Supporting Information: Tunable and Practical Homogeneous Organic Reductants for Cross-Electrophile Coupling

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Table of Contents

SI. General Methods S3
SII. Synthesis of Formamidinium Hexafluorophosphate Salts S6
SIII. Synthesis of Tetraaminoethylenes S8
SIV. Synthesis of Oxidized Tetraaminoethylenes S12
SV. Air Stability Studies of Tetraaminoethylenes S14
SVI. Solubility Studies of Tetraaminoethylenes S15
SVII. Procedure for ^{1}H NMR Yields of Products from Cross-Electrophile Coupling of Aryl and Alkyl Halides S16
SVIII. High Throughput Experimentation for Optimization of Drug-Like Aryl Halides S17
SIX. Procedure for ^{1}H NMR Yields of Cross-Electrophile Coupling of Drug-Like Aryl Halides and Alkyl Halides S25
SX. Reductant Screen for Intermolecular Three-Component Dicarbofunctionalization of Alkenes S27
SXI. Synthesis of Katritzky Salts S29
SXII. Characterization of Katritzky Salts S30
SXIII. Optimization of Cross-Electrophile Coupling of Aryl Halides and Katritzky Salts S33
SXIV. Reductant Screen for Cross-Electrophile Coupling of 2-Iodoanisole and Katritzky Salts ***1**, **3**, and **4*** S34
SXV. ^{1}H NMR Yields of Products from Cross-Electrophile Coupling of Aryl Bromides and Katritzky Salt ***4*** S37
SXVI. ^{1}H NMR Yields of Products from Cross-Electrophile Coupling of Additional Aryl Iodide Substrates and Katritzky Salt ***4*** S38
SXVII. Isolation Procedure and Characterization for Products of Cross-Electrophile Coupling of Aryl Halides and Katritzky Salts S39
SXVIII. Procedure for 1 mmol Scale Reaction to Form Product ***9f*** S43
SXIX. NMR Spectra of Isolated Compounds S44

SXX. Cyclic Voltammetry S69
SXXI. X-Ray Crystallographic Information S71
SXXII. Computational Details and Coordinates S99
SXXIII. References S123

SI. General Methods

Experiments were performed under an atmosphere of N_2 in an M-Braun glovebox or using standard Schlenk techniques, unless specified otherwise. Purging of the glovebox atmosphere was not performed between uses of pentane, benzene, toluene, diethyl ether, 1,4-dioxane and tetrahydrofuran (THF); as such, trace amounts of the solvents may have been present in the box atmosphere and intermixed in the solvent bottles.

1,4-Dioxane, *N*,*N*-dimethylformamide (DMF), acetonitrile, pentane, THF, benzene, dichloromethane, diethyl ether, and toluene were dried via passage through a column of activated alumina on an Inert Technologies PureSolv MD7 solvent purification system and subsequently stored under N_2 unless otherwise noted. EtOH was purchased as 200 proof and used as received. In cases where dry and degassed EtOH was required, EtOH was quickly transferred from a newly opened bottle of 200 proof EtOH to a Straus flask and sparged with N_2, then stored under N_2. DMAc (*N*,*N*-dimethylacetamide) was purchased as anhydrous 99.8% from Millipore Sigma and used without further purification. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were in some cases dried prior to use. C_6D_6 and CD_3CN were degassed via three consecutive freeze-pump-thaw cycles and dried by passage through a short column of neutral activated alumina and stored under an N_2 atmosphere. Neutral alumina was activated by heating at 250 °C *in vacuo* overnight. 3Å molecular sieves were activated by heating at 250 °C *in vacuo* overnight. $CDCl_3$ was degassed via three consecutive freeze-pump-thaw cycles and then dried by stirring over excess calcium hydride followed by distillation and then storage under an N_2 atmosphere. DMSO-d_6 was purchased in 1 mL ampules and used as received.

NMR spectra were recorded on Agilent-400, -500, or -600 MHz spectrometers at ambient probe temperatures unless otherwise stated. Chemical shifts for ^1H NMR and $^{13}C\{^1H\}$ NMR spectra are reported with respect to residual protio solvent in ppm. Chemical shifts for other nuclei are referenced through the gyromagnetic ratio method described by Harris *et al*.[1]

Electrochemical measurements were performed with CH Instruments potentiostats (models 600D/650D) using a 3 mm glassy carbon working electrode, a platinum wire auxiliary electrode, and a silver wire pseudo-reference electrode. To prepare the reference electrode, 0.1 M tetrabutylammonium hexafluorophosphate in DMF was added to a jacketed compartment (separated from solution with a glass frit) and allowed to equilibrate for 24 hours prior to use. A silver wire roughened with 600 grit sandpaper was then immersed in the jacketed compartment.

Glassy carbon working electrodes were polished for 30-60 seconds using 0.05 µm alumina and then rinsed with DI water and dried before every measurement. For cyclic voltammetry measurements, the potential was compensated for the internal resistance of the cell, and ferrocene was added as an internal reference.

Mass spectrometric measurements were performed with a Thermo Fisher QExactive Orbitrap LC-MS system, equipped with a Dionex UltraMate 3000 UHPLC, consisting of an LPG-3400SD pump unit, a WPS-3000 autosampler, and a Column Oven TCC-3000. Mass spectra (MS and MS/MS) were recorded with the QExactive Orbitrap mass spectrometer. Electrospray was used for desolvatization and ionization, with the electrospray needle held at +3.5kV. Compressed air was used as desolvatization gas, with capillary temperature at 250 °C, probe heater temperature at 400 °C, sheath gas at 47.5 L/min, and aux gas flow at 11 L/min. Resolution was set to 35,000 M/ΔM. Mass spectra were recorded in the range of 150 to 2000 m/z in positive ion mode. Measurements and data post-processing were performed with Thermo Xcalibur 4.1.31.9. Two methods were used for sample preparation and injection. The first method was used for all tetraaminoethylene compounds. The second method was used for all other compounds. *Method 1*: Samples were prepared in a glove box in dry and degassed THF and loaded in a gas tight, sample lock syringe, Hamilton 1725 SL SYR, for transport. Capillaries on the mass spectrometer were flushed with dry and degassed THF prior to sample injection. Samples were held at room temperature and continuously injected using a syringe pump at 15 µL/min. *Method 2*: The samples were prepared on the benchtop in CH_3CN and held at room temperature in the autosampler compartment. 1uL of each solution was directly injected into the flow path of the LC system without column separation. An isocratic flow was used with a constant rate of 0.3000 mL/min: 20% Solvent A: Water, HPLC grade Chromasolv, with 0.1% Formic Acid; 80% Solvent B: Acetonitrile, HPLC grade Chromasolv, with 0.1% Formic Acid.

Chemicals that were purchased from commercial suppliers were used as received unless otherwise stated. 4,4’-di-*tert*-butyl-2,2’-bipyridine (dtbbpy) was purchased from Sigma Aldrich or Santa Cruz at >97% purity. Aryl and alkyl halide substrates were purchased at ≥97% purity. All liquid aryl and alkyl substrates were degassed by sparging with nitrogen or by three consecutive freeze-pump-thaw cycles and then handled inside of a nitrogen filled glovebox. Liquid aryl and alkyl halide substrates that had a yellow color instead of being colorless were purified by passage through a short column of neutral activated alumina prior to use. Tetrakis(dimethylamino)ethylene

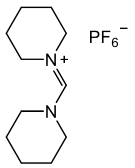
(TDAE) was purchased from Sigma-Aldrich, TCI, AstaTech, or Santa Cruz. Diisopropylamine was purchased as >99.95% from Millipore Sigma. ^{n}BuLi was purchased as 2.5 M in hexanes from Millipore Sigma. Sodium hexafluorophosphate was purchased from Oakwood Chemicals. Piperidine was purchased as >99.5% from Millipore Sigma. Morpholine was purchased from Alfa Aesar as >99%. Pyrrolidine was purchased from Oakwood Chemicals as >99%. Dimethylcarbamoyl chloride as purchased from Millipore Sigma as >98%. 4-aminotetrahydropyran was purchased from Oakwood chemicals as >98%. 4-tert-butylbenzylamine was purchased from TCI as >98%. 4-methoxybenzylamine was purchased from TCI as >97%. 4-(trifluoromethyl)benzylamine was purchased from TCI as >98%. 3-phenylpropylamine was purchased from Alfa Aesar as >98%. 2,4,6-triphenylpyrylium tetrafluoroborate was purchased from Oakwood chemicals as >95%. 3Å molecular sieves were purchased from Alfa Aesar.

The following compounds were synthesized according to literature procedures: (dtbbpy)Ni^{II}Br$_2$,[2] N,N,N',N'-tetramethylformamidinium chloride,[3] and 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate.[4]

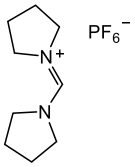
SII. Synthesis of Formamidinium Hexafluorophosphate Salts

General Procedure A:

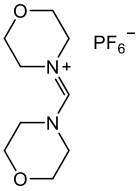
The procedure was adapted from a literature report.[5] In a glovebox under an N_2 atmosphere, to a Schlenk flask charged with a magnetic stir bar was added N,N,N',N'-tetramethylformamidinium chloride (1 equiv.), and degassed EtOH (7.5 M). The Schlenk flask was capped, attached to a Schlenk line using standard techniques, and fitted with a rubber septum. To the flask was added the corresponding amine (3 equiv.), which was degassed by sparging with N_2 prior to the addition, via syringe transfer. The rubber septum was removed from the Schlenk flask, which was then fitted with a reflux condenser against a positive pressure of N_2. The reflux condenser was fitted with a rubber septum and a gas outlet attached to a bubbler containing a 1 M HCl solution (to scrub out dimethylamine liberated during the reaction) was inserted into the top of the reflux condenser. The reaction was heated at reflux for 5 hours then allowed to cool to room temperature and volatiles were removed *in vacuo*. The resulting solid was opened to air and dissolved in 0 °C water, then quickly transferred a round bottom flask charged with a magnetic stir bar containing a nearly saturated solution of sodium hexafluorophosphate (1.2 equiv.) in water at room temperature, resulting in the formation of a precipitate. The solution was stirred for one minute at room temperature then filtered through a medium-fritted glass funnel, and the resulting solids were washed with copious water and dried *in vacuo*, resulting in the desired formamidinium hexafluorophosphate salt product.



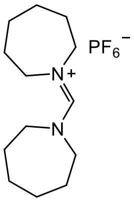
Piperidin-1-ylmethylidenepiperidinium hexafluorophosphate (2c-Pi): Synthesized according to general procedure A. 15.5 g (65%). The NMR spectra are consistent with a previous literature report.[5]



Pyrrolidin-1-ylmethylidenepyrrolidinium hexafluorophosphate (2c-Py): Synthesized according to general procedure A. 20.1 g (87%). The NMR spectra are consistent with a previous literature report.[5]



Morpholin-1-ylmethylidenemorpholinium hexafluorophosphate (2c-M): Synthesized according to general procedure A. 46.3 g (61%). The NMR spectra are consistent with a previous literature report.[6]

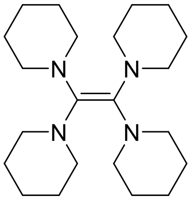


Azepan-1-ylmethylideneazepanium hexafluorophosphate (2c-Az): Synthesized according to general procedure A. 4.4 g (71%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.50 (s, 1H), 3.67 (t, J = 6.0 Hz, 4H), 3.56 (t, J = 6.1 Hz, 4H), 1.80 (m, 8 H), 1.64 (m, 8H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 156.13, 57.67, 49.74, 28.71, 27.71, 26.05, 25.50. ^{31}P{^{1}H} (161.835 MHz, CD_3CN) δ -145.5 (sep, J = 706.5 Hz). ^{19}F (376.14 MHz, CD_3CN) δ 73.81 (d, J = 706.3 Hz). (HRMS) TOF MS ES$^+$ (m/z) $[M]^+$ calculated for $[C_{13}H_{25}N_2]^+$ 209.2012; found 209.2014.

SIII. Synthesis of Tetraaminoethylenes

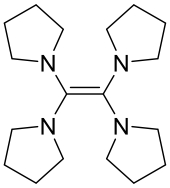
Preparation of Lithium Diisopropylamide (LDA) Solution:

All LDA solutions were prepared immediately prior to use. The following procedure details the preparation of LDA for the synthesis of TPiE as a representative procedure. A 100 mL Schlenk flask was removed from an oven at 130 °C and allowed to cool to room temperature under vacuum, then put under a positive pressure of N_2 using standard Schlenk line technique. The Schlenk flask was fitted with a rubber septum, then 30 mL of dry, degassed THF and 7.2 mL dry, degassed diisopropylamine (51.32 mmol, 1.2 equiv.) were added. The flask was cooled to -78 °C then 15.9 mL *n*BuLi (2.7 M in hexanes, 42.9 mmol, 1 equiv.) was added. The flask was allowed to warm up to room temperature and the LDA solution was used in its entirety within 30 minutes of preparation.

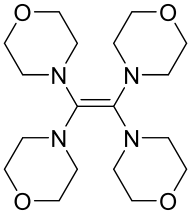


Tetrakis(piperidino)ethylene (TPiE): A 500 mL round bottom flask was charged with a magnetic stir bar and piperidin-1-ylmethylidenepiperidinium hexafluorophosphate (14.04 g, 42.9 mmol, 1 equiv.). The flask was dried *in vacuo* for 1 hour and then placed under an atmosphere of N_2. Dry, degassed THF (30 mL) was added, and the flask was cooled to -78 °C. LDA (42.9 mmol, 1 equiv.; see preparation of LDA above) was cooled to -78 °C and then added to the reaction flask via cannula transfer. The reaction mixture was allowed to warm to room temperature and left to stir under a positive pressure of N_2 for 4 hours, during which time the reaction mixture turned homogeneous and pale brown. The reaction flask was opened to air and quickly transported to a rotary evaporator, where the volatiles were removed *in vacuo*, resulting in a pale yellow solid. Hexanes (100 mL) was added to the resulting solid, and the mixture was filtered through a 60 mL medium-fritted glass funnel. The remaining contents of the round bottom flask and solids on the fritted funnel were washed with an additional 50 mL hexanes. The filtrate was transferred to a 500 mL round bottom flask and the volatiles removed *in vacuo* on a rotary evaporator, resulting in a yellow solid. A magnetic stir bar was added to the round bottom flask, which was then fitted with a rubber septum. The flask was left under active vacuum for one hour and then backfilled with N_2. Three 5-10 second cycles of vacuum followed by backfilling with N_2 were then performed.

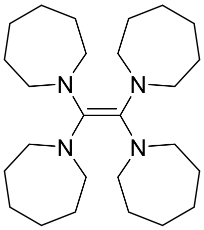
Subsequently, degassed EtOH (50 mL) was added to the flask via cannula transfer, and the contents stirred under a positive pressure of N_2 until a fine white powder was suspended in a yellow solution (about 20 minutes). Degassed H_2O (150 mL) was added to the flask via cannula transfer, the rubber septum was removed, and the solution was filtered through a 60 mL medium-fritted glass funnel. The solid was washed with 3:1 H_2O:EtOH (3 x 30 mL) and then quickly transferred to a glass scintillation vial and dried *in vacuo*. Once dry, the product was stored in a glovebox under an N_2 atmosphere as a pale yellow solid, 4.6 g (60%).[7] ^1H NMR (400 MHz, C_6D_6) δ 2.98 (br s, 16H, N-CH_2-C), 1.53 (br s, 24H, C-CH_2-C). $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6) δ 134.6, 51.6, 27.4, 25.8. (HRMS) TOF MS ES$^+$ (m/z) $[M]^+$ calculated for $[C_{22}H_{40}N_4]^+$ 360.3247; found 360.3229. Anal. Calcd. for $C_{22}H_{40}N_4$: C, 73.28; H, 11.18; N, 15.54. Found: C, 73.41; H, 11.42; N, 15.55.



Tetrakis(pyrrolidino)ethylene (TPyE): A 500 mL Schlenk flask was charged with a magnetic stir bar and pyrrolidin-1-ylmethylidenepyrrolidinium hexafluorophosphate (19.5 g, 65.4 mmol, 1 equiv.). The flask was dried *in vacuo* for 1 hour and then placed under an atmosphere of N_2. Dry, degassed THF (48 mL) was added, and the flask was cooled to -78 °C. LDA (65.4 mmol, 1 equiv.; see preparation of LDA above) was cooled to -78 °C and then added to the reaction flask via cannula transfer. The reaction mixture was allowed to warm to room temperature while stirring and left to stir at room temperature under a positive pressure of N_2 for 4 hours, during which time the reaction mixture turned brown and remained heterogeneous. Without exposing the reaction mixture to air, the volatiles were removed *in vacuo*, then dry, degassed pentane (200 mL) was added to the flask under N_2. The resulting mixture was filtered under N_2, and the volatiles were removed from the filtrate, resulting in a sticky yellow solid. The crude product mixture was transferred to a glovebox containing an N_2 atmosphere and recrystallized from dry degassed Et_2O at -35 °C to give a white solid, 2.105 g (21%). ^1H NMR (400 MHz, C_6D_6) δ 3.07 (t, J = 6.4 Hz, 16H), 1.77 (t, J = 6.4 Hz, 16H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 123.5, 49.5, 26.2. (HRMS) TOF MS ES$^+$ (m/z) $[M]^+$ calculated for $[C_{18}H_{32}N_4]^+$ 304.2621; found 304.2612. Anal. Calcd. for $C_{18}H_{32}N_4$: C, 71.01; H, 10.59; N, 18.40. Found: C, 70.67; H, 10.79; N, 18.37.

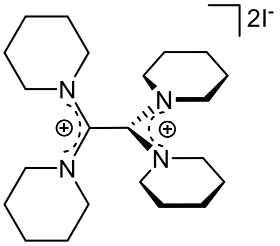


Tetrakis(morpholino)ethylene (TME): A 500 mL Schlenk flask was charged with a magnetic stir bar and morpholin-1-ylmethylidenemorpholinium hexafluorophosphate (37.05 g, 0.112 mol, 1 equiv.). The flask was dried *in vacuo* for 1 hour and then placed under an atmosphere of N_2. Dry, degassed THF (88 mL) was added, and the flask was cooled to -78 °C. LDA (0.112 mol, 1 equiv.; see preparation of LDA above) was cooled to -78 °C and added to the reaction flask via cannula transfer. The reaction mixture was allowed to warm to room temperature while stirring, then placed in a 45 °C oil bath and left to stir under an atmosphere of N_2 for 72 hours, during which time the reaction mixture turned brown and homogeneous. The reaction flask was opened to air and quickly transferred to a 1 L round bottom flask and volatiles were removed *in vacuo* on a rotary evaporator, resulting in a pale brown solid. H_2O (400 mL) was added to the flask under air and the solution was stirred rigorously for 15 minutes then filtered through a 60 mL medium-fritted glass funnel, resulting in a beige solid, which was washed with H_2O (3 x 50 mL) and then dried *in vacuo*. Once dry, the beige solid was dissolved in EtOAc (800 mL) under air and filtered through a 60 mL medium-fritted glass funnel. The filtrate was collected, and volatiles were removed *in vacuo* on a rotary evaporator to produce a pale yellow solid. The pale yellow solid was washed with hexanes (3 x 40 mL), resulting in a white solid. 6.3 g (31%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.56 (br s, Hz, 16H), 2.87 (br s, 16H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 133.3, 67.3, 50.7. (HRMS) TOF MS ES$^+$ (m/z) [M]$^+$ calculated for $[C_{18}H_{32}N_4O_4]^+$ 368.2418; found 368.2409. Anal. Calcd. for $C_{18}H_{32}N_4O_4$: C, 58.67; H, 8.75; N, 15.20. Found: C, 58.74; H, 8.54; N, 15.19.

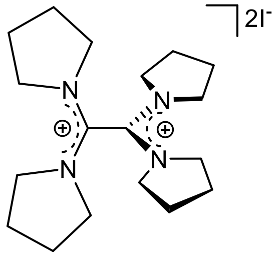


Tetrakis(azepano)ethylene (TAzE): A 500 mL round bottom flask was charged with a magnetic stir bar and azepan-1-ylmethylideneazepanium hexafluorophosphate (7.100 g, 20.0 mmol, 1 equiv.). The flask was dried *in vacuo* for 1 hour and then placed under an atmosphere of N_2. Dry, degassed THF (14 mL) was added, and the flask was cooled to -78 °C. LDA (20.0 mmol, 1 equiv.; see preparation of LDA above) was cooled to -78 °C and added to the reaction flask via cannula transfer. The reaction mixture was allowed to warm to room temperature and left to stir under a positive pressure of N_2 for 16 hours, during which time the reaction mixture turned homogeneous and pale brown. The reaction flask was opened to air and quickly transported to a rotary evaporator, where the volatiles were removed *in vacuo*, resulting in a sticky yellow solid. Hexanes (75 mL) was added to the resulting solid, and the mixture was filtered through a 60 mL medium-fritted glass funnel. The remaining contents of the round bottom flask and solids on the fritted funnel were washed with an additional 25 mL hexanes. The filtrate was transferred to a 500 mL round bottom flask and the volatiles were removed *in vacuo* on a rotary evaporator, resulting in a yellow oil. A magnetic stir bar was added to the round bottom flask, which was then fitted with a rubber septum. The flask was left under active vacuum for one hour and then backfilled with N_2. Three 5-10 second cycles of vacuum followed by backfilling with N_2 were then performed. Subsequently, degassed EtOH (25 mL) was added to the flask via cannula transfer, and the contents stirred under a positive pressure of N_2 until a fine white powder was suspended in a yellow solution (about 10 minutes). Degassed H_2O (75 mL) was added to the flask via cannula transfer, the rubber septum was removed, and the solution was filtered through a 60 mL medium-fritted glass funnel. The solid was washed with H_2O (3 x 30 mL) and then quickly transferred to a glass scintillation vial and dried *in vacuo*. Once dry, the white solid product was stored in a glovebox under an N_2 atmosphere, 1.6 g (39%). ^1H NMR (500 MHz, C_6D_6) δ 3.13 (t, J = 5.0 Hz, 16H), 1.67 (m, 32H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ 136.7, 52.6, 30.4, 28.7. (HRMS) TOF MS ES$^+$ (m/z) $[M]^+$ calculated for $[C_{26}H_{48}N_4]^+$ 416.3873; found 416.3857. Anal. Calcd. for $C_{26}H_{48}N_4$: C, 74.93; H, 11.61; N, 13.45. Found: C, 75.04; H, 11.72; N, 13.32.

SIV. Synthesis of Oxidized Tetraaminoethylenes



1,1'-(1,2-di(piperidin-1-yl)ethane-1,2-diylidene)bis(piperidin-1-ium) diiodide, [TPiE]$^{2+}$2[I]$^{-}$: Under air, a solution of iodine (0.0770 g, 0.306 mmol) in diethyl ether (5 mL) was prepared in a 2 dram vial and cooled to 0 °C. Under N_2, to a separate 2 dram vial was added a magnetic stir bar and TPiE (0.100 g, 0.278 mmol), which was then cooled to 0 °C. The 2 dram vial containing TPiE was opened to air and the diethyl ether solution of iodine was added quickly. The reaction was stirred for 10 minutes, during which time a yellow precipitate formed. The reaction was filtered through a 60 mL medium-fritted glass funnel. The resulting solid was rinsed with diethyl ether (3 x 10 mL) and dried *in vacuo* to give a yellow solid, 0.1660 g (97%). ^{1}H NMR (400 MHz, CD_3CN) δ 3.88 (t, J = 5.69 Hz, 4H), 3.66 (t, J = 5.77. Hz, 4H), 1.89-1.71 (m, 24H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 155.32, 54.51, 53.99, 26.42, 26.07, 22.69. (HRMS) TOF MS ES^{+} (m/z) [M]$^{2+}$ calculated for $[C_{22}H_{40}N_4]^{2+}$ 180.1621; found 180.1622.



1,1'-(1,2-di(pyrrolidin-1-yl)ethane-1,2-diylidene)bis(pyrrolidin-1-ium) diiodide, $[TPyE]^{2+}2[I]^{-}$: In a glovebox under an N_2 atmosphere, a solution of iodine (0.015 g, 0.059 mmol) in diethyl ether (1.5 mL) was prepared in a 2-dram vial. To a separate 2 dram vial under an N_2 atmosphere, a solution of TPyE (0.025 g, 0.082 mmol) in diethyl ether (1.5 mL) was prepared. The iodine solution was added dropwise to the TPyE solution with constant stirring over 5 minutes at room temperature, resulting in a white precipitate. *Note: If the iodine solution was added too quickly or if iodine was added in excess, triiodide counterions were formed, resulting in a deep red precipitate.* The reaction was removed from the glovebox and filtered through a 60 mL medium-fritted glass funnel. The resulting solid was rinsed with diethyl ether (3 x 10 mL) and dried *in vacuo* to give a white solid, 0.020 g (61%). ^{1}H NMR (600 MHz, Methanol-d_4) δ 4.31 (t, J = 6.81 Hz, 8H), 3.74 (t, J = 6.51 Hz, 8H), 2.21-2.12 (m, 16H). ^{13}C{^{1}H} NMR (150 MHz, Methanol-d_4) δ 151.51, 54.87, 53.97, 26.67, 25.41. (HRMS) TOF MS ES^{+} (m/z) $[M]^{2+}$ calculated for $[C_{18}H_{32}N_4]^{2+}$ 152.1308; found 152.1308.

SV. Air Stability Studies of Tetraaminoethylenes

Air Stability Studies Procedure:

A sample of tetraaminoethylene was prepared in a 2 dram vial inside a glovebox under an N_2 atmosphere. If the sample was a solid, it was crushed up into a fine powder using the side of a spatula. The samples were removed from the glovebox and opened to air. The head space of the vial was sparged with air using a 20 mL syringe 5 times, then the sample was allowed to sit on the benchtop uncapped for an additional 5 minutes. A cap was then fitted to the vial and the sample was stored at room temperature. To take a time point, an aliquot of the sample was pumped into a glovebox and an NMR sample was prepared under a N_2 atmosphere in a solvent where all species present in the sample were soluble to monitor decomposition using ^{1}H NMR spectroscopy (data for TDAE decomposition were collected in C_6D_6; data for TME, TPyE, and TAzE decomposition were collected in DMSO-d_6; data for TPiE decomposition were collected in 1:1 DMSO-d_6:C_6D_6). Decomposition is reported as integration of all unknown signals divided by integrations of all signals present in the spectrum. See Table 1 in the manuscript for percent decomposition results.

SVI. Solubility Studies of Tetraaminoethylenes

Solubility Studies Procedure:

In a glovebox under an N_2 atmosphere, a 2 dram vial with a PTFE seal cap was charged with a magnetic stir bar and a 0.0375 mmol sample of tetraaminoethylene. The solid was ground to a fine powder inside the vial using the side of a spatula. 250 µL of the appropriate solvent was added to the vial and the solution was allowed to stir at room temperature for 5 minutes. Vials which contained undissolved tetraaminoethylene were then heated to 80 °C in an aluminum heating block with a thermocouple and allowed to stir for five minutes.

Table S1. Solubility data for all reductants at 0.15M concentration. No = not soluble at 80 °C, RT = soluble at room temperature, 80 °C = soluble at 80 °C. IPAc = isopropyl acetate.

Solvent	**TME**	**TPiE**	**TAzE**	**TPyE**
Pentane	No	RT	RT	RT
Benzene	RT	RT	RT	RT
1,4-Dioxane	RT	80 °C	RT	RT
IPAc	80 °C	80 °C	RT	RT
2-MeTHF	80 °C	RT	RT	RT
THF	RT	RT	RT	RT
DMAc	80 °C	No	80 °C	80 °C
Acetonitrile	80 °C	No	No	80 °C

SVII. Procedure for ^{1}H NMR Yields of Products from Cross-Electrophile Coupling of Aryl and Alkyl Halides

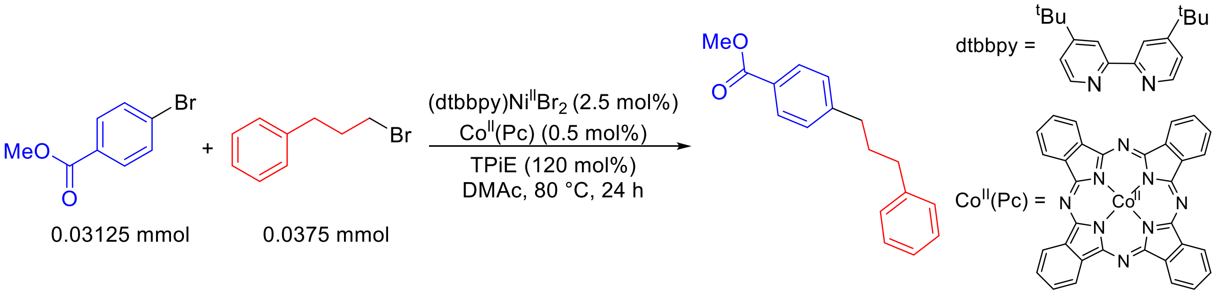


Figure S1. Cross-electrophile coupling of methyl 4-bromobenzoate and 1-bromo-3-phenylpropane.

Representative Procedure:

In a glovebox under an N_2 atmosphere, methyl 4-bromobenzoate (6.7 mg, 0.03125 mmol) and TPiE (17.5 mg, 0.0375 mmol) were added to a 1 dram vial charged with a magnetic stir bar. A separate 2 dram vial was charged with Co^{II}(Pc) (1.8 mg, 0.003125 mmol), (dtbbpy)Ni^{II}Br$_2$ (7.6 mg, 0.0156 mmol), 1-bromo-3-phenylpropane (114 µL, 0.75 mmol), and DMAc (5 mL) to make a stock solution in a glovebox under an N_2 atmosphere. 0.27 mL of the stock solution was added to the vial containing methyl 4-bromobenzoate and the reductant to initiate catalysis. The reaction was capped tightly with a PTFE seal cap and stirred at 80 °C for 24 hours. The reactions were opened to air and passed through a short plug of silica, which was washed with 5 mL EtOAc. The volatiles were removed, and the crude reaction mixture was dissolved in a solution of $CDCl_3$ containing a known amount of hexamethylbenzene. Product yields were determined by integration of select peaks in the ^{1}H NMR spectrum against the hexamethylbenzene external standard.

SVIII. High Throughput Experimentation for Optimization of Drug-Like Aryl Halides

Analytical Details for Analysis of High Throughput Experimentation:

UPLC/MS (ESI) was performed using a Waters Acquity UPLC I-Class system equipped with a binary pump, sample manager, column manager, sample organizer, a photodiode array detector, Single Quad Detector 2 with ESI source and MassLynx® software.

Analytical Separations Method:

Inject volume: 1 µL

Column Temperature: 45 °C

UV scan: 210 – 400 nM

CORTECS UPLC C18 1.6 µM 2.1x50 mm

Mobile Phase A: 0.1% TFA in Water

Mobile Phase B: 0.1% TFA in Acetonitrile

Details of Elution

Time (min)	Flow (mL/min)	% A	% B
0.00	0.700	95	5
1.70	0.700	0	100
1.95	0.700	0	100
1.96	0.700	95	100
2.00	0.700	95	5

Hardware for High Throughput Experimentation:

The reactions were performed in a 96 well reaction block (Analytical Sales & Services, Inc. catalog # 96960) using 1 mL reaction vials (Analytical Sales & Services, Inc. catalog # 884001), a PFA sheet (Analytical Sales & Services, Inc. catalog #: 96967) and rubber mat (Analytical Sales & Services, Inc. catalog #: 96965) for sealing the block, and 96 parylene coated stir dowels (1.98mm diameter, 4.80 mm length, V&P Scientific, Inc. product # VP 711D-1) for stirring. The reaction block was stirred using a tumble stirrer (tumble stirrer: V&P Scientific, Inc. Model # VP710 S) and heating was applied using a heating jacket (V&P Scientific, Inc. Model VP

741ABZ-R-MB). The analytical samples were filtered through a 0.45 um filter plate (Millipore Sigma, Part# MSRLN0450).

Figure S2. Representative image of a reaction block, reaction vessels, stir bar, PFA sheet, and rubber mat used in high throughput experimentation.

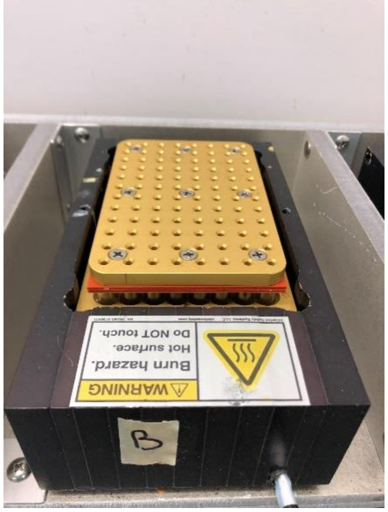


Figure S3. Representative image of a reaction block inside a heating jacket on a tumble stirrer used in high throughput experimentation.

Reaction Components Used in High Through Put Experimentation:

All coupling partners, catalysts, and reductants were dosed as mixtures in DMAc inside a nitrogen filled glovebox. If the mixture in DMAc was not soluble, the mixture was dosed while it was stirred. The DMAc that was used in all experiments was purchased from Millipore Sigma in an air free, sure seal bottle, and used as is, after opening inside a nitrogen filled glove box. Aryl and alkyl halide DMAc mixtures were prepared by weighing the aryl and alkyl halides into respective dram vials open to air (each with a stir bar), then bringing the vials inside a nitrogen filled glove box and adding DMAc. The mixtures of CoPc and organic reductant were prepared by weighing CoPc and organic reductant into respective dram vials (each with a stir bar) inside a nitrogen filled glovebox, then adding DMAc. The mixture of (dtbbpy)Ni^{II}Br$_2$ was prepared by weighing Ni^{II}Br$_2$ (1 equiv.) and dtbbpy (1 equiv.) in a dram vial (with a stir bar) inside a nitrogen filled glove box followed by adding DMAc. The (dtbbpy)Ni^{II}Br$_2$ DMAc mixture was allowed to stir for 20 min at 25 °C before use. The concentration of the mixtures of each reaction component in DMAc is shown below.

General Procedure for High Throughput Cross-Electrophile Coupling Using Dual Ni-Co-Catalysis with Organic Reductants:

Each reaction component was added as a stock mixture using DMAc as solvent. Using Eppendorf pipettes in a nitrogen filled glove box, each 1 mL reaction vial (containing a parylene coated stir dowel) was charged with an aliquot of stock mixture of aryl halide (14 uL, 7 umol, 1 equiv, 0.5 M), 1-Br-3-Ph-Propane (22 ul, 11 umol, 1.6 equiv., 0.5 M), (dtbbpy)Ni^{II}Br$_2$ (14 uL, 0.35 umol, 0.05 equiv., 0.025 M, *for 5 mol%, volumes scaled appropriately for other loadings*), CoPc (14 uL, 0.35 umol, 0.05 equiv, 0.025 M, *for 5 mol% loading, volumes scaled appropriately for other loadings*), and organic reductant (18 uL, 11 umol, 1.6 equiv., 0.6 M). DMAc was added to vials, where required, to reach a final concentration of 0.1 M. The reaction plate was then sealed and placed in a preheated (80 °C) tumble stirrer. The reaction block was stirred at 80 °C for 18 hours. At this time, the reaction block was allowed to cool to 25 ° C and removed from the tumble stirrer and glove box. The plate was centrifuged, opened to air and 4 uL of the crude mixture was diluted in 200 uL DMSO. These mixtures then were forced through a 0.45 uM filter plate (Millipore Sigma part# MSRLN0450). These mixtures were injected into the UPLC/MS for analytical analysis. The yield of the reaction under optimal conditions, as judged by Liquid Chromatography Area Percent (LCAP) at 254 nm, was then measured using NMR spectroscopy (see section SIX).

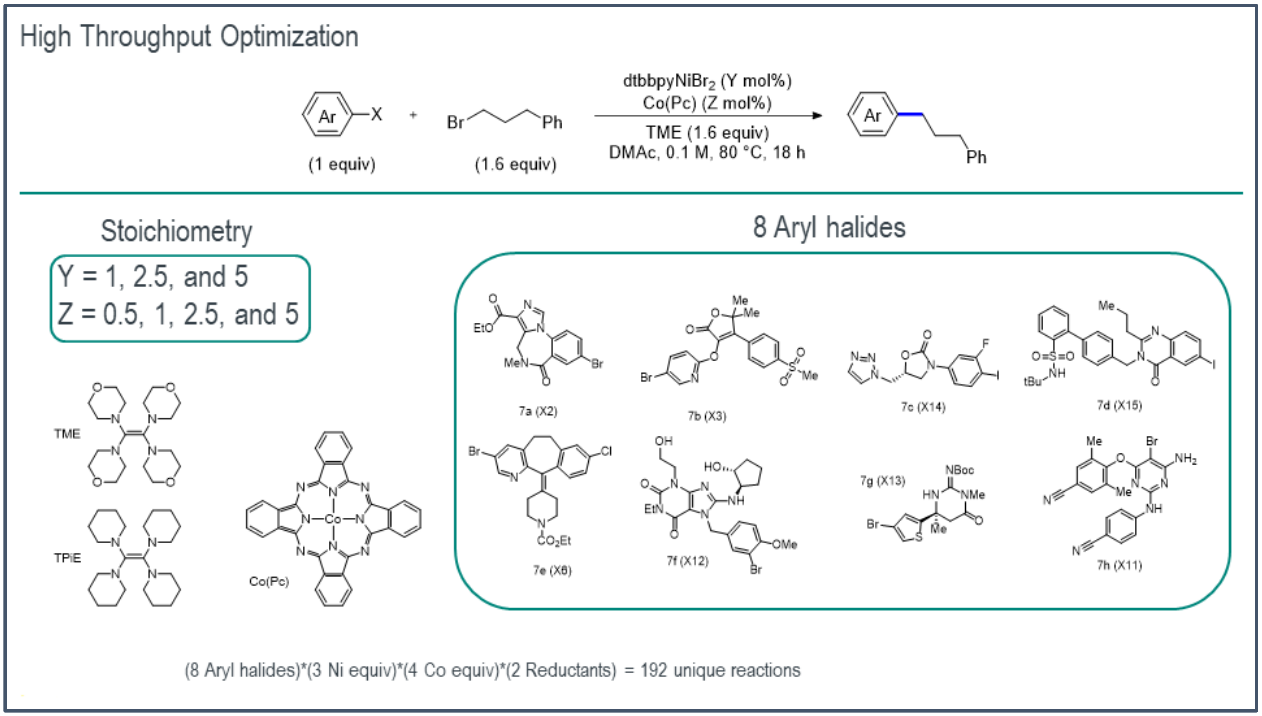
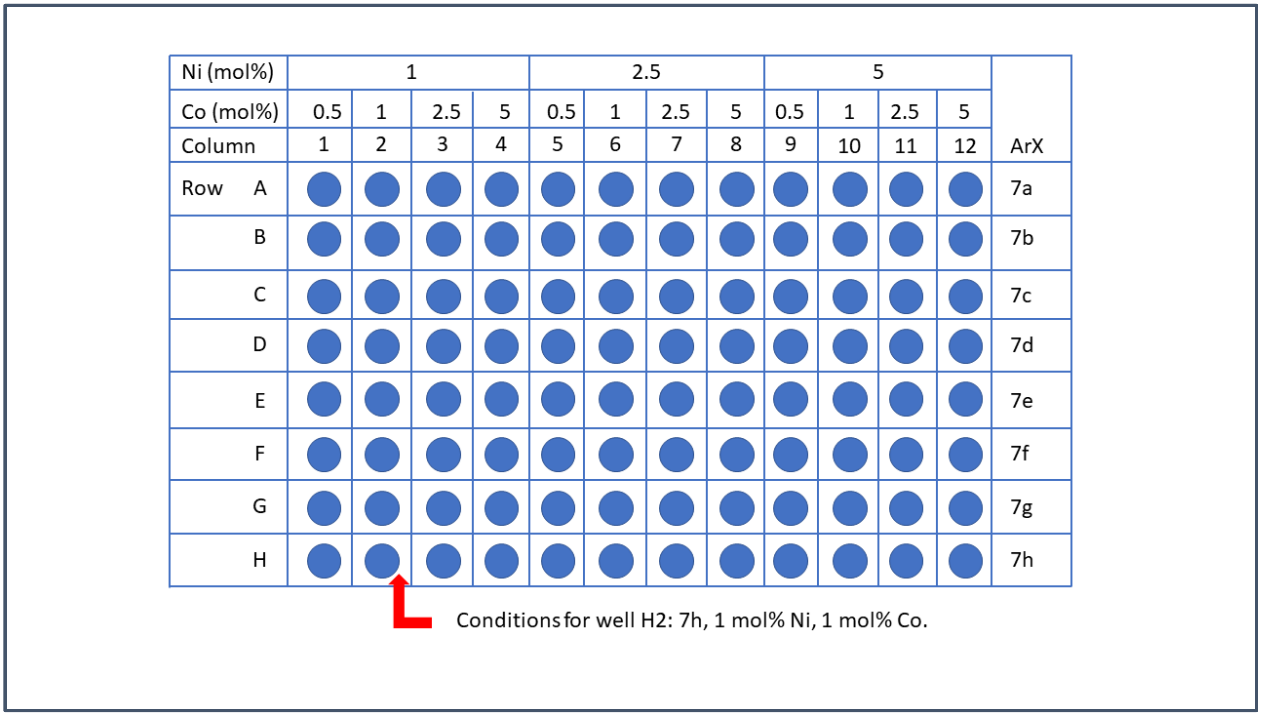


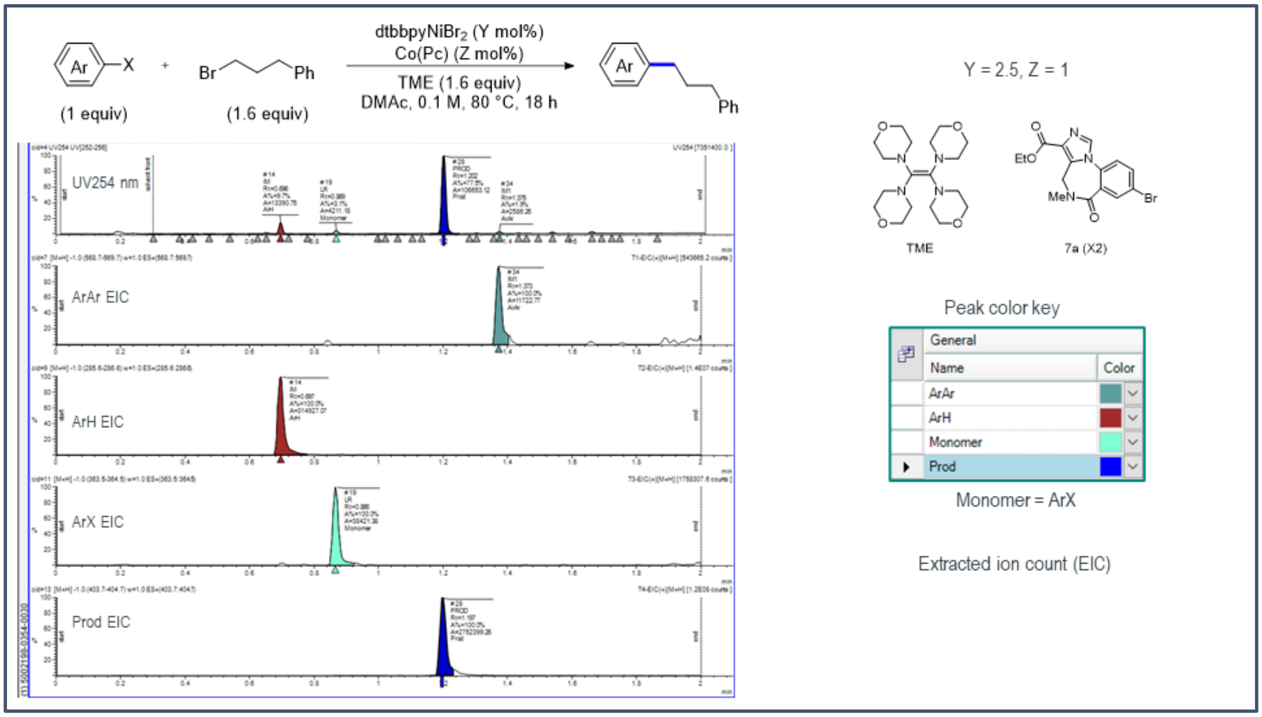
Figure S4. High throughput optimization of Ni/Co-catalyzed cross-electrophile reductive coupling promoted by organic reductants TME and TPiE.

