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Regioselective Formation of α-Vinylpyrroles from the Ruthenium-Catalyzed Coupling Reaction of Pyrroles and Terminal Alkynes Involving C–H Bond Activation

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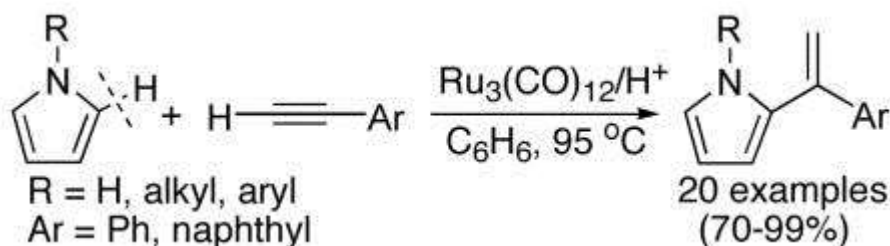
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Abstract:

The cationic ruthenium catalyst, $Ru_3(CO)_{12}/NH_4PF_6$, was found to be highly effective for the intermolecular coupling reaction of pyrroles and terminal alkynes to give *gem*-selective α-vinylpyrroles. The carbon isotope effect on the α-pyrrole carbon and the Hammett correlation from a series of *para*-substituted *N*-arylpyrroles (ρ = −0.90) indicate a rate-limiting C−C bond formation step of the coupling reaction.

C-Vinylated pyrroles are important building blocks for forming porphyrins and related nitrogen macrocycles as well as for serving as precursors for photoactive polymeric materials.[1] Compared to the traditional arene substitution methods using stoichiometric reagents, transition metal catalyzed C−H bond activation methods have been shown to exhibit a number of salient features such as increasing efficiency and reducing wasteful byproducts in introducing the vinyl group directly to pyrroles and related heteroarene compounds.[2] Pd catalysts have been found to be particularly versatile in mediating C−H oxidative coupling reactions of substituted pyrroles, pyridines and indoles, where the regioselectivity has often been found to be dictated by both steric and electronic nature of the arene substituents.[3] The direct oxidative arylation of indoles and quinoline-*N*-oxides has also been achieved by using Pd catalysts.[4] Cationic Ruallyl and -vinylidene complexes have been successfully utilized as catalysts for allylation and alkenylation of indoles and pyridine derivatives, respectively.[5] A novel regioselective insertion of alkynes to both Ar−H and Ar−CN bonds of *N*-protected 3-cyanoindoles and related heteroarenes has been achieved by using Ni-phosphine catalysts.[6] Though *gem*-selective oxidative coupling reaction of indolizines and alkenes has recently been accomplished by using Pd catalysts with bidentate nitrogen ligands,[7] lack of generally reliable *cis*- and *gem*-selective vinylation methods continues to be a major problem in catalytic C-H alkenylation methods for pyrroles and related nitrogen arene compounds, since the

formation of *trans*-selective vinyl products is normally favored for these catalytic reactions.
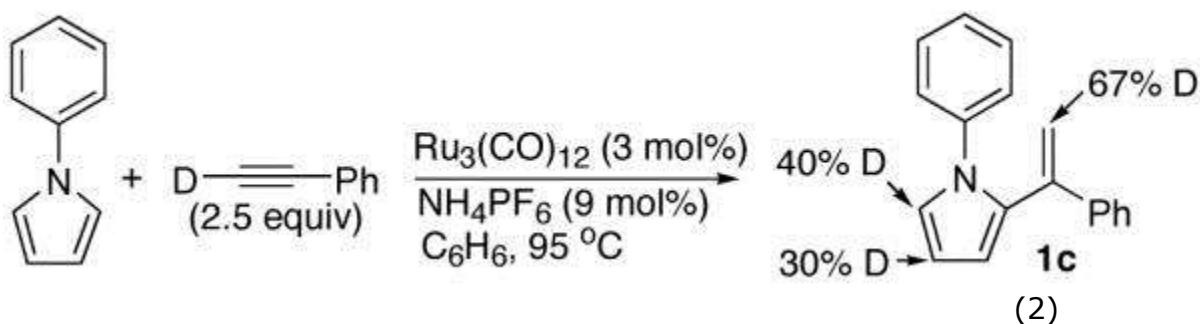
While exploring the scope of the ruthenium-catalyzed coupling reactions involving C−H bond activation, we have recently developed a number of regioselective cyclization methods from the coupling reaction of arylamines and pyrroles with terminal alkynes by using the cationic ruthenium catalytic system $Ru_3(CO)_{12}$/NH_4PF_6[8]. Here we report a highly regioselective formation of α-*gem*-vinylpyrroles from the ruthenium-catalyzed intermolecular coupling reaction of pyrroles and terminal alkynes.

$$(1)$$
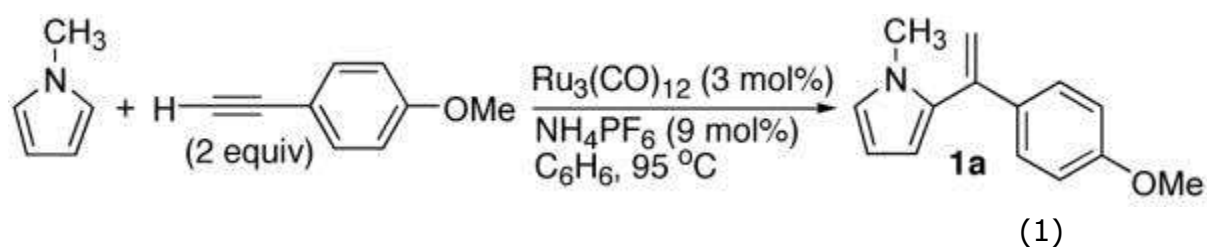
The treatment of *N*-methylpyrrole (1.0 mmol) with 4-ethynylanisole (2.0 mmol) in the presence of $Ru_3(CO)_{12}$/NH_4PF_6 (1:3, 3 mol % Ru) in benzene (3 mL) at 95 °C for 8 h cleanly produced the α-*gem*-vinylpyrrole product **1a** ([Eq 1](#)). The product was isolated in 99% yield after a simple silica gel column chromatography (CH_2Cl_2/hexanes), and was fully characterized by both spectroscopic methods and elemental analysis. The initial survey of ruthenium catalysts showed that both $Ru_3(CO)_{12}$ and NH_4PF_6 are essential for the catalytic activity. Other selected neutral and cationic ruthenium catalysts, such as $RuCl_3 \cdot 3H_2O$, $(PPh_3)_3RuHCl$, $[(COD)RuCl_2]_x$ $(PCy_3)_2(CO)RuHCl$ and $[(PCy_3)_2(CO)(CH_3CN)_2 RuH]^+BF^-_4$, were not effective in giving the coupling product under the similar reaction conditions.

The scope of the coupling reaction was explored by using $Ru_3(CO)_{12}$/NH_4PF_6 catalytic system ([Table 1](#)). Both *N*-alkyl- and *N*-arylpyrroles were found to react smoothly with aryl-substituted terminal alkynes to give the coupling products, in which arylalkynes with *para*-electron donating group were found to promote the coupling reaction. Neither aliphatic-substituted terminal alkynes nor internal alkynes gave the coupling products under the similar reaction

conditions. The regioselective α-insertion products **1q** and **1r** were obtained for 3-methylindole substrate (entries 17, 18), while the analogous coupling reaction of *N*-methylindole led to the 2:1 coupling products **1s** and **1t**, resulting from regioselective insertion to the β-carbon (entries 19, 20). The molecular structure of **1d** was also established by X-ray crystallography (Figure S3, Supporting Information).[9]

(2)

Table 1. Coupling reaction of pyrroles and indoles with terminal alkynes.[a]


[a]Reaction conditions: pyrrole/indole (1.0 mmol), alkyne (2.0 mmol), $Ru_3(CO)_{12}$/NH_4PF_6 (1:3, 3 mol % Ru), benzene (3 mL), 95 °C, 12-15 h.

We performed the following kinetic experiments to gain mechanistic insights on the coupling reaction. First, the deuterium labeling pattern was examined from the treatment of *N*-phenylpyrrole with DC≡CPh (2.5 equiv) and $Ru_3(CO)_{12}$/NH_4PF_6 (1:3, 3.0 mol% Ru) in benzene (3 mL) at 95 °C. The coupling product **1c** showed 67% D on the vinyl as well as 40% on the α-pyrrole positions as determined by both ^1H and ^2H NMR ([Eq 2](#)). Extensive H/D exchange at the β-carbon of pyrrole may be due to a direct metallation by the ruthenium catalyst during or after the coupling reaction. Conversely, the treatment of α,α-dideuterated *N*-phenylpyrrole with HC≡CC_6H_4-*p*-OMe (2 equiv) yielded the product with an extensive H/D exchange on both vinyl (33% D) and α-pyrrole positions. The extensive H/D exchange pattern on the vinyl positions is indicative of a rapid and reversible alkynyl and α-pyrrole C−H activation steps.

The deuterium isotope effect study also supported the notion of rapid H/D exchange steps. The rate of the reaction of *N*-phenylpyrrole and 2,5-d_2-*N*-phenylpyrrole with 4-ethynylanisole at 95 °C led to a virtually identical k_{obs} = 0.14 h^{-1}, which translated to k_{CH}/k_{CD} = 1.1±0.2. Similar experiments from the reaction of *N*-phenylpyrrole with HC≡CPh and DC≡CPh also gave a negligible isotope effect of k_{CH}/k_{CD} = 1.1±0.1 ([Figure S2, Supporting Information](#)).[9] These results indicate that the α-C−H bond activation of pyrrole is not the rate-limiting step for the catalytic reaction.

To discern the rate-limiting step of the coupling reaction, we next measured the carbon isotope effect from the coupling reaction of *N*-phenylpyrrole with HC≡CPh by employing Singleton's isotope measurement technique at natural abundance.[10] The most pronounced carbon isotope effect was observed on the α-pyrrole carbon when the ^{13}C ratio of unreacted *N*-phenylpyrrole isolated at 75% conversion was compared to that of the virgin sample (^{13}C(recovered)/^{13}C(virgin) at $C_α$ = 1.019, average of 3 runs) ([Eq 3](#)) ([Table S1, Supporting Information](#)). This result is consistent with the C−C bond rate-limiting step of the coupling reaction.

