

Light induced catalytic intramolecular hydrofunctionalization of allylphenol mediated by porphyrin rhodium(III) complexes

Xu Liu, Zikuan Wang and Xuefeng Fu*

Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications, Peking University, Beijing, 100871, China. Fax: +86 10 6275 1708; Tel: +86 10 6275 6035; E-mail: fuxf@pku.edu.cn

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1. General considerations

C₆D₆ and CDCl₃ were purchased from Cambridge Isotope Laboratory Inc.; (Rh(CO)₂Cl)₂ from Strem Chemicals Inc.; and all other chemicals were purchased from Alfa Aesar or J&K Scientific Ltd. and used as received unless otherwise noted. ¹H NMR spectra were recorded on a Bruker AVII-400 spectrometer at ambient temperature. GC-MS results were obtained by the Agilent 7980A/5975C GC/MSD system equipped with the DB-17MS (30m, 0.25mm, 0.25 μm) column. ESI-MS results were obtained by a Bruker Apex IV FTMS spectrometer. Light in the irradiation experiments was provided by a 500W high-pressure mercury lamp (CHF-XM35-500W, Beijing Trusttech Co., Ltd.) and the glass vessel was positioned about 20.0 cm away from the light source.

2. Preparation of (TAP)Rh^{III}-I

TAPH₂ was synthesized according to Adler's report.¹ [RhCl(CO)₂]₂ (42.0 mg) dissolved in 2 mL of chloroform was added dropwise into a two-neck flask containing 80.0 mg of TAPH₂ and 90.0 mg of sodium acetate suspended in 30 mL of chloroform under N₂ atmosphere. The mixture was stirred at room temperature for 1 h, and then 56.0 mg of I₂ dissolved in 2 mL of chloroform was added to the solution. The reaction mixture was further stirred for another 3 h. The crude product was filtrated to remove sodium acetate, and then concentrated by rotary evaporation. Subsequent

chromatography on neutral alumina using 4:1 (v/v) dichloromethane vs ethyl acetate gave the (TAP)Rh^{III}-I with a yield of 60%. ¹H NMR (400 MHz, CDCl₃) δ(ppm): 8.89 (8H, s), 8.07-8.15 (8H, m), 7.23-7.29 (8H, m), 4.08 (12H, s).

3. Independent synthesis of the key intermediate (2,3-dihydrobenzofuran-2-yl)methyl rhodium porphyrin complex 3

A 0.3 mL C₆D₆ solution of (TAP)Rh-I (0.017 M), 2-allylphenol (0.33 M) and 2,6-di-*tert*-butylpyridine (0.20 M) was heated at 60 °C for 12 hours, producing complex 3 with a NMR yield of 95% with dibromomethane as internal standard. The crude product was concentrated by rotary evaporation after reaction, and chromatographed on neutral alumina using dichloromethane as the eluent, giving complex 3 in an overall yield of 85%. ¹H NMR (400 MHz, C₆D₆) δ (ppm): 9.03 (8H, s), 8.20 (4H, m), 7.96 (4H, m), 7.17 (4H, m), 7.04 (4H, m), 6.34 (1H, m), 6.12 (2H, m), 5.78 (1H, m), 3.56 (12H, s), -0.01 (1H, m), -1.04 (1H, m), -1.68 (1H, m), -4.31 (1H, m), -4.51 (1H, m). ESI-MS results (C₅₇H₄₅N₄O₅RhNa, m/z = 991.232, calcd 991.233; Figure 2S) also confirmed the formation of (2,3-dihydrobenzofuran-2-yl)methyl rhodium porphyrin complex. In addition, the ¹H NMR spectrum of independently synthesized (2,3-dihydrobenzofuran-2-yl)methyl rhodium porphyrin complex agreed very well with that observed *in situ*.

