Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Atom-Efficient Transition-Metal-Free Arylation of *N,O*-Acetals using Diarylzinc Reagents through Zn/Zn Cooperativity

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Experimental

General Considerations

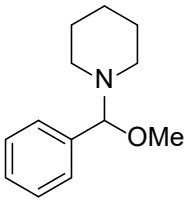
All manipulations were carried out under an inert atmosphere of argon using standard Schlenk line[1] or glove-box techniques (MBraun UNILab Pro ECO, <0.5 ppm H_2O and O_2). THF was dried and distilled from Na/benzophenone and stored over 4 Å molecular sieves. Hexane, Et_2O, toluene and benzene were dried using a MBraun SPS 5 and stored over 4 Å molecular sieves. THF-d_8, toluene-d_8 and C_6D_6 were dried and distilled over $NaK_{2.8}$ and stored over 4 Å molecular sieves in a glove-box prior to use. $Zn(C_6F_5)_2$ was purchased from Sigma Aldrich and used as received unless other specified. MeOH was degassed and stored over 4 Å molecular sieves. All other reagents were used as supplied unless otherwise stated.

NMR spectra were recorded on a Bruker Avance III HD 300 MHz spectrometer at 300 K unless otherwise specified. ^{1}H NMR spectra were referenced internally to the corresponding residual *protio* solvent peaks. CHN elemental microanalyses were performed on a Flash 2000 Organic Elemental Analyser (Thermo Scientific). High resolution mass spectra were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer (HRMS ESI, nano-electrospray) in positive ionisation mode (samples were diffused in a stream of MeCN).

Synthesis of *N,O*-Acetals (1a-m)

N,O-acetals were prepared following the general procedure: Freshly distilled secondary amine (20 mmol) was added to a mixture of aldehyde (20 mmol), K_2CO_3 (5.53 g, 40 mmol) and Na_2SO_4 (5.68 g, 40 mmol) in anhydrous MeOH (10 mL) at 0 °C. After warming to room temperature and stirring overnight, the solids were removed by filtration and evaporation of the volatiles from the filtrate afforded the crude *N,O*-acetal. Specific purification methods, if necessary, are detailed below.

1-Methoxy-(phenyl)methyl-piperidine (1a)



Distillation at 130 °C (0.1 mbar) afforded **1a** as a colourless oil (54%).

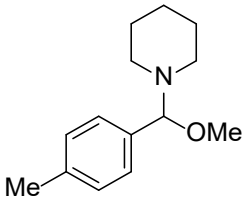
Analytical data in accordance with the literature.[2]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.38-7.34 (m, 4H, Ph-C*H*), 7.33-7.28 (m, 1H, Ph-C*H*), 4.74 (s, 1H, C*H*), 3.39 (s, 3H, OCH_3), 2.59-2.52 (m, 4H, CH_2), 1.57-1.47 (m, 4H, CH_2), 1.46-1.37 (m, 4H, CH_2).

^{1}H NMR (300.1 MHz, 298 K, Tol-d_8): δ 7.46-7.35 (m, 2H, Ph-C*H*), 7.26-7.16 (m, 2H, Ph-C*H*), 7.15-7.06 (m, 1H, Ph-C*H*), 4.63 (s, 1H, C*H*), 3.26 (s, 3H, OCH_3), 2.60-2.52 (m, 4H, CH_2), 1.49-1.38 (m, 4H, CH_2), 1.35-1.25 (m, 4H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 138.4 (quaternary-*C*), 127.8 (Ph-*C*H), 127.5 (Ph-*C*H), 127.4 (Ph-*C*H), 98.4 (*C*H), 56.4 (O*C*H_3), 48.6 (*C*H_2), 26.2 (*C*H_2), 24.8 (*C*H_2).

1-Methoxy-(*p*-tolyl)methyl-piperidine (1b)



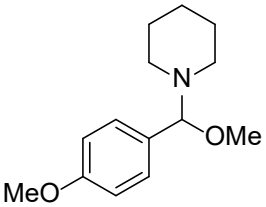
Recrystallisation from MeOH/Et_2O afforded **1b** as a yellow solid (28%).

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.26 (d, *J* =7.8 Hz, 2H, Ar-C*H*), 7.15 (d, *J* = 7.8 Hz, 2H, Ar-C*H*), 4.69 (s, 1H, C*H*), 3.36 (s, 3H, OCH_3), 2.60-2.47 (m, 4H, CH_2), 2.35 (s, 3H, CH_3), 1.58-1.47 (m, 4H, CH_2), 1.45-1.35 (m, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, $CDCl_3$): δ 137.3 (quaternary-*C*), 135.5 (quaternary-*C*), 128.7 (Ar-*C*H), 127.5 (Ar-*C*H), 98.6 (*C*H), 56.5 (O*C*H_3), 48.8 (*C*H_2), 26.3 (*C*H_2), 25.0 (*C*H_2), 21.3 (*C*H_3).

HRMS *m/z* calculated for $C_{14}H_{22}NO$ $[M+H]^+$ 220.1701; found 220.1691.

1-Methoxy-(4-methoxyphenyl)methyl-piperidine (1c)



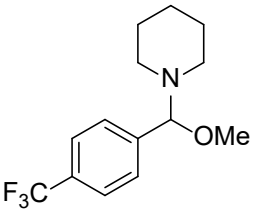
Recrystallisation from MeOH/Et_2O afforded **1c** as a yellow solid (38%).

^1H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.27 (d, *J* = 8.6 Hz, 2H, Ar-C*H*), 6.88 (d, *J* = 8.6 Hz, 2H Ar-C*H*), 4.67 (s, 1H, C*H*), 3.81 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 2.58-2.47 (m, 4H, CH_2), 1.58-1.46 (m, 4H, CH_2), 1.45-1-36 (m, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, $CDCl_3$): δ 159.1 (quaternary-*C*), 130.7 (quaternary-*C*), 128.7(Ar-*C*H), 113.3 (Ar-*C*H), 98.4 (*C*H), 56.4 (O*C*H_3), 55.3 (O*C*H_3), 48.7 (*C*H_2), 26.3 (*C*H_2), 24.9 (*C*H_2).

HRMS *m/z* calculated for $C_{14}H_{21}NO_2$ $[M]^+$ 235.1572; found 235.1519.

1-Methoxy-(4-trifluoromethylphenyl)methyl-piperidine (1d)



Recrystallisation from MeOH/Et_2O afforded **1d** as a yellow solid (47%).

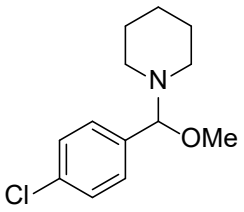
^1H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.61 (d, *J* = 8.1 Hz, 2H, Ar-C*H*), 7.49 (d, *J* = 8.1 Hz, 2H Ar-C*H*), 4.80 (s, 1H, C*H*), 3.42 (s, 3H, OCH_3), 2.61-2.48 (m, 4H, CH_2), 1.58-1.47 (m, 4H, CH_2), 1.47-1-86 (m, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, $CDCl_3$): δ 129.9 (quaternary-*C*), 127.6 (Ar-*C*H), 124.8 (q, $J_{C\text{-}F}$ = 3.9 Hz, quaternary-*C*-CF_3), 97.7 (*C*H), 56.8 (O*C*H_3), 48.6 (*C*H_2), 26.2 (*C*H_2), 24.7 (*C*H_2). The *C*F_3 signal could not be observed.

$^{19}F\{^1H\}$ NMR (282.4 MHz, 198 K, $CDCl_3$): δ -62.4 (s).

HRMS *m/z* calculated for $C_{13}H_6F_3N$ $[M\text{-}OMe]^+$ 243.1235; found 243.1179.

1-Methoxy-(4-chlorophenyl)methyl-piperidine (1e)



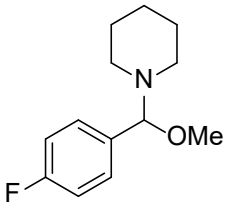
Recrystallisation from MeOH/Et_2O afforded **1e** as a yellow solid (50%).

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.34-7.28 (m, 4H, Ar-C*H*), 4.70 (s, 1H, C*H*), 3.38 (s, 3H, OCH_3), 2.58-2.47 (m, 4H, CH_2), 1.58-1.36 (m, 6H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 137.3 (quaternary-*C*), 133.4 (quaternary-*C*), 128.9 (Ar-*C*H), 128.2 (Ar-*C*H), 97.9 (*C*H), 56.8 (O*C*H_3), 48.7 (*C*H_2), 26.3 (*C*H_2), 24.9 (*C*H_2).

HRMS *m/z* calculated for $C_{13}H_{19}ClNO$ $[M+H]^+$ 240.1155; found 240.1144.

1-Methoxy-(4-fluorophenyl)methyl-piperidine (1f)



Distillation at 155 °C (0.1 mbar) afforded **1f** as a colourless oil (32%).

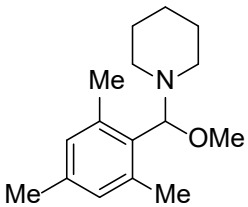
^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.37-7.29 (m, 2H, Ar-C*H*), 7.08-6-97 (m, 2H, Ar-C*H*), 4.71 (s, 1H, C*H*), 3.38 (s, 3H, OCH_3), 2.52 (t, *J* = 5.3 Hz, 4H, CH_2), 1.57-1.46 (m, 4H, CH_2), 1.45-1.35 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 162.4 (d, $J_{C\text{-}F}$ = 245.2 Hz, Ar-*C*F), 134.4 (quaternary-*C*) 129.5 (d, $J_{C\text{-}F}$ = 8.0 Hz, Ar-*C*), 114.8 (d, $J_{C\text{-}F}$ = 21.3 Hz, Ar-*C*), 98.0 (*C*H), 56.7 (O*C*H_3), 48.7 (*C*H_2), 26.3 (*C*H_2), 24.9 (*C*H_2).

^{19}F{^{1}H} NMR (282.4 MHz, 298 K, $CDCl_3$): δ -115.3 (s).

HRMS *m/z* calculated for $C_{13}H_{19}FNO$ $[M+H]^+$ 224.1451; found 224.1441.

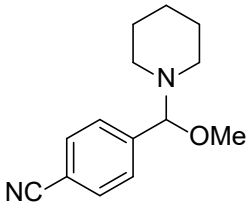
1-Methoxy-(mesityl)methyl-piperidine (1g)



Crude product used without further purification.

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 6.81 (s, 2H, Ar-C*H*), 4.82 (s, 1H, C*H*), 3.15 (s, 3H, OCH_3), 2.77-2.66 (m, 2H, CH_2), 2.46-2.36 (m, 4H, CH_2), 2.41 (s, 6H, CH_3), 2.27 (s, 3H, CH_3), 1.55-1.40 (m, 4H, CH_2).

1-Methoxy-(4-cyanophenyl)methyl-piperidine (1h)



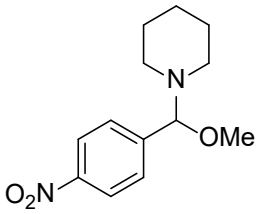
Recrystallisation from MeOH/Et_2O afforded **1h** as a yellow solid (41%).

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.63 (d, *J* = 8.2 Hz, 2H, Ar-C*H*), 7.47 (d, *J* = 8.2 Hz, 2H, Ar-C*H*), 4.78 (s, 1H, C*H*), 3.42 (s, 3H, OCH_3), 2.63-2.40 (m, 4H, CH_2), 1.60-1.32 (m, 6H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 144.4 (quaternary-*C*), 131.9 (Ar-*C*H), 128.1 (Ar-*C*H), 119.1 (*C*≡N), 111.4 (quaternary-*C*), 97.5 (*C*H), 57.2 (O*C*H_3), 48.7 (*C*H_2), 26.3 (*C*H_2), 24.8 (*C*H_2).

HRMS *m/z* calcd for $C_{14}H_{19}N_2O$ $[M+H]^+$ 231.1497, found 231.1491.

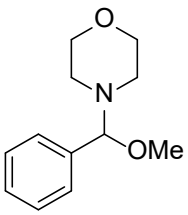
1-Methoxy-(4-nitrophenyl)methyl-piperidine (1i)



Crude product used without further purification.

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 8.20 (d, *J* = 8.8 Hz, 2H, Ar-C*H*), 7.54 (d, *J* = 8.6 Hz, 2H, Ar-C*H*), 4.83 (s, 1H, C*H*), 3.47 (s, 3H, OCH_3), 2.63-2.51 (m, 4H, CH_2), 1.57-1.46 (m, 4H, CH_2), 1.45-1.37 (m, 2H, CH_2).

1-Methoxy-(phenyl)methyl-morpholine (1j)



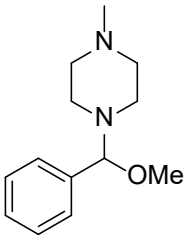
Recrystallisation from MeOH/Et_2O afforded **1j** as an orange solid (77%).

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.39-7.30 (m, 5H, Ar-C*H*), 4.68 (s, 1H, C*H*), 3.71-3.63 (m, 4H, CH_2), 3.37 (s, 3H, OCH_3), 2.68-2.52 (m, 4H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 137.8 (quaternary-*C*), 128.9 (Ar-*C*H), 128.2 (Ar-*C*H), 127.6 (Ar-*C*H), 98.2 (*C*H), 67.3 (O*C*H_2), 56.5 (O*C*H_3), 48.2 (*C*H_2).

HRMS *m/z* calculated for $C_{12}H_{21}NNaO_3$ $[M+Na+MeOH]^+$ 262.1419; found 262.1626.

1-Methoxy-(phenyl)methyl-4-methylpiperazine (1k)



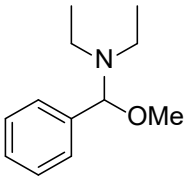
Recrystallisation from MeOH/Et_2O afforded **1k** as a yellow solid (27%).

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.37-7.28 (m, 5H, Ar-C*H*), 4.68 (s, 1H, C*H*), 3.36 (s, 3H, OCH_3), 2.67-2.51 (m, 4H, CH_2), 2.43-2.33 (m, 4H, CH_2), 2.23 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 138.0 (quaternary-*C*), 128.7 (Ar-*C*H), 128.0 (Ar-*C*H), 127.4 (Ar-*C*H), 97.8 (*C*H), 56.4 (O*C*H_3), 55.3 (*C*H_2), 47.4 (*C*H_3), 46.1 (*C*H_2).

HRMS *m/z* calculated for $C_{13}H_{20}N_2NaO$ $[M+Na]^+$ 243.1468; found 243.0894.

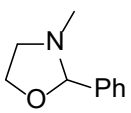
1-Methoxy-(phenyl)methyl-4-methylpiperazine (1l)



Crude product used without further purification.

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.45-7.30 (m, 5H, Ar-C*H*), 5.04 (s, 1H, C*H*), 3.38 (s, 3H, OCH_3), 2.69 (q, *J* = 7.2 Hz, 4H, NC$H_2$$CH_3$), 1.03 (t, *J* = 7.2 Hz, 6H, NCH_2CH_3).

1-Methyl-2-phenyloxazolidine (1m)



To a solution of benzaldehyde (0.8 mL, 7.87 mmol) in 10 mL benzene containing activated 4 Å molecular sieves was added 2-methylaminoethanol (0.6 mL, 7.5 mmol), and the reaction

was left to stir at room temperature overnight. The reaction mixture was filtered through celite, and all volatiles were removed *in vacuo* to give **1m** as a colourless oil (1.1 g, 90% yield).

Analytical data in accordance with the literature.[3]

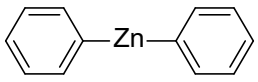
^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.51-7.43 (m, 2H, Ar-C*H*), 7.41-7.30 (m, 3H, Ar-C*H*), 4.66 (s, 1H, C*H*), 4.17-3.99 (m, 2H, CH_2), 3.39-3.29 (m, 1H, CH_2), 2.71 (td, *J* = 9.1, 7.8 Hz, 1H, CH_2), 2.30 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 139.2 (quaternary-*C*), 128.9 (Ar-*C*H), 128.4 (Ar-*C*H), 127.7 (Ar-*C*H), 98.5 (*C*H), 65.5 (*C*H_2), 54.8 (*C*H_2), 38.4 (N*C*H_3).

Synthesis of Diarylzinc Reagents (2a-g)

Diarylzinc reagents were prepared following the general procedure: To a solution of ArLi (20 mmol) in Et_2O (40 mL) was added $ZnCl_2$ (1.36 g, 10 mmol) at -78 °C. The reaction mixture was warmed to room temperature and allowed to stir overnight. The insoluble solids were removed by filtration and the filtrate was evaporated to dryness to give the crude product. Specific purification methods, if necessary, are detailed below. For **2e** and **2f**, the ArLi reagents were prepared *in situ* from the corresponding aryl-iodide and ^{n}BuLi at -78 °C. For **2g**, 2-lithiothiophene was prepared *in situ* directly from thiophene and ^{n}BuLi at -78 °C.

