Supporting Information

The mechanistic studies on the atmosphere and light tuned synthesis of cyclobuta/penta[*b*]indoles

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1. General Remarks.

^{1}H NMR spectra were recorded on a Agilent DD2 400-MR spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. ^{13}C NMR spectra were recorded at 100 MHz. Data for ^{1}H, ^{13}C NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

Compounds **1**[1], were prepared according to the previous literatures.

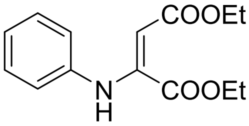
2. General procedure for the argon controlled synthesis of cyclobuta[*b*]indoles 3 from aniline-tethered alkylidenecyclopropanes 1 with alkynes 2

To a flame dried Schlenk tube was added aniline-tethered alkylidenecycopropanes **1** (0.2 mmol), alkynes (0.4 mmol) and DMSO (2.0 mL) under Argon. Then, the resulting solution was degassed, set under argon and stirred at 80 °C for 2 h. After cooling down to room temperature and the mixture was diluted with water (15 mL) followed by extraction with ethyl acetate (15 mL x 3). The combined organic collection was washed with brine (30 mL), and then dried over $NaSO_4$. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (PE/EA: 20:1 ~ 15/1) to give the desired products **3**.

3. General procedure for the oxygen controlled synthesis of cyclopenta[*b*]indoles 4 from aniline-tethered alkylidenecyclopropanes 1 with alkynes 2

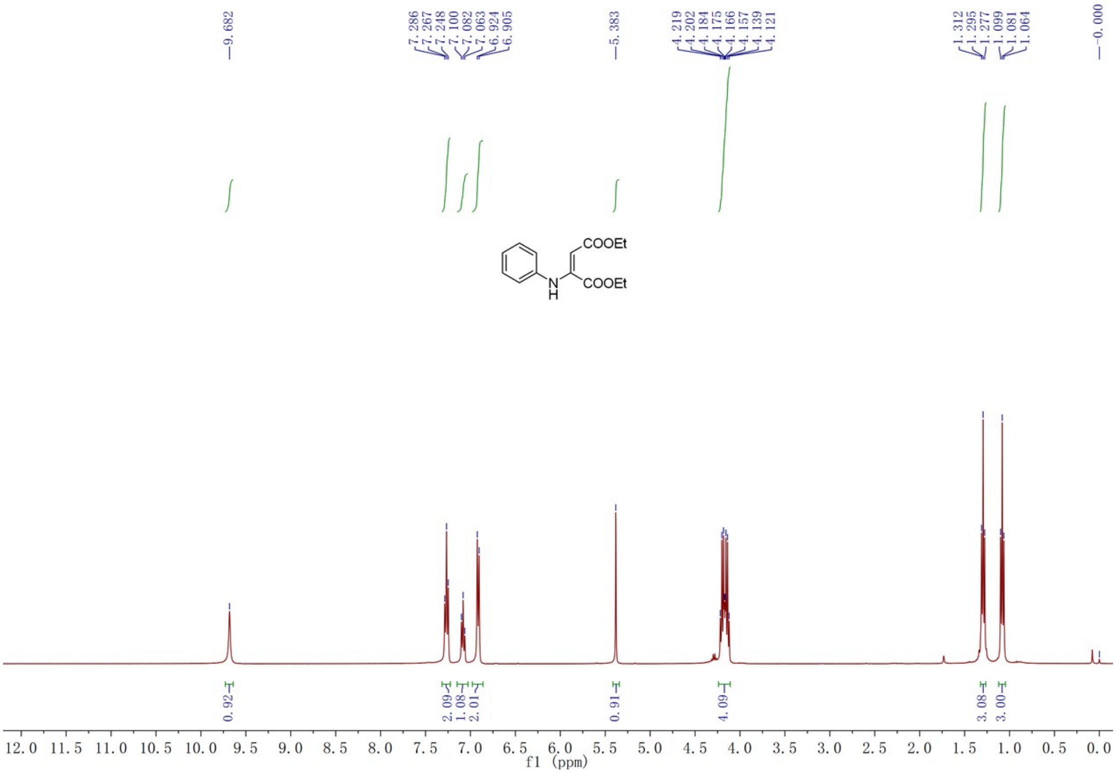
To a flame dried Schlenk tube was added aniline-tethered alkylidenecycopropanes **1** (0.2 mmol), alkynes (0.4 mmol). Then, the tube was evacuated and backfilled with O_2 for 3 times, and inserted an O_2 balloon. The solvent DMSO (2.0 mL) was added under O_2. Next, the resulting solution was allowed to stir at 80 °C for 12 h. After cooling down to room temperature and the mixture was diluted with water (15 mL) followed by extraction with ethyl acetate (15 mL x 3). The combined organic collection was washed with brine (30 mL), and then dried over $NaSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (PE/EA: 15:1 ~ 10/1) to give the desired products **4**.