(3)
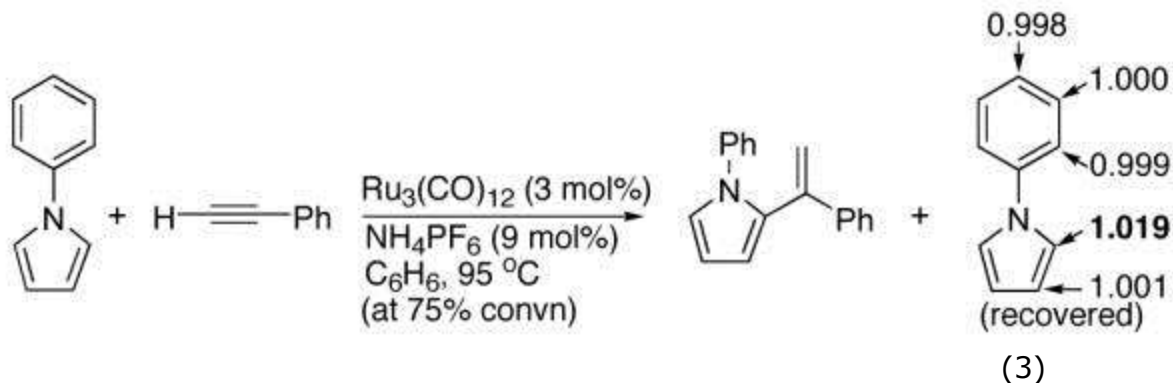
To examine the electronic influence on the pyrrole substrate, the Hammett plot was constructed from the correlation of the relative rates with σ_p for a series of *para*-substituted *N*-arylpyrroles *p*-X-$C_6H_4NC_4H_4$ (X = OMe, CH_3, H, Cl, F), which led to $\rho = -0.90$ ([Figure 1](#)). The promotional effect by electron-releasing group is indicative of a nucleophilic nature of the pyrrole group. An analogous correlation from the reaction of *N*-phenylpyrrole with *para*-substituted arylalkynes *p*-Y-$C_6H_4C\equiv CH$ (Y = OMe, CH_3, H, Br, F) resulted in a similar electronic promotional effect, but with a considerably less negative Hammett ρ value of -0.42. In this case, the negative ρ value suggests a considerable cationic character on the internal alkynyl carbon, which is stabilized by electron-releasing group of the aryl substituent. These results are consistent with the notion that the C–C bond formation step is promoted by a nucleophilic pyrrole substrate via a cationic transition state.
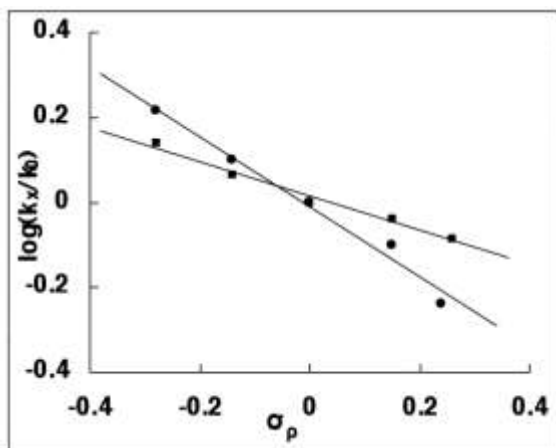
Figure 1. Hammett plots of the coupling reaction of *para*-substituted *p*-X-$C_6H_4NC_4H_4$ (X = OMe, CH_3, H, Cl, F) with PhC≡CH (●), and the reaction of *N*-phenylpyrrole with *p*-Y-$C_6H_4C\equiv CH$ (Y = OMe, CH_3, H, Br, F) (■).

A plausible mechanistic rationale for the coupling reaction is illustrated on the basis of these results (Scheme 1). We propose that the catalytically active cationic Ru-pyrrolyl species **2** is initially formed from an α-C–H insertion of pyrrole followed by the elimination of an arylalkene. In support of this hypothesis, the formation of styrene (3%) was observed from the catalytic coupling reaction of *N*-phenylpyrrole with PhC≡CH as detected by both ^{1}H NMR and GC-MS.[9] Both negligible k_H/k_D isotope effect and rapid H/D exchange patterns on the coupling reaction are consistent with a rapid and reversible C–H bond activation step. The observation of the pronounced α-carbon isotope effect on the pyrrole substrate provides a strong evidence for the rate-limiting C–C bond formation step. A relatively high negative Hammett ρ value from the correlation of *para*-substituted *N*-arylpyrroles indicates that the C–C bond formation step is promoted by the nucleophilic nature of the α-metallated pyrrolyl species **2**. The formation of *gem*-selective pyrrole product **1** can readily be rationalized by invoking a regioselective insertion of pyrrole to the internal alkynyl carbon in forming sterically less demanding Ru-vinyl species.[11] The migratory insertion of alkynes constitutes one of the well-known organometallic elementary reactions,[12] and C–C bond forming rate-determining step has been proposed in other ruthenium-catalyzed arene C–H coupling reactions.[13]
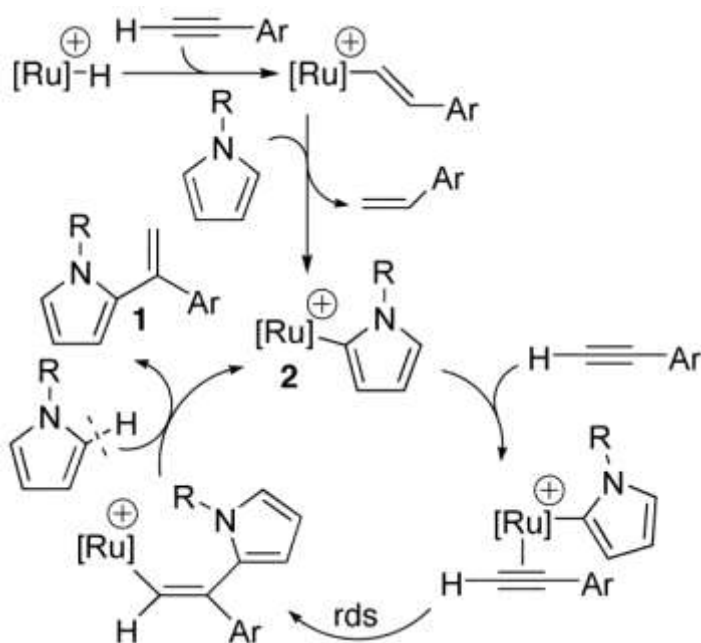
Scheme 1

In summary, the cationic ruthenium catalyst $Ru_3(CO)_{12}$/NH_4PF_6 was found to be highly effective for mediating the regioselective intermolecular coupling reaction of pyrroles and alkynes to give α-*gem*-vinylpyrroles. Both carbon isotope effect and Hammett study support a mechanism of the coupling reaction involving rate-limiting C–C bond formation step. The catalytic coupling reaction provides a reliable, atom-economical method for directly introducing synthetically useful *gem*-vinyl group to pyrroles and indoles.

Experimental Section

Representative Procedure of the Catalytic Reaction

In a glove box, $Ru_3(CO)_{12}$ (22 mg, 0.030 mmol), NH_4PF_6 (16 mg, 0.10 mmol), pyrrole (1.0 mmol) and an alkyne (2.0 mmol, 2 equiv) were dissolved in 3 mL benzene solution in a 25 mL Schlenk tube equipped with a magnetic stirring bar. The tube was brought out of the glove box, and was stirred in an oil bath set at 95 °C for 12-15 h. The tube was cooled to room temperature, and the crude product mixture was analyzed by GC-MS. The solvent was removed under a rotary evaporator, and analytically pure organic product was isolated by a column chromatography on silica gel (CH_2Cl_2/hexanes).

2-[1-(4-Methoxyphenyl)ethenyl-1-methylpyrrole

(1a) was synthesized from the reaction of *N*-methylpyrrole (81 mg) with 4-ethynylanisole (265 mg) following the general procedure. For **1a**: ^1H NMR (400 MHz, acetone-d_6) σ 7.2-6.9 (m, 4H), 6.7-6.1 (m, 3H), 5.46 (d, *J* = 1.6 Hz), 5.15 (d, *J* = 1.6 Hz), 3.81 (s, 3H), 3.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) σ 160.5, 142.4, 134.6, 134.4, 129.1, 124.4, 114.8, 113.8, 110.9, 107.9, 55.4, 35.1; HREI (*m/z*): Calcd for $C_{14}H_{15}NO$ (M$^+$) 213.1154. Found 213.1144.

Acknowledgment

Footnotes

Supporting Information Available: Experimental details, characterization data of the products and X-ray crystallographic data of **1d** (47 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] See Supporting Information for the experimental details.

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[11] As the reviewers pointed out, alternative mechanistic pathways involving cationic Ru-acetylide or direct metallation of pyrrole substrate, can also be considered (for example, see recently proposed mechanisms in ref. [8]). While these mechanistic paths cannot readily explain the *gem*-selective formation of the coupling products, they could not be rigorously ruled out on the basis of available data.

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Supplementary Material

Supporting Information

Regioselective Formation of α-Vinylpyrroles from the Ruthenium-Catalyzed Coupling

Reaction of Pyrroles and Terminal Alkynes Involving C-H Bond Activation

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General Information. All operations were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Tetrahydrofuran, benzene, hexanes and Et$_2$O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All organic substrates were received from commercial sources and used without further purification. The ^{1}H, ^{2}H, ^{13}C and ^{31}P NMR spectra were recorded on a 300 or 400 MHz FT-NMR spectrometer. Mass spectra were recorded from a GC/MS spectrometer. The conversion of organic products was measured from a GC spectrometer. The purity of organic products was determined from a combustion analysis.

Representative Procedure of the Catalytic Reaction. In a glove box, Ru$_3$(CO)$_{12}$ (22 mg, 0.030 mmol), NH$_4$PF$_6$ (16 mg, 0.10 mmol), pyrrole (1.0 mmol) and alkyne (2.0 mmol, 2 equiv) were dissolved in 3 mL benzene solution in a 25 mL Schlenk tube equipped with a magnetic stirring bar. The tube was brought out of the glove box, and was stirred in an oil bath set at 95 °C for 12-15 h. The tube was cooled to room temperature, and the crude product mixture was analyzed by GC-MS. The solvent was removed under a rotary evaporator, and analytically pure organic product was isolated by a column chromatography on silica gel (*n*-hexanes/CH$_2$Cl$_2$). Freshly distilled phenylacetylene (>99% pure by GC) was used in case of styrene detection and other kinetic experiments.

Deuterium Labeling Study. In a glove box, Ru$_3$(CO)$_{12}$ (22 mg, 0.030 mmol), NH$_4$PF$_6$ (16 mg, 0.10 mmol), pyrrole (1.0 mmol) and DC≡CPh (2.5 mmol, 2.5 equiv) were dissolved in 3 mL benzene solution in a 25 mL Schlenk tube equipped with a magnetic stirring bar. The tube was brought out of the glove box, and was stirred in an oil bath set at 95 °C for 12 h. The tube was cooled to room temperature, and the crude product mixture was analyzed by GC-MS. The solvent was removed under a rotary evaporator, and analytically pure organic product was isolated by a column chromatograph on silica gel (CH$_2$Cl$_2$/*n*-hexanes). The deuterium content of

2

the product **1c** was estimated by both ^{1}H and ^{2}H NMR (Figure S1).

