8448	5.15079
F	-0.72254	-4.01705	2.74608
F	3.52062	-4.624	-1.55207
F	3.37	-3.89146	-4.24195
F	2.17537	-1.4459	-4.8893



$INT1_{B\text{-}C}$ (Figure 10)

Zero-point correction= 0.432447 (Hartree/Particle)
Thermal correction to Energy= 0.477973
Thermal correction to Enthalpy= 0.478917
Thermal correction to Gibbs Free Energy= 0.351938
Sum of electronic and zero-point Energies= -3031.673138
Sum of electronic and thermal Energies= -3031.627612
Sum of electronic and thermal Enthalpies= -3031.626668
Sum of electronic and thermal Free Energies= -3031.753646

Cartesian Coordinates

Atom	X	Y	Z
C	-0.6507	0.24909	-0.83768
H	-0.60096	0.98154	-1.63463
C	-1.88622	-0.53988	-0.87929
O	-1.74598	-1.35652	-1.80308

N	-2.93396	-0.39935	-0.06079
C	-2.98886	0.70601	0.90636
H	-4.05195	0.89233	1.09661
H	-2.53376	0.4	1.85549
C	-2.33127	1.97073	0.3867
C	-1.42562	2.698	1.18356
C	-2.76925	2.55588	-0.8205
H	-1.08517	2.28557	2.12638
C	-2.29419	3.792	-1.231
H	-3.49625	2.03223	-1.43673
C	-1.37873	4.49194	-0.42673
H	-2.63487	4.2245	-2.16941
B	0.70229	-0.18176	-0.03661
C	0.24057	-0.62814	1.49187
C	-0.49315	-1.79628	1.7316
C	0.48001	0.12807	2.64317
C	-0.94049	-2.20295	2.9847
C	0.05602	-0.23874	3.92135
C	-0.65713	-1.41776	4.09811
C	1.87543	0.97815	-0.09076
C	1.85795	2.17101	-0.81265
C	3.09057	0.72594	0.55864
C	2.93112	3.05976	-0.87805
C	4.18679	1.58027	0.52631
C	4.10854	2.76261	-0.20492
C	1.33679	-1.42918	-0.95586
C	1.92075	-2.58821	-0.43479
C	1.44408	-1.29657	-2.34292
C	2.54131	-3.55171	-1.23047
C	2.05423	-2.23152	-3.17091
C	2.60683	-3.37727	-2.60741
F	3.23443	-0.40465	1.28043
F	0.75498	2.56039	-1.50636
F	1.11536	1.31985	2.57829
F	-0.82679	-2.606	0.70165
F	1.93249	-2.83715	0.88686

F	0.9497	-0.19363	-2.95451
C	-0.95376	3.94168	0.78842
H	-0.24606	4.49356	1.3976
O	-0.87976	5.70366	-0.76907
H	-1.20542	5.95916	-1.64688
C	-5.28346	-0.84514	-0.75489
C	-6.43955	-0.61566	-0.00183
C	-5.29752	-0.56058	-2.12909
C	-7.59233	-0.10648	-0.60584
H	-6.44352	-0.84558	1.06162
C	-6.44592	-0.0502	-2.73197
H	-4.40744	-0.75477	-2.7232
C	-7.59611	0.17925	-1.97062
H	-8.48423	0.06424	-0.00927
H	-6.44817	0.15945	-3.7982
H	-8.49185	0.57334	-2.44265
C	-4.02547	-1.38744	-0.10813
H	-4.22505	-1.71554	0.91802
H	-3.63542	-2.24491	-0.66219
F	2.83105	4.19264	-1.58954
F	5.15046	3.60027	-0.2547
F	5.31376	1.27485	1.18328
F	0.31696	0.54991	4.97348
F	-1.0801	-1.78302	5.31272
F	-1.64318	-3.33628	3.12524
F	3.07998	-4.64396	-0.67134
F	3.19892	-4.29395	-3.38042
F	2.11737	-2.03646	-4.49557

参考文献

1. For reviews, see: (a) Xia, Z.-L.; Xu-Xu, Q.-F.; Zheng, C.; You, S.-L. Chiral phosphoric acid-catalyzed asymmetric dearomatization reactions. *Chem. Soc. Rev.* **2020**, *49*, 286. (b) Wertjes, W. C.; Southgate, E. H.; Sarlah, D. Recent advances in chemical dearomatization of nonactivated arenes. *Chem. Soc. Rev.* **2018**, *47*, 7996. (c) Liebov, B. K.; Harman, W. D. Group 6 Dihapto-Coordinate Dearomatization Agents for Organic Synthesis. *Chem. Rev.* **2017**, *117*, 13721. (d) Nemoto, T.; Hamada, Y. Synthesis of Spirocyclic and Fused Cyclic Compounds by Transition-Metal-Catalyzed Intramolecular Friedel-Crafts-Type Reactions of Phenol Derivatives. *Synlett* **2016**, *27*, 2301. (e) Nemoto, T.; Hamada, Y. Synthesis of Spirocyclic or Fused Cyclic Compounds Using Transition Metal Catalyzed Dearomatization of Phenols. *Yuki Gosei Kagaku Kyokaishi* **2015**, *73*, 977.

2. (a) Wu, W.-T.; Zhang, L.; You, S.-L. Catalytic asymmetric dearomatization (CADA) reactions of phenol and aniline derivatives. *Chem. Soc. Rev.* **2016**, *45*, 1570. (b) Xu, R.-Q.; Gu, Q.; Wu, W.-T.; Zhao, Z.-A.; You, S.-L. Construction of Erythrinane Skeleton via Pd(0)-Catalyzed Intramolecular Dearomatization of *para*-Aminophenols. *J. Am. Chem. Soc.* **2014**, *136*, 15469. (c) Wu, Q.-F.; Liu, W.-B.; Zhuo, C.-X.; Rong, Z.-Q.; Ye, K.-Y.; You, S.-L. Iridium Catalyzed Intramolecular Asymmetric Allylic Dearomatization of Phenols. *Angew. Chem., Int. Ed.* **2011**, *50*, 4455. (d) Nan, J.; Yuan, Y.; Bai, L.; Liu, J.; Luan, X. Highly Chemoselective Construction of Spiro[4,5]decane-Embedded Polycyclic Scaffolds by a Palladium/ Norbornene-Catalyzed C−H Activation/Arene Dearomatization Reaction. *Org. Lett.* **2018**, *20*, 7731. (e) Hu, W.; Wang, H.; Bai, L.; Liu, J.; Luan, X. Pd(0)-Catalyzed Intermolecular Dearomatizing [3 + 2] Spiroannulation of Phenol-Based Biaryls and Allenes. *Org. Lett.* **2018**, *20*, 880. (f) Fan, L.; Liu, J.; Bai, L.; Wang, Y.; Luan, X. Rapid Assembly of Diversely Functionalized Spiroindenes by a ThreeComponent Palladium-Catalyzed C−H Amination/Phenol Dearomatization Domino Reaction. *Angew. Chem., Int. Ed.* **2017**, *56*, 14257. (g) Zuo, Z.; Wang, J.; Liu, J.; Wang, Y.; Luan, X. Palladium-Catalyzed [2+2+1] Spiroannulation *via* Alkyne-Directed Remote C−H Arylation and Subsequent Arene Dearomatization. *Angew. Chem., Int. Ed.* **2020**, *59*, 653. (h) Luo, L.; Zheng, H.; Liu, J.; Wang, H.; Wang, Y.; Luan, X. Highly Chemo- and Regioselective Construction of Spirocarbocycles by a Pd(0)-Catalyzed Dearomatization of Phenol Based Biaryls with 1,3-Dienes. *Org. Lett.* **2016**, *18*, 2082. (i) Zuo, Z.; Yang, X.; Liu, J.; Nan, J.; Bai, L.; Wang, Y.; Luan, X. J. Ru(II)-Catalyzed Oxidative Spiroannulation of 2-Arylphenols with Alkynes *via* a C−H Activation/Dearomatization Strategy. *Org. Chem.* **2015**, *80*, 3349. (j) McLaughlin, M. F.; Massolo, E.; Liu, S.; Johnson, J. S. Enantioselective Phenolic α-Oxidation Using H_2O_2 *via* an Unusual Double Dearomatization Mechanism. *J. Am. Chem. Soc.* **2019**, *141*, 2645.