Diphenylzinc (2a)



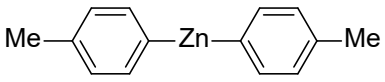
Sublimed in vacuo (140 °C, 0.1 mbar) to give **2a** as a colourless solid (43%).

Analytical data in accordance with the literature.[4]

^{1}H NMR (300.1 MHz, 298 K, Tol-d_8): δ 7.27-7.16 (m, 10H, Ar-C*H*).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, Tol-d_8): δ 148.3 (quaternary-*C*), 137.8 (Ar-*C*H), 137.5 (Ar-*C*H), 127.9 (Ar-*C*H).

Di-*p*-tolylzinc (2b)



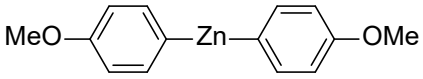
Colourless solid (59%).

Analytical data in accordance with the literature.[4]

^{1}H NMR (300.1 MHz, 298 K, Tol-d_8): δ 7.71 (d, *J* = 7.6 Hz, 4H, Ar-C*H*), 7.21 (d, *J* = 7.6 Hz, 4H, Ar-C*H*), 2.31 (s, 6H, CH_3).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, Tol-d_8): δ 150.1 (quaternary-C), 139.2 (quaternary-*C*), 135.6 (Ar-*C*H), 128.3 (Ar-*C*H), 21.7 (*C*H_3).

Di-(4-methoxyphenyl)zinc (2c)



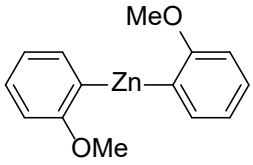
Colourless solid (81%).

Analytical data in accordance with the literature.[4]

^1H NMR (300.1 MHz, 298 K, Tol-d_8): δ 7.64 (d, *J* = 8.3 Hz, 4H, Ar-C*H*), 7.0 (d, *J* = 8.3 Hz, 4H, Ar-C*H*), 3.49 (s, 6H, OCH_3).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, Tol-d_8): δ 159.7 (quaternary-*C*), 143.4 (quaternary-*C*), 140.0 (Ar-*C*H), 113.6 (Ar-*C*H), 54.3 (O*C*H_3).

Di-(2-methoxyphenyl)zinc (2d)



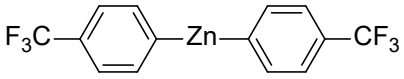
Colourless solid (81%).

Analytical data in accordance with the literature.[4]

^1H NMR (300.1 MHz, 298 K, THF-d_8): δ 7.46 (dd, *J* = 6.8, 1.8 Hz, 2H, Ar-C*H*), 7.09-7-00 (m, 2H, Ar-C*H*), 6.81-6.73 (m, 2H, Ar-C*H*), 6.69 (d, *J* = 8.1 Hz, 2H, Ar-C*H*), 3.69 (s, 6H, OCH_3).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, THF-d_8): δ 167.2 (quaternary*C*), 143.4 (quaternary-*C*), 139.6 (Ar-*C*H), 127.6 (Ar-*C*H), 121.0 (Ar-*C*H), 109.0 (Ar-*C*H), 55.2 (O*C*H_3).

Di-(4-trifluoromethylphenyl)zinc (2e)



Pale orange solid (40%).

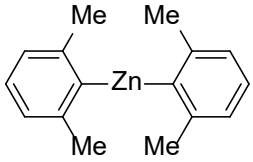
Analytical data in accordance with the literature.[4]

^1H NMR (300.1 MHz, 298 K, Tol-d_8): δ 7.49 (d, *J* = 8.2 Hz, 4H, Ar-C*H*), 7.46 (d, *J* = 8.2 Hz, 4H, Ar-C*H*).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, Tol-d_8): δ 154.0 (quaternary-*C*), 138.0 (Ar-*C*H), 130.1 (q, J_{C-F} = 32.1 Hz, quaternary-*C*), 123.8 (q, J_{C-F} = 3.9 Hz, quaternary-*C*). The *C*F_3 signal could not be observed.

$^{19}F\{^1H\}$ NMR (282.4 MHz, 298 K, Tol-d_8): δ -62.5 (s).

Di-(2,6-dimethylphenyl)zinc (2f)



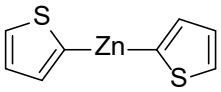
Colourless solid (74%).

Analytical data in accordance with the literature.[4]

^1H NMR (300.1 MHz, 298 K, THF-d_8): δ 6.86-6.68 (m, 6H Ar-C*H*), 2.38 (s, 12H, CH_3).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, THF-d_8): δ 145.2 (quaternary-*C*), 127.4 (Ar-*C*H), 125.3 (Ar-*C*H), 27.3 (*C*H_3).

Di-(thiophen-2-yl)zinc (2g)



Yellow solid (72%).

Analytical data in accordance with the literature.[4]

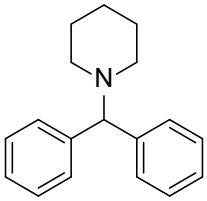
^1H NMR (300.1 MHz, 298 K, THF-d_8): δ 7.48 (d, *J* = 4.5 Hz, 1H, Ar-C*H*), 7.21 (d, *J* = 3.1 Hz, 1H, Ar-C*H*), 7.17-7.12 (m, 1H, Ar-C*H*).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, THF-d_8): δ 132.3 (Ar-*C*H), 125.6 (Ar-*C*H), 124.7 (Ar-*C*H). The quaternary carbon signal was not observed.

Synthesis of Diarylmethanamines (3a-p)

Diarylmethanamines were prepared following the general procedure: *N*,*O*-acetal (0.5 mmol), $ZnAr_2$ (0.25 mmol) and $Zn(C_6F_5)_2$ (100 mg, 0.25 mmol) were combined in toluene (5 mL) and allowed to stir at room temperature. The reaction mixture was quenched with MeOH (1 mL) then evaporated to dryness. The diarylmethanamine product was isolated and purified by silica gel column chromatography. Specific solvent systems are detailed for each product.

1-Benzhydrylpiperidine (3a)



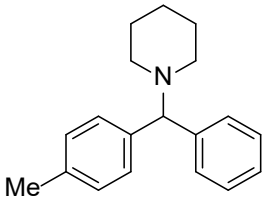
Colourless solid (91%). EtOAc/hexane (1:10).

Analytical data in accordance with the literature.[5]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.45-7.36 (m, 4H, Ar-C*H*), 7.30-7.22 (m, 4H, Ar-C*H*), 7.20-7.12 (m, 2H, Ar-C*H*), 4.22 (s, 1H, C*H*), 2.46-2.18 (m, 4H, CH_2), 1.63-1.50 (m, 4H, CH_2), 1.49-1.38 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 143.4 (quaternary-*C*), 128.4 (Ar-*C*H), 128.1 (Ar-*C*H), 126.8 (Ar-*C*H), 76.9 (*C*H), 53.3 (*C*H_2), 26.4 (*C*H_2), 24.8 (*C*H_2).

1-Phenyl-(*p*-tolyl)-methyl-piperidine (3b)



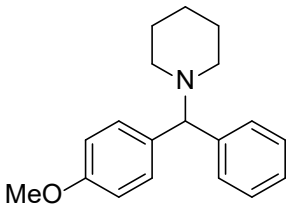
Colourless oil (88% from **1a** and **2b**; 83% from **1b** and **2a**). EtOAc/hexane (1:20).

Analytical data in accordance with the literature.[5]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.39 (d, *J* = 7.3 Hz, 2H, Ar-C*H*), 7.31-7.21 (m, 4H, Ar-C*H*), 7.14 (t, *J* = 7.3 Hz, 1H, Ar-C*H*), 7.07 (d, *J* = 7.8 Hz, 2H, Ar-C*H*), 4.18 (s, 1H, C*H*), 2.34-2.28 (m, 4H, CH_2), 2.28 (s, 3H, CH_3), 1.62-1.50 (m, 4H, CH_2), 1.47-1.38 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 143.7 (quaternary-*C*), 140.1 (quaternary-*C*), 136.3 (quaternary-*C*), 129.2 (Ar-*C*H), 128.4 (Ar-*C*H), 128.0 (Ar-*C*H), 126.7 (Ar-*C*H), 76.6 (*C*H), 53.3 (*C*H_2), 26.4 (*C*H_2), 24.9 (*C*H_2), 21.2 (*C*H_3).

1-Phenyl-(4-methoxyphenyl)-methyl-piperidine (3c)



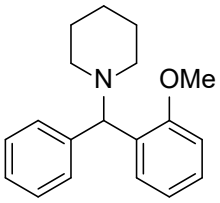
Colourless oil (90% from **1a** and **2c**; 83% from **1c** and **2a**). EtOAc/hexane (1:20).

Analytical data in accordance with the literature.[5]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.42 (d, *J* = 7.2 Hz, 2H, Ar-C*H*), 7.36-7.24 (m, 4H, Ar-C*H*), 7.18 (t, *J* = 7.2 Hz, 1H, Ar-C*H*), 6.87-6-80 (m, 2H, Ar-C*H*), 4.21 (s, 1H, C*H*), 3.77 (s, 3H, OCH_3), 2.42-2-.25 (m, 4H, CH_2), 1.66-1.54 (m, 4H, CH_2), 1.52-1.42 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 158.5 (quaternary-*C*), 143.8 (quaternary-*C*), 135.5 (quaternary-*C*), 129.2 (Ar-*C*H), 128.4 (Ar-*C*H), 128.0 (Ar-*C*H), 126.7 (Ar-*C*H), 113.8 (Ar-*C*H), 76.1 (*C*H), 55.3 (O*C*H_3), 53.2 (*C*H_2), 26.4 (*C*H_2), 24.9 (*C*H_2).

1-Phenyl-(2-methoxyphenyl)-methyl-piperidine (3d)



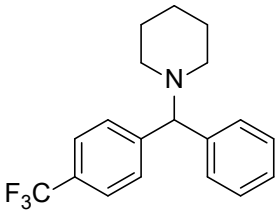
Colourless oil (92%). EtOAc/hexane (1:10).

Analytical data in accordance with the literature.[6]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.64 (dd, *J* = 7.5, 1.8 Hz, 1H, Ar-C*H*), 7.48-7.38 (m, 2H, Ar-C*H*), 7.27-7.08 (m, 4H, Ar-C*H*), 6.93 (td, *J* = 7.6, 1.2 Hz, 1H, Ar-C*H*), 6.79 (dd, *J* = 8.2, 1.2 Hz, 1H, Ar-C*H*), 4.76 (s, 1H, C*H*), 3.77 (s, 3H, OCH_3), 2.47-2.21 (m, 4H, CH_2), 1.61-1.50 (m, 4H, CH_2), 1.48-1.37 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 157.2 (quaternary-*C*), 143.5 (quaternary-*C*), 131.8 (quaternary-*C*), 128.4 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 127.3 (Ar-*C*H), 126.4 (Ar-*C*H), 120.8 (Ar-*C*H), 110.8 (Ar-*C*H), 67.4 (*C*H), 55.6 (O*C*H_3), 53.3 (*C*H_2), 26.4 (*C*H_2), 25.0 (*C*H_2).

1-Phenyl-(4-trifluoromethylphenyl)-methyl-piperidine (3e)



Colourless solid (84% from **1a** and **2e**; 82% from **1d** and **2a**). EtOAc/hexane (1:20).

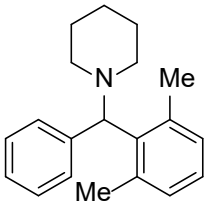
Analytical data in accordance with the literature.[3]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.50-7.41 (m, 4H, Ar-C*H*), 7.33-7.26 (m, 2H, Ar-C*H*), 7.24-7.16 (m, 2H, Ar-C*H*), 7.15-7.08 (m, 1H, Ar-C*H*), 4.21 (s, 1H, C*H*), 2.30-2.15 (m, 4H, CH_2), 1.55-1.44 (m, 4H, CH_2), 1.42-1.32 (m, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, $CDCl_3$): δ 147.9 (quaternary-*C*), 139.2 (quaternary-*C*), 136.7 (Ar-*C*H), 129.2 (Ar-*C*H), 128.1 (Ar-*C*H), 127.9 (Ar-*C*H), 125.3 (q, $J_{C\text{-}F}$ = 3.9 Hz, Ar-*C*-CF_3), 76.0 (*C*H), 53.1 (*C*H_2), 26.2 (*C*H_2), 24.6 (*C*H_2). The *C*F_3 signal could not be observed.

$^{19}F\{^1H\}$ NMR (282.4 MHz, 298 K, $CDCl_3$): δ -62.4 (s).

1-Phenyl-(2,6-dimethylphenyl)-methyl-piperidine (3f)



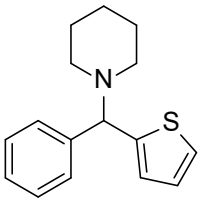
Colourless solid (90% yield). EtOAc/hexane (1:20).

^1H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.40-7.33 (m, 2H, Ar-C*H*), 7.27-7.18 (m, 2H, Ar-C*H*), 7.15-7.07 (m, 1H, Ar-C*H*), 7.03-6.89 (m, 3H, Ar-C*H*), 4.91 (s, 1H, C*H*), 2.60-2.44 (m, 2H, CH_2), 2.43 (s, 6H, CH_3), 2.34-2.19 (m, 2H, CH_2), 1.70-1.42 (m, 6H, CH_2).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, $CDCl_3$): δ 142.3 (quaternary-*C*), 139.4 (quaternary-*C*), 137.6 (quaternary-*C*), 129.4 (Ar-*C*H), 128.6 (Ar-*C*H), 127.6 (Ar-*C*H), 126.8 (Ar-*C*H), 125.9 (Ar-*C*H), 69.5 (*C*H), 53.6 (*C*H_2), 26.7 (*C*H_2), 25.0 (*C*H_2), 21.9 (*C*H_3).

HRMS *m/z* calculated for $C_{20}H_{26}N$ $[M+H]^+$ 280.2065; found 280.2056.

1-Phenyl-(thiophen-2-yl)-methyl-piperidine (3g)



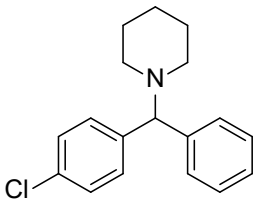
Yellow solid (89%). EtOAc/hexane (1:10).

Analytical data in accordance with the literature.[7]

^1H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.42 (d, *J* = 7.3 Hz, 2H, Ar-C*H*), 7.31 (t, *J* = 7.3 Hz, 2H, Ar-C*H*), 7.27-7.17 (m, 2H, Ar-C*H*), 6.94-6.81 (m, 2H, Ar-C*H*), 4.64 (s, 1H, C*H*), 2.48-2.24 (m, 4H, CH_2), 1.67-1.50 (m, 4H, CH_2), 1.47-1.33 (m, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, $CDCl_3$): δ 147.9 (quaternary-*C*), 141.4 (quaternary-*C*), 128.5 (Ar-*C*H), 128.3 (Ar-*C*H), 127.3 (Ar-*C*H), 126.3 (Ar-*C*H), 125.2 (Ar-*C*H), 124.9 (Ar-*C*H), 71.5 (*C*H), 52.7 (*C*H_2), 26.3 (*C*H_2), 24.7 (*C*H_2).

1-Phenyl-(4-chlorophenyl)-methyl-piperidine (3h)



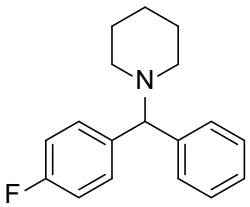
Colourless oil (85% yield). EtOAc/hexane (1:20).

Analytical data in accordance with the literature.[5]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.39-7.32 (m, 4H, Ar-C*H*), 7.29-7.12 (m, 5H, Ar-C*H*), 4.19 (s, 1H, C*H*), 2.43-2.14 (m, 4H, CH_2), 1.63-1.48 (m, 4H, CH_2) 1.47-1.36 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 142.7 (quaternary-*C*), 141.9 (quaternary-*C*), 132.3 (quaternary-*C*), 129.3 (Ar-*C*H), 128.54 (Ar-*C*H), 128.48 (Ar-*C*H), 128.0 (Ar-*C*H), 127.0 (Ar-*C*H), 76.0 (*C*H), 53.1 (*C*H_2), 26.3 (*C*H_2), 24.7 (*C*H_2).

1-Phenyl-(4-fluorophenyl)-methyl-piperidine (3i)



Colourless solid (86%). EtOAc/hexane (1:10).