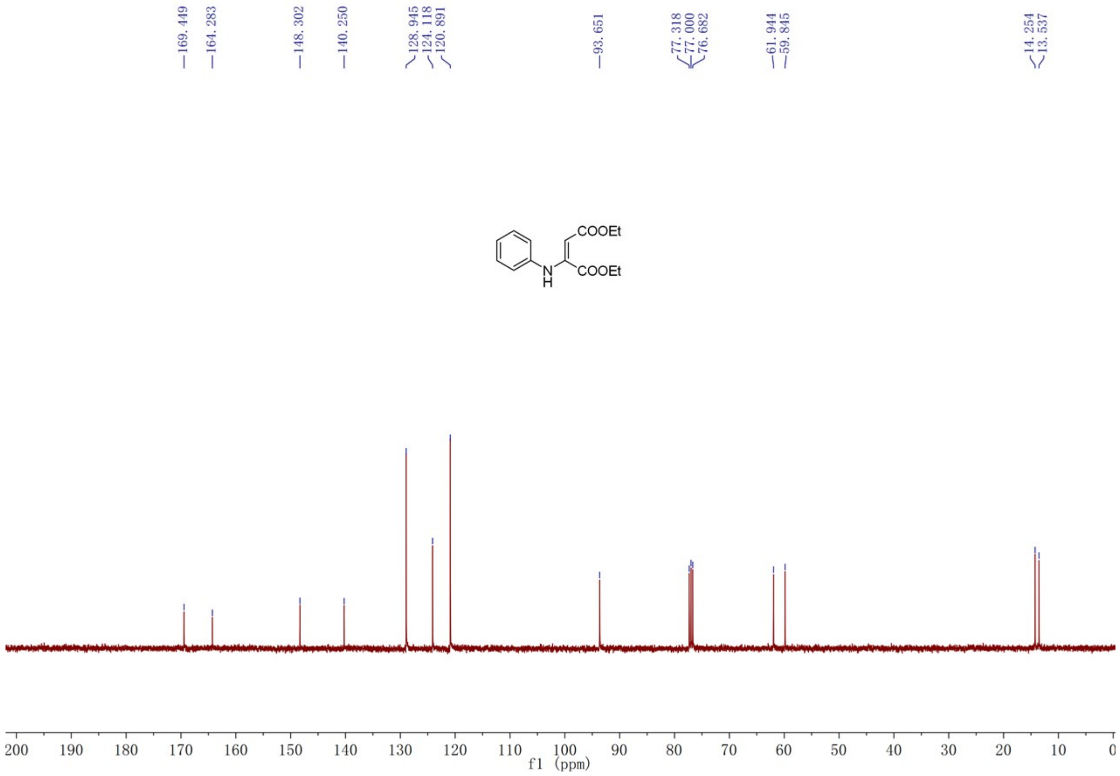
4. Characterization and spectra charts for 3ac, 3a and 4a.

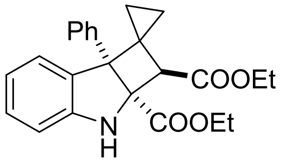


diethyl 2-(phenylamino)maleate 3ac

^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.08 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.38 (s, 1H), 6.91 (d, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 9.68 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.5, 14.3, 59.8, 61.9, 93.7, 120.9, 124.1, 128.9, 140.3, 148.3, 164.3, 169.4.