3. (a) Xia, Z.-L.; Zheng, C.; Xu, R.-Q.; You, S.-L. Chiral phosphoric acid catalyzed aminative dearomatization of *α*-naphthols/Michael addition sequence. *Nat. Commun.* **2019**, *10*, 3150. (b) Xu, R.-

Q.; Gu, Q.; You, S.-L. Construction of the Benzomesembrine Skeleton: Palladium(0)-Catalyzed Intermolecular Arylative Dearomatization of *α*-Naphthols and Subsequent Aza-Michael Reaction. *Angew. Chem., Int. Ed.* **2017**, *56*, 7252. (c) Wu, W.-T.; Xu, R.-Q.; Zhang, L.; You, S.- L. Construction of spirocarbocycles *via* gold-catalyzed intramolecular dearomatization of naphthols. *Chem. Sci.* **2016**, *7*, 3427. (d) Dohi, T.; Takenaga, N.; Nakae, T.; Toyoda, Y.; Yamasaki, M.; Shiro, M.; Fujioka, H.; Maruyama, A.; Kita, Y. Asymmetric Dearomatizing Spirolactonization of Naphthols Catalyzed by Spirobiindane-Based Chiral Hypervalent Iodine Species. *J. Am. Chem. Soc.* **2013**, *135*, 4558. (e) Dohi, T.; Maruyama, A.; Takenaga, N.; Senami, K.; Minamitsuji, Y.; Fujioka, H.; Caemmerer, S. B.; Kita, Y. A Chiral Hypervalent Iodine(III) Reagent for Enantioselective Dearomatization of Phenols. *Angew. Chem., Int. Ed.* **2008**, *47*, 3787.

4. (a) Zhang, H.-J.; Gu, Q.; You, S.-L. Ni-Catalyzed Allylic Dearomatization Reaction of *β*-Naphthols with Allylic Alcohols. *Org. Lett.* **2020**, *22*, 3297. (b) Tang, S.-B.; Tu, H.-F.; Zhang, X.; You, S.-L. Rhodium-Catalyzed Asymmetric Allylic Dearomatization of *β*-Naphthols: Enantioselective Control of Prochiral Nucleophiles. *Org. Lett.* **2019**, *21*, 6130. (c) Ding, L.; You, S.-L. Palladium(0)-Catalyzed Intermolecular Cascade Dearomatization Reaction of *β*-Naphthol Derivatives with Propargyl Carbonates. *Org. Lett.* **2018**, *20*, 6206. (d) Cheng, Y.-Z.; Zhou, K.; Zhu, M.; Li, L.-A.-C.; Zhang, X.; You, S.-L. Visible-Light-Promoted Intermolecular Oxidative Dearomatization of *β*-Naphthols with N-Hydroxycarbamates. *Chem. - Eur. J.* **2018**, *24*, 12519. (e) Tu, H.-F.; Zheng, C.; Xu, R.-Q.; Liu, X.-J.; You, S.-L. L. Iridium-Catalyzed Intermolecular Asymmetric Dearomatization of *β*-Naphthols with Allyl Alcohols or Allyl Ethers. *Angew. Chem., Int. Ed.* **2017**, *56*, 3237. (f) Xu, R.-Q.; Yang, P.; Tu, H.-F.; Wang, S.-G.; You, S.-L. Palladium(0)-Catalyzed Intermolecular Arylative Dearomatization of *β*-Naphthols. *Angew. Chem., Int. Ed.* **2016**, *55*, 15137. (g) Cheng, Q.; Wang, Y.; You, S.-L. Chemo-, Diastereo-, and Enantioselective Iridium-Catalyzed Allylic Intramolecular Dearomatization Reaction of Naphthol Derivatives. *Angew. Chem., Int. Ed.* **2016**, *55*, 3496. (h) Wang, S.-G.; Liu, X.-J.; Zhao, Q.-C.; Zheng, C.; Wang, S.-B.; You, S.-L. Asymmetric Dearomatization of *β*-Naphthols through a Bifunctional-Thiourea-Catalyzed Michael Reaction. *Angew. Chem., Int. Ed.* **2015**, *54*, 14929. (i) Yin, Q.; Wang, S.-G.; Liang, X.-W.; Gao, D.-W.; Zheng, J.; You, S.-L. Organocatalytic asymmetric chlorinative dearomatization of naphthols. *Chem. Sci.* **2015**, *6*, 4179. (j) Zheng, J.; Wang, S.-B.; Zheng, C.; You, S.-L. Asymmetric Dearomatization of Naphthols via a Rh-Catalyzed C(sp^2)−H Functionalization/Annulation Reaction. *J. Am. Chem. Soc.* **2015**, *137*, 4880. (k) Wang, S.-G.; Yin, Q.; Zhuo, C.-X.; You, S.-L. Asymmetric Dearomatization of *β*-Naphthols through an Amination Reaction Catalyzed by a Chiral Phosphoric Acid. *Angew. Chem., Int. Ed.* **2015**, *54*, 647. (l) Zhuo, C.-X.; You, S.-L. Palladium-Catalyzed Intermolecular Asymmetric Allylic Dearomatization Reaction of Naphthol Derivatives. *Angew. Chem., Int. Ed.* **2013**, *52*, 10056. (m) Han, L.; Wang, H.; Luan, X. Pd(II)-Catalyzed [3+2] spiroannulation of *α*-aryl-*β*-naphthols with alkynes *via* a C−H

activation/dearomatization approach. *Org. Chem. Front.* **2018**, *5*, 2453. (n) Gu, S.; Luo, L.; Liu, J.; Bai, L.; Zheng, H.; Wang, Y.; Luan, X. Palladium(II)-Catalyzed Oxidative Dearomatization of Free Naphthols with Two Alkyne Units. *Org. Lett.* **2014**, *16*, 6132. (o) Nan, J.; Zuo, Z.; Luo, L.; Bai, L.; Zheng, H.; Yuan, Y.; Liu, J.; Luan, X.; Wang, Y. Ru^{II}-Catalyzed Vinylative Dearomatization of Naphthols via a $C(sp^2)$−H Bond Activation Approach. *J. Am. Chem. Soc.* **2013**, *135*, 17306. (p) Zheng, H.; Bai, L.; Liu, J.; Nan, J.; Zuo, Z.; Yang, L.; Wang, Y.; Luan, X. Pd(0)-catalyzed chemoselective construction of spirocarbocycles *via* an alkyne insertion/*β*-naphthol dearomatization cascade. *Chem. Commun.* **2015**, *51*, 3061. (q) Tan, B.; Bai, L.; Ding, P.; Liu, J.; Wang, Y.; Luan, X. Palladium-Catalyzed Intermolecular [4+1] Spiroannulation by $C(sp^3)$−H Activation and Naphthol Dearomatization. *Angew. Chem., Int. Ed.* **2019**, *58*, 1474. (r) Zuo, Z.; Wang, H.; Fan, L.; Liu, J.; Wang, Y.; Luan, X. Modular Assembly of Spirocarbocyclic Scaffolds through Pd^0-Catalyzed Intermolecular Dearomatizing [2+2+1] Annulation of Bromonaphthols with Aryl Iodides and Alkynes. *Angew. Chem., Int. Ed.* **2017**, *56*, 2767. (s) Egami, H.; Rouno, T.; Masuda, K.; Yamashita, K.; Hamashima, Y. Asymmetric Dearomative Fluorination of 2-Naphthols with a Dicarboxylate Phase-Transfer Catalyst. *Angew. Chem., Int. Ed.* **2020**, *59*, 14101.

