Electronic Supplementary Information

Mechanistic Insights into the Visible-Light-Driven *O*-Arylation of Carboxylic Acids Catalyzed by Xanthine-Based Nickel Complexes

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CONTENTS OF THE SUPPORTING INFORMATION

1. General Information

The experiments were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun UniLab glovebox. Solvents were dried and degassed with an MBraun SPS800 solvent purification system. Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), and toluene were stored over molecular sieves (3 Å). Diethyl ether (Et_2O), benzene and *n*-hexane were stored over a potassium mirror. All chemicals were purchased from commercial suppliers and used as received, unless stated otherwise. Liquid substrates for catalysis were degassed *via* freeze-pump-thaw. The aryloxy radical $^{\bullet}$OAr* (Ar* = 2,4,6-(^{t}Bu)$_3$-C_6H_2) was prepared as described in the literature.[1] Solution ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on Bruker Avance 300 or 400 MHz spectrometers at Regensburg University. Peak positions are relative to tetramethylsilane (^{1}H and ^{13}C{^{1}H}), trichlorofluoromethane (^{19}F{^{1}H}) or phosphoric acid (^{31}P{^{1}H}). The chemical shifts (δ) are measured according to IUPAC, expressed in parts per million (ppm) and calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). Coupling constants $^nJ_{xx}$ are given in Hertz (Hz) as absolute values. The multiplicity of the signals is indicated as *s, d, t, q, or m* for singlets, doublets, triplets, quartets, or multiplets, respectively. The abbreviation br. is given for broadened signals. H^{Ar} and C^{Ar} denote aromatic protons/carbons, while C^{quat} is used for quaternary carbon atoms. NMR spectra were recorded at room temperature (25 °C), unless otherwise stated.

X-band EPR measurements were carried out using a MiniScope MS400 device with a frequency of 9.5 GHz and rectangular resonator TE102 from the company Magnettech GmbH. LIFDI-MS analysis was performed using a JeolAccuTOF GCX at University of Regensburg (Zentrale Analytik, Massenspektrometrie). Elemental analyses were carried out in an Elementar Vario Micro Cube instrument, at the University of Regensburg. Gas chromatography coupled to a flame ionization detector (GC-FID) was performed on a Shimadzu GC2025 using H_2 as carrier gas. Colum: Restek Rxi®-5Sil MS, 30 m x 0.25 mm x 0.25 µm. Standard heating program: 50 °C (2 min), heating ramp 25 °C/min for 9 min, 280 °C (5 min). Autosampler AOC-20s and injector AOC-20i. The calibration of substrates and products was conducted with 1,3,5-trimethoxybenzene as internal standard and analytically pure samples. Gas chromatography coupled to a mass-selective detector (GC-MS) was performed on an *Agilent 7820A GC system, mass detector 5977B*. Carrier gas: H_2. Column: HP-5MS (30 m × 0.25 mm × 0.25 µm), 5% phenylmethylsiloxane. Standard heating program: 50 °C (2 min), heating ramp 25 °C/min for 10 min, 300 °C (5 min).

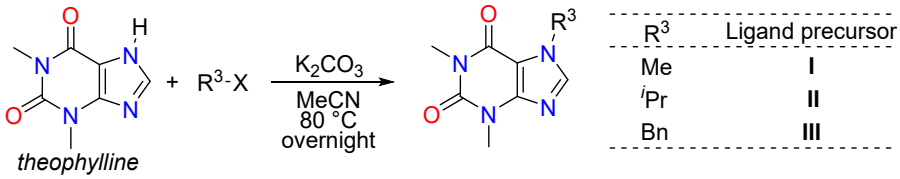
Single crystal X-ray diffraction data were recorded on an Agilent Technologies SuperNova with Cu Kα radiation (λ = 1.54184 Å), a Bruker SMART Apex II diffractometer equipped with a CCD area detector and MoKα radiation (λ = 0.71073 Å) from a fine-focus sealed tube or a Rigaku Synergy Dual Wavelength Rotating Anode diffractometer equipped with a HyPix Arc 150° detector. The structures were solved

and refined with SHELXT and SHELXL. The crystallographic tables and solid-state molecular structures are shown below (Tables S9-S11, Figures S16-S24). Deposition Numbers 2354532 (for ligand ^{Pyr}**NN**^{H}), 2354529 (for ligand $^{p\text{-Anis}}$**NN**^{H}), 2354533 (for ligand ^{Pyr}**NN**^{4Me}), 2354534 (for complex **6**^{Br}), 2354527 (for complex **6**^{Br}·MeCN), 2354530 (for complex **7**^{Br}), 2354528 (for complex **11**^{Br}·PPh_3), and 2354531 (for complex **11**^{OAr*}) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

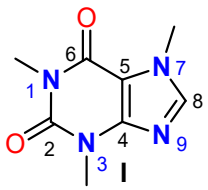
2. Synthesis and characterization of *N*7-theophylline derivatives I-VIII

2.1. *N7*-Alkylation reactions. Caffeine (R^3 = Me, **I**) was used as received from a commercial supplier. The other *N7*-alkylated xanthine derivatives (theophylline derivatives **II**, R^3 = ^{i}Pr, and **III**, R^3 = Bn) were synthesized using slightly modified literature procedures (Scheme S1).[2,3] A round bottom flask equipped with a stirring bar was loaded with theophylline (1.8 g, 10.0 mmol, 1.0 equiv.) and K_2CO_3 (1.7 g, 12.0 mmol, 1.2 equiv.). Then, the corresponding alkyl halide (for **II**: isopropyl iodide, 3.4 g, 2.0 mL, 20.0 mmol, 2.0 equiv.; for **III**: benzyl bromide, 3.4 g, 2.4 mL, 20.0 mmol, 2.0 equiv. Caution: lachrymatory) in acetonitrile (MeCN, 30 mL) was added and the mixture was refluxed for 18 h. Upon cooling to room temperature, the suspension was filtered through frit (P4) and the filter cake was washed with MeCN (3 x 10 mL). The filtrate was dried in vacuo to give a yellowish crude product which was re-dissolve in dichloromethane (100 mL) and washed with water (3 x 100 mL). After drying the organic phase with $MgSO_4$, removal of the solvent yielded a white powder that was washed with *n*-hexane (3 x 10 mL) and diethyl ether (2 x 10 mL). Each product was dried in vacuo for 1 h giving the corresponding *N7*-alkylated theophylline derivative, as confirmed by ^{1}H and ^{13}C{^{1}H} NMR, sufficiently pure for the next reaction step. NOTE. The *N7*-alkyation of theophylline with -COPh, -SO_2Tol and -CF_3 groups is possible, but it turned out useless for the subsequent C8-arylation step (*vide infra*).

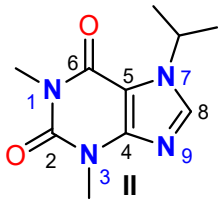
Scheme S1. Synthesis of the ligand precursors **I**-**III** *via N7*-alkylation of theophylline.



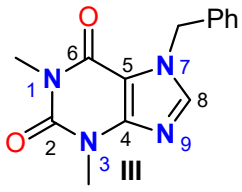
R^3	Ligand precursor
Me	**I**
^{i}Pr	**II**
Bn	**III**



1,3,7-Trimethylxanthine, **I**. Commercial product. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ [ppm] = 7.55 (s, 1H, H8), 3.99 (s, 3H, NCH_3), 3.58 (s, 3H, NCH_3), 3.40 (s, 3H, NCH_3).



1,3-Dimethyl-7-isopropyl-xanthine, **II**. Yield: 1.1 g, 5.0 mmol, 50%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ [ppm] = 7.63 (s, 1H, H8), 5.01 (sep, $^{3}J_{HH}$ = 6.7 Hz, 1H, N7CH), 3.56 (s, 3H, NCH_3), 3.38 (s, 3H, NCH_3), 1.55 (d, $^{3}J_{HH}$ = 6.7 Hz, 6H, 2 x CH_3). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ [ppm] = 155.1 (s, C=O), 151.7 (s, C=O), 149.2 (s, C^{quat}), 138.2 (s, C8), 106.8 (s, C^{quat}), 50.1 (s, NCH_3), 29.8 (s, NCH_3), 28.1 (s, NCH_3), 23.1 (s, 2 x CH_3).

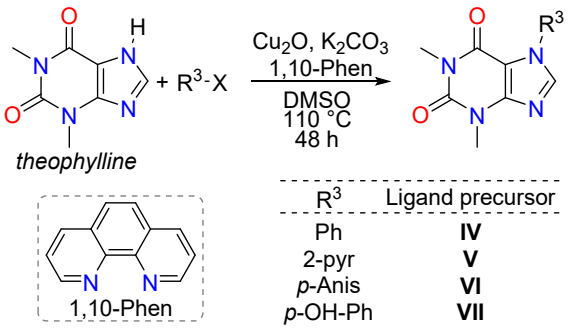


1,3-Dimethyl-7-benzyl-xanthine, **III**. Yield: 2.2 g, 8.1 mmol, 81%. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 7.57 (s, 1H, H8), 7.39-7.30 (m, 5H, H^{Ar}), 5.50 (s, 2H, CH_2), 3.58 (s, 3H, NCH_3), 3.40 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 155.3 (s, C=O), 151.7 (s, C=O), 148.8 (s, C^{quat}), 140.8 (s, C8), 135.3 (s, C^{quat}/C^{Ar}), 129.1 (s, C^{Ar}), 128.7 (s, C^{Ar}), 128.0 (s, C^{Ar}), 107.0 (s, C^{quat}), 50.4 (s, N7CH_2), 29.8 (s, NCH_3), 28.0 (s, NCH_3).

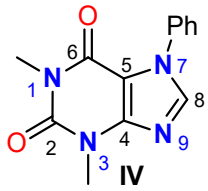
2.2. *N7*-Arylation reactions. The *N7*-arylated theophylline derivatives **IV**-**VII** were prepared following slightly adapted reported protocols (Scheme S2).[4,5] A Schlenk flask equipped with a stirring bar was loaded with theophylline (1.8 g, 10.0 mmol, 1.0 equiv.), arylating agent (11.6 mmol, 1.2 equiv.), 1,10-phenanthroline (180.0 mg, 1.0 mmol, 10 mol%), Cu_2O (71.5 mg, 0.5 mmol, 5 mol%) and K_2CO_3 (2.1 g, 15.0 mmol, 1.5 equiv.). Air was removed by three vacuum-argon cycles and then freshly degassed dimethyl sulfoxide (DMSO, 7.5 mL) was added. The suspension was vigorously stirred at 110 °C for 2 days. Upon cooling to 60 °C, chloroform ($CHCl_3$, 20 mL) was added, the suspension was filtered through a P4 frit, and the filter cake was washed with $CHCl_3$ (3 x 15 mL). The collected clear filtrate was treated with EDTA-Na_2 (558.4 mg, 1.5 mmol, 1.5 equiv. with respect to Cu) in H_2O (100 mL) and vigorously stirred for 1 h. The resulting green/blue aqueous phase was separated, the organic phase was washed with H_2O (3 x 100 mL) and finally dried over $MgSO_4$. Upon filtration, all volatiles were removed under reduced pressure to give colorless or slightly brownish powders, which were washed with *n*-hexane (2 x 10 mL) and Et_2O (3 x 10 mL). The respective products were dried in vacuo and analyzed by NMR, yielding sufficiently pure substances for the next reaction step. However, for precursor **VI** flash chromatography was necessary to remove molecular iodine and other unidentified impurities, that seemed to affect the subsequent synthetic stage. Chromatography was performed on silica gel with

ethyl acetate as eluent. NOTE. The *N7*-arylation of theophylline with 4-X-bromobenzenes (X = -NO_2, -CO_2Me) takes place with yields around only 1%, thus returning unamenable amounts for the next step.

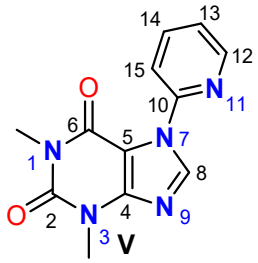
Scheme S2. Synthesis of the ligand precursors **IV**-**VII** *via N7*-arylation of theophylline.



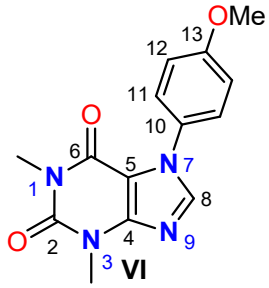
R^3	Ligand precursor
Ph	**IV**
2-pyr	**V**
p-Anis	**VI**
p-OH-Ph	**VII**



1,3-Dimethyl-7-phenyl-xanthine, **IV**. Bromobenzene as an arylating agent. Yield: 0.7 g, 2.7 mmol, 27%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ [ppm] = 7.74 (s, 1H, H8), 7.53-7.43 (m, 5H, H^{Ar}), 3.64 (s, 3H, NCH_3), 3.38 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ [ppm] = 154.4 (s, C=O), 151.6 (s, C=O), 149.6 (s, C^{quat}), 141.2 (s, C8), 134.8 (s, C^{quat}/C^{Ar}), 129.3 (s, C^{Ar}), 129.1 (s, C^{Ar}), 125.1 (s, C^{Ar}), 107.2 (s, C^{quat}), 30.0 (s, NCH_3), 28.2 (s, NCH_3).

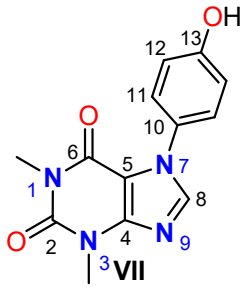


1,3-Dimethyl-7-(2-pyridyl)-xanthine, **V**. 2-Bromopyridine as an arylating agent. Yield: 2.3 g, 8.8 mmol, 88%. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.48 (ddd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.7 Hz, $^5J_{HH}$ = 0.7 Hz, 1H, H12), 8.43 (s, 1H, H8), 8.03 (dt, $^3J_{HH}$ = 8.2 Hz, $^{4,5}J_{HH}$ = 0.7 Hz, 1H, H15), 7.88 (td, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, H14), 7.34 (ddd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, H13), 3.64 (s, 3H, N3CH_3), 3.42 (s, 3H, N1CH_3). $^{13}C\{^1H\}$ NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 154.6 (s, C6), 151.3 (s, C2), 150.8 (s, C4), 148.6 (s, C12), 147.6 (s, C10), 141.9 (s, C8), 138.7 (s, C14), 123.4 (s, C13), 118.4 (s, C15), 105.9 (s, C5), 30.1 (s, N3CH_3), 28.5 (s, N1CH_3).



1,3-Dimethyl-7-(4-anisyl)-xanthine, **VI**. 4-Iodoanisole as an arylating agent. Flashed chromatographed over silica gel, using ethyl acetate as eluent. Yield: 1.5 g, 5.4 mmol, 54%. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 7.69 (s, 1H, H8), 7.38 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H11), 7.00 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H12), 3.86 (s, 3H, OCH_3), 3.65 (s, 3H, N3CH_3), 3.39 (s, 3H, N1CH_3). $^{13}C\{^1H\}$ NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 160.1 (s, C13), 154.5 (s, C6), 151.6 (s, C2),

149.4 (s, C4), 141.2 (s, C8), 127.7 (s, C10), 126.5 (s, C11), 114.4 (s, C12), 107.5 (s, C5), 55.6 (s, OCH_3), 29.9 (s, $N3CH_3$), 28.1 (s, $N1CH_3$).

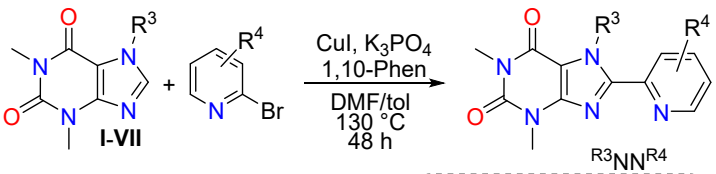


1,3-Dimethyl-7-(4-hydroxyphenyl)-xanthine, **VII**. 4-bromophenol as an arylating agent. Yield: 0.5 g, 2.0 mmol, 20%. ^{1}H NMR (400.3 MHz, DMSO-d_6): δ [ppm] = 9.87 (s, 1H, OH), 8.21 (s, 1H, H8), 7.34 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H11), 6.86 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H12), 3.47 (s, 3H, $N3CH_3$), 3.19 (s, 3H, $N1CH_3$). ^{13}C{^{1}H} NMR (100.7 MHz, DMSO-d_6): δ [ppm] = 162.3 (s, C13), 158.9 (s, C6), 156.0 (s, C2), 153.9 (s, C4), 147.8 (s, C8), 131.8 (s, C11), 120.4 (s, C12), 111.4 (s, C5), 34.7 (s, $N3CH_3$), 33.0 (s, $N1CH_3$), C10 not resolved.

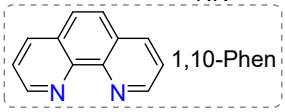
3. *C*8-arylation of theophylline derivatives with 2-bromopyridines. Synthesis of ^{R3}NN^{R4}

The C-C coupling reaction between theophylline derivatives and 2-bromo-pyridines was carried out by adapting the procedure from You and co-workers (Scheme S3).[6] A Schlenk flask equipped with a stirring bar was loaded with **I**-**VII** (2.0 mmol, 1.0 equiv.), the corresponding 2-bromopyridine (3.0 mmol, 1.5 equiv.), CuI (76.1 mg, 0.4 mmol, 20 mol%), 1,10-phenanthroline (72.0 mg, 0.4 mmol, 20 mol%) and K_3PO_4 (848.0 mg, 4.0 mmol, 2.0 equiv.). Air was purged by three vacuum/argon cycles. Then, degassed *N*,*N*-dimethylformamide/toluene (1:1, 3 mL) was added and the mixture was heated to 130 °C for 2 days. Upon cooling down to 60 °C, $CHCl_3$ (20 mL) was added and stirred for an additional 10 min. The suspension was filtered through frit (P4) and the filter cake was washed with $CHCl_3$ (3 x 20 mL). Subsequently, the filtrate was treated with EDTA-Na_2 (223.3 mg, 0.6 mmol, 1.5 equiv. with respect Cu) in water (100 mL), and vigorously stirred until the aqueous phase turned greenish and the organic phase brownish (ca. 1 h). The organic phase was washed with water (3 x 100 mL), dried over $MgSO_4$, filtrated and the solvent was removed under reduced pressure. The resulting crude product was washed with *n*-hexane (1 x 20 mL) and diethyl ether (3 x 20 mL). Caffeine derivatives were washed with hot water (60 °C, 3 x 5 mL), which proved efficient to remove unreacted **I**. Most of the products can be easily recrystallized from hot acetone, hot acetonitrile, or the mixture dichloromethane/*n*-hexane. If required, further purification can be done by flash chromatography using a silica plug and ethyl acetate as eluent.

Scheme S3. Synthesis of the ligands $^{R3}NN^{R4}$ by *C8*-arylation of precursors **I-VII** with 2-bromopyridine derivatives.

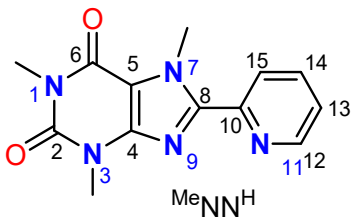


R^3	R^4	Ligand
Me		$^{Me}NN^{H}$
^{i}Pr		$^{iPr}NN^{H}$
Bn		$^{Bn}NN^{H}$
Ph	H	$^{Ph}NN^{H}$
2-pyr		$^{Pyr}NN^{H}$
p-Anis		$^{p\text{-Anis}}NN^{H}$
p-OH-Ph		$^{p\text{-OHPh}}NN^{H}$

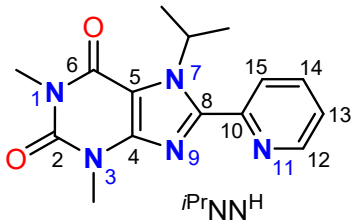


R^3	R^4	Ligand
Me		$^{Me}NN^{4Me}$
2-pyr	4-Me	$^{Pyr}NN^{4Me}$
p-OH-Ph		$^{p\text{-OHPh}}NN^{4Me}$
p-Anis	6-Me	$^{p\text{-Anis}}NN^{6Me}$

NOTE. The preparation of xanthine scaffolds $^{R3}NN^{R4}$ bearing electron-withdrawing groups has been so far unsuccessful. The functionalization of the *N7* with acyl, tosyl or trifluoromethyl groups proceeded relatively well, but in the subsequent *C8*-arylation step the -COPh, -SO_2Tol and -CF_3 groups are substituted by the corresponding aryl moiety. Likewise, as stated before, the *N7*-arylation of theophylline with 4-X-bromobenzenes (X = -NO_2, -CO_2Me) took place very poorly with yields around only 1%, thus hampering the next *C8*-arylation reaction step.

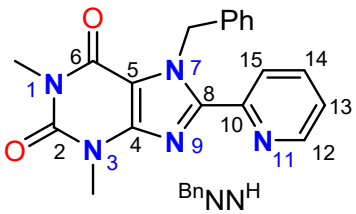


1,3,7-Trimethyl-8-(2-pyridyl)-xanthine, $^{Me}NN^{H}$. Coupling of **I** with 2-bromopyridine. Yield: 330.0 mg, 1.2 mmol, 60%. Ten-fold reaction scale, 20.0 mmol, afforded 2.7 g of product, 50% yield. The crude of reaction is a mixture of product and unreacted caffeine, which can be effectively removed by washing with hot water (60 °C, 3 x 5 mL for 2.0 mmol scale). ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.68 (d, $^{3}J_{HH}$ = 4.2 Hz, 1H, H12), 8.21 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, H15), 7.83 (td, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1H, H14), 7.35 (ddd, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 0.8 Hz, 1H, H13), 4.47 (s, 3H, N7CH_3), 3.63 (s, 3H, N3CH_3), 3.43 (s, 3H, N1CH_3). $^{13}C\{^{1}H\}$ NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 155.7 (s, C6), 151.7 (s, C2), 149.1 (s, C4), 148.8 (s, C12), 148.2 (s, C8), 147.7 (s, C10), 136.9 (s, C14), 124.6 (s, C15), 124.1 (s, C13), 109.4 (s, C5), 35.2 (s, N7CH_3), 29.7 (s, N3CH_3), 28.0 (s, N1CH_3). Anal. Calcd. for $C_{13}H_{13}N_5O_2$: C, 57.56; H, 4.83; N, 25.82; found: C, 57.32; H, 5.01; N, 25.78.



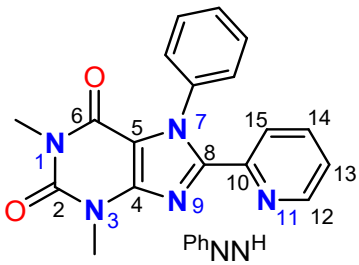
1,3-Dimethyl-7-isopropyl-8-(2-pyridyl)-xanthine, $^{iPr}NN^{H}$. Coupling of **II** with 2-bromopyridine. Yield: 121.6 mg, 0.4 mmol, 20%. The crude of

reaction is a mixture of product and unreacted **II**, which can be effectively removed by washing with hot acetone (45 °C, 3 x 1.5 mL). ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.72 (dt, $^{3}J_{HH}$ = 4.8 Hz, $^{4,5}J_{HH}$ = 0.8 Hz, 1H, H12), 8.07 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, H15), 7.86 (td, $^{3}J_{HH}$ = 7.8vHz, $^{4}J_{HH}$ = 1.8 Hz, 1H, H14), 7.38 (ddd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 4.8 Hz, $^{4}J_{HH}$ = 0.9 Hz, 1H, H13), 5.82 (sep, $^{3}J_{HH}$ = 6.9 Hz, 1H, N7CH), 3.64 (s, 3H, N3CH_3), 3.47 (s, 3H, N1CH_3), 1.68 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, 2 x CH_3). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 154.8 (s, C6), 151.8 (s, C2), 149.7 (s, C4), 149.3 (s, C10), 149.2 (s, C12), 148.9 (s, C8), 137.1 (s, C14), 125.8 (s, C15), 124.3 (s, C13), 108.8 (s, C5), 50.9 (s, N7CH), 29.9 (s, N3CH_3), 28.7 (s, N1CH_3), 21.6 (s, 2 x CH_3). Anal. Calcd. for $C_{15}H_{17}N_5O_2$: C, 60.19; H, 5.72; N, 23.40; found: C, 59.85; H, 5.75; N, 23.10. UV-vis ($CHCl_3$, 5.10^{-6} mol.L^{-1}): λ_{max} = 312 nm.



^{Bn}NN^{H}

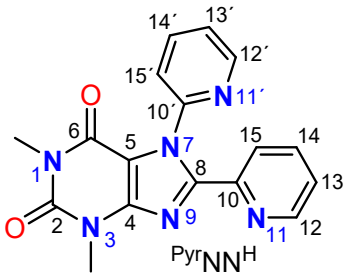
1,3-Dimethyl-7-benzyl-8-(2-pyridyl)-xanthine, ^{Bn}NN^{H}. Coupling of **III** with 2-bromopyridine. Yield: 241.7 mg, 0.7 mmol, 35%. The crude reaction is a mixture of product and unreacted **III**, which can be effectively removed by washing with acetonitrile (3 x 1.5 mL). ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.65 (d, $^{3}J_{HH}$ = 3.5 Hz, 1H, H12), 8.23 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H15), 7.82 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, H14), 7.34 (m, 1H, H13), 7.21 (br., 5H, H^{Ar}), 6.41 (s, 2H, CH_2), 3.64 (s, 3H, N3CH_3), 3.42 (s, 3H, N1CH_3). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 155.4 (s, C6), 151.7 (s, C2), 149.2 (s, C4), 148.8 (s, C12), 148.1 (s, C8), 147.9 (s, C10), 137.5 (s, C^{quat}/C^{Ar}), 137.1 (s, C14), 128.5 (s, C^{Ar}), 127.6 (s, C^{Ar}), 127.5 (s, C^{Ar}), 124.8 (s, C15), 124.3 (s, C13), 108.9 (s, C5), 49.8 (s, N7CH_2), 29.8 (s, N3CH_3), 28.1 (s, N1CH_3).



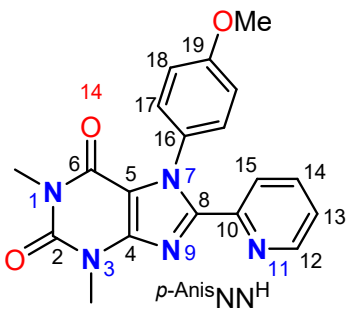
^{Ph}NN^{H}

1,3-Dimethyl-7-phenyl-8-(2-pyridyl)-xanthine, ^{Ph}NN^{H}. Coupling of **IV** with 2-bromopyridine. Yield: 460.0 mg, 1.4 mmol, 69%. The product was sufficiently pure after the washing step and neither recrystallization nor column chromatography were required. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.47 (dt, $^{3}J_{HH}$ = 4.7 Hz, $^{4}J_{HH}$ = 1.3 Hz,1H, H12), 7.68-7.66 (m, 2H, H15+H14), 7.47-7.40 (m, 3H, H^{Ar}), 7.34-7.31 (m, 2H, H^{Ar}), 7.27-7.22 (m, 1H, H13), 3.73 (s, 3H, N3CH_3), 3.37 (s, 3H, N1CH_3). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 154.6 (s, C6), 151.7 (s, C2), 149.5 (s, C12), 149.2 (s, C8), 148.5 (s, C4), 147.6 (s, C10), 136.6 (s, C14 or C15), 136.2 (s, C^{quat}/C^{Ar}), 129.2 (s, C^{Ar}), 128.8 (s, C^{Ar}), 127.5 (s, C^{Ar}), 124.7 (s, C15 or C14), 124.2 (s, C13), 109.8 (s, C5), 30.0 (s, N3CH_3), 28.1 (s, N1CH_3). Anal. Calcd. for $C_{18}H_{15}N_5O_2 \cdot (H_2O)_{0.34}$: C, 63.69; H, 4.66; N, 20.63; found: C, 64.05; H, 4.73; N, 20.80. The amount of water was confirmed

independently by ^{1}H NMR in dry $CDCl_3$ using acetone as standard, returning a molar fraction $H_2O/^{Ph}NN^H$ = 0.31.



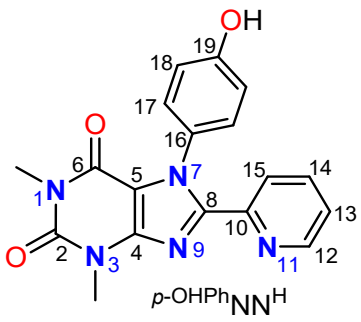
1,3-Dimethyl-7,8-di(2-pyridyl)-xanthine, $^{Pyr}NN^H$. Coupling of **V** with 2-bromopyridine. Yield: 541.6 mg, 1.6 mmol, 81%. The product was sufficiently pure after the washing step and neither recrystallization nor column chromatography were required. Five-fold reaction scale, 10.0 mmol, retrieved 2.5 g of $^{Pyr}NN^H$, 74% yield. In this case, recrystallization from acetone was necessary. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of $^{Pyr}NN^H$ in chloroform. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.46 (ddd, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 1.9 Hz, $^{5}J_{HH}$ = 0.7 Hz, 1H, H12´), 8.22 (dt, $^{3}J_{HH}$ = 4.7 Hz, $^{4,5}J_{HH}$ = 0.7 Hz, 1H, H12), 8.09 (dt, $^{3}J_{HH}$ = 7.9 Hz, $^{4,5}J_{HH}$ = 0.9 Hz, 1H, H15), 7.90 (td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.9 Hz, 1H, H14´), 7.74 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H, H14), 7.56 (dt, $^{3}J_{HH}$ = 8.0 Hz, $^{4,5}J_{HH}$ = 0.7 Hz, 1H, H15´), 7.41 (ddd, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 1.0 Hz, 1H, H13´), 7.19 (ddd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 4.8 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, H13), 3.71 (s, 3H, N3CH_3), 3.36 (s, 3H, N1CH_3). $^{13}C\{^{1}H\}$ NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 154.6 (s, C6), 151.7 (s, C2), 149.8 (s, C10´), 149.2 (s, C8), 148.8 (s, C12), 148.6 (s, C12´), 148.3 (s, C4), 147.7 (s, C10), 138.0 (s, C14´), 136.8 (s, C14), 124.4 (s, C15), 124.2 (s, C13 and C13´), 122.8 (s, C15´), 109.8 (s, C5), 30.1 (s, N3CH_3), 28.1 (s, N1CH_3). Anal. Calcd. for $C_{17}H_{14}N_6O_2$: C, 61.07; H, 4.22; N, 25.14; found: C, 60.85; H, 4.30; N, 25.25. HRMS (ESI) for $(C_{17}H_{14}N_6O_2+H)^+$ [$(M+H)^+$]: calc.: 335.1251; found: 335.1252. UV-vis ($CHCl_3$, 5.10^{-6} mol.L^{-1}): λ_{max} = 325 nm.



1,3-Dimethyl-7-(4-anisyl)-8-(2-pyridyl)-xanthine, $^{p\text{-Anis}}NN^H$. Coupling of **VI** with 2-bromopyridine. Yield: 484.5 mg, 1.3 mmol, 66%. The crude of reaction is a mixture of product and unreacted **VI**, which can be effectively removed by recrystallization in hot acetone (45 °C,). Five-fold reaction scale, 10.0 mmol, retrieved 2.3 g of $^{p\text{-Anis}}NN^H$, 63% yield. In this case, alternatively to recrystallization from acetone, protonation of $^{p\text{-Anis}}NN^H$ with $HBF_4{\cdot}Et_2O$ was used to separate the product from **VI**. For instance, a 9:1 m/m mixture of $^{p\text{-Anis}}NN^H$ and **VI** (2.0 g = 1.8 g $^{p\text{-Anis}}NN^H$ + 0.2 g **VI**) was dissolved in $CHCl_3$ (20 mL). Under stirring, $HBF_4{\cdot}Et_2O$ (754 µL, 5.5 mmol, 1.1 equiv.) was slowly added, forming $^{p\text{-Anis}}NN^H{\cdot}HBF_4$ within few hours as a light-yellow precipitate. Upon filtration and washing with $CHCl_3$ (3 x 5 mL), $^{p\text{-Anis}}NN^H{\cdot}HBF_4$ and **VI** are successfully separated. Yield: 2.0 g, 4.5 mmol, 90% $^{p\text{-Anis}}NN^H{\cdot}HBF_4$. ^{1}H NMR (400.3 MHz, CD_3CN): δ [ppm] = 8.75 (dd, $^{3}J_{HH}$ = 5.8 Hz, $^{5}J_{HH}$ = 0.8 Hz, 1H,

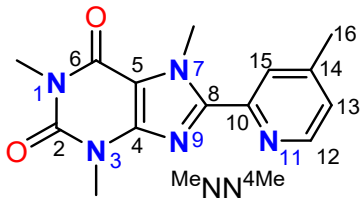
H12), 8.32 (td, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, H14), 7.95 (t, $^{3}J_{HH}$ = 6.5 Hz, 1H, H13), 7.44 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H, H17), 7.23 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, H15), 7.15 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H, H18), 3.92 (s, 3H, OCH_3), 3.64 (s, 3H, $N3CH_3$), 3.27 (s, 3H, $N1CH_3$). $^{p\text{-Anis}}NN^{H}\cdot HBF_4$ can be easily deprotonated with aqueous $NaHCO_3$ (20 mL, 0.25 mM, 5.0vmmol, 1.1 equiv.) in $MeCN/CHCl_3$ (1:3, 40 mL), returning $^{p\text{-Anis}}NN^{H}$ in high yield (1.6 g, 4.3 mmol, 95%; 88% overall the initial 1.8 g in the crude mixture). The recovered starting material **VI** (177.8 mg, 89%) can be reused in another reaction to prepare $^{p\text{-Anis}}NN^{H}$.

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into a THF solution of $^{p\text{-Anis}}NN^{H}$. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.53 (d, $^{3}J_{HH}$ = 4.7 Hz, 1H, H12), 7.70-7.63 (m, 2H, H15+H14), 7.27-7.24 (m, 3H, H13+H17), 6.93 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, H18), 3.85 (s, 3H, OCH_3), 3.73 (s, 3H, $N3CH_3$), 3.38 (s, 3H, $N1CH_3$). $^{13}C\{^{1}H\}$ NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 159.9 (s, C19), 154.7 (s, C6), 151.7 (s, C2), 149.6 (s, C12), 149.3 (s, C8), 148.4 (s, C4), 147.6 (s, C10), 136.6 (s, C14), 128.7 (s, C16), 128.5 (s, C17), 124.7 (s, C15), 124.2 (s, C13), 114.0 (s, C18), 109.9 (s, C5), 55.5 (s, OCH_3), 30.0 (s, $N3CH_3$), 28.1 (s, $N1CH_3$). Anal. Calcd. for $C_{19}H_{17}N_5O_3$: C, 62.80; H, 4.72; N, 19.27; found: C, 62.51; H, 4.81; N, 19.25. HRMS (ESI) for $(C_{19}H_{17}N_5O_3+H)^{+}$ [$(M+H)^{+}$]: calc.: 364.1404; found: 364.1407. UV-vis ($CHCl_3$, 5.10^{-6} mol.L^{-1}): λ_{max} = 315 nm.

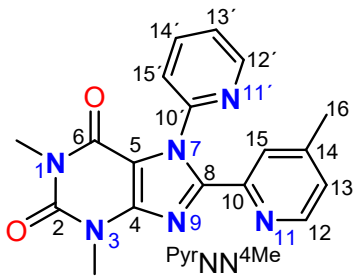


1,3-Dimethyl-7-(4-hydroxyphenyl)-8-(2-pyridyl)-xanthine, $^{p\text{-OHPh}}NN^{H}$. Coupling of **VII** with 2-bromopyridine. Yield: 652.9 mg, 1.9 mmol, 93%. The product was sufficiently pure after the washing step. However, recrystallization from dichloromethane/ethanol was required to obtain an analytically pure sample. ^{1}H NMR (400.3 MHz, DMSO-d_6): δ [ppm] = 8.38 (s, 1H, OH), 8.17 (d, $^{3}J_{HH}$ = 3.6 Hz, 1H, H12), 7.89 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, H14), 7.60 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, H17), 7.30 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, H18), 7,16 (dd, $^{3}J_{HH}$ = 6.7 Hz, $^{3}J_{HH}$ = 5.0 Hz, 1H, H13), 7.11 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, H15), 3.49 (s, 3H, $N3CH_3$), 3.22 (s, 3H, $N1CH_3$). $^{13}C\{^{1}H\}$ NMR (100.7 MHz, DMSO-d_6): δ [ppm] = 163.2 (s, C19), 154.3 (s, C6), 154.2 (s, C10), 151.4 (s, C2), 149.6 (s, C4), 147.9 (s, C12), 143.3 (s, C8), 140.9 (s, C14), 131.6 (s, C16), 127.0 (s, C17), 122.1 (s, C18), 119.8 (s, C13), 112.2 (s, C15),106.7 (s, C5), 30.1 (s, $N3CH_3$), 28.3 (s, $N1CH_3$). Anal. Calcd. for $C_{18}H_{15}N_5O_3$: C, 61.89; H, 4.33; N, 20.05; found: C, 62.19; H, 4.46; N, 19.67.

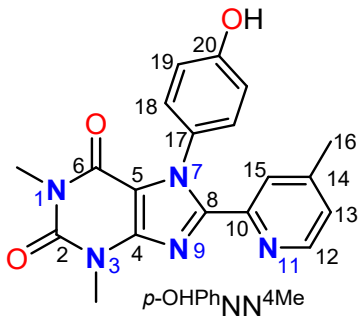
NOTE. In solution, $^{p\text{-OHAr}}NN^{H}$ experiences intermolecular hydrogen bonding, involving the OH group of one molecule as the donor and N9/N11 of another one as the acceptor. In the ^{1}H-^{13}C HMBC spectrum, the OH resonance (8.38 ppm) clearly correlates with C5 (106.7 ppm), C8 (143.3 ppm), C4 (149.6 ppm) and C10 (154.2 ppm).



1,3,7-Trimethyl-8-(4-methyl-pyridin-2-yl)-xanthine, $^{Me}NN^{4Me}$. Coupling of caffeine (**I**) with 2-bromo-4-methyl-pyridine. Yield: 427.9 mg, 1.5 mmol, 75%. Ten-fold reaction scale, 20.0 mmol, retrieved 3.5 g of product, 61% yield. The crude of reaction is a mixture of product and unreacted caffeine, which can be effectively removed by washing with hot water (60 °C, 3 x 5 mL for 2.0 mmol scale). ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.49 (d, $^{3}J_{HH}$ = 5.0 Hz, 1H, H12), 8.00 (s, 1H, H15), 7.14 (d, $^{3}J_{HH}$ = 4.9 Hz, 1H, H13), 4.42 (s, 3H, N7CH_3), 3.61 (s, 3H, N3CH_3), 3.39 (s, 3H, N1CH_3), 2.42 (s, 3H, H16). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 155.6 (s, C6), 151.7 (s, C2), 148.9 (s, C4), 148.7 (s, C12), 148.5 (s, C8), 148.3 (s, C10), 147.7 (s, C14), 125.3 (s, C15), 125.1 (s, C13), 109.3 (s, C5), 35.1 (s, N7CH_3), 29.7 (s, N3CH_3), 28.0 (s, N1CH_3), 21.1 (s, C16). Anal. Calcd. for $C_{14}H_{15}N_5O_2$: C, 58.94; H, 5.30; N, 24.55; found: C, 59.12; H, 5.23; N, 24.70.



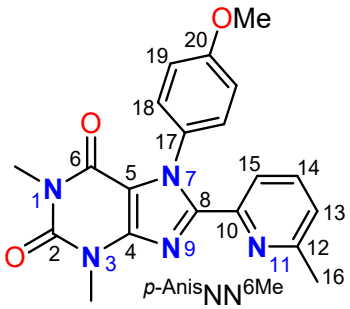
1,3-Dimethyl-7-(2-pyridyl)-8-(4-methyl-pyridin-2-yl)-xanthine, $^{Pyr}NN^{4Me}$. Coupling of **V** with 2-bromo-4-methyl-pyridine. Yield: 396.2 mg, 1.1 mmol, 57%. The product was sufficiently pure after the washing step and neither recrystallization nor column chromatography were required. However, recrystallization from dichloromethane/*n*-hexane was required to obtain an analytically pure sample and crystals suitable for X-ray diffraction analysis. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.43 (dd, $^{3}J_{HH}$ = 4.7 Hz, $^{4}J_{HH}$ = 1.0 Hz, 1H, H12´), 8.05 (d, $^{3}J_{HH}$ = 4.9 Hz, 1H, H12), 7.93 (br., 1H, H15), 7.88 (td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1H, H14´), 7.56 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, H15´), 7.39 (dd, $^{3}J_{HH}$ = 7.1 Hz, $^{3}J_{HH}$ = 5.1 Hz, 1H, H13´), 7.00 (d, $^{3}J_{HH}$ = 4.7 Hz, 1H, H13), 3.70 (s, 3H, N3CH_3), 3.35 (s, 3H, N1CH_3), 2.37 (s, 3H, H16). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 154.6 (s, C6), 151.7 (s, C2), 149.9 (s, C10´), 149.6 (s, C10 or C8), 148.7 (s, C12), 148.6 (s, C12´), 148.3 (s, C4), 148.1 (s, C14), 147.6 (s, C10 or C8), 137.9 (s, C14´), 125.3 (s, C15), 125.2 (s, C15´), 124.2 (s, C13´), 122.9 (s, C15´), 109.7 (s, C5), 30.1 (s, N3CH_3), 28.2 (s, N1CH_3), 21.1 (s, C16). Anal. Calcd. for $C_{18}H_{16}N_6O_2 \cdot (CH_2Cl_2)_{0.05}$: C, 61.48; H, 4.60; N, 23.83; found: C, 61.35; H, 4.83; N, 23.53. Amount of dichloromethane confirmed independently by ^{1}H NMR in $CDCl_3$ using ethyl acetate as standard, returning a molar fraction CH_2Cl_2/ $^{Pyr}NN^{4Me}$ = 0.051.



1,3-Dimethyl-7-(4-hydroxyphenyl)-8-(4-methyl-pyridin-2-yl)-xanthine, $^{p\text{-}OHPh}NN^{4Me}$. Coupling of **VII** with 2-bromo-4-methyl-pyridine. Yield: 550.2 mg, 1.5 mmol, 76%. The product was sufficiently pure after the washing step and neither recrystallization

nor column chromatography were required. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 8.05 (d, $^{3}J_{HH}$ = 5.1 Hz, 1H, H12), 7.74 (br., 1H, OH), 7.48 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, H18), 7.25 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, H19), 6.87 (d, $^{3}J_{HH}$ = 5.0 Hz, 1H, H13), 6.80 (s, 1H, H15), 3.65 (s, 3H, N3CH_3), 3.40 (s, 3H, N1CH_3), 2.37 (s, 3H, H16). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 163.2 (s, C20), 154.8 (s, C6), 154.5 (s, C2), 151.7 (s, C14), 151.6 (s, C4), 149.6 (s, C10), 147.0 (s, C12), 141.3 (s, C8), 130.9 (s, C17), 126.4 (s, C18), 121.7 (s, C19), 120.6 (s, C13), 112.3 (s, C15), 107.3 (s, C5), 29.9 (s, N3CH_3), 28.2 (s, N1CH_3), 21.1 (s, C16).

NOTE. As described for $^{p\text{-OHPh}}$NN^{H}, in solution $^{p\text{-OHPh}}$NN^{4Me} experiences intermolecular hydrogen bonding, involving the OH group of one molecule as the donor and N9/N11 of another one as the acceptor. In the ^{1}H-^{13}C HMBC spectrum, the OH resonance (7.74 ppm) clearly correlates with C5 (107.3 ppm), C8 (141.3 ppm), C4 (151.6 ppm) and C10 (149.6 ppm).

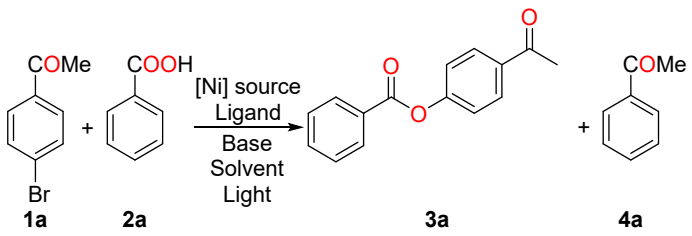


1,3-Dimethyl-7-(4-anisyl)-8-(6-methyl-pyridin-2-yl)-xanthine, $^{p\text{-Anis}}$NN^{6Me}. Coupling of **VI** with 2-bromo-6-methyl-pyridine. Yield: 396.2 mg, 1.1 mmol, 57%. The product was sufficiently pure after the washing step and neither recrystallization nor column chromatography were required. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 7.55 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, H14), 7.46 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, H15), 7.24 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, H18), 7.10 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H13), 6.92 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, H19), 3.84 (s, 3H, OCH_3), 3.71 (s, 3H, N3CH_3), 3.37 (s, 3H, N1CH_3), 2.38 (s, 3H, H16). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 159.9 (s, C20), 158.5 (s, C12), 154.7 (s, C6), 151.7 (s, C2), 149.3 (s, C8 or C10), 148.3 (s, C4), 146.7 (s, C8 or C10), 136.8 (s, C14), 129.0 (s, C17), 128.6 (s, C18), 124.0 (s, C13), 121.8 (s, C15), 113.8 (s, C19), 109.8 (s, C5), 55.5 (s, OCH_3), 30.0 (s, N3CH_3), 28.1 (s, N1CH_3), 24.2 (s, C16). HRMS (ESI) for $(C_{20}H_{19}N_5O_3+H)^+$ [$(M+H)^+$]: calc.: 378.1561; found: 378.1564.

4. Nickel catalyzed arylation of carboxylates: optimization and control experiments

Unless otherwise stated, all photocatalytic reactions were carried out in septum capped vials from 'WICOM Germany GmbH', which were filled in the glovebox. Usually, unless otherwise noted, the vials were irradiated with blue LED's (455 nm, 7 W nominal power) in the photoreactor 'TAK-120' from 'HK Testsysteme GmbH'. In a typical experiment, the vial was loaded with a stirring bar, 4-bromoacetophenone (39.9 mg, 0.20 mmol, 1.00 equiv.), benzoic acid (49.0 mg, 0.40 mmol, 2.00 equiv.), *N*,*N*-diisopropylethylamine (DIPEA, 105.0 mg, 0.82 mmol, 4.07 equiv.), nickel precursor (10.0 µmol, 0.05 equiv.) and ligand (20.0 µmol, 0.10 equiv.). The mixture was suspended in DMF (0.5 mL), the vials were sealed and the photoreactor was set up for irradiation with blue LED (7 W), for 18 h (Scheme S4). Once the reaction was completed, 1,3,5-trimethoxybenzene was added (8.4 mg, 0.050 mmol, 0.25 equiv.). An aliquot (0.32 mL) was taken, filtered through a silica plug, eluted with EtOAc (0.70 + 0.30 mL) and collected in a GC-vial for GC-FID analysis, using appropriate calibration curves. The optimization of the reaction conditions for the catalytic *O*-arylation of carboxylates are summarized in Tables S1-S6

Scheme S4. Coupling between 4'-bromoacetophenone (**1a**) and benzoic acid (**2a**) as model reaction for the nickel catalyzed arylation of carboxylates.

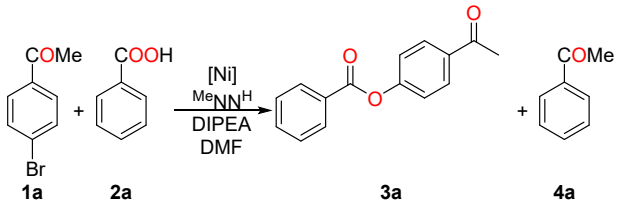


NOTE 1. For the numerous optimization experiments, stock solutions of 4-bromoacetophenone (1.00 mmol/mL, 200 µL), benzoic acid (2.00 mmol/mL, 200 µL), and some nickel precursors (0.10 mmol/mL, 100 µL) were used, having thus always a roughly reaction volume of 0.5 mL. In this case, the standard was also added from a stock solution (0.50 mmol/mL, 100 µL). The relatively low solubility of most ^{R3}NN^{R4} in DMF hampered the preparation of their corresponding stock solutions in such a solvent. DIPEA was added neat.

NOTE 2. When operating at maximum power (7 W), the TAK photoreactor reached a temperature around 40 °C.

NOTE 3. For experiments in the dark, the samples were stirred in an oil bath at 65 °C while covered from light for 18 h.

Table S1. Coupling reaction between 4'-bromoacetophenone (1a) and benzoic acid (2a): screening of nickel precursors.[a]

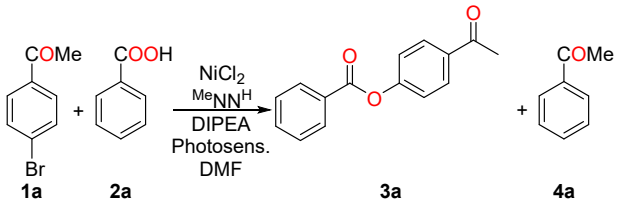


1a 2a 3a 4a

Nickel precursor	Conversion[b] (%)	**3a**[b] (%)	**4a**[b] (%)	Selectivity **3a**/**4a**
$NiCl_2$	26	14	10	1.40
$NiBr_2$	17	12	6	2.00
NiI_2	52	23	29	0.78
$Ni(TFA)_2$[c]	3	2	1	2.00
$[Ni(cod)_2]$	16	7	9	0.78
$Ni(OTf)_2$	10(2)[d]	6(1)[d]	3(1)[d]	2.25(5)[d]

[a] Conditions: 4-bromoacetophenone (159.4 mg, 0.80 mmol), benzoic acid (195.6 mg, 1.60 mmol, 2 equiv.), nickel source (40.0 µmol, 5 mol %), $^{Me}NN^{H}$ (21.7 mg, 80.0 µmol, 10 mol %), DIPEA (282 µL, 209.2 mg, 1.60 mmol, 2 equiv.), DMF (4 mL, ca. 0.2 mM), 18 h, room temperature, blue LED plate (20.3 V, 1.0 A). [b] Conversion, yield and selectivity determined by GC-FID using 1,3,5-trimethoxybenzene as internal standard (33.6 mg, 0.20 mmol) and appropriate calibration curves. [c] TFA refers to the trifluoroacetate anion, $CF_3CO_2^-$. [d] Average of three independent reactions. Shown errors correspond to the last significant figures.

Table S2. Coupling reaction between 4'-bromoacetophenone (1a) and benzoic acid (2a): screening of external photosensitizer.[a]

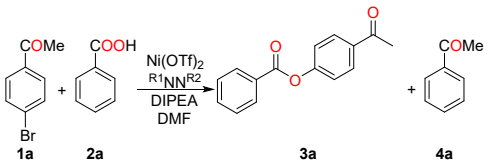


1a 2a 3a 4a

Photosensitizer	Conversion[b] (%)	**3a**[b] (%)	**4a**[b] (%)	Selectivity **3a**/**4a**
None	26	14	10	1.40
$[Ir(ppy)_3]$[c]	> 99	9	90	0.10
$[Ru(bpy)_3]$[d]	47	< 1	45	-
EOSIN Y	6	-	5	-
4CzIPN[e]	> 99	< 1	97	-
3DPA2FBN[f]	> 99	< 1	95	-
None[g]	> 99	64	32	2.00
$[Ir(dtbbpy)(ppy)_2]PF_6$[g]	93	-	45	-

[a] Conditions: 4-bromoacetophenone (39.9 mg, 0.20 mmol), benzoic acid (48.9 mg, 0.40 mmol, 2 equiv.), nickel(II) chloride (10.0 µmol, 5 mol %), $^{Me}NN^{H}$ (5.4 mg, 20.0 µmol, 10 mol %), DIPEA (71 µL, 0.40 mmol, 2 equiv.), photosensitizer (20.0 µmol, 1 mol %), DMF (1 mL, ca. 0.2 mM), 18 h, room temperature, blue LED plate (19.0 V, 0.7 A). [b] Conversion, yield and selectivity determined by GC-FID using 1,3,5-trimethoxybenzene as internal standard (8.4 mg, 0.05 mmol) and appropriate calibration curves. [c] ppy = ortho-metalated 2-phenylpyridine. [d] bpy = 2,2'-bipyridine. [e] 4CzIPN = 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene. [f] 3DPA2FBN = 2,4,6-tris(diphenylamino)-3,5-difluorobenzonitrile. [g] Conditions: 4-bromoacetophenone (39.9 mg, 0.20 mmol), benzoic acid (48.9 mg, 0.40 mmol, 2 equiv.), $Ni(OTf)_2$ (3.6 mg, 10.0 µmol, 5 mol %), ligand $^{p\text{-}Anis}NN^{H}$ (20.0 µmol, 10 mol %), DIPEA (142 µL, 0.81 mmol, 4 equiv.), DMF (0.5 mL, ca. 0.4 mM), 18 h, 40 °C, blue LED (7.0 W, TAK photoreactor).

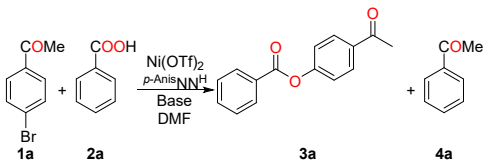
Table S3. Coupling between 4'-bromoacetophenone (1a) and benzoic acid (2a): screening of ligands.[a]



Ligand	Conversion[b] (%)	**3a**[b] (%)	**4a**[b] (%)	Selectivity[b] **3a/4a**
$^{Me}NN^{H}$	70	41	29	1.41
$^{iPr}NN^{H}$	36	17	18	0.94
$^{Bn}NN^{H}$	42	25	17	1.47
$^{Me}NN^{4Me}$	97	48	50	0.96
$^{Ph}NN^{H}$	99(2)[c]	62(2)[c]	35(1)[c]	1.77(3)[c]
$^{Pyr}NN^{H}$	97(3)[c]	60(1)[c]	37(3)[c]	1.61(4)[c]
$^{Pyr}NN^{4Me}$	99	62	36	1.72
$^{p\text{-}Anis}NN^{H}$	99(3)[c]	66(4)[c]	33(2)[c]	2.00(7)[c]
$^{p\text{-}Anis}NN^{6Me}$	44	15	28	0.54
$^{p\text{-}OHPh}NN^{H}$	60	44	16	2.75
$^{p\text{-}OHPh}NN^{4Me}$	73	47	23	2.04
dtbbpy[d]	50	30	20	1.5
dtbbpy[e]	99	34	65	0.52
None	27	15	12	1.25

[a] Conditions: 4-bromoacetophenone (39.9 mg, 0.20 mmol), benzoic acid (48.9 mg, 0.40 mmol, 2 equiv.), $Ni(OTf)_2$ (3.6 mg, 10.0 µmol, 5 mol %), ligand (20.0 µmol, 10 mol %), DIPEA (142 µL, 0.81 mmol, 4 equiv.), DMF (0.5 mL, ca. 0.4 mM), 18 h, 40 °C, blue LED (7.0 W, TAK photoreactor). [b] Conversion, yield and selectivity determined by GC-FID using 1,3,5-trimethoxybenzene as internal standard (8.4 mg, 0.05 mmol) and appropriate calibration curves. [c] Average of three independent reactions. Shown errors correspond to the last significant figures. [d] dtbbpy = 4,4'-di-*tert*butyl-2,2'-bipyridine. [e] Ligand dtbbpy used in combination with the photocatalyst $Ir(ppy)_3$ (1.3 mg, 2.0 µmol, 1 mol%) (ppy = ortho-metalated 2-phenylpyridine).

Table S4. Coupling reaction between 4'-bromoacetophenone (1a) and benzoic acid (2a): screening of amount and nature of the base.[a]

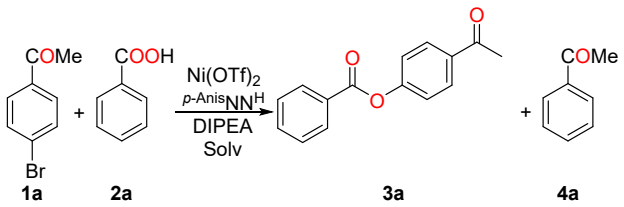


Base, equiv.	Conversion[b] (%)	**3a**[b] (%)	**4a**[b] (%)	Selectivity[b] **3a/4a**
DIPEA, 2	74	42	32	1.31
DIPEA, 3	80	50	30	1.66
DIPEA, 4	99(3)[c]	66(4)[c]	33(2)[c]	2.00(7)[c]
TEA, 4[d]	66	45	17	2.65
DIPA, 4[e]	52	36	16	2.25
TBIPA, 4[f]	43	22	21	1.05
DABCO, 4[g]	10	5	3	1.66
Cs_2CO_3, 2	63	20	43	0.47
$PhCO_2K$, 2 / DIPEA, 2	88	25	55	0.45

[a] Conditions: 4-bromoacetophenone (39.9 mg, 0.20 mmol), benzoic acid (48.9 mg, 0.40 mmol, 2 equiv.), $Ni(OTf)_2$ (3.6 mg, 10.0 µmol, 5 mol %), $^{p\text{-}Anis}NN^{H}$ (7.3 mg, 20.0 µmol, 10 mol %), base (0.40 mmol, 2 equiv.; 0.60 mmol, 3 equiv.; 0.80 mmol, 4 equiv.), DMF (0.5 mL, ca. 0.4 mM), 18 h, 40 °C, blue LED (7.0 W, TAK photoreactor). [b] Conversion, yield and selectivity determined by GC-FID using 1,3,5-trimethoxybenzene as internal standard (8.4 mg, 0.05 mmol) and appropriate calibration curves. [c] Average of three independent reactions. Shown errors correspond to the last

significant figures. [d] TEA = triethylamine, NEt_3. [e] DIPA = diisopropylamine, HN^iPr_2. [f] TBIPA = *N*-tertbutylisopropylamine, HN^tBu^iPr. [g] DABCO = 1,4-diazabicyclo[2.2.2]octane, $N(CH_2CH_2)_3N$.

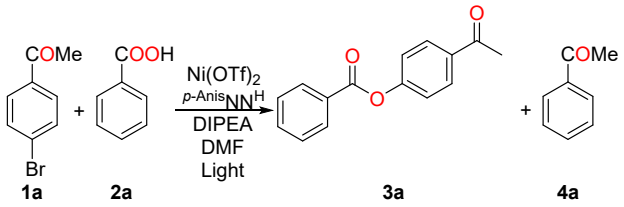
Table S5. Coupling reaction between 4'-bromoacetophenone (1a) and benzoic acid (2a): screening of solvents and concentration.[a]



Solvent, mM	Conversion[b] (%)	**3a**[b] (%)	**4a**[b] (%)	Selectivity[b] **3a**/**4a**
DMSO, 0.2	76	33	43	0.77
MeCN, 0.2	53	26	27	0.96
DMF, 0.2	85(5)[c]	52(6)[c]	33(2)[c]	1.57(5)[c]
DMF, 0.4	99(3)[c]	66(4)[c]	33(2)[c]	2.00(7)[c]
DMF, 0.8	99(3)[c]	62(4)[c]	35(5)[c]	1.9(3)[c]
DMF, 0.1	68	41	27	1.52

[a] Conditions: 4-bromoacetophenone (39.9 mg, 0.20 mmol), benzoic acid (48.9 mg, 0.40 mmol, 2 equiv.), $Ni(OTf)_2$ (3.6 mg, 10.0 µmol, 5 mol %), $^{p\text{-Anis}}NN^H$ (7.3 mg, 20.0 µmol, 10 mol %), DIPEA (142 µL, 0.81 mmol, 4 equiv.), solvent (2.0 mL, ca. 0.1 mM; 1.0 mL, ca. 0.2 mM; 0.5 mL, ca. 0.4 mM, 250 µL, ca. 0.8 mM), 18 h, 40 °C, blue LED (7.0 W, TAK photoreactor). [b] Conversion, yield and selectivity determined by GC-FID using 1,3,5-trimethoxybenzene as internal standard (8.4 mg, 0.05 mmol) and appropriate calibration curves. [c] Average of three independent reactions. Shown errors correspond to the last significant figures.

Table S6. Coupling reaction between 4'-bromoacetophenone (1a) and benzoic acid (2a): screening of light wavelength and photochemical setup (intensity).[a]



Wavelenght (nm), setup	Conversion[b] (%)	**3a**[b] (%)	**4a**[b] (%)	Selectivity[b] **3a**/**4a**
365, LED plate (3.3 W)	97[c]	-	20[c]	-
400, LED plate (3.3 W)	15	8	8	1.00
420, LED plate (3.3 W)	23	9	14	0.64
455, LED plate (3.3 W)	20	16	2	8.00
455, LED plate (2.5 W)	21	20	1	20.00
520, LED plate (3.3 W)	<1	-	-	-
White, LED plate (3.3 W)	4	3	1	3.00
455, TAK device (7.0 W)	99(3)[d]	66(4)[d]	33(2)[d]	2.00(7)[d]
455, TAK device (6.0 W)	69	46	23	2.00

[a] Conditions: 4-bromoacetophenone (39.9 mg, 0.20 mmol), benzoic acid (48.9 mg, 0.40 mmol, 2 equiv.), $Ni(OTf)_2$ (3.6 mg, 10.0 µmol, 5 mol %), $^{p\text{-Anis}}NN^H$ (7.3 mg, 20.0 µmol, 10 mol %), DIPEA (142 µL, 0.81 mmol, 4 equiv.), DMF (0.5 mL, ca. 0.4 mM), 18 h, 40 °C, LED as light source. [b] Conversion, yield and selectivity determined by GC-FID using 1,3,5-trimethoxybenzene as internal standard (8.4 mg, 0.05 mmol) and appropriate calibration curves. [c] Photochemical reduction and homocoupling of acetophenone, from hydrodehalogenation of **1a**, led to the formation of 2,3-diphenylbutane-2,3-diol as the main product [d] Average of three independent reactions. Shown errors correspond to the last significant figures.

Table S7. Coupling reaction between 4'-bromoacetophenone (1a) and benzoic acid (2a): control experiments.[a]

Deviation from optimal conditions	Conversion[b] (%)	**3a**[b] (%)	**4a**[b] (%)	Selectivity[b] **3a**/**4a**
None	99(3)[c]	66(4)[c]	33(2)[c]	2.00(7)[c]
Only $Ni(OTf)_2$, no ligand	27	15	12	1.25
Only ligand, no $Ni(OTf)_2$	41	-	39	-
No base	<1	-	-	-
$PhCO_2K$ as base, no amine	2	-	-	-
Reaction temperature: 18 °C	23	15	8	1.88
Heating 65 °C, no light	6	3	3	1.00
Zn (0.5 equiv.), no light	53	25	27	0.93

[a] Conditions: 4-bromoacetophenone (39.9 mg, 0.20 mmol), benzoic acid (48.9 mg, 0.40 mmol, 2 equiv.), $Ni(OTf)_2$ (3.6 mg, 10.0 µmol, 5 mol %), $^{p\text{-Anis}}NN^{H}$ (7.3 mg, 20.0 µmol, 10 mol %), DIPEA (142 µL, 0.81 mmol, 4 equiv.), DMF (0.5 mL, ca. 0.4 mM), 18 h, 40 °C, blue LED (7.0 W, TAK photoreactor). [b] Conversion, yield and selectivity determined by GC-FID using 1,3,5-trimethoxybenzene as internal standard (8.4 mg, 0.05 mmol) and appropriate calibration curves. [c] Average of three independent reactions. Shown errors correspond to the last significant figures.

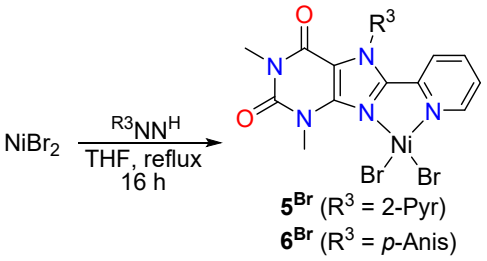
For most of the reactions within the substrate scope, twin experiments were set up to use one of them for GC-FID quantification by adding the internal standard and the other one to isolate the product of reaction. The test intended for product isolation was analyzed by GC-FID without adding internal standard, just to have a rough overlook of how the catalytic transformation proceeded. For substrates returning low product yields, several 0.2 mmol-scale batches were used and combined for the workup, rather than scaling up the reactions.

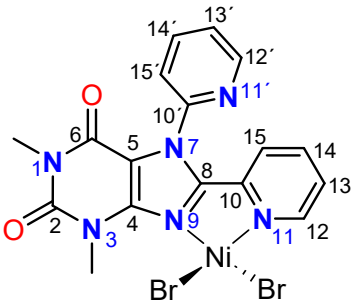
The crude of reaction was diluted with dichloromethane (10 mL) and washed with aqueous sodium bicarbonate (0.2 M, 10 mL), diluted HCl (0.2 M, 10 mL), and water (10 mL). The aqueous workup removes DMF, the nickel source, ammonium salts, unreacted carboxylic acid and unreacted DIPEA. The organic layer was dried over magnesium sulfate and evaporated to dryness under reduced pressure. The obtained residue typically consists of the hydrodehalogenation side product (**4a**-**z**), the starting material (if not fully consumed, **1a**-**z**), the desired product (**3a**-**z**) and the ligand $^{p\text{-Anis}}NN^{H}$. Such a mixture can be separated by column chromatography on silica gel using hexane/ethyl acetate 9:1, and the mixture elutes as listed above, namely **4a**-**z**, **1a**-**z**, **3a**-**z**, and $^{p\text{-Anis}}NN^{H}$.

5. Synthesis of nickel complexes bearing selected $^{R3}NN^{R4}$ ligands

5.1. Synthesis of complexes with the formula [$NiBr_2$($^{R3}NN^{H}$)], 5^{Br} (R^3 = 2-Pyr) and 6^{Br} (R^3 = *p*-Anis). A Schlenk flask equipped with a stirring bar was loaded with $NiBr_2$ (109.0 mg, 0.50 mmol, 1.02 equiv.) and the corresponding ligand (0.49 mmol, 1.00 equiv.). Air was purged by three vacuum/argon cycles. Then, dry THF (5 mL) was added, and the mixture was heated to 65 °C for 16 h (Scheme S5). Upon cooling down to room temperature, the resulting orange suspension was filtered through frit (P4) and the solid was washed with THF (3 x 1 mL), Et_2O (3 x 1 mL) and *n*-hexane (3 x 1 mL). Once dried under vacuum overnight, the products are obtained as orange or reddish solids.

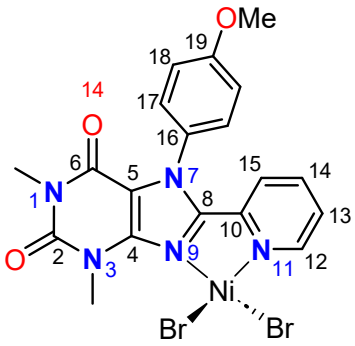
Scheme S5. Synthesis of Ni^{2+}-xanthine complexes [$NiBr_2$($^{R3}NN^{H}$)], 5^{Br} and 6^{Br}.





[$NiBr_2$($^{Pyr}NN^{H}$)], 5^{Br}. Yield: 224.7 mg, 0.41 mmol, 83%, as a pale orange solid. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ [ppm] = 59.3 (br., 1 H, H^{Pyr} = H15, H14, H13 or H12), 40.0 (br., 1 H, H^{Pyr} = H15, H14, H13 or H12), 15.6 (br., 1 H, H^{Pyr} = H15, H14, H13 or H12), 8.5 (br., 1 H, $H^{Pyr'}$ = H15', H14', H13' or H12'), 8.1 (br., 1 H, $H^{Pyr'}$ = H15', H14', H13' or H12'), 7.3 (br., 1 H, $H^{Pyr'}$ = H15', H14', H13' or H12'), 6.7 (br., 1 H, $H^{Pyr'}$ = H15', H14', H13' or H12'), 3.8 (br., 3H, Me = N1CH_3 or N3CH_3), 3.1 (br., 3H, Me = N1CH_3 or N3CH_3). One H^{pyr} resonance (H15, H14, H13 or H12) is not properly resolved. Both the poor solubility of **5** in $CDCl_3$ and its paramagnetic nature hampered the detection of any ^{13}C resonances. ^{1}H NMR (300.1 MHz, CD_3CN): δ [ppm] = 60.2 (br., 1 H, H^{Pyr} = H15, H14, H13 or H12), 39.2 (br., 1 H, H^{Pyr} = H15, H14, H13 or H12), 15.6 (br., 1 H, H^{Pyr} = H15, H14, H13 or H12), 8.7 (br., 1 H, $H^{Pyr'}$ = H15', H14', H13' or H12'), 8.2 (br., 1 H, $H^{Pyr'}$ = H15', H14', H13' or H12'), 7.6 (br., 1 H, $H^{Pyr'}$ = H15', H14', H13' or H12'), 7.1 (br., 1 H, $H^{Pyr'}$ = H15', H14', H13' or H12'), 4.3 (br., 3H, Me = N1CH_3 or N3CH_3), 3.0 (br., 3H, Me = N1CH_3 or N3CH_3). Again, one H^{pyr} resonance (H15, H14, H13 or H12) is not properly resolved. In CD_3CN, the complex slowly changes its initial yellow-orange color to pale green, thus indicating that likely the complex reacts with acetonitrile (see below, for the findings in this regard when using the related

compound **6^{Br}**). In DMSO-d_6 the sample was fully soluble and only the well-defined resonances of the free ligand $^{Pyr}NN^{H}$ were detected, thus suggesting that the complex decomposes in this solvent (ligand exchange/dissociation). Anal. Calcd. for $C_{17}H_{14}Br_2N_6NiO_2 \cdot (C_4H_8O)_{0.20} \cdot (CHCl_3)_{0.15}$: C, 36.64; H, 2.70; N, 14.28; found: C, 36.82; H, 2.69; N, 14.09. The amount of tetrahydrofuran and chloroform was confirmed independently by ^{1}H NMR in DMSO-d_6 using acetonitrile as standard, returning the following molar fractions C_4H_8O/**5^{Br}** = 0.18 and $CHCl_3$/**5^{Br}** = 0.16. HRMS (ESI) for $(C_{17}H_{14}Br_2N_6NiO_2–2Br)^{2+}$ [$(M–2Br)^{2+}$]: calc.: 196.0266; found: 196.0259.