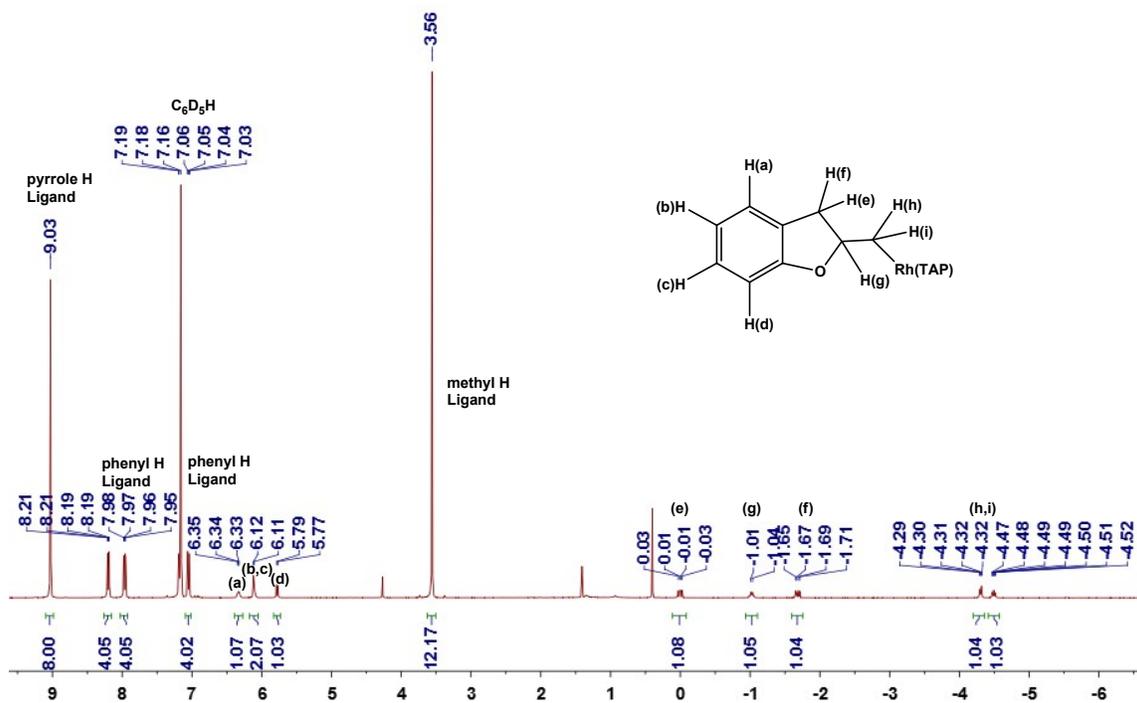


Figure 1S ¹H NMR spectrum of complex 3 (400 MHz, C₆D₆)

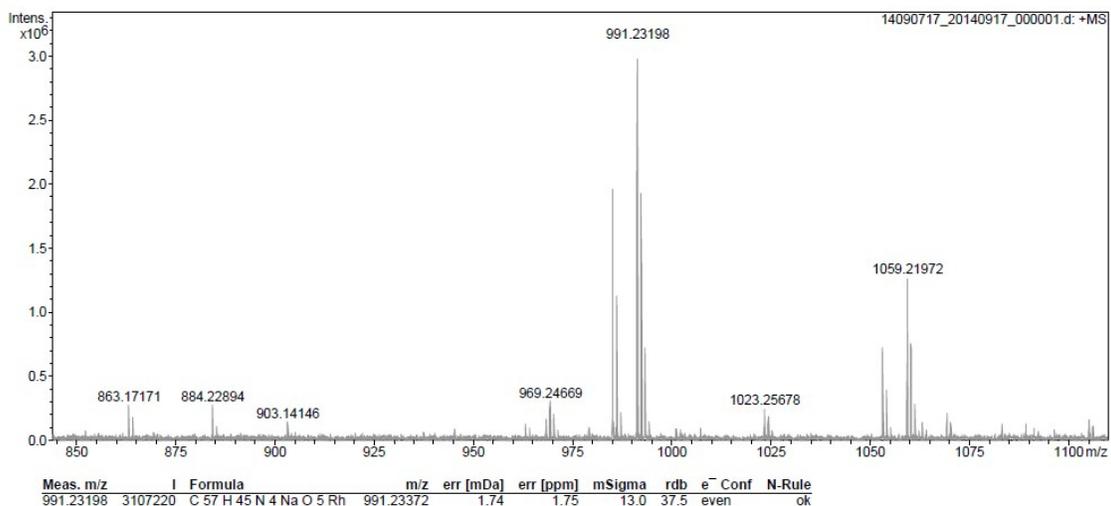


Figure 2S ESI-MS spectrum of complex **3** (ESI-MS: 991.232 and Exact Mass: 991.233).