5. (a) Wu, W.-T.; Ding, L.; Zhang, L.; You, S.-L. Gold-Catalyzed Intramolecular Dearomatization Reactions of Indoles for the Synthesis of Spiroindolenines and Spiroindolines. *Org. Lett.* **2020**, *22*, 1233. (b) Zhang, H.-J.; Gu, Q.; You, S.-L. Ni-Catalyzed Intermolecular Allylic Dearomatization Reaction of Tryptophols and Tryptamines. *Org. Lett.* **2019**, *21*, 9420. (c) Zhu, M.; Zheng, C.; Zhang, X.; You, S.-L. Synthesis of Cyclobutane-Fused Angular Tetracyclic Spiroindolines *via* Visible-Light-Promoted Intramolecular Dearomatization of Indole Derivatives. *J. Am. Chem. Soc.* **2019**, *141*, 2636. (d) Tu, H.-F.; Zhang, X.; Zheng, C.; Zhu, M.; You, S.-L. Enantioselective dearomative prenylation of indole derivatives. *Nat. Catal.* **2018**, *1*, 601. (e) Bai, L.; Liu, J.; Hu, W.; Li, K.; Wang, Y.; Luan, X. Palladium/Norbornene-Catalyzed C−H Alkylation/Alkyne Insertion/Indole Dearomatization Domino Reaction: Assembly of Spiroindolenine-Containing Pentacyclic Frameworks. *Angew. Chem., Int. Ed.* **2018**, *57*, 5151.

6. (a) Smith, K. L.; Padgett, C. L.; Mackay, W. D.; Johnson, J. S. Catalytic, Asymmetric Dearomative Synthesis of Complex Cyclohexanes *via* a Highly Regio- and Stereoselective Arene Cyclopropanation Using *α*-Cyanodiazoacetates. *J. Am. Chem. Soc.* **2020**, *142*, 6449. (b) Farndon, J. J.; Ma, X.; Bower, J. F. Transition Metal Free C−N Bond Forming Dearomatizations and Aryl C−H Aminations by in Situ Release of a Hydroxylamine-Based Aminating Agent. *J. Am. Chem. Soc.* **2017**, *139*, 14005. (c) Ma, X.; Farndon, J. J.; Young, T. A.; Fey, N.; Bower, J. F. A Simple and Broadly Applicable C−N Bond Forming Dearomatization Protocol Enabled by Bifunctional Amino Reagents. *Angew. Chem., Int. Ed.* **2017**, *56*, 14531.

7. Ma, S.-G.; Gao, R.-M.; Li, Y.-H.; Jiang, J.-D.; Gong, N.-B.; Li, L.; Lü, Y.; Tang W.-Z.; Liu, Y.-B.; Qu, J.; Lü, H.-N.; Li, Y.; Yu, S.-S. Antiviral Spirooliganones A and B with Unprecedented Skeletons from the Roots of *Illicium oligandrum*. *Org. Lett.* **2013**, *15*, 4450.

8. Song, L.; Yao, H.; Tong, R. Biomimetic Asymmetric Total Syntheses of Spirooliganones A and B. *Org. Lett.* **2014**, *16*, 3740.

9. (a) Nemoto, T.; Ishige, Y.; Yoshida, M.; Kohno, Y.; Kanematsu, M.; Hamada, Y. Novel Method for Synthesizing Spiro[4.5]-cyclohexadienones through a Pd-Catalyzed Intramolecular *ipso*-Friedel−Crafts Allylic Alkylation of Phenols. *Org. Lett.* **2010**, *12*, 5020. (b) Yoshida, M.; Nemoto, T.; Zhao, Z.; Ishige, Y.; Hamada, Y. Enantioselective construction of all-carbon quaternary spirocenters through a Pd-catalyzed asymmetric intramolecular *ipso*-Friedel−Crafts allylic alkylation of phenols. *Tetrahedron: Asymmetry* **2012**, *23*, 859. (c) Nemoto, T.; Nozaki, T.; Yoshida, M.; Hamada, Y. Palladium Catalyzed Intramolecular *ipso*-Friedel-Crafts Allylic Alkylation of Phenols *via* Arylative Activation of Allenes. *Adv. Synth. Catal.* **2013**, *355*, 2693. (d) Nemoto, T.; Wu, R.; Zhao, Z.; Yokosaka, T.; Hamada, Y. Synthesis of spiro[4.5]cyclohexadienones with an allene motif *via* a base-promoted intramolecular *ipso*-Friedel−Crafts addition of phenols to propargyl bromides. *Tetrahedron* **2013**, *69*, 3403. (e) Nemoto, T.; Zhao, Z.; Yokosaka, T.; Suzuki, Y.; Wu, R.; Hamada, Y. Palladium-Catalyzed Intramolecular *ipso*-Friedel-Crafts Alkylation of Phenols and Indoles: Rearomatization-Assisted Oxidative Addition. *Angew. Chem., Int. Ed.* **2013**, *52*, 2217. (f) Yokosaka, T.; Nakayama, H.; Nemoto, T.; Hamada, Y. Acidpromoted Cascade Cyclization to Produce Fused-polycyclic Indole Derivatives. *Org. Lett.* **2013**, *15*, 2978. (g) Yokosaka, T.; Nemoto, T.; Hamada, Y. A novel method for synthesizing 3-arylpyrrolidine and 4- arylpiperidine derivatives through an acid-promoted skeletal rearrangement. *Tetrahedron Lett.* **2013**, *54*, 1562. (h) Yokosaka, T.; Nemoto, T.; Nakayama, H.; Shiga, N.; Hamada, Y. Synthesis of nitrogen-containing fused-polycyclic compounds from tyramine derivatives using phenol dearomatization and cascade cyclization. *Chem. Commun.* **2014**, *50*, 12775. (i) Nemoto, T.; Matsuo, N.; Hamada, Y. Gold-Catalyzed Carbocyclization of Phenols with a Terminal Alkyne *via* an Intramolecular ipso-Friedel-Crafts Alkenylation. *Adv. Synth. Catal.* **2014**, *356*, 2417. See also ref 1d, e.