[$NiBr_2$($^{p\text{-Anis}}NN^{H}$)], **6^{Br}**

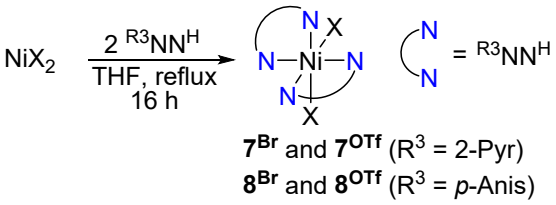
[$NiBr_2$($^{p\text{-Anis}}NN^{H}$)], **6^{Br}**. Yield: 179.6 mg, 0.31 mmol, 63%, as an orange-reddish solid. Crystals suitable for X-ray diffraction analysis were obtained upon slow diffusion of *n*-hexane into a dichloromethane solution of **6^{Br}**. In the solid-state, species **6^{Br}** is a dimer [$NiBr_2$($^{p\text{-Anis}}NN^{H}$)]$_2$. ^{1}H NMR (400.3 MHz, $CDCl_3$): δ [ppm] = 64.0 (br., 1 H, H^{Pyr} = H15, H14, H13 or H12), 52.7 (br., 1 H, H^{Pyr} = H15, H14, H13 or H12), 16.9 (br., 1 H, H^{Pyr} = H15, H14, H13 or H12), 15.4 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3), 8.2 (br., 2H, H^{Anis} = H17 or H18), 7.2 (br., 2H, H^{Anis} = H17 or H18), 4.9 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3), 3.9 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ [ppm] = 120.7, 118.7, 56.4, 31.7. Due to the paramagnetic nature of the sample, one ^{1}H resonance is not observed and not all ^{13}C resonances are properly resolved. The few ^{13}C signals detected could not be reliably assigned by 2D-NMR techniques. Anal. Calcd. for $C_{19}H_{17}Br_2N_5NiO_3 \cdot (C_4H_8O)_{0.60} \cdot (CHCl_3)_{0.35}$: C, 39.17; H, 3.35; N, 10.50; found: C, 39.11; H, 3.42; N, 10.61. The amount of tetrahydrofuran and chloroform was confirmed independently by ^{1}H NMR in DMSO-d_6 using dichloromethane as standard, returning the following molar fractions C_4H_8O/**6^{Br}** = 0.57 and $CHCl_3$/**6^{Br}** = 0.36. UV-vis ($CHCl_3$, 20.10^{-6} mol.L^{-1}): λ_{max} = 320 nm.

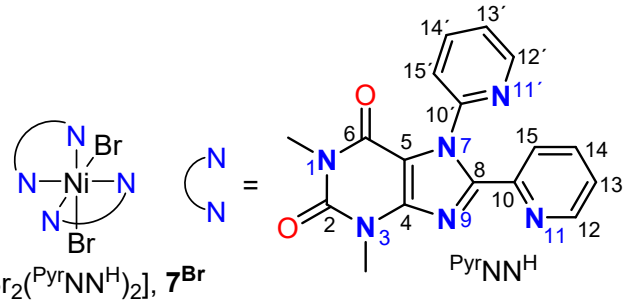
Alternatively, **6^{Br}** can be crystallized by slow diffusion of diethyl ether into an acetonitrile solution, returning a dimer where MeCN is coordinated to the metal center. The resulting pale-green octahedral nickel(II) compound is NMR silent. It is presumed that the related complex **5^{Br}** (vide supra) follows a similar reactivity against acetonitrile. In fact, by means of HRMS (ESI), the species [Ni(MeCN)($^{Pyr}NN^{H}$)]$^{2+}$, [**5^{Br}**+MeCN–2Br]$^{2+}$, was observed (calc.: 216.5398; found: 216.5390).

5.2. Synthesis of complexes with the formula [NiX_2($^{R3}NN^{H}$)$_2$], 7^{X} (R^3 = 2-pyr, X = Br, OTf) and 8^{X} (R^3 = *p*-Anis, X = Br, OTf). A Schlenk flask equipped with a stirring bar was loaded with NiX_2 (X = Br: 52.0 mg;

X = OTf: 85.8 mg, 0.24 mmol, 0.49 equiv.) and the corresponding ligand ($^{Pyr}NN^{H}$ = 164.0 mg; $^{p\text{-}Anis}NN^{H}$ = 178.1 mg, 0.49 mmol, 1.00 equiv.). Air was purged by three vacuum/argon cycles. Then, dry THF (5 mL) was added, and the mixture was heated to 65 °C for 16 h (Scheme S6). Upon cooling down to room temperature, the resulting pale green-yellow suspension was filtered through frit (P4) and the solid was washed with THF (3 x 1 mL), Et_2O (3 x 1 mL) and *n*-hexane (3 x 1 mL). Once dried under vacuum overnight, the products are obtained as light green solids.

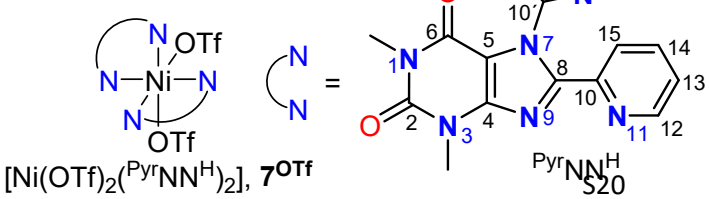
Scheme S6. Synthesis of Ni^{2+}-xanthine complexes $[NiBr_2(^{R3}NN^{H})_2]$, $\mathbf{7^{X}}$ (R^3 = 2-pyr, X = Br, OTf) and $\mathbf{8^{X}}$ (R^3 = *p*-Anis, X = Br, OTf).





$[NiBr_2(^{Pyr}NN^{H})_2]$, $\mathbf{7^{Br}}$

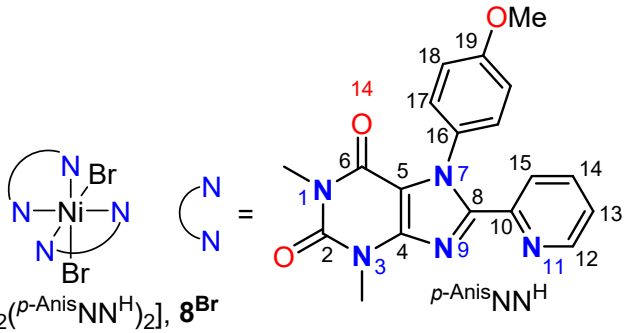
$[NiBr_2(^{Pyr}NN^{H})_2]$, $\mathbf{7^{Br}}$. Yield: 151.0 mg, 0.17 mmol, 71%. Slow diffusion of diethyl ether into an acetonitrile solution of $\mathbf{7^{Br}}$ returned yellow-greenish crystalline plates suitable for X-ray diffraction analysis. ^{1}H NMR (300.1 MHz, $CDCl_3$ or CD_3CN): δ [ppm] = silent. In DMSO-d_6 only the well-defined resonances of the free ligand $^{Pyr}NN^{H}$ were detected, thus suggesting that the complex decomposes in this solvent (ligand exchange/dissociation). Anal. Calcd. for $C_{34}H_{28}Br_2N_{12}NiO_4 \cdot (C_4H_8O)_{0.70} \cdot (CHCl_3)_{0.92}$: C, 43.25; H, 3.32; N, 16.05; found: C, 43.54; H, 3.25; N, 16.05. The amount of tetrahydrofuran and chloroform was confirmed independently by ^{1}H NMR in DMSO-d_6 using dichloromethane as standard, returning the following molar fractions $C_4H_8O/\mathbf{7^{Br}}$ = 0.67 and $CHCl_3/\mathbf{7^{Br}}$ = 0.91. HRMS (ESI) for $(C_{34}H_{28}Br_2N_{12}NiO_4–2Br)^{2+}$ $[(M–2Br)^{2+}]$: calc.: 363.0855; found: 363.0851.



$[Ni(OTf)_2(^{Pyr}NN^{H})_2]$, $\mathbf{7^{OTf}}$

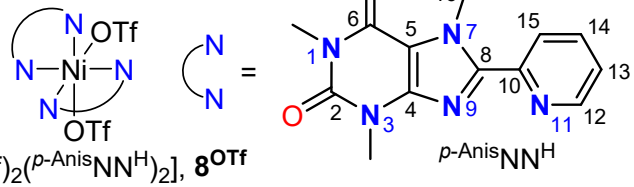
$[Ni(OTf)_2(^{Pyr}NN^{H})_2]$, $\mathbf{7^{OTf}}$. Yield: 184.6 mg, 0.18 mmol, 75%. Slow diffusion of diethyl ether into an acetonitrile solution of $\mathbf{7^{OTf}}$ returned yellow-greenish crystalline plates. The quality

of the crystallographic data is not sufficient to be publishable but confirms the proposed connectivity for this complex. ^{1}H NMR (300.1 MHz, $CDCl_3$ or CD_3CN): δ [ppm] = silent. In DMSO-d_6 only the well-defined resonances of the free ligand $^{Pyr}NN^{H}$ were detected, thus suggesting that the complex decomposes in this solvent (ligand exchange/dissociation). ^{19}F{^{1}H} NMR (282.4 MHz, $CDCl_3$): δ [ppm] = –41.0 (br., OTf). Anal. Calcd. for $C_{36}H_{28}F_6N_{12}NiO_{10}S_2\cdot(CH_3CN)_{0.15}$: C, 42.26; H, 2.78; N, 16.50; found: C, 41.94; H, 2.85; N, 16.51. The amount of acetonitrile was confirmed independently by ^{1}H NMR in DMSO-d_6 using dichloromethane as standard, returning the molar fraction $CH_3CN/\mathbf{7}^{\mathbf{OTf}}$ = 0.16. HRMS (ESI) for $(C_{36}H_{28}F_6N_{12}NiO_{10}S_2–OTf)^{+}$ [(M–OTf)$^{+}$]: calc.: 875.1231; found: 875.1211. UV-vis (CH_3CN, 20.10^{-6} mol.L^{-1}): λ_{max} = 355 nm.



$[NiBr_2(^{p\text{-Anis}}NN^{H})_2]$, $\mathbf{8}^{\mathbf{Br}}$

$[NiBr_2(^{p\text{-Anis}}NN^{H})_2]$, $\mathbf{8}^{\mathbf{Br}}$. Yield: 185.9 mg, 0.20 mmol, 83%, as a yellow-greenish solid. ^{1}H NMR (300.1 MHz, $CDCl_3$ or CD_3CN): δ [ppm] = silent. In DMSO-d_6 only the well-defined resonances of the free ligand $^{p\text{-Anis}}NN^{H}$ were detected, thus suggesting that the complex decomposes in this solvent (ligand exchange/dissociation). Anal. Calcd. for $C_{38}H_{34}Br_2N_{10}NiO_6\cdot(C_6H_{14})_{0.55}\cdot(H_2O)_{1.95}$: C, 48.26; H, 4.47; N, 13.63; found: C, 48.07; H, 4.56; N, 13.20. The amount of *n*-hexane and water was confirmed independently by ^{1}H NMR in dry DMSO-d_6 using dichloromethane as standard, returning the following molar fractions $C_6H_{14}/\mathbf{8}^{\mathbf{Br}}$ = 0.52 and $H_2O/\mathbf{8}^{\mathbf{Br}}$ = 2.01. HRMS (ESI) for $(C_{38}H_{34}Br_2N_{10}NiO_6–2Br)^{2+}$ [(M–2Br)$^{2+}$]: calc.: 392.1014; found: 392.1008.



$[Ni(OTf)_2(^{p\text{-Anis}}NN^{H})_2]$, $\mathbf{8}^{\mathbf{OTf}}$

$[Ni(OTf)_2(^{p\text{-Anis}}NN^{H})_2]$, $\mathbf{8}^{\mathbf{OTf}}$. Yield: 104.0 mg, 0.10 mmol, 40%, as a yellow-greenish solid. ^{1}H NMR (300.1 MHz, $CDCl_3$ or CD_3CN): δ [ppm] = silent. In DMSO-d_6 only the well-defined resonances of the free ligand $^{p\text{-Anis}}NN^{H}$ were detected, thus suggesting that the complex decomposes in this solvent (ligand exchange/dissociation). Anal. Calcd. for $C_{40}H_{34}F_6N_{10}NiO_{12}S_2\cdot(CHCl_3)_{0.35}\cdot(H_2O)_{4.05}$: C, 40.44; H, 3.57; N, 11.69; found: C, 40.39; H, 3.78; N, 11.62.

The amount of chloroform and water was confirmed independently by ^{1}H NMR in dry DMSO-d_6 using dichloromethane as standard, returning the following molar fractions $CHCl_3$/**8**^{OTf} = 0.30 and H_2O/**8**^{OTf} = 4.00. HRMS (ESI) for $(C_{40}H_{34}F_6N_{10}NiO_{12}S_2–OTf)^+$ [(M–OTf)$^+$]: calc.: 933.1534; found: 933.1537.

5.3. Synthesis of the formally Ni(I) complexes [NiX(*p*-^{Anis}NN^H)], **11**^{Br} (X = Br) or **11**^{OAr*} (X = 2,4,6-(^{t}Bu)$_3$-C$_6$H$_2$O, OAr*), and [NiBr(*p*-^{Anis}NN^H)(PPh$_3$)], **11**^{Br}·PPh$_3$

Complexes **11**^{Br}, **11**^{Br}·PPh$_3$ and **11**^{OAr*} were prepared *via* two alternative strategies involving an *in situ* generated Ni(0)-*p*-^{Anis}NN^H species (oxidative route, Figure S1) or Ni(II)–Ar bond homolysis (reductive route, Figure S2).

Synthesis of **11**^{Br} and **11**^{OAr*} *via* the oxidative route

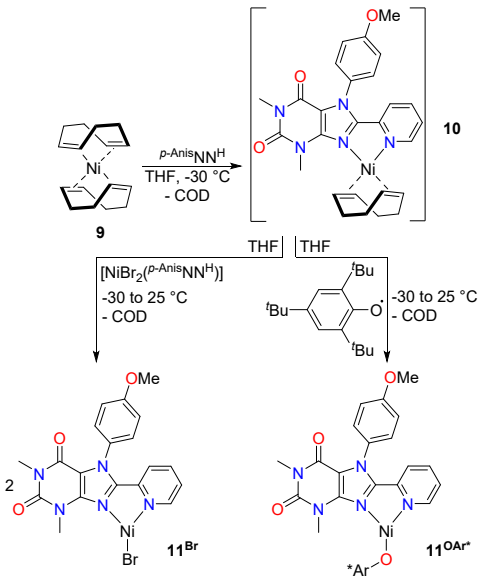
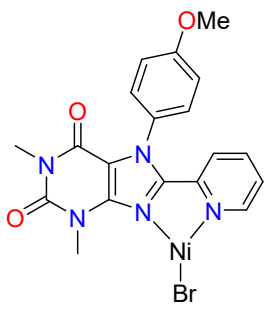
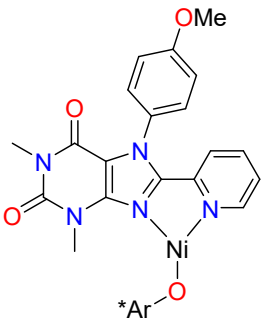


Figure S1. Synthesis of **11**^{Br} **and 11**^{OAr*} from an *in situ* generated Ni(0)-*p*-^{Anis}NN^H species (oxidative route).



Synthesis of 11^{Br}**:** In the glovebox and in darkness, a cold solution of *p*-^{Anis}NN^H (37.5 mg, 0.10 mmol, 1.03 equiv.) in THF (3 mL) was slowly added to a cold solution of [Ni(cod)$_2$] (**9**; 27.5 mg, 0.10 mmol, 1.00 equiv) in the same solvent (1 mL) while stirring. The mixture was left at –30 °C for 2 h, yielding a dark green solution, presumed to be [Ni(cod)(*p*-^{Anis}NN^H)], **10**. Further characterization of **10** was hampered by its low thermal stability and light-sensitivity. Above –30 °C or unprotected from light, metallic mirrors are typically obtained along with the corresponding free ligands *p*-^{Anis}NN^H and 1,5-COD. This freshly prepared intermediate was then

treated with [$NiBr_2$($^{p\text{-Anis}}NN^H$)] (58.2 mg, 0.10 mmol, 1.00 equiv.) in THF (3 mL). The mixture was left at –30 °C for 2 h and then slowly warmed up to room temperature overnight. The product precipitated as a dark grey solid. The material obtained by this route is typically contaminated with metallic nickel (likely due to decomposition of **10**), from which it could not be separated given the poor solubility of **11^{Br}** in common organic solvents. The poor solubility is likely a consequence of the formation of a halide-bridged dimer (**11^{Br}**)$_2$. Yield: 43.7 mg. Anal. Calcd. for $C_{19}H_{17}BrN_5NiO_3{\cdot}(C_4H_{10}O)_{0.12}(Ni)_{0.62}$: C, 42.75; H, 3.35; N, 12.80; found: C, 42.67; H, 3.38; N, 12.91.



Synthesis of 11^{OAr*}, [Ni(OAr*)($^{p\text{-Anis}}NN^H$)] (Ar* = 2, 4, 6-(^{t}Bu)$_3$-C_6H_2): In the glovebox and in darkness, a cold solution of $^{p\text{-Anis}}NN^H$ (37.5 mg, 0.10 mmol, 1.03 equiv.) in THF (3 mL) was slowly added to a cold solution of [Ni(cod)$_2$] (27.5 mg, 0.10 mmol, 1.00 equiv) in the same solvent (1 mL) while stirring. The mixture was left at –30 °C for 2 h, yielding a dark green solution, presumed to be [Ni(cod)($^{p\text{-Anis}}NN^H$)], **10**. This freshly prepared intermediate was then treated with $^{\cdot}$OAr* (28.0 mg, 0.11 mmol, 1.07 equiv.) in THF (3 mL). The mixture was left at –30 °C for 2 h and then slowly warmed up to room temperature overnight, affording a deep red-brown solution. The solution was filtered through Whatman paper and Celite to remove any possible traces of metallic nickel. The solvent was evaporated under reduced pressure to afford **11^{OAr*}** as a red brown solid. Recrystallization from Et_2O/hexane (2:3, 2.5 mL) at –30 °C furnished crystals suitable for X-ray diffraction analysis. Yield: 41.5 mg, 0.06 mmol, 61%. ^{1}H NMR (400.3 MHz, THF-d_8): δ [ppm] = 64.0 (br., 1H, H^{Pyr} = H15, H14, H13 or H12), 40.5 (br., 1H, H^{Pyr} = H15, H14, H13 or H12), 34.3 (br., 2H, 2 x H^{Ar*}), 29.4 (br., 1H, H^{Pyr} = H15, H14, H13 or H12), 20.8 (br., 1H, H^{Pyr} = H15, H14, H13 or H12), 7.7 (br., 2H, H^{Anis} = H17 or H18), 6.9 (br., 2H, H^{Anis} = H17 or H18), 4.7 (br., 27H, 3 x ^{t}Bu), 4.2 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3), 3.6 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3), 3.1 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3). Due to the paramagnetic nature of the sample, the ^{13}C{^{1}H} NMR spectrum is silent. Magnetic susceptibility (Evans method, 298 K, THF-d_8): μ_{eff} = 2.0(3) μ_B. Anal. Calcd. for $C_{37}H_{46}N_5NiO_4{\cdot}(C_8H_{16})_{0.10}$: C, 65.46; H, 6.77; N, 10.10; found: C, 65.77; H, 6.62; N, 10.31. UV-vis (THF, 20.10^{-6} mol.L^{-1}): λ_{max} = 520, 690 nm.

Preparation of 11^{Br} and 11^{Br}·PPh_3 *via* Ni(II)–Ar bond homolysis (reductive route)

According to our experimental observations, the following procedures lead to complexes **11^{Br}** and **11^{Br}**·PPh_3 *via* a (bromo)(aryl)Ni(II) intermediate (**13^{Ar,Br}**), that could not be isolated. This proposed intermediate **13^{Ar,Br}**, shown in Figure S2, is accessible either from a suitable Ni(0) precursor upon treatment with an aryl bromide (4'-bromoacetophenone) or from phosphine-stabilized (bromo)(aryl)Ni(II) complexes (aryl = C_6H_5, 3,5-$(CF_3)_2$-C_6H_3). In any of the cases, the proposed

intermediate undergoes bond homolysis to afford the corresponding Ni(I) complexes **11^{Br}** and **11^{Br}**·PPh_3 (see also Scheme S8 below).

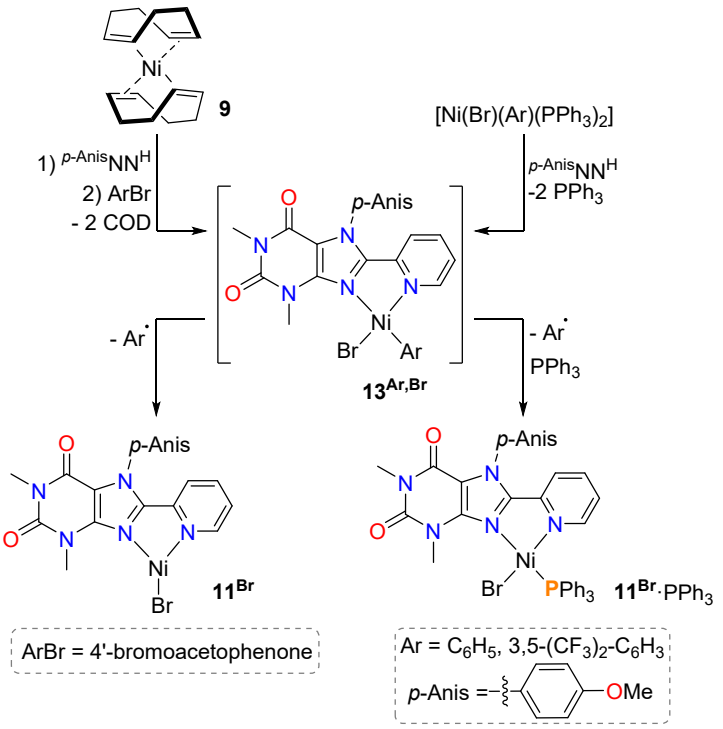
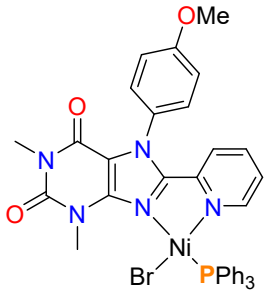


Figure S2. Preparation of **11^{Br} and 11^{Br}**·PPh_3 *via* Ni(II)−Ar bond homolysis (reductive route).

Synthesis of 11^{Br}: In the glovebox and in darkness, a cold solution of $^{p\text{-Anis}}NN^{H}$ (37.5 mg, 0.10 mmol, 1.03 equiv.) in THF (3 mL) was slowly added to a cold solution of [Ni(cod)$_2$] (**9**; 27.5 mg, 0.10 mmol, 1.00 equiv.) in the same solvent (1 mL) while stirring. The mixture was left at –30 °C for 2 h, yielding a dark green solution, presumed to be [Ni(cod)($^{p\text{-Anis}}NN^{H}$)], **10**. The freshly prepared intermediate **10** was then treated with 4'-bromoacetophenone (20.9 mg, 0.105 mmol, 1.05 equiv.) in THF (3 mL), which oxidatively added to **10** yielding the proposed Ni(II) species (Figure S2). The mixture was left at –30 °C for 2 h and then slowly warmed up to room temperature overnight. Once the reaction mixture was left to react overnight, the product precipitated. It was isolated by filtration and washing (THF: 2 x 1 mL; Et_2O: 2 x 1 mL; *n*-hexane 1 x2 mL). Complex **11^{Br}** is a very insoluble grey material that can be cleanly obtained *via* the reductive route. The poor solubility is likely a consequence of the formation of a halide-bridged dimer (**11^{Br}**)$_2$. Yield: 46.0 mg, 0.09 mmol, 92%. Anal. Calcd. for $C_{19}H_{17}BrN_5NiO_3\cdot(C_6H_{14})_{0.09}$: C, 46.04; H, 3.61; N, 13.74; found: C, 46.27; H, 3.60; N, 13.81.

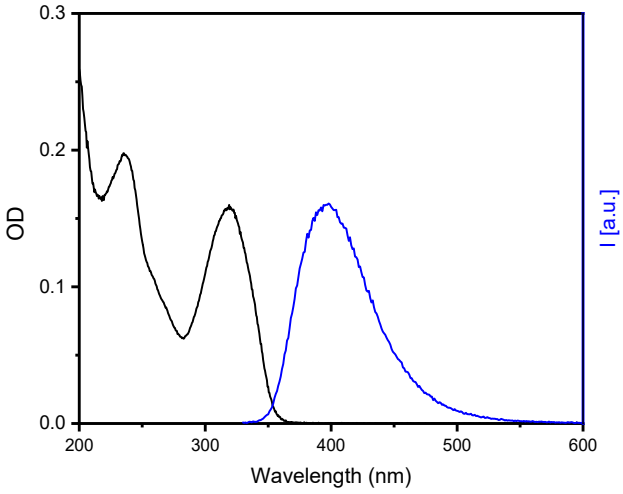


Synthesis of $\mathbf{11^{Br}}$·$\mathbf{PPh_3}$: A cold solution of $^{p\text{-Anis}}NN^{H}$ (75.0 mg, 0.21 mmol, 1.02 equiv.) in THF (6 mL) was slowly added to a cold solution of [Ni(Ar)Br(PPh_3)$_2$] (**14**, Ar = C_6H_5: 150.0 mg, 0.20 mmol, 1.00 equiv.; 3,5-$(CF_3)_2$-C_6H_3: 175.3 mg, 0.20 mmol, 1.00 equiv.) in the same solvent (2 mL) while stirring. The mixture was left at –30 °C for 2 h and then slowly warmed up to room temperature overnight, affording a precipitate. The solid was isolated by filtration and washed with THF, Et_2O and *n*-hexane (THF: 3 x 0.5 mL; Et_2O: 3 x 0.5 mL; *n*-hexane 3 x 0.5 mL). Recrystallization from acetonitrile and drying under vacuum, furnished a deep dark microcrystalline solid. Yield: 60.0 mg, 0.08 mmol, 39%. ^{1}H NMR (300.1 MHz, C_6D_6): δ [ppm] = 8.5 (br., 15H, PPh_3), 5.9 (br., 2H, H^{Anis} = H17 or H18), 4.9 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3), 3.3 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3), 2.9 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3). Due to overlapping with the solvent residual signal, not all expected ^{1}H resonances are observed. ^{13}C{^{1}H} NMR and ^{31}P{^{1}H} NMR spectra: silent. Magnetic susceptibility (Evans method, 298 K, THF-d_8): μ_{eff} = 1.7(2) μ_B. Anal. Calcd. for $C_{37}H_{32}BrN_5NiO_3P\cdot(CH_3CN)_{0.20}$: C, 58.15; H, 4.25; N, 9.43; found: C, 58.12; H, 4.17; N, 9.46. The insoluble material recovered from the acetonitrile recrystallization was found to be a mixture of $\mathbf{11^{Br}}$·PPh_3 contaminated with metallic nickel: Anal. Calcd. for $C_{37}H_{32}BrN_5NiO_3P\cdot(CH_3CN)_{0.55}(Ni)_{0.18}$: C, 57.39; H, 4.25; N, 9.75; found: C, 57.41; H, 4.22; N, 9.75. UV-vis (THF, 20.10^{-6} mol.L^{-1}): λ_{max} = 505, 720 nm.

6. Photophysical studies

Absorption spectra of selected ligands $^{R3}NN^{R4}$ and nickel complexes. UV-vis spectra were recorded using either a Cary 60 or a Cary 300 (Agilent) spectrophotometer. The xanthine-based ligands $^{Pyr}NN^{H}$ and $^{p\text{-Anis}}NN^{H}$ were dissolved in MeCN and diluted such that the optical density of the first absorption maximum over a path length of 2 mm was less than 0.2 and greater than 0.1. Emission spectra were recorded using a Fluorolog 3 (Horiba) spectrofluorometer. The excitation wavelength was chosen to be the first absorption maximum. A 2x10 mm quartz cuvette (Starna Scientific GmbH) was used, with the excitation light traversing the 2 mm direction. Both $^{Pyr}NN^{H}$ and $^{p\text{-Anis}}NN^{H}$ show similar spectra (Figure S3). The first absorption maximum is at around 320 nm and the second maximum in the spectral region close to 230 nm. The maximum emission is around 400 nm.

a



b

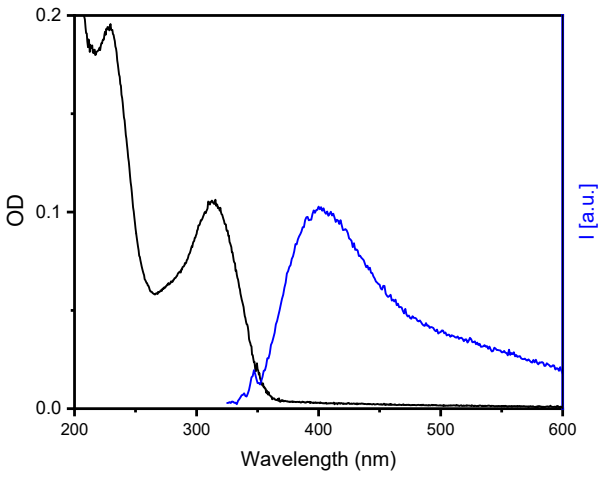


Figure S3. UV-vis absorption (black) and emission (blue, λ_{ex}= 320 nm) spectrum of **a** $^{Pyr}NN^{H}$ and **b** $^{p\text{-Anis}}NN^{H}$ in MeCN.

Absorption spectra of [$NiBr_2$($^{p\text{-Anis}}NN^H$)], **6^{Br}**, in DMF were recorded in a 0.05 mm demountable short path cuvette (20/C Q Starna) as shown in Figure S4. The spectrum of **6^{Br}** is very similar to the one of free $^{p\text{-Anis}}NN^H$ (Figure S3b).

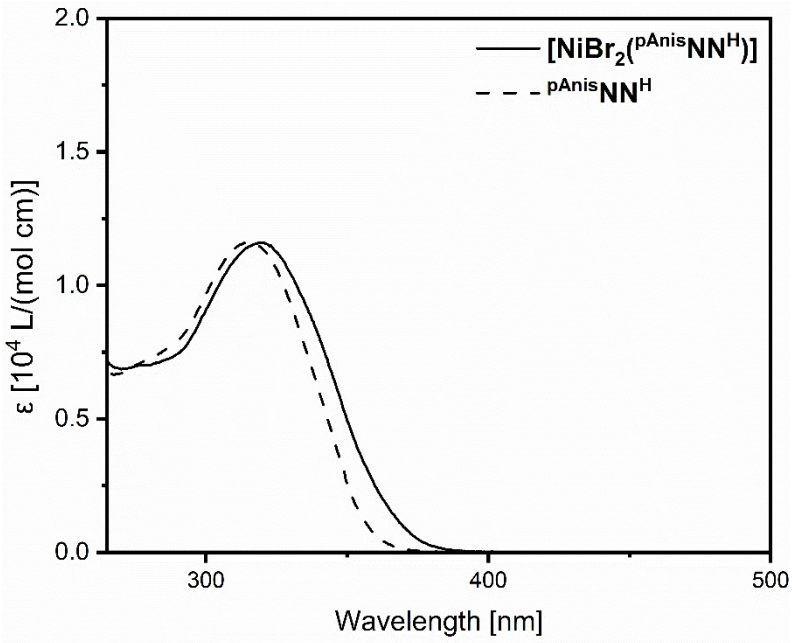


Figure S4. UV-vis absorption of [$NiBr_2$($^{p\text{-Anis}}NN^H$)], **6^{Br}**, in DMF and the scaled spectrum of $^{p\text{-Anis}}NN^H$ (black dashed) for comparison.

5.1 mg of [$Ni(OTf)_2$($^{Pyr}NN^H$)$_2$], **7^{OTf}**, were dissolved in 1 mL of MeCN yielding a 4.6 mM stock solution. The solution was diluted to 3.7 mM, 2.8 mM, 1.8 mM, 0.9 mM and 0.4 mM. Absorption spectra were recorded in a 0.05 mm demountable short path cuvette (20/C Q Starna). The spectrum of **7^{OTf}** is almost identical to that of $^{Pyr}NN^H$, except for a slight bathochromic shift (Figure S5). Upon dilution, the maximum extinction coefficient ε_{max} of the first absorption peak stays constant but a hypsochromic shift occurs. This is attributed to dissociation of the ligand $^{Pyr}NN^H$ from the complex **7^{OTf}** in acetonitrile (solution equilibrium).

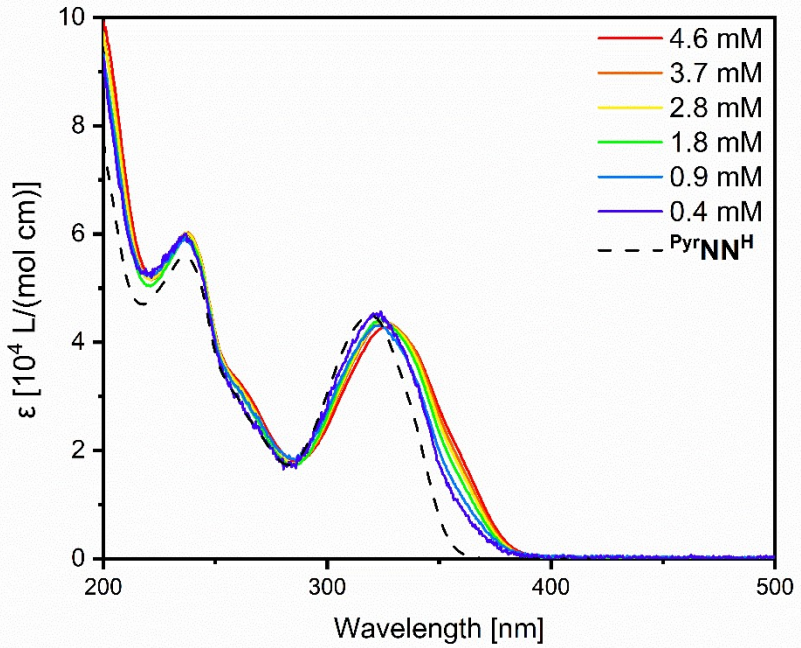


Figure S5. Molar extinction coefficient ε [L/(mol cm)] of $[Ni(OTf)_2(^{Pyr}NN^H)_2]$, $\mathbf{7^{OTf}}$, in MeCN at different concentrations (4.6 mM,3.7 mM, 2.8 mM, 1.8 mM, 0.9 mM, 0.4 mM) and the scaled spectrum of $^{Pyr}NN^H$ (black dashed) for comparison.

The UV-vis spectrum of $NiBr_2$ in DMF (20 mM) was recorded (Figure S6). The peaks are attributed to a ligand-field transition of Ni(II) in an octahedral coordination environment.[7] The broad peak from 600-800 nm corresponds to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^1E_g$ transition. The peak at 410 nm corresponds to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition.

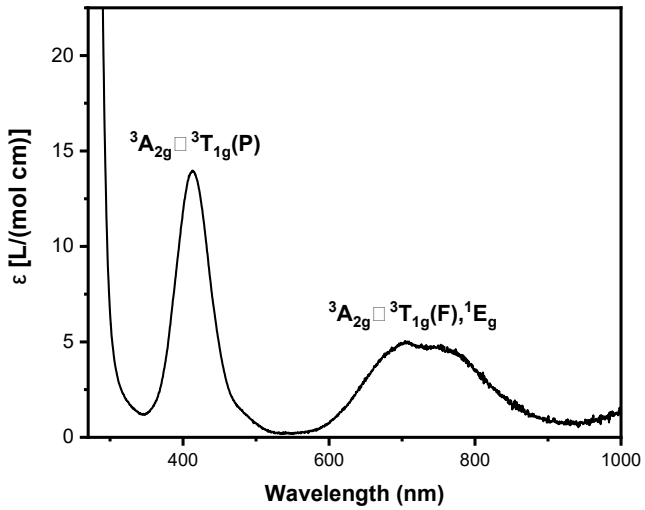


Figure S6. UV-vis spectrum of $NiBr_2$ in DMF (ca. 20 mM).

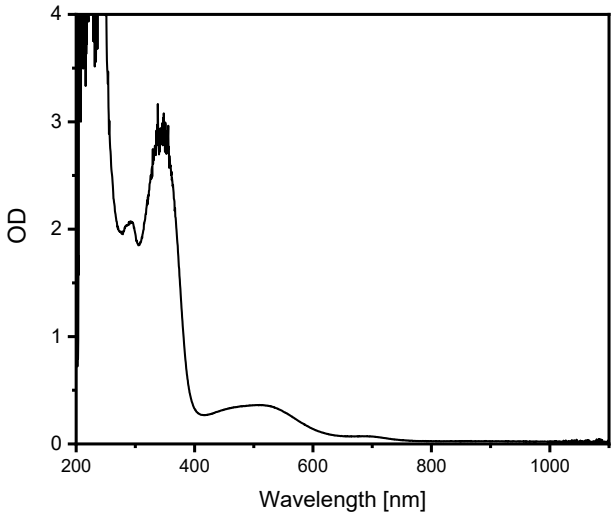


Figure S7. UV-vis absorption of [Ni(OAr*)($^{p\text{-Anis}}$NN^{H})], **11^{OAr*}**, in THF (ca. 5 mM).

Photoreduction of nickel(II) by DIPEA. Two identical solutions of $NiBr_2$ (2.2 mg, 0.01 mmol, ca. 20 mM) or [$NiBr_2$($^{p\text{-Anis}}$NN^{H})] (**6^{Br}**, 5.9 mg, 0.01 mmol, ca. 20 mM) and DIPEA (142 µL, 0.81 mmol, 80 equiv., ca. 1.6 M,) in DMF (0.5 mL) were prepared. One sample was stirred in the dark at 65 °C for 18 h, while the second sample was irradiated in the photoreactor at 455 nm (7 W) for 18 h under exclusion of oxygen and moisture. The samples were transferred from the sealed vials to a 1 mm cuvette inside a glovebox, the cuvette was closed with a stopper and tightly sealed with parafilm.

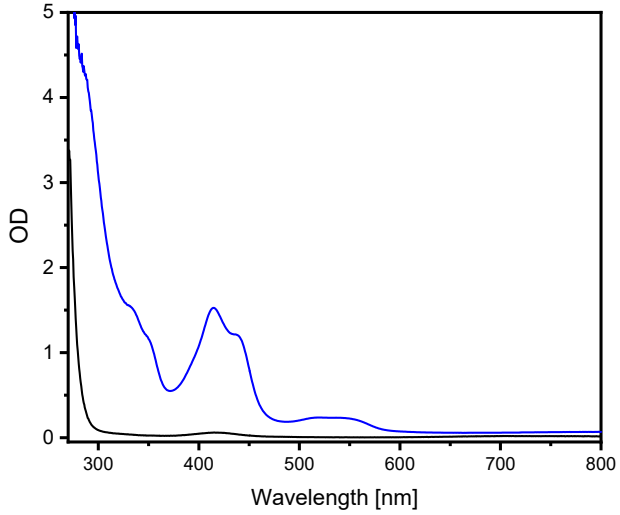


Figure S8. UV-vis spectra of $NiBr_2$ (20 mM) and DIPEA (1.60 M, 80 equiv.) in DMF in the dark (black) and after 18 h of illumination in the photoreactor at 455 nm (blue).

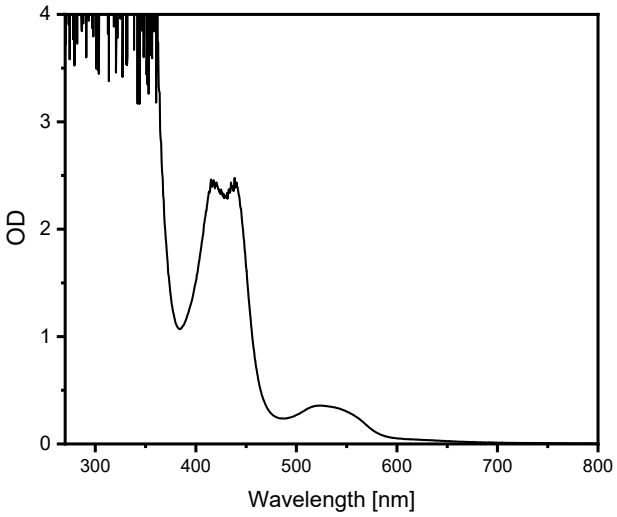


Figure S9. UV-vis spectrum of a mixture of [$NiBr_2$($^{p\text{-Anis}}NN^H$)] (**6^{Br}**, 20 mM) and DIPEA (1.6 mM, 80 equiv.) in DMF after 18 h of illumination in the photoreactor at 455 nm (blue).

The resulting spectrum of [$NiBr_2$($^{p\text{-Anis}}NN^H$)] (**6^{Br}**) and DIPEA in DMF after the illumination in the photoreactor at 455 nm (Figure S9) is remarkably similar to that of the illuminated $NiBr_2$/DIPEA mixture (Figure S8) and clearly different from the spectrum of the initial Ni-species [$NiBr_2$($^{p\text{-Anis}}NN^H$)] (**6^{Br}**) (Figure S4). The peak centered at around 530 nm (see Figure S8 and S9) is indicative of a Ni(I)-species based on the agreement with the absorption spectrum of the Ni(I)-complex [Ni(OAr*****)($^{p\text{-Anis}}NN^H$)], **11^{OAr*}** (see Figure S7) and the UV-vis spectrum recorded for the *in situ* generation of [NiBr($^{p\text{-Anis}}NN^H$)], **11^{Br}** (Figure S10). In the ^{1}H NMR of such reaction mixture, as expected, the formation of nickel-based species cannot be clearly observed due to the low concentration of nickel with respect to the other reaction components: DMF as solvent and DIPEA as reductant (80 equiv.). Regarding the formation of DIPEA-based species, for instance cyanine-type dyes or stable iminium cations, it could not be unambiguously confirmed due to the big excess of starting amine present in the reaction solution.

***In situ* formation of the nickel(I) species 11^{Br} for UV-vis measurement**. The *in-situ* generation of **11^{Br}** was performed as described in Section 5.3 (Figure S2). A cold solution of $^{p\text{-Anis}}NN^H$ (7.3 mg, 20.1 µmol, 1.02 equiv.) in THF (200 µL) was slowly added to a cold solution of [$Ni(cod)_2$] (**9**; 5.4 mg, 19.6 µmol, 1.00 equiv.) in the same solvent (200 µL) while stirring and the mixture was left at –30 °C for 2 h. The intermediate [Ni(cod)($^{p\text{-Anis}}NN^H$)] (**10**) was then treated with 4'-bromoacetophenone (4.0 mg, 20.1 µmol, 1.02 equiv.) in THF (200 µL). Upon filtration and dilution with THF (final volume ca. 1 mL), the UV-vis spectrum of the mixture was recorded (Figure S10).

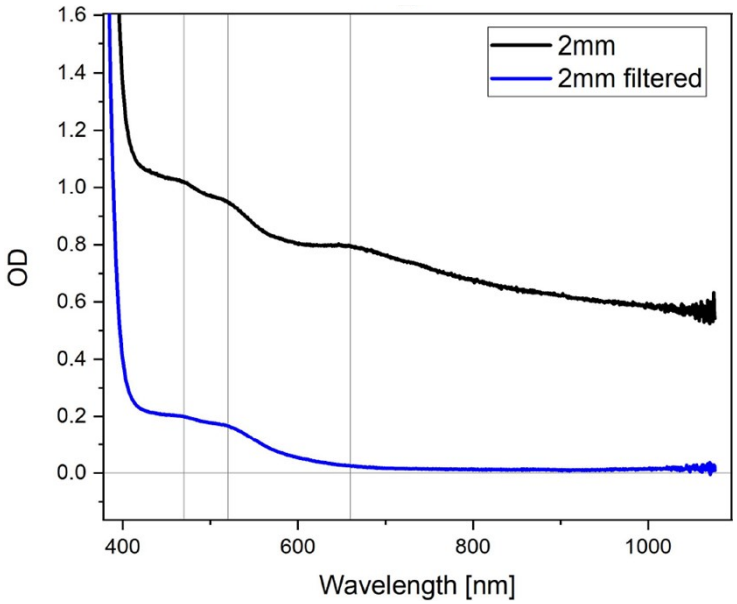


Figure S10. UV-vis spectrum of the species **11^{Br}** prepared *in situ* from $Ni(cod)_2$ + $^{p\text{-Anis}}NN^{H}$ + 4- Br- C_6H_4- COMe in THF. Black curve: unfiltered sample. Blue curve: filtered sample.

Absorption spectra of the reaction mixture for the arylation of carboxylates. Two identical reaction mixtures were prepared according to the typical procedure for catalysis (see section 4) using $^{p\text{-Anis}}NN^{H}$ as ligand. One sample was stirred in the dark at 65 °C for 18 h, while the second sample was irradiated in the photoreactor at 455 nm. The samples were transferred from the vials to a 1 mm cuvette inside a glovebox, the cuvette was closed with a stopper and tightly sealed with parafilm. Since the neat reaction mixture was used, concentrations were such that the UV regime was saturated in both cases (Figure S11).

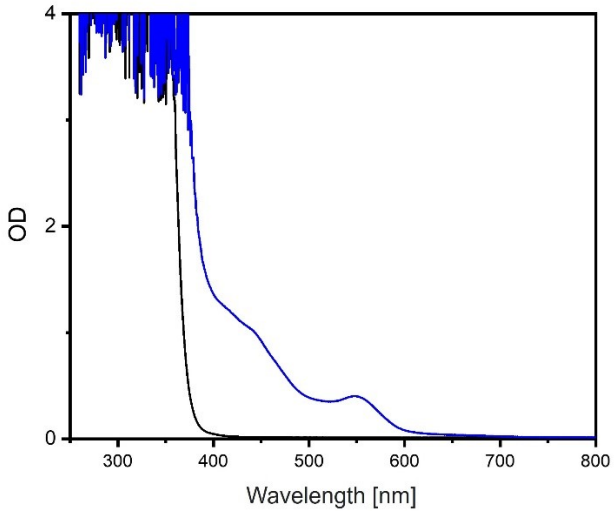


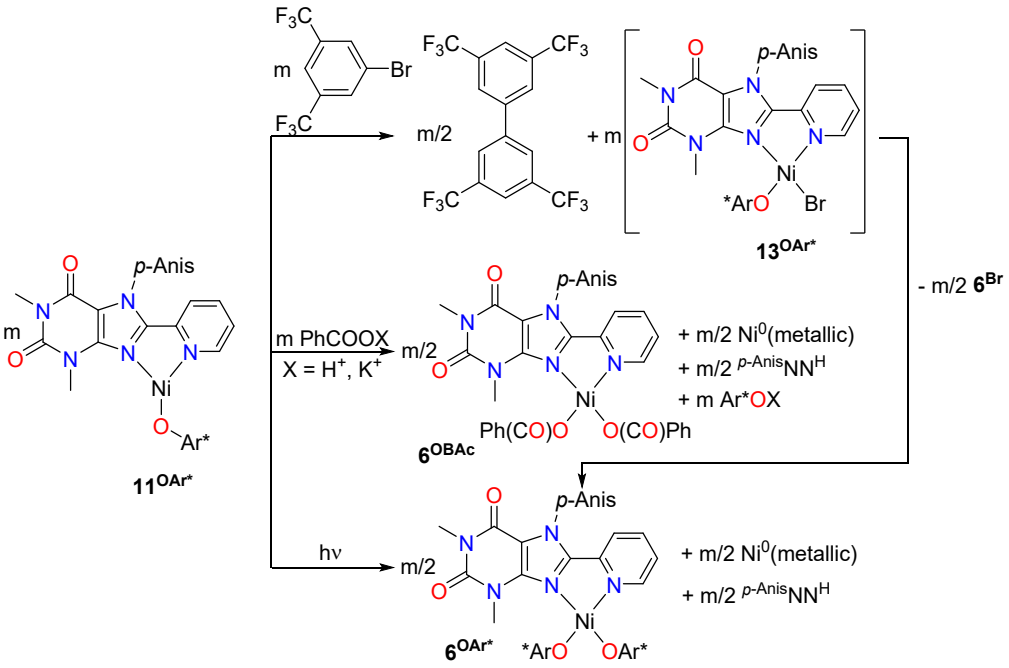
Figure S11. UV-vis absorption spectrum of the reaction mixture for the arylation of carboxylates after 18 h in the dark (black) and upon illumination in the photoreactor at 455 nm (blue).

7. Synthetic model reactions

Reaction between complex 11^{OAr*} and selected individual reaction components. In the glovebox and in darkness, a J-Young NMR tube with a C_6D_6 capillary was loaded with complex **11^{OAr*}** (13.8 mg, 0.02 mmol) and dissolved in THF (200 μL). An excess of the aryl halide or carboxylic acid source (0.08 mmol, 4.0 equiv.) in THF (400 μL) was added (Scheme S7) and the mixture was analyzed by ^{1}H and ^{19}F NMR spectroscopy (if corresponds) as shown in Figures S12-S14. The organic phase of these reactions, upon removal of Ni over silica plug or metal scavenger, were also analyzed by GC-MS.

Irradiation of complex 11^{OAr*} with blue light. In the glovebox, a WICOM septum capped vial was loaded with complex **11^{OAr*}** (13.8 mg, 0.02 mmol) and dissolved in THF (500 μL). The vial was sealed and the photoreactor was set up for irradiation with blue LED (7 W), for 18 h (Scheme S7). Once the reaction time was completed, a metallic mirror and a deep green solution were obtained. Upon filtration, the clear green solution was left in the fridge at –30 °C, returning crystals suitable for partial X-ray diffraction analysis.

Scheme S7. Summary of the reactivity tests on complex **11^{OAr*}**.



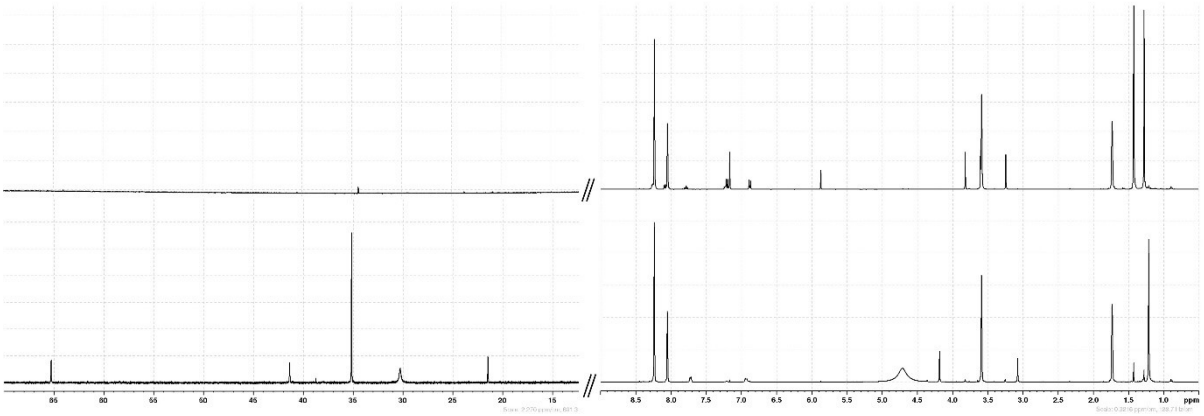


Figure S12. ^{1}H NMR spectra (400.3 MHz, THF-d_8) of the reaction mixture [Ni(OAr*)($^{p\text{-Anis}}$NN^{H})], **11^{OAr*}**, and 3,5-bis(trifluoromethyl)bromobenzene (14 μL, 0.08 mmol, 4.0 equiv.) in THF before heating (bottom) and upon heating to 65 °C for 18 h (top).

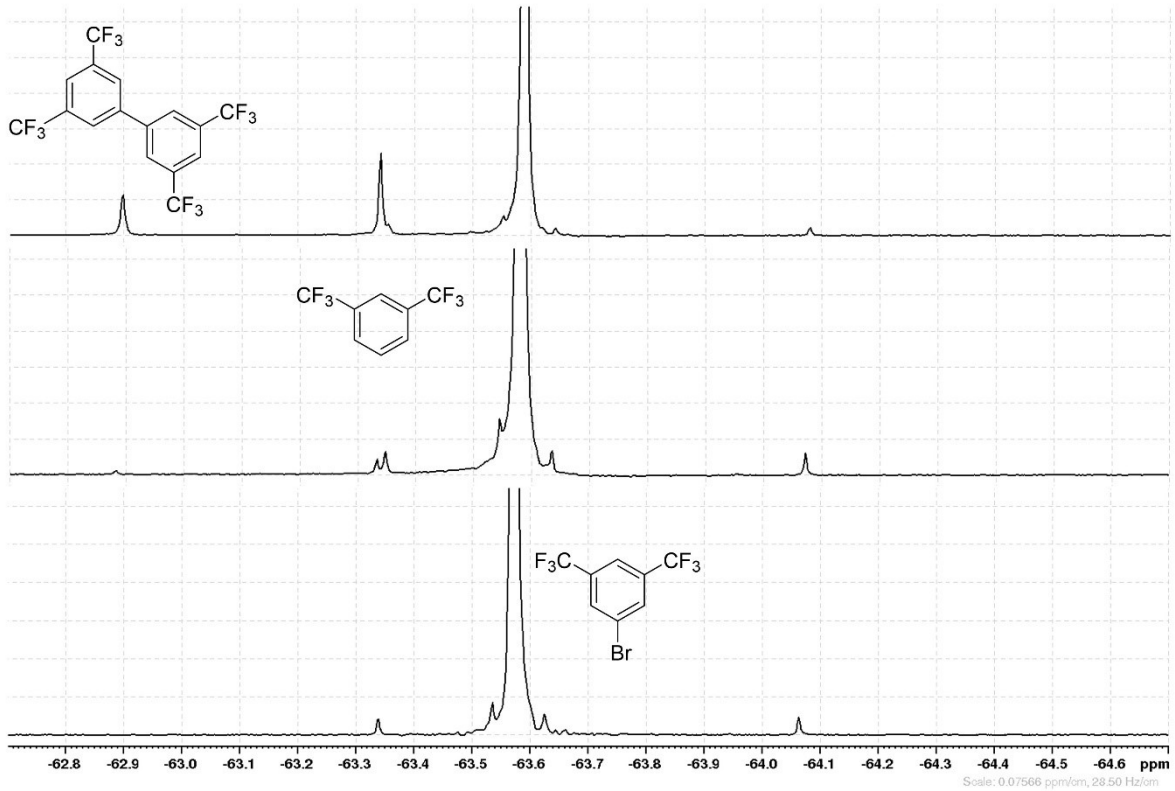


Figure S13. ^{19}F{^{1}H} NMR spectra (376.5 MHz, THF-d_8) of the reaction mixture [Ni(OAr*)($^{p\text{-Anis}}$NN^{H})], **11^{OAr*}**, and 3,5-bis(trifluoromethyl)bromobenzene (14 μL, 0.08 mmol, 4.0 equiv.) in THF before heating (bottom), upon heating to 65 °C for 2 h (middle), and upon heating to 65 °C for 18 h (top). The hydrodehalogenation product 1,3-$(CF_3)_2$-C_6H_4 was identified by spiking with a commercial sample and the homocoupling product 1,1',3,3'-$(CF_3)_4$-$C_{12}H_6$ was confirmed by GC-MS.

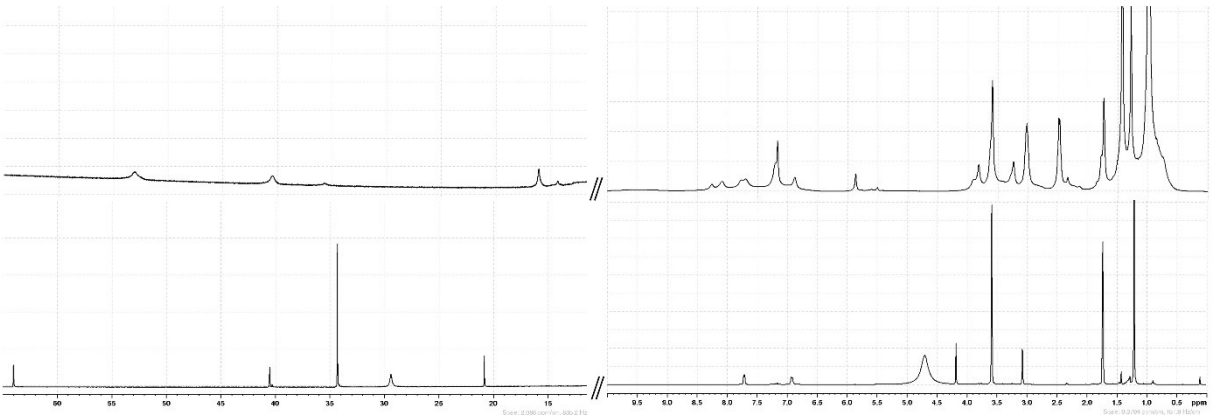
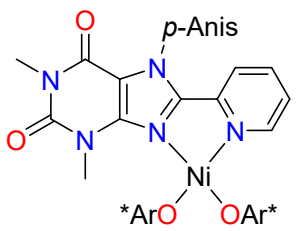
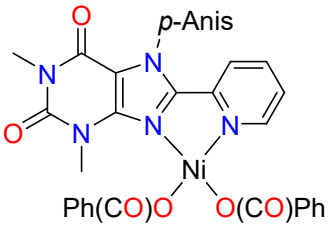


Figure S14. ^{1}H NMR spectra (400.3 MHz, THF-d_8) of Ni(OAr*)($^{p\text{-Anis}}$NN^{H})], **11^{OAr*}** (bottom), and the reaction mixture **11^{OAr*}**, $PhCO_2H$ (9.8 mg, 0.08 mmol, 4.0 equiv.) and DIPEA (14 µL, 0.08 mmol, 4.0 equiv.) in THF upon heating to 65 °C for 18 h (top).



[Ni(OAr*)$_2$($^{p\text{-Anis}}$NN^{H})], **6^{OAr*}**

[Ni(OAr*)$_2$($^{p\text{-Anis}}$NN^{H})], **6^{OAr*}**. As result of redistribution from the putative [NiBr(OAr*)($^{p\text{-Anis}}$NN^{H})], **13^{OAr*}**, the complex **6^{OAr*}** is contaminated with species **6^{Br}**. The crude of reaction was evaporated to dryness and **6^{OAr*}** was extracted with Et_2O (3 x 0.5 mL), where **6^{Br}** is poorly soluble. The green ethereal extract was left in the fridge at –30 °C, returning deep green microcrystals. Yield *via* photoinduced dismutation of **11^{OAr*}**: 6.2 mg, 6.6 µmol, 66%, as a deep green solid. Yield *via* redistribution of **13^{OAr*}**: 6.5 mg, 6.9 µmol, 69%, as a deep green solid. ^{1}H NMR (400.3 MHz, THF-d_8): δ [ppm] = 8.26 (br., 1H, H^{Pyr} = H15, H14, H13 or H12), 8.07 (br., 1H, H^{Pyr} = H15, H14, H13 or H12), 7.78 (br., 1H, H^{Pyr} = H15, H14, H13 or H12), 7.44 (br., 1H, H^{Pyr} = H15, H14, H13 or H12), 7.20 (br., 5H, H^{Anis} = H17 or H18 + 3 x H^{OAr*}), 6.87 (br., 3H, H^{Anis} = H17 or H18 + H^{OAr*}), 4.00 (br., 1H, ^{t}Bu), 3.90 (br., 2H, ^{t}Bu), 3.81 (br., 4H, Me = N1CH_3, N3CH_3 or OCH_3 + ^{t}Bu), 3.58 (br., 4H, Me = N1CH_3, N3CH_3 or OCH_3 + ^{t}Bu), 3.25 (br., 2H, ^{t}Bu), 3.23 (br., 3H, Me = N1CH_3, N3CH_3 or OCH_3), 1.62-1.19 (br., 13H, ^{t}Bu). Due to the paramagnetic nature of the sample, not all expected ^{1}H resonances for the ^{t}Bu groups are observed. ^{13}C{^{1}H} NMR spectrum: silent. Anal. Calcd. for $C_{55}H_{75}N_5NiO_5$: C, 69.91; H, 8.00; N, 7.41; found: C, 69.59; H, 8.13; N, 7.96.



[Ni(PhCO$_2$)$_2$($^{p\text{-Anis}}$NN^{H})], **6^{OBAc}**

From **11^{OAr*}** and $PhCO_2H$, upon dismutation of the putative nickel(I) complex [Ni(PhCO$_2$)($^{p\text{-Anis}}$NN^{H})]: The product was contaminated with metallic nickel, and it was extracted with THF, where **6^{OBAc}** is only partially soluble. In this sense, most of the material was lost during

the filtration step. The clear THF filtrate was evaporated to dryness and the residue was washed with THF (2 x 0.2 mL) and hexane (3 x 0.2 mL). Yield: 4.6 mg, 6.8 μmol, 68%, as a pale green solid. ^{1}H NMR (300.1 MHz, $CDCl_3$ or CD_3CN): δ [ppm] = silent. In DMSO-d_6 only the well-defined resonances of the free ligand $^{p\text{-Anis}}NN^H$ were detected, thus suggesting that the complex decomposes in this solvent (ligand exchange/dissociation). Anal. Calcd. for $C_{33}H_{27}N_5NiO_7\cdot(C_4H_8O)_{0.60}(C_6H_{14})_{0.35}$: C, 61.51; H, 5.19; N, 9.32; found: C, 61.81; H, 5.09; N, 9.35. The amount of THF and hexane was confirmed independently by ^{1}H NMR in DMSO-d_6 using dichloromethane as standard, returning the following molar fractions $C_4H_8O/\mathbf{6}^{\mathbf{OBAc}}$ = 0.57 and $C_6H_{14}/\mathbf{6}^{\mathbf{OBAc}}$ = 0.39.

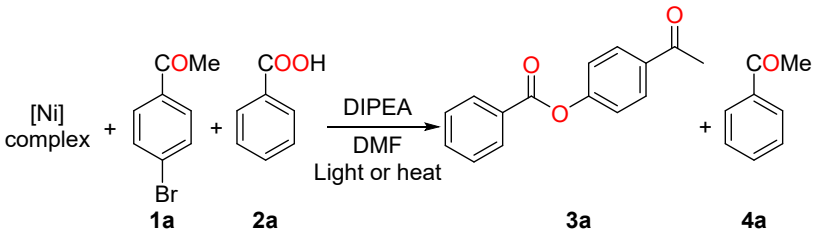
From complex [$NiBr_2(^{p\text{-Anis}}NN^H)$], $\mathbf{6}^{\mathbf{Br}}$, by treating it with potassium benzoate: A Schlenk flask equipped with a stirring bar was loaded with [$NiBr_2(^{p\text{-Anis}}NN^H)$] (58.2 mg, 0.10 mmol, 1.00 equiv.) and potassium benzoate (33.0 mg, 0.21 mmol, 2.06 equiv.). Air was purged by three vacuum/argon cycles. Then, dry THF (3 mL) was added, and the mixture was stirred at room temperature for 16 h. The initial orange suspension turned into a pale green suspension, which was filtered through frit (P4). The clear filtrate was evaporated to dryness, yielding a pale green solid that still contained KBr, as suggested by elemental analysis. This crude was suspended in acetonitrile (2 mL), filtrated, and crystalized by slow vapor diffusion with Et_2O (3 mL). Yield: 32.0 mg, 48.2 μmol, 48%, as a bright green solid. Anal. Calcd. for $C_{33}H_{27}N_5NiO_7\cdot(C_4H_{10}O)_{0.70}$: C, 60.04; H, 4.79; N, 9.78; found: C, 60.29; H, 4.70; N, 9.66. The amount of Et_2O was confirmed independently by ^{1}H NMR in DMSO-d_6 using dichloromethane as standard, returning the molar fraction $C_4H_{10}O/\mathbf{6}^{\mathbf{OBAc}}$ = 0.73.

Screening of nickel complexes for the arylation of benzoic acid. In the glovebox, two WICOM septum capped vials were loaded with an appropriate nickel complex (0.02 mmol) and a stirring bar. Then, 4-bromoacetophenone (0.20 mmol/mL, 100 μL, 0.02 mmol, 1.00 equiv.), benzoic acid (0.40 mmol/mL, 100 μL, 0.04vmmol, 2.00 equiv.), DIPEA (14.4 μL, 0.08 mmol, 4.08vequiv.) and DMF (300 μL) were added and the vials were sealed. One sample was irradiated with blue LED (7 W) and the other one heated to 65 °C. Once the reaction time was achieved, 18 h for both tests, 1,3,5-trimethoxybenzene was added (2.1 mg, 0.01 mmol, 1.00 equiv.). The whole sample was filtered through a silica plug, eluted with EtOAc (2 x 0.50 mL) and collected in a GC-vial for GC-FID analysis (Figure S15), using appropriate calibration curves.

NOTE. The presumed complex [Ni(cod)($^{p\text{-Anis}}NN^H$)] (**10**) is an extremely air-, moisture-, temperature- and light-sensitive species that could not be isolated. Above −30 °C or unprotected from light, metallic mirrors are typically obtained along with the corresponding free ligands $^{p\text{-Anis}}NN^H$ and 1,5-COD. Consequently, **10** was generated *in situ* by mixing [$Ni(cod)_2$] (11.0 mg, 40.0vμmol, 1.00vequiv.) and

$^{p\text{-Anis}}NN^{H}$ (14.6 mg, 40.0 µmol, 1.00 equiv.) in cold DMF (300 µL, –30 °C). The mixture was kept cold and in the dark for 2 h. The remaining reaction components were added and the whole sample was divided into two vials, one for the photochemical setup and the other for the thermal reaction.

Table S8. Synthetic model reactions using different nickel sources under thermal and photochemical conditions.[a]



[Ni]	Condition	Conversion[b] (%)	**3a**[b] (%)	**4a**[b] (%)	Selectivity[b] **3a**/**4a**
[Ni(cod)($^{p\text{-Anis}}NN^{H}$)], **10**	65 °C	70	-	70	-
[Ni(cod)($^{p\text{-Anis}}NN^{H}$)], **10**	455 nm	88	<1	90	-
[Ni(OAr*)($^{p\text{-Anis}}NN^{H}$)], **11**^{OAr*}	65 °C	25	-	21	-
[Ni(OAr*)($^{p\text{-Anis}}NN^{H}$)], **11**^{OAr*}	455 nm	>99	50	50	1.00
[$NiBr_2$($^{p\text{-Anis}}NN^{H}$)], **6**^{Br}	65 °C	7	-	-	-
[$NiBr_2$($^{p\text{-Anis}}NN^{H}$)], **6**^{Br}	455 nm	56	<1	57	-
No nickel	455 nm	27(2)	-	24(1)	-

[a] Conditions: 4-bromoacetophenone (3.9 mg, 20.0 µmol), benzoic acid (4.9 mg, 40.0 µmol, 2 equiv.), Ni species (20.0 µmol, 1 equiv.), DIPEA (14.2 µL, 80.0 µmol, 4 equiv.), DMF (0.50 mL, 0.04 mM), 18 h. [b] Conversion, yield and selectivity determined by GC-FID using 1,3,5-trimethoxybenzene as internal standard (8.4 mg, 50.0 µmol) and an appropriate calibration curve.

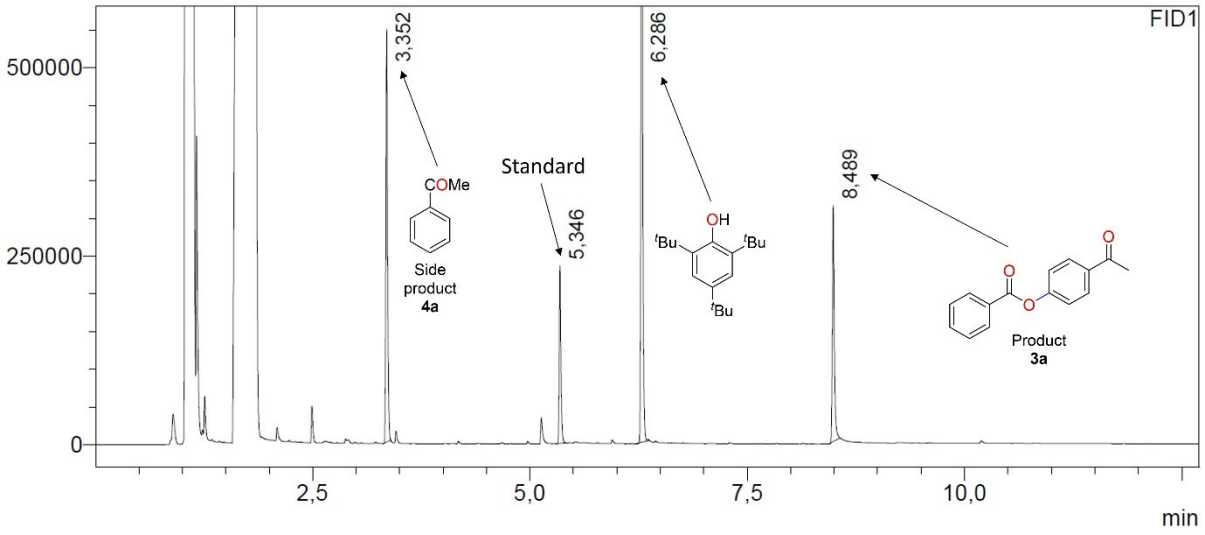


Figure S15. Representative chromatogram of a synthetic model reaction. The assignment of the FID detector signals for each relevant chemical compound is based on their retention time (min). The chromatogram indeed corresponds to the test using complex **11**$^{OAr^*}$ as nickel source, under photochemical conditions.

