Multiple deprotonations and deaminations of phenethylamines. An Unprecedented Approach to Synthesize Pyrroles

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Experimental Section

General. All reactions were carried out under air. Toluene was freshly distilled from sodium. Anhydrous $\text{Cu}(\text{OAc})_2$ was purchased from Acros Chemical and used without further purification. PdCl_2 was purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) were registered on Varian 200M spectrometers with CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm and CDCl_3 resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (J values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh. IR, X-ray, GC, MS, and HRMS were performed by the State-authorized Analytical Center in Peking University.

General procedures for syntheses of pyrroles.

PdCl_2 (0.05 mmol), anhydrous $\text{Cu}(\text{OAc})_2$ (1.0 mmol), phenethylamine (1.0 mmol), and toluene/xylene (4.0 mL) were added to an oven-dried Schlenck tube under air. Then it was heated in an oil bath at 115 °C for 16 h (155 °C for 4h in xylene). After the reaction was complete, the product was obtained by silica gel chromatography with hexanes:EtOAc.

Table 1. Deprotonation/deamination of phenethylamine under different condition. ^a

entry	cat. (mol%)	oxidant (equiv)	2a (%)
1	NiCl ₂ (5)	Cu(OAc) ₂ (1.0)	19
2	FeCl ₂ (5)	Cu(OAc) ₂ (1.0)	20
3	CoCl ₂ (5)	Cu(OAc) ₂ (1.0)	10
4	PtCl ₂ (5)	Cu(OAc) ₂ (1.0)	14
5	Pd(OAc) ₂ (5)	Cu(OAc) ₂ (1.0)	34
6	Pd(dba) ₂ (2.5)	Cu(OAc) ₂ (1.0)	16
7	Pd(CH ₃ CN) ₂ Cl ₂ (5)	Cu(OAc) ₂ (1.0)	38
8	Pd(PhCN) ₂ Cl ₂ (5)	Cu(OAc) ₂ (1.0)	37
9	PdCl₂ (5)	Cu(OAc)₂ (1.0)	42
10	PdCl ₂ (5)	MnO ₂ (1.0)	<5
11	PdCl ₂ (5)	K ₂ Cr ₂ O ₇ (1.0)	<5
12	PdCl ₂ (5)	FeCl ₃ (1.0)	<5
13	PdCl ₂ (5)	Cu(OTf) ₂ (1.0)	<5
14	PdCl ₂ (5)	Cu(acac) ₂ (1.0)	<5
15	PdCl ₂ (5)	CuBr ₂ (1.0)	<5
16	PdCl ₂ (5)	CuCl ₂ (1.0)	<5
17	-	Cu(OAc) ₂ (1.0)	22
18	PdCl ₂ (5)	-	<5
19	PdCl ₂ (5)	Cu(OAc) ₂ (0.5)	38
20	PdCl ₂ (5)	Cu(OAc) ₂ (2.0)	41

Table 2. Syntheses of pyrroles from commercial available phenethylamines. ^a

Ar-CH2-CH2-NH2 $\xrightarrow[\text{Cu(OAc)}_2 \text{ (1.0 equiv)}]{\text{PdCl}_2 \text{ (5 mol\%)}}$ Ar-c1cc(N-CH2-CH2-Ar)cc1Ar

1 **2**

entry	1	Ar	2	yield (%) ^b
1	1a	C ₆ H ₅	2a	42 (46)
2	1b	<i>p</i> -CH ₃ OC ₆ H ₄	2b	51 (51)
3	1c	<i>o</i> -CH ₃ OC ₆ H ₄	2c	64 (48)
4	1d	<i>p</i> -CH ₃ C ₆ H ₄	2d	48 (44)
5	1e	<i>m</i> -CH ₃ C ₆ H ₄	2e	45 (44)
6	1f	<i>o</i> -CH ₃ C ₆ H ₄	2f	62 (59)
7	1g	2,5-(CH ₃) ₂ C ₆ H ₃	2g	71 (64)
8	1h	<i>p</i> -FC ₆ H ₄	2h	41 (45)
9	1i	<i>m</i> -FC ₆ H ₄	2i	26 (31)
10	1j	<i>m</i> -CF ₃ C ₆ H ₄	2j	33 (40)
11 ^c	1a	C ₆ H ₅	2a	35 (38)

^a All the reactions were carried out in the scale of 1.0 mmol with 5.0 mol% of PdCl₂ and 1.0 equivalent of Cu(OAc)₂ in 4 mL of toluene or xylene unless otherwise noted. ^b Isolated Yields and the yield in parentheses were obtained in xylenes at 155 °C for 4 h. ^c This reaction was carried out in the scale of 10.0 mmol.