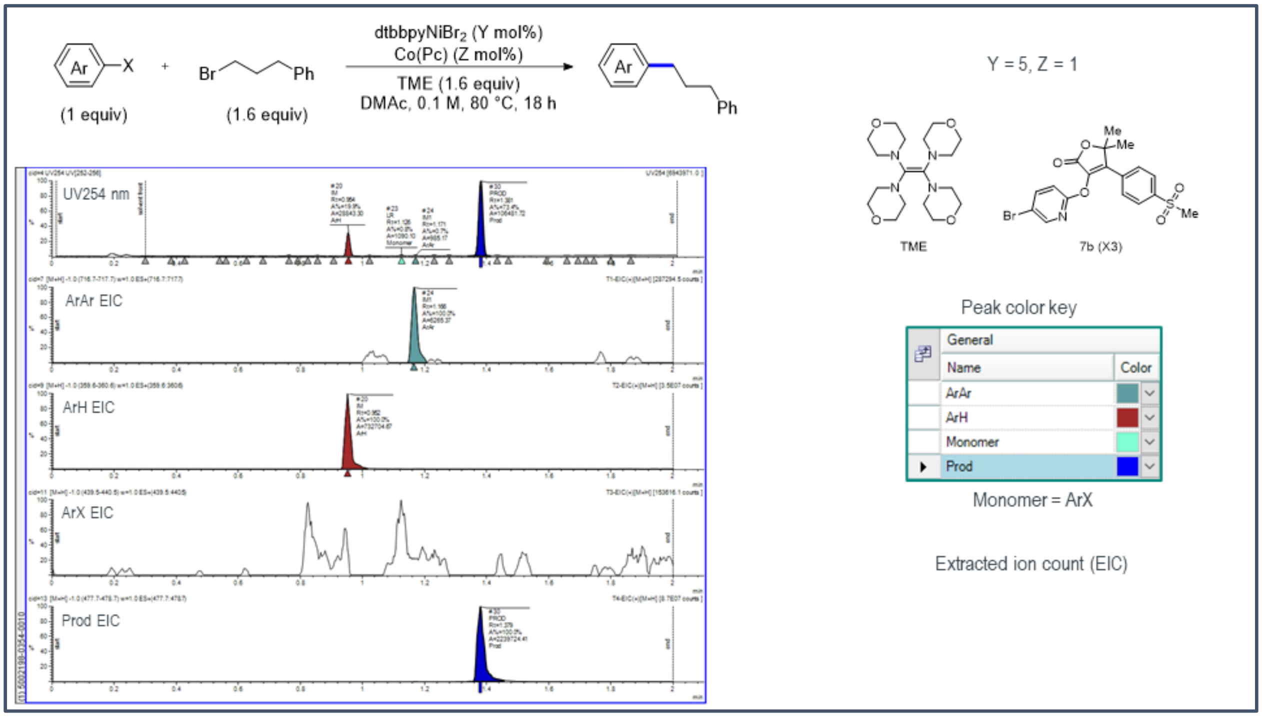


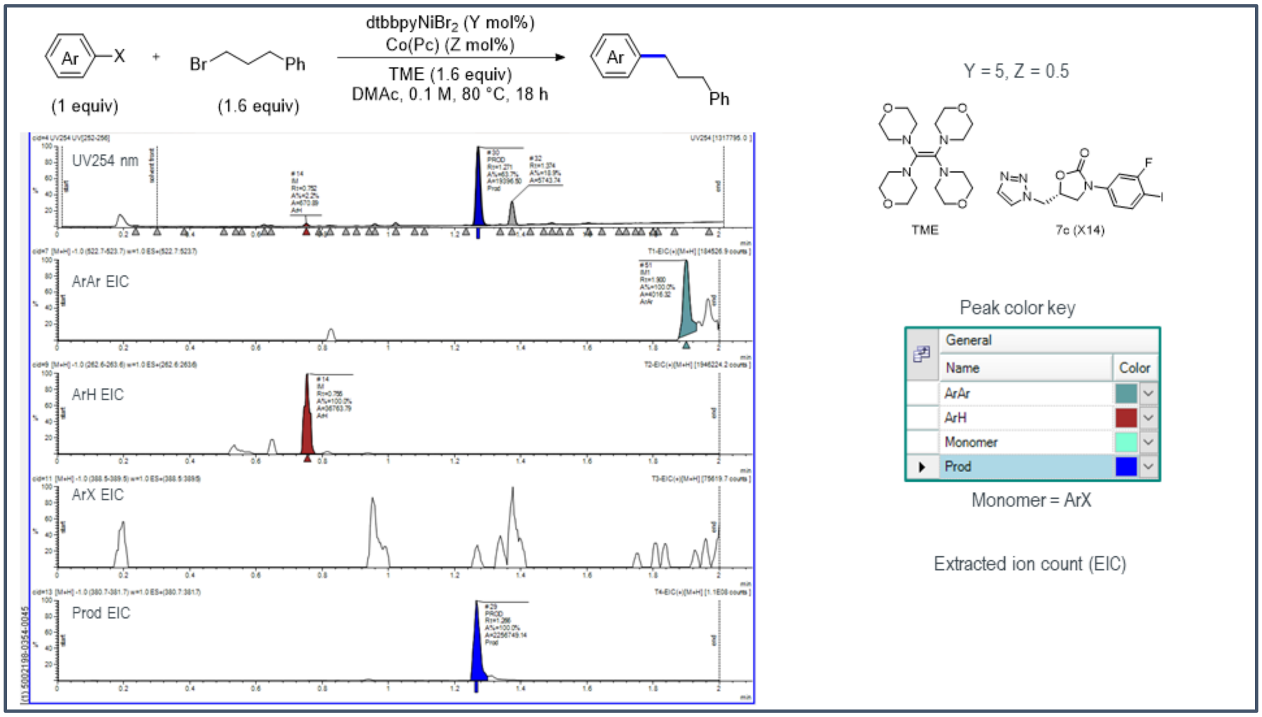
Ni (mol%)	1				2.5				5				
Co (mol%)	0.5	1	2.5	5	0.5	1	2.5	5	0.5	1	2.5	5	
Column	1	2	3	4	5	6	7	8	9	10	11	12	ArX
Row A	●	●	●	●	●	●	●	●	●	●	●	●	7a
B	●	●	●	●	●	●	●	●	●	●	●	●	7b
C	●	●	●	●	●	●	●	●	●	●	●	●	7c
D	●	●	●	●	●	●	●	●	●	●	●	●	7d
E	●	●	●	●	●	●	●	●	●	●	●	●	7e
F	●	●	●	●	●	●	●	●	●	●	●	●	7f
G	●	●	●	●	●	●	●	●	●	●	●	●	7g
H	●	●	●	●	●	●	●	●	●	●	●	●	7h

Conditions for well H2: 7h, 1 mol% Ni, 1 mol% Co.

Figure S5. Reaction array schematic used for high throughput optimization of the cross-electrophile coupling of aryl halides and 1-Br-3-Ph-propane promoted by TME and TPiE.


Ar
X
(1 equiv)
Br
Ph
(1.6 equiv)
dtbbpyNiBr2 (Y mol%)
Co(Pc) (Z mol%)
TME (1.6 equiv)
DMAc, 0.1 M, 80 °C, 18 h
Ar
Ph
Y = 2.5, Z = 1
UV254 nm
ArAr EIC
ArH EIC
ArX EIC
Prod EIC
TME
EtO
MeN
Br
7a (X2)
Peak color key
General
Name
Color
ArAr
ArH
Monomer
Prod
Monomer = ArX
Extracted ion count (EIC)


Ar
X
(1 equiv)
Br
Ph
(1.6 equiv)
dtbbpyNiBr2 (Y mol%)
Co(Pc) (Z mol%)
TME (1.6 equiv)
DMAc, 0.1 M, 80 °C, 18 h
Ar
Ph
Y = 5, Z = 1
UV254 nm
ArAr EIC
ArH EIC
ArX EIC
Prod EIC
TME
Me
Me
Br
Me
7b (X3)
Peak color key
General
Name
Color
ArAr
ArH
Monomer
Prod
Monomer = ArX
Extracted ion count (EIC)



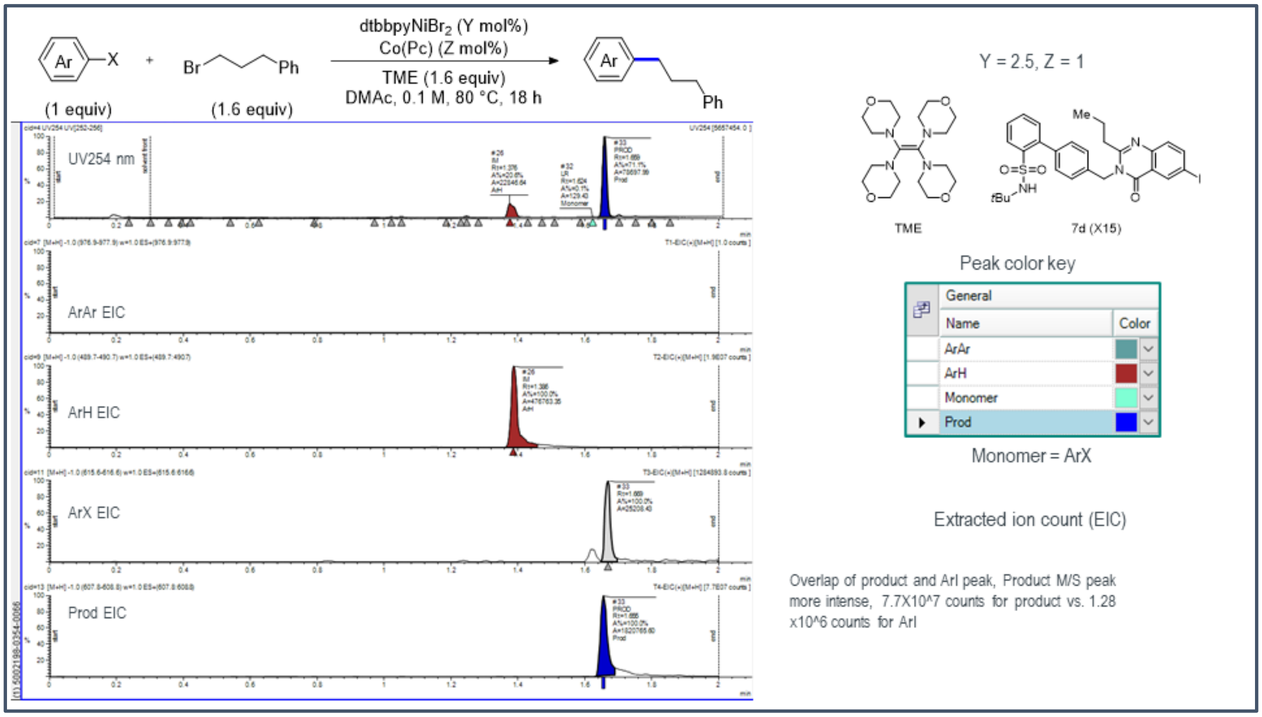
Y = 5, Z = 0.5

Peak color key

General	
Name	Color
ArAr	■
ArH	🟥
Monomer	🟩
Prod	🟦

Monomer = ArX

Extracted ion count (EIC)



Y = 2.5, Z = 1

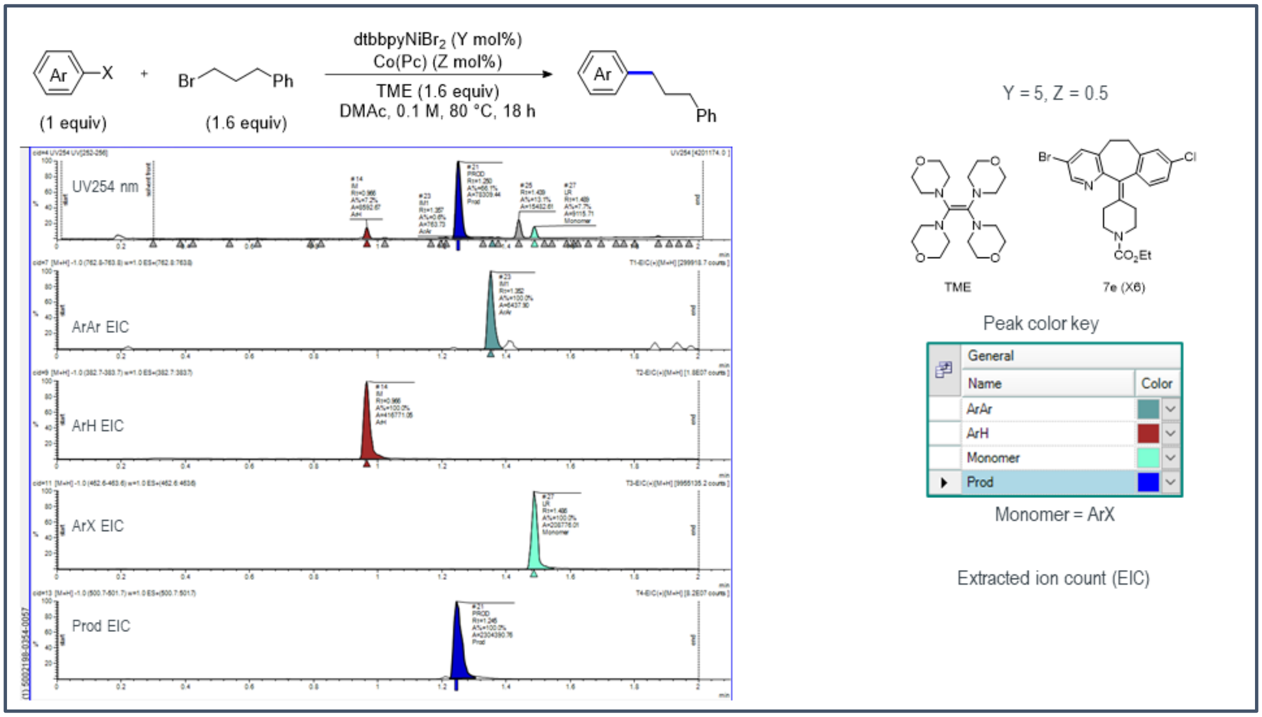
Peak color key

General	
Name	Color
ArAr	■
ArH	🟥
Monomer	🟩
Prod	🟦

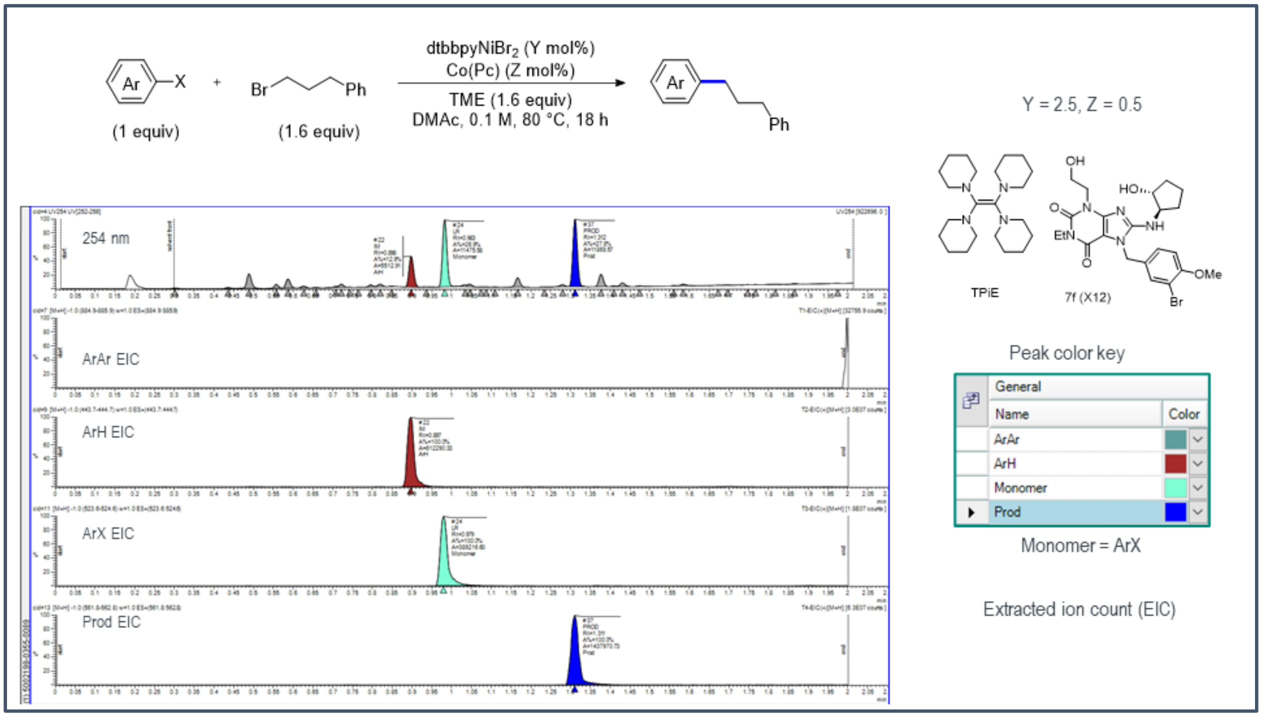
Monomer = ArX

Extracted ion count (EIC)

Overlap of product and ArI peak, Product M/S peak more intense, 7.7X10^7 counts for product vs. 1.28 x10^6 counts for ArI



General	
Name	Color
ArAr	🟦
ArH	🟥
Monomer	🟩
Prod	🟦



General	
Name	Color
ArAr	🟦
ArH	🟥
Monomer	🟩
Prod	🟦

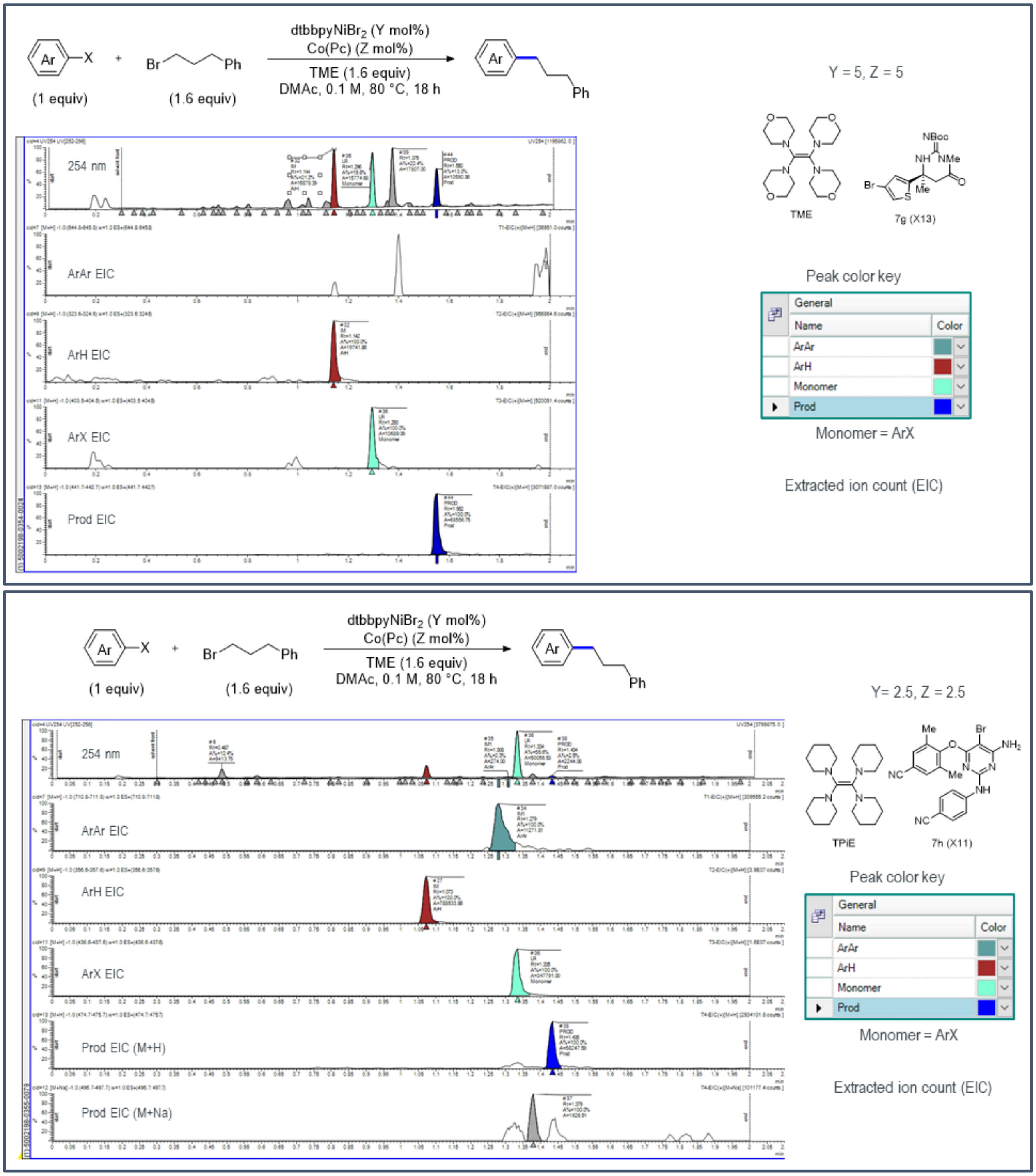


Figure S6. Representative examples of raw data from high throughput optimization experiments.

SIX. Procedure for ^{1}H NMR Yields of Cross-Electrophile Coupling of Drug-Like Aryl Halides and Alkyl Halides

Procedure:

See section SVII for representative experimental setup and workup, but the reactions were performed on a 0.03 mmol scale of the aryl electrophile with 0.048 mmol (1.6 equiv.) of the alkyl electrophile at 0.1 M concentration for 18 hours (other reagents scaled linearly). The silica plug was washed with 10 mL EtOAc instead of 5 mL during workup. For individual reactions with TPiE and TME, see Figure 7 in the manuscript. See Figure S7 below for reactions with TDAE. *Note: The conditions for TDAE were not optimized using HTE. Instead, for each substrate, the optimized conditions for TPiE or TME that required higher catalyst loadings were used with TDAE. The results are broadly comparable with the only exception being **7b** where TDAE gave a significantly lower yield. Further optimization was not attempted.* The ^{1}H NMR spectra of the compounds matched those previously reported.[8]

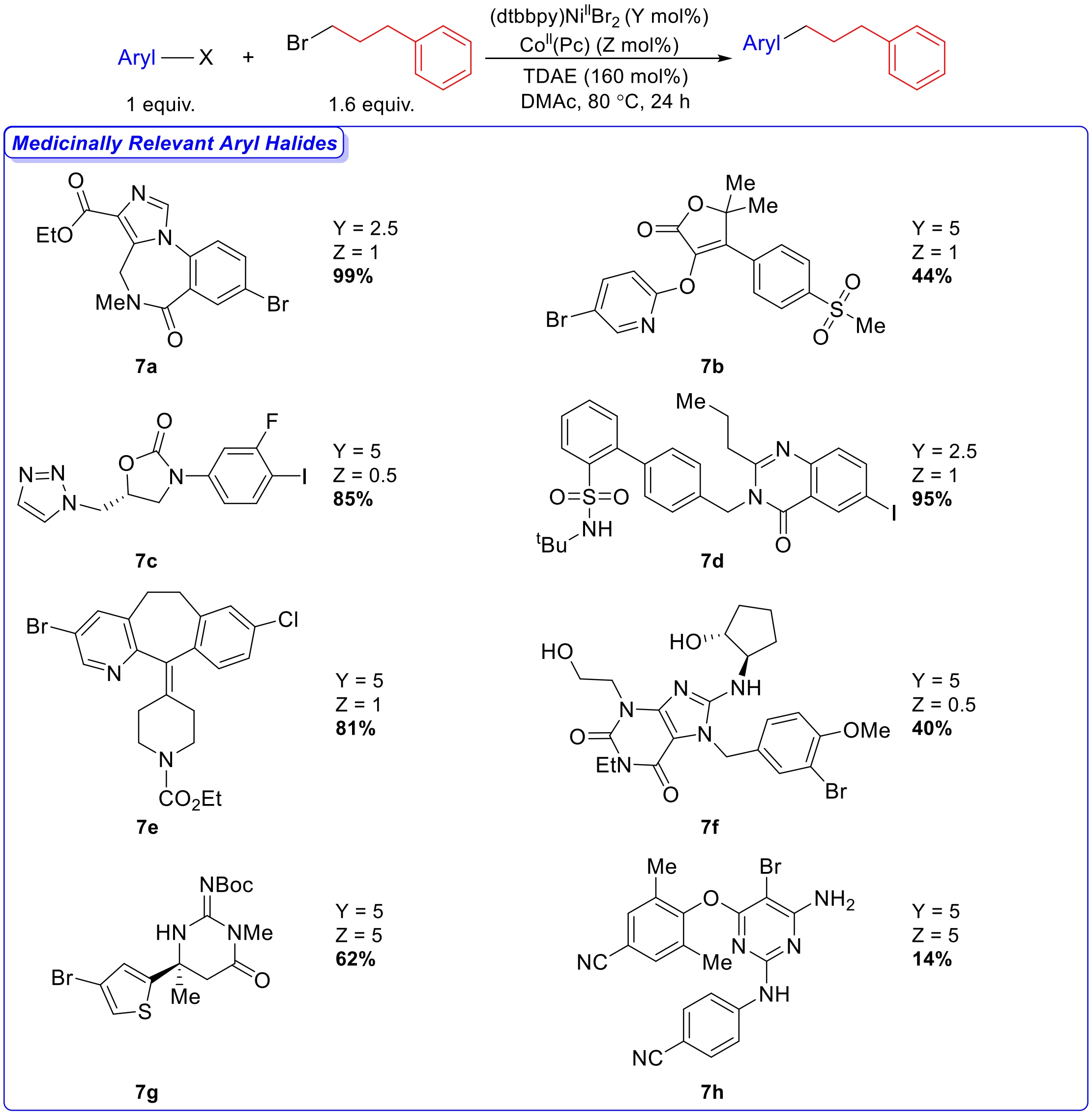


Figure S7. ^{1}H NMR yields of products from cross-electrophile coupling of drug-like aryl halides with 1-bromo-3-phenylpropane using TDAE as the reductant.

SX. Reductant Screen for Intermolecular Three-Component Dicarbofunctionalization of Alkenes

To further establish that our reductants can be used as direct and more practical replacements for TDAE, we looked at another example of a CEC reaction that uses TDAE as the electron source. The intermolecular three-component dicarbofunctionalization of alkenes[9] reported by Nevado and co-workers is an efficient pathway to construct complex molecules through the simultaneous formation of two vicinal C–C bonds by coupling alkenes with alkyl and aryl iodides (Figure S8). Using the representative procedure described below, we demonstrated that TPyE gives comparable performance to TDAE for this reaction, under essentially the optimized conditions for TDAE (Table S2). The only change was the use of a higher temperature, 60 °C, to promote solubility. TPiE and TAzE also give significant yields of product, but only a small amount of product was observed with TME. It is likely that with further optimization, higher yields could be achieved with our reductants, but overall, this result reinforces that our reductants can be used as practical replacements for TDAE with, in some cases, essentially no optimization.

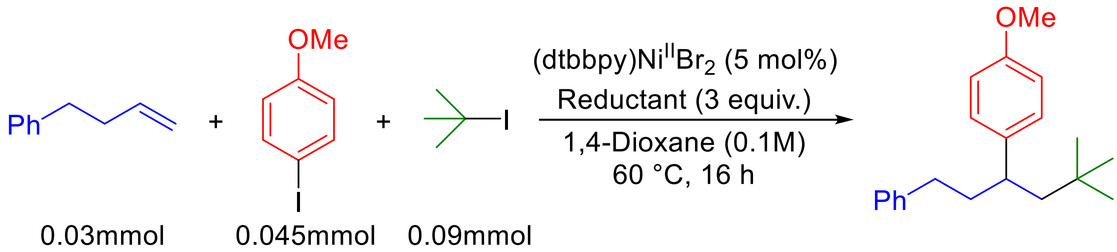


Figure S8. Intermolecular three-component dicarbofunctionalization of 4-phenyl-1-butene, 4-iodoanisole, and tert-butyl iodide.

Table S2. NMR yields of intermolecular three-component dicarbofunctionalization between 4-iodoanisole, 4-phenyl-1-butene, and tert-butyl iodide with the new reductants.

Reductant	E^o (V vs. Fc/Fc$^+$)	Product Yield (%)
TME	-0.85	9
TPiE	-1.06	31
TAzE	-1.09	25
TDAE	-1.11	62
TPyE	-1.32	51

Representative Procedure:

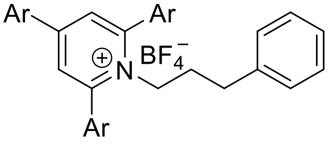
The procedure was adapted from a literature report.[9b] In a glovebox under an N_2 atmosphere, 4-iodoanisole (10.5 mg, 0.045 mmol) and the reductant (0.09 mmol) were added to a 1 dram vial charged with a magnetic stir bar. A separate 2 dram vial was charged with (dtbbpy)$Ni^{II}Br_2$ (3 mg, 0.006 mmol), 4-phenyl-1-butene (18 μL, 0.12 mmol), tert-butyl iodide (43 μL, 0.36 mmol), and 1,4-dioxane (1.2 mL) to make a stock solution in a glovebox under an N_2 atmosphere. 0.31 mL of the stock solution was added to the vial containing 4-iodoanisole and the reductant to initiate catalysis. The reaction was capped tightly with a PTFE seal cap and stirred at 60 °C for 16 hours. The reaction was opened to air and passed through a short plug of silica, which was washed with 5 mL EtOAc. The volatiles were removed, and the crude reaction mixture was dissolved in a solution of $CDCl_3$ containing a known amount of hexamethylbenzene. Product yields were determined by integration of select peaks in the ^1H NMR spectrum against the hexamethylbenzene external standard.

SXI. Synthesis of Katritzky Salts

General Procedure B:

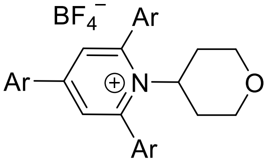
The procedure was adapted from a literature report.[11] To a 6 dram vial equipped with a magnetic stir bar was added the pyrylium cation (1 equiv.) and activated 3Å molecular sieves (0.5g per mmol of pyrylium cation) in a glovebox under an N_2 atmosphere. The vial was capped tightly with a PTFE seal cap and brought out of the glovebox. A vent needle was added to the vial, and dry, degassed DCM (0.5 M), NEt_3 (not dried or degassed) (2 equiv.), and amine (not dried or degassed) (1.2 equiv.) were added via syringes in that order. The vent needle was removed, and the reaction was allowed to stir for 20 min at room temperature. A vent needle was reinserted, then glacial acetic acid (2 equiv.) and a second portion of dry, degassed DCM (0.25 M) were added to the reaction via syringes in that order. The vent needle was removed, and the reaction was allowed to stir overnight at room temperature. The reaction was opened to air and filtered through a short pad of celite, and the vial and celite were rinsed with a small portion of DCM. The filtrate was collected and washed with 1 M HCl (4 x 8 mL per mmol of pyrylium cation), sat. $NaHCO_3$ (4 x 8 mL per mmol of pyrylium cation), and brine (1 x 8 mL per mmol of pyrylium cation). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting solid was triturated in EtOH for 20 min, filtered, triturated in EtOAc for 20 min, filtered, triturated again in diethyl ether for 20 min, and filtered. The resulting solid was dried *in vacuo* overnight. If no precipitate is formed upon trituration in EtOH, the crude product was purified by silica gel column chromatography using acetone:DCM solvent mixtures. *Note*: *The Katritzky salt product is mildly soluble in both EtOH and EtOAc, so it is important to use minimal amount of solvent during trituration to avoid loss of product during filtration.* In cases where a significant amount of product remained dissolved, the filtrate was recovered and concentrated *in vacuo*, and the resulting solid was triturated in the same order as described above with less amount of solvent.

SXII. Characterization of Katritzky Salts



Ar = 4-MeOC$_6$H$_4$

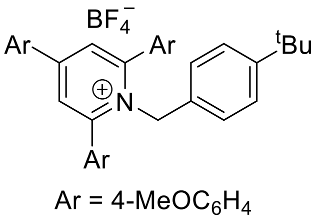
2,4,6-tris(4-methoxyphenyl)-1-(3-phenylpropyl)pyridin-1-ium tetrafluoroborate (1): The procedure was adapted from a literature report.[10] To a 2 dram vial equipped with a magnetic stir bar in a glove box under an N_2 atmosphere was added ethanol (1.25 mL, 1.0 M), 2,4,6-tris(trimethoxyphenyl)pyrylium tetrafluoroborate (500 mg, 1.0 mmol) and 3-phenyl-1-propylamine (0.18 mL, 1.2 mmol). The reaction was capped tightly with a PTFE seal cap, removed from the glove box, and heated at 80 °C with stirring for 4 hours. The reaction was allowed to cool to room temperature, and volatiles were removed in vacuo. The crude substrate was purified by silica gel column chromatography using 15:85 acetone:DCM solvent mixtures. Pale yellow solid, 0.520 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 4H), 7.62 (d, J = 8.73 Hz, 4H), 7.07 (m, 3H), 7.01 (m, 6H), 6.68 (m, 2H), 4.45 (m, 2H), 3.88 (s, 6H), 3.85 (s, 3H), 2.13. (t, J = 6.97 Hz, 2H), 1.68 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.27, 161.53, 156.53, 154.60, 139.03, 130.66, 129.92, 128.54, 128.01, 126.24, 125.88, 125.32, 125.01, 115.37, 114.85, 55.77, 55.62, 53.95, 32.40, 30.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -153.21 (minor, ^{10}BF4), -153.26 (major, ^{11}BF4). (HRMS) TOF MS ES$^+$ (m/z) [M]$^+$ calculated for $[C_{35}H_{34}NO_3]^+$ 516.2533; found 516.2537.



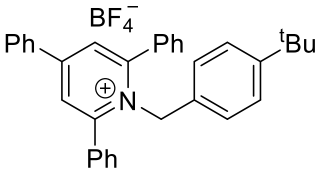
Ar = 4-MeOC$_6$H$_4$

2,4,6-tris(4-methoxyphenyl)-1-(tetrahydro-2H-pyran-4-yl)pyridin-1-ium tetrafluoroborate (2): Synthesized according to general procedure B on a 1.4 mmol scale of 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate. Pale yellow solid, 0.630 g (76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (m, 4H), 7.67 (d, J = 8.73 Hz, 4H), 7.09 (d, J = 8.75 Hz, 4H), 6.99 (d, J = 8.95 Hz, 2H), 4.88 (tt, J = 12.26, 3.10 Hz, 1H), 3.91 (s, 6H), 3.86 (s, 3H), 3.76 (dd, J = 11.54, 3.76 Hz, 2H), 2.89 (t, J = 11.36 Hz, 2H), 2.05 (qd, J = 12.07, 3.94 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ

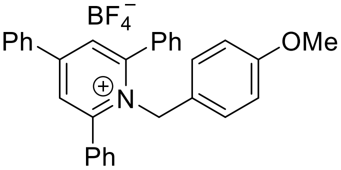
163.36, 161.62, 157.48, 154.22, 131.15, 130.15, 127.09, 126.16, 125.84, 115.36, 114.53, 68.83, 68.05, 55.77, 55.70, 34.14. ^{19}F (376 MHz, $CDCl_3$) δ -153.16 (minor, ^{10}BF4), -153.22 (major, ^{11}BF4). (HRMS) TOF MS ES$^+$ (m/z) [M]$^+$ calculated for $[C_{31}H_{32}NO_4]^+$ 482.2326; found 482.2314.



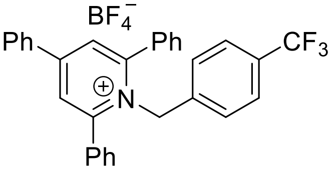
1-(4-(tert-butyl)benzyl)-2,4,6-tris(4-methoxyphenyl)pyridin-1-ium tetrafluoroborate (3): Synthesized according to general procedure B on a 1.6 mmol scale of 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate. White solid, 0.590 g (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 4H), 7.61 (d, J = 7.67 Hz, 4H), 7.05 (m, 4H), 6.96 (d, J = 8.92 Hz, 4H), 6.33 (d, J = 8.34 Hz, 2H), 5.77 (s, 2H), 3.87 (s, 3H), 3.83 (s, 6H), 1.20 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.46, 161.58, 157.64, 154.73, 151.46, 131.75, 131.69, 129.96, 126.32, 125.68, 125.64, 125.54, 124.81, 115.54, 114.70, 58.27, 55.81, 55.65, 34.61, 31.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ -152.94 (minor, ^{10}BF4), -153.00 (major, ^{11}BF4). (HRMS) TOF MS ES$^+$ (m/z) [M]$^+$ calculated for $[C_{37}H_{38}NO_3]^+$ 542.2846; found 542.2836.



1-(4-(tert-butyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (4): Synthesized according to modified general procedure B. A 250 mL Schlenk flask was removed from an oven at 130 °C and was charged with 2,4,6-triphenylpyrylium tetrafluoroborate (5.1 g, 12.6 mmol), 3Å molecular sieves (6.4 g), and a magnetic stir bar. The content of the Schlenk flask was dried *in vacuo* for 30 min and was put under a positive pressure of N_2 using standard Schlenk line techniques. The Schlenk flask was fitted with a rubber septum, and dry, degassed DCM (25 mL, 0.5 M), NEt_3 (not dried or degassed) (3.6 mL), and 4-tert-butylbenzylamine (not dried or degassed) (2.6 mL) were added via syringes in that order. The reaction was stirred at room temperature for 20 min. Glacial acetic acid (1.5 mL) and a second portion of dry, degassed DCM (25 mL, 0.25 M) were added to the reaction via syringes in that order. Under a positive pressure of N_2, the rubber septum was then replaced with a glass stopper, and the reaction was allowed to stir overnight at room temperature. See general procedure B for workup. White solid, 4.320 g (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.80 (d, J = 8.00 Hz, 2H), 7.63 (d, J = 7.29 Hz, 4H), 7.58-7.43 (m, 9H), 7.09 (d, J = 8.38 Hz, 2H), 6.36 (d, J = 8.29 Hz, 2H), 5.74 (s, 2H), 1.22 (s, 9H). The ^{1}H NMR data are consistent with a previous literature report.[12]



1-(4-methoxybenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (5): Synthesized according to general procedure B on a 2.5 mmol scale of 2,4,6-triphenylpyrylium tetrafluoroborate. White solid, 0.650 g (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.80 (d, J = 6.91 Hz, 2H), 7.66 (d, J = 6.95 Hz, 4H), 7.58-7.46 (m, 9H), 6.60 (d, J = 8.39 Hz, 2H), 6.35 (d, J= 8.32 Hz, 2H), 5.71 (s, 2H), 3.71 (s, 3H). The ^{1}H NMR data are consistent with a previous literature report.[13]



2,4,6-triphenyl-1-(4-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate (6): Synthesized according to general procedure B on a 2.5 mmol scale of 2,4,6-triphenylpyrylium tetrafluoroborate. No precipitate formed upon trituration in EtOH, and the crude product was purified by silica gel column chromatography using 5:95 acetone:DCM solvent mixtures. The product was triturated in 5 mL diethyl ether overnight after the column, filtered, and dried *in vacuo*. White solid, 0.850 g (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.82 (d, J = 8.21 Hz, 2H), 7.65 (d, J = 7.39 Hz, 4H), 7.60-7.45 (m, 9H), 7.37 (d, J = 8.01 Hz, 2H), 6.63 (d, J = 8.00 Hz, 2H), 5.85 (s, 2H). The ^{1}H NMR data are consistent with a previous literature report.[14]

SXIII. Optimization of Cross-Electrophile Coupling of Aryl Halides and Katritzky Salts

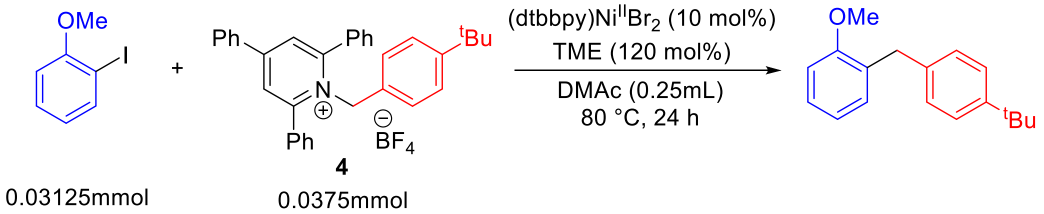


Figure S9. Cross-electrophile coupling of 2-iodoanisole and **4**.

Representative Procedure:

In a glovebox under an N_2 atmosphere, **4** (20.3 mg, 0.0375 mmol) and TME (13.8 mg, 0.0375 mmol) were added to a 1 dram vial charged with a magnetic stir bar. A separate 2 dram vial was charged with (dtbbpy)$Ni^{II}Br_2$ (6.0 mg, 0.0125 mmol), DMAc (1 mL), and 2-iodoanisole (16 μL, 0.125 mmol) to create a stock solution in a glovebox under an N_2 atmosphere. 0.26 mL of the stock solution was added to the vial containing **4** and TME to initiate catalysis. The reaction was capped tightly with a PTFE seal cap and stirred at 80 °C for 24 hours. The reaction was opened to air and passed through a short plug of silica, which was washed with 5 mL EtOAc. The volatiles were removed, and the crude reaction mixture was dissolved in a solution of $CDCl_3$ containing a known amount of hexamethylbenzene. Product yields were determined by integration of select peaks in the ^1H NMR spectrum against the hexamethylbenzene external standard.

Table S3. Yields of optimization studies for cross-electrophile coupling of 2-iodoanisole and **4**.

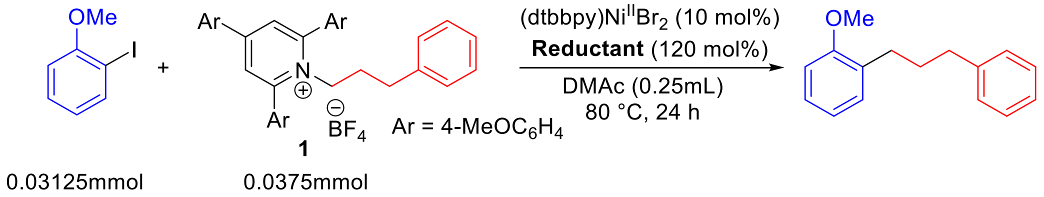
Entry	Deviation from standard conditions	Yield (%)
1	**None**	**90**
2	5 mol% catalyst loading	43
3	2.5 mol% catalyst loading	29
4	DMI	73
5	DMF	5
6	1,4-Dioxane	0
7	No Ni catalyst	0
8	No reductant	0

SXIV. Reductant Screen for Cross-Electrophile Coupling of 2-Iodoanisole and Katritzky Salts 1, 3, and 4

Procedure:

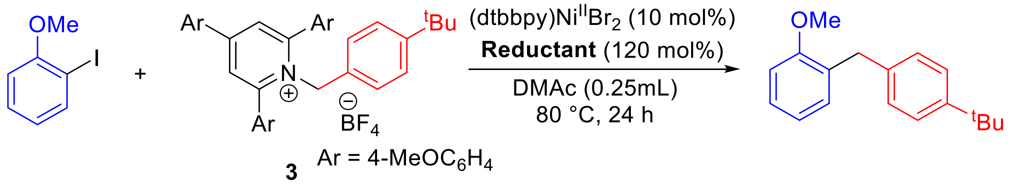
See Section SXIII for representative experimental procedure. *Note:* The product yields for the coupling between 2-iodoanisole and **2** were also determined by ^{1}H NMR spectroscopy. However, only the product could be reliably traced due to the complexity of the spectra, and thus a detailed product profile was not available. See Table 3 in the manuscript for the product yields of the reaction between 2-iodoanisole and **2**.

Table S4. Cross-electrophile coupling of 2-iodoanisole and **1**.



Reductant	E° (V vs Fc/Fc$^+$)	Product Yield (%)	ArI (%)	Biaryl (%)	1 (%)	Bialkyl (%)
TPyE	-1.32	77	<1	<1	<1	6
TDAE	-1.11	10	11	30	70	<1
TAzE	-1.09	<1	5	15	80	<1
TPiE	-1.06	<1	8	13	79	<1
TME	-0.85	<1	38	10	110	<1

Table S5. Cross-electrophile coupling of 2-iodoanisole and **3**.

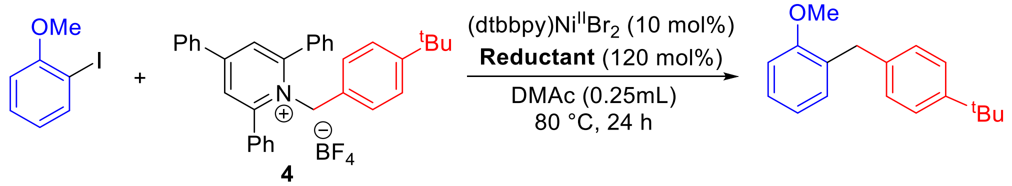


0.03125mmol 0.0375mmol

Reductant	E° (V vs Fc/Fc$^+$)	Product Yield (%)	ArI (%)	Biaryl (%)	3 (%)	Bialkyl (%)
TPyE	-1.32	57	<1	20	0	14
TDAE	-1.11	99	0	0	0	16
TAzE	-1.09	93	4	0	0	6
TPiE	-1.06	99	0	0	0	3
TME	-0.85	75	0	10	11	3
TME[a]	-0.85	93	0	2	<1	0

[a] 5 mol% (dtbbpy)Ni^{II}Br$_2$ is used.

