Supporting information

Efficient Copper Catalyzed Multicomponent Synthesis of *N*-acyl amidines via Acyl Nitrenes

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Contents

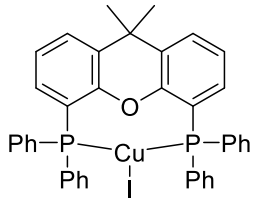
EXPERIMENTAL SECTION

General Considerations

All reactions were performed in air, unless stated otherwise. For inert experiments, solvents were distilled from sodium (toluene, tetrahydrofuran, diethyl ether) or CaH_2 (dichloromethane, hexane, methanol, acetonitrile). All chemicals were purchased from commercial suppliers and have been used without further purification. NMR spectra (^1H,^{13}C and ^{31}P) were recorded on a Bruker AV400, AV300, DRX 500 or DRX 300 spectrometer, referenced to residual solvent resonance signals. Mass spectrometry spectra were recorded on a JEOL JMS-T100LP AccuTOF 2012 (ESI), JEOL JMS-T100GCv AccuTOF 2012, (EI,CI & FD) or Bruker Impact II Q-TOF 2018 (ESI, CSI).

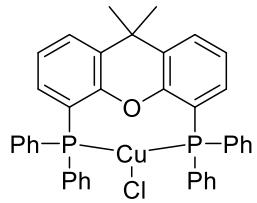
Synthesis of copper catalysts

CuCl, CuBr, CuI, $[Cu(NCMe)_4]PF_6$ and $[Cu(NCMe)_4]BF_4$, dppe and PPh_3 were purchased from commercial suppliers and have been used without further purification. $[Cu(NCMe)(TpBr_3)]$, [Cu(THF)(TpMs)] and [CuCl(IPr)] have been received from the group of Pedro J. Pérez at the University of Huelva.[1] Copper(I)acetate is a grey solid and is highly oxygen and water sensitive. As many suppliers send it as a green solid, we advise to order it from Strem Chemicals or to make it yourself as described below.



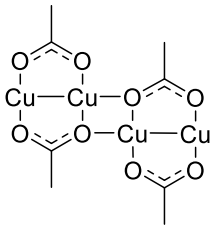
[CuI(Xantphos)]

[CuI(Xantphos)] was synthesized according to a modified literature procedure.[2] In a 100 mL round-bottomed flask, CuI (1g, 5.3 mmol) was dissolved in MeCN (50 mL) at 50 °C. To this solution was added Xantphos (3.6 g, 6.2 mmol). The reaction mixture was stirred for 2h at 50 °C, cooled to room temperature and filtered. The residue was washed with cold MeCN (25 mL) and dried *in vacuo* to give the product as a white solid (4g, 5.3 mmol, >99% yield). ^1H NMR (400 MHz, methylene chloride-d_2) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.43 (q, *J* = 6.2 Hz, 8H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.25 (t, *J* = 7.5 Hz, 8H), 7.12 (t, *J* = 7.7 Hz, 2H), 6.60 (dt, *J* = 7.8, 3.9 Hz, 2H), 1.66 (s, 6H). ^{31}P NMR (162 MHz, methylene chloride-d_2) δ -17.81.



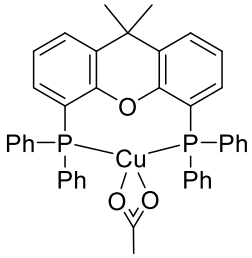
[CuCl(Xantphos)][3]

In a flame-dried Schlenk flask Xantphos (1g, 1.7 mmol) was added to a suspension of CuCl (beads, 168 mg, 1.7 mmol) in acetonitrile (20 mL). After stirring the reaction overnight, the suspension was filtered and washed with acetonitrile to give the product as a white solid. ^1H NMR (400 MHz, chloroform-*d*) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.47 – 7.39 (m, 8H), 7.35 – 7.27 (m, 4H), 7.27 – 7.20 (m, 8H), 7.11 (t, *J* = 7.7 Hz, 2H), 6.63 – 6.55 (m, 2H), 1.70 (s, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 154.58 (t, *J* = 6.2 Hz), 133.78 (t, *J* = 8.0 Hz), 133.17, 131.69 – 131.23 (m), 129.78, 128.52 (t, *J* = 4.9 Hz), 126.70, 124.75, 119.96 (t, *J* = 13.9 Hz), 35.75, 28.35. ^{31}P NMR (162 MHz, chloroform-*d*) δ -17.66.



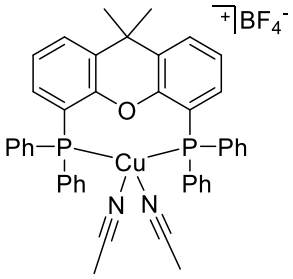
Copper(I)acetate (CuOAc) (*preferably purchased from Strem*)

CuOAc was synthesized according to a literature procedure.[4] In a N_2-filled glovebox, a 250 mL flame-dried Schlenk flask was charged with CuCl (3.3 g, 33 mmol). The schlenk flask was attached to a Schlenk line and dried *in vacuo*, after which degassed DCM (120 mL) was added. Acetic acid was dried by fractional distillation from acetic anhydride and $KMnO_3$,[5] degassed and added (1.9 mL). After stirring for 10 min at r.t., dry and degassed Et_3N (5.2 mL, distilled over CaH_2) was added, turning the white suspension in a solution. After stirring for 4h at r.t. under an atmosphere of N_2, the reaction mixture turned into a blue-grey suspension. The product was collected by inert filtration using an inversion filter. The blue filtrate was discarded and the product was washed with DCM (50 mL) and dried *in vacuo*. The product (0.79 g, 6.4 mmol, 19% yield) was stored under an atmosphere of N_2.



[Cu(OAc)(Xantphos)]

Try to avoid the use of colored batches of CuOAc as purification can be difficult. [Cu(OAc)(Xantphos)] was synthesized according to a literature procedure.[6] A flame-dried Schlenk flask was charged with Xantphos (3 g, 5.2 mmol) and flushed with nitrogen. In a N_2-filled glovebox, CuOAc (638 mg, 5.2 mmol) was added. The flask was attached to a Schlenk line and dry, degassed THF (200 mL) was added. After stirring the reaction for 4h at r.t. under an atmosphere of N_2, the reaction mixture was opened to air and solvents were removed *in vacuo*. The concentrate was dissolved in DCM, precipitated with pentane, filtered and washed with pentane to give the product as a white solid (2.7 g, 3.8 mmol, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (t, *J* = 6.6 Hz, 2H), 7.45– 7.15 (m, 20H), 7.08 (t, *J* = 7.9 Hz, 2H), 6.58 (s, 2H), 1.93 (s, 3H), 1.66 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.15, 133.86, 133.79, 133.72, 133.58, 132.17, 132.03, 131.89, 131.53, 129.58, 128.46, 128.42, 128.38, 126.31, 124.43, 99.99, 35.86, 28.01. ^{31}P NMR (121 MHz, $CDCl_3$) δ -16.80. HRMS (FD^+) *m/z* calcd. for $C_{41}H_{35}CuO_3P_2$ $[M+H]^+$ 700.1357 found 700.1379.

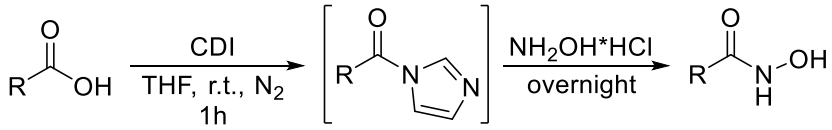


[Cu(NCMe)$_2$(Xantphos)]BF$_4$

In a 100 mL round-bottomed flask, Xantphos (1.84 g, 3.2 mmol) was added to a solution of $[Cu(NCMe)_4]BF_4$ (1 g, 3.2 mmol) in DCM (60 mL). After stirring the reaction mixture for 2h, the solvent was removed *in vacuo* to give the product as a white solid (2.6 g, 3.2 mmol, quantitative yield). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.60 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.44 – 7.21 (m, 20H), 7.17 (t, *J* = 7.7 Hz, 2H), 6.65 (ddt, *J* = 6.5, 4.1, 2.1 Hz, 2H), 2.16 (s, 6H), 1.69 (s, 6H). 13C NMR (126 MHz, chloroform-*d*) δ 154.34 (t, *J* = 6.0 Hz), 133.31 (t, *J* = 8.1 Hz), 131.47, 130.53 (t, *J* = 18.0 Hz), 130.32, 128.95 (t, *J* = 4.9 Hz), 127.23, 124.99, 121.64 – 117.86 (m), 35.82, 28.38, 2.15. ^{31}P NMR (121 MHz, chloroform-*d*) δ -14.01.

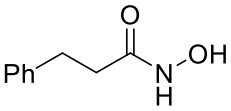
Synthesis of substrates

Hydroxamic acids



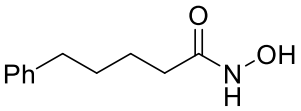
Typical procedure A

In a flame-dried Schlenk flask, carbonyldiimidazole (CDI, 7.8 g, 48 mmol, 1.5 equiv.) was added to a solution of acid acid (32 mmol, 1 equiv.) in dry THF (100 mL). After one hour of stirring at room temperature under a nitrogen atmosphere, hydroxylamine hydrochloride (4.5 g, 64 mmol, 2 equiv.) was added and the resulting solution was stirred under N_2 overnight. Subsequently, the solution was diluted with an aqueous solution of potassium bisulfate (5%, 100 mL) and extracted with ethyl acetate (2 x 100 mL). The combined organic layers were washed with brine (150 mL), dried over $MgSO_4$ and concentrated *in vacuo*. If necessary, the compound was recrystallized from either EtOAc or EtOAc/hexane mixtures.



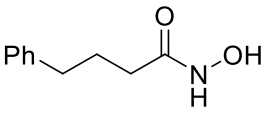
***N*-hydroxy-3-phenylpropanamide[8]**

Prepared according to typical procedure A, yielding a white solid. Isolated yield: 4.9 g (29.7 mmol, 89%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.37 (s, 1H), 8.71 (s, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 7.8 Hz, 1H), 2.25 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.24, 141.06, 128.27, 128.20, 125.92, 33.88, 32.71, 30.84.



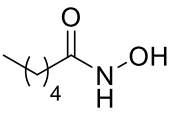
***N*-hydroxy-5-phenylpentanamide[7]**

Prepared according to typical procedure A, yielding a white solid. Isolated yield: 832 mg, (4.3 mmol, 86%). 1H NMR (400 MHz, DMSO-d_6) δ 10.38 (s, 1H), 9.77 (s, 0H), 9.04 (s, 0H), 8.71 (s, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.13 (m, 3H), 2.57 (t, *J* = 6.9 Hz, 2H), 1.98 (t, 2H), 1.61 – 1.46 (m, 4H). 13C NMR (101 MHz, DMSO-d_6) δ 169.51, 142.52, 128.73, 128.68, 126.10, 35.31, 32.59, 31.05, 25.26.



***N*-hydroxy-4-phenylbutanamide[8]**

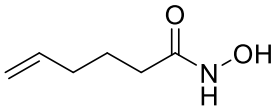
Prepared according to general procedure A, yielding a white solid. Isolated yield: 0.212 g, 1.2 mmol, 66%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.11 (m, 7H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.10 (p, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.33, 142.12, 128.76, 126.24, 99.99, 35.07, 32.25, 27.45.



***N*-hydroxyhexanamide**

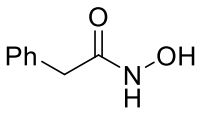
Prepared according to typical procedure A, yielding a white solid. Isolated yield: 1.9 g (14.5 mmol, 45%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.31 (s, 1H), 8.64 (s, 1H), 1.92 (t,

J = 7.4 Hz, 2H), 1.48 (p, *J* = 7.4 Hz, 2H), 1.32 – 1.15 (m, 4H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.10, 32.21, 30.78, 24.77, 21.80, 13.85.



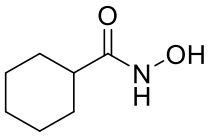
_N_-hydroxyhex-5-enamide[8]

Prepared according to typical procedure A, yielding a white solid. Isolated yield: 1.55 g, 12.0 mmol, 84%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.34 (s, 1H), 8.66 (s, 1H), 5.78 (ddt, *J* = 16.9, 9.9, 6.5 Hz, 1H), 5.08 – 4.77 (m, 2H), 2.11 – 1.82 (m, 4H), 1.57 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.91, 138.15, 115.15, 40.02, 39.95, 39.85, 39.78, 39.69, 39.61, 39.52, 39.45, 39.35, 39.19, 39.03, 39.02, 32.65, 31.68, 24.37.



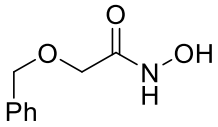
_N_-hydroxy-2-phenylacetamide

Prepared according to typical procedure A, yielding a white solid. Isolated yield: 1.7 g, 11.2 mmol, 37%. ^{1}H NMR (400 MHz, DMSO-d_6) ð 10.65 (s, 1H), 8.82 (s, 1H), 7.25 (m, 5H), 3.27 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.97, 136.06, 128.90, 128.17, 126.40, 39.39.



_N_-hydroxycyclohexanecarboxamide[7]

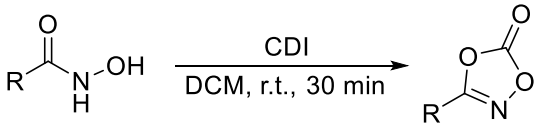
Prepared according to typical procedure A, yielding a white solid. Isolated yield: 3.06 g, 21.4 mmol, 53%. ^{z}H NMR (400 MHz, chloroform-*d*) δ 2.69 (m, 1H), 2.02 (m, 2H), 1.90 – 1.80 (m, 2H), 1.73 (m, 1H), 1.54 (qd, *J* = 11.7, 3.3 Hz, 2H), 1.46 – 1.26 (m, 3H).



2-(benzyloxy)-_N_-hydroxyacetamide

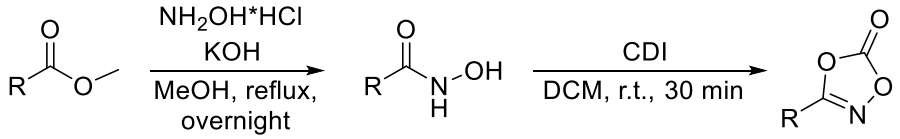
Prepared according to typical procedure A, yielding a white solid. Isolated yield: 3.51 g, 19.4 mmol, 69%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.43 – 7.17 (m, 5H), 4.52 (d, *J* = 3.4 Hz, 2H), 3.88 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.90, 138.19, 128.70, 128.12, 128.05, 72.73, 68.55.

Dioxazolones



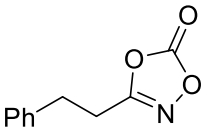
Typical procedure B

The hydroxamic acid (15 mmol, 1 equiv.) was dissolved in DCM (150 mL), followed by the addition of carbonyldiimidazole (2.4 g, 22.5 mmol, 1.5 equiv.). After stirring at room temperatures for 30 minutes, the solution was diluted with aqueous HCl solution (1 M, 100 mL) and extracted with DCM (2 x 150 mL). The combined organic layers were dried over magnesium sulfate, and concentrated under reduced pressure. The crude was purified by filtration over a plug of silica with DCM to give the product.



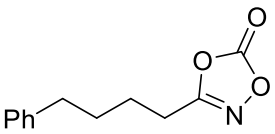
Typical procedure C

Potassium hydroxide (13.4 g, 239 mmol, 6 equiv.) was added to a suspension of methyl ester (5 mL, 40 mmol, 1 equiv.) and hydroxylamine hydrochloride (8.3 g, 119 mmol, 3 equiv.) in methanol (200 mL). After refluxing overnight, the mixture was acidified to pH 4 with HCl (1M in H_2O). The methanol was evaporated under reduced pressure and the compound was extracted with ethyl acetate (3 x 170 mL). The combined organic layers were dried over magnesium sulfate, after which the solvents were evaporated, yielding a white solid that was directly used for typical procedure B to give the dioxazolone.



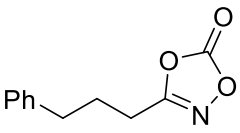
3-phenethyl-1,4,2-*d*ioxazol-5-one (1a)[8]

Prepared according to typical procedure B, resulting in a colorless oil that solidifies when solidified product was added. Isolated yield: 4.3 g, 22.6 mmol, 81%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.38 – 7.22 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.99 – 2.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.96, 154.13, 138.14, 129.05, 128.30, 127.29, 30.59, 26.79.



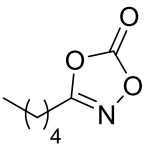
3-(4-phenylbutyl)-1,4,2-*d*ioxazol-5-one (1b)[9]

Prepared according to typical procedure B, resulting in a colorless oil. Isolated yield: 2.83 g, 12.9 mmol, 83%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.17 (m, 3H), 2.73 – 2.67 (m, 2H), 2.67 – 2.60 (m, 2H), 1.82 – 1.72 (m, 4H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 166.59, 154.21, 141.32, 128.52, 128.39, 126.13, 35.19, 30.37, 24.65, 24.02.



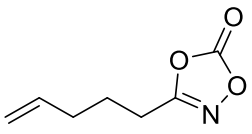
3-(3-phenylpropyl)-1,4,2-*d*ioxazol-5-one (1c)[8]

Prepared according to typical procedure B, resulting in a colorless liquid. Isolated yield: 0.212 g, 1.2 mmol, 66%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.13 (m, 5H), 2.75 (t, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.07 (p, *J* = 7.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.56, 154.19, 139.92, 128.76, 128.55, 126.62, 34.64, 25.96, 24.11.



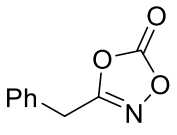
3-pentyl-1,4,2-*d*ioxazol-5-one (1d)[9]

Prepared according to typical procedure B, resulting in a colorless oil. Isolated yield: 1.7 g, 10.8 mmol, 75%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 2.61 (t, *J* = 7.6 Hz, 2H), 1.72 (q, *J* = 7.4 Hz, 2H), 1.37 (qt, *J* = 8.8, 4.5 Hz, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 166.72, 154.22, 30.79, 24.71, 24.20, 22.02, 13.73.



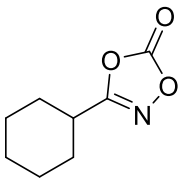
3-(pent-4-en-1-yl)-1,4,2-*d*ioxazol-5-one (1e) [8]

Prepared according to typical procedure B, resulting in a colorless liquid. Isolated yield: 0.20 g, 1.3 mmol, 17%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.13 – 5.04 (m, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.25 – 2.12 (m, 2H), 1.84 (p, *J* = 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.66, 154.27, 136.33, 116.75, 32.58, 24.09, 23.65.



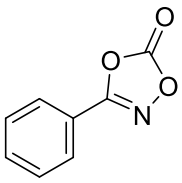
3-benzyl-1,4,2-*d*ioxazol-5-one (1f)[11]

Prepared according to typical procedure C, yielding a colorless liquid. Isolated yield: 0.62 g, 3.5 mmol, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 3.93 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.42, 154.05, 130.54, 129.41, 129.12, 128.61, 31.39.



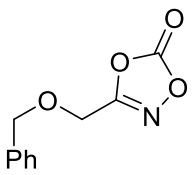
3-cyclohexyl-1,4,2-*d*ioxazol-5-one (1g)[10]

Prepared according to typical procedure B, resulting in a colorless liquid. Isolated yield: 3.22 g, 19.0 mmol, 91%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 2.66 (td, *J* = 11.2, 5.6 Hz, 1H), 1.99 (dd, *J* = 13.2, 3.9 Hz, 2H), 1.88 – 1.77 (m, 2H), 1.71 (dd, *J* = 11.7, 4.8 Hz, 1H), 1.52 (qd, *J* = 11.7, 3.3 Hz, 2H), 1.43 – 1.23 (m, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 169.32, 154.29, 34.54, 28.05, 25.21, 24.77.



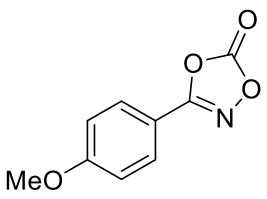
3-phenyl-1,4,2-*d*ioxazol-5-one (1h) [11]

Prepared according to typical procedure C, resulting in a white solid. Isolated yield: 1.9 g, 11.4 mmol, 28% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.68, 153.97, 133.92, 129.53, 126.76, 120.28.



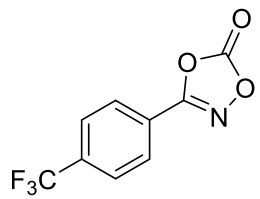
3-((benzyloxy)methyl)-1,4,2-*d*ioxazol-5-one (1i)

Prepared according to typical procedure B, resulting in a colorless oil. Isolated yield: 346 mg, 1.7 mmol, 15% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.43 – 7.31 (m, 5H), 4.66 (s, 2H), 4.45 (s, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 163.24, 153.49, 135.67, 128.65, 128.54, 128.10, 73.67, 60.17.



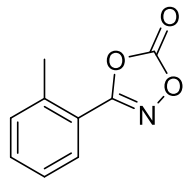
3-(4-methoxyphenyl)-1,4,2-*d*ioxazol-5-one (1j) [11]

Prepared according to typical procedure C, resulting in a colourless liquid that solidifies over time. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.00, 163.55, 154.18, 128.70, 115.01, 112.24, 55.76.



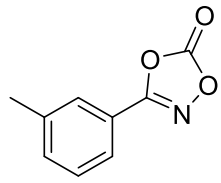
3-(4-(trifluoromethyl)phenyl)-1,4,2-*d*ioxazol-5-one (1k)

The hydroxamic acid was prepared according to the reaction in typical procedure A and was used without recrystallization to prepared **1k** according to typical procedure B, resulting in a white solid. Isolated yield: 3.20 g, 15.6 mmol, 67% yield. 1H NMR (300 MHz, chloroform-*d*) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 162.53, 153.31, 135.30 (q, *J* = 33.2 Hz), 127.12, 126.46 (q, *J* = 3.8 Hz), 123.53, 122.07 (d, *J* = 272.9 Hz).



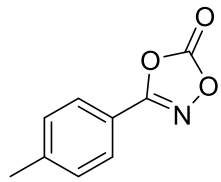
3-(o-tolyl)-1,4,2-*d*ioxazol-5-one (1l)

Prepared according to typical procedure C, resulting in a white solid. Isolated yield: 1.763 g, 9.95 mmol, 27% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 164.01, 153.69, 139.15, 133.15, 132.05, 128.78, 126.50, 119.21, 22.10.



3-(m-tolyl)-1,4,2-*d*ioxazol-5-one (1m)

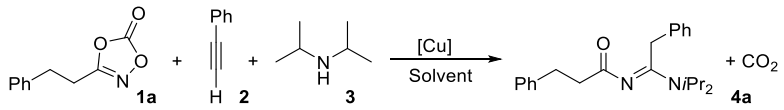
Prepared according to typical procedure C, resulting in a white solid. Isolated yield: 1.28 g, 7.23 mmol, 20%. 1H NMR (400 MHz, chloroform-*d*) δ 7.65 (m, 2H), 7.43 (m 2H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 163.67, 153.88, 139.51, 134.62, 129.27, 126.95, 123.78, 119.98, 21.25.



3-(p-tolyl)-1,4,2-*d*ioxazol-5-one (1n)

The hydroxamic acid was prepared according to the reaction in typical procedure A and was used without recrystallization to prepared **1n** according to typical procedure B, resulting in a white solid. 1.97 g, 13.0 mmol, 37%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 163.65, 153.95, 144.81, 130.08, 126.57, 117.27, 21.80.

