Peter Zhang教授在Co卟啉方面的工作

汇报人：李蔚鹏

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目录

•1981 – 1985, 安徽师范大学(Anhui Normal University), B.S., Advisor: Huai-Zhu Ma (China);

•1985 – 1988, 北京师范大学(Beijing Normal University), M.S., Advisor: Bo-Li Liu (China);

•1991 – 1996, University of Pennsylvania, Ph.D., Advisor: Bradford B. Wayland;

•1996 – 1999, Massachusetts Institute of Technology, Postdoc, Advisor: Stephen J. Lippard;

•1999 – 2001, Massachusetts Institute of Technology, Postdoc, Advisor: Stephen L. Buchwald;

•2001 – 2006, Department of Chemistry, University of Tennessee, Assistant Professor;

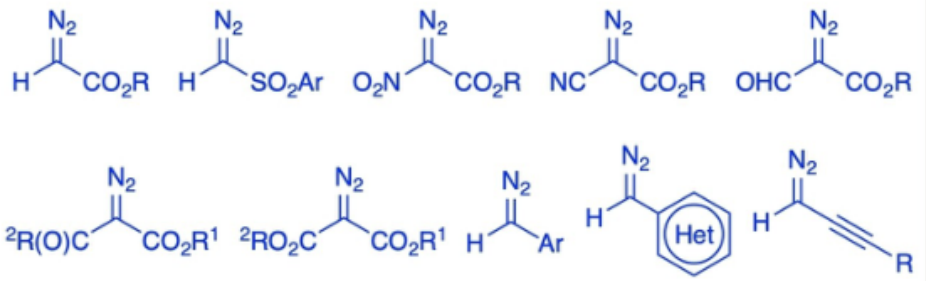
•2006 – 2010, Department of Chemistry, University of South Florida, Associate Professor;

•2010 – 2015, Department of Chemistry, University of South Florida, Professor;

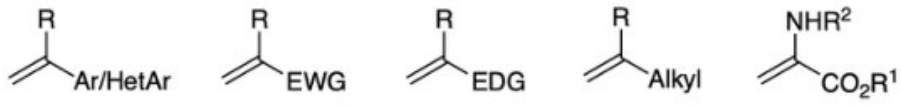
•2015 – Now, Department of Chemistry, Boston College, Professor.

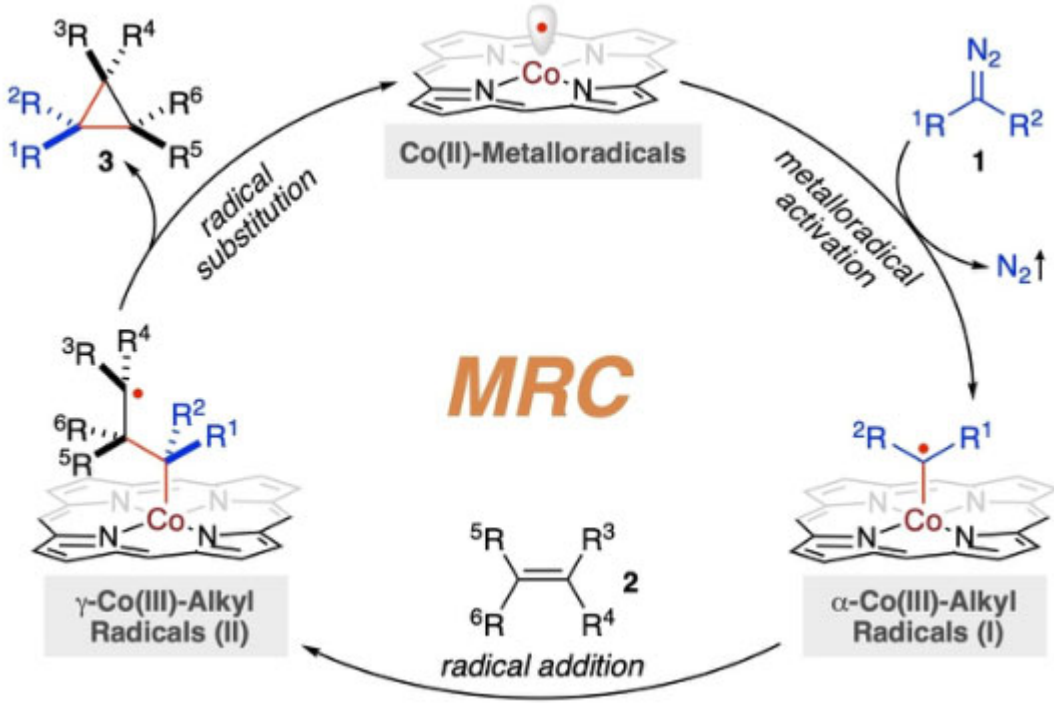
二、烯烃的自由基环丙基化

Selected Diazo Compounds

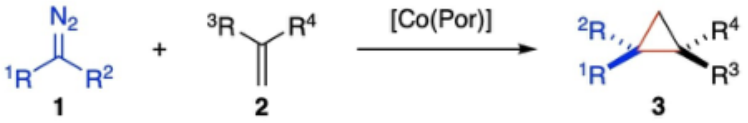


Selected Alkenes



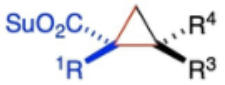


二、烯烃的自由基环丙基化



4
up to 95% yield
99:1 dr; 98% ee

5
up to 96% yield
99:1 dr; 97% ee



6
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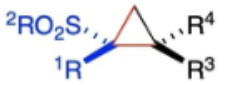

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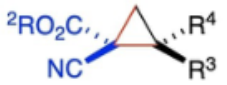
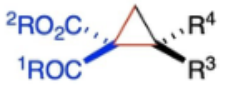
up to 99% yield
99:1 dr; 99% ee

8
up to 98% yield
99:1 dr; 95% ee



9
up to 99% yield
99:1 dr; 99% ee



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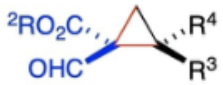
up to 94% yield
99:1 dr; 99% ee



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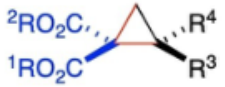
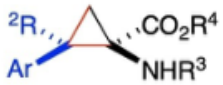
up to 99% yield
99:1 dr; 99% ee



12
up to 99% yield
99:1 dr; 99% ee

13
up to 91% yield
99:1 dr; 99% ee



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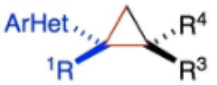
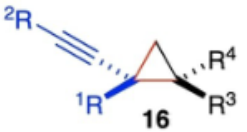
up to 99% yield
90:10 dr; 99% ee

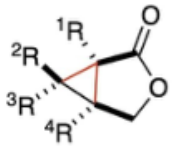


15
up to 99% yield
99:1 dr; 99% ee



16
up to 99% yield
96:4 dr; 99% ee

17
up to 96% yield
99% ee



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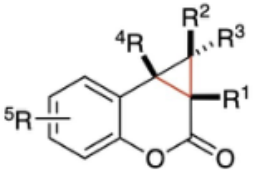
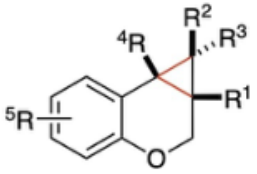
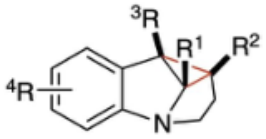
up to 99% yield
99:1 dr; 99% ee



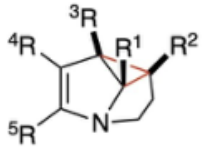
19
up to 96% yield
99:1 dr; 96% ee



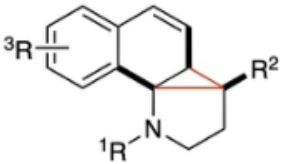
20
up to 99% yield
99:1 dr; 93% ee



21
up to 97% yield

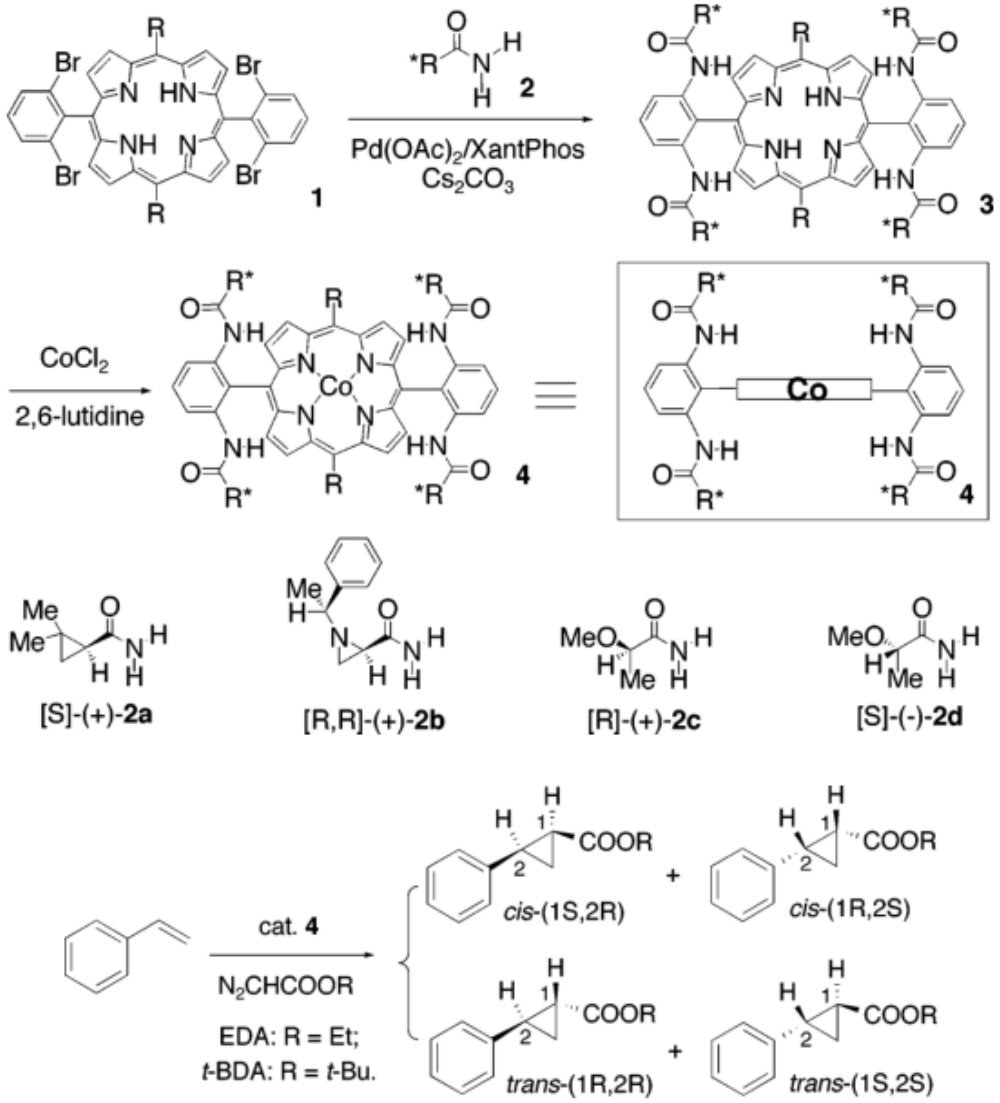


22
up to 93% yield



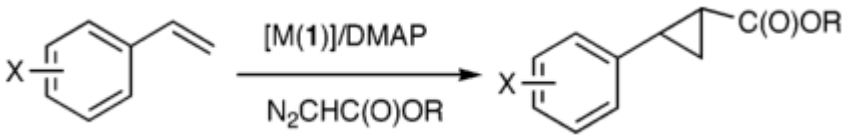
23
up to 99% yield

二、烯烃的自由基环丙基化



Y. Chen, K. B. Fields, X. P. Zhang, J. Am. Chem. Soc. 2004, 126, 14718–14719.

二、烯烃的自由基环丙基化



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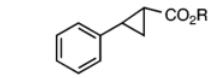
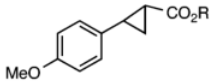
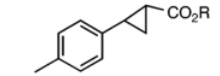
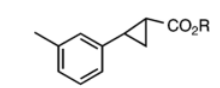
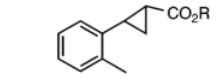
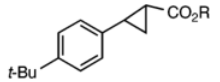
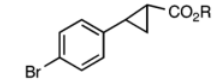
1		Et	RT	82	97:3	78
2		Et	–20	86[e]	98:2	80
3		*t*-Bu	RT	84	>99:1	95
4		*t*-Bu	–20	85[e]	>99:1	98
5		Et	RT	82	93:7	84
6		*t*-Bu	RT	86	98:2	96
7		*t*-Bu	–20	76[e]	99:1	98
8		Et	RT	71	96:4	70
9		*t*-Bu	RT	91	99:1	94
10		*t*-Bu	–20	66[e]	>99:1	92
11		Et	RT	87[c]	97:3	79
12		Et	–20	82[e]	99:1	87
13		*t*-Bu	RT	92	99:1	94
14		*t*-Bu	–20	54[e]	99:1	98
15		Et	RT	61	97:3	79
16		*t*-Bu	RT	84	>99:1	94
17		*t*-Bu	–20	76[e]	>99:1	97
18		Et	RT	95	96:4	89
19		*t*-Bu	RT	92	99:1	93
20		*t*-Bu	–20	86[e]	>99:1	91
21		Et	RT	81	95:5	73
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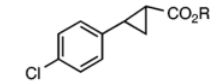
24		Et	RT	71	93:7	68
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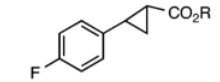
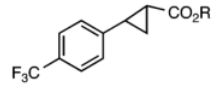
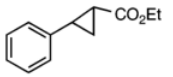
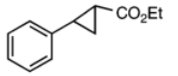
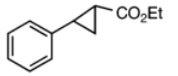
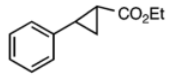
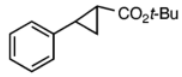
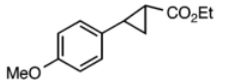
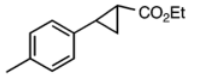
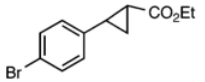
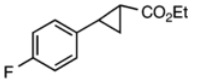
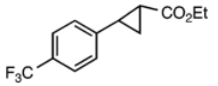
26		*t*-Bu	–20	52[e]	98:2	96
27		Et	RT	60	93:7	72
28		*t*-Bu	RT	88	98:2	86
29		*t*-Bu	–20	29[e]	97:3	94
30		Et	RT	79	95:5	77
31		*t*-Bu	RT	64	99:1	92
32		*t*-Bu	–20	65[e]	99:1	87

entry	product	alkene :diazo	DMAP	yield[b] (%)	trans:cis[c]	ee (%)[d] trans
1		1.0:1.2	yes	01[c]	nd[e]	nd[e]
2		10:1.0	yes	03[c]	nd[e]	nd[e]
3		1.0:1.2	no	41[c]	93:7	03
4		10:1.0	no	77	92:8	04
5		10:1.0	no	63	94:6	24
6		10:1.0	no	75	91:9	15
7		10:1.0	no	72	93:7	11
8		10:1.0	no	60	93:7	20
9		10:1.0	no	64	93:7	28
10		10:1.0	no	35	92:8	11

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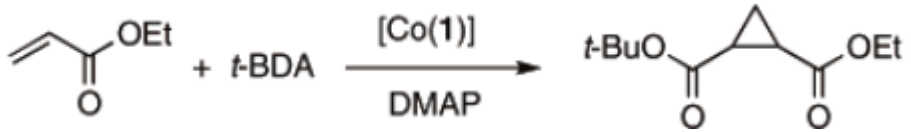
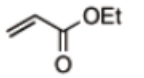
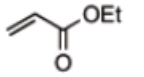
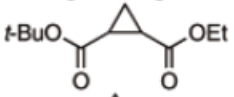
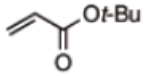
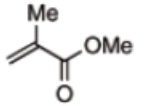
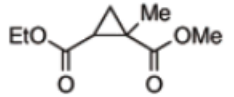
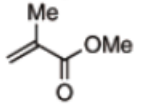
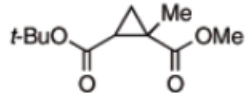
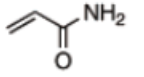
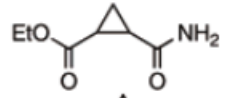
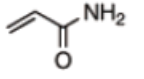
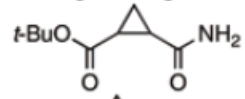
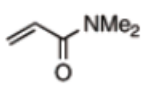
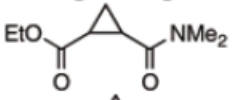
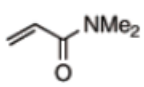
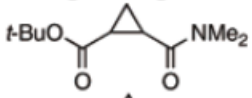
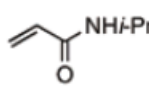
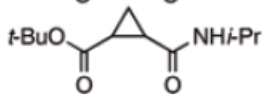
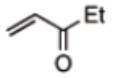
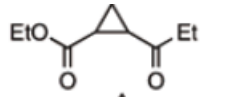
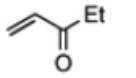
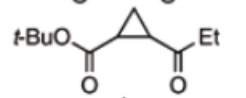
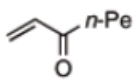
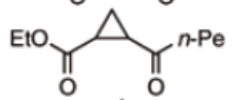
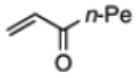
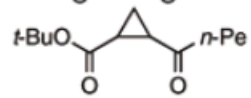
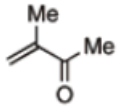
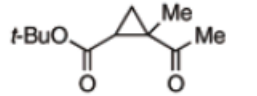
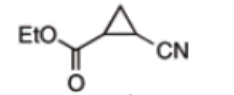
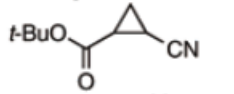
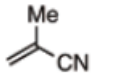
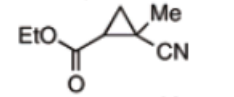
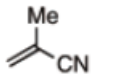
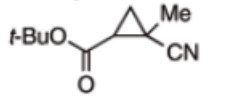
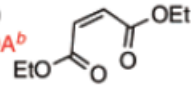
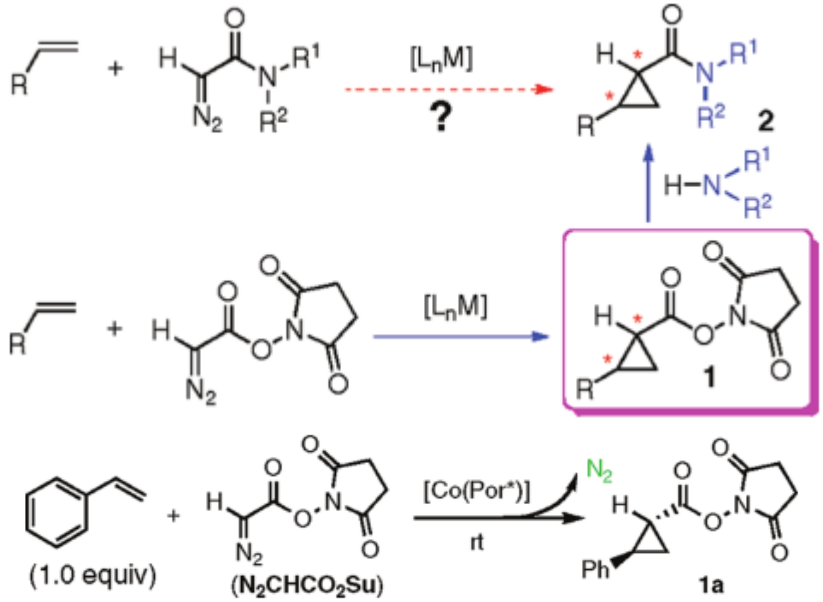


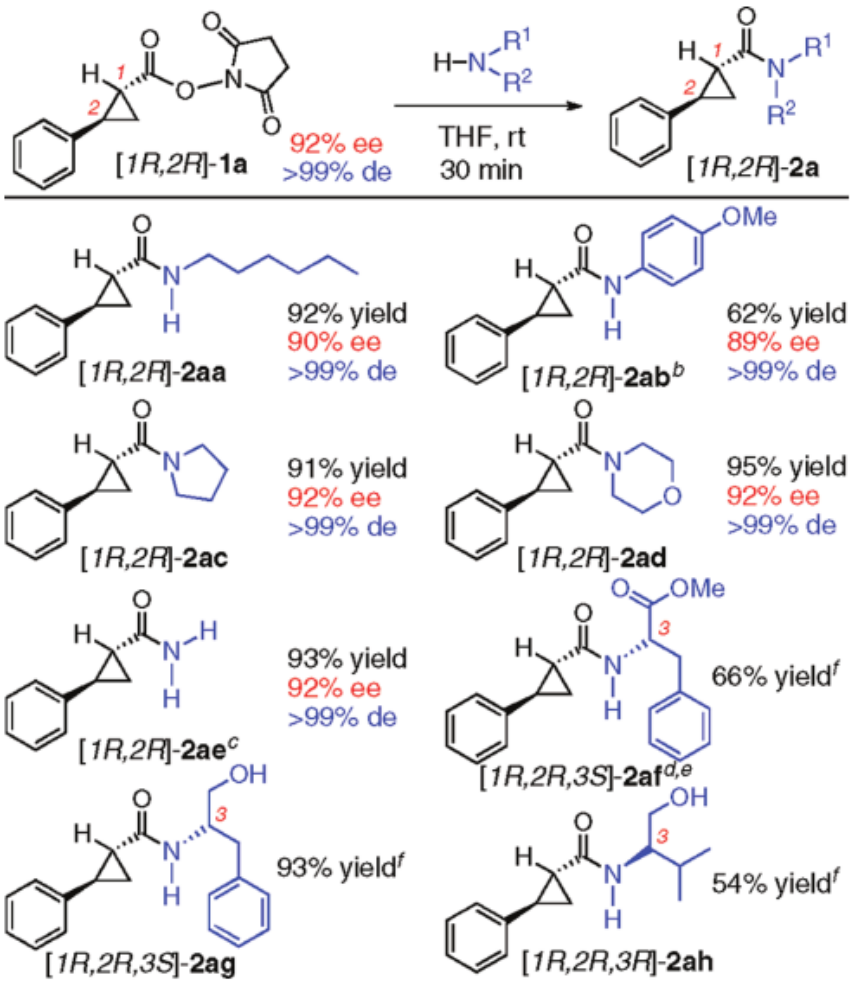
entry	alkene	diazo	product	yield (%)[c]	t:c[d]	ee (%)[e]
1		EDA		78	98:02	80[g]
1A[b]				95	97:03	81[g]
2		t-BDA		72	99:01	90
2A[b]				92	99:01	91
3		t-BDA		62	98:02	84
3A[b]				88	97:03	80
4		EDA		73	95:05	61
5		t-BDA		62	93:07	84
5A[b]				90	93:07	83
6		EDA		51	99:01	88
6A[b]				81	99:01	90
7		t-BDA		66	99:01	97
7A[b]				77	99:01	97
8		EDA		85	99:01	77
9		t-BDA		86	99:01	96
10		t-BDA		44	99:01	97
10A[b]				96	99:01	96
11		EDA		89	96:04	80
12		t-BDA		81	99:01	94
13		EDA		92	98:02	79
14		t-BDA		94	99:01	96
15		t-BDA		40	98:02	90
15A[b]				84	97:03	87
16		EDA		83	72:28	73
17		t-BDA		83	76:24	93
18		EDA		77	69:31	84
18A[b]				93	69:31	81
19		t-BDA		87	62:38	95
20		EDA		37	>99:1[f]	--
20A[b]				94	>99:1[f]	--