Table S6. Cross-electrophile coupling of 2-iodoanisole and **4**.



4

0.03125mmol

0.0375mmol

Reductant	E° (V vs Fc/Fc$^+$)	Product Yield (%)	ArI (%)	Biaryl (%)	4 (%)	Bialkyl (%)
TPyE	-1.32	25	12	31	0	25
TDAE	-1.11	29	<1	36	0	29
TAzE	-1.09	29	22	15	0	34
TPiE	-1.06	30	<1	22	0	27
TME[a]	-0.85	90	6	<1	0	10

SXV. ^{1}H NMR Yields of Products from Cross-Electrophile Coupling of Aryl Bromides and Katritzky Salt 4

Procedure:

See section SXIII for representative experimental procedure. See Figure S10 below for individual reaction conditions.

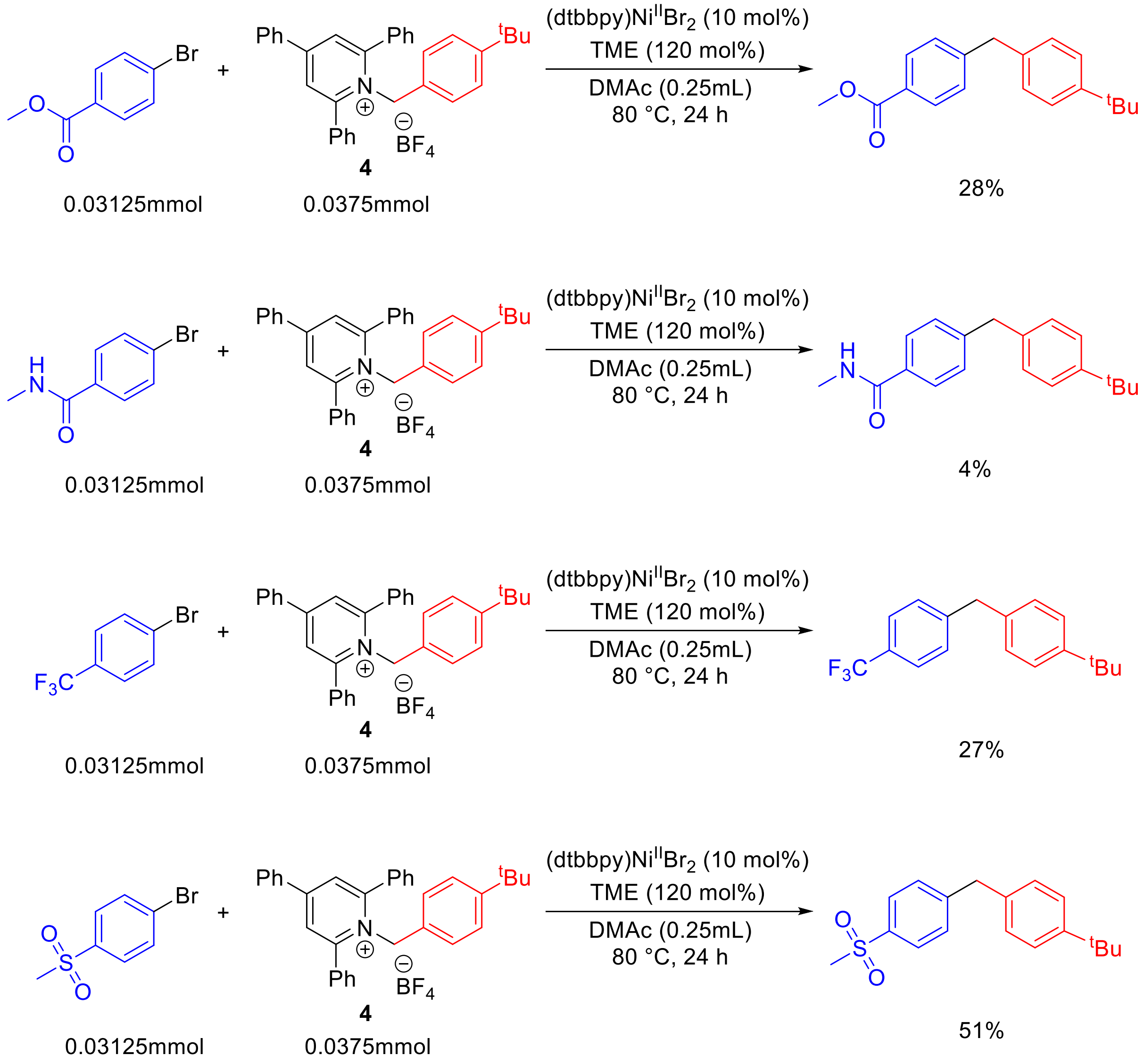


Figure S10. Cross-electrophile coupling of aryl bromides and **4**.

SXVI. ^{1}H NMR Yields of Products from Cross-Electrophile Coupling of Additional Aryl Iodide Substrates and Katritzky Salt 4

Procedure:

See section SXIII for representative experimental procedure. See Figure S11 below for individual reaction conditions.

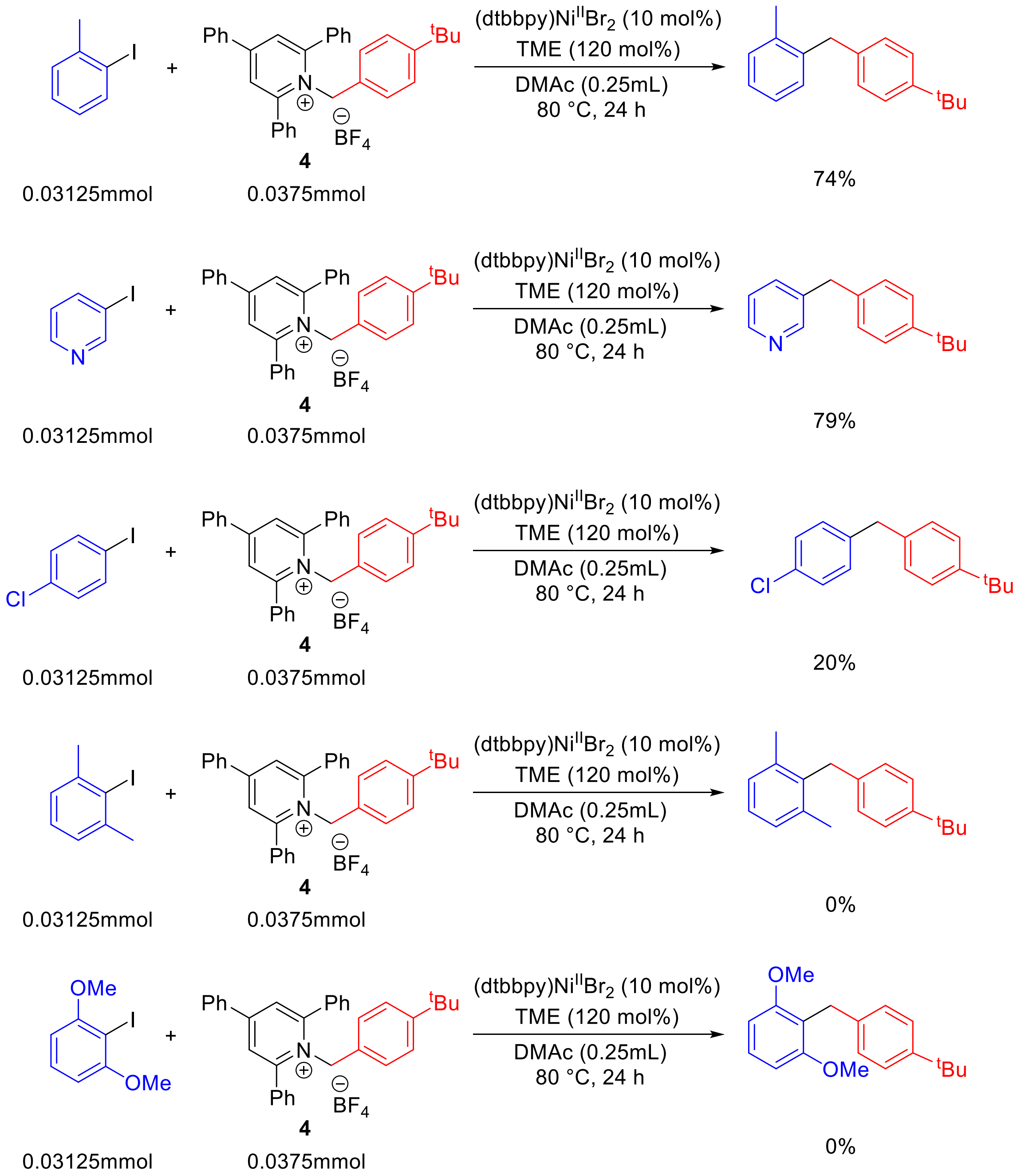
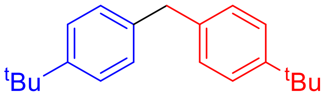


Figure S11. Cross-electrophile coupling of additional aryl iodides and **4**.

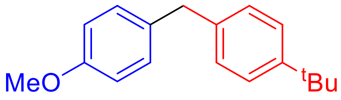
SXVII. Isolation Procedure and Characterization for Products of Cross-Electrophile Coupling of Aryl Halides and Katritzky Salts

Procedure for Isolation Scale Reactions of Following Substrates:

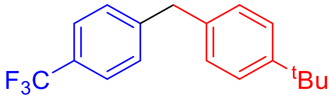
See section SXIII for experimental setup. Reactions were performed on a 0.125 mmol scale of aryl electrophile (other reagents scaled linearly), and all the reagents were added directly to the reaction vial without introducing a stock soulution. See Figure 9 in the manuscript for individual reaction conditions. The reaction vial was removed from heat, allowed to cool to room temperature, and diluted with 0.5 mL EtOAc. The mixture was passed through a short silica plug (~1.5 inches) in a glass pipette, which was rinsed with 8 mL EtOAc. The filtrate was concentrated to dryness, and the crude residue was purified by silica gel column chromatography.



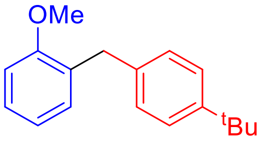
9a, bis-(4-(tert-butyl)phenyl)methane: Eluent: 1:9 toluene:hexanes. White solid, 74% yield (24.9 mg). Isolated product contains ~2% bialkyl which could not be separated. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J*=8.1 Hz, 4H), 7.14 (d, *J*=7.9 Hz, 4H), 3.93 (s, 2H), 1.31 (s, 18H). The ^{1}H NMR data are consistent with a previous literature report.[15]



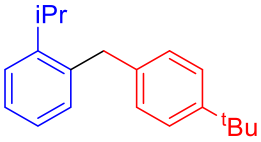
9b, 1-(tert-butyl)-4-(4-methoxybenzyl)benzene: Eluent: 1:4 toluene:hexanes. Colorless oil, 62% yield (15.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J*=8.3 Hz, 2H), 7.13-7.10 (m, 4H), 6.83 (d, *J*=8.6 Hz, 2H), 3.90 (s, 2H), 3.78 (s, 3H), 1.30 (s, 9H). The ^{1}H NMR data are consistent with a previous literature report.[16]



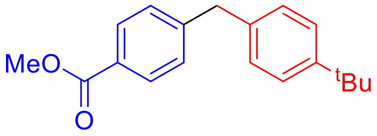
9c, 1-(tert-butyl)-4-(4-trifluoromethyl)benzyl)benzene: Eluent: 10% toluene in hexanes. Colorless oil, 88% yield (30.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J*=8.0 Hz, 2H), 7.34-7.30 (m, 4H), 7.11 (d, *J*=8.5 Hz, 2H), 4.00 (s, 2H), 1.33 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.46, 145.54, 137.08, 129.35, 128.67, 128.53 (quartet, J= 31.8 Hz), 125.69, 125.50 (quartet, J= 3.8 Hz), 124.77 (quartet, J= 271.7 Hz), 41.36, 34.55, 31.50. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.35. (LRMS) GCMS EI (*m/z*) $[M]^+$ calculated for $[C_{18}H_{19}F_3]^+$ 292.1; found 292.2.



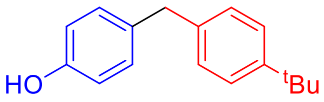
9d, 1-(4-tert-butyl)benzyl)-2-methoxybenzene: Eluent: 1% EtOAc in 1:9 toluene:hexanes. White solid, 89% yield (22.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J*=7.9 Hz, 2H), 7.19 (t, *J*=7.8 Hz, 1H), 7.15 (d, *J*=7.9 Hz, 2H), 7.08 (d, *J*=7.5 Hz, 1H), 6.89-6.86 (m, 2H), 3.95 (s, 2H), 3.83 (s, 3H), 1.30 (s, 9H). The ^{1}H NMR data are consistent with a previous literature report.[17]



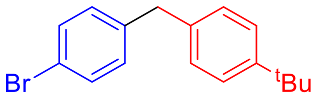
9e, 1-(4-(tert-butyl)benzyl)-2-isopropylbenzene: Eluent: 1:5 toluene:hexanes (first column) then 0-5% toluene in hexanes (second column). Colorless oil, 65% yield (17.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 3H), 7.26-7.23 (m, 1H), 7.16-7.11 (m, 2H), 7.05 (d, *J*=8.5 Hz, 2H), 4.04 (s, 2H), 3.17 (septet, *J*=6.9 Hz, 1H), 1.31 (s, 9H), 1.16 (d, *J*=6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 148.78, 147.27, 138.23, 137.58, 130.62, 128.36, 126.90, 125.80, 125.54, 125.35, 38.28, 34.48, 31.54, 29.06, 23.90. (LRMS) GCMS EI (*m/z*) $[M]^+$ calculated for $[C_{20}H_{26}]^+$ 266.2; 266.3.



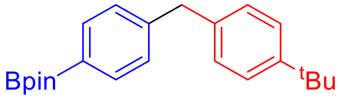
9f, methyl 4-(4-(tert-butyl)benzyl)benzoate: Eluent: 100% toluene. Colorless oil, 94% yield (26.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J*=8.2 Hz, 2H), 7.32 (d, *J*=8.3 Hz, 2H), 7.27 (d, *J*=8.0 Hz, 2H) 7.10 (d, *J*=8.2 Hz, 2H), 4.00 (s, 2H), 3.90 (s, 3H), 1.30 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 167.09, 149.18, 146.70, 137.06, 129.78, 128.96, 128.51, 127.97, 125.48, 52.00, 41.39, 34.38, 31.35. (LRMS) GCMS EI (*m/z*) $[M]^+$ calculated for $[C_{19}H_{22}O_2]^+$ 282.2; found 282.2.



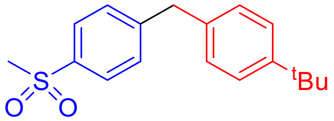
9g, 4-(4-(tert-butyl)benzyl)phenol: Eluent: 25% EtOAc in hexanes (first column) then 100% DCM (second column). White solid, 60% yield (17.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J*=8.3 Hz, 2H), 7.12-7.06 (m, 4H), 6.76 (d, *J*=8.6 Hz, 2H), 4.60 (br s, 1H), 3.89 (s, 2H), 1.31 (s, 9H). The ^{1}H NMR data are consistent with a previous literature report.[18]



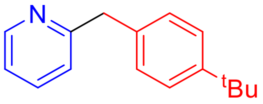
9h, 1-bromo-4-(4-(tert-butyl)benzyl)benzene: Eluent: 15:85 toluene:hexanes. White solid, 81% yield (30.7 mg). Isolated product contains ~2% bialkyl which could not be separated. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (d, *J*=8.3 Hz, 2H), 7.32 (d, *J*=8.2 Hz, 2H), 7.11-7.07 (m, 4H), 3.91 (s, 2H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ 149.25, 140.41, 137.54, 131.61, 130.83, 128.57, 125.60, 119.98, 40.92, 37.54, 34.52, 31.51. (LRMS) GCMS EI (*m/z*) [M]$^+$ calculated for [C$_{17}$H$_{19}$Br]$^+$ 302.1; 302.1.



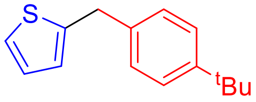
9i, 2-(4-(4-(tert-butyl)benzyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: Eluent: 100% toluene. White solid, 72% yield (31.4 mg). ^{1}H NMR (400 MHz, CDCl^3) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.96 (s, 2H), 1.33 (s, 12H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ 148.83, 144.57, 137.83, 134.97, 128.44, 125.32, 83.63, 41.62, 34.33, 31.36, 30.92, 24.82. (LRMS) GCMS EI (*m/z*) [M]$^+$ calculated for [C$_{23}$H$_{31}$BO$_2$]$^+$ 350.2; found 350.3.



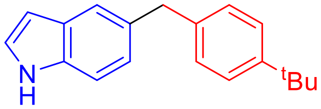
9j, 1-(tert-butyl)-4-(4-methylsulfonyl)benzyl)benzene: Eluent: gradient of 20-30% EtOAc in hexanes. White solid, 89% yield (32.3 mg). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J= 6.7 Hz, 2H), 7.39 (d, J= 8.2 Hz, 2H), 7.31 (d, J= 6.8 Hz, 2H), 7.10 (d, J= 8.2 Hz, 2H), 4.03 (s, 2H), 3.03 (s, 3H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ 149.69, 148.05, 138.36, 136.50, 129.96, 128.70, 127.73, 125.79, 44.73, 41.44, 34.57, 31.48. (LRMS) GCMS EI (*m/z*) [M]$^+$ calculated for [C$_{18}$H$_{22}$O$_2$S]$^+$ 302.1; 302.2.



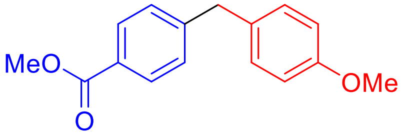
9k, 2-(4-tert-butyl)benzyl)pyridine: Eluent: gradient of 10-20% EtOAc in hexanes. Pale yellow oil, 71% yield (19.2 mg). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 (d, *J*=4.8 Hz, 1H), 7.59 (t, *J*=7.7 Hz, 1H), 7.33 (d, *J*=7.9 Hz, 2H), 7.20 (d, *J*=7.9 Hz, 2H), 7.14-7.10 (m, 2H), 4.14 (s, 2H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ 160.78, 149.53, 148.20, 137.81, 135.85, 128.90, 125.74, 123.79, 121.69, 43.55, 34.54, 31.48. (LRMS) GCMS EI (*m/z*) [M]$^+$ calculated for [C$_{16}$H$_{19}$N]$^+$ 225.2; found 225.2.



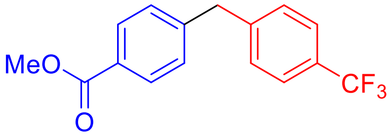
9l, 2-(4-tert-butyl)benzyl)thiophene: Eluent: gradient of 1-10% toluene in hexanes. Colorless oil, 52% yield (14.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J*=6.7 Hz, 2H), 7.19 (d, *J*=8.2 Hz, 2H), 7.15 (d, *J*=5.2 Hz, 1H), 6.94-6.92 (m, 1H), 6.82 (m, 1H), 4.13 (s, 2H), 1.31 (s, 9H). The ^{1}H NMR data are consistent with a previous literature report.[19]



9m, 5-(4-(tert-butyl)benzyl)-1*H*-indole: Eluent: gradient of 10-20% EtOAc in hexanes. Pale yellow oil, 50% yield (15.8 mg). *Note: The product slowly decomposes in air and should be stored under inert atmosphere in the dark.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (br s, 1H), 7.49 (s 1H), 7.31 (m, 3H), 7.19-7.17 (m, 3H), 7.07 (d, *J*=6.6 Hz, 1H), 6.50 (m, 1H), 4.07 (s, 2H), 1.31 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 148.64, 139.42, 134.54, 132.81, 128.58, 128.21, 125.41, 124.45, 123.67, 120.72, 111.05, 102.53, 41.64, 34.47, 31.55. (LRMS) GCMS EI (*m/z*) $[M]^+$ calculated for $[C_{19}H_{21}N]^+$ 263.2; found 263.2.



9n, methyl 4-(4-methoxybenzyl)benzoate: Eluent: gradient of 10-20% EtOAc in hexanes. Colorless oil, 84% yield (27.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J*=8.3 Hz, 2H), 7.24 (d, *J*=8.0 Hz, 2H), 7.09 (d, *J*=8.2 Hz, 2H), 6.84 (d, *J*=8.6 Hz, 2H), 3.97 (s, 2H), 3.89 (s, 3H), 3.79 (s, 3H). The ^{1}H NMR data are consistent with a previous literature report.[20]



9o, methyl 4-(4-(trifluoromethyl)benzyl)benzoate: Eluent: 1:1 toluene:hexanes. Pale yellow oil, 82% yield (31.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J*=8.3 Hz, 2H), 7.55 (d, *J*=8.0 Hz, 2H), 7.29-7.23 (m, 4H), 4.08 (s, 2H), 3.90 (s, 3H). The ^{1}H NMR data are consistent with a previous literature report.[16]

SXVIII. Procedure for 1 mmol Scale Reaction to Form Product 9f

Procedure:

A 100 mL Schlenk flask was removed from an oven at 130 °C and was immediately transferred into a glovebox under an N_2 atmosphere. The Schlenk flask was allowed to cool to room temperature and was charged with methyl 4-iodobenzoate (270 mg, 1 mmol), **4** (653 mg, 1.2 mmol), (dtbbpy)$Ni^{II}Br_2$ (48 mg, 0.1 mmol), TME (440 mg, 1.2 mmol), DMAc (8 mL) and a magnetic stir bar. The flask was sealed, quickly removed from the glovebox, and placed in an oil bath. The reaction was stirred at 80°C for 24 hours. After 24 hours, the reaction was allowed to cool to room temperature, and the reaction mixture was filtered through a short pad of celite. The flask and celite were rinsed with 15 mL of EtOAc. The filtrate was concentrated *in vacuo*, and the crude product was purified by silica gel column chromatography using 100% toluene as eluent. Product **9f** was obtained in an 85% yield (247 mg).

^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J*=8.3 Hz, 2H), 7.32 (d, *J*=8.3 Hz, 2H), 7.27 (d, *J*=7.9 Hz, 2H) 7.10 (d, *J*=8.6 Hz, 2H), 4.00 (s, 2H), 3.90 (s, 3H), 1.30 (s, 9H). The ^1H NMR data are consistent with the results collected on a smaller scale (see Section SXVII, product **9f**).

SXIX. NMR Spectra of Isolated Compounds

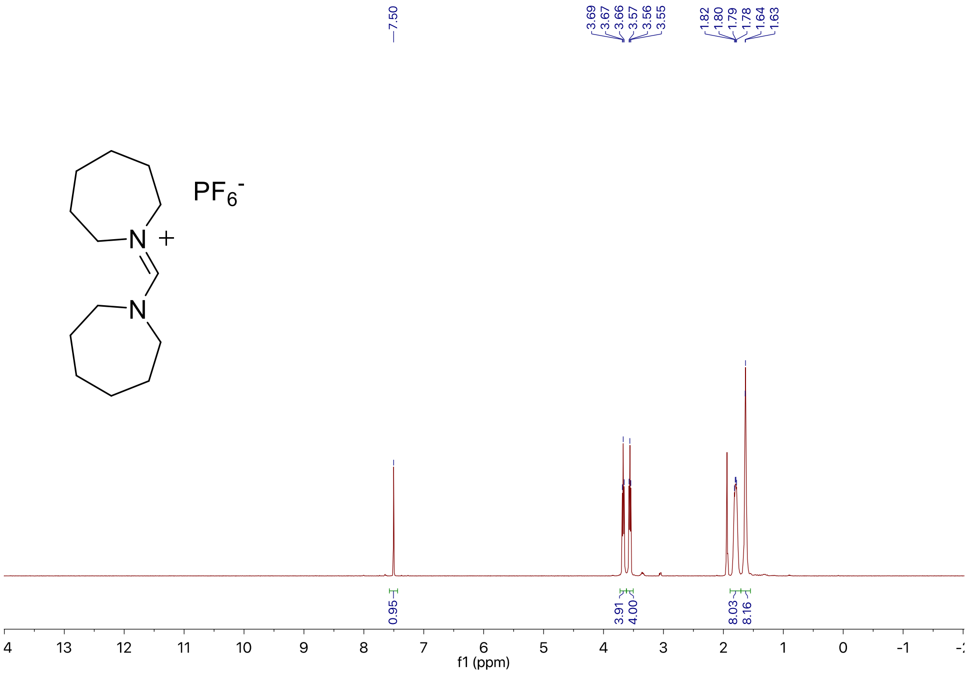


Figure S12. ^{1}H NMR spectrum (400 MHz, CD_3CN) of **2c-Az**.

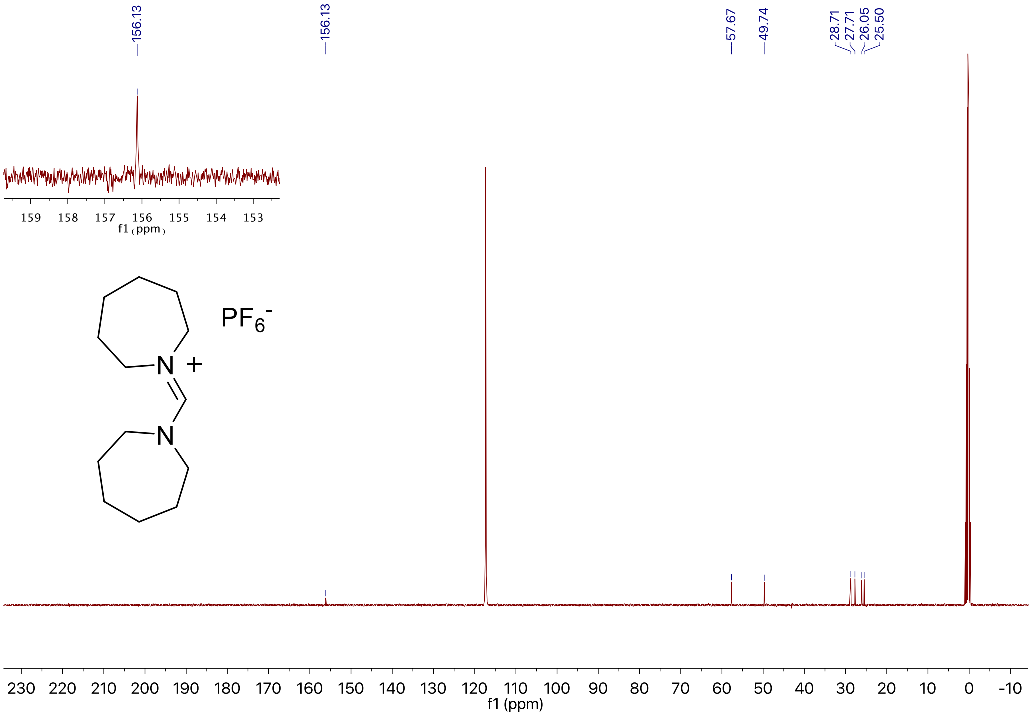


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_3CN) of **2c-Az**.

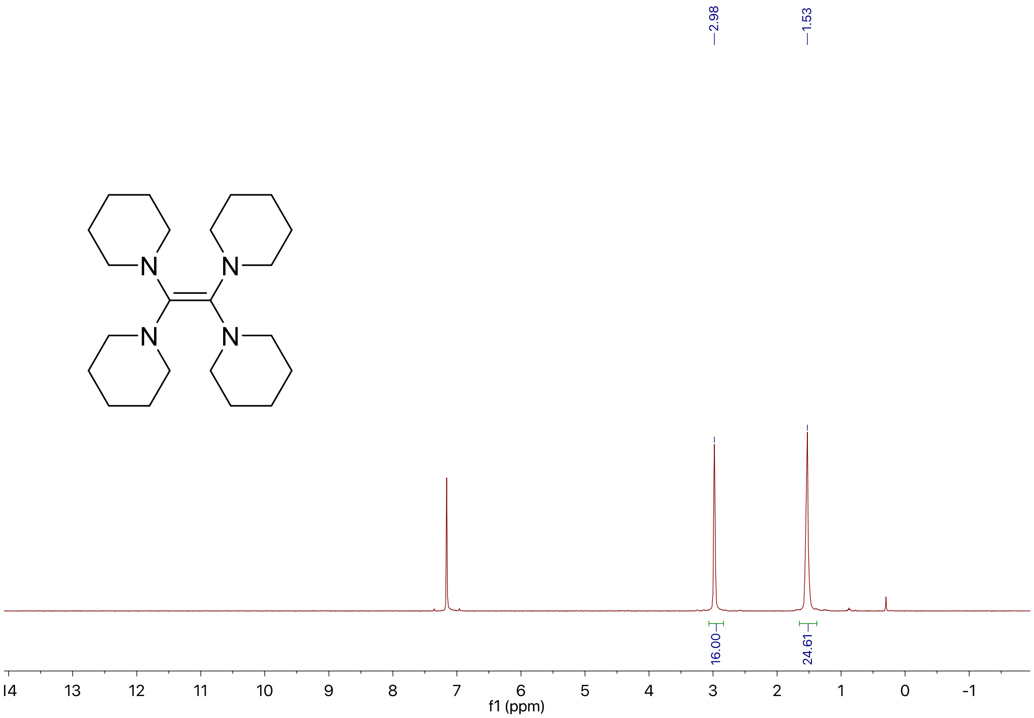


Figure S14. ^{1}H NMR spectrum (400 MHz, C_6D_6) of TPiE.

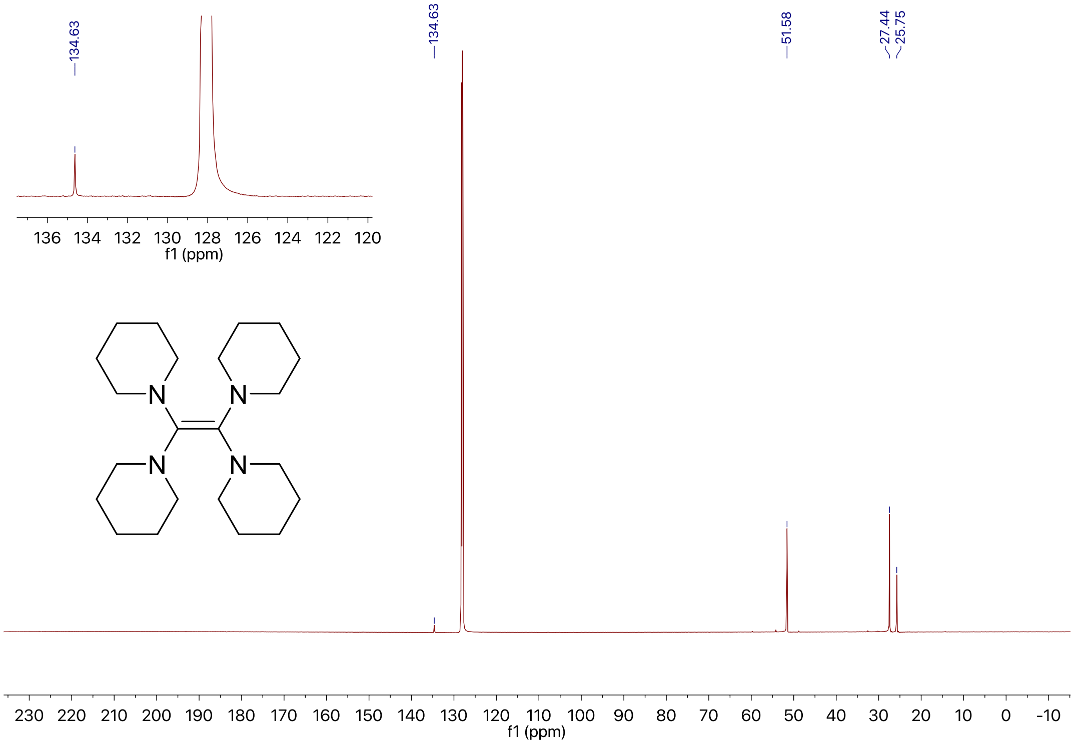


Figure S15. $^{13}C\{^1H\}$ NMR spectrum (150 MHz, C_6D_6) of TPiE.

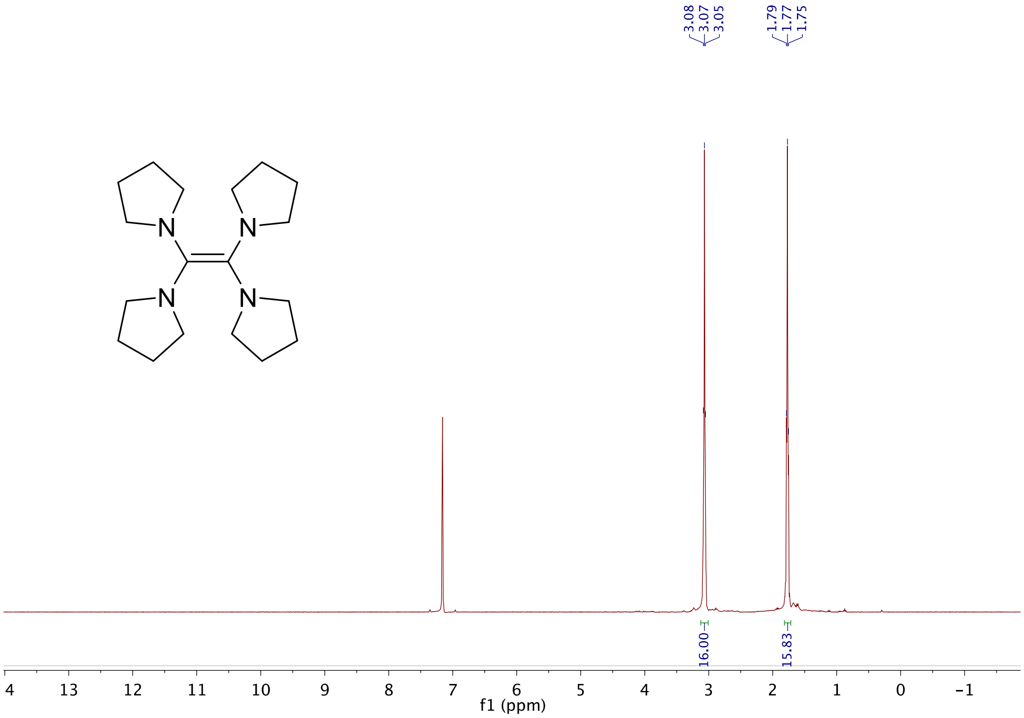


Figure S16. ^{1}H NMR spectrum (400 MHz, C_6D_6) of TPyE.

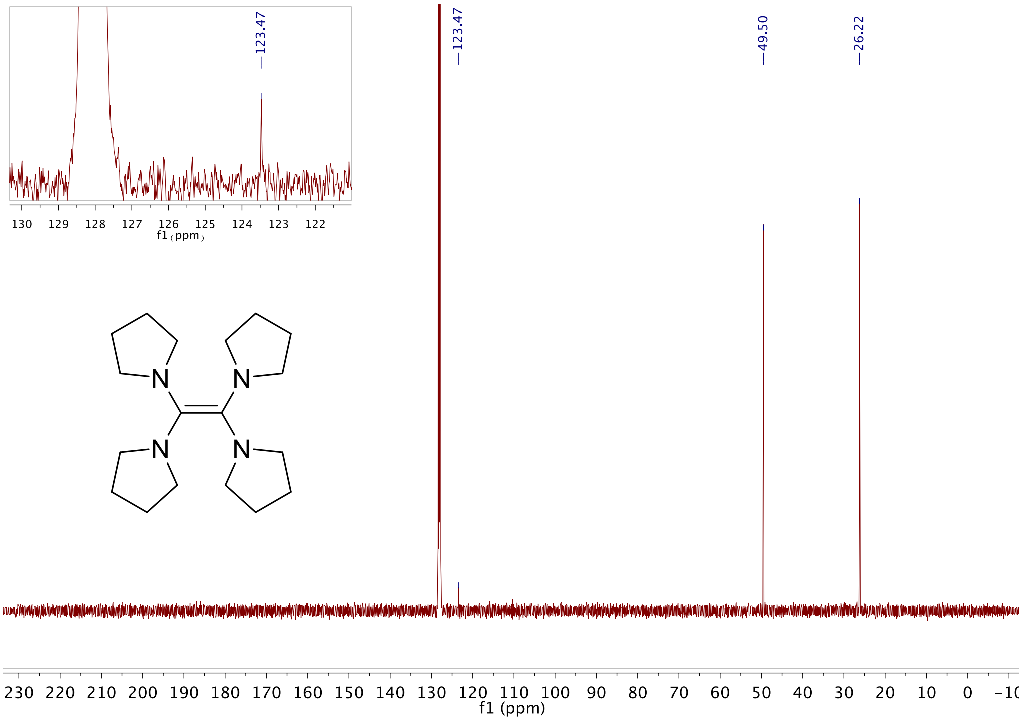


Figure S17. ^{13}C{^{1}H} NMR spectrum (100 MHz, C_6D_6) of TPyE.

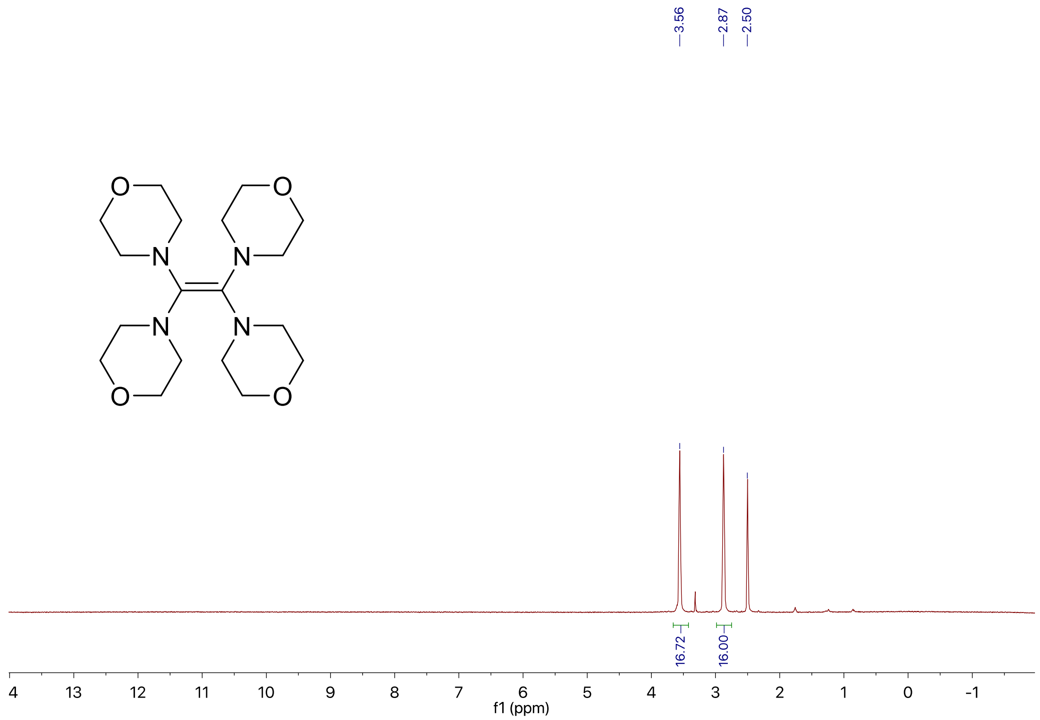


Figure S18. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of TME.

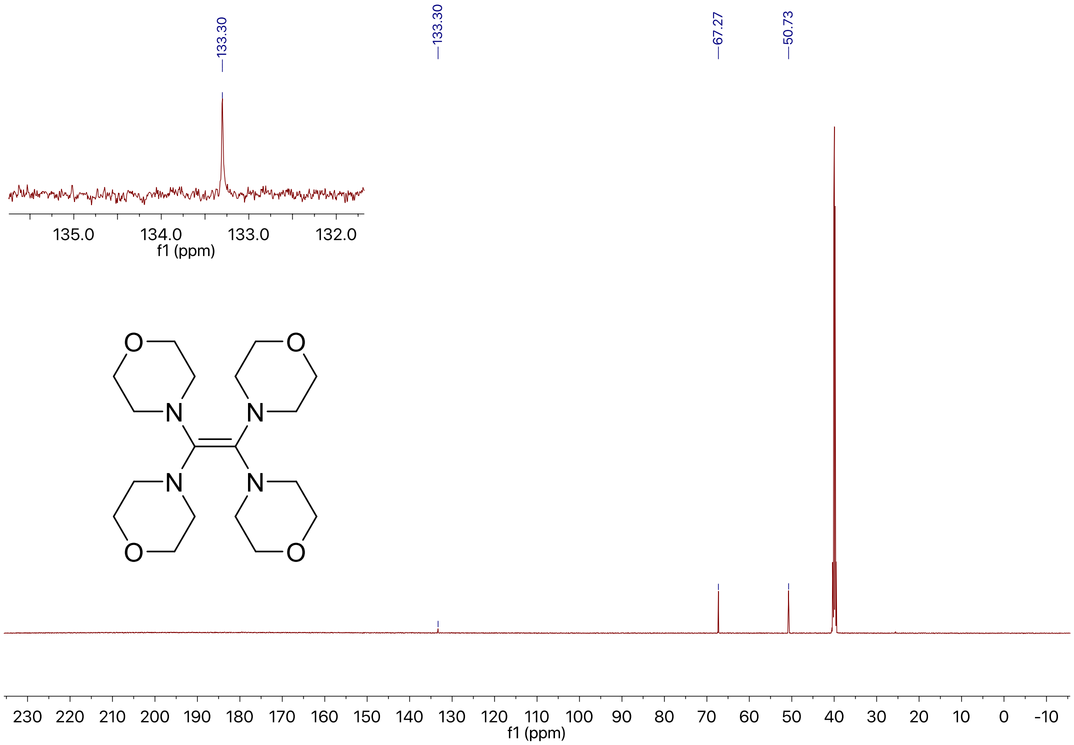


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, DMSO-d_6) of TME.

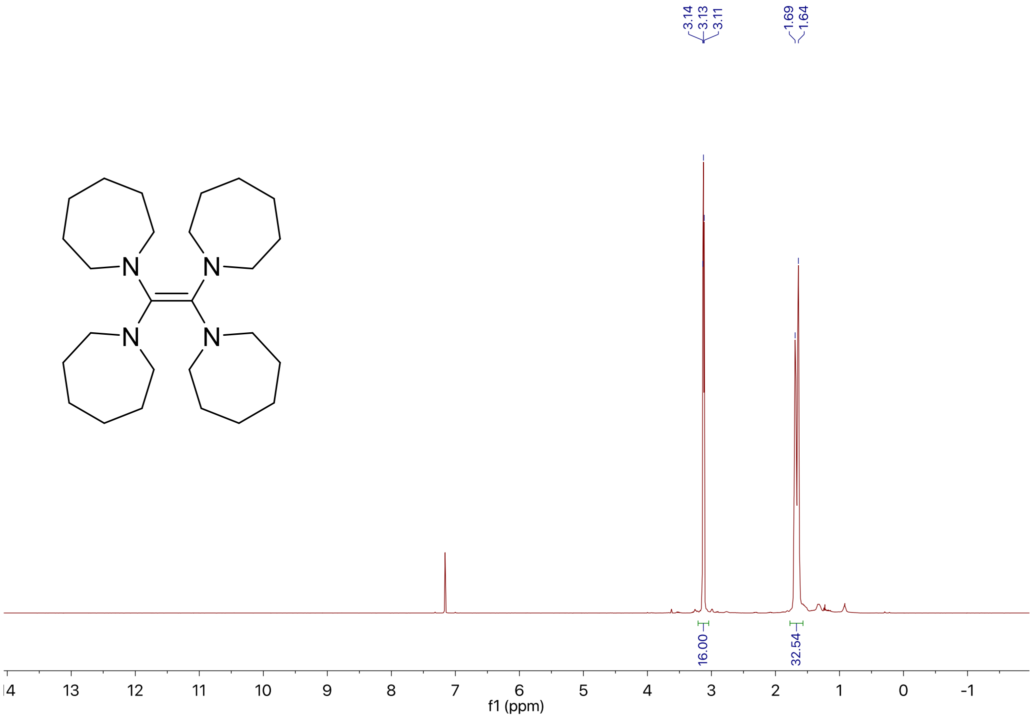


Figure S20. ^{1}H NMR spectrum (500 MHz, C_6D_6) of TAzE.