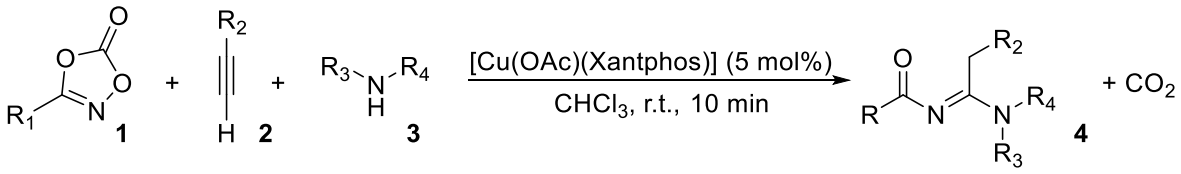
Conditions Screening Table



entry	Catalyst	Eq. 2a	Eq. 3a	loading (mol%)	Solvent	Yield (%)
1	CuCl	2	2	10	$CHCl_3$	55
2	CuBr	2	2	10	$CHCl_3$	63
3	CuI	2	2	10	$CHCl_3$	62
4	$[Cu(NCMe)_4]BF_4$	2	2	10	$CHCl_3$	65
5	$[Cu(NCMe)_4]PF_6$	2	2	10	$CHCl_3$	75
6	$[(TpBr_3)Cu(NCMe)]$	2	2	10	$CHCl_3$	5
7	[(TpMs)Cu(THF)]	2	2	10	$CHCl_3$	0
8	[(IPr)CuCl]	2	2	10	$CHCl_3$	37
9	[(Xantphos)CuI]	2	2	10	$CHCl_3$	0
10	[Cu(OAc)(Xantphos)]	2	2	10	$CHCl_3$	98
11	$[(Xantphos)Cu(NCMe)_2]BF_4$	2	2	10	$CHCl_3$	72
12	[Cu(OAc)(Xantphos)]	2	2	10	DCM	58 (97%*)
13	[Cu(OAc)(Xantphos)]	2	2	10	THF	95
14	[Cu(OAc)(Xantphos)]	2	2	10	MeCN	0
15	[Cu(OAc)(Xantphos)]	2	2	10	EtOAC	92
16	[Cu(OAc)(Xantphos)]	2	2	10	MeOH	0
17	[Cu(OAc)(Xantphos)]	2	2	10	DCE	74
19	[Cu(OAc)(Xantphos)]	2	2	10	Toluene	93
20	**[Cu(OAc)(Xantphos)]**	**2**	**2**	**5**	**$CHCl_3$**	**97**
21	[Cu(OAc)(Xantphos)]	2	2	2	$CHCl_3$	43 (94%*)
22	[Cu(OAc)(Xantphos)]	2	2	1	$CHCl_3$	10 (19%*)
23	[Cu(OAc)(Xantphos)]	2	2	0.5	$CHCl_3$	0
24	[Cu(OAc)(Xantphos)]	2	2	0.1	$CHCl_3$	0
25[#]	[Cu(OAc)(Xantphos)]	2	2	5	$CHCl_3$	0 (98%*)
26	[Cu(OAc)] + dppe	2	2	5	$CHCl_3$	79%*
27	[Cu(OAc)] + dppe	2	2	5	$CHCl_3$	82%*
28	-	2	2		$CHCl_3$	0[§]
29	-	2	-		$CHCl_3$	0[Φ]
30	-	-	2		$CHCl_3$	0[§]
31	[Cu(OAc)(Xantphos)]	1.5	1.5	5	$CHCl_3$	90
32	[Cu(OAc)(Xantphos)]	1.2	1.2	5	$CHCl_3$	71
33	[Cu(OAc)(Xantphos)]	1	1	5	$CHCl_3$	69
34	[Cu(OAc)(Xantphos)]	2	1	5	$CHCl_3$	84
35	[Cu(OAc)(Xantphos)]	1	2	5	$CHCl_3$	56

Reaction of **1a** (0.5 mmol), **2a** (2 eq.), **3** (2 eq.) and catalyst in solvent (1 mL), stirred overnight at room temperature. Yields are determined by ^{1}H-NMR spectroscopy with 1,3,5-trimethoxybenzene as external standard. [§] Full conversionn to 1,1-*d*iisopropyl-3-phenethylurea was observed. * Reactions performed in a N_2 filled glovebox. [#] 10 mL of chloroform was used. [Φ] no conversion of starting material was observed

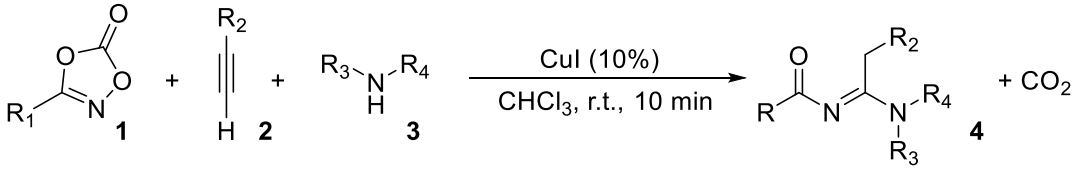
Cu-catalyzed three-component reactions



Typical procedure D

Do not use $CHCl_3$ that is stabilized with MeOH.

In a 4 mL vial, [Cu(OAc)(Xantphos)] (17.5 mg, 25 µmol, 0.05 eq) was dissolved in $CHCl_3$ (1 mL). To the resulting colorless solution was added the acetylene (**2**, 1 mmol, 2 eq). After addition of the amine (**3**, 1 mmol, 2 eq) the solution turned yellow, directly the 1,4,2-*d*ioxazol-5-one (**1**, 0.5 mmol, 1 eq) was added and the vial was capped with a screw cap. After 10 minutes of stirring, the vial was carefully opened to release the overpressure. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography (DCM, with 2% Et_3N and 3% EtOAc).

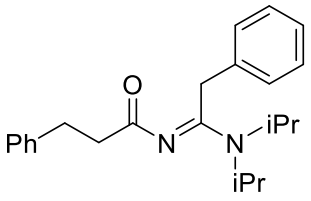


Typical procedure E

Do not use $CHCl_3$ that is stabilized with MeOH.

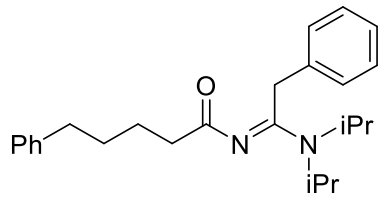
In a 4 mL vial, CuI (19 mg, 50 µmol, 0.10 eq) was suspended in $CHCl_3$ (1 mL). To the resulting suspension was added the acetylene (**2**, 1 mmol, 2 eq). After addition of the amine (**3**, 1 mmol, 2 eq) the solution turned yellow, directly the 1,4,2-*d*ioxazol-5-one (**1**, 0.5 mmol, 1 eq) was added and the vial was capped with a screw cap. After 30 minutes of stirring, the vial was carefully opened to release the overpressure. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography (DCM, with 2% Et_3N and 3% EtOAc).

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)-3-phenylpropanamide (4aaa)



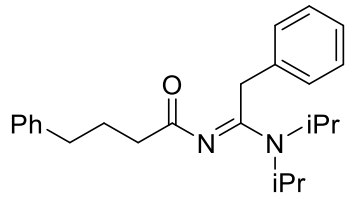
The reaction of **1a**, phenylacetylene and diisopropylamine according to procedure D yielded the product as a colorless oil: 170 mg, 0.49 mmol, 97%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.36 – 7.01 (m, 10H), 3.97 (s, 2H), 3.96 – 3.87 (m, 1H), 3.68 – 3.36 (m, 1H), 2.95 (t, *J* = 8.1 Hz, 2H), 2.68 (t, *J* = 8.1 Hz, 2H), 1.62 – 1.28 (m, 6H), 1.06 – 0.73 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 182.35, 161.05, 142.09, 136.43, 128.69, 128.33, 128.26, 128.08, 126.52, 125.69, 49.70, 47.38, 41.83, 37.26, 32.00, 20.12. MS (ESI) *m/z* calc. for $[C_{23}H_{30}N_2O+H]^+$ 351.2 found 351.2, *m/z* calc. for $[C_{23}H_{30}N_2O+Na]^+$ 373.2 found 373.1.

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)-5-phenylpentanamide (4baa)



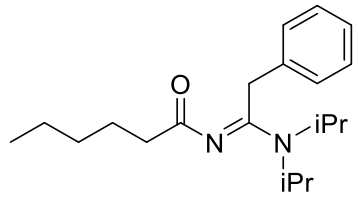
The reaction of **1b**, phenylacetylene and diisopropylamine according to procedure D yielded the product as a colorless oil: 182 mg, 0.48 mmol, 97%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.35 – 7.06 (m, 10H), 4.00 (s, 2H), 3.96 – 3.80 (m, 1H), 3.59 – 3.39 (m, 1H), 2.61 (t, *J* = 7.3 Hz, 2H), 2.38 (t, *J* = 7.1 Hz, 2H), 1.77 – 1.58 (m, 4H), 1.58 – 1.33 (m, 6H), 1.04 – 0.77 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 183.41, 160.71, 142.68, 136.47, 128.70, 128.43, 128.19, 128.05, 126.53, 125.53, 49.69, 47.32, 40.31, 37.23, 35.84, 31.33, 25.70, 20.13. MS (ESI^{+}) *m/z* calc. for $[C_{25}H_{34}N_2O+H]^{+}$ 379.3 found 379.2, *m/z* calc. for $[C_{25}H_{34}N_2O+Na]^{+}$ 401.3 found 401.2.

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)-4-phenylbutanamide (4caa)



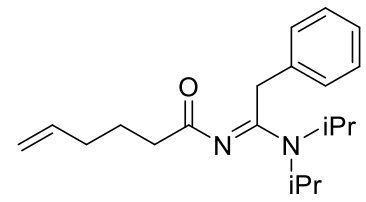
The reaction of **1c**, phenylacetylene and diisopropylamine according to procedure D yielded the product as a colorless oil: 168 mg, 0.46 mmol, 92%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.36 – 7.09 (m, 10H), 4.02 (s, 2H), 3.97 – 3.85 (m, 1H), 3.60 – 3.42 (m, 1H), 2.65 (d, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 1.96 (p, *J* = 7.6 Hz, 2H), 1.61 – 1.34 (m, 6H), 1.04 – 0.78 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 183.19, 160.81, 142.41, 136.45, 128.70, 128.51, 128.19, 128.05, 126.53, 125.60, 49.68, 47.21, 39.93, 37.23, 35.61, 27.57, 20.13. MS (ESI^{+}) *m/z* calc. for $[C_{24}H_{32}N_2O+H]^{+}$ 365.2 found 365.2, *m/z* calc. for $[C_{24}H_{32}N_2O+Na]^{+}$ 387.2 found 387.2.

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)hexanamide (4daa)



The reaction of **1d**, phenylacetylene and diisopropylamine according to procedure D yielded the product as a colorless oil: 139 mg, 0.44 mmol, 88%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.35 – 7.15 (m, 5H), 4.00 (s, 2H), 3.92 (s, 1H), 3.48 (s, 1H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.62 (t, *J* = 7.4 Hz, 2H), 1.47 (dd, *J* = 14.4, 7.1 Hz, 6H), 1.29 (q, *J* = 3.9 Hz, 4H), 0.92 (s, 6H), 0.88 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 183.70, 136.37, 128.55, 127.90, 126.37, 49.47, 47.17, 40.38, 37.08, 31.60, 25.60, 22.43, 19.99, 13.89. HRMS (FD^{+}) *m/z* calc. for $[C_{20}H_{32}N_2O]^{+}$ 316.2514 found 316.2515

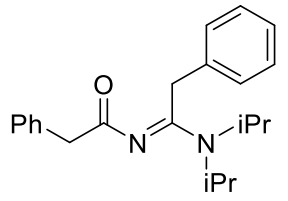
(E)-N-(1-(diisopropylamino)-2-phenylethylidene)hex-5-enamide (4eaa)



The reaction of **1e**, phenylacetylene and diisopropylamine according to procedure D yielded the product as a yellowish oil: 115 mg, 0.37 mmol, 73%. ^{1}H-NMR of the reaction mixture showed full conversion into the desired product. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.34 – 7.16 (m, 5H), 5.80 (ddt, *J* = 16.8, 9.7, 6.6 Hz, 1H), 5.04 – 4.88 (m, 2H), 4.01 (s, 2H), 3.93 (s, 1H), 3.49 (s, 1H), 2.36 (t, *J* = 7.6 Hz, 2H), 2.08 (q, *J* = 7.3 Hz, 2H), 1.73 (p, *J* = 7.6 Hz, 2H), 1.50 (s, 6H), 0.92 (s, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 183.30, 160.72, 138.66, 136.45, 128.68, 128.03, 126.51, 114.53, 99.99, 49.65,

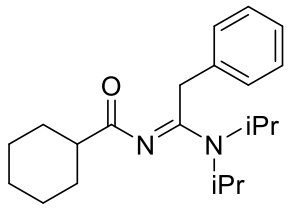
47.33, 39.83, 37.23, 33.53, 25.17, 20.11. MS (ESI$^+$) *m/z* calc. for $[C_{20}H_{30}N_2O+H]^+$ 315.2 found 316.2, *m/z* calc. for $[C_{20}H_{30}N_2O+Na]^+$ 337.2 found 337.1.

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)-2-phenylacetamide (4faa)



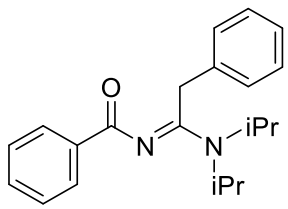
The reaction of **1f**, phenylacetylene and diisopropylamine according to procedure D under an N_2 atmosphere yielded the product as a yellowish solid: 148 mg, 0.44 mmol, 88%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.30 – 7.15 (m, 8H), 7.02 (d, *J* = 7.3 Hz, 2H), 3.96 (s, 2H), 3.94 – 3.84 (m, 1H), 3.68 (s, 2H), 3.48 – 3.35 (m, 1H), 1.46 – 1.29 (m, 6H), 0.96 – 0.76 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 180.48, 162.01, 137.10, 136.25, 129.68, 128.60, 128.18, 127.99, 126.39, 126.08, 49.87, 47.77, 47.42, 37.20, 19.92. MS (ESI$^+$) *m/z* calc. for $[C_{22}H_{28}N_2O+H]^+$ 337.2 found 337.2, *m/z* calc. for $[C_{22}H_{28}N_2O+Na]^+$ 359.2 found 359.1.

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)cyclohexanecarboxamide (4gaa)



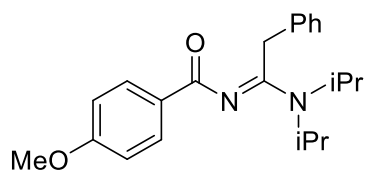
The reaction of **1g**, phenylacetylene and diisopropylamine according to procedure D under an N_2 atmosphere yielded the product as a yellowish solid: 151 mg, 0.046 mmol, 92%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.37 – 7.15 (m, 5H), 3.99 (s, 2H), 3.93 (s, 1H), 3.54 – 3.40 (m, 1H), 2.33 – 2.20 (m, 1H), 1.92 (d, *J* = 11.9 Hz, 2H), 1.80 – 1.69 (m, 2H), 1.69 – 1.60 (m, 1H), 1.59 – 1.45 (m, 6H), 1.46 – 1.35 (m, 2H), 1.33 – 1.15 (m, 3H), 1.00 – 0.81 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 186.23, 161.31, 136.68, 128.64, 128.05, 126.45, 49.79, 48.46, 47.25, 37.43, 29.96, 26.25, 26.06, 20.14. HRMS (ESI$^+$) *m/z* calc. for $[C_{21}H_{32}N_2O+H]^+$ 329.2587 found 329.259.

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)benzamide (4haa)



The reaction of **1h**, phenylacetylene and diisopropylamine according to procedure E yielded the product as a white solid: 110 mg, 0.34 mmol, 68%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.16 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.1 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.20 (t, *J* = 7.0 Hz, 1H), 4.15 (s, 2H), 4.12 – 4.02 (m, 1H), 3.67 – 3.52 (m, 1H), 1.72 – 1.53 (m, 6H), 1.08 – 0.89 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 174.32, 163.83, 138.02, 136.45, 131.07, 129.34, 128.69, 128.16, 127.90, 126.52, 50.10, 47.61, 37.83, 20.37, 20.11. HRMS (CSI$^+$) *m/z* calc. for $[C_{21}H_{26}N_2O+H]^+$ 323.2118 found 323.2122, *m/z* calc. for $[C_{21}H_{26}N_2O+Na]^+$ 345.1937 found 345.1940, *m/z* calc. for $[C_{21}H_{26}N_2O+H]^+$ 361.1677 found 361.1679.

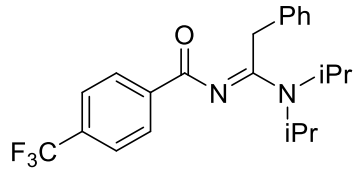
(E)-N-(1-(diisopropylamino)-2-phenylethylidene)-4-methoxybenzamide (4jaa)



The reaction of **1j**, phenylacetylene and diisopropylamine according to procedure E yielded the product as a white solid: 111 mg, 0.32 mmol, 64%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.18 (dd, *J* = 7.8, 5.6 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.11 (s, 2H), 4.08 – 4.00 (m, 1H), 3.86 (s, 3H), 3.62 – 3.50 (m, 1H), 1.67 – 1.51 (m, 6H), 1.04 – 0.86 (m, 6H). ^{13}C NMR (126 MHz,

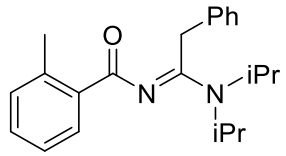
chloroform-*d*) δ 174.25, 163.10, 162.09, 136.54, 131.25, 130.77, 128.66, 128.16, 126.46, 113.12, 55.34, 49.97, 47.46, 37.77, 20.39, 20.16. HRMS (CSI$^+$) *m/z* calc. for $[C_{22}H_{28}N_2O_2+H]^+$ 353.2224 found 353.2227, *m/z* calc. for $[C_{22}H_{28}N_2O_2+Na]^+$ 375.2043 found 375.2045, *m/z* calc. for $[C_{22}H_{28}N_2O_2+K]^+$ 391.1782 found 391.1783.

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)-4-(trifluoromethyl)benzamide (4kaa)



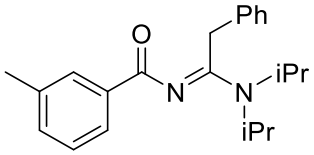
The reaction of **1k**, phenylacetylene and diisopropylamine according to procedure E yielded the product as a white solid: 113 mg, 0.29 mmol, 58%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.24 (m, 4H), 7.24 – 7.16 (m, 1H), 4.16 (s, 2H), 4.10 (p, *J* = 6.7 Hz, 1H), 3.68 – 3.55 (m, 1H), 1.60 (d, *J* = 6.8 Hz, 6H), 0.99 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 172.49, 165.38, 141.33, 136.17, 132.60 (q, *J* = 32.1 Hz), 129.52, 128.78, 128.06, 126.69, 124.11 (q, *J* = 272.5 Hz), 12z4.90 (q, *J* = 3.7 Hz), 50.41, 47.90, 37.78, 20.36, 20.05. HRMS (CSI$^+$) *m/z* calc. for $[C_{22}H_{25}F_3N_2O+H]^+$ 391.1992 found 391.1989, *m/z* calc. for $[C_{22}H_{25}F_3N_2O+Na]^+$ 413.1811 found 413.1808, *m/z* calc. for $[C_{22}H_{25}F_3N_2O+K]^+$ 429.1551 found 429.1546.

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)-2-methylbenzamide (4laa)



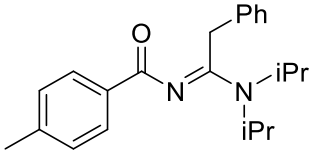
The reaction of **1l**, phenylacetylene and diisopropylamine according to procedure E yielded the product as a yellow solid: 57 mg, 0.17 mmol, 34%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.01 – 7.91 (m, 2H), 7.36 – 7.24 (m, 6H), 7.20 (t, *J* = 6.9 Hz, 1H), 4.13 (s, 2H), 4.11 – 4.01 (m, 1H), 3.67 – 3.50 (m, 1H), 2.42 (s, 3H), 1.72 – 1.51 (m, 6H), 1.07 – 0.87 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 174.57, 163.58, 137.96, 137.48, 136.48, 131.84, 129.95, 128.67, 128.18, 127.80, 126.57, 126.50, 50.07, 47.58, 37.84, 21.42, 20.35, 20.12. MS (ESI$^+$) *m/z* calc. for $[C_{22}H_{28}N_2O+H]^+$ 337.2 found 337.2.

(E)-N-(1-(diisopropylamino)-2-phenylethylidene)-3-methylbenzamide (4maa)



The reaction of **1m**, phenylacetylene and diisopropylamine according to procedure E yielded the product as a white solid: 84 mg, 0.25 mmol, 50%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.01 – 7.93 (m, 2H), 7.31 (tt, *J* = 11.7, 5.2 Hz, 6H), 7.20 (t, *J* = 7.1 Hz, 1H), 4.14 (s, 2H), 4.11 – 4.04 (m, 1H), 3.69 – 3.53 (m, 1H), 2.42 (s, 3H), 1.73 – 1.53 (m, 6H), 1.06 – 0.87 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 174.57, 163.57, 137.96, 137.48, 136.48, 131.84, 129.95, 128.67, 128.19, 127.80, 126.57, 126.50, 50.06, 47.57, 37.84, 21.42, 20.35, 20.12. (ESI$^+$) *m/z* calc. for $[C_{22}H_{28}N_2O+H]^+$ 337.2 found 337.2.

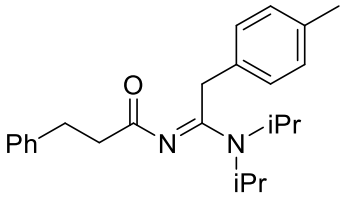
(E)-N-(1-(diisopropylamino)-2-phenylethylidene)-4-methylbenzamide (4naa)



The reaction of **1n**, phenylacetylene and diisopropylamine according to procedure E yielded the product as a white solid: 94 mg, 0.28 mmol, 56%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 4.13 (s, 2H), 4.11 – 3.99 (m, 1H), 3.65 – 3.50 (m, 1H), 2.41 (s, 3H), 1.70 – 1.52 (m, 6H), 1.06 – 0.87 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 174.48, 163.36, 141.38,

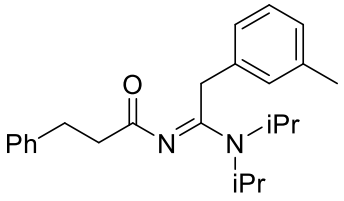
136.51, 135.36, 129.43, 128.66, 128.64, 128.17, 126.48, 50.02, 47.52, 37.81, 21.52, 20.36, 20.13. (ESI^+) *m/z* calc. for $[C_{22}H_{28}N_2O+H]^+$ 337.2 found 337.2.

(E)-N-(1-(diisopropylamino)-2-(p-tolyl)ethylidene)-3-phenylpropanamide (4aba)



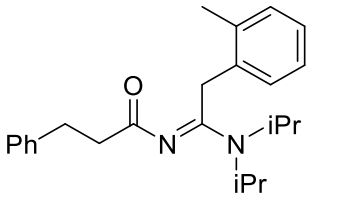
The reaction of **1a**, 4-tolylacetylene and diisopropylamine according to procedure D under an N_2 atmosphere yielded the product as a colorless oil: 177 mg, 0.49 mmol, 97%. ^1H NMR (500 MHz, chloroform-*d*) δ 7.30 – 7.08 (m, 9H), 4.04 – 3.88 (m, 1H), 3.96 (s, 2H), 3.60 – 3.43 (m, 1H), 2.98 (t, *J* = 8.2 Hz, 2H), 2.69 (t, *J* = 8.1 Hz, 2H), 2.35 (s, 3H), 1.59 – 1.39 (m, 6H), 1.10 – 0.82 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 182.33, 161.17, 142.14, 136.02, 133.28, 129.35, 128.33, 128.25, 127.91, 125.66, 49.64, 47.34, 41.85, 36.78, 32.03, 21.02, 20.18. HRMS (FD^+) *m/z* calc. for $[C_{24}H_{32}N_2O]^+$ 364.2515 found 364.2502.

(E)-N-(1-(diisopropylamino)-2-(m-tolyl)ethylidene)-3-phenylpropanamide (4aca)



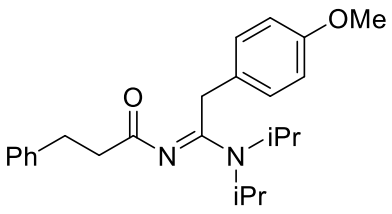
The reaction of **1a**, 3-tolylacetylene and diisopropylamine according to procedure D under an N_2 atmosphere yielded the product as a yellowish oil: 176 mg, 0.48 mmol, 97%. ^1H NMR (500 MHz, chloroform-*d*) δ 7.30 – 7.10 (m, 6H), 7.07 – 6.96 (m, 3H), 4.00 – 3.85 (m, 1H), 3.94 (s, 2H), 3.61 – 3.40 (m, 1H), 2.94 (t, *J* = 8.1 Hz, 2H), 2.67 (t, *J* = 8.2 Hz, 2H), 2.32 (s, 3H), 1.56 – 1.35 (m, 6H), 1.08 – 0.79 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 192.58, 182.36, 142.13, 138.25, 136.29, 128.82, 128.56, 128.32, 128.26, 127.22, 125.67, 124.95, 41.87, 37.04, 32.02, 21.44, 20.14. HRMS (ESI^+) *m/z* calc. for $[C_{24}H_{32}N_2O+Na]^+$ 387.2407 found 387.239

(E)-N-(1-(diisopropylamino)-2-(o-tolyl)ethylidene)-3-phenylpropanamide (4ada)



The reaction of **1a**, 2-tolylacetylene and diisopropylamine according to procedure D under an N_2 atmosphere yielded the product as a yellowish oil: 177 mg, 0.49 mmol, 97%. ^1H NMR (500 MHz, chloroform-*d*) δ 7.28 – 7.19 (m, 2H), 7.19 – 7.11 (m, 7H), 3.87 (s, 2H), 3.73 – 3.50 (m, 2H), 2.90 (t, *J* = 8.1 Hz, 2H), 2.62 (t, *J* = 8.1 Hz, 2H), 2.25 (s, 3H), 1.61 – 1.42 (m, 6H), 1.09 – 0.89 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 182.55, 161.25, 142.08, 135.50, 134.61, 130.17, 128.31, 128.22, 127.06, 126.63, 126.27, 125.64, 49.67, 47.31, 41.73, 34.07, 31.96, 20.25, 19.72. HRMS (ESI) *m/z* calc. for $[C_{24}H_{32}N_2O+Na]^+$ 387.2407 found 387.240.

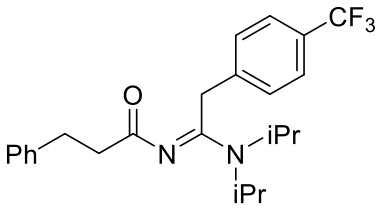
(E)-N-(1-(diisopropylamino)-2-(4-methoxyphenyl)ethylidene)-3-phenylpropanamide (4aea)



The reaction of **1a**, 4-methoxyphenylacetylene and diisopropylamine according to procedure D under an N_2 atmosphere yielded the product as a white solid: 160 mg, 0.42 mmol, 84%. ^1H NMR (400 MHz, chloroform-*d*) δ 7.31 – 7.05 (m, 9H), 4.01 – 3.86 (m, 1H), 3.56 – 3.40 (m, 1H), 2.94 (t, *J* = 8.1 Hz, 2H), 2.66 (t, *J* = 8.2 Hz, 2H), 2.31 (s, 3H), 1.56 – 1.34 (m, 6H), 1.08 – 0.82 (m, 6H). ^{13}C NMR

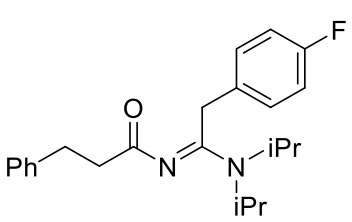
(101 MHz, chloroform-*d*) δ 182.22, 161.09, 142.01, 135.90, 133.14, 129.24, 128.22, 128.15, 127.78, 125.56, 49.57, 47.22, 41.74, 36.67, 31.92, 20.92, 20.02. HRMS (FD^+) *m/z* calc. for $[C_{24}H_{32}N_2O_2]^+$ 380.2464 found 380.2464.