1-phenethyl-3,4-diphenyl-1H-pyrrole (2a). Starting from 1 mmol **1a** to afford **2a**: 45 mg in toluene, yield 42%, 50mg in xylene, yield 46%. ¹H NMR (CDCl₃, 200 MHz): δ7.38-7.19 (m, 15 H), 6.76 (s, 2 H), 4.17 (t, *J* = 7.2 Hz, 3 H), 3.17 (t, *J* = 7.2 Hz, 3 H). ¹³C NMR (CDCl₃, 50 MHz): δ138.1, 135.9, 128.7, 128.6, 128.3, 128.1, 126.7, 125.5, 123.1, 120.1, 51.3, 38.2. MS (C₂₄H₂₁N): 323 (M⁺). HRMS: Anal. Calcd. for C₂₄H₂₁N 323.1674. Found: 323.1672. IR (KBr, cm⁻¹): 1602, 1540.

1-(4-methoxyphenethyl)-3,4-bis(4-methoxyphenyl)-1H-pyrrole (2b). Starting from 1 mmol **1b** to afford **2b** 70 mg in toluene, yield 51%; 70 mg in xylene, yield 51%. ¹H NMR (CDCl₃, 200 MHz): δ7.18-6.76 (m, 12 H), 6.61 (s, 2 H), 4.01 (t, *J* = 7.6 Hz, 3 H), 3.75 (s, 9 H), 3.01 (t, *J* = 7.6 Hz, 3 H). ¹³C NMR (CDCl₃, 50 MHz): δ158.5, 157.7, 130.4, 129.7, 129.4, 128.6, 122.6, 119.5, 114.0, 113.6, 55.2, 55.1, 51.4, 37.2. MS (C₂₇H₂₇NO₃): 413 (M⁺). HRMS: Anal. Calcd. for C₂₇H₂₇NO₃ 413.1991. Found: 413.1994. IR (KBr, cm⁻¹): v.1543, 1513.

1-(2-methoxyphenethyl)-3,4-bis(2-methoxyphenyl)-1H-pyrrole (2c). Starting from 1 mmol **1c** to afford **2c** 88 mg in toluene, yield 64 %; 66 mg in xylene, yield 48%. ¹H NMR (CDCl₃, 200 MHz): δ 7.32-7.13 (m, 6 H), 6.98-6.83 (m, 8 H), 4.15 (t, *J* = 7.8 Hz, 3 H), 3.88 (s, 3 H), 3.52 (s, 6 H), 3.22 (t, *J* = 7.8 Hz, 3 H). ¹³C NMR (CDCl₃, 50 MHz): δ157.5, 156.3, 130.4, 127.9, 126.8, 126.5, 126.3, 120.6, 120.5, 120.1, 119.4, 110.6, 110.2, 55.2, 54.9, 49.7, 33.0. MS (C₂₇H₂₇NO₃): 413 (M⁺). HRMS: Anal. Calcd. for C₂₇H₂₇NO₃ 413.1991. Found: 413.1997. IR (KBr, cm⁻¹): v.1493, 1463.

1-(4-methylphenethyl)-3,4-dip-tolyl-1H-pyrrole (2d). Starting from 1 mmol **1d** to afford **2d** 58 mg in toluene, yield 48 %; 54 mg in xylene, yield 44%. ¹H NMR (CDCl₃, 200 MHz): δ 7.25-7.10 (m, 12 H), 6.75 (s, 2 H), 4.13 (t, *J* = 7.8 Hz, 3 H), 3.13 (t, *J* = 7.8 Hz, 3 H), 2.39 (s, 9 H). ¹³C NMR (CDCl₃, 50 MHz): δ136.2, 135.1, 134.9, 133.0, 129.3, 128.8, 128.6, 128.2, 122.9, 119.8, 51.4, 37.8, 21.1, 21.0. MS (C₂₇H₂₇N): (M⁺). HRMS: Anal. Calcd. For 365.2144. Found: 365.2141. IR (KBr, cm⁻¹): v.1546, 1515.