4. General procedure for (TAP)Rh^{III} mediated catalytic intramolecular hydrofunctionalization of allylphenol

A 0.3 mL of C₆D₆ solution containing (TAP)Rh-I (1.67mM), different kinds of substituted 2-allylphenol (0.667 M) and HNEt₂ (0.233 M) was added to a J. Young Valve NMR tube. The sample was degassed by three freeze-pump-thaw cycles and refilled with 1 atm of N₂. Irradiating the solution for 36 hours (500 W Hg lamp, 20 cm distance) produced 2-methylbenzofuran which was detected and quantified by ¹H NMR.

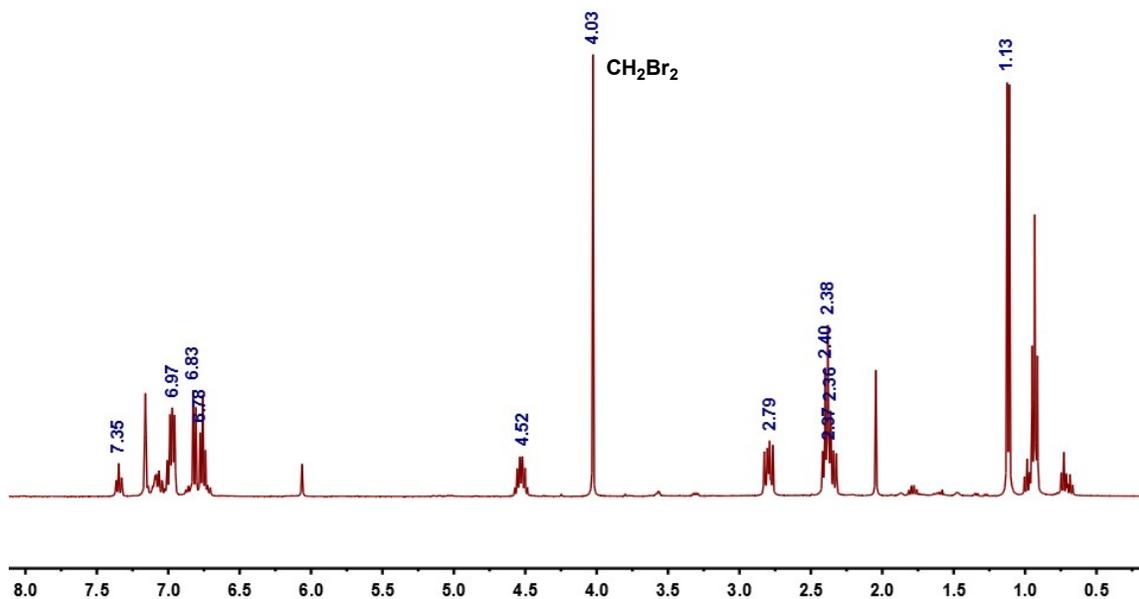


Figure 3S ¹H NMR spectrum of 2-methyl-2,3-dihydrobenzofuran (with dibromomethane as the inner standard, 400 MHz, C₆D₆), δ (ppm): 7.35 (1H, m), 6.97 (1H, m), 6.83 (1H, m), 6.78 (1H, m), 4.52

(1H, m), 2.79 (1H, m), 2.40 (1H, m), 1.13 (3H, d).