Y. Chen, J. V. Ruppel, X. P. Zhang, J. Am. Chem. Soc. 2007, 129, 12074–12075.

二、烯烃的自由基环丙基化

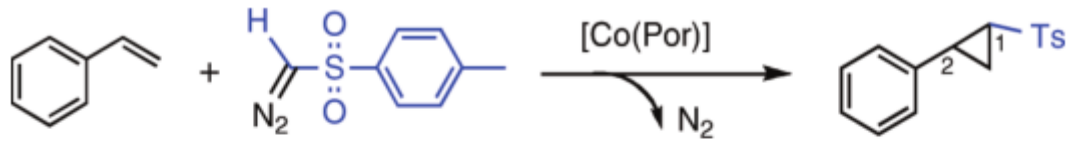


entry	[Co(Por*)][b]	additive	solvent	yield[c,i] (%)	trans:cis[d]	ee[e] (%)
1	[Co(**P1**)]	DMAP	C_6H_5Me	86	>99:1	92
2	[Co(**P2**)]	DMAP	C_6H_5Me	70	>99:1	96
3	[Co(**P3**)]	DMAP	C_6H_5Me	10	>99:1	63
4	[Co(**P4**)]	DMAP	C_6H_5Me	0		
5	[Co(**P5**)]	DMAP	C_6H_5Me	0		
6	[Co(**P6**)]	DMAP	C_6H_5Me	0		
7f	[Co(**P1**)]	DMAP	C_6H_5Me	74	>99:1	91
8[f]	[Co(**P1**)]	NMI	C_6H_5Me	85	>99:1	88
9[f]	[Co(**P1**)]		C_6H_5Me	86	>99:1	88
10[f,g]	[Co(**P1**)]	DMAP	C_6H_5Me	66	>99:1	91
11[f,h]	[Co(**P1**)]	DMAP	C_6H_5Me	64	>99:1	91
12[f]	[Co(**P1**)]	DMAP	C_6H_5Cl	67	>99:1	87

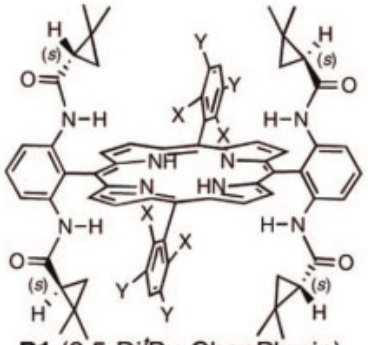


J. V. Ruppel, T. J. Gauthier, N. L. Snyder, J. A. Perman, X. P. Zhang, Org. Lett. 2009, 11, 2273–2276.

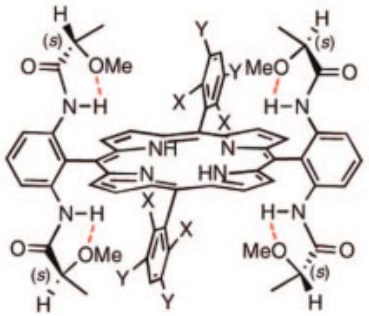
二、烯烃的自由基环丙基化



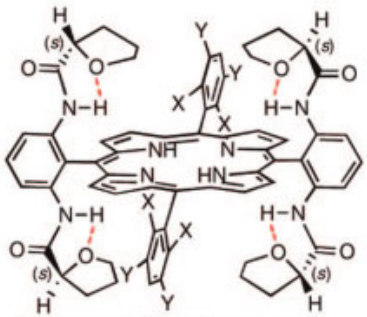
entry	[Co(Por)][b]	DMAP[c]	yield (%)[d]	trans:cis[e]	ee (%)[f]	config[g]
1	[Co(**P1**)]	+	~6[h]	>99:01	3	[1*R*,2*S*]-(−)
2	[Co(**P1**)]	−	86	>99:01	14	[1*S*,2*R*]-(+)
3	[Co(**P2**)]	−	78	>99:01	56	[1*S*,2*R*]-(+)
4	[Co(**P3**)]	−	60	>99:01	23	[1*S*,2*R*]-(+)
5	[Co(**P4**)]	−	99	>99:01	61	[1*S*,2*R*]-(+)
6	[Co(**P5**)]	−	30	>99:01	54	[1*R*,2*S*]-(−)
7	[Co(**P6**)]	−	99	>99:01	92	[1*R*,2*S*]-(−)



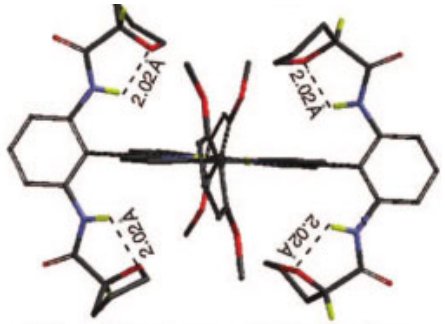
P1 (3,5-Di^{t}Bu-ChenPhyrin)
P2 (2,6-DiMeO-ChenPhyrin)



P3 (3,5-Di^{t}Bu-RuppelPhyrin)
P4 (2,6-DiMeO-RuppelPhyrin)



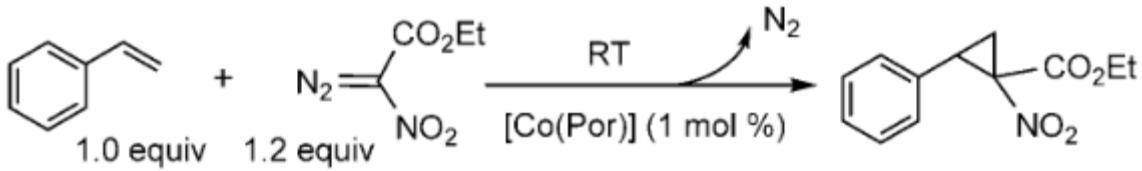
P5 (3,5-Di^{t}Bu-ZhuPhyrin)
P6 (2,6-DiMeO-ZhuPhyrin)



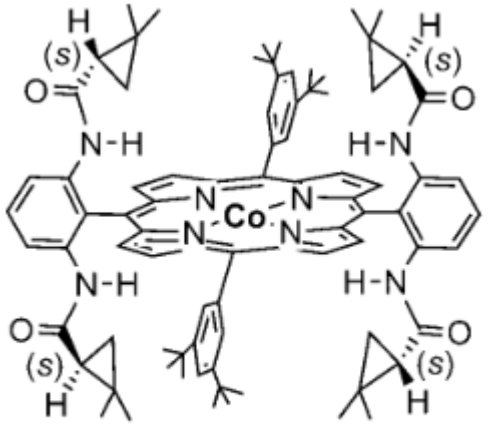
X-Ray Structure of **P6** Indicating Hydrogen Bonding Interactions

S. F. Zhu, J. V. Ruppel, H. J. Lu, L. Wojtas, X. P. Zhang, J. Am. Chem. Soc. 2008, 130, 5042–5043.

二、烯烃的自由基环丙基化



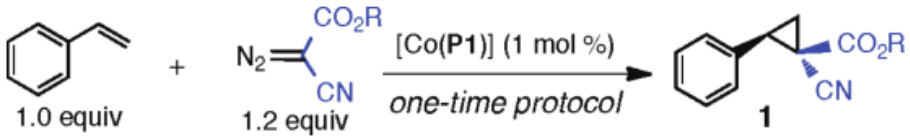
Entry	[Co(Por)][b]	Solvent	Yield [%][c]	Z/E[d]	ee [%][e]
1	[Co(tpp)]	CH_2Cl_2	15[f]	58:42	–
2	[Co(**P1**)]	CH_2Cl_2	99	91:09	81
3	[Co(**P2**)]	CH_2Cl_2	99	91:09	58
4	[Co(**P3**)]	CH_2Cl_2	20	67:33	33
5	[Co(**P4**)]	CH_2Cl_2	69	81:19	47
6	[Co(**P5**)]	CH_2Cl_2	31	66:34	−23
7	[Co(**P6**)]	CH_2Cl_2	< 5[f]	85:15	n.d.[g]
8	[Co(**P1**)]	$C_2H_4Cl_2$	91	93:07	86
9[h]	[Co(**P1**)]	$C_2H_4Cl_2$	90	92:08	90
10[i]	[Co(**P1**)]	$C_2H_4Cl_2$	98	92:08	92
11	[Co(**P1**)]	C_6H_5Cl	99	88:12	82
12	[Co(**P1**)]	*n*-C_6H_{14}	87	92:08	89



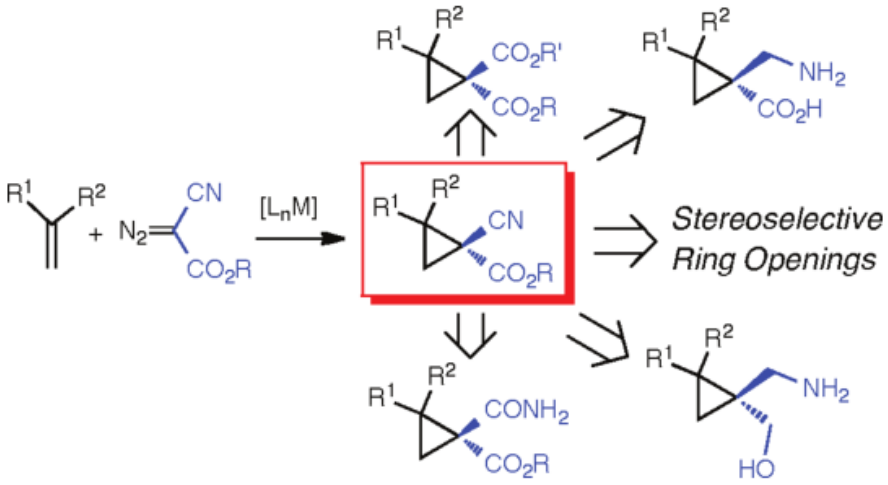
[Co(**P1**)]
(**P1** = 3,5-Di*t*Bu-ChenPhyrin)

S. F. Zhu, J. A. Perman, X. P. Zhang, Angew. Chem. Int. Ed. 2008, 47, 8460–8463.

二、烯烃的自由基环丙基化

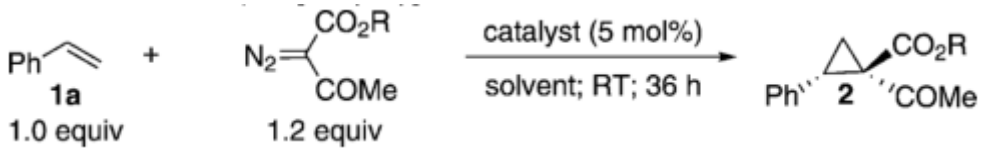


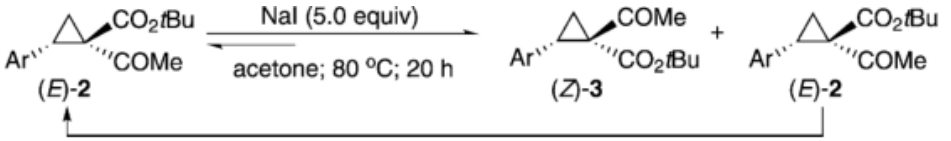
entry	R	solvent	temp (°C)	yield (%)[b]	E:Z[c]	ee (%)[d]
1	Et	CH_2Cl_2	25	99	84:16	62
2	Et	C_6H_5Cl	25	92	84:16	66
3	Et	$C_2H_4Cl_2$	25	99	81:19	71
4	Et	C_6H_5Me	25	94	85:15	70
5	Et	*n*-C_6H_{14}	25	99	88:12	74
6	*t*-Bu	*n*-C_6H_{14}	25	89	>99:1	91
7	*t*-Bu	*n*-C_6H_{14}	0	83	>99:1	95
8	*t*-Bu	*n*-C_6H_{14}	–20	96	>99:1	98

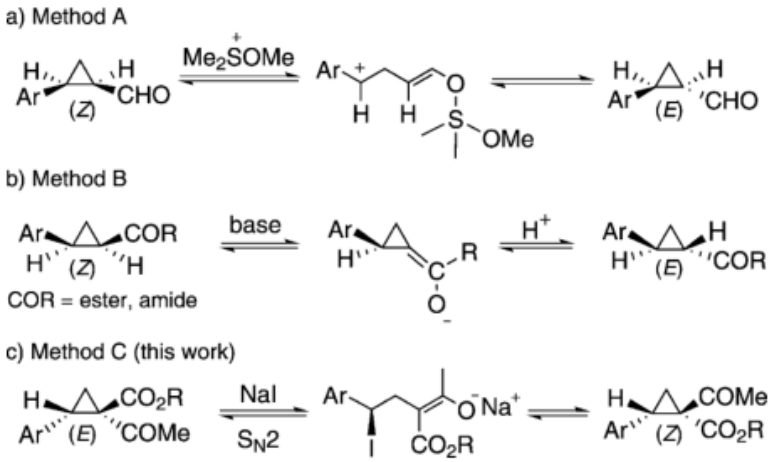


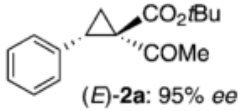
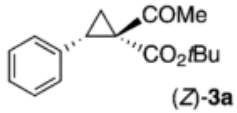
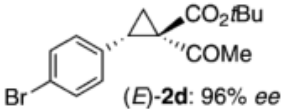
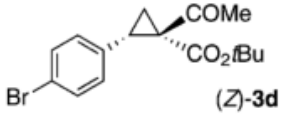
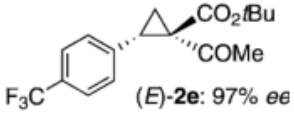
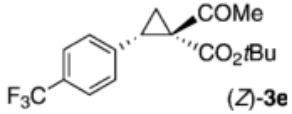
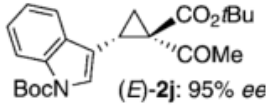
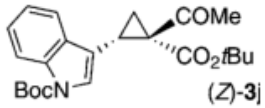
S. F. Zhu, X. Xu, J. A. Perman, X. P. Zhang, J. Am. Chem. Soc. 2010, 132, 12796–12799.

二、烯烃的自由基环丙基化







Entry	*E* cyclopropane	*Z* cyclopropane	Yield [%][a]	*ee* [%][b]
1	 (*E*)-**2a**: 95% *ee*	 (*Z*)-**3a**	70	95
2	 (*E*)-**2d**: 96% *ee*	 (*Z*)-**3d**	65	96
3	 (*E*)-**2e**: 97% *ee*	 (*Z*)-**3e**	70	97
4	 (*E*)-**2j**: 95% *ee*	 (*Z*)-**3j**	68	93[c]

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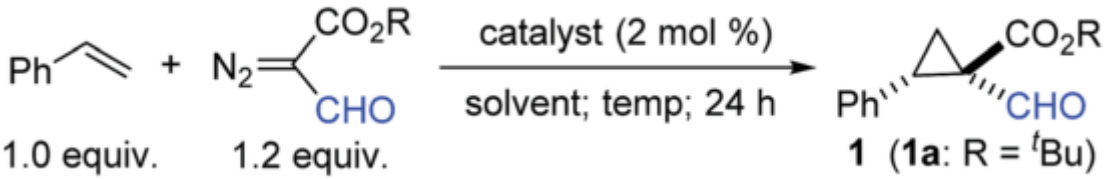
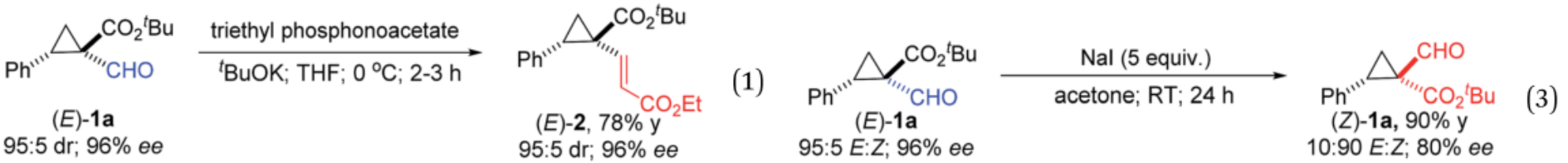
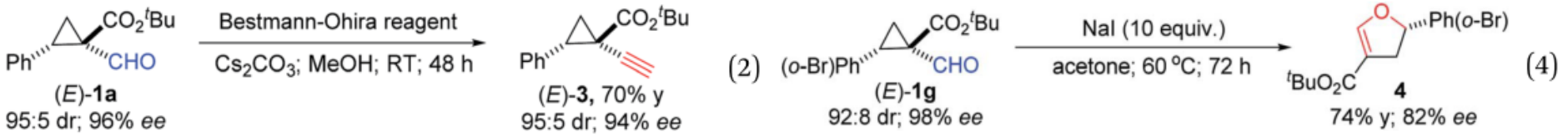
二、烯烃的自由基环丙基化







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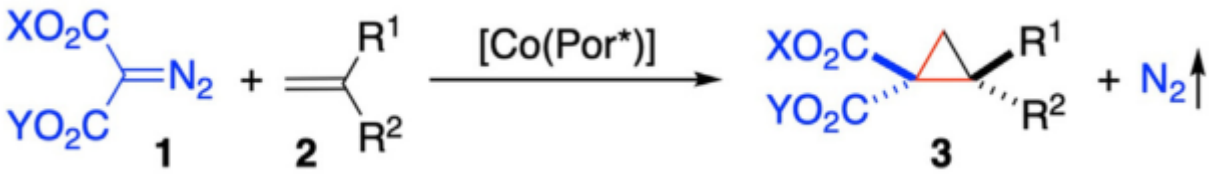
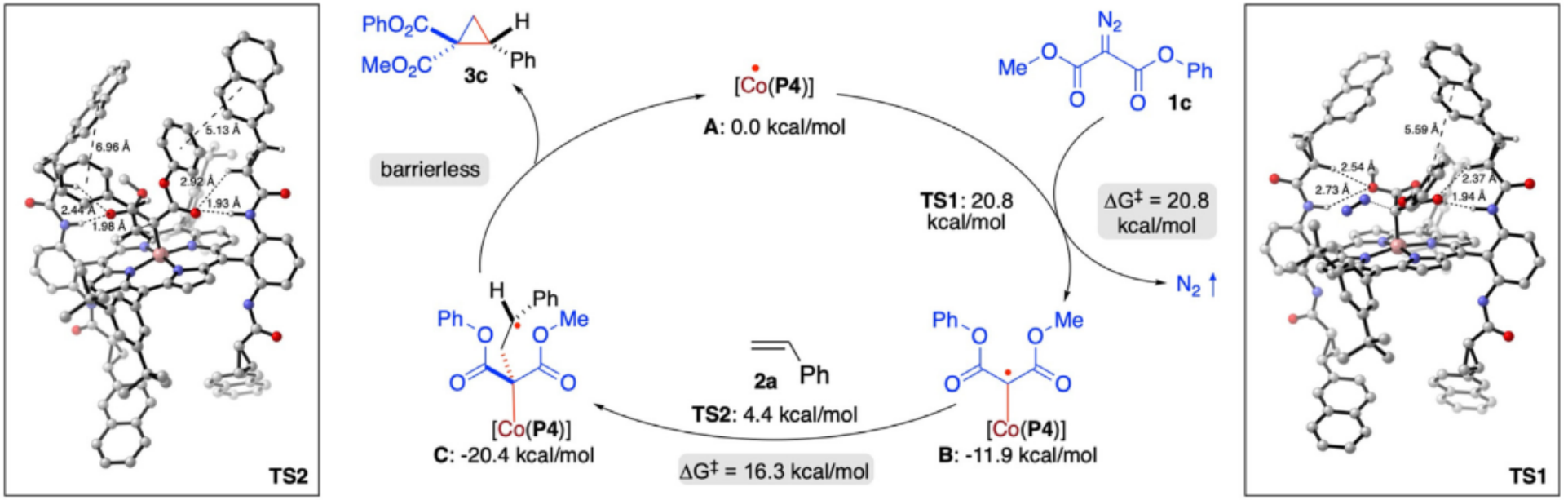
二、烯烃的自由基环丙基化





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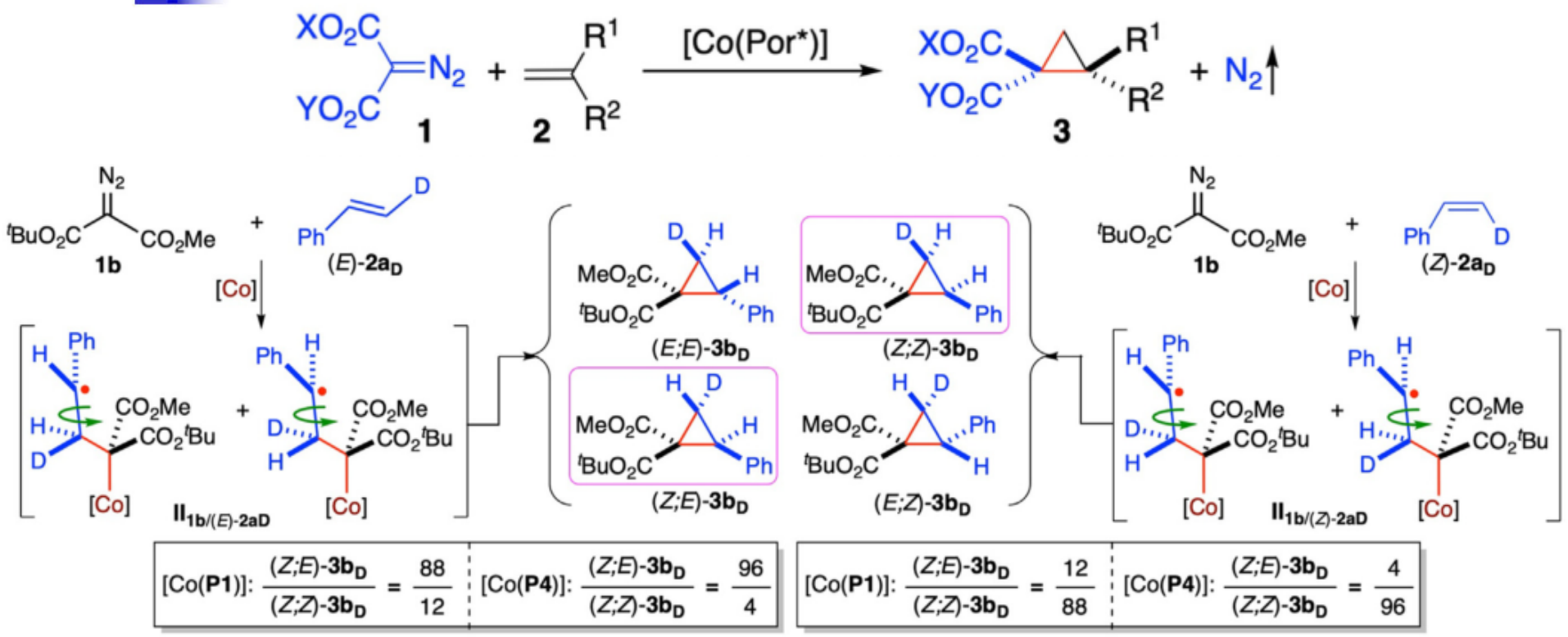
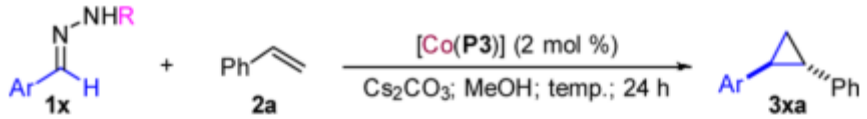
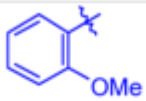
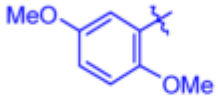
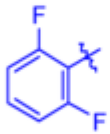
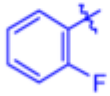
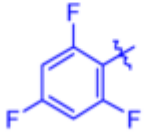
二、烯烃的自由基环丙基化



J. Y. Wang, J. J. Xie, W.-C. C. Lee, D. S. Wang, X. P. Zhang, Chem Catal. 2022, 2, 330–344.

二、烯烃的自由基环丙基化



entry	Ar	R[b]	product	temp. (°C)	yield (%)[c]	dr[d]	ee (%)[e]
1		Ts (**1b**)	**3ba**	40	78	95:5	99
2		Ts (**1f**)	**3fa**	40	91	95:5	94
3		Ts (**1g**)	**3ga**	RT	90	94:6	86
4		Ts (**1g**)	**3ga**	0	<10	-	-
5		TPS (**1g'**)	**3g'a**	0	83	>99:1	93
6		Ts (**1h**)	**3ha**	RT	58	96:4	71
7		TPS (**1h'**)	**3h'a**	0	75	>99:1	76
8		Ts (**1i**)	**3ia**	RT	85	96:4	88
9		TPS (**1i'**)	**3i'a**	0	85	>99:1	93
10		Ts (**1j**)	**3ja**	RT	82	95:5	68
11		TPS (**1j'**)	**3j'a**	0	81	>99:1	89