1-(3-methylphenethyl)-3,4-dim-tolyl-1H-pyrrole (2e). Starting from 1 mmol **1e** to afford **2e** 55 mg in toluene, yield 45 %; 53 mg in xylene, yield 44%. ¹H NMR (CDCl₃,

200 MHz): δ 7.26-6.99 (m, 12 H), 6.75 (s, 2 H), 4.13 (t, J = 7.7 Hz, 3 H), 3.11 (t, J = 7.7 Hz, 3 H), 2.37 (s, 3 H), 2.33 (s, 6 H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 138.2, 138.1, 137.5, 135.8, 129.6, 128.9, 128.5, 127.9, 127.4, 126.2, 125.7, 125.6, 123.1, 120.1, 51.4, 38.2, 21.45, 21.36. MS ($\text{C}_{27}\text{H}_{27}\text{N}$): 365 (M^+). HRMS: Anal. Calcd. For $\text{C}_{27}\text{H}_{27}\text{N}$. 365.2144. Found: 365.2139. IR (KBr, cm^{-1}): ν . 1607, 1538.

1-(2-methylphenethyl)-3,4-dio-tolyl-1H-pyrrole (2f). Starting from 1 mmol **1f** to afford **2f** 75 mg in toluene, yield 62 %; 72 mg in xylene, yield 59%. ^1H NMR (CDCl_3 , 200 MHz): δ 7.25-7.09 (m, 12 H), 6.60 (s, 2 H), 4.20 (t, J = 6.8 Hz, 3 H), 3.18 (t, J = 6.8 Hz, 3 H), 2.31 (s, 3 H), 2.11 (s, 6 H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 136.7, 136.3, 136.1, 135.9, 130.7, 130.3, 129.9, 129.3, 126.8, 126.2, 125.9, 125.2, 123.7, 119.9, 50.5, 35.6, 20.5, 19.2. MS ($\text{C}_{27}\text{H}_{27}\text{N}$): 365 (M^+). HRMS: Anal. Calcd. for $\text{C}_{27}\text{H}_{27}\text{N}$. 365.2144. Found: 365.2140. IR (KBr, cm^{-1}): 1537, 1459.

1-(2,5-dimethylphenethyl)-3,4-bis(2,5-dimethylphenyl)-1H-pyrrole (2g). Starting from 1 mmol **1g** to afford **2g** 96 mg in toluene; yield 71%; 87 mg in xylene, yield 64%. ^1H NMR (CDCl_3 , 200 MHz): δ 7.15-6.98 (m, 9 H), 6.60 (s, 2 H), 4.19 (t, J = 7.0 Hz, 3 H), 3.15 (t, J = 7.0 Hz, 3 H), 2.37 (s, 3 H), 2.29 (s, 9 H), 2.05 (s, 6 H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 136.5, 135.9, 135.4, 134.3, 133.0, 132.9, 131.4, 130.2, 129.7, 127.4, 126.6, 123.9, 119.8, 50.4, 35.7, 20.87, 20.86, 20.0, 18.7. MS ($\text{C}_{30}\text{H}_{33}\text{N}$): (M^+). HRMS: Anal. Calcd. For $\text{C}_{30}\text{H}_{33}\text{N}$: 407.2613. Found: 407.2614. IR (KBr, cm^{-1}): ν . 1536, 1449.

