

## Supporting Information

# Cobalt carbaporphyrin-catalyzed cyclopropanation

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## Experimental Section

### General Considerations.

Cobalt N-confused porphyrins and cobalt benzophthalocyanines were prepared as previously described.<sup>1</sup> All catalytic reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Toluene was distilled under nitrogen from sodium benzophenone ketyl. Toluene, styrene, and ethyl diazoacetate (EDA) were purchased from Sigma-Aldrich and used without further purification. Proton and carbon nuclear magnetic resonance spectra (<sup>1</sup>H NMR and <sup>13</sup>C NMR) were recorded on Varian Mercury 300 or Varian Inova 400 spectrometers and referenced with respect to residual solvent. GC measurements were carried out on a Hewlett-Packard G1800B GC-MS or a Shimadzu GC-MS QP2010S system equipped with a G-TA column.

General Procedures for Cyclopropanation of Styrene: Catalyst (1 mol %) was placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screw cap was replaced with a rubber septum, and 1.0 equivalent of styrene (0.25 mmol) was added via syringe, followed by toluene (0.5 mL) were added and allowed to stir 1 minute until porphyrin dissolved. Then, 1.2 equivalents of ethyl diazoacetate and toluene again (0.5 mL to rinse the walls) were added. The tube was purged with nitrogen for 1 minute while its contents were stirred at room temperature, then the rubber septum was replaced with a Teflon

screwcap and placed in an 80°C oil bath and allowed to stir. After 18 hours, the resulting mixture was given an internal standard (tridecane = 0.50 equivalent) and injected into the gas chromatograph (GC-MS). Peaks were standardized based on isolated cis and trans products purified by flash silica gel chromatography (Hexanes: Ethyl acetate = 8:2) to give the pure product. All yields reported are GC yields based on this process.

A control reaction was done using the same general procedure as above. 1.0 equivalent of styrene (0.25 mmol), 1.2 equivalents of ethyl diazoacetate (0.30 mmol) in 1 ml toluene under N<sub>2</sub> for 20 hours at 80°C, then tridecane = 0.50 equivalent was added and injected into the gas chromatograph (GC-MS). The result was 13% yield of the cyclopropanes (trans:cis = 67:33) and no dimer was formed.

The catalytic reactions generate the (Z) - maleate ethyl esters. Spectra were both compared to a standardized sample of the maleate ester and compared to the mass database structure similarities. It was found that the dimer peak corresponded with the (Z) conformation. No other peaks are found for the fumarate esters.

Ethyl 2-phenylcyclopropane-1-carboxylate trans-isomer:<sup>2</sup> <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, Figure S1): δ 7.09-7.31 (m, 5H), 4.17 (q, J = 7.2 Hz, 2H), 2.52 (ddd, J = 9.3, 6.6, 4.2 Hz, 1H), 1.90 (ddd, J = 8.7, 5.4, 4.5 Hz, 1H), 1.60 (ddd, J = 9.0, 5.1, 4.2 Hz, 1H), 1.30 (ddd, J = 8.4, 6.6, 4.8 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, Figure S2): δ 173.4, 140.1, 128.4, 126.4, 126.1, 60.7, 26.2, 24.2, 17.1, 14.3.

Ethyl 2-phenylcyclopropane-1-carboxylate cis-isomer:<sup>2</sup> <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, Figure S3): δ 7.18-7.28 (m, 5H), 3.88 (q, J = 7.2 Hz, 2H), 2.59 (m, 1H), 2.08 (ddd, J = 9.0, 7.8, 5.6 Hz, 1H), 1.72 (ddd, J = 6.3, 4.9, 4.4 Hz, 1H), 1.32 (ddd, J = 8.9, 7.9, 5.0 Hz, 1H), 0.97 (t, J = 7.2 Hz, 3H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, Figure S4): δ 170.9, 136.5, 129.2, 127.8, 126.6, 60.1, 25.4, 21.7, 14.0, 11.1.