8. X-ray analysis

Table S9. Crystal data and structure refinement for the xanthine-based scaffolds $^{Pyr}NN^{H}$, $^{p\text{-}Anis}NN^{H}$, and $^{Pyr}NN^{4Me}$.

	^{Pyr}NN^{H}	**$^{p\text{-}Anis}$NN^{H}**	**^{Pyr}NN^{4Me}**
Empirical formula	$C_{17}H_{14}N_6O_2$	$C_{19}H_{17}N_5O_3$	$C_{18}H_{16}N_6O_2$
Formula weight / g·mol^{-1}	334.34	348.38	348.37
Temperature / K	123(1)	123(1)	123(1)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	I2/a
a / Å	6.6161(4)	9.8012(2)	13.0278(2)
b / Å	11.0537(6)	8.1826(2)	14.7154(2)
c / Å	11.1219(6)	27.1202(6)	34.4476(5)
α /°	84.188(4)	90	90
β /°	74.575(5)	94.448(2)	99.1520(10)
γ /°	88.159(4)	90	90
V / Å^3	780.03(8)	2168.47(8)	6519.86(16)
Z	2	4	14
ρ_{calc} / g·cm^{-1}	1.423	1.334	1.426
μ / mm^{-1}	0.816	0.768	0.811
F(000)	348	920	2927.0
Crystal size / mm^3	0.244 × 0.178 × 0.122	0.527 × 0.141 × 0.063	0.624 × 0.489 × 0.382
Radiation / Å	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2*Θ* range for data collection /°	8.04 to 133.4	9.05 to 133.582	9.132 to 145.5
Index ranges	-6 ≤ h ≤ 7, -13 ≤ k ≤ 12, -13 ≤ l ≤ 13	-11 ≤ h ≤ 11, -7 ≤ k ≤ 9, -32 ≤ l ≤ 32	-13 ≤ h ≤ 16, -18 ≤ k ≤ 10, -42 ≤ l ≤ 38
Reflections collected	8636	30627	13874
Independent reflections	2740 [R_{int} = 0.0379, R_{sigma} = 0.0292]	3834 [R_{int} = 0.0761, R_{sigma} = 0.0310]	6280 [R_{int} = 0.0153, R_{sigma} = 0.0162]
Data/restraints/parameters	2740/0/228	3834/0/292	6280/0/481
Goodness-of-fit on F^2	1.080	1.032	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0704, wR_2 = 0.1998	R_1 = 0.0540, wR_2 = 0.1476	R_1 = 0.0361, wR_2 = 0.0902
Final R indexes [all data]	R_1 = 0.0776, wR_2 = 0.2104	R_1 = 0.0584, wR_2 = 0.1544	R_1 = 0.0380, wR_2 = 0.0913
Largest diff. peak/hole / e Å^{-3}	0.55/-0.34	0.32/-0.26	0.21/-0.18

Table S10. Crystal data and structure refinement for the nickel(II) complexes [$NiBr_2$($^{p\text{-Anis}}NN^H$)] (**6^{Br}**), [NiBr(MeCN)(μ-Br)($^{p\text{-Anis}}NN^H$)]$_2$, **6^{Br}**·MeCN and [$NiBr_2$($^{Pyr}NN^H$)$_2$] (**7^{Br}**).

	6^{Br}	**6^{Br}**·MeCN	**7^{Br}**
Empirical formula	$C_{40}H_{38}Br_4Cl_4N_{12}Ni_2O_4$	$C_{42}H_{40}Br_4N_{12}Ni_2O_6$	$C_{38}H_{35}Br_2N_{14}NiO_4$
Formula weight / g·mol^{-1}	1329.68	1245.92	970.33
Temperature / K	123(1)	123(1)	123(1)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	13.4368(3)	14.4927(8)	17.17370(10)
b / Å	9.1144(2)	9.5220(2)	13.64170(10)
c / Å	20.4830(4)	24.7089(14)	17.84950(10)
α /°	90	90	90
β /°	108.664(2)	137.895(11)	103.7100(10)
γ /°	90	90	90
V / Å^3	2376.60(9)	2286.2(4)	4062.61(5)
Z	2	2	4
ρ_{calc} / g·cm^{-1}	1.858	1.81	1.586
μ / mm^{-1}	7.455	5.636	3.489
F(000)	1316	1240	1964
Crystal size / mm^3	0.139 × 0.107 × 0.048	0.024 × 0.05 × 0.041	0.265 × 0.179 × 0.14
Radiation / Å	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2*Θ* range for data collection /°	6.944 to 151.534	7.252 to 147.032	5.296 to 152.24
Index ranges	-16 ≤ h ≤ 16, -11 ≤ k ≤ 11, -24 ≤ l ≤ 25	-17 ≤ h ≤ 17, -11 ≤ k ≤ 11, -30 ≤ l ≤ 29	-16 ≤ h ≤ 21, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22
Reflections collected	12001	13704	61114
Independent reflections	4510 [R_{int} = 0.0323, R_{sigma} = 0.0363]	4466 [R_{int} = 0.0277, R_{sigma} = 0.0232]	8417 [R_{int} = 0.0290, R_{sigma} = 0.0136]
Data/restraints/parameters	4510/0/301	4466/0/302	8417/0/538
Goodness-of-fit on F^2	1.074	1.048	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0356, wR_2 = 0.0995	R_1 = 0.0356, wR_2 = 0.0990	R_1 = 0.0429, wR_2 = 0.1206
Final R indexes [all data]	R_1 = 0.0403, wR_2 = 0.1021	R_1 = 0.0383, wR_2 = 0.1011	R_1 = 0.0465, wR_2 = 0.1228
Largest diff. peak/hole / e Å^{-3}	0.93/-0.94	0.78/-0.89	0.74/-0.67

Table S11. Crystal data and structure refinement for the nickel complexes [NiBr($^{p\text{-Anis}}$NN^{H})(PPh_3)] (**11^{Br}**·PPh_3) and [Ni(OAr*)($^{p\text{-Anis}}$NN^{H})] (**11^{OAr*}**).

	11^{Br}·PPh_3	**11^{OAr*}**
Empirical formula	$C_{37}H_{32}N_5O_3PNiBr$	$C_{39}H_{52}N_5NiO_{4.5}$
Formula weight / g·mol^{-1}	764.26	721.56
Temperature / K	123(1)	123(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c
a / Å	19.3695(2)	33.3183(3)
b / Å	17.6564(2)	9.93460(10)
c / Å	19.5992(3)	21.7721(2)
α /°	90	90
β /°	93.2970(10)	91.0070(10)
γ /°	90	90
V / Å^3	6691.75(15)	7205.54(12)
Z	8	8
ρ_{calc} / g·cm^{-1}	1.517	1.330
μ / mm^{-1}	3.056	1.169
F(000)	3128.0	3080.0
Crystal size / mm^3	0.134 × 0.13 × 0.108	0.068 × 0.055 × 0.048
Radiation / Å	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2*Θ* range for data collection /°	6.238 to 145.32	5.306 to 146.056
Index ranges	-22 ≤ h ≤ 23,	-39 ≤ h ≤ 40,
	-21 ≤ k ≤ 20,	-12 ≤ k ≤ 11,
	-23 ≤ l ≤ 22	-24 ≤ l ≤ 27
Reflections collected	56036	19803
Independent reflections	12747	6864
	[R_{int} = 0.0416,	[R_{int} = 0.0196,
	R_{sigma} = 0.0338]	R_{sigma} = 0.0202]
Data/restraints/parameters	12747/0/871	6864/77/579
Goodness-of-fit on F^2	1.051	1.262
Final R indexes [I>=2σ (I)]	R_1 = 0.0450,	R_1 = 0.0652,
	wR_2 = 0.1180	wR_2 = 0.1635
Final R indexes [all data]	R_1 = 0.0668,	R_1 = 0.0690,
	wR_2 = 0.1276	wR_2 = 0.1653
Largest diff. peak/hole / e Å^{-3}	0.74/-0.58	0.59/-0.69

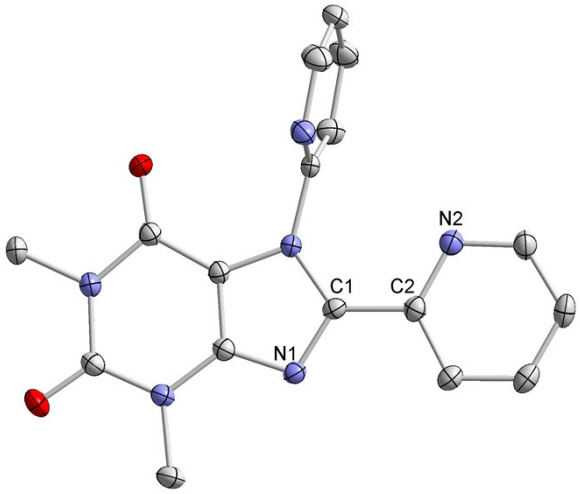


Figure S16. Solid state molecular structure of ^{Pyr}**NN**^{H}. Displacement ellipsoids are drawn at the 40% probability level. H-atoms have been omitted for clarity. Selected bond lengths [Å]: C1–N1 1.336(3), C1–C2 1.465(3), C1–N2 1.341(3)

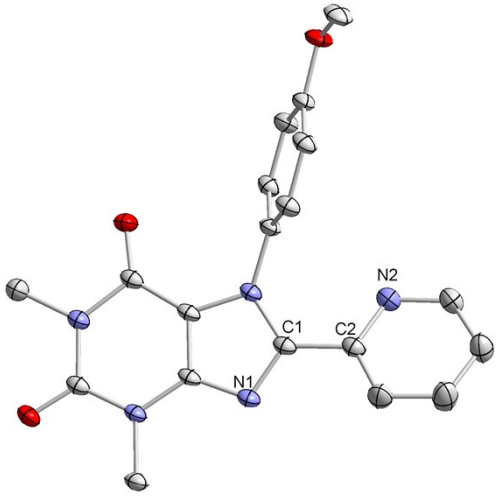


Figure S17. Solid state molecular structure of $^{p\text{-Anis}}$**NN**^{H}. Displacement ellipsoids are drawn at the 40% probability level. H-atoms have been omitted for clarity. Selected bond lengths [Å]: C1–N1 1.342(2), C1–C2 1.472(2), C1–N2 1.340(2).

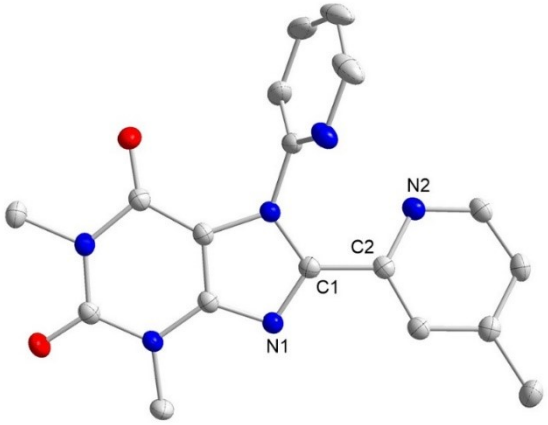


Figure S18. Solid state molecular structure of ^{Pyr}**NN**^{4Me}. Displacement ellipsoids are drawn at the 40% probability level. H-atoms have been omitted for clarity. Selected bond lengths [Å]: C1–N1 1.336(2), C1–C2 1.474(2), C1–N2 1.344(2). The values shown are an average of the corresponding parameter for the two independent molecules found within the unit cell.

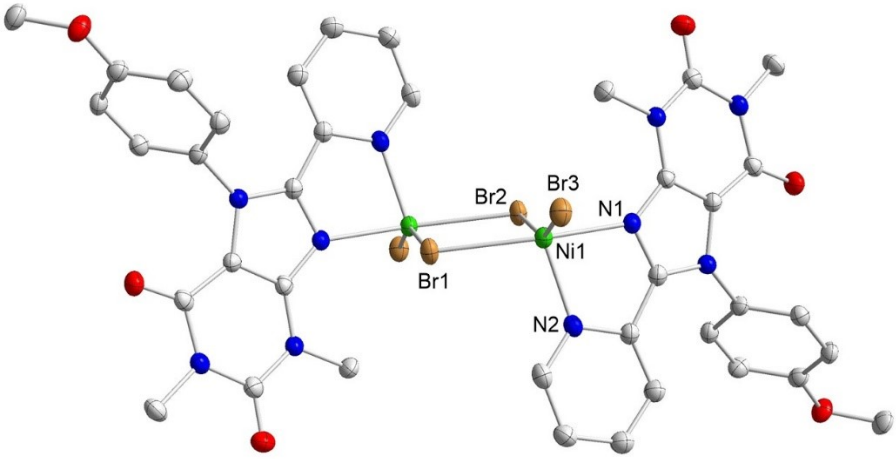


Figure S19. Solid state molecular structure of [NiBr(μ-Br)($^{p\text{Anis}}$NN^{H})]$_2$, **6**^{Br} (*included in the main manuscript of the paper in Scheme 2b*). Displacement ellipsoids are drawn at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–N1 2.052(3), Ni–N2 2.013(3), Ni–Br1 2.4875(7), Ni–Br2 2.5549(7), Ni–Br3 2.4113(7), N1–Ni–N2 80.25(11), N1–Ni–Br1 167.94(9), Br1–Ni–Br3 94.59(2), Br2–Ni–Br3 154.45(3).

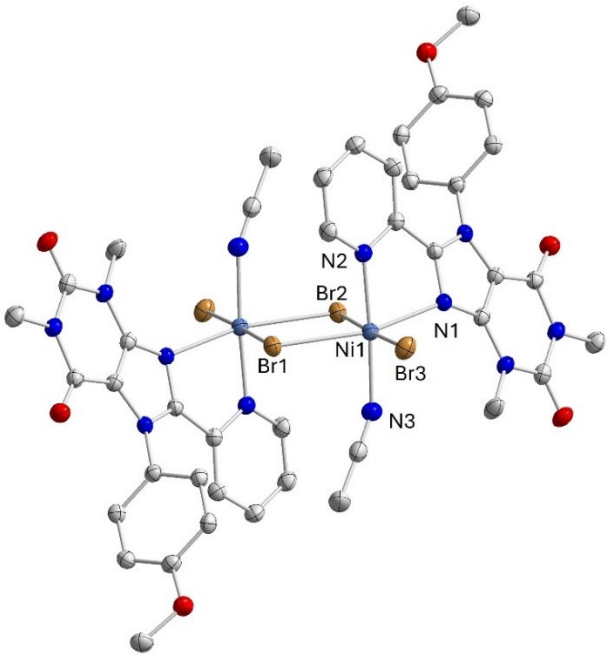


Figure S20. Solid state molecular structure of [NiBr(MeCN)(μ-Br)($^{p\text{-Anis}}$NN^{H})]$_2$, **6^{Br}**·MeCN. Displacement ellipsoids are drawn at the 40% probability level. H-atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–N1 2.179(4), Ni–N2 2.035(2), Ni–N3 2.064(3), Ni–Br1 2.6531(6), Ni–Br2 2.4907(6), Ni–Br3 2.5831(9), N1–Ni–N2 78.8(1), N1–Ni–Br1 81.39(7), Br1–Ni–Br3 86.83(2), Br2–Ni–N2 91.61(8), Br2–Ni–N3 89.02(9), Br3–Ni–N3 85.33(9).

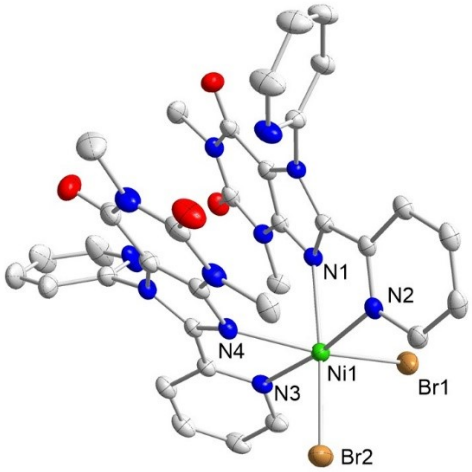


Figure S21. Solid state molecular structure of [NiBr$_2$(^{Pyr}NN^{H})$_2$], **7^{Br}** (*included in the main manuscript of the paper in Scheme 2c*). Displacement ellipsoids are drawn at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–N1 2.284(2), Ni1–N2 2.059(2), Ni1–N3 2.065(2), Ni1–N4 2.244(2), Ni1–Br1 2.504(1), Ni1–Br2 2.500(1), N1–Ni1–N2 76.72(7), N3–Ni1–N4 76.96(7), Br1–Ni1–Br2 100.11(2).

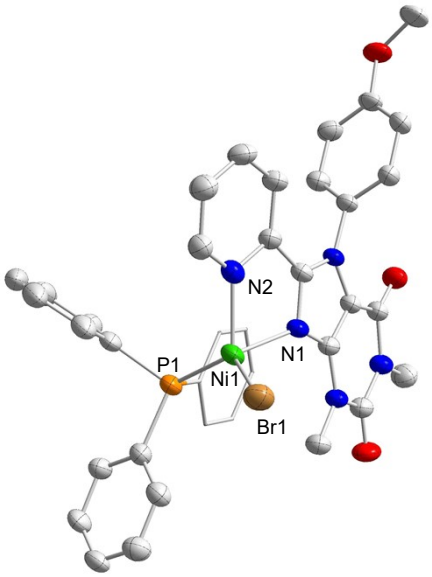


Figure S22. Solid state molecular structure of [NiBr($^{p\text{Anis}}$NN^{H})(PPh$_3$)], **11^{Br}**·PPh$_3$. Displacement ellipsoids are drawn at the 40% probability level. H-atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–N1 2.009(3), Ni–N2 2.010(3), Ni–Br1 2.3743(7), Ni–P1 2.2148(10), C1–N1 1.358(4), C1–C2 1.449(4), C1–N2 1.365(4), N1–Ni–N2 80.13(11), N1–Ni–Br1 106.22(9), N1–Ni–P1 117.06(8), N2–Ni–Br1 122.18(8), N2–Ni–P1 103.79(8), Br1–Ni–P1 120.98(3).

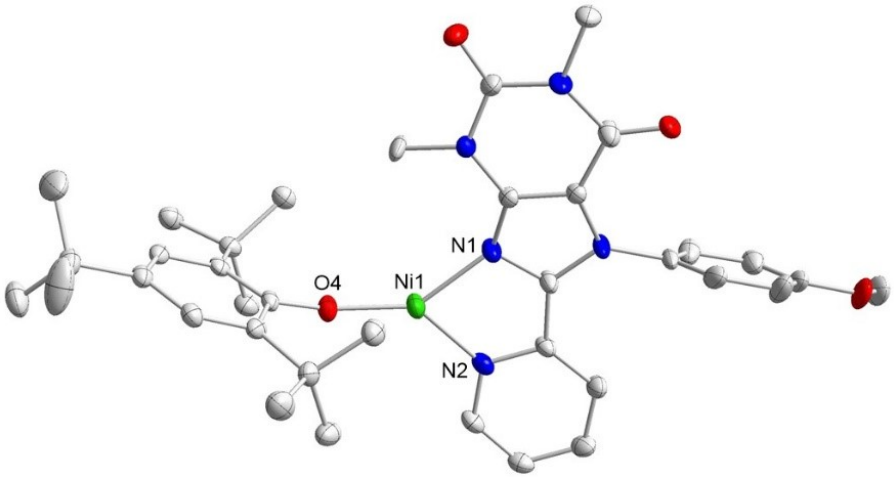


Figure S23. Solid state molecular structure of [Ni(OAr*)($^{p\text{Anis}}$NN^{H})](Ar* = 2, 4, 6-(^{t}Bu)$_3$-C$_6$H$_2$), **11^{OAr*}** (*included in the main manuscript of the paper*). Displacement ellipsoids are drawn at the 40% probability level. H-atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]. Ni–N1 1.975(3), Ni–N2 1.935(3), Ni–O4 1.819(7), C10–N2 1.366(4), C1–C2 1.463(4), C8–N1 1.349(4), N1–Ni–N2 82.21(11), N1–Ni–O4 140.59(9), N2–Ni–O4 136.84(8).

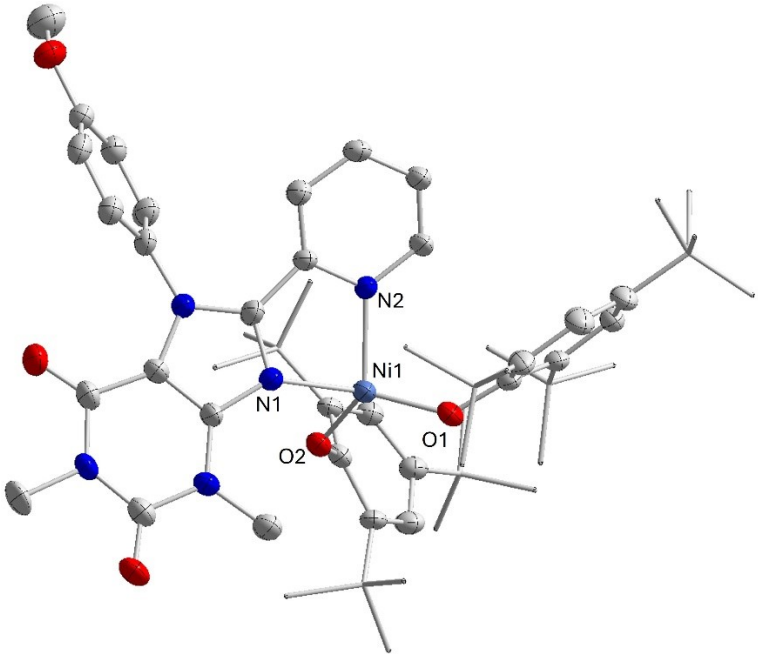


Figure S24. Solid state molecular structure of [Ni(OAr*)$_2$($^{p\text{-Anis}}$NN^{H})] (Ar* = 2,4,6-(^{t}Bu)$_3$-C$_6$H$_2$), **6^{OAr*}**. The quality of the crystallographic data is not sufficient to be publishable but confirms the proposed connectivity for this complex.

9. NMR spectra

***N*7-theophylline derivatives I-VIII**

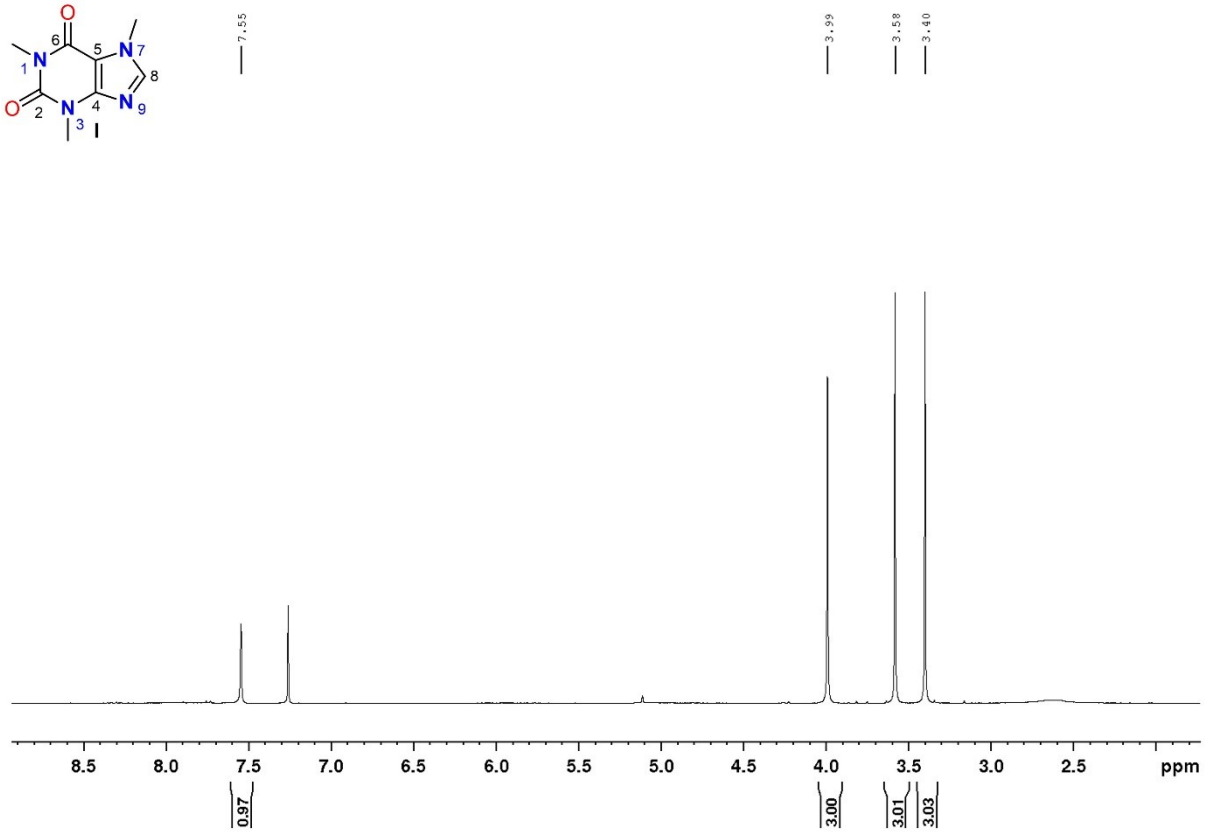


Figure S25. ^{1}H NMR spectrum (300.1 MHz, $CDCl_3$) of caffeine, **I**.

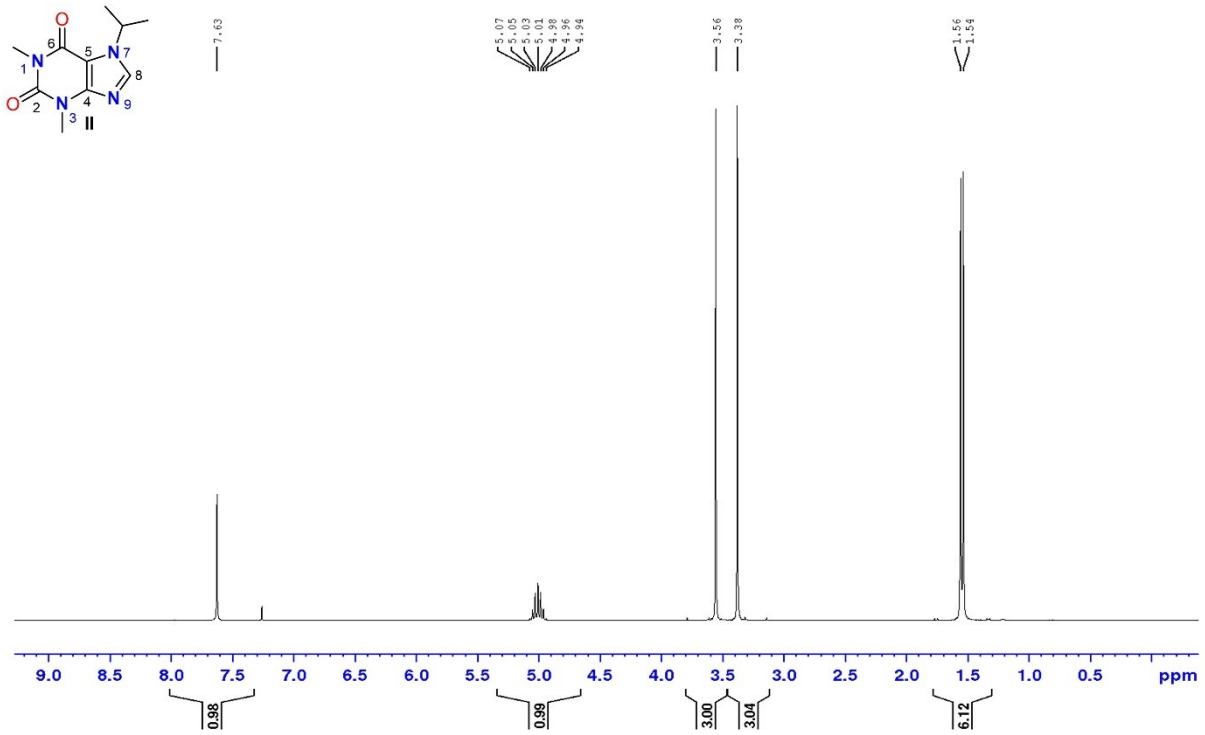


Figure S26. ^{1}H NMR spectrum (300.1 MHz, $CDCl_3$) of the *N7*-theophylline derivative **II**.

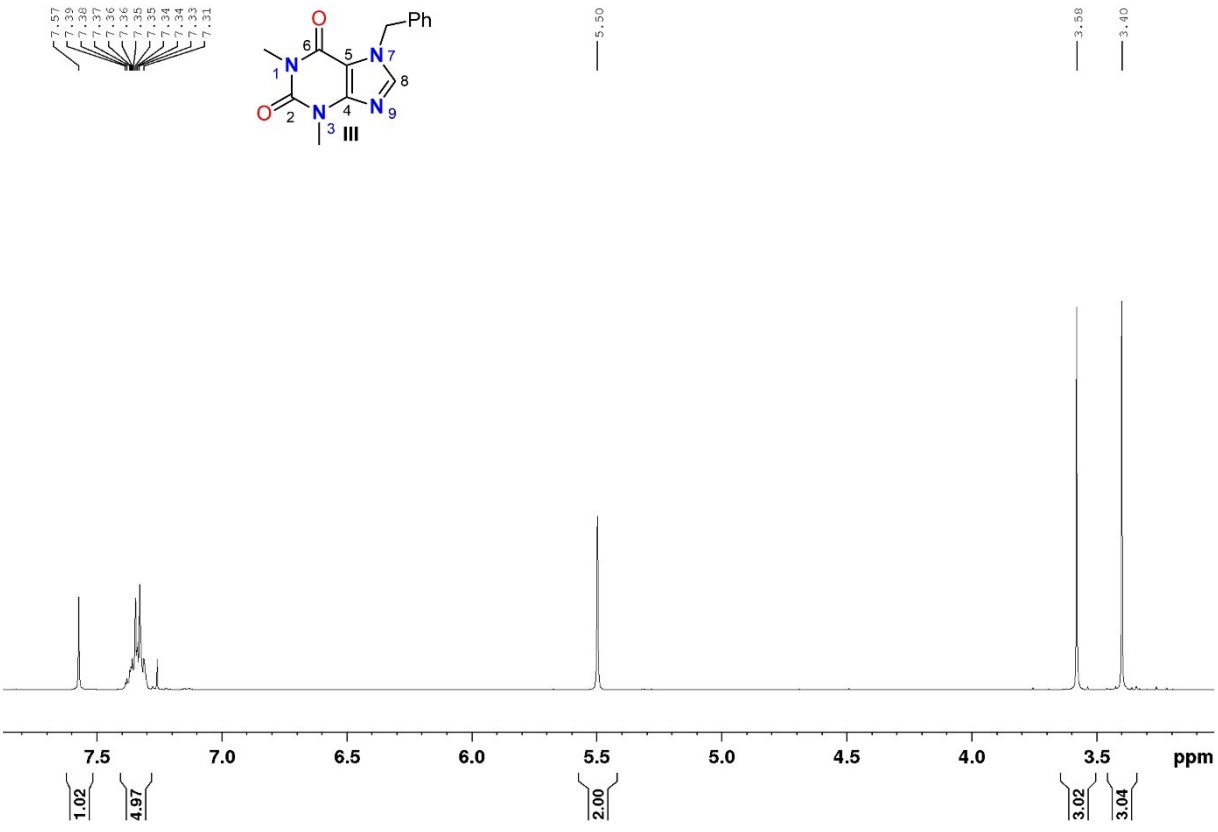


Figure S27. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the *N7*-theophylline derivative **III**.

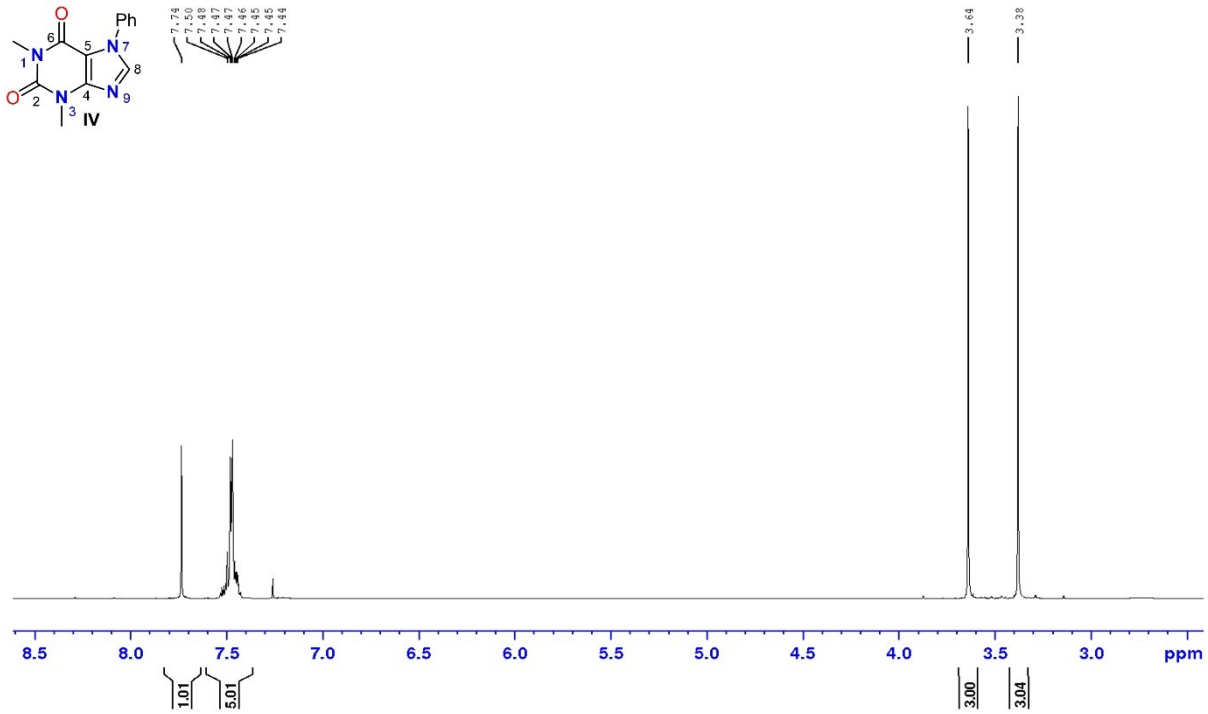


Figure S28. ^{1}H NMR spectrum (300.1 MHz, $CDCl_3$) of the *N7*-theophylline derivative **IV**.

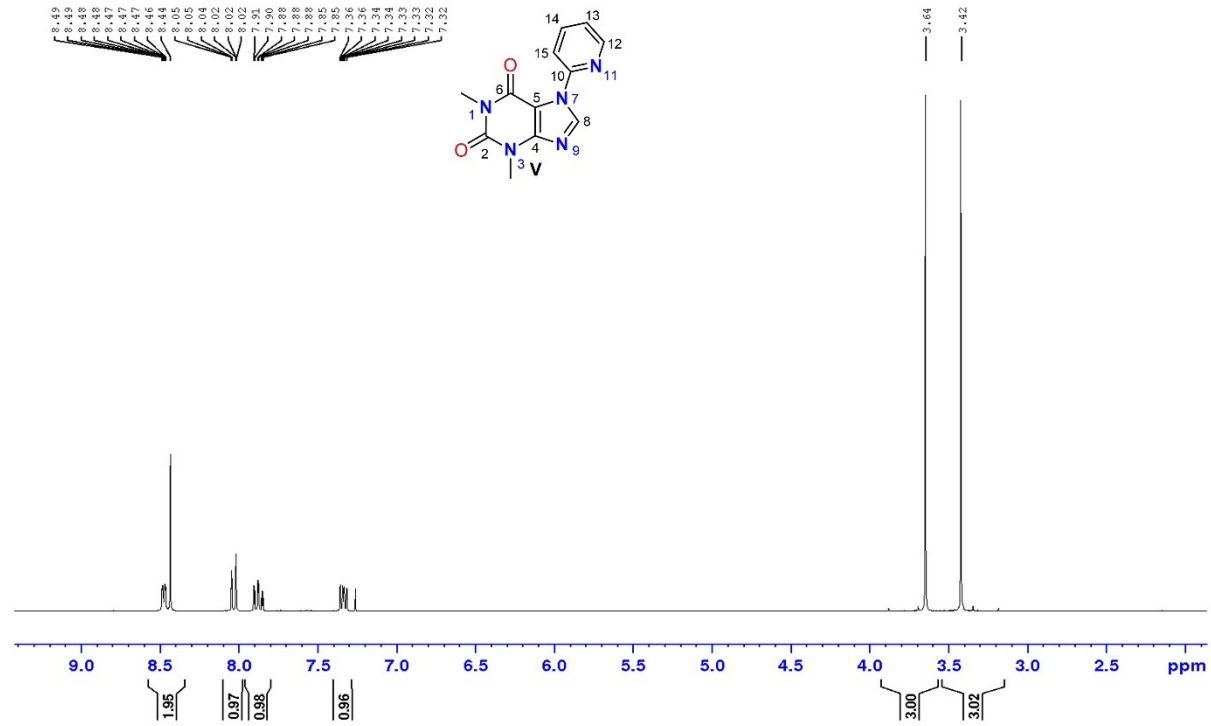


Figure S29. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the *N7*-theophylline derivative **V**.

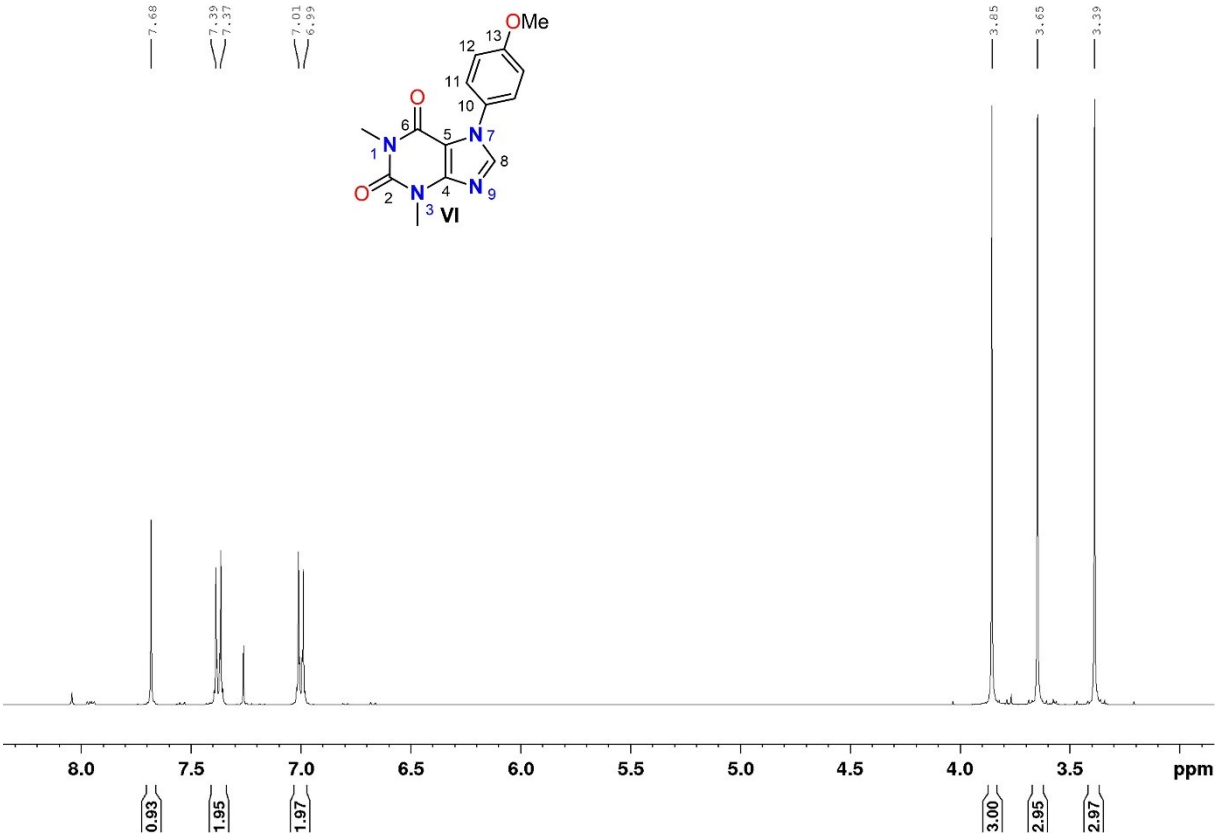


Figure S30. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the *N7*-theophylline derivative **VI**.

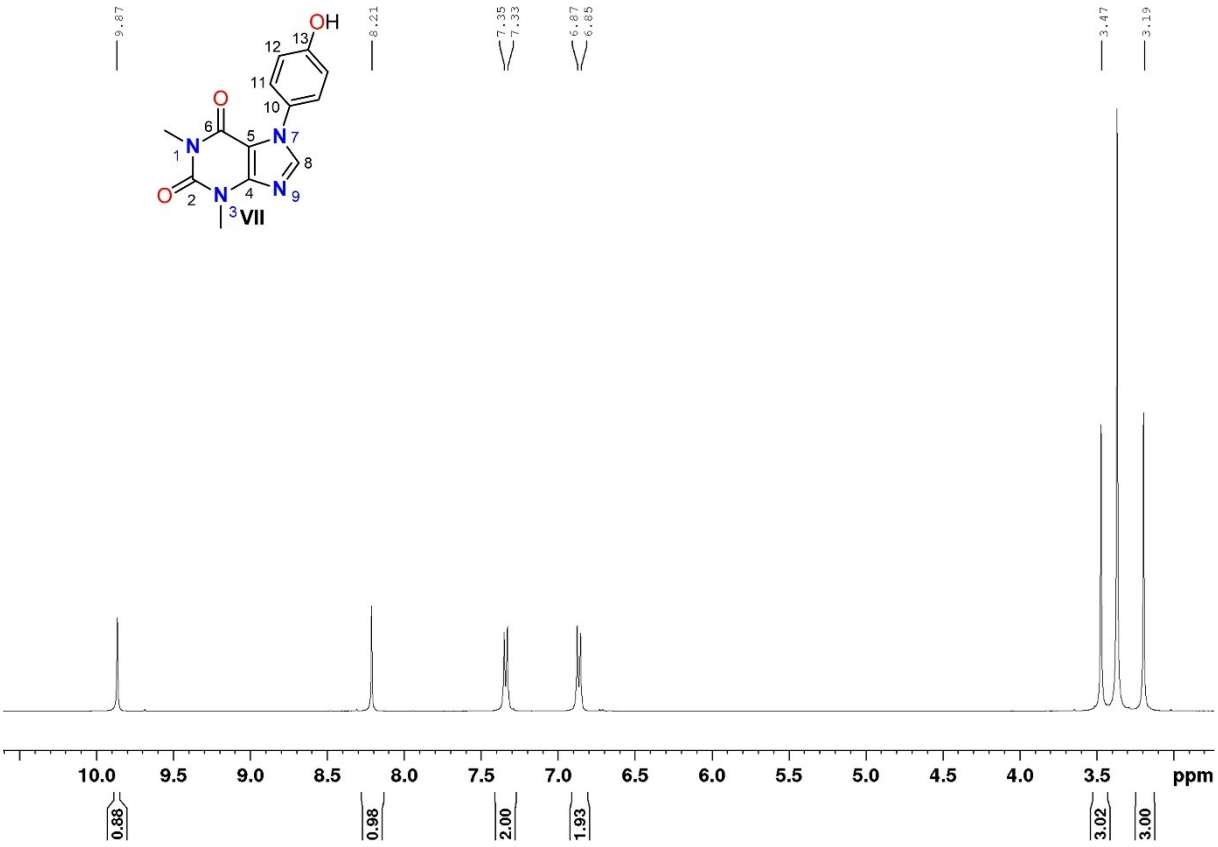


Figure S31. ^{1}H NMR spectrum (400.3 MHz, DMSO-d_6) of the *N7*-theophylline derivative **VII**.

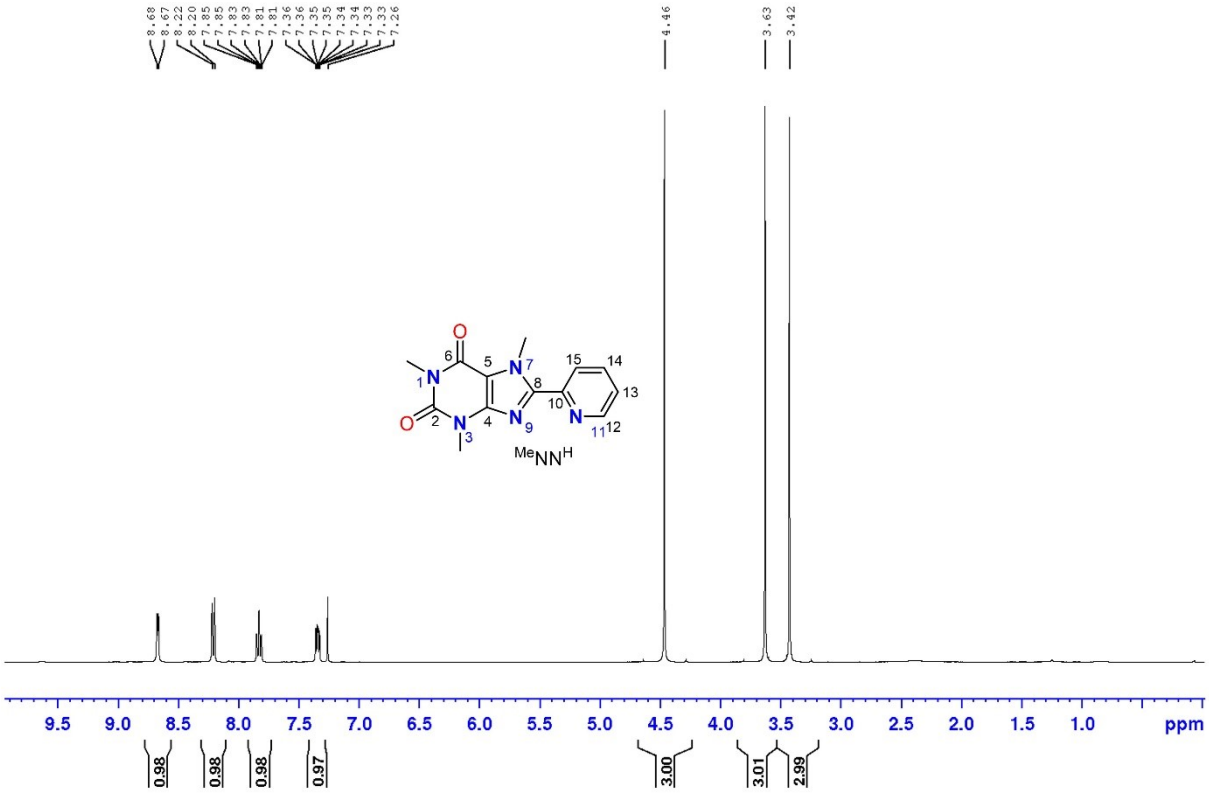


Figure S32. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{Me}NN^{H}$.

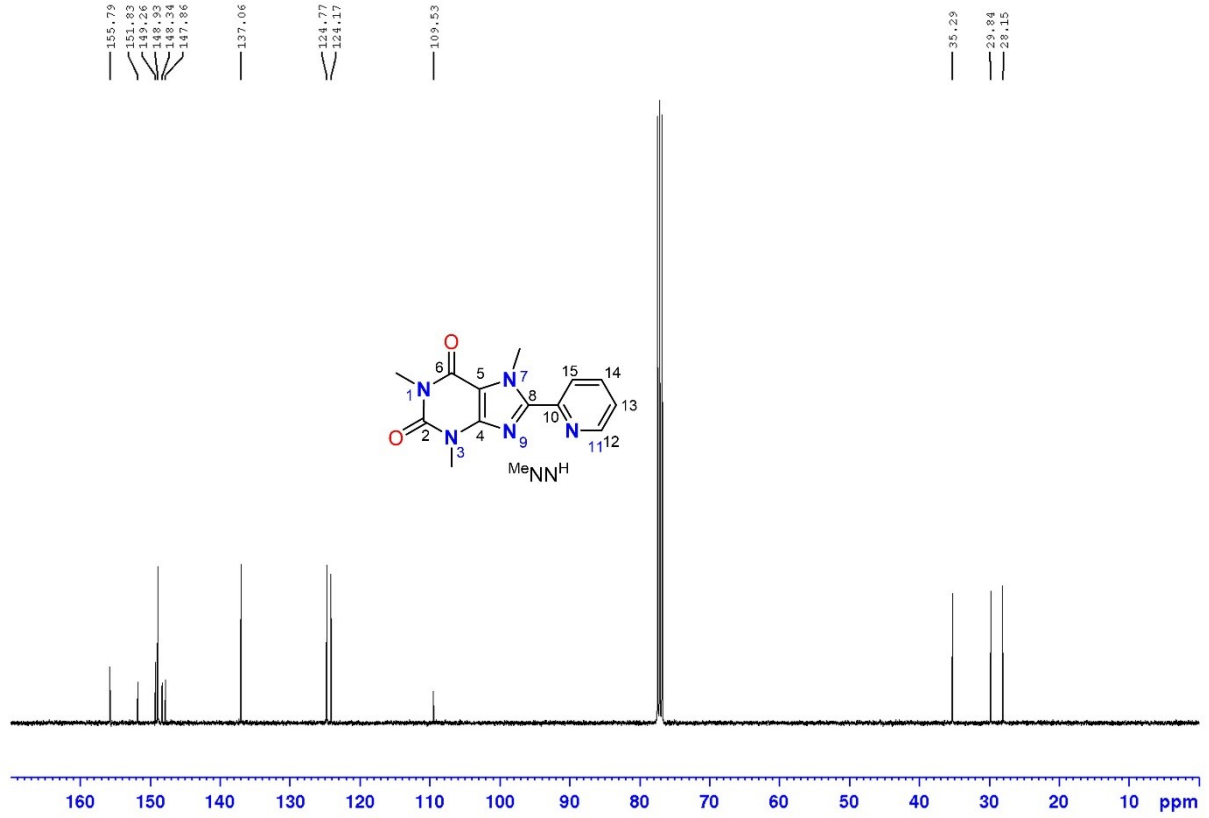


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{Me}NN^{H}$.

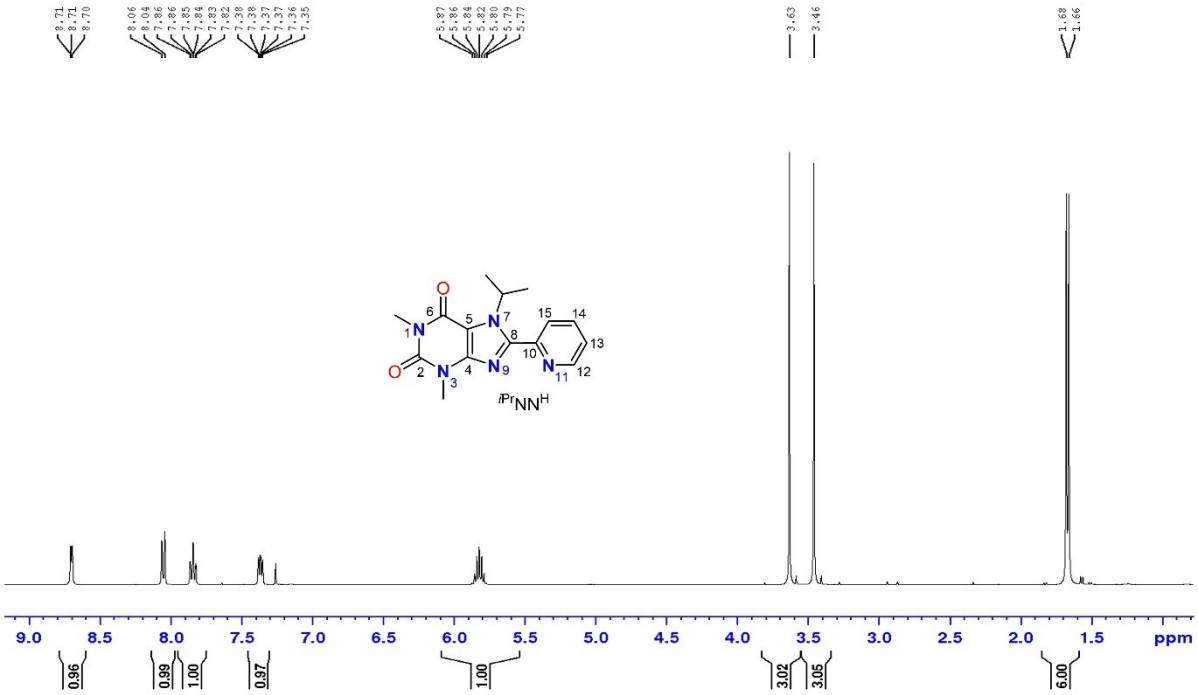


Figure S34. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{iPr}NN^{H}$.

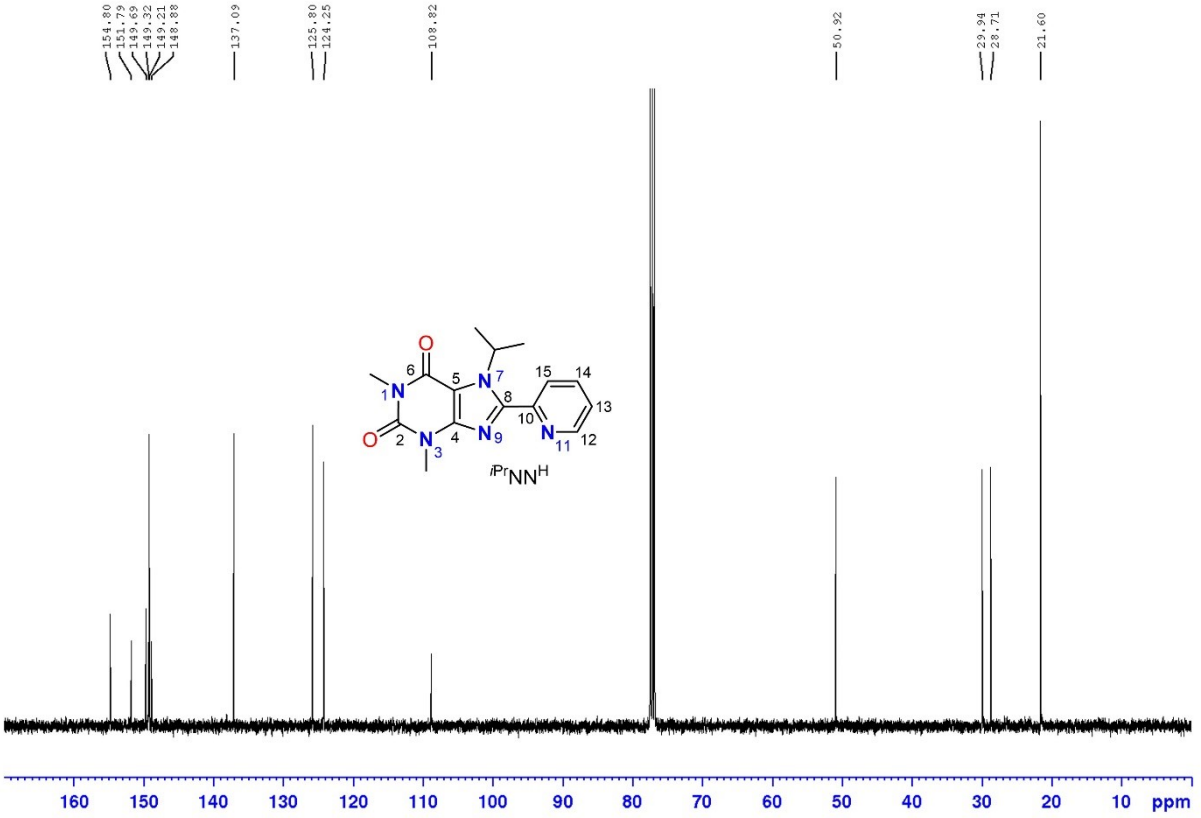


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{iPr}NN^{H}$.

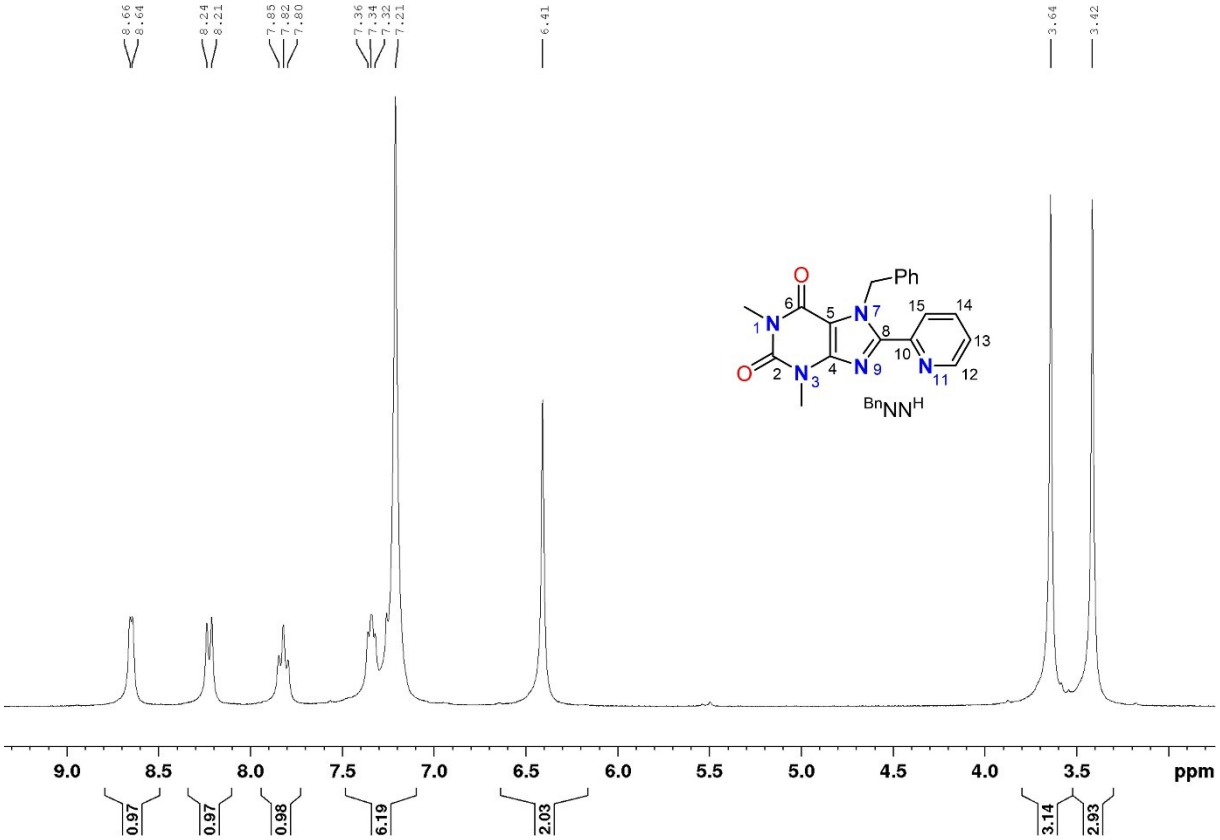


Figure S36. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{Bn}NN^{H}$.

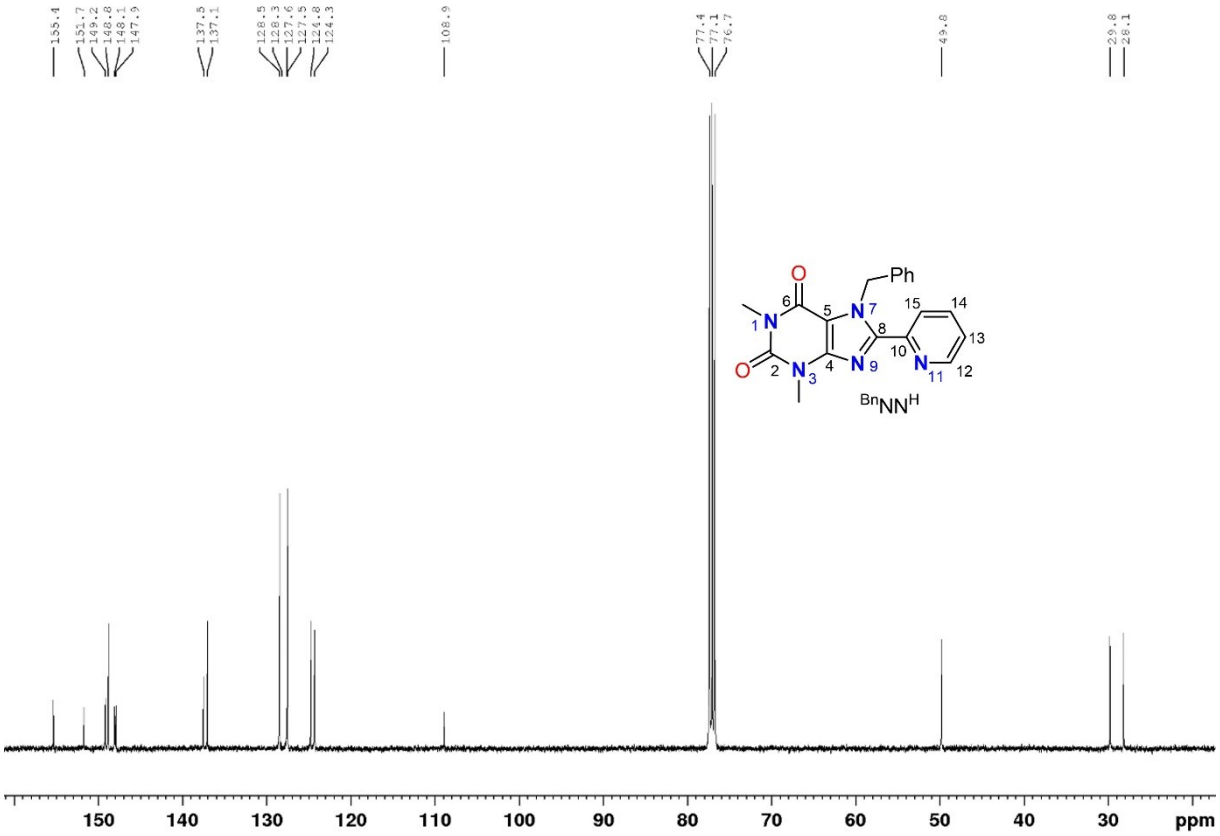


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{Bn}NN^{H}$.

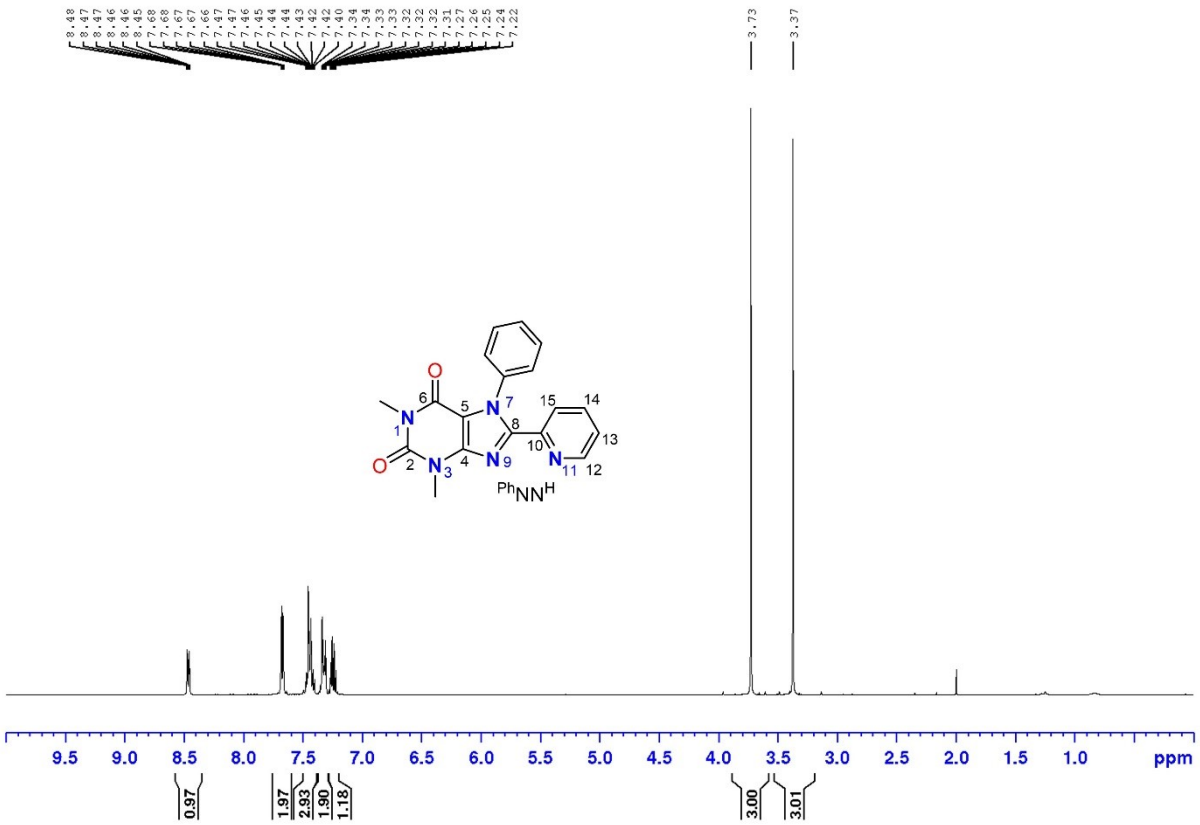


Figure S38. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{Ph}NN^{H}$.

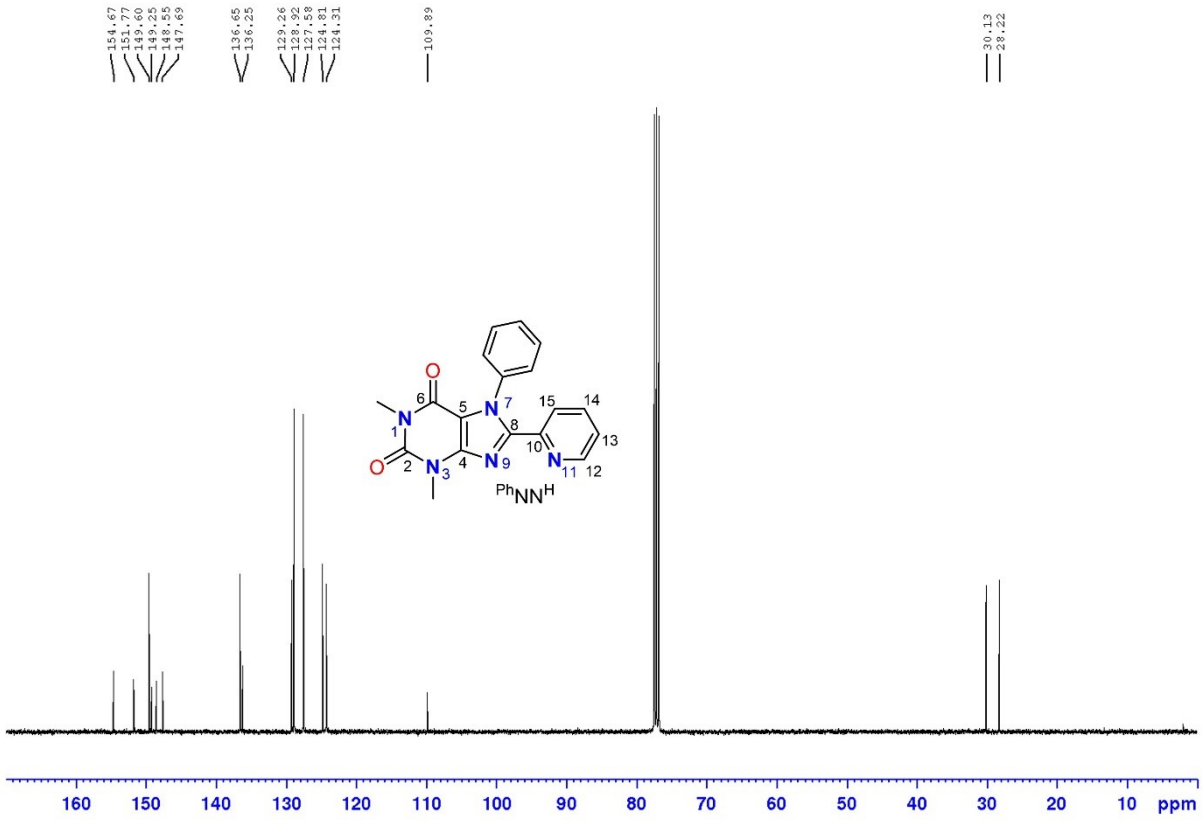


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{Ph}NN^{H}$.