10. (a) Sarkar, D.; Rout, N. Ruthenium(VIII)-Catalyzed *ipso*-Dearomative Spiro-Etherification and Spiro-Amidation of Phenols. *Org. Lett.* **2019**, *21*, 4132. (b) Oguma, T.; Doiuchi, D.; Fujitomo, C.; Kim, C.; Hayashi, H.; Uchida, T.; Katsuki, T. Iron-Catalyzed Asymmetric Inter- and Intramolecular Aerobic Oxidative Dearomatizing Spirocyclization of 2-Naphthols. *Asian J. Org. Chem.* **2020**, *9*, 404. (c) Min, X.-L.; Xu, X.-R.; He, Y. Axial-to-Central Chirality Transfer for Construction of Quaternary Stereocenters *via* Dearomatization of BINOLs. *Org. Lett.* **2019**, *21*, 9188. (d) Shibuya, T.; Noguchi,

K.; Tanaka, K. Dearomatization of Fused Arenes Using PlatinumCatalyzed Intramolecular Formation of Two C-C Bonds. *Angew. Chem., Int. Ed.* **2012**, *51*, 6219.

11. (a) Uyanik, M.; Kato, T.; Sahara, N.; Katade, O.; Ishihara, K. High-Performance Ammonium Hypoiodite/Oxone Catalysis for Enantioselective Oxidative Dearomatization of Arenols. *ACS Catal.* **2019**, *9*, 11619. (b) Yao, L.; Ishihara, K. Enantioselective [1,3] *O*-to-*C* rearrangement: dearomatization of alkyl 2-allyloxy/benzyloxy-1/3- naphthoates catalyzed by a chiral π-Cu(II) complex. *Chem. Sci.* **2019**, *10*, 2259.

12. Ogawa, N.; Yamaoka, Y.; Takikawa, H.; Takasu, K. Synthesis of Polycyclic Spirocarbocycles *via* Acid-Promoted Ring-Contraction/Dearomative Ring-Closure Cascade of Oxapropellanes. *Org. Lett.* **2019**, *21*, 7563.

13. (a) He, Y.; Tang, J.; Luo, M.; Zeng, X. Regioselective and Chemoselective Reduction of Naphthols Using Hydrosilane in Methanol: Synthesis of the 5,6,7,8-Tetrahydronaphthol Core. *Org. Lett.* **2018**, *20*, 4159. (b) Zhang, J.; Jiang, H.; Liu, Y.; Chen, R. Tuning surface properties of *N*-doped carbon with TiO_2 nano-islands for enhanced phenol hydrogenation to cyclohexanone. *Appl. Surf. Sci.* **2019**, *488*, 555. (c) Liu, C.; Rong, Z.; Sun, Z.; Wang, Y.; Du, W.; Wang, Y.; Lu, L. Quenched skeletal Ni as the effective catalyst for selective partial hydrogenation of polycyclic aromatic hydrocarbons. *RSC Adv.* **2013**, *3*, 23984. (d) Makowski, P.; Cakan, R. D.; Antonietti, M.; Goettmann, F.; Titirici, M.-M. Selective partial hydrogenation of hydroxy aromatic derivatives with palladium nanoparticles supported on hydrophilic carbon. *Chem. Commun.* **2008**, 999. (e) Guo, H.; Ding, K. Reduction of 1,1'-binaphthyls to octahydro-1,1'-binaphthyl derivatives with Raney Ni−Al alloy in aqueous solution. *Tetrahedron Lett.* **2000**, *41*, 10061. (f) Zhu, Z.; Ostashevskaya, L. A.; Koltunov, K. Y. Reactions of 2,3-naphthalenediol with cyclohexane in the presence of aluminum halides. *Tetrahedron Lett.* **2015**, *56*, 2254.

14. (a) *Contemporary Carbene Chemistry*; Moss, R. A., Doyle, M. P., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, 2014. (b) DeAngelis, A.; Panish, R.; Fox, J. M. Rh-Catalyzed Intermolecular Reactions of α-Alkyl-α-Diazo Carbonyl Compounds with Selectivity over β-Hydride Migration. *Acc. Chem. Res.* **2016**, *49*, 115. (c) Deng, Y.; Jing, C.; Arman, H.; Doyle, M. P. Reactivity and Selectivity in Catalytic Reactions of Enoldiazoacetamides. Assessment of Metal Carbenes as Intermediates. *Organometallics* **2016**, *35*, 3413.

15. $L_nM{-}C(N_2)R^3R^4$ and $L_nM{=}CR^1\ R^2$ were termed as "metal−carbenoid" and "metal−carbene", respectively. Our group has followed the nomenclature of the terms as recommended by Echavarren, Caballero, and Pérez; see: (a) Wang, Y.; Muratore, M. E.; Echavarren, A. M. Gold Carbene or

Carbenoid: Is There a Difference? *Chem. - Eur. J.* **2015**, *21*, 7332. (b) Caballero, A.; Pérez, P. J. Dimensioning the Term Carbenoid. *Chem. - Eur. J.* 2017, *23*, 14389.
16. (a) Ye, T.; McKervey, M. A. Organic Synthesis with.alpha.- Diazo Carbonyl Compounds. *Chem. Rev.* **1994**, *94*, 1091. (b) Ford, A.; Miel, H.; Ring, A.; Slattery, C. N.; Maguire, A. R.; McKervey, M. A. Modern Organic Synthesis with *α*-Diazocarbonyl Compounds. *Chem. Rev.* **2015**, *115*, 9981.

17. (a) Díaz-Requejo, M. M.; Pérez, P. J. Coinage Metal Catalyzed C−H Bond Functionalization of Hydrocarbons. *Chem. Rev.* **2008**, *108*, 3379. (b) Caballero, A.; Despagnet-Ayoub, E.; Díaz-Requejo, M. M.; Díaz-Rodríguez, A.; Gonzalez-Núñez, M. E.; Mello, R.; Muñoz, B. K.; Ojo, W. S.; Asensio, G.; Etienne, M.; Pérez, P. J. Silver-Catalyzed C-C Bond Formation Between Methane and Ethyl Diazoacetate in Supercritical CO_2. *Science* **2011**, *332*, 835. (c) Hansen, J. H.; Davies, H. M. L. Vinylogous reactivity of silver(I) vinylcarbenoids. *Chem. Sci.* **2011**, *2*, 457. (d) Liu, Z.; Sivaguru, P.; Zanoni, G.; Anderson, E. A.; Bi, X. Catalyst-Dependent Chemoselective Formal Insertion of Diazo Compounds into C−C or C−H Bonds of 1,3-Dicarbonyl Compounds. *Angew. Chem., Int. Ed.* **2018**, *57*, 8927. (e) Tskhovrebov, A. G.; Goddard, R.; Fürstner, A. Two Amphoteric Silver Carbene Clusters. *Angew. Chem., Int. Ed.* **2018**, *57*, 8089.

18. Nakayama, H.; Harada, S.; Kono, M.; Nemoto, T. Chemoselective Asymmetric Intramolecular Dearomatization of Phenols with *α*-Diazoacetamides Catalyzed by Silver Phosphate. *J. Am. Chem. Soc.* **2017**, *139*, 10188.

19. Ueda, J.; Harada, S.; Kanda, A.; Nakayama, H.; Nemoto, T. Silver-Catalyzed, Chemo- and Enantioselective Intramolecular Dearomatization of Indoles to Access Sterically Congested Azaspiro Frameworks. *J. Org. Chem.* **2020**, *85*, 10934.

20. Harada, S.; Tanikawa, T.; Homma, H.; Sakai, C.; Ito, T.; Nemoto, T. Silver-Catalyzed Asymmetric Insertion into Phenolic O−H Bonds using Aryl Diazoacetates and Theoretical Mechanistic Studies. *Chem.- Eur. J.* **2019**, *25*, 12058.