(E)-N-(1-(diisopropylamino)-2-(4-fluorophenyl)ethylidene)-3-phenylpropanamide (4afa)



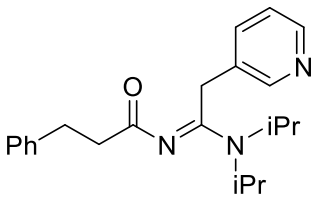
The reaction of **1a**, 4-trifluormethylphenylacetylene and diisopropylamine according to procedure D under an N_2 atmosphere yielded the product as a yellowish solid: 201 mg, 0.48 mmol, 96%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.17 (m, 4H), 7.16 – 7.11 (m, 1H), 3.99 (s, 2H), 3.89 – 3.80 (m, 1H), 3.55 – 3.46 (m, 1H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.69 (t, *J* = 7.9 Hz, 2H), 1.56 – 1.36 (m, 6H), 1.04 – 0.82 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 182.53, 160.33, 141.90, 140.64, 128.44, 128.31, 128.27, 125.76, 125.60 (q, *J* = 3.8 Hz), 49.68, 47.50, 41.69, 37.11, 31.86, 20.11. HRMS (ESI) *m/z* calc. for $[C_{24}H_{29}F_3N_2O+H]^+$ 419.2305 found 419.230.

(E)-N-(1-(diisopropylamino)-2-(4-(trifluoromethyl)phenyl)ethylidene)-3-phenylpropanamide (4aga)



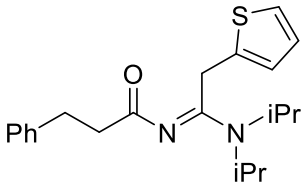
The reaction of **1a**, 3-tolylacetylene and diisopropylamine according to procedure D under an N_2 atmosphere yielded the product as a white solid: 168 mg, 0.46 mmol, 91%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.28 – 7.19 (m, 6H), 7.16 (t, *J* = 7.1 Hz, 1H), 6.99 (t, *J* = 8.5 Hz, 2H), 3.97 – 3.80 (m, 1H), 3.91 (2H), 3.58 – 3.42 (m, 1H), 2.96 (t, *J* = 8.0 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.61 – 1.33 (m, 6H), 1.08 – 0.77 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 182.34, 162.55, 160.95, 160.60, 142.00, 132.17 (d, *J* = 3.3 Hz), 129.68 (d, *J* = 7.9 Hz), 125.73, 115.50 (d, *J* = 21.3 Hz), 49.63, 47.44, 41.72, 36.68, 31.93, 20.12. HRMS (ESI^+) *m/z* calc. for $[C_{23}H_{29}FN_2O+H]^+$ 369.2337 found 369.233.

(E) -N-(1-(diisopropylamino)-2-(pyridin-3-yl)ethylidene)-3-phenylpropanamide (4aha)



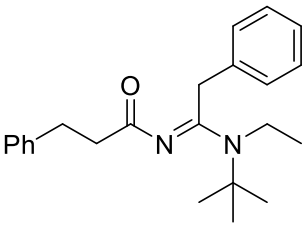
The reaction of **1a**, phenylacetylene and diisopropylamine according to procedure D yielded the product as a colorless oil: 138 mg, 0.39 mmol, 79%. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.50 – 8.44 (m, 2H), 7.65 (d, J = 7.9 Hz, 1H), 7.29 – 7.19 (m, 5H), 7.15 (t, J = 6.7 Hz, 1H), 3.93 (s, 2H), 3.90 – 3.75 (m, 1H), 3.60 – 3.37 (m, 1H), 2.96 (t, J = 7.9 Hz, 2H), 2.70 (t, J = 7.9 Hz, 2H), 1.64 – 1.33 (m, 6H), 1.10 – 0.76 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 182.48, 160.20, 149.44, 148.05, 141.86, 135.80, 132.31, 128.32, 128.28, 125.76, 123.56, 49.69, 47.60, 41.67, 34.72, 31.87, 20.17. HRMS (FD^+) *m/z* calc. for $[C_{22}H_{29}N_3O_1]^+$ 351.2311 found 351.2277.

(E)-N-(1-(diisopropylamino)-2-(thiophen-3-yl)ethylidene)-3-phenylpropanamide (4aga)



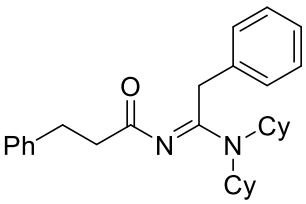
The reaction of **1a**, phenylacetylene and diisopropylamine according to procedure D yielded the product as a colorless oil: 175 mg, 0.49 mmol, 98%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.20 (m, 5H), 7.18 (t, J = 6.9 Hz, 1H), 7.07 (d, J = 1.4 Hz, 1H), 7.00 (d, J = 4.9 Hz, 1H), 4.06 – 3.94 (m, 1H), 3.94 (s, 2H), 3.59 – 3.41 (m, 1H), 2.97 (t, J = 8.0 Hz, 2H), 2.69 (t, J = 8.0 Hz, 2H), 1.60 – 1.30 (m, 7H), 1.17 – 0.82 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 182.34, 161.05, 142.06, 136.28, 128.34, 128.28, 127.91, 125.83, 125.72, 121.66, 49.71, 47.44, 41.74, 32.39, 32.00, 20.17. HRMS (FD^{+}) *m/z* calc. for $[C_{21}H_{28}N_2O_1S_1]^{+}$ 356.1922 found 356.1930.

(E)-N-(1-(tert-butyl(ethyl)amino)-2-phenylethylidene)-3-phenylpropanamide (4aag)



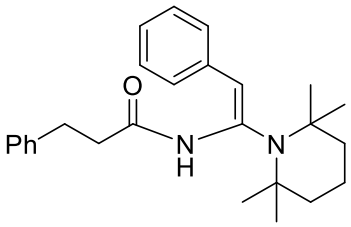
The reaction of **1a**, phenylacetylene and *N*-ethyl-*N*-tert-butylamine according to procedure D yielded the product as a white solid: 168 mg, 0.48 mmol, 96%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.21 (m, 5H), 7.21 – 7.13 (m, 3H), 3.97 (s, 2H), 3.33 (q, *J* = 7.1 Hz, 2H), 2.89 (t, *J* = 7.9 Hz, 2H), 2.62 (t, *J* = 8.3 Hz, 2H), 1.56 (s, 9H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 182.10, 160.58, 141.98, 136.61, 128.73, 128.33, 128.28, 128.14, 126.59, 125.72, 58.87, 41.57, 40.31, 37.59, 31.80, 28.79, 17.24. HRMS (FD^{+}) *m/z* calc. for $[C_{23}H_{30}N_2O_1]^{+}$ 350.2358 found 350.2356.

(E)-N-(1-(dicyclohexylamino)-2-phenylethylidene)-3-phenylpropanamide (4aah)



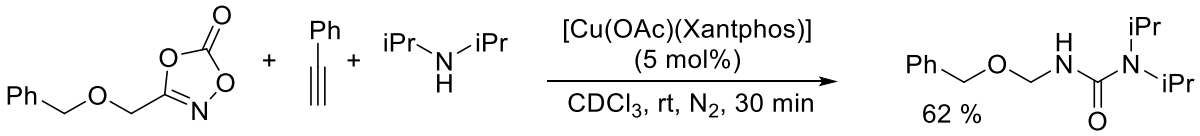
The reaction of **1a**, phenylacetylene and dicyclohexylamine according to procedure D yielded the product as a yellow solid: 204 mg, 0.48 mmol, 95%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.39 – 7.12 (m, 10H), 4.01 (s, 2H), 3.61 – 3.45 (m, 1H), 3.12 – 2.92 (m, 3H), 2.90 – 2.62 (m, 4H), 1.86 – 1.74 (m, 2H), 1.74 – 1.42 (m, 7H), 1.42 – 1.07 (m, 8H), 1.07 – 0.82 (m, 3H). 13C NMR (126 MHz, chloroform-*d*) δ 182.00, 161.70, 142.15, 136.75, 128.64, 128.34, 128.28, 128.26, 126.54, 125.72, 58.88, 57.90, 53.49, 41.87, 37.87, 32.09, 30.57, 29.17, 26.58, 25.73, 25.54, 25.13. HRMS (FD^{+}) *m/z* calc. for $[C_{29}H_{38}N_2O_1]^{+}$ 430.2984 found 430.2965.

(E)-3-phenyl-N-(2-phenyl-1-(2,2,6,6-tetramethylpiperidin-1-yl)vinyl)propanamide (4aai)



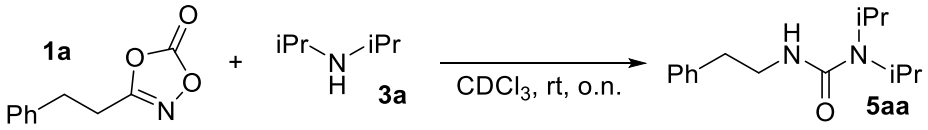
The reaction of **1a**, phenylacetylene and diisopropylamine according to procedure D yielded the product as a white solid: 180 mg, 0.46 mmol, 92%. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.37 – 7.09 (m, 11H), 6.30 (d, *J* = 6.4 Hz, 1H), 6.05 (s, 1H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.90 – 1.69 (m, 2H), 1.61 – 1.48 (m, 4H), 1.48 – 1.36 (m, 2H), 1.31 (s, 7H), 1.12 (s, 5H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 167.31, 140.92, 137.36, 134.10, 128.52, 128.05, 127.60, 126.22, 126.06, 120.07, 55.64, 41.83, 39.22, 32.22, 30.83, 25.31, 18.02. HRMS (FD^{+}) *m/z* calc. for $[C_{26}H_{34}N_2O_1]^{+}$ 390.2671 found 390.2737.

Reaction copper catalyzed reaction of 1i with 2a and 3a



In a N_2-filled glovebox, a 2 mL vial was charged with a solution of [Cu(OAc)(Xantphos)] (8.8 mg, 12.5 µmol) and phenylacetylene (55 µL, 0.5 mmol) in $CDCl_3$ (0.5 mL). Then, diisopropylamine (70 µL, 0.5 mmol) and **1i** (52 mg, 0.25 mmol) were added. After stirring for 30 minutes, the reaction mixture was removed from the glovebox and analyzed by ^{1}H-NMR. Clearly, the ureum N,N-diisopropyl-N'-benzyloxymethylurea was the main product in the crude NMR spectra (62% yield, based on trimethoxybenzene as the external standard). ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.39 – 7.14 (m, 5H), 5.15 (br, 1H), 4.86 (d, *J* = 6.8 Hz, 2H), 4.59 (s, 2H), 3.81 (hept, J = 6.9 Hz, 2H), 1.21 (d, J = 6.9 Hz, 12H). The desired product 2-(benzyloxy)-N-(1-(diisopropylamino)-2-phenylethylidene)acetamide could not be isolated.

Uncatalyzed reaction of 1a with 3a



To a solution of 1a (48 mg, 0.25 mmol) in $CDCl_3$ was added diisopropylamine (70 µL, 0.5 mmol). After stirring overnight at r.t., a ^{1}H-NMR spectrum was recorded showing full conversion of **1a** to N,N-diisopropyl-N'-phenethylurea (**3a**)[12].

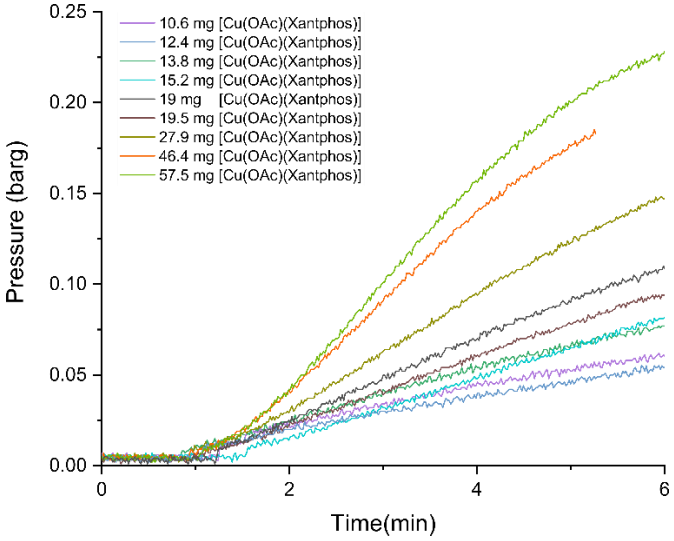
Kinetic Measurements

General experiment preparation

The Man on the Moon X102 kit[13] was used to measure the pressure buildup during the reaction. Oxygen was removed from amylene-stabilized $CHCl_3$ by 3 freeze-pump-thaw cycles in a Schlenk flask attached to a N_2-filled Schlenk line. Phenylacetylene was distilled and degassed by bubbling with N_2. Diisopropylamine was degassed by bubbling with N_2.

Determination of the kinetic order in [catalyst]

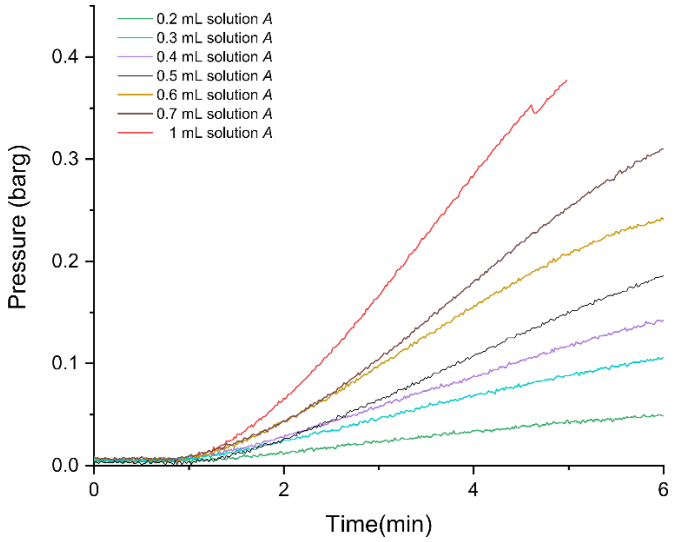
A stock solution A_{Cat} was prepared by dissolving **1a** (1.15 g, 6.03 mmol) in $CHCl_3$ (8 mL). A stock solution B_{Cat} was prepared by dissolving phenylacetylene (1.76 mL, 16 mmol) in $CHCl_3$ (40 mL). To the flask of the X102 kit, with the valve open towards a Schlenk line equipped with a magnetic stir bar, was added [Cu(OAc)(Xantphos)] (**X_{Cat}** mg, 0.0177-0.0820 mmol). The flask was purged with N_2 after which solution B_{Cat} (2.5 mL) was added. When diisopropylamine (140 µL) was added, the solution turned yellow. Then solution A_{Cat} (0.5 mL) was added and the valve was directly switched to the pressure transducer to collect the pressure buildup.



X_{Cat} (mg)	d(P)/dt (barg min^{-1})
10.6	0.01113
12.4	0.00935
13.8	0.01493
15.2	0.01595
19	0.02316
19.5	0.01921
27.9	0.03167
46.4	0.04898
57.5	0.05763

Determination of the kinetic order in [dioxazolone]

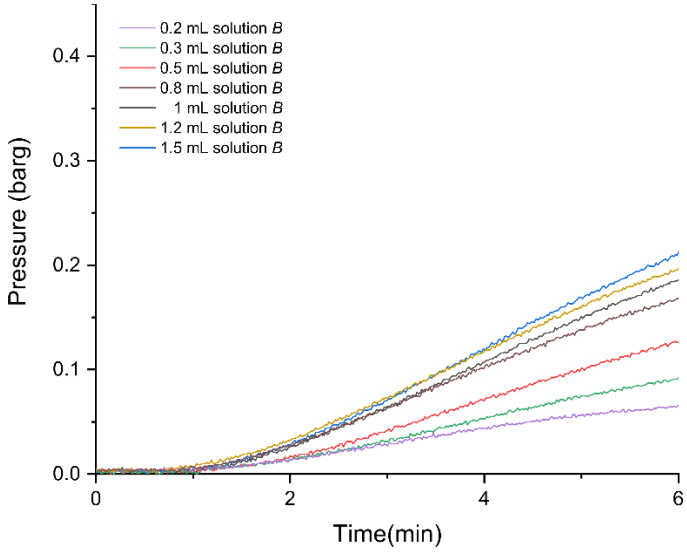
A stock solution A_{Diox} was prepared by dissolving **1a** (1.15 g, 6.03 mmol) in $CHCl_3$ (6 mL). A stock solution B_{Diox} was prepared by dissolving phenylacetylene (1.32 mL, 12 mmol) in $CHCl_3$ (12 mL). A stock solution C_{Diox} was prepared by dissolving [Cu(OAc)(Xantphos)] (210 mg, 0.30 mmol) in $CHCl_3$ (12 mL). To the flask of the X102 kit, with the valve open towards a Schlenk line equipped with a magnetic stir bar, was added solution C_{Diox} (1 mL), followed by addition of solution B_{Diox} (1 mL). Then was added $CHCl_3$ (1-**X_{Diox}** mL). When diisopropylamine (140 µL) was added, the solution turned yellow. Then solution A_{Diox} (**X_{Diox}** mL) was added and the valve was directly switched to the pressure transducer to collect the pressure buildup.



X_{Diox} (mL)	d(P)/dt (barg min^{-1})
1	0.114104
0.7	0.073457
0.6	0.056807
0.5	0.042929
0.4	0.029383
0.3	0.022037
0.2	0.009305

Determination of the kinetic order in [phenylacetylene]

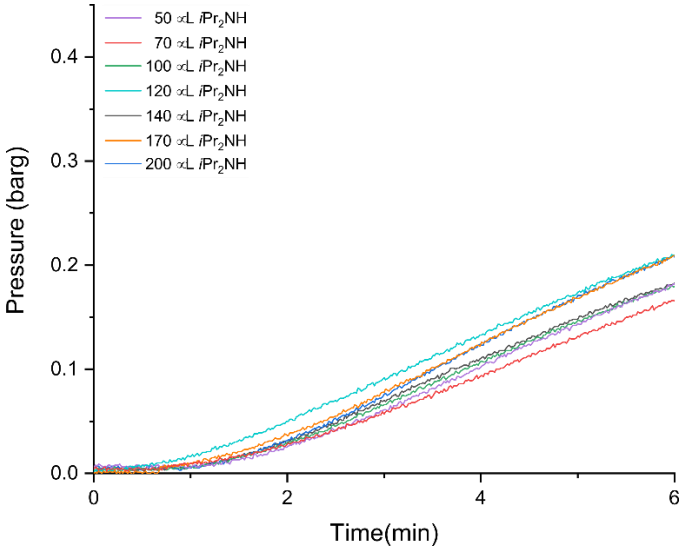
A stock solution A_{PhCCH} was prepared by dissolving **1a** (2.69 g, 6.03 mmol) in $CHCl_3$ (14 mL). A stock solution B_{PhCCH} was prepared by dissolving phenylacetylene (3.08 mL, 12 mmol) in $CHCl_3$ (28 mL). A stock solution C_{PhCCH} was prepared by dissolving [Cu(OAc)(Xantphos)] (490 mg, 0.70 mmol) in $CHCl_3$ (28 mL). To the flask of the X102 kit, with the valve open towards a Schlenk line equipped with a magnetic stir bar, was added solution C_{PhCCH} (1 mL), followed by addition of solution B_{PhCCH} (**X_{PhCCH}** mL). Then was added $CHCl_3$ (1.5-**X_{PhCCH}** mL). When diisopropylamine (140 µL) was added, the solution turned yellow. Then solution A_{PhCCH} (0.5 mL) was added and the valve was directly switched to the pressure transducer to collect the pressure buildup.



X_{PhCCH} (mL)	d(P)/dt (barg min^{-1})
1.5	0.049495
1.2	0.043565
1	0.042929
0.8	0.038057
0.5	0.029798
0.3	0.020854
0.2	0.015023

Determination of the kinetic order in [*i*Pr$_2$NH]

To the flask of the X102 kit, with the valve open towards a Schlenk line equipped with a magnetic stir bar, was added solution C_{PhCCH} (1 mL), followed by addition of solution B_{PhCCH} (1 mL). Then was added $CHCl_3$ (0.5 mL). When diisopropylamine ($\mathbf{X_{iPr2NH}}$ µL) was added, the solution turned yellow. Then solution A_{PhCCH} (0.5 mL) was added and the valve was directly switched to the pressure transducer to collect the pressure buildup.



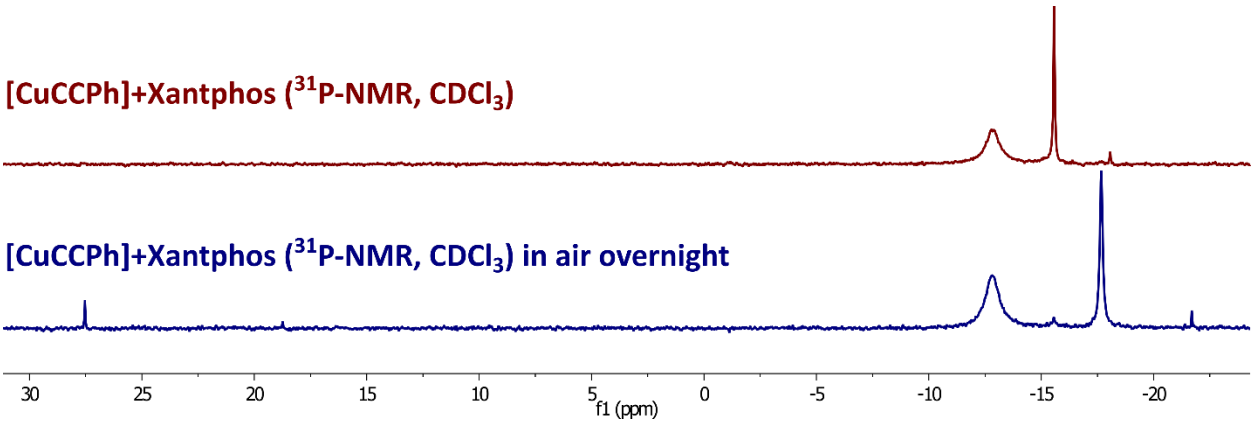
$\mathbf{X_{iPr2NH}}$ (µL)	d(P)/dt (barg min^{-1})
200	0.045989
170	0.044643
140	0.039876
120	0.041445
100	0.038501
70	0.036087
50	0.039652

Formation of [(Xantphos)Cu(CCPh)].

To investigate the formation of [(Xantphos)Cu(CCPh)], we used ^{31}P-NMR spectroscopy. We envisioned this to be the easiest way to validate the formation of this species. As a benchmark, we formed [(Xantphos)Cu(CCPh)] in different ways. All spectra for this study were measured in $CDCl_3$.

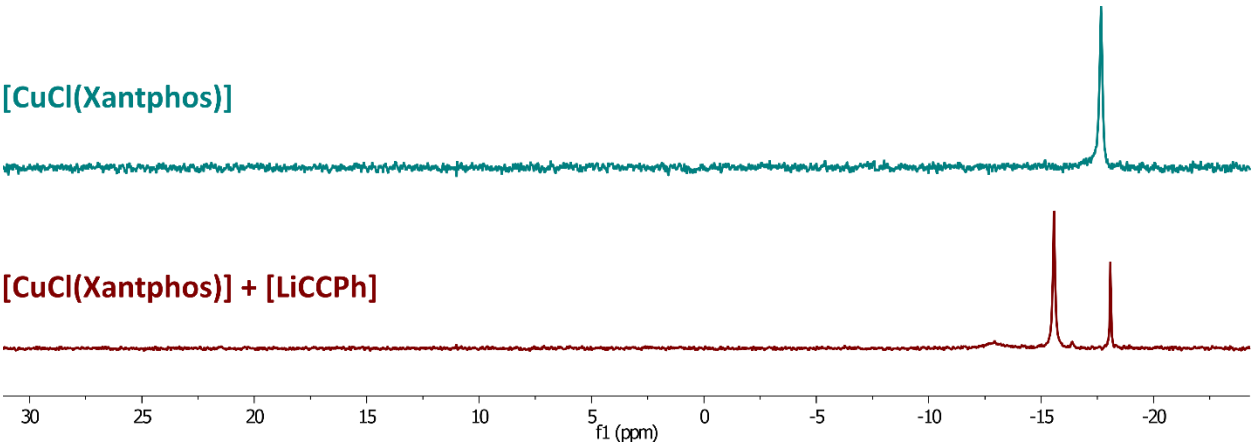
1. [CuCCPh]+Xantphos

In an N_2-filled glovebox, a vial was charged with [Cu(CCPh)] (74 mg, 0.5 mmol) and Xantphos (281 mg, 0.5 mmol). Dry, degassed DCM (6 mL) was added and after 2h of stirring under a nitrogen atmosphere, the reaction turned into a green suspension. The reaction mixture was filtered. a sample (0.5 mL) was taken from the filtrate for NMR spectroscopy and dry, degassed pentane (60 mL) was added to the remaining solution. After 1 week, small crystals were formed that were determined to be $[(Xantphos)_2Cu_3(CCPh)_3]$ by X-ray diffraction (see page S24). The collected ^{31}P-NMR spectra contains a minor signal for Xantphos (-18 ppm), a sharp signal at -15.6 ppm and a large broad signal at -12.8 ppm, which likely results from the trinuclear species $[(Xantphos)_2Cu_3(CCPh)_3]$. After exposing to air overnight, the signal at -15.6 ppm disappeared and a signal at -17.7 ppm appeared together with the formation of Xantphos-*P*-dioxide (27.5 ppm). $[(Xantphos)_2Cu_3(CCPh)_3]$ seems to be stable in air.