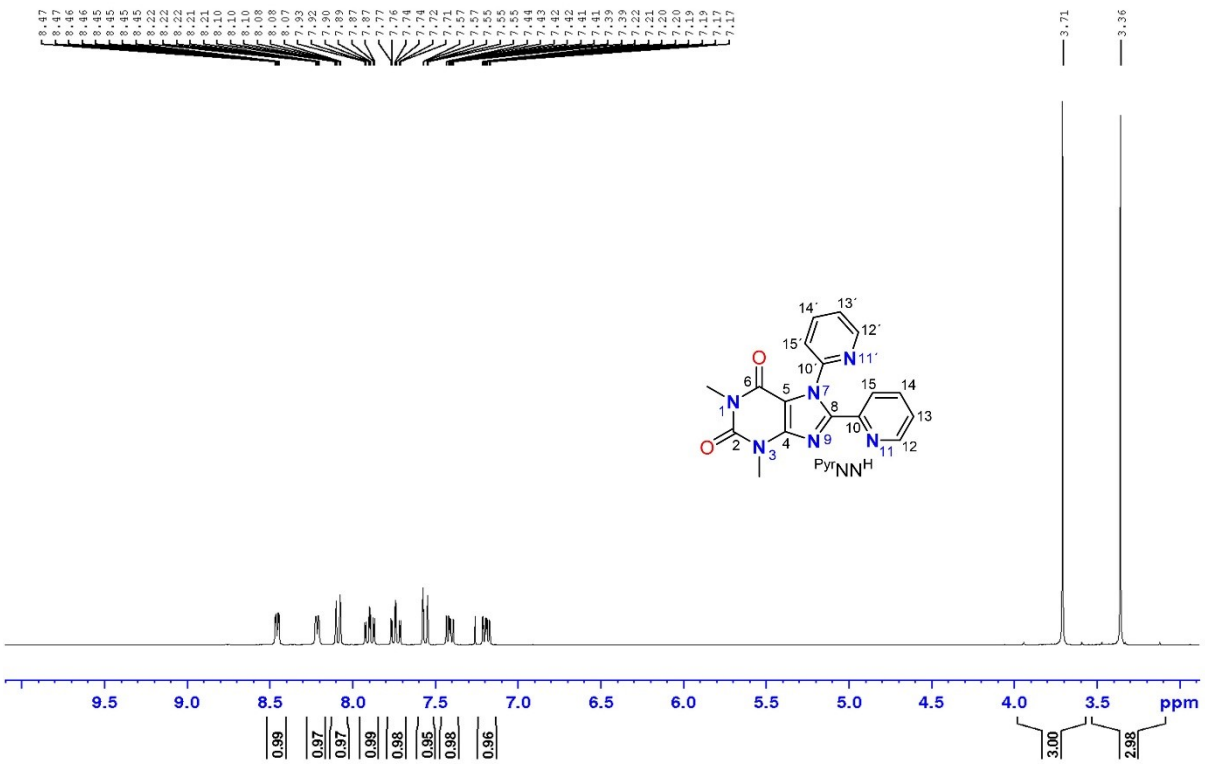


Figure S40. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{Pyr}NN^{H}$.

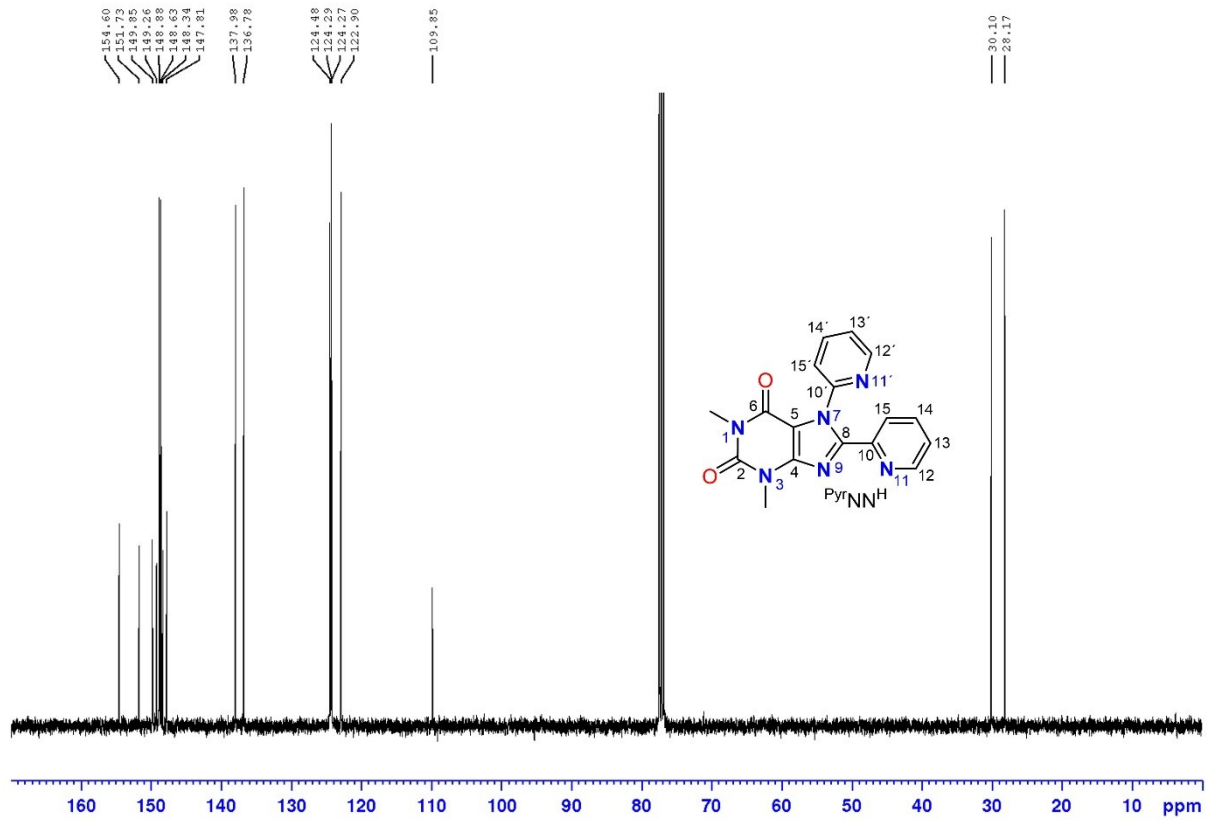


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{Pyr}NN^{H}$.

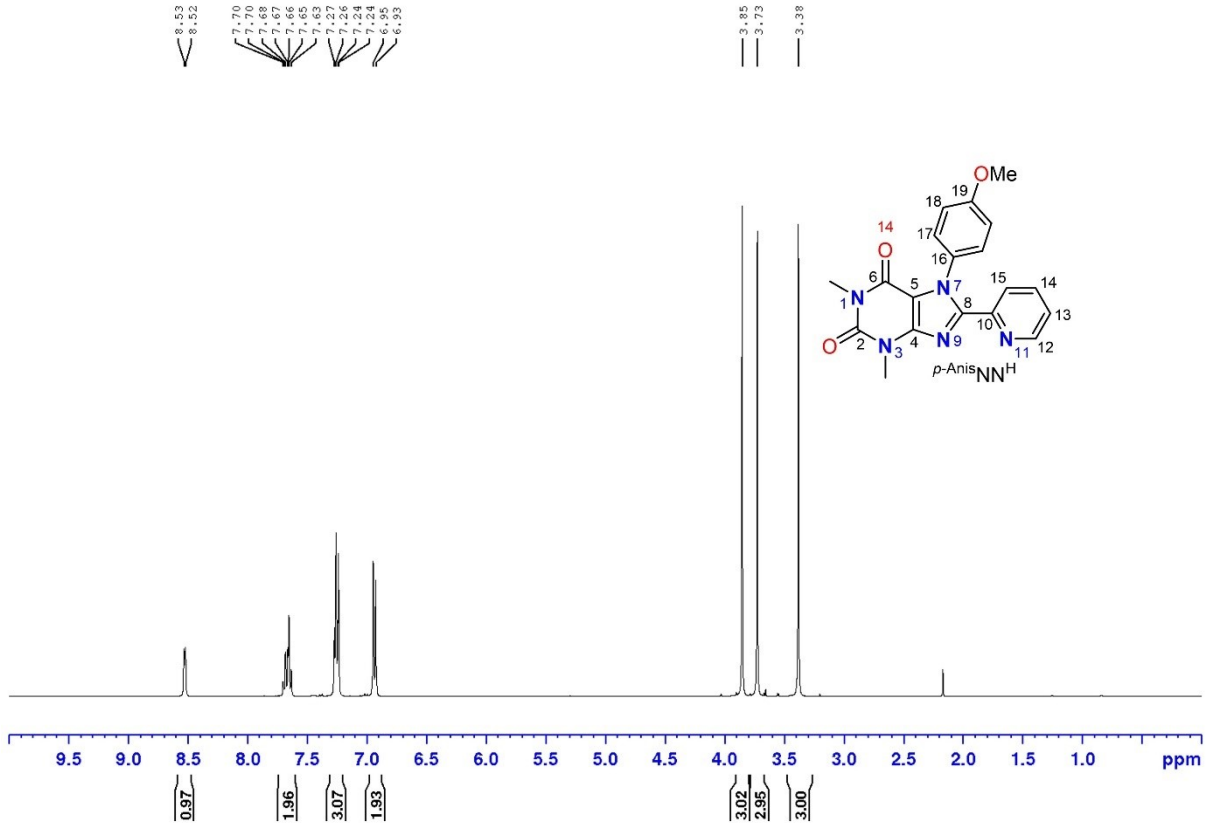


Figure S42. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{p\text{-Anis}}NN^{H}$.

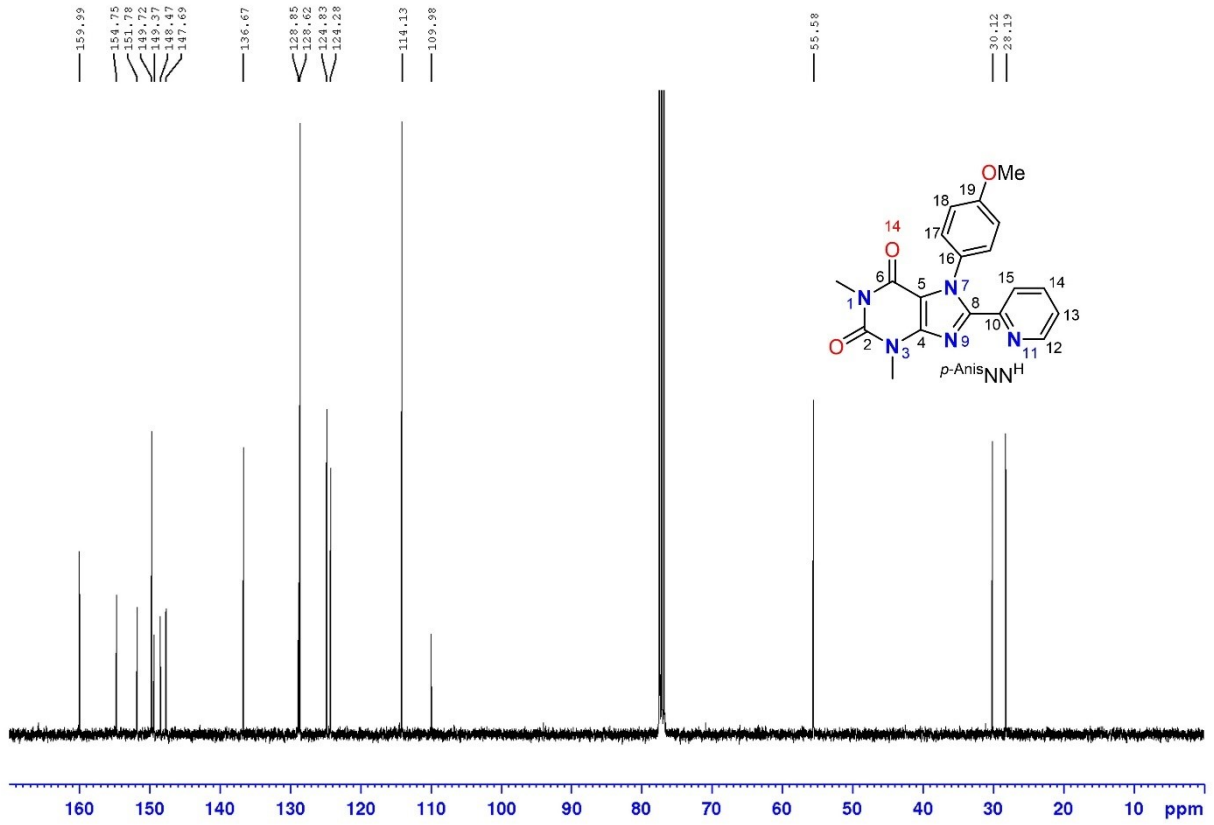


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{p\text{-Anis}}NN^{H}$.

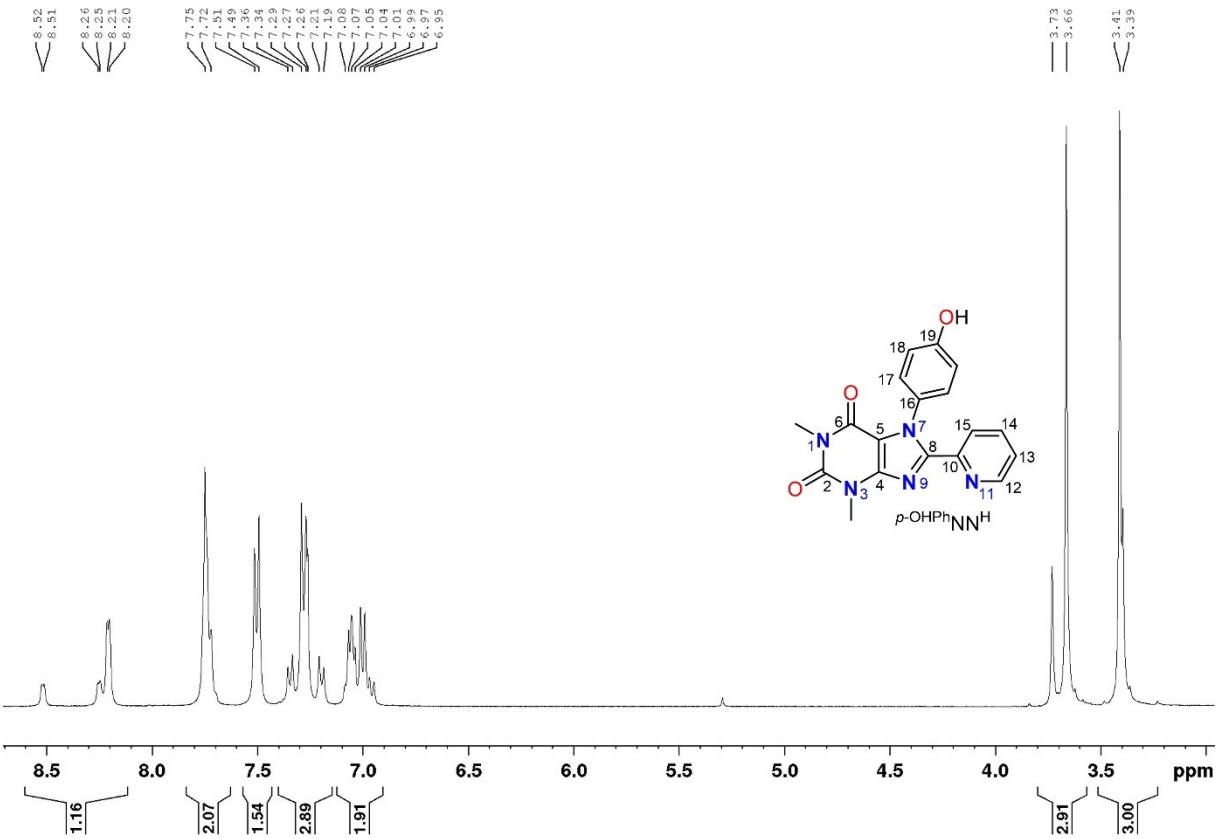


Figure S44. ^{1}H NMR spectrum (400.3 MHz, DMSO-d_6) of the ligand $^{p\text{-OHPh}}$NN^{H}.

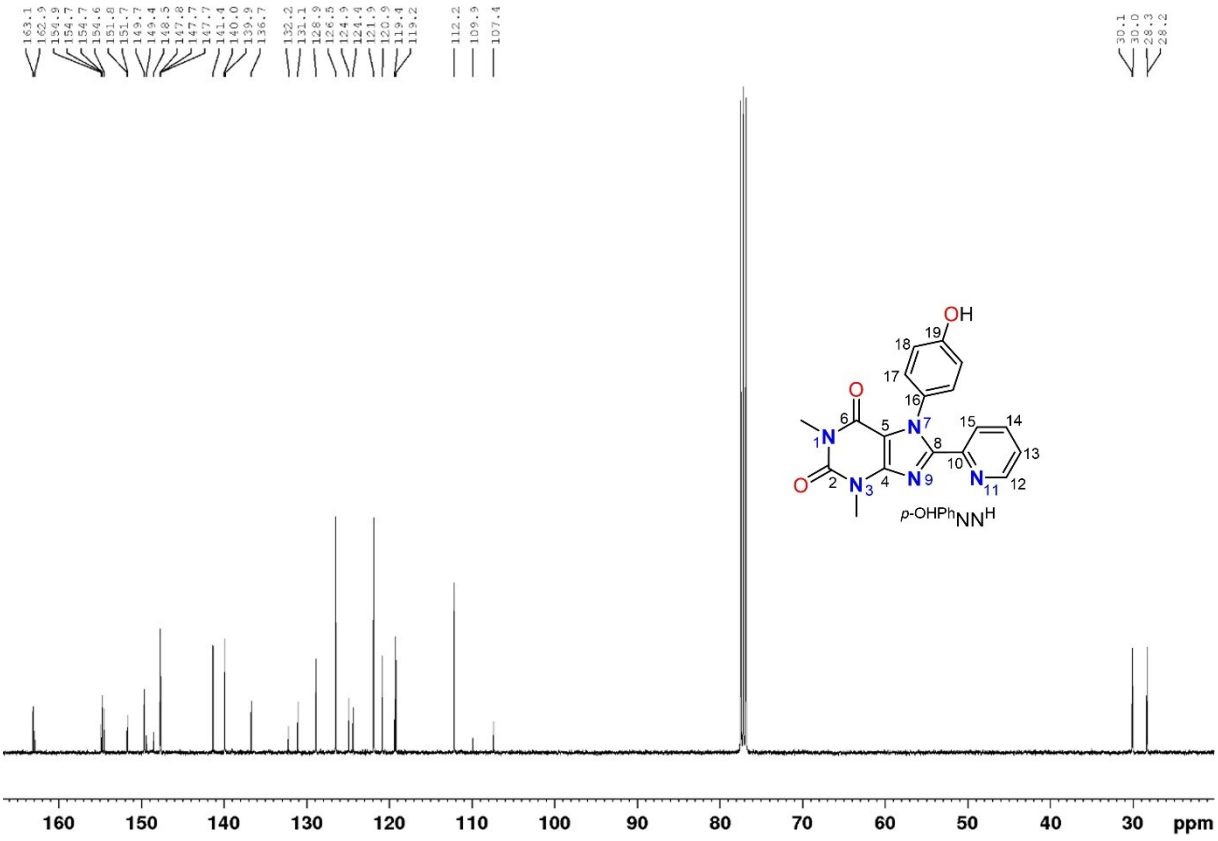


Figure S45. ^{13}C{^{1}H} NMR spectrum (100.7 MHz, DMSO-d_6) of the ligand $^{p\text{-OHPh}}$NN^{H}.

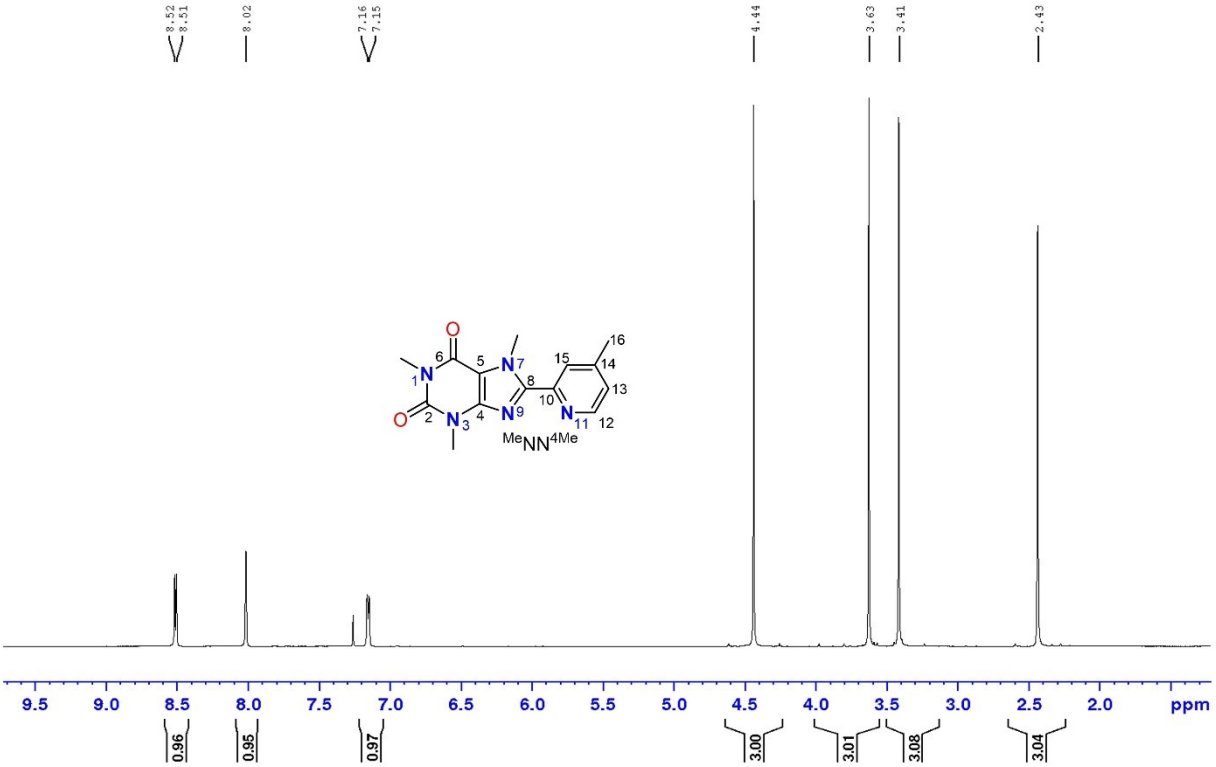


Figure S46. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{Me}NN^{4Me}$.

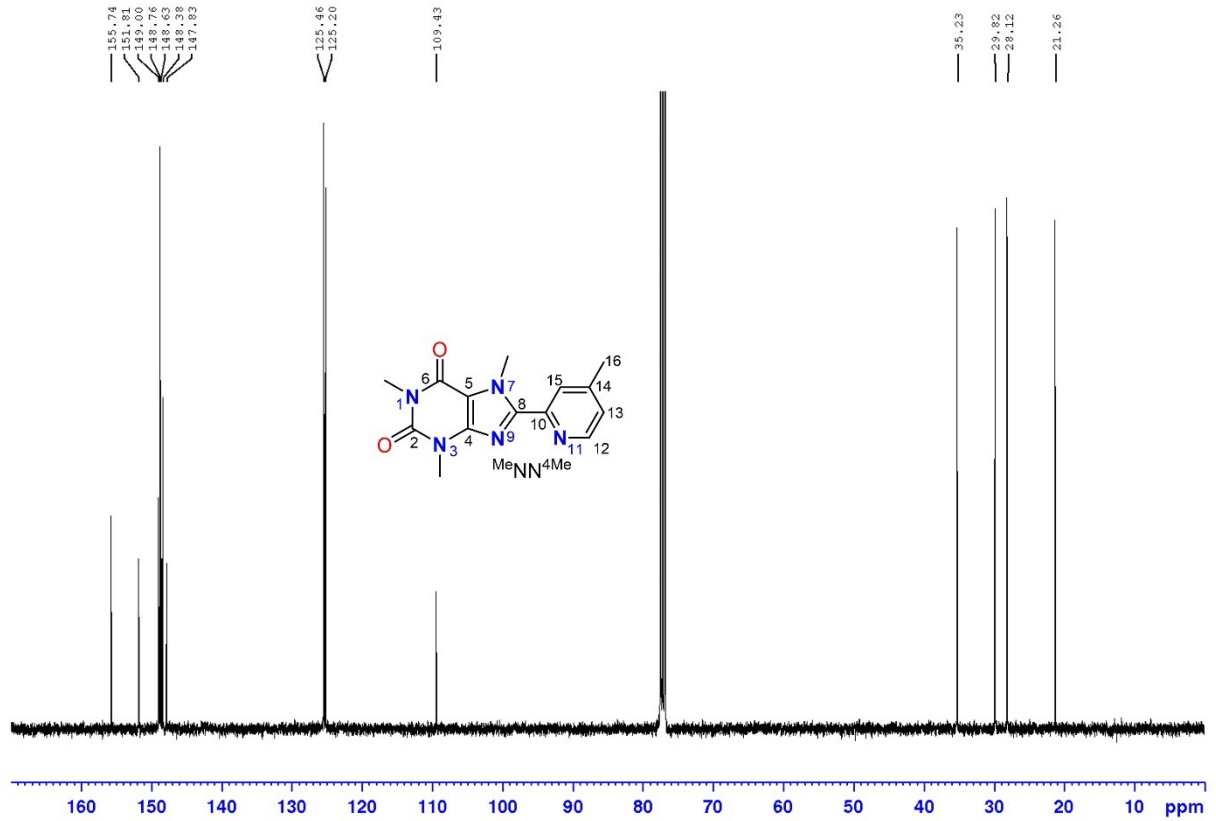


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{Me}NN^{4Me}$.

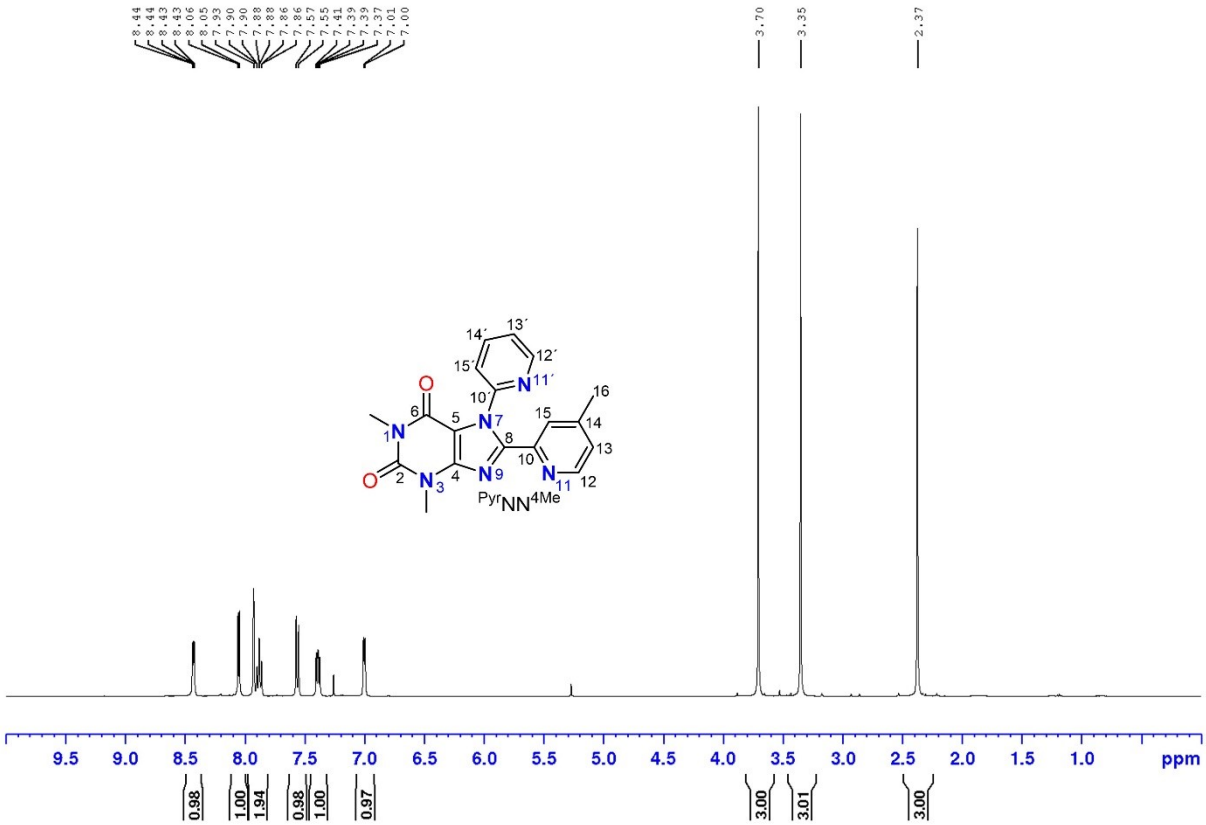


Figure S48. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{Pyr}NN^{4Me}$.

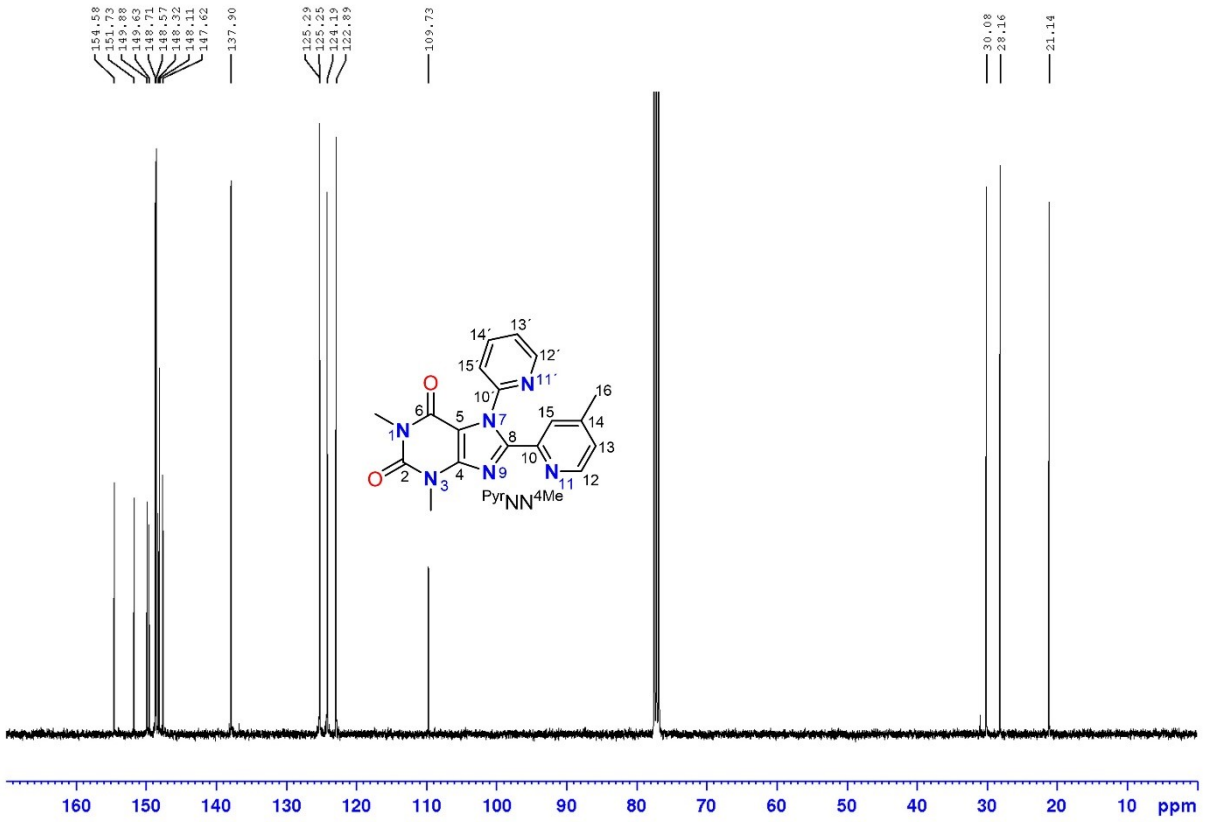


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{Pyr}NN^{4Me}$.

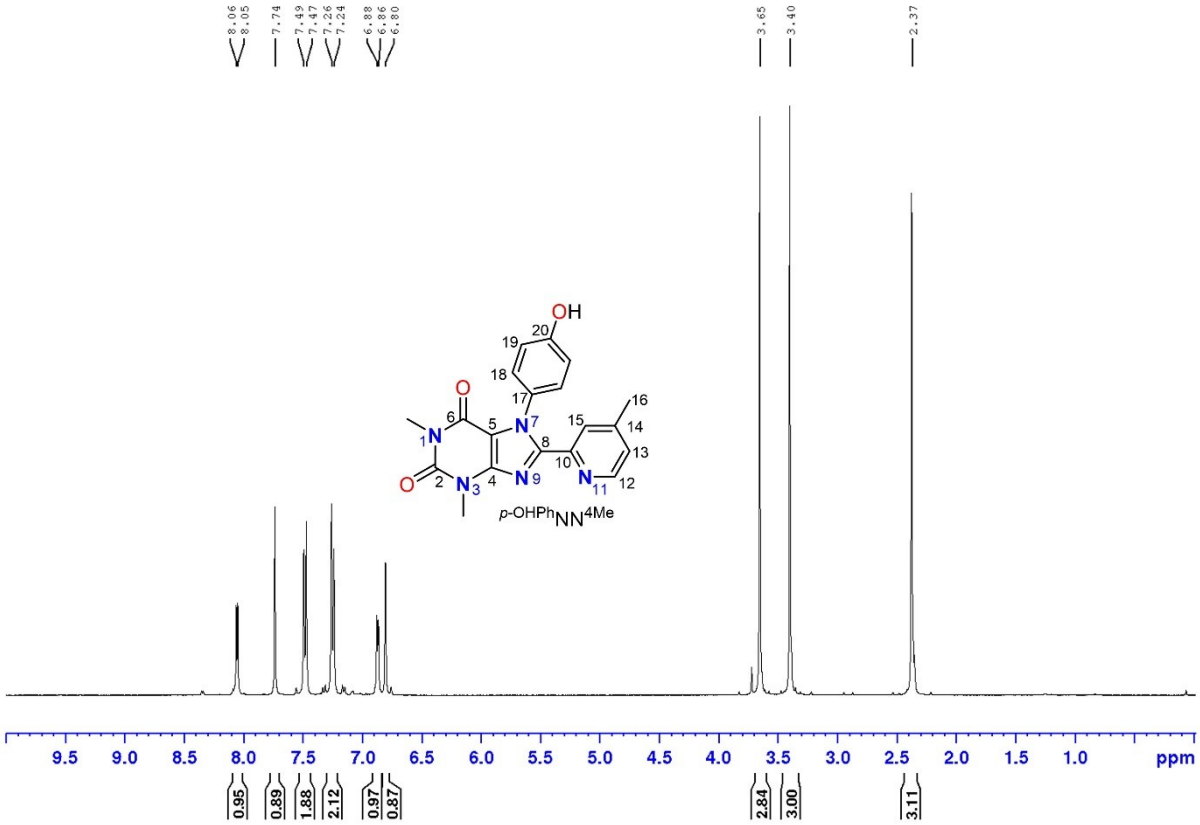


Figure S50. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{p\text{-}OHPh}NN^{4Me}$.

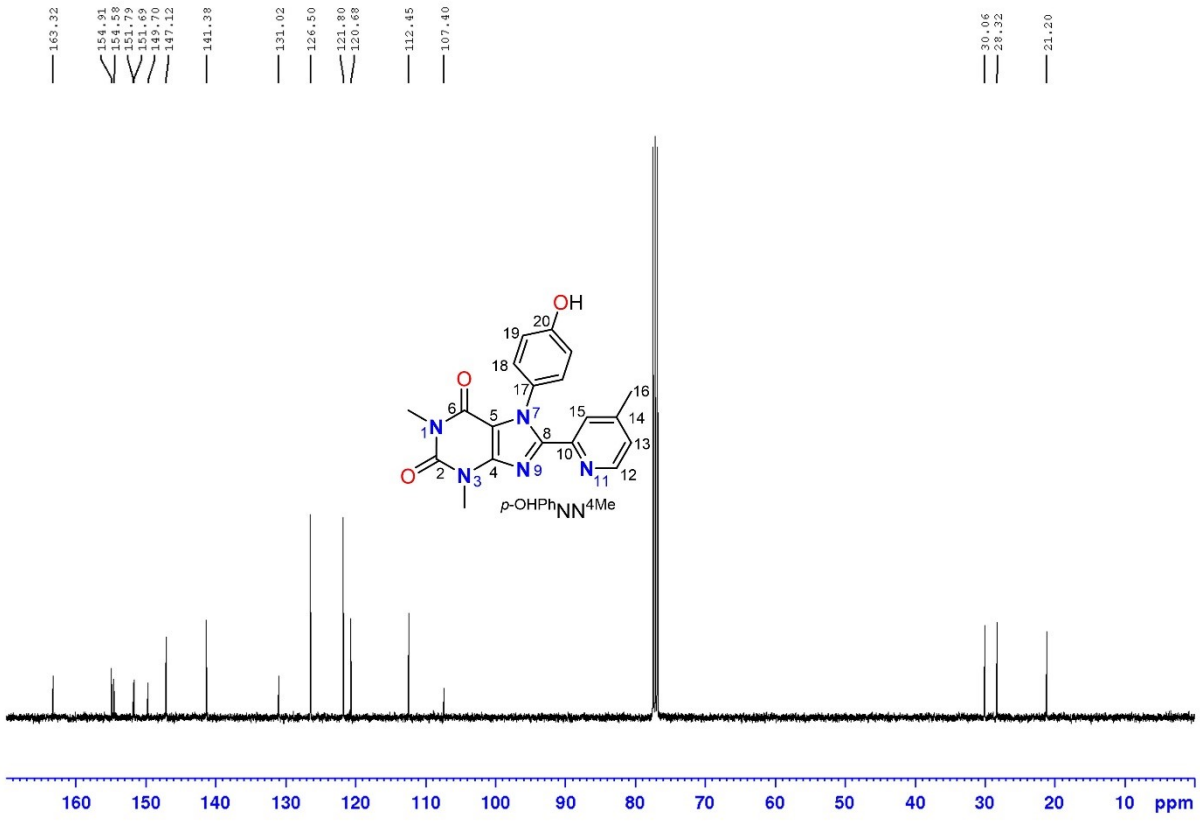


Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{p\text{-}OHPh}NN^{4Me}$.

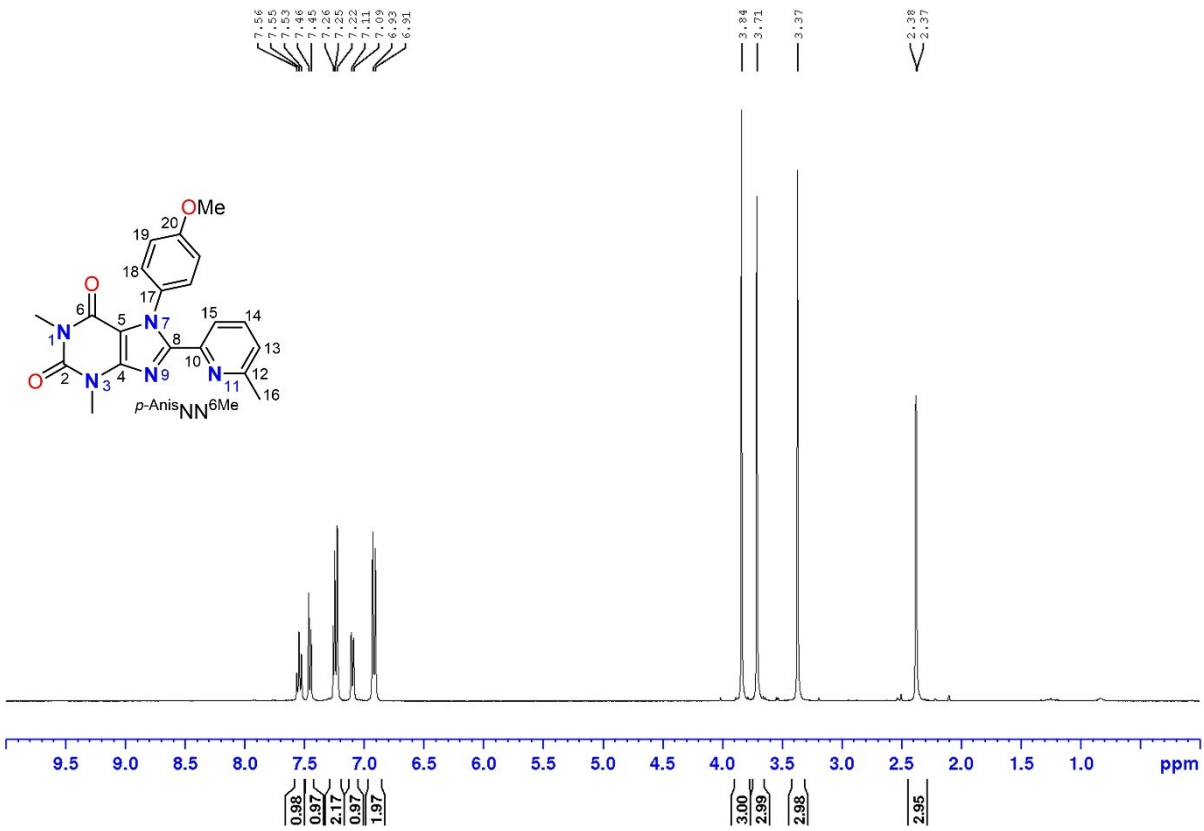


Figure S52. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the ligand $^{p\text{-Anis}}NN^{6Me}$.

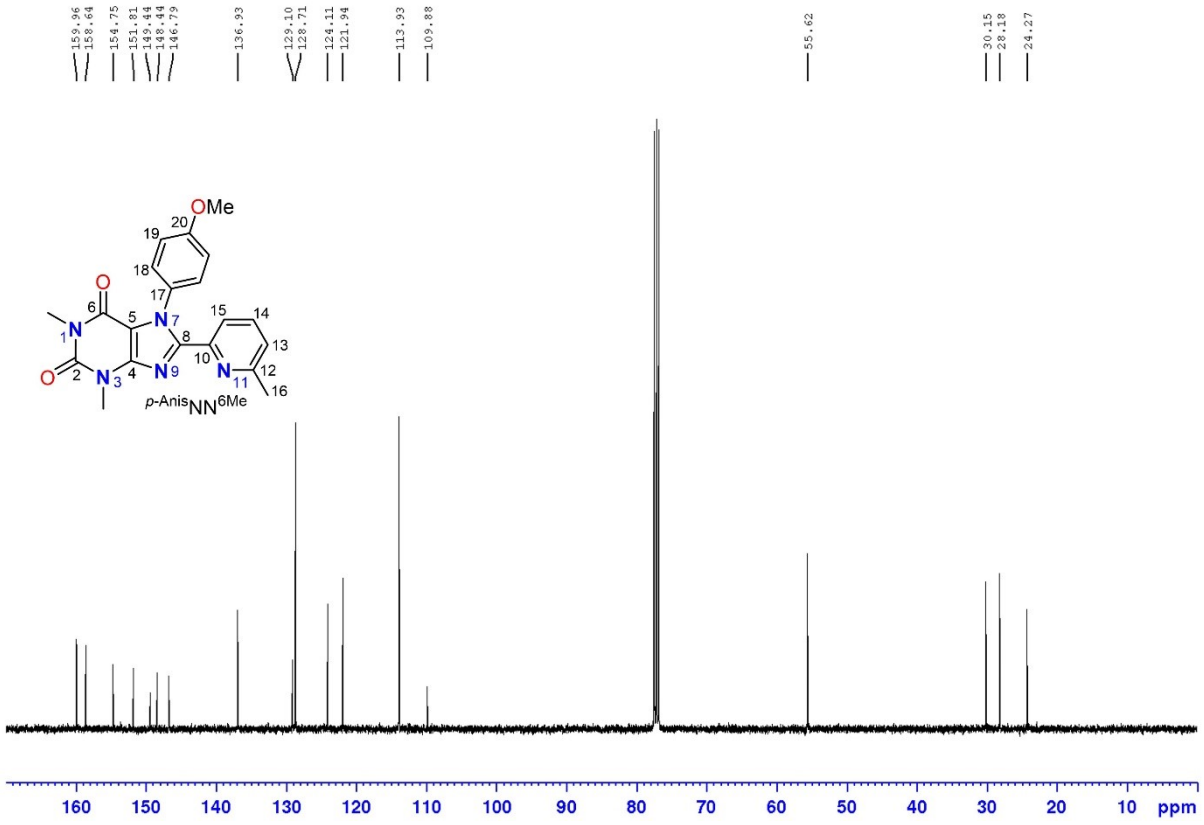


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, $CDCl_3$) of the ligand $^{p\text{-Anis}}NN^{6Me}$.

Isolated aryls esters 3a-z

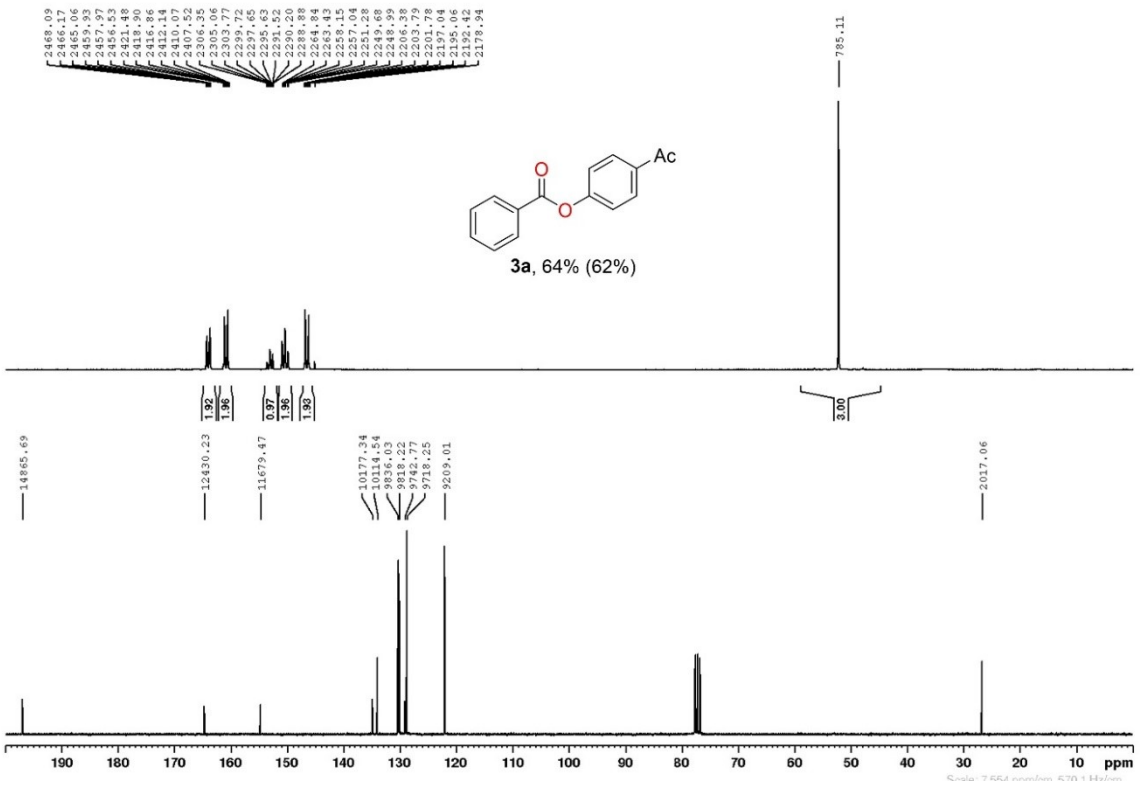


Figure S54. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3a** in $CDCl_3$.

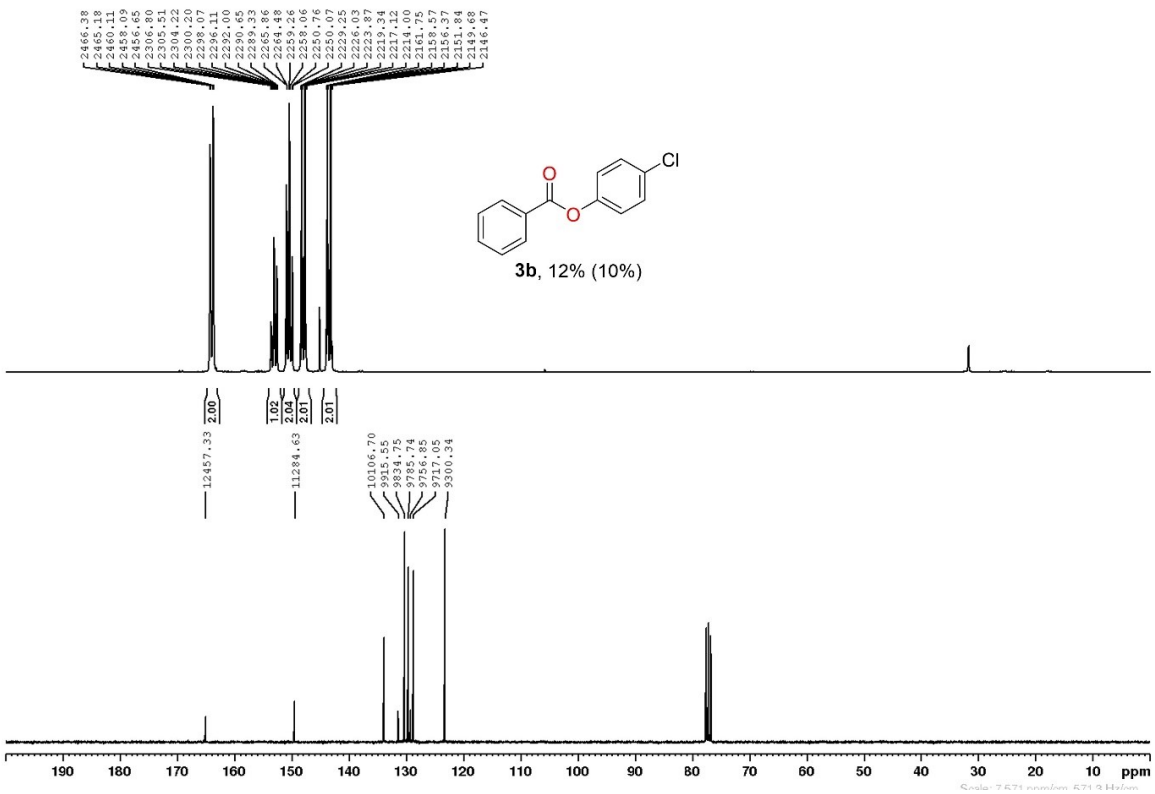


Figure S55. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3b** in $CDCl_3$.

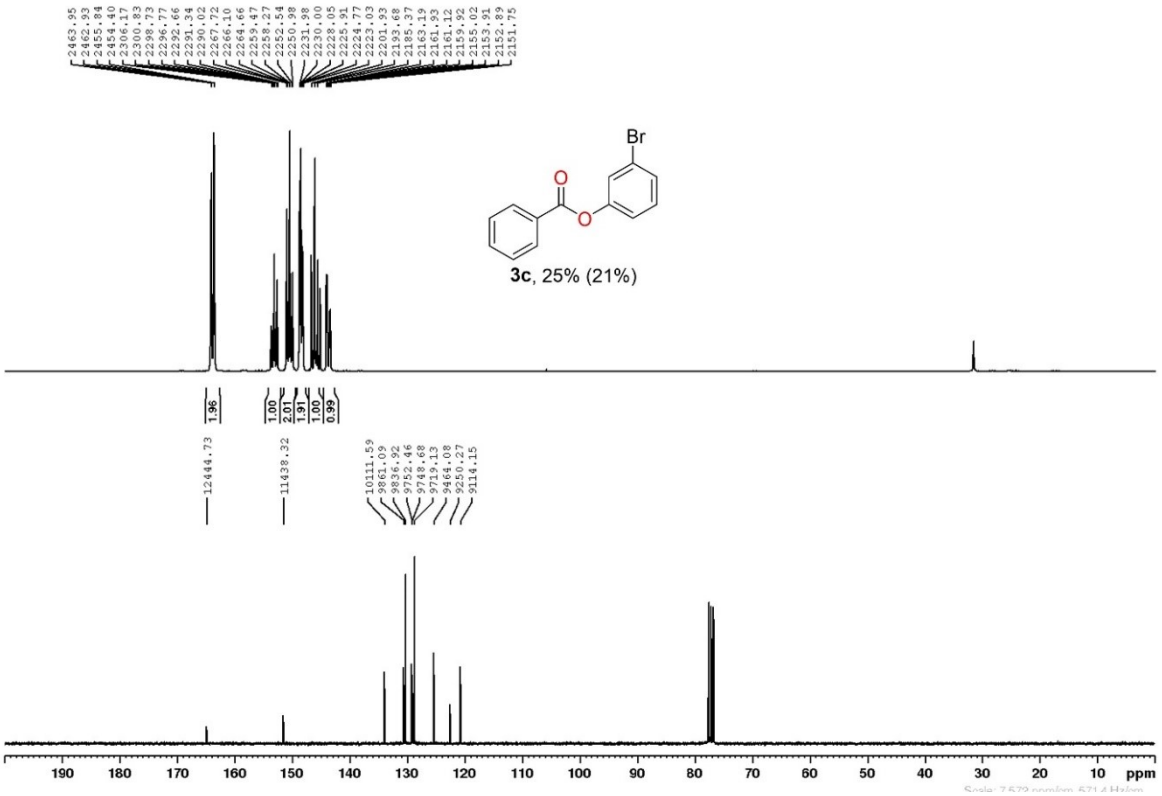


Figure S56. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3c** in $CDCl_3$.

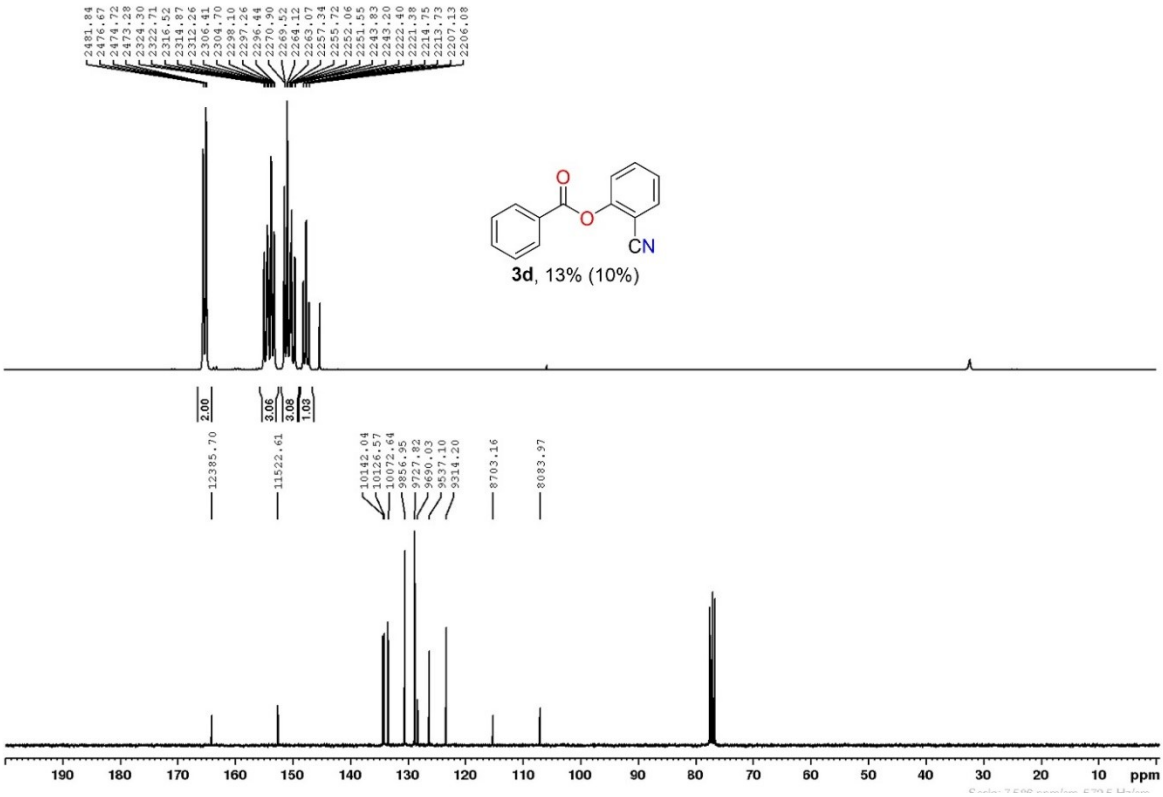


Figure S57. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3d** in $CDCl_3$.

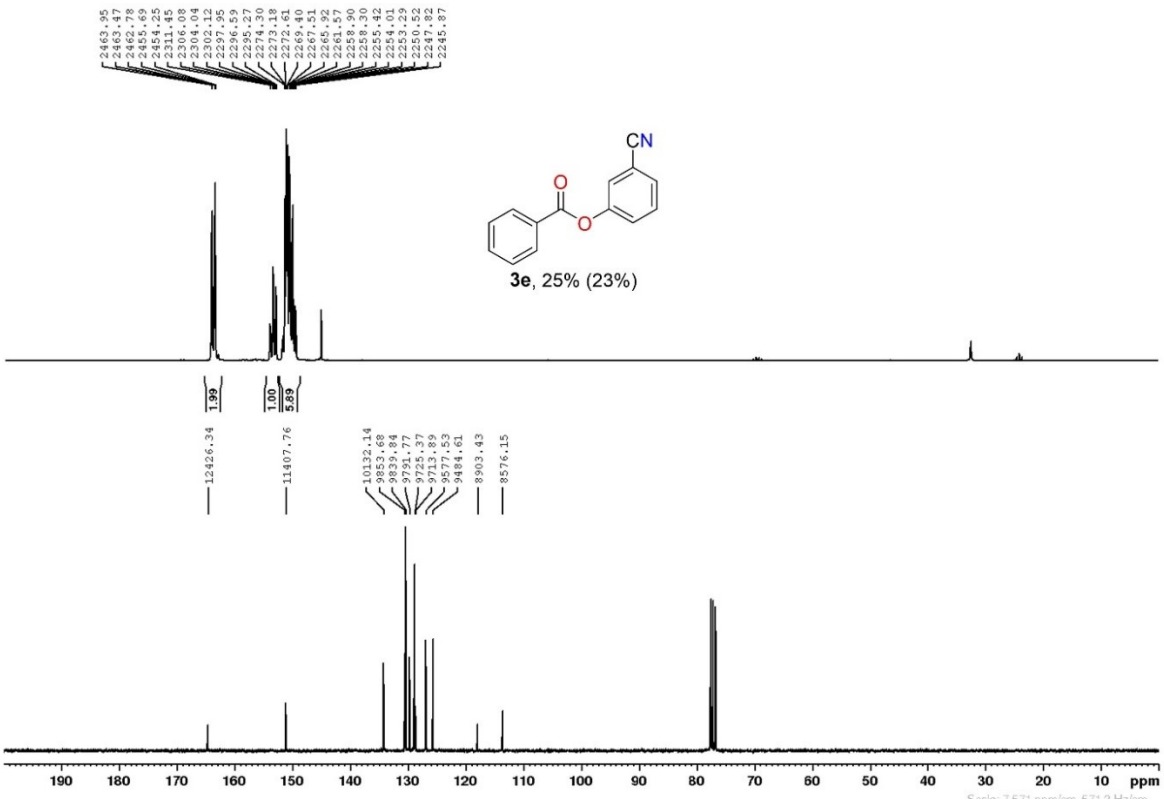


Figure S58. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3e** in $CDCl_3$.

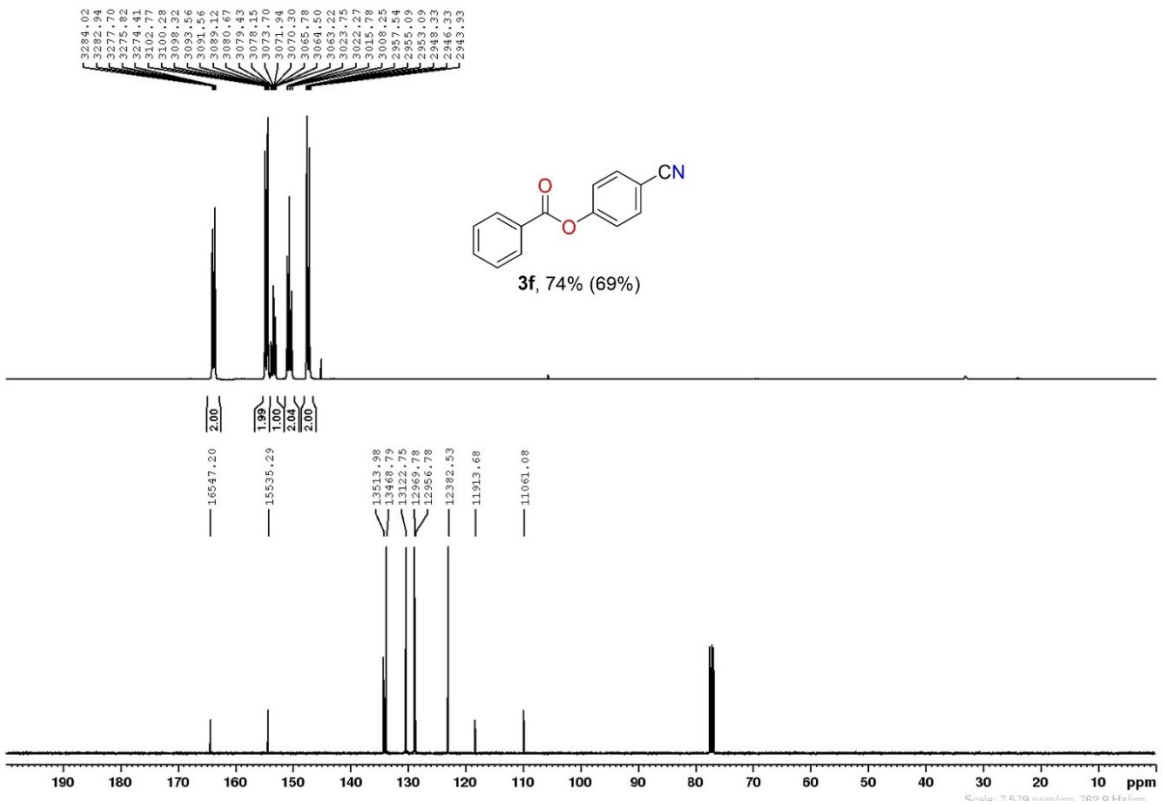


Figure S59. ^{1}H (400.3 MHz, top) and $^{13}C\{^{1}H\}$ (100.7 MHz, bottom) NMR spectra of the isolated ester **3f** in $CDCl_3$.

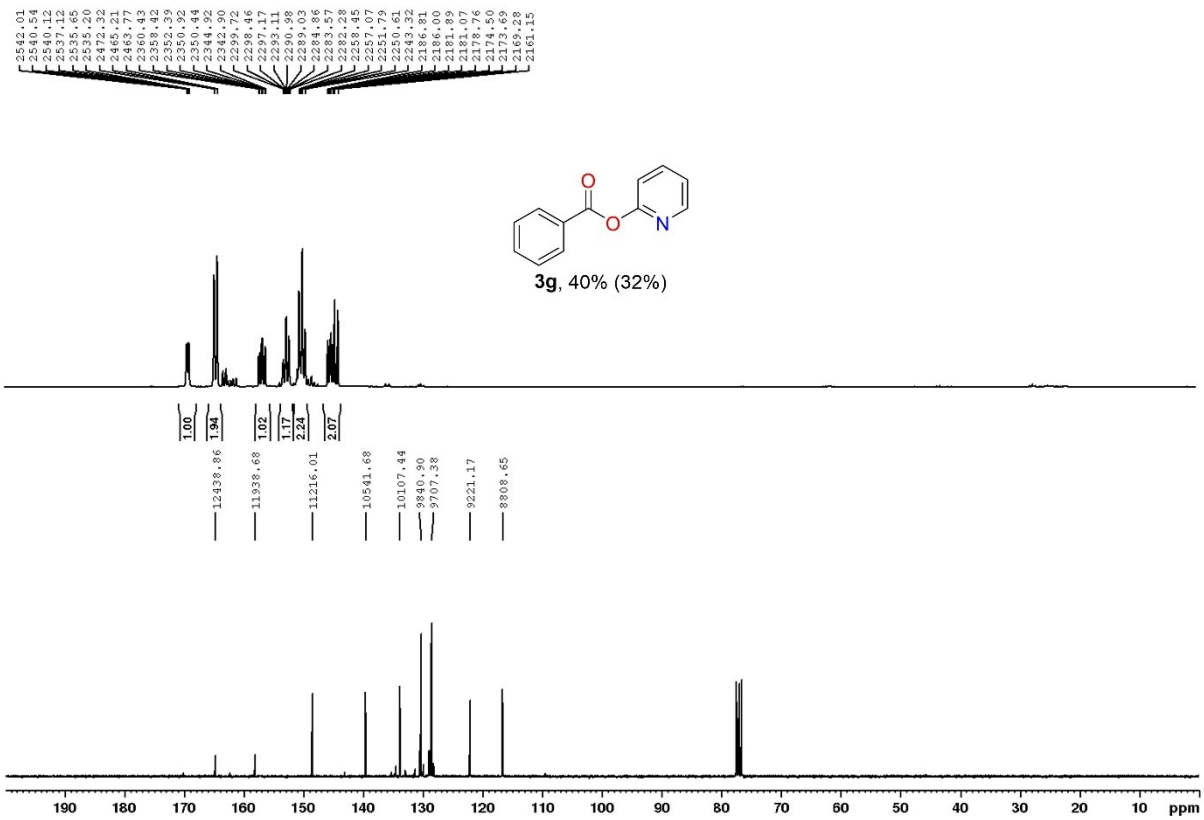


Figure S60. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3g** in $CDCl_3$.

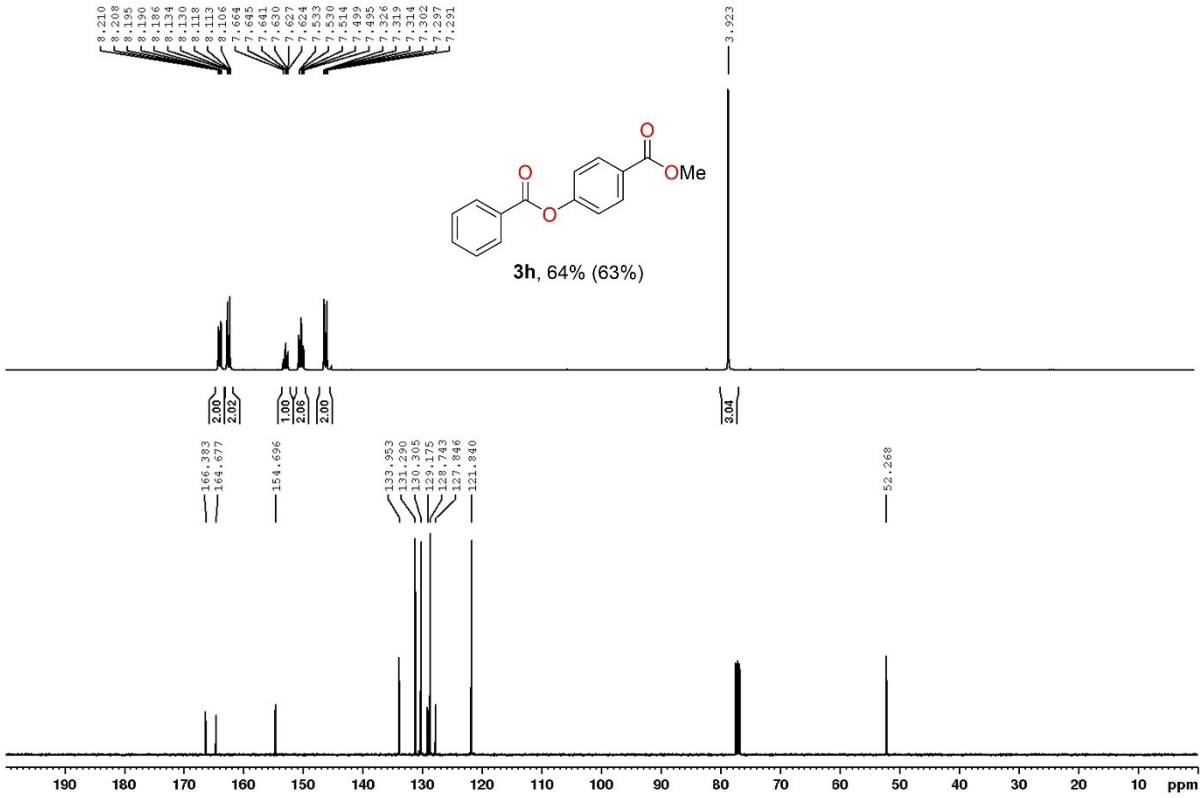


Figure S61. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3g** in $CDCl_3$.