Figure S1. Aromatic and vinyl regions of the ^{1}H and ^{2}H NMR of **1c**.
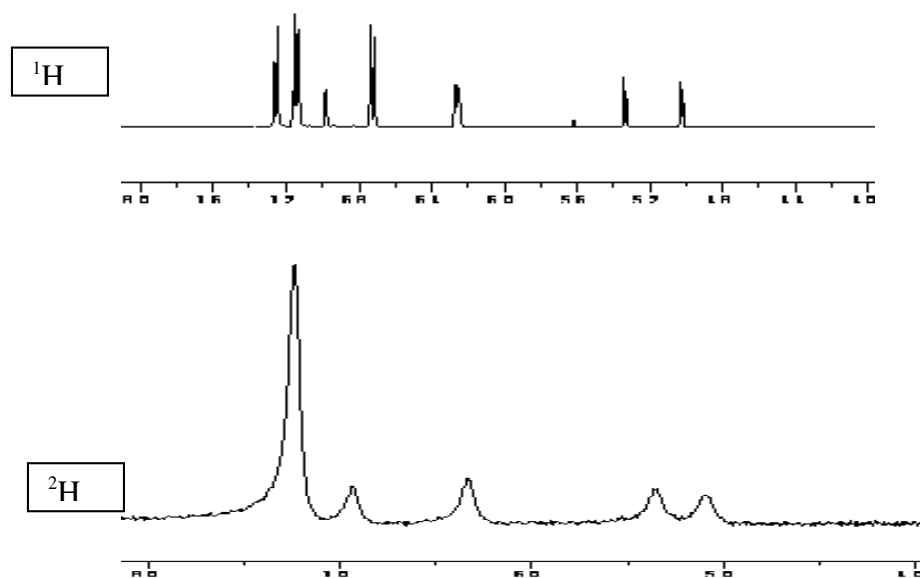
Deuterium Isotope Effect Study. In a glove box, Ru$_3$(CO)$_{12}$ (3 μmol), NH$_4$PF$_6$ (0.010 mmol), pyrrole (0.10 mmol) and DC≡CPh (0.25 mmol, 2.5 equiv) and hexamethylbenzene (26 mg, internal standard) were dissolved in benzene-d_6 (0.5 mL) solution in a J-Young NMR tube with a Teflon screw cap. The tube was brought out of the glove box, and was heated in an oil bath set at 95 °C. The reaction rate was measured by monitoring the appearance of the product peaks by ^{1}H NMR. The k_{obs} was estimated from a first-order plot of *ln*[product] vs reaction time by measuring the amount of the products against the internal standard (Figure S2).

3
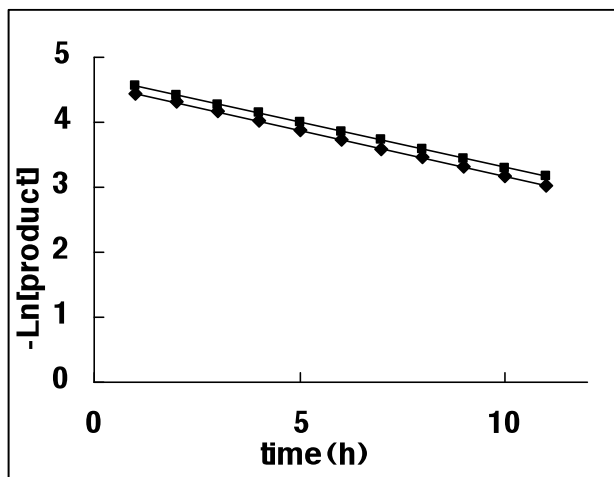
Figure S2. First order plots of *ln*[product] vs reaction time for *N*-phenylpyrrole (■) and *N*-phenylpyrrole-d_4 (◆).

Carbon Isotope Effect Study. In a glove box, $Ru_3(CO)_{12}$ (0.03 mmol), NH_4PF_6 (0.1 mmol), *N*-phenylpyrrole (1.0 mmol) and 4-ethynylanisole (2.5 mmol) were dissolved in 3 mL benzene solution in a 25 mL Schlenk tube equipped with a magnetic stirring bar. The tube was brought out of the glove box. The reaction tube was heated in an oil bath at 95 °C for 15 h. The tube was opened to air at room temperature, and the crude product mixture was analyzed by GC/MS (75% conversion). And the solvent was removed under a rotary evaporator, and the unreacted *N*-phenylpyrrole was isolated by a column chromatograph on silica gel (CH_2Cl_2/*n*-hexanes).

The ^{13}C NMR analysis of the recovered and virgin samples of N-phenylpyrrole was performed by following Singleton's ^{13}C NMR method (ref. 10, main text). The NMR sample of virgin and recovered *N*-phenylpyrrole was prepared identically by adding *N*-phenylpyrrole (75 mg) in $CDCl_3$ (0.5 mL) in a 5 mm high precision NMR tube. The ^{13}C{^{1}H} NMR spectra were recorded with H-decoupling and 45 degree pulses. A 60 s delay between pulses was imposed to minimize T_1 variations (d1 = 35 s, at = 1.0 s, np = 49020, nt = 6400). The average ^{13}C integration ratio of the recovered and virgin samples of *N*-phenylpyrrole are shown in Table S1.

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Table S1. Average ^{13}C Integration of the Recovered and Virgin Samples of *N*-Phenylpyrrole.

C#	Virgin	Recovered (75% conv.)	Recovered/Virgin	Change (%)
1	0.998(5)	1.017(5)	1.019(5)	1.90(5)
2	1.020(3)	1.025(3)	1.005(3)	0.49(3)
3	1.009(4)	1.008(4)	0.999(4)	0.11(4)
4(ref)	1.000	1.000	1.000	0.00
5	0.469(3)	0.468(3)	0.998(3)	0.22(3)

C#	Virgin	Recovered (70% conv.)	Recovered/Virgin	Change (%)
1	0.998(5)	1.011(5)	1.013(5)	1.30(5)
2	1.020(3)	1.025(3)	1.005(3)	0.47(3)
3	1.009(4)	1.007(4)	0.998(4)	0.19(4)
4(ref)	1.000	1.000	1.000	0.00
5	0.469(3)	0.468(3)	0.998(3)	0.24(3)
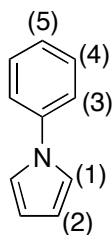
Characterization Data of Organic Products

For **1a**: ^{1}H NMR (400 MHz, acetone-d_6) δ 7.2-6.9 (m, 4H), 6.7-6.1 (m, 3H), 5.46 (d, J = 1.6 Hz), 5.15 (d, J = 1.6 Hz), 3.81 (s, 3H), 3.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 160.5, 142.4, 134.6, 134.4, 129.1, 124.4, 114.8, 113.8, 110.9, 107.9, 55.4, 35.1; HREI (*m/z*): Calcd for $C_{14}H_{15}NO$ (M$^+$) 213.1154. Found 213.1144.

For **1b**: ^{1}H NMR (400 MHz, acetone-d_6) δ 7.7-7.1 (m, 6H), 6.8-6.3 (m, 3H), 5.65 (d, J = 1.6 Hz), 5.33 (d, J = 1.6 Hz), 3.39 (s, 3H), 3.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 159.5, 143.1, 137.7, 135.9, 134.9, 131.0, 130.2, 128.2, 127.2, 125.0, 120.4, 115.8, 111.5, 108.4, 107.0, 56.1, 35.6; GC-MS *m/z* = 263 (M$^+$); Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51. Found C, 81.98; H, 6.59.

For **1c**: ^{1}H NMR (400 MHz, acetone-d_6) δ 7.3-6.7 (m, 10H), 7.0-6.3 (m, 3H), 5.34 (d, J = 1.6 Hz) 5.03 (d, J = 1.6 Hz); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 141.6, 148.4, 140.9, 134.4, 134.2, 129.7, 129.3, 127.2, 124.7, 125.6, 114.2, 114.1, 113.4, 109.6; GC-MS *m/z* = 245 (M$^+$); Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16. Found C, 87.99; H, 6.19.

For **1d**: ^{1}H NMR (400 MHz, acetone-d_6) δ 7.3-6.7 (m, 9H), 7.0-6.3 (m, 3H), 5.34 (d, J = 1.6 Hz), 5.03 (d, J = 1.6 Hz), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 160.3, 142.4, 141.6, 134.4, 134.2, 129.7, 129.3, 127.2, 125.6, 124.7, 114.2, 114.1, 113.4, 109.6, 55.6; GC-MS *m/z* = 275 (M$^+$); Anal. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22. Found C, 82.92; H, 6.27.

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For **1e**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.3-6.3 (m, 11H), 5.21 (d, *J* = 1.6 Hz), 4.90 (d, *J* = 1.6 Hz), 3.71 (s, 3H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 159.3, 140.7, 138.3, 136.2, 133.8, 129.4, 128.7, 125.0, 124.0, 114.2, 113.4, 112.5, 108.5, 55.3, 21.1; GC-MS *m/z* = 289 (M$^+$); Anal. Calcd for C$_{20}$H$_{19}$NO: C, 83.01; H, 6.62. Found C, 82.92; H, 6.71.

For **1f**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.2-6.2 (m, 11H), 5.31 (d, *J* = 1.6 Hz), 4.98 (d, *J* = 1.6 Hz), 3.73 (s, 3H), 3.72 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, acetone-*d$_6$*) δ 160.3, 159.1, 142.1, 134.7, 134.4, 134.3, 129.4, 127.0, 124.8, 114.7 114.1, 114.0, 112.8, 109.1, 55.7, 55.5; HREI (*m/z*): Calcd for C$_{14}$H$_{15}$NO (M$^+$) 305.1416. Found 305.1408.

For **1g**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.3-6.3 (m, 11H), 5.41 (d, *J* = 1.6 Hz), 5.18 (d, *J* = 1.6 Hz), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 159.3, 140.7, 139.3, 134.0, 133.4, 132.0, 129.0, 128.6, 123.8, 114.6, 113.5, 113.0, 109.2, 55.3 (OCH$_3$); GC-MS *m/z* = 309 (M$^+$); Anal. Calcd for C$_{19}$H$_{16}$ClNO: C, 73.66; H, 5.21. Found C, 73.79; H, 5.15.

For **1h**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.2-6.4 (m, 11H), 5.43 (d, *J* = 1.6 Hz), 5.18 (d, *J* = 1.6 Hz), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 162.2 (C$_{Ar}$), 159.8, 140.7, 136.8, 134.4, 133.4, 128.5, 126.6, 128.6, 123.8, 115.6, 114.6, 113.5, 112.6, 108.9, 55.3; GC-MS *m/z* = 293 (M$^+$); Anal. Calcd for C$_{19}$H$_{16}$NOF: C, 77.80; H, 5.50. Found C, 77.42; H, 5.47.

For **1i**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.7-7.15 (m, 11H), 7.0-6.3 (m, 3H), 5.48 (d, *J* = 1.6 Hz), 5.28 (d, *J* = 1.6 Hz), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 157.9, 141.3, 140.8, 136.4, 134.2, 134.0, 129.9, 128.9, 127.8, 126.7, 126.6, 126.2, 125.3, 124.2, 119.0, 115.7, 112.9,

108.9, 105.7, 56.1; GC-MS m/z = 325 (M$^+$); Anal. Calcd for C$_{23}$H$_{19}$NO: C, 84.89; H, 5.89. Found C, 85.09; H, 6.05.

For **1j**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.7-6.3 (m, 13H), 5.51 (d, J = 1.6 Hz), 5.15 (d, J = 1.6 Hz), 3.89 (s, 3H), 3.66 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 159.4, 159.3, 143.0, 137.4, 135.6, 134.8, 130.9 129.9, 127.7, 127.5, 127.4, 127.0, 125.3, 120.0, 115.9, 115.1, 113.4, 109.7, 106.9, 56.1; GC-MS m/z = 355 (M$^+$); Anal. Calcd for C$_{24}$H$_{21}$NO$_2$: C, 81.10; H, 5.96. Found C, 80.88; H, 6.02.

For **1k**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.4-7.3 (m, 5H), 6.8-6.2 (m, 3H), 5.62 (d, J = 1.6 Hz), 5.41 (d, J = 1.6 Hz), 3.82 (t, J = 7.0 Hz), 2.43 (t, J = 7.0 Hz); ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6) δ 141.9, 141.3, 133.5, 129.2, 128.6, 127.6, 123.3, 118.0, 116.7, 111.7, 108.7, 43.5, 19.9; GC-MS m/z = 222 (M$^+$); Anal. Calcd for C$_{15}$H$_{14}$N$_2$: C, 81.05; H, 6.35. Found C, 81.25; H, 6.30.