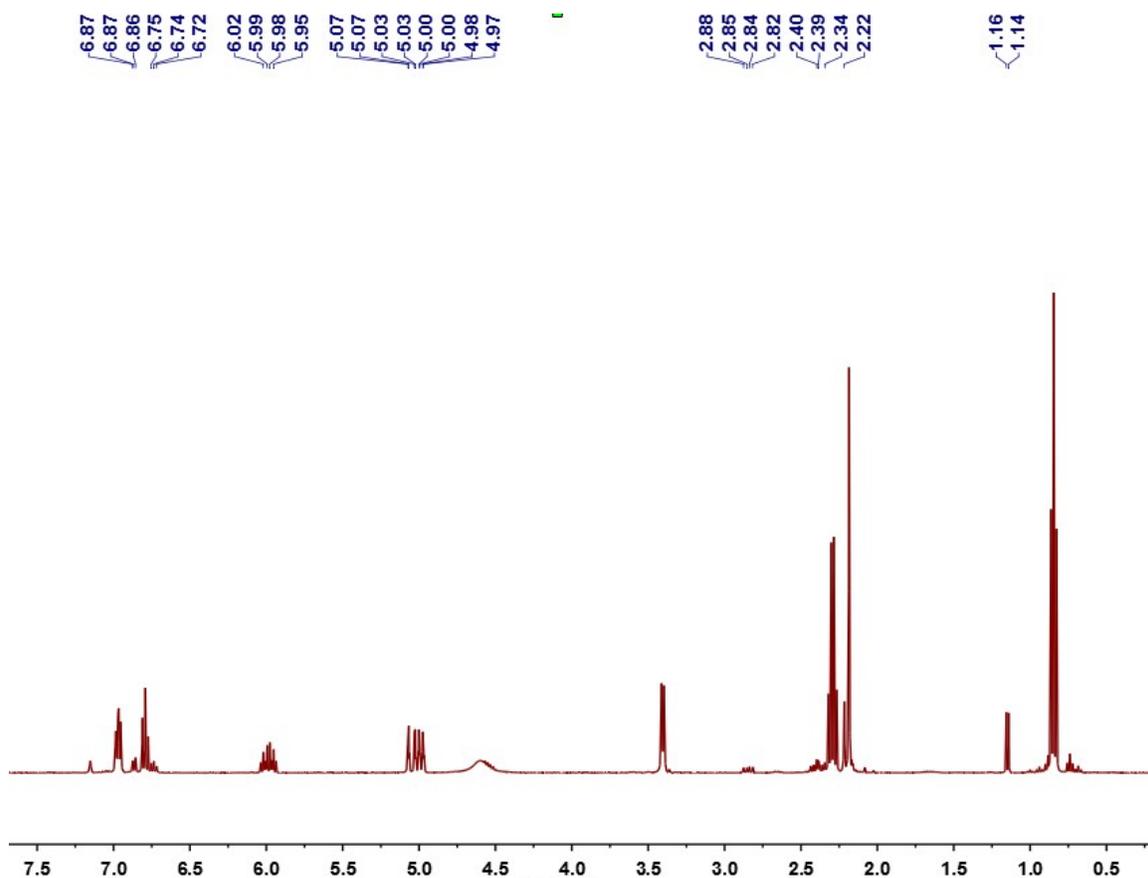


Figure 4S ¹H NMR spectrum of the reaction solution of hydrofunctionalization of 2-allyl-6-methylphenol (400 MHz, C₆D₆). The signals of products were shown as δ (ppm): 6.68 (2H, m), 6.72 (1H, m), 6.00 (1H, m), 2.85 (1H, m), 2.36 (1H, m), 2.22 (3H, s), 1.15 (2H, d). The other set of signals corresponded to the remaining 2-allyl-6-methylphenol.

- The active catalyst was (TAP)Rh^{III}-NEt₂, which was confirmed by ¹H NMR and ESI-MS (Figure 5S-6S);
- After irradiation of the reaction solution for 5h, the form of catalyst was (TAP)Rh^{III}-NEt₂ (characteristic signal at 9.16 ppm), and complex 3 (characteristic signals at 9.01, -1.05, -4.34, -4.51 ppm), which could be confirmed by ¹H NMR (Figure 7S)