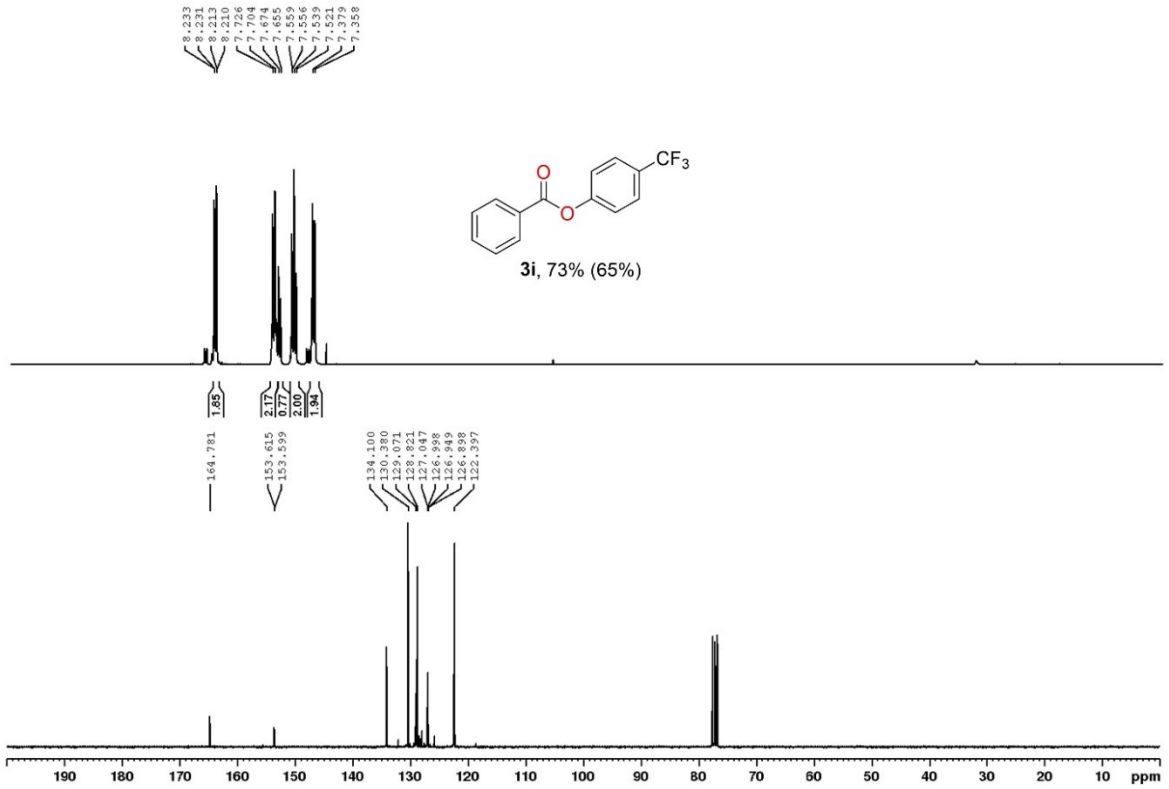


Figure S62. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3i** in $CDCl_3$.

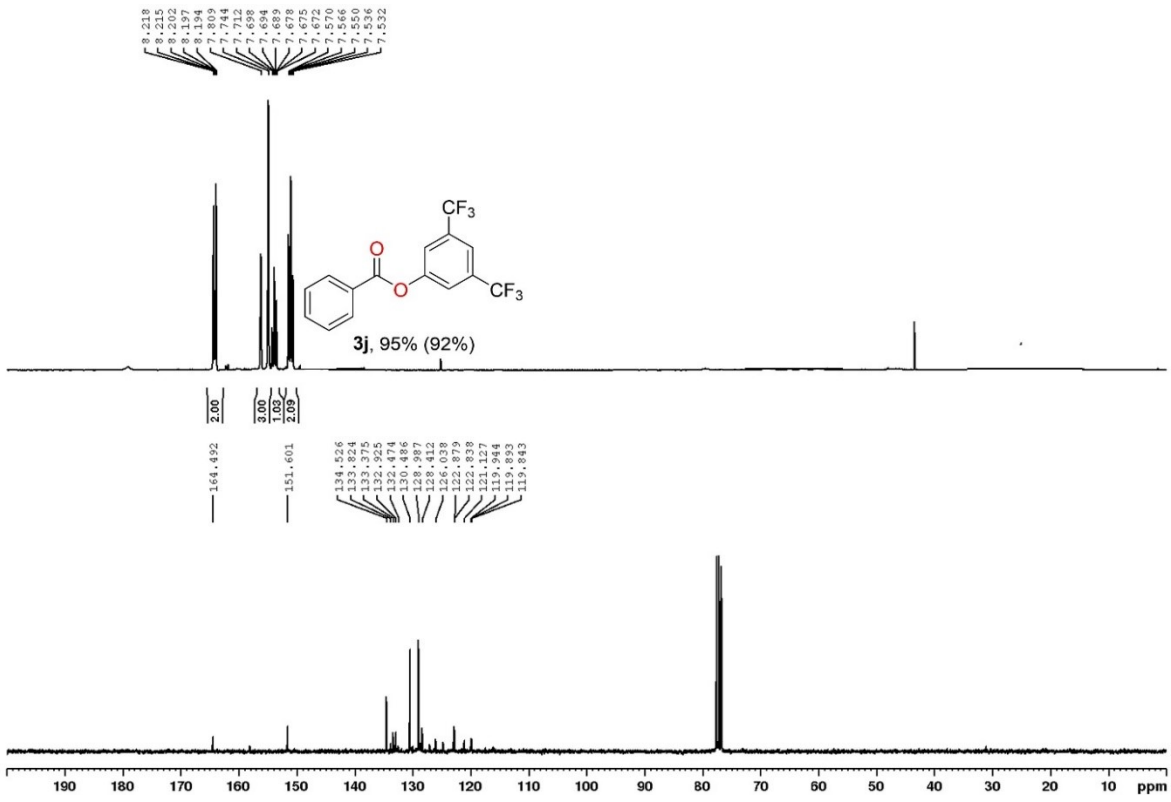


Figure S63. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3j** in $CDCl_3$.

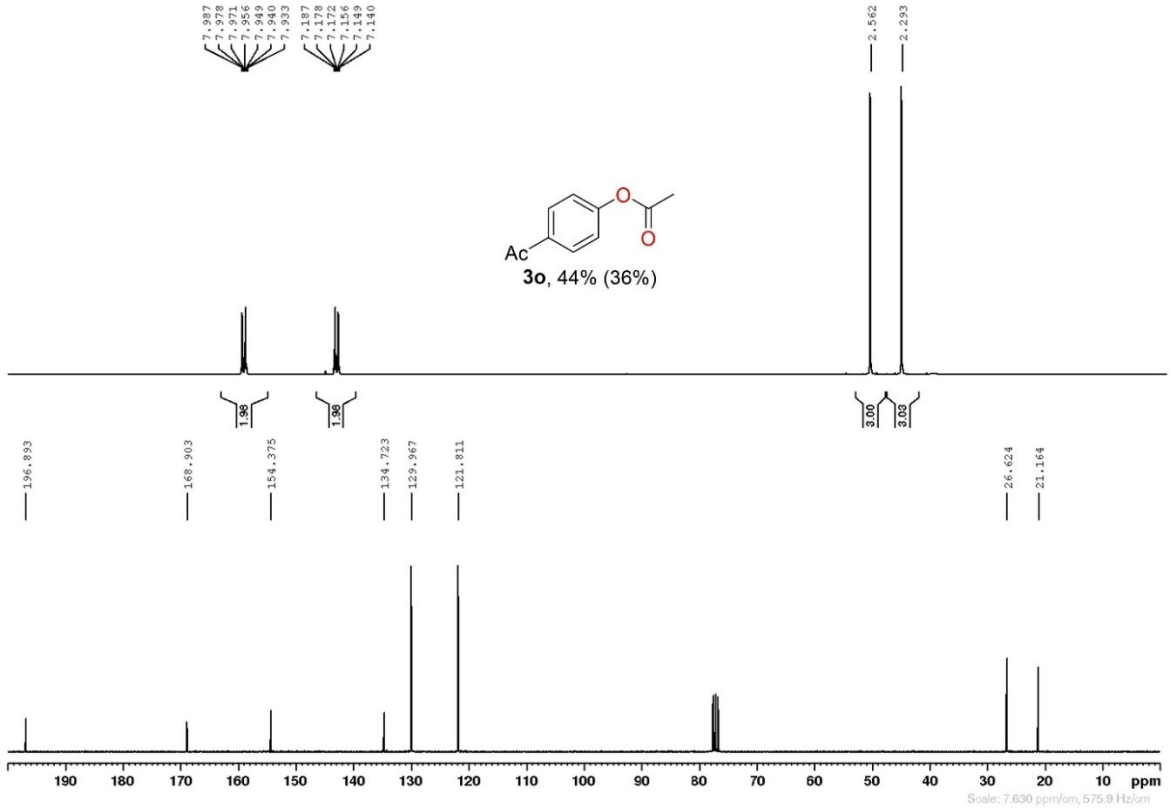


Figure S64. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3o** in $CDCl_3$.

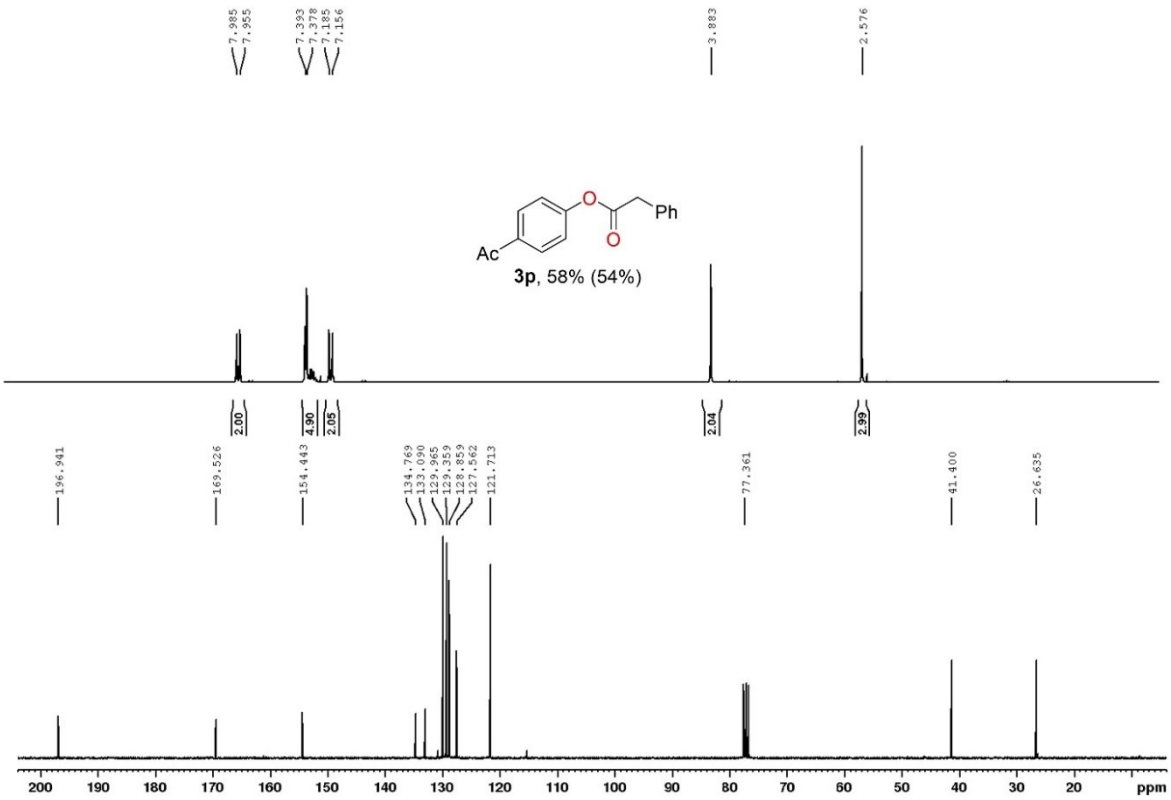


Figure S65. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3p** in $CDCl_3$.

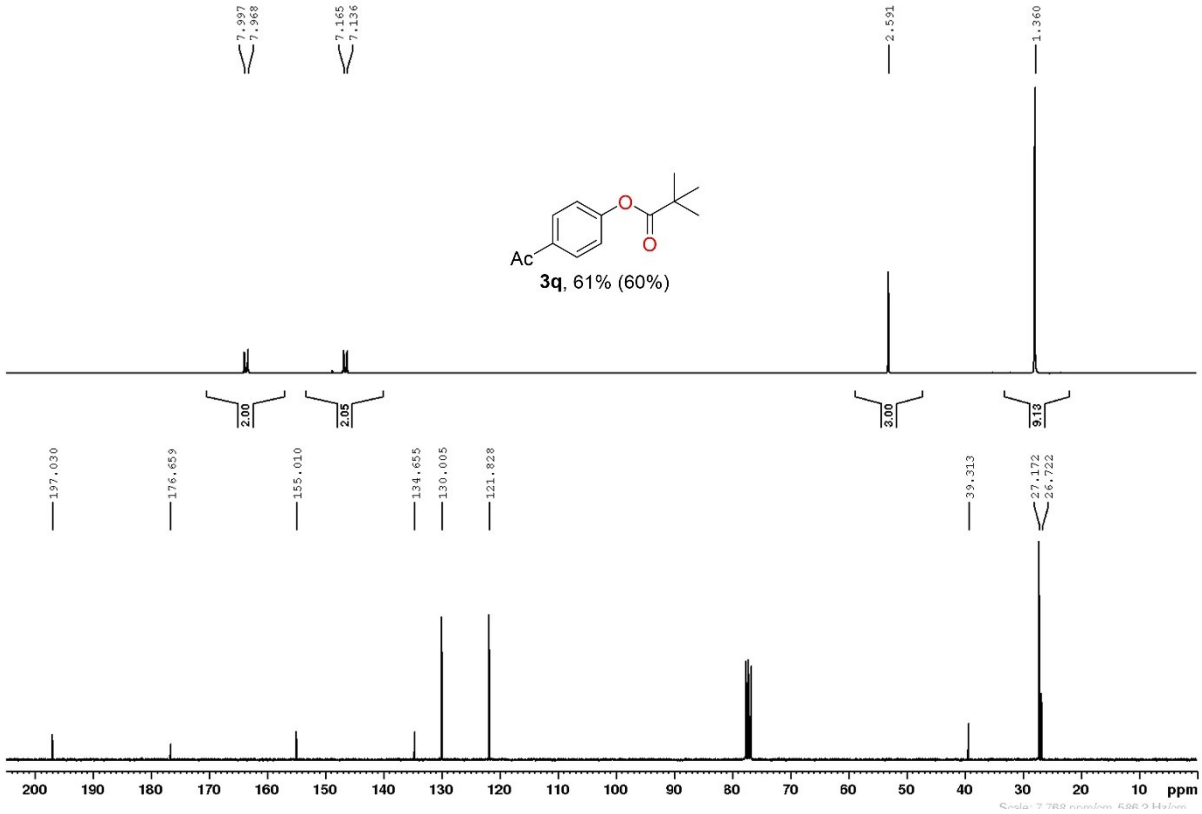


Figure S66. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3q** in $CDCl_3$.

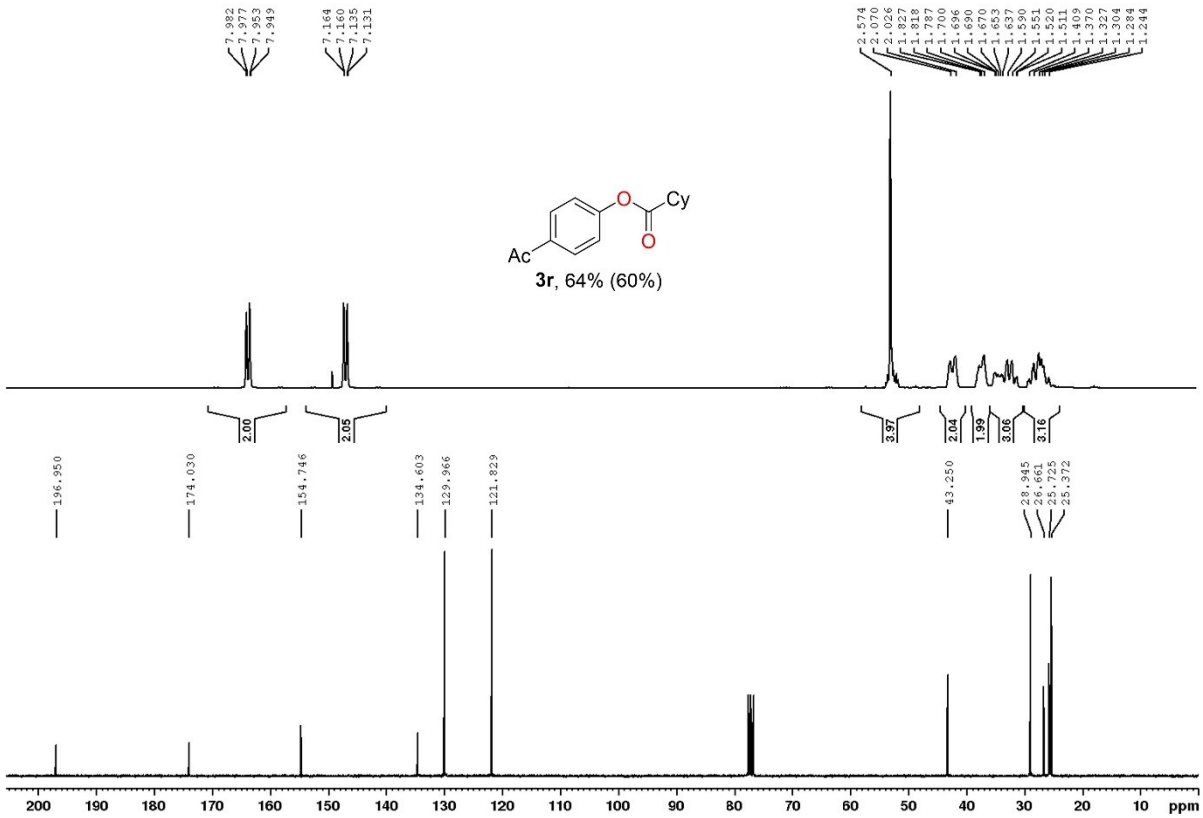


Figure S67. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3r** in $CDCl_3$.

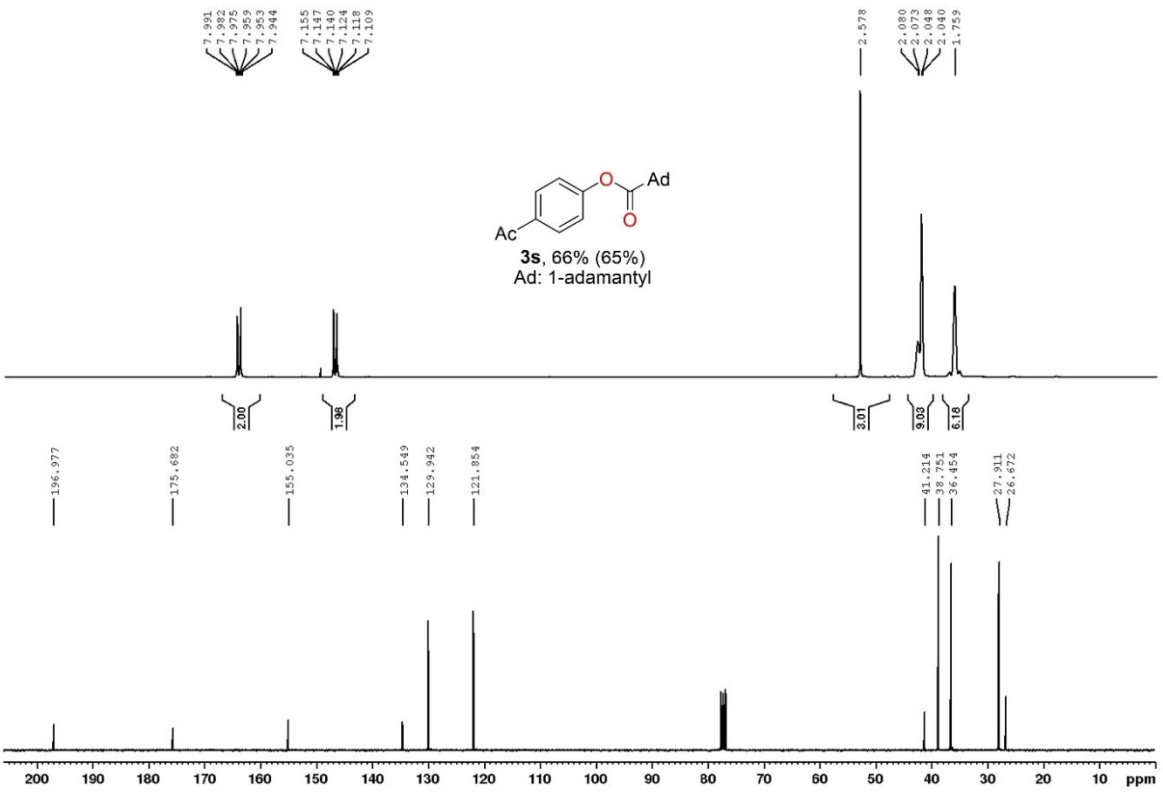


Figure S68. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3s** in $CDCl_3$.

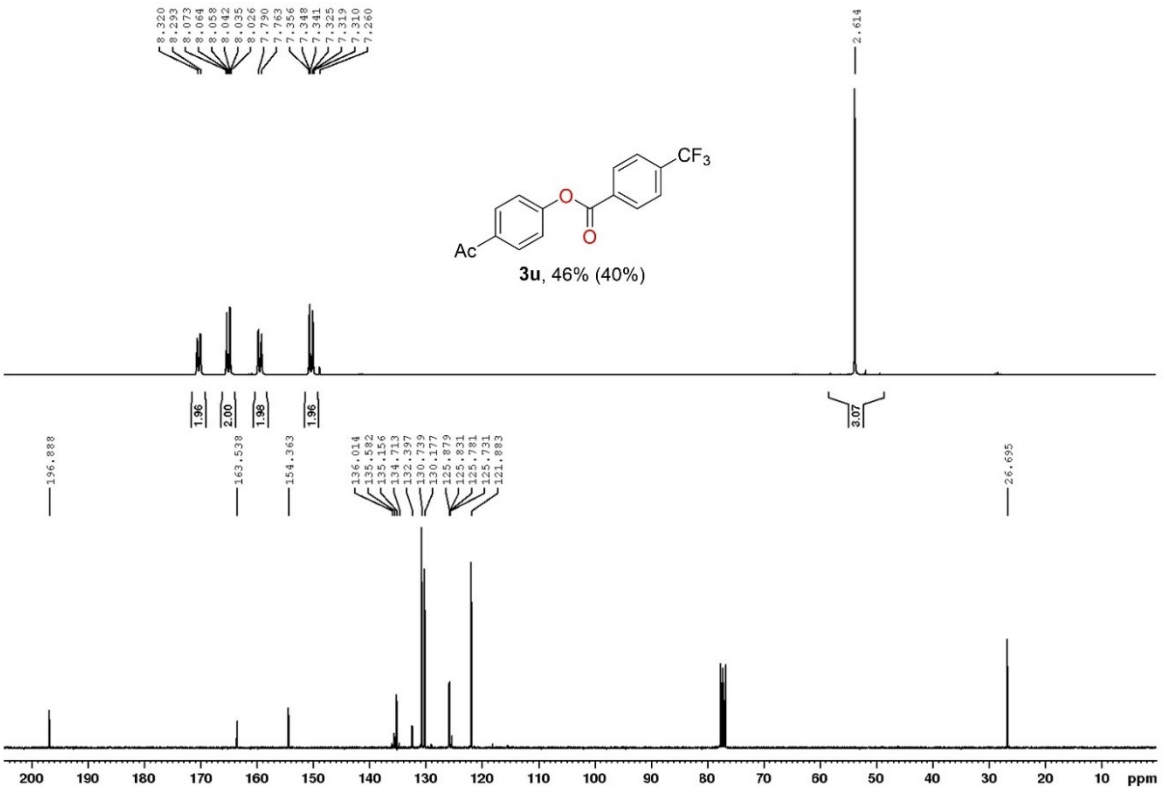


Figure S69. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3u** in $CDCl_3$.

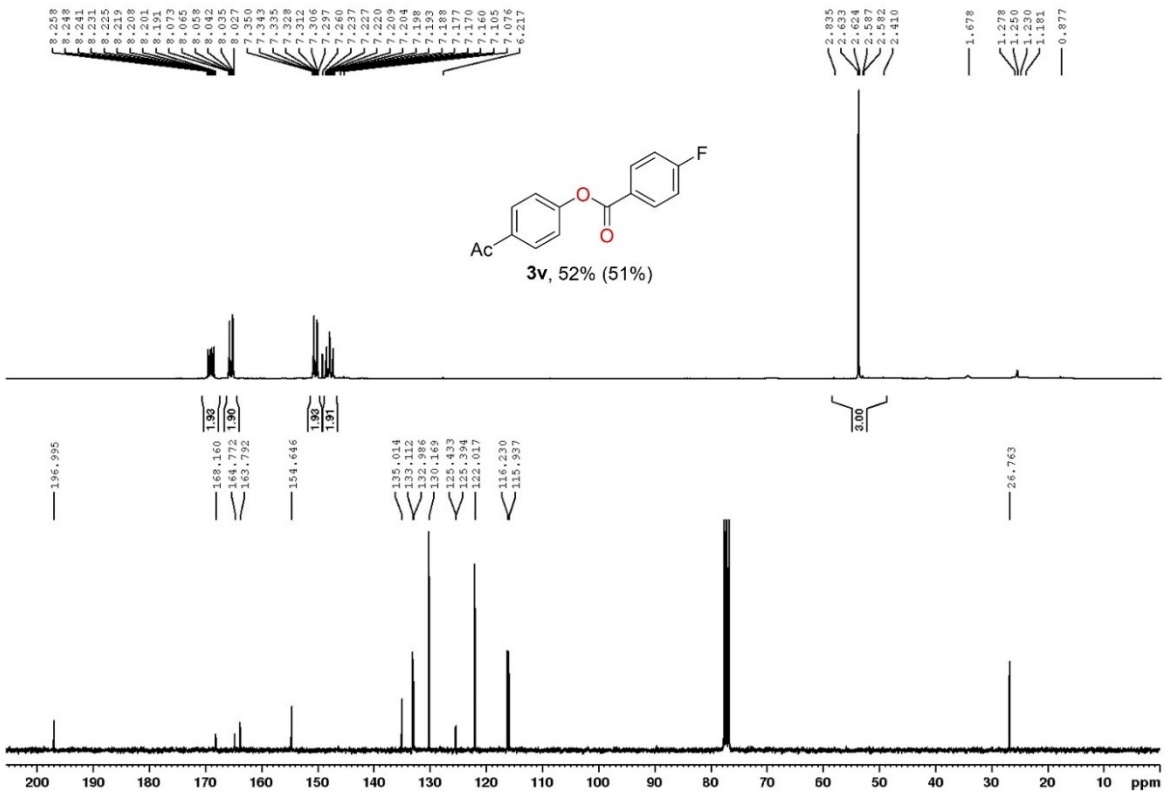


Figure S70. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3v** in $CDCl_3$.

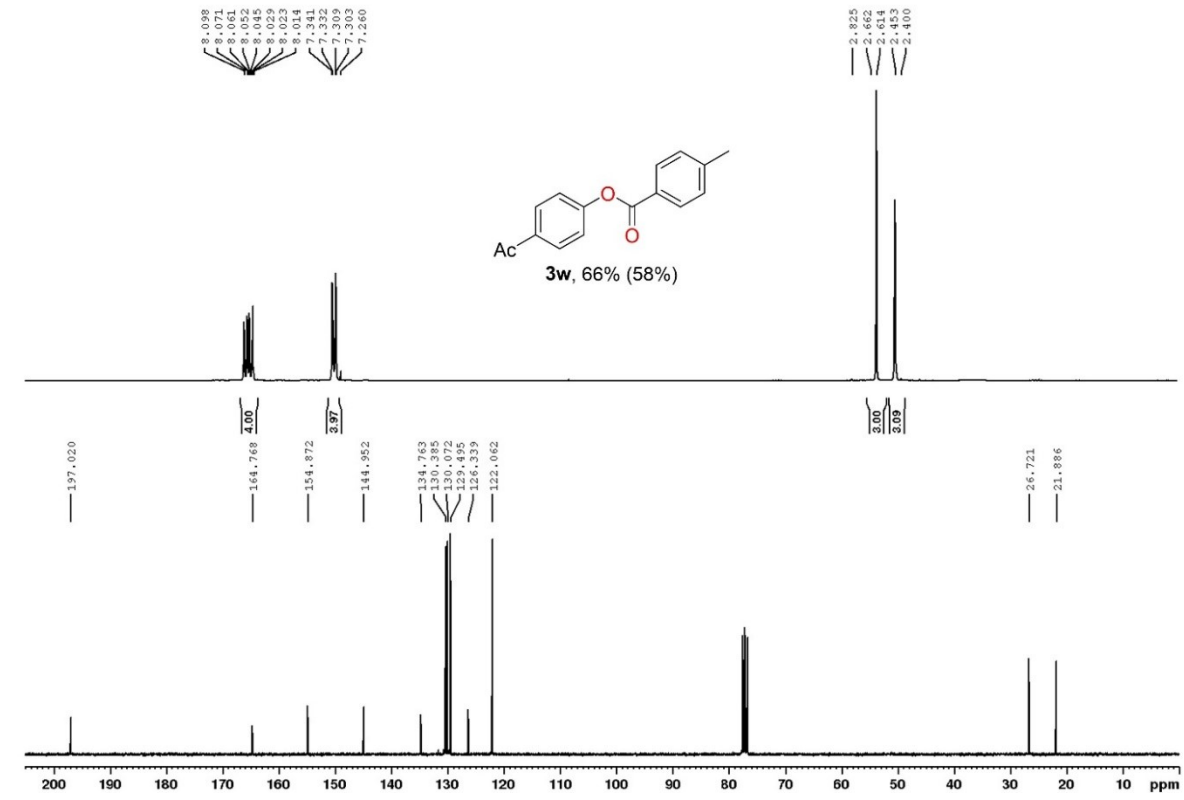


Figure S71. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3w** in $CDCl_3$.

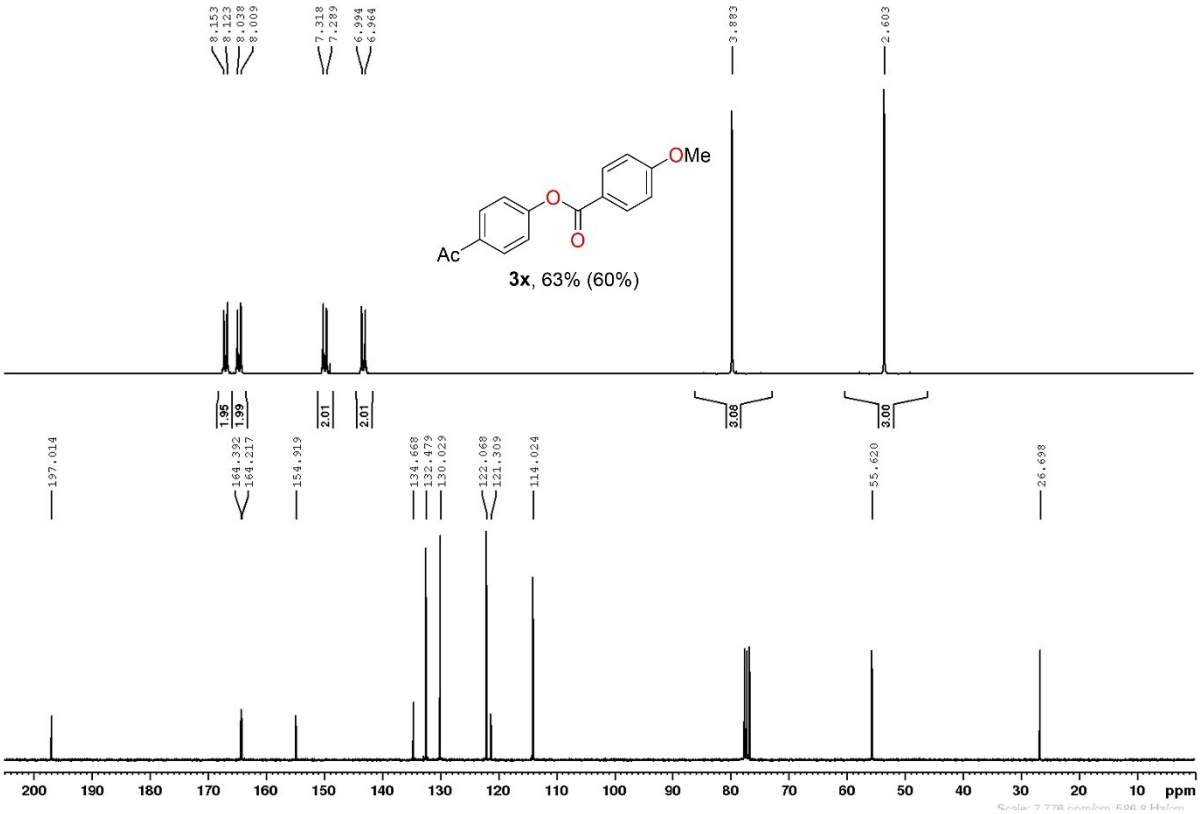


Figure S72. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3x** in $CDCl_3$.

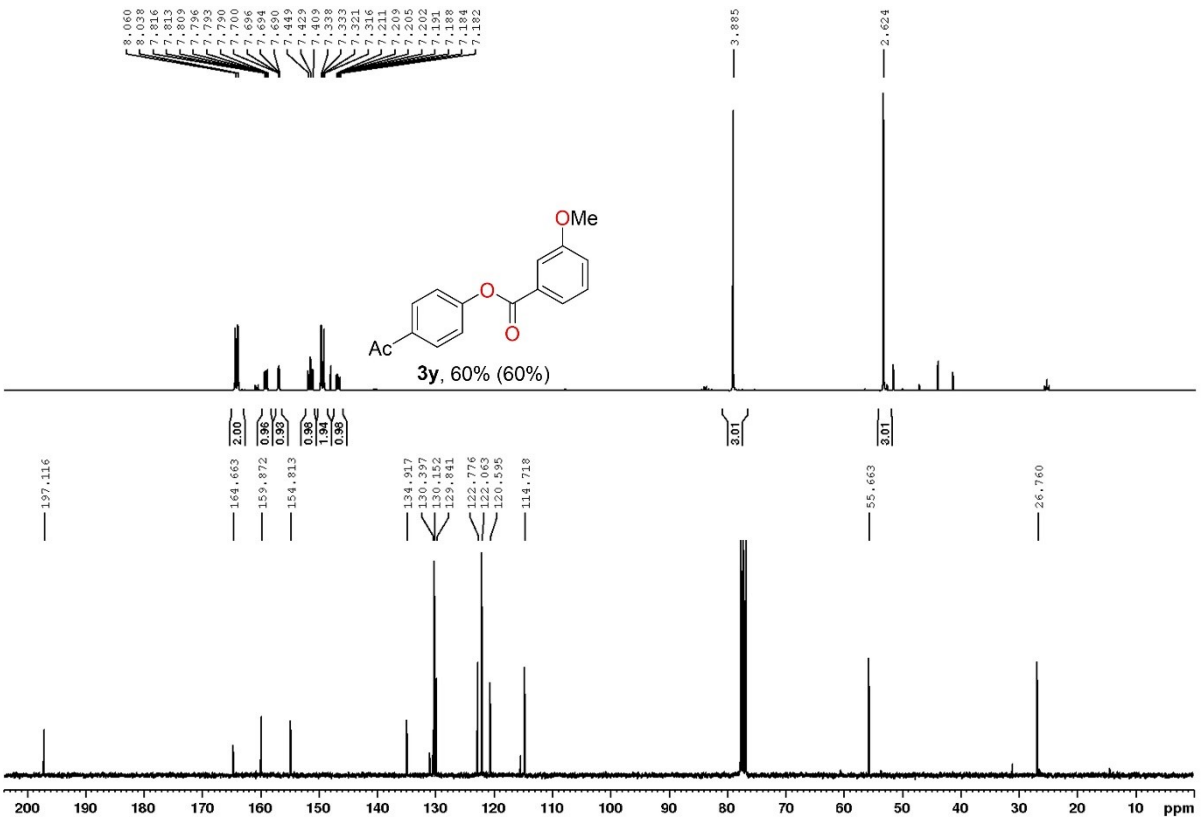


Figure S73. ^{1}H (300.1 MHz, top) and $^{13}C\{^{1}H\}$ (75.5 MHz, bottom) NMR spectra of the isolated ester **3y** in $CDCl_3$.

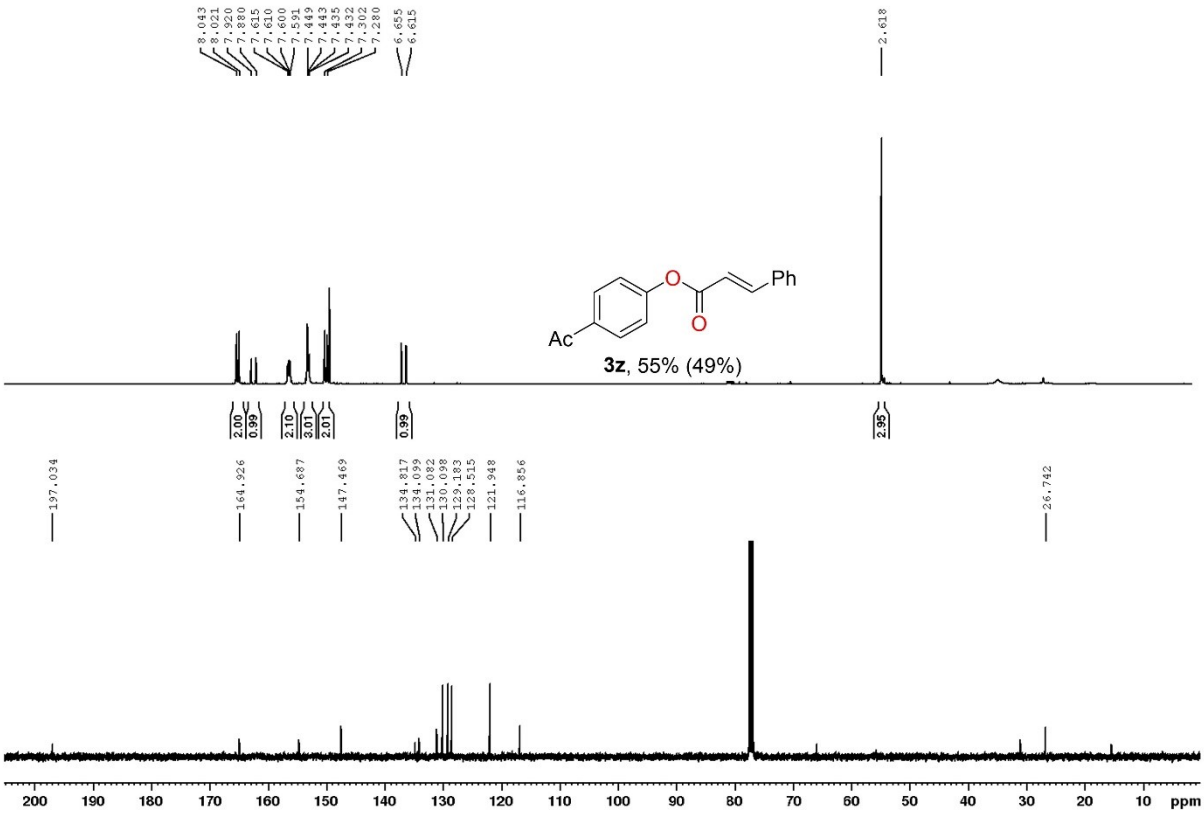


Figure S74. ^{1}H (400.3 MHz, top) and $^{13}C\{^{1}H\}$ (100.7 MHz, bottom) NMR spectra of the isolated ester **3z** in $CDCl_3$.

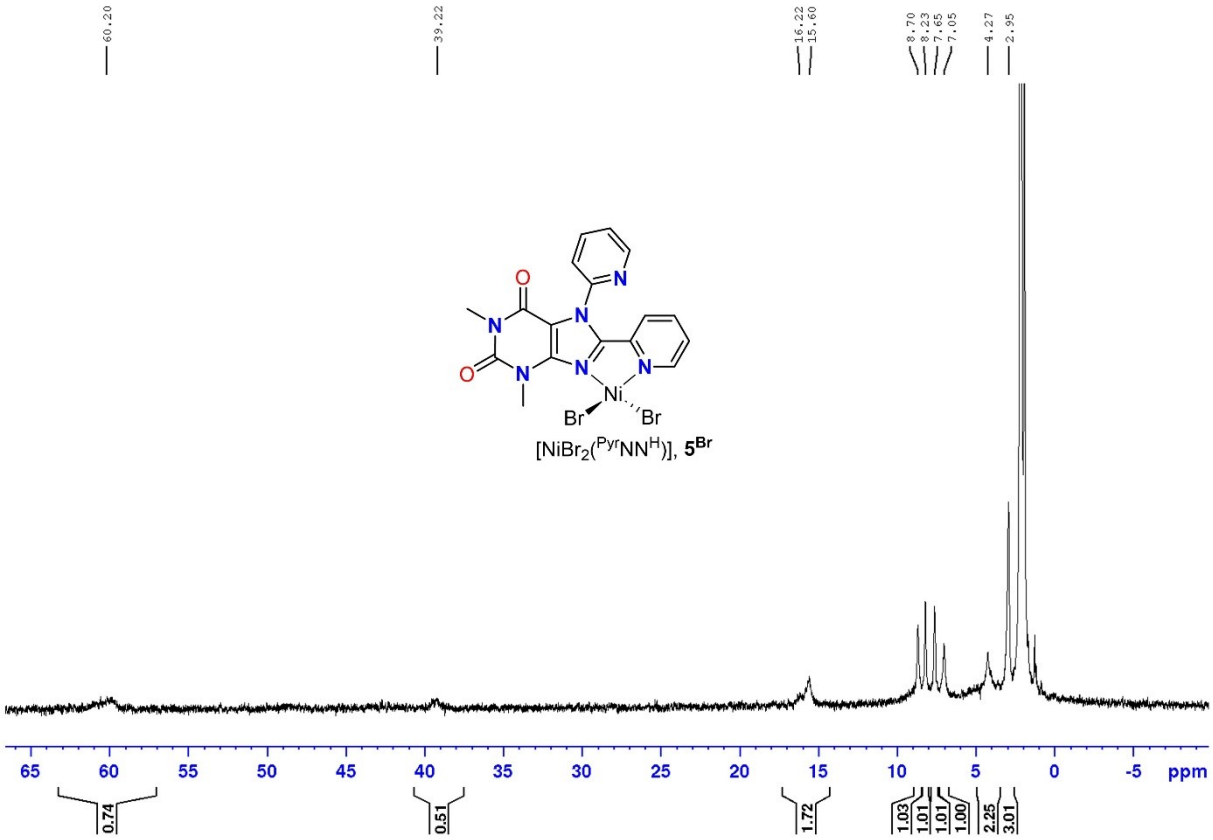


Figure S75. ^{1}H NMR spectrum (400.3 MHz, CD_3CN) of the complex [$NiBr_2(^{Pyr}NN^{H})$], $\mathbf{5^{Br}}$.

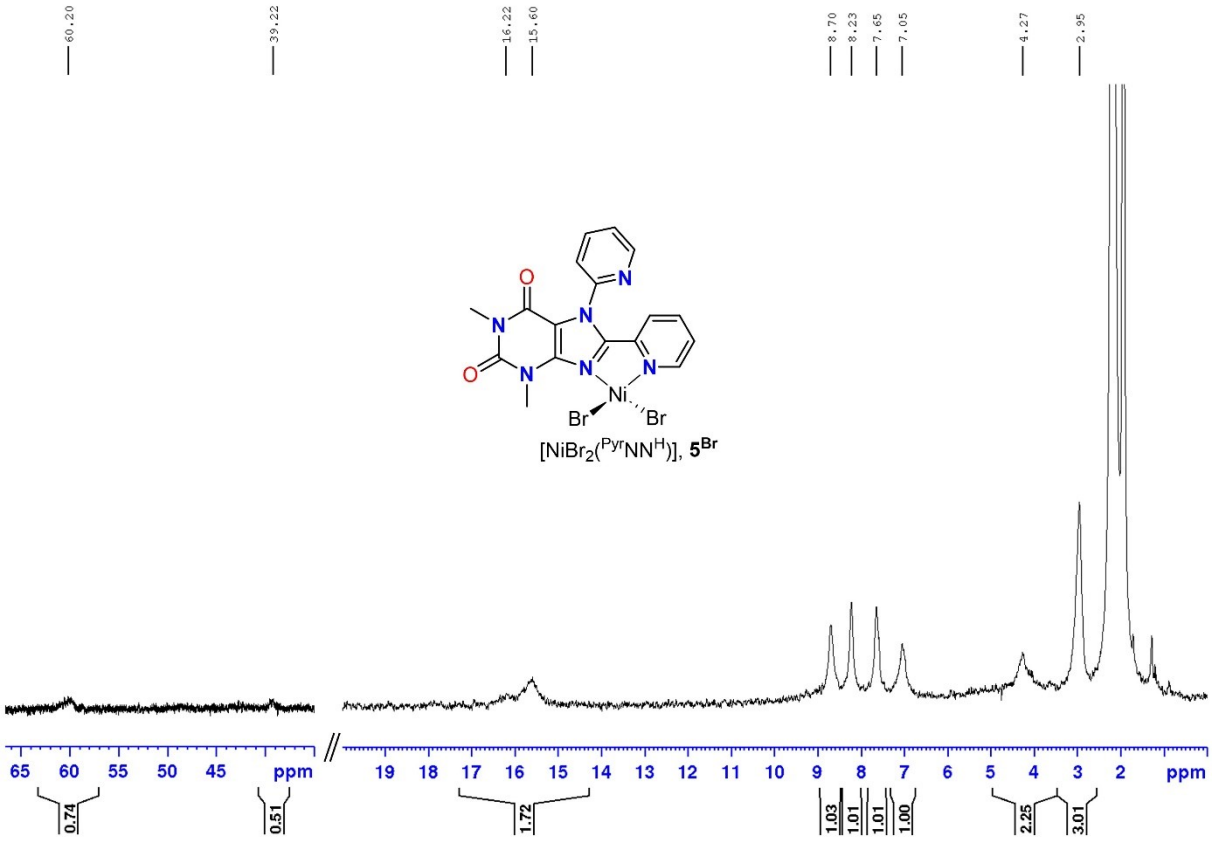


Figure S76. Partial enlarged views of the ^{1}H NMR spectrum (400.3 MHz, CD_3CN) of complex **5^{Br}**.

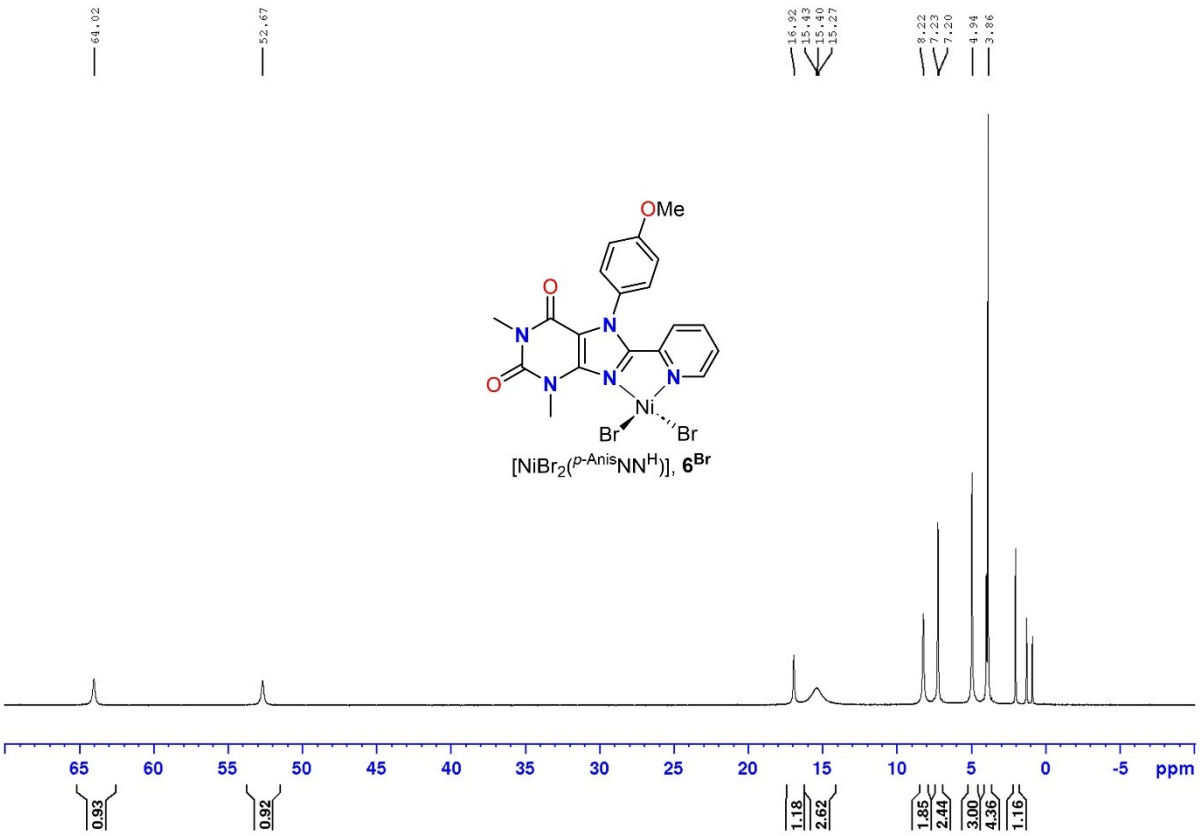


Figure S77. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of the complex [$NiBr_2$($^{p\text{-Anis}}NN^{H}$)], **6^{Br}**.

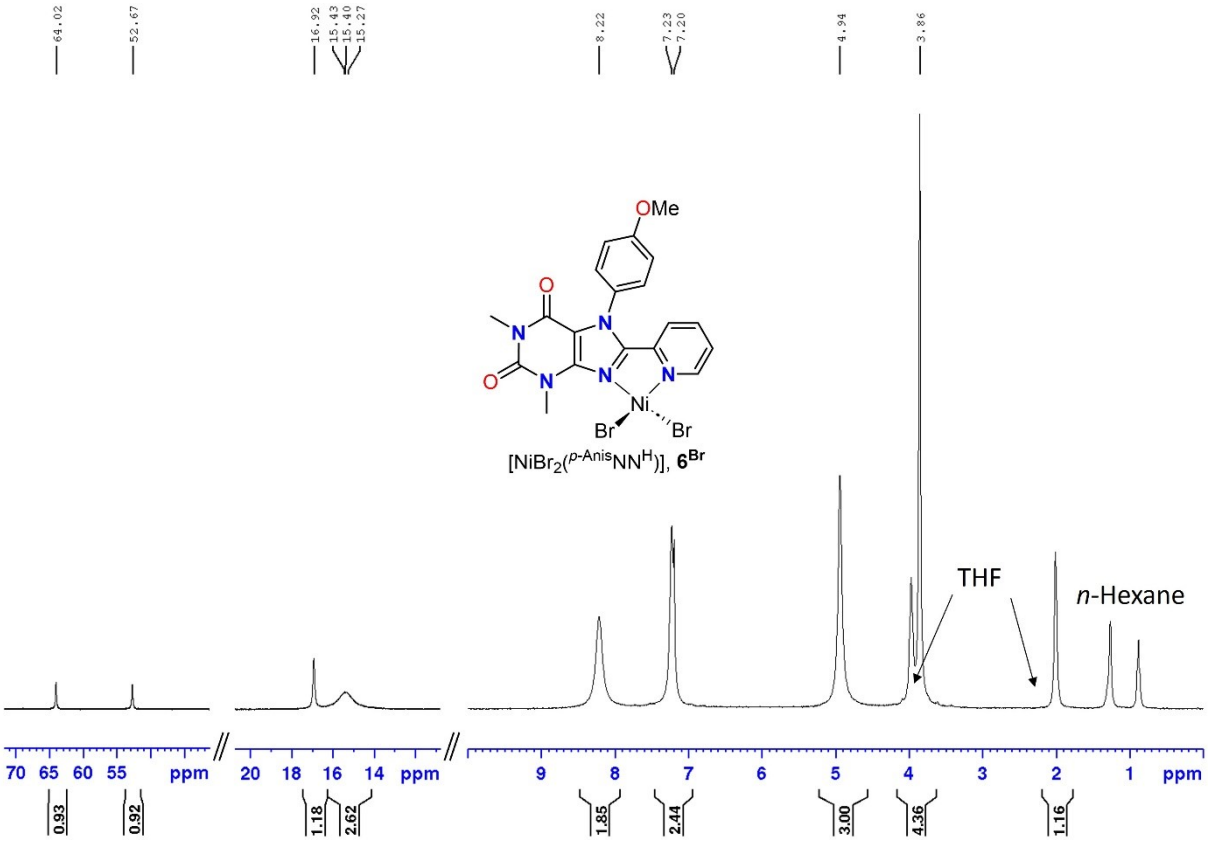


Figure S78. Partial enlarged views of the ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$) of complex **6^{Br}**.

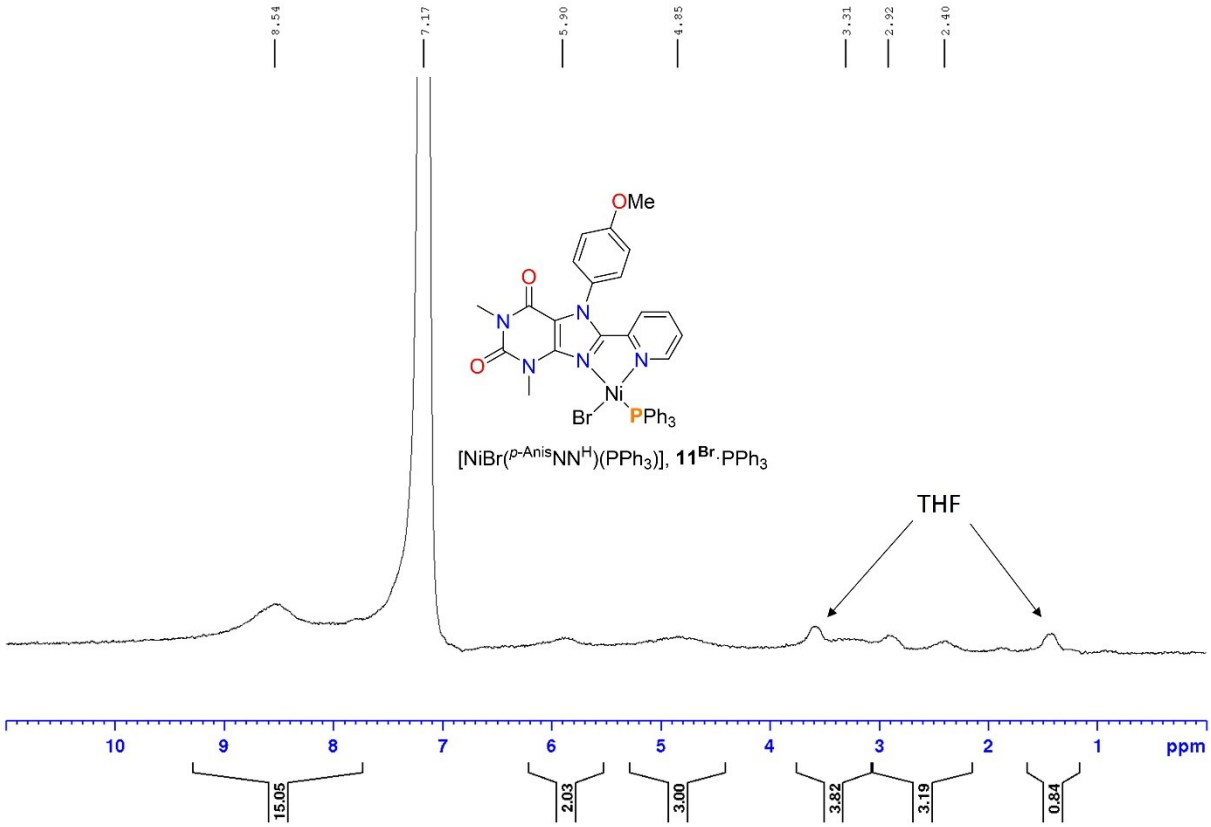


Figure S79. ^{1}H NMR spectrum (400.3 MHz, C_6D_6) of the complex [NiBr($^{p\text{-Anis}}$NN^{H})(PPh$_3$)], **11^{Br}**·PPh$_3$.

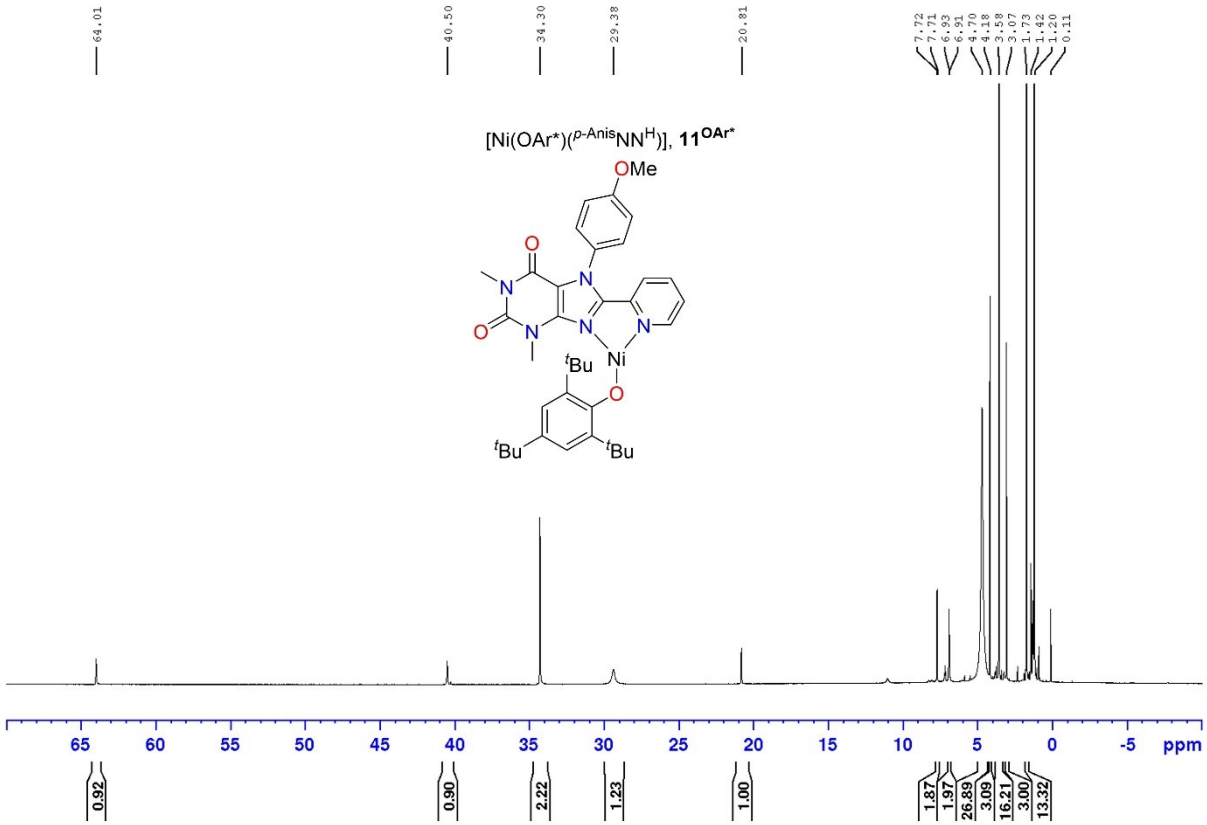


Figure S80. ^{1}H NMR spectrum (400.3 MHz, THF-d_8) of the complex [Ni(OAr*)($^{p\text{-Anis}}$NN^{H})], **11^{OAr*}**.

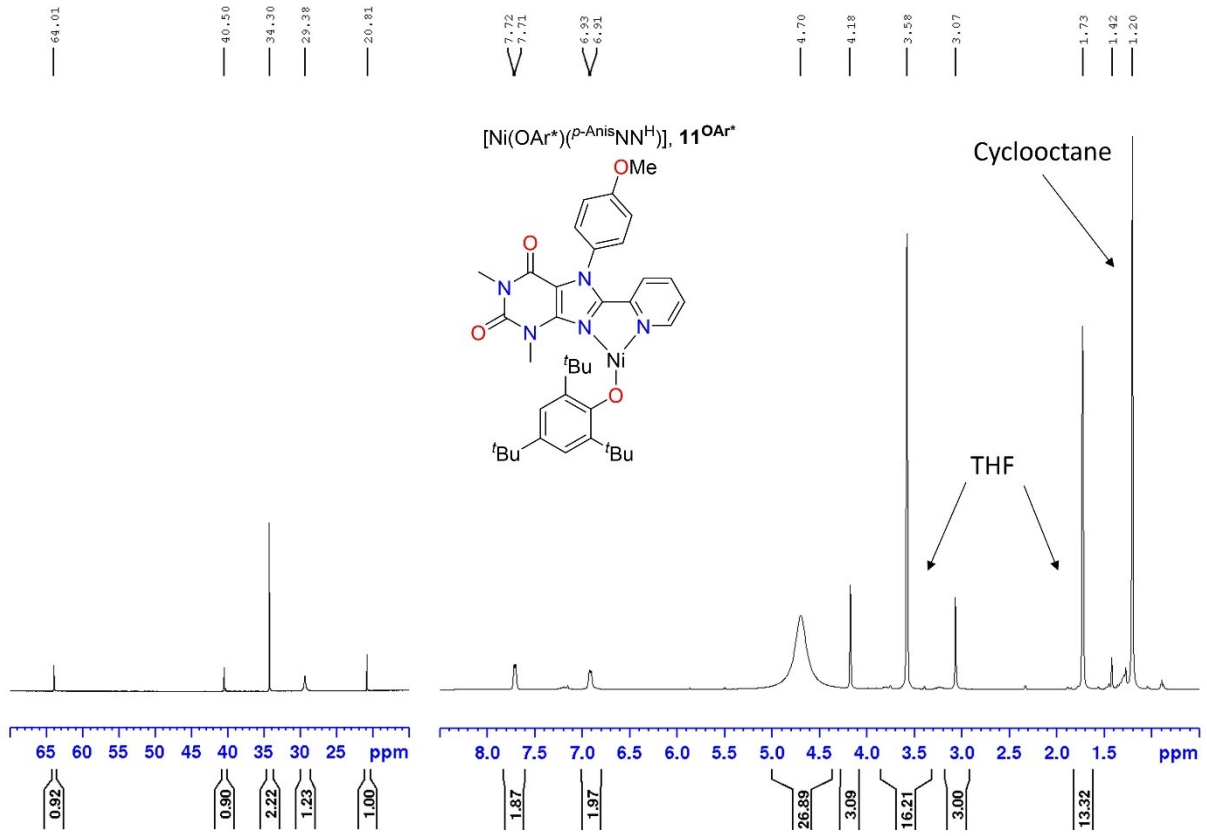


Figure S81. Partial enlarged views of the ^{1}H NMR spectrum (400.3 MHz, THF-d_8) of complex **11^{OAr*}**.

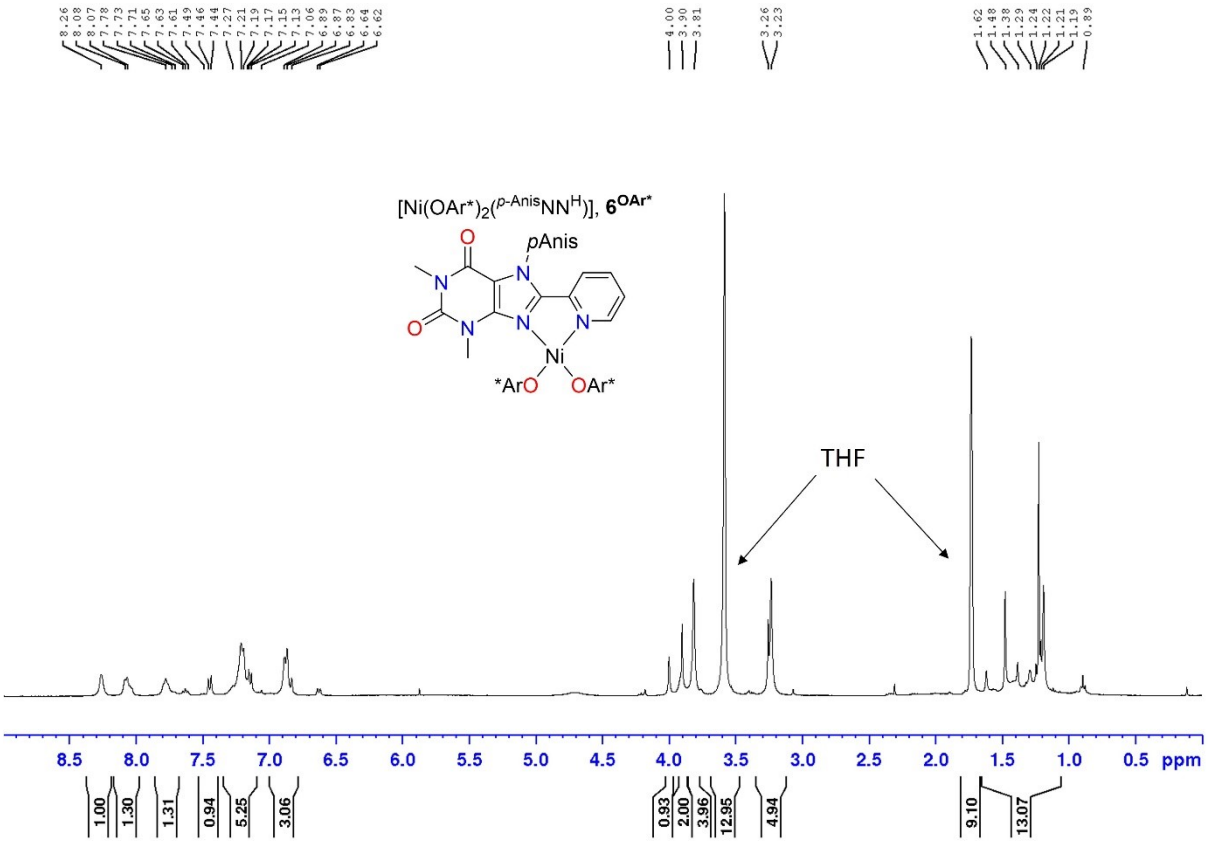
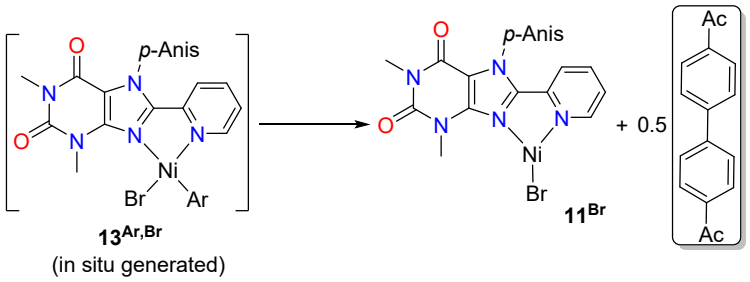


Figure S82. ^{1}H NMR spectrum (400.3 MHz, THF-d_8) of the complex [Ni(OAr*)$_2$($^{p\text{-Anis}}$NN^{H})], **6^{OAr*}**.

Formation of a biphenyl derivative (Ar-Ar) *via* Ni−Ar bond homolysis

Scheme S8. Stoichiometric test: Ni−Ar bond homolysis underwent by the putative complex [Ni(Ar)(Br)(*p*-AnisNN^{H})], yielding the species **11^{Br}** and the corresponding biphenyl Ar−Ar. The presence of the biphenyl Ar−Ar was confirmed by NMR spectroscopy (see Figure S83, below).



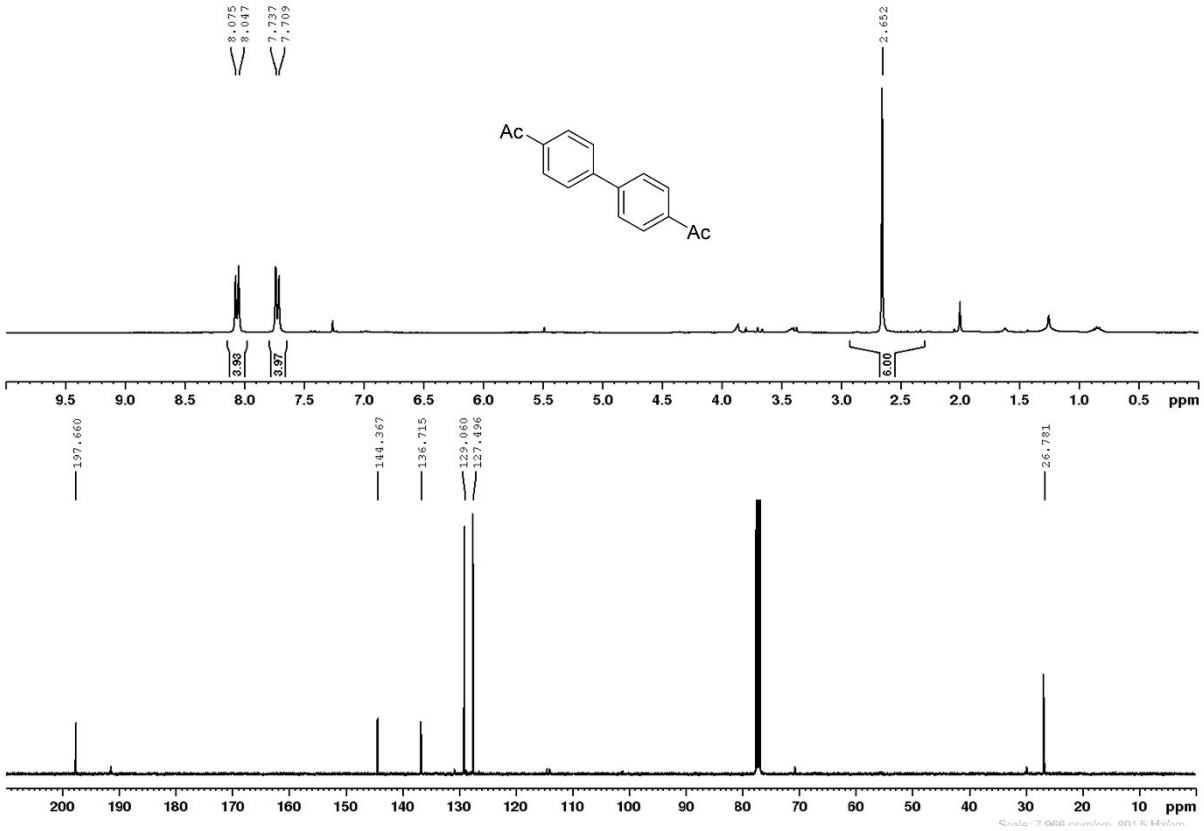


Figure S83. ^{1}H (300.1 MHz, top) and ^{13}C{^{1}H} (75.5 MHz, bottom) NMR spectra in $CDCl_3$ of the mother liquors from the reaction between the intermediate [Ni(cod)(*p*-AnisNN^{H})], **10**, and 4'-bromoacetophenone, which forms the proposed **13^{Ar,Br}** in situ. This spectroscopic data, supported also by GC-MS, suggests the formation of the corresponding biphenyl derivative as homocoupling product.