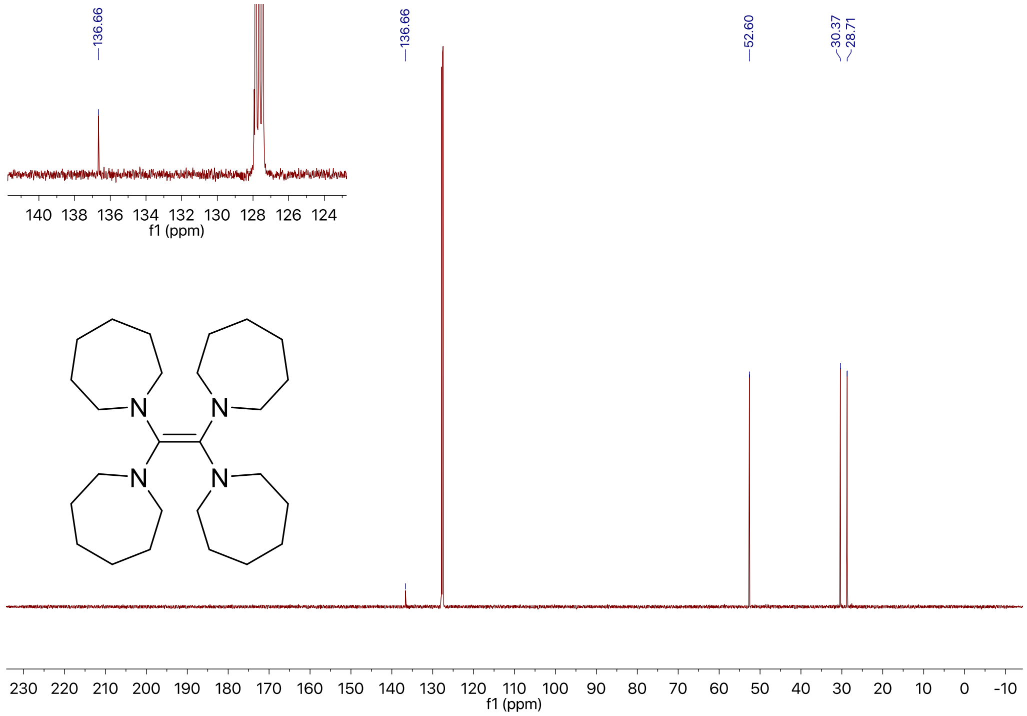


Figure S21. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, C_6D_6) of TAzE.

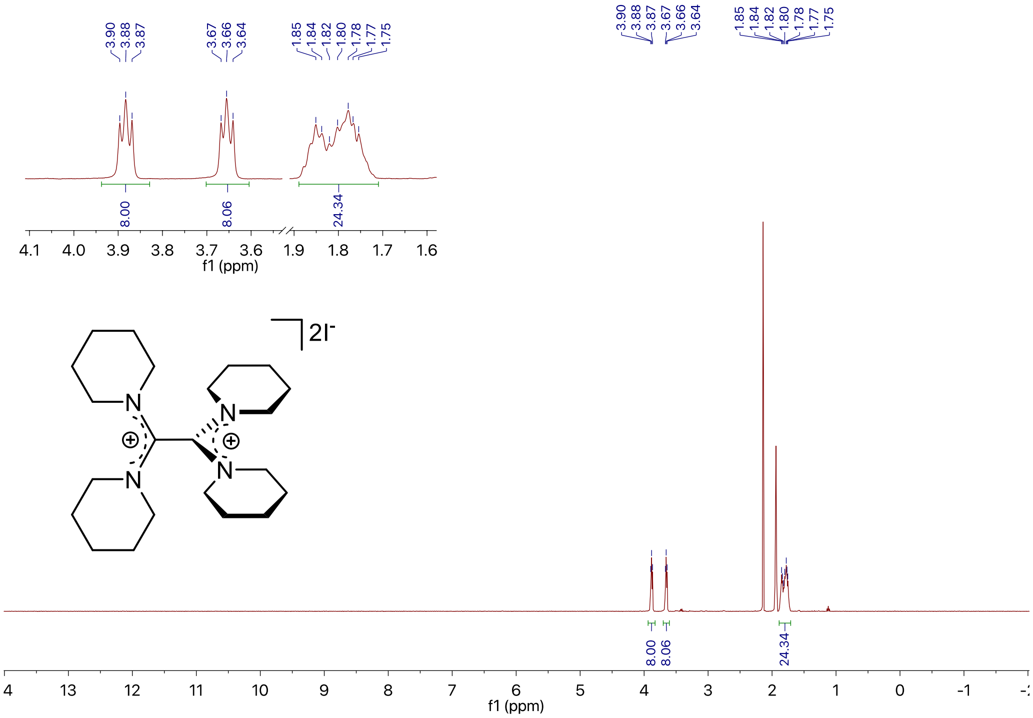


Figure S22. ^{1}H NMR spectrum (400 MHz, CD_3CN) of $[TPiE]^{2+}2[I]^-$.

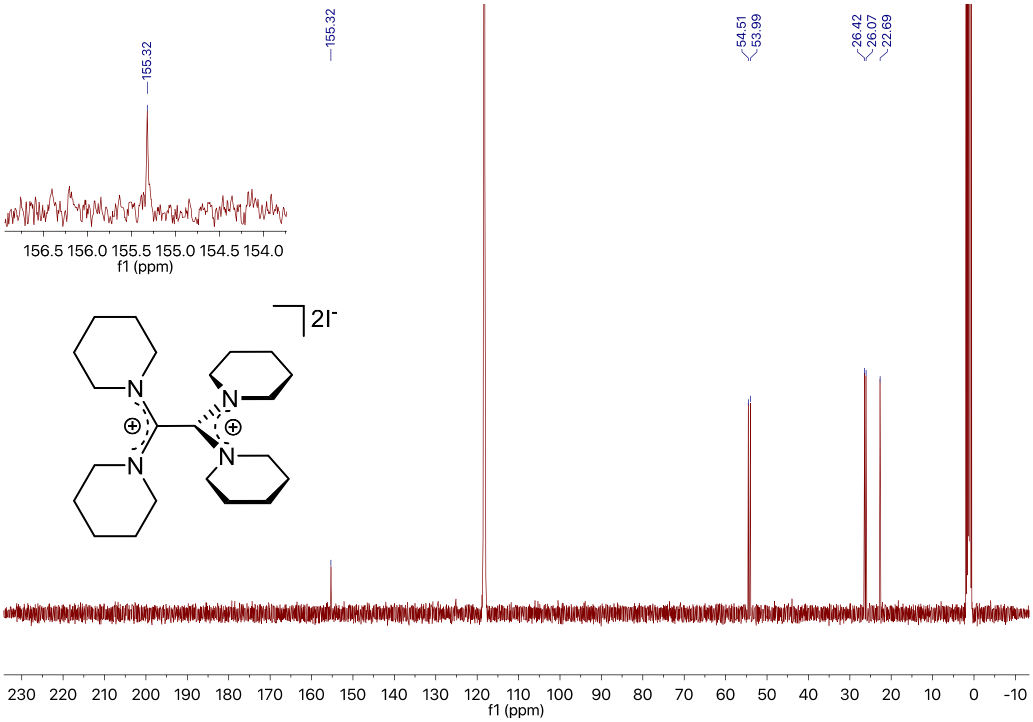


Figure S23. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, CD_3CN) of $[TPiE]^{2+}2[I]^-$.

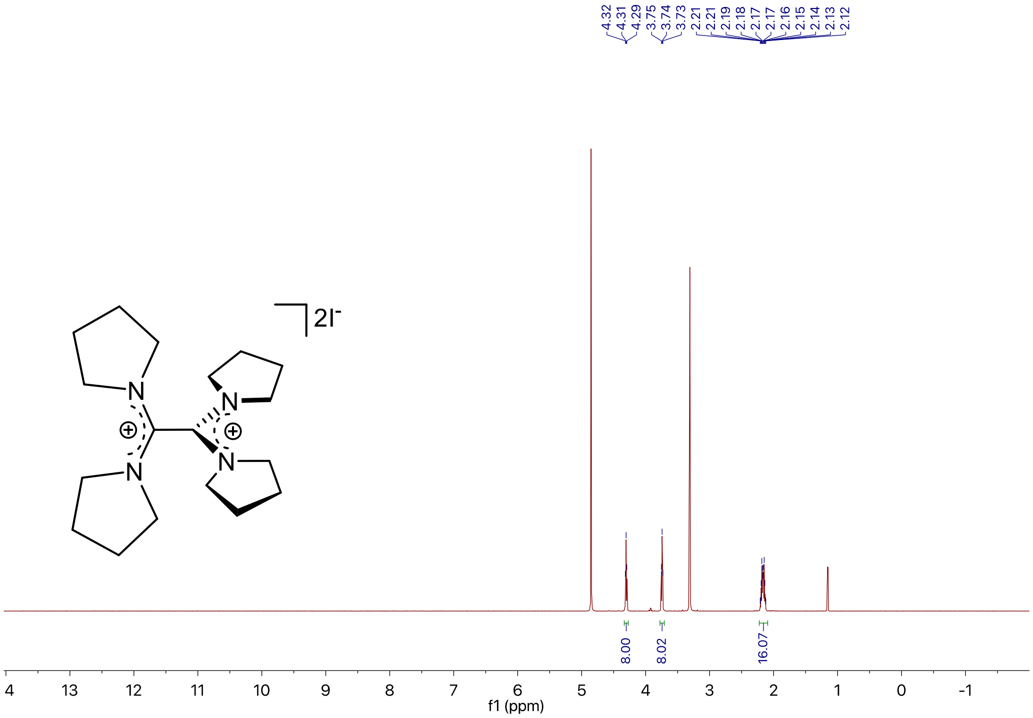


Figure S24. ^{1}H NMR spectrum (600 MHz, Methanol-d_4) of $[\mathrm{TPyE}]^{2+}2[\mathrm{I}]^-$.

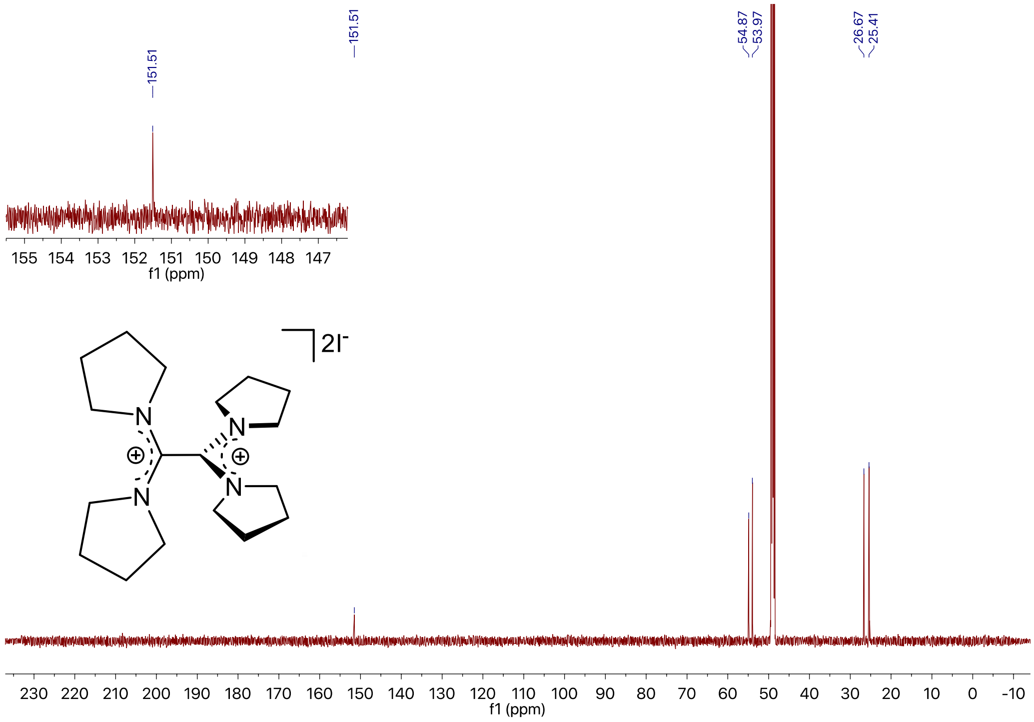


Figure S25. ^{13}C{^{1}H} NMR spectrum (150 MHz, Methanol-d_4) of $[\mathrm{TPyE}]^{2+}2[\mathrm{I}]^-$.

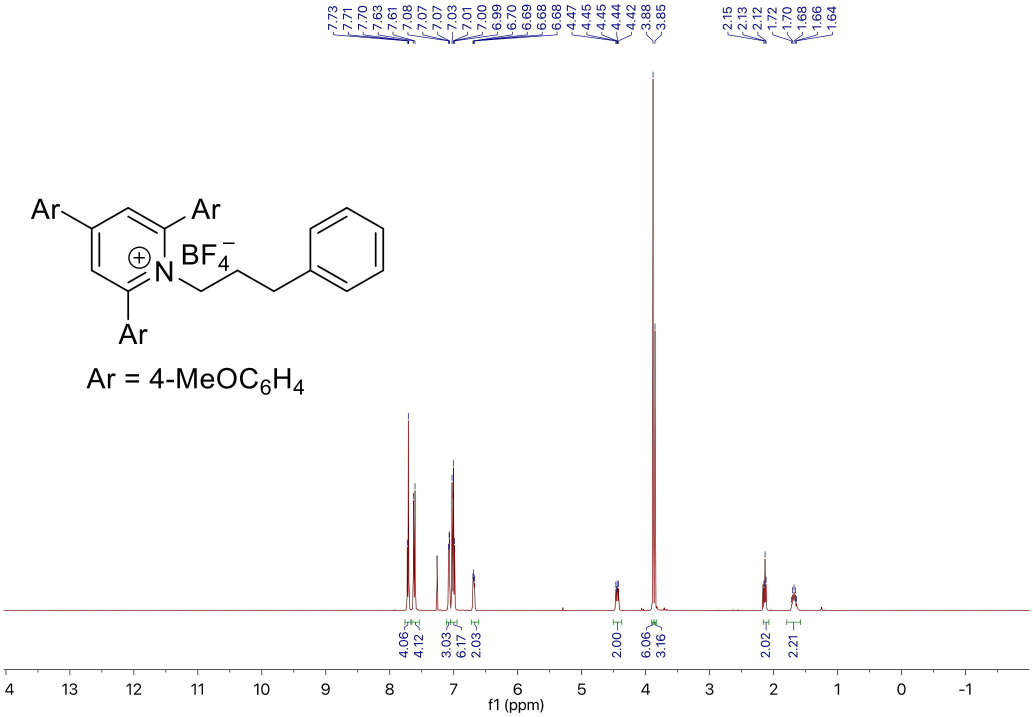


Figure S26. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **1**.

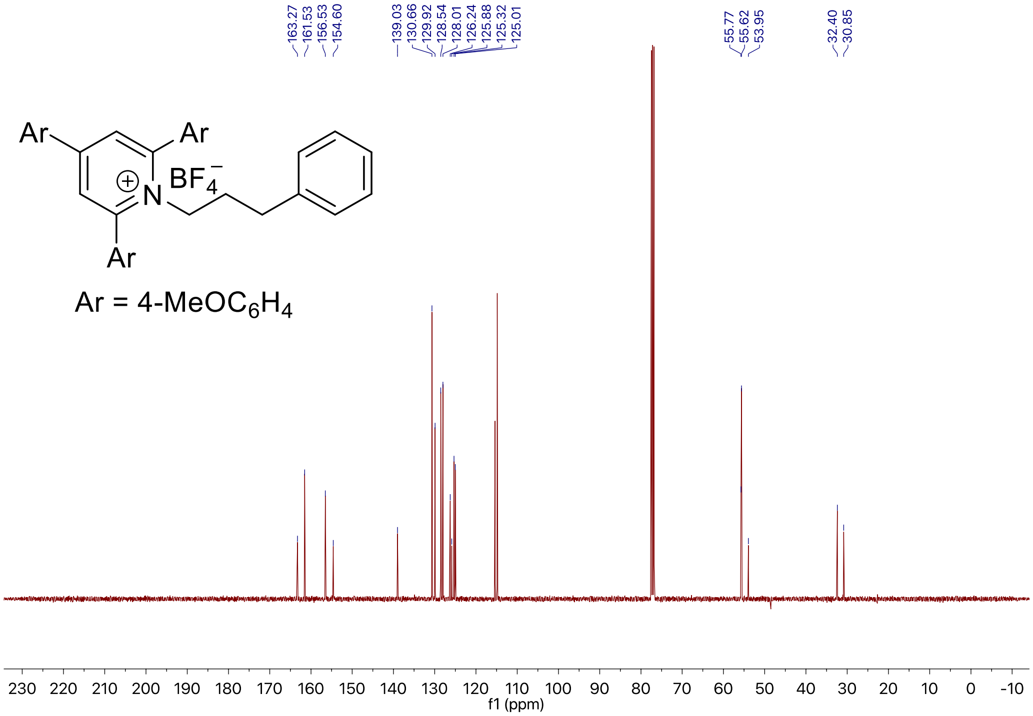


Figure S27. ^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **1**.

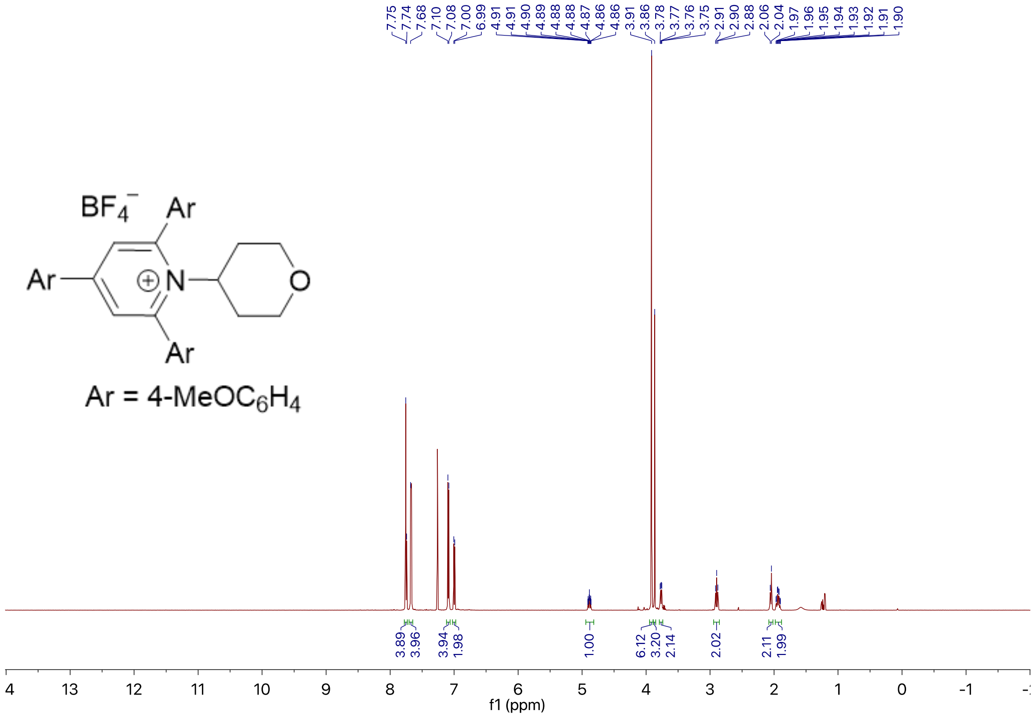


Figure S28. ^{1}H NMR spectrum (600 MHz, CDCl$_3$) of **2**.

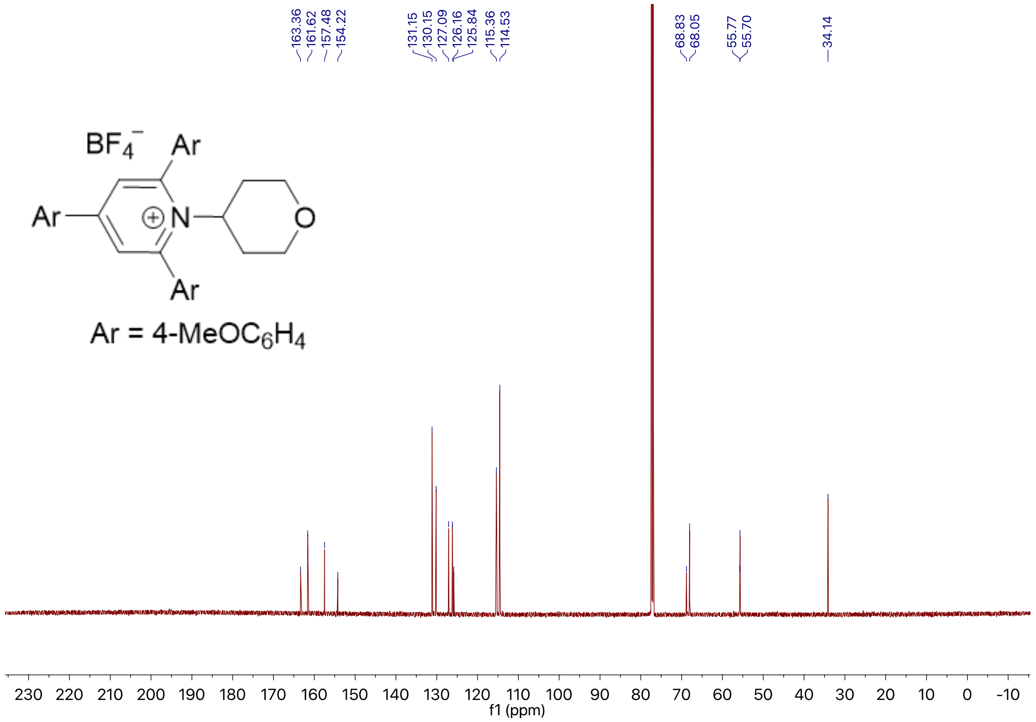


Figure S29. ^{13}C{^{1}H} NMR spectrum (150 MHz, CDCl$_3$) of **2**.

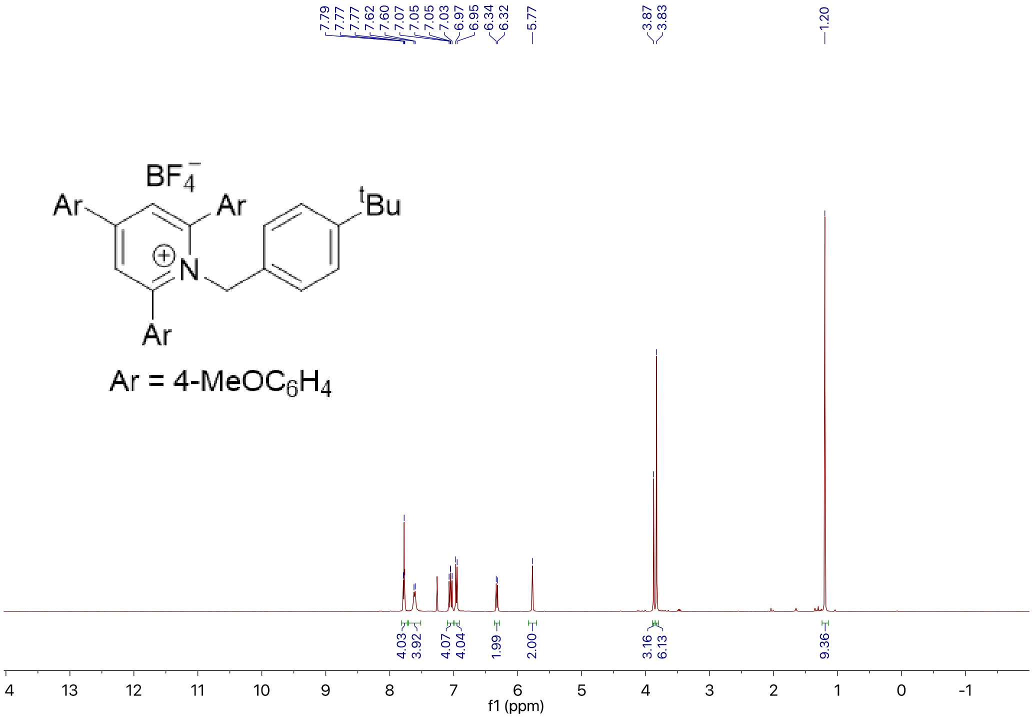


Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**.

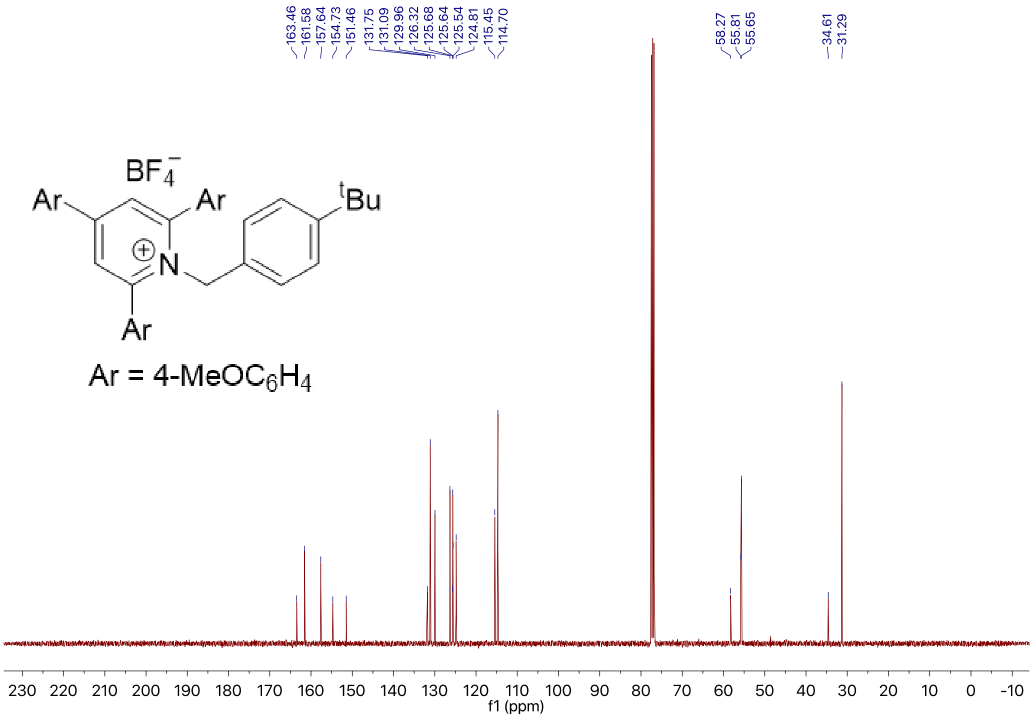


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **3**.

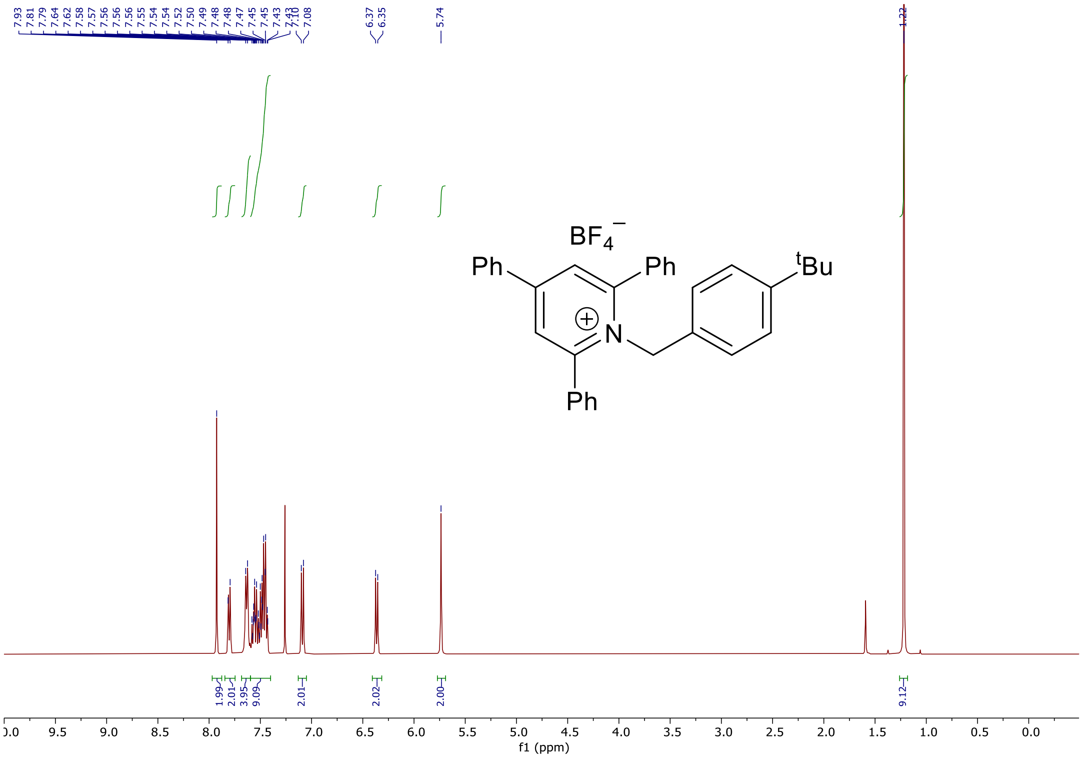


Figure S32. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **4**.

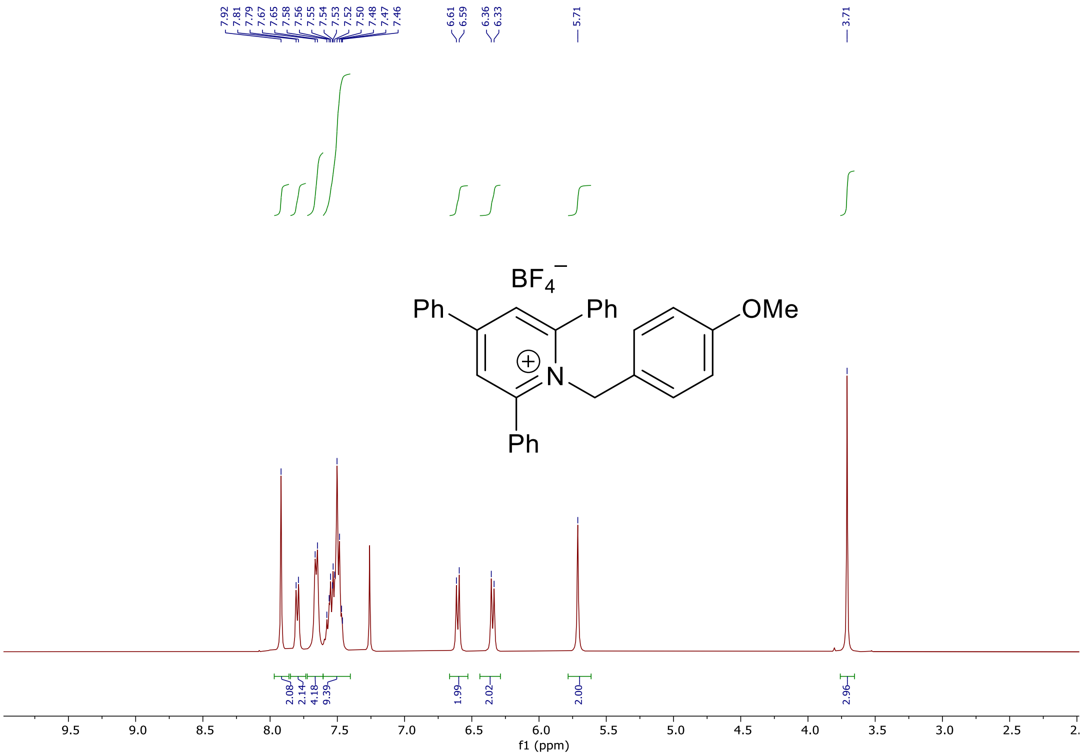


Figure S33. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **5**.

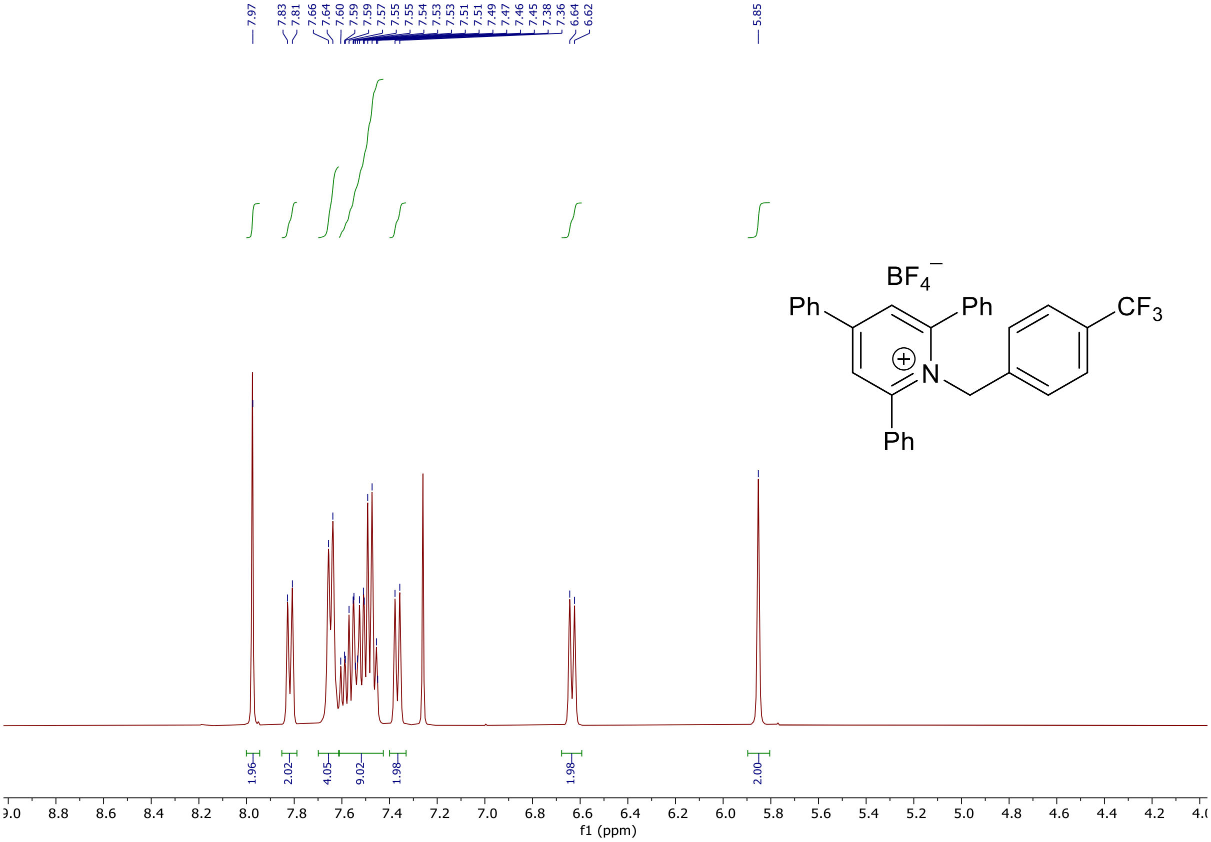


Figure S34. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **6**.

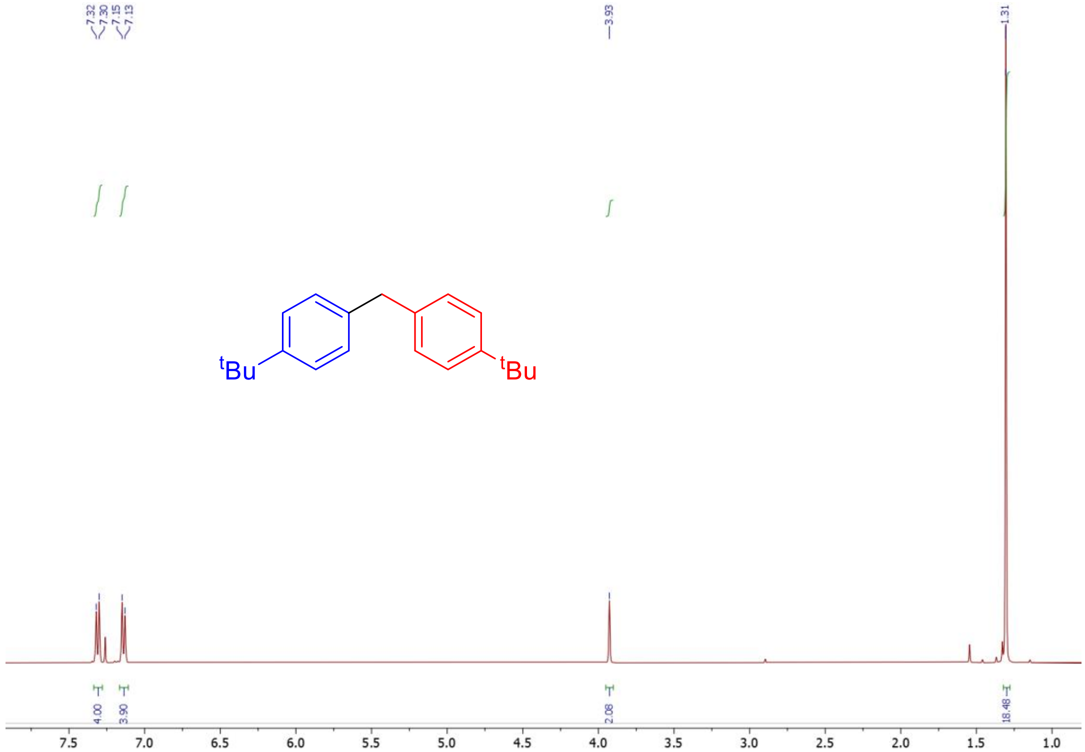


Figure S35. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9a**.

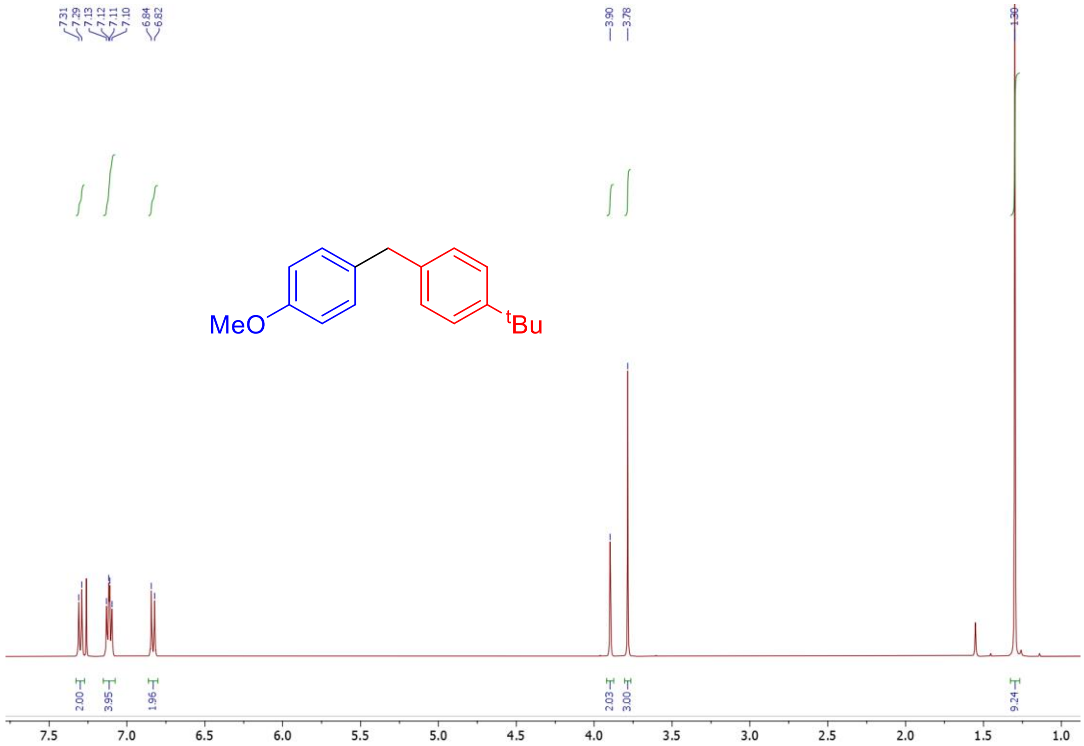


Figure S36. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9b**.

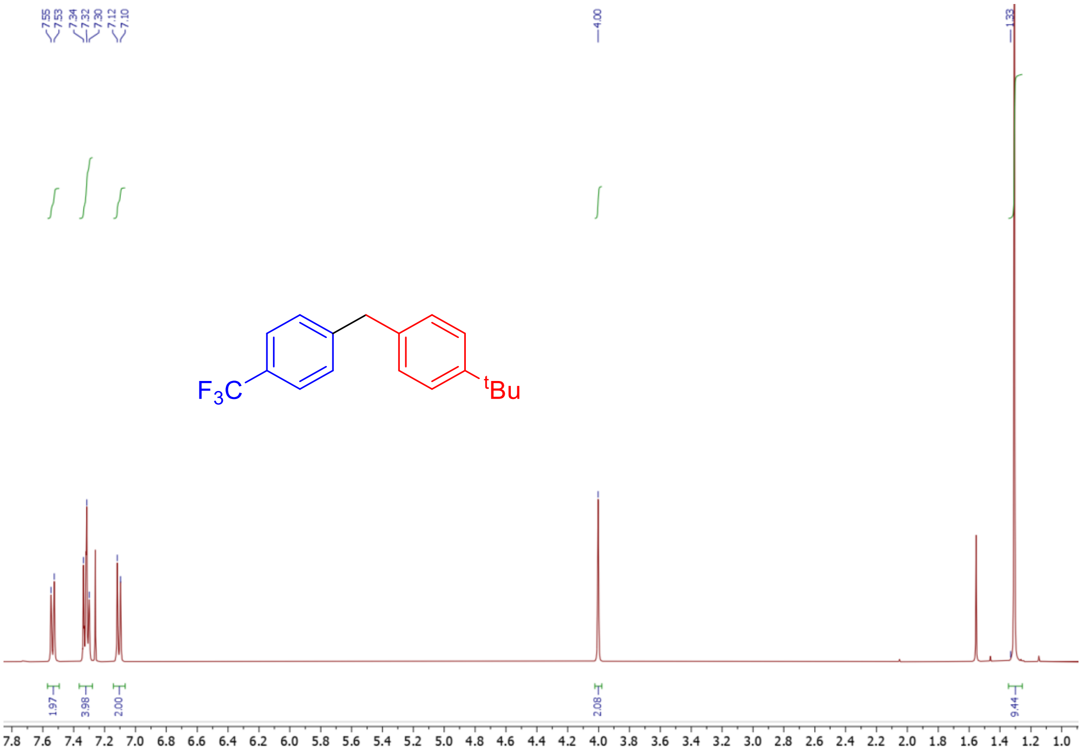


Figure S37. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **9c**.

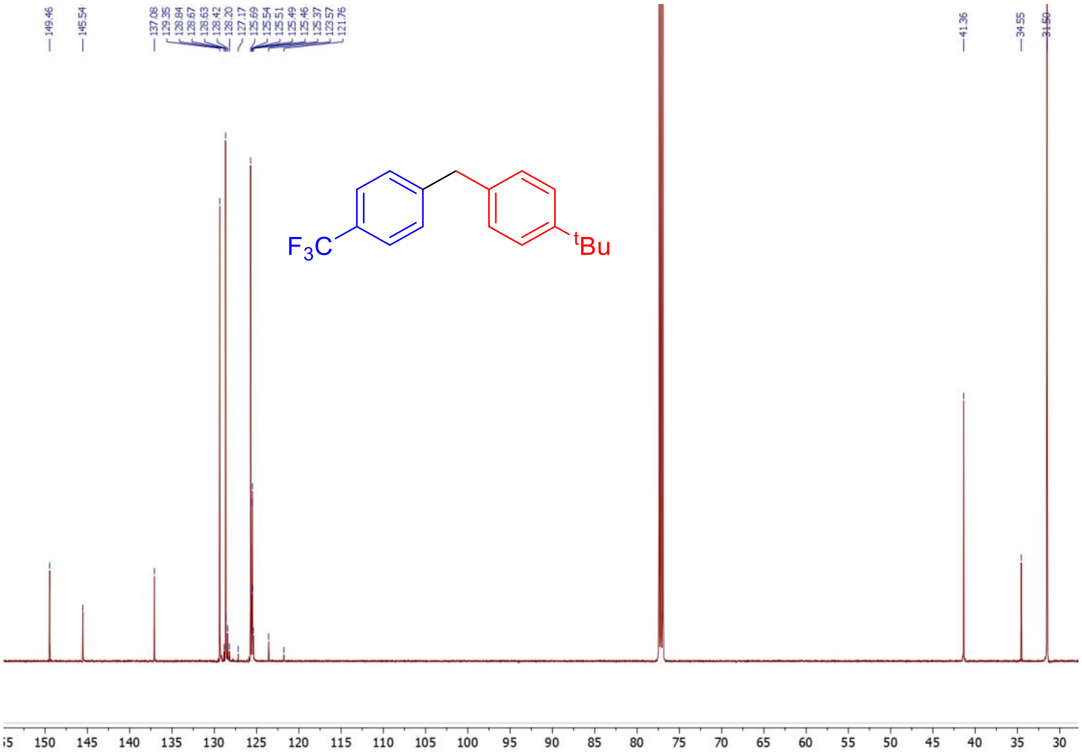


Figure S38. ^{13}C{^{1}H} NMR spectrum (150 MHz, CDCl$_3$) of **9c**.