For **1l**: ^{1}H NMR (400 MHz, acetone-d_6) δ 7.3-7.1 (m, 4H), 6.9-6.1 (m, 3H), 5.62 (d, J = 1.6 Hz), 5.40 (d, J = 1.6 Hz), 3.91 (t, J = 7.0 Hz), 2.64 (t, J = 7.0 Hz), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 141.9, 138.8, 138.7, 133.9, 130.1, 127.7, 123.3, 118.3, 116.1, 111.7, 108.7, 43.5, 21.2, 19.9; GC-MS m/z = 236 (M$^+$); Anal. Calcd for C$_{16}$H$_{16}$N$_2$: C, 81.32; H, 6.82. Found C, 81.47; H, 7.02.

For **1m**: ^{1}H NMR (400 MHz, acetone-d_6) δ 7.25-7.0 (m, 4H), 6.9-6.1 (m, 3H), 5.56 (d, J = 1.6 Hz), 5.26 (d, J = 1.6 Hz), 3.91 (t, J = 7.0 Hz, 2H), 3.81 (s, 3H), 2.64 (t, J = 7.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 160.3, 141.1, 133.5, 133.4, 128.4, 114.3, 123.0, 117.8,

114.3, 111.2, 108.3, 55.4, 43.5, 19.9; GC-MS m/z = 252 (M$^+$); Anal. Calcd for C$_{16}$H$_{16}$N$_2$O: C, 76.16; H, 6.40. Found C, 75.74; H, 6.22.

For **1n**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.25-6.8 (m, 4H), 6.7-6.2 (m, 3H), 5.45 (d, J = 1.6 Hz), 5.21 (d, J = 1.6 Hz), 3.88 (t, J = 7.0 Hz, 2H), 2.99 (s, 3H), 2.46 (t, J = 7.0 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 150.7, 140.6, 133.8, 128.1, 127.9, 122.2, 117.5, 113.7, 112.3, 111.4, 108.6, 43.2, 40.6, 19.9; GC-MS m/z = 265 (M$^+$); Anal. Calcd for C$_{17}$H$_{19}$N$_3$: C, 76.95; H, 7.22. Found C, 76.88; H, 7.29.

For **1o**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.7-7.1 (m, 6H), 6.8-6.3 (m, 3H), 5.72 (d, J = 1.6 Hz), 5.45 (d, J = 1.6 Hz), 3.93 (s, 3H), 3.84 (t, J = 7.0 Hz, 2H), 2.46 (t, J = 7.0 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6) δ 159.2, 142.1, 136.7, 135.6, 134.0, 130.7, 128.1, 126.7, 126.2, 123.5, 120.1, 118.3, 116.7, 111.9, 109.0, 106.6, 55.7, 43.8, 20.2; GC-MS m/z = 302 (M$^+$); Anal. Calcd for C$_{20}$H$_{18}$N$_2$O: C, 79.43; H, 6.00. Found C, 79.10; H, 5.90.

For **1p**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.4-7.2 (m, 6H), 6.60 (d, J = 2.0 Hz), 6.00 (d, J = 1.6 Hz), 5.36 (d, J = 1.6 Hz), 3.22 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 193.2, 140.3, 139.8, 135.5, 128.6 128.4, 128.2, 126.8, 124.8, 117.5, 110.4, 43.9, 35.6, 27.0, 21.1; GC-MS m/z = 225 (M$^+$); Anal. Calcd for C$_{15}$H$_{15}$NO: C, 79.97; H, 6.71. Found C, 79.89; H, 6.48

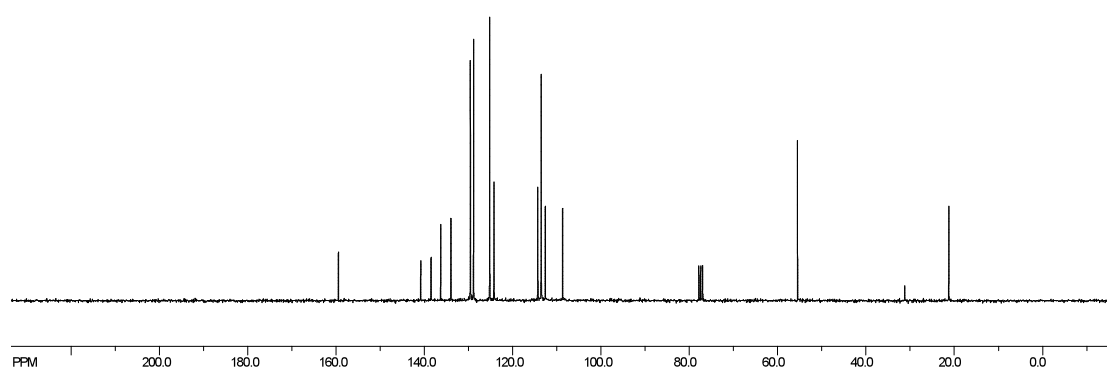For **1q**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.80 (s, 1H), 7.6-6.8 (m, 8H), 5.62 (d, J = 1.6 Hz), 5.42 (d, J = 1.6 Hz), 3.86 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 160.0, 141.1, 135.5, 134.2, 133.0, 129.8, 129.4, 122.6, 119.6, 119.2, 115.1, 114.1, 110.9, 110.8, 55.6, 10.1; GC-MS m/z = 288 (M$^+$); Anal. Calcd for C$_{18}$H$_{17}$NO: C, 82.09; H, 6.50. Found C, 81.99; H, 6.42.

For **1r**: [superscript 1]H NMR (300 MHz, CDCl$_3$) δ 7.80 (s, 1H), 7.6-7.0 (m, 10H), 5.67 (d, J = 1.6 Hz), 5.42 (d, J = 1.6 Hz), 3.86 (s, 3H), 2.26 (s, 3H); [superscript 13]C{[superscript 1]H} NMR (75 MHz, CDCl$_3$) δ 160.0, 141.1, 137.4, 135.5, 134.2, 133.0, 130.9, 129.8, 129.4, 127.7, 127.5, 127.4, 127.0, 122.6, 119.6, 119.2, 115.1, 114.1, 110.9, 110.8, 55.6, 10.1; GC-MS m/z = 313 (M[superscript +]); Anal. Calcd for C$_{22}$H$_{19}$NO: C, 84.31; H, 6.11. Found C, 84.49; H, 6.14.

For **1s**: [superscript 1]H NMR (300 MHz, CDCl$_3$) δ 7.5-6.9 (m, 13H), 6.53 (s, 2H), 3.70 (s, 3H), 2.40 (s, 3H); [superscript 13]C{[superscript 1]H} NMR (75 MHz, CDCl$_3$) δ 148.6, 138.0, 128.4, 128.0, 127.1, 126.0, 123.6, 122.5, 121.3, 118.6, 109.5, 43.9, 32.9, 29.4; GC-MS m/z = 363 (M[superscript +]).

For **1t**: [superscript 1]H NMR (400 MHz, CDCl$_3$) δ 7.5-6.9 (m, 12H), 6.53 (s, 1H), 3.70 (s, 6H), 2.40 (s, 3H); [superscript 13]C{[superscript 1]H} NMR (100 MHz, CDCl$_3$) δ 145.4, 138.0, 135.1, 128.4, 128.0, 127.1, 123.6, 122.5, 118.6, 109.5, 43.9, 32.9, 29.4, 21.1; GC-MS m/z = 378 (M[superscript +]); Anal. Calcd for C$_{18}$H$_{17}$N: C, 85.67; H, 6.92. Found C, 85.69; H, 6.82.

The ¹H and ¹³C NMR Spectra of Organic Products

The ^{1}H and ^{13}C NMR Spectra of Organic Products

1c

PPM   11.2   10.8   10.4   10.0   9.6   9.2   8.8   8.4   8.0   7.6   7.2   6.8   6.4   6.0   5.6   5.2   4.8   4.4   4.0   3.6

5.028   4.192   2.972   1.110   0.999   1.054

PPM   180.0   170.0   160.0   150.0   140.0   130.0   120.0   110.0   100.0   90.0   80.0   70.0   60.0

13

1d

PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4

3.696
2.767
0.989
1.911
1.889
1.027
0.999
3.059

159.6200
159.6030
159.5850
141.4058
141.3869
141.3824
140.8742
133.6288
133.4142
133.3980
129.9719
128.9471
128.5827
128.8960
128.4597
124.9156
124.8710
124.8527
124.8475
124.8143
123.9289
113.4780
113.4540
113.4086
113.3096
112.6590
108.8484

54.7818

PPM 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0.0

14

CH₃ ... (structure label) **1e** OMe

1g

PPM scale (¹H NMR): 11.0, 10.0, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0

Integration values: 5.968, 1.066, 1.982, 1.926, 0.999, 1.018, 2.989

¹³C peaks: 159.5340, 159.5119, 140.7076, 140.6937, 139.3825, 139.3854, 134.0644, 133.4800, 132.1184, 129.0515, 128.6859, 126.3107, 123.8605, 114.6705, 113.6040, 113.0947, 113.0780, 109.2784, 109.2626, 55.4896

PPM scale (¹³C NMR): 220.0, 200.0, 180.0, 160.0, 140.0, 120.0, 100.0, 80.0, 60.0, 40.0, 20.0, 0.0

17

1h

F

OMe

PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0

3.811

2.888
1.913

1.925

1.008
1.000

2.996

162.1989
159.7538
159.2991

140.6978
136.8312
136.8012
134.0248
133.4038
128.5361
126.6919
126.6062
123.8622

115.6261
115.4000
114.3498
113.3724
112.5540
108.8509

55.1776

PPM 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0.0

18

1i

1j

1k

1I

CN

CH₃

PPM 10.0   9.0   8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0   0.0

3.903 1.002 1.875 1.006 0.999 2.091 2.011 3.004

205.6902
205.6358

141.3212
138.2265
138.0854
133.2879
129.4567
127.0654
122.8056
117.6816
115.4812
111.1739
108.2898

43.0547

29.6985
29.5060
29.3469
29.3135
29.1480
29.1209
28.8283
20.6034
19.4802

PPM 200.0   180.0   160.0   140.0   120.0   100.0   80.0   60.0   40.0   20.0   0.0

1m

CN

N

OMe

CN

1n

NMe₂

PPM 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4

1.962 3.292 1.801 1.002 1.100 1.981 6.134 1.890

150.7597
140.7986
134.0511
130.8099
128.3373
128.2182
127.9890
122.3016
117.5974
113.8012
113.0560
112.4025
111.4347
108.7025
77.7798
77.3575
76.9347
43.3179
40.8485
20.0205

PPM 220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0.0

CN

1o

OMe

PPM   10.0   9.0   8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0

3.200
1.010
2.035
0.986
1.000
0.977
1.012
0.989
3.121
2.030
2.067

205.5619

158.4711

141.4307
136.0230
134.9095
133.2722
129.9895
129.0543
127.3490
126.0167
125.5065
122.8073
119.3818
117.6593
116.0469

111.2498
108.3371
105.9406

55.0459

43.0732
29.9870
29.8221
29.7420
29.5601
29.4859
29.3816
29.3300
29.2310
29.1025
29.0777
28.8754
28.8840
28.7919
28.7780
28.7209
28.5210
28.4641
19.4823

PPM   220.0   200.0   180.0   160.0   140.0   120.0   100.0   80.0   60.0   40.0   20.0   0.0

25

1q

H
N
CH₃

PPM 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

1.039
1.088
4.753
1.945
1.023
0.999
2.930

159.9777

141.0541
135.1547
134.2165
133.0023
129.8072
129.3516

122.6283
119.5807
119.2190

115.0529
114.0725
110.9432
110.8595

77.7331
77.3109
76.8897

55.6117

10.1417

PPM 220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0.0

1s

1t

Figure S3. Molecular Structure of **1d**.