10. Computational Details

All calculations were performed using density functional theory (DFT) as implemented in the Jaguar 9.1 quantum chemistry program.[8] Geometry optimizations to the stationary points as well as to the saddle points (transition state (TS) geometries) were performed with the B3LYP hybrid functional,[9,10] augmented with Grimme's D3 correction (B3LYP-D3).[11] We used a double-zeta quality Pople's basis set, namely, 6-31G(d,p) for main group atoms.[12,13,14] Ni atoms were described by Los Alamos relativistic effective core potentials (ECP) and its corresponding LACVP basis set.[15,16,17] Analytical vibrational frequencies within the harmonic approximation were computed at the same level of theory for the geometry optimizations to confirm proper convergence to well-defined minima or saddle points: the intermediates have all positive vibrational frequency and the transition states exhibit a single imaginary frequency. The energies of the optimized structures were refined by single-point calculations on each optimized geometry: B3LYP-D3 functional in combination with the Dunning's correlation consistent triple-ζ basis set (cc-pVTZ(-f)) was used for main group elements.[18] Of note, we used a modified version of LACVP, designated as LACV3P, for Ni, in which the exponents were decontracted to match the effective core potential with the triple- ζ quality. Solvation energies were calculated based on the optimized gas-phase structures. A self-consistent reaction field (SCRF)[19,20,21] approach was used to model the solvation shell of dielectric constant ε = 36.7 (*N,N*-dimethylformamide). The basis set 6-31G(d,p) was used for main group elements, and LANL2DZ was used for Ni.[22] For each Ni-complex, we considered spin states to find the lowest-in-energy electronic configuration.

The Gibbs free energies in solution phase, G_{sol} were calculated with the following protocol:

$$G_{sol} = G_{gas} + G_{solv} \quad (1)$$

$$G_{gas} = H_{gas} - T \cdot S_{gas} \quad (2)$$

$$H_{gas} = E_{SCF} + ZPE \quad (3)$$

$$\Delta E_{SCF} = \Sigma E_{SCF}\,(\text{products}) - \Sigma E_{SCF}\,(\text{reactants}) \quad (4)$$

$$\Delta G_{sol} = \Sigma G_{sol}\,(\text{products}) - \Sigma G_{sol}\,(\text{reactants}) \quad (5)$$

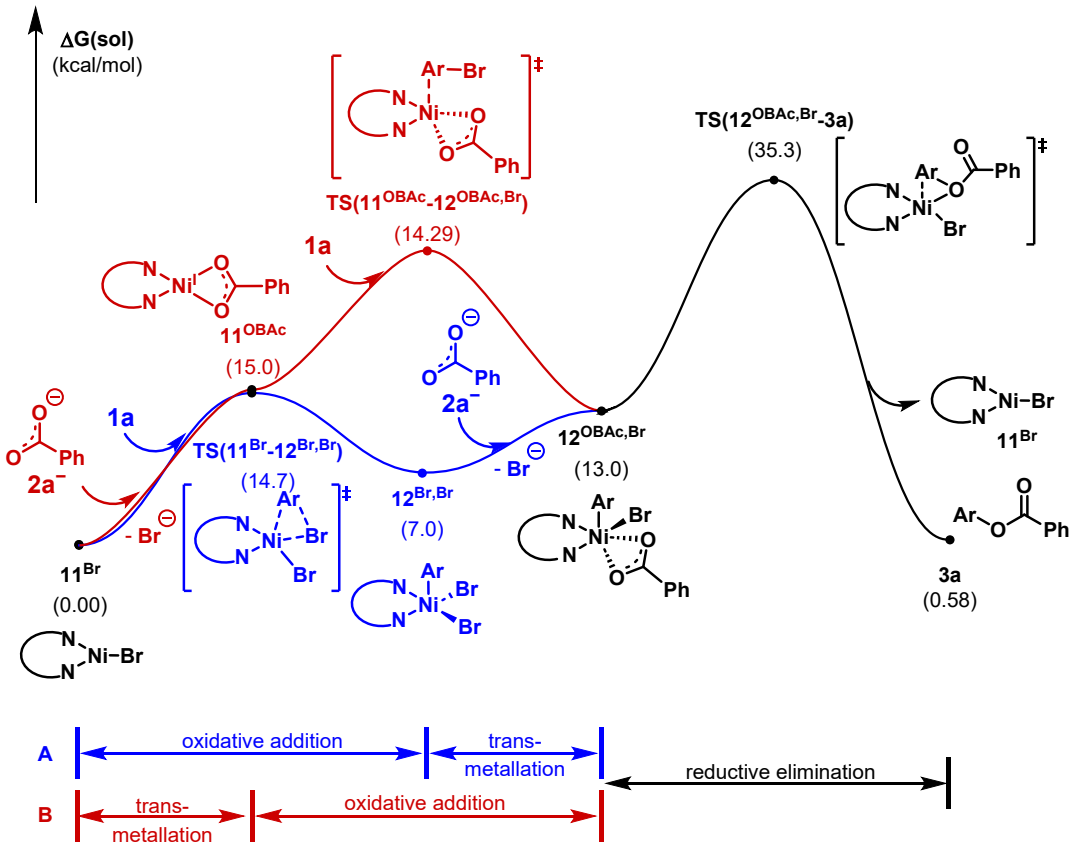
G_{gas} = free energy in the gas-phase; G_{sol} = solvation corrected Gibbs free energy of solvation as computed exploiting the continuum solvation model; H_{gas} = enthalpy in gas-phase; T = absolute temperature (313.15 K); S_{gas} = entropy in the gas-phase; E_{SCF} = self-consistent field energy, i.e., raw electronic energy as computed from the SCF procedure; and ZPE = zero-point energy. Note that by entropy here we refer specifically to the vibrational/rotational/translational entropy of the solute(s); the entropy of the solvent is implicitly incorporated in the continuum solvation model.

10.1. Gibbs Free Energy of Mononuclear Anions

The entropy of a single atomic species cannot be calculated using DFT. Instead, we calculated S_{gas} using the Sackur-Tetrode equation at 1 atm (equation 6).[23,24]

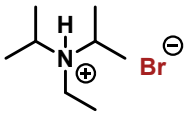
$$S_{gas} = \frac{3}{2}R\ ln(M) + \frac{5}{2}R\ln(T) - 9.686\ J \bullet mol^{-1} \bullet K^{-1} \quad (6)$$

To determine G_{sol} we combined the calculated gas-phase entropy of an ion and experimental solvation energy of the ion (G_{solv}).[25] The overall energy profile is given in Scheme S9.



Scheme S9. Energy profile for the catalytic cycle without ion pairing.

Due to the low solubility of Br^- in DMF, the overall reaction is energetically uphill. Thus, we considered an alternative pathway. We optimized the structure of the ion pair DIPEA-H^+/Br^- (Scheme S10) and calculated the energy profile for the same reaction under consideration of the ion pair formation (given in Scheme 8 in the manuscript).

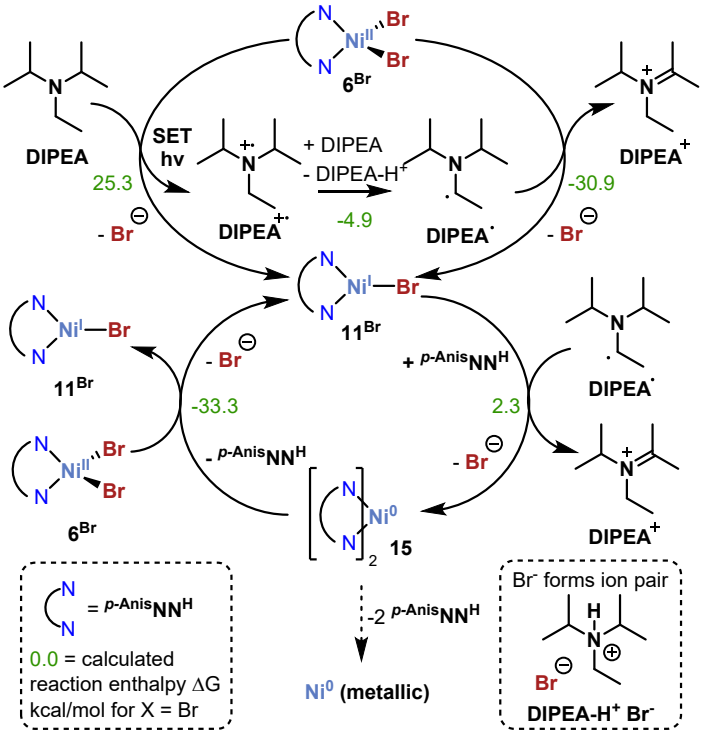


DIPEA-H$^+$ Br$^-$

Scheme S10. Ion-paring of DIPEA-H+ cation and Br- anion.

10.2. Pathways for the Reduction of Ni(II)

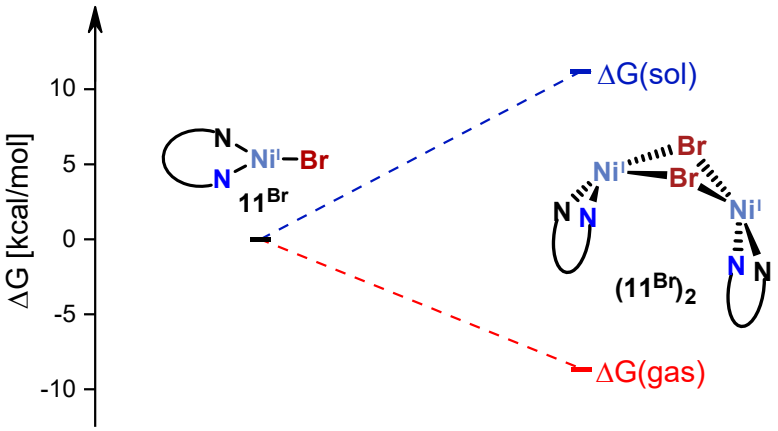
We explored possible pathways for the reduction of Ni(II) using DFT. The results are summarized in Scheme S11**.** Using **DIPEA** as sacrificial reductant, Ni(II) complex **6^{Br}** is reduced to **11^{Br}**. The reduction is endergonic by ΔG = +25.3 kcal/mol, which mandates photoactivation. **DIPEA$^{+\bullet}$** can be deprotonated by another **DIPEA** molecule, producing the radical **DIPEA$^{\bullet}$**, which is a strong reducing agent.[26,27,28] The reduction of **6^{Br}** by **DIPEA$^{\bullet}$** is downhill in energy (ΔG = −30.9 kcal/mol), leading to another equivalent of **11^{Br}**. Additionally, **11^{Br}** can be reduced by **DIPEA$^{\bullet}$** forming a Ni(0) complex **15**, which is slightly uphill in energy by 2.3 kcal/mol. When such a Ni(0) complex is formed, it will comproportionate with **6^{Br}** to regenerate **11^{Br}**.[29,30] However, precipitation of elemental Ni(0) drives the reduction in absence of other reaction partners for **11^{Br}**, as observed experimentally (*vide supra*). Notably, protonated **DIPEA-H$^+$** facilitates the removal of Br^-.



Scheme S11. Photoreduction of $\mathbf{6^{Br}}$ in the presence of DIPEA, and possible further reduction of the resulting Ni(I) compound *via* SET. DIPEA species are shown in the mesomeric structure that resembles their geometry more closely.

10.3. Dimerization of the Ni(I) Species

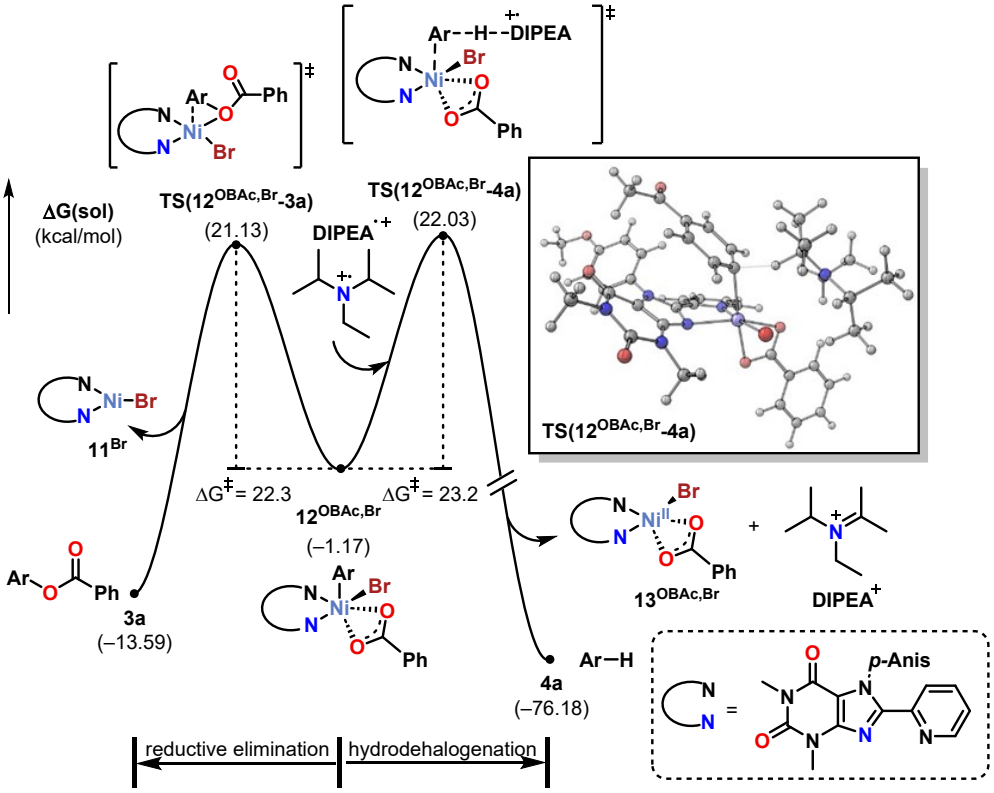
We found that the formation of a Ni(I) dimer from $\mathbf{11^{Br}}$ is energetically uphill by 11.2 kcal/mol in solution (see Scheme S12). Interestingly, the dimerization is exergonic in the gas phase (ΔG(gas) = −8.7 kcal/mol and ΔH = −1.3 kcal/mol). The precipitation of the dimer drives the dimer formation.



Scheme S12. Comparison of the energy diagram for the dimerization in solution (blue) and in the gas phase(red).

10.4. Hydrodehalogenation Side Reaction

We also investigated the mechanism of the hydrodehalogenation of the aryl bromide, which is the major side reaction of the photocatalytic O-arylation of carboxylates. Scheme S13 compares the energy profile of the reductive elimination and the HAT to the Ni(III) species **A3**. Our calculations indicate that this reaction proceeds *via* a concerted HAT where the DIPEA radical cation **DIPEA**$^{+\bullet}$ donates a hydride to Ni(III) intermediates. The computed activation energy barrier for the HAT reaction is $\Delta G^{\ddagger}$ = 23.2 kcal/mol (**C3-TS**), which is 0.9 kcal/mol higher than that of the reductive elimination ($\Delta G^{\ddagger}$ = 22.3 kcal/mol, **A3-TS**).



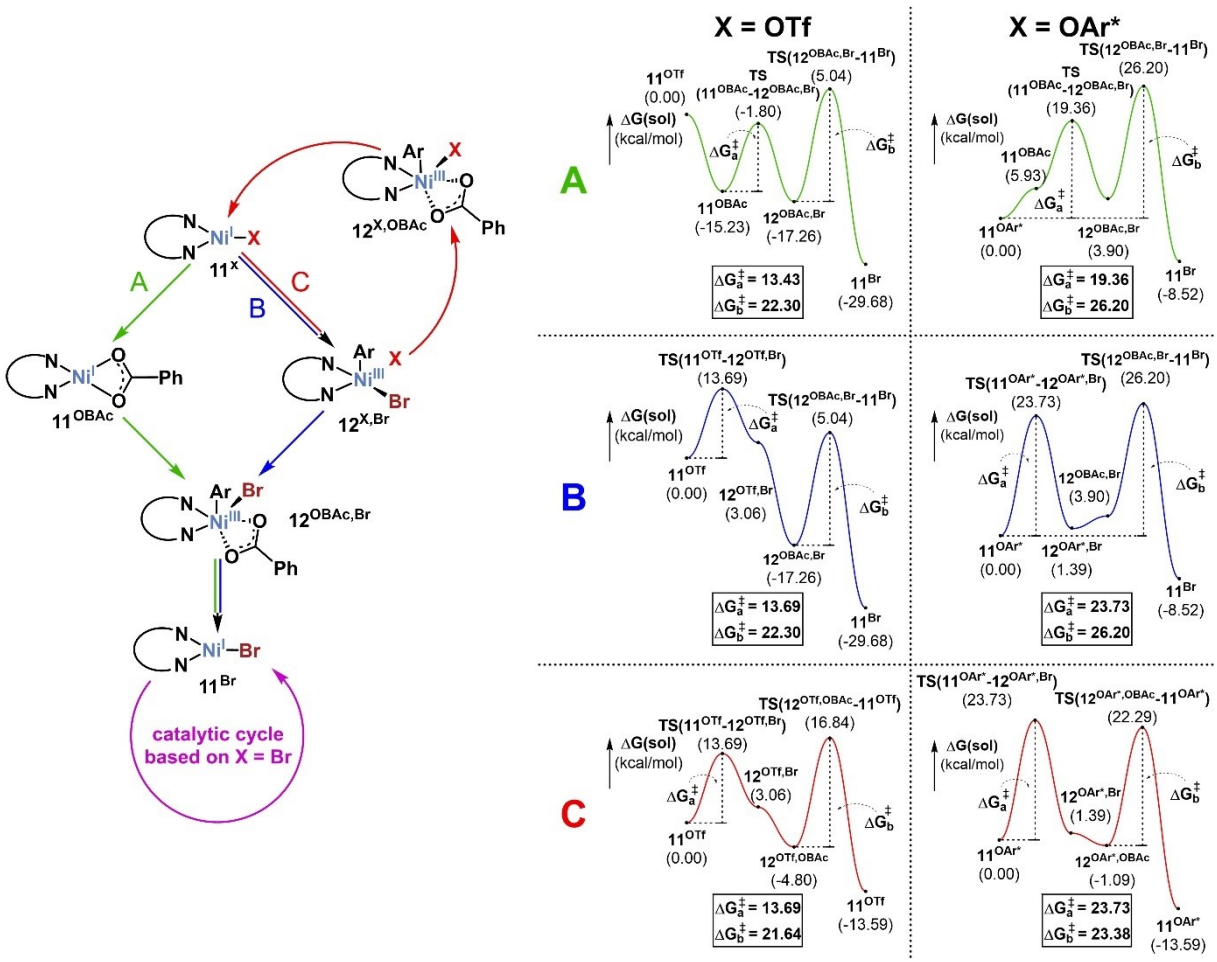
Scheme S13. a) Comparison of the energy profiles for the reductive elimination (A4) and the hydrodehalogenation (C4), including the transition state structure for the HAT reaction (C3-TS).

10.5. Alternative Catalytic Pathways Incorporating Different Counter Anions

In the publication's main text, we described the catalytic pathways starting from **11**^{Br}, where Br^- coordinates Ni(I) (reaction energy profile summarized in Scheme 8 in the main text). In the following, we will refer to this path as the standard mechanism.

When using a catalyst precursor with a different counterion X^-, three different mechanistic pathways are viable, as displayed in Scheme S14. Pathway **A** is a transmetalation-first mechanism from **11**^{X}, where counter ion X^- is replaced by benzoate in the first step. Thus Ni(I) complex **11**^{Br} with Br^- as

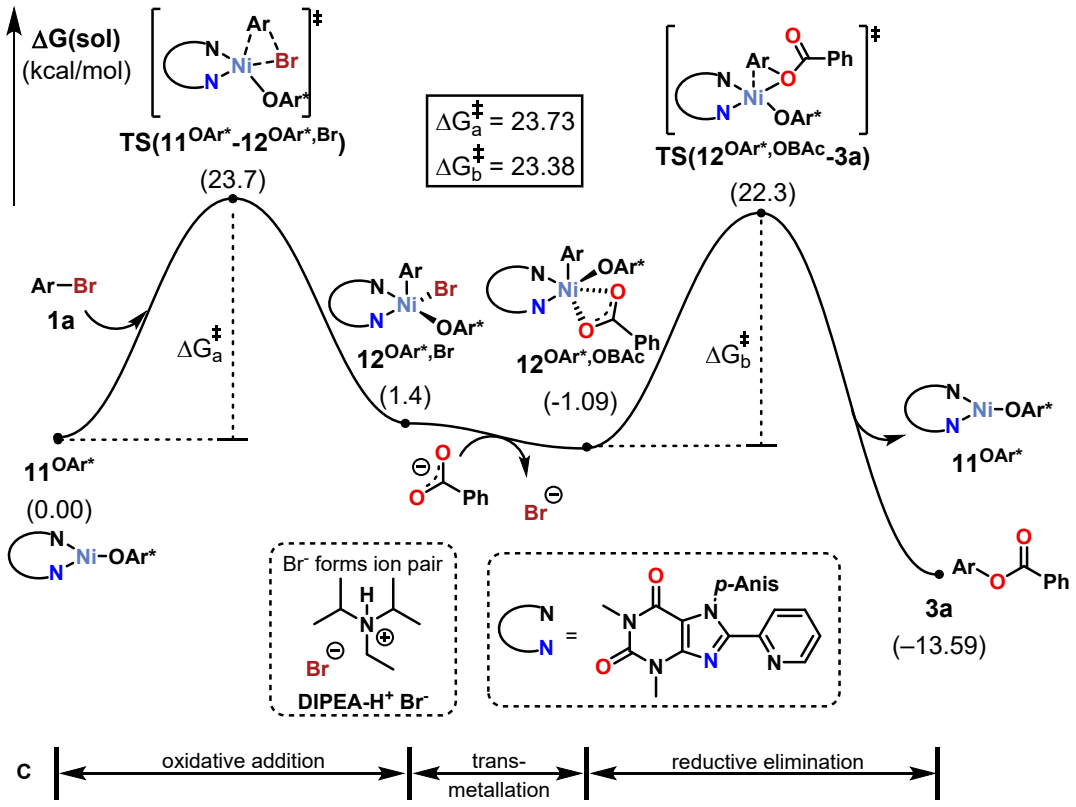
counter ion is formed instead of restoring **11^{X}**, and the reaction continues with the standard mechanism. Pathway **B** is an oxidative addition-first mechanism, but the counter ion X^- is replaced in the following transmetalation step. This also produces **11^{Br}**, and the catalytic cycle continues following the standard mechanism. Only in pathway **C**, the counterion X^- remains in the cycle. This is the oxidative addition-first mechanism where Br^- is replaced by the carboxylate in the transmetalation.



Scheme S14. Schematic depiction and energy profiles of possible mechanistic pathways, when using a metal precursor with counter ions other than Br^-. left: X = OTf^- and right: X = OAr^{*-}.

Scheme S14 summarizes computed reaction energy profiles of the alternative pathways incorporating different counter anions. For X = OTf^- (complex **11^{OTf}**), all three alternative pathways (**A**, **B**, and **C**) are thermally accessible and have slightly lower activation barriers than the standard mechanism. However, since the transmetalation of OTf^- leads to the formation of **11^{Br}** at the end of the catalytic cycle, the system will quickly equilibrate to the standard mechanism. Thus, the use of the OTf^- counter ion only provides a minor benefit, which may explain the marginally improved catalytic performance.

In the case of X = OAr*$^{-}$ (complex **11**^{OAr*}), pathways **A** and **B** are thermally inaccessible due to the high activation barrier of the reductive elimination ($\Delta G^{‡}$ = 26.2 kcal/mol). Thus, the system follows pathway **C**, where OAr*$^{-}$ stays coordinated to the Ni(I) complex, while Br^{-} is removed in the transmetalation (Scheme S15). The larger counter ion retards the catalytic cycle due to higher activation barriers (oxidative addition: $\Delta G^{‡}$ = 23.7 kcal/mol, reductive elimination: $\Delta G^{‡}$ = 23.4 kcal/mol). It is likely that a high concentration of the Ni(I) complex in combination with the decelerated oxidative addition and reductive elimination disfavor the thermal reaction relative to hydrodehalogenation and other side reactions. Previously, it was reported that counter anions other than halides accelerate disproportionation of Ni(I) complexes.[29] These findings explain the results of our stoichiometric experiments (**Table 2** entry 3 in the main text), where thermal *O*-arylation was not observed with complex **11**^{OAr*} as a catalyst.



Scheme S15. Energy profile for the *O*-arylation using **11**^{OAr*} as catalyst.

10.6. Computed Energy Components for DFT-Optimized Structures

Structure	E_{SCF} [eV] cc-pVTZ(-f)/LACV3P	ZPE [kcal/mol] 6-31G**/LACVP	S_{gas} [cal/mol] 6-31G**/LACVP	G_{solv} [kcal/mol] 6-31G**/LACVP
1a	-10819.181	80.317	96.916	-6.64
2a$^-$	-11440.132	64.107	83.287	-67.59
3a	-21899.599	146.637	121.871	-10.4
4a	-10477.282	86.829	86.717	-6.68
DIPEA-H$^+$ Br$^-$	-10476.604	174.753	114.054	-20.21
OTf$^-$	-26171.498	17.082	85.578	-60.58
OAr*$^-$	-21197.151	270.027	143.797	-46.58
***p*-Anis^{NNH}**	-33,583	215.278	164.530	-20.16
DIPEA	-10100.663	164.462	102.197	-2.47
DIPEA$^{+\bullet}$	-10093.586	165.584	104.013	-49.62
DIPEA$^\bullet$	-10082.946	156.324	106.996	-2.2
DIPEA$^+$	-10078.432	158.87	103.062	-49.68
DIPEA-H$^+$	-10111.462	175.004	102.252	-51.43
11^{Br}	-38552.074	217.004	189.432	-27.47
11^{OBAc}	-49632.138	282.386	215.407	-23.68
11^{OTf}	-64362.465	234.699	219.520	-24.17
11^{OAr*}	-59388.549	488.158	277.916	-21.85
$(11^{Br})_2$	-77105.494	435.806	313.207	-35.08
12^{Br,Br}	-49371.589	298.257	239.205	-35.08
12^{OTf,Br}	-75182.008	315.876	270.752	-34.57
12^{OAr*,Br}	-70208.248	569.109	329.077	-30.12
6^{Br}	-38911.923	218.014	193.948	-30.53
12^{OBAc,Br}	-60451.991	364.122	266.114	-32.75
12^{OTf,OBAc}	-86262.241	382.002	296.343	-36.47
12^{OAr*,OBAc}	-81288.493	635.45	350.606	-27.85
13^{Ar,Br}	-49012.7	297.142	234.037	-30.66
13^{OBAc,Br}	-49992.185	283.557	228.486	-31.95
15	-71775.343	431.127	284.835	-29.59
TS(11^{Br}-12^{Br,Br})	-49371.508	298.1	229.441	-32.17
TS(11^{OTf}-12^{OTf,Br})	-75181.864	315.904	262.672	-29.82
TS(11^{OAr*}-12^{OAr*,Br})	-70207.897	569.954	308.926	-23.03
TS(11^{OBAc}-12^{OBAc,Br})	-60451.492	363.118	262.472	-28.93
TS(12^{OBAc,Br}-3a)	-60451.017	363.495	264.139	-32.9
TS(12^{OTf,OBAc}-11^{OTf})	-86261.711	381.358	285.200	-29.9
TS(12^{OAr*,OBAc}-11^{OAr*})	-81287.569	635.121	347.346	-26.47
TS(12^{Br,Br}-6^{Br})	-59465.679	462.911	292.549	-65.04
TS(12^{OBAc,Br}-13^{OBAc,Br})	-70546.414	528.605	315.919	-55.74

10.7. DFT Optimized Geometries and Computed Vibrational Frequencies

Cartesian Coordinates

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1a

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C1	-0.5880	-0.3959	-2.7518
C2	-1.6573	-0.8877	-2.0036
C3	0.3635	0.3998	-2.1193
H4	-2.3969	-1.5072	-2.4997
C5	-1.7742	-0.5909	-0.6384
C6	0.2741	0.7131	-0.7631
H7	1.0263	1.3366	-0.2930
C8	-0.7973	0.2130	-0.0314
H9	-0.8989	0.4356	1.0257
H10	-0.4973	-0.6265	-3.8071
C11	-2.9021	-1.0933	0.2146
O12	-2.9486	-0.8178	1.4037
C13	-3.9788	-1.9489	-0.4291
H14	-3.5489	-2.8686	-0.8419
H15	-4.7218	-2.2046	0.3267
H16	-4.4629	-1.4148	-1.2542
Br17	1.8668	1.0985	-3.1622

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2a$^-$

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C1	-0.5704	-0.0259	-1.7757
C2	-1.7158	-0.4249	-1.0842
C3	0.5549	0.4164	-1.0727

H4	-2.6091	-0.7740	-1.5952
H5	1.4495	0.7288	-1.6092
C6	-1.7625	-0.3917	0.3147
C7	0.5198	0.4543	0.3257
H8	1.3929	0.7986	0.8795
C9	-0.6303	0.0533	1.0078
H10	-0.6961	0.0692	2.0922
H11	-0.5498	-0.0573	-2.8649
C12	-3.0421	-0.8349	1.0825
O13	-2.9623	-0.7594	2.3354
O14	-3.9968	-1.2132	0.3549

3a

C1	-2.7040	-0.0269	-4.2881
C2	-2.4833	-1.3998	-4.4261
C3	-1.8096	0.7509	-3.5589
H4	-3.1818	-2.0072	-4.9948
H5	-1.9606	1.8182	-3.4374
C6	-1.3659	-1.9929	-3.8336
C7	-0.6869	0.1587	-2.9624
H8	-1.1952	-3.0599	-3.9415
C9	-0.4672	-1.2191	-3.1025
H10	0.4007	-1.6744	-2.6404
H11	-3.5726	0.4348	-4.7481
C12	0.2246	1.0491	-2.1941
O13	0.0592	2.2421	-2.0526
O14	1.2737	0.3416	-1.6755
C15	2.2883	0.8679	-0.8915
C16	2.2890	2.1284	-0.2866
C17	3.3603	-0.0153	-0.7106
C18	3.3842	2.4881	0.5003
C19	4.4384	0.3609	0.0730
C20	4.4676	1.6216	0.6931
H21	1.4649	2.8086	-0.4347
H22	3.3225	-0.9856	-1.1945
H23	3.3775	3.4682	0.9662
H24	5.2798	-0.3063	0.2251
C25	5.6622	1.9706	1.5249
O26	6.5859	1.1796	1.6525
C27	5.7054	3.3276	2.2071
H28	4.8530	3.4537	2.8836
H29	6.6347	3.4059	2.7722
H30	5.6585	4.1352	1.4678

4a

C1	-0.2516	-0.2384	-2.9765
C2	-1.3244	-0.7326	-2.2353
C3	0.7149	0.5592	-2.3615
H4	-2.0681	-1.3516	-2.7265
C5	-1.4390	-0.4336	-0.8696
C6	0.6079	0.8620	-1.0006
H7	1.3592	1.4831	-0.5215
C8	-0.4611	0.3688	-0.2607
H9	-0.5662	0.5893	0.7964
H10	-0.1696	-0.4746	-4.0334
C11	-2.5675	-0.9351	-0.0185
O12	-2.6234	-0.6570	1.1701
C13	-3.6410	-1.7972	-0.6620
H14	-3.2061	-2.7115	-1.0813
H15	-4.3791	-2.0607	0.0960
H16	-4.1328	-1.2630	-1.4824
H17	1.5498	0.9444	-2.9405

DIPEA-H$^+$ Br$^-$

N1	-1.8127	-0.6115	-2.4770
C2	-2.9569	-1.1877	-1.6699
H3	-2.7413	-1.0152	-0.6133
H4	-3.8556	-0.6156	-1.9005
C5	-3.1823	-2.6683	-1.9603
H6	-2.2949	-3.2633	-1.7364
H7	-4.0176	-3.0281	-1.3511
H8	-3.4121	-2.8322	-3.0153
C9	-0.6126	-0.2486	-1.5992
H10	-0.9908	0.4555	-0.8489
C11	-0.0890	-1.5179	-0.9149
H12	0.7728	-1.2523	-0.2965
H13	-0.8280	-1.9864	-0.2605
H14	0.2273	-2.2438	-1.6705
C15	0.5046	0.4001	-2.4208
H16	0.2404	1.3919	-2.7950
H17	1.3805	0.5187	-1.7771
H18	0.7754	-0.2474	-3.2608
C19	-2.2492	0.4725	-3.4570
H20	-1.3519	0.6623	-4.0475
C21	-2.6951	1.7503	-2.7491
H22	-3.5843	1.5868	-2.1318
H23	-1.9112	2.1756	-2.1170
H24	-2.9553	2.4986	-3.5032
C25	-3.2989	-0.0818	-4.4243
H26	-3.4609	0.6569	-5.2147
H27	-2.9377	-1.0047	-4.8868
H28	-4.2653	-0.2627	-3.9437
H29	-1.4287	-1.3801	-3.1378
Br30	-0.5039	-2.6227	-4.5322

OTf$^-$

S1	-1.4625	-1.2884	0.2051
O2	-1.3423	0.1273	-0.2122
O3	-0.4001	-1.7760	1.1145
O4	-1.8790	-2.2332	-0.8569
C5	-2.9606	-1.2521	1.3208
F6	-2.7819	-0.4286	2.3790
F7	-4.0647	-0.8234	0.6673
F8	-3.2469	-2.4771	1.8180

OAr*$^-$

O1	2.7789	2.9034	-2.9941
C2	3.8890	3.5012	-3.2421
C3	4.8899	2.9322	-4.1281
C4	4.2154	4.7917	-2.6502
C5	6.0838	3.6120	-4.3710
C6	5.4288	5.4062	-2.9425
C7	6.3964	4.8519	-3.7976
H8	6.8070	3.1567	-5.0363
H9	5.6486	6.3687	-2.4881
C10	4.5999	1.5687	-4.7856
C11	3.1912	5.4464	-1.7036
C12	3.6602	6.8078	-1.1554
H13	2.8904	7.2233	-0.4923
H14	4.5859	6.7176	-0.5745
H15	3.8336	7.5345	-1.9579
C16	1.8601	5.6753	-2.4604
H17	1.5092	4.7230	-2.8613
H18	1.0961	6.0967	-1.7902
H19	2.0099	6.3775	-3.2900
C20	2.9326	4.5161	-0.4930
H21	2.1639	4.9416	0.1688
H22	2.6047	3.5403	-0.8548
H23	3.8521	4.3881	0.0918

C24	4.3828	0.5004	-3.6864
H25	4.1287	-0.4731	-4.1314
H26	5.2970	0.3751	-3.0927
H27	3.5746	0.8227	-3.0277
C28	5.7439	1.0789	-5.6953
H29	5.4768	0.1084	-6.1332
H30	5.9368	1.7740	-6.5211
H31	6.6803	0.9449	-5.1408
C32	3.3207	1.6706	-5.6524
H33	2.4936	2.0171	-5.0307
H34	3.4730	2.3844	-6.4715
H35	3.0674	0.6948	-6.0931
C36	7.7069	5.6079	-4.0671
C37	8.6409	4.8490	-5.0295
H38	9.5603	5.4244	-5.1977
H39	8.9245	3.8719	-4.6241
H40	8.1653	4.6842	-6.0022
C41	8.4770	5.8269	-2.7421
H42	9.4115	6.3823	-2.9083
H43	7.8754	6.3898	-2.0221
H44	8.7249	4.8640	-2.2826
C45	7.4017	6.9884	-4.6979
H46	6.8741	6.8630	-5.6495
H47	6.7624	7.5892	-4.0439
H48	8.3240	7.5576	-4.8856

p-AnisNN^H

N1	-0.8475	-1.5973	0.8540
C2	0.2103	-1.4726	-0.0643
N3	0.8447	-0.2372	-0.1327
C4	-1.3443	-0.5957	1.7306
C5	-0.6110	0.6304	1.5773
C6	0.4371	0.7867	0.6888
N7	-0.7226	1.8611	2.2196
C8	0.2489	2.6660	1.6669
N9	0.9673	2.0314	0.7394
C10	1.9500	-0.0838	-1.0771
O11	0.5543	-2.4081	-0.7734
O12	-2.2859	-0.8030	2.4895
C13	-1.4842	-2.9175	0.8837
H14	2.7512	-0.7850	-0.8319
H15	2.3105	0.9414	-1.0059
H16	1.6036	-0.2973	-2.0908
H17	-0.7478	-3.6791	1.1493
H18	-1.8844	-3.1592	-0.1034
H19	-2.2816	-2.8814	1.6228
H20	-1.6698	4.5569	2.1651
C21	-0.6579	4.9404	2.2238
C22	-0.4173	6.2808	2.5096
H23	-1.2465	6.9614	2.6789
C24	0.9009	6.7297	2.5648
H25	1.1366	7.7661	2.7842
C26	1.9222	5.8075	2.3244
H27	2.9638	6.1222	2.3567
N28	1.7126	4.5169	2.0541
C29	0.4388	4.0916	2.0077
C30	-1.6147	2.1743	3.2953
C31	-2.9978	2.0546	3.1151
C32	-1.1034	2.6186	4.5118
C33	-3.8568	2.3968	4.1473
C34	-1.9644	2.9726	5.5523
C35	-3.3485	2.8638	5.3703
H36	-3.3856	1.6804	2.1755
H37	-0.0293	2.6970	4.6437
H38	-4.9318	2.3065	4.0367
H39	-1.5469	3.3177	6.4900
O40	-4.2824	3.1730	6.3113
C41	-3.8379	3.6206	7.5840
H42	-3.2285	2.8596	8.0888
H43	-3.2617	4.5524	7.5092
H44	-4.7402	3.8035	8.1698

DIPEA

N1	-0.9885	0.1038	-3.2563
C2	-2.3598	-0.4371	-3.2810
H3	-2.4493	-1.2699	-2.5778
H4	-3.0683	0.3091	-2.9210
C5	-2.7963	-0.8886	-4.6736
H6	-2.1275	-1.6529	-5.0653
H7	-3.8099	-1.2960	-4.6487
H8	-2.7806	-0.0494	-5.3679
C9	-0.0484	-0.7717	-2.5295
H10	-0.4168	-0.9597	-1.5065
C11	0.0645	-2.1294	-3.2342
H12	0.7418	-2.7814	-2.6813
H13	-0.8911	-2.6437	-3.3078
H14	0.4553	-1.9940	-4.2433
C15	1.3535	-0.1712	-2.4072
H16	1.3853	0.7036	-1.7605
H17	2.0260	-0.9140	-1.9785
H18	1.7381	0.1077	-3.3895
C19	-0.9257	1.5384	-2.9175
H20	0.1169	1.8285	-3.0204
C21	-1.3613	1.8824	-1.4819
H22	-2.4207	1.6788	-1.3218
H23	-0.7961	1.3082	-0.7476
H24	-1.1957	2.9412	-1.2770
C25	-1.6921	2.3758	-3.9447
H26	-1.5187	3.4369	-3.7621
H27	-1.3566	2.1370	-4.9531
H28	-2.7684	2.2093	-3.8958

$DIPEA^{+\cdot}$

N1	-1.0936	0.0645	-2.9779
C2	-2.4337	-0.4964	-3.1738
H3	-2.4989	-1.4090	-2.5769
H4	-3.1537	0.2239	-2.7761
C5	-2.7748	-0.8080	-4.6490
H6	-2.0586	-1.4997	-5.0927
H7	-3.7620	-1.2777	-4.6618
H8	-2.8181	0.0948	-5.2566
C9	-0.0226	-0.8546	-2.5149
H10	-0.4135	-1.2401	-1.5582
C11	0.1229	-2.0512	-3.4814
H12	0.8962	-2.7112	-3.0820
H13	-0.7914	-2.6383	-3.5780
H14	0.4410	-1.7097	-4.4699
C15	1.3283	-0.1847	-2.2669
H16	1.2804	0.6303	-1.5423
H17	2.0019	-0.9410	-1.8566
H18	1.7771	0.1799	-3.1960
C19	-0.9109	1.5250	-2.9763
H20	0.1545	1.7010	-3.1252
C21	-1.3018	2.0410	-1.5631
H22	-2.3740	1.9213	-1.3874
H23	-0.7521	1.5273	-0.7716
H24	-1.0600	3.1060	-1.5189
C25	-1.6847	2.2530	-4.0790
H26	-1.4389	3.3155	-4.0044
H27	-1.3863	1.9105	-5.0718
H28	-2.7683	2.1605	-3.9715

DIPEA$^{\cdot}$			
N1	-1.0488	-0.1675	-2.9069
C2	-2.1183	-0.8091	-3.5417
H3	-2.9324	-0.1414	-3.8055
C4	-2.4867	-2.2237	-3.2124
H5	-2.6424	-2.3959	-2.1318
H6	-3.4226	-2.4785	-3.7186
H7	-1.7401	-2.9603	-3.5417
C8	0.1458	-0.9453	-2.5443
H9	-0.2006	-1.9699	-2.3900
C10	1.2044	-0.9775	-3.6620
H11	2.0261	-1.6543	-3.4026
H12	0.7556	-1.3184	-4.5996
H13	1.6339	0.0165	-3.8288
C14	0.7413	-0.4830	-1.2062
H15	-0.0295	-0.4684	-0.4301
H16	1.5383	-1.1665	-0.8942
H17	1.1808	0.5177	-1.2711
C18	-0.8754	1.2736	-3.1668
H19	0.1125	1.5403	-2.7802
C20	-1.9089	2.0931	-2.3778
H21	-2.9273	1.8633	-2.7073
H22	-1.8416	1.8678	-1.3096
H23	-1.7435	3.1663	-2.5214
C24	-0.8929	1.6406	-4.6628
H25	-0.6545	2.7019	-4.7930
H26	-0.1608	1.0509	-5.2201
H27	-1.8761	1.4588	-5.1057
DIPEA^{+}			
N1	-0.9956	0.0447	-2.9823
C2	-2.3704	-0.5125	-3.1887
H3	-2.4902	-1.3776	-2.5351
H4	-3.0690	0.2426	-2.8334
C5	-2.6524	-0.8565	-4.6517
H6	-1.9648	-1.6143	-5.0348
H7	-3.6686	-1.2513	-4.7324
H8	-2.5800	0.0263	-5.2896
C9	0.0611	-0.7154	-2.9515
C10	0.0006	-2.2031	-3.0990
H11	0.5479	-2.6548	-2.2637
H12	-0.9946	-2.6353	-3.1487
H13	0.5513	-2.4796	-4.0073
C14	1.4422	-0.1463	-2.7634
H15	1.5363	0.3388	-1.7858
H16	2.1846	-0.9426	-2.8189
H17	1.6802	0.5958	-3.5316
C18	-0.9192	1.5380	-2.7679
H19	0.1376	1.7939	-2.7891
C20	-1.4686	1.8837	-1.3788
H21	-2.5429	1.6972	-1.2990
H22	-0.9569	1.3197	-0.5939
H23	-1.3055	2.9486	-1.1944
C24	-1.6056	2.3010	-3.9037
H25	-1.4307	3.3689	-3.7492
H26	-1.1914	2.0302	-4.8783
H27	-2.6877	2.1486	-3.9215
DIPEA-H^{+}			
N1	-0.9776	0.1049	-3.2894
C2	-2.4047	-0.4577	-3.3013
H3	-2.4319	-1.2892	-2.5974
H4	-3.0650	0.3148	-2.9127
C5	-2.8289	-0.8839	-4.7002
H6	-2.1793	-1.6668	-5.1027
H7	-3.8458	-1.2833	-4.6620
H8	-2.8322	-0.0362	-5.3922
C9	-0.0016	-0.8015	-2.5043
H10	-0.4537	-0.9030	-1.5140
C11	0.0758	-2.1655	-3.1959
H12	0.7336	-2.8154	-2.6142
H13	-0.8885	-2.6706	-3.2757
H14	0.5092	-2.0738	-4.1986
C15	1.3858	-0.1704	-2.3899
H16	1.4045	0.7259	-1.7680
H17	2.0537	-0.8990	-1.9239
H18	1.8025	0.0674	-3.3751
C19	-0.9228	1.6049	-2.9230
H20	0.1301	1.8660	-3.0381
C21	-1.3509	1.8459	-1.4789
H22	-2.4040	1.6055	-1.3102
H23	-0.7449	1.2859	-0.7628
H24	-1.2217	2.9083	-1.2569
C25	-1.7214	2.4164	-3.9433
H26	-1.5440	3.4778	-3.7520
H27	-1.4000	2.2131	-4.9704
H28	-2.7991	2.2485	-3.8717
H29	-0.6492	0.0660	-4.2597
11^{Br}			
N1	-1.9987	3.7489	3.9623
C2	-2.7099	3.2347	2.8622
N3	-2.2865	3.6284	1.5913
C4	-0.8719	4.6011	3.9318
C5	-0.5319	4.9602	2.5787
C6	-1.1956	4.4410	1.4829
N7	0.5200	5.7184	2.0659
C8	0.4399	5.6080	0.7032
N9	-0.5935	4.8284	0.3295
C10	-2.9197	3.0701	0.3883
O11	-3.6427	2.4605	3.0260
O12	-0.2786	4.9469	4.9506
C13	-2.4205	3.2189	5.2661
H14	-3.7484	2.4465	0.7157
H15	-2.1870	2.4740	-0.1633
H16	-3.2682	3.8642	-0.2757
H17	-2.1730	2.1570	5.3146
H18	-3.4972	3.3502	5.3783
H19	-1.8781	3.7660	6.0335
H20	2.2561	7.7459	0.7927
C21	2.1737	7.2515	-0.1665
C22	2.9400	7.6600	-1.2518
H23	3.6326	8.4898	-1.1485
C24	2.7996	6.9917	-2.4758
H25	3.3888	7.2717	-3.3427
C26	1.8785	5.9570	-2.5674
H27	1.7185	5.4181	-3.4959
N28	1.1337	5.5430	-1.5290
C29	1.2918	6.1744	-0.3286
C30	1.5537	6.3154	2.8620
C31	1.2199	7.2875	3.8004
C32	2.8699	5.8527	2.7590
C33	2.1971	7.8099	4.6458
C34	3.8473	6.3744	3.5929
C35	3.5174	7.3493	4.5472
H36	0.1896	7.6128	3.8921
H37	3.1259	5.0613	2.0660
H38	1.9154	8.5524	5.3821

H39	4.8676	6.0092	3.5491
O40	4.5441	7.7715	5.3336
C41	4.2566	8.6650	6.4016
H42	3.8810	9.6294	6.0348
H43	3.5256	8.2361	7.0993
H44	5.2021	8.8236	6.9229
Ni45	-0.5321	4.3282	-1.6904
Br46	-2.6016	4.8553	-2.9165
N47	1.7361	2.0523	3.4065
C48	0.4767	1.4361	3.2799
C49	2.6352	2.3635	2.3575
C50	2.1317	2.3774	4.7843
N51	0.0022	1.2097	1.9903
O52	-0.1754	1.1166	4.2645
C53	0.7601	1.6086	0.9140
C54	-1.2020	0.3858	1.8329
C55	2.0391	2.1044	1.0754
O56	3.7519	2.8346	2.5600
N57	2.4938	2.3757	-0.2128
N58	0.3941	1.5829	-0.3920
C59	1.4537	2.0604	-1.0506
C60	3.8305	2.8043	-0.5254
C61	1.4559	2.2669	-2.5141
H62	-2.0183	0.7844	2.4324
H63	-0.9917	-0.6367	2.1604
H64	-1.4731	0.3864	0.7790
H65	2.1140	1.4739	5.3968
H66	1.4317	3.1072	5.1986
H67	3.1352	2.7956	4.7450
C68	2.4377	1.7346	-3.3496
H69	3.2667	1.1791	-2.9276
C70	2.3196	1.9260	-4.7267
H71	3.0694	1.5204	-5.3997
C72	1.2209	2.6251	-5.2228
H73	1.0851	2.7798	-6.2881
C74	0.2901	3.1425	-4.3199
H75	-0.5817	3.7164	-4.6253
N76	0.4166	2.9851	-2.9940
C77	4.1574	4.1536	-0.5469
C78	4.8280	1.8386	-0.6980
C79	5.4782	4.5573	-0.7412
H80	3.3890	4.8943	-0.3865
C81	6.1434	2.2290	-0.8991
H82	4.5679	0.7855	-0.6458
C83	6.4796	3.5927	-0.9100
H84	5.7075	5.6160	-0.7442
H85	6.9369	1.5000	-1.0241
O86	7.7998	3.8666	-1.0831
C87	8.2307	5.2175	-0.9774
H88	7.7989	5.8443	-1.7688
H89	7.9756	5.6449	0.0011
H90	9.3159	5.1958	-1.0895

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N1	-0.0847	-1.6184	0.9476
C2	1.0281	-1.5331	0.0851
N3	1.6585	-0.2902	-0.0092
C4	-0.6393	-0.5861	1.7444
C5	0.1000	0.6384	1.5808
C6	1.1985	0.7483	0.7500
N7	-0.0469	1.8848	2.1843
C8	0.9489	2.6755	1.6843
N9	1.7222	1.9995	0.8113
C10	2.8369	-0.1227	-0.8693
O11	1.4043	-2.5079	-0.5458
O12	-1.6191	-0.7569	2.4607
C13	-0.7100	-2.9443	1.0074
H14	3.7358	0.0186	-0.2664
H15	2.7190	0.7690	-1.4858
H16	2.9241	-1.0150	-1.4849
H17	0.0178	-3.6812	1.3538
H18	-1.0487	-3.2393	0.0121
H19	-1.5495	-2.8816	1.6964
H20	-0.4926	4.6821	3.0847
C21	0.4584	4.9877	2.6696
C22	0.9159	6.2950	2.8230
H23	0.3176	7.0161	3.3713
C24	2.1423	6.6657	2.2661
H25	2.5276	7.6742	2.3727
C26	2.8687	5.7146	1.5557
H27	3.8218	5.9249	1.0807
N28	2.4352	4.4537	1.4043
C29	1.2530	4.0805	1.9615
C30	-0.9758	2.1857	3.2351
C31	-2.3409	2.2120	2.9720
C32	-0.4973	2.4180	4.5288
C33	-3.2448	2.4836	3.9983
C34	-1.3897	2.6996	5.5518
C35	-2.7702	2.7300	5.2945
H36	-2.6975	2.0020	1.9699
H37	0.5702	2.3787	4.7217
H38	-4.3050	2.4913	3.7795
H39	-1.0475	2.8844	6.5642
O40	-3.5567	3.0032	6.3679
C41	-4.9690	2.9934	6.1973
H42	-5.2956	3.7636	5.4865
H43	-5.3260	2.0127	5.8575
H44	-5.3902	3.2100	7.1800
Ni45	3.3858	3.1302	0.2650
O46	5.1024	4.2668	-0.2774
C47	5.4647	3.2442	-0.9383
O48	4.7383	2.1926	-0.9610
C49	6.7480	3.2617	-1.7003
C50	7.5579	4.4043	-1.6857
C51	7.1474	2.1378	-2.4339
C52	8.7558	4.4221	-2.3979
C53	8.3453	2.1566	-3.1461
C54	9.1509	3.2984	-3.1290
H55	7.2292	5.2637	-1.1111
H56	6.5053	1.2634	-2.4320
H57	9.3826	5.3098	-2.3845
H58	8.6529	1.2828	-3.7141
H59	10.0847	3.3128	-3.6854

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N1	-0.7258	-1.8786	1.6448
C2	0.0017	-1.7260	0.4464
N3	0.4326	-0.4340	0.1265
C4	-1.0409	-0.8746	2.5918
C5	-0.5567	0.4093	2.1548
C6	0.1394	0.5946	0.9757
N7	-0.6408	1.6637	2.7502
C8	0.0073	2.5286	1.9182
N9	0.4780	1.9022	0.8215
C10	1.2101	-0.2053	-1.0977
O11	0.2373	-2.6866	-0.2674
O12	-1.6429	-1.1066	3.6332
C13	-1.1557	-3.2529	1.9289
H14	2.0252	0.4869	-0.8809
H15	0.5865	0.2422	-1.8731
H16	1.5946	-1.1669	-1.4307
H17	-0.2837	-3.9019	2.0363

H18	-1.7610	-3.6260	1.1006
H19	-1.7323	-3.2339	2.8511
H20	-0.2957	4.2146	4.1683
C21	0.0799	4.6924	3.2730
C22	0.4140	6.0454	3.2701
H23	0.2904	6.6340	4.1740
C24	0.9098	6.6310	2.1039
H25	1.1740	7.6824	2.0693
C26	1.0685	5.8353	0.9715
H27	1.4481	6.2167	0.0291
N28	0.7566	4.5314	0.9697
C29	0.2568	3.9605	2.0949
C30	-1.4618	1.9945	3.8807
C31	-2.6236	2.7334	3.6751
C32	-1.1044	1.5731	5.1641
C33	-3.4368	3.0771	4.7547
C34	-1.9099	1.9092	6.2415
C35	-3.0812	2.6611	6.0453
H36	-2.8912	3.0426	2.6692
H37	-0.2092	0.9778	5.3065
H38	-4.3370	3.6524	4.5779
H39	-1.6642	1.5912	7.2489
O40	-3.7973	2.9292	7.1669
C41	-5.0262	3.6349	7.0365
H42	-4.8716	4.6441	6.6331
H43	-5.7343	3.0936	6.3958
H44	-5.4365	3.7098	8.0445
Ni45	1.0118	3.3246	-0.5930
S46	1.5989	3.8062	-3.1257
O47	1.2398	2.4805	-2.4882
O48	1.0860	4.0670	-4.4649
O49	1.4082	4.8674	-2.0734
C50	3.4512	3.6890	-3.2731
F51	3.9543	4.8426	-3.7230
F52	3.9810	3.4312	-2.0641
F53	3.7906	2.7039	-4.1112

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11^{OAr*}

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N1	-4.0598	2.1288	-4.3605
C2	-2.8964	2.5175	-5.0549
N3	-1.6826	2.3944	-4.3693
C4	-4.1489	1.6135	-3.0424
C5	-2.8435	1.5270	-2.4383
C6	-1.6892	1.8989	-3.0959
N7	-2.4445	1.0697	-1.1848
C8	-1.0833	1.1924	-1.1429
N9	-0.6083	1.6946	-2.3020
C10	-0.4231	2.7578	-5.0276
O11	-2.9609	2.9402	-6.1972
O12	-5.2131	1.2999	-2.5244
C13	-5.3048	2.2802	-5.1235
H14	0.2350	1.8866	-5.0887
H15	0.0886	3.5384	-4.4596
H16	-0.6656	3.1155	-6.0259
H17	-5.2606	1.6715	-6.0292
H18	-5.4338	3.3240	-5.4173
H19	-6.1239	1.9567	-4.4849
H20	-1.4241	0.2310	1.5057
C21	-0.4053	0.4329	1.2048
C22	0.6522	0.2239	2.0862
H23	0.4561	-0.1469	3.0876
C24	1.9585	0.4950	1.6717
H25	2.8046	0.3403	2.3327
C26	2.1607	0.9825	0.3842
H27	3.1474	1.2323	0.0067
N28	1.1504	1.1911	-0.4738
C29	-0.1242	0.9106	-0.0792
C30	-3.3407	0.5608	-0.1857
C31	-4.2075	1.4315	0.4665
C32	-3.3799	-0.8114	0.0798
C33	-5.1199	0.9420	1.3995
C34	-4.2771	-1.3041	1.0159
C35	-5.1591	-0.4320	1.6757
H36	-4.1816	2.4900	0.2306
H37	-2.7112	-1.4818	-0.4513
H38	-5.7953	1.6314	1.8906
H39	-4.3333	-2.3636	1.2410
O40	-6.0087	-1.0194	2.5566
C41	-6.9864	-0.2119	3.2032
H42	-6.5221	0.5524	3.8399
H43	-7.6489	0.2751	2.4763
H44	-7.5705	-0.8914	3.8254
Ni45	1.3443	2.0651	-2.2787
O46	2.7726	2.8848	-3.0434
C47	3.9172	3.5145	-3.2598
C48	4.8975	2.9150	-4.1074
C49	4.1778	4.7986	-2.6826
C50	6.0964	3.5973	-4.3398
C51	5.3971	5.4146	-2.9663
C52	6.3794	4.8468	-3.7859
H53	6.8347	3.1357	-4.9794
H54	5.6001	6.3849	-2.5309
C55	4.6431	1.5299	-4.7425
C56	3.1492	5.4888	-1.7593
C57	2.9452	4.6472	-0.4761
H58	2.2014	5.1173	0.1804
H59	2.6027	3.6403	-0.7123
H60	3.8871	4.5690	0.0793
C61	3.6122	6.8895	-1.3009
H62	3.7729	7.5651	-2.1478
H63	2.8411	7.3367	-0.6630
H64	4.5372	6.8474	-0.7157
C65	1.8011	5.6849	-2.4954
H66	1.0666	6.1579	-1.8305
H67	1.9355	6.3331	-3.3685
H68	1.3978	4.7322	-2.8370
C69	5.8073	1.0748	-5.6464
H70	5.5708	0.0973	-6.0821
H71	5.9795	1.7722	-6.4734
H72	6.7441	0.9683	-5.0880
C73	3.3704	1.5657	-5.6247
H74	3.1604	0.5690	-6.0340
H75	2.5114	1.8980	-5.0424
H76	3.5075	2.2562	-6.4647
C77	4.4880	0.4602	-3.6323
H78	5.4013	0.4042	-3.0284
H79	3.6519	0.6966	-2.9725
H80	4.3126	-0.5292	-4.0742
C81	7.6944	5.6055	-4.0364
C82	8.4277	5.8308	-2.6930
H83	9.3678	6.3746	-2.8486
H84	7.8185	6.4113	-1.9935
H85	8.6610	4.8728	-2.2158
C86	7.3874	6.9770	-4.6822
H87	8.3125	7.5392	-4.8614
H88	6.8746	6.8456	-5.6409
H89	6.7438	7.5888	-4.0424
C90	8.6437	4.8385	-4.9752
H91	8.9196	3.8627	-4.5611
H92	8.1923	4.6752	-5.9599
H93	9.5661	5.4114	-5.1232

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$(11^{Br})_2$

N1	3.9984	-1.1754	-0.8973
C2	5.3791	-1.4123	-0.7467
N3	6.0786	-0.5381	0.0813
C4	3.2284	-0.1685	-0.2665
C5	4.0549	0.6983	0.5200
C6	5.4091	0.4823	0.6972
N7	3.7402	1.7849	1.3405
C8	4.9056	2.1334	1.9578
N9	5.9450	1.3718	1.5730
C10	7.5104	-0.7386	0.3284
O11	5.9225	-2.3388	-1.3313
O12	2.0074	-0.1016	-0.4023
C13	3.3011	-2.1235	-1.7701
H14	7.6630	-1.1383	1.3354
H15	8.0267	0.2185	0.2332
H16	7.8766	-1.4490	-0.4095
H17	3.2778	-3.1160	-1.3128
H18	3.8309	-2.1950	-2.7203
H19	2.2887	-1.7541	-1.9172
H20	3.0771	3.1967	3.7730
C21	4.0797	3.5988	3.8508
C22	4.4067	4.5514	4.8130
H23	3.6510	4.9047	5.5078
C24	5.7116	5.0406	4.8709
H25	6.0011	5.7859	5.6039
C26	6.6465	4.5697	3.9508
H27	7.6628	4.9470	3.9214
N28	6.3407	3.6547	3.0245
C29	5.0804	3.1702	2.9780
C30	2.5888	2.6335	1.1951
C31	2.7654	3.9189	0.6794
C32	1.3150	2.1597	1.5201
C33	1.6586	4.7479	0.4916
C34	0.2158	2.9831	1.3317
C35	0.3756	4.2821	0.8184
H36	3.7627	4.2717	0.4227
H37	1.1922	1.1445	1.8791
H38	1.8085	5.7388	0.0812
H39	-0.7882	2.6433	1.5616
O40	-0.7687	4.9942	0.6880
C41	-0.7185	6.2659	0.0394
H42	-0.0726	6.9684	0.5825
H43	-0.3801	6.1678	-0.9967
H44	-1.7424	6.6428	0.0528
Ni45	7.3065	3.2245	1.2976
Br46	6.3720	5.5893	0.4410
C47	3.5094	8.1472	-2.3525
N48	2.1638	7.7683	-2.5471
C49	1.6830	6.4742	-2.8525
C50	1.2068	8.8791	-2.5223
N51	4.4626	7.1319	-2.3611
O52	3.8183	9.3167	-2.1931
C53	4.0611	5.8387	-2.5514
C54	5.8742	7.5333	-2.3089
C55	2.7429	5.5074	-2.8214
O56	0.4954	6.2530	-3.0850
N57	2.7266	4.1266	-3.0113
N58	4.8412	4.7268	-2.5495
C59	4.0155	3.7103	-2.8567
C60	1.5649	3.2984	-3.1665
C61	4.5812	2.3752	-3.0536
Ni62	6.4500	3.8676	-1.4242
H63	6.4874	6.6409	-2.4099
H64	6.0917	8.0014	-1.3498
H65	6.0712	8.2406	-3.1182
H66	1.4680	9.6136	-3.2873
H67	1.2426	9.3737	-1.5490
H68	0.2176	8.4674	-2.7109
H69	3.0253	1.5209	-4.2783
C70	4.0006	1.3713	-3.8335
C71	4.7116	0.1922	-4.0385
H72	4.2866	-0.5992	-4.6482
C73	5.9711	0.0466	-3.4577
H74	6.5404	-0.8696	-3.5618
C75	6.4782	1.0919	-2.6889
H76	7.4490	1.0408	-2.2088
N77	5.8088	2.2375	-2.4884
C78	1.3000	2.3146	-2.2207
C79	0.7309	3.4601	-4.2776
C80	0.2160	1.4552	-2.3850
H81	1.9371	2.1987	-1.3553
C82	-0.3583	2.6171	-4.4399
H83	0.9321	4.2485	-4.9941
C84	-0.6178	1.6054	-3.4991
H85	0.0592	0.6872	-1.6402
H86	-1.0258	2.7190	-5.2889
O87	-1.7001	0.8251	-3.7637
C88	-2.0222	-0.2106	-2.8441
H89	-1.2082	-0.9423	-2.7577
H90	-2.2482	0.1908	-1.8478
H91	-2.9097	-0.7025	-3.2458
Br92	8.7813	2.8058	-0.6300

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N1	-0.2682	-1.2637	0.4710
C2	0.9188	-1.1700	-0.2807
N3	1.7080	-0.0281	-0.0928
C4	-0.7597	-0.3302	1.4124
C5	0.1043	0.8227	1.4908
C6	1.2648	0.9513	0.7488
N7	-0.0168	1.9971	2.2287
C8	1.0654	2.7580	1.9171
N9	1.8438	2.1542	1.0035
C10	2.9950	0.0488	-0.7955
O11	1.2529	-2.0533	-1.0504
O12	-1.7870	-0.5093	2.0545
C13	-1.0408	-2.4920	0.2458
H14	3.4351	-0.9475	-0.8127
H15	3.6520	0.7401	-0.2649
H16	2.8517	0.3798	-1.8277
H17	-0.4332	-3.3629	0.5009
H18	-1.3195	-2.5618	-0.8075
H19	-1.9264	-2.4446	0.8755
H20	0.2459	4.1536	4.2220
C21	1.0076	4.6433	3.6282
C22	1.5720	5.8541	4.0267
H23	1.2393	6.3269	4.9458
C24	2.5702	6.4431	3.2497
H25	3.0325	7.3798	3.5406
C26	2.9795	5.7979	2.0829
H27	3.7509	6.1871	1.4270
N28	2.4310	4.6434	1.6985
C29	1.4677	4.0598	2.4458
C30	-1.1975	2.4302	2.9221
C31	-1.9424	3.4725	2.3773
C32	-1.6129	1.7873	4.0911
C33	-3.1136	3.8952	3.0055
C34	-2.7770	2.2030	4.7178
C35	-3.5375	3.2557	4.1794
H36	-1.6120	3.9401	1.4542
H37	-1.0394	0.9554	4.4837
H38	-3.6877	4.7028	2.5682

H39	-3.1331	1.7197	5.6209
O40	-4.6625	3.5720	4.8680
C41	-5.5203	4.5821	4.3490
H42	-5.0148	5.5554	4.3016
H43	-5.8939	4.3178	3.3514
H44	-6.3596	4.6462	5.0428
Ni45	2.9975	3.5696	0.0339
Br46	3.8886	5.1754	-1.5118
Br47	5.1005	2.7473	1.0516
C48	1.3644	3.9421	-1.0143
C49	0.4358	4.8988	-0.6140
C50	1.0446	2.9878	-1.9800
C51	-0.8706	4.8239	-1.1022
C52	-0.2630	2.9164	-2.4578
C53	-1.2423	3.8162	-2.0059
H54	0.7120	5.6822	0.0821
H55	1.7917	2.2836	-2.3316
H56	-1.5972	5.5591	-0.7673
H57	-0.5560	2.1539	-3.1729
C58	-2.6471	3.6349	-2.4908
O59	-2.9213	2.7631	-3.3020
C60	-3.7335	4.5373	-1.9238
H61	-3.7884	4.4352	-0.8333
H62	-3.5294	5.5906	-2.1462
H63	-4.6901	4.2529	-2.3633

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12^{OTf,Br}

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N1	0.4104	-1.3807	0.7952
C2	1.5445	-1.2396	-0.0301
N3	2.1996	0.0001	-0.0011
C4	-0.1454	-0.4147	1.6690
C5	0.5850	0.8270	1.5890
C6	1.6934	0.9938	0.7815
N7	0.3907	2.0470	2.2350
C8	1.3876	2.8669	1.8088
N9	2.1711	2.2587	0.9027
C10	3.4350	0.1979	-0.7709
O11	1.9363	-2.1604	-0.7246
O12	-1.1135	-0.6411	2.3829
C13	-0.2227	-2.7052	0.7419
H14	3.8175	-0.7837	-1.0424
H15	4.1547	0.7456	-0.1626
H16	3.2335	0.7687	-1.6838
H17	0.4859	-3.4683	1.0715
H18	-0.5182	-2.9293	-0.2847
H19	-1.0910	-2.6826	1.3966
H20	0.5015	4.4008	3.9935
C21	1.2456	4.8741	3.3649
C22	1.7669	6.1317	3.6713
H23	1.4169	6.6594	4.5534
C24	2.7458	6.6947	2.8543
H25	3.1806	7.6620	3.0795
C26	3.1751	5.9852	1.7311
H27	3.9463	6.3454	1.0616
N28	2.6608	4.7911	1.4315
C29	1.7264	4.2247	2.2291
C30	-0.8416	2.4649	2.8506
C31	-1.6357	3.3771	2.1592
C32	-1.2654	1.9196	4.0645
C33	-2.8686	3.7636	2.6803
C34	-2.4914	2.3037	4.5869
C35	-3.3050	3.2189	3.8965
H36	-1.2995	3.7688	1.2045
H37	-0.6533	1.1828	4.5717
H38	-3.4823	4.4621	2.1246
H39	-2.8590	1.8901	5.5195
O40	-4.4934	3.5034	4.4853
C41	-5.4159	4.3362	3.7907
H42	-5.0179	5.3495	3.6486
H43	-5.6832	3.9110	2.8148
H44	-6.3061	4.3854	4.4190
Ni45	3.0621	3.7181	-0.2798
Br46	3.6999	5.1106	-2.1192
C47	1.2772	4.1495	-1.0244
C48	0.5893	5.3118	-0.6858
C49	0.6395	3.0904	-1.6704
C50	-0.7840	5.3817	-0.9230
C51	-0.7345	3.1654	-1.8923
C52	-1.4643	4.3028	-1.5094
H53	1.1086	6.1491	-0.2365
H54	1.1900	2.2025	-1.9663
H55	-1.3170	6.2847	-0.6417
H56	-1.2695	2.3421	-2.3553
C57	-2.9461	4.2991	-1.7293
O58	-3.5008	3.3301	-2.2246
C59	-3.7490	5.5200	-1.3078
H60	-3.6265	5.7200	-0.2365
H61	-3.4143	6.4143	-1.8453
H62	-4.8018	5.3379	-1.5259
O63	7.2497	2.8676	0.6307
O64	4.8533	2.9342	0.0056
O65	5.7887	4.7783	1.4117
C66	5.4182	2.3900	2.4895
S67	5.9298	3.3761	0.9908
F68	5.2076	1.1033	2.1621
F69	6.3566	2.4460	3.4368
F70	4.2680	2.8771	3.0072