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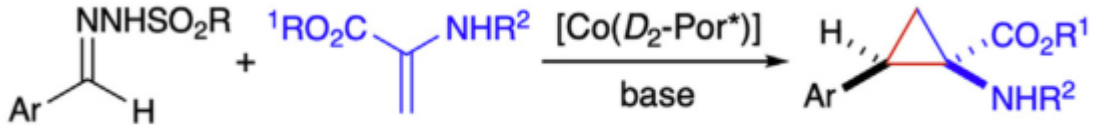
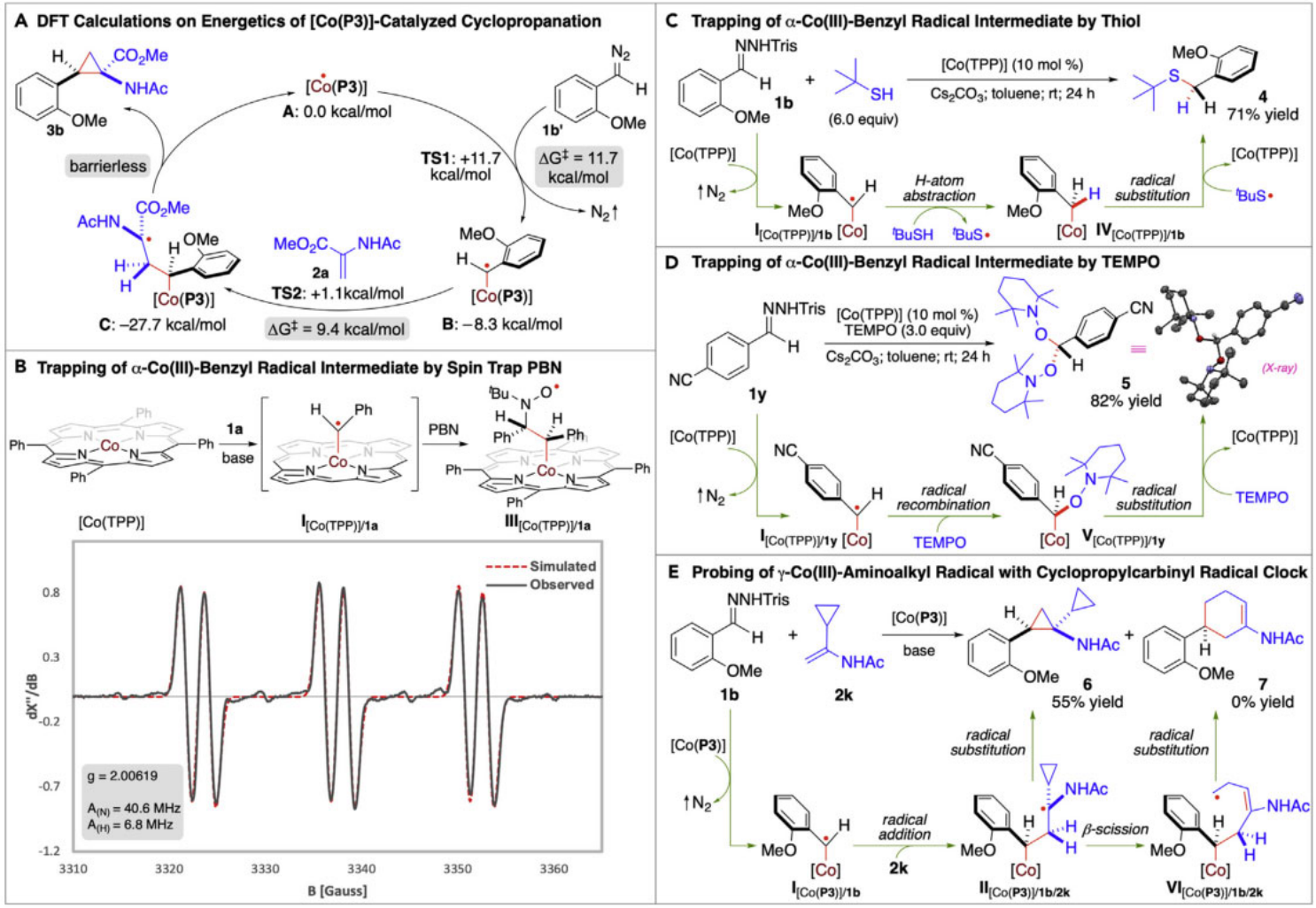
二、烯烃的自由基环丙基化





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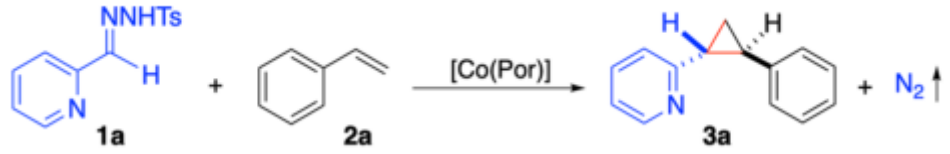
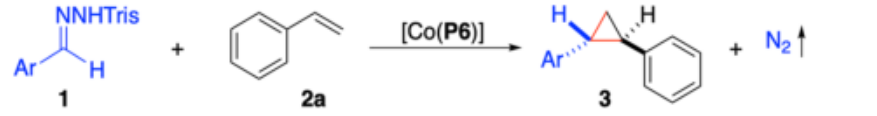
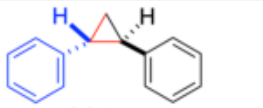
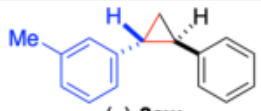
二、烯烃的自由基环丙基化



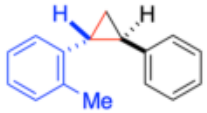



(–)-**3au**
entry 1: 97% yield
94:6 dr; 97% ee

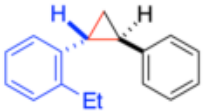
(–)-**3av**
entry 2: 95% yield
93:7 dr; 98% ee



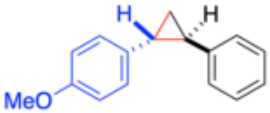
(–)-**3aw**
entry 3: 92% yield
95:5 dr; 97% ee



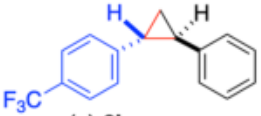
(–)-**3ax**
entry 4: 86% yield
95:5 dr; 97% ee



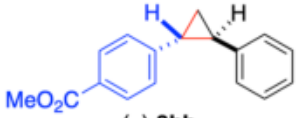
(–)-**3ay**
entry 5: 57% yield
96:4 dr; 89% ee



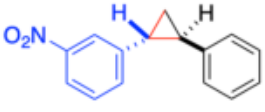
(–)-**3az**
entry 6: 94% yield
94:6 dr; 97% ee



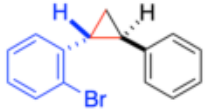
(–)-**3ba**
entry 7: 96% yield
93:7 dr; 99% ee



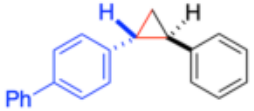
(–)-**3bb**
entry 8: 94% yield
94:6 dr; 97% ee



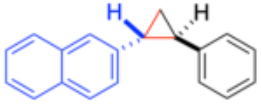
(–)-**3bc**
entry 9: 89% yield
98:2 dr; 96% ee

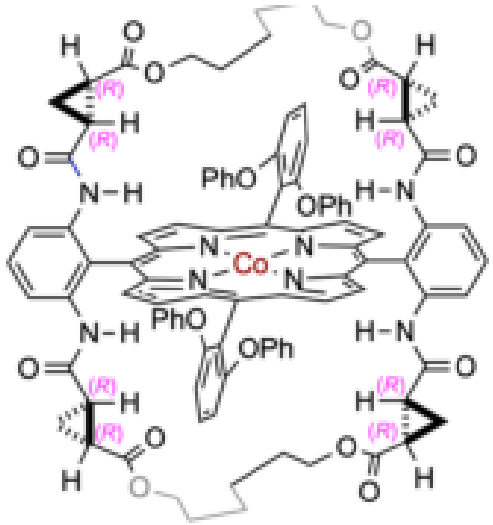


(–)-**3bd**
entry 10: 89% yield
96:4 dr; 93% ee



(–)-**3be**
entry 11: 90% yield
95:5 dr; 98% ee

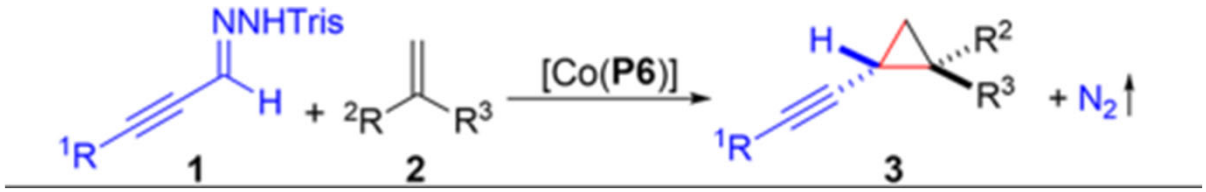

(–)-**3bf**
entry 12: 91% yield
95:5 dr; 97% ee

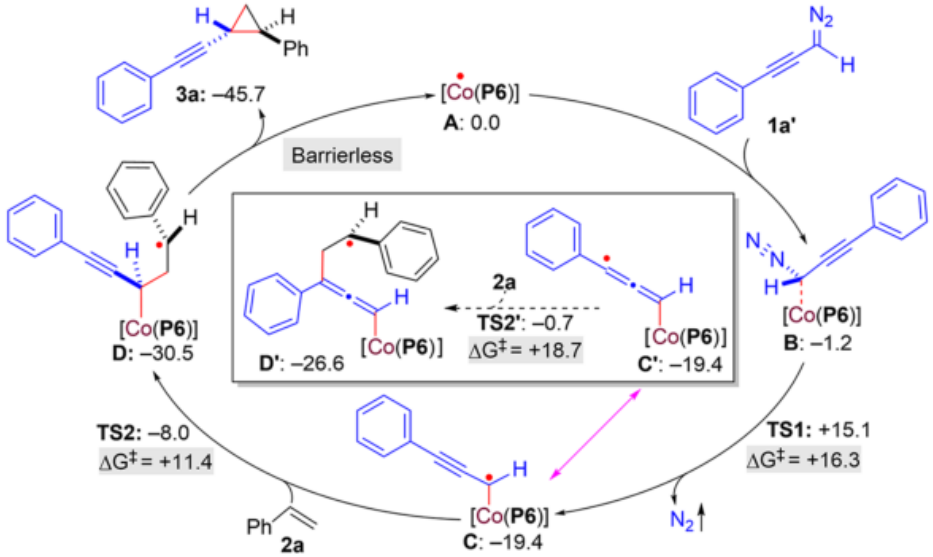


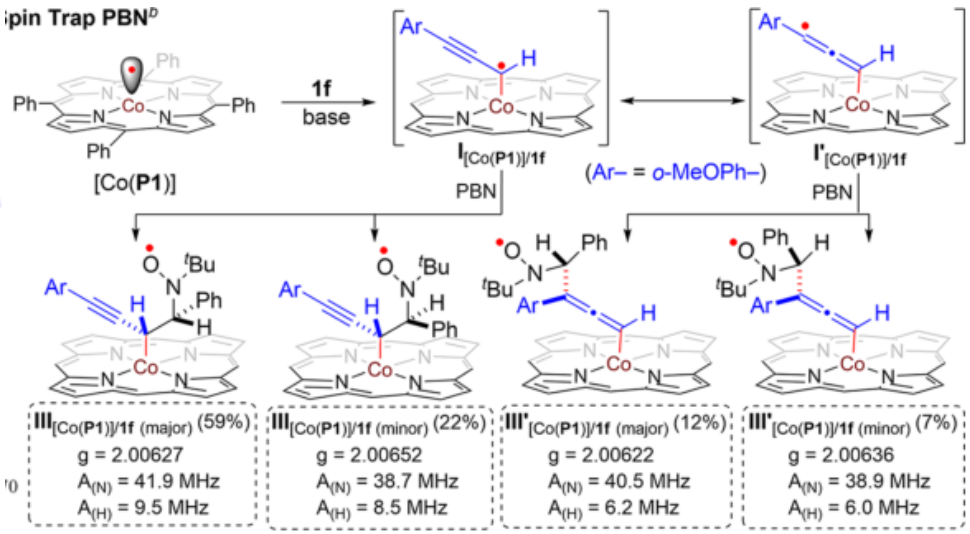
[Co(**P6**)]
(**P6** = 2,6-DiPhO-Hu(C_6)Phyrin)

X. X. Wang, J. Ke, Y. L. Zhu, A. Deb, Y. J. Xu, X. P. Zhang, J. Am. Chem. Soc. 2021, 143, 11121–11129.

二、烯烃的自由基环丙基化







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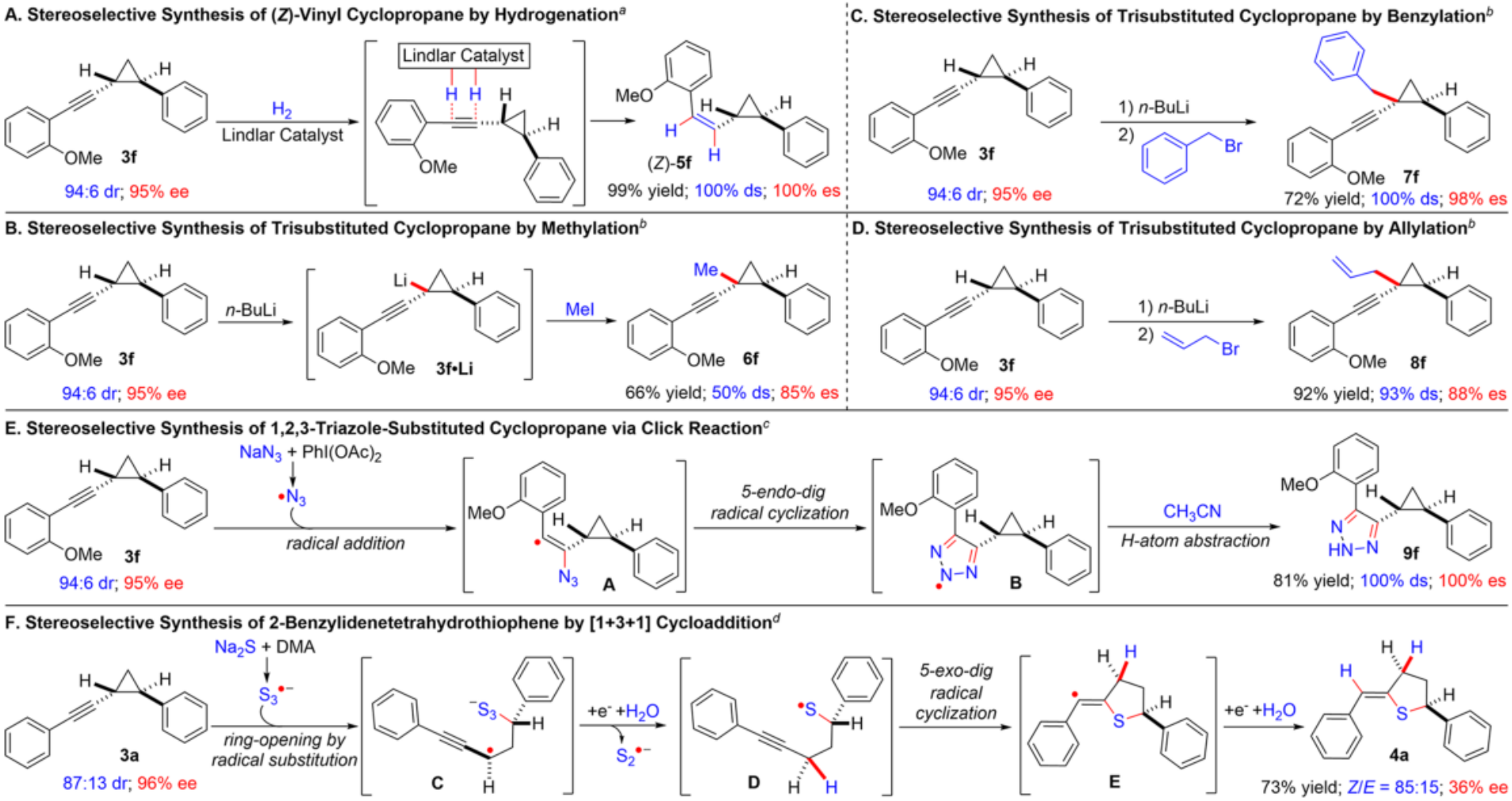

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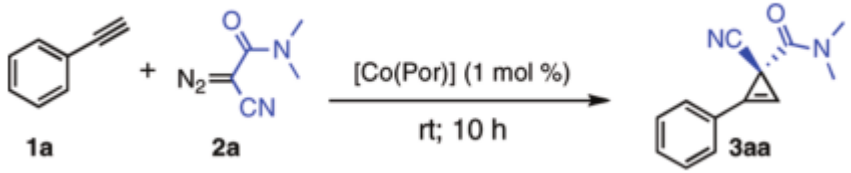
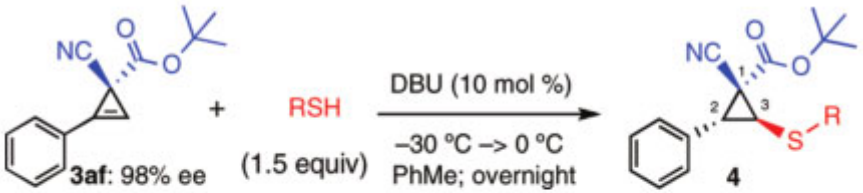
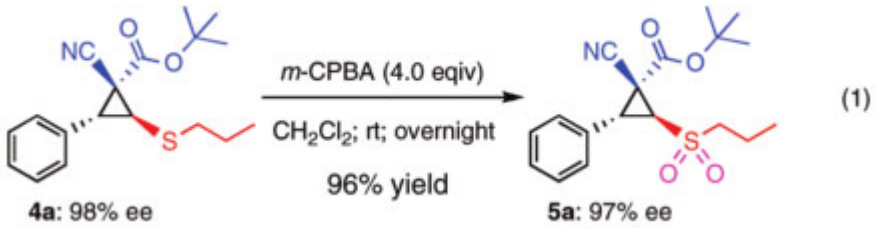


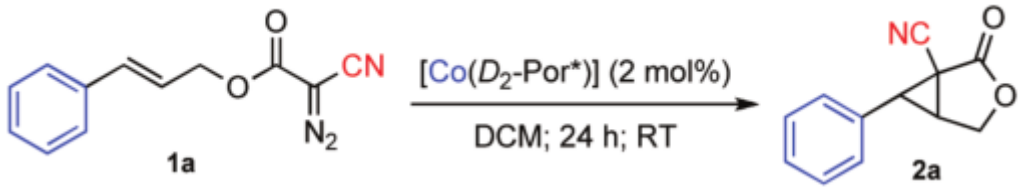


entry	thiol	product	yield (%)[b]	ee (%)[c]
1	HS	4a	98	98[d]
2	HS	4b	88	98
3[e]	HS	4c	54	98

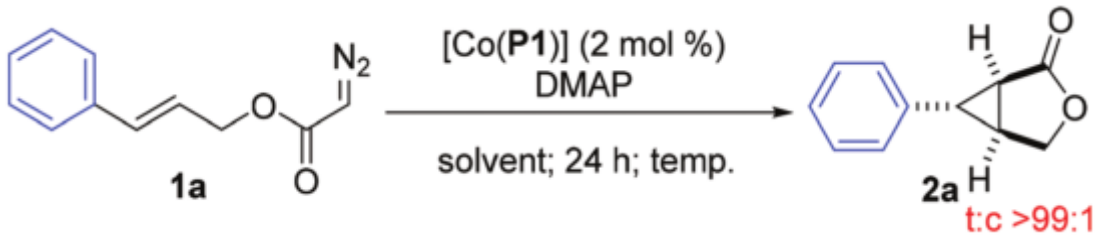


X. Cui, X. Xu, H. J. Lu, S. F. Zhu, L. Wojtas, X. P. Zhang, J. Am. Chem. Soc. 2011, 133, 3304–3307.

二、烯烃的自由基环丙基化

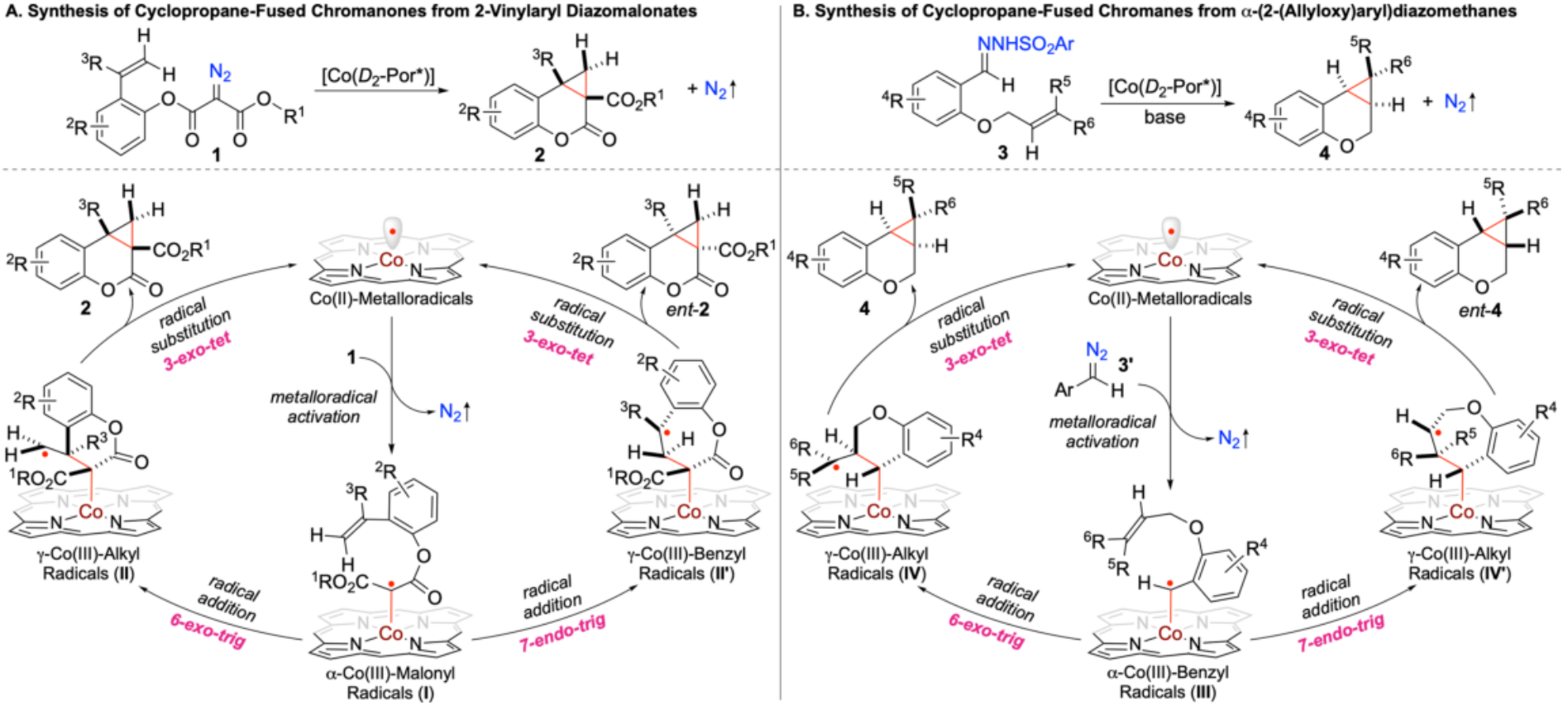


X. Xu, H. J. Lu, J. V. Ruppel, X. Cui, S. L. de Mesa, L. Wojtas, X. P. Zhang, J. Am. Chem. Soc. 2011, 133, 15292– 15295



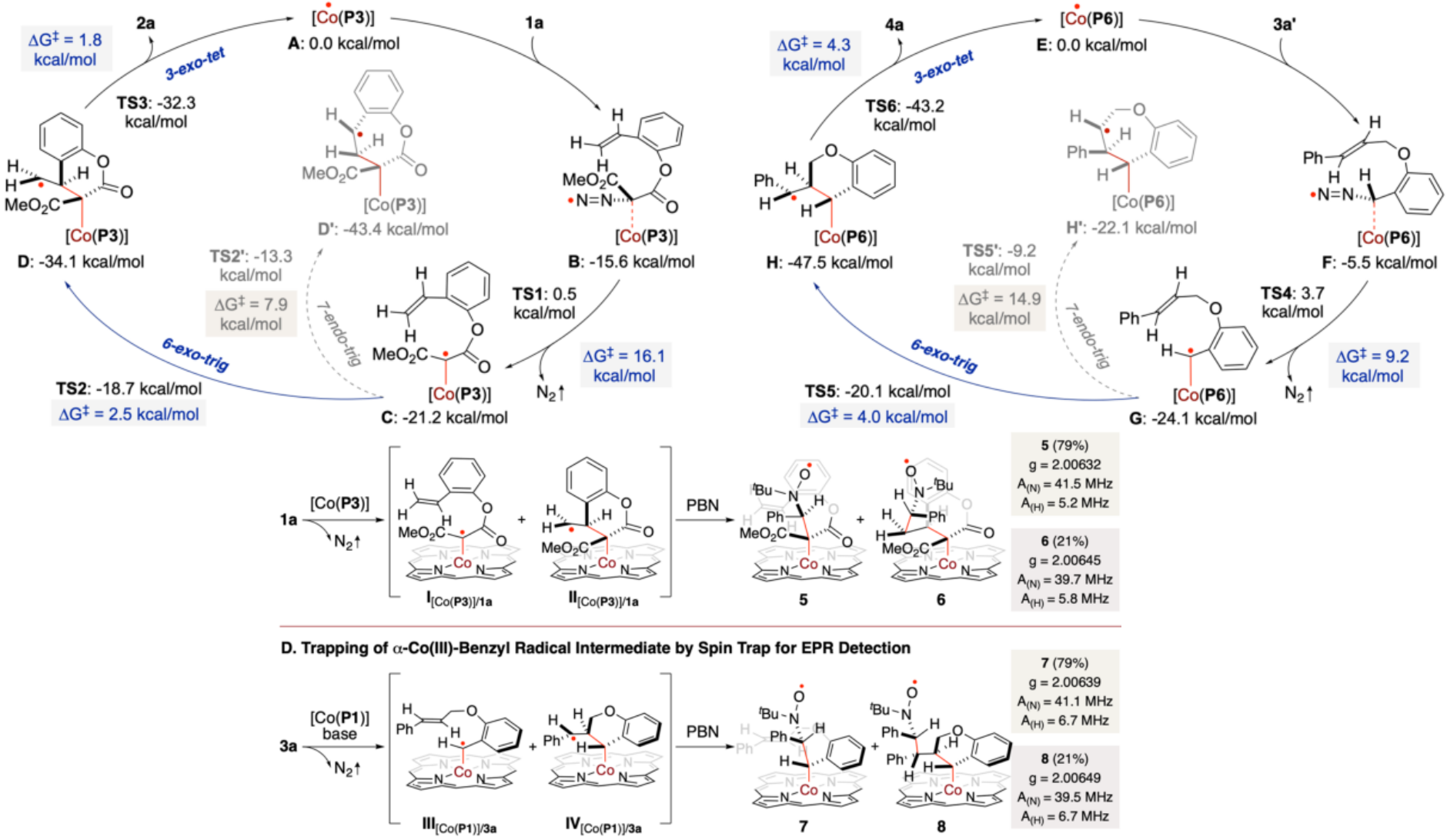
J. V. Ruppel, X. Cui, X. Xu, X. P. Zhang, Org. Chem. Front. 2014, 1, 515–520.