**X-ray Crystallography.** X-ray intensity data were measured at 100 K (Bruker KYRO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ( $\lambda = 0.71073 \text{ \AA}$ ) operated at 2000 W power. The crystals were mounted on a cryoloop using Paratone N-Exxon oil and placed under a stream of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystals. The data were corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F<sup>2</sup> converged.<sup>3</sup> Crystal data and refinement parameters for Co<sup>II</sup>(NCTTP)py and Co<sup>II</sup>(N-MeNCTTP)py are listed in tables S1 and S2. CCDC-790334 & 790335 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

Table S1. Crystal data and structure refinement for  $\text{Co}^{\text{II}}(\text{NCTTP})\text{py}$

Identification code	$\text{Co}^{\text{II}}(\text{NCTTP})\text{py}$	
Empirical formula	$\text{C}_{108}\text{H}_{76}\text{Co}_2\text{N}_{12}$	
Formula weight	1659.67	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	$a = 21.6684(15)$ Å	$\alpha = 90^\circ$ .
	$b = 17.1353(12)$ Å	$\beta = 98.6680(10)^\circ$ .
	$c = 22.1912(15)$ Å	$\gamma = 90^\circ$ .
Volume	8145.4(10) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.353 Mg/m <sup>3</sup>	
Absorption coefficient	0.469 mm <sup>-1</sup>	
F(000)	3448	
Crystal size	0.30 x 0.20 x 0.10 mm <sup>3</sup>	
Theta range for data collection	1.22 to 27.00°.	
Index ranges	-27 ≤ h ≤ 27, -21 ≤ k ≤ 21, -28 ≤ l ≤ 28	
Reflections collected	68252	
Independent reflections	17762 [R(int) = 0.0435]	
Completeness to theta = 27.00°	99.9 %	
Absorption correction	Multi-scan (SADABS)	
Max. and min. transmission	0.9546 and 0.8722	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	17762 / 0 / 1003	
Goodness-of-fit on F <sup>2</sup>	1.041	
Final R indices [I > 2σ(I)]	R1 = 0.0597, wR2 = 0.1498	
R indices (all data)	R1 = 0.0790, wR2 = 0.1580	
Largest diff. peak and hole	1.383 and -1.618 e.Å <sup>-3</sup>	

Table S2. Crystal data and structure refinement for  $\text{Co}^{\text{II}}(\text{N-MeNCTTP})\text{py}$ .

Identification code	$\text{Co}^{\text{II}}(\text{N-MeNCTTP})\text{py}$ .	
Empirical formula	C <sub>55</sub> H <sub>40</sub> Co N <sub>6</sub>	
Formula weight	843.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.6749(13) Å	$\alpha = 97.019(2)^\circ$ .
	b = 13.2874(15) Å	$\beta = 93.666(2)^\circ$ .
	c = 14.1474(16) Å	$\gamma = 107.317(2)^\circ$ .
Volume	2067.8(4) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.355 Mg/m <sup>3</sup>	
Absorption coefficient	0.463 mm <sup>-1</sup>	
F(000)	878	
Crystal size	0.09 x 0.05 x 0.03 mm <sup>3</sup>	
Theta range for data collection	1.46 to 27.00°.	
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -17 ≤ l ≤ 18	
Reflections collected	17072	
Independent reflections	8810 [R(int) = 0.0524]	
Completeness to theta = 27.00°	97.8 %	
Absorption correction	Multi-scan (SADABS)	
Max. and min. transmission	0.9862 and 0.9595	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	8810 / 0 / 596	
Goodness-of-fit on F <sup>2</sup>	1.087	
Final R indices [I > 2σ(I)]	R1 = 0.0755, wR2 = 0.1471	
R indices (all data)	R1 = 0.1221, wR2 = 0.1629	
Largest diff. peak and hole	0.789 and -0.516 e.Å <sup>-3</sup>	