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12$^{OAr^*,Br}$

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N1	-0.3279	-1.4634	0.6823
C2	0.9180	-1.4944	0.0315
N3	1.7638	-0.3988	0.2234
C4	-0.8312	-0.4339	1.5176
C5	0.1053	0.6580	1.6044
C6	1.3376	0.6579	0.9807
N7	0.0115	1.8822	2.2565
C8	1.1798	2.5387	2.0018
N9	2.0048	1.8184	1.2225
C10	3.0574	-0.3883	-0.4574
O11	1.2502	-2.4409	-0.6642
O12	-1.9189	-0.5064	2.0750
C13	-1.1719	-2.6415	0.4530
H14	3.4884	-1.3884	-0.4138
H15	3.7006	0.3366	0.0376
H16	2.9381	-0.1049	-1.5077
H17	-0.6614	-3.5398	0.8075
H18	-1.3642	-2.7538	-0.6161
H19	-2.1022	-2.4904	0.9962
H20	0.1762	4.0463	4.1139
C21	0.9701	4.5247	3.5549
C22	1.4277	5.7943	3.8967
H23	0.9876	6.3198	4.7390
C24	2.4501	6.3762	3.1494
H25	2.8279	7.3662	3.3810
C26	2.9932	5.6595	2.0847
H27	3.7777	6.0544	1.4466
N28	2.5636	4.4339	1.7581
C29	1.5578	3.8731	2.4664
C30	-1.2252	2.4733	2.6930
C31	-1.8078	3.4433	1.8818
C32	-1.8563	2.0384	3.8599
C33	-3.0321	4.0044	2.2399

C34	-3.0736	2.5972	4.2210
C35	-3.6721	3.5775	3.4114
H36	-1.3153	3.7471	0.9646
H37	-1.4073	1.2537	4.4589
H38	-3.4800	4.7464	1.5903
H39	-3.5984	2.2752	5.1138
O40	-4.8719	4.0419	3.8483
C41	-5.5815	4.9615	3.0263
H42	-5.0304	5.9033	2.9041
H43	-5.7929	4.5362	2.0369
H44	-6.5219	5.1604	3.5426
Ni45	3.1054	3.4025	-0.0121
Br46	4.4379	5.3174	-1.0244
O47	4.8524	2.2402	0.2795
C48	1.3429	3.7816	-0.8847
C49	0.7731	5.0642	-0.7940
C50	0.5318	2.7619	-1.4216
C51	-0.5519	5.3082	-1.1562
C52	-0.7906	2.9923	-1.7947
C53	-1.3625	4.2674	-1.6447
H54	1.3810	5.8850	-0.4225
H55	0.9295	1.7537	-1.5282
H56	-0.9575	6.3105	-1.0431
H57	-1.4185	2.1932	-2.1788
C58	-2.8111	4.4359	-1.9547
O59	-3.4903	3.5047	-2.3695
C60	-3.4532	5.7980	-1.7156
H61	-3.3481	6.1028	-0.6674
H62	-2.9716	6.5713	-2.3237
H63	-4.5113	5.7372	-1.9741
C64	6.0709	2.6097	0.2446
C65	6.8128	2.6184	-1.0229
C66	6.7368	3.0784	1.4561
C67	7.9697	3.3632	-1.0716
C68	7.8954	3.8228	1.3001
C69	8.5026	4.0394	0.0534
H70	8.4936	3.4586	-2.0127
H71	8.3526	4.2533	2.1816
C72	6.2424	2.7962	2.8897
C73	6.3433	1.7644	-2.2135
C74	9.7159	4.9550	-0.1258
C75	7.3898	2.0729	3.6456
H76	7.0773	1.8541	4.6727
H77	7.6384	1.1246	3.1575
H78	8.3022	2.6737	3.6961
C79	4.9964	1.8941	2.9896
H80	5.1410	0.9429	2.4701
H81	4.8059	1.6765	4.0476
H82	4.1133	2.3637	2.5652
C83	5.9263	4.1315	3.6051
H84	5.5859	3.9360	4.6286
H85	6.8003	4.7875	3.6635
H86	5.1350	4.6706	3.0803
C87	4.9324	2.1468	-2.7230
H88	4.7031	1.5627	-3.6220
H89	4.1654	1.9326	-1.9808
H90	4.8725	3.2091	-2.9655
C91	6.3514	0.2833	-1.7548
H92	5.9885	-0.3620	-2.5629
H93	7.3650	-0.0395	-1.4919
H94	5.7120	0.1329	-0.8840
C95	7.3061	1.8890	-3.4127
H96	8.3275	1.5896	-3.1544
H97	6.9654	1.2304	-4.2179
H98	7.3282	2.9092	-3.8102
C99	10.1828	5.5844	1.2001
H100	9.3937	6.1863	1.6628
H101	10.5072	4.8255	1.9207
H102	11.0353	6.2450	1.0125
C103	10.8969	4.1520	-0.7230
H104	11.1886	3.3327	-0.0572
H105	10.6527	3.7230	-1.6989
H106	11.7641	4.8081	-0.8569
C107	9.3165	6.0963	-1.0952
H108	10.1601	6.7817	-1.2346
H109	9.0268	5.7134	-2.0776
H110	8.4694	6.6649	-0.6989

6^{Br}

Ni1	1.8540	6.5641	-0.5874
Br2	2.9280	8.7213	-0.3459
N3	4.9390	3.3903	3.2053
C4	3.9821	4.3774	3.5270
C5	5.3779	3.0000	1.9179
C6	5.5455	2.7285	4.3677
N7	3.3619	5.0278	2.4537
O8	3.7140	4.6361	4.6866
C9	3.7306	4.6984	1.1857
C10	2.3577	6.0749	2.6917
C11	4.6861	3.7462	0.8938
O12	6.2319	2.1427	1.7351
N13	4.7594	3.6818	-0.4945
N14	3.2333	5.2123	0.0362
C15	3.8662	4.5927	-0.9749
C16	5.5926	2.7606	-1.2180
C17	3.5428	4.9795	-2.3508
H18	1.4024	5.7745	2.2497
H19	2.6885	7.0132	2.2357
H20	2.2541	6.1928	3.7679
H21	4.7643	2.2692	4.9764
H22	6.0721	3.4635	4.9801
H23	6.2362	1.9753	3.9953
C24	4.1446	4.4883	-3.5126
H25	4.9272	3.7449	-3.4541
C26	3.7134	4.9759	-4.7452
H27	4.1678	4.6047	-5.6585
C28	2.7028	5.9346	-4.7961
H29	2.3428	6.3313	-5.7386
C30	2.1578	6.3866	-3.5957
H31	1.3772	7.1391	-3.5611
N32	2.5699	5.9240	-2.4133
C33	6.9704	2.9488	-1.2413
C34	5.0131	1.6417	-1.8247
C35	7.7886	2.0207	-1.8830
H36	7.4045	3.8086	-0.7425
C37	5.8212	0.7208	-2.4735
H38	3.9381	1.4977	-1.7764
C39	7.2151	0.8981	-2.4983
H40	8.8606	2.1731	-1.8849
H41	5.4033	-0.1602	-2.9482
O42	7.9133	-0.0723	-3.1383
C43	9.3362	-0.0155	-3.1201
H44	9.7111	0.8759	-3.6390
H45	9.7241	-0.0291	-2.0938
H46	9.6766	-0.9079	-3.6469
Br47	-0.2705	5.4438	-0.3044

12^{OBAc,Br}

N1	-0.7139	-1.6980	1.1608
C2	-0.3903	-1.7387	-0.2148
N3	-0.2681	-0.5092	-0.8670

C4	-1.0428	-0.5587	1.9256
C5	-0.8730	0.6497	1.1589
C6	-0.4632	0.6437	-0.1640
N7	-1.0603	1.9894	1.4963
C8	-0.7584	2.7062	0.3772
N9	-0.3580	1.9143	-0.6295
C10	-0.0763	-0.5227	-2.3257
O11	-0.2354	-2.7882	-0.8155
O12	-1.4143	-0.6498	3.0901
C13	-0.8238	-2.9837	1.8597
H14	-0.1967	0.4915	-2.7041
H15	-0.8169	-1.1935	-2.7658
H16	0.9253	-0.8757	-2.5668
H17	-0.3312	-2.9010	2.8291
H18	-0.3545	-3.7465	1.2438
H19	-1.8751	-3.2353	2.0265
H20	-2.1749	4.6984	1.7683
C21	-1.6189	5.0446	0.9068
C22	-1.6501	6.3823	0.5183
H23	-2.2342	7.0974	1.0896
C24	-0.9332	6.7900	-0.6054
H25	-0.9349	7.8238	-0.9330
C26	-0.2024	5.8378	-1.3139
H27	0.3839	6.0709	-2.1959
N28	-0.1732	4.5549	-0.9418
C29	-0.8578	4.1499	0.1499
C30	-1.3037	2.5005	2.8158
C31	-2.4646	2.1549	3.4997
C32	-0.3466	3.3346	3.4053
C33	-2.6896	2.6543	4.7817
C34	-0.5717	3.8414	4.6760
C35	-1.7430	3.5028	5.3739
H36	-3.1779	1.4792	3.0426
H37	0.5623	3.5782	2.8631
H38	-3.5917	2.3692	5.3082
H39	0.1501	4.4905	5.1598
O40	-1.8602	4.0449	6.6131
C41	-2.9979	3.7100	7.4006
H42	-3.0529	2.6301	7.5885
H43	-2.8707	4.2342	8.3489
H44	-3.9292	4.0440	6.9253
Ni45	1.0030	3.1152	-1.8681
Br46	2.7401	1.5308	-2.4826
C47	2.3422	3.5339	-0.4975
C48	2.4188	2.8744	0.7265
C49	3.0490	4.7104	-0.7397
C50	3.1747	3.4440	1.7553
C51	3.7899	5.2735	0.2963
C52	3.8560	4.6562	1.5569
H53	1.9186	1.9243	0.8797
H54	3.0032	5.1787	-1.7175
H55	3.2312	2.9273	2.7092
H56	4.3355	6.2009	0.1507
C57	4.6637	5.3214	2.6259
O58	5.2004	6.4022	2.4258
C59	4.8110	4.6249	3.9708
H60	5.2753	3.6397	3.8484
H61	5.4342	5.2427	4.6185
H62	3.8357	4.4695	4.4460
C63	0.0253	4.4737	-5.4013
C64	0.7050	5.5571	-5.9718
C65	-1.0673	3.9038	-6.0669
C66	0.2910	6.0694	-7.1996
C67	-1.4794	4.4188	-7.2942
C68	-0.8022	5.5024	-7.8604
H69	1.5514	5.9800	-5.4408
H70	-1.5783	3.0648	-5.6066
H71	0.8183	6.9096	-7.6429
H72	-2.3283	3.9784	-7.8100
H73	-1.1258	5.9043	-8.8169
C74	0.4422	3.9505	-4.0729
O75	1.4007	4.5050	-3.4348
O76	-0.1804	2.9722	-3.5436

12^{OTf,OBAc}

N1	-0.5020	-1.7125	1.3286
C2	0.0406	-1.6717	0.0249
N3	0.2088	-0.4141	-0.5612
C4	-0.9726	-0.6217	2.0908
C5	-0.7469	0.6218	1.3946
C6	-0.1402	0.6960	0.1501
N7	-0.9946	1.9363	1.7833
C8	-0.5377	2.7229	0.7722
N9	0.0057	1.9962	-0.2163
C10	0.6619	-0.3678	-1.9625
O11	0.3379	-2.6955	-0.5638
O12	-1.4903	-0.7496	3.1941
C13	-0.6266	-3.0599	1.8968
H14	1.7156	-0.6327	-2.0221
H15	0.5330	0.6449	-2.3383
H16	0.0678	-1.0809	-2.5360
H17	0.3514	-3.5446	1.9029
H18	-1.3040	-3.6610	1.2860
H19	-1.0141	-2.9576	2.9081
H20	-2.1309	4.6641	2.0440
C21	-1.4215	5.0502	1.3235
C22	-1.3454	6.4127	1.0394
H23	-2.0022	7.1084	1.5523
C24	-0.4294	6.8723	0.0938
H25	-0.3459	7.9261	-0.1481
C26	0.3928	5.9470	-0.5460
H27	1.1367	6.2159	-1.2879
N28	0.3197	4.6425	-0.2681
C29	-0.5629	4.1818	0.6468
C30	-1.4490	2.3682	3.0743
C31	-2.7294	2.0449	3.5085
C32	-0.5816	3.1110	3.8829
C33	-3.1682	2.4791	4.7581
C34	-1.0168	3.5514	5.1236
C35	-2.3125	3.2390	5.5695
H36	-3.3746	1.4421	2.8796
H37	0.4241	3.3294	3.5341
H38	-4.1647	2.2146	5.0886
H39	-0.3706	4.1290	5.7756
O40	-2.6364	3.7157	6.7980
C41	-3.9168	3.4031	7.3361
H42	-4.7251	3.8123	6.7162
H43	-4.0543	2.3196	7.4424
H44	-3.9481	3.8694	8.3217
Ni45	1.5056	3.2506	-1.1191
C46	2.6343	3.4530	0.4517
C47	2.5858	2.5714	1.5223
C48	3.4951	4.5418	0.4122
C49	3.4119	2.8203	2.6245
C50	4.3024	4.7818	1.5218
C51	4.2662	3.9329	2.6398
H52	1.9564	1.6896	1.5051
H53	3.5545	5.1640	-0.4731
H54	3.3859	2.1285	3.4611
H55	4.9852	5.6255	1.5380
C56	5.1614	4.2558	3.7976
O57	5.8212	5.2846	3.8065
C58	5.2363	3.2764	4.9585

H59	4.2558	3.1524	5.4326
H60	5.5600	2.2880	4.6137
H61	5.9468	3.6578	5.6927
C62	1.6392	4.6747	-4.7269
C63	2.7398	5.4554	-5.1036
C64	0.6684	4.3217	-5.6721
C65	2.8639	5.8858	-6.4224
C66	0.7940	4.7590	-6.9888
C67	1.8906	5.5405	-7.3639
H68	3.4909	5.6948	-4.3582
H69	-0.1670	3.7039	-5.3596
H70	3.7216	6.4824	-6.7198
H71	0.0434	4.4864	-7.7253
H72	1.9899	5.8756	-8.3930
C73	1.5183	4.2101	-3.3252
O74	2.3414	4.6320	-2.4372
O75	0.6144	3.3813	-2.9764
O76	3.9902	1.3190	-3.6292
S77	4.0180	1.7824	-2.2423
O78	2.6059	1.7546	-1.6222
O79	4.8021	2.9636	-1.8858
C80	4.7438	0.3890	-1.2444
F81	4.0599	-0.7499	-1.4506
F82	6.0186	0.1914	-1.5923
F83	4.6938	0.6802	0.0652

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12^{OAr*,OBAc}

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N1	-0.6215	-1.3769	2.2368
C2	0.1919	-1.4776	1.0942
N3	0.2677	-0.3582	0.2687
C4	-1.4231	-0.2704	2.6242
C5	-1.2216	0.8429	1.7329
C6	-0.3698	0.7916	0.6452
N7	-1.7099	2.1476	1.7674
C8	-1.1311	2.8026	0.7199
N9	-0.2889	2.0028	0.0396
C10	1.0099	-0.4802	-0.9887
O11	0.8020	-2.5036	0.8327
O12	-2.1593	-0.3018	3.6022
C13	-0.6456	-2.5746	3.0825
H14	2.0094	-0.8620	-0.7859
H15	1.0733	0.4989	-1.4582
H16	0.4929	-1.1802	-1.6507
H17	0.3716	-2.8236	3.3917
H18	-1.0521	-3.4211	2.5240
H19	-1.2685	-2.3552	3.9471
H20	-3.1851	4.6350	1.3114
C21	-2.3926	5.0167	0.6820
C22	-2.4193	6.3282	0.2138
H23	-3.2430	6.9821	0.4842
C24	-1.3830	6.7895	-0.5964
H25	-1.3672	7.8083	-0.9691
C26	-0.3545	5.9090	-0.9288
H27	0.4895	6.1926	-1.5480
N28	-0.3329	4.6476	-0.4904
C29	-1.3160	4.2022	0.3158
C30	-2.4797	2.7185	2.8362
C31	-3.7746	2.2728	3.0741
C32	-1.9025	3.7085	3.6399
C33	-4.5218	2.8274	4.1125
C34	-2.6444	4.2665	4.6696
C35	-3.9575	3.8307	4.9127
H36	-4.1926	1.4834	2.4594
H37	-0.8833	4.0326	3.4515
H38	-5.5271	2.4668	4.2911
H39	-2.2249	5.0342	5.3109
O40	-4.5939	4.4431	5.9457
C41	-5.9103	4.0225	6.2791
H42	-6.6118	4.1949	5.4519
H43	-5.9361	2.9613	6.5586
H44	-6.2098	4.6281	7.1357
Ni45	1.3526	3.2865	-0.7355
O46	3.0970	1.8060	-1.3338
C47	2.0205	3.9999	1.0210
C48	2.8629	5.1262	0.9684
C49	1.6322	3.5677	2.3044
C50	3.3038	5.7751	2.1236
C51	2.0542	4.2082	3.4664
C52	2.9024	5.3262	3.3944
H53	3.1748	5.5019	-0.0043
H54	1.0022	2.6856	2.4083
H55	3.9609	6.6366	2.0318
H56	1.7505	3.8592	4.4502
C57	3.3239	5.9799	4.6654
O58	2.9077	5.5918	5.7513
C59	4.2930	7.1536	4.5941
H60	5.2210	6.8634	4.0897
H61	3.8608	7.9840	4.0240
H62	4.5165	7.4875	5.6084
C63	1.3843	4.6494	-4.4521
C64	2.1985	5.7387	-4.7856
C65	0.5623	4.0693	-5.4253
C66	2.1956	6.2387	-6.0866
C67	0.5579	4.5729	-6.7249
C68	1.3757	5.6564	-7.0570
H69	2.8306	6.1684	-4.0155
H70	-0.0553	3.2226	-5.1439
H71	2.8326	7.0798	-6.3468
H72	-0.0789	4.1206	-7.4805
H73	1.3749	6.0461	-8.0718
C74	1.4041	4.0967	-3.0667
O75	2.1044	4.6808	-2.1698
O76	0.7293	3.0579	-2.7913
C77	4.0363	0.9744	-1.4817
C78	4.5152	0.6128	-2.8296
C79	4.6504	0.2707	-0.3358
C80	5.1494	-0.6085	-2.9857
C81	5.2985	-0.9160	-0.5944
C82	5.4892	-1.4352	-1.9005
H83	5.4039	-0.9338	-3.9836
H84	5.6735	-1.4977	0.2367
C85	4.2606	1.5187	-4.0363
C86	4.5246	0.8193	1.0871
C87	6.0999	-2.8283	-2.0730
C88	3.0667	0.6577	1.5754
H89	2.7860	-0.4012	1.5845
H90	2.9649	1.0545	2.5904
H91	2.3822	1.2063	0.9332
C92	5.4345	0.0624	2.0764
H93	5.1257	-0.9793	2.2167
H94	6.4826	0.0743	1.7575
H95	5.3776	0.5505	3.0544
C96	4.9538	2.3038	1.0963
H97	4.8202	2.7277	2.0967
H98	6.0130	2.3933	0.8266
H99	4.3625	2.8989	0.4041
C100	5.1603	-3.8606	-1.3999
H101	4.1668	-3.8424	-1.8597
H102	5.5711	-4.8706	-1.5099
H103	5.0340	-3.6630	-0.3315
C104	6.2685	-3.2208	-3.5527
H105	6.9602	-2.5519	-4.0762
H106	6.6762	-4.2347	-3.6205

H107	5.3119	-3.2122	-4.0854
C108	7.4930	-2.8770	-1.3980
H109	7.4418	-2.6595	-0.3273
H110	7.9299	-3.8751	-1.5134
H111	8.1737	-2.1521	-1.8566
C112	2.7997	1.3174	-4.5038
H113	2.5877	1.9716	-5.3569
H114	2.6506	0.2798	-4.8238
H115	2.0815	1.5536	-3.7193
C116	4.5390	2.9959	-3.6740
H117	4.3350	3.6305	-4.5427
H118	3.9286	3.3497	-2.8474
H119	5.5948	3.1249	-3.4057
C120	5.1896	1.1582	-5.2176
H121	6.2438	1.1736	-4.9207
H122	4.9671	0.1764	-5.6490
H123	5.0522	1.8955	-6.0150

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13^{Ar,Br}

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N1	-0.2281	-0.5381	1.5941
C2	0.6897	-0.5958	0.5249
N3	0.8870	0.5867	-0.1984
C4	-0.9561	0.5889	2.0495
C5	-0.6492	1.7527	1.2534
C6	0.2374	1.7179	0.1972
N7	-1.0592	3.0791	1.3675
C8	-0.4150	3.7669	0.3813
N9	0.3684	2.9515	-0.3484
C10	1.8850	0.6452	-1.2722
O11	1.2683	-1.6319	0.2487
O12	-1.7333	0.5395	2.9935
C13	-0.4004	-1.8042	2.3185
H14	2.7306	1.2651	-0.9588
H15	1.4341	1.0821	-2.1673
H16	2.2154	-0.3714	-1.4736
H17	0.5587	-2.1277	2.7279
H18	-0.7611	-2.5752	1.6347
H19	-1.1192	-1.6323	3.1165
H20	-2.1282	5.8508	1.2256
C21	-1.3338	6.1440	0.5518
C22	-1.1913	7.4673	0.1380
H23	-1.8819	8.2224	0.5007
C24	-0.1668	7.8114	-0.7443
H25	-0.0341	8.8320	-1.0855
C26	0.6884	6.8076	-1.1969
H27	1.4923	6.9871	-1.9042
N28	0.5618	5.5407	-0.7922
C29	-0.4259	5.1978	0.0700
C30	-1.8507	3.5998	2.4489
C31	-3.1823	3.2207	2.5796
C32	-1.2486	4.4348	3.3965
C33	-3.9343	3.6817	3.6593
C34	-1.9949	4.9048	4.4663
C35	-3.3405	4.5248	4.6095
H36	-3.6235	2.5475	1.8531
H37	-0.2016	4.7026	3.2921
H38	-4.9661	3.3685	3.7565
H39	-1.5555	5.5483	5.2205
O40	-3.9723	5.0240	5.7014
C41	-5.3096	4.6129	5.9658
H42	-5.9951	4.9328	5.1704
H43	-5.3778	3.5246	6.0883
H44	-5.5918	5.0998	6.9003
Ni45	1.8316	4.0151	-1.3908
Br46	2.5286	4.5400	-3.6420
C47	3.2078	3.8983	0.0256
C48	4.5620	3.7818	-0.3300
C49	2.8986	3.9195	1.3979
C50	5.5635	3.6890	0.6408
C51	3.8867	3.8368	2.3727
C52	5.2379	3.7162	2.0064
H53	4.8372	3.7751	-1.3826
H54	1.8602	4.0097	1.7188
H55	6.5993	3.6006	0.3252
H56	3.6449	3.8599	3.4314
C57	6.2595	3.6302	3.0935
O58	5.9314	3.6601	4.2729
C59	7.7267	3.5069	2.7084
H60	7.8995	2.6087	2.1051
H61	8.0462	4.3669	2.1090
H62	8.3250	3.4552	3.6189

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13^{OBAc,Br}

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Ni1	1.7022	6.5842	-0.6316
Br2	3.0695	8.6095	-0.4572
N3	5.0495	3.6938	3.2583
C4	4.0962	4.6931	3.5533
C5	5.4091	3.1894	1.9840
C6	5.7146	3.1215	4.4352
N7	3.4330	5.2699	2.4663
O8	3.8726	5.0228	4.7055
C9	3.7240	4.8313	1.2093
C10	2.4031	6.2977	2.6728
C11	4.6575	3.8484	0.9453
O12	6.2468	2.3107	1.8269
N13	4.6330	3.6560	-0.4324
N14	3.1474	5.2447	0.0580
C15	3.7019	4.5218	-0.9275
C16	5.4170	2.6758	-1.1308
C17	3.2460	4.7296	-2.3055
H18	1.4540	5.9512	2.2505
H19	2.7034	7.2230	2.1725
H20	2.3064	6.4551	3.7448
H21	4.9729	2.6622	5.0923
H22	6.2243	3.9108	4.9912
H23	6.4259	2.3780	4.0826
C24	3.7635	4.1259	-3.4547
H25	4.5938	3.4366	-3.3898
C26	3.1835	4.4337	-4.6850
H27	3.5693	3.9744	-5.5901
C28	2.1142	5.3255	-4.7456
H29	1.6407	5.5787	-5.6877
C30	1.6613	5.9009	-3.5588
H31	0.8380	6.6064	-3.5124
N32	2.2179	5.6081	-2.3813
C33	6.7728	2.9013	-1.3404
C34	4.8197	1.4813	-1.5447
C35	7.5502	1.9343	-1.9763
H36	7.2225	3.8257	-0.9936
C37	5.5853	0.5193	-2.1860
H38	3.7637	1.3136	-1.3565
C39	6.9574	0.7356	-2.3987
H40	8.6066	2.1190	-2.1247
H41	5.1530	-0.4194	-2.5151
O42	7.6165	-0.2761	-3.0183
C43	9.0247	-0.1655	-3.1949
H44	9.2849	0.6796	-3.8453
H45	9.5421	-0.0561	-2.2334
H46	9.3397	-1.0951	-3.6707
C47	-2.1167	5.8115	-0.8314
C48	-2.6158	4.7072	-0.1282
C49	-2.9727	6.5728	-1.6375

C50	-0.6753	6.1620	-0.7356
C51	-3.9621	4.3652	-0.2338
H52	-1.9354	4.1319	0.4907
C53	-4.3189	6.2277	-1.7415
H54	-2.5660	7.4262	-2.1699
C55	-4.8138	5.1238	-1.0415
H56	-4.3493	3.5089	0.3115
H57	-4.9837	6.8173	-2.3665
H58	-5.8634	4.8545	-1.1254
O59	0.1045	5.4578	-0.0017
O60	-0.1951	7.1411	-1.3931

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15

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N1	2.4511	-1.7871	3.4391
C2	3.3056	-1.2616	4.4158
N3	3.2609	0.1247	4.6066
C4	1.5275	-1.0683	2.6168
C5	1.5790	0.3330	2.8936
C6	2.4215	0.8864	3.8352
N7	0.9178	1.4142	2.2979
C8	1.3917	2.5518	2.9184
N9	2.3344	2.2341	3.8548
C10	4.1222	0.7599	5.6016
O11	4.0559	-1.9807	5.0613
O12	0.8158	-1.6355	1.7930
C13	2.5288	-3.2409	3.2680
H14	4.6681	1.5883	5.1385
H15	4.8122	0.0052	5.9739
H16	3.5203	1.1580	6.4238
H17	2.2775	-3.7427	4.2053
H18	3.5443	-3.5299	2.9870
H19	1.8235	-3.5156	2.4864
H20	-0.7593	3.6527	1.5013
C21	-0.0961	4.3719	1.9652
C22	-0.3363	5.7306	1.8563
H23	-1.1913	6.0869	1.2893
C24	0.5275	6.6398	2.4947
H25	0.3644	7.7106	2.4451
C26	1.6029	6.1282	3.2121
H27	2.2854	6.7934	3.7279
N28	1.8811	4.8206	3.3084
C29	1.0256	3.9281	2.6992
C30	0.2054	1.3348	1.0596
C31	0.7943	1.8180	-0.1075
C32	-1.0535	0.7292	1.0134
C33	0.1187	1.7261	-1.3266
C34	-1.7276	0.6302	-0.1942
C35	-1.1488	1.1295	-1.3705
H36	1.7875	2.2530	-0.0685
H37	-1.4862	0.3257	1.9218
H38	0.5987	2.1012	-2.2219
H39	-2.7031	0.1604	-0.2590
O40	-1.8998	0.9726	-2.4972
C41	-1.4214	1.5216	-3.7135
H42	-1.3149	2.6121	-3.6427
H43	-0.4590	1.0844	-4.0127
H44	-2.1709	1.2836	-4.4706
Ni45	3.7188	3.7677	3.4609
N46	4.0064	9.1260	1.5443
C47	4.3495	8.8281	2.8688
C48	3.9205	8.2160	0.4432
C49	3.7069	10.5379	1.2882
N50	4.6434	7.4889	3.1534
O51	4.3840	9.6961	3.7300
C52	4.5508	6.5521	2.1571
C53	5.0002	7.0831	4.5111
C54	4.2214	6.8820	0.8588
O55	3.6161	8.5895	-0.6855
N56	4.2037	5.6721	0.1556
N57	4.7243	5.2210	2.3068
C58	4.5205	4.6861	1.0679
C59	3.5589	5.5049	-1.1115
C60	4.6447	3.2650	0.8631
H61	4.3481	6.2646	4.8340
H62	4.8785	7.9488	5.1592
H63	6.0355	6.7314	4.5398
H64	4.5696	11.1562	1.5463
H65	2.8614	10.8580	1.9019
H66	3.4690	10.6344	0.2308
C67	4.6810	2.6205	-0.3922
H68	4.6061	3.2029	-1.3020
C69	4.8194	1.2442	-0.4407
H70	4.8432	0.7342	-1.3991
C71	4.9445	0.5191	0.7583
H72	5.0693	-0.5580	0.7617
C73	4.9139	1.2240	1.9562
H74	5.0178	0.7047	2.9023
N75	4.7493	2.5517	2.0381
C76	2.2719	4.9733	-1.1658
C77	4.1967	5.9294	-2.2800
C78	1.6195	4.8397	-2.3940
H79	1.7707	4.6813	-0.2476
C80	3.5554	5.8007	-3.5024
H81	5.1848	6.3719	-2.2169
C82	2.2643	5.2555	-3.5667
H83	0.6164	4.4320	-2.4138
H84	4.0243	6.1281	-4.4240
O85	1.7284	5.1879	-4.8177
C86	0.4694	4.5580	-4.9816
H87	0.5053	3.5086	-4.6615
H88	-0.3252	5.0764	-4.4278
H89	0.2452	4.5995	-6.0490

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TS(11^{Br}-$12^{Br,Br}$)

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N1	-0.7842	-0.7149	-0.0025
C2	0.4948	-0.7428	-0.5946
N3	1.4374	0.1806	-0.1274
C4	-1.2304	0.1670	0.9992
C5	-0.1808	1.0647	1.4132
C6	1.0630	1.1008	0.8064
N7	-0.2211	2.1594	2.2718
C8	0.9808	2.7876	2.1437
N9	1.7708	2.1741	1.2484
C10	2.7844	0.1250	-0.7052
O11	0.7784	-1.5393	-1.4710
O12	-2.3840	0.1689	1.4209
C13	-1.7628	-1.6399	-0.5915
H14	3.1548	-0.8989	-0.6381
H15	3.4403	0.7989	-0.1543
H16	2.7515	0.4140	-1.7574
H17	-1.2995	-2.6189	-0.7109
H18	-2.0731	-1.2598	-1.5680
H19	-2.6173	-1.6894	0.0799
H20	0.2596	3.9596	4.5888
C21	1.0008	4.5057	4.0190
C22	1.5553	5.6901	4.4991
H23	1.2418	6.0836	5.4613
C24	2.5188	6.3557	3.7410
H25	2.9705	7.2791	4.0862
C26	2.9057	5.8055	2.5201
H27	3.6508	6.2665	1.8806
N28	2.3726	4.6716	2.0542

C29	1.4335	4.0244	2.7808
C30	-1.3699	2.5958	3.0121
C31	-1.9462	3.8318	2.7328
C32	-1.9167	1.7642	3.9940
C33	-3.0700	4.2581	3.4420
C34	-3.0349	2.1791	4.6980
C35	-3.6219	3.4269	4.4269
H36	-1.5137	4.4621	1.9643
H37	-1.4724	0.7937	4.1842
H38	-3.5070	5.2220	3.2125
H39	-3.4858	1.5513	5.4586
O40	-4.7152	3.7288	5.1717
C41	-5.3998	4.9500	4.9182
H42	-4.7589	5.8199	5.1123
H43	-5.7711	4.9957	3.8865
H44	-6.2458	4.9664	5.6067
Ni45	3.0523	3.6794	0.3574
Br46	3.3138	5.7274	-1.1415
Br47	5.2721	2.7302	0.6683
C48	1.5479	4.0957	-0.9479
C49	0.3340	4.5759	-0.4435
C50	1.5818	3.0993	-1.9310
C51	-0.8380	3.9044	-0.7737
C52	0.4012	2.4256	-2.2374
C53	-0.8146	2.7885	-1.6327
H54	0.3262	5.4120	0.2472
H55	2.5255	2.8159	-2.3854
H56	-1.7750	4.2296	-0.3330
H57	0.4038	1.5818	-2.9211
C58	-2.0166	1.9324	-1.8750
O59	-1.9391	0.9486	-2.6011
C60	-3.3092	2.2573	-1.1482
H61	-3.1829	2.0963	-0.0710
H62	-3.6168	3.2963	-1.3065
H63	-4.0880	1.5863	-1.5116

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TS(11^{OTf}-$12^{OTf,Br}$)

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N1	-0.2891	-0.9450	0.0147
C2	0.9281	-0.8873	-0.6926
N3	1.8268	0.1256	-0.3360
C4	-0.7320	-0.0512	1.0077
C5	0.2764	0.9314	1.3180
C6	1.4621	1.0349	0.6104
N7	0.2341	2.0429	2.1589
C8	1.3804	2.7397	1.9281
N9	2.1257	2.1627	0.9741
C10	3.1263	0.1490	-1.0159
O11	1.2012	-1.6836	-1.5725
O12	-1.8530	-0.1129	1.5055
C13	-1.2478	-1.9441	-0.4753
H14	3.5820	-0.8384	-0.9401
H15	3.7708	0.8729	-0.5247
H16	2.9887	0.3948	-2.0711
H17	-0.7175	-2.8738	-0.6769
H18	-1.7067	-1.5756	-1.3966
H19	-2.0080	-2.0820	0.2907
H20	0.8361	3.7997	4.4573
C21	1.5278	4.3789	3.8589
C22	2.1357	5.5262	4.3625
H23	1.9119	5.8595	5.3713
C24	3.0436	6.2271	3.5696
H25	3.5430	7.1176	3.9350
C26	3.3176	5.7495	2.2898
H27	4.0217	6.2405	1.6264
N28	2.7320	4.6539	1.8003
C29	1.8555	3.9672	2.5663
C30	-0.8870	2.4587	2.9489
C31	-1.4700	3.7006	2.7107
C32	-1.4007	1.6131	3.9368
C33	-2.5637	4.1212	3.4676
C34	-2.4911	2.0214	4.6870
C35	-3.0815	3.2760	4.4586
H36	-1.0643	4.3418	1.9362
H37	-0.9544	0.6382	4.0953
H38	-3.0045	5.0903	3.2693
H39	-2.9156	1.3828	5.4539
O40	-4.1448	3.5716	5.2486
C41	-4.8233	4.8050	5.0454
H42	-4.1647	5.6635	5.2314
H43	-5.2332	4.8762	4.0296
H44	-5.6423	4.8180	5.7659
Ni45	3.3307	3.6639	0.0837
Br46	3.6194	5.6767	-1.4798
C47	1.9199	4.2252	-1.2344
C48	0.7209	4.7059	-0.6840
C49	1.9281	3.1602	-2.1519
C50	-0.4324	3.9571	-0.8673
C51	0.7617	2.4162	-2.3062
C52	-0.4177	2.7710	-1.6310
H53	0.7308	5.5855	-0.0511
H54	2.8458	2.8836	-2.6599
H55	-1.3473	4.2754	-0.3785
H56	0.7534	1.5217	-2.9216
C57	-1.5783	1.8318	-1.6864
O58	-1.4881	0.7745	-2.2996
C59	-2.8347	2.1666	-0.9042
H60	-2.6279	2.1154	0.1711
H61	-3.2067	3.1703	-1.1343
H62	-3.5984	1.4262	-1.1424
O63	5.1384	2.8357	0.3716
S64	5.3279	2.0534	1.6711
O65	5.0907	0.6119	1.5122
O66	4.7225	2.7233	2.8356
C67	7.1617	2.2537	1.9032
F68	7.8267	1.7373	0.8637
F69	7.4713	3.5539	2.0131
F70	7.5471	1.6255	3.0211

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TS(11^{OAr*}-$12^{OAr*,Br}$)

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N1	-1.0994	-0.3938	1.5483
C2	0.0350	-0.9403	0.9100
N3	1.1384	-0.0958	0.7520
C4	-1.2480	0.9147	2.0538
C5	-0.0463	1.6875	1.8638
C6	1.0483	1.1950	1.1750
N7	0.2343	3.0324	2.1094
C8	1.4643	3.2702	1.5745
N9	1.9649	2.1721	0.9868
C10	2.3446	-0.6310	0.1106
O11	0.0608	-2.0936	0.5228
O12	-2.2938	1.3196	2.5557
C13	-2.2703	-1.2810	1.5747
H14	2.5737	-1.6013	0.5524
H15	3.1727	0.0624	0.2652
H16	2.1721	-0.7639	-0.9596
H17	-1.9766	-2.2546	1.9679
H18	-2.6457	-1.4001	0.5551
H19	-3.0239	-0.8160	2.2065
H20	1.4502	5.4804	3.3132
C21	2.2092	5.5043	2.5414
C22	3.1678	6.5167	2.4965
H23	3.1503	7.3091	3.2389

C24	4.1597	6.4871	1.5179
H25	4.9394	7.2386	1.4760
C26	4.1523	5.4484	0.5864
H27	4.9026	5.3593	-0.1915
N28	3.2196	4.4903	0.6147
C29	2.2768	4.4904	1.5851
C30	-0.6630	3.9880	2.6870
C31	-1.0142	5.1301	1.9725
C32	-1.1836	3.7635	3.9653
C33	-1.8700	6.0761	2.5389
C34	-2.0399	4.6938	4.5292
C35	-2.3858	5.8586	3.8238
H36	-0.6119	5.2855	0.9773
H37	-0.9252	2.8557	4.4985
H38	-2.1314	6.9611	1.9717
H39	-2.4617	4.5435	5.5170
O40	-3.2240	6.7032	4.4763
C41	-3.6310	7.9008	3.8255
H42	-2.7733	8.5469	3.5970
H43	-4.1818	7.6893	2.9000
H44	-4.2903	8.4131	4.5277
Ni45	3.2989	2.8009	-0.5628
Br46	3.3329	4.3334	-2.7897
O47	4.8979	1.7655	-0.1396
C48	1.7156	3.1293	-1.8137
C49	0.5989	3.8668	-1.3714
C50	1.5471	1.8193	-2.3119
C51	-0.6210	3.2264	-1.2286
C52	0.3177	1.1887	-2.1403
C53	-0.7746	1.8634	-1.5706
H54	0.7274	4.9048	-1.0827
H55	2.3793	1.2965	-2.7707
H56	-1.4582	3.7788	-0.8120
H57	0.1826	0.1508	-2.4302
C58	-2.0290	1.1020	-1.3104
O59	-2.0714	-0.1105	-1.4994
C60	-3.2370	1.8409	-0.7597
H61	-3.0503	2.1638	0.2714
H62	-3.4760	2.7283	-1.3551
H63	-4.0889	1.1599	-0.7598
C64	5.9585	2.5839	-0.1766
C65	6.4950	3.1020	1.0502
C66	6.5718	2.9837	-1.4043
C67	7.3263	4.2195	0.9904
C68	7.3919	4.1234	-1.3855
C69	7.7293	4.8073	-0.2169
H70	7.6767	4.6582	1.9174
H71	7.7971	4.4712	-2.3255
C72	6.5780	2.1085	-2.6849
C73	7.8557	1.2323	-2.5779
C74	5.3784	1.1517	-2.8554
C75	6.6811	2.9550	-3.9756
C76	6.2125	2.3983	2.3953
C77	4.7526	2.5919	2.8496
C78	6.4997	0.8844	2.2412
C79	7.1251	2.9264	3.5219
C80	8.5599	6.1012	-0.1976
C81	9.8784	5.8707	0.5769
C82	8.9128	6.5929	-1.6128
C83	7.7505	7.2187	0.5042
H84	5.5289	0.5475	-3.7587
H85	4.4515	1.7131	-2.9843
H86	5.2614	0.4918	-1.9972
H87	7.9659	0.5962	-3.4656
H88	7.8070	0.5858	-1.6951
H89	8.7512	1.8564	-2.4884
H90	6.6221	2.2994	-4.8515
H91	7.6288	3.4965	-4.0502
H92	5.8660	3.6805	-4.0407
H93	5.8644	0.4477	1.4693
H94	6.3124	0.3634	3.1885
H95	7.5470	0.7191	1.9648
H96	8.1853	2.8421	3.2610
H97	6.9562	2.3400	4.4319
H98	6.9160	3.9739	3.7678
H99	10.4688	5.0810	0.1007
H100	9.6926	5.5685	1.6120
H101	10.4833	6.7857	0.5993
H102	6.8300	7.4322	-0.0529
H103	8.3308	8.1479	0.5630
H104	7.4732	6.9319	1.5239
H105	8.0131	6.7785	-2.2093
H106	9.5332	5.8674	-2.1492
H107	9.4762	7.5308	-1.5540
H108	4.0707	2.1905	2.1040
H109	4.5317	3.6549	3.0003
H110	4.5758	2.0752	3.8020

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TS(11^{OBAc}-$12^{OBAc,Br}$)

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N1	-1.1275	-1.6016	1.1889
C2	-0.5261	-1.5739	-0.0859
N3	-0.0890	-0.3330	-0.5572
C4	-1.3957	-0.4984	2.0358
C5	-0.8994	0.7224	1.4534
C6	-0.2442	0.7678	0.2371
N7	-0.8915	2.0273	1.9395
C8	-0.2422	2.7859	1.0106
N9	0.1815	2.0285	-0.0187
C10	0.4601	-0.2526	-1.9186
O11	-0.4006	-2.5917	-0.7460
O12	-1.9646	-0.6115	3.1146
C13	-1.5382	-2.9353	1.6423
H14	1.5205	-0.5106	-1.9180
H15	0.3355	0.7631	-2.2976
H16	-0.0822	-0.9615	-2.5436
H17	-0.6748	-3.6034	1.6425
H18	-2.2894	-3.3456	0.9638
H19	-1.9460	-2.8313	2.6455
H20	-1.0277	4.8635	2.7893
C21	-0.4325	5.1681	1.9405
C22	-0.0843	6.5061	1.7610
H23	-0.4059	7.2473	2.4861
C24	0.6763	6.8820	0.6558
H25	0.9680	7.9138	0.4952
C26	1.0697	5.8934	-0.2446
H27	1.6642	6.0929	-1.1305
N28	0.7475	4.6103	-0.0687
C29	0.0142	4.2332	1.0003
C30	-1.4065	2.4209	3.2203
C31	-2.7787	2.4560	3.4391
C32	-0.5127	2.7173	4.2539
C33	-3.2750	2.8021	4.6955
C34	-0.9985	3.0737	5.5022
C35	-2.3841	3.1114	5.7334
H36	-3.4581	2.1996	2.6331
H37	0.5540	2.6674	4.0666
H38	-4.3459	2.8166	4.8547
H39	-0.3290	3.3097	6.3221
O40	-2.7547	3.4562	6.9924
C41	-4.1381	3.4314	7.3275
H42	-4.7092	4.1610	6.7391
H43	-4.5680	2.4321	7.1824
H44	-4.1941	3.6988	8.3835

Ni45	1.5519	3.0627	-1.2321
Br46	3.7210	1.4777	-1.5661
C47	3.2736	2.8827	-0.0230
C48	2.9807	2.3138	1.2378
C49	3.9098	4.1436	-0.0945
C50	3.0634	3.1047	2.3711
C51	3.9706	4.9197	1.0490
C52	3.5038	4.4431	2.2943
H53	2.6225	1.2923	1.2955
H54	4.2255	4.5231	-1.0590
H55	2.7737	2.6762	3.3262
H56	4.3503	5.9360	1.0063
C57	3.4595	5.3786	3.4415
O58	3.7938	6.5540	3.3210
C59	2.9358	4.8727	4.7814
H60	1.8800	4.5876	4.6961
H61	3.4894	3.9941	5.1302
H62	3.0288	5.6745	5.5152
C63	1.0221	4.7798	-4.7370
C64	1.8878	5.8181	-5.1034
C65	-0.0660	4.4591	-5.5579
C66	1.6658	6.5297	-6.2809
C67	-0.2874	5.1725	-6.7344
C68	0.5789	6.2071	-7.0979
H69	2.7248	6.0513	-4.4537
H70	-0.7252	3.6531	-5.2530
H71	2.3382	7.3352	-6.5636
H72	-1.1341	4.9241	-7.3687
H73	0.4047	6.7644	-8.0147
C74	1.2379	4.0357	-3.4600
O75	2.2020	4.3859	-2.6919
O76	0.4518	3.0963	-3.1297

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TS($12^{OBAc,Br}$-3a)

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N1	1.3476	-0.8587	2.7331
C2	1.5429	-1.1969	1.3810
N3	0.9067	-0.4060	0.4237
C4	0.5478	0.1968	3.2435
C5	-0.0118	0.9750	2.1669
C6	0.1950	0.6894	0.8310
N7	-0.7440	2.1551	2.1978
C8	-0.9241	2.5329	0.8980
N9	-0.3691	1.6469	0.0529
C10	1.0304	-0.8095	-0.9807
O11	2.2398	-2.1459	1.0584
O12	0.4029	0.3960	4.4414
C13	2.0139	-1.7447	3.6941
H14	2.0706	-0.7315	-1.3033
H15	0.3971	-0.1716	-1.5973
H16	0.7168	-1.8500	-1.0823
H17	3.0838	-1.7833	3.4803
H18	1.6127	-2.7575	3.6096
H19	1.8330	-1.3455	4.6898
H20	-2.6595	4.4053	2.0810
C21	-2.3633	4.6297	1.0661
C22	-2.8360	5.7714	0.4206
H23	-3.5043	6.4483	0.9444
C24	-2.4528	6.0288	-0.8923
H25	-2.8038	6.9048	-1.4262
C26	-1.5829	5.1364	-1.5176
H27	-1.2135	5.2995	-2.5214
N28	-1.1145	4.0506	-0.8977
C29	-1.5018	3.7762	0.3720
C30	-1.1386	2.8234	3.4091
C31	-2.4377	2.6720	3.8825
C32	-0.1915	3.5603	4.1269
C33	-2.8246	3.2948	5.0697
C34	-0.5711	4.1743	5.3105
C35	-1.8868	4.0507	5.7874
H36	-3.1464	2.0667	3.3250
H37	0.8361	3.6227	3.7816
H38	-3.8395	3.1723	5.4268
H39	0.1407	4.7448	5.8969
O40	-2.1476	4.6948	6.9545
C41	-3.4428	4.5692	7.5281
H42	-4.2181	4.9848	6.8708
H43	-3.6839	3.5226	7.7545
H44	-3.4156	5.1412	8.4567
Ni45	0.2406	2.7096	-1.8363
Br46	-0.8334	1.3877	-3.5927
C47	1.9186	3.2355	-0.8215
C48	2.7887	2.1544	-0.7114
C49	1.8388	4.2519	0.1296
C50	3.4015	1.9404	0.5241
C51	2.4640	4.0213	1.3491
C52	3.1979	2.8421	1.5839
H53	2.9090	1.4609	-1.5365
H54	1.2485	5.1379	-0.0646
H55	4.0064	1.0495	0.6615
H56	2.3656	4.7358	2.1602
C57	3.6614	2.5792	2.9783
O58	3.2943	3.3002	3.8998
C59	4.5459	1.3754	3.2414
H60	3.9987	0.4545	3.0098
H61	5.4428	1.3908	2.6132
H62	4.8292	1.3673	4.2942
C63	2.8377	5.4143	-4.0102
C64	3.6202	4.4794	-4.7014
C65	3.0097	6.7836	-4.2530
C66	4.5701	4.9153	-5.6236
C67	3.9625	7.2150	-5.1720
C68	4.7438	6.2813	-5.8581
H69	3.4724	3.4225	-4.5098
H70	2.3919	7.4882	-3.7064
H71	5.1751	4.1898	-6.1600
H72	4.0986	8.2773	-5.3539
H73	5.4873	6.6186	-6.5752
C74	1.8203	4.9934	-2.9958
O75	1.7815	3.6798	-2.8055
O76	1.1156	5.8065	-2.4006

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TS($12^{OTf,OBAc}$-11^{OTf})

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N1	1.0272	-1.0469	2.7629
C2	1.3741	-1.4765	1.4703
N3	0.7378	-0.8409	0.4006
C4	0.1443	0.0035	3.0982
C5	-0.3393	0.6771	1.9167
C6	-0.0067	0.2830	0.6349
N7	-1.0357	1.8720	1.7836
C8	-1.0867	2.1387	0.4506
N9	-0.4725	1.1840	-0.2768
C10	0.9830	-1.3585	-0.9487
O11	2.1810	-2.3744	1.2706
O12	-0.1212	0.2703	4.2614
C13	1.6602	-1.7142	3.9096
H14	1.9728	-1.0694	-1.3012
H15	0.2377	-0.9424	-1.6209
H16	0.9149	-2.4462	-0.9189
H17	2.2968	-0.9972	4.4337
H18	2.2452	-2.5499	3.5345
H19	0.8837	-2.0604	4.5937
H20	-3.1424	3.9138	1.1802

C21	-2.6371	4.1502	0.2521
C22	-3.0106	5.2472	-0.5221
H23	-3.8204	5.8911	-0.1929
C24	-2.3494	5.5018	-1.7237
H25	-2.6229	6.3423	-2.3517
C26	-1.3160	4.6521	-2.1113
H27	-0.7690	4.7859	-3.0370
N28	-0.9402	3.6147	-1.3573
C29	-1.5900	3.3484	-0.2056
C30	-1.4268	2.7219	2.8734
C31	-2.3470	2.2649	3.8102
C32	-0.8293	3.9786	3.0151
C33	-2.6861	3.0640	4.9006
C34	-1.1701	4.7817	4.0919
C35	-2.0940	4.3266	5.0469
H36	-2.7757	1.2749	3.7042
H37	-0.0949	4.3115	2.2905
H38	-3.3924	2.6887	5.6304
H39	-0.7168	5.7569	4.2328
O40	-2.3397	5.1811	6.0724
C41	-3.1834	4.7473	7.1333
H42	-4.2063	4.5559	6.7839
H43	-2.7894	3.8432	7.6146
H44	-3.1980	5.5642	7.8562
Ni45	0.5119	2.2481	-1.9107
O46	1.2884	0.6943	-3.1982
C47	2.1035	2.4740	-0.7247
C48	3.0219	1.4415	-0.8894
C49	1.9407	3.1633	0.4778
C50	3.6191	0.9184	0.2570
C51	2.5326	2.6113	1.6106
C52	3.3404	1.4604	1.5237
H53	3.1890	1.0161	-1.8711
H54	1.3266	4.0528	0.5089
H55	4.2698	0.0559	0.1564
H56	2.3540	3.0386	2.5930
C57	3.8159	0.8234	2.7892
O58	3.4201	1.2279	3.8768
C59	4.7481	-0.3707	2.6946
H60	4.2376	-1.2120	2.2102
H61	5.6368	-0.1350	2.0998
H62	5.0488	-0.6611	3.7020
C63	2.3354	5.4053	-3.7415
C64	2.5271	4.6666	-4.9183
C65	2.4925	6.7979	-3.7535
C66	2.8771	5.3252	-6.0963
C67	2.8532	7.4481	-4.9308
C68	3.0452	6.7117	-6.1035
H69	2.3889	3.5910	-4.9105
H70	2.3286	7.3461	-2.8313
H71	3.0162	4.7533	-7.0092
H72	2.9838	8.5268	-4.9370
H73	3.3229	7.2200	-7.0232
C74	1.9223	4.7477	-2.4591
O75	2.0101	3.4221	-2.5215
O76	1.5291	5.3875	-1.4886
O77	1.1177	1.2592	-5.6602
O78	-0.4957	2.1756	-3.9329
C79	-0.6825	-0.3916	-4.5674
S80	0.4332	1.0867	-4.3822
F81	0.0377	-1.4821	-4.8465
F82	-1.3431	-0.5986	-3.4111
F83	-1.5745	-0.1892	-5.5384

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TS($12^{OAr*,OBAc}$-11^{OAr*})

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N1	1.9355	-1.2600	3.0588
C2	2.2763	-1.6103	1.7404
N3	1.5923	-0.9648	0.7081
C4	0.9696	-0.3062	3.4649
C5	0.4189	0.3764	2.3196
C6	0.7333	0.0558	1.0136
N7	-0.4464	1.4575	2.2556
C8	-0.5961	1.7556	0.9296
N9	0.0972	0.8970	0.1574
C10	1.7845	-1.4295	-0.6676
O11	3.1419	-2.4451	1.5184
O12	0.6833	-0.1111	4.6367
C13	2.6565	-1.9921	4.1058
H14	2.7939	-1.8229	-0.7615
H15	1.6459	-0.5956	-1.3471
H16	1.0608	-2.2075	-0.9213
H17	3.7313	-1.8515	3.9815
H18	2.4378	-3.0600	4.0331
H19	2.3275	-1.5993	5.0654
H20	-2.5387	3.5047	1.9815
C21	-2.2734	3.6774	0.9486
C22	-2.8946	4.6862	0.2149
H23	-3.6464	5.3101	0.6890
C24	-2.5559	4.8781	-1.1216
H25	-3.0268	5.6470	-1.7237
C26	-1.5717	4.0635	-1.6756
H27	-1.2412	4.1799	-2.6995
N28	-0.9600	3.1071	-0.9713
C29	-1.3088	2.8857	0.3190
C30	-0.9371	2.1364	3.4251
C31	-2.2493	1.9424	3.8416
C32	-0.0483	2.9068	4.1813
C33	-2.7109	2.5635	5.0033
C34	-0.5013	3.5201	5.3383
C35	-1.8332	3.3579	5.7543
H36	-2.9094	1.3031	3.2627
H37	0.9948	2.9750	3.8868
H38	-3.7354	2.4073	5.3177
H39	0.1631	4.1160	5.9544
O40	-2.1669	4.0027	6.9024
C41	-3.4780	3.8297	7.4256
H42	-4.2428	4.2083	6.7345
H43	-3.6857	2.7760	7.6526
H44	-3.5107	4.4099	8.3489
Ni45	0.5180	1.8888	-1.8466
O46	0.2047	0.6936	-3.2822
C47	2.1531	2.6328	-0.9202
C48	3.1614	1.6785	-0.9867
C49	1.9990	3.4988	0.1614
C50	3.8470	1.3718	0.1910
C51	2.6904	3.1770	1.3237
C52	3.5612	2.0700	1.3756
H53	3.3344	1.1240	-1.9016
H54	1.3004	4.3233	0.1046
H55	4.5568	0.5503	0.1868
H56	2.5341	3.7516	2.2313
C57	4.0487	1.6249	2.7158
O58	3.5497	2.0837	3.7384
C59	5.1291	0.5606	2.7860
H60	4.7844	-0.3783	2.3360
H61	6.0239	0.8737	2.2364
H62	5.3827	0.3860	3.8325
C63	2.0967	5.1798	-4.2078
C64	2.8040	4.4212	-5.1494
C65	1.8994	6.5497	-4.4232
C66	3.3115	5.0323	-6.2948
C67	2.4056	7.1566	-5.5700
C68	3.1166	6.3994	-6.5053

H69	2.9479	3.3619	-4.9752
H70	1.3510	7.1163	-3.6777
H71	3.8609	4.4416	-7.0229
H72	2.2523	8.2200	-5.7338
H73	3.5143	6.8738	-7.3987
C74	1.5344	4.5632	-2.9586
O75	1.6941	3.2538	-2.9090
O76	0.9764	5.2501	-2.1009
C77	0.0964	-0.6294	-3.4166
C78	1.1659	-2.7880	-3.7328
C79	-1.0594	-2.7034	-2.9153
C80	2.4293	-0.8193	-4.6492
C81	1.1928	-1.3955	-3.9116
C82	-2.4716	-0.5904	-2.9043
C83	-1.1145	-1.3187	-3.0703
C84	-2.6378	0.5043	-3.9849
H85	-3.6071	1.0045	-3.8652
H86	-1.8419	1.2464	-3.9216
H87	-2.6087	0.0609	-4.9864
C88	-3.6581	-1.5689	-3.0722
H89	-3.7328	-2.2835	-2.2455
H90	-4.5961	-1.0027	-3.0903
H91	-3.5858	-2.1348	-4.0067
C92	-2.5983	0.0499	-1.5080
H93	-3.5920	0.4990	-1.3763
H94	-2.4500	-0.6946	-0.7176
H95	-1.8540	0.8283	-1.3795
C96	2.5306	-1.5219	-6.0298
H97	3.3989	-1.1457	-6.5842
H98	2.6367	-2.6070	-5.9435
H99	1.6337	-1.3212	-6.6255
C100	3.7195	-1.1170	-3.8478
H101	4.5975	-0.7109	-4.3643
H102	3.6763	-0.6651	-2.8519
H103	3.8807	-2.1908	-3.7103
C104	2.3813	0.6940	-4.9339
H105	1.4641	0.9777	-5.4546
H106	2.4236	1.2963	-4.0297
H107	3.2369	0.9573	-5.5697
C108	0.0859	-3.4684	-3.1771
C109	-1.0270	-5.6736	-3.7030
C110	-0.1794	-5.2022	-1.3751
C111	0.0847	-4.9775	-2.8838
H112	-0.2073	-6.2732	-1.1394
H113	0.6108	-4.7432	-0.7699
H114	-1.1343	-4.7669	-1.0635
C115	1.4290	-5.6411	-3.2348
H116	-1.9497	-3.2213	-2.5796
H117	2.0379	-3.3531	-4.0396
H118	1.6567	-5.5553	-4.3029
H119	1.3946	-6.7082	-2.9887
H120	2.2563	-5.1956	-2.6719
H121	-0.8672	-5.5232	-4.7759
H122	-1.0373	-6.7526	-3.5053
H123	-2.0180	-5.2809	-3.4556

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TS($12^{Br,Br}$-6^{Br})

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N1	-0.5131	-0.7348	-0.7131
C2	0.6883	-0.5150	-1.4033
N3	1.5047	0.5250	-0.9333
C4	-1.0091	-0.0244	0.4192
C5	-0.1153	1.0534	0.7809
C6	1.0637	1.2891	0.1087
N7	-0.2281	2.0685	1.7264
C8	0.8641	2.8636	1.5780
N9	1.6548	2.4068	0.5882
C10	2.8662	0.6928	-1.4455
O11	1.0043	-1.1822	-2.3756
O12	-2.0640	-0.2992	0.9630
C13	-1.3210	-1.8528	-1.2263
H14	3.0590	-0.1148	-2.1487
H15	3.5819	0.6711	-0.6209
H16	2.9606	1.6589	-1.9545
H17	-0.7541	-2.7829	-1.1508
H18	-1.5659	-1.6786	-2.2755
H19	-2.2256	-1.9099	-0.6252
H20	-0.1967	4.1474	3.8667
C21	0.6584	4.6311	3.4135
C22	1.2040	5.7938	3.9588
H23	0.7629	6.2268	4.8513
C24	2.3189	6.3846	3.3658
H25	2.7702	7.2807	3.7770
C26	2.8600	5.7922	2.2255
H27	3.7268	6.1889	1.7066
N28	2.3334	4.6839	1.6980
C29	1.2573	4.0914	2.2741
C30	-1.3159	2.2270	2.6605
C31	-2.4087	3.0133	2.3145
C32	-1.2562	1.5761	3.8965
C33	-3.4633	3.1678	3.2126
C34	-2.3010	1.7298	4.7939
C35	-3.4155	2.5206	4.4570
H36	-2.4555	3.5107	1.3538
H37	-0.3989	0.9579	4.1445
H38	-4.3061	3.7830	2.9238
H39	-2.2907	1.2376	5.7603
O40	-4.3795	2.5930	5.4014
C41	-5.5763	3.3121	5.1092
H42	-5.3725	4.3769	4.9402
H43	-6.0883	2.8941	4.2340
H44	-6.2109	3.2010	5.9887
Ni45	3.1149	3.7084	0.0762
Br46	4.4115	5.3337	-1.1865
Br47	4.8940	2.4277	1.1809
C48	1.0291	6.1704	-0.9244
C49	1.1015	4.8527	-1.3439
C50	0.0177	3.9893	-1.4090
C51	-0.2151	6.6215	-0.4607
C52	-1.2063	4.4570	-0.9340
C53	-1.3293	5.7683	-0.4419
H54	1.9074	6.8046	-0.9097
H55	0.1126	2.9753	-1.7813
H56	-0.2941	7.6407	-0.0948
H57	-2.0826	3.8160	-0.9421
C58	-2.6677	6.1826	0.1108
O59	-3.5237	5.3337	0.3157
C60	-2.9177	7.6437	0.4127
H61	-2.2552	7.9871	1.2157
H62	-2.7188	8.2686	-0.4646
H63	-3.9539	7.7682	0.7275
N64	2.5287	3.5246	-4.6864
C65	3.8977	3.1933	-4.2609
C66	1.9146	4.7070	-4.1438
C67	1.7482	2.5174	-5.4400
H68	4.0614	3.6581	-3.2841
H69	3.9468	2.1083	-4.1371
C70	5.0024	3.6520	-5.2319
H71	4.9584	4.7263	-5.4143
H72	5.9642	3.4284	-4.7619
H73	4.9558	3.1308	-6.1883
H74	1.9110	4.5521	-2.9970
C75	2.7642	5.9809	-4.3357
C76	0.4639	4.9452	-4.5575

H77	2.2752	6.7949	-3.7961
H78	3.7690	5.8859	-3.9299
H79	2.8070	6.2371	-5.3986
H80	-0.1919	4.1018	-4.3319
H81	0.0914	5.8016	-3.9908
H82	0.3847	5.1900	-5.6215
H83	0.9190	3.0570	-5.8962
C84	1.1711	1.4544	-4.4798
C85	2.5611	1.8706	-6.5684
H86	1.9482	0.8078	-4.0704
H87	0.6255	1.9127	-3.6517
H88	0.4765	0.8182	-5.0345
H89	1.8938	1.2036	-7.1209
H90	2.9453	2.6187	-7.2654
H91	3.3917	1.2663	-6.1951

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TS($12^{OBAc,Br}$-$13^{OBAc,Br}$)

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N1	-1.2137	-1.2003	1.9892
C2	-0.8264	-1.4680	0.6591
N3	-0.3567	-0.3907	-0.1024
C4	-1.3204	0.0661	2.5960
C5	-0.9531	1.1177	1.6744
C6	-0.3717	0.8615	0.4453
N7	-0.8199	2.4856	1.8905
C8	-0.1528	2.9765	0.8125
N9	0.1669	2.0024	-0.0641
C10	-0.1834	-0.6261	-1.5455
O11	-0.8854	-2.5912	0.1957
O12	-1.6381	0.2176	3.7709
C13	-1.5952	-2.3854	2.7709
H14	0.6207	-1.3395	-1.7132
H15	0.0693	0.3183	-2.0220
H16	-1.1157	-1.0279	-1.9504
H17	-0.7678	-3.0972	2.7844
H18	-2.4583	-2.8697	2.3097
H19	-1.8349	-2.0547	3.7790
H20	-1.2628	5.4093	1.6532
C21	-0.3909	5.4992	1.0185
C22	0.1055	6.7462	0.6476
H23	-0.3811	7.6498	1.0014
C24	1.2217	6.8203	-0.1857
H25	1.6336	7.7751	-0.4940
C26	1.7986	5.6356	-0.6360
H27	2.6506	5.6136	-1.3056
N28	1.3270	4.4341	-0.2776
C29	0.2552	4.3554	0.5417
C30	-1.3614	3.1898	3.0204
C31	-2.7203	3.0716	3.3022
C32	-0.5270	3.9380	3.8567
C33	-3.2590	3.7003	4.4215
C34	-1.0558	4.5655	4.9728
C35	-2.4251	4.4478	5.2683
H36	-3.3561	2.4759	2.6555
H37	0.5305	4.0182	3.6425
H38	-4.3160	3.5928	4.6300
H39	-0.4212	5.1274	5.6489
O40	-2.8363	5.0874	6.3859
C41	-4.1996	4.9652	6.7889
H42	-4.8788	5.3897	6.0390
H43	-4.4682	3.9182	6.9752
H44	-4.2866	5.5319	7.7162
Ni45	2.0145	2.5893	-1.0524
Br46	3.0278	0.4778	-1.9288
C47	3.1124	2.1308	0.8851
C48	2.7214	0.9062	1.4272
C49	3.2858	3.2722	1.6774
C50	2.3605	0.8587	2.7763
C51	2.9429	3.1979	3.0242
C52	2.4496	2.0031	3.5797
H53	2.6345	0.0307	0.7954
H54	3.6393	4.2034	1.2488
H55	1.9903	-0.0766	3.1848
H56	3.0326	4.0662	3.6709
C57	1.9885	2.0375	5.0190
O58	2.0843	3.0804	5.6473
C59	1.3604	0.7997	5.6146
H60	0.4114	0.5837	5.1059
H61	2.0082	-0.0770	5.5063
H62	1.1653	0.9804	6.6719
C63	2.3804	4.2776	-4.5576
C64	3.5161	5.0201	-4.9083
C65	1.3331	4.1248	-5.4761
C66	3.6050	5.6036	-6.1693
C67	1.4262	4.7078	-6.7373
C68	2.5605	5.4464	-7.0844
H69	4.3160	5.1393	-4.1848
H70	0.4611	3.5480	-5.1862
H71	4.4835	6.1816	-6.4412
H72	0.6163	4.5878	-7.4506
H73	2.6300	5.9016	-8.0683
C74	2.2729	3.6635	-3.2145
O75	3.2533	3.7253	-2.3854
O76	1.2035	3.0765	-2.8530
N77	6.0988	2.4182	-1.3151
C78	6.0259	3.8748	-1.4759
C79	5.7928	1.8651	-0.0407
C80	6.4035	1.5669	-2.4914
H81	5.4650	4.0765	-2.3847
H82	5.4170	4.2662	-0.6608
C83	7.4042	4.5507	-1.5040
H84	7.9719	4.2674	-2.3925
H85	7.2584	5.6346	-1.5308
H86	7.9970	4.3045	-0.6197
H87	4.6204	2.0286	0.0540
C88	5.9889	0.3607	0.1345
C89	6.4065	2.6319	1.1451
H90	5.4310	-0.2259	-0.5939
H91	7.0482	0.0915	0.0956
H92	5.6116	0.0909	1.1239
H93	5.9681	2.2500	2.0689
H94	7.4861	2.4541	1.1730
H95	6.2331	3.7077	1.1198
H96	5.8615	0.6372	-2.3232
C97	7.9187	1.2626	-2.5265
C98	5.9011	2.1569	-3.8082
H99	8.4979	2.1531	-2.7803
H100	8.2860	0.8691	-1.5761
H101	8.0972	0.5080	-3.2979
H102	6.0331	1.3998	-4.5856
H103	4.8396	2.3984	-3.7409
H104	6.4653	3.0434	-4.1144

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Frequencies

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67.73 78.77 157.63 189.87 239.68 243.36 290.85 418.42 422.06 467.05 494.23 598.18 611.77 638.18 726.31 754.84 834.28 854.66 965.01 967.51 997.61 1018.76 1049.67 1080.9 1100.39 1149.85 1219.91 1287.22 1332.78 1347.68 1396.5 1438.81 1483.74 1492.53 1526.29 1620.52 1640.31 1782.05 3046.69 3110.73 3169.2 3206.67 3212.34 3224.67 3226.05

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80.09 163.17 229.52 370.65 426.54 451.59 503.95 631.94 678.49 696.67 721.67 815.66 816.55 863.71 929.81 988.84 992.06 1014.82 1047.62 1080.64 1124.35 1177.86 1186.02 1314.44 1354.68 1357.34 1478.63 1513.02 1629.35 1643.62 1743.33 3127.38 3138.7 3161.54 3193.57 3195.95

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-3.44 31.24 54.53 70.9 76.1 116.17 165.71 177.48 189.97 220.86 284.06 309.48 358.49 407.78 415.45 422.13 448.17 450.43 501.17 510.51 588.68 601.58 630.69 639.66 677.38 694.79 716.88 724.37 735.85 808.84 835.48 847.38 863.22 868 873.87 959.34 965.67 977.96 992.54 995.95 1014.29 1017.04 1033.17 1049.16 1053.68 1093.57 1105.47 1123.84 1151.95 1198.37 1201.26 1214.83 1258.48 1282.44 1293.82 1336.56 1349.44 1363.91 1370.35 1396.49 1457.69 1484.45 1492 1492.93 1535.27 1546.85 1625.88 1639.6 1659.37 1662.13 1775.62 1802.53 3046.45 3110.86 3167.64 3183.01 3195.52 3204.24 3205.91 3208.05 3221.14 3224.27 3230.64 3285.23

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68.28 154.97 193.01 230.31 373.54 414.55 431.78 467.83 596.54 603.98 630.92 707.01 743.59 778.7 866.89 947.79 963.37 991.32 1012.88 1016.53 1049.55 1053.2 1100.58 1120.61 1197.75 1217.54 1287.66 1347.37 1370.02 1396.77 1484.02 1490.47 1492.77 1535.82 1637.56 1659.07 1779.55 3046.69 3110.94 3167.81 3178.57 3190.33 3200.04 3210.67 3218.35

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72.79 74.98 106.99 129.44 145.88 151.19 209.39 219.11 228.86 262.76 275.15 276.86 316.55 340.38 367.91 380.8 417.17 450.4 482.37 504.13 587.09 783.81 793.68 858.25 895.61 935.99 947.22 963.54 969.55 974.57 978.87 1038.6 1102.34 1126.35 1142.12 1163.7 1194.36 1209.46 1211.13 1220.43 1330.7 1356.45 1364.48 1372.76 1397.36 1408.66 1428.92 1439.34 1444.82 1448 1454.45 1489.55 1492.86 1502.1 1502.67 1506.14 1510.61 1512.62 1517.81 1526.6 1528.4 1542.07 1544.03 1548.24 2465.53 3049.42 3052.59 3054.8 3057.3 3060.31 3063.74 3098.29 3116.44 3123.25 3129.72 3135.6 3137.02 3137.78 3138.8 3141.48 3142.9 3145.3 3146.66 3165.25