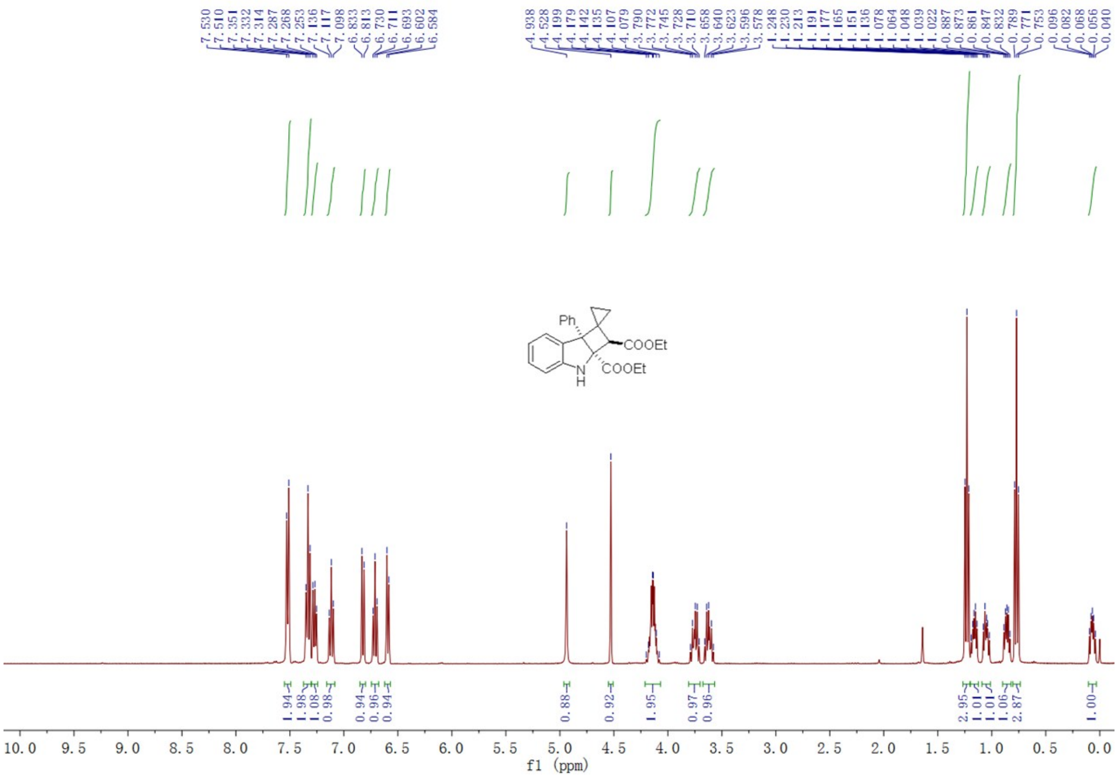






Diethyl-7*b*-phenyl-3,7*b*-dihydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane]-2,2*a*(2*H*)-dicarboxylate 3a