2. [(Xantphos)CuCl] + [LiCCPh]

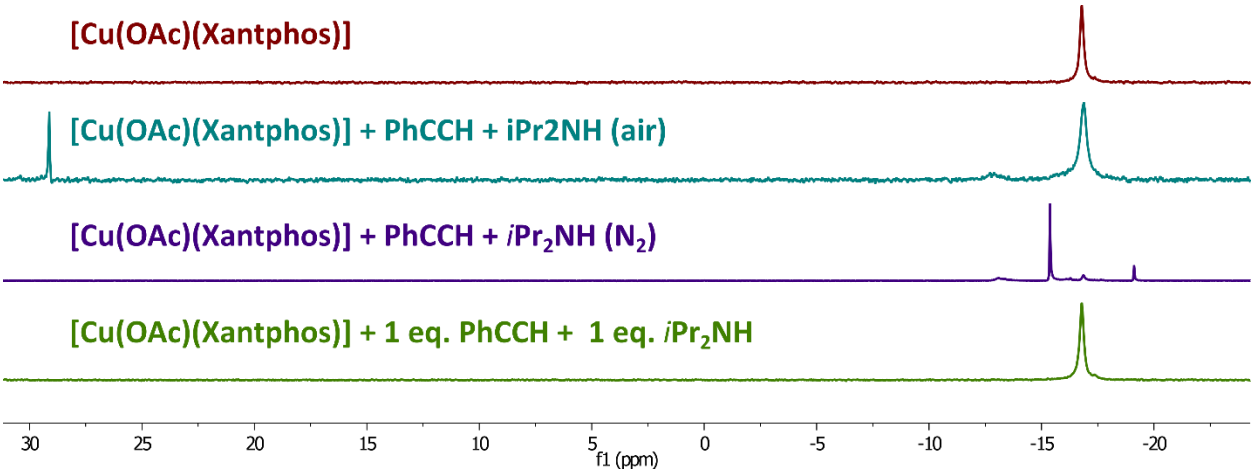
In an N_2-filled glovebox, [(Xantphos)CuCl] (339 mg, 0.5 mmol) was suspended in dry, degassed THF. Then, dropwise, a solution of [LiCCPh] in THF (0.5 mL, 1M, 0.5 mmol) was added dropwise and the reaction mixture turned yellow. After stirring for 1h, the solvent was removed *in vacuo* and dry, degassed DCM (2 mL) was added. The suspension was filtered and the filtrate was concentrated *in vacuo* to give yellow powder. The collected ^{31}P-NMR spectra contained a minor broad signal at -12.8 ppm, a sharp signal at -15.6 ppm and a Xantphos signal (-18 ppm). Formation of insoluble polymeric $[CuCCPh]_n$ could be an explanation for the dissociation of Xantphos.



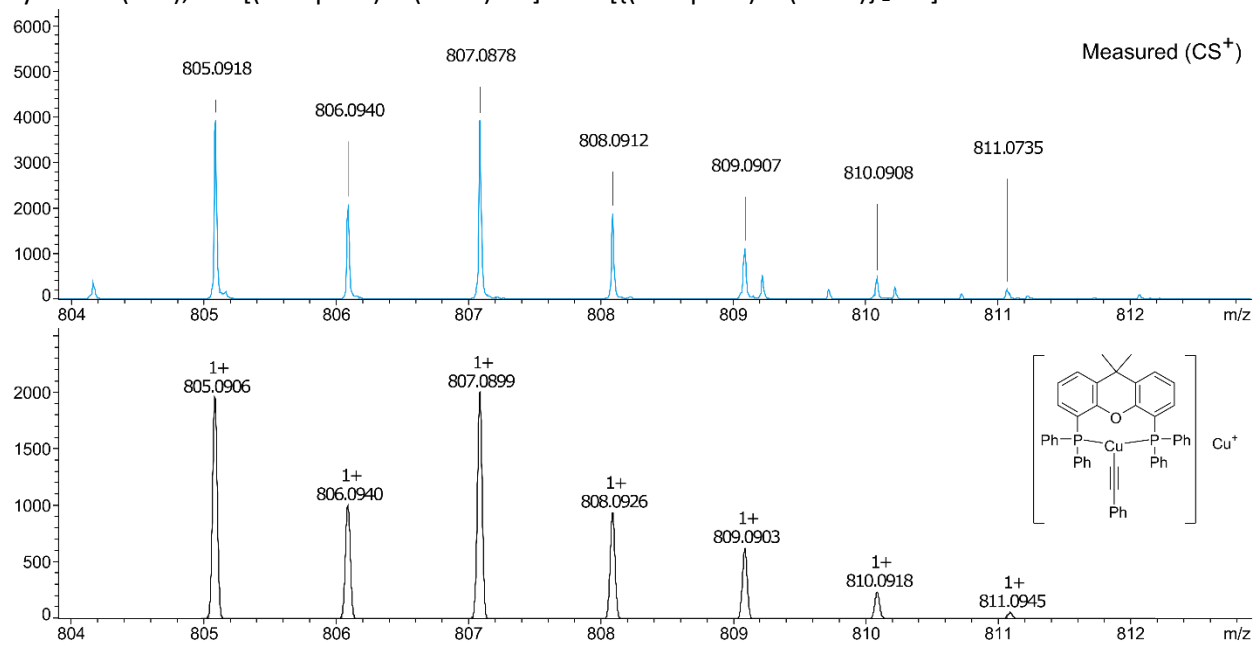
3. [Cu(OAc)(Xantphos)] + PhCCH + *i*Pr_2NH

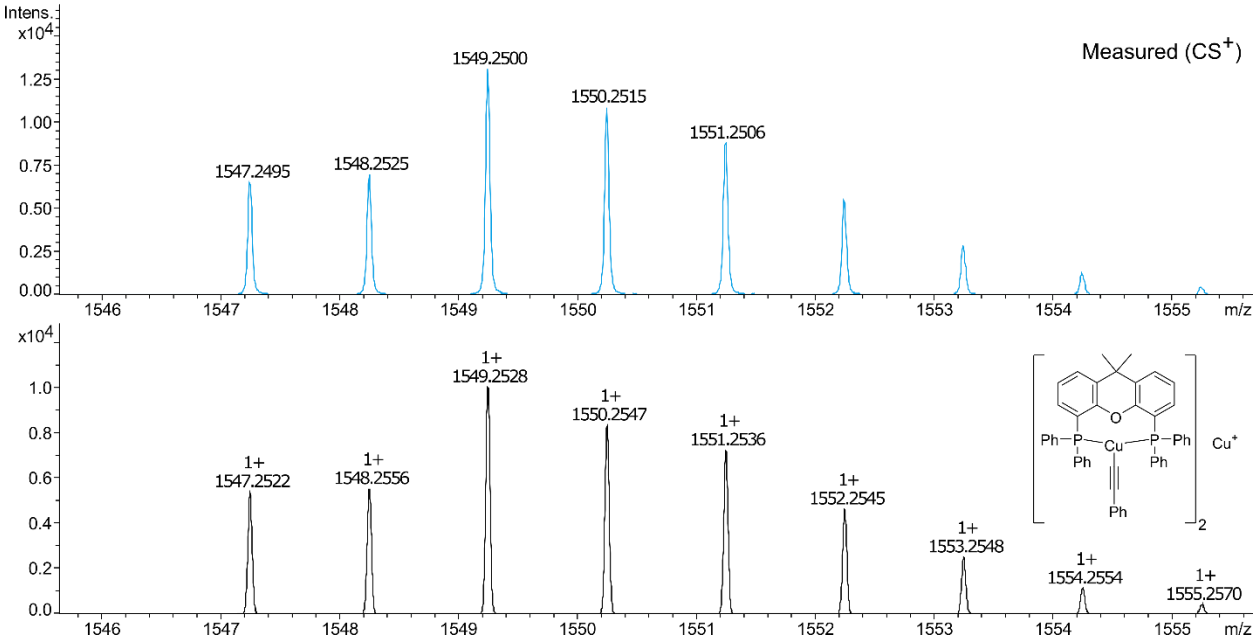
In a 2 mL vial, a stock solution of [Cu(OAc)(Xantphos)] (8.8 mg, 12.5 µmol) was dissolved in $CDCl_3$ (1 mL). No reaction was observed when to 0.5 mL of the stock solution was added either PhCCH (55 µL, 0.5 mmol) or *i*Pr_2NH (70 µL, 0.5 mmol). When to the solution of [Cu(OAc)(Xantphos)], $CDCl_3$ and PhCCH was added *i*Pr_2NH (70 µL, 0.5 mmol), direct color change to yellow was observed. After 5 minutes of stirring, a ^{31}P-NMR spectrum was recorded which did not show a signal at -15.6 ppm. We did observe Xantphos-*P*-dioxide (27.5 ppm) and the broad signal at -12.8 ppm.

Performing the same reaction under an atmosphere of N_2, does show a ^{31}P-NMR signal at -15.6 ppm. If only one equivalent of phenylacetylene and *i*Pr_2NH is used, no reaction was observed.



By HRMS (CS+), the [(Xantphos)Cu(CCPh)-Cu]$^+$ and [{(Xantphos)Cu(CCPh)}$_2$-Cu]$^+$ were observed.

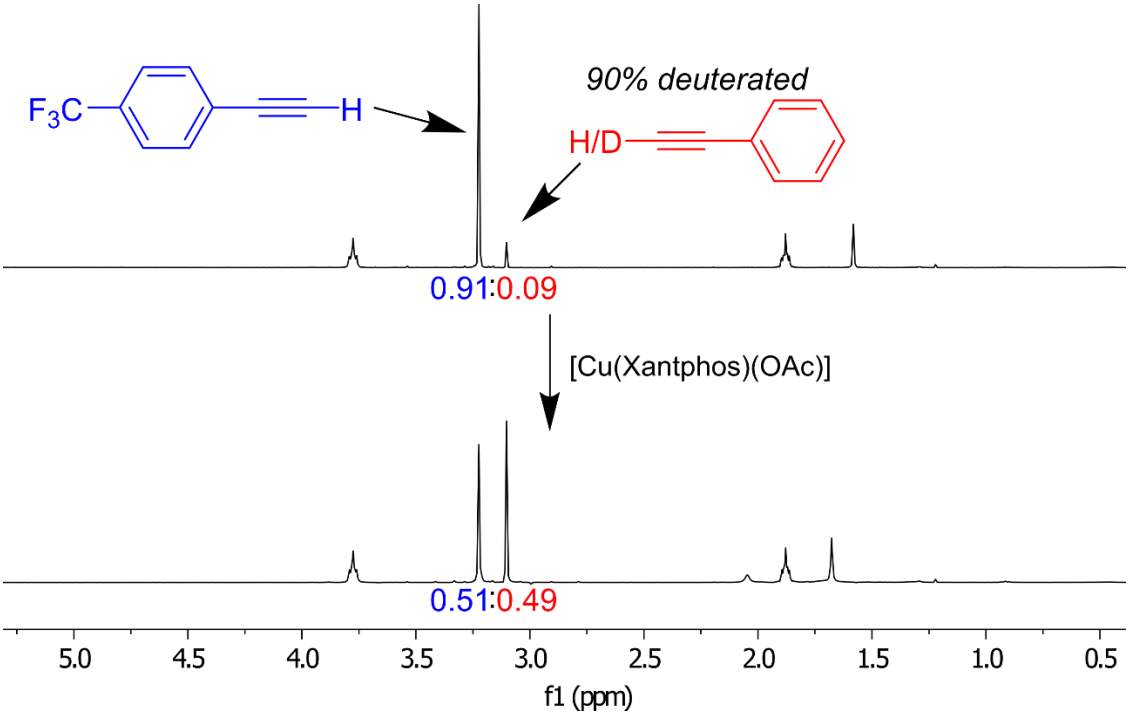




H/D-Exchange Experiment

The (ethynyl-D)benzene used for this experiment was 94% pure (with THF residue) and 90% deuterated.

A stock solution (Stock A) was prepared by adding (ethynyl-D)benzene (0.12 mL, 1.0 mmol) and 4-ethynyl-α,α,α-trifluorotoluene (0.16 mL, 1.0 mmol) to dry, degassed $CDCl_3$ (2 mL). To [Cu(OAc)(Xantphos)] (17.5 mg, 0.025 mmol) was added a part of stock A (1 mL). After stirring both mixtures for 1 h, 1H-NMR spectra were recorded, which showed H/D scrambling only for the solution containing the catalyst. Combined with the ^{31}P-NMR studies described in the main text, these data confirm the presence of (slightly) endergonic equilibrium reactions of the type [Cu(OAc)(Xantphos)] + HCC(Aryl) ⇌ [Cu(CCAryl)(Xantphos)] + HOAc, in good agreement with the proposed mechanism shown in Scheme 3 and Figure 6 of the main text.



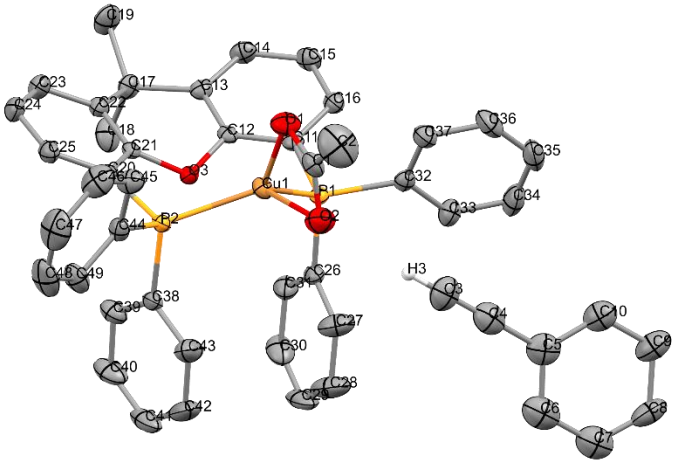
X-ray Crystal Structure Determination

X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å) and a CMOS Photon 100 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX3 software.[14] Absorption correction and scaling was performed with SADABS.[15] The structures were solved using intrinsic phasing with the program SHELXT.[16] Least-squares refinement was performed with SHELXL-2014[17] against F2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times Ueq of the attached C atoms. CCDC 1937520 contain the supplementary crystallographic

data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

[Cu(OAc)(Xantphos)]-HCCPh

The single crystal of [Cu(OAc)(Xantphos)]-HCCPh was obtained by slow vapor diffusion of pentane into a solution of [Cu(OAc)(Xantphos)] in phenylacetylene, and the molecular structure of the interaction species was determined by X-ray diffraction measurements. The figure below shows a displacement ellipsoid plot (50% probability level). Selected bond lengths are shown in the table below.



Atoms	*Bond length (Å)*
Cu1-O1	2.1124(18)
Cu1-O2	2.313(2)
C3-H3	0.95
O2-H3	2.222
O2-C3	3.160

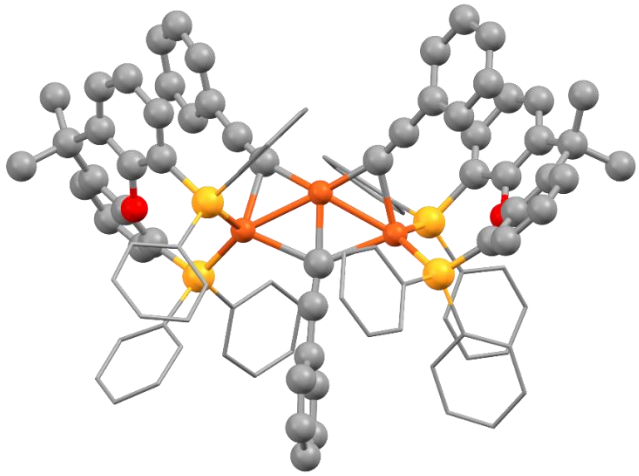
Atoms	*Angle (°)*
O2-H3-C3	169.62

$C_{49}H_{41}CuO_3P_2$, Fw = 803.30, shape, 0.429×0.362x×0.178 mm, monoclinic, $P2_1/c$ (No: 14)), a = 13.1535(7), b = 18.2025(9), c = 17.8085(9) Å, β = 107.602(2)°, V = 4064.2(4) Å^3, Z = 4, D_x = 1.313 g/cm^3, μ = 0.658 mm^{-1}. 163955 Reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.81 Å^{-1}. 7973 Reflections were unique (R_{int} = 0.0448), of which 6537 were observed [I>2σ(I)]. 563 Parameters were refined with 243 restraints. R1/wR2 [I > 2σ(I)]: 0.0389/0.0949. R1/wR2 [all refl.]: 0.0540/ 0.1087. S = 1.054. Residual electron density between -0.336 and 0.654 e/Å^3. CCDC 1937520.

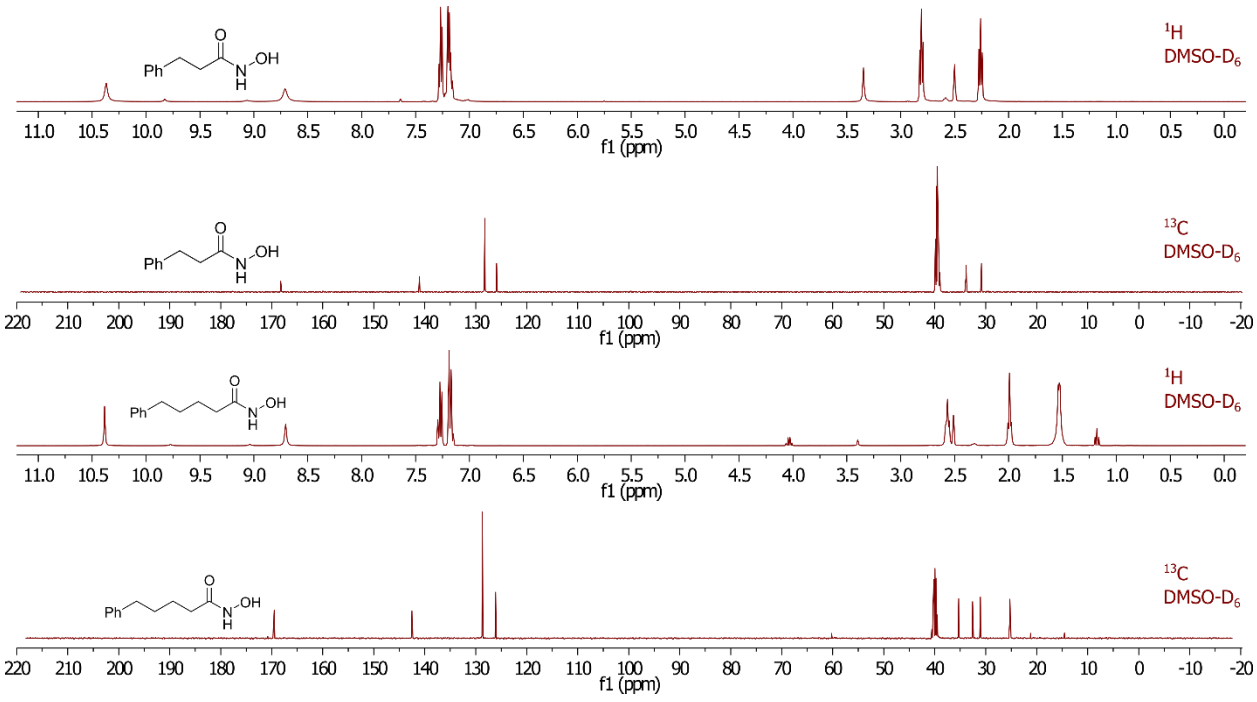
[(Xantphos)$_2$Cu$_3$(CCPh)$_3$]

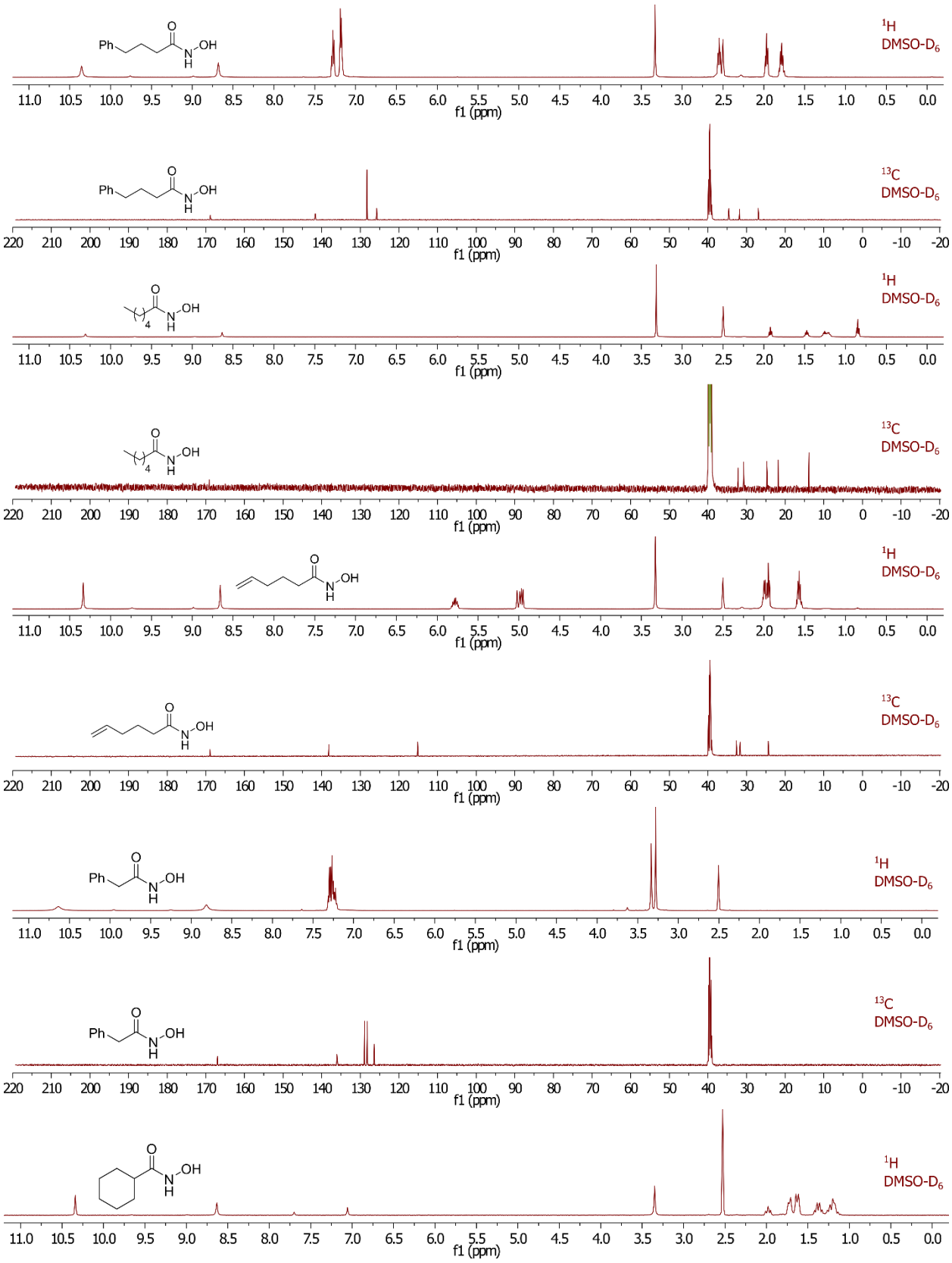
Single crystals obtained from the reaction on page S21 proved of insufficient quality for a fully refined structure (R1 = 0.14030). Therefore, only a preliminary connectivity plot is depicted to illustrate the

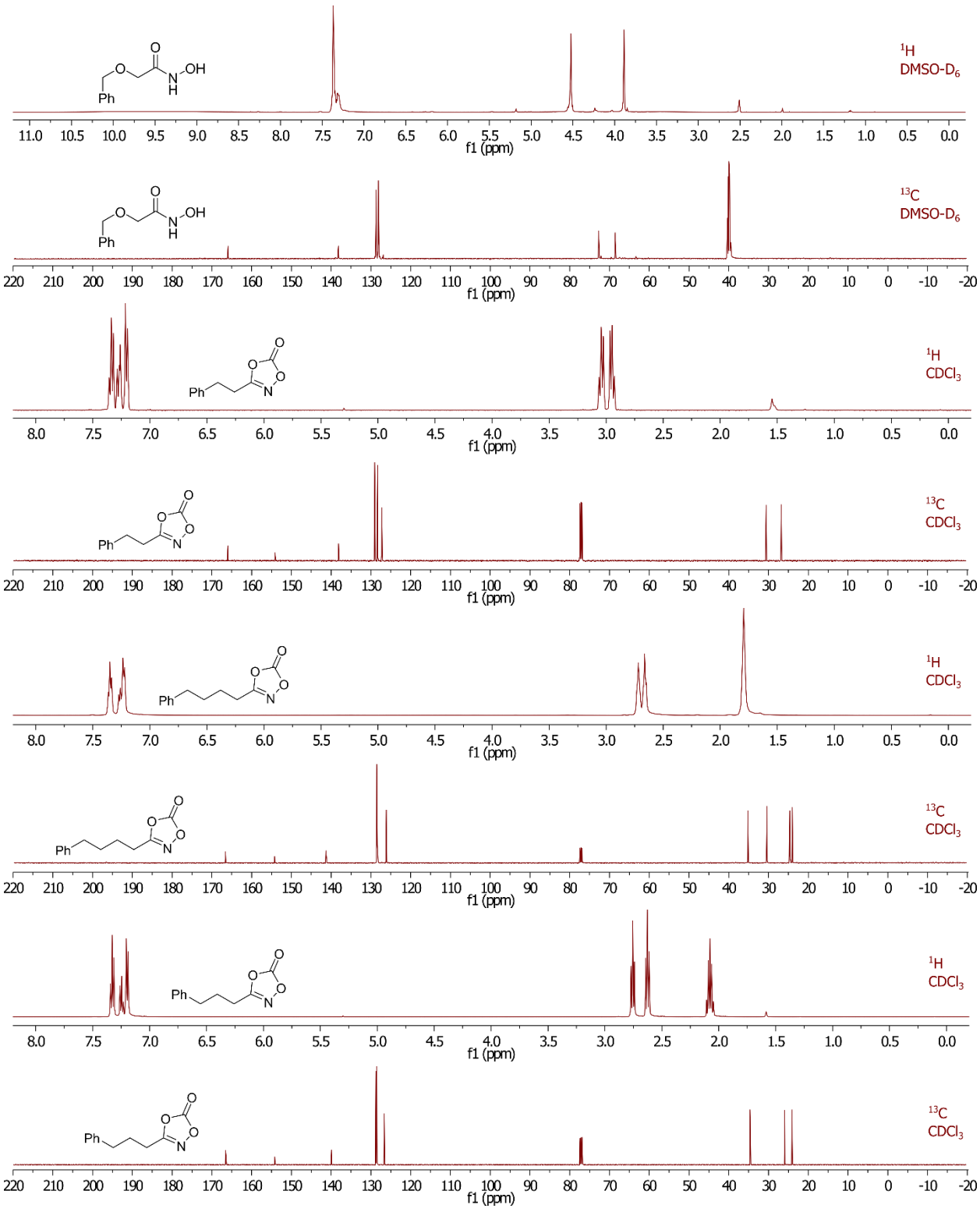
trinuclear nature of the complex. For clarity, protons and lattice solvent molecules are not displayed.