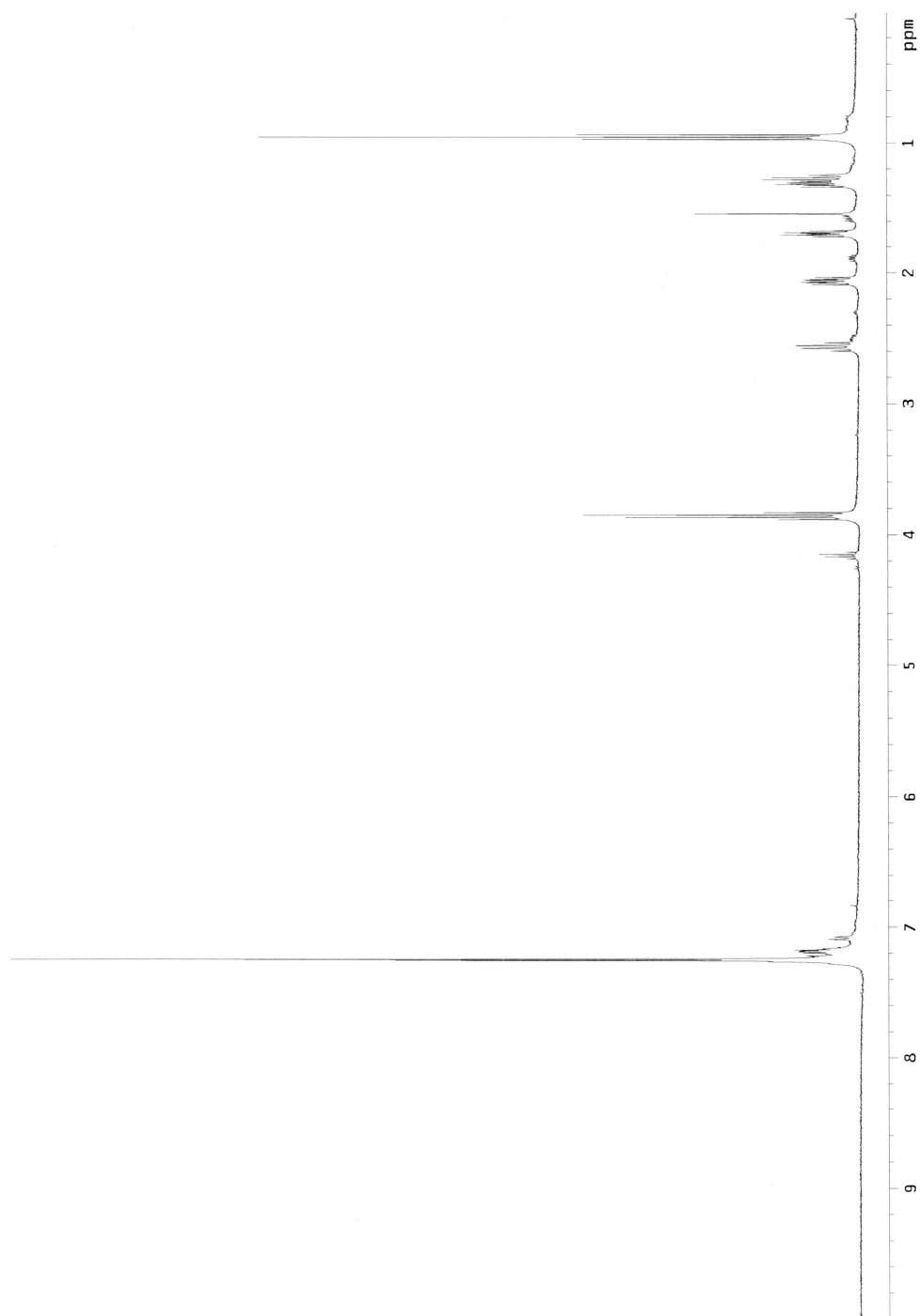


Figure S1: <sup>1</sup>H-NMR (400MHz) Ethyl 2-phenylcyclopropane-1-carboxylate *cis*-isomers