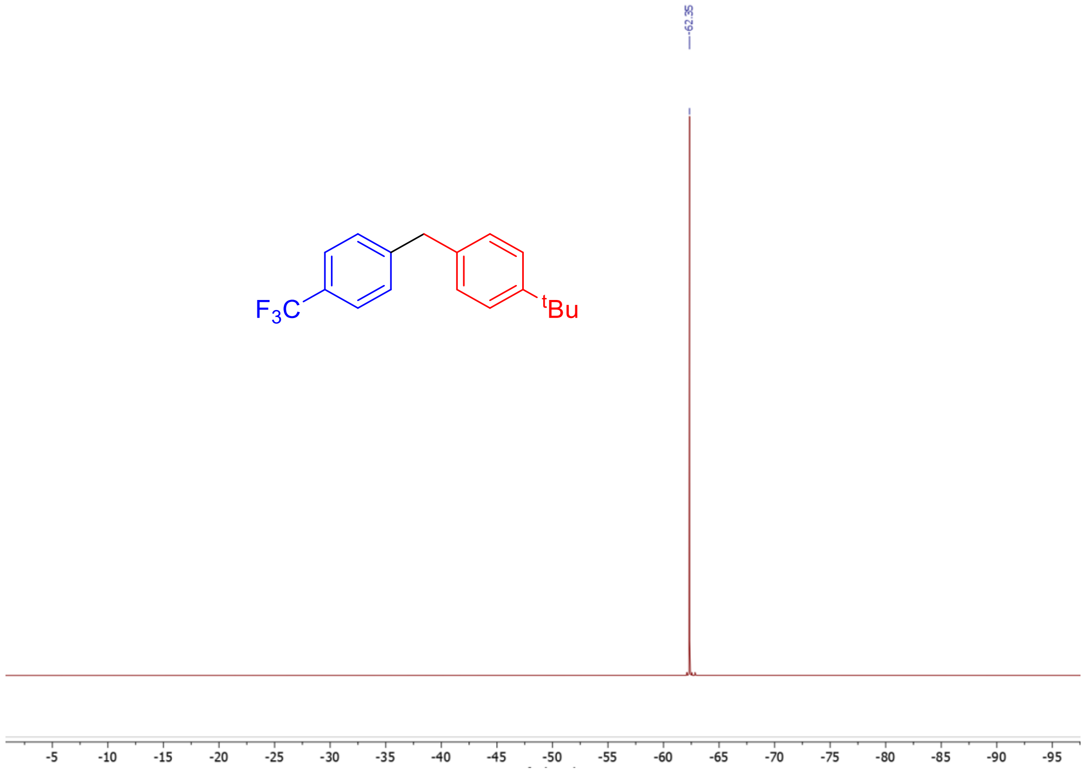


Figure S39. $^{19}F\{^1H\}$ NMR spectrum (376 MHz, $CDCl_3$) of **9c**.

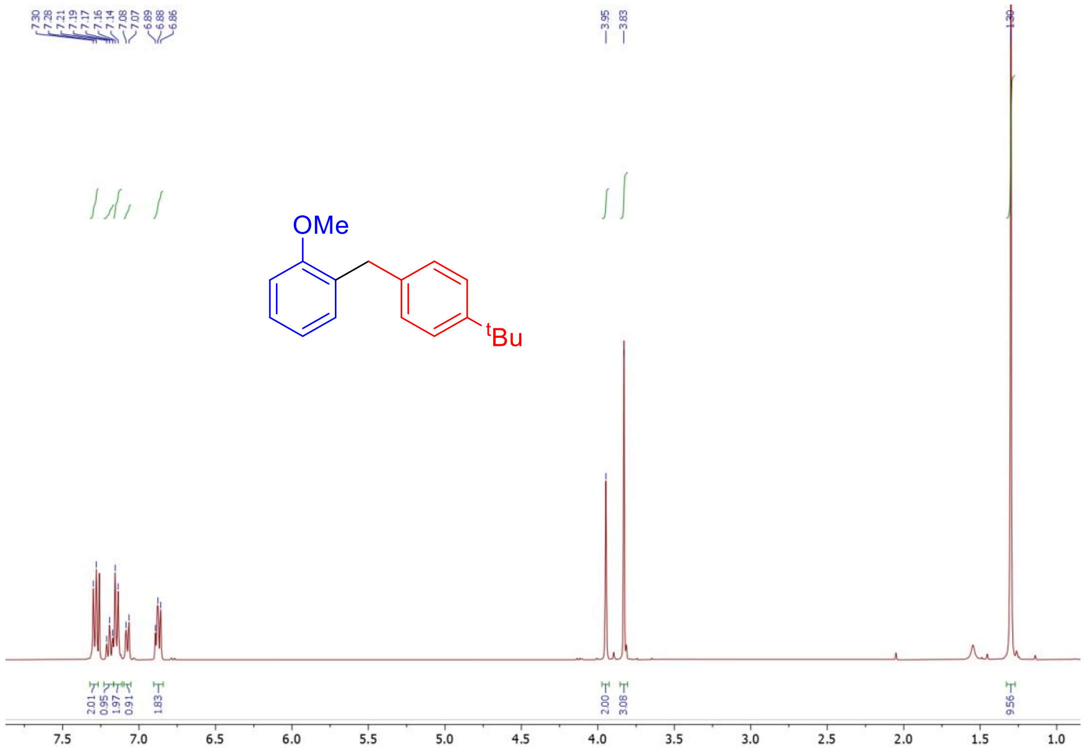


Figure S40. ^1H NMR spectrum (400 MHz, $CDCl_3$) of **9d**.

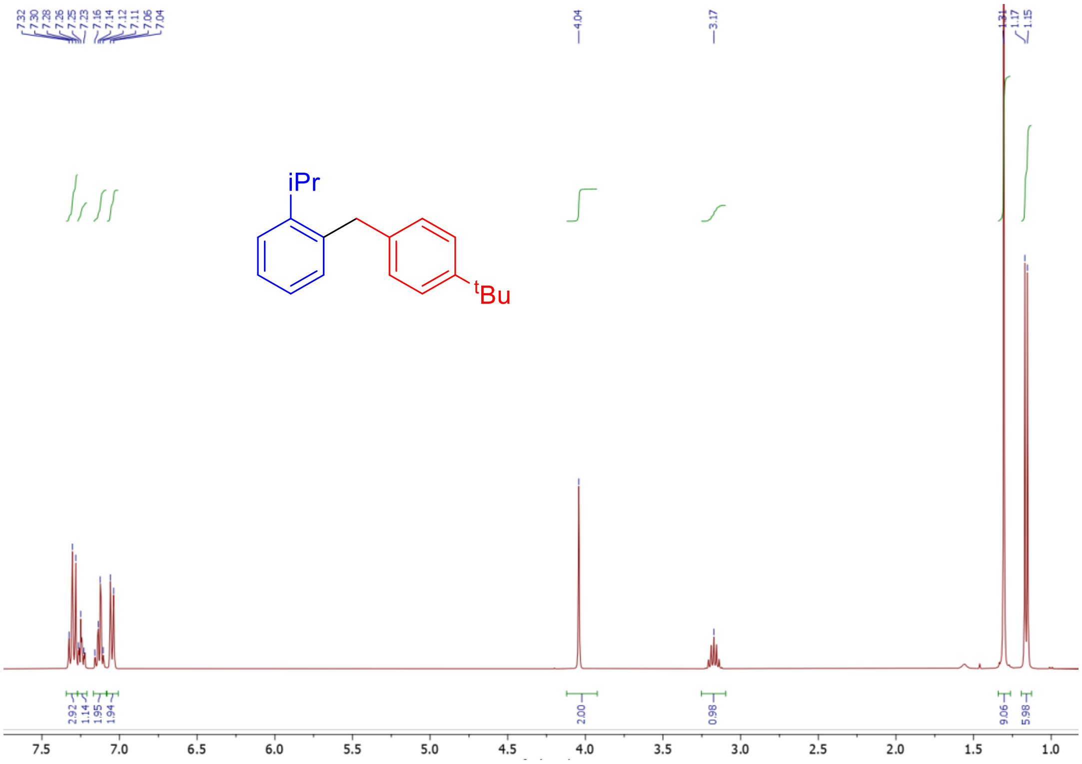


Figure S41. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9e**.

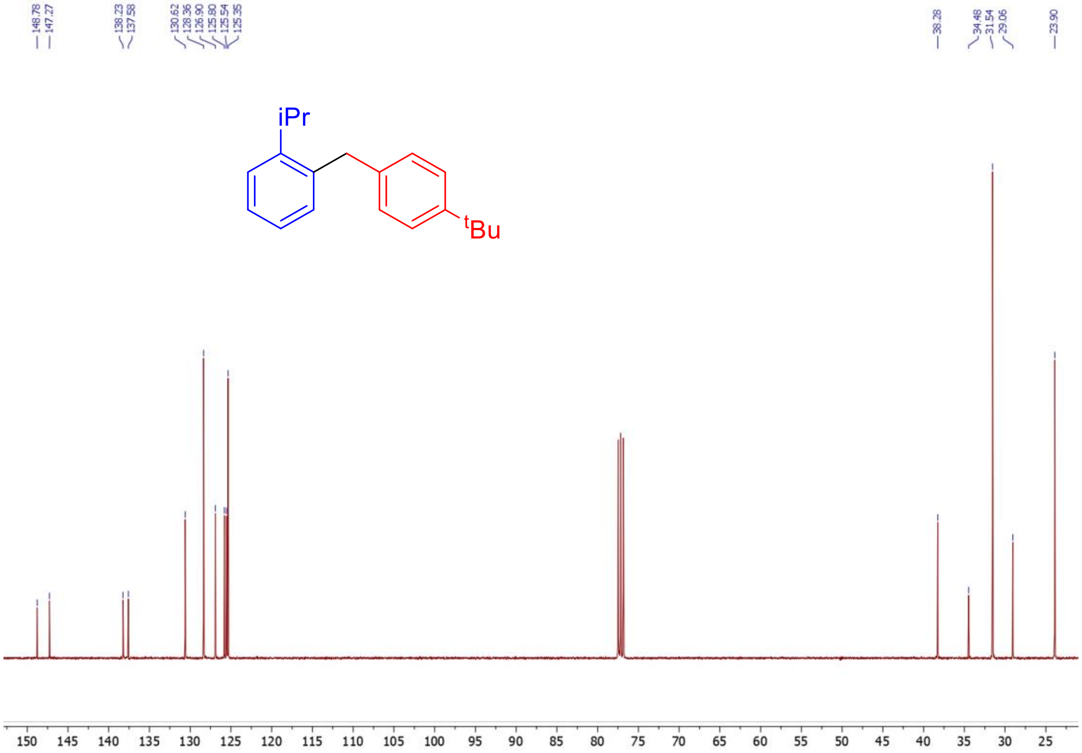


Figure S42. $^{13}C\{^1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of **9e**.

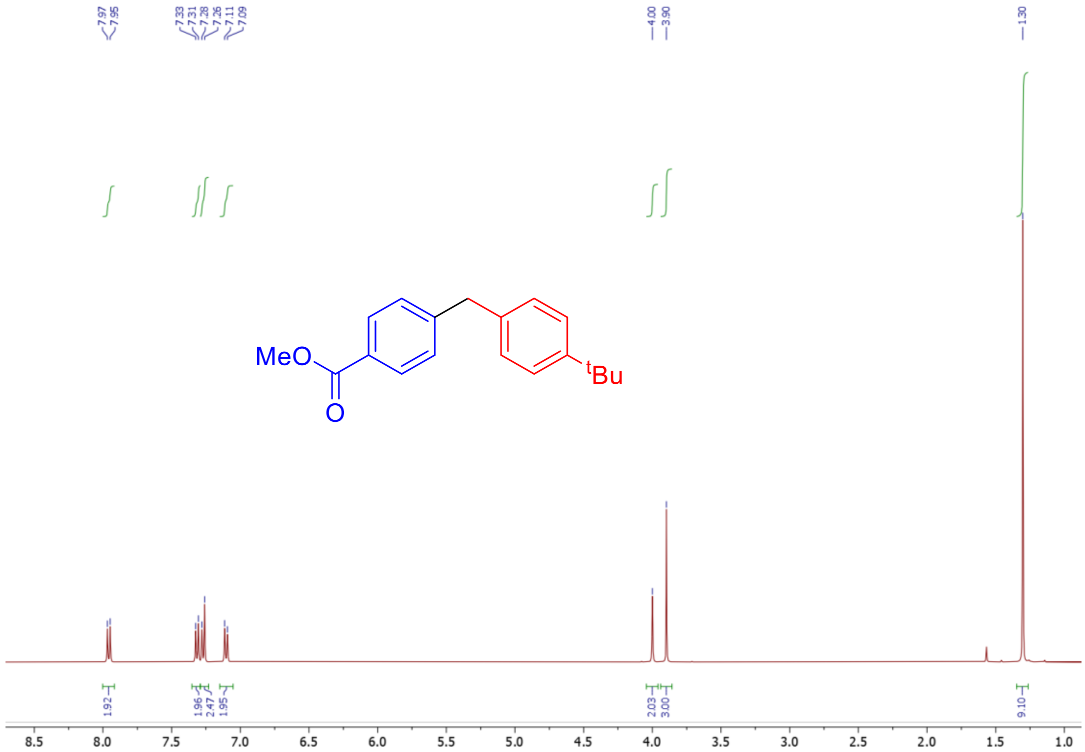


Figure S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9f**.

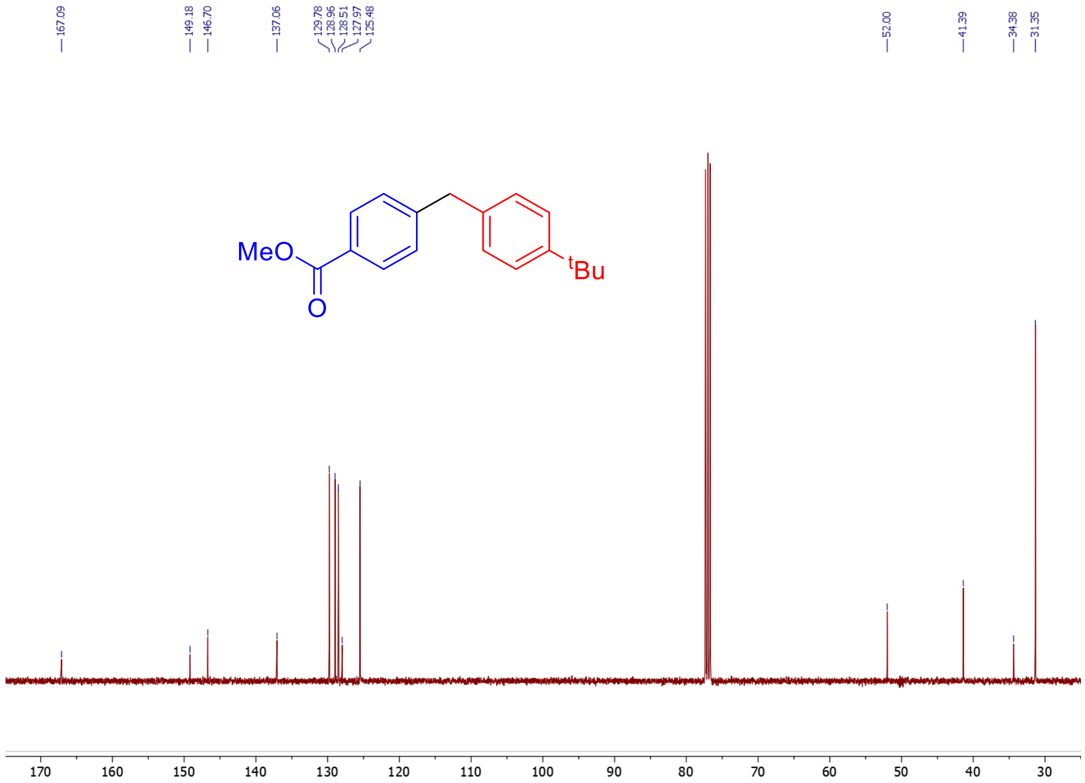


Figure S44. $^{13}C\{^1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of **9f**.

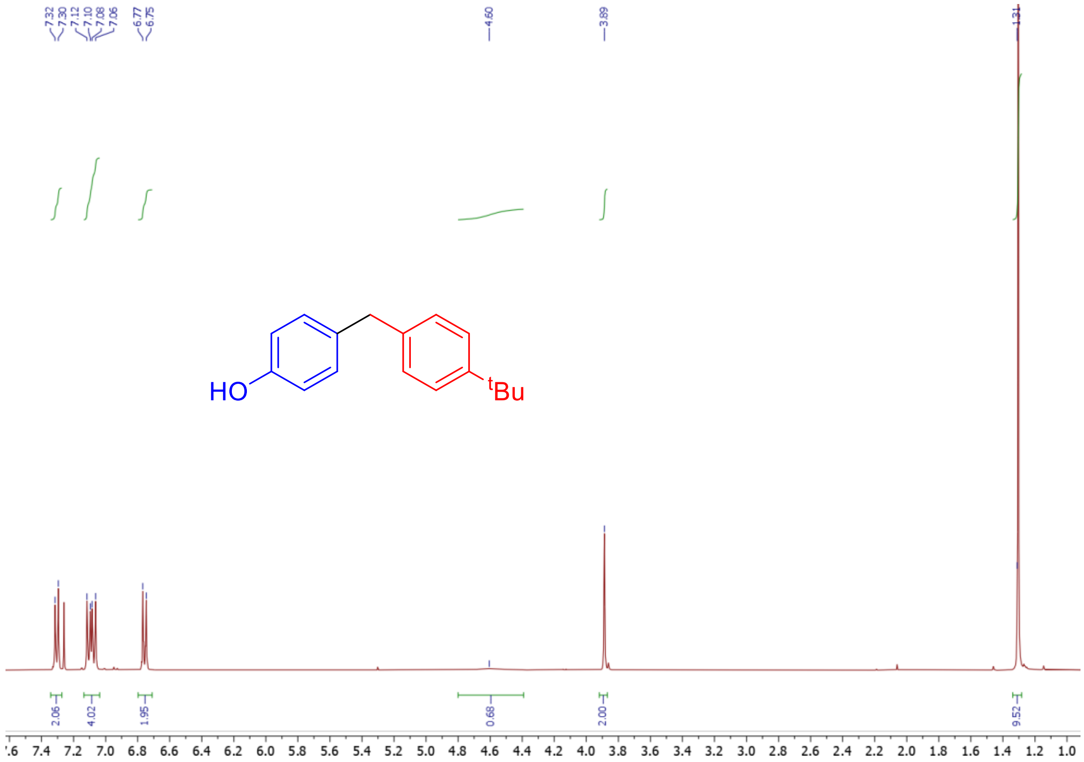


Figure S45. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9g**.

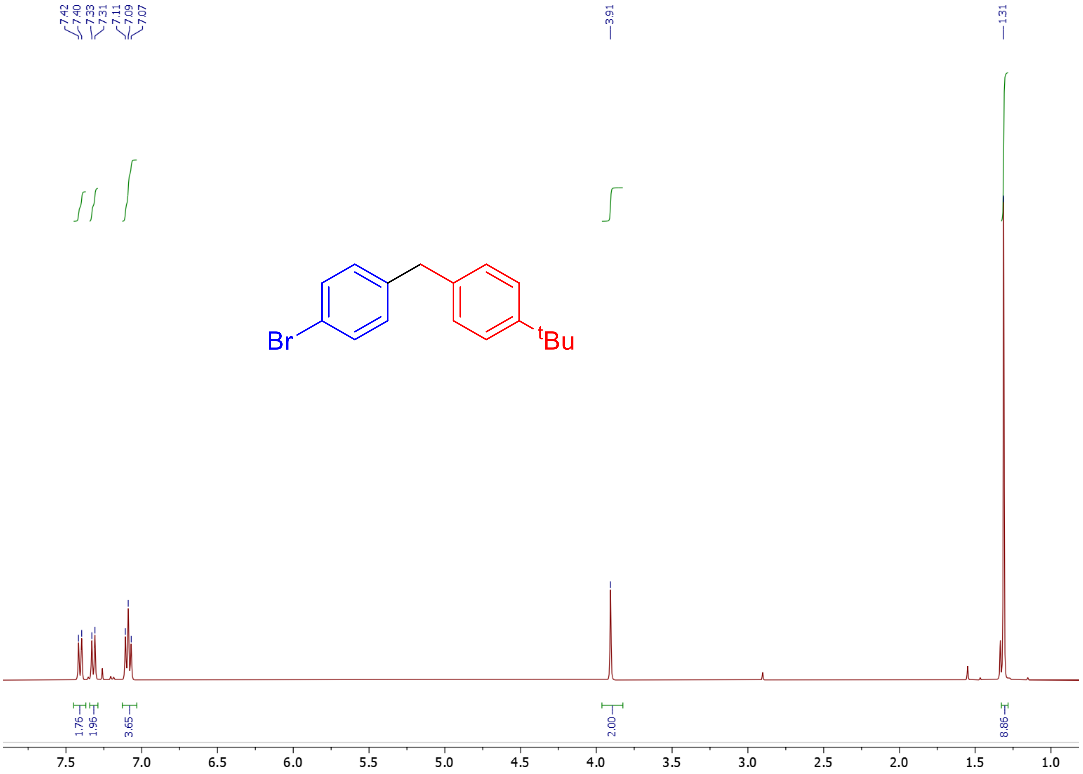


Figure S46. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **9h**.

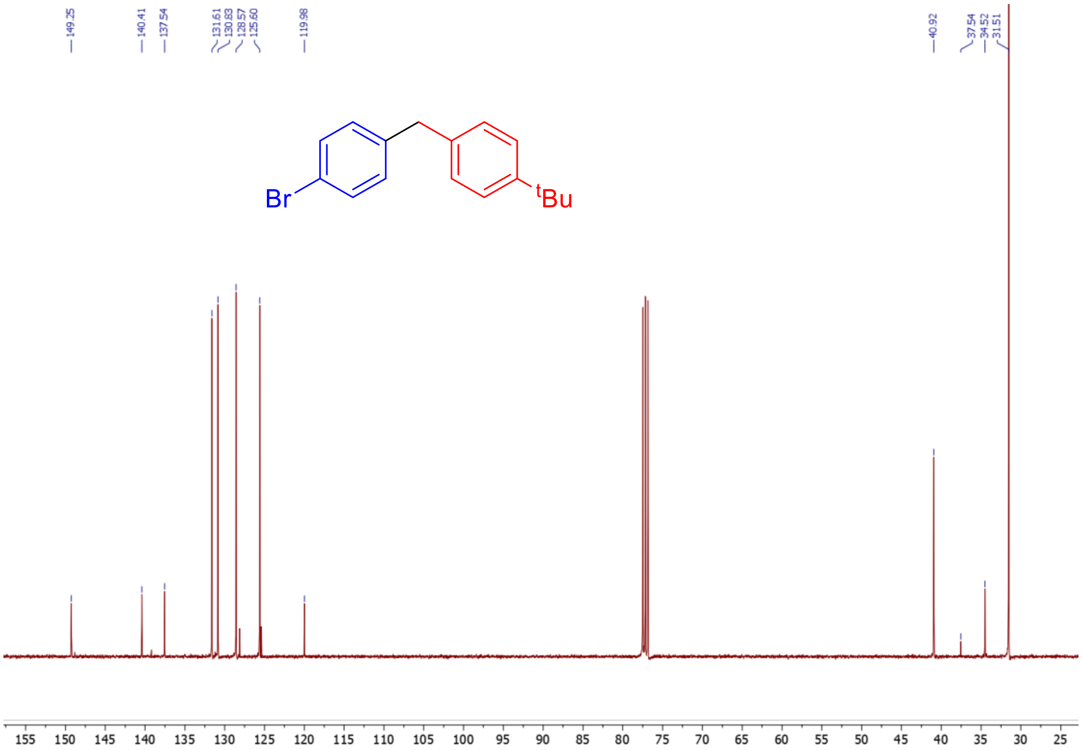


Figure S47. ^{13}C{^{1}H} NMR spectrum (150 MHz, CDCl$_3$) of **9h**.

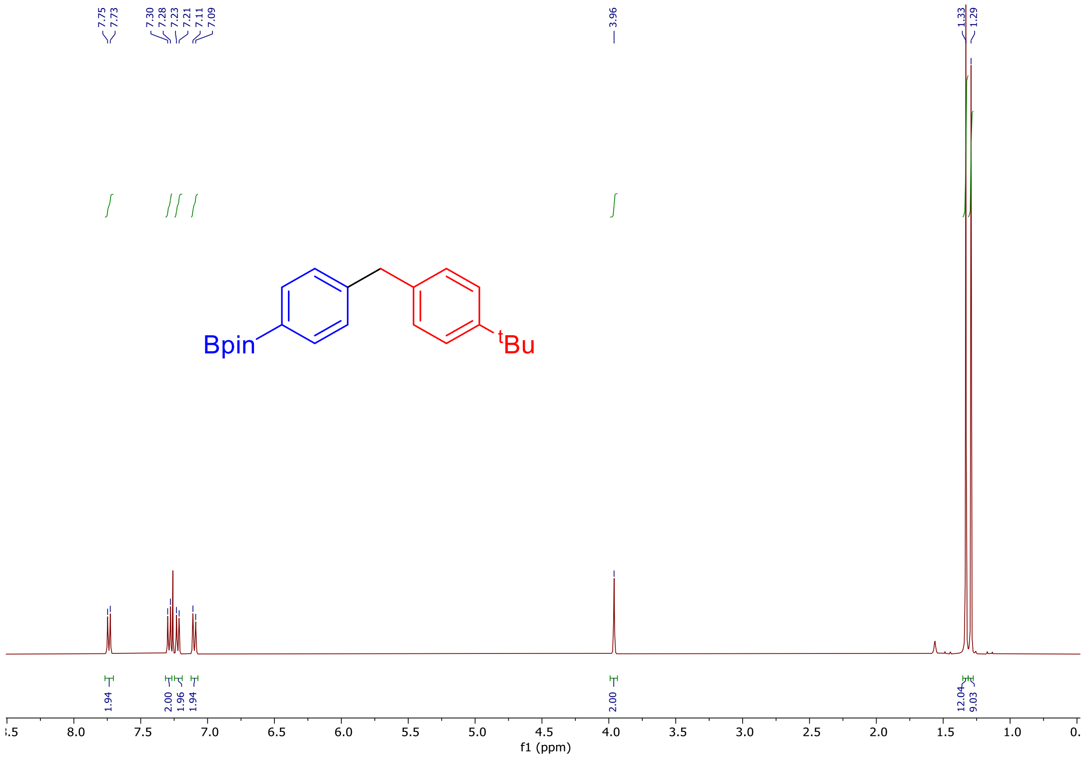


Figure S48. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **9i**.

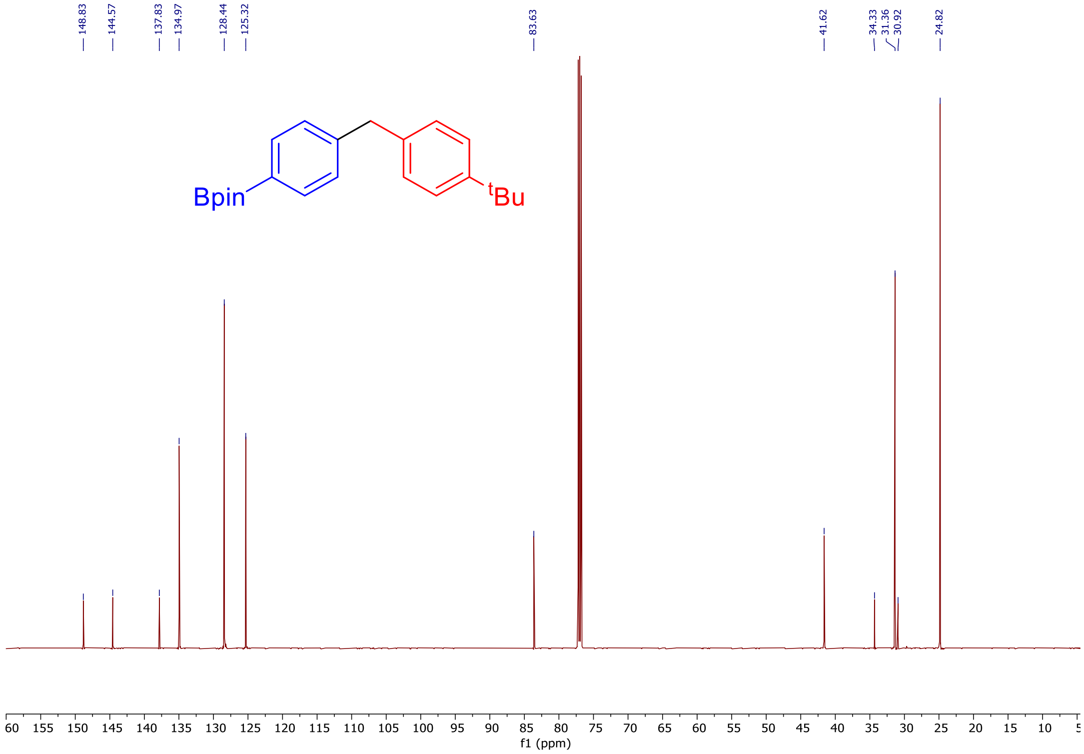


Figure S49. ^{13}C{^{1}H} NMR spectrum (150 MHz, CDCl$_3$) of **9i**.

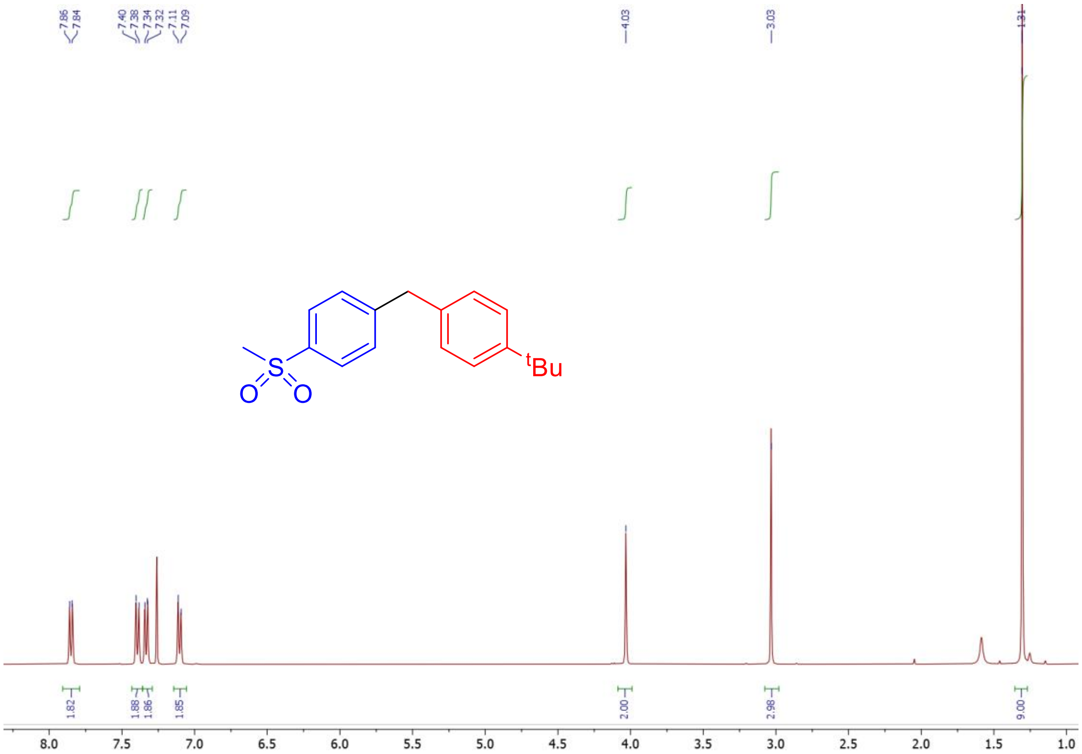


Figure S50. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9j**.

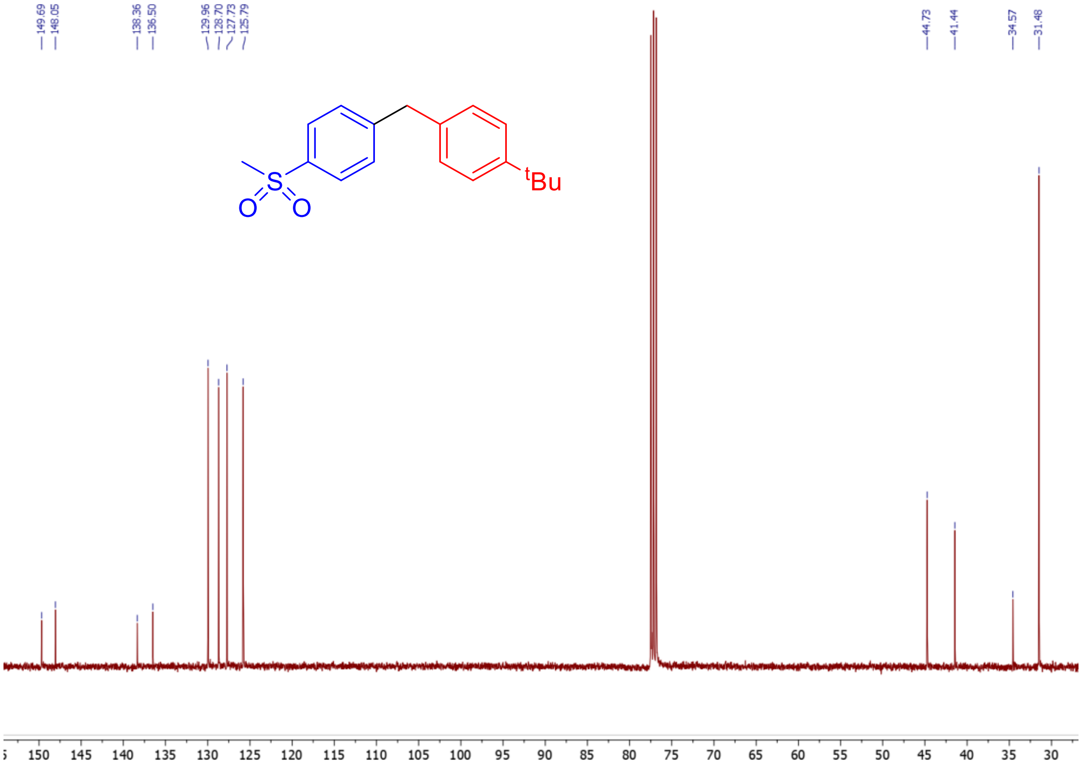


Figure S51. $^{13}C\{^1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of **9j**.

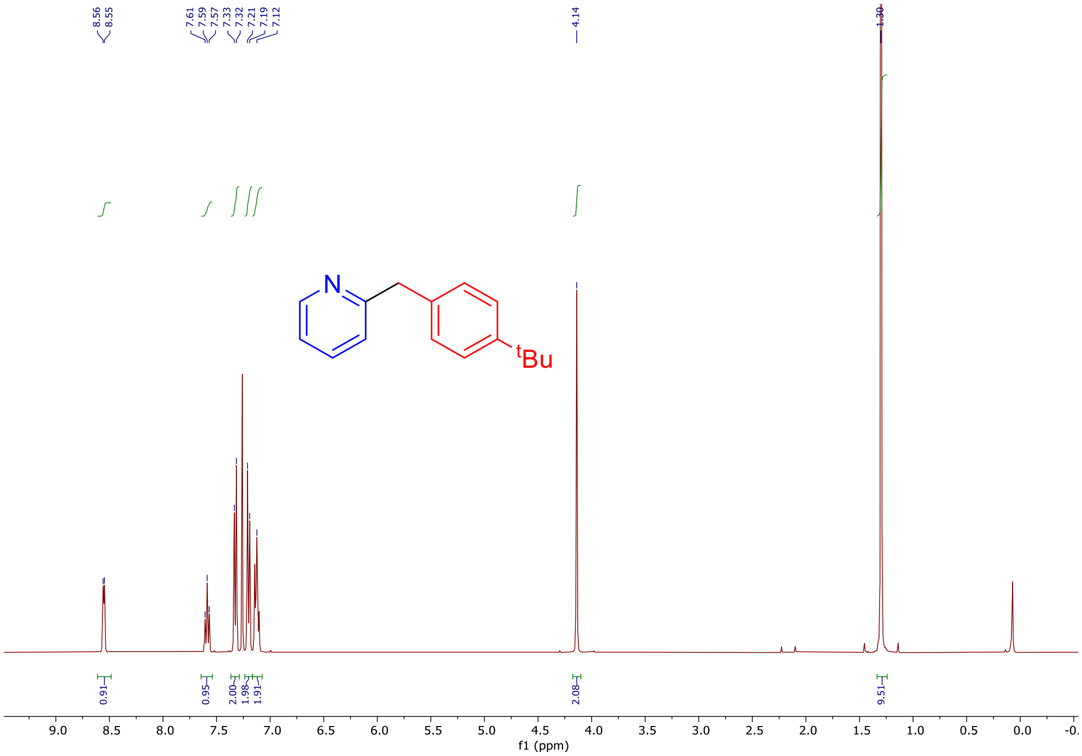


Figure S52. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9k**.

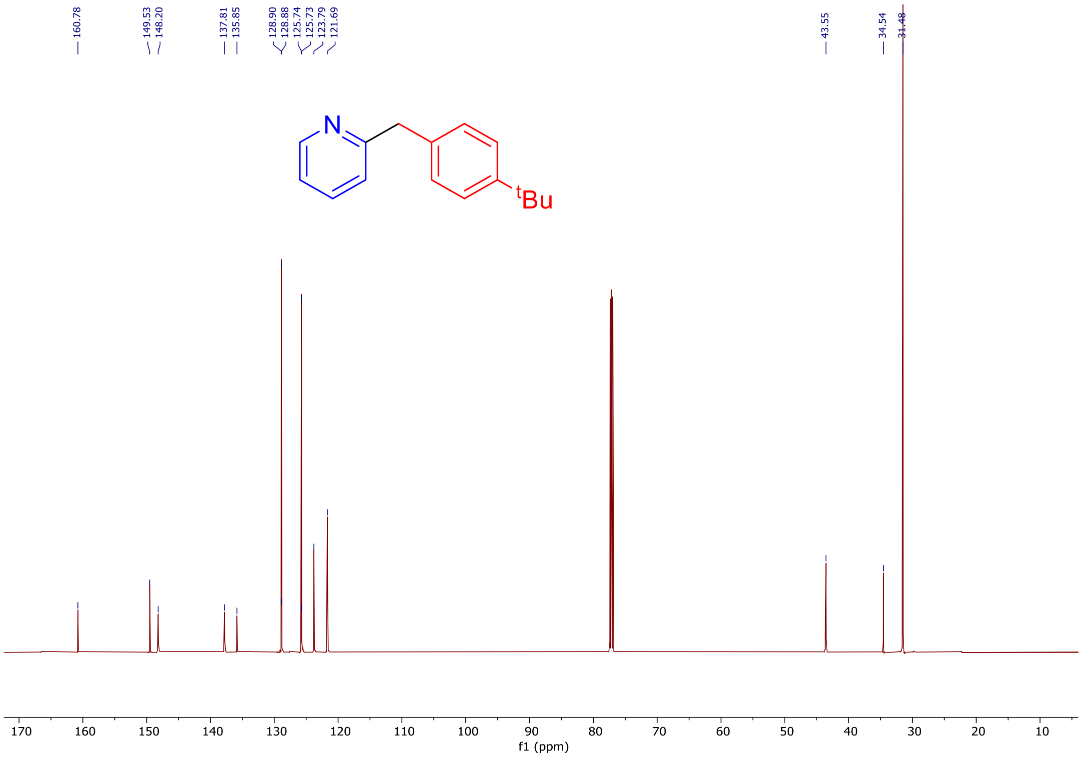


Figure S53. $^{13}C\{^1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of **9k**.

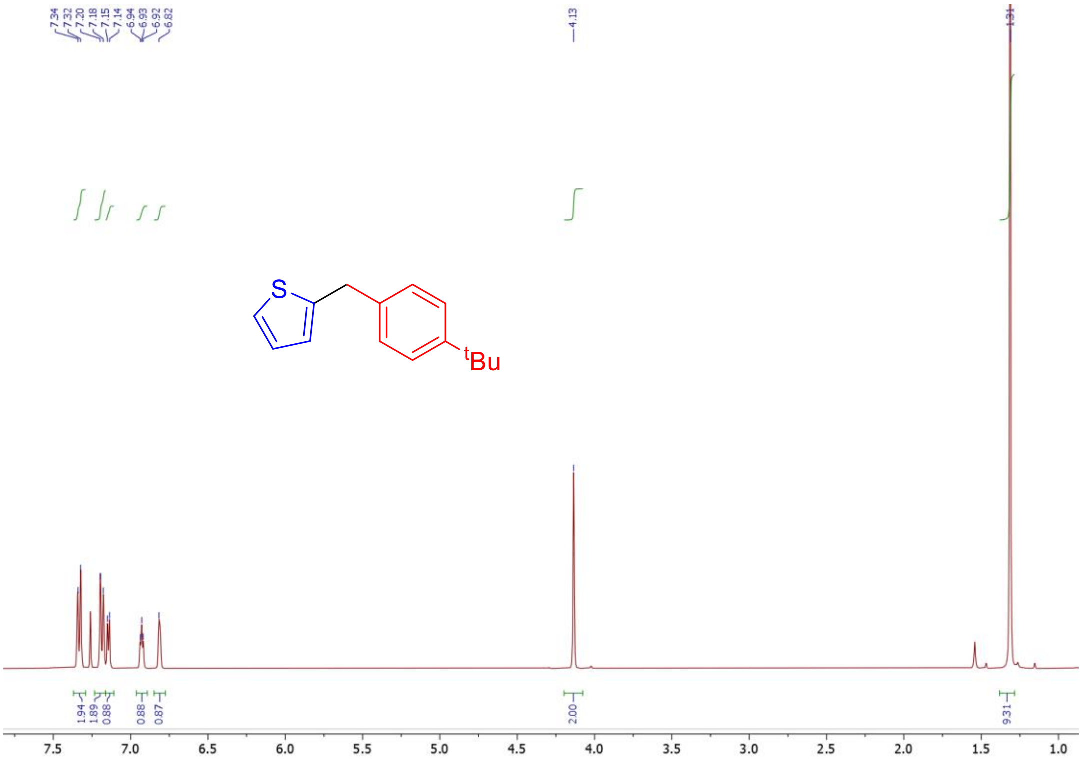


Figure S54. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9l**.

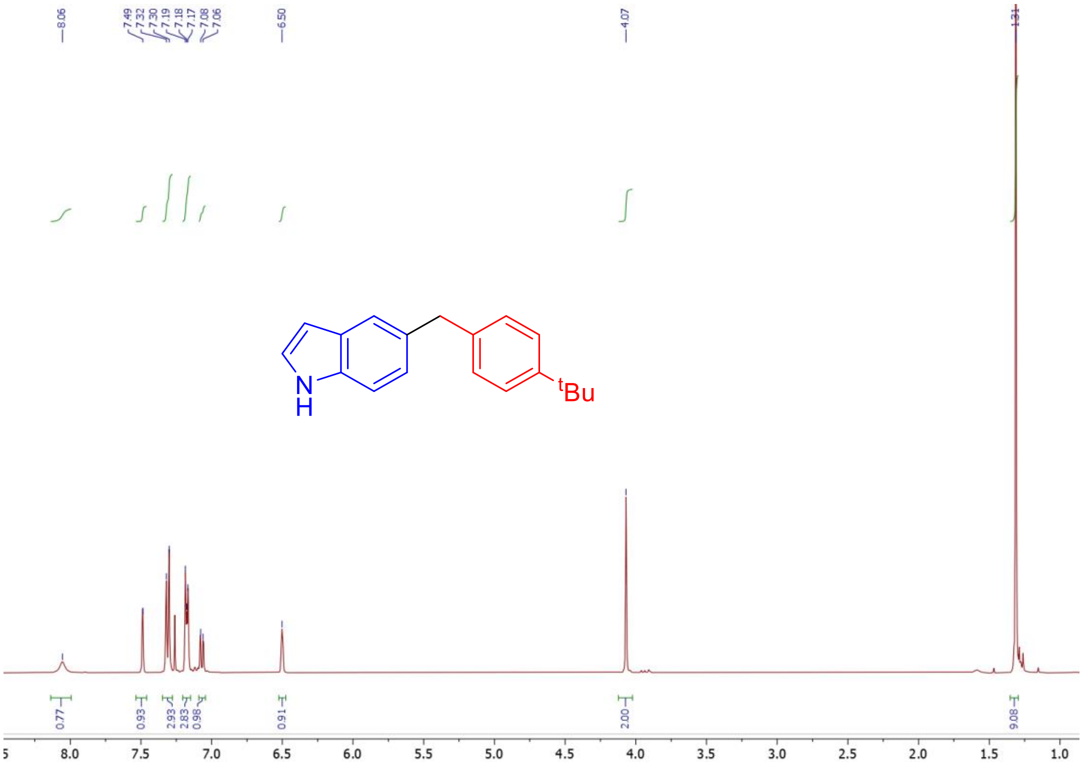


Figure S55. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **9m**.