^{1}H NMR (CDCl$_3$, TMS, 400 MHz) δ 0.04-0.10 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H), 0.83-0.89 (m, 1H), 1.02-1.08 (m, 1H), 1.13-1.20 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 3.57-3.66 (m, 1H), 3.71-3.79 (m, 1H), 4.07-4.20 (m, 2H), 4.53 (s, 1H), 4.94 (s, 1H), 6.59 (d, *J* = 7.2 Hz, 1H), 6.71 (dd, *J* = 7.2 Hz, 7.2 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 7.12 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.25-7.29 (m, 1H), 7.33 (dd, *J* = 7.6 Hz, 7.6 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (CDCl$_3$, TMS, 100 MHz) δ 7.5, 10.2, 13.6, 14.3, 29.2, 48.0, 60.2, 61.5, 66.6, 76.2, 110.3, 118.8, 124.7, 127.4, 128.0, 128.3, 129.3, 130.9, 137.4, 153.4, 169.7, 170.0.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6.730
6.711
6.693
6.602
6.584
4.938
4.528
4.199
4.179
4.142
4.135
4.107
4.079
3.790
3.772
3.745
3.728
3.710
3.658
3.640
3.623
3.596
3.578
1.248
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1.191
1.177
1.165
1.151
1.136
1.078
1.064
1.048
1.039
1.022
0.887
0.873
0.861
0.847
0.832
0.789
0.771
0.753
0.096
0.082
0.068
0.056
0.040
Ph
COOEt
COOEt
N
H
1.94
1.98
1.08
0.98
0.94
0.96
0.94
0.88
0.92
1.95
0.97
0.96
2.95
1.01
1.01
1.06
2.87
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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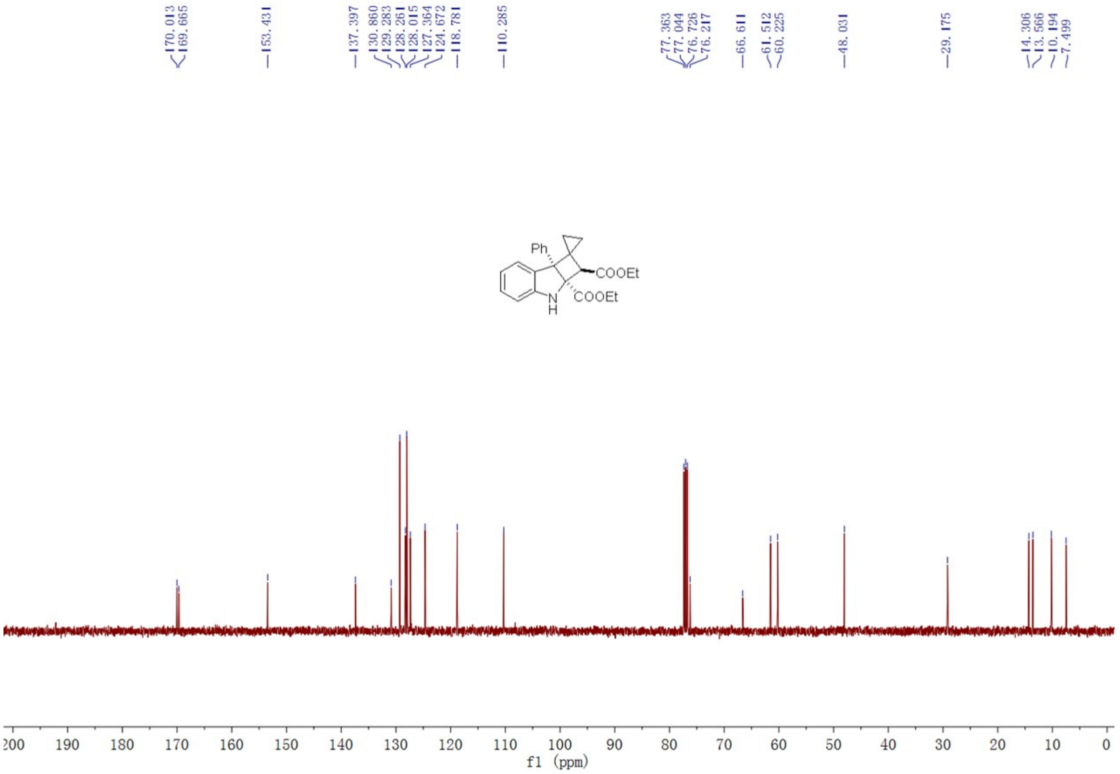
f1 (ppm)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77.044
76.726
76.217
66.611
61.512
60.225
48.031
29.175
14.306
13.566
10.194
7.499
Ph
COOEt
COOEt
N
H
200
190
180
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50
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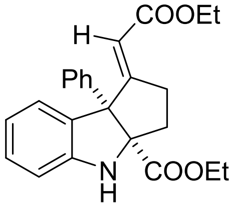
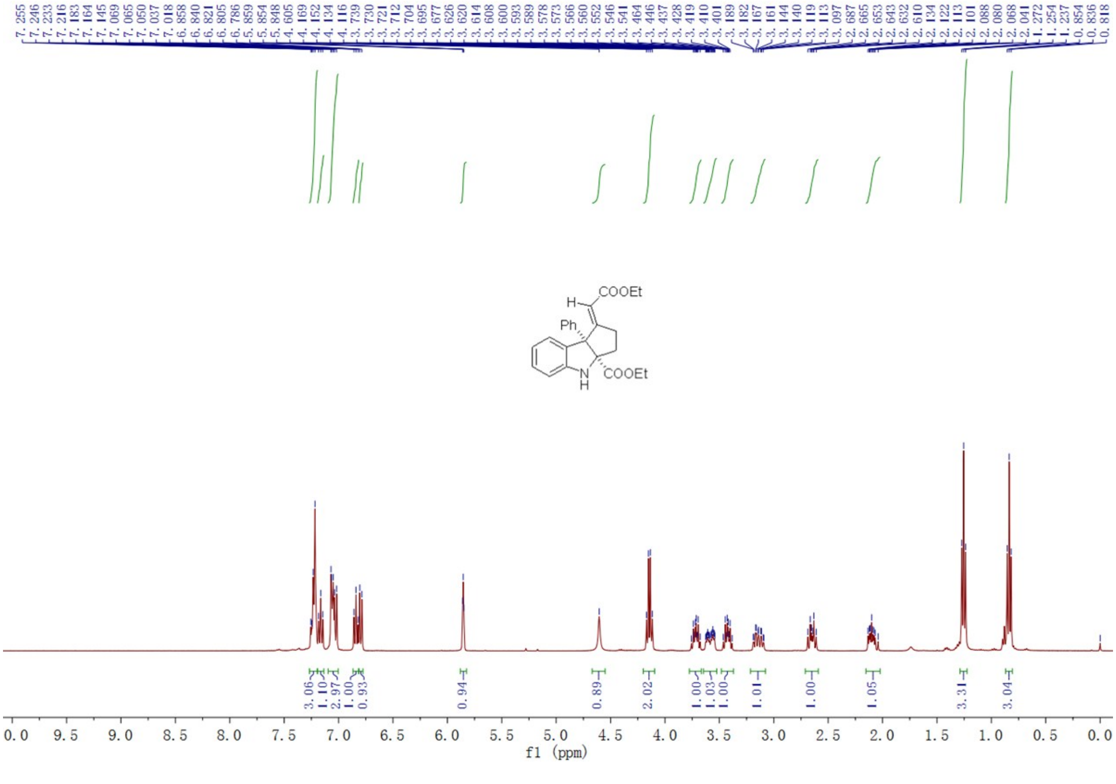
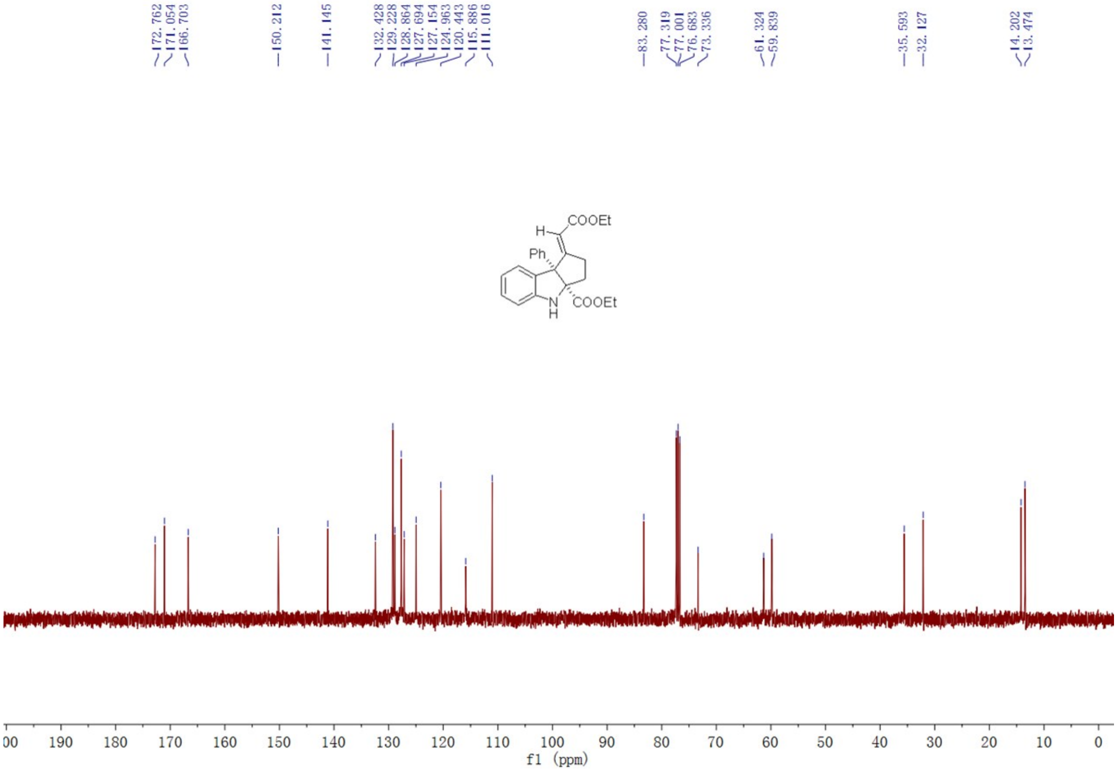
20
10
0
f1 (ppm)