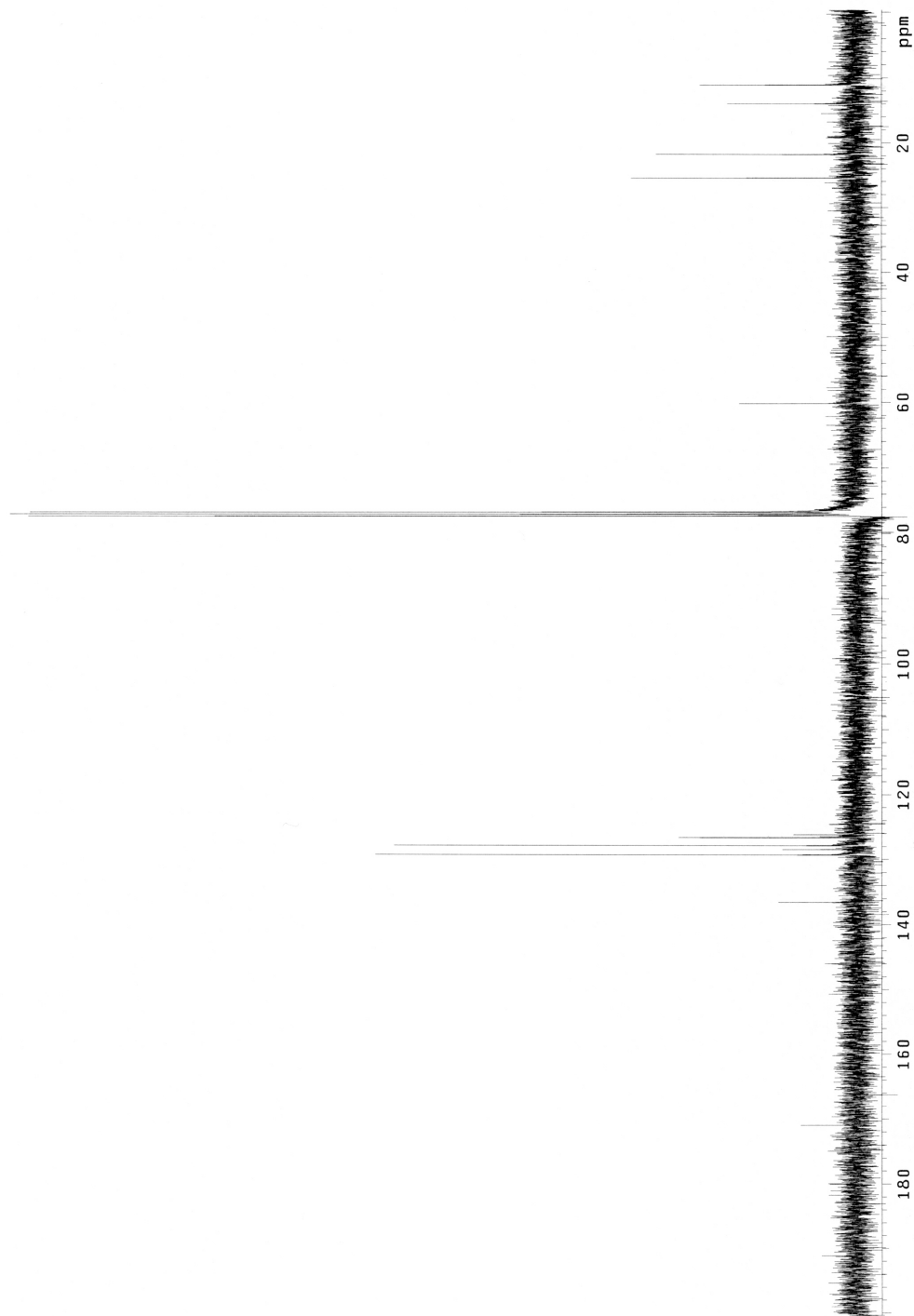


Figure S2:  $^{13}\text{C}$ -NMR (400MHz) Ethyl 2-phenylcyclopropane-1-carboxylate *cis*-isomers