21. Yu, Z.; Ma, B.; Chen, M.; Wu, H.-H.; Liu, L.; Zhang, J. Highly Site-Selective Direct C–H Bond Functionalization of Phenols with *α*-Aryl-*α*-diazoacetates and Diazooxindoles *via* Gold Catalysis. *J. Am. Chem. Soc.* **2014**, *136*, 6904.

22. マリケン電子密度解析により電子の局在化の程度を見積もることができ、値が負であるほど電子がその原子に局在化していることを示す。

23. Zhao, C.; Sun, M.; Bennani, Y. L.; Miller, T. R.; Witte, D. G.; Esbenshade, T. A.; Wetter, J.; Marsh, K. C.; Hancock, A. A.; Brioni, J. D.; Cowart, M. D. Design of a New Histamine H_3 Receptor

Antagonist Chemotype: (3a*R*,6a*R*)-5-Alkyl-1-aryl-octahydropyrrolo- [3,4-*b*]pyrroles, Synthesis, and Structure−Activity Relationships. *J. Med. Chem.* **2009**, *52*, 4640.

24. Ng, P.-Y.; Davis, H.; Bair, K. W.; Millan, D. S.; Rudnitskaya, A.; Zheng, X.; Han, B.; Barczak, N.; Lancia, D., Jr. Preparation of 3-spiro7-hydroxamic acid tetralins as histone deacetylase inhibitors. From PCT Int. Appl. 2016, WO 2016168660 A1 20161020.

25. (a) Jiang, B.; Xu, M. Highly Enantioselective Construction of Fused Pyrrolidine Systems That Contain a Quaternary Stereocenter: Concise Formal Synthesis of (+)-Conessine. *Angew. Chem., Int. Ed.* **2004**, *43*, 2543. (b) Kopach, M. E.; Fray, A. H.; Meyers, A. I. An Asymmetric Route to the Conanine BCDE Ring System. A Formal Total Synthesis of (+)-Conessine. *J. Am. Chem. Soc.* **1996**, *118*, 9876.

26. Zimmerman, H. E.; Lamers, P. H. Photochemistry of some extended .pi.-systems: type A and aryl rearrangements of systems with extended conjugation related to cyclohexadienones and cyclohexenones. Mechanistic and exploratory organic photochemistry. *J. Org. Chem.* **1989**, *54*, 5788.

27. (a) Sakai, T.; Matsuoka, J.; Shintai, M.; Mori, Y. C_{Ar}−O Rotamers in 3,3′-Disubstituted BINOL Esters. *J. Org. Chem.* **2017**, *82*, 3276−3283. (b) Mishiro, K.; Furuta, T.; Sasamori, T.; Hayashi, K.; Tokitoh, N.; Futaki, S.; Kawabata, T. A Cyclochiral Conformational Motif Constructed Using a Robust Hydrogen-Bonding Network. *J. Am. Chem. Soc.* **2013**, *135*, 13644.

28. (a) Chen, Y.-H.; Li, H.-H.; Zhang, X.; Xiang, S.-H.; Li, S.; Tan, B. Organocatalytic Enantioselective Synthesis of Atropisomeric Aryl-*p*-Quinones: Platform Molecules for Diversity-Oriented Synthesis of Biaryldiols. *Angew. Chem., Int. Ed.* **2020**, *59*, 11374. (b) Yan, S.; Xia, W.; Li, S.; Song, Q.; Xiang, S.-H.; Tan, B. Michael Reaction Inspired Atroposelective Construction of Axially Chiral Biaryls. *J. Am. Chem. Soc.* **2020**, *142*, 7322. (c) Qi, L.-W.; Li, S.; Xiang, S.-H.; Wang, J.; Tan, B. Asymmetric construction of atropisomeric biaryls *via* a redox neutral cross-coupling strategy. *Nat. Catal.* **2019**, *2*, 314. (d) Wang, Y.-B.; Tan, B. Construction of Axially Chiral Compounds *via* Asymmetric Organocatalysis. *Acc. Chem. Res.* **2018**, *51*, 534. (e) Shibuya, T.; Shibata, Y.; Noguchi, K.; Tanaka, K. PalladiumCatalyzed Enantioselective Intramolecular Hydroarylation of Alkynes To Form Axially Chiral 4-Aryl 2-Quinolinones. *Angew. Chem., Int. Ed.* **2011**, *50*, 3963. (f) Yoshimura, R.; Tanaka, K. Rhodium-Catalyzed ortho-Olefination of Sterically Demanding Benzamides: Application to the Asymmetric Synthesis of Axially Chiral Benzamides. *Chem. - Eur. J.* **2020**, *26*, 4969.

29. Jesuraj, J. L.; Sivaguru, J. Photochemical type II reaction of atropchiral benzoylformamides to point chiral oxazolidin-4-ones. Axial chiral memory leading to enantiomeric resolution of photoproducts. *Chem. Commun.* **2010**, *46*, 4791.

30. (a) Zhang, H.-H.; Wang, C.-S.; Li, C.; Mei, G.-J.; Li, Y.; Shi, F. Design and Enantioselective Construction of Axially Chiral NaphthylIndole Skeletons. *Angew. Chem., Int. Ed.* **2017**, *56*, 116. (b) Jiang, F.; Chen, K.-W.; Wu, P.; Zhang, Y.-C.; Jiao, Y.; Shi, F. A Strategy for Synthesizing Axially Chiral Naphthyl-Indoles: Catalytic Asymmetric Addition Reactions of Racemic Substrates. *Angew. Chem., Int. Ed.* **2019**, *58*, 15104. (c) He, Y.-P.; Wu, H.; Wang, Q.; Zhu, J. Palladium Catalyzed Enantioselective Cacchi Reaction: Asymmetric Synthesis of Axially Chiral 2,3-Disubstituted Indoles. *Angew. Chem., Int. Ed.* **2020**, *59*, 2105.

31. Sharma, K.; Baral, E. R.; Akhtar, M. S.; Lee, Y. R.; Kim, S. H.; Wee, Y.-J. 3-Naphthylindoles as new promising candidate antioxidant, antibacterial, and antibiofilm agents. *Res. Chem. Intermed.* **2017**, *43*, 2387.

32. Jiang, F.; Luo, G.-Z.; Zhu, Z.-Q.; Wang, C.-S.; Mei, G.-J.; Shi, F. Application of Naphthylindole-Derived Phosphines as Organocatalysts in [4+1] Cyclizations of *o*-Quinone Methides with Morita−Baylis−Hillman Carbonates. *J. Org. Chem.* **2018**, *83*, 10060.

33. (a) Beer, P. D.; Gale, P. A. Anion Recognition and Sensing: The State of the Art and Future Perspectives. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (b) Caltagirone, C.; Gale, P. A. Anion receptor chemistry: highlights from 2007. *Chem. Soc. Rev.* **2009**, *38*, 520. (c) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. Signaling Recognition Events with Fluorescent Sensors and Switches. *Chem. Rev.* **1997**, *97*, 1515. (d) Martinez-Manez, R.; Sancenón, F. Fluorogenic and Chromogenic Chemosensors and Reagents for Anions. C *Chem. Rev.* **2003**, *103*, 4419.