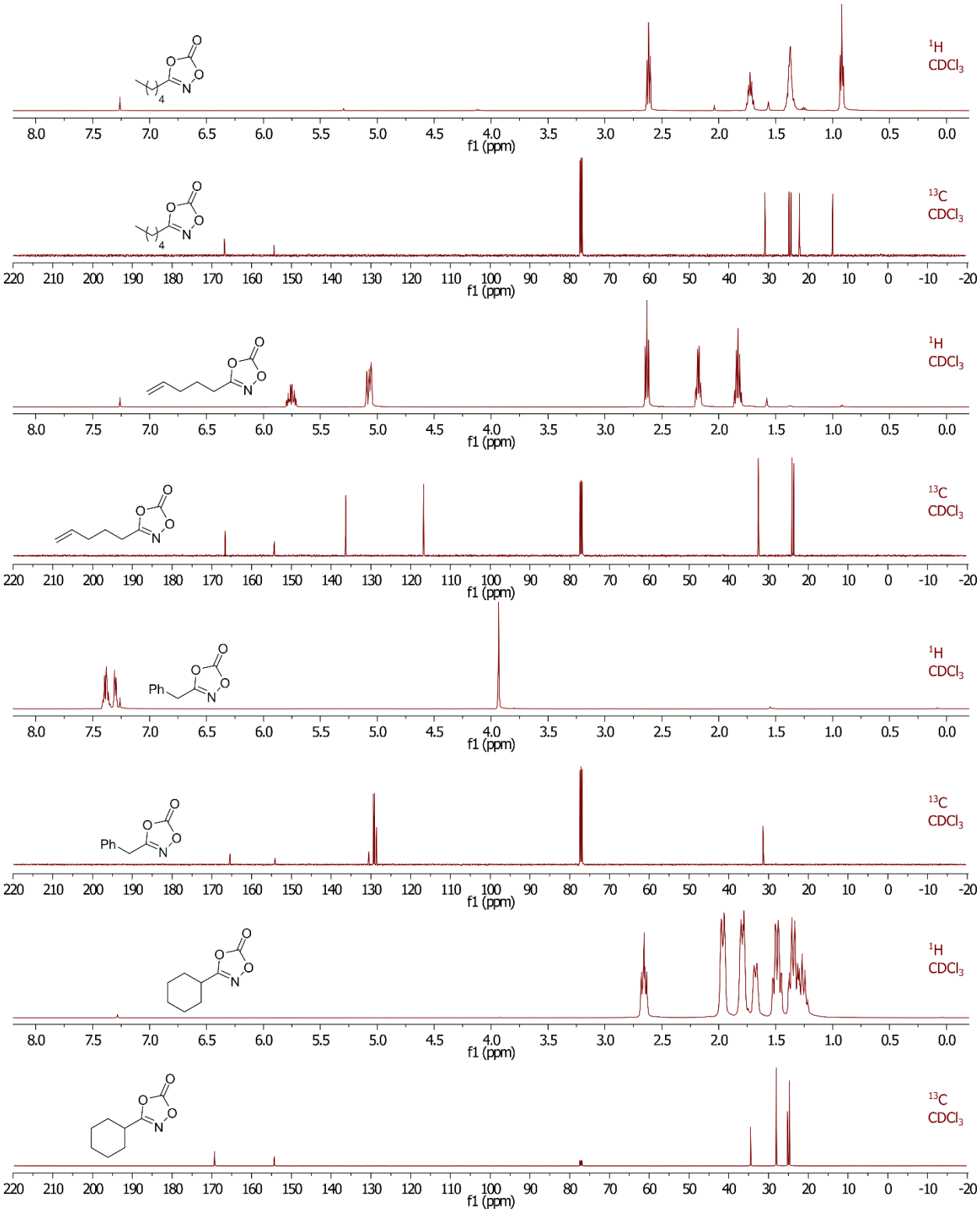


Product NMR spectra




Ph
O
N
OH
H
^{1}H
DMSO-D$_6$
^{13}C
DMSO-D$_6$
f1 (ppm)


^{1}H
DMSO-D$_6$
f1 (ppm)
^{13}C
DMSO-D$_6$
f1 (ppm)
^{1}H
CDCl$_3$
f1 (ppm)
^{13}C
CDCl$_3$
f1 (ppm)
^{1}H
CDCl$_3$
f1 (ppm)
^{13}C
CDCl$_3$
f1 (ppm)
^{1}H
CDCl$_3$
f1 (ppm)
^{13}C
CDCl$_3$
f1 (ppm)


^{1}H
$CDCl_3$
f1 (ppm)
^{13}C
$CDCl_3$
f1 (ppm)
^{1}H
$CDCl_3$
f1 (ppm)
^{13}C
$CDCl_3$
f1 (ppm)
Ph
^{1}H
$CDCl_3$
f1 (ppm)
Ph
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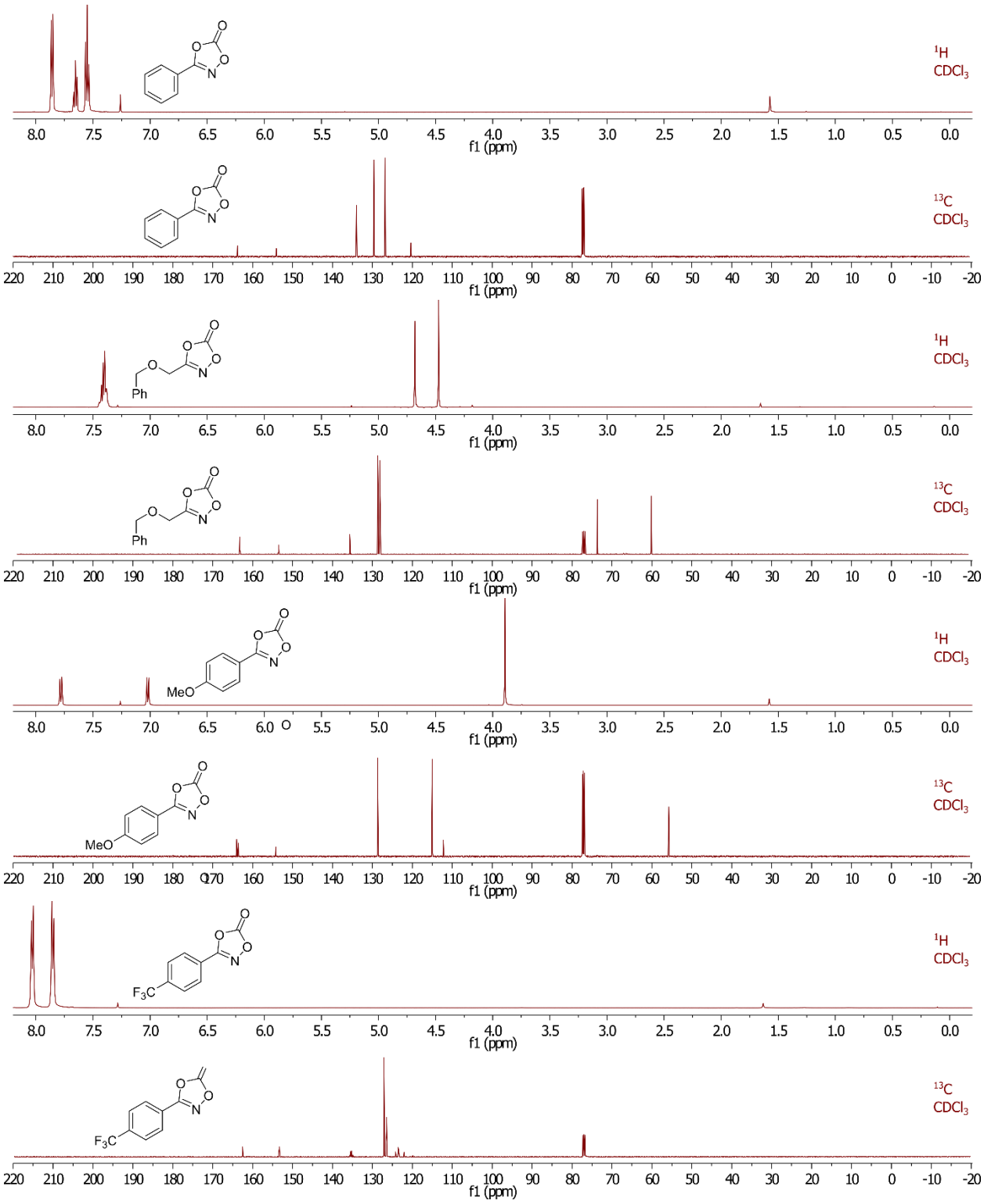
f1 (ppm)
^{13}C
$CDCl_3$
f1 (ppm)


^{1}H
$CDCl_3$
f1 (ppm)
^{13}C
$CDCl_3$
f1 (ppm)
Ph
^{1}H
$CDCl_3$
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Ph
^{13}C
$CDCl_3$
f1 (ppm)
MeO
^{1}H
$CDCl_3$
f1 (ppm)
MeO
^{13}C
$CDCl_3$
f1 (ppm)
F_3C
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$CDCl_3$
f1 (ppm)
F_3C
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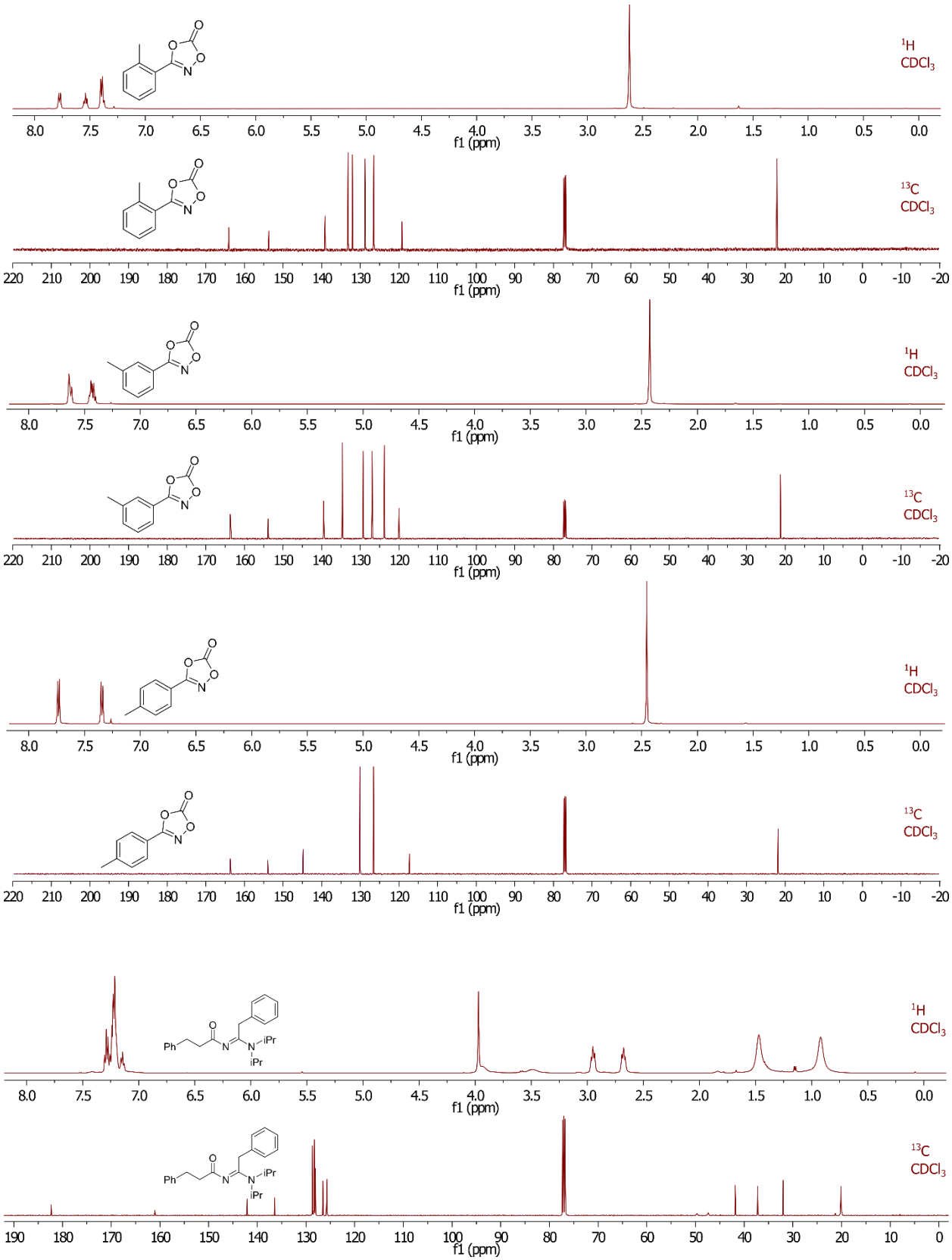
$CDCl_3$
f1 (ppm)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f1 (ppm)
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f1 (ppm)
Ph
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iPr
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iPr
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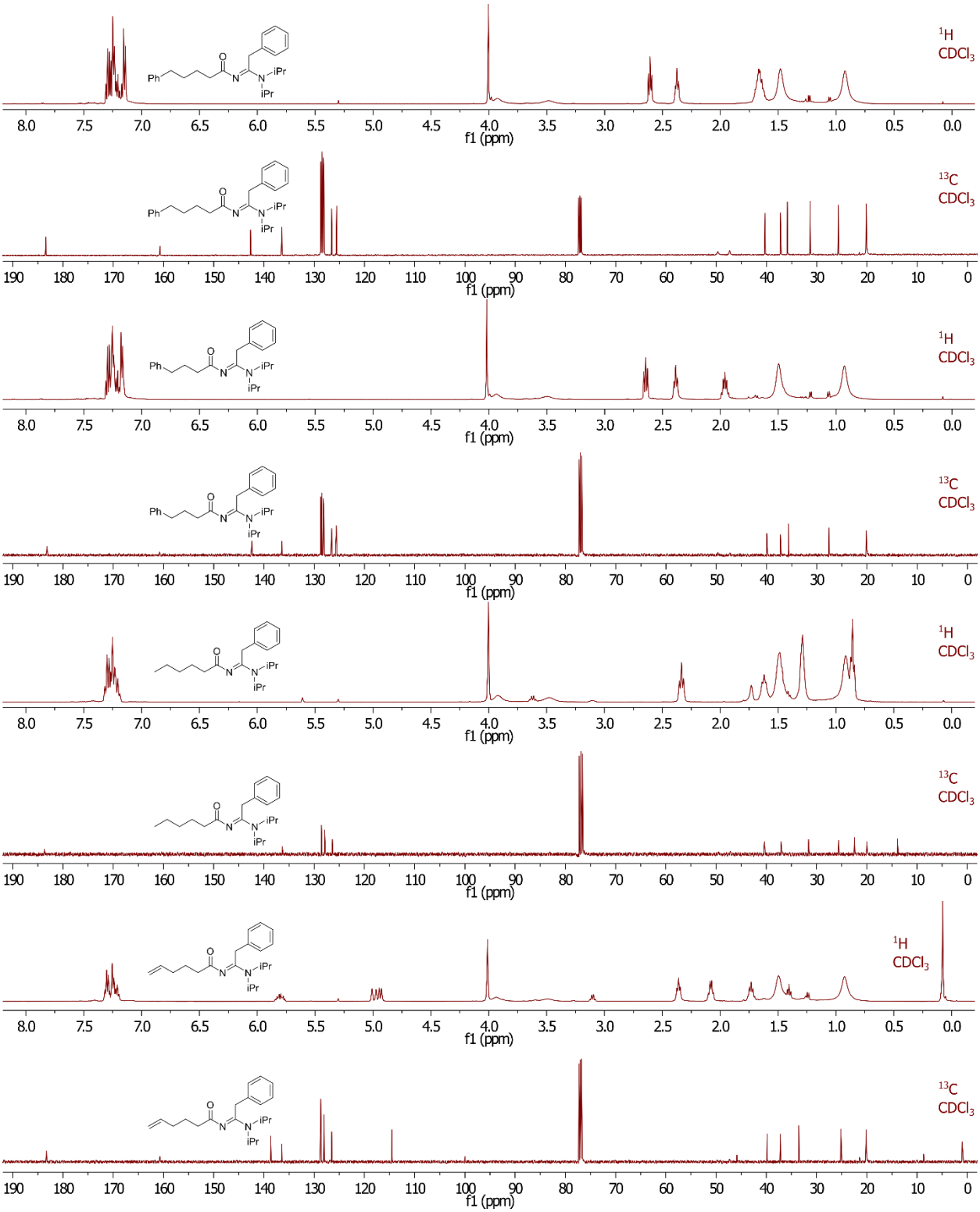
f1 (ppm)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iPr
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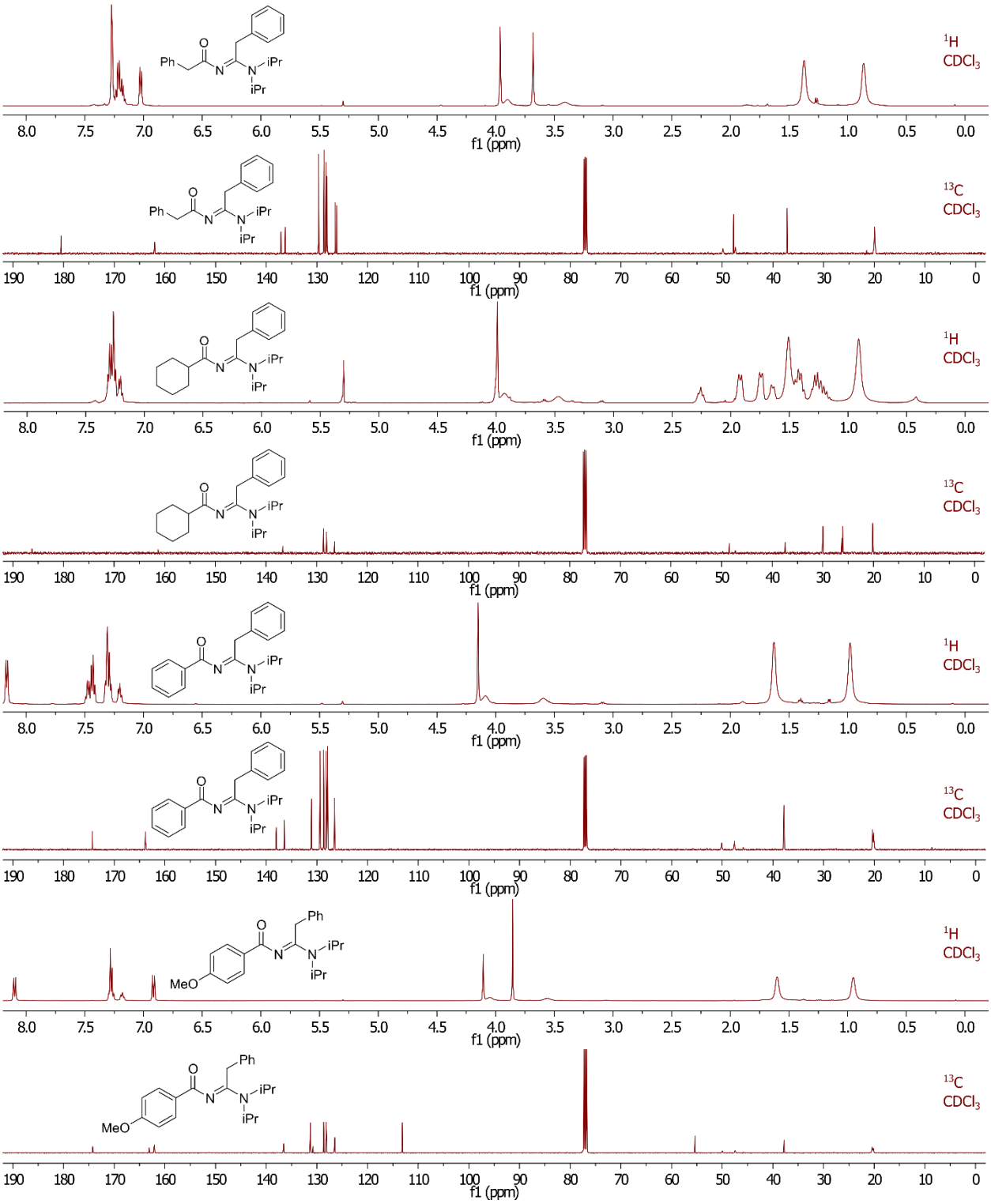
f1 (ppm)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iPr
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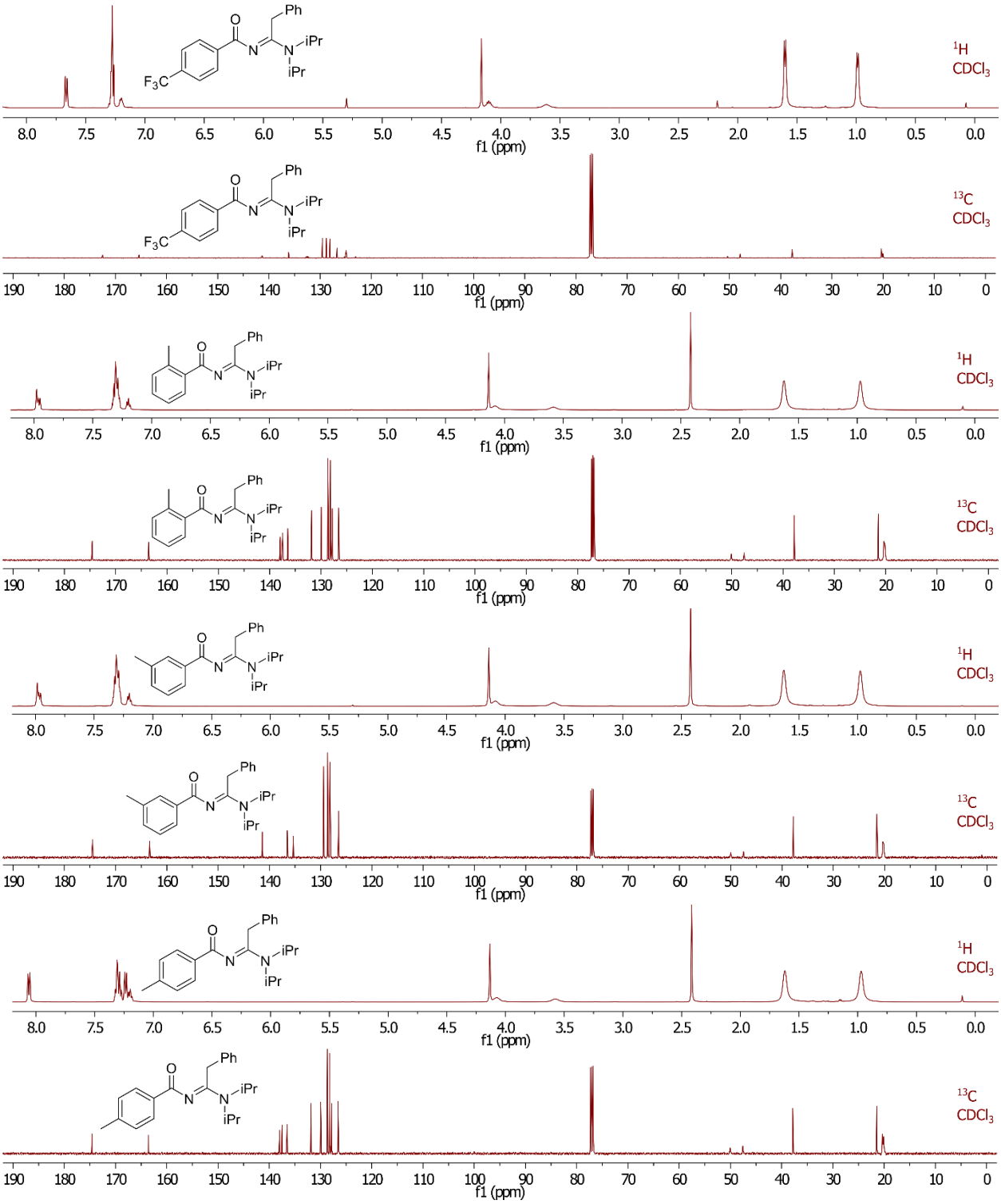
CDCl$_3$
MeO
f1 (ppm)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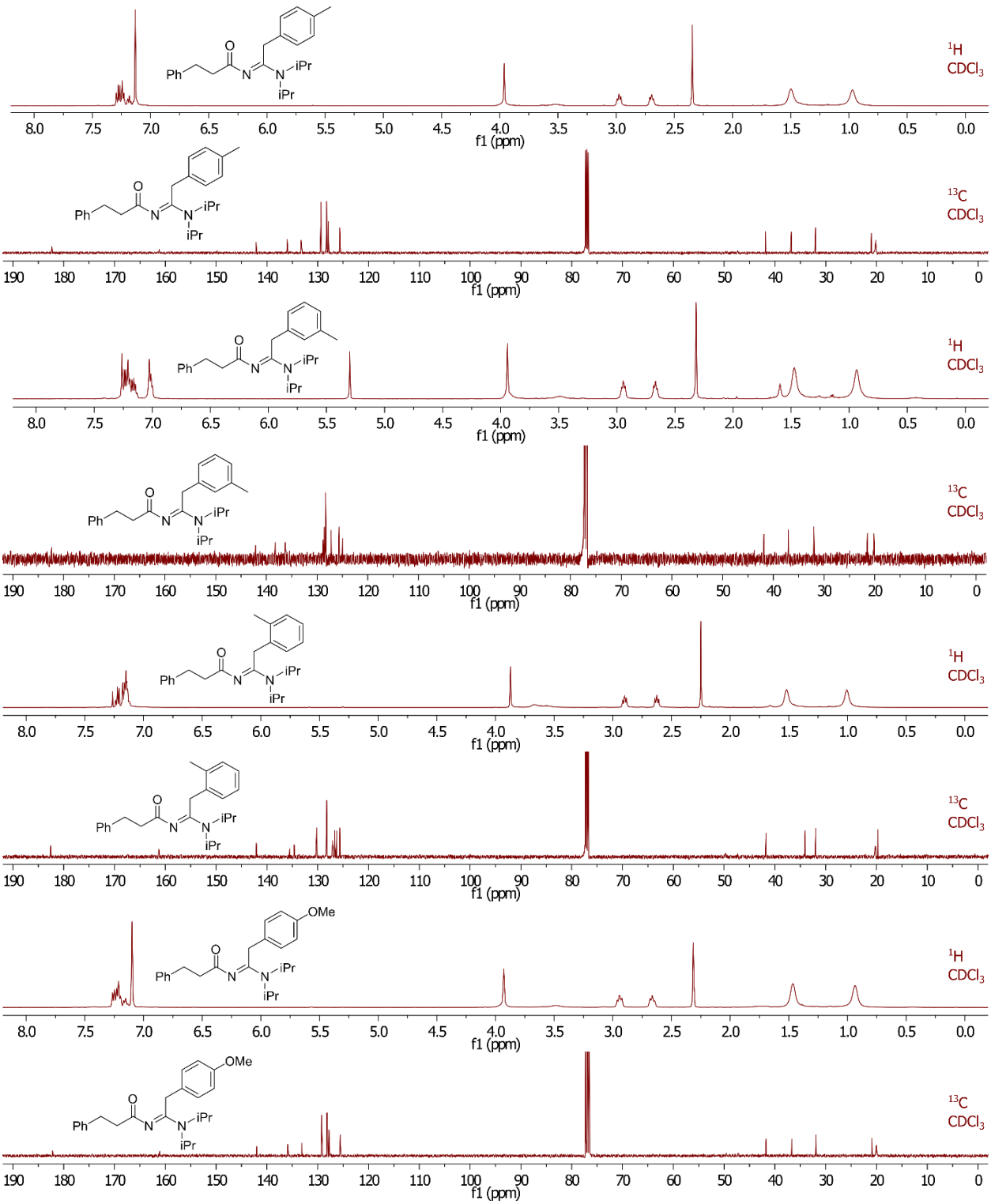
CDCl3
13C
CDCl3
f1 (ppm)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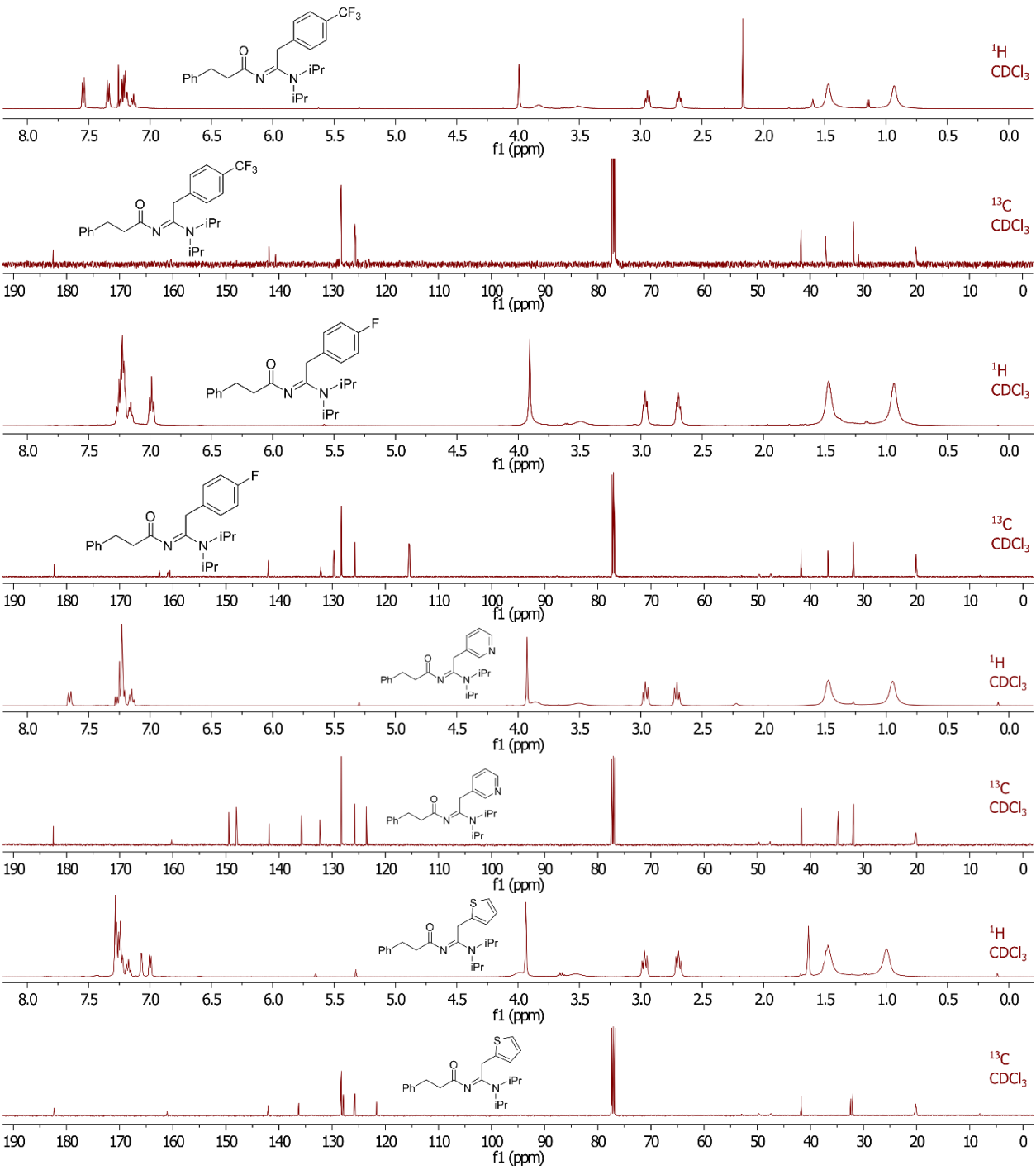
f1 (ppm)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f1 (ppm)
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f1 (ppm)
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f1 (ppm)
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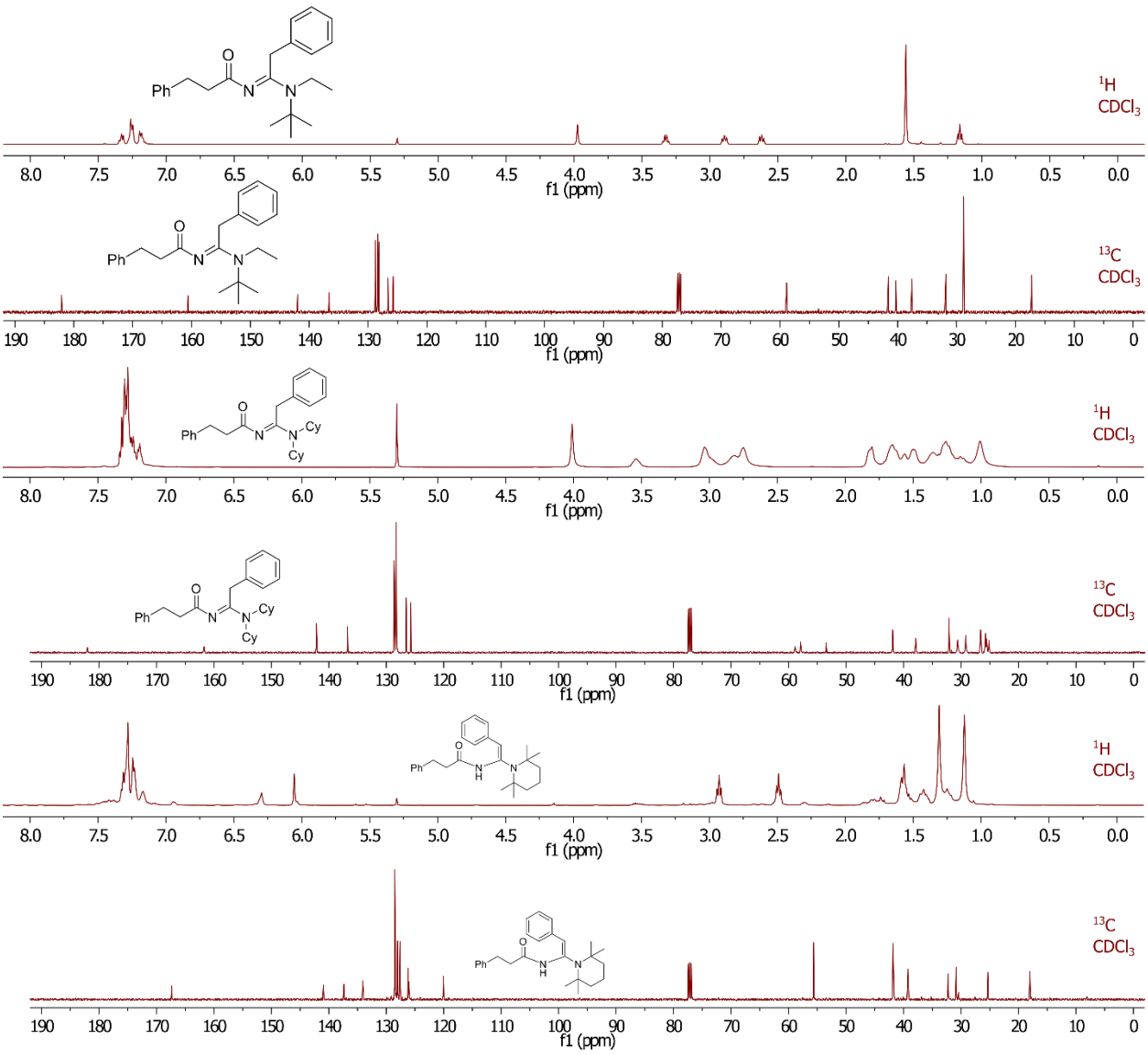
f1 (ppm)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N
^{1}H
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f1 (ppm)
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CDCl$_3$
Cy
Cy