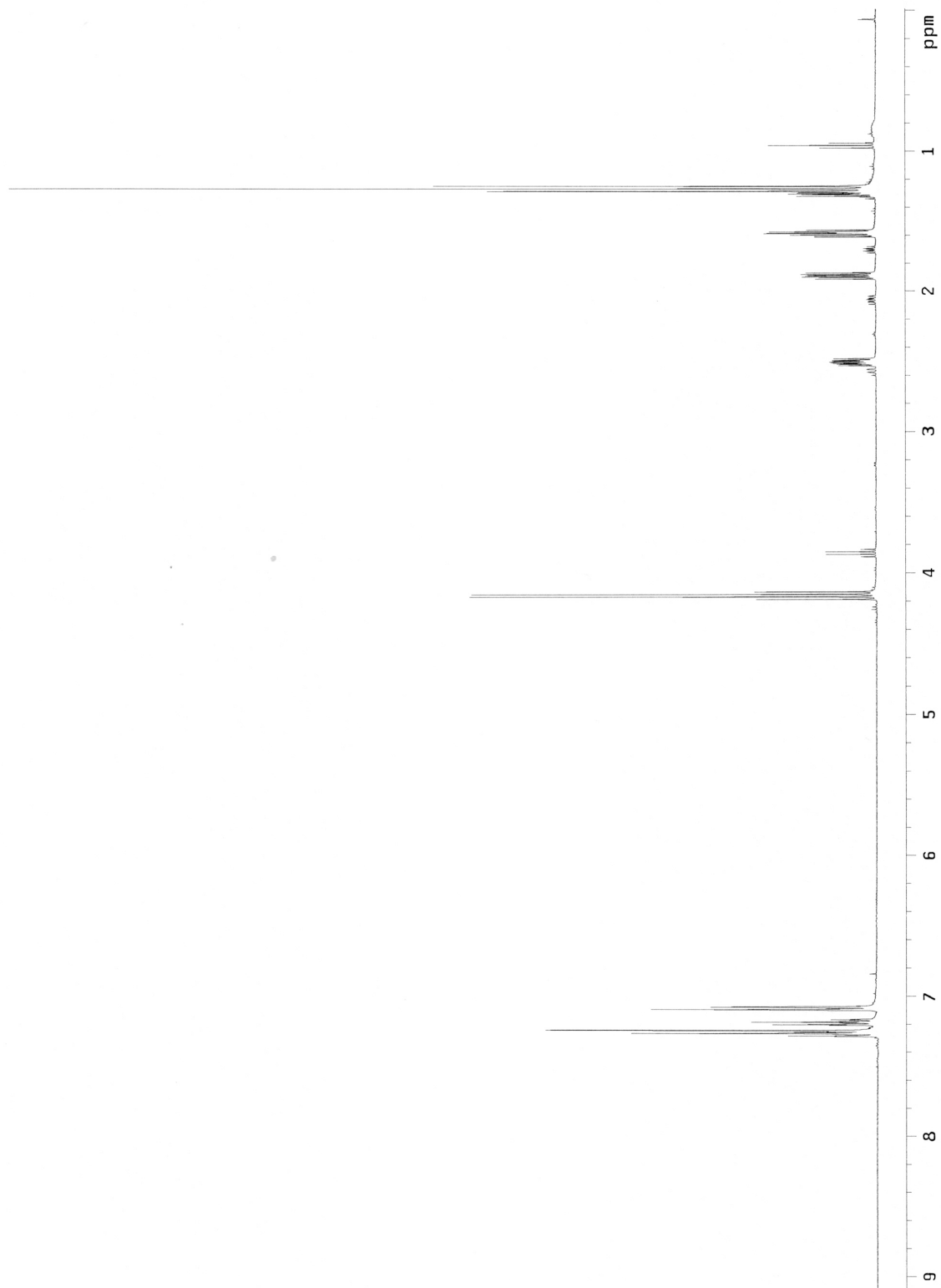


Figure S3:  $^1\text{H-NMR}$  (400MHz) Ethyl 2-phenylcyclopropane-1-carboxylate *trans*-isomers