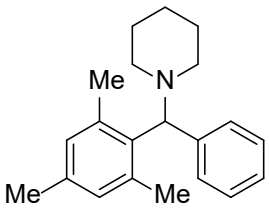
Analytical data in accordance with the literature.[5]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.39-7.31 (m, 4H, Ar-C*H*), 7.26 (t, *J* = 7.2 Hz, 2H, Ar-C*H*), 7.17 (t, *J* = 7.2 Hz, 1H, Ar-C*H*), 7.00-6.88 (m, 2H, Ar-C*H*), 4.21 (s, 1H, C*H*), 2.43-2.16 (m, 4H, CH_2), 1.63-1.51 (m, 4H, CH_2), 1.49-1.37 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 161.8 (d, $J_{C\text{-}F}$ = 244.7 Hz, quaternary-*C*F), 143.2 (quaternary-*C*), 139.1 (quaternary-*C*), 129.5 (d, $J_{C\text{-}F}$ = 7.8 Hz, Ar-*C*H), 128.5 (Ar-*C*H), 128.1 (Ar-*C*H), 126.9 (Ar-*C*H), 115.2 (d, $J_{C\text{-}F}$ = 21.2 Hz, Ar-*CH*), 76.0 (Ph-*C*H), 53.2 (*C*H_2), 26.4 (*C*H_2), 24.8 (*C*H_2).

^{19}F{^{1}H} NMR (282.4 MHz, 298 K, $CDCl_3$): δ -116.5 (s).

1-Phenyl-(mesityl)-methyl-piperidine (3j)



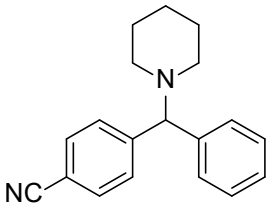
Colourless solid (73%). EtOAc/hexane (1:20).

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.28 (m, 2H, Ar-C*H*), 7.17-7.10 (m, 2H, Ar-C*H*), 7.06-6.98 (m, 1H, Ar-C*H*), 6.68 (s, 2H, Ar-C*H*), 4.79 (s, 1H, C*H*), 2.49-2.34 (m, 2H, CH_2), 2.31 (s, 6H, CH_3), 2.25-2.15 (m, 2H, CH_2); 2.13 (s, 3H, CH_3), 1.59-1.31 (m, 6H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 142.6 (quaternary-*C*), 137.4 (quaternary-*C*), 136.4 (quaternary-*C*), 136.1 (quaternary-*C*), 130.2 (Ar-*C*H), 128.5 (Ar-*C*H), 127.6 (Ar-*C*H), 125.8 (Ar-*C*H), 69.3 (*C*H), 53.6 (*C*H_2), 26.7 (*C*H_2), 25.0 (*C*H_2), 21.8 (CH_3), 20.9 (*C*H_3).

HRMS *m/z* calculated for $C_{21}H_{28}N$ $[M+H]^+$ 294.222; found 294.2215.

1-Phenyl-(4-cyanophenyl)-methyl-piperidine (3k)



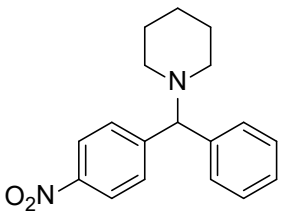
Colourless oil (81%). EtOAc/hexane (1:5).

Analytical data in accordance with the literature.[8]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.60-7.51 (m, 4H, Ar-C*H*), 7.37-7.16 (m, 5H, Ar-C*H*), 4.28 (s, 1H, C*H*), 2.42-2.16 (m, 4H, CH_2), 1.66-1.52 (m, 4H, CH_2), 1.50-1.39 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 149.3 (quaternary-*C*), 141.7 (quaternary-*C*), 132.4 (Ar-*C*H), 128.8 (Ar-*C*H), 128.7 (Ar-*C*H), 128.2 (Ar-*C*H), 127.4 (Ar-*C*H), 119.1 (*C*≡N), 110.5 (quaternary-*C*), 76.5 (*C*H), 53.2 (*C*H_2), 26.4 (*C*H_2), 24.7 (*C*H_2).

1-Phenyl-(4-nitrophenyl)-methyl-piperidine (3l)



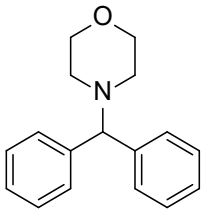
Colourless oil (58%). EtOAc/hexane (1:10).

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 8.13 (d, *J* = 8.8 Hz, 2H, Ar-C*H*), 7.61 (d, *J* = 8.8 Hz, 2H, Ar-C*H*), 7.40-7.16 (m, 5H, Ar-C*H*), 4.34 (s, 1H, C*H*), 2.48-2.16 (m, 4H, CH_2), 1.66-1.52 (m, 4H, CH_2), 1.50-1.38 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 151.4 (quaternary-*C*), 146.9 (quaternary-*C*), 141.5 (quaternary-*C*), 128.8 (Ar-*C*H), 128.7 (Ar-*C*H), 128.2 (Ar-*C*H), 127.5 (Ar-*C*H), 123.9 (Ar-*C*H), 76.2 (*C*H), 53.2 (*C*H_2), 26.3 (*C*H_2), 24.7 (*C*H_2).

HRMS *m/z* calculated for $C_{18}H_{21}N_2O_2$ $[M+H]^+$ 297.1603; found 297.1594.

1-Benzhydrylmorpholine (3m)



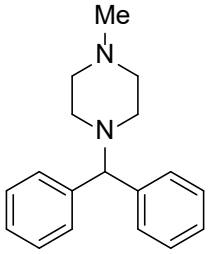
Colourless oil (86%). EtOAc/hexane (1:10).

Analytical data in accordance with the literature.[9]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.47-7.37 (m, 4H, Ar-C*H*), 7.31-7.22 (m, 4H, Ar-C*H*), 7.20-7.12 (m, 2H, Ar-C*H*), 4.19 (s, 1H, C*H*), 3.79-3.61 (m, 4H, CH_2), 2.46-2.31 (m, 4H, CH_2).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 142.5 (quaternary-*C*), 128.7 (Ar-*C*H), 128.0 (Ar-*C*H), 127.1 (Ar-*C*H), 76.8 (*C*H), 67.3 (*C*H_2), 52.8 (*C*H_2).

1-Benzhydryl-4-methylpiperazine (3n)



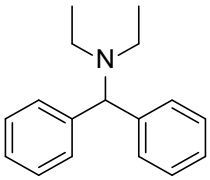
Colourless solid (72%). MeOH/CH_2Cl_2 (1:20 with 3% Et_3N).

Analytical data in accordance with the literature.[10]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.46-7.38 (m, 4H, Ar-C*H*), 7.31-7.22 (m, 4H, Ar-C*H*), 7.20-7.13 (m, 2H, Ar-C*H*), 4.21 (s, 1H, C*H*), 2.58-2.34 (m, 8H, CH_2), 2.28 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 143.0 (quaternary-*C*), 128.6 (Ar-*C*H), 128.0 (Ar-*C*H), 127.0 (Ar-*C*H), 76.4 (*C*H), 55.5 (*C*H_2), 52.1 (*C*H_2), 46.1 (*C*H_3).

1-Benzhydryl-*N,N*-diethylamine (3o)



Colourless solid (76%). EtOAc/hexane (1:20).

Analytical data in accordance with the literature.[8]

^{1}H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 7.46-7.38 (m, 4H, Ar-C*H*), 7.31-7.23 (m, 4H, Ar-C*H*), 7.22-7.12 (m, 2H, Ar-C*H*), 4.71 (s, 1H, C*H*), 2.57 (q, *J* = 7.1 Hz, 4H, CH_2), 0.98 (t, *J* = 7.1 Hz, 6H, CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, $CDCl_3$): δ 143.6 (quaternary-*C*), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 126.8 (Ar-*C*H), 71.4 (*C*H), 42.9 (*C*H_2), 11.2 (*C*H_3).

Synthesis of Aryl Zinc Alkoxides (4, 5 and 8)

$[PhZnOMe]_4$ (4)

$ZnPh_2$ (0.44 g, 2 mmol) was dissolved in toluene (5 mL) and MeOH (81 µL, 2 mmol) was slowly added using a microliter syringe. The reaction mixture was stirred for 15 minutes then filtered to remove any insoluble material. The filtrate was layered with hexane (10 mL) and stored at -40 °C for 72 hours. The colourless crystals were isolated by cannula filtration, washed with cold hexane (2 x 2.5 mL) and dried *in vacuo* (0.20 g, 58%). The isolated solids contained approximately 15% $[(PhZnOMe)_6ZnOMe_2]$ (**5**), which could be independently isolated and characterised by changing the reaction conditions (see below).

^{1}H NMR (300.1 MHz, 298 K, Tol-d_8): δ 7.61-7.53 (m, 8H, Ph-C*H*), 7.39-7.27 (m, 12H, Ph-C*H*), 3.62 (s, 12H, OCH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, Tol-d_8): δ 145.1 (quaternary-*C*), 139.5 (Ph-*C*H), 137.5 (Ph-*C*H), 128.2 (Ph-*C*H), 57.1 (O*C*H_3).

Elemental Analysis: Calculated for $(C_7H_8OZn)_4$; C, 48.45; H, 4.65. Found; C, 46.06; H, 4.56. The low carbon content is attributed to the presence of methoxy-rich **5**.

$[(PhZnOMe)_6ZnOMe_2]$ (5)

$ZnPh_2$ (0.27 g, 1.24 mmol) was dissolved in toluene (5 mL) and MeOH (50 µL, 1.24 mmol) was slowly added using a microliter syringe. The reaction mixture was stirred for 1 hour then concentrated by half *in vacuo*. Storage at 4 °C for 24 hours afforded colourless crystals that were isolated by filtration and dried *in vacuo* (0.04 g, 18%).

^{1}H NMR (300.1 MHz, 298 K, Tol-d_8): δ 7.61-7.52 (m, 12H, Ph-C*H*), 7.38-7.26 (m, 18H, Ph-C*H*), 3.84 (s, 18H, OCH_3), 3.63 (s, 6H, OCH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 298 K, Tol-d_8): δ 145.0 (quaternary-*C*), 139.5 (Ph-*C*H), 137.5 (Ph-*C*H), 128.3 (Ph-*C*H), 57.0 (O*C*H_3), 56.3 (O*C*H_3).

[(C_6F_5)ZnOMe]$_4$ (8)

Freshly sublimed Zn(C_6F_5)$_2$ (0.20 g, 0.5 mmol) was dissolved in toluene (2.5 mL) and MeOH (20 µL, 0.5 mmol) was added slowly using a microliter syringe. The reaction mixture was stirred for 15 minutes then filtered to remove any insoluble material. The filtrate was stored at -40 °C for 24 hours and the colourless crystals were isolated by cannula filtration, washed with cold pentane (1 mL) and dried *in vacuo* (0.04 g, 34%).

^{1}H NMR (300.1 MHz, 298 K, Tol-d_8): δ 3.57 (s, 12H, OCH_3).

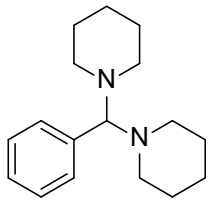
^{13}C{^{1}H} NMR (75.5 MHz, 298 K, Tol-d_8): δ 57.8 (OCH_3). Due to the poor solubility of the compound, signals for C_6F_5 could not be observed.

^{19}F{^{1}H} NMR (282.4 MHz, 298 K, Tol-d_8): δ -116.4 (m, *o*-C*F*), -151.4 (t, *p*-C*F*), -159.2 (m, *m*-C*F*). Minor signals are observed at d -116.3, -151.6 and -159.4.

Elemental Analysis: Calculated for ($C_7H_3F_5OZn$)$_4$; C, 31.91; H, 1.15. Found; C, 31.00; H, 1.11.

Synthesis of *N,N'*-Aminal and Zinc Adduct (6-7)

1,1'-(Phenylmethylene)bis-piperidine (6)



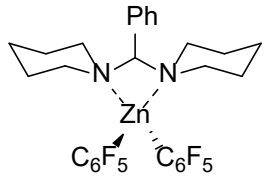
Freshly distilled piperidine (7.4 mL, 75 mmol) was added to a suspension containing benzaldehyde (3 mL, 30 mmol) and Al_2O_3 (10 g, 98 mmol) in anhydrous Et_2O (20 mL) at 0 ºC. The reaction mixture was warmed to room temperature and allowed to stir overnight. The suspension was filtered, and the filtrate was evaporated to dryness to give the crude solid that was recrystallised from petroleum ether (6.03 g, 78%).

Analytical data in accordance with the literature.[11]

^{1}H NMR (300.1 MHz, 298 K, Tol-d_8): δ 7.25-7.16 (m, 4H, Ar-C*H*), 7.15-7-08 (m, 1H, Ar-C*H*), 3.55 (s, 1H, C*H*), 2.51-2.30 (m, 8H, CH_2), 1.60-1.45 (m, 8H, CH_2), 1.36-1.24 (m, 4H, CH_2).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, Tol-d_8): δ 136.8 (quaternary-*C*), 129.3 (Ar-*C*H), 128.1 (Ar-*C*H), 127.8 (Ar-*C*H), 90.6 (*C*H), 50.9 (*C*H_2), 27.1 (*C*H_2), 26.2 (*C*H_2).

***N,N'*-Aminal-Zn(C_6F_5)$_2$ (7)**



Zn(C_6F_5)$_2$ (100 mg, 0.255 mmol) and **6** (65 mg, 0.25 mmol) were dissolved in toluene (2.5 mL) and stirred for 15 minutes at room temperature. Hexane (2.5 mL) was added, and the solution was stored at -40 ºC for 24 hours to give **7** as colourless crystals that were isolated by filtration, washed hexane (2.5 mL), and dried *in vacuo* (100 mg, 61%).

^1H NMR (300.1 MHz, 298 K, Tol-d_8): δ 7.21-7.11 (m, 3H, Ar-C*H*), 6.85-6.75 (m, 2H, Ar-C*H*), 4.49 (s, 1H, C*H*), 3.60-3.35 (m, 2H, C*H*$_2$), 3.06-2.83 (m, 2H, C*H*$_2$), 2.07-1.93 (m, 2H, C*H*$_2$), 1.77-1.60 (m, 2H, C*H*$_2$), 1.58-1.34 (m, 4H, C*H*$_2$), 1.20-0.97 (m, 6H, C*H*$_2$), 0.50-0.31 (m, 2H, C*H*$_2$).

$^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, Tol-d_8): δ 132.9 (quaternary-*C*), 130.0 (Ar-*C*H), 128.4 (Ar-*C*H), 126.3 (Ar-*C*H), 93.6 (*C*H), 56.8 (*C*H_2), 25.6 (*C*H_2), 24.9 (*C*H_2). Signals for C_6F_5 could not be observed.

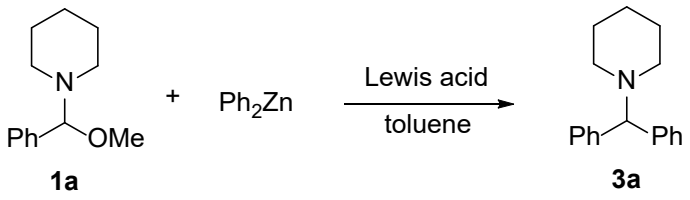
$^{19}F\{^1H\}$ NMR 282.4 MHz, 298 K, Tol-d_8): δ 114.9, 115.9, 156.5, 161.1.

Elemental Analysis: Calculated for $C_{29}H_{26}F_{10}N_2Zn$; C, 52.94; H, 3.98; N, 4.26. Found: C, 52.78; H, 4.05; N, 4.33.

Reaction Optimisation

Lewis Acid Optimisation

1a (100 mg, 0.488 mmol) was dissolved in toluene (5 ml) and $ZnPh_2$ (0.5 to 1 equivalents) and Lewis acid (0.1 to 0.5 equivalents) were added. After stirring at room temperature or heating for the specified period of time, the reaction was quenched with MeOH (1 mL) then evaporated to dryness. The yield of **3a** was determined by ^1H NMR spectroscopy against hexamethylcyclotrisiloxane as the internal standard. The results are summarised in **Table S1**.