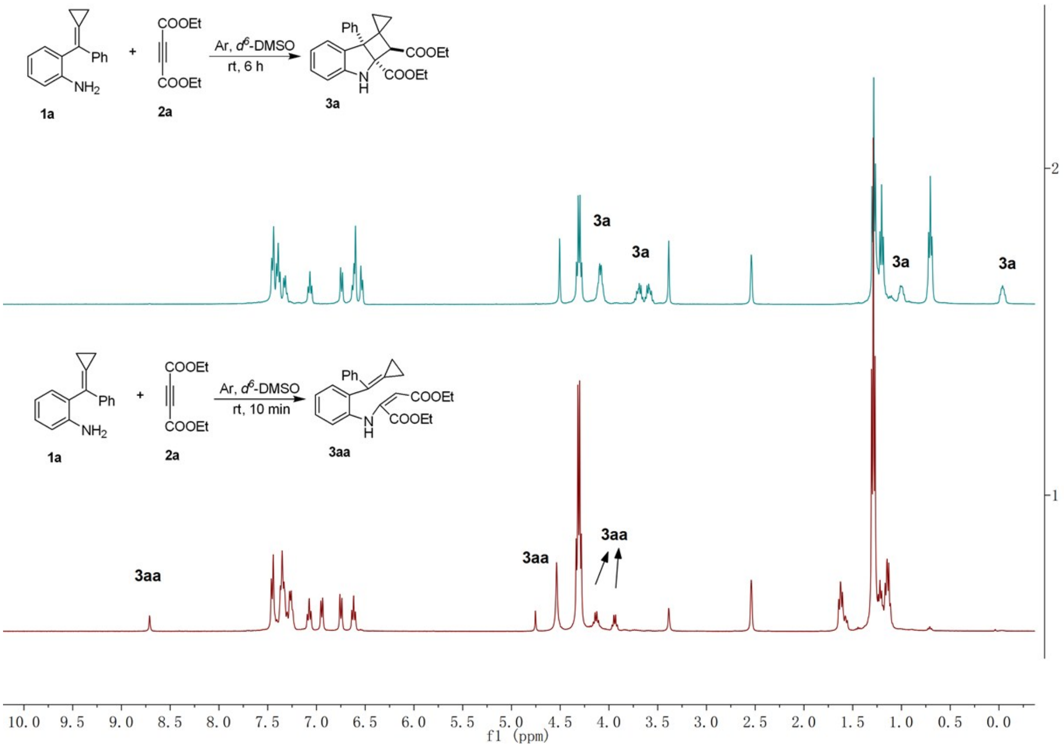
ethyl-(*E*)-1-(2-ethoxy-2-oxoethylidene)-8*b*-phenyl-2,3,4,8*b*-tetrahydrocyclopenta[*b*]indole-3a(1*H*)-carboxylate 4a

^{1}H NMR (CDCl$_3$, TMS, 400 MHz) δ 0.84 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 2.04-2.14 (m, 1H), 2.61-2.69 (m, 1H), 3.09-3.19 (m, 1H), 3.38-3.46 (m, 1H), 3.54-3.63 (m, 1H), 3.67-3.76 (m, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.61 (s, 1H), 5.85 (t, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.84 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.01-7.07 (m, 3H), 7.16 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.21-7.26 (m, 3H). ^{13}C NMR (CDCl$_3$, TMS, 100 MHz) δ 13.4, 14.2, 32.1, 35.6, 59.8, 61.3, 73.3, 83.3, 111.0, 115.9, 120.4, 125.0, 127.2, 127.7, 128.9, 129.2, 132.4, 141.1, 150.2, 166.7, 171.1, 172.8.