二、烯烃的自由基环丙基化



W.-C. C. Lee, J. Y. Wang, Y. L. Zhu, X. P. Zhang, J. Am. Chem. Soc. 2023, 145, 11622–11632.

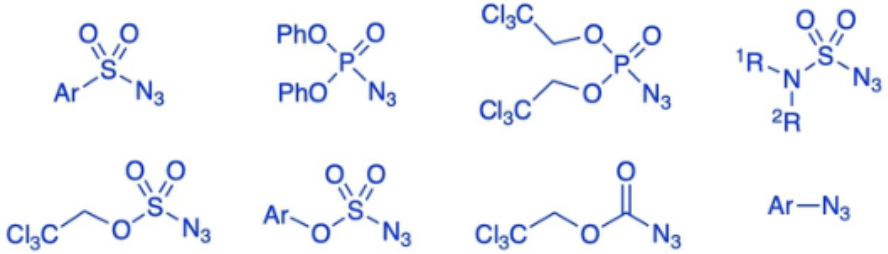
二、烯烃的自由基环丙基化



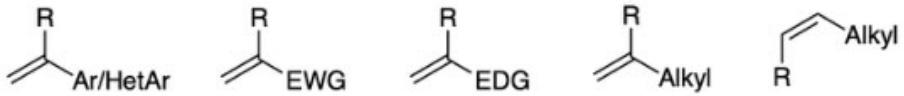
W.-C. C. Lee, J. Y. Wang, Y. L. Zhu, X. P. Zhang, J. Am. Chem. Soc. 2023, 145, 11622–11632.

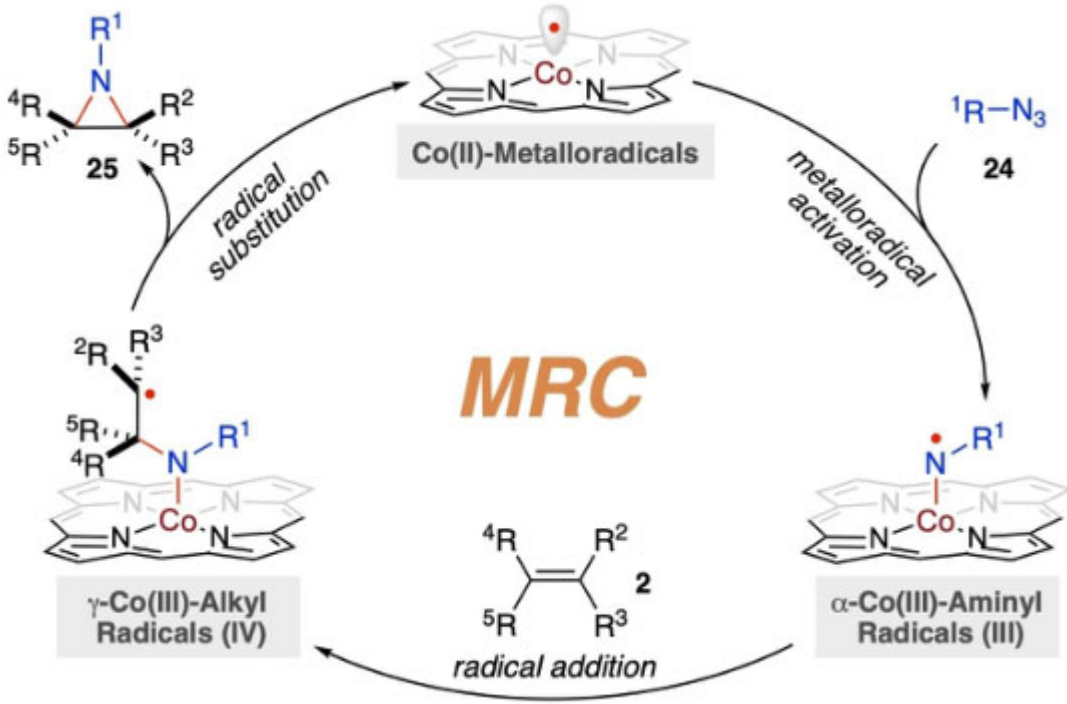
三、烯烃的自由基氮杂环丙烷化

Selected Organic Azides

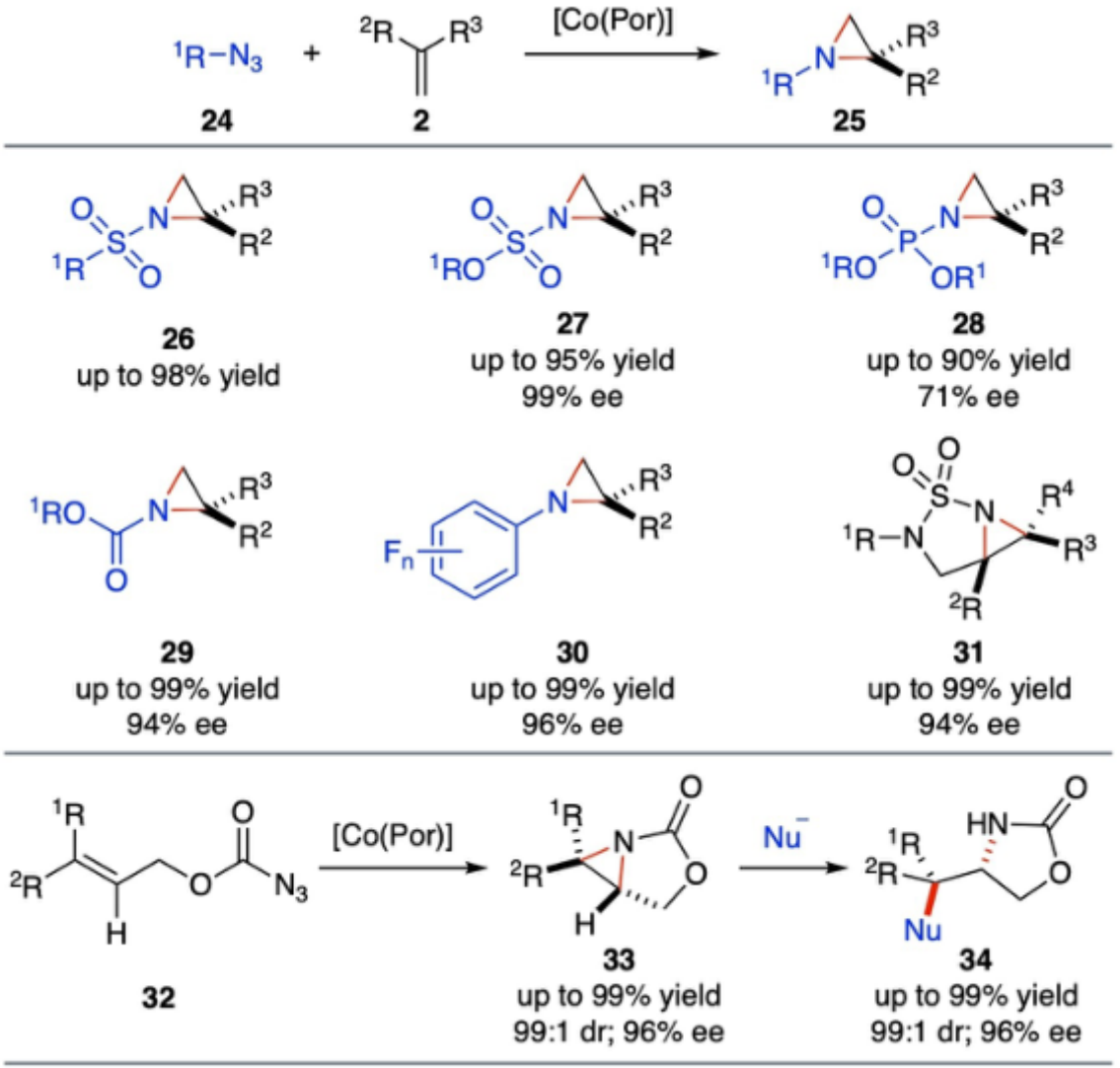


Selected Alkenes

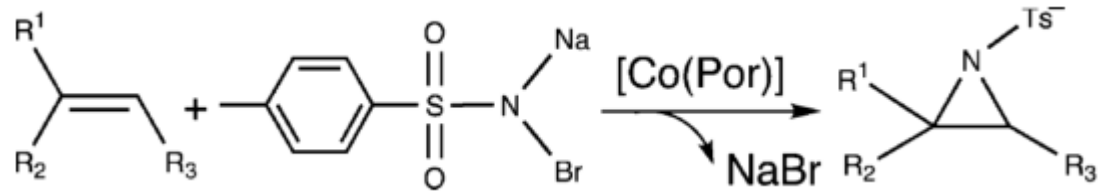


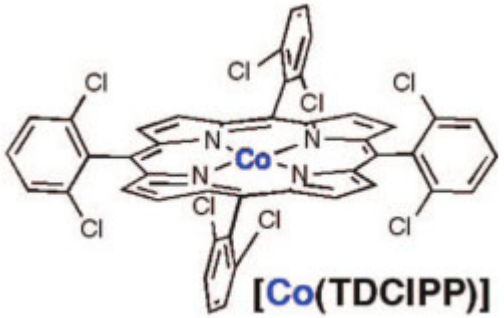


三、烯烃的自由基氮杂环丙烷化

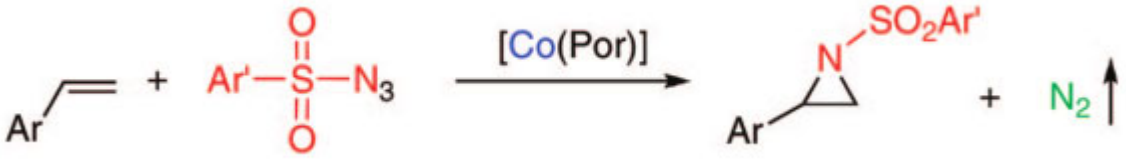


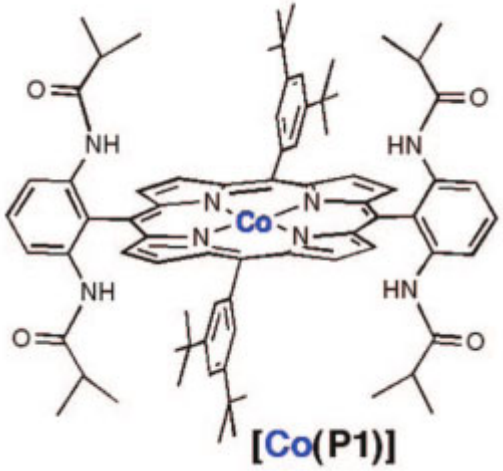
三、烯烃的自由基氮杂环丙烷化





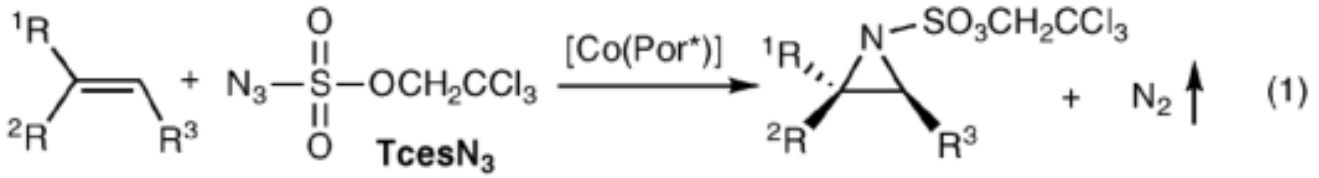
G. Y. Gao, J. D. Harden, X. P. Zhang, Org. Lett. 2005, 7, 3191–3193.

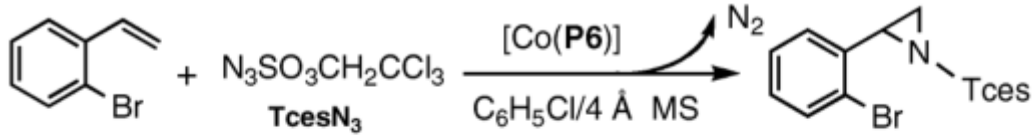




J. V. Ruppel, J. E. Jones, C. A. Huff, R. M. Kamble, Y. Chen, X. P. Zhang, Org. Lett. 2008, 10, 1995–1998.

三、烯烃的自由基氮杂环丙烷化

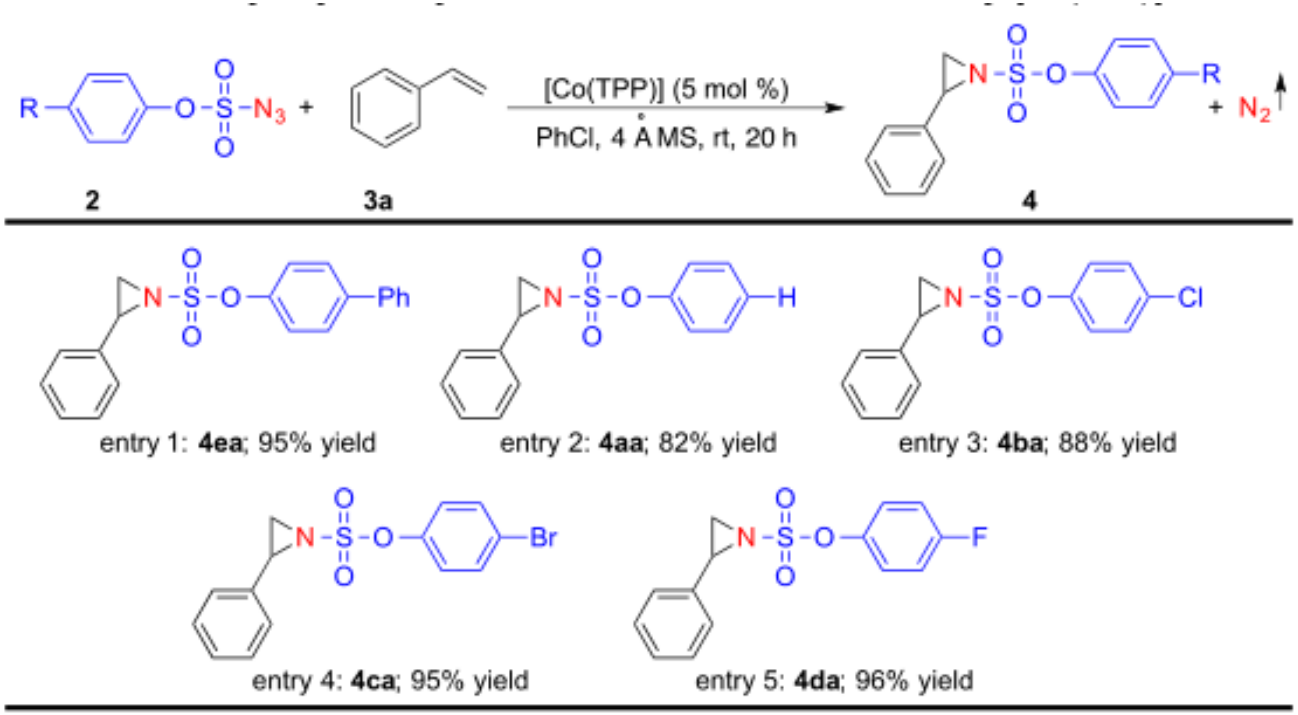




Entry	Cycle	Temp/°C	Yield[b] (%)	ee[c] (%)
1	First	RT	95	96
2	Second	RT	89	94
3	Third	RT	81	94

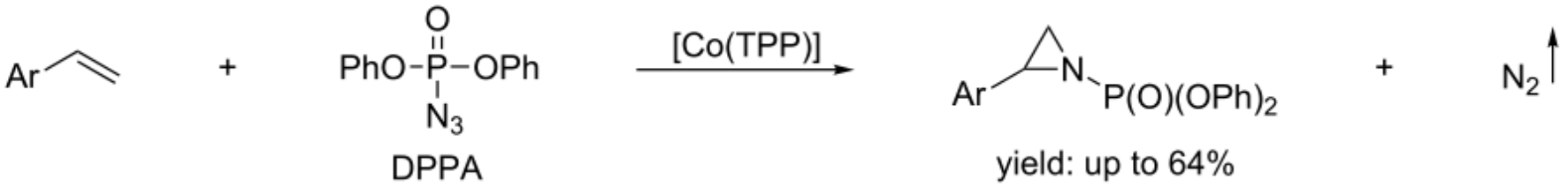
V. Subbarayan, J. V. Ruppel, S. Zhu, J. A. Perman, X. P. Zhang, Chem. Commun. 2009, 4266–4268.

三、烯烃的自由基氮杂环丙烷化

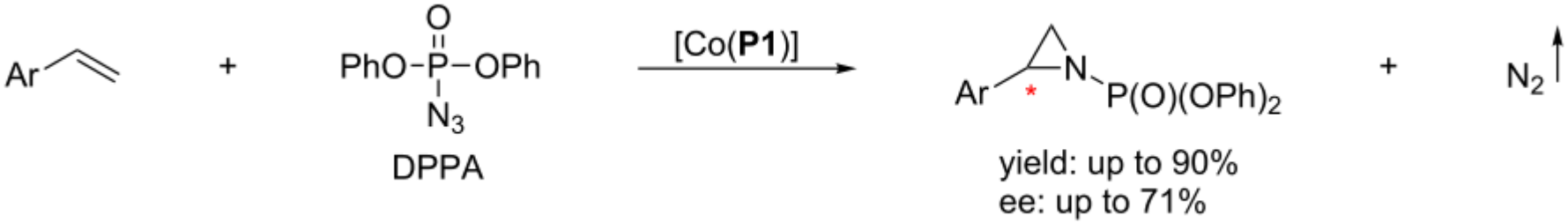


V. Subbarayan, L. M. Jin, X. Cui, X. P. Zhang, Tetrahedron Lett. 2015, 56, 3431–3434.

三、烯烃的自由基氮杂环丙烷化



G. Y. Gao, J. E. Jones, R. Vyas, J. D. Harden, X. P. Zhang, J. Org. Chem. 2006, 71, 6655–6658.



J. E. Jones, J. V. Ruppel, G. Y. Gao, T. M. Moore, X. P. Zhang, J. Org. Chem. 2008, 73, 7260–7265.

The Yang Research Group
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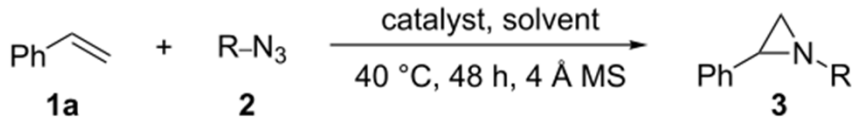
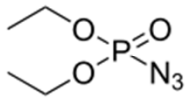
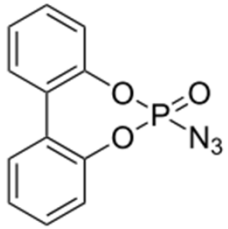
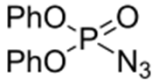
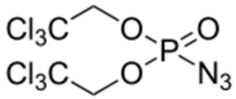
三、烯烃的自由基氮杂环丙烷化



entry	R–N_3	catalyst	solvent	yield (%)[b]	ee (%)[c]
1[d]	 **2a**	[Co(TPP)]	PhCl	0	–
2[d]	 **2b**	[Co(TPP)]	PhCl	0	–
3[d]	 **2c**	[Co(TPP)]	PhCl	0	–
4[d]	 **2d**	[Co(TPP)]	PhCl	11	–
13[e]	**2d**	[Co(**P6**)]	C_6H_6	99	82

J. R. Tao, L. M. Jin, X. P. Zhang, Beilstein J. Org. Chem. 2014, 10, 1282–1289.

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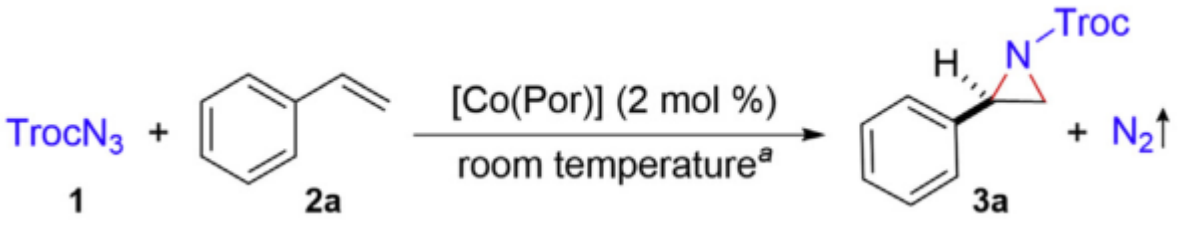
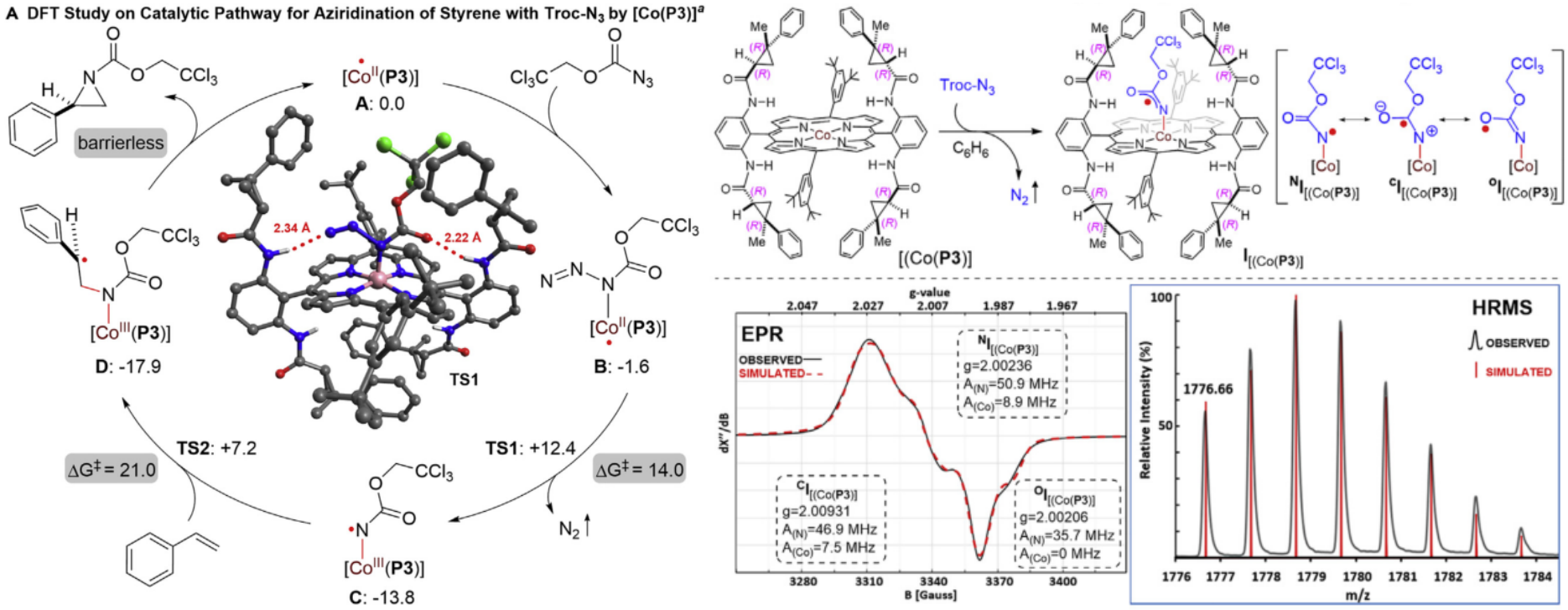
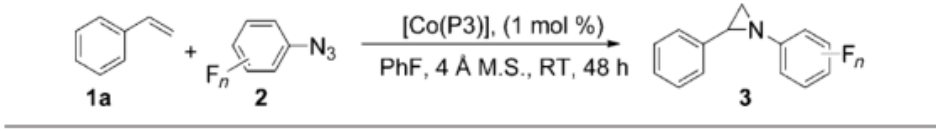
三、烯烃的自由基氮杂环丙烷化

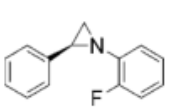




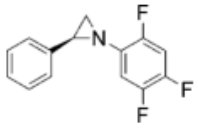
X. Riart-Ferrer, P. Sang, J. R. Tao, H. Xu, L. M. Jin, H. J. Lu, X. Cui, L. Wojtas, X. P. Zhang, Chem 2021, 7, 1120–1134.