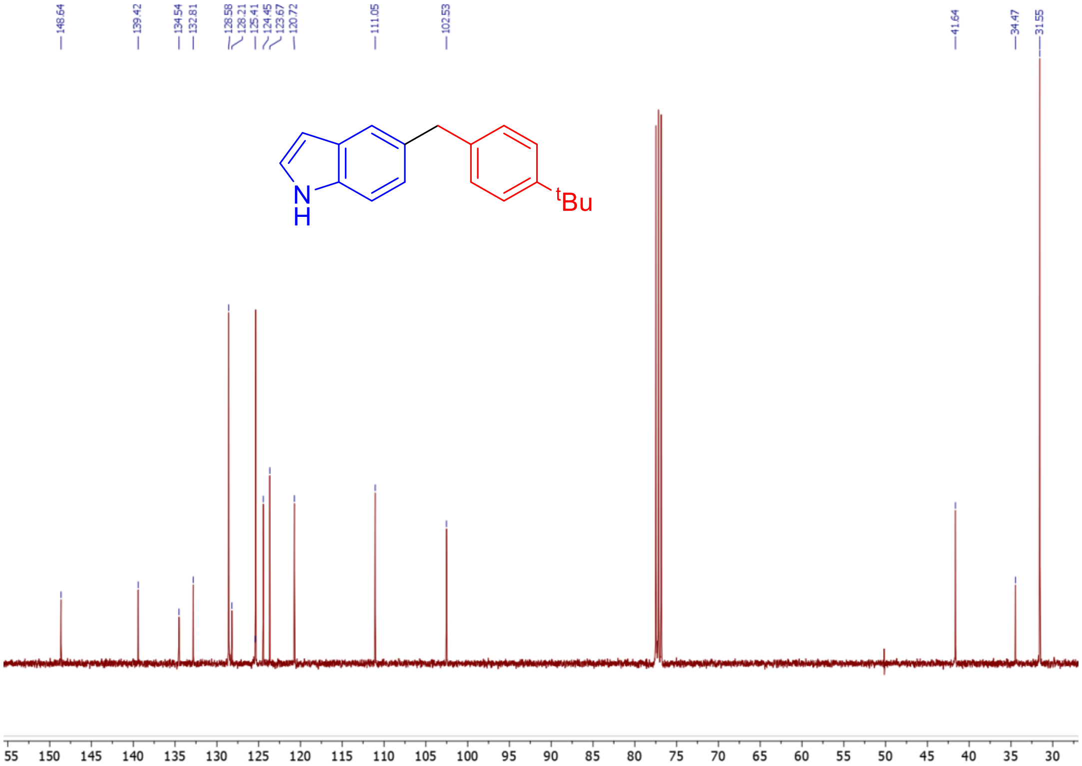


Figure S56. ^{13}C{^{1}H} NMR spectrum (150 MHz, CDCl$_3$) of **9m**.

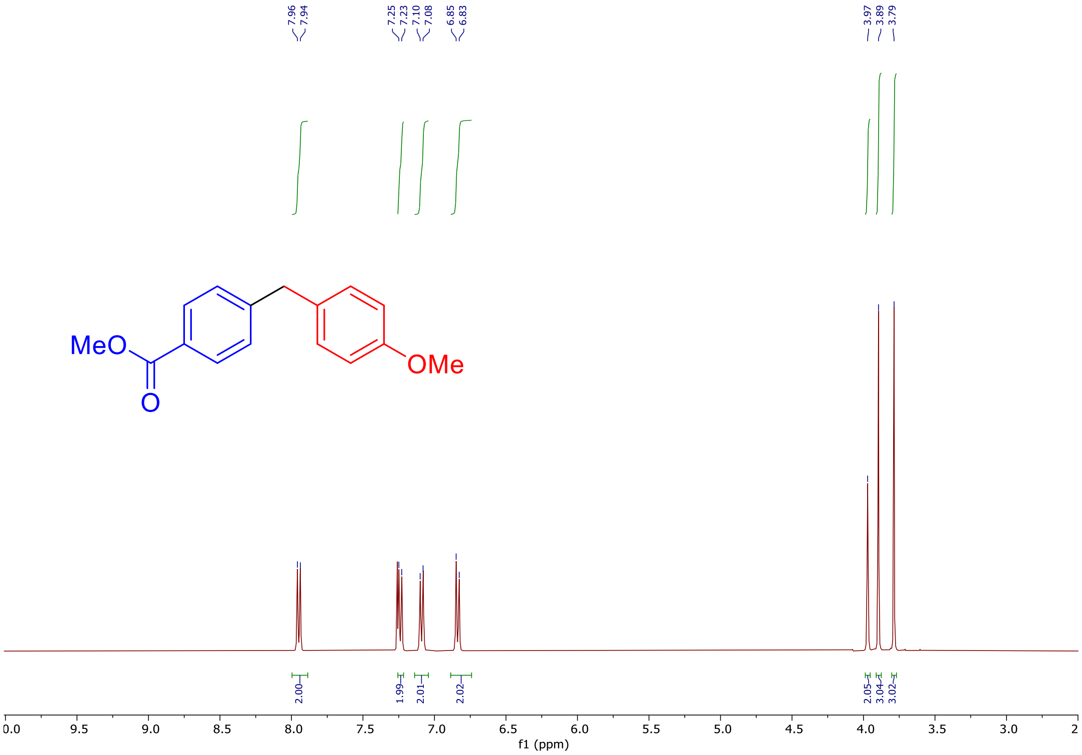


Figure S57. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9n**.

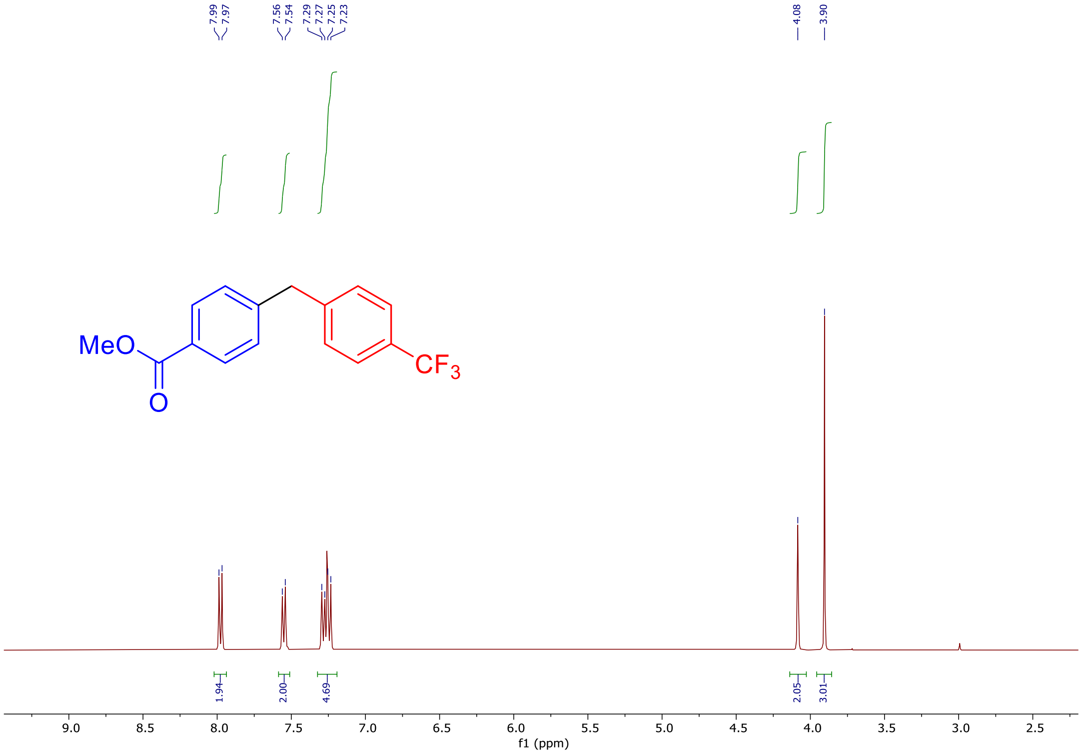


Figure S58. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9o**.

SXX. Cyclic Voltammetry

Cyclic voltammograms were recorded in an M-Braun glovebox under an N_2 atmosphere in DMF using concentrations of 0.1 mM tetraaminoethylene and 0.1 mM tetrabutylammonium hexafluorophosphate at a scan rate of 100 mVs^{-1}. Reduction potentials were calibrated against a ferrocene (Fc) internal standard and are reported versus Fc/Fc^+.

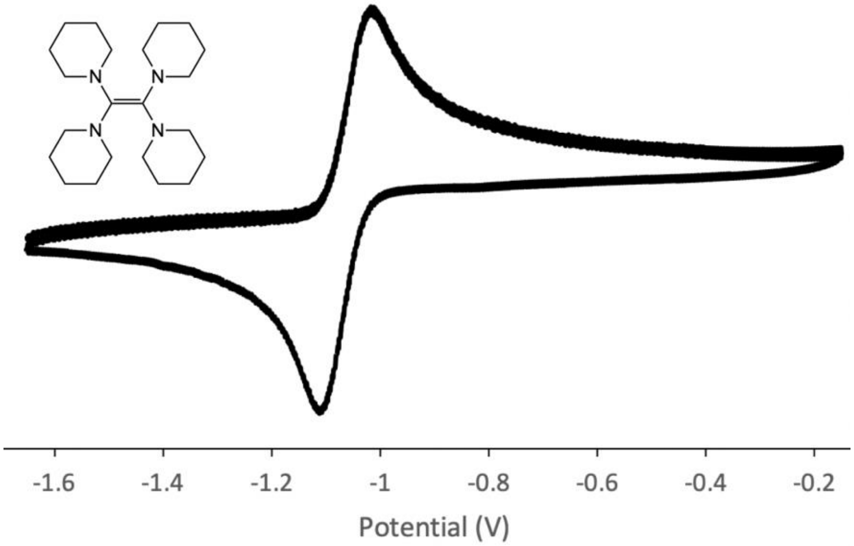


Figure S59. Cyclic voltammogram of TPiE.

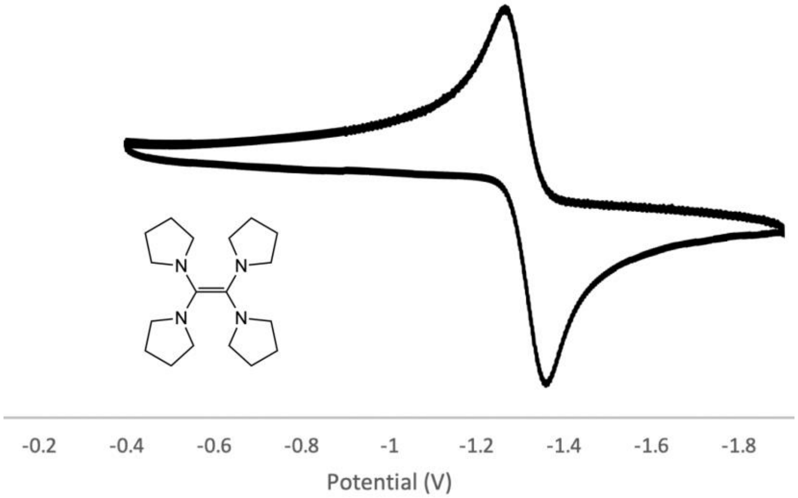


Figure S60. Cyclic voltammogram of TPyE.

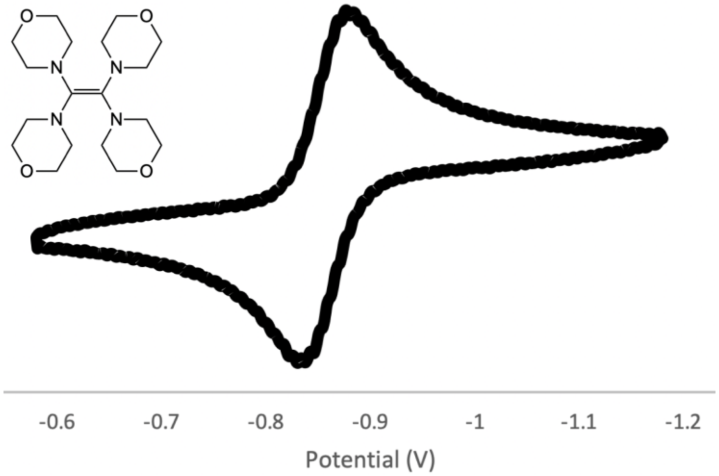


Figure S61. Cyclic voltammogram of TME.

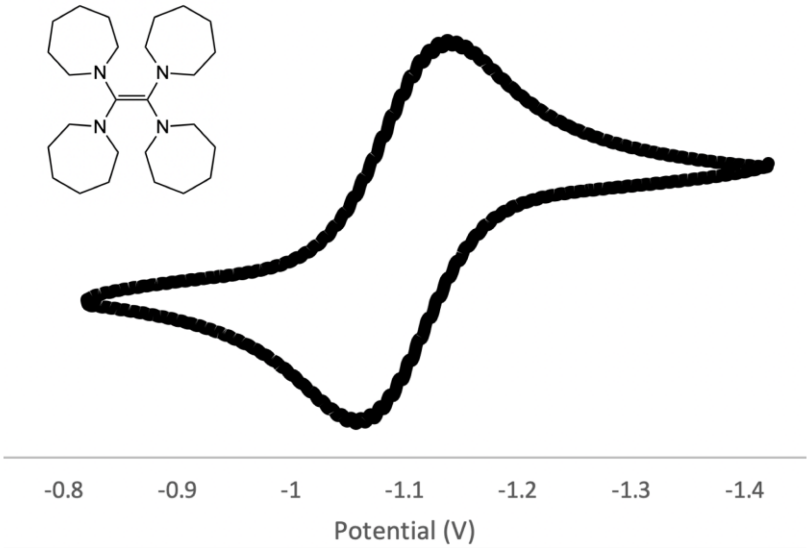


Figure S62. Cyclic voltammogram of TAzE.

SXXI. X-Ray Crystallographic Information

X-Ray Diffraction of TPiE: Crystals suitable for X-ray diffraction were grown by heating a supersaturated mixture of TPiE in DMAc at 80 °C. Once all TPiE had dissolved, the solution was allowed to cool slowly to room temperature, resulting in colorless crystals. Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα ($\lambda = 0.71073$ Å) for the structure of TPiE. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[21] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Both piperidine models are disordered over two positions. Their site occupancies were freely refined and converged to nearly equal population distributions (~50/50). All chemically equivalent C-C and C-N distances were restrained to be similar. The full numbering scheme of TPiE can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 2111617 contains the supplementary crystallographic data for this paper.

Table S7. Crystal data and structure refinement for TPiE.

Empirical formula	$C_{22}H_{40}N_4$	
Formula weight	360.58	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2/n	
Unit cell dimensions	a = 12.3100(3) Å	α= 90°
	b = 6.2310(2) Å	β= 92.468(3)°
	c = 14.1848(4) Å	γ = 90°
Volume	1087.02(5) Å^3	
Z	2	
Density (calculated)	1.102 Mg/m^3	
Absorption coefficient	0.066 mm^{-1}	
F(000)	400	
Crystal size	0.200 x 0.200 x 0.080 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	3.269 to 27.481°.	
Index ranges	-15<=h<=15, -8<=k<=8, -18<=l<=18	
Reflections collected	21240	
Independent reflections	2490 [R(int) = 0.0325]	
Observed reflections (I > 2sigma(I))	2110	
Completeness to theta = 25.242°	99.8%	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.38634
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	2490 / 40 / 210
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1017
R indices (all data)	R1 = 0.0505, wR2 = 0.1080
Largest diff. peak and hole	0.215 and -0.148 e.Å^{-3}

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for TPiE. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	3979(1)	6816(1)	2337(1)	25(1)
N(2)	3044(1)	7722(1)	3734(1)	26(1)
C(1)	2978(1)	7269(1)	2755(1)	22(1)
C(2)	4025(2)	5162(3)	1573(2)	32(1)
C(3)	5153(9)	4165(17)	1559(7)	52(2)
C(4)	5967(5)	5833(14)	1456(4)	49(1)
C(5)	5884(8)	7574(15)	2202(6)	57(2)
C(6)	4773(2)	8477(4)	2240(2)	32(1)
C(7)	2300(2)	9383(3)	4121(1)	32(1)
C(8)	2811(5)	10381(8)	5014(4)	45(1)
C(9)	3091(5)	8628(10)	5744(5)	45(1)
C(10)	3796(5)	6952(11)	5331(4)	49(1)
C(11)	3301(2)	6072(3)	4401(1)	30(1)
C(2B)	4204(2)	4657(3)	2145(2)	28(1)
C(3B)	5063(9)	4486(15)	1421(6)	35(1)
C(4B)	6125(5)	5769(12)	1749(4)	40(1)
C(5B)	5841(8)	8017(13)	2004(6)	43(1)
C(6B)	4921(2)	8092(4)	2700(2)	31(1)
C(7B)	2910(3)	9811(4)	4030(2)	37(1)
C(8B)	2568(6)	9829(11)	5045(5)	48(1)
C(9B)	3385(6)	8648(16)	5676(8)	54(2)
C(10B)	3579(7)	6394(13)	5290(6)	49(2)
C(11B)	3892(3)	6466(5)	4283(2)	38(1)

Table S9. Bond lengths [Å] and angles [°] for TPiE.

N(1)-C(2B)	1.403(2)
N(1)-C(1)	1.4177(11)
N(1)-C(6)	1.435(2)
N(1)-C(6B)	1.480(2)
N(1)-C(2)	1.499(2)
N(2)-C(7B)	1.380(3)
N(2)-C(1)	1.4161(12)
N(2)-C(11)	1.4237(19)
N(2)-C(11B)	1.496(3)
N(2)-C(7)	1.502(2)
C(1)-C(1)#1	1.3549(17)
C(2)-C(3)	1.522(11)

C(3)-C(4)	1.455(13)
C(4)-C(5)	1.522(12)
C(5)-C(6)	1.482(10)
C(7)-C(8)	1.523(5)
C(8)-C(9)	1.534(7)
C(9)-C(10)	1.494(8)
C(10)-C(11)	1.530(6)
C(2B)-C(3B)	1.511(11)
C(3B)-C(4B)	1.585(11)
C(4B)-C(5B)	1.492(12)
C(5B)-C(6B)	1.535(8)
C(7B)-C(8B)	1.517(7)
C(8B)-C(9B)	1.509(10)
C(9B)-C(10B)	1.530(10)
C(10B)-C(11B)	1.495(9)

C(2B)-N(1)-C(1)	117.03(10)
C(1)-N(1)-C(6)	120.30(12)
C(2B)-N(1)-C(6B)	115.12(15)
C(1)-N(1)-C(6B)	115.45(11)
C(1)-N(1)-C(2)	120.01(10)
C(6)-N(1)-C(2)	112.28(16)
C(7B)-N(2)-C(1)	118.95(13)
C(1)-N(2)-C(11)	120.62(10)
C(7B)-N(2)-C(11B)	115.2(2)
C(1)-N(2)-C(11B)	114.57(13)
C(1)-N(2)-C(7)	119.05(10)
C(11)-N(2)-C(7)	112.11(14)
C(1)#1-C(1)-N(2)	122.36(10)
C(1)#1-C(1)-N(1)	121.85(10)
N(2)-C(1)-N(1)	115.79(7)
N(1)-C(2)-C(3)	110.7(4)
C(4)-C(3)-C(2)	110.0(7)
C(3)-C(4)-C(5)	111.9(7)
C(6)-C(5)-C(4)	112.7(7)
N(1)-C(6)-C(5)	111.3(4)
N(2)-C(7)-C(8)	110.4(3)
C(7)-C(8)-C(9)	110.1(4)
C(10)-C(9)-C(8)	110.5(6)
C(9)-C(10)-C(11)	111.9(5)
N(2)-C(11)-C(10)	112.5(3)
N(1)-C(2B)-C(3B)	110.5(4)
C(2B)-C(3B)-C(4B)	110.9(6)
C(5B)-C(4B)-C(3B)	110.2(7)
C(4B)-C(5B)-C(6B)	111.8(6)
N(1)-C(6B)-C(5B)	110.5(4)
N(2)-C(7B)-C(8B)	109.7(3)
C(9B)-C(8B)-C(7B)	110.8(7)
C(8B)-C(9B)-C(10B)	110.2(8)
C(11B)-C(10B)-C(9B)	111.4(7)
N(2)-C(11B)-C(10B)	108.1(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y,-z+1/2

Table S10. Anisotropic displacement parameters ($Å^2 \times 10^3$) for TPiE. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	21(1)	24(1)	29(1)	-3(1)	2(1)	-1(1)
N(2)	24(1)	28(1)	25(1)	-2(1)	1(1)	0(1)
C(1)	24(1)	17(1)	27(1)	1(1)	3(1)	-1(1)
C(2)	34(1)	24(1)	38(2)	-8(1)	9(1)	-2(1)
C(3)	41(2)	40(4)	77(5)	-6(2)	26(3)	12(2)
C(4)	22(2)	69(3)	57(3)	-27(3)	1(2)	8(2)
C(5)	32(2)	71(5)	68(3)	-12(3)	17(2)	-23(3)
C(6)	32(1)	31(1)	35(1)	-5(1)	4(1)	-10(1)
C(7)	42(1)	23(1)	33(1)	-5(1)	10(1)	4(1)
C(8)	62(2)	34(2)	40(1)	-17(1)	17(1)	-17(1)
C(9)	48(3)	61(2)	26(2)	-12(1)	9(2)	-20(2)
C(10)	48(2)	74(3)	24(1)	-3(2)	-8(1)	-4(2)
C(11)	32(1)	33(1)	26(1)	2(1)	1(1)	2(1)
C(2B)	28(1)	24(1)	31(1)	-1(1)	4(1)	3(1)
C(3B)	44(3)	26(2)	36(2)	-7(2)	10(1)	6(2)
C(4B)	22(2)	51(2)	49(3)	-8(2)	6(2)	-1(2)
C(5B)	37(2)	33(2)	62(3)	-14(2)	29(2)	-12(2)
C(6B)	25(1)	35(1)	34(1)	-9(1)	4(1)	-7(1)
C(7B)	44(2)	28(1)	38(1)	-6(1)	10(1)	-7(1)
C(8B)	61(3)	39(3)	46(2)	-19(2)	18(2)	-11(2)
C(9B)	52(4)	83(4)	27(2)	-11(2)	6(3)	-29(3)
C(10B)	48(3)	63(4)	35(2)	1(2)	-5(2)	14(3)
C(11B)	26(2)	52(2)	37(1)	4(1)	0(1)	4(1)

Table S11. Torsion angles [°] for TPiE.

C(7B)-N(2)-C(1)-C(1)#1	-73.5(2)
C(11)-N(2)-C(1)-C(1)#1	109.71(14)
C(11B)-N(2)-C(1)-C(1)#1	144.56(17)
C(7)-N(2)-C(1)-C(1)#1	-36.30(15)
C(7B)-N(2)-C(1)-N(1)	106.4(2)
C(11)-N(2)-C(1)-N(1)	-70.39(16)
C(11B)-N(2)-C(1)-N(1)	-35.5(2)
C(7)-N(2)-C(1)-N(1)	143.60(14)
C(2B)-N(1)-C(1)-C(1)#1	-77.09(15)
C(6)-N(1)-C(1)-C(1)#1	111.02(17)
C(6B)-N(1)-C(1)-C(1)#1	142.50(16)
C(2)-N(1)-C(1)-C(1)#1	-36.62(16)
C(2B)-N(1)-C(1)-N(2)	103.01(15)
C(6)-N(1)-C(1)-N(2)	-68.88(19)
C(6B)-N(1)-C(1)-N(2)	-37.40(18)
C(2)-N(1)-C(1)-N(2)	143.48(15)
C(1)-N(1)-C(2)-C(3)	-152.6(4)
C(6)-N(1)-C(2)-C(3)	57.3(5)
N(1)-C(2)-C(3)-C(4)	-56.0(7)
C(2)-C(3)-C(4)-C(5)	53.7(9)
C(3)-C(4)-C(5)-C(6)	-52.9(9)
C(1)-N(1)-C(6)-C(5)	154.7(4)
C(2)-N(1)-C(6)-C(5)	-55.4(5)

C(4)-C(5)-C(6)-N(1)	52.6(7)
C(1)-N(2)-C(7)-C(8)	-153.4(2)
C(11)-N(2)-C(7)-C(8)	57.9(3)
N(2)-C(7)-C(8)-C(9)	-56.5(5)
C(7)-C(8)-C(9)-C(10)	54.9(6)
C(8)-C(9)-C(10)-C(11)	-52.7(6)
C(1)-N(2)-C(11)-C(10)	155.9(3)
C(7)-N(2)-C(11)-C(10)	-56.0(4)
C(9)-C(10)-C(11)-N(2)	54.1(6)
C(1)-N(1)-C(2B)-C(3B)	160.4(4)
C(6B)-N(1)-C(2B)-C(3B)	-59.1(5)
N(1)-C(2B)-C(3B)-C(4B)	55.3(7)
C(2B)-C(3B)-C(4B)-C(5B)	-52.6(8)
C(3B)-C(4B)-C(5B)-C(6B)	51.1(9)
C(2B)-N(1)-C(6B)-C(5B)	57.2(5)
C(1)-N(1)-C(6B)-C(5B)	-161.7(4)
C(4B)-C(5B)-C(6B)-N(1)	-52.4(7)
C(1)-N(2)-C(7B)-C(8B)	157.7(3)
C(11B)-N(2)-C(7B)-C(8B)	-60.6(5)
N(2)-C(7B)-C(8B)-C(9B)	56.6(6)
C(7B)-C(8B)-C(9B)-C(10B)	-53.4(8)
C(8B)-C(9B)-C(10B)-C(11B)	53.9(9)
C(7B)-N(2)-C(11B)-C(10B)	59.8(5)
C(1)-N(2)-C(11B)-C(10B)	-156.8(4)
C(9B)-C(10B)-C(11B)-N(2)	-53.8(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y,-z+1/2

X-Ray Diffraction of TPyE: Crystals suitable for X-ray diffraction were grown by heating a supersaturated mixture of TPyE in DMAc at 80 °C. Once all TPyE had dissolved, the solution was allowed to cool slowly to room temperature, resulting in colorless crystals. Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα ($\lambda = 0.71073$ Å) for the structure of TPyE. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[21] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 2111616 contains the supplementary crystallographic data for this paper.

Table S12. Crystal data and structure refinement for TPyE.

Empirical formula	C18 H32 N4	
Formula weight	304.47	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.9752(2) Å	α= 92.009(3)°
	b = 11.9721(4) Å	β= 96.897(3)°
	c = 12.2482(5) Å	γ = 94.606(3)°
Volume	866.15(5) Å^3	
Z	2	
Density (calculated)	1.167 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	336	
Crystal size	0.350 x 0.240 x 0.120 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	3.354 to 28.279°.	
Index ranges	-7<=h<=7, -15<=k<=15, -16<=l<=16	
Reflections collected	17242	
Independent reflections	4276 [R(int) = 0.0344]	
Observed reflections (I > 2sigma(I))	3512	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.51122	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	4276 / 0 / 199	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1249	

R indices (all data)	R1 = 0.0606, wR2 = 0.1327
Extinction coefficient	n/a
Largest diff. peak and hole	0.381 and -0.204 e.Å^{-3}

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for TPyE. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	1723(2)	7738(1)	3889(1)	24(1)
N(2)	2022(2)	5998(1)	2945(1)	26(1)
N(3)	1725(2)	8798(1)	1770(1)	22(1)
N(4)	3457(2)	7256(1)	1146(1)	31(1)
C(1)	2053(2)	7171(1)	2907(1)	20(1)
C(2)	2393(2)	7722(1)	1985(1)	21(1)
C(3)	-147(2)	7412(1)	4494(1)	23(1)
C(4)	111(2)	8293(1)	5443(1)	26(1)
C(5)	2660(2)	8607(1)	5634(1)	34(1)
C(6)	3328(2)	8585(1)	4468(1)	29(1)
C(7)	3444(2)	5457(1)	3784(1)	23(1)
C(8)	3222(2)	4233(1)	3368(1)	25(1)
C(9)	885(2)	4089(1)	2695(1)	30(1)
C(10)	675(2)	5217(1)	2162(1)	24(1)
C(11)	-260(2)	9224(1)	2162(1)	22(1)
C(12)	-324(2)	10353(1)	1641(1)	26(1)
C(13)	2170(3)	10782(1)	1740(2)	37(1)
C(14)	3441(2)	9724(1)	1675(1)	24(1)
C(15)	2842(2)	7431(1)	-10(1)	28(1)
C(16)	4340(2)	6702(1)	-590(1)	24(1)
C(17)	6406(2)	6646(1)	261(1)	25(1)
C(18)	5382(2)	6594(1)	1344(1)	22(1)

Table S14. Bond lengths [Å] and angles [°] for TPyE.

N(1)-C(1)	1.4027(15)
N(1)-C(6)	1.4422(16)
N(1)-C(3)	1.4489(15)
N(2)-C(1)	1.4055(15)
N(2)-C(10)	1.4393(16)
N(2)-C(7)	1.4568(15)
N(3)-C(2)	1.4044(15)
N(3)-C(11)	1.4541(14)
N(3)-C(14)	1.4656(16)
N(4)-C(2)	1.3948(15)
N(4)-C(15)	1.4457(16)
N(4)-C(18)	1.4499(15)
C(1)-C(2)	1.3556(17)
C(3)-C(4)	1.5276(17)
C(4)-C(5)	1.5269(19)
C(5)-C(6)	1.5288(18)
C(7)-C(8)	1.5252(17)
C(8)-C(9)	1.5282(18)
C(9)-C(10)	1.5282(17)

C(11)-C(12)	1.5163(17)
C(12)-C(13)	1.526(2)
C(13)-C(14)	1.5322(18)
C(15)-C(16)	1.5184(17)
C(16)-C(17)	1.5241(18)
C(17)-C(18)	1.5280(17)

C(1)-N(1)-C(6)	124.11(10)
C(1)-N(1)-C(3)	122.06(10)
C(6)-N(1)-C(3)	113.33(10)
C(1)-N(2)-C(10)	124.55(10)
C(1)-N(2)-C(7)	121.98(10)
C(10)-N(2)-C(7)	113.44(10)
C(2)-N(3)-C(11)	122.94(10)
C(2)-N(3)-C(14)	119.77(10)
C(11)-N(3)-C(14)	110.22(9)
C(2)-N(4)-C(15)	123.72(10)
C(2)-N(4)-C(18)	123.44(10)
C(15)-N(4)-C(18)	112.76(10)
C(2)-C(1)-N(1)	122.00(11)
C(2)-C(1)-N(2)	122.31(11)
N(1)-C(1)-N(2)	115.69(10)
C(1)-C(2)-N(4)	122.31(11)
C(1)-C(2)-N(3)	124.45(11)
N(4)-C(2)-N(3)	113.24(10)
N(1)-C(3)-C(4)	103.25(10)
C(5)-C(4)-C(3)	103.10(10)
C(4)-C(5)-C(6)	102.95(10)
N(1)-C(6)-C(5)	103.26(11)
N(2)-C(7)-C(8)	103.41(10)
C(7)-C(8)-C(9)	103.56(10)
C(8)-C(9)-C(10)	103.47(10)
N(2)-C(10)-C(9)	103.41(10)
N(3)-C(11)-C(12)	101.96(10)
C(11)-C(12)-C(13)	102.99(10)
C(12)-C(13)-C(14)	104.93(11)
N(3)-C(14)-C(13)	104.45(10)
N(4)-C(15)-C(16)	104.12(10)
C(15)-C(16)-C(17)	103.41(10)
C(16)-C(17)-C(18)	102.90(10)
N(4)-C(18)-C(17)	102.86(9)

Symmetry transformations used to generate equivalent atoms:

Table S15. Anisotropic displacement parameters (Å^2 x 10^3) for TPyE. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	27(1)	25(1)	21(1)	-5(1)	9(1)	-6(1)
N(2)	38(1)	18(1)	20(1)	1(1)	-9(1)	4(1)
N(3)	19(1)	19(1)	31(1)	4(1)	10(1)	6(1)
N(4)	40(1)	40(1)	18(1)	7(1)	8(1)	28(1)
C(1)	24(1)	19(1)	19(1)	-1(1)	3(1)	4(1)
C(2)	22(1)	20(1)	22(1)	1(1)	5(1)	7(1)

C(3)	22(1)	24(1)	24(1)	-1(1)	7(1)	-1(1)
C(4)	30(1)	26(1)	25(1)	-2(1)	10(1)	2(1)
C(5)	30(1)	45(1)	24(1)	-10(1)	0(1)	0(1)
C(6)	20(1)	37(1)	29(1)	-10(1)	4(1)	-3(1)
C(7)	23(1)	24(1)	20(1)	2(1)	-4(1)	4(1)
C(8)	27(1)	23(1)	24(1)	3(1)	-2(1)	8(1)
C(9)	30(1)	21(1)	34(1)	4(1)	-8(1)	-1(1)
C(10)	23(1)	21(1)	27(1)	2(1)	-6(1)	3(1)
C(11)	17(1)	22(1)	29(1)	1(1)	7(1)	6(1)
C(12)	28(1)	25(1)	26(1)	3(1)	3(1)	13(1)
C(13)	36(1)	21(1)	58(1)	5(1)	18(1)	3(1)
C(14)	19(1)	25(1)	28(1)	1(1)	6(1)	2(1)
C(15)	25(1)	41(1)	19(1)	-2(1)	0(1)	14(1)
C(16)	25(1)	28(1)	21(1)	-3(1)	6(1)	2(1)
C(17)	21(1)	27(1)	29(1)	2(1)	8(1)	7(1)
C(18)	21(1)	23(1)	23(1)	3(1)	3(1)	10(1)

Table S16. Torsion angles [°] for TPyE.

C(6)-N(1)-C(1)-C(2)	-58.75(18)
C(3)-N(1)-C(1)-C(2)	129.93(14)
C(6)-N(1)-C(1)-N(2)	120.89(14)
C(3)-N(1)-C(1)-N(2)	-50.42(16)
C(10)-N(2)-C(1)-C(2)	-51.11(19)
C(7)-N(2)-C(1)-C(2)	126.87(14)
C(10)-N(2)-C(1)-N(1)	129.25(13)
C(7)-N(2)-C(1)-N(1)	-52.77(17)
N(1)-C(1)-C(2)-N(4)	157.77(12)
N(2)-C(1)-C(2)-N(4)	-21.8(2)
N(1)-C(1)-C(2)-N(3)	-22.4(2)
N(2)-C(1)-C(2)-N(3)	157.94(12)
C(15)-N(4)-C(2)-C(1)	144.56(14)
C(18)-N(4)-C(2)-C(1)	-39.0(2)
C(15)-N(4)-C(2)-N(3)	-35.25(19)
C(18)-N(4)-C(2)-N(3)	141.17(13)
C(11)-N(3)-C(2)-C(1)	-31.46(19)
C(14)-N(3)-C(2)-C(1)	116.21(14)
C(11)-N(3)-C(2)-N(4)	148.36(12)
C(14)-N(3)-C(2)-N(4)	-63.98(15)
C(1)-N(1)-C(3)-C(4)	-176.89(11)
C(6)-N(1)-C(3)-C(4)	10.93(14)
N(1)-C(3)-C(4)-C(5)	-29.89(13)
C(3)-C(4)-C(5)-C(6)	37.68(14)
C(1)-N(1)-C(6)-C(5)	-159.35(12)
C(3)-N(1)-C(6)-C(5)	12.64(15)
C(4)-C(5)-C(6)-N(1)	-30.86(14)
C(1)-N(2)-C(7)-C(8)	-168.66(11)
C(10)-N(2)-C(7)-C(8)	9.53(15)
N(2)-C(7)-C(8)-C(9)	-27.88(13)
C(7)-C(8)-C(9)-C(10)	35.87(13)
C(1)-N(2)-C(10)-C(9)	-168.99(12)
C(7)-N(2)-C(10)-C(9)	12.87(15)
C(8)-C(9)-C(10)-N(2)	-29.83(14)
C(2)-N(3)-C(11)-C(12)	-175.71(11)

C(14)-N(3)-C(11)-C(12)	33.95(13)
N(3)-C(11)-C(12)-C(13)	-39.02(13)
C(11)-C(12)-C(13)-C(14)	30.87(14)
C(2)-N(3)-C(14)-C(13)	-165.97(11)
C(11)-N(3)-C(14)-C(13)	-14.55(14)
C(12)-C(13)-C(14)-N(3)	-10.87(14)
C(2)-N(4)-C(15)-C(16)	-176.23(13)
C(18)-N(4)-C(15)-C(16)	7.01(16)
N(4)-C(15)-C(16)-C(17)	-27.44(14)
C(15)-C(16)-C(17)-C(18)	37.22(13)
C(2)-N(4)-C(18)-C(17)	-160.50(13)
C(15)-N(4)-C(18)-C(17)	16.27(15)
C(16)-C(17)-C(18)-N(4)	-32.58(13)

X-Ray Diffraction of TME: Crystals suitable for X-ray diffraction were grown by heating a supersaturated mixture of TME in DMAc at 80 °C. Once all TME had dissolved, the solution was allowed to cool slowly to room temperature, resulting in colorless crystals. Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of TME. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[21] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 2111618 contains the supplementary crystallographic data for this paper.

Table S17. Crystal data and structure refinement for TME.

Empirical formula	C18 H32 N4 O4	
Formula weight	368.47	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2/c	
Unit cell dimensions	a = 11.8750(10) Å	α= 90°
	b = 6.0835(2) Å	β= 134.314(14)°
	c = 18.3743(15) Å	γ = 90°
Volume	949.8(2) Å^3	
Z	2	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	400	
Crystal size	0.500 x 0.500 x 0.100 mm^3	
Crystal color and habit	colorless block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	3.099 to 28.278°.	
Index ranges	-15<=h<=15, -8<=k<=8, -24<=l<=24	
Reflections collected	18066	
Independent reflections	2354 [R(int) = 0.0293]	
Observed reflections (I > 2sigma(I))	2153	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.58947	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	2354 / 0 / 118	
Goodness-of-fit on F^2	1.050	

Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0920
R indices (all data)	R1 = 0.0385, wR2 = 0.0940
Extinction coefficient	n/a
Largest diff. peak and hole	0.371 and -0.217 e.Å^{-3}

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for TME. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9345(1)	757(1)	5851(1)	20(1)
O(2)	7261(1)	3770(1)	1258(1)	16(1)
N(1)	6890(1)	2214(1)	3820(1)	10(1)
N(2)	6411(1)	3229(1)	2359(1)	10(1)
C(1)	5780(1)	2720(1)	2768(1)	9(1)
C(2)	8414(1)	3309(2)	4500(1)	13(1)
C(3)	9182(1)	3027(2)	5590(1)	17(1)
C(4)	7056(1)	-108(2)	4088(1)	15(1)
C(5)	7845(1)	-294(2)	5181(1)	19(1)
C(6)	5545(1)	4721(2)	1495(1)	13(1)
C(7)	6635(1)	5553(2)	1392(1)	15(1)
C(8)	7103(1)	1415(2)	2256(1)	12(1)
C(9)	8130(1)	2324(2)	2114(1)	15(1)

Table S19. Bond lengths [Å] and angles [°] for TME.

O(1)-C(5)	1.4265(12)
O(1)-C(3)	1.4302(12)
O(2)-C(7)	1.4300(11)
O(2)-C(9)	1.4309(11)
N(1)-C(1)	1.4169(11)
N(1)-C(2)	1.4563(11)
N(1)-C(4)	1.4630(11)
N(2)-C(1)	1.4182(10)
N(2)-C(6)	1.4560(11)
N(2)-C(8)	1.4653(11)
C(1)-C(1)#1	1.3616(16)
C(2)-C(3)	1.5235(12)
C(4)-C(5)	1.5155(13)
C(6)-C(7)	1.5202(12)
C(8)-C(9)	1.5172(12)
C(5)-O(1)-C(3)	110.38(7)
C(7)-O(2)-C(9)	109.84(7)
C(1)-N(1)-C(2)	118.98(7)
C(1)-N(1)-C(4)	116.52(7)
C(2)-N(1)-C(4)	111.03(7)
C(1)-N(2)-C(6)	118.83(7)
C(1)-N(2)-C(8)	117.12(7)
C(6)-N(2)-C(8)	111.21(7)
C(1)#1-C(1)-N(1)	119.11(9)
C(1)#1-C(1)-N(2)	124.86(9)
N(1)-C(1)-N(2)	116.02(7)

N(1)-C(2)-C(3)	108.64(7)
O(1)-C(3)-C(2)	111.50(8)
N(1)-C(4)-C(5)	109.31(8)
O(1)-C(5)-C(4)	110.71(8)
N(2)-C(6)-C(7)	109.20(7)
O(2)-C(7)-C(6)	111.05(7)
N(2)-C(8)-C(9)	109.77(7)
O(2)-C(9)-C(8)	111.34(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

Table S20. Anisotropic displacement parameters (Å^2 x 10^3) for TME. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	15(1)	26(1)	11(1)	6(1)	6(1)	5(1)
O(2)	19(1)	20(1)	16(1)	2(1)	15(1)	3(1)
N(1)	8(1)	11(1)	7(1)	1(1)	4(1)	-1(1)
N(2)	11(1)	11(1)	10(1)	3(1)	8(1)	3(1)
C(1)	10(1)	9(1)	8(1)	1(1)	6(1)	0(1)
C(2)	9(1)	16(1)	9(1)	-1(1)	5(1)	-2(1)
C(3)	14(1)	23(1)	10(1)	-1(1)	6(1)	-1(1)
C(4)	15(1)	12(1)	13(1)	3(1)	9(1)	0(1)
C(5)	19(1)	21(1)	16(1)	7(1)	12(1)	3(1)
C(6)	14(1)	14(1)	14(1)	5(1)	11(1)	4(1)
C(7)	19(1)	15(1)	16(1)	2(1)	14(1)	1(1)
C(8)	13(1)	13(1)	13(1)	1(1)	10(1)	3(1)
C(9)	13(1)	19(1)	15(1)	1(1)	11(1)	2(1)

Table S21. Torsion angles [°] for TME.

C(2)-N(1)-C(1)-C(1)#1	-145.90(6)
C(4)-N(1)-C(1)-C(1)#1	76.82(8)
C(2)-N(1)-C(1)-N(2)	33.16(11)
C(4)-N(1)-C(1)-N(2)	-104.13(9)
C(6)-N(2)-C(1)-C(1)#1	28.34(10)
C(8)-N(2)-C(1)-C(1)#1	-109.90(6)
C(6)-N(2)-C(1)-N(1)	-150.65(8)
C(8)-N(2)-C(1)-N(1)	71.11(10)
C(1)-N(1)-C(2)-C(3)	163.53(8)
C(4)-N(1)-C(2)-C(3)	-57.03(9)
C(5)-O(1)-C(3)-C(2)	-58.81(10)
N(1)-C(2)-C(3)-O(1)	57.39(10)
C(1)-N(1)-C(4)-C(5)	-161.58(7)
C(2)-N(1)-C(4)-C(5)	57.90(9)
C(3)-O(1)-C(5)-C(4)	58.84(10)
N(1)-C(4)-C(5)-O(1)	-58.14(10)
C(1)-N(2)-C(6)-C(7)	163.14(7)
C(8)-N(2)-C(6)-C(7)	-56.35(9)
C(9)-O(2)-C(7)-C(6)	-59.84(9)
N(2)-C(6)-C(7)-O(2)	58.57(9)

C(1)-N(2)-C(8)-C(9)	-163.17(7)
C(6)-N(2)-C(8)-C(9)	55.57(9)
C(7)-O(2)-C(9)-C(8)	58.86(10)
N(2)-C(8)-C(9)-O(2)	-56.56(9)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

X-Ray Diffraction of TAzE: Crystals suitable for X-ray diffraction were grown by heating a supersaturated mixture of TAzE in DMAc at 80 °C. Once all TAzE had dissolved, the solution was allowed to cool slowly to room temperature, resulting in colorless crystals. Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of TAzE. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[21] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 2111619 contains the supplementary crystallographic data for this paper.

Table S22. Crystal data and structure refinement for TAzE.