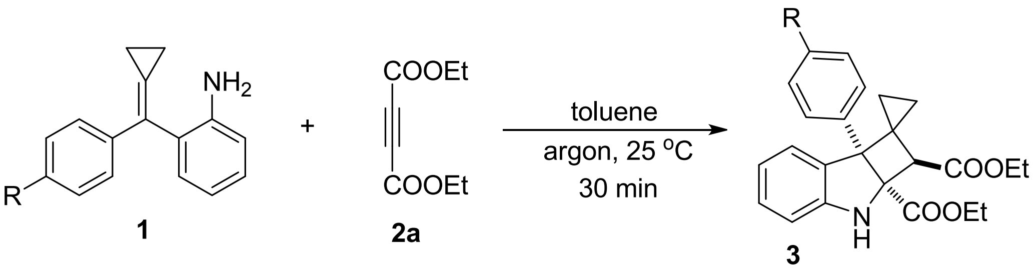




5. The reaction of 1a with 2a monitored by ^{1}H NMR spectroscopy (400 MHz, d^6-DMSO).



6. Hammett correlation



To a flame dried Schlenk tube was added aniline-tethered alkylidenecycopropanes **1** (0.2 mmol), alkynes **2a** (0.4 mmol) and toluene (2.0 mL) under Argon. Then, the resulting solution was degassed, set under argon and stirred at 25 °C for 30 min. Then, the solvent was removed under reduced pressure and the yield was determined by ^{1}H NMR using 1,3,5-trimethoxybeneze as an internal standard.

Table SI-1. Relative Rates $\log(k_X/k_H)$ with σ_p Scales for the [2+2] Cycloaddition of *Para*-Substituted **1** with **2a**

substituent	yield (%)	$\log(k_X/k_H)$	σ_p
***p*-t-Bu**	26	0.26885	-0.2
***p*-Me**	25	0.25181	-0.17
***p*-H**	14	0	0
***p*-Ph**	13	-0.03218	-0.01
***p*-Cl**	8	-0.24304	0.23
***p*-Br**	8	-0.24304	0.23
***p*-CF_3**	4	-0.54417	0.54