1-(4-fluorophenethyl)-3,4-bis(4-fluorophenyl)-1H-pyrrole (2h). Starting from 1 mmol **1h** to afford **2h** 52 mg in toluene; yield 41%; 57 mg in xylene, yield 45%,. ^1H NMR (CDCl_3 , 200 MHz): δ 7.26-6.91 (m, 12 H), 6.65 (s, 2 H), 4.10 (t, J = 7.1 Hz, 3 H), 3.09 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 164.2, 163.7, 159.3, 158.9, 133.8, 133.7, 131.63, 131.57, 130.2, 130.1, 129.8, 129.7, 122.2, 119.9, 115.6, 115.23, 115.20, 114.8, 51.4, 51.3, 37.4. MS ($\text{C}_{24}\text{H}_{18}\text{NF}_3$): 377 (M^+). HRMS: Anal. Calcd. For $\text{C}_{24}\text{H}_{18}\text{NF}_3$. 377.1391. Found: 377.1394. IR (KBr, cm^{-1}): ν . 1544, 1510.

1-(3-fluorophenethyl)-3,4-bis(3-fluorophenyl)-1H-pyrrole (2i). Starting from 1

mmol **1i** to afford **2i** 33 mg in toluene, yield 26%; 39 mg in xylene, yield 31%. ¹H NMR (CDCl₃, 200 MHz): δ 7.30-6.83 (m, 12 H), 6.68 (s, 2 H), 4.13 (t, *J* = 7.2 Hz, 3 H), 3.11 (t, *J* = 7.2 Hz, 3 H). ¹³C NMR (CDCl₃, 50 MHz): δ 165.2, 160.5, 160.3, 140.5, 140.3, 137.8, 137.6, 130.2, 130.0, 129.6, 129.5, 124.4, 124.3, 124.02, 123.97, 122.3, 120.5, 115.8, 115.4, 115.1, 114.7, 114.0, 113.6, 112.7, 112.3, 51.1, 37.88, 37.86. MS (C₂₄H₁₈NF₃): 377 (M⁺). HRMS: Anal. Calcd. For C₂₄H₁₈NF₃: 377.1391. Found: 377.1393. IR (KBr, cm⁻¹): ν.1614, 1586.

1-(3-(trifluoromethyl)phenethyl)-3,4-bis(3-(trifluoromethyl)phenyl)-1H-pyrrole (2j). Starting from 1 mmol **1j** to afford **2j** 58 mg in toluene, yield 33%; 71 mg in xylene, yield 40%. ¹H NMR (CDCl₃, 200 MHz): δ 7.57-7.26 (m, 12 H), 6.73 (s, 2 H), 4.18 (t, *J* = 7.0 Hz, 3 H), 3.19 (t, *J* = 7.0 Hz, 3 H). ¹³C NMR (CDCl₃, 50 MHz): δ 138.8, 136.0, 132.13, 132.10, 131.6, 131.5, 131.4, 131.0, 130.7, 130.3, 129.2, 128.6, 126.9, 126.7, 125.6, 125.53, 125.45, 125.4, 125.0, 124.83, 124.76, 124.7, 123.94, 123.86, 123.8, 123.7, 122.6, 122.54, 122.47, 122.4, 122.2, 121.5, 120.7, 51.2, 38.0. MS (C₂₇H₁₈NF₉): 527 (M⁺). HRMS: Anal. Calcd. For C₂₇H₁₈NF₉: 527.1296. Found: 527.1298. IR (KBr, cm⁻¹): ν.1332, 1324.

X-ray crystal data for 2b.Table 1. Crystal data and structure refinement for **2b**

Empirical formula	C ₂₇ H ₂₇ N O ₃
Formula weight	413.50
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 13.370(3) Å α = 90°. b = 16.407(3) Å β = 91.85(3)°. c = 10.255(2) Å γ = 90°.
Volume	2248.5(8) Å ³
Z	4
Density (calculated)	1.222 mg/m ³
Absorption coefficient	0.079 mm ⁻¹
F(000)	880
Crystal size	0.50 x 0.10 x 0.08 mm ³
Theta range for data collection	2.34 to 25.02
Index ranges	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -12 ≤ l ≤ 12
Reflections collected	12452
Independent reflections	3959 [R(int) = 0.0332]
Completeness to theta = 25.02	99.7 %
Absorption correction	Empirical
Max. and min. transmission	0.994 and 0.961
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3959 / 0 / 281
Goodness-of-fit on F ²	0.954
Final R indices [I > 2σ(I)]	R1 = 0.0392, wR2 = 0.0661
R indices (all data)	R1 = 0.1060, wR2 = 0.0723