Table S2. Crystal data and structure refinement for **1d**.

Identification code	yis
Empirical formula	$C_{19}H_{17}NO$
Formula weight	275.34
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 19.3228(3) Å $\quad\quad$ $\alpha = 90°$.
	b = 17.3708(2) Å $\quad\quad$ $\beta = 96.4510(10)°$.
	c = 8.83840(10) Å $\quad\quad$ $\gamma = 90°$.
Volume	2947.85(7) $Å^3$
Z	8
Density (calculated)	1.241 Mg/m^3
Absorption coefficient	0.596 mm^{-1}
F(000)	1168
Crystal size	0.50 x 0.40 x 0.20 mm^3
Theta range for data collection	3.43 to 67.84°.
Index ranges	$-23<=h<=23, 0<=k<=20, 0<=l<=10$
Reflections collected	24399
Independent reflections	5215 [R(int) = 0.0186]
Completeness to theta = 67.84°	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8901 and 0.7548
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5215 / 0 / 516
Goodness-of-fit on F^2	0.993
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0768
R indices (all data)	R1 = 0.0335, wR2 = 0.0787
Extinction coefficient	0.00105(10)
Largest diff. peak and hole	0.194 and -0.165 e.$Å^{-3}$

Table S3. Atomic coordinates x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **1d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3480(1)	7628(1)	9746(1)	28(1)
N(1)	6234(1)	9937(1)	5960(1)	18(1)
C(1)	6344(1)	8258(1)	6921(1)	21(1)
C(2)	5885(1)	8763(1)	7376(1)	19(1)
C(3)	5979(1)	9601(1)	7212(1)	19(1)
C(4)	5891(1)	10184(1)	8234(1)	21(1)
C(5)	6093(1)	10883(1)	7599(1)	21(1)
C(6)	6295(1)	10719(1)	6203(1)	20(1)
C(7)	5256(1)	8500(1)	8053(1)	18(1)
C(8)	4625(1)	8894(1)	7783(1)	21(1)
C(9)	4018(1)	8621(1)	8308(1)	23(1)
C(10)	4039(1)	7945(1)	9149(1)	22(1)
C(11)	4669(1)	7552(1)	9469(1)	22(1)
C(12)	5263(1)	7822(1)	8919(1)	20(1)
C(13)	2827(1)	8015(1)	9445(2)	34(1)
C(14)	6313(1)	9588(1)	4523(1)	18(1)
C(15)	6938(1)	9665(1)	3903(1)	24(1)
C(16)	6997(1)	9365(1)	2464(1)	27(1)
C(17)	6438(1)	8987(1)	1664(1)	23(1)
C(18)	5818(1)	8908(1)	2299(1)	21(1)
C(19)	5752(1)	9209(1)	3730(1)	19(1)
O(1A)	1658(1)	2636(1)	5753(1)	27(1)
N(1A)	349(1)	6261(1)	9270(1)	20(1)
C(1A)	1836(1)	6109(1)	8467(1)	26(1)
C(2A)	1302(1)	5656(1)	7949(1)	20(1)
C(3A)	578(1)	5929(1)	7986(1)	20(1)
C(4A)	55(1)	6016(1)	6811(1)	23(1)
C(5A)	-501(1)	6415(1)	7379(1)	24(1)
C(6A)	-313(1)	6554(1)	8883(1)	23(1)
C(7A)	1406(1)	4878(1)	7318(1)	19(1)
C(8A)	2015(1)	4679(1)	6692(1)	20(1)

C(9A)	2119(1)	3941(1)	6151(1)	21(1)
C(10A)	1610(1)	3381(1)	6238(1)	21(1)
C(11A)	999(1)	3567(1)	6854(1)	23(1)
C(12A)	898(1)	4305(1)	7371(1)	21(1)
C(13A)	2249(1)	2427(1)	5011(2)	29(1)
C(14A)	672(1)	6225(1)	10802(1)	20(1)
C(15A)	937(1)	5530(1)	11406(1)	22(1)
C(16A)	1220(1)	5496(1)	12917(1)	25(1)
C(17A)	1235(1)	6147(1)	13831(1)	26(1)
C(18A)	965(1)	6834(1)	13226(1)	27(1)
C(19A)	687(1)	6879(1)	11710(1)	23(1)

_____

Table S4. Bond lengths [Å] and angles [°] for **1d**.

_____

O(1)-C(10)	1.3710(14)
O(1)-C(13)	1.4280(15)
N(1)-C(6)	1.3782(14)
N(1)-C(3)	1.3905(14)
N(1)-C(14)	1.4314(13)
C(1)-C(2)	1.3402(16)
C(1)-H(1A)	0.974(15)
C(1)-H(1B)	0.977(14)
C(2)-C(3)	1.4768(15)
C(2)-C(7)	1.4850(15)
C(3)-C(4)	1.3794(15)
C(4)-C(5)	1.4118(16)
C(4)-H(4)	0.969(13)
C(5)-C(6)	1.3654(16)
C(5)-H(5)	0.966(13)
C(6)-H(6)	0.970(14)
C(7)-C(8)	1.3957(15)
C(7)-C(12)	1.4031(15)
C(8)-C(9)	1.3910(16)
C(8)-H(8)	0.975(13)
C(9)-C(10)	1.3884(16)
C(9)-H(9)	0.977(14)
C(10)-C(11)	1.3959(16)
C(11)-C(12)	1.3793(16)
C(11)-H(11)	0.970(14)
C(12)-H(12)	0.980(13)
C(13)-H(13A)	0.977(15)
C(13)-H(13B)	1.001(15)
C(13)-H(13C)	1.011(16)
C(14)-C(15)	1.3864(16)
C(14)-C(19)	1.3901(15)
C(15)-C(16)	1.3917(16)
C(15)-H(15)	0.971(14)
C(16)-C(17)	1.3883(17)

C(16)-H(16)	0.977(15)
C(17)-C(18)	1.3863(16)
C(17)-H(17)	0.970(14)
C(18)-C(19)	1.3870(15)
C(18)-H(18)	0.985(14)
C(19)-H(19)	0.986(13)
O(1A)-C(10A)	1.3701(13)
O(1A)-C(13A)	1.4250(14)
N(1A)-C(6A)	1.3834(14)
N(1A)-C(3A)	1.3900(14)
N(1A)-C(14A)	1.4274(14)
C(1A)-C(2A)	1.3372(16)
C(1A)-H(1C)	0.969(15)
C(1A)-H(1D)	0.990(14)
C(2A)-C(3A)	1.4815(15)
C(2A)-C(7A)	1.4842(15)
C(3A)-C(4A)	1.3734(16)
C(4A)-C(5A)	1.4168(16)
C(4A)-H(4A)	0.945(13)
C(5A)-C(6A)	1.3600(17)
C(5A)-H(5A)	0.934(14)
C(6A)-H(6A)	0.951(14)
C(7A)-C(8A)	1.3988(15)
C(7A)-C(12A)	1.4013(15)
C(8A)-C(9A)	1.3907(16)
C(8A)-H(8A)	0.963(14)
C(9A)-C(10A)	1.3902(16)
C(9A)-H(9A)	0.966(13)
C(10A)-C(11A)	1.3926(15)
C(11A)-C(12A)	1.3819(16)
C(11A)-H(11A)	0.965(14)
C(12A)-H(12A)	0.977(14)
C(13A)-H(13D)	0.997(15)
C(13A)-H(13E)	0.996(15)
C(13A)-H(13F)	1.006(14)
C(14A)-C(19A)	1.3893(16)

C(14A)-C(15A)	1.3947(15)
C(15A)-C(16A)	1.3859(17)
C(15A)-H(15A)	0.969(13)
C(16A)-C(17A)	1.3883(17)
C(16A)-H(16A)	0.979(14)
C(17A)-C(18A)	1.3842(18)
C(17A)-H(17A)	0.970(14)
C(18A)-C(19A)	1.3883(17)
C(18A)-H(18A)	0.982(14)
C(19A)-H(19A)	0.944(14)
C(10)-O(1)-C(13)	117.23(10)
C(6)-N(1)-C(3)	108.77(9)
C(6)-N(1)-C(14)	122.69(9)
C(3)-N(1)-C(14)	127.70(9)
C(2)-C(1)-H(1A)	121.6(8)
C(2)-C(1)-H(1B)	121.6(8)
H(1A)-C(1)-H(1B)	116.8(11)
C(1)-C(2)-C(3)	121.50(10)
C(1)-C(2)-C(7)	121.25(10)
C(3)-C(2)-C(7)	117.25(9)
C(4)-C(3)-N(1)	107.06(9)
C(4)-C(3)-C(2)	129.36(10)
N(1)-C(3)-C(2)	123.43(9)
C(3)-C(4)-C(5)	108.17(10)
C(3)-C(4)-H(4)	125.0(7)
C(5)-C(4)-H(4)	126.8(7)
C(6)-C(5)-C(4)	107.42(9)
C(6)-C(5)-H(5)	124.2(8)
C(4)-C(5)-H(5)	128.4(8)
C(5)-C(6)-N(1)	108.57(10)
C(5)-C(6)-H(6)	130.9(8)
N(1)-C(6)-H(6)	120.4(8)
C(8)-C(7)-C(12)	117.38(10)
C(8)-C(7)-C(2)	121.24(10)
C(12)-C(7)-C(2)	121.29(9)

C(9)-C(8)-C(7)	121.89(10)
C(9)-C(8)-H(8)	118.2(8)
C(7)-C(8)-H(8)	119.8(8)
C(10)-C(9)-C(8)	119.48(10)
C(10)-C(9)-H(9)	120.9(8)
C(8)-C(9)-H(9)	119.6(8)
O(1)-C(10)-C(9)	124.72(10)
O(1)-C(10)-C(11)	115.60(10)
C(9)-C(10)-C(11)	119.66(10)
C(12)-C(11)-C(10)	120.20(10)
C(12)-C(11)-H(11)	121.6(8)
C(10)-C(11)-H(11)	118.2(8)
C(11)-C(12)-C(7)	121.36(10)
C(11)-C(12)-H(12)	120.6(7)
C(7)-C(12)-H(12)	118.0(7)
O(1)-C(13)-H(13A)	111.3(8)
O(1)-C(13)-H(13B)	110.5(8)
H(13A)-C(13)-H(13B)	108.3(12)
O(1)-C(13)-H(13C)	106.0(9)
H(13A)-C(13)-H(13C)	110.8(12)
H(13B)-C(13)-H(13C)	110.0(12)
C(15)-C(14)-C(19)	120.77(10)
C(15)-C(14)-N(1)	119.62(9)
C(19)-C(14)-N(1)	119.54(9)
C(14)-C(15)-C(16)	119.29(10)
C(14)-C(15)-H(15)	119.7(8)
C(16)-C(15)-H(15)	121.0(8)
C(17)-C(16)-C(15)	120.26(11)
C(17)-C(16)-H(16)	120.6(8)
C(15)-C(16)-H(16)	119.1(8)
C(18)-C(17)-C(16)	119.95(10)
C(18)-C(17)-H(17)	119.4(8)
C(16)-C(17)-H(17)	120.6(8)
C(17)-C(18)-C(19)	120.27(10)
C(17)-C(18)-H(18)	120.0(8)
C(19)-C(18)-H(18)	119.7(8)