三、烯烃的自由基氮杂环丙烷化

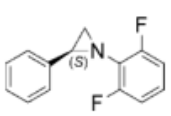




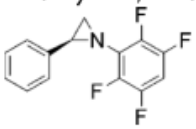
entry 1:[e] **3aa**;
52% yield, 75% *ee*



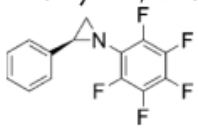
entry 2: **3ac**;
64% yield, 80% *ee*



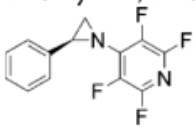
entry 3:[d] **3ad**;
80% yield, 96% *ee*



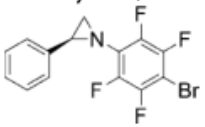
entry 4: **3ae**;
95% yield, 89% *ee*



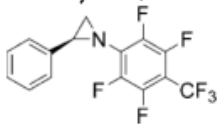
entry 5: **3af**;
99% yield, 92% *ee*



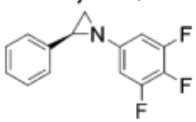
entry 6: **3ag**;
96% yield, 90% *ee*



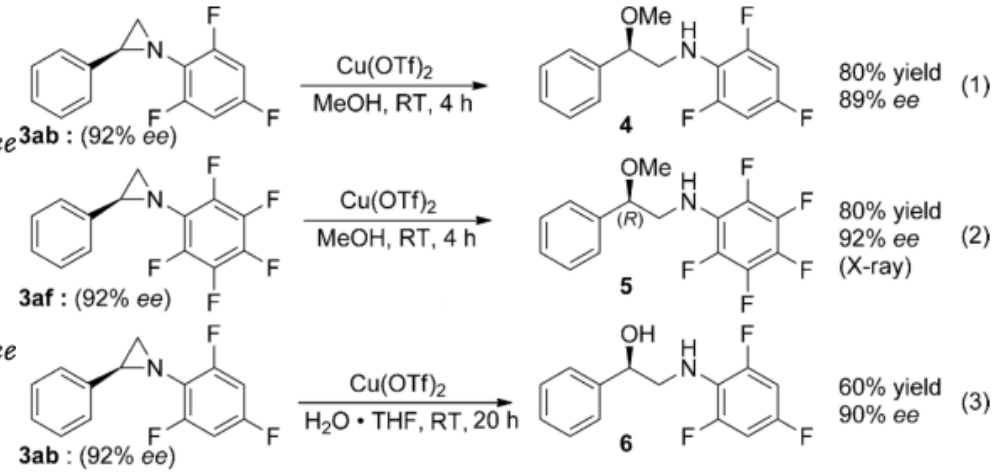
entry 7: **3ah**;
95% yield, 80% *ee*



entry 8: **3ai**;
99% yield, 68% *ee*

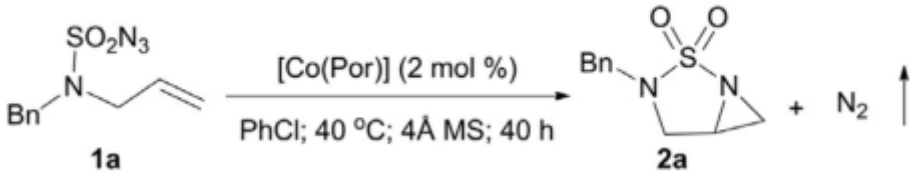


entry 9: **3aj**;
no reaction

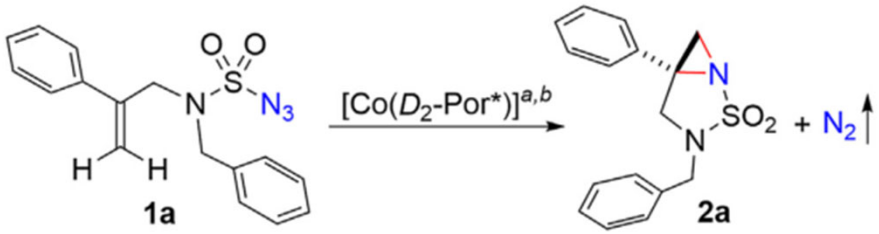


L. M. Jin, X. Xu, H. J. Lu, X. Cui, L. Wojtas, X. P. Zhang, Angew. Chem. Int. Ed. 2013, 52, 5309–5313.

三、烯烃的自由基氮杂环丙烷化

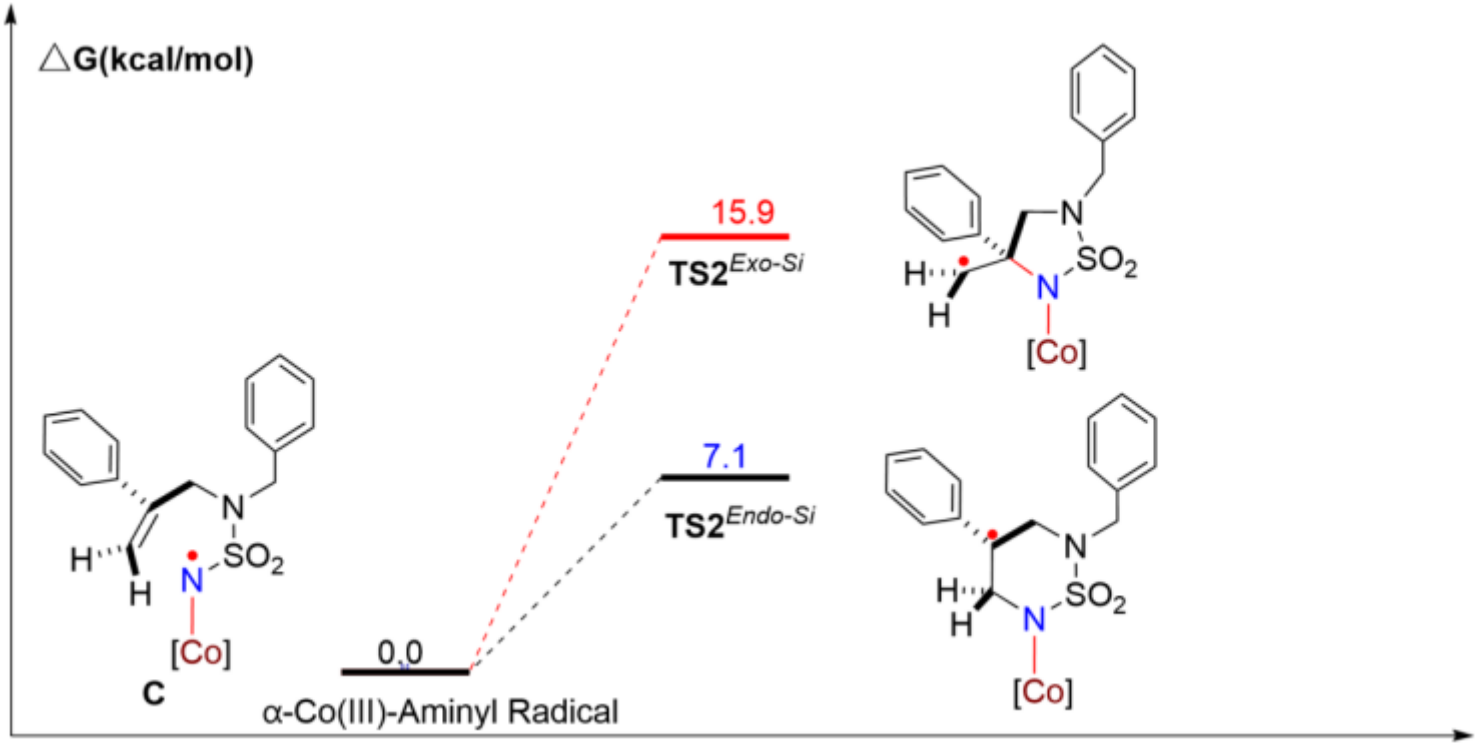


H. L. Jiang, K. Lang, H. J. Lu, L. Wojtas, X. P. Zhang, Angew. Chem. Int. Ed. 2016, 55, 11604–11608.



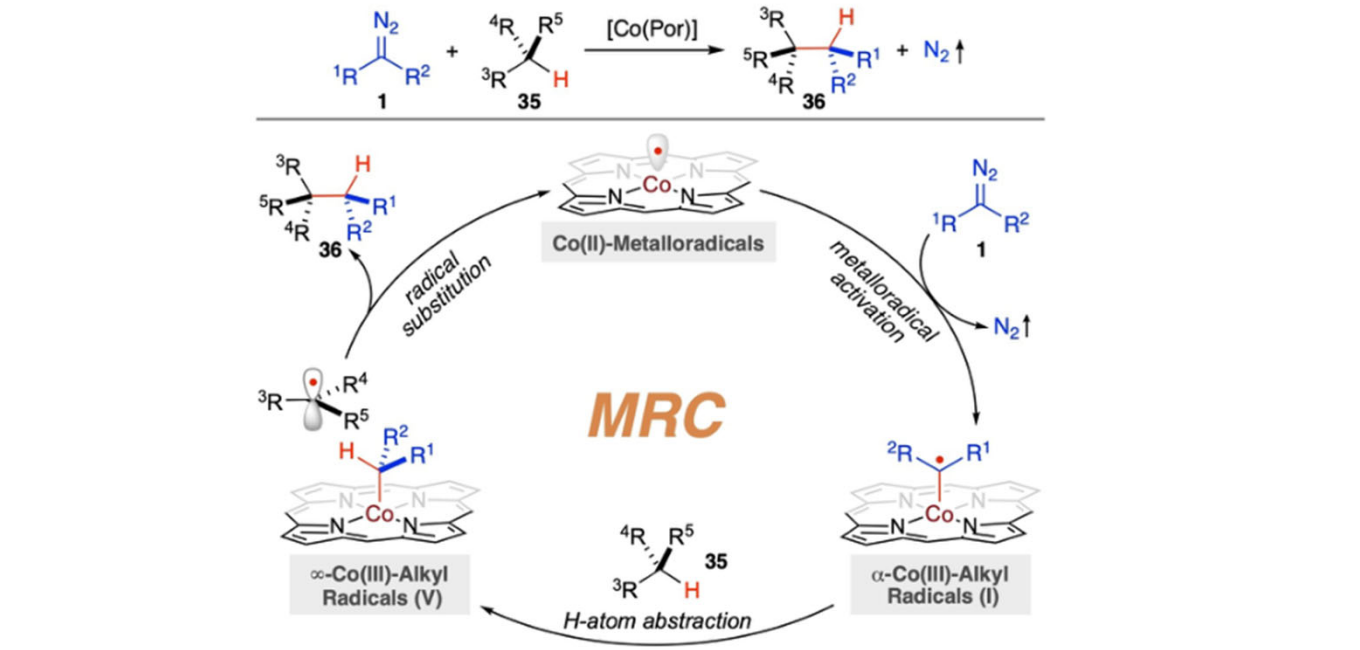
H. Xu, D.-S. Wang, Z. Zhu, A. Deb, X. P. Zhang, Chem 2024, 10, 283–298.

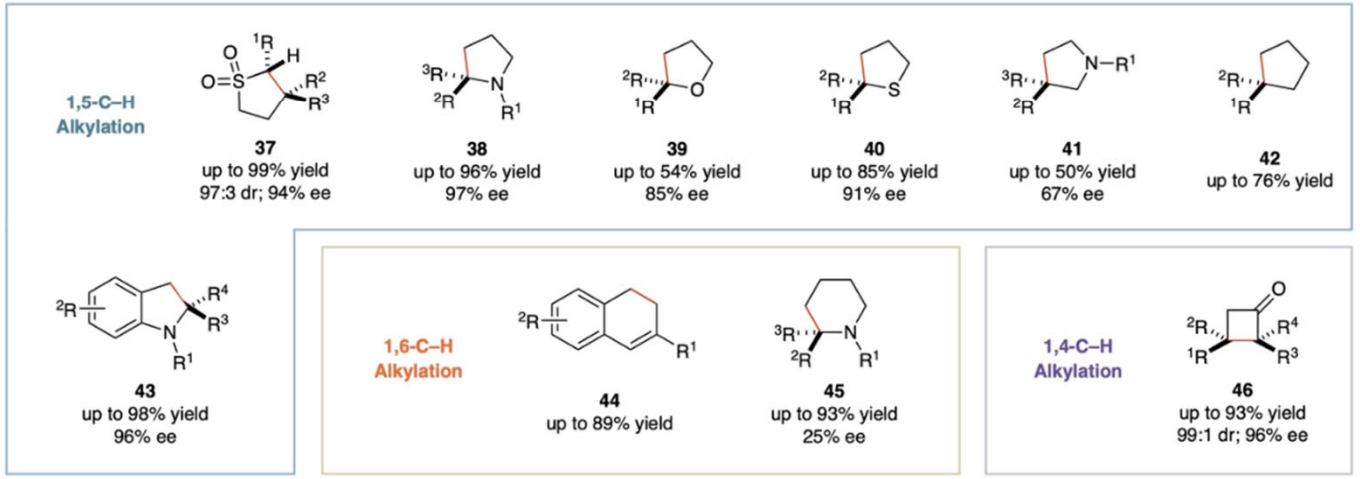
三、烯烃的自由基氮杂环丙烷化



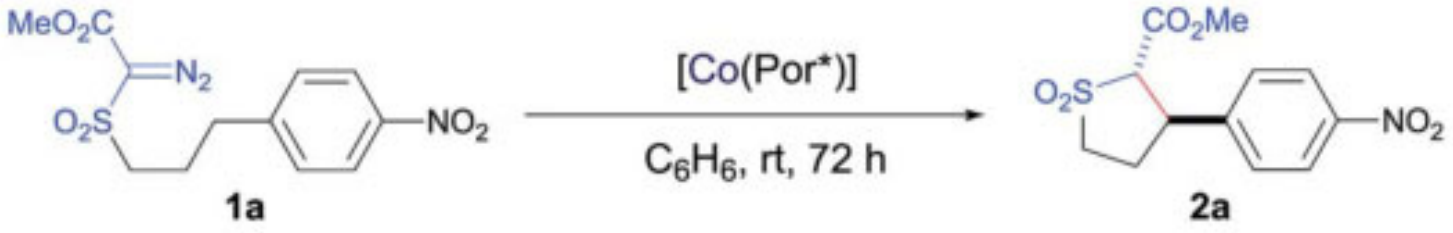
H. Xu, D.-S. Wang, Z. Zhu, A. Deb, X. P. Zhang, Chem 2024, 10, 283–298.