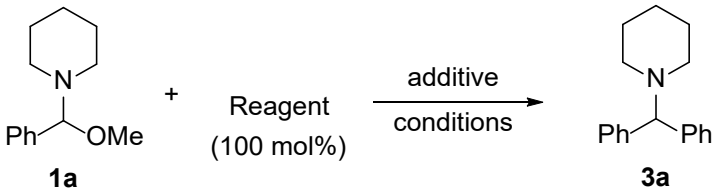


Entry	Conditions	$ZnPh_2$ (mol %)	Lewis acid (mol %)	Yield of **3a** (%)
1	1 h, rt	50	$Zn(C_6F_5)_2$ (10)	63
2	4 h, rt	50	$Zn(C_6F_5)_2$ (10)	67
3	24 h, rt	50	$Zn(C_6F_5)_2$ (10)	67
4	30 h, 80 ºC	50	$Zn(C_6F_5)_2$ (10)	68
5	24 h, rt	50	$B(C_6F_5)_3$ (10)	43
6	24 h, rt	50	$GaCl_3$ (10)	52
7	24 h, rt	50	$ZnBr_2$ (10)	47
8	1 h, rt	50	$Zn(C_6F_5)_2$ (20)	72
9	1 h, rt	50	$Zn(C_6F_5)_2$ (30)	81
10	1 h, rt	50	$Zn(C_6F_5)_2$ (50)	94
11	1 h, rt	50	−	47
12	1 h, rt	60	−	53
13	1 h, rt	70	−	68
14	1 h, rt	100	−	93

Table S1: Lewis acid optimisation for the arylation of *N,O*-acetals.

Reagent, Solvent and Additive Controls

To a 0.1 M solution of compound **1a** (100 mg, 0.488 mmol) was added the corresponding amount of reagent and/or additive. After stirring at room temperature or 0 °C for the specified period of time, the reaction was quenched with MeOH (1 mL) then evaporated to dryness. The yield of **3a** was determined by ^{1}H NMR spectroscopy against hexamethylcyclotrisiloxane as the internal standard. The results are summarised in **Table S2**.



1a **3a**

Entry	Conditions	Reagent	Additive (mol%)	Yield of **3a** (%)
1	toluene, rt, 16 h	$ZnPh_2$	THF (100)	–
2	toluene, rt, 16 h	$ZnPh_2$	TMEDA (100)	–
3	toluene, rt, 16 h	$ZnPh_2$	Bu_4NBr (100)	traces
4	THF, 0 ºC, 1 h	$Ph_3ZnMgCl$	–	–[a]
5	THF, 0 ºC, 1 h	Ph_3ZnLi	–	–[a]
6	toluene, rt, 16 h	PhZnBr	–	21

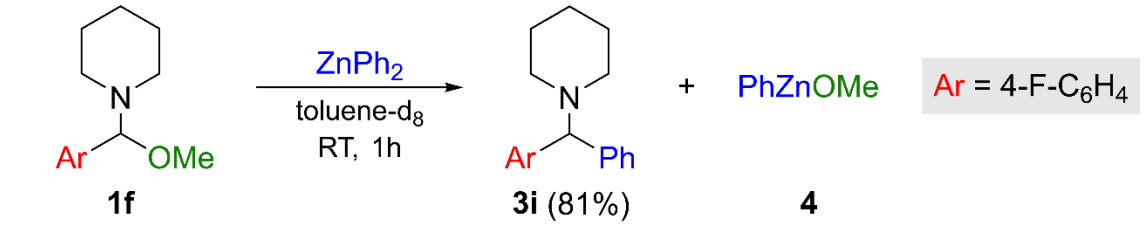
Table S2: Reagent, solvent and additive controls for the arylation of *N,O*-acetals. [a] The reaction resulted in decomposition of the starting material and gave a complex mixture of products.

Reaction Monitoring and Determining the Role of $Zn(C_6F_5)_2$

A series of NMR scale reactions were carried out to investigate the nature of the intermediates and elucidate the role of $Zn(C_6F_5)_2$ in enabling the atom-efficient transfer of both aryl groups from the diarylzinc reagent.

N,O-Acetal + 0.5 or 1 equivalents of $ZnPh_2$

A new species is observed when treating *N,O*-acetal (**1f**) with 0.5 equivalents of $ZnPh_2$ in toluene-d_8 (**Figure S1**). This species does not correlate with the starting material (**1f**) or arylated product (**3i**) but attempts to isolate this compound were unsuccessful. On addition of a second 0.5 equivalents of $ZnPh_2$, the arylated product (**3i**) is clearly observed alongside a new sharp signal at δ 3.63 (together with broad aromatic signals) which is attributed to the 'PhZnOMe' by-product (**4**).



1f **3i** (81%) **4**

^{1}H NMR

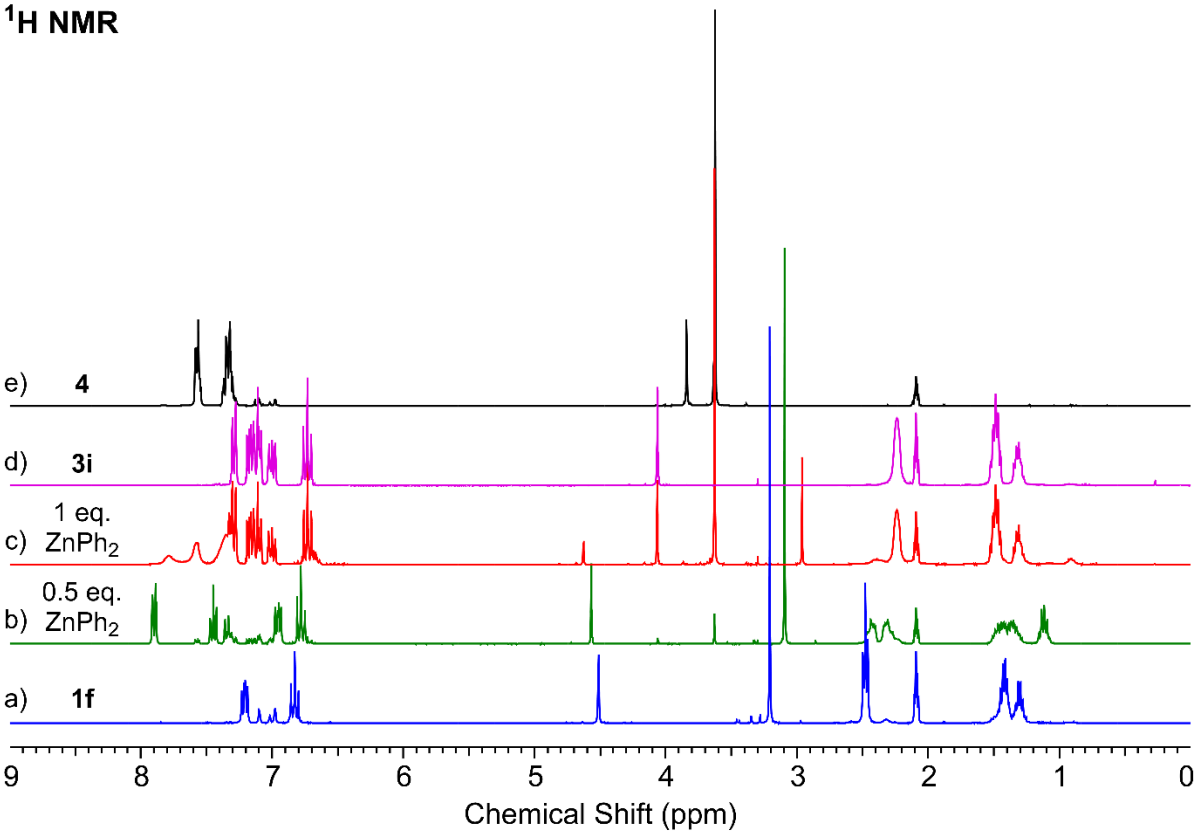


Figure S1: Stacked ^{1}H NMR spectra showing the reaction of *N,O*-acetal (**1f**) with 0.5 and 1 equivalent of $ZnPh_2$. Reference spectra of the arylated product (**3i**) and $[PhZnOMe]_4$ (**4**) in toluene-d_8 is included.

Evidence For Adduct Formation Between *N,O*-Acetal and $Zn(C_6F_5)_2$

When **1f** is combined with 1 equivalent of $Zn(C_6F_5)_2$ in toluene-d_8, significant broadening and shifting of the signals in the ^{1}H and ^{19}F NMR spectra are observed (**Figures S1 and S2**), indicative of adduct formation. Attempts however to isolate this species or grow crystals suitable for single-crystal X-ray diffraction were unsuccessful.

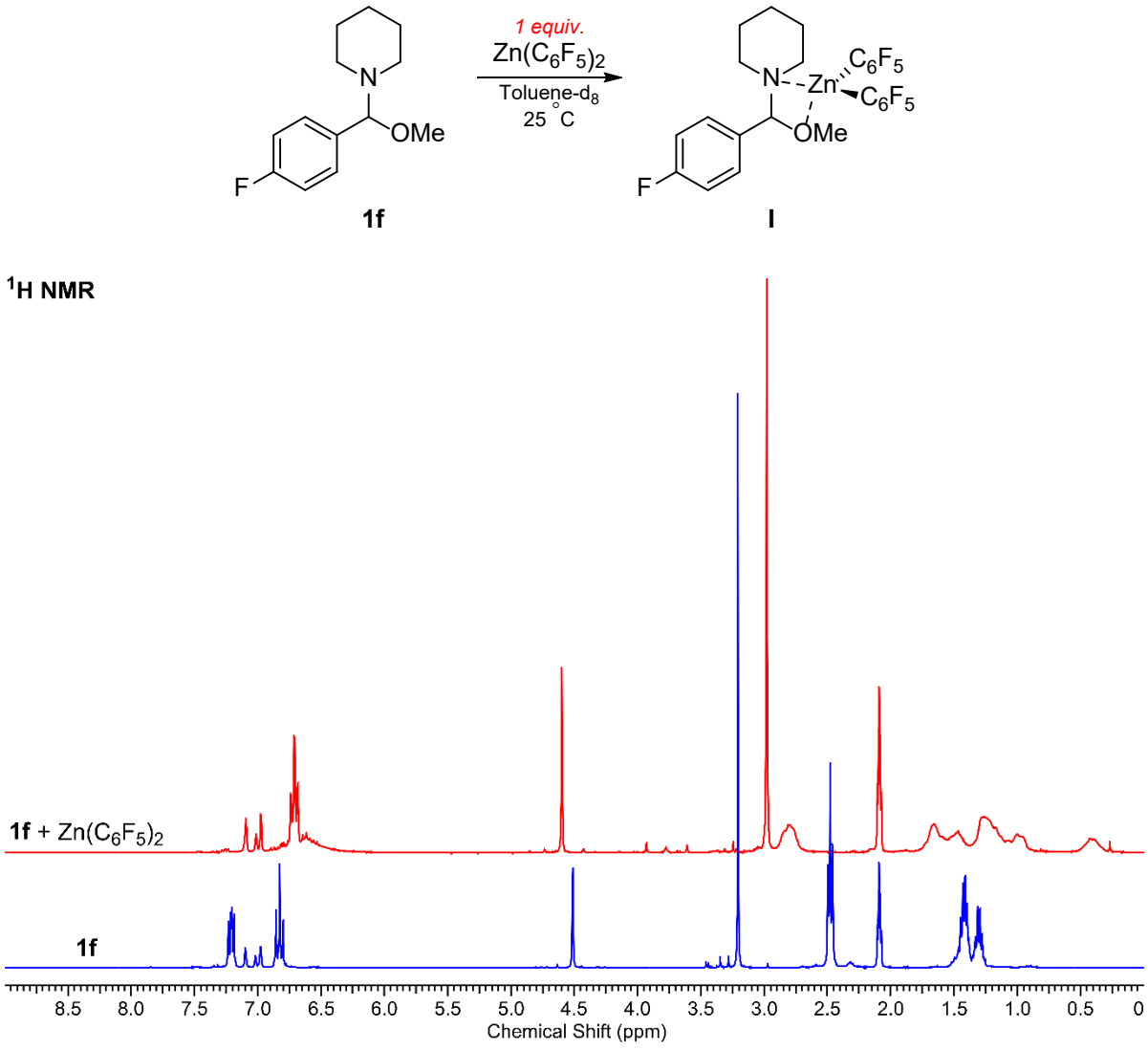


Figure S2: Stacked ^{1}H NMR spectra showing evidence for adduct formation between *N,O*-acetal **1f** and $Zn(C_6F_5)_2$.

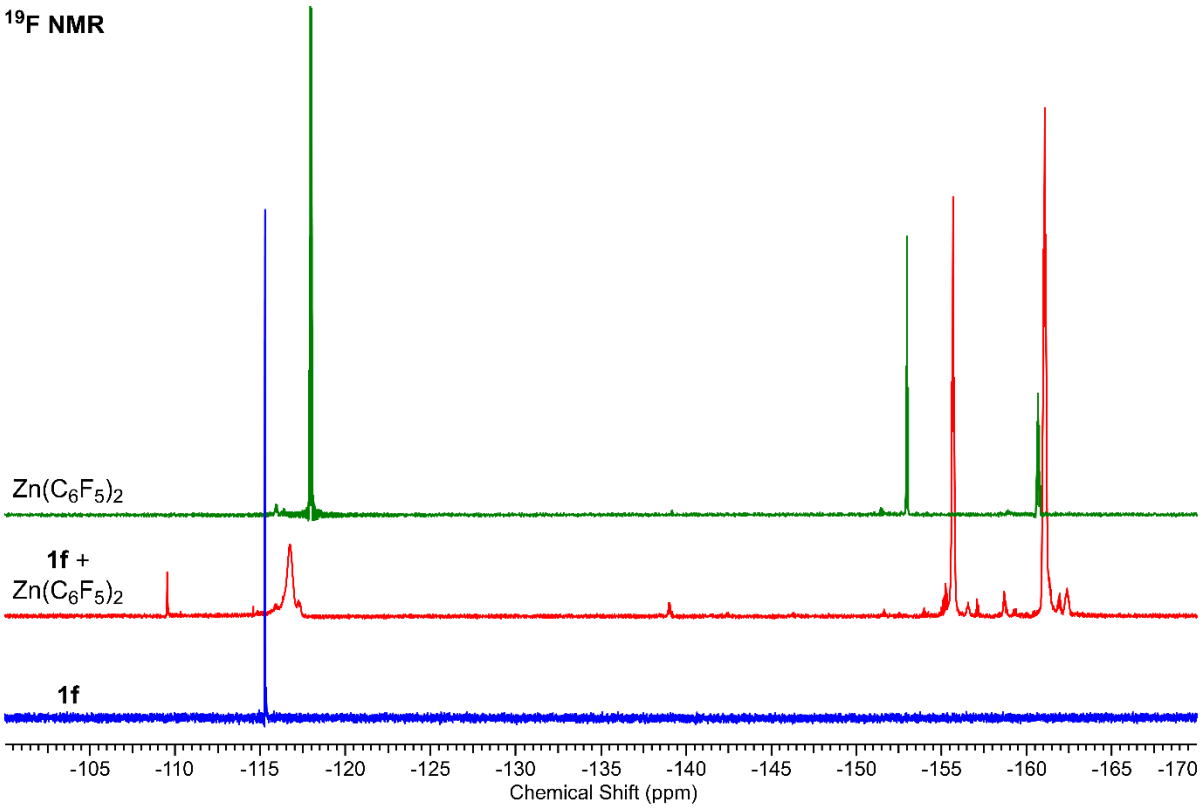
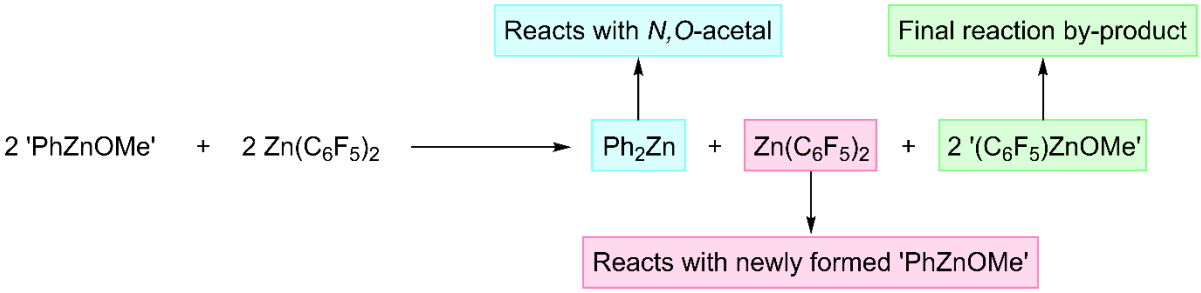


Figure S3: Stacked ^{19}F NMR spectra showing evidence for adduct formation between *N,O*-acetal **1f** and $Zn(C_6F_5)_2$.

Investigating the $ZnPh_2$ Regeneration

It was hypothesised that $Zn(C_6F_5)_2$ reacts with the inactive 'PhZnOMe' by-product to form '(C_6F_5)ZnOMe' and regenerate the nucleophilic $ZnPh_2$ reagent, allowing it to continue reacting with the *N,O*-acetal substrate (**Scheme S1**).



Scheme S1: Proposed role of $Zn(C_6F_5)_2$ in regenerating the nucleophilic $ZnPh_2$ species.