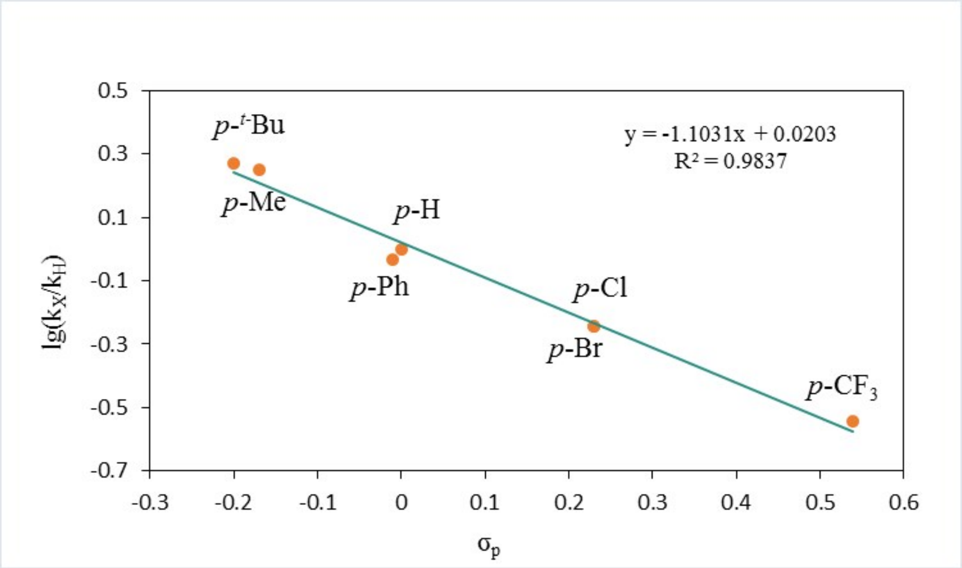


Figure SI-1. Linear-Free-Energy Correlation of $\log(k_X/k_H)$ vs σ_p for **3a**

7. UV-absorption spectra of 3a

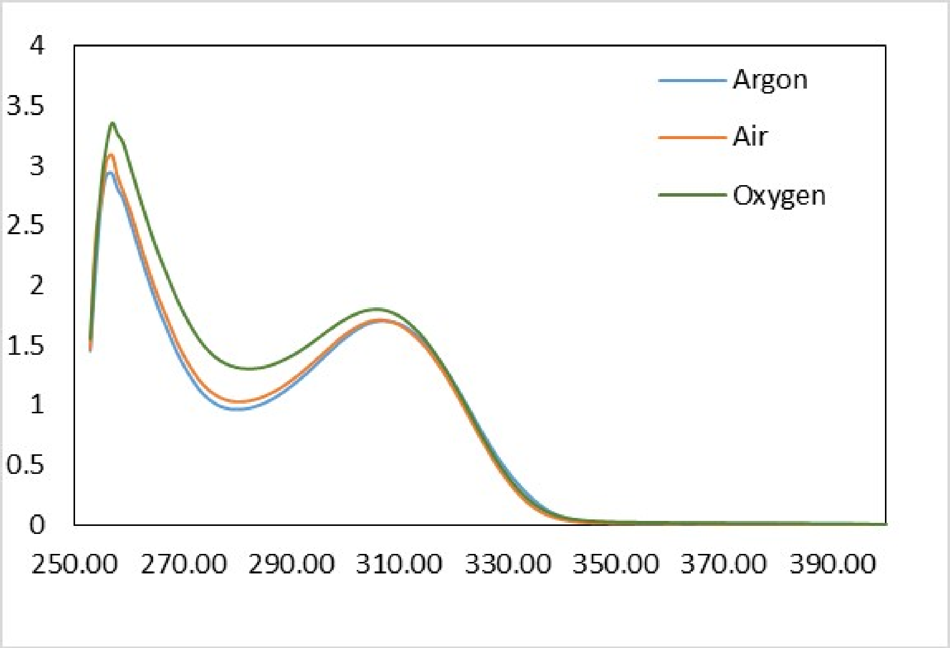


Figure SI-2. UV-Absorption Spectra of **3a** (5.0×10^{-4} M) in DMSO

8. Transient absorption spectroscopy

The transient absorption spectra (TAS) were determined on Edinburgh LP920 specteophotometer with a laser at 355 nm for excitation and a xenon lamp as probe.

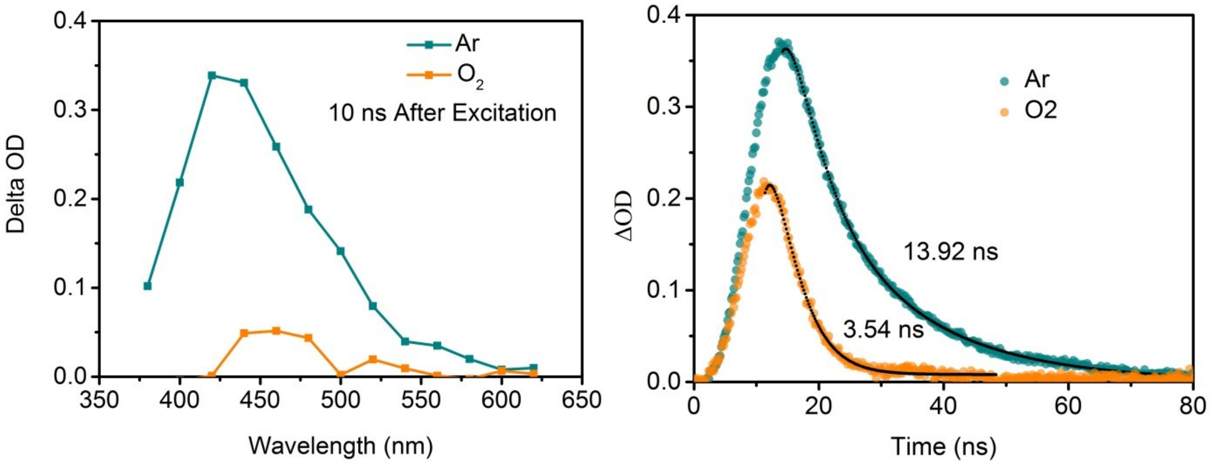


Figure SI-3. **A**: Transient absorption spectra obtained upon LFP at 355 nm of **3a** (10^{-2} M) in acetonitrile under argon (■) and under oxygen (■). **B**: Decay trace at 420 nm and 450 nm under argon.

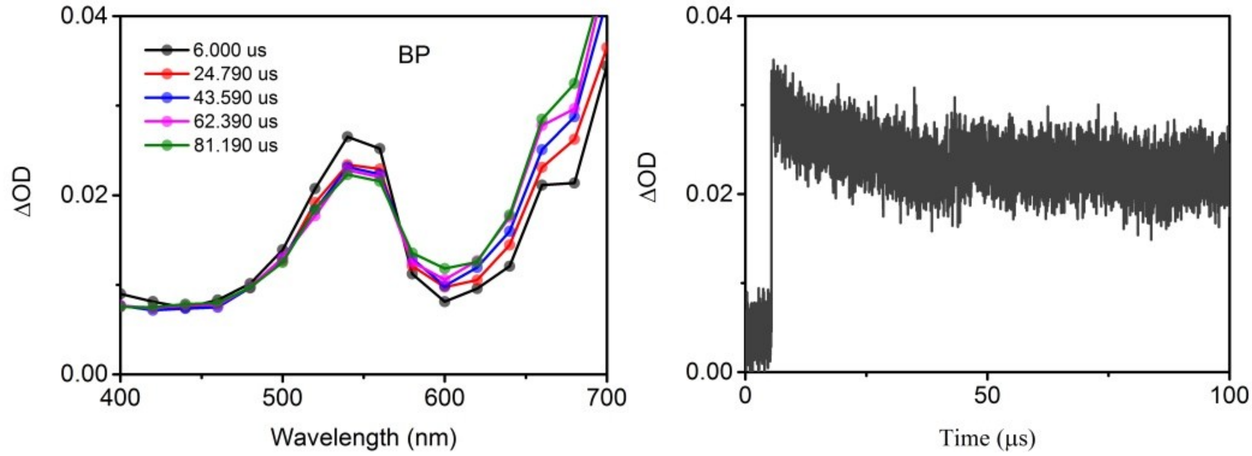


Figure SI-4. **A**: Transient absorption spectra obtained upon LFP at 355 nm of $Ph_2C=O$ (10^{-3} M) in DMSO under argon. **B**: Decay trace at 540 nm under argon.