Empirical formula	C104 H192 N16	
Formula weight	1666.72	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P2/c	
Unit cell dimensions	a = 20.0666(5) Å	α= 90°
	b = 6.57270(10) Å	β= 91.303(2)°
	c = 18.5611(4) Å	γ = 90°
Volume	2447.42(9) Å^3	
Z	1	
Density (calculated)	1.131 Mg/m^3	
Absorption coefficient	0.500 mm^{-1}	
F(000)	928	
Crystal size	0.200 x 0.080 x 0.020 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	2.202 to 66.598°.	
Index ranges	-23<=h<=23, -7<=k<=7, -22<=l<=22	
Reflections collected	73896	
Independent reflections	4292 [R(int) = 0.0868]	
Observed reflections (I > 2sigma(I))	3597	
Completeness to theta = 66.598°	99.3%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.63774	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	4292 / 0 / 272	

Goodness-of-fit on F^2	1.156
Final R indices [I>2sigma(I)]	R1 = 0.0960, wR2 = 0.2564
R indices (all data)	R1 = 0.1110, wR2 = 0.2690
Extinction coefficient	0.0012(3)
Largest diff. peak and hole	0.698 and -0.283 e.Å^{-3}

Table S23. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for TAzE. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	6984(2)	2524(5)	4193(2)	28(1)
N(2)	6635(2)	2657(5)	5398(2)	26(1)
N(3)	8337(2)	1667(5)	4795(2)	29(1)
N(4)	8032(2)	3548(5)	5817(2)	27(1)
C(1)	7173(2)	2608(6)	4927(2)	27(1)
C(2)	7817(2)	2622(6)	5165(2)	26(1)
C(3)	6546(2)	853(6)	3962(2)	31(1)
C(4)	6302(2)	957(6)	3185(2)	31(1)
C(5)	5930(2)	2927(7)	2992(2)	33(1)
C(6)	6386(2)	4643(7)	2755(2)	34(1)
C(7)	6877(2)	5406(7)	3333(2)	35(1)
C(8)	7324(2)	3754(6)	3676(2)	30(1)
C(9)	6136(2)	4238(6)	5271(2)	30(1)
C(10)	5564(2)	4276(6)	5790(2)	29(1)
C(11)	5131(2)	2352(7)	5792(3)	38(1)
C(12)	5410(2)	645(7)	6270(2)	36(1)
C(13)	6075(2)	-184(6)	6057(2)	33(1)
C(14)	6639(2)	1377(6)	6036(2)	29(1)
C(15)	8179(2)	-173(6)	4396(2)	31(1)
C(16)	8773(2)	-1523(7)	4227(3)	38(1)
C(17)	9152(2)	-896(7)	3563(3)	42(1)
C(18)	9572(2)	1023(7)	3649(3)	40(1)
C(19)	9192(2)	2891(7)	3914(3)	40(1)
C(20)	8962(2)	2742(7)	4676(2)	35(1)
C(21)	8346(2)	2272(6)	6375(2)	31(1)
C(22)	9052(2)	2900(7)	6583(2)	33(1)
C(23)	9117(2)	4905(7)	7002(2)	36(1)
C(24)	8751(2)	6695(6)	6671(2)	34(1)
C(25)	8000(2)	6475(6)	6681(2)	32(1)
C(26)	7677(2)	5372(6)	6042(2)	28(1)

Table S24. Bond lengths [Å] and angles [°] for TAzE.

N(1)-C(1)	1.407(5)
N(1)-C(8)	1.439(5)
N(1)-C(3)	1.465(5)
N(2)-C(1)	1.405(5)
N(2)-C(14)	1.453(5)
N(2)-C(9)	1.459(5)
N(3)-C(2)	1.409(5)
N(3)-C(15)	1.449(5)
N(3)-C(20)	1.459(5)

N(4)-C(2)	1.414(5)
N(4)-C(26)	1.462(5)
N(4)-C(21)	1.463(5)
C(1)-C(2)	1.357(6)
C(3)-C(4)	1.514(6)
C(4)-C(5)	1.533(6)
C(5)-C(6)	1.522(6)
C(6)-C(7)	1.525(6)
C(7)-C(8)	1.538(6)
C(9)-C(10)	1.517(6)
C(10)-C(11)	1.534(6)
C(11)-C(12)	1.528(6)
C(12)-C(13)	1.504(6)
C(13)-C(14)	1.529(6)
C(15)-C(16)	1.525(6)
C(16)-C(17)	1.519(6)
C(17)-C(18)	1.523(7)
C(18)-C(19)	1.532(6)
C(19)-C(20)	1.502(6)
C(21)-C(22)	1.518(6)
C(22)-C(23)	1.535(6)
C(23)-C(24)	1.510(6)
C(24)-C(25)	1.516(6)
C(25)-C(26)	1.522(6)
C(1)-N(1)-C(8)	120.1(3)
C(1)-N(1)-C(3)	117.4(3)
C(8)-N(1)-C(3)	121.2(3)
C(1)-N(2)-C(14)	120.3(3)
C(1)-N(2)-C(9)	116.7(3)
C(14)-N(2)-C(9)	122.4(3)
C(2)-N(3)-C(15)	117.7(3)
C(2)-N(3)-C(20)	120.4(3)
C(15)-N(3)-C(20)	120.4(3)
C(2)-N(4)-C(26)	117.2(3)
C(2)-N(4)-C(21)	118.5(3)
C(26)-N(4)-C(21)	118.2(3)
C(2)-C(1)-N(2)	122.4(4)
C(2)-C(1)-N(1)	123.4(4)
N(2)-C(1)-N(1)	114.2(3)
C(1)-C(2)-N(3)	123.3(4)
C(1)-C(2)-N(4)	123.5(4)
N(3)-C(2)-N(4)	113.2(3)
N(1)-C(3)-C(4)	115.1(3)
C(3)-C(4)-C(5)	114.0(3)
C(6)-C(5)-C(4)	113.7(3)
C(5)-C(6)-C(7)	115.0(3)
C(6)-C(7)-C(8)	114.9(4)
N(1)-C(8)-C(7)	113.0(3)
N(2)-C(9)-C(10)	115.9(3)
C(9)-C(10)-C(11)	115.1(4)
C(12)-C(11)-C(10)	114.0(4)
C(13)-C(12)-C(11)	115.3(4)
C(12)-C(13)-C(14)	115.2(4)
N(2)-C(14)-C(13)	114.7(3)
N(3)-C(15)-C(16)	115.3(4)

C(17)-C(16)-C(15)	114.7(4)
C(16)-C(17)-C(18)	115.1(4)
C(17)-C(18)-C(19)	114.8(4)
C(20)-C(19)-C(18)	114.6(4)
N(3)-C(20)-C(19)	117.2(4)
N(4)-C(21)-C(22)	114.1(3)
C(21)-C(22)-C(23)	115.5(4)
C(24)-C(23)-C(22)	115.3(3)
C(23)-C(24)-C(25)	113.3(4)
C(24)-C(25)-C(26)	116.2(4)
N(4)-C(26)-C(25)	114.3(3)

Table S25. Anisotropic displacement parameters (Å^2 x 10^3) for TAzE. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	35(2)	21(2)	28(2)	0(1)	-1(1)	-3(1)
N(2)	32(2)	16(2)	29(2)	3(1)	2(1)	2(1)
N(3)	29(2)	26(2)	32(2)	-5(2)	4(1)	-1(1)
N(4)	32(2)	20(2)	29(2)	1(1)	-1(1)	2(1)
C(1)	34(2)	13(2)	33(2)	0(2)	2(2)	2(2)
C(2)	33(2)	15(2)	31(2)	-1(2)	2(2)	0(2)
C(3)	37(2)	22(2)	35(2)	0(2)	-2(2)	-5(2)
C(4)	37(2)	25(2)	32(2)	-3(2)	-1(2)	-4(2)
C(5)	34(2)	32(2)	34(2)	0(2)	-4(2)	1(2)
C(6)	39(2)	30(2)	32(2)	6(2)	0(2)	5(2)
C(7)	45(2)	23(2)	36(2)	3(2)	-1(2)	-3(2)
C(8)	34(2)	27(2)	29(2)	-1(2)	-1(2)	-5(2)
C(9)	34(2)	22(2)	35(2)	4(2)	-3(2)	3(2)
C(10)	32(2)	23(2)	33(2)	0(2)	-3(2)	3(2)
C(11)	31(2)	30(2)	52(3)	6(2)	1(2)	-2(2)
C(12)	37(2)	28(2)	42(2)	8(2)	4(2)	-4(2)
C(13)	41(2)	19(2)	38(2)	2(2)	1(2)	-2(2)
C(14)	32(2)	25(2)	30(2)	4(2)	1(2)	0(2)
C(15)	39(2)	22(2)	33(2)	-3(2)	4(2)	1(2)
C(16)	42(3)	25(2)	48(3)	-6(2)	3(2)	2(2)
C(17)	47(3)	32(2)	46(3)	-9(2)	10(2)	4(2)
C(18)	43(3)	36(3)	43(3)	-3(2)	15(2)	1(2)
C(19)	48(3)	26(2)	47(3)	-1(2)	6(2)	-3(2)
C(20)	36(2)	29(2)	39(2)	-5(2)	5(2)	-5(2)
C(21)	38(2)	21(2)	33(2)	2(2)	-1(2)	3(2)
C(22)	36(2)	32(2)	31(2)	2(2)	-2(2)	6(2)
C(23)	35(2)	33(2)	39(2)	1(2)	-9(2)	-1(2)
C(24)	41(2)	21(2)	41(2)	-1(2)	-5(2)	-4(2)
C(25)	42(2)	20(2)	35(2)	-3(2)	1(2)	0(2)
C(26)	34(2)	19(2)	33(2)	-2(2)	2(2)	1(2)

Table S26. Torsion angles [°] for TAzE.

C(14)-N(2)-C(1)-C(2)	-44.5(5)
C(9)-N(2)-C(1)-C(2)	126.8(4)

C(14)-N(2)-C(1)-N(1)	134.9(4)
C(9)-N(2)-C(1)-N(1)	-53.7(4)
C(8)-N(1)-C(1)-C(2)	-43.3(5)
C(3)-N(1)-C(1)-C(2)	123.5(4)
C(8)-N(1)-C(1)-N(2)	137.3(4)
C(3)-N(1)-C(1)-N(2)	-56.0(5)
N(2)-C(1)-C(2)-N(3)	149.3(4)
N(1)-C(1)-C(2)-N(3)	-30.0(6)
N(2)-C(1)-C(2)-N(4)	-29.0(6)
N(1)-C(1)-C(2)-N(4)	151.6(4)
C(15)-N(3)-C(2)-C(1)	-32.8(5)
C(20)-N(3)-C(2)-C(1)	133.0(4)
C(15)-N(3)-C(2)-N(4)	145.7(3)
C(20)-N(3)-C(2)-N(4)	-48.5(5)
C(26)-N(4)-C(2)-C(1)	-33.1(5)
C(21)-N(4)-C(2)-C(1)	118.9(4)
C(26)-N(4)-C(2)-N(3)	148.4(3)
C(21)-N(4)-C(2)-N(3)	-59.6(5)
C(1)-N(1)-C(3)-C(4)	174.1(4)
C(8)-N(1)-C(3)-C(4)	-19.3(5)
N(1)-C(3)-C(4)-C(5)	-57.0(5)
C(3)-C(4)-C(5)-C(6)	87.4(5)
C(4)-C(5)-C(6)-C(7)	-64.3(5)
C(5)-C(6)-C(7)-C(8)	54.9(5)
C(1)-N(1)-C(8)-C(7)	-113.7(4)
C(3)-N(1)-C(8)-C(7)	80.1(5)
C(6)-C(7)-C(8)-N(1)	-76.8(5)
C(1)-N(2)-C(9)-C(10)	-179.5(3)
C(14)-N(2)-C(9)-C(10)	-8.3(5)
N(2)-C(9)-C(10)-C(11)	-61.6(5)
C(9)-C(10)-C(11)-C(12)	83.9(5)
C(10)-C(11)-C(12)-C(13)	-62.5(5)
C(11)-C(12)-C(13)-C(14)	58.5(5)
C(1)-N(2)-C(14)-C(13)	-118.0(4)
C(9)-N(2)-C(14)-C(13)	71.2(5)
C(12)-C(13)-C(14)-N(2)	-78.7(5)
C(2)-N(3)-C(15)-C(16)	-160.0(4)
C(20)-N(3)-C(15)-C(16)	34.3(5)
N(3)-C(15)-C(16)-C(17)	-83.1(5)
C(15)-C(16)-C(17)-C(18)	72.5(5)
C(16)-C(17)-C(18)-C(19)	-54.1(6)
C(17)-C(18)-C(19)-C(20)	67.9(6)
C(2)-N(3)-C(20)-C(19)	-125.5(4)
C(15)-N(3)-C(20)-C(19)	39.8(6)
C(18)-C(19)-C(20)-N(3)	-83.3(5)
C(2)-N(4)-C(21)-C(22)	120.4(4)
C(26)-N(4)-C(21)-C(22)	-87.9(4)
N(4)-C(21)-C(22)-C(23)	70.1(5)
C(21)-C(22)-C(23)-C(24)	-50.5(5)
C(22)-C(23)-C(24)-C(25)	67.5(5)
C(23)-C(24)-C(25)-C(26)	-87.7(5)
C(2)-N(4)-C(26)-C(25)	-170.9(3)
C(21)-N(4)-C(26)-C(25)	37.0(5)
C(24)-C(25)-C(26)-N(4)	42.8(5)

X-Ray Diffraction of $[TPiE]^{2+}2[I]^{-}$: Crystals suitable for X-ray diffraction were grown by slow vapor diffusion of Et_2O into a nearly saturated solution of $[TPiE^{2+}][I^{-}]_2$ in CH_3CN. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of $[TPiE^{2+}][I^{-}]_2$. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[21] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 2111621 contains the supplementary crystallographic data for this paper.

Table S27. Crystal data and structure refinement for $[TPiE]^{2+}2[I]^{-}$.

Empirical formula	C22 H40 I2 N4	
Formula weight	614.38	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.9860(6) Å	α= 90°
	b = 9.6755(3) Å	β= 109.077(5)°
	c = 19.7003(8) Å	γ = 90°
Volume	2519.46(18) $Å^3$	
Z	4	
Density (calculated)	1.620 Mg/m^3	
Absorption coefficient	2.511 mm^{-1}	
F(000)	1224	
Crystal size	0.450 x 0.450 x 0.080 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	Rigaku Mercury275R CCD	
Theta range for data collection	4.573 to 27.484°.	
Index ranges	-18<=h<=18, -12<=k<=12, -25<=l<=25	
Reflections collected	42357	
Independent reflections	5742 [R(int) = 0.0935]	
Observed reflections (I > 2sigma(I))	4667	
Completeness to theta = 25.242°	99.4%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.67404	
Solution method	SHELXT-2018/2 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	5742 / 0 / 253	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0348, wR2 = 0.0741	

R indices (all data)	R1 = 0.0501, wR2 = 0.0798
Extinction coefficient	n/a
Largest diff. peak and hole	1.110 and -0.651 e.Å^{-3}

Table S28. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [TPiE]$^{2+}$2[I]$^-$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	1492(1)	7516(1)	1857(1)	21(1)
I(2)	7424(1)	9893(1)	3354(1)	19(1)
N(1)	4909(2)	7975(3)	2096(2)	13(1)
N(2)	4570(2)	7383(3)	3151(2)	12(1)
N(3)	4520(2)	4880(3)	1936(2)	12(1)
N(4)	5952(2)	5110(3)	2975(2)	12(1)
C(1)	4836(2)	7078(3)	2582(2)	12(1)
C(2)	5114(2)	5576(3)	2494(2)	12(1)
C(3)	4389(3)	9326(3)	1969(2)	17(1)
C(4)	3890(3)	9556(4)	1163(2)	19(1)
C(5)	4646(3)	9420(4)	758(2)	19(1)
C(6)	5121(3)	7988(4)	893(2)	18(1)
C(7)	5630(3)	7747(4)	1692(2)	16(1)
C(8)	4672(3)	8792(3)	3472(2)	17(1)
C(9)	5132(3)	8685(4)	4284(2)	18(1)
C(10)	4528(3)	7734(4)	4608(2)	20(1)
C(11)	4421(3)	6310(4)	4264(2)	16(1)
C(12)	4009(3)	6373(4)	3451(2)	16(1)
C(13)	3418(2)	5179(4)	1642(2)	16(1)
C(14)	3020(3)	5177(4)	828(2)	18(1)
C(15)	3329(3)	3867(4)	523(2)	22(1)
C(16)	4474(3)	3696(4)	823(2)	19(1)
C(17)	4849(3)	3631(3)	1639(2)	15(1)
C(18)	6804(3)	6049(3)	3339(2)	16(1)
C(19)	7165(3)	5857(4)	4149(2)	19(1)
C(20)	7383(3)	4344(4)	4352(2)	21(1)
C(21)	6475(3)	3450(4)	3962(2)	17(1)
C(22)	6165(3)	3623(3)	3152(2)	14(1)

Table S29. Bond lengths [Å] and angles [°] for [TPiE]$^{2+}$2[I]$^-$.

N(1)-C(1)	1.320(4)
N(1)-C(3)	1.477(4)
N(1)-C(7)	1.491(4)
N(2)-C(1)	1.325(4)
N(2)-C(8)	1.490(4)
N(2)-C(12)	1.490(4)
N(3)-C(2)	1.325(4)
N(3)-C(17)	1.480(4)
N(3)-C(13)	1.486(4)
N(4)-C(2)	1.322(4)
N(4)-C(18)	1.483(4)
N(4)-C(22)	1.487(4)
C(1)-C(2)	1.530(4)

C(3)-C(4)	1.527(5)
C(4)-C(5)	1.524(5)
C(5)-C(6)	1.522(5)
C(6)-C(7)	1.519(5)
C(8)-C(9)	1.520(5)
C(9)-C(10)	1.524(5)
C(10)-C(11)	1.521(5)
C(11)-C(12)	1.517(5)
C(13)-C(14)	1.516(5)
C(14)-C(15)	1.525(5)
C(15)-C(16)	1.525(5)
C(16)-C(17)	1.521(5)
C(18)-C(19)	1.520(5)
C(19)-C(20)	1.522(5)
C(20)-C(21)	1.521(5)
C(21)-C(22)	1.520(5)

C(1)-N(1)-C(3)	123.7(3)
C(1)-N(1)-C(7)	121.0(3)
C(3)-N(1)-C(7)	115.0(3)
C(1)-N(2)-C(8)	123.2(3)
C(1)-N(2)-C(12)	121.3(3)
C(8)-N(2)-C(12)	115.0(3)
C(2)-N(3)-C(17)	123.4(3)
C(2)-N(3)-C(13)	120.9(3)
C(17)-N(3)-C(13)	115.0(3)
C(2)-N(4)-C(18)	121.4(3)
C(2)-N(4)-C(22)	124.0(3)
C(18)-N(4)-C(22)	114.3(3)
N(1)-C(1)-N(2)	125.2(3)
N(1)-C(1)-C(2)	117.4(3)
N(2)-C(1)-C(2)	117.3(3)
N(4)-C(2)-N(3)	126.2(3)
N(4)-C(2)-C(1)	116.2(3)
N(3)-C(2)-C(1)	117.6(3)
N(1)-C(3)-C(4)	109.8(3)
C(5)-C(4)-C(3)	111.8(3)
C(6)-C(5)-C(4)	109.0(3)
C(7)-C(6)-C(5)	110.6(3)
N(1)-C(7)-C(6)	111.1(3)
N(2)-C(8)-C(9)	109.5(3)
C(8)-C(9)-C(10)	112.3(3)
C(11)-C(10)-C(9)	110.3(3)
C(12)-C(11)-C(10)	112.5(3)
N(2)-C(12)-C(11)	112.2(3)
N(3)-C(13)-C(14)	112.8(3)
C(13)-C(14)-C(15)	111.4(3)
C(16)-C(15)-C(14)	109.5(3)
C(17)-C(16)-C(15)	111.7(3)
N(3)-C(17)-C(16)	109.9(3)
N(4)-C(18)-C(19)	111.8(3)
C(18)-C(19)-C(20)	111.3(3)
C(21)-C(20)-C(19)	110.6(3)
C(22)-C(21)-C(20)	111.9(3)
N(4)-C(22)-C(21)	108.6(3)

Symmetry transformations used to generate equivalent atoms:

Table S30. Anisotropic displacement parameters (Å^2 x 10^3) for [TPiE]$^{2+}$2[I]$^-$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

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

Table S31. Torsion angles [°] for [TPiE]$^{2+}$2[I]$^-$.

C(3)-N(1)-C(1)-N(2)	-21.8(5)
C(7)-N(1)-C(1)-N(2)	151.1(3)
C(3)-N(1)-C(1)-C(2)	160.5(3)
C(7)-N(1)-C(1)-C(2)	-26.6(4)
C(8)-N(2)-C(1)-N(1)	-22.8(5)
C(12)-N(2)-C(1)-N(1)	148.3(3)
C(8)-N(2)-C(1)-C(2)	155.0(3)
C(12)-N(2)-C(1)-C(2)	-33.9(4)
C(18)-N(4)-C(2)-N(3)	149.1(3)
C(22)-N(4)-C(2)-N(3)	-25.2(5)
C(18)-N(4)-C(2)-C(1)	-28.5(4)
C(22)-N(4)-C(2)-C(1)	157.1(3)
C(17)-N(3)-C(2)-N(4)	-18.9(5)
C(13)-N(3)-C(2)-N(4)	150.9(3)
C(17)-N(3)-C(2)-C(1)	158.7(3)

C(13)-N(3)-C(2)-C(1)	-31.5(4)
N(1)-C(1)-C(2)-N(4)	110.6(3)
N(2)-C(1)-C(2)-N(4)	-67.4(4)
N(1)-C(1)-C(2)-N(3)	-67.3(4)
N(2)-C(1)-C(2)-N(3)	114.7(3)
C(1)-N(1)-C(3)-C(4)	-134.0(3)
C(7)-N(1)-C(3)-C(4)	52.7(4)
N(1)-C(3)-C(4)-C(5)	-55.0(4)
C(3)-C(4)-C(5)-C(6)	58.4(4)
C(4)-C(5)-C(6)-C(7)	-57.7(4)
C(1)-N(1)-C(7)-C(6)	133.0(3)
C(3)-N(1)-C(7)-C(6)	-53.5(4)
C(5)-C(6)-C(7)-N(1)	55.0(4)
C(1)-N(2)-C(8)-C(9)	-134.6(3)
C(12)-N(2)-C(8)-C(9)	53.8(4)
N(2)-C(8)-C(9)-C(10)	-55.8(4)
C(8)-C(9)-C(10)-C(11)	56.0(4)
C(9)-C(10)-C(11)-C(12)	-52.4(4)
C(1)-N(2)-C(12)-C(11)	136.6(3)
C(8)-N(2)-C(12)-C(11)	-51.6(4)
C(10)-C(11)-C(12)-N(2)	50.0(4)
C(2)-N(3)-C(13)-C(14)	138.6(3)
C(17)-N(3)-C(13)-C(14)	-50.8(4)
N(3)-C(13)-C(14)-C(15)	51.0(4)
C(13)-C(14)-C(15)-C(16)	-54.6(4)
C(14)-C(15)-C(16)-C(17)	58.1(4)
C(2)-N(3)-C(17)-C(16)	-137.1(3)
C(13)-N(3)-C(17)-C(16)	52.5(4)
C(15)-C(16)-C(17)-N(3)	-56.3(4)
C(2)-N(4)-C(18)-C(19)	130.4(3)
C(22)-N(4)-C(18)-C(19)	-54.7(4)
N(4)-C(18)-C(19)-C(20)	51.7(4)
C(18)-C(19)-C(20)-C(21)	-53.0(4)
C(19)-C(20)-C(21)-C(22)	56.6(4)
C(2)-N(4)-C(22)-C(21)	-129.0(3)
C(18)-N(4)-C(22)-C(21)	56.3(4)
C(20)-C(21)-C(22)-N(4)	-56.8(4)

Symmetry transformations used to generate equivalent atoms:

X-Ray Diffraction of [TPyE]$^{2+}$2[I]$^{-}$: Crystals suitable for X-ray diffraction were grown by slow vapor diffusion of Et_2O into a solution of [TPyE^{2+}][I^{-}]$_2$ in methanol. Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of [TPyE^{2+}][I^{-}]$_2$. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[21] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The program SQUEEZE[23] was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (158 e/A^3^), it is likely that ~8.5 methanols, ~4 ethers, or some combination of these solvent molecules are present in the unit cell. See "_platon_squeeze_details" in the .cif for more information. The full numbering scheme can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 2111620 contains the supplementary crystallographic data for this paper.

Table S32. Crystal data and structure refinement for [TPyE]$^{2+}$2[I]$^{-}$.

Empirical formula	C18 H32 I2 N4	
Formula weight	558.27	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 14.2990(4) Å	α= 90°
	b = 13.0573(3) Å	β= 114.849(3)°
	c = 14.8142(4) Å	γ = 90°
Volume	2509.83(13) Å^3	
Z	4	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	2.513 mm^{-1}	
F(000)	1096	
Crystal size	0.100 x 0.100 x 0.070 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.279 to 30.504°.	
Index ranges	-20<=h<=20, -18<=k<=18, -20<=l<=21	
Reflections collected	48356	
Independent reflections	3719 [R(int) = 0.0419]	

Observed reflections (I > 2sigma(I))	3390
Completeness to theta = 25.242°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.75624
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	3719 / 0 / 110
Goodness-of-fit on F^2	1.268
Final R indices [I>2sigma(I)]	R1 = 0.0571, wR2 = 0.1374
R indices (all data)	R1 = 0.0619, wR2 = 0.1386
Extinction coefficient	n/a
Largest diff. peak and hole	3.198 and -1.548 e.Å^{-3}

Table S33. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [TPyE]$^{2+}$2[I]$^-$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	7023(1)	8637(1)	11529(1)	27(1)
N(1)	5169(3)	7638(3)	6783(3)	14(1)
N(2)	5833(3)	9686(3)	8153(3)	13(1)
C(1)	5000	8078(5)	7500	14(1)
C(2)	5000	9245(5)	7500	14(1)
C(3)	4999(4)	6543(4)	6493(4)	19(1)
C(4)	4975(4)	6555(4)	5453(4)	20(1)
C(5)	5744(4)	7389(4)	5528(4)	23(1)
C(6)	5491(4)	8214(4)	6098(4)	18(1)
C(7)	6805(4)	9115(4)	8744(4)	18(1)
C(8)	7559(4)	9969(4)	9286(4)	19(1)
C(9)	6868(4)	10765(4)	9464(4)	18(1)
C(10)	5904(4)	10775(4)	8479(4)	17(1)

Table S34. Bond lengths [Å] and angles [°] for [TPyE]$^{2+}$2[I]$^-$.

N(1)-C(1)	1.316(5)
N(1)-C(3)	1.482(6)
N(1)-C(6)	1.483(6)
N(2)-C(2)	1.311(5)
N(2)-C(10)	1.492(6)
N(2)-C(7)	1.494(6)
C(1)-N(1)#1	1.316(5)
C(1)-C(2)	1.524(9)
C(2)-N(2)#1	1.311(5)
C(3)-C(4)	1.527(8)
C(4)-C(5)	1.519(7)
C(5)-C(6)	1.504(7)
C(7)-C(8)	1.524(7)
C(8)-C(9)	1.531(7)
C(9)-C(10)	1.529(7)
C(1)-N(1)-C(3)	126.2(5)
C(1)-N(1)-C(6)	123.1(4)
C(3)-N(1)-C(6)	110.6(4)

C(2)-N(2)-C(10)	125.1(4)
C(2)-N(2)-C(7)	123.1(4)
C(10)-N(2)-C(7)	111.5(4)
N(1)-C(1)-N(1)#1	128.3(7)
N(1)-C(1)-C(2)	115.9(3)
N(1)#1-C(1)-C(2)	115.9(3)
N(2)#1-C(2)-N(2)	127.9(7)
N(2)#1-C(2)-C(1)	116.1(3)
N(2)-C(2)-C(1)	116.1(3)
N(1)-C(3)-C(4)	102.4(4)
C(5)-C(4)-C(3)	103.0(4)
C(6)-C(5)-C(4)	102.5(4)
N(1)-C(6)-C(5)	103.8(4)
N(2)-C(7)-C(8)	102.8(4)
C(7)-C(8)-C(9)	102.9(4)
C(10)-C(9)-C(8)	103.3(4)
N(2)-C(10)-C(9)	102.2(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+3/2

Table S35. Anisotropic displacement parameters (Å^2 x 10^3) for [TPyE]$^{2+}$2[I]$^-$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	23(1)	36(1)	20(1)	2(1)	9(1)	5(1)
N(1)	16(2)	7(2)	20(2)	-3(1)	9(2)	-1(1)
N(2)	13(2)	8(2)	16(2)	0(1)	5(2)	0(1)
C(1)	8(3)	14(3)	18(3)	0	3(2)	0
C(2)	15(3)	13(3)	15(3)	0	9(2)	0
C(3)	23(2)	4(2)	29(3)	-3(2)	11(2)	-2(2)
C(4)	28(3)	6(2)	27(3)	-5(2)	11(2)	-2(2)
C(5)	27(3)	17(2)	29(3)	-8(2)	17(2)	-2(2)
C(6)	21(2)	13(2)	21(2)	-4(2)	10(2)	-4(2)
C(7)	12(2)	18(2)	22(2)	4(2)	4(2)	4(2)
C(8)	14(2)	20(2)	20(2)	-1(2)	3(2)	-2(2)
C(9)	19(2)	14(2)	18(2)	-3(2)	4(2)	-5(2)
C(10)	17(2)	12(2)	19(2)	-2(2)	6(2)	0(2)

Table S36. Torsion angles [°] for [TPyE]$^{2+}$2[I]$^-$.

C(3)-N(1)-C(1)-N(1)#1	13.5(4)
C(6)-N(1)-C(1)-N(1)#1	-171.4(5)
C(3)-N(1)-C(1)-C(2)	-166.5(4)
C(6)-N(1)-C(1)-C(2)	8.6(5)
C(10)-N(2)-C(2)-N(2)#1	17.6(3)
C(7)-N(2)-C(2)-N(2)#1	-169.3(5)
C(10)-N(2)-C(2)-C(1)	-162.4(3)
C(7)-N(2)-C(2)-C(1)	10.7(5)
N(1)-C(1)-C(2)-N(2)#1	77.4(3)
N(1)#1-C(1)-C(2)-N(2)#1	-102.6(3)
N(1)-C(1)-C(2)-N(2)	-102.6(3)

N(1)#1-C(1)-C(2)-N(2)	77.4(3)
C(1)-N(1)-C(3)-C(4)	162.0(4)
C(6)-N(1)-C(3)-C(4)	-13.6(5)
N(1)-C(3)-C(4)-C(5)	34.3(5)
C(3)-C(4)-C(5)-C(6)	-42.7(5)
C(1)-N(1)-C(6)-C(5)	171.6(4)
C(3)-N(1)-C(6)-C(5)	-12.6(5)
C(4)-C(5)-C(6)-N(1)	33.7(5)
C(2)-N(2)-C(7)-C(8)	173.6(4)
C(10)-N(2)-C(7)-C(8)	-12.5(5)
N(2)-C(7)-C(8)-C(9)	33.2(5)
C(7)-C(8)-C(9)-C(10)	-42.3(5)
C(2)-N(2)-C(10)-C(9)	160.5(4)
C(7)-N(2)-C(10)-C(9)	-13.3(5)
C(8)-C(9)-C(10)-N(2)	33.8(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+3/2

SXXII. Computational Details and Coordinates

DFT calculations were carried out with the Gaussian16 software package.[24] The hybrid meta-GGA M06 functional[25] was selected, given its proven track record to model the structures and energies of main group compounds.[25] Structures were fully optimized without any geometry or symmetry constraints, using the 6-31+G** basis set for all elements.[26] Vibrational frequencies were computed at the same level of theory to classify all stationary points as energy minima, with only real frequencies. These calculations were also used to obtain the thermochemistry corrections (zero-point, thermal, and entropy energies) at 298.15K. The energies reported were obtained by adding the thermochemistry corrections to the refined potential energies.

To test hypotheses about the structures of reductants, a number of compounds were considered computationally in addition to TPyE, TPiE, TME, TAzE. Specifically, we performed calculations on: (i) the known reductant TDAE, (ii) a variant of TDAE in which two nitrogen atoms are part of the same five-membered heterocyclic ring (TDAE 2.0), and (iii) TAzetE, in which the nitrogen atoms of the tetraaminoethylene scaffold are incorporated into four-membered azetidine rings (Figure S63).

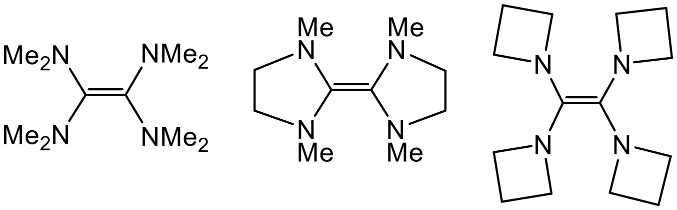
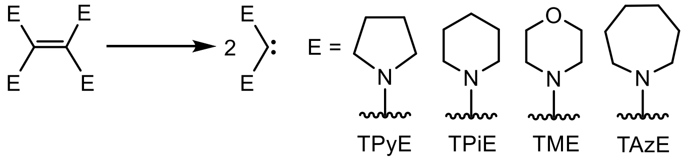


Figure S63: Reductants in addition to TPiE, TPyE, TME, and TAzE used in calculations.

Initially, we explored the ability of the tetraminoethylene scaffolds to undergo the Wanzlick equilibrium and form free carbenes.[27] The formation of carbenes would represent a problem in catalysis as the reactive carbenes could either undergo deleterious side reactions with substrates or bind to a transition metal catalyst. The formation of a free carbene from TDAE is uphill by 40.8 kcal mol^{-1}, consistent with its compatibility with transition metal catalyzed reactions. In contrast, for TDAE 2.0, the formation of a free carbene is uphill by just 14.1 kcal mol^{-1}. This likely explains why attempts to use TDAE 2.0 in catalysis were not successful. In contrast, as shown in Table S37, it requires at least 36 kcal mol^{-1} to generate a carbene from TPyE, TPiE, TME, or TAzE, which is consistent with their excellent performance in catalysis.

Table S37. Calculated gas phase free energies for formation of free carbenes from TPyE, TPiE, TME, or TAzE.



Reductant	ΔG (kcal mol^{-1})
TPyE	36.6
TPiE	45.6
TME	54.2
TAzE	38.1

We analyzed the calculated geometries of TDAE, TDAE 2.0, TAzetE, TPyE, TME, and TAzE, as well as their oxidized forms. In general, good agreement is observed between the calculated and experimental structures. For all of the reductants calculated, the molecules contained a central C–C double bond and four C–N single bonds from the central C–C double bond. The major difference between the structures is related to their planarity. As described in the paper, we quantify planarity by measuring the angle formed by the planes defined by N(1)-C(1)-C(2)-N(2) and N(3)-C(2)-C(1)-N(4). As this angle approaches 0°, the molecule become more planar. Figure S64 shows the two planes used for the measurements in TAzetE and TPiE, while the calculated angles between the planes are given for all reductants in Table S38. The calculated data clearly shows that the angle between the planes is the smallest in TAzetE and TDAE 2.0, which are the reductants with the least steric bulk. On this basis, we propose that the reason for the larger deviation from planarity in TDAE, TPyE, TPiE, TME, and TAzE, is related to steric factors.

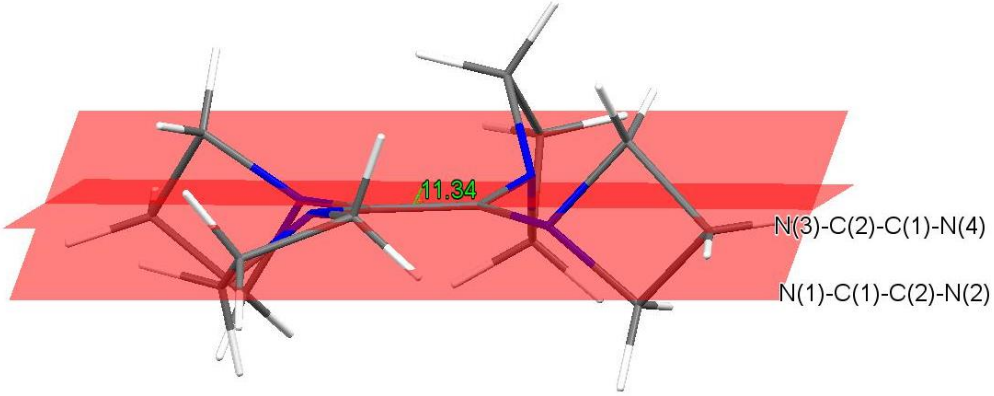
We also calculated the angle formed by the planes defined by N(1)-C(1)-C(2)-N(2) and N(3)-C(2)-C(1)-N(4) for the oxidized forms of the reductants, specifically $TDAE^{2+}$, TDAE 2.0^{2+}, $TAzetE^{2+}$, $TPyE^{2+}$, TME^{2+}, and $TAzE^{2+}$. These values are provided in Table S39. By comparing the data in Tables S38 and S39, it can be seen that the strongest reductants, TDAE 2.0, TAzetE, and TPyE, are those with the largest difference in the magnitude of this angle between the neutral and oxidized forms. Given that we do not have experimental data for TDAE 2.0 and TAzetE, in these cases we calculated the reduction potentials using DFT,[28] whereas for other compounds we used the experimental values. Finally, the HOMOs for all reductants and the LUMOs for the oxidized forms of all reductants are shown in Figures S65 and S66. The character of the orbitals is the same across the series, indicating that electrons are being removed from similar types of orbitals on oxidation.

Table S38. Calculated angles between planes formed by N(1)-C(1)-C(2)-N(2) and N(3)-C(2)-C(1)-N(4) for different reductants.

Reductant	Angle (°)
TAzetE	11.3
TPyE	23.7
TPiE	20.1
TME	24.7
TAzE	24.6
TDAE	27.8
TDAE 2.0	4.85

Figure S64. Angles between planes formed by N(1)-C(1)-C(2)-N(2) and N(3)-C(2)-C(1)-N(4) for **a)** TAzetE and **b)** TPiE.

a)



b)

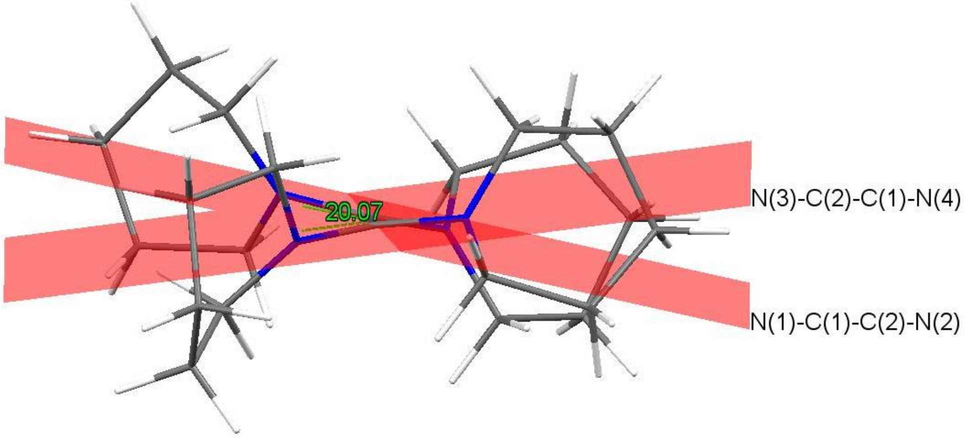


Table S39. Calculated angles between planes formed by N(1)-C(1)-C(2)-N(2) and N(3)-C(2)-C(1)-N(4) for oxidized versions of reductants.

Reductant	**Angle (°)**
TAzetE^{2+}	89.9
TPyE^{2+}	79.5
TPiE^{2+}	72.5
TME^{2+}	69.3
TAzE^{2+}	78.7
TDAE^{2+}	69.1
TDAE 2.0^{2+}	86.2

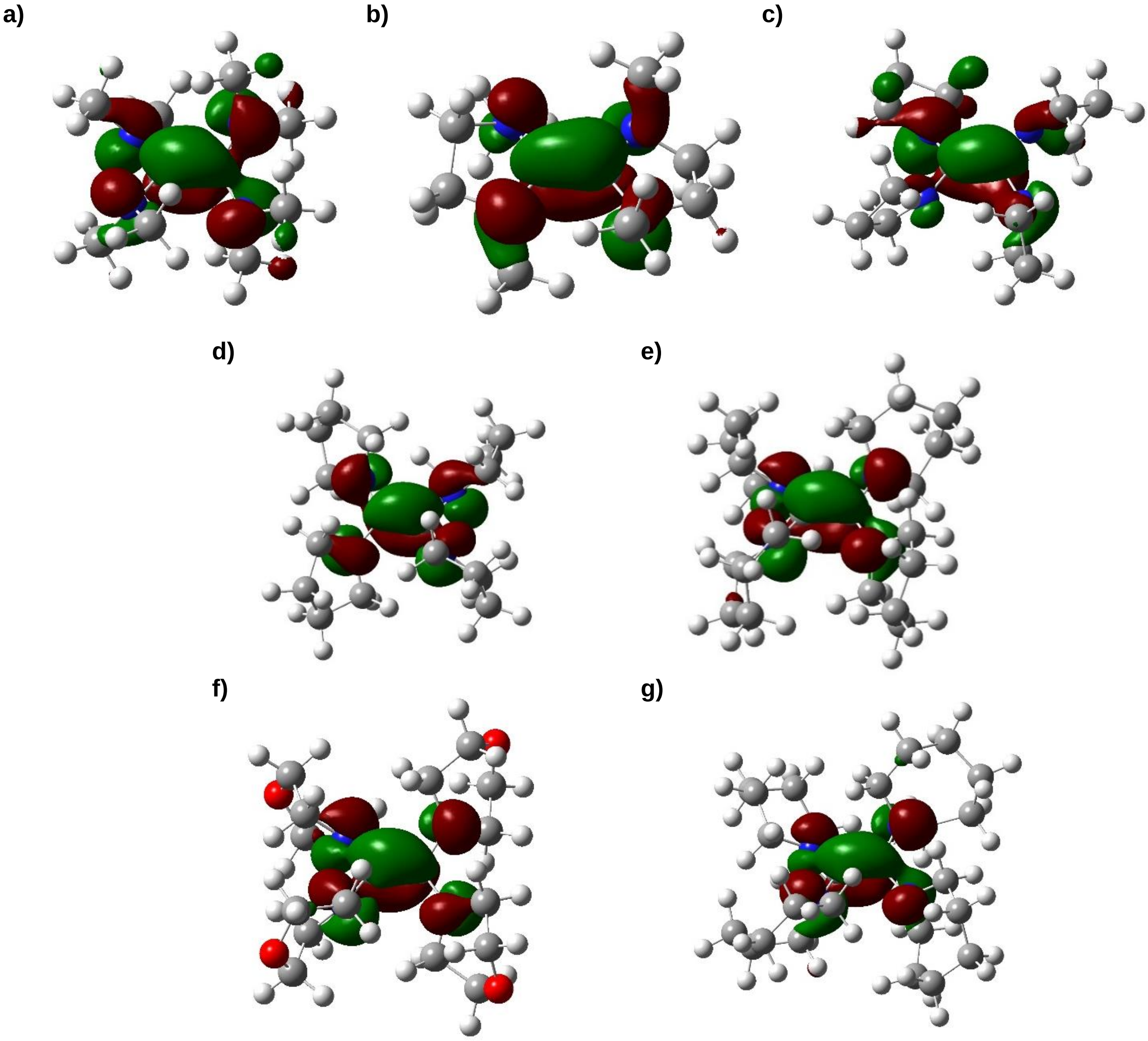


Figure S65: DFT calculated HOMOs of **a)** TDAE, **b)** TDAE 2.0, **c)** TAzetE, **d)** TPyE, **e)** TPiE, **f)** TME, and **g)** TAzE.