$[PhZnOMe]_4$ (**4**) and $[(C_6F_5)ZnOMe]_4$ (**8**) can be independently prepared by treating $ZnPh_2$ or $Zn(C_6F_5)_2$ with 1 equivalent of MeOH. When $[PhZnOMe]_4$ is treated with 0.5 or 1 equivalent of $Zn(C_6F_5)_2$ (**Figures S4-5**, **A** and **B**), signals closely matching the isolated $[(C_6F_5)ZnOMe]_4$ compound (**C**) are observed in the ^{19}F NMR spectra, however other signals are also present. When the 'PhZnOMe' by-product (from the reaction mixture) is treated with 1 equivalent of

$Zn(C_6F_5)_2$, the ^{19}F NMR spectrum (**D**) closely matches the spectrum obtained by treating isolated $[PhZnOMe]_4$ with $Zn(C_6F_5)_2$, but again, other signals are also present.

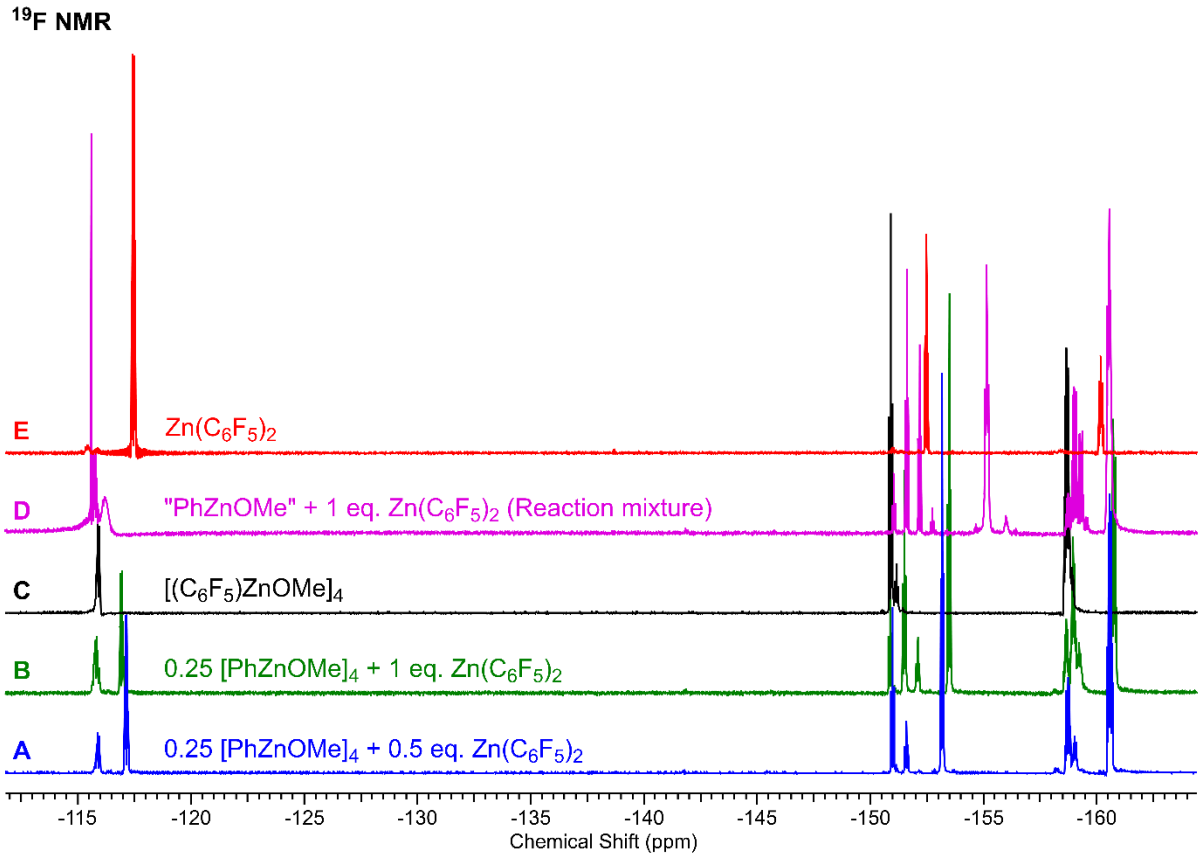


Figure S4: Stacked ^{19}F NMR spectra for the reaction of 'PhZnOMe' with $Zn(C_6F_5)_2$. Reference spectra for $[(C_6F_5)ZnOMe]_4$ and $Zn(C_6F_5)_2$ are shown.

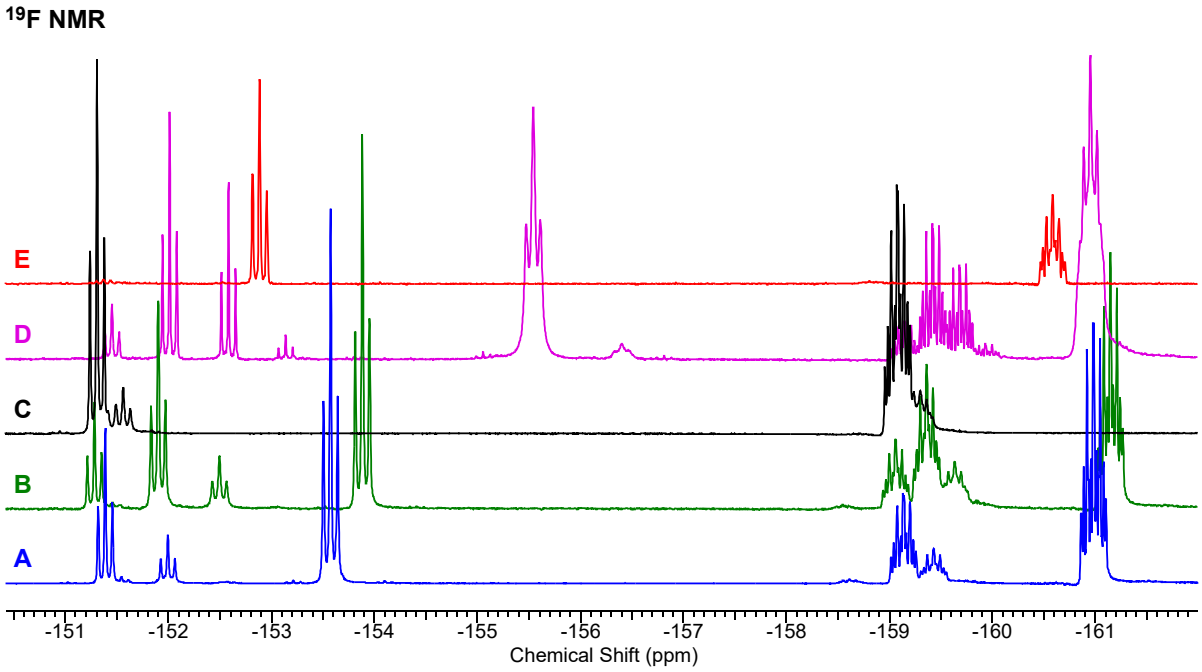


Figure S5: Stacked ^{19}F NMR spectra (highfield expansion) for the reaction of 'PhZnOMe' with $Zn(C_6F_5)_2$. Reference spectra for $[(C_6F_5)ZnOMe]_4$ and $Zn(C_6F_5)_2$ are shown.

These subtle differences and mixture of species are attributed to the formation of different aggregates. For example, the 'PhZnOMe' species formed in the reaction may not be tetrameric due to the presence of donor atoms in the *N,O*-acetal and arylated product. This hypothesis is supported by spiking each sample with THF, since this is likely to displace other donors and breakdown higher unsolvated aggregates. The stacked ^{19}F NMR spectra shown in **Figure S6** shows that on addition of THF, the speciation of products changes drastically and similar ^{19}F spectra are obtained in each case.

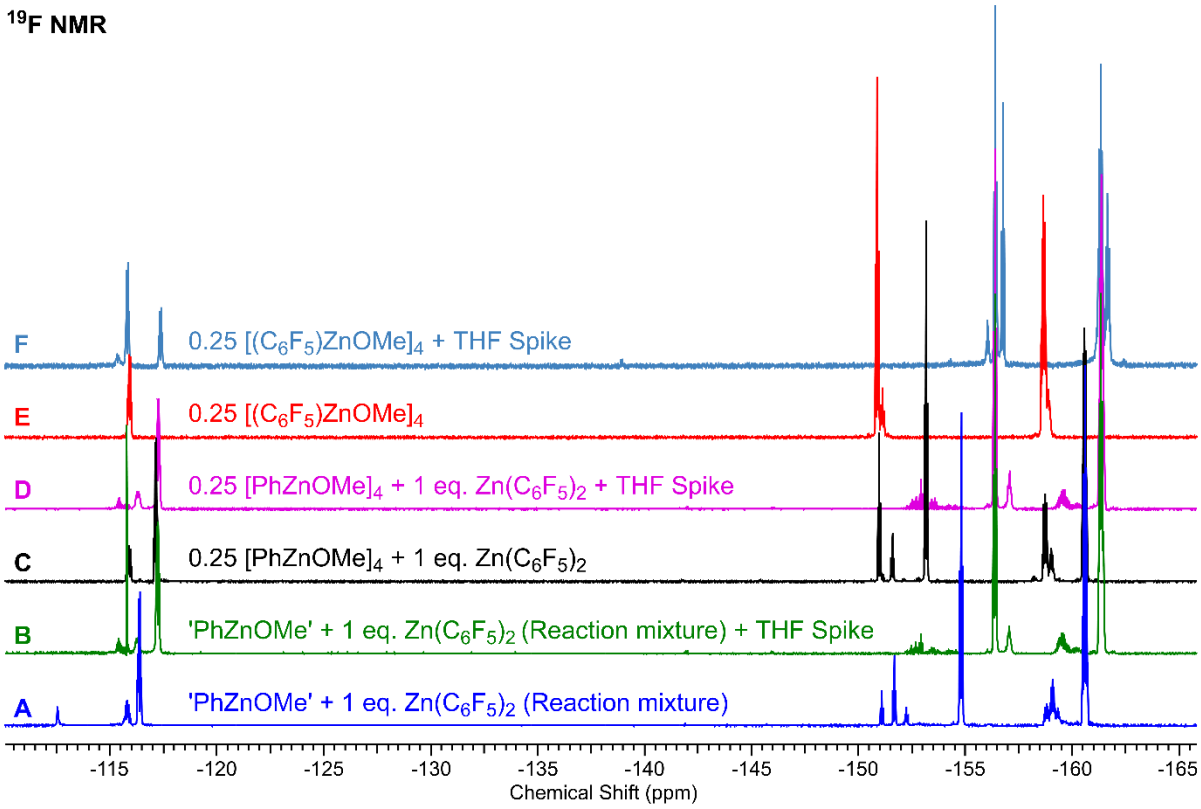


Figure S6: Stacked ^{19}F NMR spectra showing the formation of '$(C_6F_5)ZnOMe$' under different reaction conditions and the influence of spiking with THF.

THF spiking experiments can also identity the regeneration of $ZnPh_2$ when $[PhZnOMe]_4$ is treated with $Zn(C_6F_5)_2$ (**Figure S7**). $ZnPh_2$ can be observed as the bis-THF adduct (**D**).

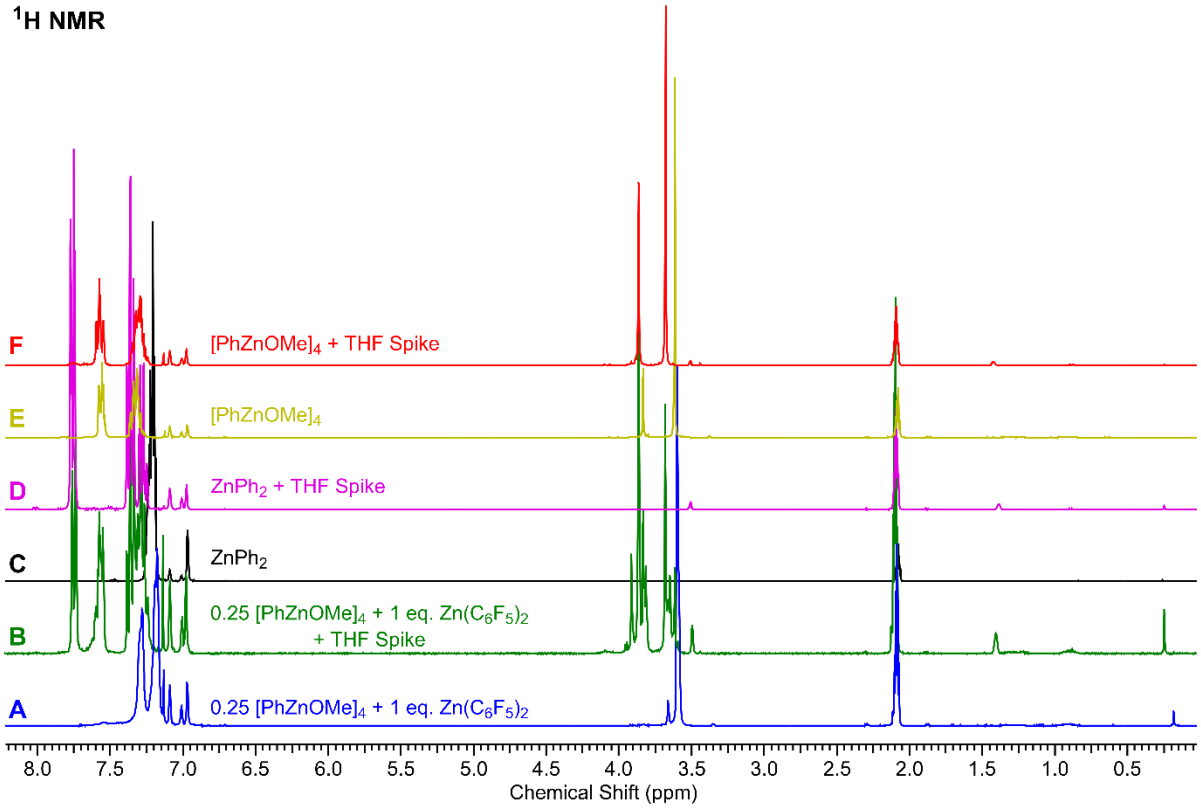
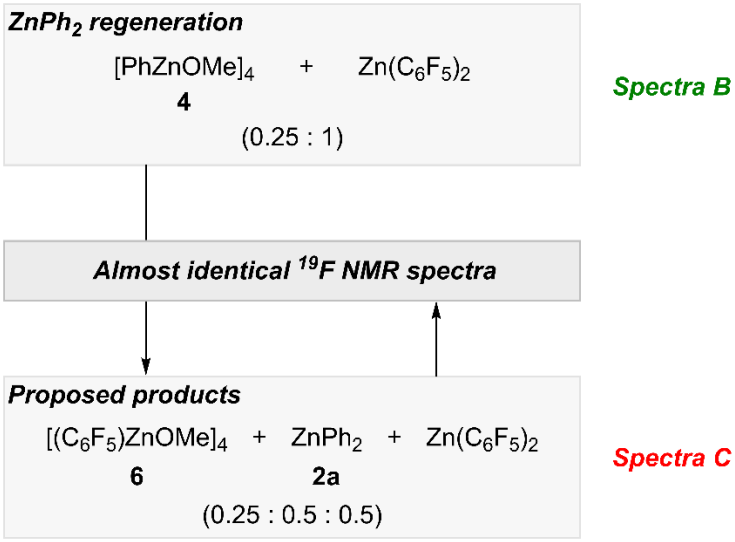


Figure S7: Stacked ^{1}H NMR spectra identifying the regeneration of $ZnPh_2$ when $[PhZnOMe]_4$ is treated with $Zn(C_6F_5)_2$.

It should also be noted that although the individual proposed products from the reaction of $[PhZnOMe]_4$ with $Zn(C_6F_5)_2$ can not be directly observed (**Scheme S2**), combining each component in the anticipated ratio together affords almost identical ^{19}F NMR spectra (**Figure S8**).



Scheme S2: Proposed product distribution when $[PhZnOMe]_4$ is treated with $Zn(C_6F_5)_2$.