COMPUTATIONAL SECTION

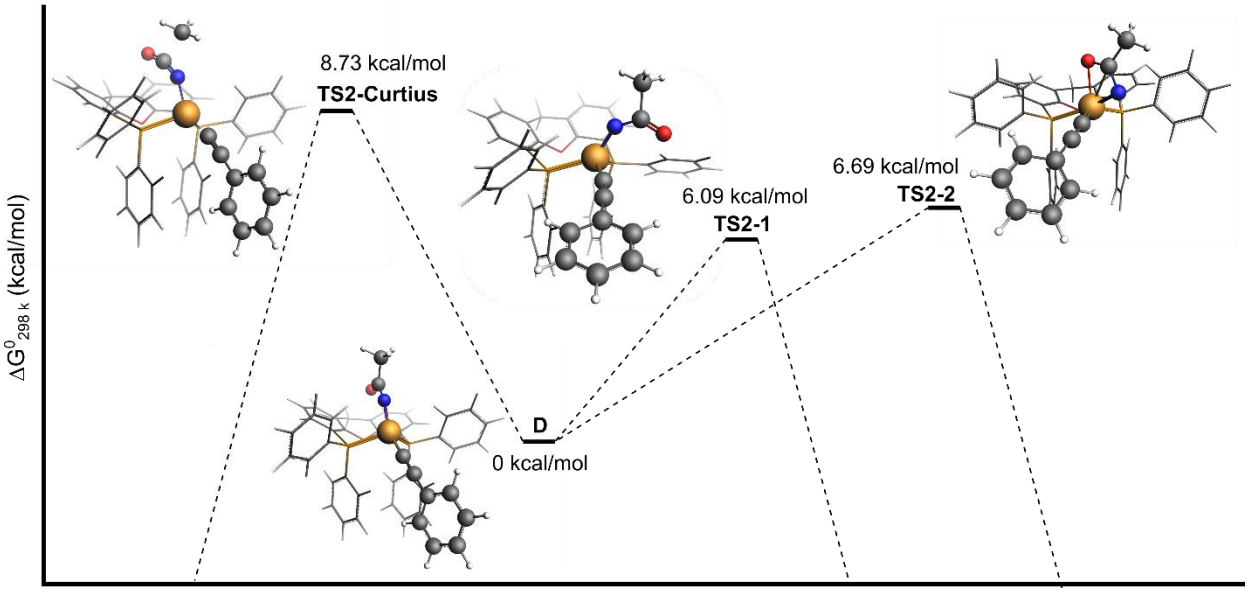
General Considerations.

For the computational analysis, we used the Amsterdam Density Functional 2018 program[18], based on Kohn-Sham density functional theory.[19] We optimized the geometries at the BLYP-*D*3(BJ)/TZ2P level in the gas phase.[20] An analytical frequency analysis was performed on the same level for all species to obtain the internal energy (U) and the entropy energy (ΔS).[21] More accurate bonding energies were obtained by a self-consistent field procedure at the B3LYP-D3/TZ2P level.[22] The Conductor like Screening Model (COSMO) was used to find solvation corrections for the optimized structures.[23] The zeroth order regular approximation (ZORA) was used to correct for relativistic effects.[24] To correct for the standard state concentrations, adjustments for 1 atm. (1/24.5 M) to 1 M concentration change of 1.9 kcal/mol (*RT*ln{24.5}) was used for reaction steps involving a change in the number of species.[25]

Energies.

Species	***U*** **(kcal/mol)**	***pV/n = RT*** **(kcal/mol)**	***-TΔS*** **(kcal/mol)**	***Bonding energy*** **(kcal/mol)**	***ΔH*** **(kcal/mol)**	***ΔG^{GP}*** **(kcal/mol)**	***ΔG^{LP}*** **(kcal/mol)**
A	385.31	0.59	-72.83	-13026.18	-12640.28	-12713.11	-12707.11
B	415.40	0.59	-72.04	-14142.72	-13726.73	-15052.17	-15046.17
C	460.24	0.59	-81.15	-15940.02	-15479.19	-13798.77	-13796.87
TS1	459.69	0.59	-82.22	-15918.96	-15458.68	-15560.34	-15558.44
D	450.57	0.59	-81.13	-15285.87	-14834.71	-15540.9	-15539
TS2-1	450.19	0.59	-81.94	-15278.59	-14827.81	-14915.84	-14913.94
TS2-2	450.48	0.59	-80.81	-15279.41	-14828.34	-14909.75	-14907.85
TS2-Curtius	448.24	0.59	-80.62	-15275.32	-14826.49	-14907.11	-14905.21
E	451.00	0.59	-79.43	-15349.53	-14897.94	-14977.37	-14975.47
TS3	451.54	0.59	-80.90	-15343.7	-14891.57	-14972.47	-14970.57
F	450.95	0.59	-76.98	-15349.46	-14897.92	-14974.9	-14973
2a	70.71	0.59	-23.50	-2391.96	-2320.66	-2344.16	-2342.26
Dioxazolone	43.45	0.59	-23.08	-1785.73	-1741.69	-1764.77	-1762.87
CO2	8.66	0.59	-15.26	-648.53	-639.28	-654.54	-652.64
3a	130.75	0.59	-28.11	-3083.2	-2951.86	-2979.97	-2978.07
[iPr2NH][HOAc]	173.09	0.59	-39.06	-4364.22	-4190.54	-4229.6	-4227.7

Energy Comparision Between Nitrene Insertion and Curtius Rearrangement.

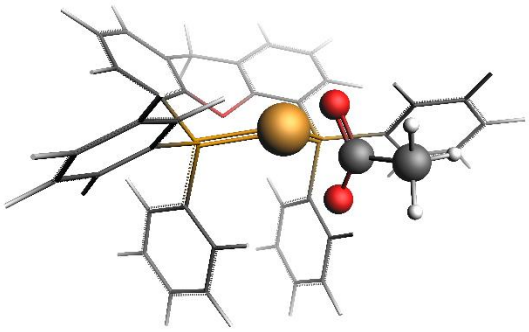


DFT (B3LYP-D3; TZ2P)

We also computed the transition state of the hypothetical Curtius rearrangement from intermediate **D** in order to compare the barrier of that process with the barriers for acyl nitrene insertion into the Cu–C bond of intermediate **D**. The results are shown in the figure above, revealing that the undesired Curtius rearrangement has an approximately 2-3 kcal/mol higher energy barrier than the desired acyl nitrene insertion via either **TS2-1** or **TS2-2**. The DFT results are thus in line with the experimental observations (absence of products derived from undesired Curtius rearrangements).

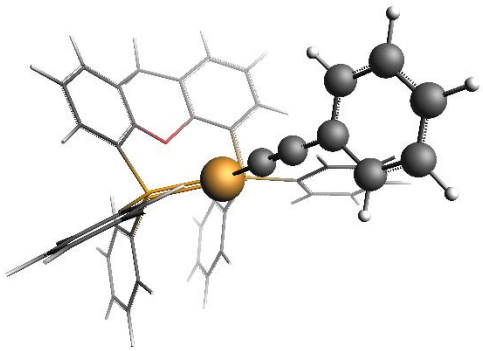
Coordinates.

A



Atom	X	Y	Z (Angstrom)
1.O	0.012766	0.719021	0.376133
2.C	0.312556	3.476281	0.057560
3.C	-1.060976	2.836117	-0.053049
4.C	-1.144152	1.449880	0.105128
5.C	3.208219	0.595569	-1.399060
6.C	3.450287	1.959622	-1.595371
7.C	2.535315	2.917636	-1.144099
8.C	1.372930	2.524602	-0.470324
9.C	1.164771	1.157233	-0.278220
10.C	2.045333	0.167509	-0.740188
11.C	-2.242857	3.534044	-0.321137
12.C	-2.338405	0.725216	-0.029946
13.H	3.910603	-0.141867	-1.775619
14.H	4.352112	2.275725	-2.113948
15.H	2.722703	3.975962	-1.315242
16.C	-3.460941	2.851151	-0.418310
17.C	-3.508756	1.460485	-0.281814
18.H	-4.375921	3.402540	-0.620529
19.H	-4.452680	0.938250	-0.400169
20.H	-1.678523	0.262231	2.530080
21.H	-2.208113	4.613584	-0.455494
22.P	-2.237895	-1.115788	-0.093675
23.P	1.504164	-1.583809	-0.583652
24.H	4.317826	-2.258737	0.214182
25.H	0.524368	3.704113	1.115518
26.H	2.840925	-0.195867	1.735051
27.H	0.340670	4.428462	-0.483314
28.H	-3.298863	-2.059220	-2.594489
29.Cu	-0.554338	-2.010704	-1.241493
30.O	-1.032601	-3.194635	-2.857803
31.C	-1.309024	-4.266822	-2.192130
32.C	-1.846750	-5.457712	-2.977991
33.H	-1.444897	-5.468031	-3.995308
34.H	-1.617028	-6.394026	-2.461847
35.H	-2.938990	-5.362840	-3.045138
36.O	-1.184491	-4.339970	-0.936049
37.C	1.693779	-1.949547	1.205921
38.C	1.096744	-3.129922	1.681050
39.C	1.211520	-3.474130	3.028045
40.C	1.905360	-2.641890	3.912989
41.C	2.488883	-1.460624	3.445564
42.C	2.386958	-1.115515	2.094411
43.H	0.530309	-3.761074	0.999406
44.H	0.738893	-4.382585	3.390904
45.H	1.980814	-2.907840	4.965029
46.H	3.023148	-0.806124	4.131137
47.C	2.860745	-2.549244	-1.357302
48.C	2.591408	-3.173975	-2.585408
49.C	3.576932	-3.947128	-3.207292
50.C	4.828248	-4.106762	-2.603646
51.C	5.095691	-3.494601	-1.372757
52.C	4.115824	-2.719282	-0.749788
53.H	1.604326	-3.072558	-3.032954
54.H	3.361812	-4.434196	-4.155791
55.H	5.590872	-4.716527	-3.083496
56.H	6.064457	-3.628873	-0.896296
57.C	-2.140291	-1.660731	1.657212
58.C	-2.326708	-3.032106	1.912633
59.C	-2.246525	-3.515404	3.217729
60.C	-1.948017	-2.648258	4.275375
61.C	-1.730484	-1.292311	4.019440
62.C	-1.834089	-0.796048	2.716421
63.H	-2.508252	-3.713986	1.085577
64.H	-2.399645	-4.575609	3.407233
65.H	-1.872966	-3.030301	5.291009
66.H	-1.484101	-0.615593	4.834515
67.C	-3.935653	-1.616106	-0.579853
68.C	-5.012840	-1.616709	0.321888
69.C	-6.284297	-2.004773	-0.104195
70.C	-6.489181	-2.397215	-1.432842
71.C	-5.417409	-2.407395	-2.331162
72.C	-4.141825	-2.021929	-1.907830
73.H	-4.850959	-1.322916	1.355880
74.H	-7.114467	-2.004841	0.599055
75.H	-7.479660	-2.703472	-1.762181
76.H	-5.570706	-2.726106	-3.359871

B



Atom	X	Y	Z (Angstrom)
1.O	-0.291245	0.336811	0.221158
2.C	0.197320	2.775633	-1.044325
3.C	-1.218676	2.231496	-0.951327
4.C	-1.395881	1.003935	-0.311290
5.C	2.856064	-0.634730	-1.367748
6.C	3.202454	0.559502	-2.006828

7.C	2.366850	1.679659	-1.927940
8.C	1.186233	1.629138	-1.179826
9.C	0.880706	0.429721	-0.530909
10.C	1.670810	-0.725054	-0.619145
11.C	-2.354748	2.856656	-1.478307
12.C	-2.634579	0.359312	-0.194792
13.H	3.490180	-1.508798	-1.474457
14.H	4.119484	0.609619	-2.588749
15.H	2.629645	2.596105	-2.452972
16.C	-3.614961	2.260194	-1.350282
17.C	-3.756527	1.019050	-0.719509
18.H	-4.490765	2.757691	-1.759354
19.H	-4.732743	0.548821	-0.653016
20.H	-1.887339	-3.194791	2.547711
21.H	-2.251187	3.810361	-1.992278
22.P	-2.629587	-1.355609	0.479363
23.P	0.980278	-2.305588	0.041854
24.H	3.741358	-3.098441	0.899768
25.H	0.427769	3.349095	-0.130807
26.H	1.445910	-0.100914	2.037931
27.H	0.291832	3.469750	-1.886435
28.H	-5.051570	-1.008534	2.222434
29.Cu	-1.134969	-2.616529	-0.667935
30.C	-7.065366	-2.617472	-0.007470
31.C	-6.680591	-1.925935	1.147200
32.C	-5.348299	-1.543621	1.324187
33.H	-4.028081	-2.834302	-1.548400
34.H	-6.404714	-3.482116	-1.875111
35.H	-8.103047	-2.915576	-0.141999
36.H	-7.417717	-1.685868	1.910417
37.C	1.283380	-2.248515	1.855371
38.C	1.264872	-3.464009	2.564427
39.C	1.431598	-3.477205	3.949350
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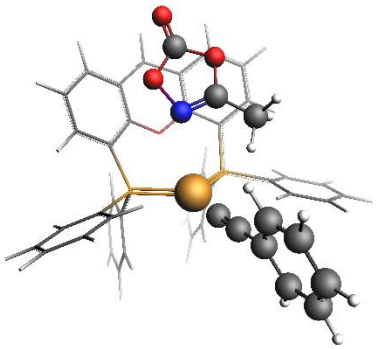
41.C	1.592196	-1.065390	3.953556
42.C	1.440353	-1.049201	2.564391
43.H	1.136355	-4.401231	2.027771
44.H	1.429069	-4.425193	4.482936
45.H	1.719530	-2.286827	5.729574
46.H	1.707935	-0.127120	4.491087
47.C	2.188794	-3.565986	-0.533062
48.C	1.818043	-4.384925	-1.611928
49.C	2.710752	-5.346038	-2.097298
50.C	3.969373	-5.499040	-1.508263
51.C	4.340358	-4.686606	-0.428671
52.C	3.455063	-3.723239	0.057533
53.H	0.829571	-4.275603	-2.054913
54.H	2.415088	-5.979892	-2.930280
55.H	4.659054	-6.252029	-1.883482
56.H	5.317723	-4.806249	0.033893
57.C	-2.376100	-1.108411	2.280879
58.C	-2.505854	0.135262	2.915918
59.C	-2.289782	0.247559	4.292582
60.C	-1.951410	-0.880547	5.045076
61.C	-1.818319	-2.122988	4.415781
62.C	-2.019523	-2.234425	3.040702
63.H	-2.773309	1.014230	2.335651
64.H	-2.388970	1.216749	4.776687
65.H	-1.780933	-0.791094	6.115414
66.H	-1.534678	-2.999369	4.991989
67.C	-4.391859	-1.854452	0.344315
68.C	-4.777285	-2.562210	-0.807383
69.C	-6.113133	-2.933918	-0.982005
70.C	-2.065953	-4.330601	-3.091127
71.C	-2.559246	-5.109705	-4.172314
72.C	-3.054705	-6.419562	-3.959158
73.C	-3.546574	-7.179889	-5.019575
74.C	-3.561906	-6.660805	-6.319962
75.C	-3.074974	-5.367359	-6.547793
76.C	-2.580470	-4.600224	-5.493368
77.C	-1.661267	-3.654844	-2.143117
78.H	-3.045331	-6.822348	-2.949642
79.H	-3.922118	-8.184047	-4.830874
80.H	-3.947272	-7.255936	-7.144751
81.H	-3.081722	-4.954380	-7.554729
82.H	-2.203914	-3.596094	-5.671734