Largest diff. peak and hole	0.142 and -0.126 e.Å ⁻³
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Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	3924(1)	7096(1)	699(1)	66(1)
O(2)	12805(1)	4989(1)	8220(1)	82(1)
O(3)	12705(1)	10484(1)	8559(1)	72(1)
N(1)	8884(1)	7766(1)	4722(2)	67(1)
C(1)	9390(1)	7088(1)	5114(2)	60(1)
C(2)	10144(1)	7317(1)	5984(2)	50(1)
C(3)	10085(1)	8183(1)	6128(2)	51(1)
C(4)	9288(2)	8430(2)	5327(2)	64(1)
C(5)	8006(1)	7756(1)	3827(2)	75(1)
C(6)	7076(1)	7463(1)	4483(2)	70(1)
C(7)	6197(1)	7376(2)	3532(2)	57(1)
C(8)	5601(2)	8028(1)	3188(2)	68(1)
C(9)	4830(1)	7967(1)	2252(2)	63(1)
C(10)	4659(1)	7233(1)	1645(2)	50(1)
C(11)	5233(1)	6568(1)	1991(2)	61(1)
C(12)	5998(2)	6643(1)	2924(2)	64(1)
C(13)	10835(1)	6723(1)	6605(2)	45(1)
C(14)	11210(1)	6076(1)	5892(2)	53(1)
C(15)	11852(2)	5502(1)	6453(2)	56(1)
C(16)	12145(2)	5570(1)	7755(2)	53(1)
C(17)	11770(1)	6195(1)	8493(2)	54(1)
C(18)	11115(1)	6759(1)	7920(2)	51(1)

C(19)	10769(2)	8755(1)	6816(2)	47(1)
C(20)	11773(1)	8576(1)	7051(2)	49(1)
C(21)	12435(1)	9127(1)	7633(2)	50(1)
C(22)	12110(2)	9889(1)	7979(2)	52(1)
C(23)	11118(2)	10089(1)	7749(2)	62(1)
C(24)	10461(2)	9534(1)	7185(2)	61(1)
C(25)	3482(1)	7797(1)	85(2)	78(1)
C(26)	13113(2)	5048(1)	9557(2)	97(1)
C(27)	13711(2)	10270(1)	8879(2)	86(1)

Table 3. Bond lengths [Å] and angles [deg] for **2b**.

O(1)-C(10)	1.376(2)
O(1)-C(25)	1.430(2)
O(2)-C(16)	1.374(2)
O(2)-C(26)	1.422(2)
O(3)-C(22)	1.382(2)
O(3)-C(27)	1.419(2)
N(1)-C(1)	1.356(2)
N(1)-C(4)	1.356(2)
N(1)-C(5)	1.467(2)
C(1)-C(2)	1.377(2)
C(1)-H(1)	0.9300
C(2)-C(3)	1.431(2)
C(2)-C(13)	1.473(2)
C(3)-C(4)	1.385(2)
C(3)-C(19)	1.475(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.511(2)

C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-C(7)	1.509(2)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.373(3)
C(7)-C(12)	1.376(3)
C(8)-C(9)	1.390(2)
C(8)-H(8)	0.9300
C(9)-C(10)	1.372(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.375(3)
C(11)-C(12)	1.383(2)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-C(18)	1.389(2)
C(13)-C(14)	1.392(2)
C(14)-C(15)	1.388(2)
C(14)-H(14)	0.9300
C(15)-C(16)	1.383(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.379(2)
C(17)-C(18)	1.391(2)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-C(20)	1.387(2)
C(19)-C(24)	1.399(3)
C(20)-C(21)	1.387(2)
C(20)-H(20)	0.9300
C(21)-C(22)	1.373(2)