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56.46 190.83 191.57 288.67 330.6 330.84 498.52 498.78 555.54 555.78 621.55 738.9 998.09 1178.58 1178.88 1225.34 1254.68 1255.26

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41.28 46.91 70.56 78.55 132.74 135.86 159.34 171.78 241.56 258.82 260.54 267.25 273.34 280.03 280.64 291.72 308.57 317.08 321.49 328.47 348.38 350.11 355.84 360.98 365.21 379.74 387.33 388.45 409.27 416.56 437.67 453.78 476.96 486.7 517.68 547.01 568.14 610.95 632.15 665.2 739.34 765.96 806.03 827.52 841.81 890.08 902.01 906.07 923.64 932.05 933.2 934.4 943.44 945.2 947.69 966.77 970.48 971.07 1051.12 1052.49 1058.08 1060.6 1068.42 1068.8 1138.8 1181.51 1207.82 1228.52 1229.93 1230.13 1239.64 1244.16 1246.34 1278.25 1294.69 1316.16 1338.8 1376.51 1384.84 1385.28 1393.75 1404.95 1406.21 1409.41 1419.89 1424.99 1437.79 1471.47 1482.02 1482.24 1489.53 1492.5 1499.62 1505 1505.31 1509.54 1510.07 1513.81 1514.28 1515.42 1519.44 1535.53 1536.21 1536.77 1545.9 1553.62 1561.4 1566.36 1651.08 2995.62 2996.24 3001.3 3002.59 3003.19 3009.58 3016.7 3017.44 3025.22 3065.21 3065.77 3068.17 3068.48 3079.64 3080.26 3082.73 3083.88 3090.71 3090.95 3092.02 3108.06 3114.63 3116.66 3146.57 3147.14 3149.24 3149.7 3163.35 3209.25

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***p*-Anis^{H}NN^{H}**

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30.38 34.54 47.03 49.46 56.64 74.73 81.46 95.79 102.03 106.61 128.31 147.2 162.32 175.74 211.53 237.44 248.52 253.23 265.38 272.99 313.06 319.59 337.76 362.85 380.44 407.25 416.52 427.85 441.82 461.46 473.69 505.2 523.97 533.45 558.62 612.23 627.7 645.42 650.07 686.2 715.94 727.85 740.03 746.32 751.96 759.09 764.99 804.78 814.6 817.45 826.79 849.52 919.04 944.95 955.95 974.46 984.25 991.72 1008.4 1009.27 1014.37 1037.11 1070.01 1076.94 1077.73 1123.79 1132.65 1146.96 1161.36 1163.13 1179.98 1182.73 1193.51 1206.7 1215.68 1253.59 1275.04 1286.61 1302.04 1313.43 1318.94 1331.92 1336.69 1353.02 1373.41 1396.08 1438.58 1450.79 1457.49 1467.42 1470.85 1491 1495.87 1498.51 1507.22 1507.77 1512.57 1514.71 1518.16 1538.25 1562.06 1575.46 1627.32 1635.71 1637.52 1643.93 1671.97 1754.65 1790.24 3012.53 3071.04 3074.59 3076.19 3139.31 3141 3147.57 3165.06 3186.58 3192.04 3196.69 3205.78 3211.29 3214.84 3224.93 3230.41 3234.34

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73.48 105.26 127.13 181.82 217.01 222.73 239.42 264.3 265.69 304.96 330.26 358.23 375.8 416.2 448.14 481.56 510.94 579.18 716.67 789.18 846.94 883.62 929.36 945.83 953.52 955.34 962.86 1003.25 1054.75 1104.27 1120.08 1132.1 1151.18 1180.98 1198.2 1229.27 1237.61 1339.4 1364.16 1366.67 1378.01 1393.88 1405.24 1408.16 1416.73 1422.66 1426.45 1428.32 1489.91 1491.96 1496.75 1501.18 1502.82 1508.44 1512.15 1514.77 1520.98 1530.79 1534.09 2891.31 3009.24 3028.09 3029.92 3032.63 3035.88 3038.12 3056.03 3072.58 3084.77 3089.37 3091.7 3092.67 3098.42 3099.58 3105.44 3110.17 3111.31 3115.16

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47.15 106.8 153.49 179.62 218.27 229.88 253.27 271.28 306.48 318.08 322.69 330.45 345.45 399.66 431.08 475.57 523.57 599.33 692.92 807.16 849.45 873.67 932.11 941.86 953.86 962.16 968.42 970.12 1007.53 1079.94 1088.24 1117.25 1141.08 1155.83 1189.94 1205.03 1217.83 1293.73 1319.07 1337.05 1344.29 1383.57 1410.13 1415.94 1427.2 1433.17 1441.86 1452.2 1489.58 1491.35 1496.12 1498.84 1501.77 1507.21 1518.75 1520.41 1524.82 1531.96 1533.15 2985.81 3064.78 3065.94 3068.81 3072.7 3081.57 3085.91 3131.04 3138.13 3140.8 3145.51 3153.04 3154.6 3155.68 3158.13 3160.99 3163.88 3167.79 3193.54

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53.65 75.91 97.63 160.94 208.94 224.25 227.89 241.26 253.18 256.07 290.41 327.25 340.74 377.61 437.8 501.73 545.93 564.47

590.68 701.65 864.64 895.05 933.04 937.17 952.06 954.98 988.51 1021.06 1026.97 1115.98 1137.89 1147.96 1159.86 1192.9 1203.1 1231.16 1311.98 1350.25 1358.12 1407.33 1409.4 1410.19 1414.8 1427.21 1429.76 1446.32 1481.14 1491.01 1496.03 1498.04 1502.66 1507.94 1509.54 1515.16 1518.63 1522.02 1526.34 2941.02 3019.47 3037.43 3043.4 3044.54 3050.86 3075.9 3090.7 3105.5 3106.31 3114.23 3119.17 3123.14 3124.11 3127.82 3128.91 3139.74 3183.91

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50.78 104.62 142.27 176.62 185.47 206.55 227.56 236.84 257.47 290.45 320.46 346.61 415.35 437.7 459.31 503.57 539.43 630.9 680.4 805.63 868.42 907.03 937.27 947.66 954.41 967.37 997.42 1027.22 1095.78 1105.37 1114.61 1154.39 1159.42 1177.69 1217.18 1302.34 1342.64 1353.89 1383.32 1409.99 1412.84 1415.61 1426.99 1439.04 1448.04 1475.45 1489.96 1493.4 1498.26 1502.08 1504.82 1509.05 1513.53 1520.12 1525.71 1545.99 1694.72 3050.91 3059.66 3062.34 3066.03 3074.66 3104.63 3118.71 3126.09 3137.37 3142.93 3144.69 3147.51 3148.58 3160.28 3166.89 3172.82 3179.5 3210.32

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67.83 104.83 131.31 198.93 228.71 237.79 242.1 260.03 265.82 304.36 326.33 357.19 370.01 406.86 441.46 469.18 492.6 577.62 769.92 789.07 848.82 881.72 914.96 924.83 956.49 962.01 969.19 972.8 1018.29 1081.04 1104.64 1131.58 1155.17 1181.81 1199.62 1206.35 1213.2 1316.51 1341.33 1344.46 1374.39 1392.96 1399.5 1426.63 1434.01 1439.96 1443.42 1445.4 1455.55 1460.5 1488.97 1494.7 1502.47 1508.01 1510.03 1514.83 1517.7 1517.91 1526.34 1534.61 1542.56 3055.17 3056.32 3058.98 3060.65 3069.49 3104.46 3122.21 3128.01 3133.16 3133.45 3135.48 3141.19 3143.66 3147.31 3149.66 3151.79 3156.86 3158.75 3185.65 3427.29

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16.17 22.2 27.17 32.63 38.94 49.21 64.49 89.77 94.33 99.88 107.49 113.64 130.18 135.82 141.93 153.66 169.01 176.05 188.85 228.64 245.29 263.33 265.06 269.01 287.15 297.9 323.28 332.08 339.33 376.36 395.15 418.71 423.93 429.97 440.61 474.02 488.73 518.21 524.22 528.64 557.83 617.82 641.68 649.31 660.57 681.73 711.27 716 741.91 747.52 749.18 757.75 761.81 796.27 810.71 823.39 830.08 855.74 909.04 948.02 961.69 971.13 984.79 998.56 1008.24 1010.44 1023.97 1037.74 1064.89 1070.95 1076.45 1115.83 1133.64 1144.4 1144.55 1162.69 1179.65 1186.93 1195.21 1203.3 1215.49 1264.1 1272.41 1288.57 1307.37 1316.09 1320.31 1328.33 1334.7 1360.71 1365.8 1410.61 1434.51 1450.84 1463.47 1467.58 1479.42 1491.51 1494.42 1502 1506.88 1508.52 1508.59 1513.96 1517.54 1524.76 1561.41 1576.71 1617.67 1634.89 1645.29 1651.88 1670.07 1764.37 1801.05 3018.18 3074.23 3078.04 3084.22 3143.97 3146.47 3154.4 3199.38 3201.05 3201.6 3201.63 3210.65 3212.38 3221.27 3226 3235.09 3252.37

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11.49 16.83 25.74 33.1 35.59 41.05 42.94 49.97 69.21 75.5 90.72 97.26 108.77 111.59 119.75 130.13 137.48 139.76 150.85 156.41 174.83 176 191.2 206.55 220.14 234.67 245.11 254.12 264.12 269.79 287.48 298.97 302.14 320.69 324.78 327.88 341.42 366.86 376.84 396.66 418 427.13 432.26 443.05 469.09 482.52 489.32 515.12 519.33 525.77 531.34 554.3 559.32 569.12 612.77 617.5 642.13 649.29 657.85 682.34 712.89 717.92 742.95 745.5 749 757.15 759.47 762.29 797.99 806.21 818.62 821.79 855.02 916.91 947.83 962.06 965.44 972.1 993.31 995.95 1008.27 1014.31 1031.5 1035.6 1064.99 1070.91 1077.97 1101.59 1119.23 1135.43 1145.69 1151.7 1162.59 1179.67 1189.71 1196 1204.69 1205.96 1215.19 1226.32 1246.52 1262.2 1272.35 1286.76 1305.82 1309.46 1316.39 1325.48 1330.27 1334.64 1357.24 1368.93 1411.8 1434.59 1453.85 1463.75 1468.59 1483.8 1491.64 1494.44 1498.56 1506.38 1508.47 1513.11 1515.14 1517.47 1530.09 1560.61 1574.26 1618.48 1634.66 1645.21 1650.52 1668.81 1762.85 1800.05 3016.58 3077.76 3081.89 3087.74 3146.49 3153.98 3164.32 3198.97 3200.14 3200.64 3200.91 3212.85 3215.46 3226.7 3227.73 3232.49 3246.98

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11.86 15.2 20.73 23.99 30.39 33.32 40.53 42.86 44.62 51.67 69.24 74.19 76.94 91.53 93.13 94.69 102.82 108 114.12 121.52 131.77 137.77 142.67 148.6 159.49 165.74 168.78 171.13 177.39 190.67 202.75 220.15 224.87 233.71 243.48 245.01 249.89 256.52 262.4 264.95 267.57 275.83 278.66 282.32 288.15 295.94 303.93 314.9 318.01 327.36 330.28 339.64 346.12 354.89 359.77 373.43 376.68 377.61 387.27 394.57 396.78 403.98 419.25 420.71 421.06 423.17 430.68 438.8 440.34 474.91 477.06 478.49 484.29 490.67 519.31 524.44 531.63 550.87 559.15 563.68 571.27 619.26 628.59 640.41 647.9 648.42 655.45 661.46 679.34 706.36 716.47 741.71 746.72 750.15 753.37 762.31 765.49 766.33 790.46 793.7 811.14 823.67 829.81 832.32 856.6 877.5 903.19 905.69 906.81 914.97 934.69 937.61 938.44 939.74 942.34 943.26 948.82 951.81 961.32 970.68 971.98 972.76 973.07 980.71 1001.23 1006.95 1008.74 1021.24 1037.5 1051.45 1054.75 1059.25 1061.07 1062.68 1064.61 1065.62 1071.41 1075.72 1115.42 1133.33 1144.67 1150.53 1153.59 1162.84 1179.9 1185.51 1186.84 1193.5 1203.82 1215.56 1221.85 1229.97 1230.92 1234.71 1236.26 1242.64 1256.99 1263.63 1273.73 1280.56 1289.6 1300.36 1306.56 1315.62 1319.71 1321.07 1327.67 1328.59 1335.07 1350.74 1360.38 1364.51 1397.44 1400.29 1405.5 1408.62 1412.48 1412.64 1414.72 1428.99 1434.45 1438.03 1446.7 1449.08 1463.29 1467.46 1467.5 1475.82 1480.11 1488.31 1488.97 1490.83 1493.13 1496.77 1501.13 1505.44 1506.37 1506.97 1507.32 1507.94 1508.67 1508.69 1510.5 1510.85 1511.57 1513.22 1514.54 1517.88 1519.32 1523.66 1524.63 1525.39 1527.84 1538.88 1543.57 1547.04 1561.79 1576.1 1594.88 1612.88 1634.54

1641.9 1653.37 1655.43 1670.39 1764.91 1800.3 3017.99 3023.99 3024.3 3026.3 3026.99 3027.49 3029.26 3034.09 3035.16 3037.02 3068.91 3077.74 3083.93 3086.39 3087.13 3090.34 3091.4 3096.89 3097.82 3099.83 3100.45 3105.7 3106.77 3108.75 3109.3 3116.07 3118.48 3137.71 3146.02 3150.16 3153.6 3163.78 3166.22 3167.35 3198.44 3198.91 3199.9 3201.06 3208.15 3210.6 3216.77 3221.34 3223.73 3234.78 3246.68 3254.36

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15.8 26.56 29.61 31.4 34.78 36.53 40.6 43.39 51.25 55.08 57.26 63.72 67.99 71.87 72.46 77.02 81.33 85.81 91.53 96.31 97.35 103.19 110.25 112.45 113.15 118.26 121.88 125.47 126.97 130.15 136.75 141.52 144.27 147.4 149.61 162.92 166.73 170.06 174.39 181.36 183.78 186 198.08 201.79 215.35 236.86 243.25 245.75 247.37 251.15 255.83 261.5 271.16 273.24 278.5 279.54 291.24 293.75 317.53 325.35 333.71 335.49 340.48 346.73 374.38 375.04 390.13 401.35 410.38 419.11 431.98 432.26 432.95 435.48 446.17 447.31 468.68 471.6 484.65 485.88 513.3 518.5 524.35 530.48 534.81 538.79 562.61 564.26 620.39 621.19 639.9 642.97 651.61 651.97 654.25 655.26 684.4 689.53 713.47 714.63 718.62 721.2 741.97 746.37 747.35 747.76 752 753.45 760.43 762.54 764.14 766.42 797.24 798.69 810.2 811.17 829.4 829.82 831.89 832.7 858.63 859.47 909.74 916.01 952.03 953.39 970.93 974.78 975.64 978.88 985.6 992.81 996.98 1001.96 1009.13 1010.2 1011.22 1017.6 1024.09 1032.04 1037.17 1038.83 1060.61 1069.91 1071.11 1076.04 1076.85 1081.02 1120.19 1125.15 1134.98 1140.42 1148.57 1150.13 1160.05 1161.15 1162.8 1166.89 1180.42 1184.67 1189.69 1190.25 1193.94 1199.18 1206.1 1212.8 1217.22 1218.27 1253.26 1261.58 1274.83 1275.06 1285.31 1286.16 1306.59 1311.67 1315.54 1317 1323.77 1326.82 1327.98 1331.79 1333.19 1341.3 1356.59 1360.16 1368.84 1374.09 1406.29 1412.16 1436.8 1439.17 1451.49 1454.17 1462.87 1464.43 1470.09 1477.06 1477.62 1481.64 1489.63 1491.74 1494.91 1495.85 1496.18 1502.63 1505.31 1506.53 1506.83 1509.93 1514.23 1514.69 1515.34 1517.06 1517.84 1530.31 1531.27 1537.16 1558.12 1561.31 1569.8 1571.03 1617.03 1625.44 1630.47 1638.31 1641.7 1642.31 1647.99 1650.89 1665.2 1667.96 1740.45 1745.92 1785.95 1797.01 3016.05 3022.96 3063.2 3075.32 3078.54 3078.67 3080.01 3113.87 3142.23 3142.58 3148.12 3151.63 3155.22 3167.12 3167.53 3196.27 3198.42 3199.92 3199.94 3201.22 3204.38 3210.59 3212.65 3213.78 3217.43 3226.01 3227.32 3229.96 3232.09 3234.81 3234.96 3242.89 3256.15 3268.52

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14.81 17.97 25.87 28.46 36.89 42.12 45.49 53.02 54.61 68.55 75.21 82.32 86.77 91.88 95.92 100.64 111.71 114.81 125.01 133.7 139.02 143.41 146.78 156 162.19 175.69 192.47 196.26 213.63 237.46 244.61 253.31 256.41 264.94 269.26 279.91 282.07 283.85 317.86 328.74 332 342.63 376.03 398.58 404.02 414.64 415.71 430.58 434.28 448.7 470.25 472.76 482.97 484.68 518.23 525.63 534.1 561.38 601.4 604.48 619.99 630.8 645.48 650.6 661.24 682.02 716.25 721.55 727.75 741.93 744.68 748.24 754.63 763.89 769.75 801.06 811.26 823.64 830.97 831.55 841.63 854.14 918.03 954.67 959.35 960.52 971.69 973.61 995.07 996.37 1001.68 1009.43 1012.23 1019.67 1039.61 1041.72 1049.44 1061.87 1068.42 1075.29 1077.71 1096.1 1122.47 1137.75 1143.27 1148.14 1154.88 1162.79 1179.58 1193.77 1197.54 1208.26 1213.81 1215.88 1253.97 1278.48 1286.61 1289.83 1308.83 1316.56 1327.8 1328.69 1334.04 1338.52 1341.48 1360.39 1370.47 1393.09 1412.52 1419.28 1445.23 1457.53 1467.98 1478.09 1483.51 1488.62 1493.09 1493.82 1500.13 1505.96 1506.44 1508.52 1512.76 1513.13 1516.24 1516.8 1547.66 1563.44 1571.96 1601.31 1615.42 1626.85 1634.64 1648.58 1655.24 1669.24 1764.31 1777.79 1804.52 3017.24 3041.5 3063.92 3079.33 3083.02 3105.73 3145.82 3149.09 3155.23 3166.01 3179.55 3185.81 3197.1 3197.31 3200.92 3202.79 3213.74 3215.38 3218.98 3219.85 3228.52 3229.77 3231.54 3240

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12.55 18.81 21.19 27.75 28.77 34.61 36.53 42.1 49.04 49.87 56.7 61.42 65.29 72.72 82.99 88.97 93.36 96.73 99.93 106.07 112.46 118.31 121.33 131.21 139.1 142.83 152.75 161.98 168.3 177.77 191.11 194.83 198.27 213.91 217.44 240.09 246.17 252.66 258.28 267.17 269.53 281.15 281.95 285.22 301.48 318.34 328.3 330.92 336.78 343.33 355.83 376.27 398.26 402.13 415.49 418.26 429.32 439.24 450.79 470.72 472.2 482.34 484.85 496.12 518.05 522.56 525.64 531.89 556.69 560.85 578.07 600.91 603.78 610.31 618.78 630.93 643.93 651.49 661.72 684.77 714.55 723.35 728.04 741.28 743.76 747.43 750.69 754.6 762.96 767.36 798.78 810.69 818.92 831.94 832.98 843.04 852.46 912.88 945.15 958.64 959.04 965.87 972 973.91 983.43 996.61 1000.72 1007.82 1011.43 1019.51 1039.72 1041.51 1047.34 1061.41 1066.46 1071.9 1077.72 1097.03 1118.24 1136.09 1147.23 1148.73 1150.84 1156.6 1162.44 1179.48 1185.2 1193.44 1198.34 1209.56 1215.06 1215.87 1217.48 1248.47 1263.33 1274.41 1286.25 1287.13 1309.87 1316.91 1322.79 1330.33 1331.01 1334.74 1339.52 1341.95 1360.45 1366.77 1393.93 1407.33 1421.02 1445.5 1456.66 1468.44 1472.67 1482.49 1487.61 1492.12 1492.57 1500.77 1504.13 1506.47 1508.66 1512.87 1513.26 1517.04 1517.49 1547.45 1561.75 1573.9 1602.98 1615.87 1627.76 1635.01 1652.34 1656.87 1667.71 1765.23 1780.49 1804.75 3016.92 3041.97 3059.62 3079.54 3082.78 3105.3 3149.38 3155.59 3155.77 3167.38 3191.12 3197.06 3201.05 3203.08 3205.68 3211.93 3213 3217.38 3226.75 3229.72 3230.55 3231.81 3238.86 3251.23

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14.51 19.68 20.7 24.97 27.46 31 36.02 39.14 40.93 45.27 49.86 54.01 54.66 59.15 61.33 66.86 77.02 80.76 85.6 89.05 90.14 96.43 99.17 103.55 107.29 117.28 118.99 125.55 131.76 135.75 139.29 140.62 144.63 152.7 162.75 173.08 176.7 182.15 190.63 195.16 204.9 224.1 234.25 235.8 246.07 248.86 251.65 254.61 255.99 259.5 266.77 269.04 271.4 273.24 276.7 278.95 286.7 293.56 296.77 304.37 313.2 323.26 325.49 330.99 338.98 350.76 352.93 361.7 364.92 371.24 377.8 378.62 385.16 396.1 401.4 404.04 407.96 411.78 413.02 417.51 421.53 429.74 435.88 446.63 448.08 468.34 469.65 476.14 481.21 482.9 488.28 518.25 527.87 528.43 531.33 536.77 560.92 564.38 593.49 605.47 609.89 617.5 641.01 644.11 651.06 653.91 670.43 672.27 685.78 715.12 725.09 737.14 740.74 744.1 745.75 746.17 752.05 753.17 762.9 769.57 802.94 804.37 811.23 820.94 824.24 830.28 834.74 837.18 852.26 872.73 890.87 911.44 915.43 920.5 920.86 935.67 941.08 941.28 944.45 948.61 951.33 953.71 954.72 958.35 972.78 975.4 976.89 977.44 979.07 999.47 1001.07 1007.02 1011.47 1021.09 1026.04 1032.25 1040.02 1045.21 1051.45 1055.91 1056.91 1058.54 1060.53 1065.27 1065.79 1069.36 1077.8 1083.16 1101.85 1126.73 1129.31 1139.19 1140.33 1147.13 1150.7 1159.77 1163.25 1180 1192.49 1198.69 1208.61 1213.09 1216.38 1221.6 1223.07 1226.14 1227.63 1234.31 1236.68 1237.47 1256.81 1276.6 1278.94 1287.56 1288.44 1293.26 1308.2 1311.26 1315.07 1316.76 1328.02 1329.84 1330.7 1336.46 1341.09 1359.25 1367.91 1391.4 1399.85 1408.21 1409.38 1414.92 1415.53 1416.99 1419.07 1423.43 1425.67 1439.72 1440.85 1449.76 1451.49 1456.1 1467.03 1469.62 1471.08 1477.54 1479.95 1481.53 1483.81 1491.7 1492.18 1492.58 1495.81 1496.94 1497.46 1499.92 1500.19

1500.74 1503.55 1506.78 1506.81 1508.26 1509.26 1512.1 1513.6 1517.19 1518.38 1518.5 1520.1 1521.16 1521.94 1524.76 1526.14 1529.66 1535.27 1539.13 1543.14 1547.31 1561.4 1572.24 1583.07 1620.42 1625.01 1627.47 1636.76 1646.36 1654.47 1668.26 1763.41 1765.56 1798.74 3016.01 3036.78 3036.97 3038.48 3040.07 3041.31 3041.91 3042.02 3045.15 3048.41 3050.61 3067.28 3076.29 3081.51 3103.8 3105.62 3108.01 3108.65 3110.12 3111.92 3112.38 3113.07 3114.71 3116.48 3118.7 3123.73 3124.47 3130.14 3141.09 3144.41 3144.52 3148.77 3151.03 3152.55 3160.19 3160.68 3169.1 3180.7 3186.8 3196.88 3196.95 3198.05 3198.28 3202.46 3209.56 3211.05 3221.39 3221.5 3225.42 3227.32 3233.18 3237.7 3242.6

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7.33 21.48 25.33 29.24 42.6 46.54 48.3 59.63 63.89 90.43 95.68 106.83 107.73 114.93 136.76 154.96 156.55 172.17 176.41 197.65 212.42 215.67 247.17 250.86 264.55 268.58 276.4 294.12 298.93 306.49 332.05 339.81 374.9 395.71 417.51 425.9 430.75 443.04 474.98 487.13 519.24 524.82 530.36 557.72 618.54 641.56 656.07 662 680.88 714.36 716.79 741.97 748.3 748.81 763.56 764.24 799.53 810.66 824.42 831.4 856.51 909.68 949.81 963.58 970.9 985.25 1001.54 1011.67 1018.79 1032.58 1040.78 1065.34 1071.9 1077.21 1118.62 1137.62 1145.89 1162.04 1167.39 1179.43 1188.7 1199.07 1203.95 1215.54 1269.68 1276.69 1290.37 1309.63 1319.14 1325.09 1332.49 1337.43 1361.76 1369.58 1410.99 1445.37 1454.11 1466.36 1468.84 1483.54 1492.56 1501.21 1506.39 1508.82 1513.6 1514.44 1517.23 1530.47 1540.59 1562.32 1583.07 1627.16 1634.4 1654.2 1662.96 1669.66 1767.4 1805.97 3019.91 3053.35 3079.63 3086.73 3125.22 3149.29 3155.92 3198.73 3200.82 3202.09 3205.77 3212.11 3217.64 3222.68 3232.41 3235.02 3258.73

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17.86 20.02 22.19 24.55 25.4 32.55 37.22 39.68 40.84 49.78 53.8 62.79 71.37 79.04 83.82 92.76 98.17 106.47 113.95 122.23 126.56 132.11 132.62 138.08 145.09 147.33 166.88 178.49 180.39 189.92 191.48 210.09 215.11 220.69 229.72 234.97 248.17 257.19 266.77 268.76 274.76 286.3 299.66 306.81 319.04 320.72 338.96 344.86 373.76 388.43 405.74 417.26 418.65 420.09 431.1 434.86 443.98 454.6 459.4 473.31 478.55 484.47 490.08 519.67 524.89 528.26 533.96 558.5 602.65 605.69 622.04 631.01 631.59 642.47 654.93 661.78 683.19 695.87 702.62 718.32 719.01 727.52 732.38 743.26 744.56 747.98 752.15 761.69 773.09 803.68 810.82 823.48 827.43 830.05 833.61 861.33 864.38 867.98 870.03 922.5 941.84 957.78 959.91 968.85 974.72 982.09 985.21 997.4 1008.27 1008.45 1011.01 1012.24 1013.9 1018.24 1034.2 1037.41 1039.5 1048.09 1053.8 1062.83 1066.87 1074.42 1081.28 1096.3 1108.33 1125.13 1137.56 1147.71 1151.45 1159.95 1162.55 1170.24 1179.63 1191.19 1195.98 1198.07 1207.6 1208.95 1215.47 1215.5 1253.57 1281.8 1285.75 1289.03 1308.12 1313.07 1327.24 1329.9 1332.39 1340.31 1341.57 1343.87 1363.64 1365.58 1366.58 1393.96 1406.44 1421.23 1443.53 1455.34 1469.25 1472.28 1481.64 1483.7 1483.85 1484.53 1492.58 1493.54 1496.35 1497.69 1502.61 1508.71 1508.88 1515.01 1517.3 1518.03 1541.63 1543.32 1561.98 1568.98 1571.6 1601.52 1615.86 1628.16 1635.68 1647.11 1648.63 1655.23 1661.3 1669.95 1761.51 1772.91 1801.72 3018.05 3044.09 3073.88 3082.96 3084.15 3107.81 3147.38 3152.61 3163.87 3170.77 3175.63 3187.69 3187.94 3197.79 3199.15 3200.19 3201.93 3202.58 3207.77 3210.24 3216.4 3216.73 3218.64 3219.76 3219.89 3223.26 3231.33 3237.8 3245.92

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10.28 15.92 21.04 22.25 23.92 28.4 32.62 34.3 37.21 40.25 46.49 50.91 56.87 61.58 62.97 77.05 86.21 94.21 99.18 102.94 107.2 113.28 117.99 120.96 127.54 135.39 140.52 147.55 150.75 158.22 168.25 177.97 184.81 187.78 191.81 195.59 207.88 223.26 234.09 236.25 239.35 250.86 254.95 260.66 268.25 269.37 278.27 289.94 299.71 312.61 315.14 321.73 330.21 337.12 343.88 347.61 375.82 391.92 397.64 409.08 409.21 414.75 416.02 430.62 435.31 446.93 454.99 457.74 475.01 477.59 487.54 489.93 495.03 519.83 521.56 525.95 531.48 533.32 553.61 559.11 581.97 599.84 604.53 614.75 618.98 623.17 628.72 641.14 656.12 661.54 680.61 696.98 700.49 717.37 718.58 723.76 731.25 733.15 744.12 748.61 751.04 754.78 760.57 773.66 802.96 810.23 822.82 825.06 827.76 829.73 850.86 861.31 867.94 868.27 923.72 927.51 943.26 957.93 959.07 961.51 970.65 979.07 984.6 996.31 998.91 1004.41 1008.47 1010.73 1014.34 1017.8 1032.78 1037.21 1041.43 1049.1 1053.69 1062 1067.11 1075.06 1079.7 1095.22 1109.98 1123.84 1138.3 1142.3 1149.84 1151.61 1161.7 1162.84 1170.98 1179.53 1191.74 1196.75 1198.26 1206.18 1209.91 1211.42 1215.59 1218.1 1220.36 1245.89 1253.37 1276.22 1285.01 1287.19 1309.23 1314.11 1327.92 1331.8 1332.73 1334.86 1338.77 1343.84 1346.9 1364.14 1367.45 1371.22 1393.81 1404.57 1419.02 1445.49 1457.1 1469.29 1473.21 1482.38 1483.67 1484.09 1486.48 1493.18 1493.38 1494.57 1498.89 1505.41 1508.68 1511.67 1514.47 1514.87 1517.43 1542.7 1546.69 1554.51 1562.3 1570.61 1607.69 1616.67 1627.08 1635.48 1645.72 1647.08 1657.15 1661.91 1669.9 1763.02 1777.37 1805.15 3018.32 3044.84 3078.31 3084.4 3094.76 3108.71 3147.55 3155.67 3165.79 3177.02 3188.13 3190.06 3192.6 3193.72 3199.33 3200.35 3204.88 3208.65 3214.06 3216.68 3219.25 3220.04 3220.89 3221.33 3224.49 3230.85 3233.04 3237.5 3245.06

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14.53 16.91 20.2 23.29 25.82 28.4 31.12 35.57 38.18 39.01 45.42 50.56 53.44 58.57 62.18 63.79 66.73 77.79 84.68 85.74 93 97.25 100.61 105.68 109.93 112.83 116.14 121.94 130.37 132.79 135.98 138.72 142.75 148.84 151.09 155.96 163.46 168.6 172.04 178.82 184.76 189.47 197.99 205.69 210.98 225.13 230.41 233.85 247.66 249.23 251.69 256.69 258.51 262.99 265.22 267.5 273.04 274.92 276 284.42 287.64 289.26 292.15 294.39 312.69 321.75 324.05 326.91 333.2 335.82 337.45 344.31 352.57 357.22 358.35 361.73 372.38 384.73 388.08 391.76 398.91 401.06 406.53 413.04 415.38 417.82 419.72 421.58 429.4 433.91 441.61 444.3 450.64 459.33 467.79 471.61 481.31 481.77 483.95 485.61 514.22 521.73 523.99 529.14 531.79 537.13 555.5 570.8 592.45 594.22 610.23 613.32 631.17 636.27 638.2 641.98 658.15 667.84 670.24 682.41 697.2 704.27 714.87 720.09 727.6 736.55 737.31 741.24 745.25 745.41 751.57 752.71 757.36 768.79 803.09 808.18 810.26 819.16 823.63 825.9 835.34 835.55 844.24 865.23 866.13 872.8 888.31 896.43 907.22 915.18 919.95 925.68 939.18 939.68 945.55 949.91 951.52 953.01 955.07 956.17 958.7 973.21 976.34 983.8 988.36 989.59 990.81 992.15 992.86 1003.28 1006.17 1007.8 1009.89 1015.98 1018.64 1025.68 1027.3 1037.02 1047.77 1050.61 1050.79 1054.1 1054.78 1056.18 1060.37 1065.61 1069.07 1071.97 1075.49 1080.36 1102.2 1106.9 1121.57 1129.46 1135.57 1142 1152.04 1162.46 1163.28 1164.12 1169.36 1180.16 1187.48 1195.21 1196.06 1204.84 1207.42 1207.69 1215.73 1225.29 1225.64 1229.06 1233.54 1235.1 1240.86 1249.37 1254.02 1272.54 1280.84 1281.56 1288.19 1293.22 1306.29 1314.45 1315.07 1315.45 1320.98 1326.09 1330.52 1339.78 1340.47 1345.54 1363.04 1365.24 1366.07 1392.27 1400.44 1406.78 1414.28 1417.68 1418.37 1419.61 1420.79 1423.92 1425.28 1437.59 1447.6 1448.87

1451.64 1455.55 1460.9 1465.15 1468.62 1477.92 1480.3 1480.93 1484.88 1485.62 1492.01 1493 1493.27 1493.41 1496.19 1496.67 1497.52 1500.75 1502.46 1506.06 1506.84 1508.09 1508.2 1509.16 1512.27 1514.25 1517.11 1518.12 1519.44 1520.87 1521.74 1522.87 1525.65 1529.79 1531.54 1535.44 1537.09 1539.22 1539.53 1549.3 1559.17 1561.39 1570.92 1583.81 1593.07 1621.4 1623.11 1629.63 1635.64 1641.21 1649.42 1652.25 1661.06 1670.41 1760.49 1762.38 1792.05 3014.41 3034.6 3035.28 3036.98 3037.91 3039.66 3041.71 3042.43 3045.27 3045.45 3049.06 3074.85 3075.54 3078.8 3100.69 3102.39 3105.34 3107.66 3108.07 3109.37 3109.73 3111.06 3112.91 3114.13 3116.22 3117.42 3117.8 3123.91 3126.7 3142.43 3146.53 3150.88 3159.19 3159.98 3162.03 3173.08 3178.13 3181.05 3185.37 3188.77 3193.79 3197.17 3197.21 3198.32 3203.26 3205.16 3207.06 3211.98 3214.95 3215.88 3216.26 3217.98 3221.31 3229.45 3234.54 3234.55 3249.81 3255.37

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12.61 16.83 21.81 29.39 30.55 33.81 40.4 43.09 52.14 64.1 73.31 81.39 88.46 97 101.32 109.37 115.03 121.24 138.91 143.84 153.46 169.31 178.28 187.89 190.94 193.13 218.21 228 234.07 254.2 257.42 264.52 269.73 274.63 279.57 307.07 315.2 334.49 337.31 372.83 395.1 405.1 413.58 415 427.09 433.22 441.74 464.36 465.21 484.54 487.98 516.43 522.26 527.3 554.85 607.1 608.2 612.39 640.37 643.35 652.18 660.27 680.8 714.99 716.63 739.95 742.2 747.17 748.34 756.16 757.64 767.72 800.12 807.94 821.22 827.6 831.76 854.64 864 917.89 943.91 962.51 962.78 969.56 987.57 991.07 995.34 998.4 1005.49 1019.71 1027.96 1032.25 1038.1 1048.59 1063.98 1069.85 1070.74 1076.01 1103.44 1114.37 1134.87 1141.93 1147 1160.39 1162.73 1179.16 1188.35 1197.1 1204.27 1215.24 1221.91 1265.11 1270.46 1285.5 1292.49 1308.08 1314.59 1316.83 1326.42 1331.55 1337.06 1342.42 1362.78 1364.33 1393.48 1405 1422.28 1440.15 1449.6 1462.33 1468.59 1481.78 1484.52 1491.98 1492.76 1497.01 1506.8 1507.02 1508.43 1513.08 1517.05 1520.81 1522.7 1536.63 1560.28 1576.83 1587.87 1624.65 1626.8 1634.95 1651.52 1655.69 1668.66 1766.22 1768.8 1802.4 3018.96 3045.39 3059.7 3079.3 3085.38 3109.35 3128.04 3129.47 3148.59 3155.32 3163.18 3166.88 3191.76 3198.3 3198.86 3200.19 3200.45 3203.15 3212.6 3216.4 3222.88 3228.58 3236.4 3246.7

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10.56 19.46 20.7 28.75 30.84 38.27 43.62 46.28 51.09 73.32 87.28 89.6 92.01 100.73 111.35 115.71 130.6 138.32 140.04 146.38 156.19 172.74 179.83 191.24 205.79 217.03 227.2 244.82 254.72 264.19 265.13 272.63 279.7 298.71 309.18 312.53 333.51 338.72 376.02 394.75 415.26 417.61 426.62 430.99 442.37 455.96 461.72 471.7 484.5 517.32 523.31 525.44 529.89 556.69 614.86 630.66 642.44 654.35 660.19 682.35 698.74 702.48 715.3 718.77 731.94 742.7 746.6 748.74 762.11 765.25 802.69 809.9 825.04 827.55 830.63 856.58 870.34 871.79 915.14 951.38 959.07 962.61 971.04 986.18 997.24 1006.39 1009.43 1009.96 1017.54 1022.1 1031.68 1039.09 1053.66 1064.34 1071.21 1076.44 1108.2 1119.92 1135.88 1144.45 1162.67 1168.9 1171.97 1179.6 1188.86 1196.17 1198.29 1203.34 1208.85 1215.45 1268.35 1274.47 1288.14 1307.79 1321.6 1327.91 1332.4 1338.9 1341.41 1360.92 1365.18 1370.6 1411.34 1444.58 1453.63 1465.57 1467.53 1470.8 1482.89 1484.84 1492.57 1499.48 1506.96 1508.59 1513.21 1513.89 1517.51 1531.69 1540.51 1541.22 1563.22 1570.46 1583.34 1628.61 1635.06 1647.53 1652.77 1658.38 1660.51 1670.15 1766.43 1802.48 3018.74 3053.35 3078.09 3084.94 3126.13 3146.74 3154.82 3176.19 3188.82 3197.32 3199.26 3199.69 3201.57 3202.03 3210.87 3217.72 3218.26 3219.45 3221.65 3230.09 3235.45 3258.38

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18.09 19.38 26.42 29.05 31.27 36.54 39.59 42.24 48.19 59.05 61.34 64.38 69.4 77.47 85.41 91.65 95.17 100.63 107.49 109.28 114.02 121.47 128.31 129.77 132.39 134.88 142.2 148.2 150.78 158.61 159.32 161.58 171 185.45 186.82 201.14 206.9 236.39 243.65 247.23 248.76 252.63 258.39 262.08 263.42 266.56 275.67 284.67 286.38 298.62 310.44 333.17 334.59 336.25 337.08 373.32 375.57 395.17 396.08 416.05 416.79 422.2 431.75 432.16 434.61 437.33 445.83 469.28 470.97 482.05 483.84 496.44 499.56 517.04 518.53 534.5 542.32 552.3 555.52 610.76 615.17 630.07 634.53 635.76 638.96 646.34 649.05 667.41 671.43 694.69 695.57 712.73 718.01 724.27 727.71 734.74 735.77 736.69 741.33 742.28 743.48 756.13 760.79 765.52 768.27 805.02 808.02 816.26 817.74 825.53 839.65 852.09 867.03 870.83 872.31 928.31 940.21 956.37 961.98 964.36 973.69 975.66 976.63 980.67 983.5 984.73 989.62 993.61 1003.77 1004.56 1006.15 1030.96 1035.44 1060.27 1061.14 1062.8 1065.71 1078.29 1082.95 1111.46 1115.21 1133.65 1134.44 1142.17 1144.63 1162.87 1163.05 1165.18 1166.06 1168.54 1172.9 1177.63 1180.63 1190.16 1194.11 1201.33 1205.51 1212.76 1216.37 1247.79 1260.11 1261.71 1275.04 1277.33 1279.91 1292.55 1296.55 1304.67 1306.26 1314.48 1322.03 1325.56 1327.88 1330.63 1331.84 1336.78 1348.53 1357.02 1361.62 1373.82 1401.8 1406.4 1429.35 1432.91 1445.23 1445.28 1453.2 1456.73 1465.98 1466.16 1466.52 1466.89 1482.38 1488.82 1490.88 1493.24 1502.84 1505.65 1505.89 1506.81 1508.28 1508.63 1513.42 1513.88 1516.51 1517.19 1518.05 1521.89 1539.55 1553.75 1555.98 1560.77 1562.33 1580.62 1585.38 1605.85 1621.47 1632.65 1634.1 1642.4 1645.19 1666.88 1669.02 1751.84 1755.8 1780.68 1788.27 3009.12 3012.61 3050.33 3051.82 3071.74 3071.87 3072.02 3077.3 3113.38 3114.13 3137.33 3137.67 3144.49 3146.28 3190.62 3190.96 3192.99 3193.78 3194.25 3194.68 3200.63 3209.73 3210.98 3211.76 3212.01 3213.74 3225.6 3227.06 3227.44 3228.94 3230.11 3234.17 3235.12 3235.65

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-53.1 20.29 25.22 29.19 41.32 42.84 51.13 59.27 67.01 73.47 79.44 86.52 98.09 100.26 108.97 109.63 116.29 118.65 130.99 136.55 145.31 152.31 154.11 167.14 176.42 183.32 184.42 188.08 195.22 205.05 240.53 242.44 256.98 260.05 264.03 271.87 275.57 285.17 304.75 328 334.03 340.51 375.13 392.37 398.39 412.31 429.57 433.29 435.22 448.92 463.57 470.5 472.76 482.41 514.98 527.69 535.22 560.19 594.85 607.87 619.85 620.26 645.6 648.97 657.82 683.13 713.69 717.32 719.21 727.16 744.7 750.58 751.46 762.14 771.17 800.41 809.79 819.25 825.46 829.8 848.99 854.06 918.65 945.35 962.12 963.03 972.1 974.91 986.55 993.01 998.72 1003.97 1011.04 1019.68 1035.21 1036.44 1040.12 1056.3 1070.2 1077.8 1082.04 1092.35 1121.31 1136.9 1138.38 1146.98 1159.43 1168.89 1179.5 1191.02 1197.24 1204.56 1205.72 1215.21 1248.48 1282.9 1283.81 1290.18 1307.15 1313.55 1322.87 1327.33 1331.32 1335.58 1342.71 1358.8 1373.31 1403.11 1410.85 1421.64 1445.03 1458.96 1464.69 1479.55 1479.8 1486.16 1492.09 1492.98 1498.08 1500.44 1502.25 1502.71 1508.36 1512.53 1516.57 1524.6 1547.47 1563.02 1570.78 1585.25 1606.5 1625.92 1635.15 1648.23 1656.81 1670.4 1748.69 1760.85 1802.67 3016.92 3046.42 3075.65 3082.49 3083.65 3114.86 3154.61 3155.27 3165.04 3166.56 3180.67 3196.06 3200.04 3200.44 3202.29 3212.35 3213.66 3214.11 3218.74 3219.61 3227.99 3230.91 3234.32 3239.75

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-87.32 13.64 20.21 24.5 28.31 33.97 40.42 41.8 50.62 55.45 61.78 65.91 71.51 79.43 88.9 91.66 91.94 100.4 102.77 109.62 117.03 120.55 129.11 141.67 143.28 146.73 156.48 161.1 169.81 177.32 183.31 188.47 190.73 203.17 209.49 220.76 246.46 252.3 264.13 264.52 265.7 273.81 278 285.65 303.88 313.6 328.36 333.13 336.64 344.79 375.05 392.46 401.75 409.56 414.69 430.5 431.48 441.5 449.88 466.2 472.05 480.95 486.24 493.34 503.47 515.22 527.83 536.08 555.95 562.7 566.78 595.08 605.24 620.87 622.19 624.11 647.06 650.95 659.53 682.65 716.23 719.41 728.83 732.75 745.69 750.58 753.65 759.19 764.68 768.94 798.47 810.71 815.67 822.78 831.62 838.56 854.98 915.78 950.74 952.61 964.71 971.23 974.83 977.64 986.12 987.82 1000.88 1002.67 1014.57 1017.94 1025.99 1038.78 1042.45 1053.16 1071.26 1079.59 1083.22 1093.86 1122.96 1137.83 1140.48 1141.96 1149.43 1161.63 1166.06 1179.65 1193.36 1198.47 1206.06 1207.32 1215.71 1224.24 1232.79 1241.61 1251 1286.06 1286.16 1290.5 1292.12 1308.14 1316 1321.48 1328.98 1333.11 1338.8 1344.48 1360.13 1374.59 1403.38 1412.6 1425.03 1448.77 1458.92 1465.97 1474.66 1482.44 1488.26 1490.76 1492.58 1492.63 1496.94 1499.66 1502.88 1508.35 1512.87 1516.95 1525.87 1549.83 1563.66 1572.32 1577.19 1607.29 1628.8 1635.87 1651.96 1660.33 1671.14 1749.47 1758.6 1803.79 3015.57 3048.16 3080.48 3082.48 3084.56 3115.98 3153.95 3159.86 3165.95 3170.07 3201.13 3201.18 3202.17 3203.96 3214.17 3216.22 3216.46 3218.01 3222.91 3225.37 3228.57 3232.35 3233.89 3240.98

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-72.9 20.88 24.85 27.66 33.22 40.11 43.56 45.65 50.2 55 60.15 65.86 68.73 70.79 79.25 87.08 92.95 95.67 96.99 100.07 104.74 108.44 117.25 121.35 129.14 134.46 138.48 141.57 148.31 150.59 153.15 157.47 160 170.07 173.65 178.22 186.59 190.27 195.25 201.03 203.81 217.12 232.83 245.84 255.08 260.28 262.74 267.42 268.49 271.77 274.77 277.16 281.21 284 287.32 300.61 304.8 307.44 315.02 317.9 328.96 332.36 337.58 343.58 345.32 347.85 355.94 363.88 372.64 373.43 377.65 386.59 390.41 398.35 405.58 409.69 410.58 421.06 429.47 431.45 437.92 440.01 442.19 450.43 456.55 468.4 471.49 478.77 480.68 482.59 496.24 516.22 529.63 535.99 543.33 545.8 561.94 573.3 594.11 606.54 610.99 618.63 623.89 645.24 650.75 652.72 653.85 669.43 681.96 716.72 719.51 727.77 728.37 730.14 744.28 749.22 751.39 757.6 762.23 768.29 801.77 810.54 811.29 819.55 822.32 827.78 831.43 836.42 838.94 854.7 888.69 902.95 909.8 918.09 927.6 933.25 935.59 944.9 949.27 950.12 953.22 954.13 961.7 965.96 971.28 974.54 975.56 979.66 980.92 982.7 996.06 996.54 997.2 1009.45 1018.01 1020.7 1022.6 1039.04 1054.71 1054.89 1056.47 1059.32 1062.43 1064.26 1068.15 1069.58 1074.27 1077.98 1094.21 1122.12 1135.82 1145.31 1148.39 1149.79 1160.23 1170.19 1175.44 1179.68 1184.51 1198.68 1206.32 1210.95 1215.89 1219.59 1224.84 1233.86 1236.46 1238.79 1244.06 1253.14 1254.32 1277.15 1280.68 1288 1289.34 1291.88 1293.55 1308.5 1313.25 1317.23 1320.76 1325.91 1329.27 1331.63 1338.64 1341.52 1359.95 1375.26 1404.29 1406.66 1409.59 1410.52 1410.97 1411.44 1414.41 1414.85 1428.93 1436.18 1443.16 1443.52 1446.46 1450.7 1458.92 1462.16 1464.94 1480.36 1484.28 1485.56 1492.04 1492.15 1493.35 1493.62 1495.18 1497.41 1499.53 1499.74 1502.46 1502.8 1503.56 1507.3 1508.36 1509.93 1514.39 1515.35 1515.63 1517.24 1517.36 1519.74 1521.38 1523.7 1524.16 1527.31 1536.78 1538.39 1539.17 1540.92 1556.76 1563.5 1564.45 1574.28 1580.75 1604.4 1623.89 1636.56 1641.55 1653.69 1656.3 1671.46 1742.1 1751.33 1806.31 3016.38 3022.13 3023.75 3025.19 3028.77 3031.04 3035.43 3038.07 3038.42 3046.64 3047.72 3075.81 3080 3081.51 3086.3 3088.81 3094.63 3096.82 3098.73 3100.31 3104.84 3106.09 3107.79 3110.8 3112.45 3113.7 3114.16 3120.16 3130.48 3136.84 3153.52 3154.19 3155.09 3158.97 3163.71 3176.9 3179.44 3188.42 3199.43 3200.01 3200.71 3203 3205.24 3206.45 3214.78 3215.92 3216.48 3224.5 3230.55 3232.99 3237.31 3239.89 3240.01

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TS(11^{OBAc}-$12^{OBAc,Br}$)

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-41.72 16.6 21.22 22.28 25.66 29.87 34.87 38.47 42.96 48.93 56.12 60.25 65.61 78.22 85.47 87.01 94.06 104.51 109.74 120.9 125.45 129.95 136.83 145.48 148.4 151.63 153.32 162.67 173.23 175.17 192.09 194.38 198.4 203.39 220.78 224.86 242.16 253.54 259.07 264.98 270.68 273.71 277.69 296.83 304.63 311.09 328.59 347.25 376.37 394.4 398.15 413.98 418.74 426.37 430.67 440.25 441.38 444.85 453.93 458.36 473.12 480.69 487.44 517.13 523.76 527.35 527.9 558.09 593.2 595.6 618.02 627.45 632.09 642.58 650.54 660.82 681.33 695.21 702.17 713.9 716.1 719.54 728.11 730.54 742.35 747.89 750.07 761.01 762.44 801.55 811.39 814.85 824.43 824.6 830.41 840.69 856.08 864.58 869.98 912.02 948.97 955.05 955.91 962.72 967.3 974.82 978.07 984.46 996.99 998.45 1004.27 1006.44 1011.13 1018.55 1019.71 1023.65 1032.66 1039.58 1043.33 1054.01 1066.83 1073.07 1079.24 1089.91 1106.79 1124.06 1136.77 1143.2 1144.82 1160.68 1162.87 1167.19 1179.48 1188.17 1194.87 1198.75 1202.11 1207.36 1208.53 1215.42 1258.49 1275.61 1289.01 1299.34 1308.07 1316.59 1318.78 1326.43 1331.64 1337.13 1339.74 1340.26 1361.65 1363.85 1367.35 1392.68 1412.21 1437.53 1443.71 1455.95 1457.29 1467.5 1479.71 1483.47 1485.91 1486.16 1492.52 1494.35 1494.94 1499.75 1506.1 1508.53 1509.24 1514.47 1517.5 1518.55 1534.57 1538.12 1554.3 1562.73 1576.46 1586.38 1608.58 1630.17 1635.26 1647.9 1651.04 1652.28 1660.57 1670.63 1744.03 1764.36 1801.59 3018.75 3040.73 3077.6 3082.12 3084.8 3105.82 3145.96 3155.15 3160.89 3165.76 3173.09 3183.38 3185.13 3186.01 3197.29 3198.98 3203.22 3203.77 3210.92 3213.62 3214.91 3215.09 3216.3 3218.16 3227.54 3228.64 3231.53 3235.41 3263.57

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TS($12^{OBAc,Br}$-3a)

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-177.64 12 20.13 24.18 28.5 32.1 36.87 39.57 42.14 49.85 51.52 57.73 63.52 72.28 74.51 84.33 97.27 101.55 104.84 109.5 116.56 122.98 133.62 139.64 148 151.79 160.28 163.26 167.51 172.7 176.08 181.98 187.34 190.05 206.74 229.5 249.18 256.51 257.63 263.37 268.02 269.2 279.98 288.93 315.28 322.95 335.34 348.47 378.02 387.84 389.68 406.65 416.83 429.53 431.33 435.31 440.76 447.38 454.17 466.8 481.68 481.94 488.68 518.97 521.73 535.56 558.94 583.79 596.23 603.84 615.98 625.94 629.07 639.33 653.34 677.83 682.7 698.83 701.62 711.95 713.64 722.09 726.2 738.29 745.37 750.41 758.51 765.22 796.51 803.05 815.02 819.33 820.68 827.26 835.21 850.61 857.05 867.99 869.06 910.14 944.35 958.58 958.95 965.94 969.72 980.31 984.6 986.88 988.74 1003.63 1005.2 1009.31 1013.28 1014.89 1017.89 1036.37 1037.87 1047.73 1053.14 1068.9 1073.39 1082.16 1092.48 1100.32 1110.5 1133.7 1138.1 1138.61 1149.27 1159.07 1162.78 1165.43 1179.7 1196.47 1197.44 1199.98 1204.21 1209.22 1214.05 1215.39 1253.54 1278.08 1287.73 1294.57 1303.05 1312.78 1317.72 1322.13 1328.23 1335.7 1345.39 1348.94 1349.78 1359.63 1366.22 1371.57 1394.18 1419.69 1423.05 1443.12 1459.13 1465.09 1476.43 1480.68 1482.44 1490.03 1490.34 1491.98 1495.7 1500.77 1502.95 1505.42 1508.49 1512.54 1516.96 1517.54 1532.78 1537.68 1561.53 1575.47 1597.59 1604.79 1630.22 1633.26 1637.23 1645.68 1656.47 1657.81 1668.57 1711.77 1754.7 1767.72 1799.78 3014.84 3050.49 3072.81 3075.42 3079.36 3115.38 3142.58 3148.9 3152.64 3170.7 3177.46 3179.71 3189.78 3197.22

3197.92 3198.23 3201.14 3201.31 3206.69 3209.4 3216.76 3218.15 3224.01 3224.61 3225.8 3232.43 3247.03 3256.86 3258.22

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TS(12^{OTf,OBAc} -11^{OTf})

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-159.56 19.06 21.87 24.13 28.9 33.45 37.75 43.2 44.26 47.03 52.81 55.86 67.01 72.57 80.05 81.79 82.76 95.27 100.54 108.33 112.17 113.64 121.86 131.12 133.24 138.09 143.03 145.07 152.37 156.7 166.26 171.49 178.78 181.17 188.24 194.2 203.41 206.37 217.63 224.36 231.5 242.81 245.72 259.34 266.58 269.69 270.74 281.83 287.16 297.33 305.45 309.58 328.41 329.59 339.64 341.99 357.18 372.75 383.6 385.69 416.93 421.13 423.72 428.57 436.87 437.15 443.19 457.93 471.73 478.25 483.1 484.81 489.51 513.4 516.82 523.77 531.03 554.91 555.63 557.06 565.5 590.99 607.6 614.51 616.43 617.47 630.44 640.43 655.42 662.31 681.97 683.63 701.08 709.03 714.74 719.98 723.03 732.28 740.66 750.14 752.68 755.95 763.24 770 798.95 807.85 819.41 825.08 827.72 831.29 840.02 845.71 853.32 871.83 915.18 941.46 957.55 959.57 961.01 969.87 971.58 972.68 985.68 988.42 989.59 991.22 998.41 1010.33 1010.77 1016.9 1018.37 1036.41 1038.8 1042.29 1053.48 1056.99 1069.46 1078.3 1082.8 1090.49 1111.18 1112.68 1121.7 1137.15 1137.49 1142.55 1148.48 1153.3 1172.63 1179.61 1190.82 1196.02 1197.09 1198.59 1205.48 1206.9 1211.78 1215.78 1225.76 1249 1254.76 1280.65 1281.85 1287.04 1292.24 1302.45 1309.04 1309.91 1322.25 1328.74 1332.62 1336.5 1346.22 1349.34 1359.65 1365.25 1365.96 1401.56 1407.88 1422.24 1439.88 1456.67 1468.89 1479.23 1485.21 1488.26 1488.79 1490.07 1493.2 1495.39 1497.33 1498.92 1508.3 1508.59 1512.25 1517.54 1524.94 1532.4 1548.5 1561.55 1568.8 1597.94 1603.66 1629.25 1636.61 1637.03 1643.72 1656.52 1658.6 1670.59 1725.11 1750.41 1762.3 1792.98 3017.72 3044.06 3079.83 3083.75 3099.93 3112.45 3151.7 3153.78 3163.3 3174.92 3175.8 3189.78 3201.12 3202.67 3202.88 3207.49 3207.98 3213.89 3214.86 3218.43 3222.87 3224.98 3226.82 3229.92 3236.44 3237.97 3239.8 3240.46 3252.58

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TS(12^{OAr*,OBAc}-11^{OAr*})

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-112.7 17.11 18.48 20.29 22.77 29.68 32.51 34.73 38.93 40.46 42.53 43.91 47.89 51.97 53.91 58.6 65.66 66.01 72.38 80.5 85.1 90.7 93.75 95.64 102.35 104.53 106.33 112.76 116.38 122.01 123.75 135.26 138.3 144.76 150.03 153.08 156.84 164.67 169.12 173.69 177 191.43 197.38 202.55 215.41 218.92 228.85 233.71 243.67 250.32 254.73 256.94 257.96 262.52 266.03 266.93 269.76 271.65 279.62 280.82 283.19 290.96 297.24 306.06 312.57 315.1 320.32 328.83 337.5 341.07 348.84 352.2 354.49 358.26 365.42 378.17 378.45 381.21 392.06 393.11 398.02 412.04 416.52 417.3 418.35 423.74 430.99 432.99 434.73 436.75 439.51 445.51 448.95 460.39 467.04 482.51 484.19 486.59 489.36 491.77 519.67 521.95 536.34 550.36 553.21 556.84 574.2 581.09 598.68 602.67 610.01 612.59 626.45 631 639.06 650.21 656.09 668.43 677.2 681.53 694.36 699.53 708.04 710.56 714.99 726.83 731.8 745.1 748.14 749.99 757.53 758.38 761.5 790.21 795.59 796.84 809.53 821.78 822.78 826.77 831.03 833.22 840.71 845.9 864.56 864.95 870.98 901.78 904.11 908.81 915.85 928.56 934.23 935.95 941.9 945.21 946.64 950.62 953.61 954.23 957.84 965.84 968.14 973.32 973.75 975.59 977.54 978.66 981.89 986.87 999.39 1004.44 1008.78 1012.92 1016.75 1017.9 1033.53 1039.55 1050.65 1053.66 1054.65 1058.58 1059.8 1062.81 1065.73 1067.62 1069.61 1073.16 1082.95 1089.19 1094 1111.37 1130.24 1134.31 1138.92 1148.47 1149.55 1153.19 1163.43 1164.22 1179.71 1181.5 1194.37 1195.78 1200.33 1203.03 1206.54 1209.78 1215.11 1221.34 1223.85 1233.42 1234.67 1236.18 1242.87 1252.86 1265.12 1277.02 1279.07 1284.34 1291.33 1296.7 1301.95 1306.24 1311.63 1315.64 1316.91 1325.18 1326.91 1329.78 1337.79 1344.93 1347.46 1351.53 1358.29 1366.88 1371.8 1398.8 1406.82 1411.43 1412.75 1412.91 1416.02 1416.9 1419.09 1423.31 1437.32 1439.33 1448.15 1452.11 1453.68 1456.61 1462.41 1467.94 1470.72 1477.67 1485.65 1490.03 1490.75 1491.71 1491.84 1493.2 1495.22 1495.92 1497.27 1498.59 1499.14 1500.21 1501.16 1504.06 1506.25 1506.8 1508.52 1511.19 1513.5 1515.95 1517.2 1517.55 1519.77 1521.83 1524.05 1524.61 1524.92 1533.4 1533.57 1534.17 1538.93 1543.75 1561.79 1572.22 1589.8 1597.91 1602.52 1630.17 1634.42 1637.8 1640.41 1647.77 1656.01 1657.95 1669.89 1700.82 1749.82 1763.07 1795.68 3014.46 3024.19 3026.94 3027.34 3029.91 3030.87 3033.15 3037.5 3037.87 3040.08 3043.06 3078.97 3079.49 3087.94 3095.11 3095.16 3095.88 3099.9 3100.37 3101.13 3105.43 3106.81 3107.34 3109.28 3112.35 3115.73 3118.08 3118.33 3121.89 3125.94 3149.46 3151.76 3159.25 3162.2 3173.65 3184.9 3186.16 3196.22 3198.15 3198.41 3199.47 3199.71 3201.22 3203 3208.36 3210.12 3211.46 3215.13 3223.45 3225.1 3225.52 3231.09 3235.94 3237.53 3245.98 3248.95 3251.95 3262.9

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TS(12^{Br,Br}-6^{Br})

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-213.05 4.06 15.98 23.64 26.16 28.14 32.17 33.01 35.02 39.8 49.53 54.6 58.42 63.97 65.33 72.42 75.36 79.42 80.87 88.74 97.64 99 101.97 107.82 109.77 114.85 122.61 125.45 137.34 142.88 149.64 155.79 159.4 169.62 170.65 179.07 179.73 191.62 202.54 219.48 225.66 235.03 240.09 245.72 252.46 258.41 261.38 264.13 267.96 280.79 282.01 287.7 311.25 314.34 320.12 324.67 328.1 331.25 341.95 343.67 357.73 366.6 376.66 395.59 412.42 414.93 417.14 427.32 430.51 432.54 441.77 448.85 474.34 476.28 490.06 490.84 519.69 526.92 536.05 540.12 562.38 587.58 590.77 593.08 611 619.11 644.25 655.17 664.05 681.78 692.51 703.29 711.45 716.57 721.67 740.64 748.06 752.77 766.61 767.56 805.17 812.5 814.64 829.56 832.11 835.72 842.46 860.61 862.7 887.87 920.68 941.77 947.98 953.45 959.4 962.98 963.15 968.9 971.35 974.71 979.56 981.68 997.18 999.94 1003.37 1005.52 1011.23 1024.26 1027.05 1038.41 1041.92 1046.71 1048.7 1062.51 1069.17 1079.29 1088.31 1091.41 1105.03 1118.02 1126.87 1132.44 1138.44 1144.76 1148.26 1157.33 1161.31 1166.98 1179.07 1191.39 1194.35 1199.39 1201.49 1203.74 1211.96 1214.87 1220.31 1260.14 1268.68 1275.89 1280.08 1288.51 1298.92 1315.22 1315.84 1322.47 1328.28 1330.17 1337.87 1338.42 1341.85 1358.62 1363.15 1369.17 1388.85 1394.9 1407.4 1411.34 1411.87 1412.9 1424.38 1434.83 1439.44 1443.19 1446.52 1454.03 1465.7 1467.13 1477.63 1484.66 1486.7 1487.04 1489.16 1491.18 1492.93 1496.41 1496.65 1500.39 1502.25 1506.14 1506.9 1509.77 1510.46 1512.53 1513.76 1515.26 1519.38 1522.86 1531 1531.45 1535.74 1545.14 1558.98 1580.16 1591.73 1605.28 1626.68 1632.85 1653.31 1661.58 1665.97 1769.57 1772.89 1807.69 2120.23 3024.32 3045.05 3048.6 3060.31 3061.58 3066.01 3068.49 3075.59 3081.23 3082.35 3093.16 3112.5 3121.65 3127.73 3132.69 3138.1 3143.55 3147.33 3149.5 3152.4 3154.04 3155.35 3159.9 3163.61 3174.27 3177.26 3180.47 3193.88 3195.17 3200.68 3202.28 3203.76 3204.14 3207.93 3214.76 3216.56 3225.24 3229.5 3231.14 3234.72 3249.16 3254.05

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TS(12^{OBAc,Br}-13^{OBAc,Br})

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-473.55 17.58 20.52 26.32 27.11 31.62 36 39.08 43.01 45.16 49.59 54.72 57.61 63.73 73.51 77.04 81.99 85.56 88.14 92.88

99.82 104.63 105.71 107.12 110.57 115.02 122.4 125.31 130.23
131 137.05 141 148.49 153.61 161.73 170.08 174.38 180.73
186.12 190.15 194.04 200.45 209.83 223.67 224.15 227.7 232.53
235.35 246.32 251.84 252.72 255.18 258.75 262.33 265.27
271.03 271.5 282.32 302.95 316.64 324.11 325.11 331.53 339.55
347.26 356.08 370.72 374.07 384.39 396.9 409.27 411.7 416.56
425.84 428.73 435.96 440.09 447.15 449.07 456.93 458.85
468.16 475.9 485.4 488.92 521.8 526.45 531.4 535.97 546.54
558.2 569.02 584.63 600.63 618.54 622.4 631.12 639.75 651.41
663.46 678.79 685.47 698.99 704.18 705.58 712.81 716.51 727.1
737.17 748.01 749.27 753.19 765.46 773.87 786.47 805.97
811.92 820.57 827.16 831.05 833.31 850.73 854.06 859.78
867.89 870.79 886.72 911.08 928.28 946.74 953.87 959.52
959.68 963.83 967.38 969.83 973.27 985.02 986.53 994.96
998.19 1002.36 1004.32 1010.77 1016.05 1018.69 1021.7
1024.88 1028.98 1032.61 1033.31 1039.24 1043.19 1055.23
1056.94 1062.67 1074.66 1079.48 1095.45 1103.28 1111.46
1113.63 1122.13 1129.27 1137.41 1138.51 1142.7 1148.83
1160.19 1161.4 1163.5 1172.1 1178.3 1184.75 1188.84 1199.97
1200.9 1205.03 1205.45 1208.83 1211.94 1215.95 1225.58
1246.58 1255.82 1274.35 1276.38 1284.99 1292.11 1304.53
1315.46 1320.92 1322.57 1324.05 1328.64 1335.57 1336.21
1344.28 1353.64 1362.22 1369.51 1369.63 1373.25 1401.71
1402.85 1407.96 1414.78 1417.46 1421.33 1432.38 1437.7
1439.86 1442.11 1457.85 1466.72 1471.08 1478.74 1479.63
1483.11 1484.84 1485.31 1486.75 1490.2 1491.43 1493 1494.21
1494.53 1494.67 1502.14 1504.67 1505.65 1507.18 1507.81
1509.7 1514.02 1514.14 1515.94 1517.9 1522.86 1533.15
1541.33 1543.48 1548.73 1557.84 1560.33 1565.26 1580.65
1595.98 1624.41 1633.5 1643.59 1645.35 1654.77 1660.3
1667.37 1712.82 1753.62 1779.18 1808.23 3024.29 3037.54
3060.99 3064.42 3066.52 3067.79 3072.71 3080.95 3082.1 3093
3106.47 3123.18 3128.07 3137.78 3139.2 3143.26 3147.34
3149.28 3152.58 3152.97 3160.82 3162.95 3168.11 3170.67
3173.42 3176.29 3178.7 3185.44 3192.14 3196.05 3197.65
3202.54 3204.28 3206.33 3208.07 3210.06 3210.31 3214.18
3214.71 3221.89 3222.55 3225.59 3230.43 3234.63 3237.29
3248.93 3255.1
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11. Cyclic Voltammetry of 11^{OAr*}

Cyclic voltammetry (CV) experiments were conducted by means of a three-electrode setup using a CHI 600E potentiostat. The electrochemical cell comprised a glassy carbon (GC) disk working electrode (Ø = 1.6 mm), a platinum wire counter electrode, and a silver wire pseudo-reference electrode. The supporting electrolyte, electrochemical grade tetrabutylammonium hexafluorophosphate $[N(^nBu)_4]PF_6$, was dried in vacuo at 110 °C for three days. All measurements were conducted at room temperature in a glovebox under N_2 atmosphere. The working electrode was polished with 1.0 µm diamond paste (AES, C3) and 0.05 µm alumina paste (AES, C3), rinsed with acetone and deionized water, and allowed to dry. Initially a blank sample only containing electrolyte in THF (0.25 M) was measured and the potential cycled for 3-5 scans until a stable potential was reached. Then, the electrochemical cell was filled with **11^{OAr*}** (0.67 mM) in THF and the CV was recorded (Figure S84). Ferrocene was used as an internal standard and all redox potentials are reported against the Fc/Fc^+ redox couple.

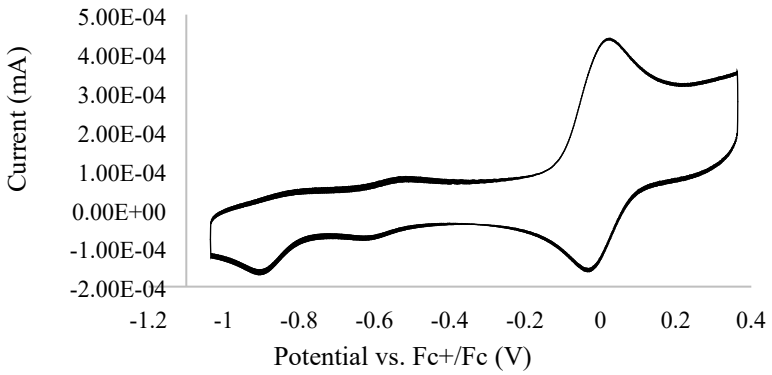

Figure S84. Cyclic voltammetry of [Ni(OAr*)($^{p\text{-Anis}}$NN^{H})] (0.67 mM) in THF (0.25 M $TBAPF_6$ supporting electrolyte) recorded at 100 mV/s.

A quasi-reversible event assigned for the redox couple Ni(II)/Ni(I) can be observed at −1.036 V vs. Fc+/Fc (Figure S84). Toward more negative potentials, two other irreversible processes can be seen, likely involving the reduction to Ni(0) and then the reduction of the ligand itself.

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