C



Atom	X	Y	Z (Angstrom)
1.O	-0.801728	0.740034	-0.390813
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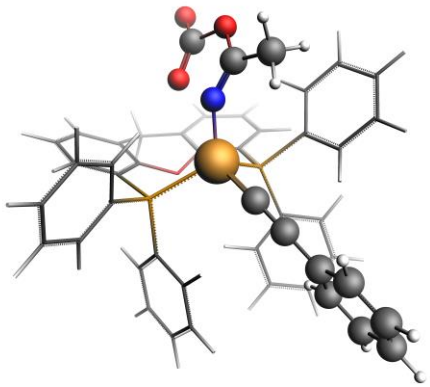
3.C	-1.902197	1.870802	-2.217753
4.C	-1.851248	0.815855	-1.303877
5.C	2.802497	0.777511	-1.019129
6.C	2.908262	1.894251	-1.852430
7.C	1.769480	2.611554	-2.231688
8.C	0.511755	2.244511	-1.744796
9.C	0.443262	1.148302	-0.882392
10.C	1.552170	0.370049	-0.524571
11.C	-2.962678	1.885997	-3.131884
12.C	-2.797261	-0.219791	-1.258287
13.H	3.687647	0.196890	-0.782075
14.H	3.882586	2.184458	-2.237580
15.H	1.851151	3.442980	-2.928072
16.C	-3.937430	0.882611	-3.102565
17.C	-3.860225	-0.161917	-2.174251
18.H	-4.756313	0.905697	-3.817209
19.H	-4.614733	-0.942914	-2.168914
20.H	-1.812177	-2.637972	2.480084
21.H	-3.015445	2.678777	-3.874447
22.P	-2.441374	-1.617062	-0.116078
23.P	1.263800	-1.236693	0.339304

24.H	3.827527	-0.827723	1.842296
25.H	-1.063053	3.684507	-1.425708
26.H	0.584278	1.285203	1.833183
27.H	-0.675180	3.398482	-3.128795
28.H	-5.344783	-1.389515	0.576854
29.Cu	-0.412548	-2.562963	-0.402272
30.C	-6.056493	-4.476164	-0.681481
31.C	-6.260441	-3.225616	-0.082776
32.C	-5.185904	-2.353553	0.099812
33.H	-2.687780	-4.290481	-1.183954
34.H	-4.606017	-5.831217	-1.535357
35.H	-6.895061	-5.155387	-0.819201
36.H	-7.255821	-2.934539	0.245774
37.C	1.070047	-0.800856	2.114387
38.C	1.217283	-1.832261	3.059923
39.C	1.040694	-1.573059	4.418958
40.C	0.692834	-0.288239	4.849861
41.C	0.521287	0.733464	3.912591
42.C	0.711577	0.481300	2.551195
43.H	1.484144	-2.833535	2.729208
44.H	1.171299	-2.375417	5.141902
45.H	0.549578	-0.087739	5.909042
46.H	0.239603	1.731818	4.239231
47.C	2.919757	-2.030187	0.289859
48.C	3.116462	-3.070782	-0.631043
49.C	4.367302	-3.687547	-0.730914
50.C	5.421667	-3.277514	0.090572
51.C	5.225740	-2.246379	1.018138
52.C	3.980082	-1.624254	1.118517
53.H	2.284644	-3.408202	-1.244805
54.H	4.511318	-4.497339	-1.442489
55.H	6.391930	-3.763540	0.015844
56.H	6.042551	-1.929778	1.663288
57.C	-2.710548	-0.903956	1.555029
58.C	-3.297693	0.348503	1.779933
59.C	-3.474709	0.816908	3.085812
60.C	-3.071325	0.036300	4.172667
61.C	-2.480582	-1.212517	3.952181
62.C	-2.292895	-1.677288	2.650957
63.H	-3.613839	0.958982	0.938435
64.H	-3.928450	1.791755	3.252239
65.H	-3.205868	0.403197	5.187638
66.H	-2.146207	-1.814345	4.792686
67.C	-3.897023	-2.723962	-0.320969
68.C	-3.693370	-3.984600	-0.904241
69.C	-4.773665	-4.854526	-1.086690
70.C	-0.085557	-5.437660	-1.557165
71.C	0.013766	-6.714936	-2.172719
72.C	0.502094	-6.847348	-3.495674
73.C	0.585259	-8.098190	-4.106414
74.C	0.189665	-9.252326	-3.418633
75.C	-0.291489	-9.138982	-2.108279
76.C	-0.380865	-7.891682	-1.491186
77.C	-0.185628	-4.319904	-1.047157
78.H	0.815411	-5.952938	-4.028697
79.H	0.963768	-8.174962	-5.124051
80.H	0.257675	-10.226840	-3.896203
81.H	-0.599025	-10.029998	-1.563978
82.H	-0.754954	-7.805308	-0.474139
83.O	0.855385	-0.225858	-3.747519
84.C	-0.081102	0.350713	-4.558869
85.O	-1.140841	-0.565534	-4.669896
86.C	-0.786655	-1.646084	-3.892124
87.N	0.361505	-1.535101	-3.310561
88.O	-0.028535	1.426323	-5.084334
89.C	-1.706029	-2.804293	-3.808250
90.H	-1.865737	-3.222899	-4.809197
91.H	-2.674341	-2.479329	-3.413269
92.H	-1.271775	-3.558865	-3.146132

TS1

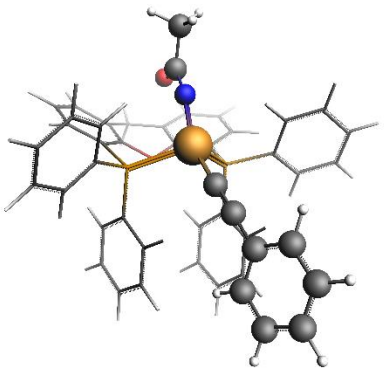
Imaginairy frequency: -32.86 cm^{-1}



Atom	X	Y	Z (Angstrom)
1.O	-0.118457	0.455560	0.167120
2.C	-0.137002	3.297493	0.248080
3.C	-1.422389	2.495277	0.151283
4.C	-1.347589	1.101915	0.071384
5.C	3.212250	0.967729	-1.231341
6.C	3.279248	2.364069	-1.260930
7.C	2.203863	3.134163	-0.806612
8.C	1.047598	2.525530	-0.303570
9.C	1.003915	1.130937	-0.297606
10.C	2.061048	0.326359	-0.751003
11.C	-2.693342	3.077916	0.144329
12.C	-2.475218	0.283287	-0.095113
13.H	4.041741	0.373481	-1.602044
14.H	4.169452	2.853046	-1.648066
15.H	2.260378	4.220530	-0.841439
16.C	-3.844204	2.284169	0.084607
17.C	-3.736455	0.897465	-0.038194
18.H	-4.825952	2.749992	0.110802
19.H	-4.632743	0.290439	-0.123005
20.H	-0.460129	-1.974998	1.752275
21.H	-2.782133	4.161382	0.197341
22.P	-2.173699	-1.494705	-0.487394
23.P	1.776154	-1.485073	-0.830642
24.H	4.534284	-2.325435	-0.028348

25.H	0.057156	3.549379	1.304110
26.H	2.423083	-0.193695	1.799785
27.H	-0.248825	4.250488	-0.282453
28.H	-3.328086	-4.082976	-1.083505
29.CU	-0.207542	-2.099682	-1.828875
30.C	-5.387417	-2.896233	-3.521975
31.C	-4.755620	-3.807779	-2.667270
32.C	-3.839168	-3.363019	-1.714506
33.H	-3.915633	-0.028745	-2.436031
34.H	-5.542013	-0.820001	-4.104185
35.H	-6.104332	-3.245478	-4.261467
36.H	-4.970168	-4.871001	-2.746562
37.C	2.004747	-2.101988	0.875921
38.C	1.816711	-3.479687	1.094264
39.C	1.917162	-4.002376	2.383033
40.C	2.192487	-3.157977	3.465797
41.C	2.371723	-1.787743	3.253009
42.C	2.282257	-1.258591	1.961438
43.H	1.555347	-4.126853	0.261985
44.H	1.758035	-5.065909	2.543159
45.H	2.261088	-3.565907	4.471799
46.H	2.582072	-1.127913	4.091715
47.C	3.232846	-2.118803	-1.740259
48.C	3.114127	-2.281155	-3.129850
49.C	4.198784	-2.745048	-3.877072
50.C	5.404197	-3.060575	-3.240773
51.C	5.523763	-2.908499	-1.855230
52.C	4.442784	-2.437852	-1.105361
53.H	2.169115	-2.052168	-3.617195
54.H	4.100054	-2.870746	-4.952840
55.H	6.245776	-3.431062	-3.821930
56.H	6.458298	-3.158289	-1.357772
57.C	-2.497114	-2.320395	1.123993
58.C	-3.740019	-2.858446	1.491410
59.C	-3.902811	-3.460405	2.741986
60.C	-2.833163	-3.517573	3.641562
61.C	-1.596750	-2.969081	3.285646
62.C	-1.426255	-2.380748	2.030779
63.H	-4.576868	-2.818712	0.800895
64.H	-4.866843	-3.885700	3.012604
65.H	-2.962513	-3.989951	4.612665
66.H	-0.756044	-3.013372	3.972428
67.C	-3.549369	-1.988883	-1.589636
68.C	-4.159717	-1.084888	-2.476772
69.C	-5.077822	-1.535686	-3.429369
70.C	-0.674895	-5.028097	-1.000504
71.C	-1.064305	-6.205181	-0.303705
72.C	-1.004658	-7.487875	-0.895145
73.C	-1.407427	-8.618225	-0.182804
74.C	-1.878581	-8.499933	1.130633
75.C	-1.942653	-7.235044	1.728794
76.C	-1.541170	-6.100322	1.025769
77.C	-0.389525	-3.947554	-1.507665
78.H	-0.640367	-7.579377	-1.915302
79.H	-1.354766	-9.597553	-0.654034
80.H	-2.192667	-9.383953	1.681082
81.H	-2.309330	-7.130655	2.748245
82.H	-1.589700	-5.120441	1.488192
83.O	-0.533953	0.777441	-3.134451
84.C	-1.320592	1.221363	-4.043435
85.O	-1.865406	0.068955	-4.859622
86.C	-1.439515	-1.097770	-4.362198
87.N	-0.657011	-1.187034	-3.349330
88.O	-1.689463	2.329406	-4.349982
89.C	-1.923626	-2.343244	-5.058390
90.H	-1.468601	-3.224988	-4.605219
91.H	-1.673213	-2.281651	-6.123216
92.H	-3.012057	-2.398883	-4.951385

D

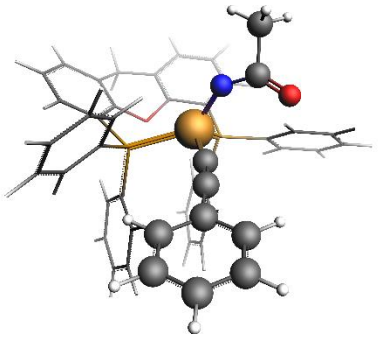


Atom	X	Y	Z (Angstrom)
1.O	-0.502795	0.160069	-0.167453
2.C	-0.798581	2.891768	0.451938
3.C	-1.982452	2.063804	-0.015609
4.C	-1.767496	0.721253	-0.327879
5.C	2.823889	1.211834	-1.246616
6.C	2.766716	2.582824	-0.980446
7.C	1.608217	3.153046	-0.437710
8.C	0.496633	2.361935	-0.135345
9.C	0.578975	1.000049	-0.420825
10.C	1.715935	0.396729	-0.970826
11.C	-3.268278	2.574927	-0.204813
12.C	-2.767677	-0.119802	-0.830136
13.H	3.716965	0.774198	-1.681794
14.H	3.624413	3.211644	-1.205864
15.H	1.565766	4.224595	-0.252033
16.C	-4.301484	1.755462	-0.675674
17.C	-4.053762	0.419592	-0.996829
18.H	-5.298463	2.166213	-0.814405
19.H	-4.848689	-0.198498	-1.401184
20.H	-1.772068	-1.260198	1.454470
21.H	-3.460884	3.624824	0.007241
22.P	-2.280982	-1.780396	-1.429693
23.P	1.588304	-1.375529	-1.394816
24.H	2.350849	-1.230271	-4.152615
25.H	-0.738322	2.856029	1.552981
26.H	2.061334	-0.476023	1.415068
27.H	-0.940060	3.943439	0.178704
28.H	-4.872841	-3.071983	-0.680131
29.Cu	-0.324594	-1.886621	-2.688425
30.C	-5.925943	-3.159147	-3.919998
31.C	-5.948674	-3.332103	-2.531292
32.C	-4.855875	-2.934472	-1.757636
33.H	-2.830676	-1.761121	-4.240053

34.H	-4.783315	-2.460223	-5.615070
35.H	-6.777191	-3.472588	-4.520399
36.H	-6.816962	-3.776778	-2.050260
37.C	1.674673	-2.237569	0.223016
38.C	1.485263	-3.629695	0.247607
39.C	1.550514	-4.321853	1.456545
40.C	1.791269	-3.636852	2.651531
41.C	1.970187	-2.251106	2.632822
42.C	1.914332	-1.551728	1.423708
43.H	1.265456	-4.154772	-0.676532
44.H	1.398218	-5.398226	1.468930
45.H	1.830557	-4.179512	3.593307
46.H	2.156299	-1.711170	3.558826
47.C	3.169251	-1.757586	-2.225445
48.C	4.297329	-2.216743	-1.528990
49.C	5.483587	-2.480704	-2.218576
50.C	5.549692	-2.284699	-3.601836
51.C	4.424385	-1.829250	-4.298875
52.C	3.233859	-1.571380	-3.616584
53.H	4.244733	-2.371356	-0.454915
54.H	6.355100	-2.839929	-1.675668
55.H	6.473787	-2.492945	-4.136436
56.H	4.471829	-1.684271	-5.375728
57.C	-2.183070	-2.853704	0.049317
58.C	-2.305991	-4.245790	-0.109485
59.C	-2.157409	-5.092927	0.988567
60.C	-1.865592	-4.565144	2.250605
61.C	-1.728347	-3.183930	2.410036
62.C	-1.887132	-2.329351	1.317429
63.H	-2.506474	-4.664206	-1.089173
64.H	-2.257253	-6.166543	0.850592
65.H	-1.737775	-5.228131	3.103283
66.H	-1.488250	-2.767127	3.385009
67.C	-3.730090	-2.365015	-2.373669
68.C	-3.708056	-2.196196	-3.767314
69.C	-4.806062	-2.590480	-4.535599
70.C	-0.260319	-4.984959	-2.585553
71.C	-0.311882	-6.398777	-2.450593
72.C	-0.015063	-7.010633	-1.209424
73.C	-0.080574	-8.395453	-1.062661
74.C	-0.444320	-9.206046	-2.144652
75.C	-0.741638	-8.614687	-3.378636
76.C	-0.678155	-7.230458	-3.534180
77.C	-0.232653	-3.760672	-2.655925
78.H	0.255023	-6.382319	-0.366933
79.H	0.152041	-8.846353	-0.099776
80.H	-0.494840	-10.286062	-2.027806
81.H	-1.025683	-9.237506	-4.224543
82.H	-0.909531	-6.770326	-4.491168
83.H	-0.386237	0.604043	-6.026517
84.H	0.232849	2.144817	-5.357104
85.O	-0.837477	1.633919	-2.881783
86.C	-0.610125	0.857610	-3.858269
87.N	-0.389115	-0.430165	-3.733539
88.H	-1.521480	1.888910	-5.507005
89.C	-0.565975	1.396148	-5.290696

TS2-1

Imaginairy frequency: -38.02 cm^{-1}

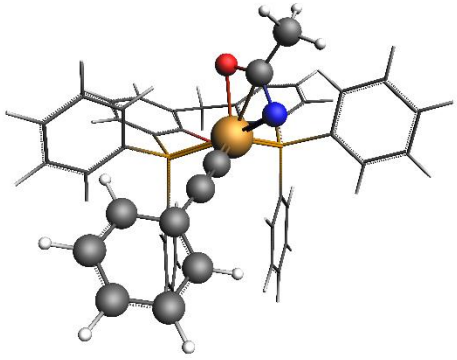


Atom	X	Y	Z (Angstrom)
1.O	-0.447934	0.437821	0.809829
2.C	-0.143555	3.219166	1.020808
3.C	-1.484144	2.616064	0.635717
4.C	-1.572461	1.226235	0.554612
5.C	2.955400	0.597448	-0.507613
6.C	3.215123	1.966498	-0.397075
7.C	2.233719	2.840664	0.084416
8.C	0.989991	2.352473	0.497826
9.C	0.770851	0.975047	0.404679
10.C	1.710777	0.075122	-0.117173
11.C	-2.637580	3.354751	0.345584
12.C	-2.739857	0.539168	0.193696
13.H	3.706201	-0.064541	-0.926675
14.H	4.180594	2.356617	-0.709338
15.H	2.432599	3.909278	0.137616
16.C	-3.826240	2.704442	-0.004974
17.C	-3.880016	1.308265	-0.083800
18.H	-4.715408	3.288476	-0.229104
19.H	-4.800311	0.813995	-0.378782
20.H	-2.637608	-0.151032	2.744132
21.H	-2.602270	4.441501	0.392421
22.P	-2.584892	-1.271695	-0.068058
23.P	1.161793	-1.648078	-0.474648
24.H	3.856042	-2.799214	0.085579
25.H	-0.075420	3.285034	2.119723
26.H	1.411080	-0.882204	2.413507
27.H	-0.054788	4.241798	0.637842
28.H	-5.102171	-1.157442	1.479270
29.Cu	-0.889036	-1.970215	-1.546663
30.C	-6.878834	-2.798495	-0.918789
31.C	-6.604088	-2.129862	0.282129
32.C	-5.316667	-1.658623	0.538560
33.H	-3.787029	-2.728517	-2.333197
34.H	-6.057187	-3.531828	-2.781087
35.H	-7.883027	-3.168056	-1.116078
36.H	-7.390847	-1.983398	1.019134
37.C	1.346026	-2.586709	1.085542
38.C	1.355058	-3.991920	1.003640
39.C	1.493204	-4.756722	2.160685
40.C	1.596619	-4.133173	3.409240

41.C	1.554116	-2.739419	3.495301
42.C	1.433498	-1.965107	2.338198
43.H	1.250204	-4.476734	0.037838
44.H	1.511250	-5.841687	2.086252
45.H	1.697591	-4.731701	4.311686
46.H	1.615505	-2.250458	4.464447
47.C	2.509165	-2.306341	-1.532015
48.C	2.315015	-2.326804	-2.922168
49.C	3.312726	-2.831308	-3.759191
50.C	4.505015	-3.321705	-3.216942
51.C	4.702299	-3.303263	-1.831913
52.C	3.707932	-2.796998	-0.990662
53.H	1.373533	-1.983851	-3.342845
54.H	3.147859	-2.861972	-4.833369
55.H	5.273250	-3.728839	-3.870314
56.H	5.625466	-3.688850	-1.405464
57.C	-2.295285	-1.958894	1.612022
58.C	-1.980726	-3.326589	1.685011
59.C	-1.796728	-3.936834	2.925025
60.C	-1.905877	-3.187744	4.100799
61.C	-2.202796	-1.823790	4.031896
62.C	-2.400455	-1.210262	2.791337
63.H	-1.873446	-3.906057	0.770372
64.H	-1.548483	-4.993426	2.972494
65.H	-1.749229	-3.663998	5.065916
66.H	-2.282753	-1.235364	4.943593
67.C	-4.293328	-1.845767	-0.409536
68.C	-4.565403	-2.531568	-1.601675
69.C	-5.860360	-3.001672	-1.852453
70.C	-0.031245	-4.795491	-2.411262
71.C	0.580855	-6.044851	-2.689579
72.C	-0.161622	-7.124525	-3.221300
73.C	0.458481	-8.343664	-3.490435
74.C	1.824901	-8.516393	-3.234989
75.C	2.571927	-7.454039	-2.711112
76.C	1.962284	-6.230028	-2.440699
77.C	-0.505354	-3.714597	-2.082528
78.H	-1.219601	-6.981036	-3.422397
79.H	-0.124882	-9.164233	-3.903064
80.H	2.303975	-9.469937	-3.445647
81.H	3.634661	-7.580888	-2.514992
82.H	2.542497	-5.401843	-2.044669
83.H	-1.870704	-0.039898	-5.037899
84.H	-3.499153	-0.734711	-5.328178
85.O	-2.909472	-3.162066	-4.328358
86.C	-2.283399	-2.093897	-4.169741
87.N	-1.490148	-1.616786	-3.246430
88.H	-2.076994	-1.389830	-6.199544
89.C	-2.428679	-0.952703	-5.259275

TS2-2

Imaginairy frequency: -203.75 cm^{-1}

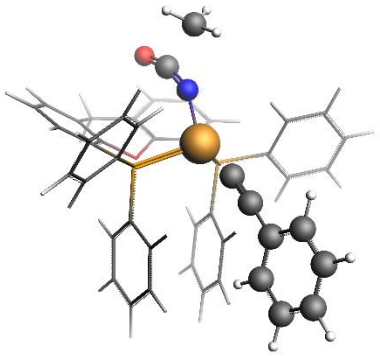


Atom	X	Y	Z (Angstrom)
1.O	-0.507595	0.310141	0.960418
2.C	-0.075237	3.011181	1.564516
3.C	-1.424648	2.544043	1.047043
4.C	-1.571583	1.186524	0.756574
5.C	2.947945	0.458742	-0.210705
6.C	3.265220	1.789005	0.077524
7.C	2.312102	2.643280	0.644447
8.C	1.033945	2.169596	0.955662
9.C	0.754085	0.830016	0.671962
10.C	1.668544	-0.045776	0.077241
11.C	-2.528612	3.375148	0.825491
12.C	-2.740859	0.626165	0.230652
13.H	3.683710	-0.183112	-0.683652
14.H	4.256986	2.166620	-0.158322
15.H	2.560551	3.683794	0.843994
16.C	-3.732033	2.842111	0.348051
17.C	-3.840702	1.479412	0.049629
18.H	-4.587386	3.494858	0.192773
19.H	-4.768570	1.081165	-0.347398
20.H	-3.363416	-0.484936	2.538603
21.H	-2.446248	4.440786	1.030247
22.P	-2.659959	-1.133871	-0.298483
23.P	1.079016	-1.716738	-0.441303
24.H	3.697519	-3.079473	0.059285
25.H	-0.050299	2.906724	2.662108
26.H	0.952033	-1.128099	2.479044
27.H	0.078669	4.073208	1.344412
28.H	-5.079888	-2.704511	0.500060
29.Cu	-0.938374	-2.011805	-1.566380
30.C	-6.742407	-1.860673	-2.351839
31.C	-6.489675	-2.458460	-1.114217
32.C	-5.273451	-2.235299	-0.460037
33.H	-3.793672	-0.206798	-2.766706
34.H	-5.960056	-0.582009	-3.909850
35.H	-7.687409	-2.038789	-2.860023
36.H	-7.237743	-3.101337	-0.655498
37.C	1.168481	-2.753755	1.066718
38.C	1.264627	-4.150220	0.923357
39.C	1.253378	-4.972444	2.050309

40.C	1.129666	-4.416820	3.327940
41.C	1.018872	-3.031600	3.473094
42.C	1.040048	-2.201391	2.350463
43.H	1.344184	-4.588677	-0.064254
44.H	1.337872	-6.049548	1.924719
45.H	1.115808	-5.060074	4.204929
46.H	0.913273	-2.592765	4.462456
47.C	2.450178	-2.282670	-1.516195
48.C	2.333138	-2.043389	-2.895577
49.C	3.374553	-2.408488	-3.751218
50.C	4.528425	-3.016458	-3.242616
51.C	4.642433	-3.258399	-1.870028
52.C	3.607945	-2.887717	-1.006021
53.H	1.424636	-1.594227	-3.293202
54.H	3.277606	-2.229791	-4.819476
55.H	5.331833	-3.309406	-3.914915
56.H	5.532646	-3.738934	-1.470797
57.C	-2.664619	-2.086358	1.267762
58.C	-2.246942	-3.427393	1.217993
59.C	-2.222457	-4.194538	2.382960
60.C	-2.598853	-3.628840	3.604936
61.C	-3.007345	-2.292934	3.659601
62.C	-3.045107	-1.523098	2.493961
63.H	-1.928194	-3.861516	0.272754
64.H	-1.885637	-5.226424	2.338298
65.H	-2.563260	-4.224567	4.514164
66.H	-3.296680	-1.848303	4.609489
67.C	-4.303030	-1.413177	-1.046494
68.C	-4.553971	-0.826906	-2.299486
69.C	-5.772880	-1.040271	-2.941468
70.C	0.098803	-4.818548	-2.276072
71.C	0.817508	-6.038381	-2.325014
72.C	0.230851	-7.256601	-1.905579
73.C	0.966667	-8.441051	-1.919532
74.C	2.299379	-8.444038	-2.349926
75.C	2.891529	-7.245903	-2.769094
76.C	2.166647	-6.055625	-2.756630
77.C	-0.397007	-3.708725	-2.115551
78.H	-0.804450	-7.252322	-1.574398
79.H	0.498361	-9.368438	-1.595465
80.H	2.869457	-9.370141	-2.360114
81.H	3.926962	-7.239295	-3.104209
82.H	2.627406	-5.125385	-3.072825
83.H	-3.293064	-2.261512	-5.265010
84.H	-1.752290	-1.732223	-5.998096
85.O	-0.790307	-0.869751	-3.532435
86.C	-1.720157	-1.711495	-3.856688
87.N	-2.125010	-2.706012	-3.092810
88.H	-2.833709	-0.526503	-5.265189
89.C	-2.462711	-1.554790	-5.180841