34. フッ素アニオンの過剰摂取はフッ素症や尿路結石の原因となり、また発がんのリスクが高まると報告されている。(a) Ayoob, S.; Gupta, A. K. Fluoride in Drinking Water: A Review on the Status and Stress Effects. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 433. (b) Singh, P. P.; Barjatiya, M. K.; Dhing, S.; Bhatnagar, R.; Kothari, S.; Dhar, V. Evidence suggesting that high intake of fluoride provokes nephrolithiasis in tribal populations. *Urol. Res.* **2001**, *29*, 238. (c) Jagtap, S.; Yenkie, M.; Labhsetwar, N.; Rayalu, S. Fluoride in Drinking Water and Defluoridation of Water. *Chem. Rev.* **2012**, *112*, 2454. (d) Lin, Q.; Lu, T.-T.; Zhu, X.; Wei, T.-B.; Li, H.; Zhang, Y.-M. Rationally introduce multi-competitive binding interactions in supramolecular gels: a simple and efficient approach to develop multi-analyte sensor array. *Chem. Sci.* **2016**, *7*, 5341.

35. (a) Lee, D. H.; Im, J. H.; Son, S. U.; Chung, Y. K.; Hong, J.-I. An Azophenol-based Chromogenic Pyrophosphate Sensor in Water. *J. Am. Chem. Soc.* **2003**, *125*, 7752. (b) Beer, P. D.; Szemes, F. Remarkable chloride over dihydrogen phosphate anion selectivity exhibited by novel macrocyclic bis[ruthenium(II) bipyridyl] and ruthenium(II) bipyridyl−metallocene receptors. *J. Chem. Soc., Chem.*

Commun. **1995**, *21*, 2245. (c) Cho, E. J.; Moon, J. W.; Ko, S. W.; Lee, J. Y.; Kim, S. K.; Yoon, J.; Nam, K. C. A New Fluoride Selective Fluorescent as Well as Chromogenic Chemosensor Containing a Naphthalene Urea Derivative. *J. Am. Chem. Soc.* **2003**, *125*, 12376. (d) Lee, J. Y.; Cho, E. J.; Mukamel, S.; Nam, K. C. Efficient FluorideSelective Fluorescent Host: Experiment and Theory. *J. Org. Chem.* **2004**, *69*, 943. (e) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. Efficient and Simple Colorimetric Fluoride Ion Sensor Based on Receptors Having Urea and Thiourea Binding Sites. *Org. Lett.* **2004**, *6*, 3445. (f) He, X.; Hu, S.; Liu, K.; Guo, Y.; Xu, J.; Shao, S. Oxidized Bis(indolyl)methane: A Simple and Efficient Chromogenic-Sensing Molecule Based on the Proton Transfer Signaling Mode. *Org. Lett.* **2006**, *8*, 333. (g) Yamaguchi, S.; Akiyama, S.; Tamao, K. Photophysical Properties Changes Caused by Hypercoordination of Organosilicon Compounds: From Trianthrylfluorosilane to Trianthryldifluorosilicate. *J. Am. Chem. Soc.* **2000**, *122*, 6793. (h) Choi, K.; Hamilton, A. D. A Dual Channel Fluorescence Chemosensor for Anions Involving Intermolecular Excited State Proton Transfer. *Angew. Chem., Int. Ed.* **2001**, *40*, 3912. (i) Li, B.; Tian, H. A ratiometric fluorescent chemosensor for fluoride ions based on a proton transfer signaling mechanism. *J. Mater. Chem.* **2005**, *15*, 2681. (j) Piatek, P.; Jurczak, J. A selective colorimetric anion sensor based on an amide group containing macrocycle. *J. Chem. Commun.* **2002**, 2450. (k) Anzenbacher, P.; Nishiyabu, R.; Palacios, M. A. *N*-confused calix[4]pyrroles. C *Coord. Chem. Rev.* **2006**, *250*, 2929.

36. (a) Chen, P.; Nan, J.; Hu, Y.; Kang, Y.; Wang, B.; Ma, Y.; Szostak, M. Metal-free tandem carbene N–H insertions and C–C bond cleavages. *Chem. Sci.* **2021**, *12*, 803. (b) Gallo, R. D. C.; Burtoloso, A. C. B. Silica-supported $HClO_4$ promotes catalytic solvent- and metal-free O–H insertion reactions with diazo compounds. *Green Chem.* **2018**, *20*, 4547. (c) Zhai, C.; Xing, D.; Jing, C.; Zhou, J.; Wang, C.; Wang, D.; Hu, W. Facile Synthesis of 3-Aryloxindoles *via* Brønsted Acid Catalyzed Friedel–Crafts Alkylation of Electron-Rich Arenes with 3-Diazooxindoles. *Org. Lett.* **2014**, *16*, 2934. (d) So, S. S.; Mattson, A. E. Stereoselective N-H Insertion-Arylation Reactions of Nitrodiazoesters. *Asian J. Org. Chem.* **2014**, *3*, 425. (d) Krishna, P. R.; Prapurna, Y. L.; Alivelu, M. $InCl_3$ catalyzed carbene insertion into O–H bonds: efficient synthesis of ethers. *Tetrahedron Lett.* **2011**, *52*, 3460. (e) Johnston, J. N.; Muchalski, H.; Troyer, T. L. To Protonate or Alkylate? Stereoselective Brønsted Acid Catalysis of C-C Bond Formation Using Diazoalkanes. *Angew., Chem., Int. Ed.* **2010**, *49*, 2290.

37. (a) Hu, M.; Ni, C.; Li, L.; Han, Y.; Hu, J. *gem*-Difluoroolefination of Diazo Compounds with $TMSCF_3$ or $TMSCF_2Br$: Transition-Metal-Free Cross-Coupling of Two Carbene Precursors. *J. Am. Chem. Soc.* **2015**, *137*, 14496. (b) Wang, Q.; Ni, C.; Hu, M.; Xie, Q.; Liu, Q.; Pan, S.; Hu, J. From C_1 to C_3: Copper-Catalyzed *gem*-Bis(trifluoromethyl)olefination of *α*-Diazo Esters with $TMSCF_3$. *Angew., Chem., Int. Ed.* **2020**, *59*, 8507.

38. (a) Ovalles, S. R.; Hansen, J. H.; Davies, H. M. L. Thermally Induced Cycloadditions of Donor/Acceptor Carbenes. *Org. Lett.* **2011**, *13*, 4284. (b) Hansen, S. R.; Spangler, J. E.; Hansen, J. H.; Davies, H. M. L. Metal-Free N–H Insertions of Donor/Acceptor Carbenes. *Org. Lett.* **2012**, *14*, 4626. (c) Tortoreto, C.; Rackl, D.; Davies, H. M. L. Metal-Free C–H Functionalization of Alkanes by Aryldiazoacetates. *Org. Lett.* **2017**, *19*, 770. (d) Liu, Z.; Tan, H.; Wang, L.; Fu, T.; Xia, Y.; Zhang, Y.; Wang, J. Transition-Metal-Free Intramolecular Carbene Aromatic Substitution/Büchner Reaction: Synthesis of Fluorenes and [6,5,7]Benzo-fused Rings. *Angew. Chem., Int. Ed.* **2015**, *54*, 3056. (e) Zhang, Z.; Yu, W.; Wu, C.; Wang, C.; Zhang, Y.; Wang, J. Reaction of Diazo Compounds with Difluorocarbene: An Efficient Approach towards 1,1-Difluoroolefins. *Angew. Chem., Int. Ed.* **2016**, *55*, 273. (f) Barroso, R.; Jiménez, A.; Pérez-Aguilar, M. C.; Cabal, M.-P.; Valdés, C. *Chem. Commun.* **2016**, *52*, 3677. (g) Deng, Y.; Jingab, C.; Doyle, M. P. Synthesis of 1,3-diaryl-3-trifluoromethylcyclopropenes by transition-metal-free reaction of 2,2,2-trifluoroacetophenone tosylhydrazones with alkynes: the effect of the trifluoromethyl group. *Chem. Commun.* **2015**, *51*, 12924 (h) Alford, J. S.; Davies, H. M. L. Expanding the Scope of Donor/Acceptor Carbenes to *N*-Phthalimido Donor Groups: Diastereoselective Synthesis of 1-Cyclopropane α-Amino Acids. *Org. Lett.* **2012**, *14*, 6020. (i) Zhang, X.; Cao, W.-B.; Li, H.-Y.; Xu, X.-P.; Ji, S.-J. Synthesis of Polysubstituted Maleimides *via* Metal-Free Cascade Reaction of Isocyanides and *α*-Diazoketones. *J. Org. Chem.* **2019**, *84*, 16237.