C(18)-C(19)-C(14)	119.46(10)
C(18)-C(19)-H(19)	119.8(7)
C(14)-C(19)-H(19)	120.7(7)
C(10A)-O(1A)-C(13A)	118.07(9)
C(6A)-N(1A)-C(3A)	108.72(9)
C(6A)-N(1A)-C(14A)	123.01(9)
C(3A)-N(1A)-C(14A)	127.68(9)
C(2A)-C(1A)-H(1C)	122.2(8)
C(2A)-C(1A)-H(1D)	120.6(8)
H(1C)-C(1A)-H(1D)	117.2(11)
C(1A)-C(2A)-C(3A)	119.92(10)
C(1A)-C(2A)-C(7A)	122.24(10)
C(3A)-C(2A)-C(7A)	117.83(9)
C(4A)-C(3A)-N(1A)	107.26(9)
C(4A)-C(3A)-C(2A)	129.46(10)
N(1A)-C(3A)-C(2A)	122.64(9)
C(3A)-C(4A)-C(5A)	108.02(10)
C(3A)-C(4A)-H(4A)	125.7(8)
C(5A)-C(4A)-H(4A)	126.2(8)
C(6A)-C(5A)-C(4A)	107.64(10)
C(6A)-C(5A)-H(5A)	124.9(8)
C(4A)-C(5A)-H(5A)	127.4(8)
C(5A)-C(6A)-N(1A)	108.35(10)
C(5A)-C(6A)-H(6A)	131.9(8)
N(1A)-C(6A)-H(6A)	119.7(8)
C(8A)-C(7A)-C(12A)	117.42(10)
C(8A)-C(7A)-C(2A)	121.90(10)
C(12A)-C(7A)-C(2A)	120.66(9)
C(9A)-C(8A)-C(7A)	121.64(10)
C(9A)-C(8A)-H(8A)	118.6(8)
C(7A)-C(8A)-H(8A)	119.8(8)
C(10A)-C(9A)-C(8A)	119.64(10)
C(10A)-C(9A)-H(9A)	120.9(7)
C(8A)-C(9A)-H(9A)	119.5(7)
O(1A)-C(10A)-C(9A)	124.71(10)
O(1A)-C(10A)-C(11A)	115.58(10)

C(9A)-C(10A)-C(11A)	119.71(10)
C(12A)-C(11A)-C(10A)	120.08(10)
C(12A)-C(11A)-H(11A)	122.0(8)
C(10A)-C(11A)-H(11A)	117.9(8)
C(11A)-C(12A)-C(7A)	121.50(10)
C(11A)-C(12A)-H(12A)	119.0(8)
C(7A)-C(12A)-H(12A)	119.5(8)
O(1A)-C(13A)-H(13D)	111.2(8)
O(1A)-C(13A)-H(13E)	105.4(8)
H(13D)-C(13A)-H(13E)	110.3(11)
O(1A)-C(13A)-H(13F)	112.2(8)
H(13D)-C(13A)-H(13F)	108.8(11)
H(13E)-C(13A)-H(13F)	108.8(11)
C(19A)-C(14A)-C(15A)	120.30(10)
C(19A)-C(14A)-N(1A)	119.38(10)
C(15A)-C(14A)-N(1A)	120.23(10)
C(16A)-C(15A)-C(14A)	119.52(11)
C(16A)-C(15A)-H(15A)	120.9(7)
C(14A)-C(15A)-H(15A)	119.5(7)
C(15A)-C(16A)-C(17A)	120.44(11)
C(15A)-C(16A)-H(16A)	119.4(8)
C(17A)-C(16A)-H(16A)	120.1(8)
C(18A)-C(17A)-C(16A)	119.66(11)
C(18A)-C(17A)-H(17A)	119.5(8)
C(16A)-C(17A)-H(17A)	120.8(8)
C(17A)-C(18A)-C(19A)	120.63(11)
C(17A)-C(18A)-H(18A)	120.7(8)
C(19A)-C(18A)-H(18A)	118.7(8)
C(18A)-C(19A)-C(14A)	119.44(11)
C(18A)-C(19A)-H(19A)	120.1(8)
C(14A)-C(19A)-H(19A)	120.5(8)

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Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1d**. The anisotropic displacement factor exponent takes the form: $-2p^2[\,h^2a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	24(1)	23(1)	40(1)	-1(1)	8(1)	-3(1)
N(1)	20(1)	17(1)	18(1)	-2(1)	2(1)	0(1)
C(1)	26(1)	19(1)	19(1)	0(1)	2(1)	2(1)
C(2)	22(1)	19(1)	14(1)	-1(1)	-2(1)	1(1)
C(3)	18(1)	20(1)	18(1)	0(1)	1(1)	1(1)
C(4)	22(1)	21(1)	20(1)	-2(1)	3(1)	1(1)
C(5)	21(1)	17(1)	25(1)	-5(1)	0(1)	1(1)
C(6)	19(1)	16(1)	24(1)	0(1)	1(1)	-1(1)
C(7)	23(1)	16(1)	15(1)	-4(1)	-1(1)	0(1)
C(8)	27(1)	16(1)	21(1)	0(1)	2(1)	2(1)
C(9)	23(1)	20(1)	26(1)	-3(1)	1(1)	3(1)
C(10)	24(1)	20(1)	23(1)	-6(1)	4(1)	-4(1)
C(11)	28(1)	16(1)	20(1)	-1(1)	1(1)	-1(1)
C(12)	23(1)	17(1)	18(1)	-2(1)	-1(1)	2(1)
C(13)	22(1)	32(1)	48(1)	-4(1)	5(1)	-2(1)
C(14)	22(1)	15(1)	18(1)	2(1)	2(1)	2(1)
C(15)	22(1)	24(1)	25(1)	-3(1)	3(1)	-3(1)
C(16)	25(1)	30(1)	28(1)	-3(1)	10(1)	-2(1)
C(17)	30(1)	21(1)	19(1)	-2(1)	5(1)	1(1)
C(18)	24(1)	17(1)	20(1)	0(1)	-1(1)	0(1)
C(19)	20(1)	16(1)	21(1)	2(1)	3(1)	1(1)
O(1A)	24(1)	23(1)	37(1)	-7(1)	10(1)	0(1)
N(1A)	19(1)	18(1)	23(1)	1(1)	4(1)	3(1)
C(1A)	21(1)	25(1)	31(1)	-4(1)	4(1)	1(1)
C(2A)	20(1)	22(1)	18(1)	2(1)	4(1)	1(1)
C(3A)	21(1)	16(1)	23(1)	1(1)	4(1)	-1(1)
C(4A)	22(1)	23(1)	24(1)	1(1)	2(1)	-1(1)
C(5A)	19(1)	23(1)	31(1)	5(1)	0(1)	2(1)
C(6A)	20(1)	19(1)	31(1)	3(1)	6(1)	4(1)
C(7A)	19(1)	22(1)	15(1)	2(1)	0(1)	1(1)
C(8A)	19(1)	22(1)	20(1)	3(1)	3(1)	-2(1)

C(9A)	17(1)	26(1)	19(1)	2(1)	4(1)	4(1)
C(10A)	22(1)	21(1)	19(1)	-1(1)	1(1)	3(1)
C(11A)	20(1)	22(1)	28(1)	-1(1)	5(1)	-3(1)
C(12A)	18(1)	24(1)	22(1)	0(1)	5(1)	2(1)
C(13A)	26(1)	28(1)	34(1)	-9(1)	7(1)	4(1)
C(14A)	17(1)	22(1)	22(1)	1(1)	6(1)	0(1)
C(15A)	20(1)	20(1)	26(1)	0(1)	5(1)	1(1)
C(16A)	21(1)	26(1)	28(1)	5(1)	4(1)	1(1)
C(17A)	23(1)	35(1)	21(1)	1(1)	5(1)	-5(1)
C(18A)	30(1)	26(1)	26(1)	-6(1)	11(1)	-5(1)
C(19A)	25(1)	20(1)	27(1)	1(1)	9(1)	1(1)

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Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **1d**.

	x	y	z	U(eq)
H(1A)	6274(7)	7705(8)	6996(15)	30(3)
H(1B)	6764(7)	8428(8)	6498(15)	30(3)
H(4)	5726(6)	10114(7)	9220(15)	21(3)
H(5)	6086(7)	11395(8)	8025(14)	24(3)
H(6)	6430(7)	11055(8)	5411(15)	25(3)
H(8)	4599(7)	9368(8)	7189(14)	23(3)
H(9)	3587(7)	8915(8)	8103(15)	27(3)
H(11)	4673(7)	7087(8)	10081(15)	28(3)
H(12)	5708(7)	7552(7)	9150(14)	22(3)
H(13A)	2858(7)	8546(9)	9808(16)	35(4)
H(13B)	2671(8)	8022(8)	8326(18)	36(4)
H(13C)	2486(8)	7711(9)	9996(17)	40(4)
H(15)	7326(7)	9930(8)	4475(15)	27(3)
H(16)	7437(8)	9421(8)	2029(16)	33(4)
H(17)	6472(7)	8787(8)	649(16)	28(3)
H(18)	5415(7)	8659(8)	1715(15)	29(3)
H(19)	5303(7)	9171(7)	4154(14)	23(3)
H(1C)	2317(8)	5948(8)	8468(15)	32(4)
H(1D)	1753(7)	6632(8)	8848(15)	31(3)
H(4A)	72(7)	5854(7)	5795(15)	24(3)
H(5A)	-926(7)	6557(8)	6841(15)	27(3)
H(6A)	-555(7)	6788(8)	9643(15)	28(3)
H(8A)	2369(7)	5061(8)	6610(14)	24(3)
H(9A)	2546(7)	3822(7)	5730(14)	20(3)
H(11A)	654(7)	3168(8)	6894(15)	26(3)
H(12A)	465(7)	4426(8)	7793(15)	27(3)
H(13D)	2280(7)	2746(8)	4082(17)	32(4)
H(13E)	2178(7)	1876(8)	4728(15)	32(3)
H(13F)	2698(7)	2479(8)	5701(16)	30(3)
H(15A)	905(6)	5072(8)	10775(14)	23(3)

H(16A)	1385(7)	5003(8)	13352(15)	26(3)
H(17A)	1428(7)	6127(8)	14891(16)	29(3)
H(18A)	960(7)	7296(8)	13864(15)	29(3)
H(19A)	505(7)	7350(8)	11307(14)	23(3)

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Table S7. Torsion angles [°] for **1d**.