TS2-Curtius

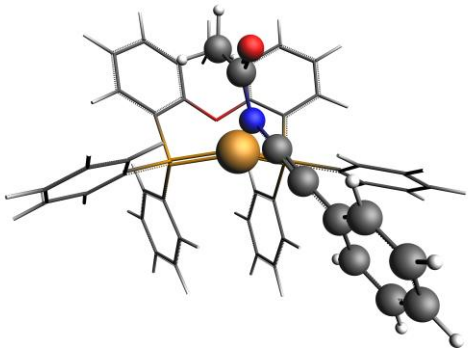
Imaginairy frequency: -398.34 cm^{-1}



Atom	X	Y	Z (Angstrom)
1.O	0.302873	0.248059	0.035757
2.C	0.916995	2.992288	-0.004490
3.C	-0.517684	2.516135	-0.141696
4.C	-0.757403	1.143036	-0.116438
5.C	3.503969	-0.040887	-1.707588
6.C	3.901408	1.298158	-1.749526
7.C	3.086757	2.298874	-1.209236
8.C	1.875034	1.972169	-0.593545
9.C	1.512867	0.624984	-0.549657
10.C	2.284877	-0.402865	-1.111294
11.C	-1.617100	3.362266	-0.322334
12.C	-2.029395	0.576821	-0.278574
13.H	4.124768	-0.804312	-2.165271
14.H	4.842566	1.564296	-2.224381
15.H	3.388724	3.342549	-1.273385
16.C	-2.906000	2.835062	-0.456739
17.C	-3.114198	1.452186	-0.437715
18.H	-3.751817	3.504397	-0.592900
19.H	-4.113367	1.048064	-0.569774
20.H	-1.707531	-3.911093	0.568828
21.H	-1.460955	4.438446	-0.364352
22.P	-2.119600	-1.249042	-0.444479
23.P	1.528197	-2.076265	-1.238229
24.H	4.228576	-3.272756	-0.780861
25.H	1.151825	3.141532	1.062815
26.H	1.990126	-1.022673	1.534074
27.H	1.046226	3.963049	-0.495388
28.H	-4.571493	-1.634317	1.233471
29.Cu	-0.671890	-2.209230	-1.975478
30.C	-6.557373	-2.041811	-1.507314
31.C	-6.190197	-1.943807	-0.160608
32.C	-4.858314	-1.702490	0.187477
33.H	-3.493583	-1.589460	-2.934825
34.H	-5.870418	-1.991909	-3.555000
35.H	-7.593383	-2.235413	-1.775801
36.H	-6.940138	-2.059929	0.618803
37.C	1.724781	-2.851178	0.410906
38.C	1.606326	-4.250570	0.495168
39.C	1.705365	-4.886996	1.732181
40.C	1.895462	-4.138050	2.898129

41.C	1.988631	-2.746383	2.820686
42.C	1.909163	-2.103495	1.582537
43.H	1.424305	-4.832598	-0.402847
44.H	1.623385	-5.970122	1.784109
45.H	1.960418	-4.636213	3.862616
46.H	2.122341	-2.156364	3.724353
47.C	2.702677	-3.010461	-2.289082
48.C	2.330450	-3.279413	-3.614438
49.C	3.196356	-3.979787	-4.459090
50.C	4.434239	-4.421953	-3.982493
51.C	4.806681	-4.163645	-2.657663
52.C	3.944679	-3.462159	-1.812680
53.H	1.356123	-2.954826	-3.970667
54.H	2.898580	-4.191691	-5.483377
55.H	5.104163	-4.974526	-4.637364
56.H	5.765912	-4.513498	-2.282466
57.C	-1.884758	-1.874072	1.262830
58.C	-1.861445	-1.025557	2.379452
59.C	-1.682532	-1.557782	3.659571
60.C	-1.531851	-2.936362	3.831768
61.C	-1.552766	-3.783176	2.718878
62.C	-1.721032	-3.258564	1.437710
63.H	-1.982573	0.046173	2.250721
64.H	-1.662468	-0.893471	4.520986
65.H	-1.388598	-3.348422	4.828301
66.H	-1.421436	-4.854600	2.845783
67.C	-3.885672	-1.561287	-0.813364
68.C	-4.255927	-1.672190	-2.163607
69.C	-5.589131	-1.904033	-2.507966
70.C	-1.107969	-5.270493	-1.593996
71.C	-1.232208	-6.635586	-1.218977
72.C	-1.627227	-7.630577	-2.143694
73.C	-1.738908	-8.964716	-1.752513
74.C	-1.461086	-9.345338	-0.433649
75.C	-1.070805	-8.372344	0.494307
76.C	-0.958652	-7.036135	0.112017
77.C	-0.984362	-4.076798	-1.863250
78.H	-1.844179	-7.335808	-3.167052
79.H	-2.046024	-9.713378	-2.480172
80.H	-1.548054	-10.386934	-0.133012
81.H	-0.853257	-8.657988	1.521836
82.H	-0.654973	-6.282076	0.831941
83.H	-1.143594	-1.096497	-5.508079
84.H	0.123437	0.207143	-5.712801
85.O	-0.058570	1.569812	-3.273244
86.C	-0.382454	0.421558	-3.449860
87.N	-0.644737	-0.773911	-3.214459
88.H	-1.632795	0.663587	-5.401899
89.C	-0.841786	-0.076322	-5.298275

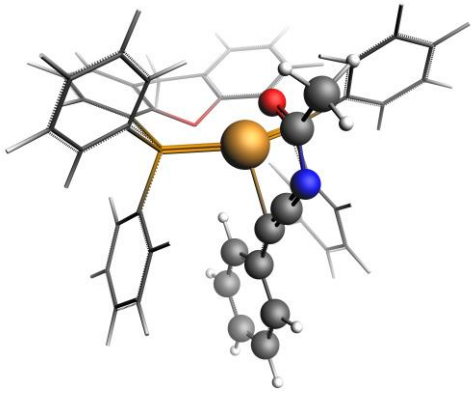
E



Atom	X	Y	Z (Angstrom)
1.O	-0.620637	-0.000348	-0.201112
2.C	-1.258318	2.697825	0.204949
3.C	-2.280871	1.742794	-0.388188
4.C	-1.903671	0.409717	-0.569118
5.C	2.678333	1.343703	-1.019850
6.C	2.459961	2.710946	-0.820627
7.C	1.200816	3.182779	-0.432651
8.C	0.146218	2.290199	-0.206854
9.C	0.400872	0.930973	-0.393766
10.C	1.636666	0.424923	-0.821730
11.C	-3.572221	2.110969	-0.780008
12.C	-2.737532	-0.561630	-1.144268
13.H	3.646435	0.989296	-1.360690
14.H	3.271433	3.414497	-0.988360
15.H	1.033454	4.250735	-0.307642
16.C	-4.445138	1.162424	-1.323434
17.C	-4.032001	-0.159938	-1.511894
18.H	-5.447346	1.458582	-1.622469
19.H	-4.703453	-0.875573	-1.975249
20.H	-1.950878	-1.506116	1.335359
21.H	-3.893081	3.144243	-0.661993
22.P	-2.002349	-2.192931	-1.602738
23.P	1.701788	-1.353307	-1.294445
24.H	2.582816	-1.350366	-4.028368
25.H	-1.336259	2.675895	1.304808
26.H	2.209153	-0.523264	1.546804
27.H	-1.467728	3.727364	-0.105403
28.H	-4.593718	-3.449247	-0.803311
29.Cu	-0.061845	-1.742144	-2.615009
30.C	-5.320893	-4.361577	-4.006151
31.C	-5.470166	-4.206439	-2.621247
32.C	-4.484686	-3.553332	-1.879861
33.H	-2.310798	-2.827771	-4.412608
34.H	-4.050534	-3.994512	-5.717467
35.H	-6.085526	-4.881494	-4.579051
36.H	-6.351394	-4.600459	-2.119699
37.C	1.802307	-2.242291	0.304686
38.C	1.603079	-3.632404	0.286333
39.C	1.689869	-4.370792	1.465497
40.C	1.953834	-3.726511	2.678888
41.C	2.134250	-2.340990	2.706580

42.C	2.062761	-1.599709	1.523231
43.H	1.370739	-4.130984	-0.652215
44.H	1.529743	-5.445259	1.441762
45.H	2.007996	-4.302091	3.599964
46.H	2.333657	-1.835098	3.648895
47.C	3.371479	-1.547575	-2.025052
48.C	4.522345	-1.752208	-1.247453
49.C	5.770215	-1.869324	-1.864507
50.C	5.875585	-1.782802	-3.257691
51.C	4.730066	-1.587372	-4.035767
52.C	3.478227	-1.477047	-3.424564
53.H	4.440096	-1.825677	-0.166117
54.H	6.659559	-2.030946	-1.259267
55.H	6.847942	-1.876994	-3.735666
56.H	4.805571	-1.531892	-5.119081
57.C	-1.912006	-3.168478	-0.046215
58.C	-1.794787	-4.565398	-0.160864
59.C	-1.668197	-5.360233	0.977761
60.C	-1.636350	-4.769853	2.245806
61.C	-1.731485	-3.381680	2.364463
62.C	-1.872435	-2.582526	1.226419
63.H	-1.819211	-5.031036	-1.143313
64.H	-1.590880	-6.440424	0.874698
65.H	-1.530164	-5.388154	3.133892
66.H	-1.696930	-2.915165	3.346062
67.C	-3.342026	-3.043752	-2.522900
68.C	-3.198854	-3.197897	-3.909545
69.C	-4.185228	-3.860627	-4.647386
70.N	0.060518	-1.342331	-4.544623
71.H	1.233463	1.079375	-3.623453
72.H	-0.064424	-4.113228	-8.457350
73.O	0.340795	0.092883	-6.354754
74.C	0.225377	-0.095713	-5.141271
75.H	-0.692750	-6.264089	-9.523344
76.C	0.264262	1.056391	-4.136197
77.H	-0.511048	0.946283	-3.368680
78.H	0.127293	2.000850	-4.667106
79.C	-0.799881	-6.144004	-8.446924
80.C	-0.443392	-4.933893	-7.854048
81.C	-0.061311	-2.435258	-5.298021
82.H	-1.184511	-5.696254	-4.612013
83.H	-1.808676	-7.846957	-5.675205
84.H	-1.569456	-8.143898	-8.140271
85.C	-0.244501	-3.515059	-5.840255
86.C	-0.573533	-4.746234	-6.455747
87.C	-1.071816	-5.827298	-5.685099
88.C	-1.425106	-7.033153	-6.288080
89.C	-1.293136	-7.201943	-7.672126

F



Atom	X	Y	Z (Angstrom)
1.O	-0.698798	0.290894	-0.776895
2.C	-0.418294	3.033359	-1.124324
3.C	-1.617260	2.484473	-0.375069
4.C	-1.699909	1.094096	-0.221556
5.C	2.932989	0.443140	-0.266670
6.C	3.162037	1.811790	-0.423049
7.C	2.098079	2.678906	-0.695264
8.C	0.799152	2.181138	-0.823973
9.C	0.596666	0.805005	-0.661026
10.C	1.637614	-0.089852	-0.375760
11.C	-2.626602	3.273270	0.181522
12.C	-2.736564	0.467774	0.484124
13.H	3.762436	-0.218553	-0.039655
14.H	4.171438	2.204035	-0.326154
15.H	2.275324	3.746574	-0.810245
16.C	-3.692124	2.678004	0.866203
17.C	-3.743132	1.291261	1.017988
18.H	-4.477011	3.297223	1.293441
19.H	-4.558057	0.839486	1.574892
20.H	-1.906667	-1.464741	3.490770
21.H	-2.576779	4.355695	0.078306
22.P	-2.711074	-1.365461	0.731306
23.P	1.255279	-1.883923	-0.138184
24.H	1.540389	-4.597867	-1.091071
25.H	-0.238293	4.080642	-0.859629
26.H	4.015375	-2.776924	-0.923953
27.H	-0.621497	3.006396	-2.208205
28.H	-3.963244	-3.935901	0.298182
29.CU	-0.733305	-2.460449	0.756408
30.C	-5.383116	-3.046721	-2.664748
31.C	-5.027312	-3.840832	-1.569435
32.C	-4.265333	-3.304780	-0.532200
33.H	-3.916146	-0.125186	-1.715545
34.H	-5.262426	-1.084412	-3.556705
35.H	-5.959035	-3.473110	-3.482520
36.H	-5.323173	-4.886403	-1.533865
37.C	2.729621	-2.480991	0.789163
38.C	2.630799	-2.571724	2.187130
39.C	3.729315	-2.993296	2.941531

40.C	4.929691	-3.333471	2.309901
41.C	5.029597	-3.253921	0.916488
42.C	3.935658	-2.829772	0.158231
43.H	1.686475	-2.347228	2.675303
44.H	3.642041	-3.067236	4.023450
45.H	5.781244	-3.668073	2.898602
46.H	5.958918	-3.523594	0.419194
47.C	1.530326	-2.563979	-1.824052
48.C	1.570244	-1.753821	-2.967245
49.C	1.659738	-2.332198	-4.236625
50.C	1.713185	-3.721151	-4.374912
51.C	1.688598	-4.533455	-3.236720
52.C	1.593804	-3.960826	-1.969254
53.H	1.525542	-0.673103	-2.870955
54.H	1.680456	-1.694726	-5.117985
55.H	1.764494	-4.170011	-5.363743
56.H	1.716680	-5.615432	-3.337340
57.C	-3.691584	-1.553408	2.277996
58.C	-5.087770	-1.705619	2.289302
59.C	-5.771912	-1.832278	3.501396
60.C	-5.070213	-1.803282	4.711538
61.C	-3.679124	-1.652840	4.704948
62.C	-2.990292	-1.534445	3.495553
63.H	-5.637047	-1.733039	1.352714
64.H	-6.852964	-1.954599	3.499907
65.H	-5.603963	-1.905945	5.653771
66.H	-3.126740	-1.642048	5.641990
67.C	-3.854329	-1.960861	-0.576046
68.C	-4.226487	-1.165031	-1.669273
69.C	-4.987303	-1.707671	-2.708552
70.H	-2.340974	-4.514187	-5.647448
71.H	-1.366563	-2.333256	-2.066903
72.O	-0.439322	-3.169752	2.710726
73.C	-0.602265	-4.424467	2.915463
74.N	-0.929554	-5.316698	1.966361
75.H	-1.864158	-2.359019	-4.485733
76.C	-0.408972	-4.943166	4.322716
77.H	-0.583876	-6.019890	4.375873
78.H	-1.095786	-4.420620	5.000067
79.C	-1.857508	-3.292825	-3.928541
80.C	-1.577588	-3.271892	-2.566329
81.C	-1.102256	-4.899023	0.739154
82.H	-1.820122	-6.606568	-1.913627
83.H	-2.318670	-6.640110	-4.343886
84.H	0.611922	-4.717746	4.655956
85.C	-1.267443	-4.467944	-0.415337
86.C	-1.556363	-4.464603	-1.812394
87.C	-1.831746	-5.680474	-2.482621
88.C	-2.110809	-5.693669	-3.848073
89.C	-2.124985	-4.500808	-4.581728

TS3

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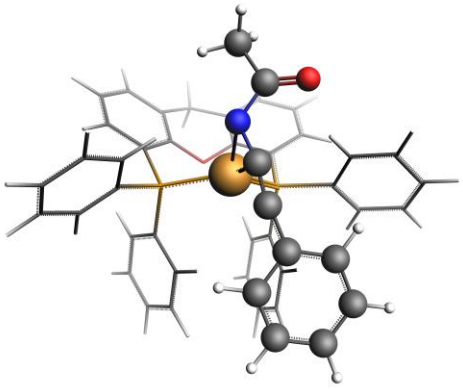

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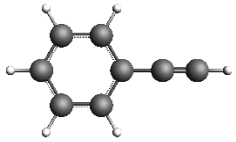
6.C	2.521864	2.530498	-0.368009
7.C	1.266654	2.930520	0.104156
8.C	0.198209	2.026652	0.136425
9.C	0.432461	0.730014	-0.326971
10.C	1.669248	0.301895	-0.832558
11.C	-3.525559	2.020339	-0.432495
12.C	-2.722963	-0.515846	-1.372402
13.H	3.693260	0.930670	-1.224840
14.H	3.344770	3.240769	-0.383198
15.H	1.113598	3.950826	0.451016
16.C	-4.414100	1.219654	-1.159067
17.C	-4.015952	-0.033800	-1.632993
18.H	-5.415917	1.582251	-1.375241
19.H	-4.696218	-0.629877	-2.232990
20.H	-2.221163	-1.981012	0.838600
21.H	-3.833182	3.006743	-0.090464
22.P	-2.021596	-2.023312	-2.167439
23.P	1.747778	-1.376892	-1.581168
24.H	2.786649	-0.883523	-4.207347
25.H	-1.270808	2.106719	1.705644
26.H	2.220786	-1.041694	1.369017
27.H	-1.393879	3.433078	0.549342
28.H	-4.465920	-3.706261	-1.807945
29.Cu	0.035367	-1.723704	-2.939876
30.C	-5.329222	-3.430177	-5.091130
31.C	-5.396334	-3.817553	-3.746920
32.C	-4.414902	-3.397270	-2.848110
33.H	-2.467748	-1.596221	-5.014443
34.H	-4.213229	-2.314844	-6.573370
35.H	-6.092562	-3.763805	-5.790913
36.H	-6.211459	-4.448969	-3.399663
37.C	1.739007	-2.510373	-0.139865
38.C	1.449464	-3.862230	-0.386332

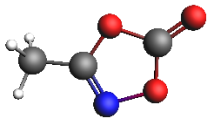
39.C	1.457324	-4.783060	0.660372
40.C	1.730311	-4.360302	1.965666
41.C	1.999237	-3.012186	2.219627
42.C	2.008380	-2.088593	1.169790
43.H	1.201325	-4.188055	-1.393146
44.H	1.224712	-5.824796	0.460188
45.H	1.720877	-5.077232	2.783581
46.H	2.202772	-2.677911	3.234709
47.C	3.452726	-1.486245	-2.239231
48.C	4.545458	-1.884878	-1.452900
49.C	5.822297	-1.950352	-2.016008
50.C	6.013864	-1.617681	-3.361982
51.C	4.924163	-1.227437	-4.148327
52.C	3.642714	-1.164825	-3.594616
53.H	4.395952	-2.151108	-0.409904
54.H	6.666832	-2.263633	-1.405818
55.H	7.008637	-1.672697	-3.798307
56.H	5.068171	-0.982394	-5.198172
57.C	-1.997513	-3.309472	-0.853069
58.C	-1.820319	-4.646228	-1.253433
59.C	-1.773099	-5.664359	-0.302659
60.C	-1.875304	-5.360470	1.059688
61.C	-2.025200	-4.031232	1.463249
62.C	-2.091455	-3.008120	0.512572
63.H	-1.733778	-4.893290	-2.306407
64.H	-1.644774	-6.692572	-0.632284
65.H	-1.829244	-6.153820	1.802318
66.H	-2.093805	-3.786527	2.520725
67.C	-3.352988	-2.590126	-3.291149
68.C	-3.287884	-2.202501	-4.638612
69.C	-4.279339	-2.618670	-5.531519
70.N	0.557275	-0.928433	-5.051004
71.H	0.864132	1.535497	-4.766286
72.H	-2.056417	-4.673640	-5.434146
73.O	-1.256249	-0.385141	-6.425695
74.C	-0.305941	-0.055757	-5.700461
75.H	-2.722936	-6.973973	-4.796709
76.C	0.012793	1.413689	-5.441024
77.H	-0.872099	1.898032	-5.010681
78.H	0.222072	1.910936	-6.395640
79.C	-1.742694	-6.598365	-4.510507
80.C	-1.371606	-5.306795	-4.879305
81.C	0.326579	-2.233207	-5.062167
82.H	1.743930	-5.233786	-3.489347
83.H	1.071755	-7.529847	-2.833932
84.H	-1.170391	-8.411682	-3.476573
85.C	0.230613	-3.434887	-4.788953
86.C	-0.108694	-4.782321	-4.505358
87.C	0.767577	-5.619536	-3.771131
88.C	0.385013	-6.908296	-3.405013
89.C	-0.873555	-7.406424	-3.765964

2a



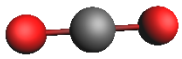
Atom	X	Y	Z (Angstrom)
1.C	2.001503	-0.000002	0.000381
2.C	0.575201	-0.000008	0.000148
3.C	-0.141956	-1.215878	-0.000010
4.C	-1.536754	-1.210816	-0.000237
5.C	-2.239052	0.000005	-0.000312
6.C	-1.536762	1.210834	-0.000157
7.C	-0.141961	1.215860	0.000071
8.C	3.212203	0.000005	0.000579
9.H	0.407103	-2.153372	0.000049
10.H	-2.077742	-2.154281	-0.000357
11.H	-3.326492	-0.000003	-0.000490
12.H	-2.077734	2.154308	-0.000214
13.H	0.407111	2.153347	0.000192
14.H	4.278233	0.000004	0.000753

Dioxazolone



Atom	X	Y	Z (Angstrom)
1.O	-0.423706	-0.062479	0.683514
2.C	-0.623719	0.978937	-0.187368
3.O	-1.935234	0.826699	-0.699641
4.C	-2.435179	-0.301192	-0.097898
5.N	-1.629916	-0.885546	0.722544
6.O	0.137581	1.852693	-0.473576
7.C	-3.815660	-0.741922	-0.426305
8.H	-4.047743	-1.651007	0.133577
9.H	-3.902005	-0.939550	-1.501034
10.H	-4.534016	0.043987	-0.165392

CO_2



Atom	X	Y	Z (Angstrom)
1.C	0.000000	0.000000	0.000000
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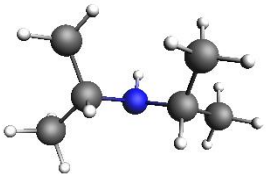
3.O	0.000001	0.000005	1.172533

iPr_2NH



Atom	X	Y	Z (Angstrom)
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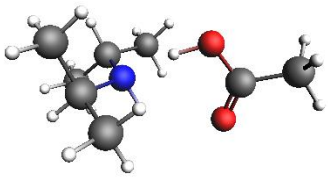
3.C	1.229335	-0.184438	-0.225156
4.C	2.163052	-1.408384	-0.278574
5.C	-1.460704	1.435329	-0.391209
6.C	1.894470	0.978164	0.539403
7.N	-0.081004	-0.580615	0.344390
8.H	-2.629616	-0.450985	1.335055
9.H	-2.416929	-1.857824	0.271011
10.H	-3.437979	-0.487457	-0.241541
11.H	-1.208689	-0.461716	-1.385609
12.H	-0.126198	-0.330837	1.333887
13.H	1.043619	0.143014	-1.258009
14.H	3.123133	-1.156993	-0.748054
15.H	1.693128	-2.219654	-0.844352
16.H	2.362760	-1.777232	0.735935
17.H	-2.369341	1.713967	-0.940724
18.H	-0.611036	1.920308	-0.884236
19.H	-1.541439	1.839043	0.627135
20.H	1.255698	1.867318	0.553726
21.H	2.856553	1.251363	0.087924
22.H	2.090122	0.681397	1.579348

$[AcOH][HNiPr_2]$



Atom	X	Y	Z (Angstrom)
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3.O	-2.729221	-1.166972	0.152408
4.O	-4.641059	-1.821086	1.196390
5.C	-4.290890	0.535060	0.742173
6.H	-4.214039	0.954011	-0.267292
7.H	-5.302534	0.663425	1.131536
8.H	-1.277156	-2.310229	2.305287
9.H	-0.773424	-3.638529	3.374464
10.H	-0.493985	-4.225838	0.948502
11.H	-3.401949	-3.817223	0.865745
12.H	-2.750625	-5.661283	-0.652316
13.H	-1.381239	-4.967925	-2.628481
14.H	-0.421437	-4.918503	-1.144220
15.H	-1.041903	-3.407605	-1.844949
16.H	-0.933948	-6.041082	2.615280
17.H	-1.637305	-6.460893	1.047380
18.H	-2.681150	-5.864632	2.355833
19.H	-4.696993	-4.113376	-1.056293
20.H	-3.917757	-4.642192	-2.562695
21.H	-2.537071	-2.191426	0.207105
22.H	-3.619031	-3.007836	-1.927834
23.H	-2.498503	-3.328494	3.090492
24.C	-1.507102	-3.332762	2.620244
25.C	-1.478790	-4.299092	1.425871
26.C	-2.573407	-4.592682	-0.856776
27.C	-1.273080	-4.464019	-1.661532
28.C	-1.696880	-5.754299	1.881831
29.C	-3.775880	-4.055968	-1.647982
30.N	-2.476869	-3.832498	0.420945

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