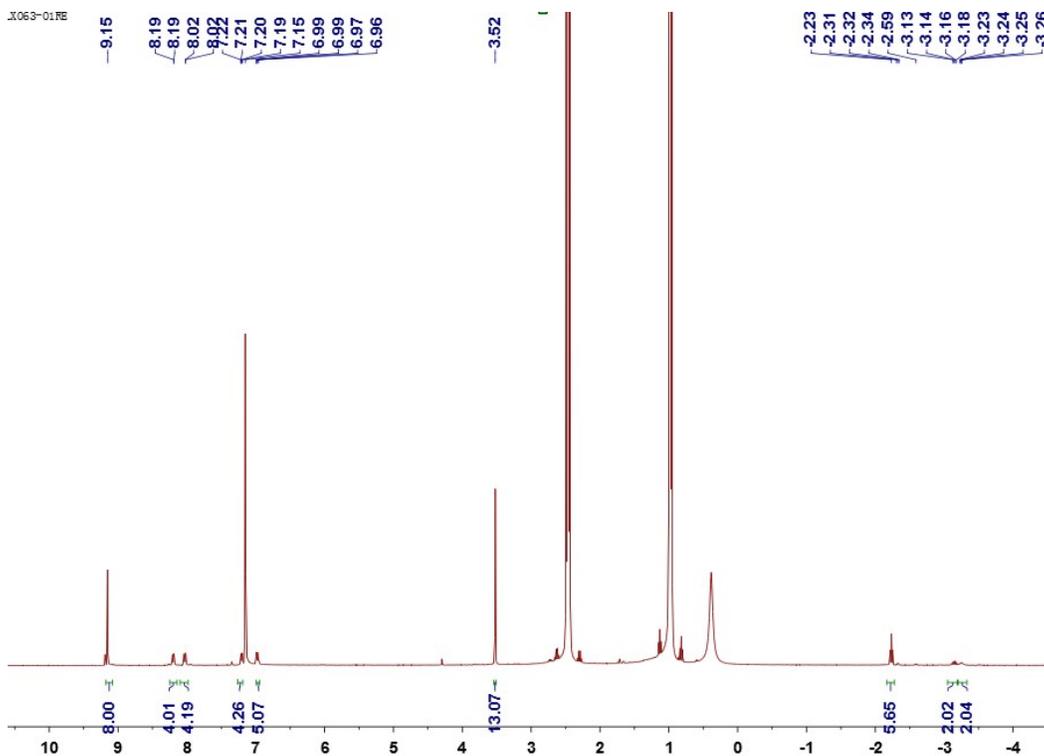


Figure 5S. ^1H NMR spectrum of the mixed solution of (TAP)Rh-I (1.67mM) and HNEt_2 (0.233 M) (400 MHz, C_6D_6).