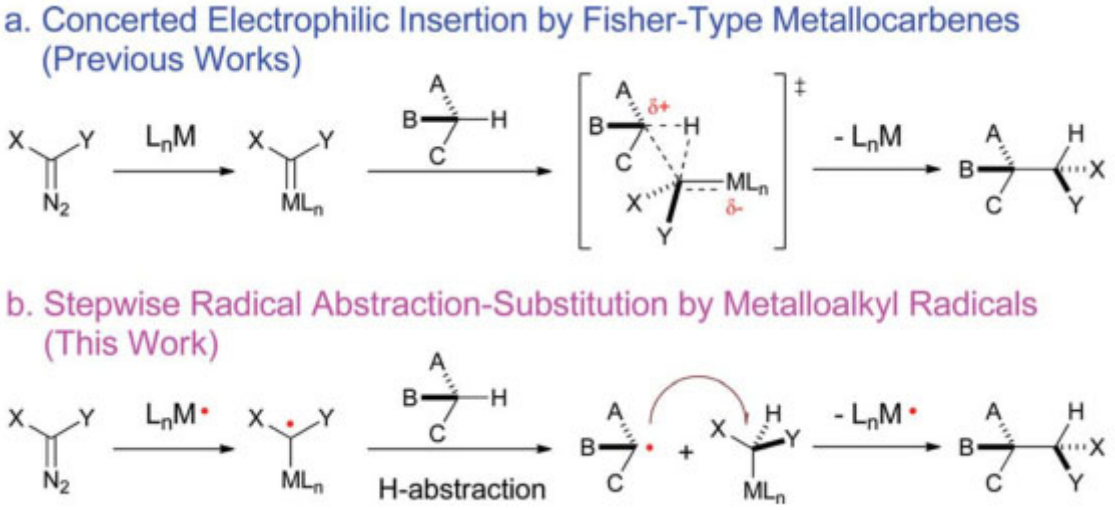
四、Csp3-H的自由基烷基化





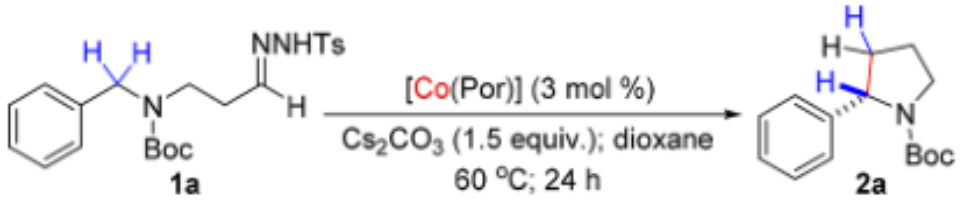
四、Csp3-H的自由基烷基化



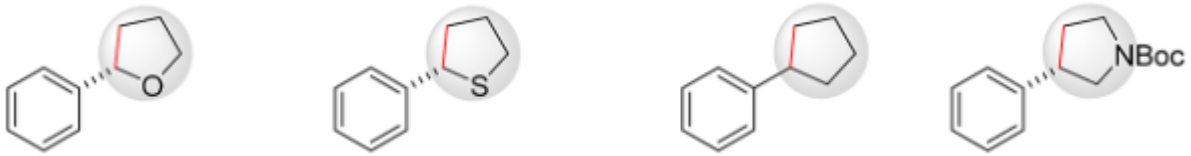


X. Cui, X. Xu, L. M. Jin, L. Wojtas, X. P. Zhang, Chem. Sci. 2015, 6, 1219–1224.

四、Csp3-H的自由基烷基化



Other common 5-membered cyclic structures



2y
54% y; 85% *ee*

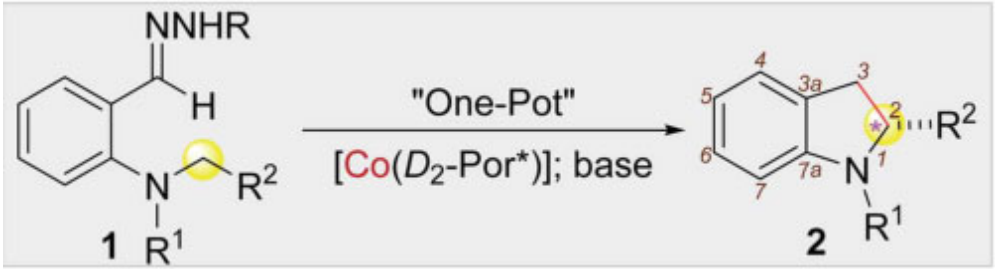
2z
85% y; 91% *ee*

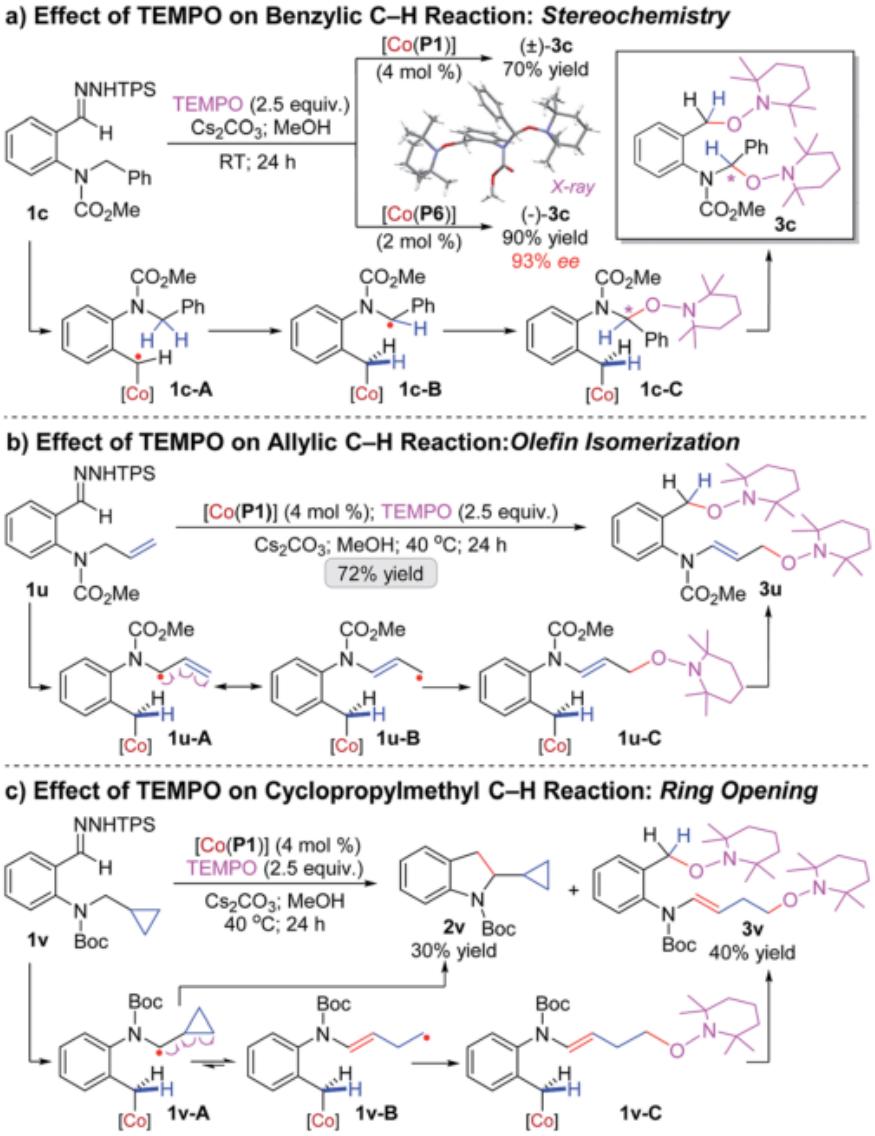
2aa[d]
76% y; *ee*: n/a

2ab
50% y; 67% *ee*

Y. Wang, X. Wen, X. Cui, X. P. Zhang, J. Am. Chem. Soc. 2018, 140, 4792–4796.

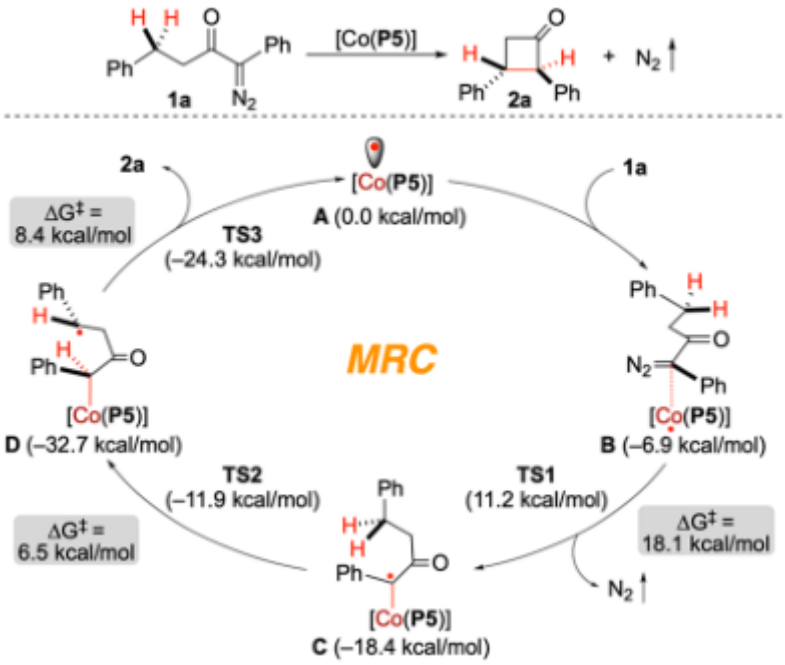
四、Csp3-H的自由基烷基化

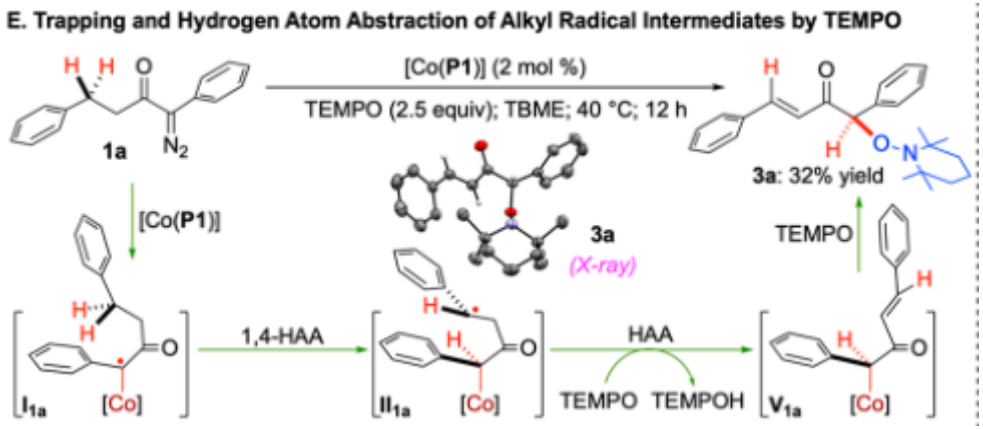




X. Wen, Y. Wang, X. P. Zhang, Chem. Sci. 2018, 9, 5082– 5086.

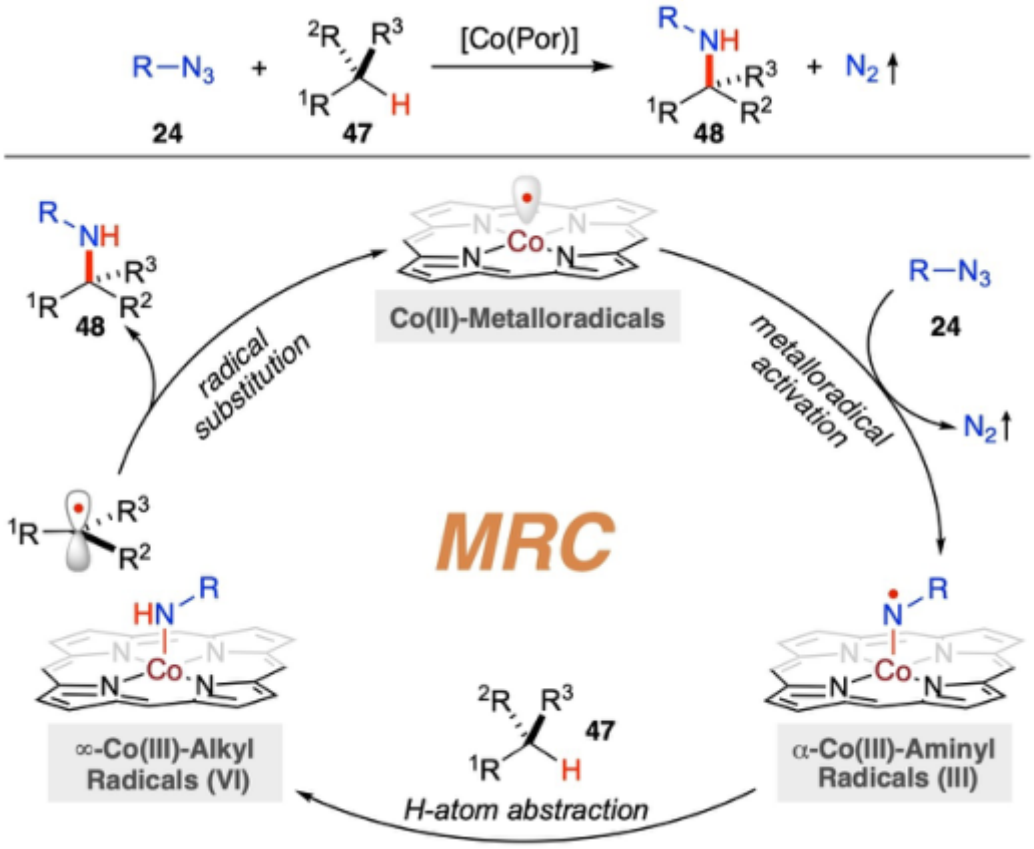
四、Csp3-H的自由基烷基化



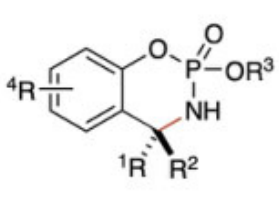


J. J. Xie, P. Xu, Y. L. Zhu, J. Y. Wang, W.-C. C. Lee, X. P. Zhang, J. Am. Chem. Soc. 2021, 143, 11670–11678.

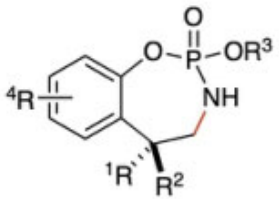
五、Csp3-H的自由基胺化



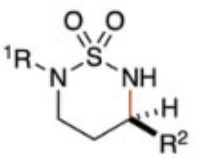
五、Csp3-H的自由基胺化



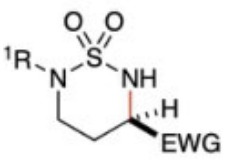
49
up to 99% yield



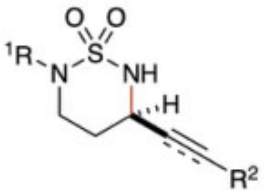
50
up to 99% yield



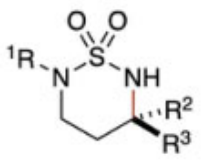
51
up to 94% yield
96% ee



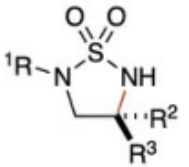
52
up to 95% yield
98% ee



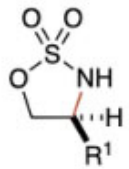
53
up to 88% yield
94% ee



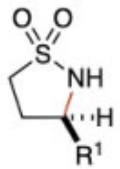
54
Enantioconvergent
up to 95% yield
86% ee



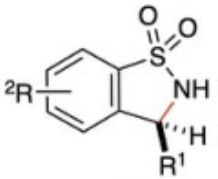
55
Enantiodivergent
up to 98% yield
96% ee



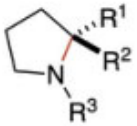
56
up to 98% yield
99% ee



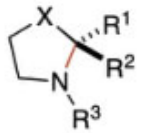
57
up to 98% yield
99% ee



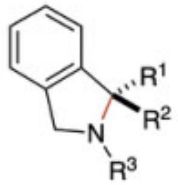
58
up to 99% yield
93% ee



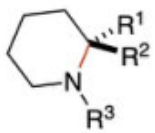
59
up to 89% yield



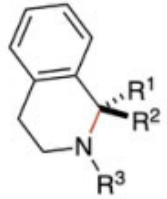
60
X = O, NR^4
up to 96% yield



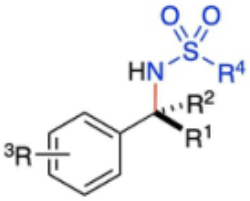
61
up to 93% yield



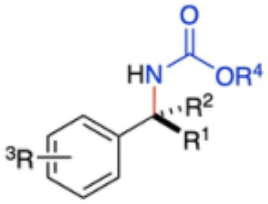
62
up to 38% yield



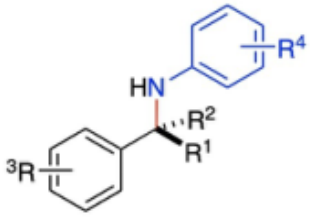
63
up to 28% yield



64
up to 73% yield

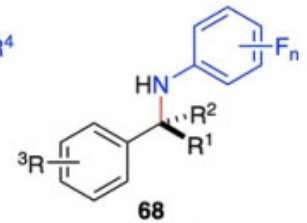


65
up to 92% yield



66
up to 55% yield

67
up to 60% yield



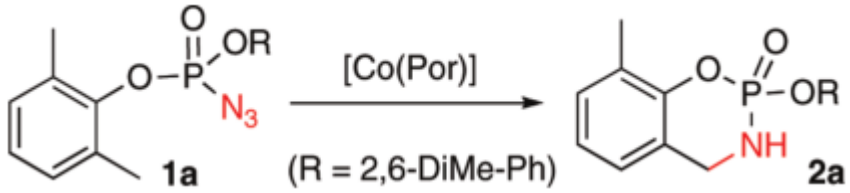
68
up to 95% yield
99% ee

69
Diastereoconvergent
up to 96% yield
97% ee

70

71
up to 95% yield

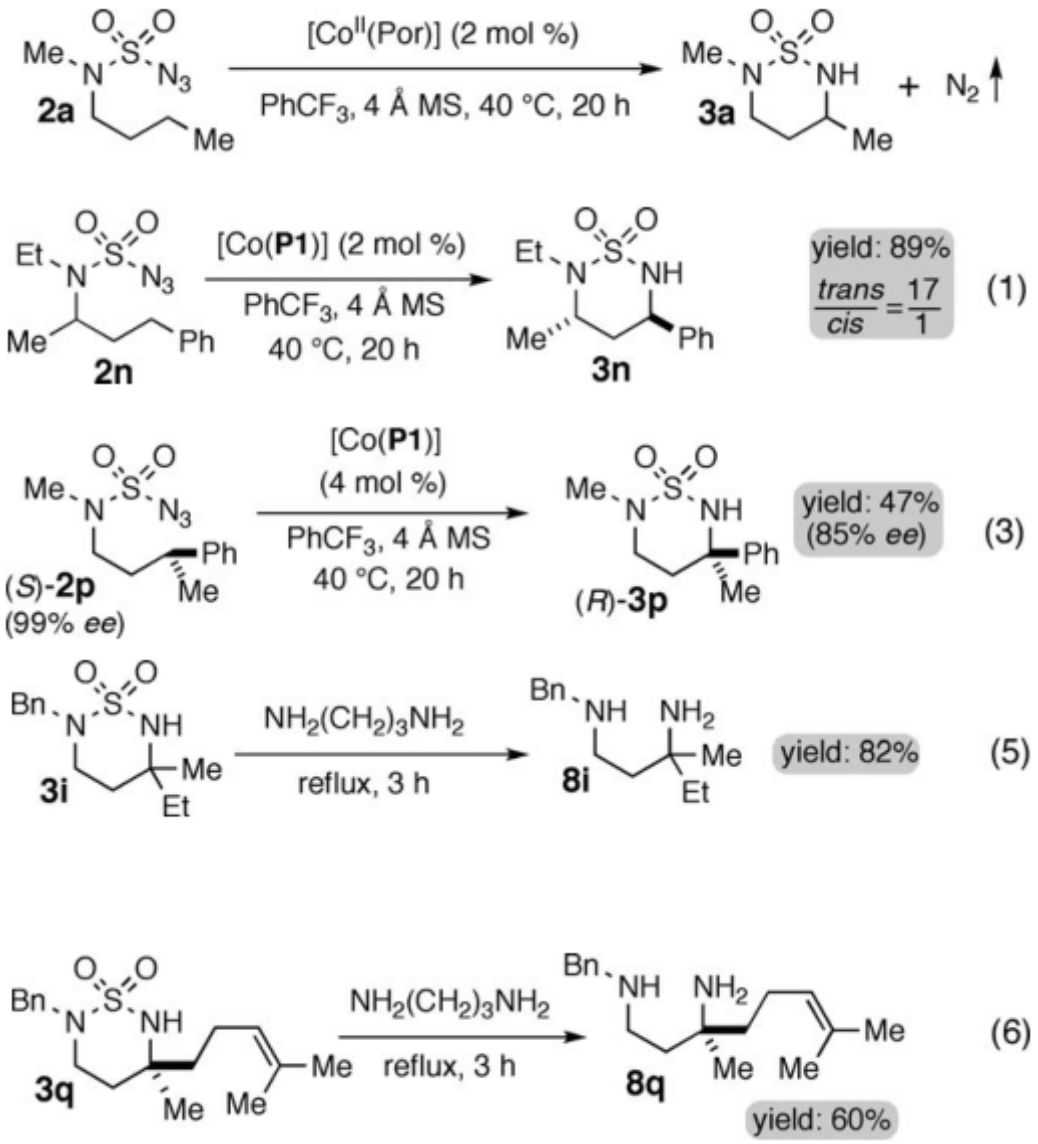
五、Csp3-H的自由基胺化



1	1a	Me, Me	2a	99
2				94[d]
3	1b	Me, Me, Me	2b	92
4				99[d]
5	1c	Et	2c	94[c,d,f,g]
6	1d	Et	2d	90[c,d,h]
7	1e	Allyl	2e	74[c,e,i]
8	1f	Bn	2f	83[c,e,j]
9	1g	*i*-Pr	2g	85[e]
10	1h		2ha	90%[d] 2ha/2hb = 84/16
11			2hb	96%[e] 2ha/2hb = 76/24
12	1i	*t*-Bu	2i	96
13	1j		2j	55
14				85[e]
15				97[d]
16	1k	Et	2k	37
17				95[d]
18	1l	Me, *t*-Bu	2l	99
19	1m	Me, *t*-Bu	2m	99
20	1n	MeO	2n	97
		OMe, *t*-Bu	MeO	
21	1o	Me, N, Ph	2o	80[d,k]
22	1p	Br	2p	70[d,k]

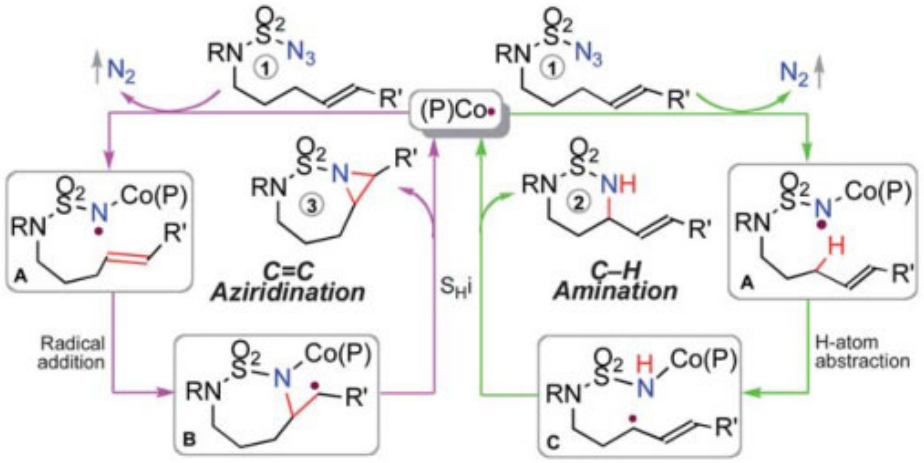
H. J. Lu, J. R. Tao, J. E. Jones, L. Wojtas, X. P. Zhang, Org. Lett. 2010, 12, 1248–1251.

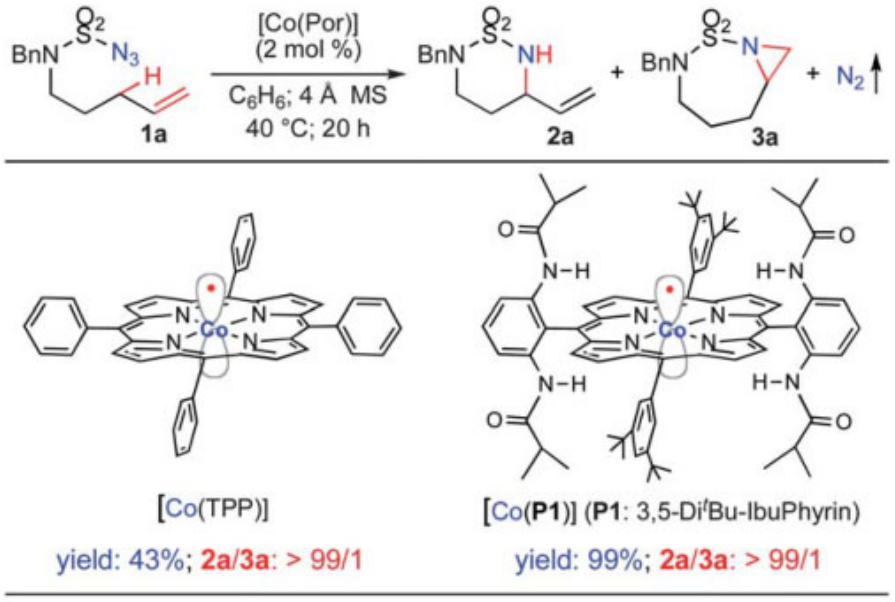
五、Csp3-H的自由基胺化



H. J. Lu, H. L. Jiang, L. Wojtas, X. P. Zhang, Angew. Chem. Int. Ed. 2010, 49, 10192–10196.

五、Csp3-H的自由基胺化





H. J. Lu, H. L. Jiang, Y. Hu, L. Wojtas, X. P. Zhang, Chem. Sci. 2011, 2, 2361–2366.

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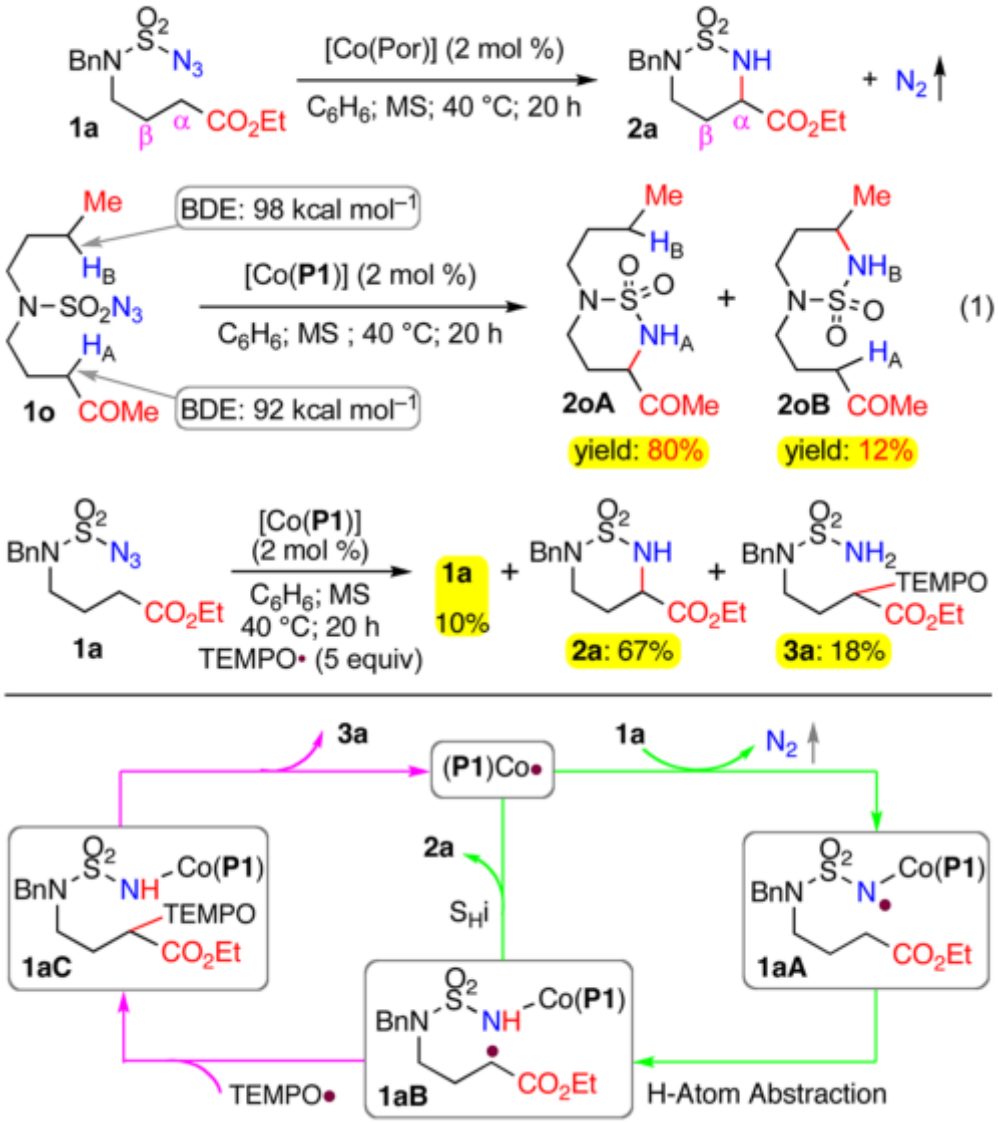
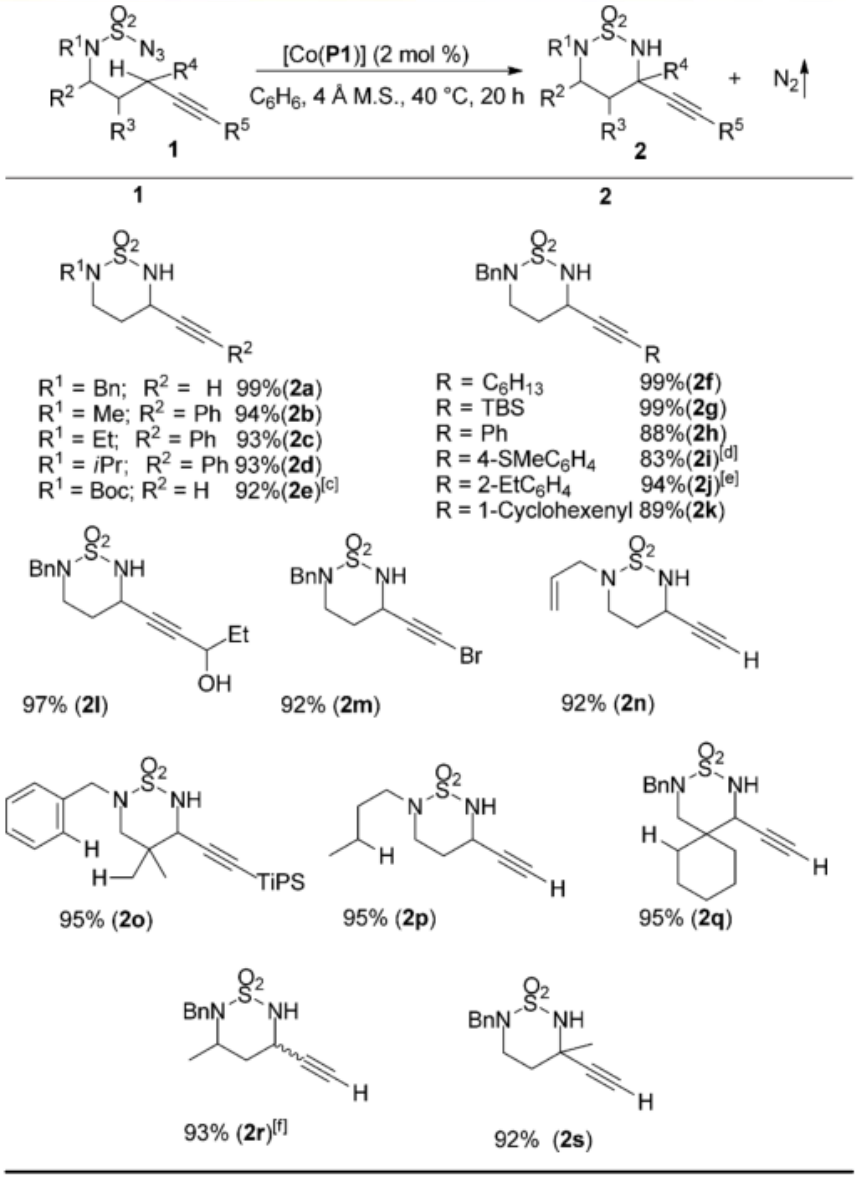
Precise Synthesis Lab at Tongji University