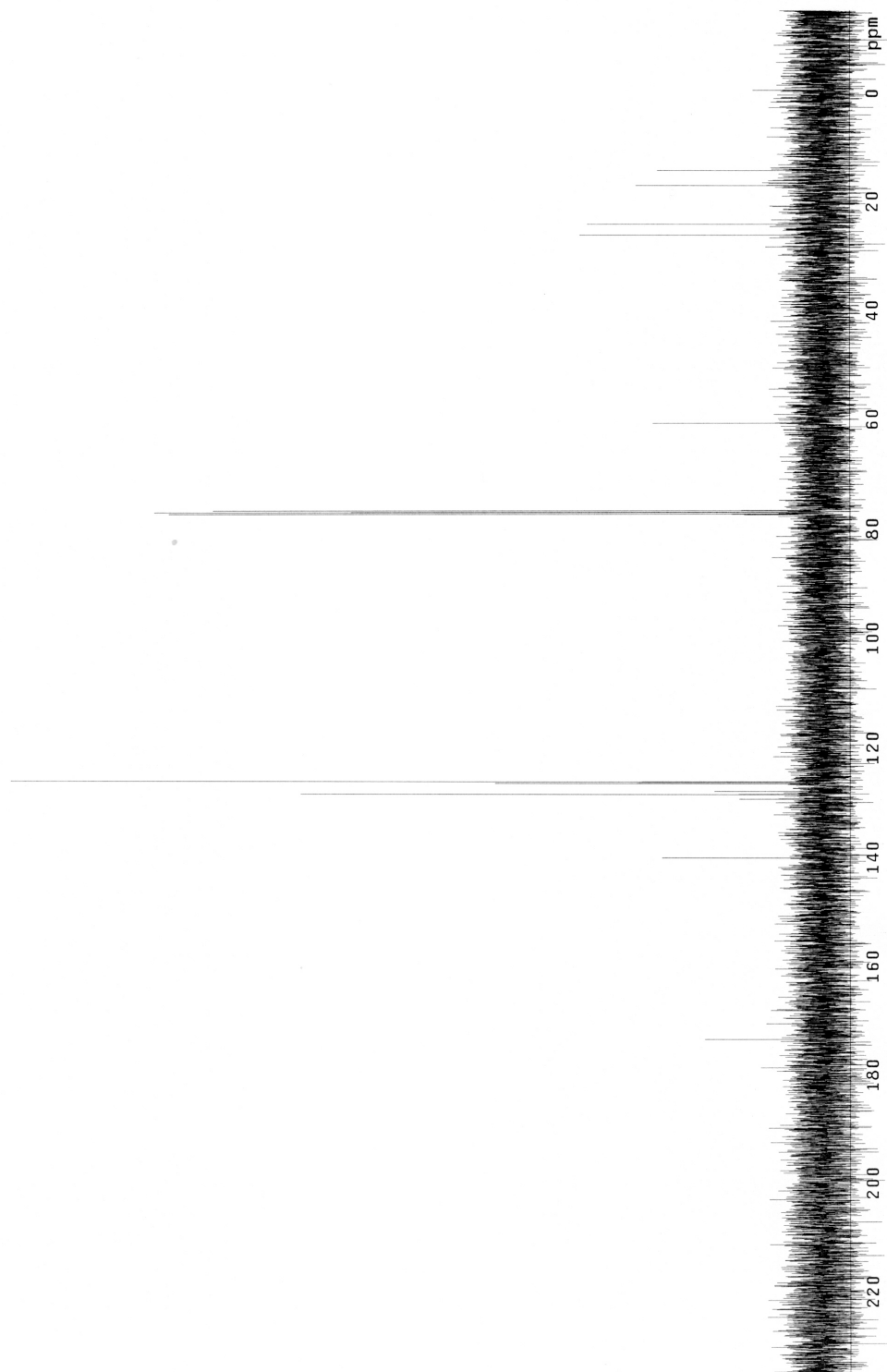


Figure S4:  $^{13}\text{C}$ -NMR (400MHz) Ethyl 2-phenylcyclopropane-1-carboxylate *trans*-isomers



## References

- 1) J. D. Harvey, C. J. Ziegler, *Chem. Commun.*, 2004, **14**, 1666; W.-C. Qu, T. Ding, A. A. Çetin, J. D. Harvey, M. J. Taschner, C. J. Ziegler *J. Org. Chem.* 2006, **71**, 811; A. Çetin, S. Sripathongnak, M. Kawa, W. S. Durfee, C. J. Ziegler, *Chem. Commun.*, 2007, **41**, 4289.
- 2) L. Huang, Y. Chen, G.-Y. Gao, X. P. Zhang, *J. Org. Chem.* 2003, **68**, 8179.
- 3) Sheldrick, G. M. SHELXTL, Crystallographic Software Package, Version 6.10, Bruker-AXS: Madison, WI, 2000.