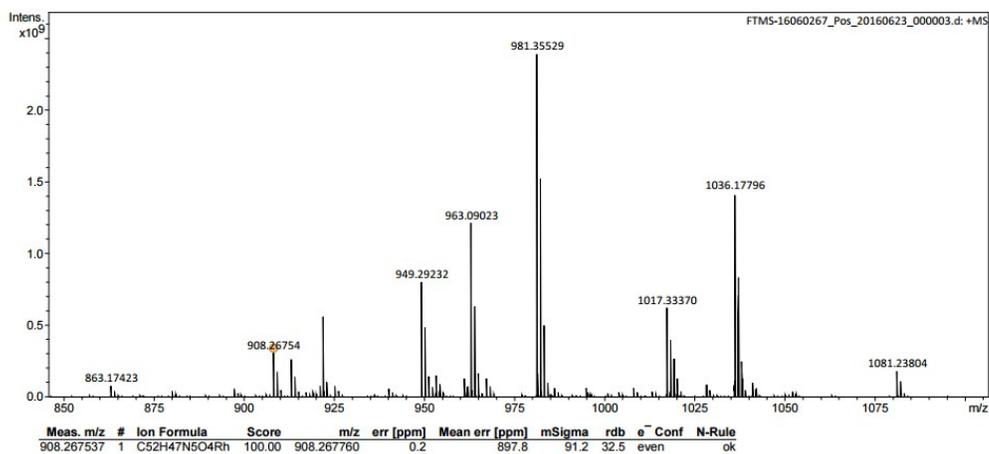


Figure 6S. ESI-MS spectrum of (TAP)Rh^{III}-NEt₂ complex

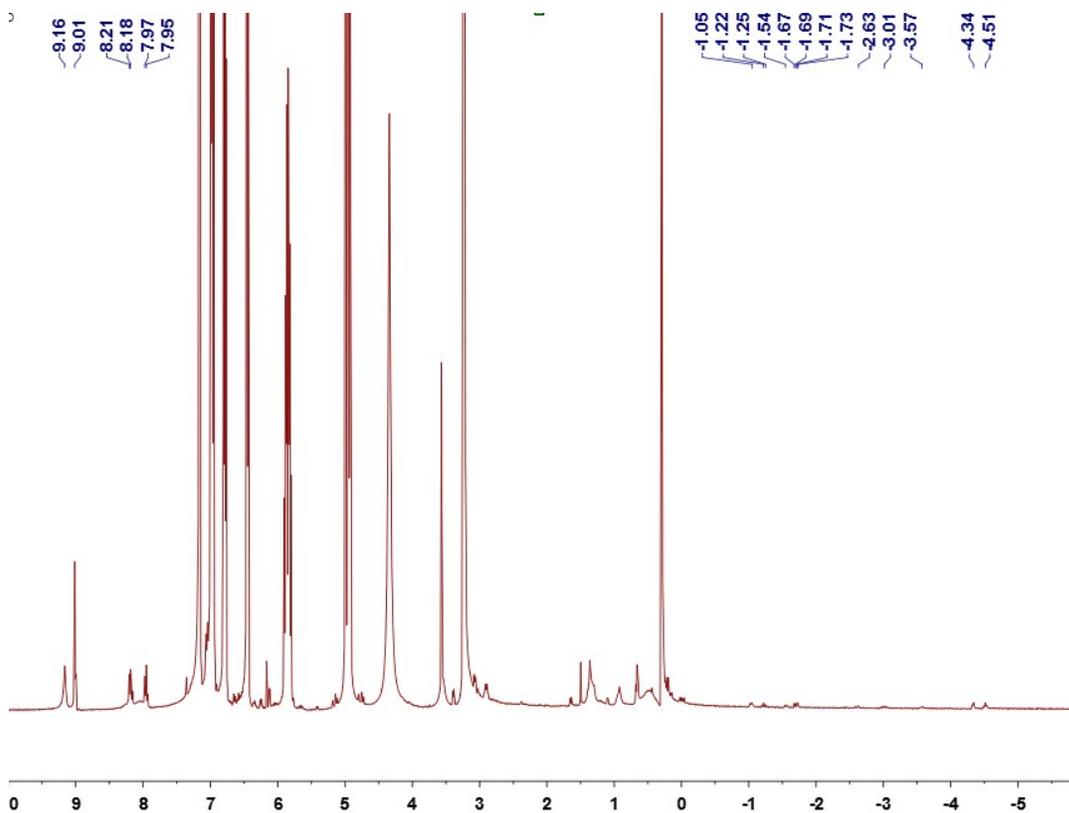


Figure 7S. ¹H NMR spectrum of the reaction solution after irradiation for 5 hours. (400 MHz, C₆D₆)

5. Characterization of complex 3 by Single crystal X-ray diffraction

Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of 0.5ml water into 0.3 mL THF of complex 3 (0.01 M).

Selected bond lengths [Å] and angles[°]: Rh2-N5 2.031, Rh2-N6 2.037, Rh2-N7 2.038, Rh2-N8 2.022, Rh2-C1A 2.151; N5-Rh2-N6 90.20, N6-Rh2-N7 90.46, N7-Rh2-N8 89.57, N8-Rh2-N5 89.76, N5-Rh2-C1A 90.62, N5-Rh2-C1A 87.28, N5-Rh2-C1A 89.67, N5-Rh2-C1A 96.98.

The deposition number of CCDC is 1476559.

Crystal data and structure refinement for complex 3

Empirical formula	C117.4 H97.4 I0.1 N8 O10.9 Rh2
Formula weight	2009.45
Temperature	173.1500 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 12.1532(17) Å a = 68.884(4)°. b = 21.943(3) Å b = 81.902(6)°.

	$c = 22.090(3) \text{ \AA}$	$g = 80.570(5)^\circ$.
Volume	5399.5(12) \AA^3	
Z	2	
Density (calculated)	1.236 Mg/m ³	
Absorption coefficient	0.386 mm ⁻¹	
F(000)	2078	
Crystal size	0.22 x 0.13 x 0.09 mm ³	
range for data collection	0.992 to 27.507°.	
Index ranges	-15 ≤ h ≤ 15, -28 ≤ k ≤ 28, -28 ≤ l ≤ 28	
Reflections collected	62197	
Independent reflections	24524 [R(int) = 0.0599]	
Completeness to theta	25.242° 99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. & min. transmission	1.0000 and 0.8981	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	24524 / 36 / 1270	
Goodness-of-fit on F ²	1.194	
Final R indices [I > 2σ(I)]	R1 = 0.0983, wR2 = 0.2582	
R indices (all data)	R1 = 0.1187, wR2 = 0.2858	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.328 and -1.086 e.Å ⁻³	

Reference

- (1) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.