五、Csp3-H的自由基胺化



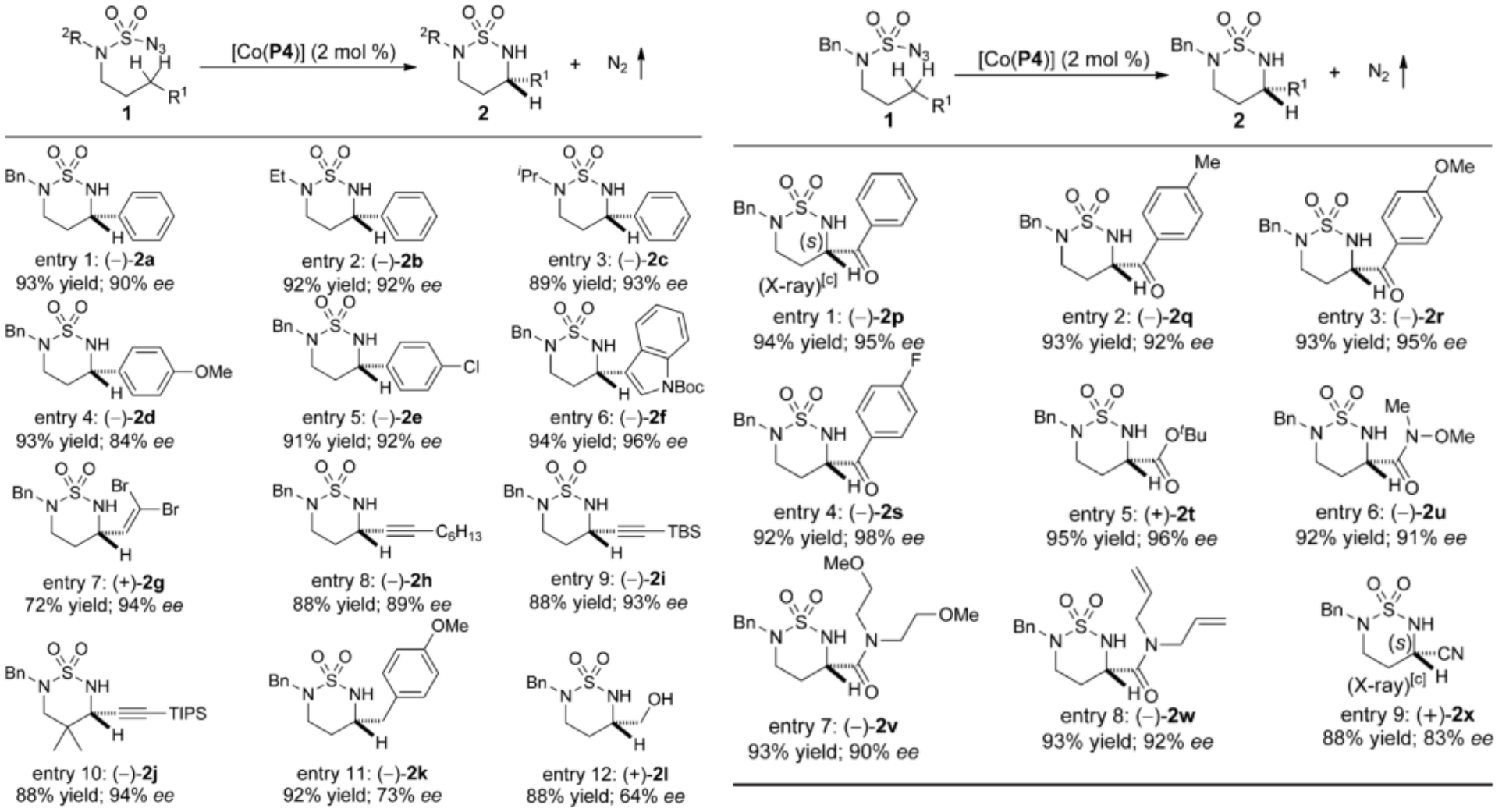
H. J. Lu, Y. Hu, H. L. Jiang, L. Wojtas, X. P. Zhang, Org. Lett. 2012, 14, 5158–5161.

五、Csp3-H的自由基胺化



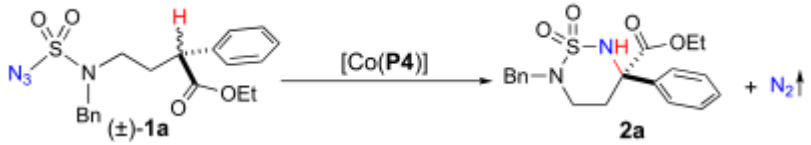
H. J. Lu, C. Q. Li, H. L. Jiang, C. L. Lizardi, X. P. Zhang, Angew. Chem. Int. Ed. 2014, 53, 7028–7032.

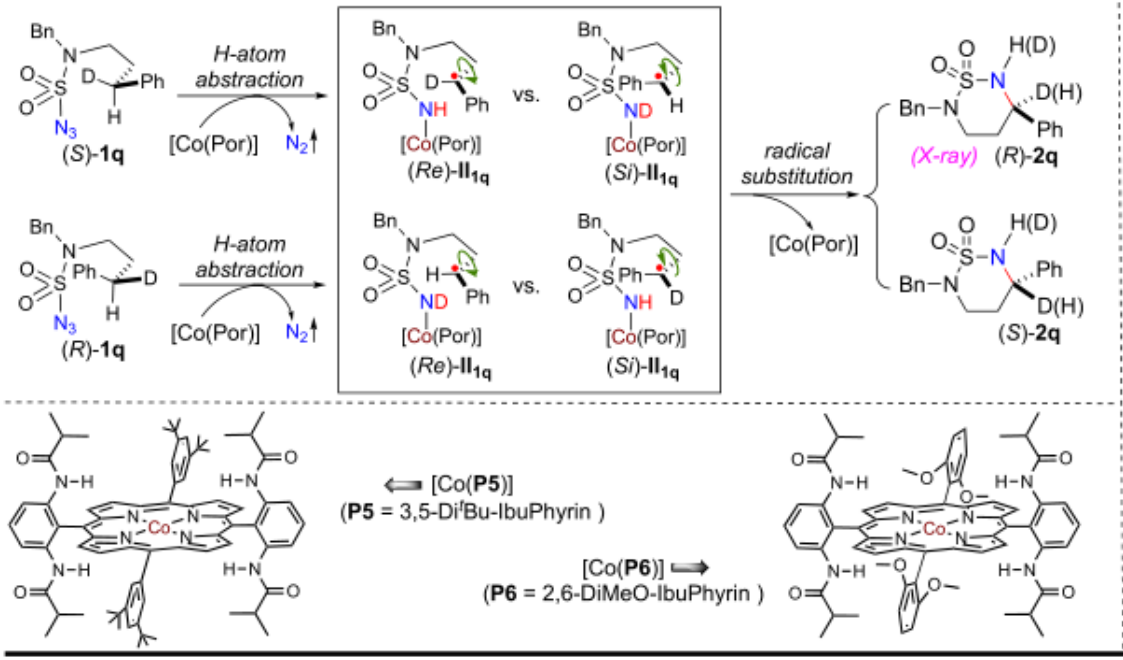
五、Csp3-H的自由基胺化



C. Q. Li, K. Lang, H. J. Lu, Y. Hu, X. Cui, L. Wojtas, X. P. Zhang, Angew. Chem. Int. Ed. 2018, 57, 16837–16841.

五、Csp3-H的自由基胺化

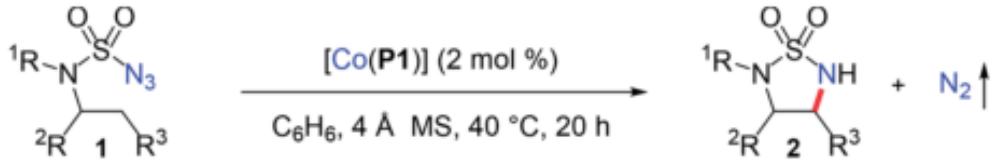




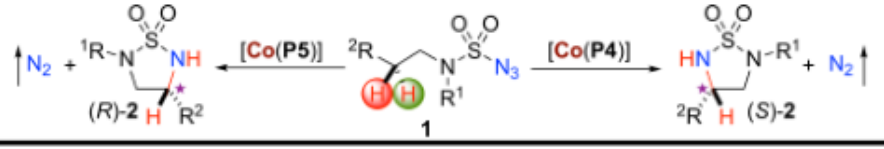
entry	azide	catalyst	KIE[c]	*Re*:*Si* of II_{1q}[d]	ee%[cal,e]	ee%[exp,f]
1	(*S*)-**1q**	[Co(**P5**)]	13.0	93:07	−86(*R*)	−10(*R*)
2	(*R*)-**1q**	[Co(**P5**)]	13.0	07:93	+86(*S*)	+10(*S*)
3[b]	(*S*)-**1q**	[Co(**P6**)]	11.0	92:08	−84(*R*)	−2(*R*)
4[b]	(*R*)-**1q**	[Co(**P6**)]	11.0	08:92	+84(*S*)	+2(*S*)
5	(*S*)-**1q**	[Co(**P1**)]	12.0	92:08	−84(*R*)	+26(*S*)
6	(*R*)-**1q**	[Co(**P1**)]	12.0	08:92	+84(*S*)	+28(*S*)
7[b]	(*S*)-**1q**	[Co(**P2**)]	27.0	96:04	−92(*R*)	+10(*S*)
8[b]	(*R*)-**1q**	[Co(**P2**)]	10.0	09:91	+82(*S*)	+10(*S*)
9	(*S*)-**1q**	[Co(**P3**)]	13.0	93:07	−86(*R*)	−56(*R*)
10	(*R*)-**1q**	[Co(**P3**)]	8.0	11:89	+78(*S*)	−6(*R*)
11[b]	(*S*)-**1q**	[Co(**P4**)]	15.0	94:06	−88(*R*)	−94(*R*)[g]
12[b]	(*R*)-**1q**	[Co(**P4**)]	3.0	25:75	+50(*S*)	−46(*R*)
13[b]	(±)-**1q**	[Co(**P4**)]	9.0	--	--	−70(*R*)

K. Lang, C. Q. Li, I. Kim, X. P. Zhang, J. Am. Chem. Soc. 2020, 142, 20902–20911.

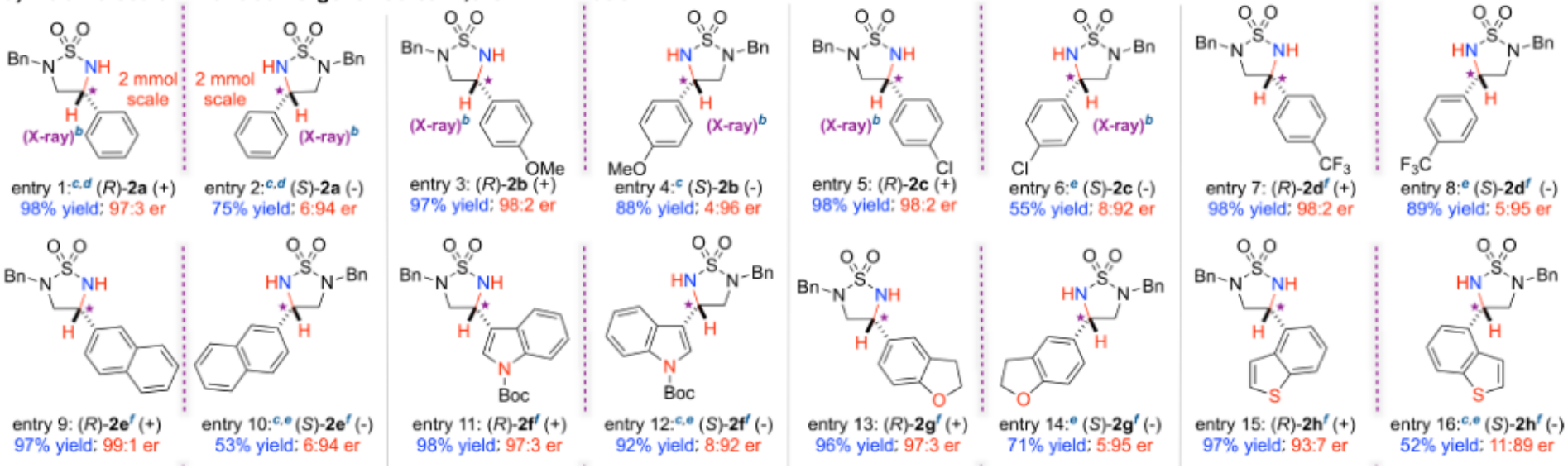
五、Csp3-H的自由基胺化



H. J. Lu, K. Lang, H. L. Jiang, L. Wojtas, X. P. Zhang, Chem. Sci. 2016, 7, 6934–6939.

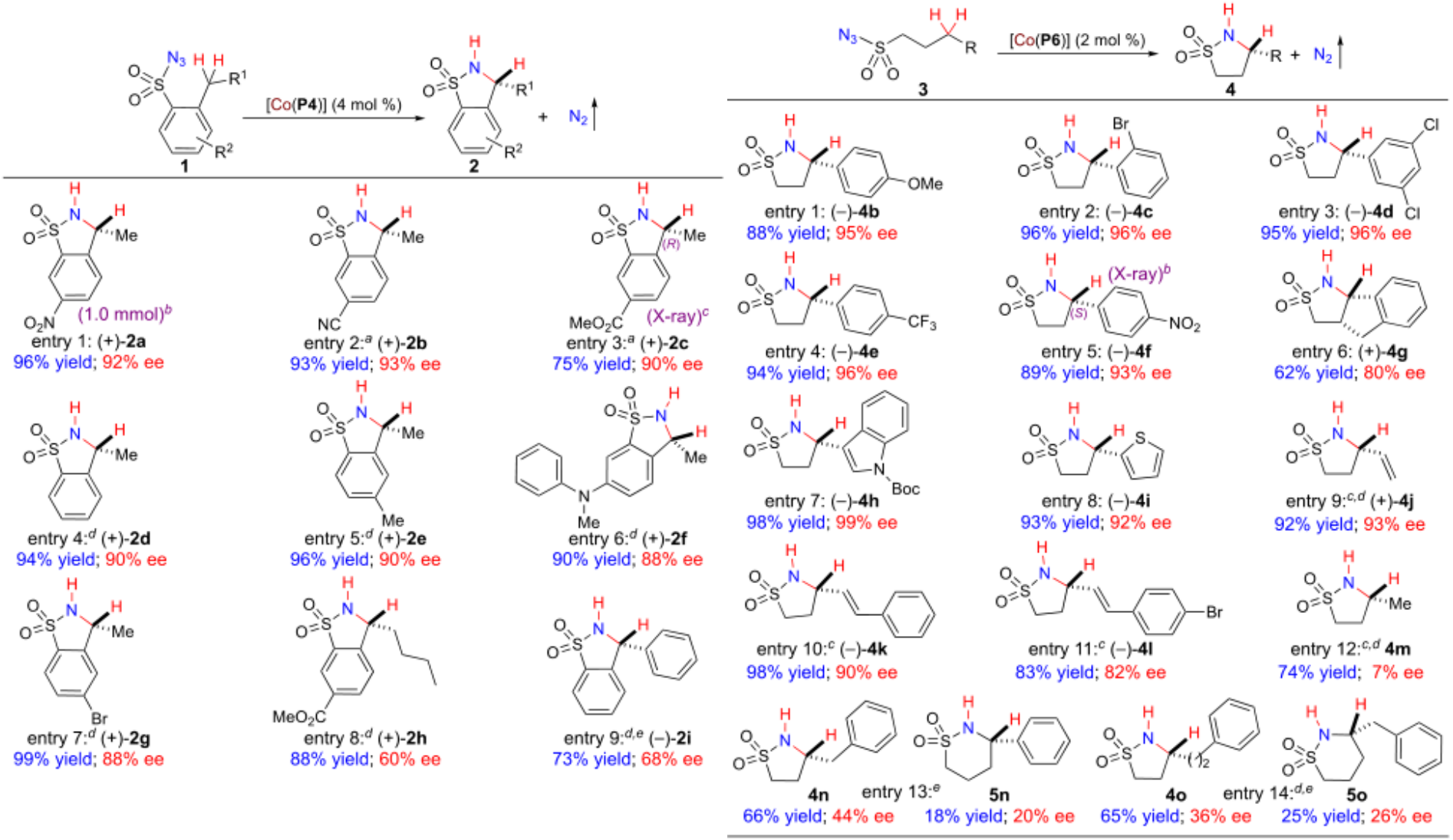


a) Intramolecular Enantiodivergent Radical 1,5-C–H Amination



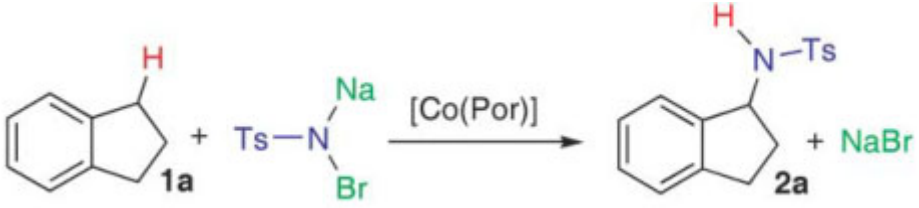
K. Lang, S. Torker, L. Wojtas, X. P. Zhang, J. Am. Chem. Soc. 2019, 141, 12388–12396.

五、Csp3-H的自由基胺化

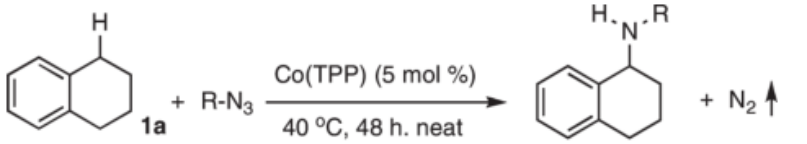


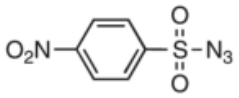
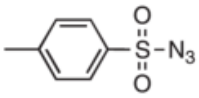
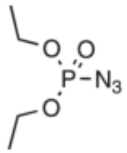
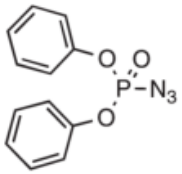
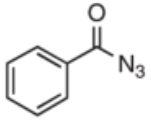
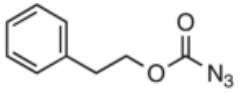
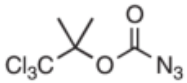
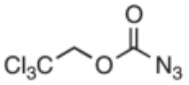
Y. Hu, K. Lang, C. Q. Li, J. B. Gill, I. Kim, H. J. Lu, K. B. Fields, M. Marshall, Q. G. Cheng, X. Cui, L. Wojtas, X. P. Zhang, J. Am. Chem. Soc. 2019, 141, 18160–18169.

五、Csp3-H的自由基胺化



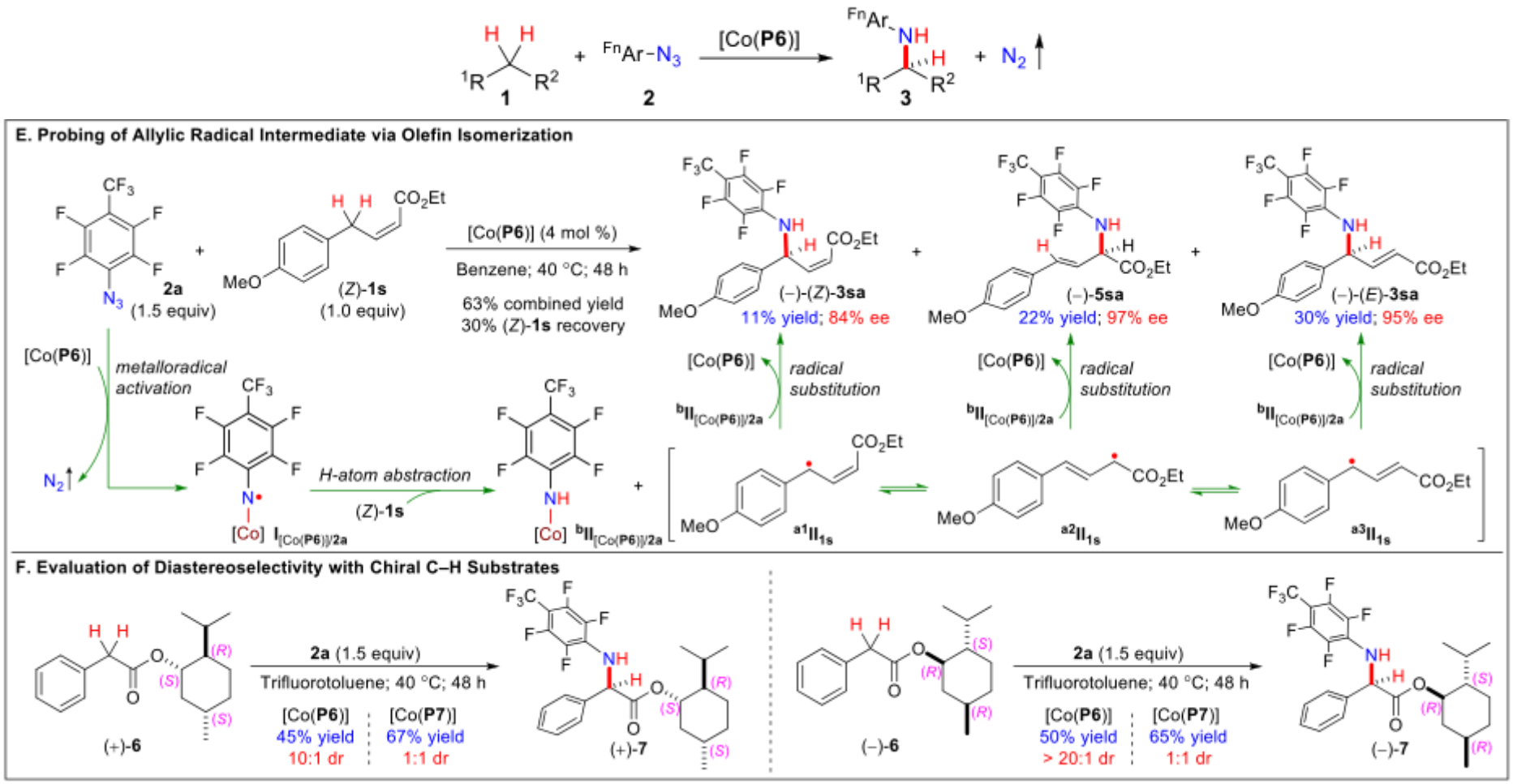
J. D. Harden, J. V. Ruppel, G. Y. Gao, X. P. Zhang, Chem. Commun. 2007, 4644–4646.



entry	R-N_3	yield[b]	entry	R-N_3	yield[b]
1		<5%	2		32%
3		0%	4		0%
5		0%	6		0%
7		0%	8		85%

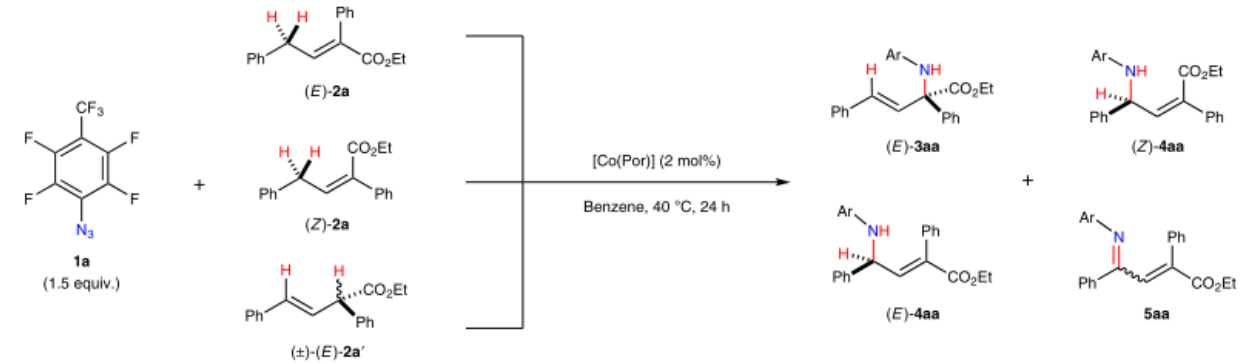
H. J. Lu, V. Subbarayan, J. R. Tao, X. P. Zhang, Organometallics 2010, 29, 389–393.