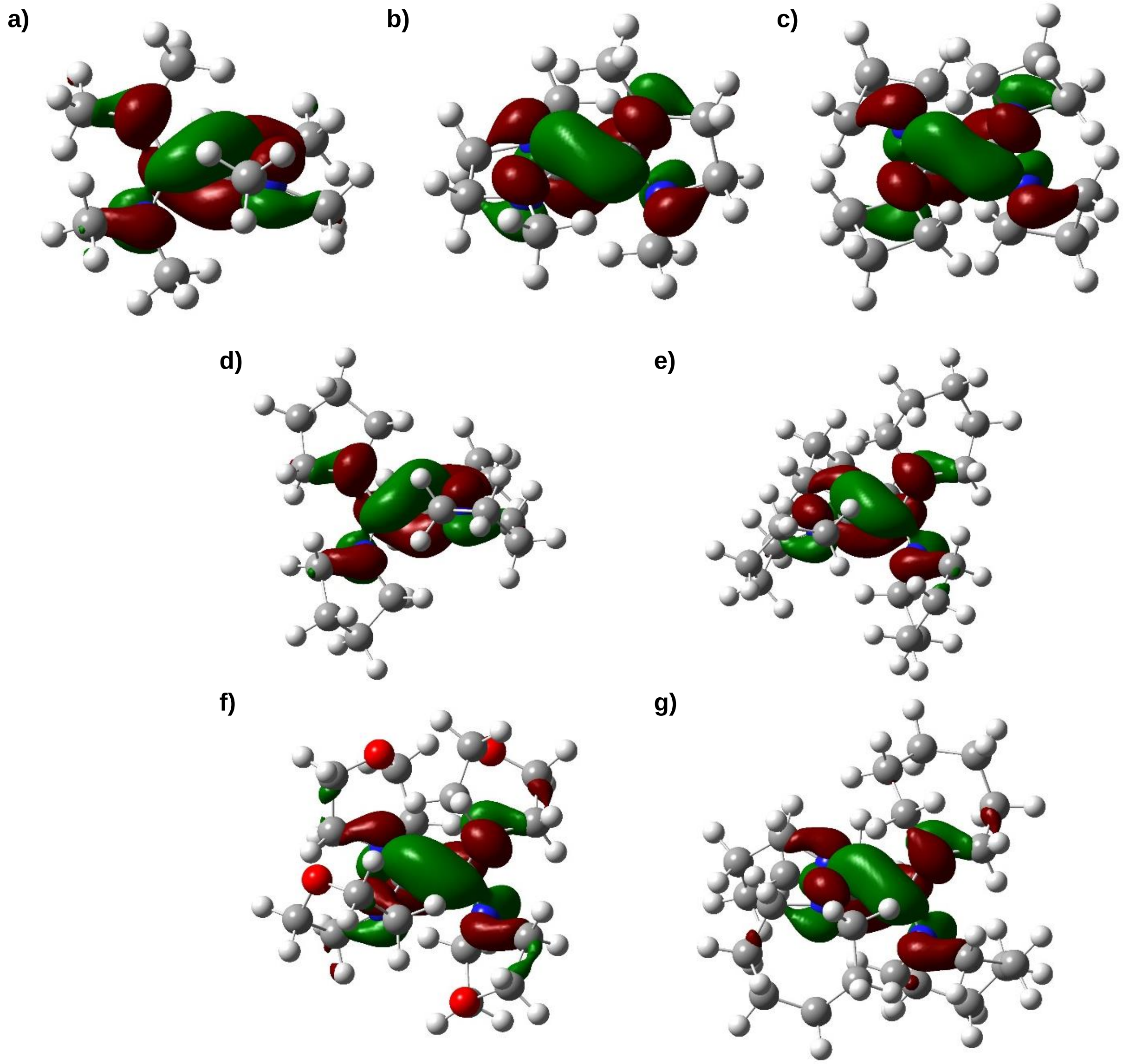


Figure S66: DFT calculated LUMOs of **a)** $TDAE^{2+}$, **b)** TDAE 2.0^{2+}, **c)** $TAzetE^{2+}$, **d)** $TPyE^{2+}$, **e)** $TPiE^{2+}$, **f)** TME^{2+}, and **g)** $TAzE^{2+}$.

Optimized Coordinates and DFT Energies

TPiE   G = -680461.3507 kcal/mol

C	-0.126000	-0.706000	0.070000
C	-0.009000	0.649000	-0.044000
C	1.941000	0.917000	-1.517000
C	1.553000	2.536000	0.312000
C	3.222000	1.734000	-1.652000
H	1.286000	1.068000	-2.399000
H	2.195000	-0.157000	-1.491000
C	3.035000	2.609000	0.697000
H	1.306000	3.379000	-0.367000
H	0.913000	2.664000	1.192000
C	3.914000	1.838000	-0.300000
H	2.998000	2.743000	-2.030000
H	3.873000	1.263000	-2.399000
H	3.177000	2.204000	1.708000
H	3.337000	3.665000	0.738000
H	4.096000	0.819000	0.075000
H	4.899000	2.313000	-0.396000
C	-1.459000	2.328000	-1.082000
C	-2.115000	1.335000	1.090000
C	-2.629000	3.250000	-0.753000
H	-1.699000	1.691000	-1.956000
H	-0.587000	2.937000	-1.375000
C	-2.524000	2.685000	1.693000
H	-3.006000	0.812000	0.691000
H	-1.696000	0.676000	1.861000
C	-2.452000	3.812000	0.651000
H	-3.579000	2.697000	-0.815000
H	-2.686000	4.049000	-1.502000
H	-1.868000	2.926000	2.540000
H	-3.543000	2.602000	2.098000
H	-1.470000	4.307000	0.702000
H	-3.201000	4.584000	0.865000
C	-2.171000	-1.130000	-1.281000
C	-1.809000	-2.328000	0.876000
C	-2.926000	-2.402000	-1.635000
H	-1.504000	-0.826000	-2.103000
H	-2.894000	-0.299000	-1.144000
C	-3.328000	-2.401000	0.875000
H	-1.398000	-3.340000	0.687000
H	-1.438000	-2.022000	1.867000
C	-3.866000	-2.828000	-0.498000
H	-2.187000	-3.195000	-1.828000
H	-3.485000	-2.262000	-2.569000
H	-3.720000	-1.409000	1.143000
H	-3.668000	-3.092000	1.656000
H	-4.862000	-2.389000	-0.651000
H	-4.004000	-3.917000	-0.529000
C	1.772000	-1.259000	1.549000
C	1.120000	-2.827000	-0.248000
C	2.950000	-2.226000	1.637000
H	1.144000	-1.324000	2.459000
H	2.154000	-0.225000	1.497000

C	2.563000	-3.079000	-0.697000
H	0.807000	-3.628000	0.452000
H	0.431000	-2.882000	-1.100000
C	3.567000	-2.416000	0.258000
H	2.623000	-3.199000	2.033000
H	3.684000	-1.833000	2.352000
H	2.710000	-2.696000	-1.716000
H	2.735000	-4.164000	-0.743000
H	3.853000	-1.427000	-0.132000
H	4.492000	-3.004000	0.318000
N	1.241000	1.254000	-0.285000
N	0.986000	-1.518000	0.353000
N	-1.353000	-1.357000	-0.106000
N	-1.097000	1.527000	0.081000

TPiE^{2+} G = -680151.4524 kcal/mol

C	-0.082000	-0.796000	0.195000
C	-0.010000	0.704000	-0.024000
C	1.846000	0.227000	-1.560000
C	1.534000	2.549000	-0.619000
C	2.453000	0.996000	-2.719000
H	1.216000	-0.594000	-1.921000
H	2.632000	-0.204000	-0.922000
C	3.039000	2.541000	-0.810000
H	1.059000	3.199000	-1.363000
H	1.266000	2.905000	0.381000
C	3.423000	2.073000	-2.216000
H	1.638000	1.439000	-3.308000
H	2.956000	0.286000	-3.384000
H	3.499000	1.905000	-0.040000
H	3.408000	3.554000	-0.618000
H	4.449000	1.689000	-2.204000
H	3.422000	2.919000	-2.912000
C	-1.370000	2.775000	-0.024000
C	-1.882000	0.871000	1.552000
C	-2.857000	2.991000	0.178000
H	-1.107000	2.787000	-1.088000
H	-0.803000	3.564000	0.487000
C	-2.367000	1.996000	2.449000
H	-2.730000	0.370000	1.063000
H	-1.333000	0.120000	2.129000
C	-3.228000	2.995000	1.663000
H	-3.415000	2.219000	-0.369000
H	-3.125000	3.941000	-0.296000
H	-1.491000	2.489000	2.891000
H	-2.925000	1.562000	3.285000
H	-3.099000	3.999000	2.083000
H	-4.291000	2.754000	1.772000
C	-1.713000	-0.796000	-1.638000
C	-1.598000	-2.746000	-0.039000
C	-2.261000	-1.869000	-2.562000
H	-0.997000	-0.157000	-2.166000
H	-2.528000	-0.159000	-1.262000
C	-3.083000	-2.774000	-0.351000
H	-1.094000	-3.573000	-0.557000
H	-1.409000	-2.840000	1.035000

C	-3.338000	-2.705000	-1.860000
H	-1.427000	-2.499000	-2.902000
H	-2.657000	-1.384000	-3.460000
H	-3.578000	-1.946000	0.176000
H	-3.501000	-3.690000	0.078000
H	-4.331000	-2.280000	-2.043000
H	-3.354000	-3.712000	-2.289000
C	1.446000	-0.476000	2.088000
C	1.251000	-2.737000	1.003000
C	2.661000	-1.165000	2.685000
H	0.701000	-0.251000	2.863000
H	1.752000	0.473000	1.627000
C	2.762000	-2.794000	0.776000
H	0.962000	-3.218000	1.945000
H	0.739000	-3.254000	0.194000
C	3.533000	-1.733000	1.577000
H	2.355000	-1.952000	3.385000
H	3.203000	-0.425000	3.284000
H	2.971000	-2.700000	-0.296000
H	3.081000	-3.804000	1.057000
H	3.850000	-0.910000	0.918000
H	4.454000	-2.154000	1.989000
N	1.010000	1.154000	-0.742000
N	0.797000	-1.323000	1.040000
N	-1.025000	-1.441000	-0.479000
N	-0.979000	1.435000	0.508000

TPiE Carbene G = -340207.8826 kcal/mol

C	0.000000	-1.039000	-0.001000
C	-2.197000	-1.206000	0.927000
C	-1.418000	1.033000	0.632000
C	-3.475000	-0.678000	0.246000
H	-2.316000	-1.206000	2.023000
H	-1.962000	-2.226000	0.610000
C	-2.298000	1.381000	-0.572000
H	-1.991000	1.153000	1.563000
H	-0.549000	1.684000	0.739000
C	-3.112000	0.148000	-0.985000
H	-4.054000	-0.051000	0.941000
H	-4.126000	-1.518000	-0.022000
H	-1.681000	1.722000	-1.416000
H	-2.963000	2.216000	-0.308000
H	-2.513000	-0.475000	-1.664000
H	-4.010000	0.445000	-1.539000
C	2.197000	-1.205000	-0.929000
C	1.418000	1.034000	-0.632000
C	3.475000	-0.678000	-0.244000
H	2.318000	-1.202000	-2.024000
H	1.962000	-2.225000	-0.615000
C	2.298000	1.382000	0.572000
H	1.991000	1.155000	-1.563000
H	0.549000	1.684000	-0.738000
C	3.111000	0.147000	0.986000
H	4.056000	-0.052000	-0.938000
H	4.125000	-1.520000	0.025000
H	1.682000	1.724000	1.416000

H	2.965000	2.215000	0.307000
H	2.509000	-0.475000	1.664000
H	4.008000	0.444000	1.542000
N	-1.034000	-0.386000	0.563000
N	1.034000	-0.386000	-0.564000

TPyE G = -581540.4649 kcal/mol

C	-0.073000	-0.678000	-0.151000
C	0.074000	0.678000	-0.151000
C	1.304000	-2.609000	0.591000
C	2.087000	-1.297000	-1.274000
C	2.726000	-3.033000	0.213000
H	0.596000	-3.453000	0.516000
H	1.241000	-2.233000	1.627000
C	2.848000	-2.615000	-1.254000
H	2.736000	-0.467000	-0.928000
H	1.707000	-1.014000	-2.266000
H	3.455000	-2.471000	0.813000
H	2.912000	-4.099000	0.381000
H	3.886000	-2.519000	-1.589000
H	2.345000	-3.347000	-1.901000
C	1.850000	2.357000	-0.698000
C	2.073000	1.032000	1.313000
C	3.186000	2.654000	-0.023000
H	1.193000	3.247000	-0.695000
H	1.965000	2.048000	-1.751000
C	2.920000	2.293000	1.438000
H	2.717000	0.133000	1.230000
H	1.399000	0.866000	2.169000
H	3.966000	1.995000	-0.430000
H	3.516000	3.689000	-0.166000
H	3.833000	2.148000	2.026000
H	2.329000	3.088000	1.916000
C	-2.087000	1.296000	-1.275000
C	-1.304000	2.609000	0.591000
C	-2.848000	2.615000	-1.254000
H	-2.735000	0.467000	-0.929000
H	-1.706000	1.014000	-2.267000
C	-2.726000	3.031000	0.212000
H	-0.596000	3.453000	0.514000
H	-1.240000	2.233000	1.627000
H	-2.345000	3.347000	-1.901000
H	-3.886000	2.518000	-1.589000
H	-2.913000	4.097000	0.381000
H	-3.455000	2.469000	0.813000
C	-1.849000	-2.357000	-0.698000
C	-2.073000	-1.031000	1.313000
C	-3.187000	-2.653000	-0.023000
H	-1.194000	-3.247000	-0.693000
H	-1.964000	-2.048000	-1.750000
C	-2.922000	-2.291000	1.438000
H	-2.717000	-0.131000	1.229000
H	-1.400000	-0.865000	2.169000
H	-3.966000	-1.993000	-0.431000
H	-3.517000	-3.687000	-0.166000
H	-3.835000	-2.145000	2.025000

H	-2.331000	-3.086000	1.917000
N	-0.983000	1.564000	-0.376000
N	1.307000	1.278000	0.108000
N	0.984000	-1.564000	-0.376000
N	-1.306000	-1.278000	0.108000

TPyE^{2+} *G = -581232.1278 kcal/mol*

C	-0.000000	0.756000	-0.000000
C	0.000000	-0.756000	-0.000000
C	-1.399000	2.749000	-0.590000
C	-1.765000	0.606000	-1.729000
C	-2.781000	2.696000	-1.224000
H	-0.743000	3.446000	-1.123000
H	-1.410000	3.000000	0.475000
C	-2.597000	1.707000	-2.367000
H	-2.401000	-0.108000	-1.185000
H	-1.142000	0.053000	-2.440000
H	-3.519000	2.323000	-0.503000
H	-3.110000	3.685000	-1.554000
H	-3.538000	1.323000	-2.767000
H	-2.046000	2.169000	-3.196000
C	-1.397000	-2.750000	0.590000
C	-1.764000	-0.607000	1.729000
C	-2.779000	-2.698000	1.225000
H	-0.741000	-3.447000	1.123000
H	-1.408000	-3.001000	-0.476000
C	-2.595000	-1.709000	2.367000
H	-2.401000	0.106000	1.185000
H	-1.142000	-0.054000	2.441000
H	-3.517000	-2.325000	0.503000
H	-3.108000	-3.687000	1.554000
H	-3.537000	-1.326000	2.768000
H	-2.044000	-2.171000	3.196000
C	1.765000	-0.606000	-1.729000
C	1.399000	-2.749000	-0.590000
C	2.597000	-1.707000	-2.367000
H	2.401000	0.108000	-1.185000
H	1.142000	-0.053000	-2.441000
C	2.781000	-2.696000	-1.224000
H	0.743000	-3.446000	-1.123000
H	1.410000	-3.000000	0.476000
H	2.046000	-2.170000	-3.195000
H	3.538000	-1.323000	-2.767000
H	3.111000	-3.685000	-1.554000
H	3.519000	-2.323000	-0.503000
C	1.397000	2.750000	0.590000
C	1.764000	0.607000	1.729000
C	2.778000	2.699000	1.224000
H	0.740000	3.447000	1.122000
H	1.408000	3.001000	-0.476000
C	2.595000	1.709000	2.367000
H	2.401000	-0.106000	1.185000
H	1.142000	0.054000	2.440000
H	3.517000	2.325000	0.503000
H	3.108000	3.687000	1.554000

H	3.537000	1.326000	2.768000
H	2.044000	2.171000	3.195000
N	0.909000	-1.348000	-0.755000
N	-0.908000	-1.349000	0.755000
N	-0.909000	1.348000	-0.755000
N	0.908000	1.349000	0.755000

TPyE Carbene G = -290751.9042 kcal/mol

C	0.000000	-1.077000	0.000000
C	-2.385000	-1.158000	-0.326000
C	-1.469000	1.011000	0.236000
C	-3.483000	-0.108000	-0.349000
H	-2.508000	-1.854000	0.517000
H	-2.326000	-1.753000	-1.242000
C	-2.944000	0.949000	0.610000
H	-1.316000	1.707000	-0.603000
H	-0.832000	1.329000	1.068000
H	-3.586000	0.319000	-1.356000
H	-4.458000	-0.510000	-0.054000
H	-3.442000	1.920000	0.524000
H	-3.053000	0.602000	1.646000
C	1.469000	1.011000	-0.236000
C	2.385000	-1.158000	0.325000
C	2.944000	0.949000	-0.610000
H	1.315000	1.707000	0.602000
H	0.832000	1.329000	-1.068000
C	3.483000	-0.108000	0.349000
H	2.508000	-1.853000	-0.518000
H	2.326000	-1.754000	1.241000
H	3.053000	0.602000	-1.646000
H	3.442000	1.920000	-0.524000
H	4.458000	-0.509000	0.054000
H	3.586000	0.319000	1.356000
N	1.142000	-0.385000	0.142000
N	-1.142000	-0.385000	-0.142000

TME G = -770976.3827 kcal/mol

C	-0.000000	-0.801000	0.000000
C	0.000000	0.564000	0.000000
C	1.971000	1.169000	-1.404000
C	1.524000	2.382000	0.700000
C	2.418000	2.542000	-1.864000
H	1.350000	0.701000	-2.182000
H	2.856000	0.516000	-1.266000
C	2.960000	2.798000	0.452000
H	0.864000	3.262000	0.575000
H	1.417000	2.050000	1.746000
H	1.526000	3.144000	-2.114000
H	3.041000	2.471000	-2.764000
H	3.634000	1.959000	0.699000
H	3.231000	3.641000	1.098000
C	-1.524000	2.382000	-0.700000
C	-1.971000	1.169000	1.404000
C	-2.960000	2.799000	-0.453000
H	-1.417000	2.049000	-1.747000

H	-0.864000	3.262000	-0.576000
C	-2.417000	2.543000	1.863000
H	-2.856000	0.517000	1.266000
H	-1.350000	0.702000	2.183000
H	-3.634000	1.959000	-0.698000
H	-3.231000	3.641000	-1.098000
H	-1.526000	3.144000	2.114000
H	-3.041000	2.472000	2.763000
C	-2.098000	-1.124000	-1.283000
C	-1.537000	-2.657000	0.567000
C	-2.896000	-2.325000	-1.745000
H	-1.563000	-0.681000	-2.137000
H	-2.778000	-0.342000	-0.896000
C	-3.049000	-2.743000	0.601000
H	-1.125000	-3.626000	0.230000
H	-1.156000	-2.479000	1.583000
H	-2.212000	-3.059000	-2.205000
H	-3.635000	-2.032000	-2.500000
H	-3.460000	-1.823000	1.054000
H	-3.371000	-3.589000	1.219000
C	2.098000	-1.125000	1.283000
C	1.536000	-2.658000	-0.566000
C	2.896000	-2.325000	1.745000
H	1.564000	-0.681000	2.138000
H	2.778000	-0.343000	0.895000
C	3.048000	-2.744000	-0.601000
H	1.124000	-3.626000	-0.230000
H	1.155000	-2.479000	-1.582000
H	2.212000	-3.059000	2.206000
H	3.636000	-2.031000	2.499000
H	3.459000	-1.824000	-1.054000
H	3.369000	-3.590000	-1.219000
N	1.181000	1.296000	-0.197000
N	1.127000	-1.565000	0.307000
N	-1.127000	-1.565000	-0.306000
N	-1.181000	1.297000	0.197000
O	-3.609000	-2.943000	-0.684000
O	3.183000	3.222000	-0.880000
O	3.608000	-2.944000	0.684000
O	-3.182000	3.223000	0.880000

TME^{2+} G = -770638.714 kcal/mol

C	-0.264000	-0.946000	-0.009000
C	-0.158000	0.531000	-0.390000
C	1.688000	0.003000	-1.933000
C	1.344000	2.320000	-1.234000
C	3.157000	0.404000	-1.707000
H	1.409000	0.057000	-2.995000
H	1.508000	-1.017000	-1.581000
C	2.700000	2.329000	-0.495000
H	1.438000	2.595000	-2.291000
H	0.670000	3.023000	-0.751000
H	3.520000	1.065000	-2.509000
H	3.788000	-0.487000	-1.685000
H	2.564000	2.646000	0.545000

H	3.375000	3.043000	-0.989000
C	-1.663000	2.519000	-0.554000
C	-1.782000	1.075000	1.372000
C	-1.474000	3.672000	0.467000
H	-2.729000	2.334000	-0.754000
H	-1.181000	2.692000	-1.518000
C	-1.273000	2.230000	2.282000
H	-2.869000	1.090000	1.230000
H	-1.512000	0.098000	1.786000
H	-2.447000	4.003000	0.860000
H	-0.989000	4.541000	0.012000
H	-0.523000	1.874000	2.994000
H	-2.114000	2.651000	2.852000
C	-1.879000	-1.210000	-1.844000
C	-2.092000	-2.624000	0.152000
C	-3.407000	-1.154000	-1.698000
H	-1.569000	-1.944000	-2.601000
H	-1.471000	-0.241000	-2.148000
C	-3.477000	-1.992000	0.452000
H	-2.170000	-3.510000	-0.490000
H	-1.613000	-2.923000	1.085000
H	-3.875000	-2.101000	-2.008000
H	-3.827000	-0.363000	-2.325000
H	-3.532000	-1.649000	1.490000
H	-4.260000	-2.752000	0.305000
C	1.480000	-0.638000	1.704000
C	0.912000	-2.903000	0.948000
C	2.905000	-1.213000	1.637000
H	1.083000	-0.657000	2.729000
H	1.459000	0.396000	1.345000
C	2.353000	-3.101000	0.416000
H	0.813000	-3.201000	1.999000
H	0.215000	-3.497000	0.358000
H	3.103000	-1.894000	2.480000
H	3.637000	-0.403000	1.669000
H	2.338000	-3.458000	-0.619000
H	2.863000	-3.859000	1.031000
N	0.821000	0.937000	-1.182000
N	0.592000	-1.463000	0.856000
N	-1.282000	-1.610000	-0.553000
N	-1.168000	1.273000	0.051000
O	-3.715000	-0.864000	-0.356000
O	3.262000	1.038000	-0.455000
O	3.061000	-1.887000	0.411000
O	-0.641000	3.224000	1.511000

TME Carbene G = -385461.1095 kcal/mol

C	-0.000000	-1.246000	0.000000
C	2.348000	-1.364000	-0.449000
C	1.384000	0.809000	-0.707000
C	3.573000	-0.494000	-0.126000
H	2.422000	-1.750000	-1.480000
H	2.274000	-2.218000	0.228000
C	2.353000	1.461000	0.277000
H	1.835000	0.761000	-1.712000

H	0.465000	1.383000	-0.827000
H	3.989000	-0.032000	-1.039000
H	4.369000	-1.099000	0.319000
H	1.820000	1.891000	1.135000
H	2.912000	2.273000	-0.222000
C	-2.348000	-1.364000	0.450000
C	-1.384000	0.809000	0.708000
C	-3.573000	-0.494000	0.124000
H	-2.424000	-1.748000	1.481000
H	-2.274000	-2.218000	-0.226000
C	-2.353000	1.461000	-0.277000
H	-1.836000	0.761000	1.712000
H	-0.465000	1.382000	0.828000
H	-3.991000	-0.032000	1.037000
H	-4.368000	-1.099000	-0.322000
H	-1.819000	1.892000	-1.134000
H	-2.913000	2.273000	0.222000
N	1.127000	-0.570000	-0.287000
N	-1.128000	-0.570000	0.288000
O	3.247000	0.506000	0.815000
O	-3.245000	0.506000	-0.816000

TAzE G = -779388.1049 kcal/mol

C	0.427000	0.531000	0.050000
C	0.504000	2.916000	-0.506000
C	-0.306000	2.207000	1.689000
C	-0.474000	4.031000	-0.846000
H	1.382000	3.361000	0.007000
H	0.885000	2.474000	-1.436000
C	-1.677000	2.800000	2.002000
H	0.478000	2.924000	2.008000
H	-0.172000	1.309000	2.308000
C	-1.149000	4.719000	0.339000
H	-1.256000	3.635000	-1.511000
H	0.082000	4.780000	-1.430000
C	-2.205000	3.851000	1.021000
H	-1.607000	3.239000	3.009000
H	-2.415000	1.987000	2.078000
H	-0.392000	5.053000	1.068000
H	-1.633000	5.634000	-0.029000
H	-2.922000	4.491000	1.554000
H	-2.787000	3.352000	0.231000
C	2.280000	-0.508000	-1.222000
C	2.735000	0.643000	0.890000
C	3.355000	0.072000	-2.133000
H	2.661000	-1.432000	-0.744000
H	1.420000	-0.809000	-1.834000
C	3.726000	1.795000	0.720000
H	3.301000	-0.296000	1.045000
H	2.159000	0.796000	1.813000
C	4.584000	0.656000	-1.437000
H	2.905000	0.860000	-2.758000
H	3.671000	-0.728000	-2.820000
C	4.299000	1.959000	-0.687000
H	4.545000	1.625000	1.436000

H	3.254000	2.741000	1.023000
H	5.027000	-0.090000	-0.756000
H	5.347000	0.850000	-2.203000
H	5.219000	2.554000	-0.615000
H	3.604000	2.556000	-1.297000
N	1.808000	0.424000	-0.215000
N	-0.063000	1.840000	0.297000
C	-0.427000	-0.531000	0.050000
C	-2.280000	0.508000	-1.222000
C	-2.735000	-0.643000	0.890000
C	-3.356000	-0.072000	-2.132000
H	-2.661000	1.432000	-0.744000
H	-1.420000	0.809000	-1.833000
C	-3.726000	-1.795000	0.720000
H	-3.301000	0.296000	1.045000
H	-2.159000	-0.797000	1.813000
C	-4.584000	-0.656000	-1.437000
H	-2.905000	-0.860000	-2.758000
H	-3.671000	0.728000	-2.820000
C	-4.300000	-1.958000	-0.687000
H	-4.545000	-1.625000	1.436000
H	-3.255000	-2.742000	1.023000
H	-5.027000	0.090000	-0.756000
H	-5.347000	-0.849000	-2.203000
H	-5.220000	-2.554000	-0.615000
H	-3.605000	-2.556000	-1.297000
N	-1.808000	-0.425000	-0.215000
C	-0.504000	-2.916000	-0.506000
C	0.307000	-2.207000	1.689000
C	0.474000	-4.031000	-0.846000
H	-1.382000	-3.361000	0.007000
H	-0.885000	-2.474000	-1.435000
C	1.678000	-2.800000	2.002000
H	-0.478000	-2.924000	2.008000
H	0.172000	-1.309000	2.308000
C	1.149000	-4.719000	0.339000
H	1.256000	-3.635000	-1.511000
H	-0.082000	-4.780000	-1.430000
C	2.205000	-3.851000	1.021000
H	1.608000	-3.238000	3.009000
H	2.415000	-1.987000	2.077000
H	0.392000	-5.053000	1.068000
H	1.633000	-5.634000	-0.029000
H	2.921000	-4.491000	1.555000
H	2.788000	-3.353000	0.231000
N	0.063000	-1.841000	0.297000

TAzE^{2+} *G = -779071.6502 kcal/mol*

C	0.668000	-0.374000	0.465000
C	2.954000	-0.378000	1.528000
C	1.197000	1.162000	2.329000
C	3.985000	0.529000	0.881000
H	3.117000	-0.433000	2.611000
H	3.060000	-1.387000	1.154000
C	1.603000	2.592000	1.956000

H	1.695000	0.860000	3.256000
H	0.125000	1.123000	2.548000
C	4.057000	1.945000	1.438000
H	3.810000	0.563000	-0.207000
H	4.952000	0.026000	1.017000
C	2.840000	2.790000	1.081000
H	1.751000	3.113000	2.912000
H	0.755000	3.101000	1.482000
H	4.208000	1.918000	2.528000
H	4.953000	2.424000	1.029000
H	3.099000	3.853000	1.133000
H	2.591000	2.603000	0.025000
C	-0.186000	-1.594000	-1.488000
C	1.713000	-2.569000	-0.245000
C	0.422000	-1.448000	-2.876000
H	-0.618000	-2.596000	-1.359000
H	-1.011000	-0.881000	-1.381000
C	3.007000	-2.532000	-1.053000
H	1.107000	-3.412000	-0.595000
H	1.883000	-2.763000	0.819000
C	1.627000	-2.321000	-3.212000
H	0.707000	-0.398000	-3.038000
H	-0.397000	-1.652000	-3.579000
C	2.883000	-1.919000	-2.444000
H	3.327000	-3.579000	-1.138000
H	3.813000	-2.024000	-0.509000
H	1.397000	-3.387000	-3.059000
H	1.813000	-2.215000	-4.286000
H	3.778000	-2.197000	-3.011000
H	2.915000	-0.819000	-2.369000
N	0.787000	-1.404000	-0.374000
N	1.548000	0.089000	1.351000
C	-0.698000	0.323000	0.496000
C	0.097000	1.924000	-1.184000
C	-1.719000	2.600000	0.395000
C	-0.557000	2.005000	-2.555000
H	0.500000	2.905000	-0.899000
H	0.943000	1.225000	-1.214000
C	-2.957000	2.981000	-0.431000
H	-1.042000	3.462000	0.439000
H	-1.981000	2.366000	1.433000
C	-1.723000	2.975000	-2.682000
H	-0.897000	1.004000	-2.862000
H	0.241000	2.285000	-3.256000
C	-2.958000	2.548000	-1.891000
H	-3.031000	4.075000	-0.387000
H	-3.870000	2.617000	0.056000
H	-1.414000	3.990000	-2.387000
H	-1.981000	3.044000	-3.745000
H	-3.858000	2.968000	-2.353000
H	-3.076000	1.452000	-1.966000
N	-0.832000	1.506000	-0.103000
C	-3.089000	-0.023000	1.077000
C	-1.314000	-1.350000	2.216000
C	-3.918000	-1.174000	0.525000
H	-3.434000	0.271000	2.078000

H	-3.223000	0.828000	0.415000
C	-1.361000	-2.816000	1.804000
H	-2.046000	-1.165000	3.011000
H	-0.337000	-1.120000	2.653000
C	-3.867000	-2.514000	1.251000
H	-3.653000	-1.326000	-0.533000
H	-4.949000	-0.796000	0.520000
C	-2.574000	-3.278000	0.993000
H	-1.324000	-3.365000	2.755000
H	-0.438000	-3.090000	1.277000
H	-4.048000	-2.384000	2.329000
H	-4.706000	-3.117000	0.888000
H	-2.725000	-4.345000	1.192000
H	-2.354000	-3.213000	-0.084000
N	-1.636000	-0.322000	1.182000

TAzE Carbene G = -389674.9805 kcal/mol

C	0.103000	-1.267000	-0.624000
C	1.398000	0.873000	-1.283000
C	2.458000	-1.260000	-0.708000
C	1.697000	1.724000	-0.054000
H	2.235000	0.940000	-1.994000
H	0.533000	1.281000	-1.805000
C	2.828000	-1.336000	0.769000
H	3.248000	-0.743000	-1.270000
H	2.379000	-2.271000	-1.121000
C	2.847000	1.249000	0.833000
H	0.790000	1.777000	0.569000
H	1.893000	2.750000	-0.400000
C	2.548000	-0.061000	1.564000
H	3.897000	-1.590000	0.832000
H	2.277000	-2.167000	1.228000
H	3.775000	1.159000	0.244000
H	3.042000	2.036000	1.574000
H	3.121000	-0.104000	2.500000
H	1.488000	-0.053000	1.865000
C	-2.197000	-1.655000	-0.200000
C	-1.697000	0.381000	-1.466000
C	-2.697000	-1.147000	1.141000
H	-3.035000	-1.726000	-0.914000
H	-1.763000	-2.653000	-0.084000
C	-1.878000	1.631000	-0.598000
H	-2.679000	0.075000	-1.851000
H	-1.098000	0.593000	-2.358000
C	-3.233000	0.284000	1.144000
H	-1.866000	-1.216000	1.862000
H	-3.479000	-1.833000	1.497000
C	-2.165000	1.348000	0.875000
H	-2.708000	2.214000	-1.025000
H	-0.995000	2.282000	-0.663000
H	-4.054000	0.383000	0.414000
H	-3.684000	0.477000	2.126000
H	-2.458000	2.296000	1.347000
H	-1.233000	1.037000	1.376000
N	-1.151000	-0.804000	-0.782000

N	1.193000	-0.557000	-0.975000

TAzetE G = -482535.8924 kcal/mol

C	0.763000	-0.076000	0.008000
C	-0.566000	0.209000	-0.072000
C	2.751000	0.878000	1.175000
C	2.783000	1.072000	-0.900000
C	3.764000	1.495000	0.201000
H	3.006000	-0.169000	1.411000
H	2.511000	1.415000	2.102000
H	3.040000	0.085000	-1.322000
H	2.566000	1.776000	-1.716000
H	4.768000	1.063000	0.177000
H	3.835000	2.583000	0.304000
C	1.110000	-2.452000	0.907000
C	0.965000	-2.318000	-1.192000
C	1.192000	-3.491000	-0.223000
H	0.120000	-2.428000	1.391000
H	1.885000	-2.481000	1.687000
H	-0.081000	-2.244000	-1.527000
H	1.633000	-2.235000	-2.061000
H	0.438000	-4.282000	-0.221000
H	2.186000	-3.937000	-0.319000
C	-2.334000	-1.164000	1.141000
C	-2.673000	-0.917000	-0.935000
C	-3.461000	-1.606000	0.192000
H	-2.598000	-0.284000	1.750000
H	-1.903000	-1.925000	1.807000
H	-3.078000	0.065000	-1.223000
H	-2.493000	-1.496000	-1.852000
H	-4.459000	-1.215000	0.404000
H	-3.518000	-2.692000	0.075000
C	-2.232000	2.068000	0.450000
C	-0.465000	2.774000	-0.451000
C	-1.816000	3.431000	-0.122000
H	-2.095000	2.011000	1.545000
H	-3.232000	1.687000	0.200000
H	0.305000	2.965000	0.306000
H	-0.028000	2.941000	-1.445000
H	-1.800000	4.275000	0.572000
H	-2.388000	3.699000	-1.015000
N	-1.506000	-0.849000	-0.040000
N	-1.114000	1.467000	-0.288000
N	1.718000	0.973000	0.122000
N	1.287000	-1.390000	-0.096000

TAzetE^{2+} *G = -482229.0623 kcal/mol*

C	0.754000	-0.000000	0.001000
C	-0.754000	-0.000000	-0.000000
C	2.762000	-1.325000	-0.964000
C	0.801000	-2.065000	-1.505000
C	2.246000	-2.496000	-1.820000
H	3.304000	-1.600000	-0.054000
H	3.304000	-0.543000	-1.503000
H	0.208000	-2.769000	-0.910000

H	0.208000	-1.713000	-2.356000
H	2.514000	-3.484000	-1.441000
H	2.514000	-2.436000	-2.875000
C	2.760000	1.327000	0.964000
C	0.799000	2.065000	1.507000
C	2.244000	2.497000	1.821000
H	3.302000	1.603000	0.054000
H	3.304000	0.544000	1.503000
H	0.204000	2.768000	0.912000
H	0.207000	1.711000	2.358000
H	2.511000	3.484000	1.443000
H	2.512000	2.437000	2.876000
C	-2.761000	-0.966000	1.323000
C	-0.801000	-1.506000	2.064000
C	-2.246000	-1.821000	2.495000
H	-3.304000	-1.505000	0.540000
H	-3.303000	-0.056000	1.597000
H	-0.208000	-2.358000	1.713000
H	-0.208000	-0.910000	2.767000
H	-2.513000	-2.876000	2.435000
H	-2.515000	-1.442000	3.482000
C	-2.761000	0.967000	-1.324000
C	-0.800000	1.506000	-2.065000
C	-2.244000	1.820000	-2.497000
H	-3.303000	1.507000	-0.543000
H	-3.303000	0.056000	-1.597000
H	-0.207000	2.358000	-1.714000
H	-0.206000	0.909000	-2.767000
H	-2.512000	2.875000	-2.439000
H	-2.513000	1.440000	-3.484000
N	-1.346000	-0.692000	0.946000
N	-1.345000	0.692000	-0.946000
N	1.346000	-0.948000	-0.689000
N	1.345000	0.948000	0.691000

TAzetE Carbene G = -241257.693 kcal/mol

C	0.000000	-1.093000	-0.000000
C	-1.552000	1.027000	-0.111000
C	-2.496000	-0.894000	0.076000
C	-3.015000	0.556000	-0.031000
H	-1.250000	1.429000	-1.087000
H	-1.224000	1.716000	0.677000
H	-2.706000	-1.534000	-0.791000
H	-2.766000	-1.438000	0.989000
H	-3.621000	0.771000	-0.914000
H	-3.547000	0.908000	0.857000
C	1.552000	1.027000	0.111000
C	2.496000	-0.894000	-0.075000
C	3.015000	0.556000	0.030000
H	1.250000	1.428000	1.088000
H	1.224000	1.716000	-0.676000
H	2.706000	-1.534000	0.792000
H	2.767000	-1.438000	-0.989000
H	3.621000	0.772000	0.913000
H	3.546000	0.907000	-0.858000

N	-1.124000	-0.386000	0.084000
N	1.124000	-0.386000	-0.084000

TDAE G = -386657.2401kcal/mol

C	-0.775000	0.000000	-0.000000
C	0.589000	0.000000	-0.000000
N	-1.553000	-1.112000	0.373000
N	1.323000	-1.182000	-0.192000
N	-1.553000	1.113000	-0.373000
N	1.323000	1.182000	0.191000
C	-1.008000	-2.082000	1.287000
H	-1.834000	-2.618000	1.775000
H	-0.353000	-2.830000	0.803000
H	-0.418000	-1.573000	2.059000
C	-2.471000	-1.662000	-0.603000
H	-1.988000	-2.408000	-1.263000
H	-3.310000	-2.157000	-0.095000
H	-2.869000	-0.853000	-1.222000
C	1.213000	-1.954000	-1.400000
H	2.158000	-1.939000	-1.977000
H	0.972000	-3.012000	-1.197000
H	0.418000	-1.539000	-2.028000
C	2.451000	-1.484000	0.647000
H	2.402000	-2.521000	1.020000
H	3.414000	-1.369000	0.116000
H	2.459000	-0.813000	1.513000
C	1.215000	1.954000	1.400000
H	2.160000	1.936000	1.977000
H	0.975000	3.012000	1.198000
H	0.419000	1.539000	2.028000
C	2.451000	1.484000	-0.647000
H	2.404000	2.521000	-1.018000
H	3.414000	1.365000	-0.116000
H	2.457000	0.814000	-1.515000
C	-2.470000	1.663000	0.603000
H	-1.988000	2.408000	1.263000
H	-3.309000	2.157000	0.096000
H	-2.868000	0.853000	1.223000
C	-1.008000	2.082000	-1.287000
H	-1.834000	2.618000	-1.775000
H	-0.353000	2.830000	-0.803000
H	-0.418000	1.573000	-2.059000

TDAE $^{2+}$ *G = -386323.3975 kcal/mol*

C	-0.759000	-0.000000	0.000000
C	0.759000	-0.000000	-0.000000
N	-1.361000	-0.973000	-0.670000
N	1.360000	-0.973000	0.670000
N	-1.360000	0.973000	0.670000
N	1.360000	0.973000	-0.670000
C	-2.731000	-1.437000	-0.394000
H	-3.438000	-1.091000	-1.154000
H	-2.709000	-2.531000	-0.417000
H	-3.052000	-1.120000	0.599000
C	-0.660000	-1.777000	-1.684000

H	-0.488000	-2.792000	-1.307000
H	-1.296000	-1.841000	-2.573000
H	0.288000	-1.323000	-1.981000
C	2.730000	-1.437000	0.394000
H	3.437000	-1.091000	1.155000
H	2.709000	-2.531000	0.417000
H	3.052000	-1.120000	-0.598000
C	0.660000	-1.778000	1.684000
H	0.488000	-2.792000	1.307000
H	1.296000	-1.840000	2.573000
H	-0.289000	-1.324000	1.980000
C	2.730000	1.437000	-0.395000
H	3.437000	1.092000	-1.155000
H	2.708000	2.531000	-0.418000
H	3.052000	1.120000	0.598000
C	0.659000	1.777000	-1.684000
H	0.487000	2.792000	-1.307000
H	1.295000	1.841000	-2.573000
H	-0.289000	1.323000	-1.980000
C	-0.658000	1.778000	1.684000
H	-0.484000	2.791000	1.306000
H	-1.295000	1.843000	2.572000
H	0.289000	1.323000	1.981000
C	-2.730000	1.437000	0.395000
H	-3.437000	1.092000	1.155000
H	-2.708000	2.531000	0.418000
H	-3.052000	1.120000	-0.597000

TDAE Carbene G = -193308.1857 kcal/mol

C	-0.000000	-0.827000	0.000000
N	-1.161000	-0.139000	0.026000
N	1.161000	-0.139000	-0.025000
C	-2.375000	-0.919000	0.205000
H	-2.975000	-0.515000	1.033000
H	-2.992000	-0.902000	-0.706000
H	-2.094000	-1.948000	0.433000
C	-1.437000	1.250000	-0.346000
H	-2.345000	1.270000	-0.962000
H	-1.612000	1.901000	0.522000
H	-0.625000	1.662000	-0.948000
C	1.437000	1.250000	0.346000
H	2.345000	1.270000	0.962000
H	1.612000	1.901000	-0.522000
H	0.626000	1.662000	0.949000
C	2.375000	-0.919000	-0.205000
H	2.974000	-0.515000	-1.033000
H	2.993000	-0.902000	0.706000
H	2.093000	-1.948000	-0.433000

TDAE2.0 G = -385168.1532 kcal/mol

C	-0.672000	-0.027000	-0.045000
C	-2.872000	0.652000	-0.310000
C	-2.656000	-0.751000	-0.864000
H	-3.414000	0.617000	0.655000
H	-3.433000	1.308000	-0.987000

H	-3.491000	-1.432000	-0.670000
H	-2.485000	-0.711000	-1.949000
C	0.672000	-0.027000	0.045000
C	2.872000	0.652000	0.310000
C	2.656000	-0.751000	0.864000
H	3.414000	0.617000	-0.655000
H	3.434000	1.309000	0.987000
H	3.491000	-1.432000	0.670000
H	2.486000	-0.711000	1.949000
N	1.505000	1.128000	0.112000
N	1.436000	-1.220000	0.205000
N	-1.436000	-1.220000	-0.205000
N	-1.505000	1.128000	-0.112000
C	-1.371000	2.078000	0.980000
H	-1.962000	2.975000	0.760000
H	-1.725000	1.649000	1.937000
H	-0.324000	2.367000	1.110000
C	1.371000	2.078000	-0.980000
H	1.962000	2.975000	-0.761000
H	1.725000	1.649000	-1.937000
H	0.323000	2.367000	-1.110000
C	1.674000	-1.918000	-1.057000
H	2.221000	-1.306000	-1.799000
H	2.248000	-2.832000	-0.864000
H	0.707000	-2.200000	-1.484000
C	-1.674000	-1.918000	1.057000
H	-2.221000	-1.306000	1.799000
H	-2.248000	-2.832000	0.864000
H	-0.707000	-2.200000	1.484000

TDAE2.0^{2+} *G = -384846.4223 kcal/mol*

C	-0.744000	-0.000000	-0.000000
C	-2.898000	0.602000	-0.477000
C	-2.898000	-0.602000	0.477000
H	-3.305000	1.514000	-0.024000
H	-3.431000	0.416000	-1.415000
H	-3.431000	-0.416000	1.414000
H	-3.305000	-1.514000	0.024000
C	0.744000	-0.000000	-0.000000
C	2.898000	-0.602000	-0.477000
C	2.898000	0.602000	0.477000
H	3.305000	-1.514000	-0.024000
H	3.431000	-0.416000	-1.414000
H	3.431000	0.416000	1.414000
H	3.305000	1.514000	0.024000
N	1.458000	-0.809000	-0.757000
N	1.458000	0.809000	0.757000
N	-1.458000	-0.809000	0.757000
N	-1.458000	0.809000	-0.757000
C	-0.995000	1.878000	-1.633000
H	-1.478000	1.778000	-2.610000
H	-1.256000	2.852000	-1.205000
H	0.088000	1.817000	-1.771000
C	0.995000	-1.878000	-1.633000
H	1.476000	-1.776000	-2.610000

H	1.259000	-2.852000	-1.207000
H	-0.088000	-1.818000	-1.769000
C	0.995000	1.878000	1.634000
H	1.477000	1.777000	2.610000
H	1.257000	2.852000	1.206000
H	-0.088000	1.817000	1.770000
C	-0.995000	-1.878000	1.634000
H	-1.477000	-1.777000	2.610000
H	-1.258000	-2.852000	1.206000
H	0.088000	-1.817000	1.770000

TDAE2.0 Carbene G = -192577.0291 kcal/mol

C	0.000000	1.026000	0.000000
C	-0.759000	-1.221000	0.065000
C	0.759000	-1.221000	-0.065000
H	-1.101000	-1.591000	1.045000
H	-1.265000	-1.811000	-0.710000
H	1.265000	-1.811000	0.710000
H	1.101000	-1.590000	-1.046000
N	1.069000	0.208000	0.071000
N	-1.069000	0.208000	-0.071000
C	-2.437000	0.648000	-0.005000
H	-3.030000	0.213000	-0.821000
H	-2.905000	0.359000	0.949000
H	-2.453000	1.737000	-0.090000
C	2.437000	0.648000	0.004000
H	3.030000	0.213000	0.821000
H	2.904000	0.359000	-0.950000
H	2.453000	1.737000	0.090000

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