39. Yang, Z.; Stivanin, M. L.; Jurberg, I. D.; Koenigs, R. M. Visible light-promoted reactions with diazo compounds: a mild and practical strategy towards free carbene intermediates. *Chem. Soc. Rev.* **2020**, *49*, 6833.

40. Catalyst-free reaction. Li, J.; Ma, C.; Xing, D.; Hu, W. Catalyst-Free *gem*-Difunctionalization of Fluoroalkyl-Substituted Diazo Compound with Diselenide or Disulfide and NFSI. *Org. Lett.* **2019**, *21*, 2101.

41. Metal-free reaction with protic acid. Yi, X.; Feng, J.; Huang, F.; Baell, J. B. Metal-free C–C, C–O, C–S and C–N bond formation enabled by SBA-15 supported TFMSA. *Chem. Commun.* **2020**, *56*, 1243.

42. (a) Harada, S.; Kwok, I. M.-Y.; Nakayama, H.; Kanda, A.; Nemoto, T. Merging Brønsted Acid and Hydrogen-Bonding Catalysis: Metal-Free Dearomatization of Phenols *via ipso*-Friedel-Crafts Alkylation to Produce Functionalized Spirolactams. *Adv. Synth. Catal.* **2018**, *360*, 801. (b) Yanagawa, M.; Kobayashi, M.; Ikeda, M.; Harada, S.; Nemoto, T. Computational Study on the Synergic Effect of Brønsted Acid and Hydrogen-Bonding Catalysis for the Dearomatization Reaction of Phenols with Diazo Functionality. *Chem. Pharm. Bull.* **2020**, *68*, 1104.

43. (a) Peng, C.; Zhang, W.; Yan, G.; Wang, J. Arylation and Vinylation of *α*-Diazocarbonyl Compounds with Boroxines. *Org. Lett.* **2009**, *11*, 1667. (b) Barluenga, J.; Tomás-Gamasa, M.; Aznar, F.; Valdés, C. Metal-free carbon–carbon bond-forming reductive coupling between boronic acids and tosylhydrazones. *Nat. Chem.* **2009**, *1*, 494. (c) Pérez-Aguilar, M. C.; Valdés, C. Olefination of Carbonyl Compounds through Reductive Coupling of Alkenylboronic Acids and Tosylhydrazones. *Angew. Chem., Int. Ed.* **2012**, *51*, 5953. (d) Li, H.; Wang, L.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 2943. (e) Argintaru, O. A.; Ryu, D.; Aron, I.; Molander, G. A. Transition-Metal-Free Synthesis of Pinacol Alkylboronates from Tosylhydrazones. *Angew. Chem., Int. Ed.* **2013**, *52*, 13656. (f) Molander, G. A.; Ryu, D. Diastereoselective Synthesis of Vicinally Bis(trifluoromethylated) Alkylboron Compounds through Successive Insertions of 2,2,2-Trifluorodiazoethane. *Angew. Chem., Int. Ed.* **2014**, *53*, 14181. (g) Wu, G.; Deng, Y.; Wu, C.; Zhang, Y.; Wang, J. Synthesis of *α*-Aryl Esters and Nitriles: Deaminative Coupling of *α*-Aminoesters and *α*-Aminoacetonitriles with Arylboronic Acids. *Angew. Chem., Int. Ed.* **2014**, *53*, 10510. (h) Poh, J.-S.; Lau, S.-H.; Dykes, I. G.; Tran, D. N.; Battilocchio, C.; Ley, S. V. A multicomponent approach for the preparation of homoallylic alcohols. *Chem. Sci.* **2016**, *7*, 6803. (i) Plaza, M.; Valdés, C. Stereoselective Domino Carbocyclizations of *γ*- and *δ*-Cyano-*N*-tosylhydrazones with Alkenylboronic Acids with Formation of Two Different C(sp^3)–C(sp^2) Bonds on a Quaternary Stereocenter. *J. Am. Chem. Soc.* **2016**, *138*, 12061. (j) Battilocchio, C.; Feist, F.; Hafner, A.; Simon, M.; Tran, D. N.; Allwood, D. M.; Blakemore, D. C.; Ley, S. V. Iterative reactions of transient boronic acids enable sequential C–C bond formation. *Nat. Chem.* **2016**, *8*, 360. (k) Bomio, C.; Kabeshov, M. A.; Lit, A. R.; Lau, S.-H.; Ehlert, J.; Battilocchio, C.; Ley, S. V. Unveiling the role of boroxines in metal-free carbon–carbon homologations using diazo compounds and boronic acids. *Chem. Sci.* **2017**, *8*, 6071. (l) Lgbcke, M.; Bezhan, D.; Szabl, K. J. Trifluoromethylthiolation–arylation of diazocarbonyl compounds by modified Hooz multicomponent coupling. *Chem. Sci.* **2019**, *10*, 5990. (m) Santi, M.; Ould, D. M. C.; Wenz, J.; Soltani, Y.; Melen, R. L.; Wirth, T. Metal-Free Tandem Rearrangement/Lactonization: Access to 3,3-Disubstituted Benzofuran-2-(3*H*)-ones. *Angew. Chem., Int. Ed.* **2019**, *58*, 7861. (n) Ma, Y.; Reddy, B. R. P.; Bi, X. Coupling of Trifluoroacetaldehyde *N*-Triftosylhydrazone with Organoboronic Acids for the Synthesis of *gem*-Difluoroalkenes. *Org. Lett.* **2019**, *21*, 9860. (o) Wu, K.; Wu, L.-L.; Zhou, C.-Y.; Che, C.-M. Transition-Metal-Free C(sp^2)–C(sp^2) Cross-Coupling of Diazo Quinones with Catechol Boronic Esters. *Angew. Chem., Int. Ed.* **2020**, *59*, 16202.

44. Empel, C.; Nguyen, T. V.; Koenigs, R. M. Tropylium-Catalyzed O–H Insertion Reactions of Diazoalkanes with Carboxylic Acids. *Org. Lett.* **2021**, *23*, 548.

45. (a) Tayama, E.; Ishikawa, M.; Iwamoto, H.; Hasegawa, E. Copper(II)–acid co-catalyzed intermolecular substitution of electron-rich aromatics with diazoesters. *Tetrahedron Lett.* **2012**, *53*,

5159. (b) Li, H.; Zhang, Y.; Wang, J. Reaction of Diazo Compounds with Organoboron Compounds. *Synthesis* **2013**, 3090.