五、Csp3-H的自由基胺化

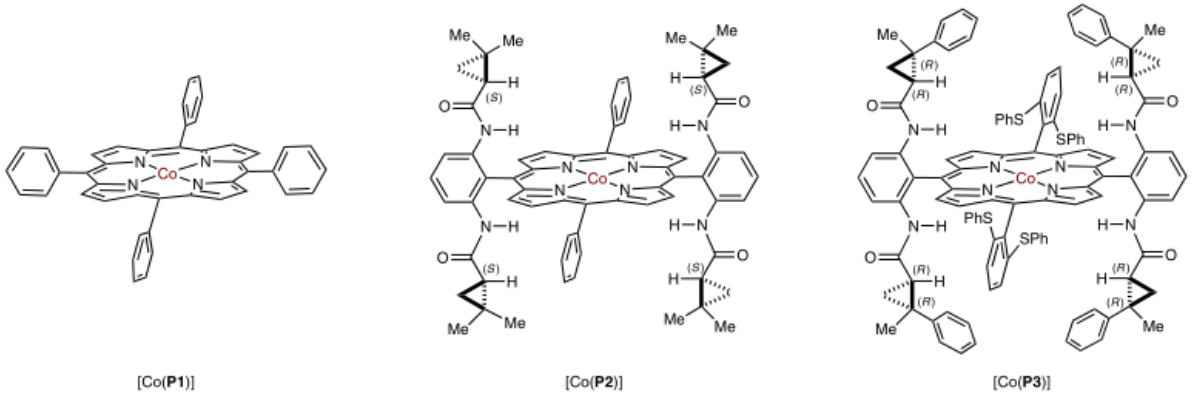


L. M. Jin, P. Xu, J. J. Xie, X. P. Zhang, J. Am. Chem. Soc. 2020, 142, 20828–20836.

五、Csp3-H的自由基胺化



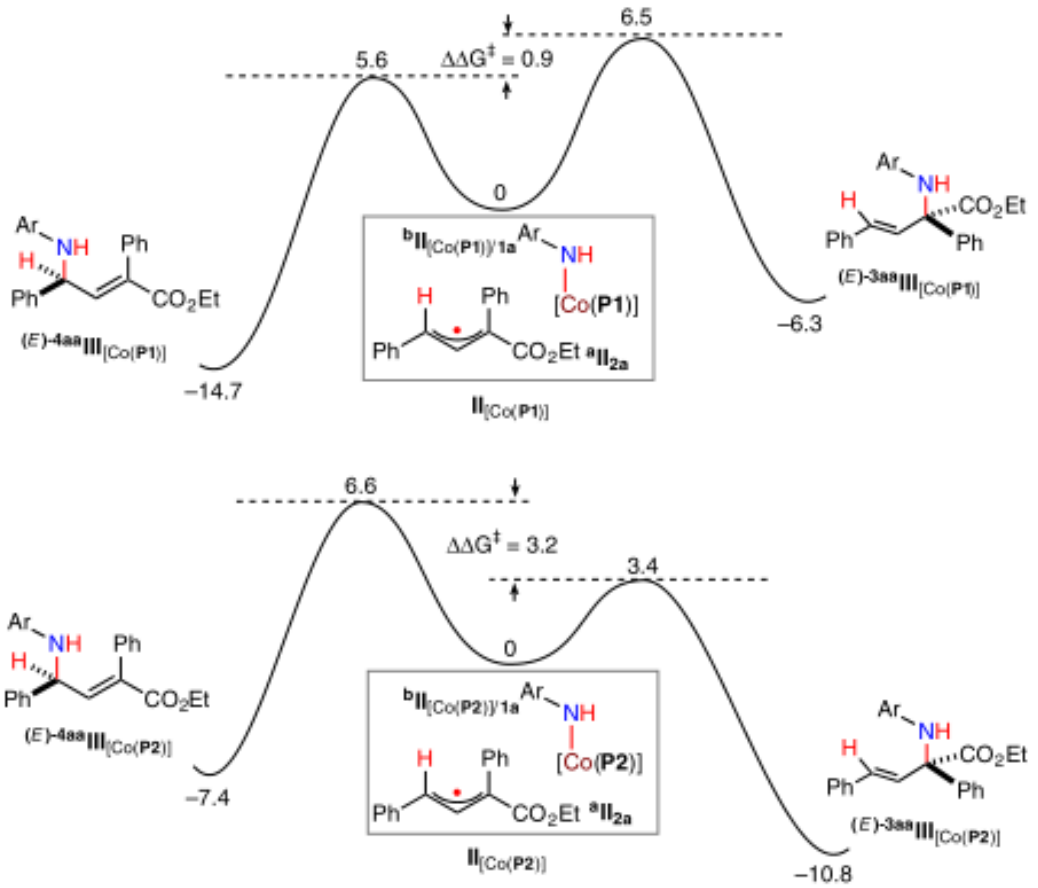
Entry	Substrate	Catalyst	Conversion (%)	Yield (%) (*E*)-**3aa**	Yield (%) (*E*)-**4aa**	Yield (%) (*Z*)-**4aa**	Yield (%) **5aa**	e.e. (%) (*E*)-**3aa**
1	(*E*)-**2a**	[Co(**P1**)]	99	22	47	8	10	–
2	(*E*)-**2a**	[Co(**P2**)]	99	99	0	0	0	82
3	(*E*)-**2a**	[Co(**P3**)]	0	0	0	0	0	–
4	(*Z*)-**2a**	[Co(**P1**)]	99	22	46	4	16	–
5	(*Z*)-**2a**	[Co(**P2**)]	99	99	0	0	0	82
6	(*Z*)-**2a**	[Co(**P3**)]	0	0	0	0	0	–
7	(±)-(*E*)-**2a′**	[Co(**P1**)]	99	24	43	9	16	–
8	(±)-(*E*)-**2a′**	[Co(**P2**)]	99	99	0	0	0	82
9	(±)-(*E*)-**2a′**	[Co(**P3**)]	0	0	0	0	0	–



[Co(**P1**)] [Co(**P2**)] [Co(**P3**)]

P. Xu, J. Xie, D. S. Wang, X. P. Zhang, Nat. Chem. 2023, 15,498–507.

五、Csp3-H的自由基胺化



P. Xu, J. Xie, D. S. Wang, X. P. Zhang, Nat. Chem. 2023, 15,498–507.

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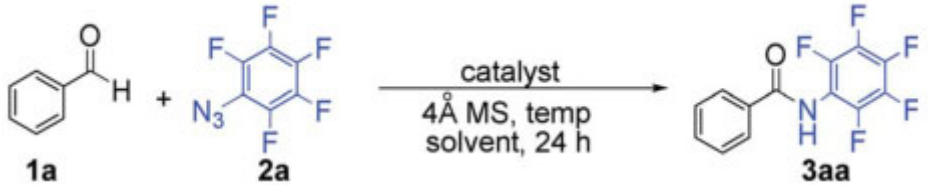
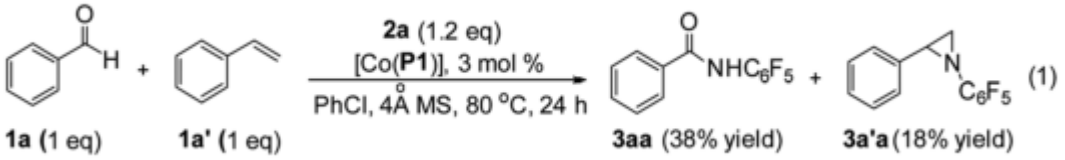
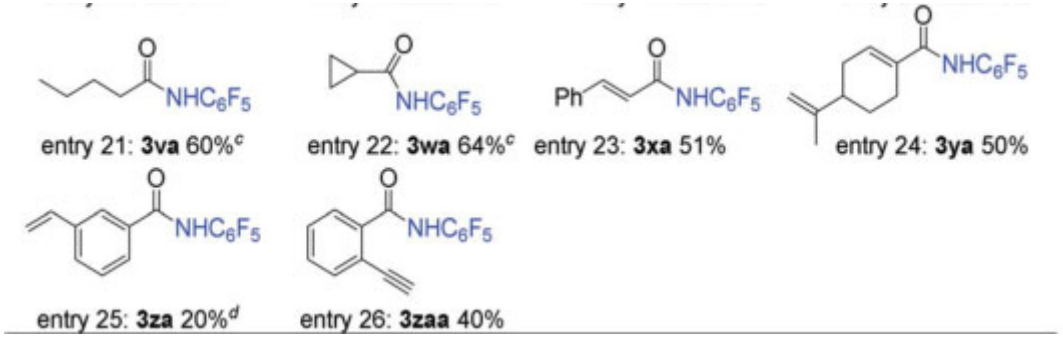
五、Csp3-H的自由基胺化







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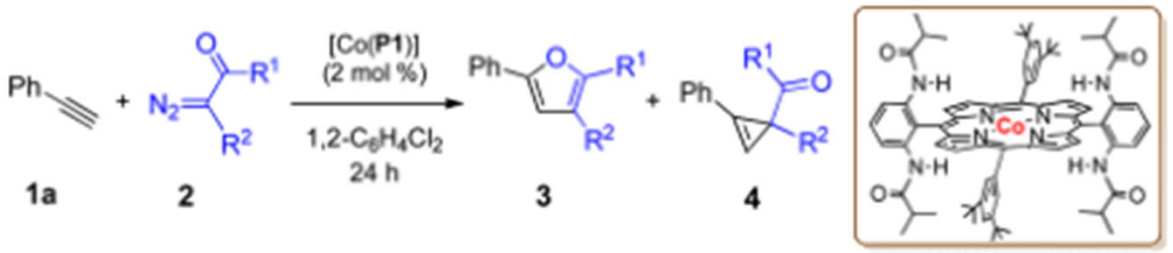
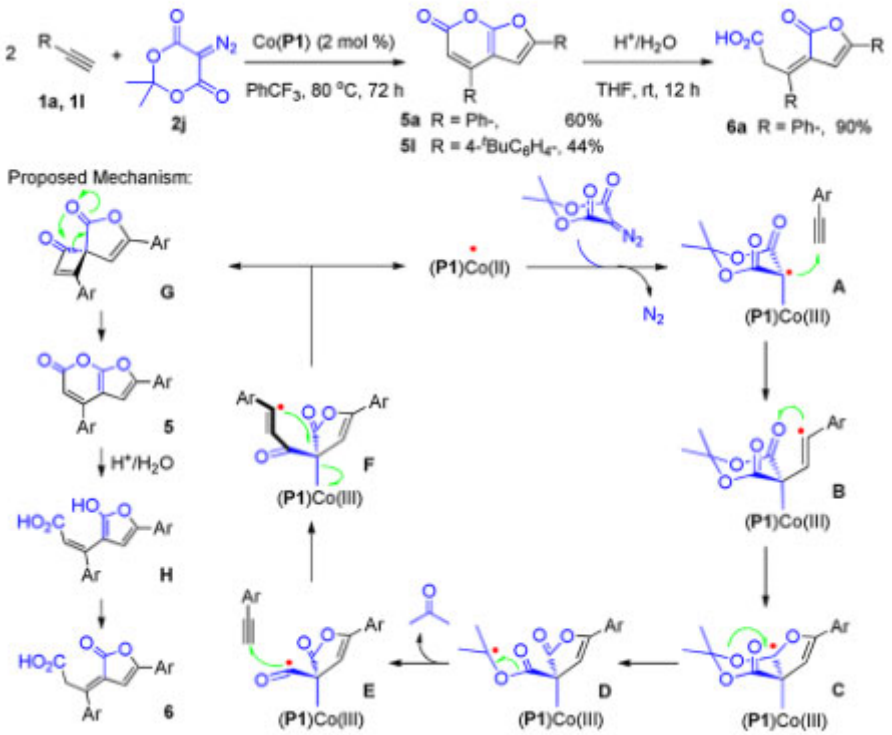
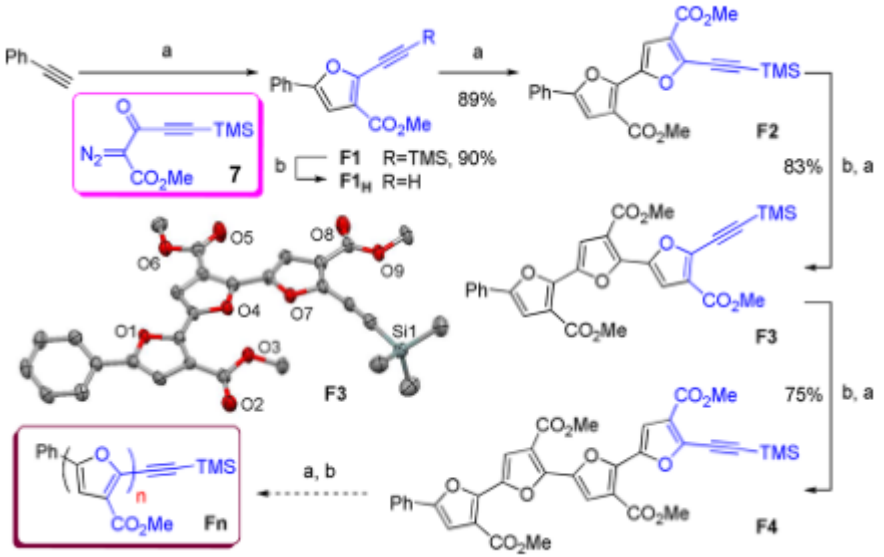
六、自由基环化







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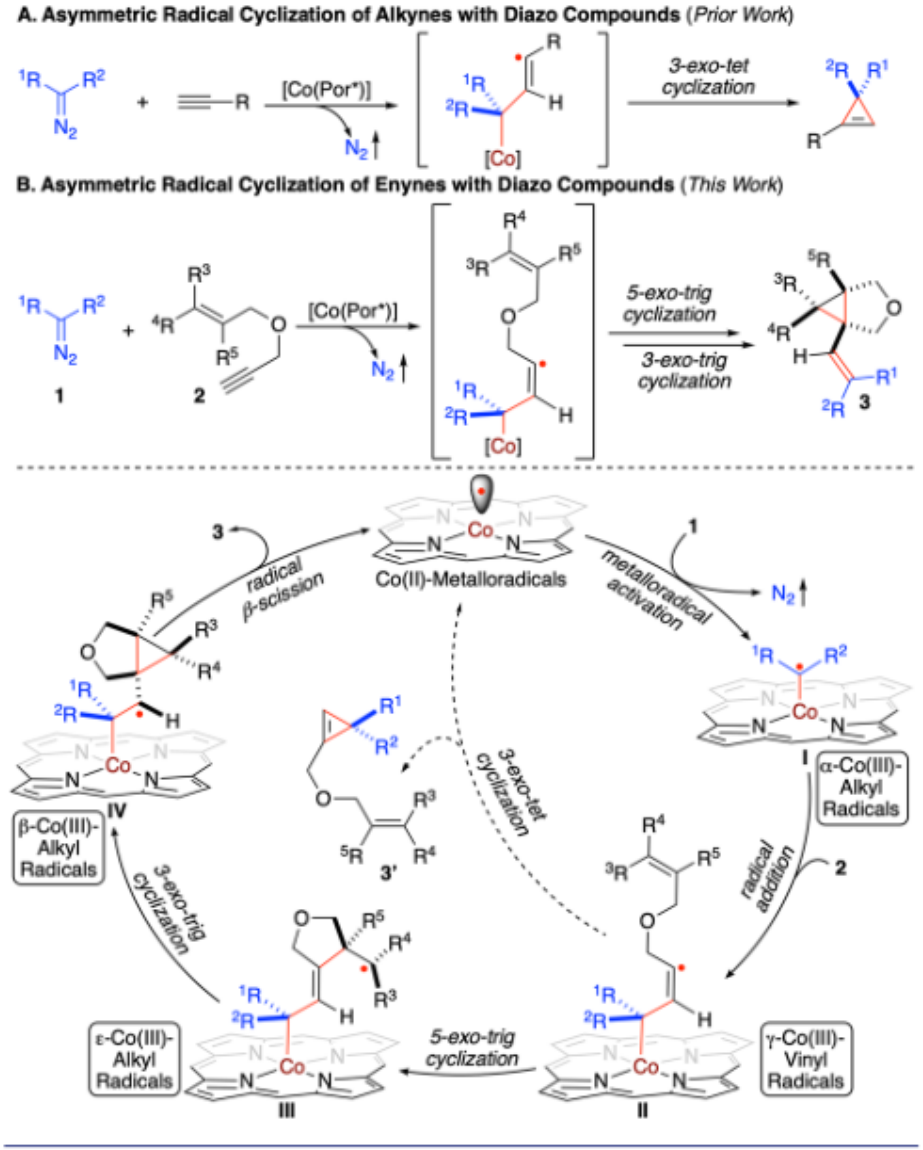
六、自由基环化



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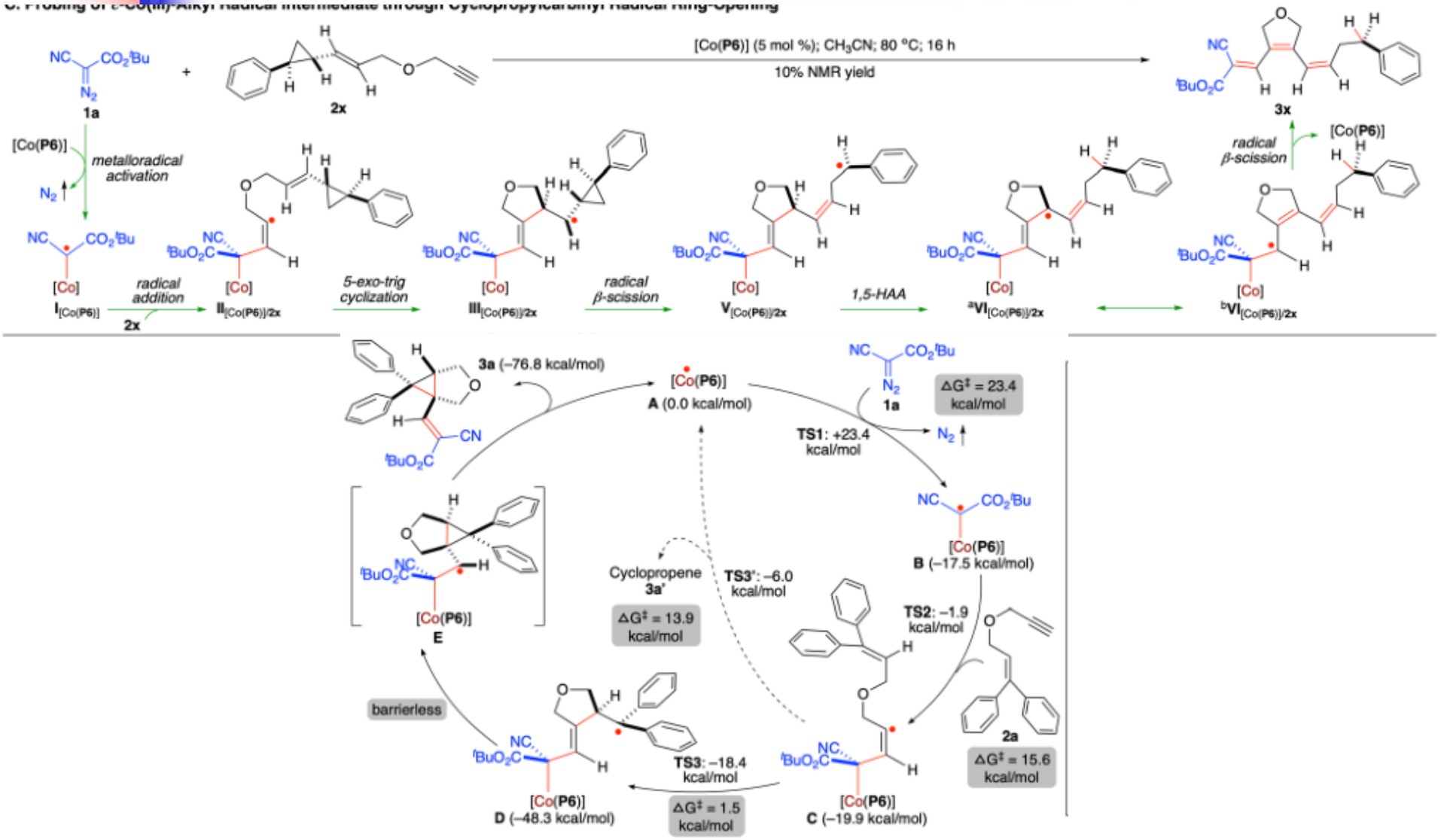
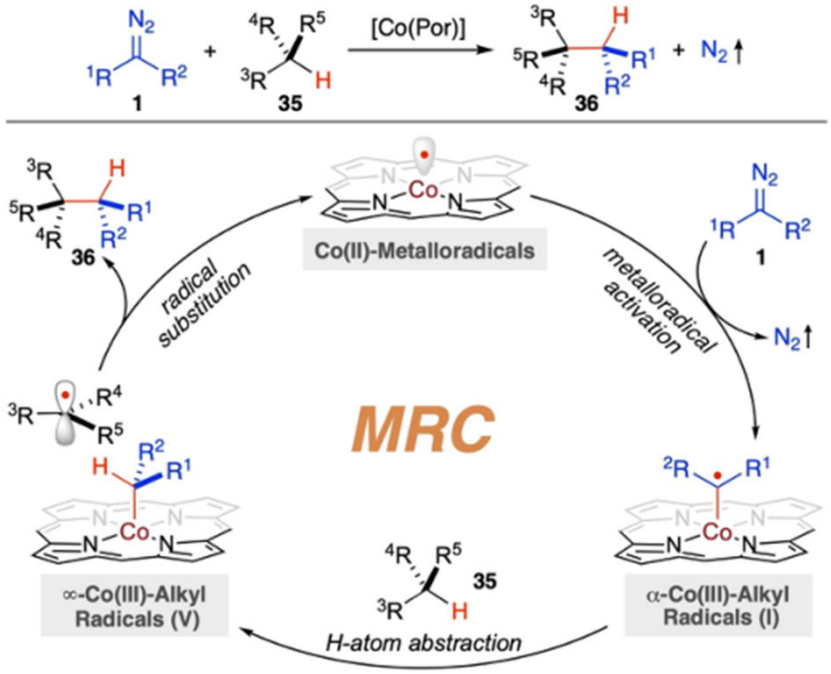
六、自由基环化

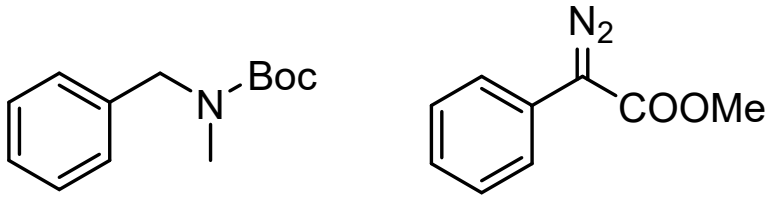


C. Z. Zhang, D. S. Wang, W.-C. C. Lee, A. M. McKillop, X. P. Zhang, J. Am. Chem. Soc. 2021, 143, 11130–11140.

七、proposal



该反应用于分子间C-C键构筑



The Yang Research Group
Precise Synthesis Lab at Tongji University

谢谢大家

请老师和各位同学批评指正