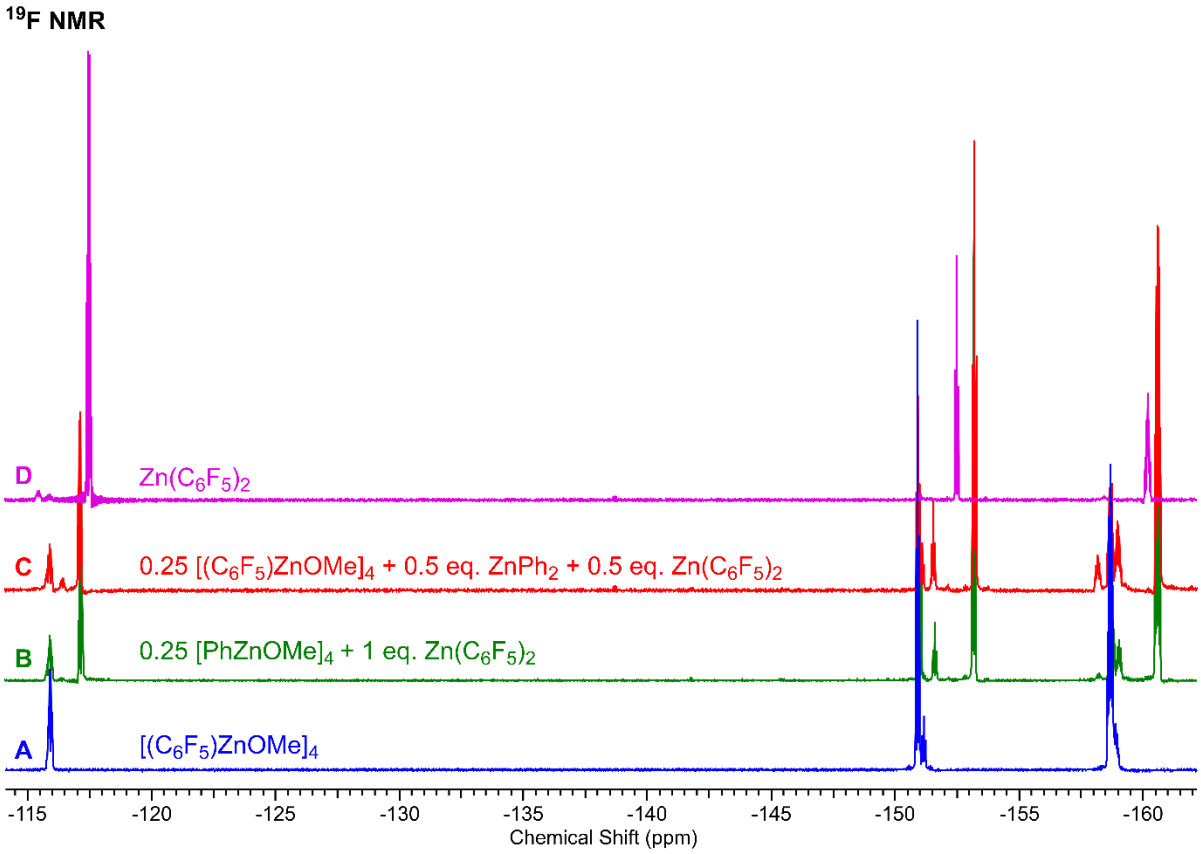
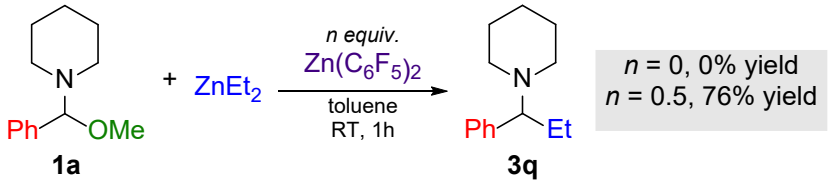


Figure S8: Stacked ^{19}F NMR spectra comparing the combination of $[PhZnOMe]_4$ with $Zn(C_6F_5)_2$ (**spectra B**) and $[(C_6F_5)ZnOMe]_4$ with $ZnPh_2$ and $Zn(C_6F_5)_2$ (**spectra C**). Reference ^{19}F NMR spectra for $[(C_6F_5)ZnOMe]_4$ (**spectra A**) and $Zn(C_6F_5)_2$ (**spectra D**) are shown.

Reactions of *N,O*-Acetal with $ZnEt_2$

N,O-Acetal **1a** (100 mg, 0.48 mmol) and $Zn(C_6F_5)_2$ (96 mg, 0.24 mmol) were combined in toluene (5 mL) and $ZnEt_2$ (0.5 M, 0.48 mL, 0.24 mmol) was added. After stirring for 1 hour at room temperature, the reaction was quenched by the addition of MeOH (1 mL) and then all volatiles were removed *in vacuo*. The residue was analysed by ^1H NMR spectroscopy and the yield of **3q** was calculated to be 76% against an internal standard (hexamethylcyclotrisiloxane). In the absence of $Zn(C_6F_5)_2$, no **3q** is formed.



X-ray Crystallography

The crystal structures have been deposited into the Cambridge Crystallographic Data Centre (CCDC) and have been assigned the following numbers: **4** – 2099646; **5** – 2099647; **7** – 2099648; **8** –2099649. Selected crystallographic and refinement parameters are presented below (**Tables S3-4**). In all cases, crystals immersed in an inert oil were mounted at ambient conditions and transferred into the nitrogen stream (173 K).

All measurements were made on a *RIGAKU Synergy S* area-detector diffractometer using mirror optics monochromated Cu Kα radiation (λ = 1.54184 Å) or on an *Oxford Diffraction SuperNova* area-detector diffractometer using mirror optics monochromated Mo *K*α radiation (λ = 0.71073 Å) and Al filtered. Data reduction was performed using the *CrysAlisPro* program.[12] The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the Gaussian method using SCALE3 ABSPACK in *CrysAlisPro* was applied. The structure was solved by direct methods or intrinsic phasing using *SHELXT*,[13] which revealed the positions of all non-hydrogen atoms of the compounds. All non-hydrogen atoms were refined anisotropically. H-atoms were assigned in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2Ueq of its parent atom (1.5Ueq for methyl groups). Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the *SHELXL-2014/7*[14] program in OLEX2.[15]

Identification code	**4**	**5**
Empirical formula	$C_{28}H_{32}O_4Zn_4$	$C_{51}H_{63}O_8Zn_7$
Formula weight	694.01	1261.6
Temperature/K	173.01(10)	173.00(10)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	*P*-1
a/Å	13.63748(12)	12.8055(5)
b/Å	16.05559(14)	14.5382(10)
c/Å	13.67121(12)	16.1933(10)
α/°	90	66.616(6)
β/°	90.1859(8)	75.238(4)
γ/°	90	85.544(4)
Volume/Å^3	2993.40(5)	2674.8(3)
Z	4	1
ρ_{calc}g/cm^3	1.54	1.566
μ/mm^{-1}	3.76	3.133
F(000)	1408	1286

Crystal size/mm^3	0.172 × 0.147 × 0.041	0.15 × 0.075 × 0.05
Radiation	Cu Kα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.466 to 145.584	3.25 to 56.34
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -16 ≤ l ≤ 16	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	76825	19320
Independent reflections	5939 [R_{int} = 0.0466, R_{sigma} = 0.0191]	19320 [R_{int} = ?, R_{sigma} = 0.5302]
Data/restraints/parameters	5939/0/330	19320/0/320
Goodness-of-fit on F^2	1.094	0.903
Final R indexes [I>=2σ (I)]	R_1 = 0.0525, wR_2 = 0.1487	R_1 = 0.0619, wR_2 = 0.0780
Final R indexes [all data]	R_1 = 0.0536, wR_2 = 0.1493	R_1 = 0.2263, wR_2 = 0.0841
Largest diff. peak/hole / e Å^{-3}	0.69/-0.75	1.26/-0.90

Table S3: Crystal data and structure refinement details for compounds **4-5**.

Identification code	**7**	**8**
Empirical formula	$C_{29}H_{26}F_{10}N_2Zn$	$C_{35}H_{20}F_{20}O_4Zn_4$
Formula weight	657.89	1145.99
Temperature/K	173.01(10)	173.00(10)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P-1
a/Å	9.4666(4)	10.17870(10)
b/Å	17.7242(7)	10.3481(2)
c/Å	16.3037(5)	19.0323(3)
α/°	90	85.6520(10)
β/°	96.154(3)	82.5450(10)
γ/°	90	84.9310(10)
Volume/Å^3	2719.80(18)	1975.75(5)
Z	4	2
ρ_{calc}g/cm^3	1.607	1.926
μ/mm^{-1}	2.094	3.998
F(000)	1336	1124
Crystal size/mm^3	0.321 × 0.248 × 0.102	0.141 × 0.103 × 0.052
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.39 to 154.846	4.692 to 136.494
Index ranges	-11 ≤ h ≤ 11, -22 ≤ k ≤ 22, -20 ≤ l ≤ 15	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -22 ≤ l ≤ 22
Reflections collected	23035	49800
Independent reflections	5586 [R_{int} = 0.1065, R_{sigma} = 0.0494]	7249 [R_{int} = 0.0322, R_{sigma} = 0.0161]
Data/restraints/parameters	5586/0/379	7249/0/574

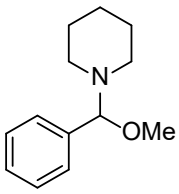
Goodness-of-fit on F^2	2.419	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.1933, wR_2 = 0.5125	R_1 = 0.0289, wR_2 = 0.0791
Final R indexes [all data]	R_1 = 0.1983, wR_2 = 0.5157	R_1 = 0.0308, wR_2 = 0.0803
Largest diff. peak/hole / e $Å^{-3}$	4.50/-1.00	0.36/-0.43

Table S4: Crystal data and structure refinement details for compounds **7-8**.

NMR Spectra of Reported Compounds

^{1}H NMR

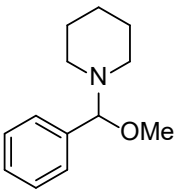
(300.1 MHz, 298 K, $CDCl_3$)



1a

^{13}C{^{1}H} NMR

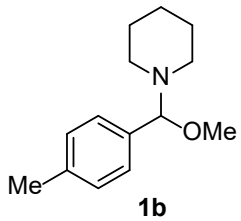
(75.5 MHz, 298 K, $CDCl_3$)



1a

^{1}H NMR

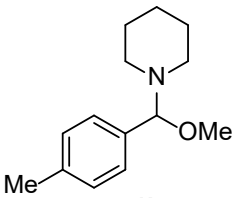
(300.1 MHz, 298 K, $CDCl_3$)



1b

^{13}C{^{1}H} NMR

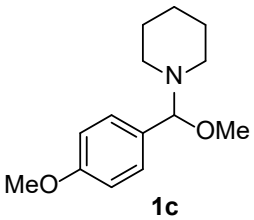
(75.5 MHz, 298 K, $CDCl_3$)



1b

^{1}H NMR

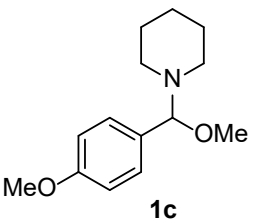
(300.1 MHz, 298 K, $CDCl_3$)



1c

$^{13}C\{^1H\}$ NMR

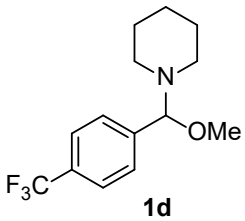
(75.5 MHz, 298 K, $CDCl_3$)



1c

^{1}H NMR

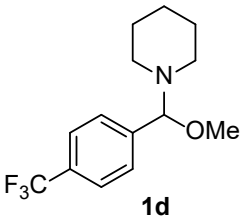
(300.1 MHz, 298 K, $CDCl_3$)



1d

^{13}C{^{1}H} NMR

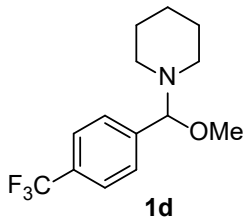
(75.5 MHz, 298 K, $CDCl_3$)



1d

^{19}F NMR

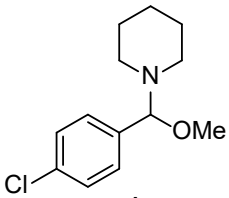
(282.4 MHz, 298 K, $CDCl_3$)



1d

^{1}H NMR

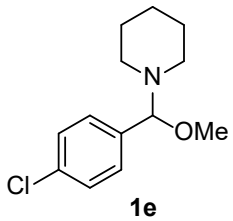
(300.1 MHz, 298 K, $CDCl_3$)



1e

$^{13}C\{^{1}H\}$ NMR

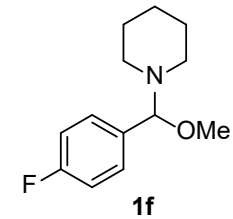
(75.5 MHz, 298 K, $CDCl_3$)



1e

^{1}H NMR

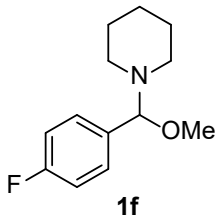
(300.1 MHz, 298 K, $CDCl_3$)



1f

$^{13}C\{^{1}H\}$ NMR

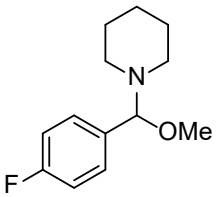
(75.5 MHz, 298 K, $CDCl_3$)



1f

^{19}F NMR

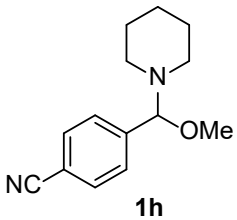
(282.4 MHz, 298 K, $CDCl_3$)



1f

^{1}H NMR

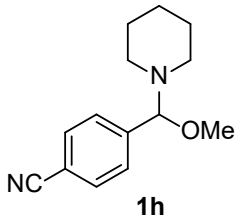
(300.1 MHz, 298 K, $CDCl_3$)



1h

^{13}C{^{1}H} NMR

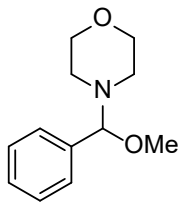
(75.5 MHz, 298 K, $CDCl_3$)



1h

^{1}H NMR

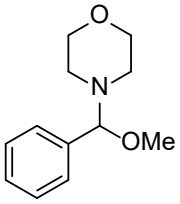
(300.1 MHz, 298 K, $CDCl_3$)



1j

^{13}C{^{1}H} NMR

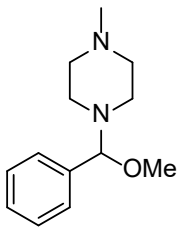
(75.5 MHz, 298 K, $CDCl_3$)



1j

^{1}H NMR

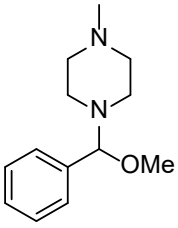
(300.1 MHz, 298 K, $CDCl_3$)



1k

$^{13}C\{^1H\}$ NMR

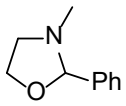
(75.5 MHz, 298 K, $CDCl_3$)



1k

^{1}H NMR

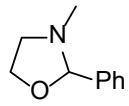
(300.1 MHz, 298 K, $CDCl_3$)



1m

^{13}C{^{1}H} NMR

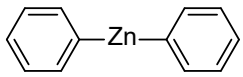
(75.5 MHz, 298 K, $CDCl_3$)



1m

^{1}H NMR

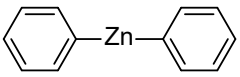
(300.1 MHz, 298 K, Tol-d_8)



2a

^{13}C{^{1}H} NMR

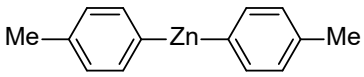
(75.5 MHz, 298 K, Tol-d_8)



2a

^{1}H NMR

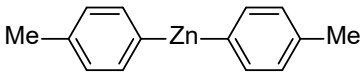
(300.1 MHz, 298 K, Tol-d_8)



2b

^{13}C{^{1}H} NMR

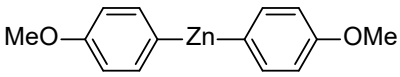
(75.5 MHz, 298 K, Tol-d_8)



2b

^{1}H NMR

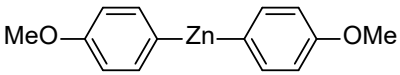
(300.1 MHz, 298 K, Tol-d_8)



2c

^{13}C{^{1}H} NMR

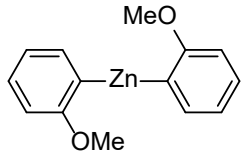
(75.5 MHz, 298 K, Tol-d_8)



2c

^{1}H NMR

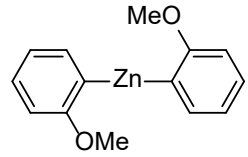
(300.1 MHz, 298 K, THF-d_8)



2d

^{13}C{^{1}H} NMR

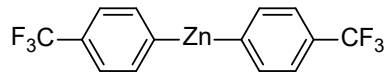
(75.5 MHz, 298 K, THF-d_8)



2d

^{1}H NMR

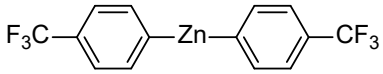
(300.1 MHz, 298 K, Tol-d_8)