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C(6)-N(1)-C(3)-C(4)	-0.68(12)
C(14)-N(1)-C(3)-C(4)	-170.29(10)
C(6)-N(1)-C(3)-C(2)	-176.56(9)
C(14)-N(1)-C(3)-C(2)	13.83(16)
C(1)-C(2)-C(3)-C(4)	-136.62(12)
C(7)-C(2)-C(3)-C(4)	43.99(15)
C(1)-C(2)-C(3)-N(1)	38.29(15)
C(7)-C(2)-C(3)-N(1)	-141.11(10)
N(1)-C(3)-C(4)-C(5)	0.16(12)
C(2)-C(3)-C(4)-C(5)	175.71(10)
C(3)-C(4)-C(5)-C(6)	0.43(13)
C(4)-C(5)-C(6)-N(1)	-0.85(12)
C(3)-N(1)-C(6)-C(5)	0.96(12)
C(14)-N(1)-C(6)-C(5)	171.20(9)
C(1)-C(2)-C(7)-C(8)	-144.56(11)
C(3)-C(2)-C(7)-C(8)	34.83(14)
C(1)-C(2)-C(7)-C(12)	31.91(15)
C(3)-C(2)-C(7)-C(12)	-148.70(10)
C(12)-C(7)-C(8)-C(9)	-1.85(16)
C(2)-C(7)-C(8)-C(9)	174.76(10)
C(7)-C(8)-C(9)-C(10)	1.26(17)
C(13)-O(1)-C(10)-C(9)	1.51(16)
C(13)-O(1)-C(10)-C(11)	179.87(10)
C(8)-C(9)-C(10)-O(1)	178.83(10)
C(8)-C(9)-C(10)-C(11)	0.53(16)
O(1)-C(10)-C(11)-C(12)	179.88(9)
C(9)-C(10)-C(11)-C(12)	-1.67(16)
C(10)-C(11)-C(12)-C(7)	1.05(16)
C(8)-C(7)-C(12)-C(11)	0.69(15)
C(2)-C(7)-C(12)-C(11)	-175.92(10)
C(6)-N(1)-C(14)-C(15)	60.27(14)
C(3)-N(1)-C(14)-C(15)	-131.44(11)
C(6)-N(1)-C(14)-C(19)	-116.57(11)
C(3)-N(1)-C(14)-C(19)	51.72(15)

C(19)-C(14)-C(15)-C(16)	0.71(16)
N(1)-C(14)-C(15)-C(16)	-176.09(10)
C(14)-C(15)-C(16)-C(17)	-0.55(18)
C(15)-C(16)-C(17)-C(18)	0.05(18)
C(16)-C(17)-C(18)-C(19)	0.30(17)
C(17)-C(18)-C(19)-C(14)	-0.14(16)
C(15)-C(14)-C(19)-C(18)	-0.37(16)
N(1)-C(14)-C(19)-C(18)	176.43(9)
C(6A)-N(1A)-C(3A)-C(4A)	-0.15(12)
C(14A)-N(1A)-C(3A)-C(4A)	171.15(10)
C(6A)-N(1A)-C(3A)-C(2A)	171.45(10)
C(14A)-N(1A)-C(3A)-C(2A)	-17.25(16)
C(1A)-C(2A)-C(3A)-C(4A)	121.66(13)
C(7A)-C(2A)-C(3A)-C(4A)	-57.98(15)
C(1A)-C(2A)-C(3A)-N(1A)	-47.93(15)
C(7A)-C(2A)-C(3A)-N(1A)	132.43(10)
N(1A)-C(3A)-C(4A)-C(5A)	0.61(12)
C(2A)-C(3A)-C(4A)-C(5A)	-170.23(11)
C(3A)-C(4A)-C(5A)-C(6A)	-0.85(13)
C(4A)-C(5A)-C(6A)-N(1A)	0.75(13)
C(3A)-N(1A)-C(6A)-C(5A)	-0.38(12)
C(14A)-N(1A)-C(6A)-C(5A)	-172.18(10)
C(1A)-C(2A)-C(7A)-C(8A)	-24.72(16)
C(3A)-C(2A)-C(7A)-C(8A)	154.91(10)
C(1A)-C(2A)-C(7A)-C(12A)	153.36(11)
C(3A)-C(2A)-C(7A)-C(12A)	-27.00(14)
C(12A)-C(7A)-C(8A)-C(9A)	-0.47(15)
C(2A)-C(7A)-C(8A)-C(9A)	177.68(10)
C(7A)-C(8A)-C(9A)-C(10A)	-0.41(16)
C(13A)-O(1A)-C(10A)-C(9A)	-4.43(16)
C(13A)-O(1A)-C(10A)-C(11A)	175.51(10)
C(8A)-C(9A)-C(10A)-O(1A)	-179.54(10)
C(8A)-C(9A)-C(10A)-C(11A)	0.52(16)
O(1A)-C(10A)-C(11A)-C(12A)	-179.69(10)
C(9A)-C(10A)-C(11A)-C(12A)	0.25(17)
C(10A)-C(11A)-C(12A)-C(7A)	-1.17(17)

C(8A)-C(7A)-C(12A)-C(11A)	1.26(16)
C(2A)-C(7A)-C(12A)-C(11A)	-176.91(10)
C(6A)-N(1A)-C(14A)-C(19A)	-50.38(14)
C(3A)-N(1A)-C(14A)-C(19A)	139.45(11)
C(6A)-N(1A)-C(14A)-C(15A)	126.18(11)
C(3A)-N(1A)-C(14A)-C(15A)	-43.98(15)
C(19A)-C(14A)-C(15A)-C(16A)	-0.46(16)
N(1A)-C(14A)-C(15A)-C(16A)	-177.00(10)
C(14A)-C(15A)-C(16A)-C(17A)	0.61(17)
C(15A)-C(16A)-C(17A)-C(18A)	-0.03(17)
C(16A)-C(17A)-C(18A)-C(19A)	-0.70(17)
C(17A)-C(18A)-C(19A)-C(14A)	0.85(17)
C(15A)-C(14A)-C(19A)-C(18A)	-0.26(16)
N(1A)-C(14A)-C(19A)-C(18A)	176.30(10)

_____

Symmetry transformations used to generate equivalent atoms:

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;
_chemical_name_common           ?
_chemical_melting_point         ?
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 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
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 'H'   'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'   'N'   0.0311   0.0180
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'   'O'   0.0492   0.0322
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M   'P 21/c'

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

_cell_length_a                  19.3228(3)
_cell_length_b                  17.3708(2)
_cell_length_c                  8.83840(10)
_cell_angle_alpha               90.00
_cell_angle_beta                96.4510(10)
_cell_angle_gamma               90.00
_cell_volume                    2947.85(7)
_cell_formula_units_Z           8
_cell_measurement_temperature   100(2)
_cell_measurement_reflns_used   6910
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_exptl_crystal_size_min         0.20
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_exptl_absorpt_correction_type  multi-scan
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_exptl_absorpt_correction_T_min    0.7548
_exptl_absorpt_correction_T_max    0.8901
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;
 SADABS. Program for empirical absorption correction of
 area-detector data. University of Goetingen. Germany.
 Sheldrick, G. M. 1996
;

_exptl_special_details
;
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;

_diffrn_ambient_temperature         100(2)
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_diffrn_measurement_method          '\w scans'
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_diffrn_reflns_number               24399
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_diffrn_reflns_av_sigmaI/netI       0.0128
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_diffrn_reflns_theta_min            3.43
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_reflns_threshold_expression        >2sigma(I)

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_computing_cell_refinement          'SAINT v7.23A (Bruker, 2005)'
_computing_data_reduction           'SADABS-2004/1 (Bruker, 2005)'
_computing_structure_solution       'XS/SHELXTL v6.12 (Bruker, 2001)'
_computing_structure_refinement     'SHELXL-97 v.97-2 (Sheldrick, 1993-1997)'
_computing_molecular_graphics       'XP v5.1 (Bruker, 1998)'
_computing_publication_material     'XCIF v6.12 (Bruker, 2001)'