46. (a) Yu, Z.; Li, Y.; Shi, J.; Ma, B.; Liu, L.; Zhang, J. $(C_6F_5)_3B$ Catalyzed Chemoselective and ortho-Selective Substitution of Phenols with *α*-Aryl *α*-Diazoesters. *Angew. Chem., Int. Ed.* **2016**, *55*, 14807. (b) Xu, G.; Tang, S.; Shao, Y.; Sun, J. *Chem. Commun.* **2019**, *55*, 9096. (c) San, H. H.; Wang, C.-Y.; Zeng, H.-P.; Fu, S.-T.; Jiang, M.; Tang, X.-Y. $B(C_6F_5)_3$-Catalyzed formal (4+1)-annulation of *ortho*-quinone methides with diazoacetates: access to 2,3-dihydrobenzofurans. *J. Org. Chem.* **2019**, *84*, 4478. (d) Rao, S.; Kapanaiah, R.; Prabhu, K. R. Boron-Catalyzed C−C Functionalization of Allyl Alcohols. *Adv. Synth. Catal.* **2019**, *361*, 1301. (e) Mancinelli, J. P.; Wilkerson-Hill, S. M. Tris(pentafluorophenyl)borane-Catalyzed Cyclopropanation of Styrenes with Aryldiazoacetates. *ACS Catal.* **2020**, *10*, 11171. (f) Dasgupta, A.; Babaahmadi, R.; Slater, B.; Yates, B. F.; Ariafard, A.; Melen, R. L. Borane-Catalyzed Stereoselective C–H Insertion, Cyclopropanation, and Ring-Opening Reactions. *Chem* **2020**, *6*, 2364.

47. Zhang, Q.; Zhang, X.-F.; Li, M.; Li, C.; Liu, J.-Q.; Jiang, Y.-Y.; Ji, X.; Liu, L.; Wu. Y.-C. Mechanistic Insights into the Chemo- and Regio-Selective $B(C_6F_5)_3$ Catalyzed C–H Functionalization of Phenols with Diazoesters. *J. Org. Chem.* **2019**, *84*, 14508.

48. 量子化学計算を用いて、ジアゾ基を持たない基質と $B(C_6F_5)_3$ の反応メカニズムを解析している。Wang, G.; Gao, L.; Chen, H.; Liu, X.; Cao, J.; Chen, S.; Cheng, X.; Li, S. Chemoselective Borane-Catalyzed Hydroarylation of 1,3-Dienes with Phenols. *Angew. Chem., Int. Ed.* **2019**, *58*, 1694.

49. (a) Balogh, L.; Wang, L.; Faust, R. Initiation *via* Haloboration in Living Cationic Polymerization. 1. The Polymerization of Isobutylene. *Macromolecules* **1994**, *27*, 3453. (b) Kostjuk, S. V. Cationic polymerization of *p*-methoxystyrene co-initiated by $B(C_6F_5)_3$: Effect of acetonitrile and proton traps. *Eur. Polym. J.* **2020**, *129*, 109632.

50. 量子化学計算を用いて、ジフェニルジアゾメタンと $B(C_6F_5)_3$ の反応メカニズムを解析している。Tang, C.; Liang, Q.; Jupp, A. R.; Johnstone, T. C.; Neu, R. C.; Song, D.; Grimme, S.; Stephan, D. W. 1,1-Hydroboration and a Borane Adduct of Diphenyldiazomethane: A Potential Prelude to FLP-N_2 Chemistry. *Angew. Chem., Int. Ed.* **2017**, *56*, 16588.

51. Zuo, Z.; Wang, H.; Fan, L.; Liu, J.; Wang, Y.; Luan, X. Modular Assembly of Spirocarbocyclic Scaffolds through Pd^0-Catalyzed Intermolecular Dearomatizing [2+2+1] Annulation of Bromonaphthols with Aryl Iodides and Alkynes. *Angew. Chem., Int. Ed.* **2017**, *56*, 2767.

52. Han, L.; Wang, H.; Luan, X. Pd(II)-Catalyzed [3+2] spiroannulation of *α*-aryl-*β*-naphthols with alkynes *via* a C–H activation/dearomatization approach. *Org. Chem. Front.* **2018**, *5*, 2453.

53. Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Supporting Information S123 Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.

54. (a) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev.* **1988**, *A38*, 3098. (b) Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*. 1372. (c) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev.* **1988**, *B37*, 785.

55. (a) Fukui, K. The path of chemical reactions - the IRC approach. *Acc. Chem. Res.* **1981**, *14*, 363. (b) Ishida, K.; Morokuma, K.; Komornicki, A. The intrinsic reaction coordinate. An *ab initio* calculation for HNC→HCN and H−+CH4→CH4+H− . *J. Chem. Phys.* **1977**, *66*, 2153. (c) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (d) Gonzalez, C. H.; Schlegel, B. Reaction path following in mass-weighted internal coordinates. *J. Phys. Chem.* **1990**, *94*, 5523.

56. SDD: Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. H. Energy-adjusted *ab initio* pseudopotentials for the second and third row transition elements. *Theoret. Chim. Acta* **1990**, *77*, 123.

主論文目録

本学位論文内容は下記の発表論文による。

1. Homma, H.; Harada, S.; Ito, T.; Kanda, A.; Nemoto, T. Atypical Dearomative Spirocyclization of *β*-Naphthols with Diazoacetamides Using a Silver Catalyst. *Org. Lett.* **2020**, *22*, 8132.

謝辞

本研究を行うにあたり、終始御懇篤なるご指導とご鞭撻を賜りました千葉大学大学院薬学研究院 根本哲宏教授に深甚なる感謝の意を表します。

本研究を行うにあたり、時には厳しくも温かいご指導と多大なる御助言、御討論を賜りました千葉大学大学院薬学研究院 原田慎吾講師に深謝致します。

本研究、発表を行う上で貴重なご助言を賜りました千葉大学大学院薬学研究院 中島誠也助教に感謝致します。

学部から修士課程にかけて、研究の基礎をご教授下さった西田篤司先生、千葉大学大学院薬学研究院　荒井秀准教授、原田真至助教に深く感謝致します。

まだ科学者として未熟な私を受け入れ、ドイツでの研究生活という貴重な機会を与えて下さったビーレフェルト大学化学科 Harald Gröger 教授に心より御礼申し上げます。

日々の研究生活をご支援いただきました公益社団法人公益財団法人 双葉電子記念財団に深謝致します。

ビーレフェルト大学への短期留学は日本学術振興会－ドイツ学術交流会（JSPS-DAAD）二国間交流事業のご支援を受けて遂行したものであり、厚く御礼申し上げます。

研究生活を送るにあたり、数々のご協力をいただいた千葉大学大学院薬学研究院の教員、職員、学生の皆様に感謝致します。

最後に、永きに亘る学生生活を支え、応援してくれた家族に心より御礼申し上げます。

2021 年 3 月 本間　榛花

本学位論文の審査は千葉大学大学院薬学研究院で指名された下記の審査委員により行われた。

主査 千葉大学大学院教授（薬学研究院） 理学博士 石橋正己
副査 千葉大学大学院准教授（薬学研究院） 薬学博士 荒井秀
副査 千葉大学大学院准教授（薬学研究院） 薬学博士 北島満里子