2e

^{1}H NMR

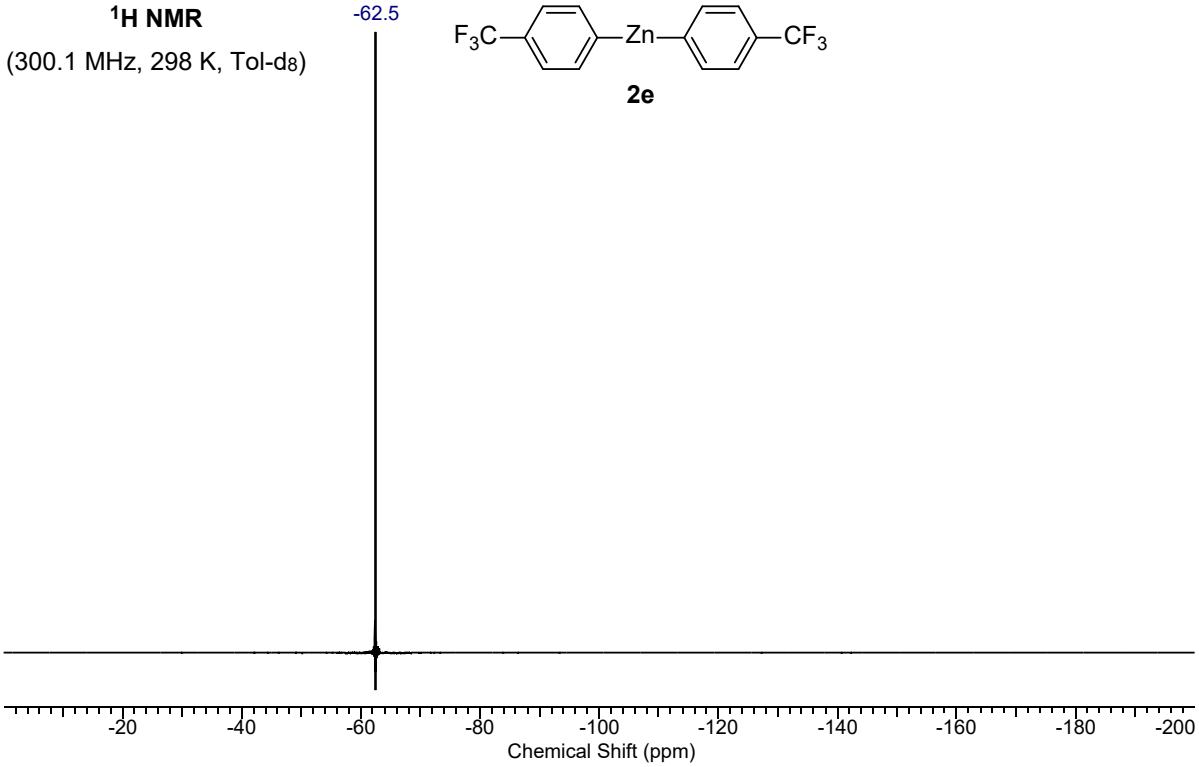
(300.1 MHz, 298 K, Tol-d_8)



2e

^{1}H NMR

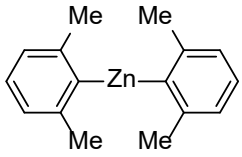
(300.1 MHz, 298 K, Tol-d_8)



2e

^{1}H NMR

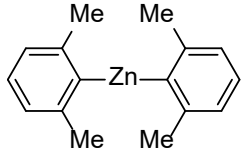
(300.1 MHz, 298 K, THF-d_8)



2f

$^{13}C\{^{1}H\}$ NMR

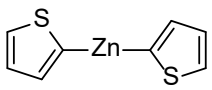
(75.5 MHz, 298 K, THF-d_8)



2f

^{1}H NMR

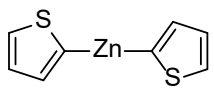
(300.1 MHz, 298 K, THF-d_8)



2g

$^{13}C\{^{1}H\}$ NMR

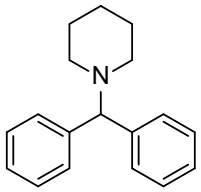
(75.5.1 MHz, 298 K, THF-d_8)



2g

^{1}H NMR

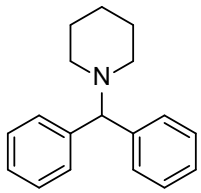
(300.1 MHz, 298 K, $CDCl_3$)



3a

$^{13}C\{^{1}H]$ NMR

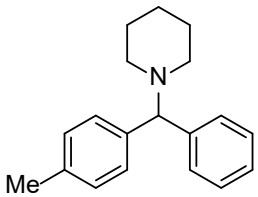
(75.5 MHz, 298 K, $CDCl_3$)



3a

^{1}H NMR

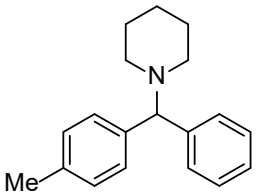
(300.1 MHz, 298 K, $CDCl_3$)



3b

$^{13}C\{^{1}H\}$ NMR

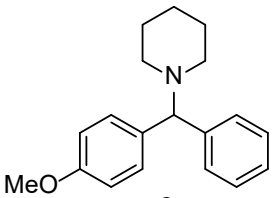
(75.5 MHz, 298 K, $CDCl_3$)



3b

^{1}H NMR

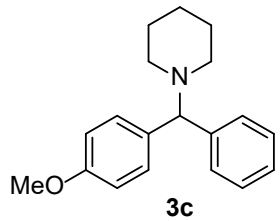
(300.1 MHz, 298 K, $CDCl_3$)



3c

$^{13}C\{^{1}H\}$ NMR

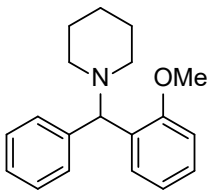
(75.5 MHz, 298 K, $CDCl_3$)



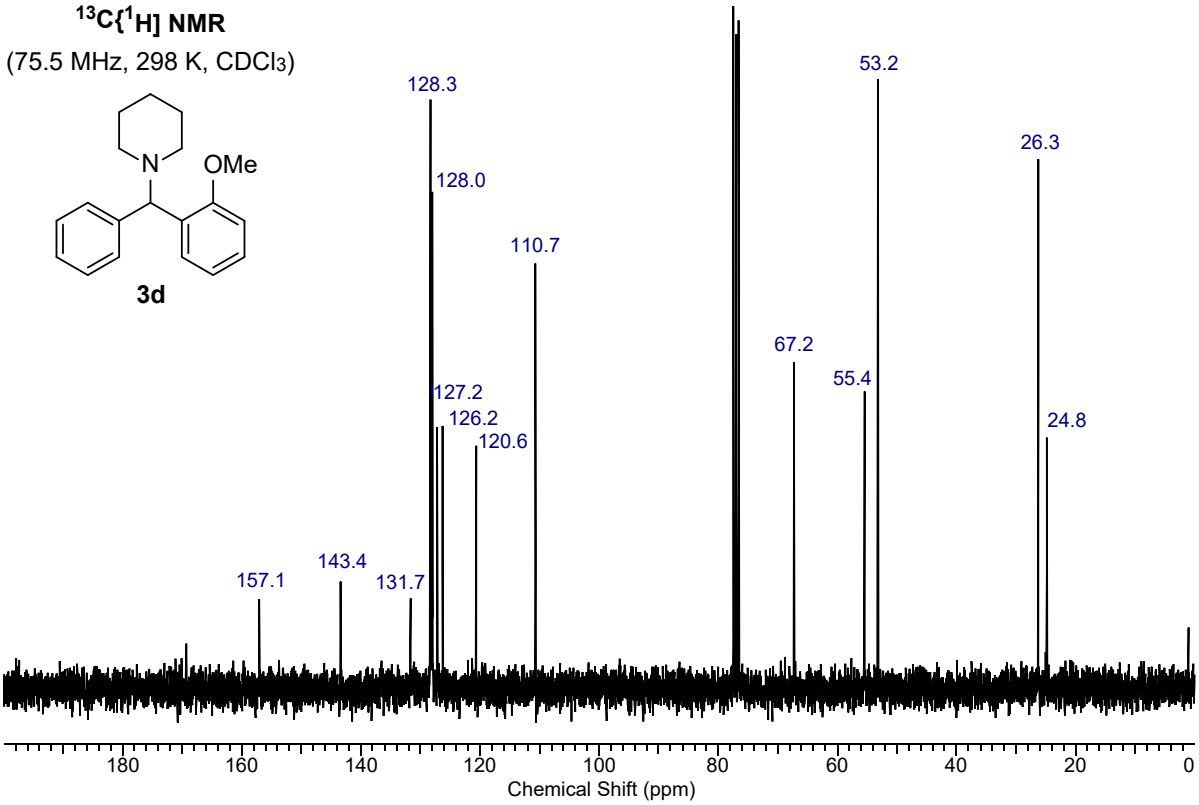
3c

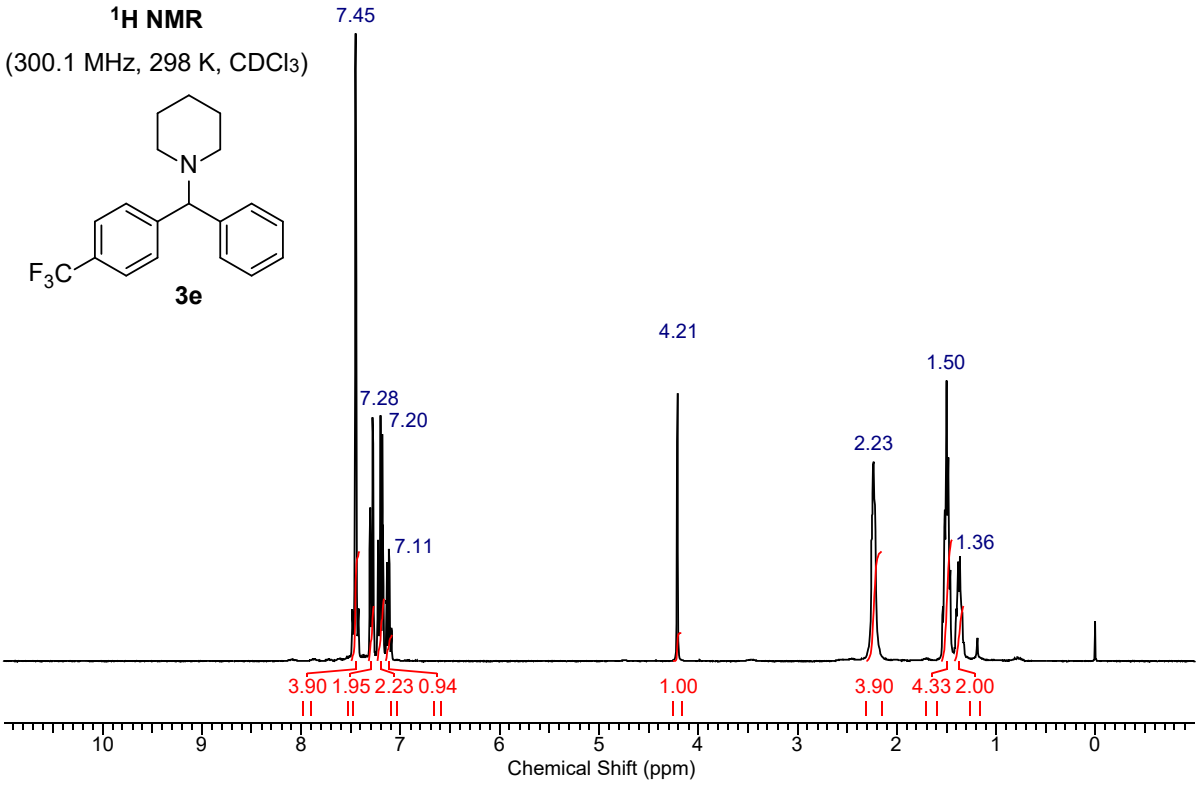
^{1}H NMR

(300.1 MHz, 298 K, $CDCl_3$)



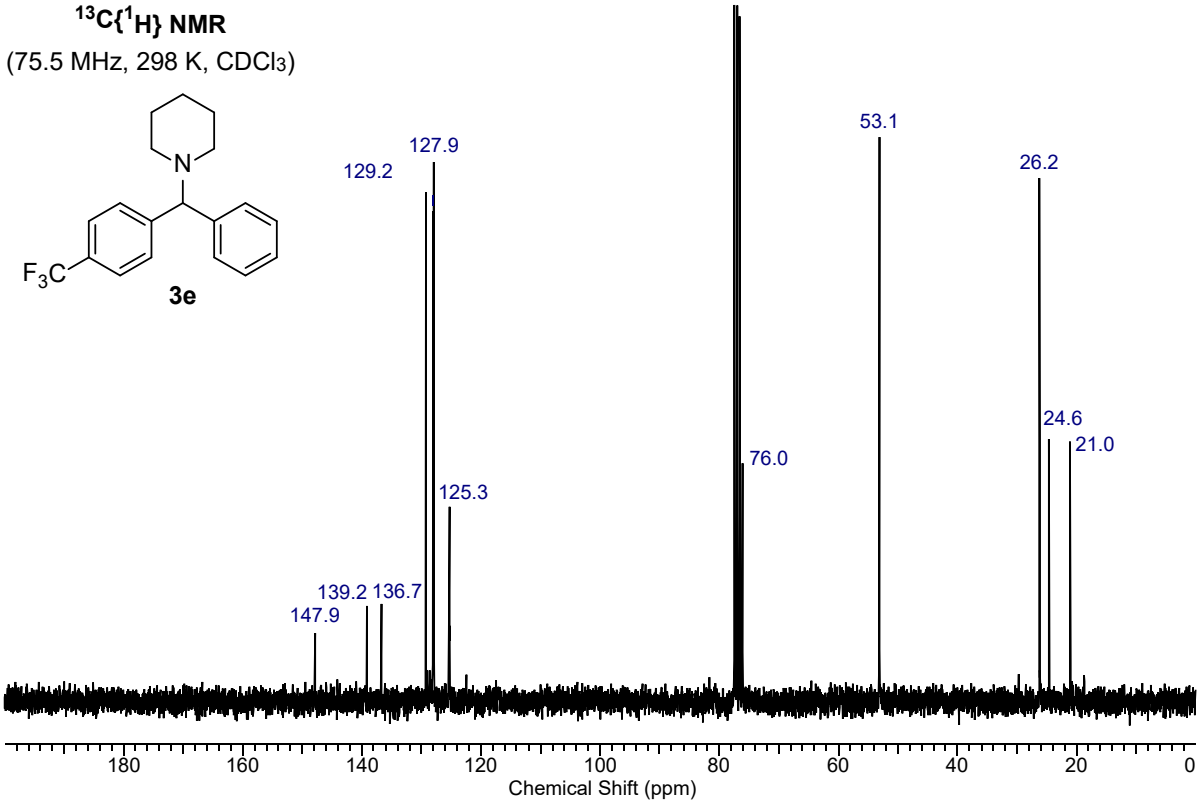
3d


$^{13}C\{^{1}H]$ NMR
(75.5 MHz, 298 K, $CDCl_3$)
N
OMe
3d
128.3
128.0
110.7
53.2
26.3
67.2
55.4
127.2
126.2
120.6
24.8
157.1
143.4
131.7
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


^{1}H NMR
(300.1 MHz, 298 K, $CDCl_3$)
N
F_3C
3e
7.45
4.21
1.50
7.28
7.20
2.23
7.11
1.36
3.90 1.95 2.23 0.94
1.00
3.90 4.33 2.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