_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_matrix_type              full
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_atom_sites_solution_secondary     difmap
_atom_sites_solution_hydrogens     difmap
_refine_ls_hydrogen_treatment      refall
_refine_ls_extinction_method       SHELXL
_refine_ls_extinction_coef         0.00105(10)
_refine_ls_extinction_expression
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_refine_ls_number_reflns           5215
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_refine_ls_R_factor_all            0.0335
_refine_ls_R_factor_gt             0.0310
_refine_ls_wR_factor_ref           0.0787
_refine_ls_wR_factor_gt            0.0768
_refine_ls_goodness_of_fit_ref     0.993
_refine_ls_restrained_S_all        0.993
_refine_ls_shift/su_max            0.001
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N1 N 0.62341(4) 0.99374(5) 0.59599(10) 0.01821(19) Uani 1 1 d . . .
C1 C 0.63437(6) 0.82583(7) 0.69206(12) 0.0213(2) Uani 1 1 d . . .
C2 C 0.58847(6) 0.87626(6) 0.73761(11) 0.0186(2) Uani 1 1 d . . .
C3 C 0.59785(5) 0.96010(6) 0.72123(12) 0.0185(2) Uani 1 1 d . . .
C4 C 0.58907(6) 1.01838(6) 0.82335(12) 0.0208(2) Uani 1 1 d . . .
C5 C 0.60925(6) 1.08834(6) 0.75986(13) 0.0211(2) Uani 1 1 d . . .
C6 C 0.62947(5) 1.07194(6) 0.62027(13) 0.0197(2) Uani 1 1 d . . .
C7 C 0.52561(6) 0.84996(6) 0.80530(11) 0.0184(2) Uani 1 1 d . . .
C8 C 0.46250(6) 0.88942(6) 0.77834(12) 0.0214(2) Uani 1 1 d . . .
C9 C 0.40185(6) 0.86211(6) 0.83075(13) 0.0231(2) Uani 1 1 d . . .
C10 C 0.40393(6) 0.79449(6) 0.91489(12) 0.0221(2) Uani 1 1 d . . .
C11 C 0.46686(6) 0.75515(6) 0.94688(12) 0.0215(2) Uani 1 1 d . . .
C12 C 0.52632(6) 0.78221(6) 0.89189(12) 0.0196(2) Uani 1 1 d . . .
C13 C 0.28269(7) 0.80150(8) 0.94454(18) 0.0341(3) Uani 1 1 d . . .
C14 C 0.63134(6) 0.95883(6) 0.45225(12) 0.0182(2) Uani 1 1 d . . .
C15 C 0.69379(6) 0.96652(7) 0.39033(13) 0.0236(2) Uani 1 1 d . . .
C16 C 0.69970(6) 0.93648(7) 0.24637(14) 0.0269(3) Uani 1 1 d . . .
C17 C 0.64378(6) 0.89867(6) 0.16636(13) 0.0233(2) Uani 1 1 d . . .
C18 C 0.58176(6) 0.89080(6) 0.22991(12) 0.0207(2) Uani 1 1 d . . .
C19 C 0.57518(6) 0.92087(6) 0.37297(12) 0.0190(2) Uani 1 1 d . . .
H1A H 0.6274(7) 0.7705(8) 0.6996(15) 0.030(3) Uiso 1 1 d . . .
H1B H 0.6764(7) 0.8428(8) 0.6498(15) 0.030(3) Uiso 1 1 d . . .
H4 H 0.5726(6) 1.0114(7) 0.9220(15) 0.021(3) Uiso 1 1 d . . .
H5 H 0.6086(7) 1.1395(8) 0.8025(14) 0.024(3) Uiso 1 1 d . . .
H6 H 0.6430(7) 1.1055(8) 0.5411(15) 0.025(3) Uiso 1 1 d . ^ .
H8 H 0.4599(7) 0.9368(8) 0.7189(14) 0.023(3) Uiso 1 1 d . . .
H9 H 0.3587(7) 0.8915(8) 0.8103(15) 0.027(3) Uiso 1 1 d . . .
H11 H 0.4673(7) 0.7087(8) 1.0081(15) 0.028(3) Uiso 1 1 d . . .
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H12 H 0.5708(7) 0.7552(7) 0.9150(14) 0.022(3) Uiso 1 1 d . . .
H13A H 0.2858(7) 0.8546(9) 0.9808(16) 0.035(4) Uiso 1 1 d . . .
H13B H 0.2671(8) 0.8022(8) 0.8326(18) 0.036(4) Uiso 1 1 d . . .
H13C H 0.2486(8) 0.7711(9) 0.9996(17) 0.040(4) Uiso 1 1 d . . .
H15 H 0.7326(7) 0.9930(8) 0.4475(15) 0.027(3) Uiso 1 1 d . . .
H16 H 0.7437(8) 0.9421(8) 0.2029(16) 0.033(4) Uiso 1 1 d . . .
H17 H 0.6472(7) 0.8787(8) 0.0649(16) 0.028(3) Uiso 1 1 d . . .
H18 H 0.5415(7) 0.8659(8) 0.1715(15) 0.029(3) Uiso 1 1 d . . .
H19 H 0.5303(7) 0.9171(7) 0.4154(14) 0.023(3) Uiso 1 1 d . . .
O1A O 0.16585(4) 0.26361(5) 0.57525(10) 0.02739(19) Uani 1 1 d . . .
N1A N 0.03489(5) 0.62612(5) 0.92703(10) 0.0200(2) Uani 1 1 d . . .
C1A C 0.18364(6) 0.61088(7) 0.84670(14) 0.0258(3) Uani 1 1 d . . .
C2A C 0.13023(6) 0.56557(6) 0.79488(12) 0.0199(2) Uani 1 1 d . . .
C3A C 0.05780(6) 0.59287(6) 0.79856(12) 0.0199(2) Uani 1 1 d . . .
C4A C 0.00549(6) 0.60157(6) 0.68111(13) 0.0230(2) Uani 1 1 d . . .
C5A C -0.05011(6) 0.64148(7) 0.73785(14) 0.0244(2) Uani 1 1 d . . .
C6A C -0.03133(6) 0.65536(6) 0.88829(13) 0.0229(2) Uani 1 1 d . . .
C7A C 0.14055(5) 0.48777(6) 0.73175(11) 0.0188(2) Uani 1 1 d . . .
C8A C 0.20146(6) 0.46785(6) 0.66919(12) 0.0204(2) Uani 1 1 d . . .
C9A C 0.21189(6) 0.39405(6) 0.61513(12) 0.0207(2) Uani 1 1 d . . .
C10A C 0.16102(6) 0.33812(6) 0.62382(12) 0.0207(2) Uani 1 1 d . . .
C11A C 0.09990(6) 0.35669(7) 0.68540(13) 0.0229(2) Uani 1 1 d . . .
C12A C 0.08982(6) 0.43049(6) 0.73705(12) 0.0214(2) Uani 1 1 d . . .
C13A C 0.22490(6) 0.24274(7) 0.50112(15) 0.0288(3) Uani 1 1 d . . .
C14A C 0.06721(5) 0.62252(6) 1.08024(12) 0.0199(2) Uani 1 1 d . . .
C15A C 0.09368(6) 0.55296(6) 1.14061(13) 0.0220(2) Uani 1 1 d . . .
C16A C 0.12196(6) 0.54963(7) 1.29167(13) 0.0250(2) Uani 1 1 d . . .
C17A C 0.12345(6) 0.61474(7) 1.38306(13) 0.0262(3) Uani 1 1 d . . .
C18A C 0.09650(6) 0.68338(7) 1.32260(13) 0.0268(3) Uani 1 1 d . . .
C19A C 0.06869(6) 0.68792(7) 1.17105(13) 0.0234(2) Uani 1 1 d . . .
H1C H 0.2317(8) 0.5948(8) 0.8468(15) 0.032(4) Uiso 1 1 d . . .
H1D H 0.1753(7) 0.6632(8) 0.8848(15) 0.031(3) Uiso 1 1 d . . .
H4A H 0.0072(7) 0.5854(7) 0.5795(15) 0.024(3) Uiso 1 1 d . . .
H5A H -0.0926(7) 0.6557(8) 0.6841(15) 0.027(3) Uiso 1 1 d . . .
H6A H -0.0555(7) 0.6788(8) 0.9643(15) 0.028(3) Uiso 1 1 d . . .
H8A H 0.2369(7) 0.5061(8) 0.6610(14) 0.024(3) Uiso 1 1 d . . .
H9A H 0.2546(7) 0.3822(7) 0.5730(14) 0.020(3) Uiso 1 1 d . . .
H11A H 0.0654(7) 0.3168(8) 0.6894(15) 0.026(3) Uiso 1 1 d . . .
H12A H 0.0465(7) 0.4426(8) 0.7793(15) 0.027(3) Uiso 1 1 d . . .
H13D H 0.2280(7) 0.2746(8) 0.4082(17) 0.032(4) Uiso 1 1 d . . .
H13E H 0.2178(7) 0.1876(8) 0.4728(15) 0.032(3) Uiso 1 1 d . . .
H13F H 0.2698(7) 0.2479(8) 0.5701(16) 0.030(3) Uiso 1 1 d . . .
H15A H 0.0905(6) 0.5072(8) 1.0775(14) 0.023(3) Uiso 1 1 d . . .
H16A H 0.1385(7) 0.5003(8) 1.3352(15) 0.026(3) Uiso 1 1 d . . .
H17A H 0.1428(7) 0.6127(8) 1.4891(16) 0.029(3) Uiso 1 1 d . . .
H18A H 0.0960(7) 0.7296(8) 1.3864(15) 0.029(3) Uiso 1 1 d . . .
H19A H 0.0505(7) 0.7350(8) 1.1307(14) 0.023(3) Uiso 1 1 d . . .

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N1 0.0195(4) 0.0166(4) 0.0184(4) -0.0015(3) 0.0018(3) -0.0002(3)
C1 0.0258(6) 0.0188(6) 0.0193(5) 0.0001(4) 0.0025(4) 0.0015(4)
C2 0.0224(5) 0.0187(5) 0.0138(5) -0.0006(4) -0.0017(4) 0.0005(4)
C3 0.0181(5) 0.0196(5) 0.0177(5) 0.0000(4) 0.0010(4) 0.0007(4)
C4 0.0224(5) 0.0205(5) 0.0195(5) -0.0021(4) 0.0027(4) 0.0013(4)
C5 0.0209(5) 0.0170(5) 0.0249(6) -0.0048(4) 0.0001(4) 0.0006(4)
C6 0.0185(5) 0.0162(5) 0.0241(6) -0.0003(4) 0.0006(4) -0.0012(4)
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C7 0.0234(5) 0.0162(5) 0.0149(5) -0.0040(4) -0.0006(4) 0.0001(4)
C8 0.0269(6) 0.0163(5) 0.0208(5) -0.0003(4) 0.0015(4) 0.0018(4)
C9 0.0226(6) 0.0198(5) 0.0264(6) -0.031(4) 0.0009(5) 0.0034(4)
C10 0.0240(6) 0.0195(5) 0.0233(5) -0.0059(4) 0.0039(4) -0.0037(4)
C11 0.0280(6) 0.0159(5) 0.0202(5) -0.0008(4) 0.0011(4) -0.0010(4)
C12 0.0226(5) 0.0172(5) 0.0182(5) -0.0023(4) -0.0006(4) 0.0023(4)
C13 0.0222(6) 0.0323(7) 0.0481(8) -0.0039(6) 0.0053(6) -0.0023(5)
C14 0.0224(5) 0.0146(5) 0.0177(5) 0.0017(4) 0.0022(4) 0.0022(4)
C15 0.0220(6) 0.0239(6) 0.0248(6) -0.0028(4) 0.0026(5) -0.0029(4)
C16 0.0251(6) 0.0295(6) 0.0278(6) -0.0030(5) 0.0102(5) -0.0023(5)
C17 0.0304(6) 0.0214(5) 0.0187(5) -0.0015(4) 0.0050(5) 0.0010(5)
C18 0.0245(6) 0.0168(5) 0.0201(5) 0.0003(4) -0.0007(4) 0.0003(4)
C19 0.0201(5) 0.0161(5) 0.0210(5) 0.0019(4) 0.0033(4) 0.0009(4)
O1A 0.0240(4) 0.0226(4) 0.0371(5) -0.0070(3) 0.0098(3) 0.0004(3)
N1A 0.0190(4) 0.0181(4) 0.0231(5) 0.0011(4) 0.0035(4) 0.0028(3)
C1A 0.0210(6) 0.0253(6) 0.0313(6) -0.0040(5) 0.0037(5) 0.0006(5)
C2A 0.0200(5) 0.0219(5) 0.0183(5) 0.0025(4) 0.0038(4) 0.0012(4)
C3A 0.0213(5) 0.0160(5) 0.0225(5) 0.0006(4) 0.0036(4) -0.0006(4)
C4A 0.0220(6) 0.0232(6) 0.0237(6) 0.0006(4) 0.0022(5) -0.0012(4)
C5A 0.0185(5) 0.0227(6) 0.0313(6) 0.0048(5) -0.0003(5) 0.0022(4)
C6A 0.0197(5) 0.0189(5) 0.0307(6) 0.0030(4) 0.0059(5) 0.0040(4)
C7A 0.0186(5) 0.0223(5) 0.0152(5) 0.0025(4) 0.0004(4) 0.0014(4)
C8A 0.0190(5) 0.0223(6) 0.0201(5) 0.0028(4) 0.0027(4) -0.0017(4)
C9A 0.0170(5) 0.0264(6) 0.0192(5) 0.0015(4) 0.0042(4) 0.0038(4)
C10A 0.0220(5) 0.0206(5) 0.0192(5) -0.0006(4) 0.0011(4) 0.0030(4)
C11A 0.0197(5) 0.0218(6) 0.0277(6) -0.0006(4) 0.0047(4) -0.0029(4)
C12A 0.0183(5) 0.0243(6) 0.0223(5) 0.0002(4) 0.0052(4) 0.0015(4)
C13A 0.0255(6) 0.0282(7) 0.0337(7) -0.0087(5) 0.0075(5) 0.0037(5)
C14A 0.0170(5) 0.0215(5) 0.0222(5) 0.0009(4) 0.0059(4) -0.0004(4)
C15A 0.0201(5) 0.0201(6) 0.0260(6) -0.0004(4) 0.0045(4) 0.0005(4)
C16A 0.0210(5) 0.0264(6) 0.0279(6) 0.0048(5) 0.0038(5) 0.0013(5)
C17A 0.0230(6) 0.0346(7) 0.0214(6) 0.0010(5) 0.0049(5) -0.0047(5)
C18A 0.0296(6) 0.0265(6) 0.0262(6) -0.0056(5) 0.0108(5) -0.0053(5)
C19A 0.0249(6) 0.0195(6) 0.0273(6) 0.0010(4) 0.0094(5) 0.0005(4)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C3 1.3905(14) . ?
N1 C14 1.4314(13) . ?
C1 C2 1.3402(16) . ?
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C1 H1B 0.977(14) . ?
C2 C3 1.4768(15) . ?
C2 C7 1.4850(15) . ?
C3 C4 1.3794(15) . ?
C4 C5 1.4118(16) . ?
C4 H4 0.969(13) . ?
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C5 H5 0.966(13) . ?
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C7 C12 1.4031(15) . ?
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C9 H9 0.977(14) . ?
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C13 H13B 1.001(15) . ?
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C14 C19 1.3901(15) . ?
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