The triplet transient absorption spectra of benzophenone were obtained upon LFP at 540 nm in DMSO, and the lifetime was more than 100 μs. Because the spectrophotometer was unstable in the above lifetime range, we did not calculate its triplet lifetime (Figure SI-4).

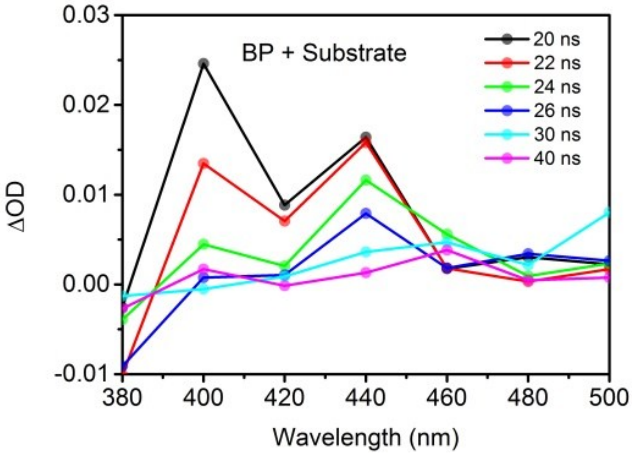


Figure SI-5. **A**: Transient absorption spectra obtained upon LFP at 355 nm of $Ph_2C=O$ (BP) (10^{-3} M) + Substrate **3a** (10^{-2} M) in acetonitrile under argon

When substrate **3a** was added together, the triplet transient absorption spectra of benzophenone were gradually faded away. This fact indicated that the triplet benzophenone reacted with substrate **3a**. We also detected a new transient absorption spectrum at 400 nm which was near to the above result, but it had weaker signal strength. In anyway, its lifetime was so short that we could not calculate it out (Figure SI-5).

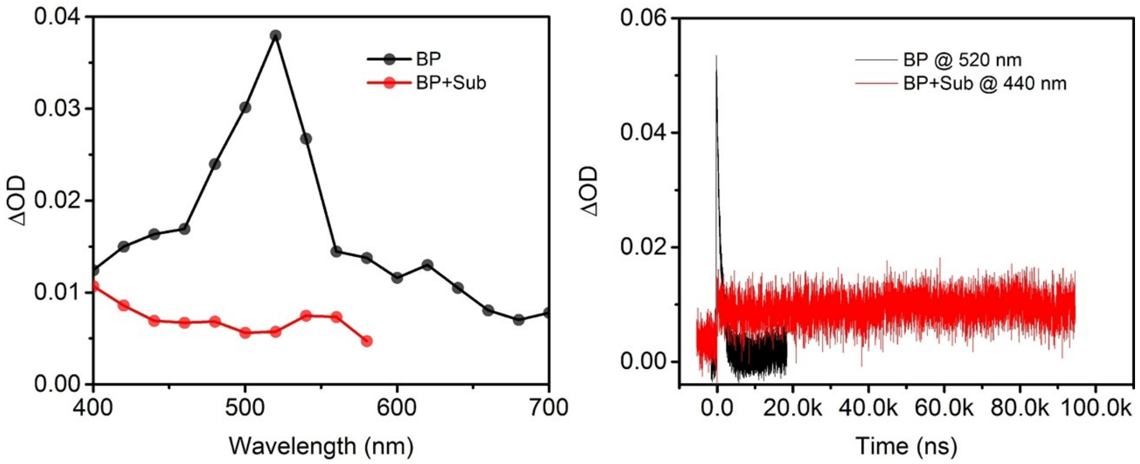


Figure SI-6. **A**: Transient absorption spectra obtained upon LFP at 355 nm of $Ph_2C{=}O$ (BP)(10^{-3} M) (●) and $Ph_2C{=}O$ (BP) (10^{-3}M) + **3a** (Sub) (10^{-2} M) (●) in acetonitrile under argon atmosphere. **B**: Decay trace BP (●) at 520 nm and BP+Sub (●) at 440 nm.

We also detected the triplet transient absorption spectra of benzophenone + substrate **3a** in MeCN, and found a new transient absorption at 420-440 nm with a long lifetime, but it could not be calculated because of the stability of the test instrument in this range (Figure SI-6).

9. EPR spectra

EPR measurements. EPR spectra were recorded at room temperature with the addition of the radical trap 5-,5-dimethyl-1-pyrroline *N*-oxide (DMPO) on a Bruker E500 spectrometer operating at 9.37 GHz. Typical spectrometer parameters were: scan range, 50 G; field set, 3480 G; time constant, 5.12 ms; scan time, 5.24s; modulation amplitude 3.0 G; modulation frequency 100 kHz; receiver gain 2.00×10^4; microwave power, 7.96 mW.

10. References

[1] (a) B. Cao, M. Simaan, I. Marek, Y. Wei, M. Shi, *Chem. Commun.*, **2017**, *53*, 216; (b) B. Cao, Y. Wei, M. Shi, *Chem. Commun.*, **2018**, *54*, 3870.