C(21)-H(21)	0.9300
C(22)-C(23)	1.380(2)
C(23)-C(24)	1.379(3)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(10)-O(1)-C(25)	117.06(16)
C(16)-O(2)-C(26)	116.75(17)
C(22)-O(3)-C(27)	116.92(17)
C(1)-N(1)-C(4)	109.60(16)
C(1)-N(1)-C(5)	123.8(2)
C(4)-N(1)-C(5)	126.5(2)
N(1)-C(1)-C(2)	108.46(19)
N(1)-C(1)-H(1)	125.8
C(2)-C(1)-H(1)	125.8
C(1)-C(2)-C(3)	107.20(18)
C(1)-C(2)-C(13)	122.4(2)
C(3)-C(2)-C(13)	130.36(19)
C(4)-C(3)-C(2)	105.83(18)
C(4)-C(3)-C(19)	123.5(2)
C(2)-C(3)-C(19)	130.24(19)

N(1)-C(4)-C(3)	108.91(19)
N(1)-C(4)-H(4)	125.5
C(3)-C(4)-H(4)	125.5
N(1)-C(5)-C(6)	112.24(17)
N(1)-C(5)-H(5A)	109.2
C(6)-C(5)-H(5A)	109.2
N(1)-C(5)-H(5B)	109.2
C(6)-C(5)-H(5B)	109.2
H(5A)-C(5)-H(5B)	107.9
C(7)-C(6)-C(5)	112.17(17)
C(7)-C(6)-H(6A)	109.2
C(5)-C(6)-H(6A)	109.2
C(7)-C(6)-H(6B)	109.2
C(5)-C(6)-H(6B)	109.2
H(6A)-C(6)-H(6B)	107.9
C(8)-C(7)-C(12)	117.50(19)
C(8)-C(7)-C(6)	121.7(2)
C(12)-C(7)-C(6)	120.7(2)
C(7)-C(8)-C(9)	122.2(2)
C(7)-C(8)-H(8)	118.9
C(9)-C(8)-H(8)	118.9
C(10)-C(9)-C(8)	119.02(19)
C(10)-C(9)-H(9)	120.5
C(8)-C(9)-H(9)	120.5
O(1)-C(10)-C(11)	115.6(2)
O(1)-C(10)-C(9)	124.6(2)
C(11)-C(10)-C(9)	119.79(18)
C(10)-C(11)-C(12)	120.1(2)
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9

C(7)-C(12)-C(11)	121.3(2)
C(7)-C(12)-H(12)	119.3
C(11)-C(12)-H(12)	119.3
C(18)-C(13)-C(14)	116.87(19)
C(18)-C(13)-C(2)	122.5(2)
C(14)-C(13)-C(2)	120.57(18)
C(15)-C(14)-C(13)	121.89(18)
C(15)-C(14)-H(14)	119.1
C(13)-C(14)-H(14)	119.1
C(16)-C(15)-C(14)	119.8(2)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
O(2)-C(16)-C(15)	116.0(2)
O(2)-C(16)-C(17)	124.44(19)
C(15)-C(16)-C(17)	119.60(19)
C(16)-C(17)-C(18)	119.81(19)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1
C(17)-C(18)-C(13)	121.94(19)
C(17)-C(18)-H(18)	119.0
C(13)-C(18)-H(18)	119.0
C(20)-C(19)-C(24)	116.0(2)
C(20)-C(19)-C(3)	122.00(19)
C(24)-C(19)-C(3)	121.81(19)
C(21)-C(20)-C(19)	122.47(19)
C(21)-C(20)-H(20)	118.8
C(19)-C(20)-H(20)	118.8
C(22)-C(21)-C(20)	120.12(19)
C(22)-C(21)-H(21)	119.9
C(20)-C(21)-H(21)	119.9

C(21)-C(22)-O(3)	124.91(19)
C(21)-C(22)-C(23)	118.9(2)
O(3)-C(22)-C(23)	116.2(2)
C(24)-C(23)-C(22)	120.7(2)
C(24)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7
C(23)-C(24)-C(19)	121.8(2)
C(23)-C(24)-H(24)	119.1
C(19)-C(24)-H(24)	119.1
O(1)-C(25)-H(25A)	109.5
O(1)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
O(1)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
O(2)-C(26)-H(26A)	109.5
O(2)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
O(2)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
O(3)-C(27)-H(27A)	109.5
O(3)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
O(3)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5