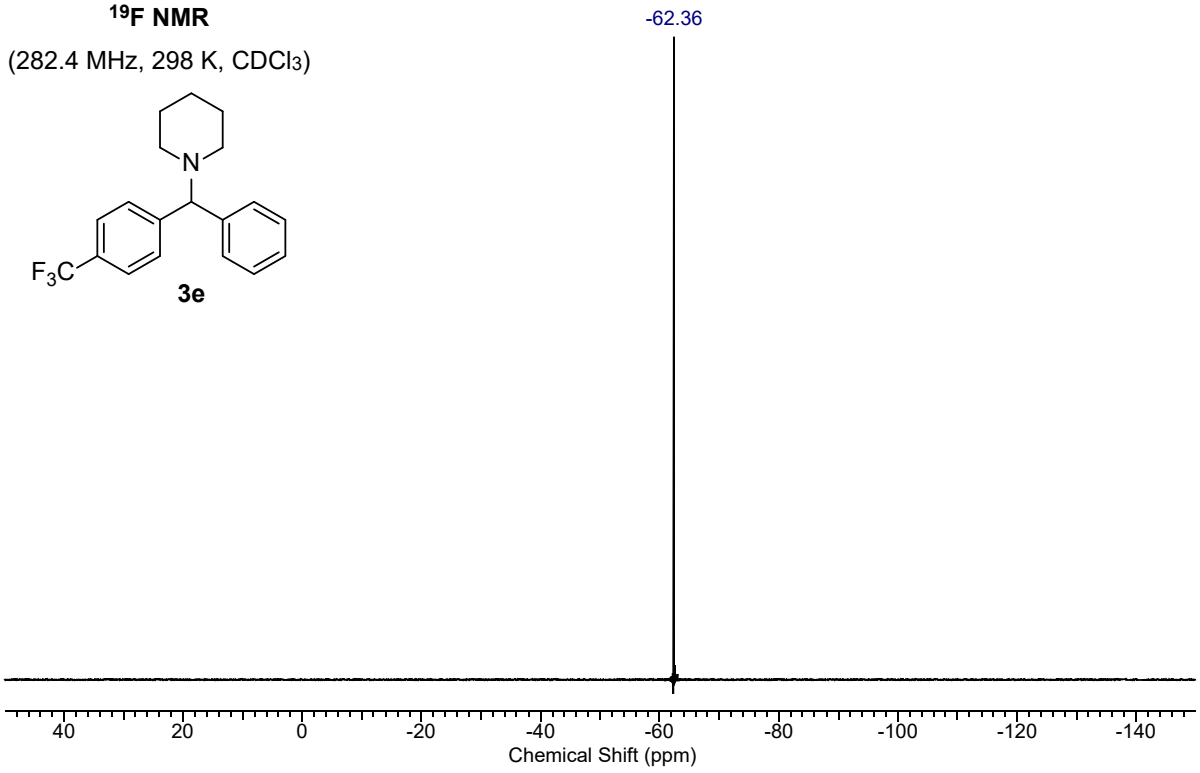
$^{13}C\{^{1}H\}$ NMR

(75.5 MHz, 298 K, $CDCl_3$)



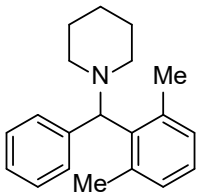
^{19}F NMR

(282.4 MHz, 298 K, $CDCl_3$)



^{1}H NMR

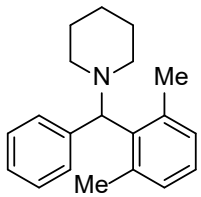
(300.1 MHz, 298 K, $CDCl_3$)



3f

$^{13}C\{^1H\}$ NMR

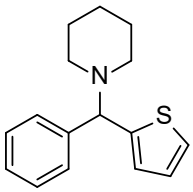
(75.5 MHz, 298 K, $CDCl_3$)



3f

^{1}H NMR

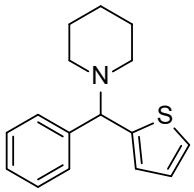
(300.1 MHz, 298 K, $CDCl_3$)



3g

^{13}C{^{1}H} NMR

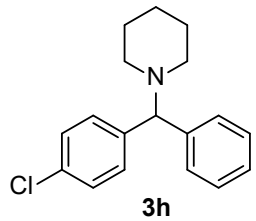
(75.5 MHz, 298 K, $CDCl_3$)



3g

^{1}H NMR

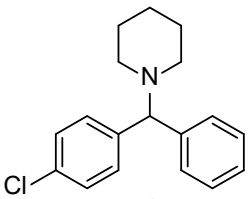
(300.1 MHz, 298 K, $CDCl_3$)



3h

$^{13}C\{^1H\}$ NMR

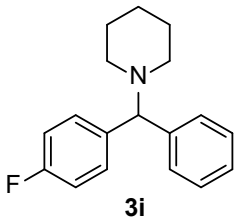
(75.5 MHz, 298 K, $CDCl_3$)



3h

^{1}H NMR

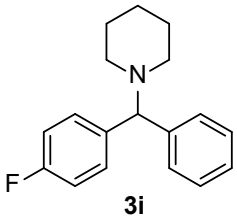
(300.1 MHz, 298 K, $CDCl_3$)



3i

$^{13}C\{^1H\}$ NMR

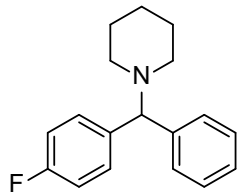
(75.5 MHz, 298 K, $CDCl_3$)



3i

^{19}F NMR

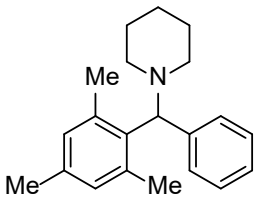
(282.4 MHz, 298 K, $CDCl_3$)



3i

^{1}H NMR

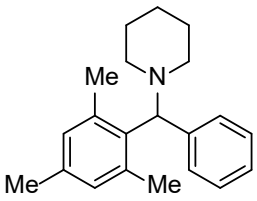
(300.1 MHz, 298 K, $CDCl_3$)



3j

$^{13}C\{^{1}H\}$ NMR

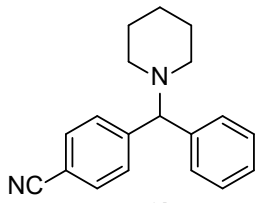
(75.5 MHz, 298 K, $CDCl_3$)



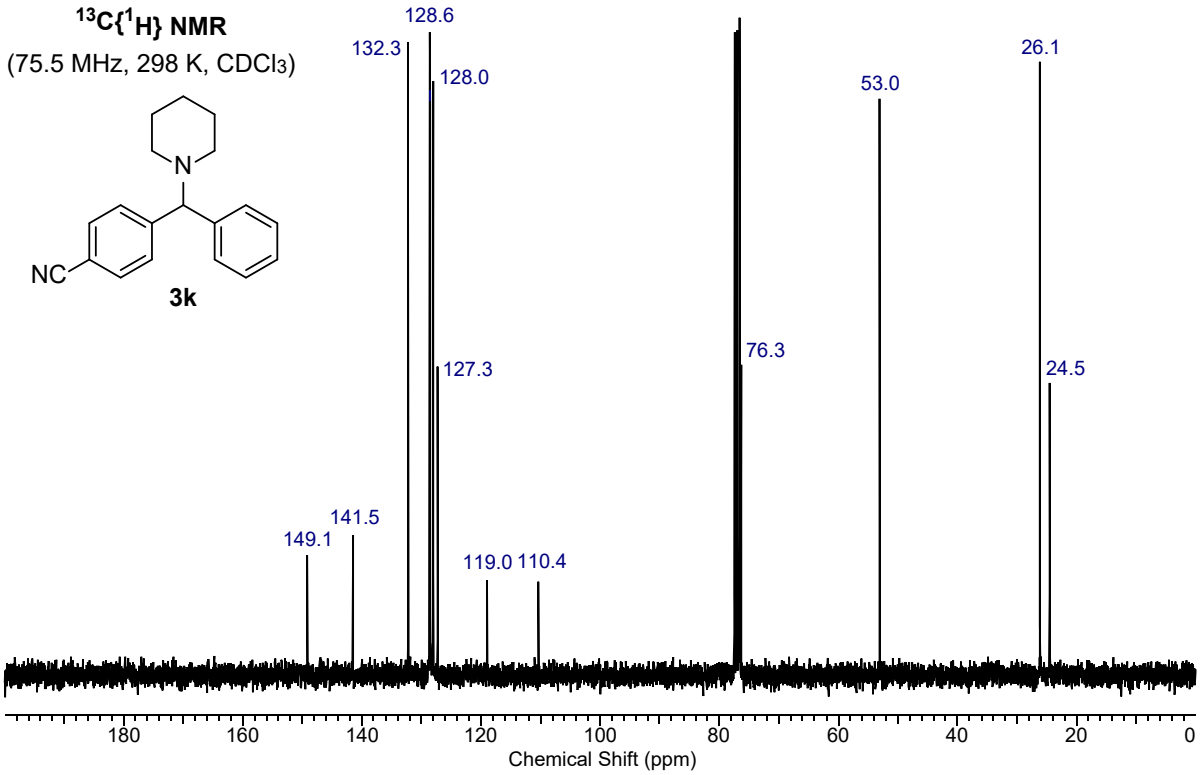
3j

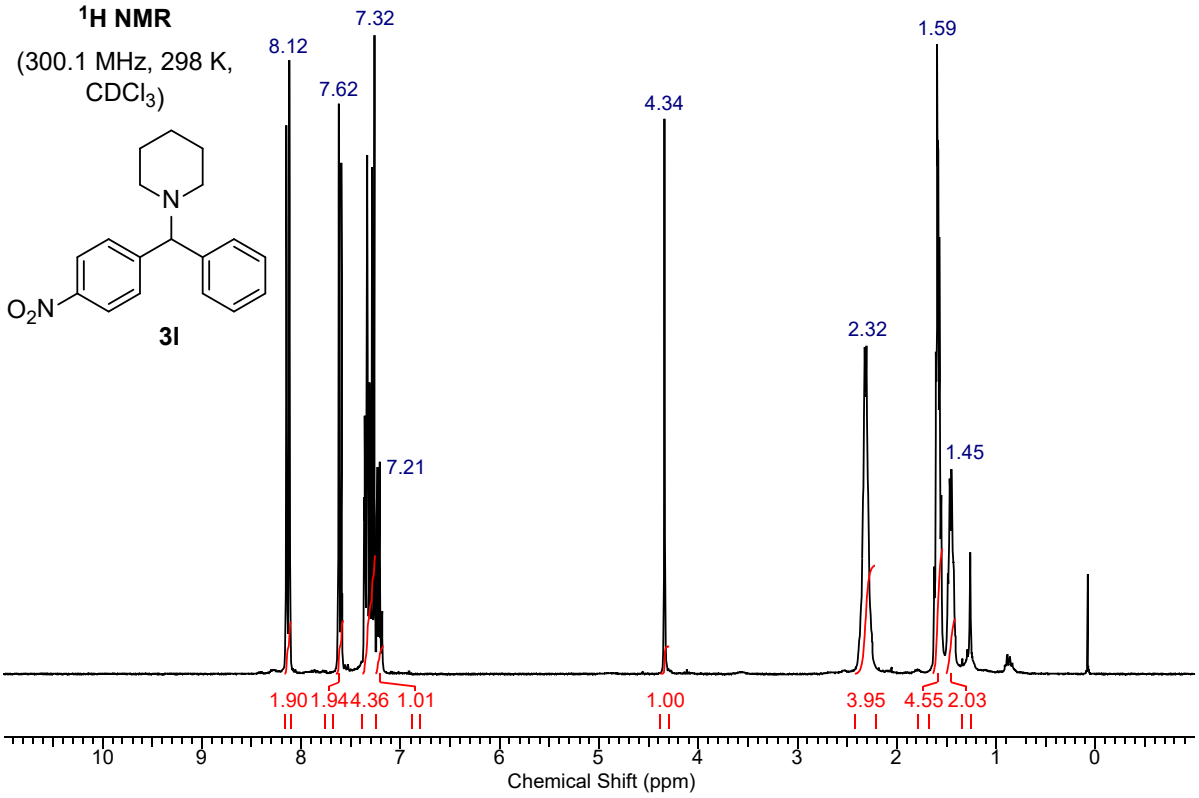
^{1}H NMR

(300.1 MHz, 298 K, $CDCl_3$)



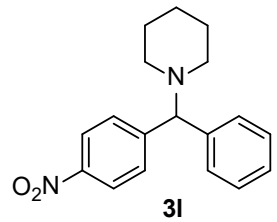
3k


$^{13}C\{^{1}H\}$ NMR
(75.5 MHz, 298 K, $CDCl_3$)
N
NC
3k
128.6
132.3
128.0
127.3
76.3
53.0
26.1
24.5
149.1
141.5
119.0
110.4
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


^{1}H NMR
(300.1 MHz, 298 K, $CDCl_3$)
N
O_2N
3l
8.12
7.62
7.32
7.21
4.34
2.32
1.59
1.45
1.90
1.94
4.36
1.01
1.00
3.95
4.55
2.03
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

$^{13}C\{^{1}H\}$ NMR

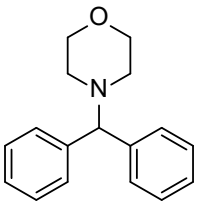
(75.5 MHz, 298 K, $CDCl_3$)



3l

^{1}H NMR

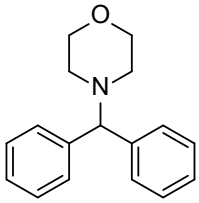
(300.1 MHz, 298 K, $CDCl_3$)



3m

$^{13}C\{^{1}H\}$ NMR

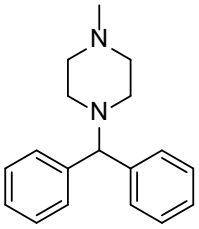
(75.5 MHz, 298 K, $CDCl_3$)



3m

^{1}H NMR

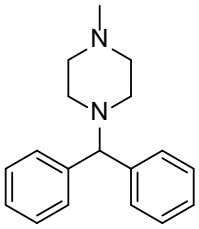
(300.1 MHz, 298 K, $CDCl_3$)



3n

$^{13}C\{^{1}H]$ NMR

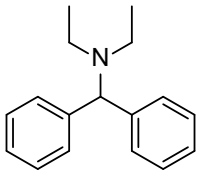
(75.5 MHz, 298 K, $CDCl_3$)



3n

^{1}H NMR

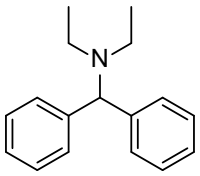
(300.1 MHz, 298 K, $CDCl_3$)



3o

$^{13}C\{^{1}H\}$ NMR

(75.5 MHz, 298 K, $CDCl_3$)



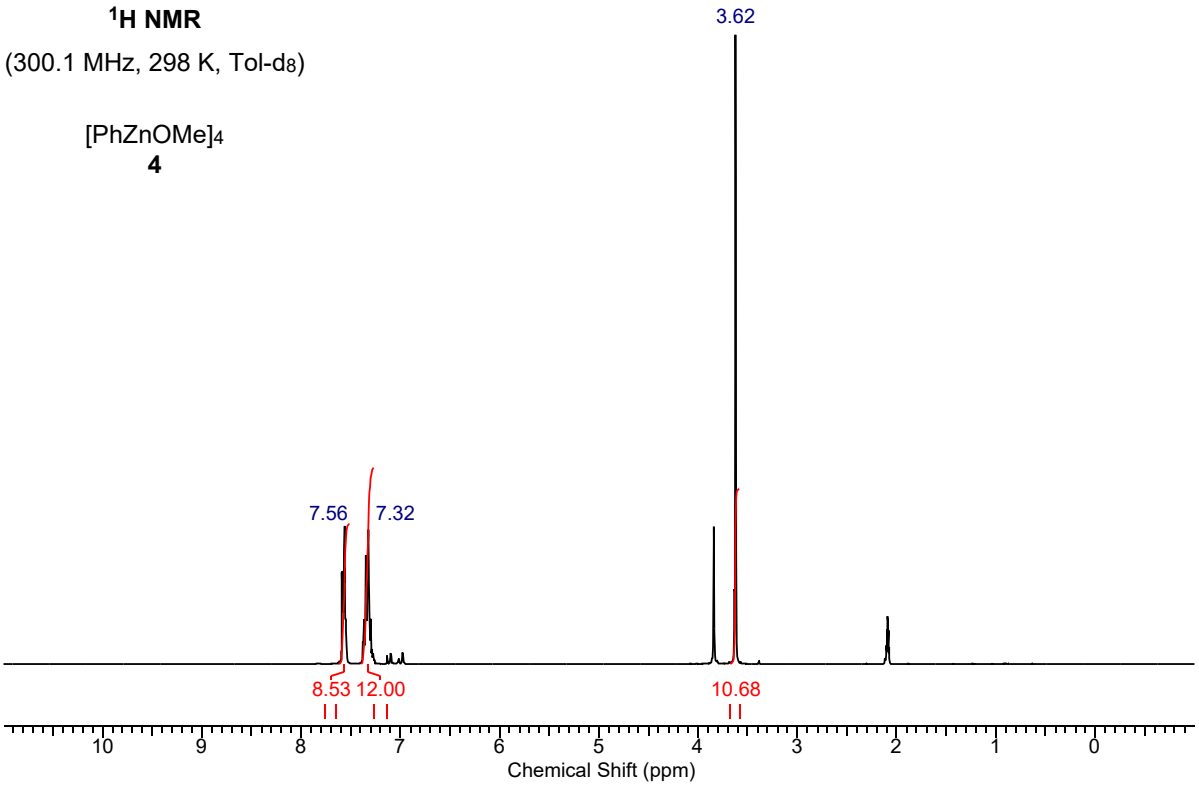
3o

^{1}H NMR

(300.1 MHz, 298 K, Tol-d_8)

$[PhZnOMe]_4$

4

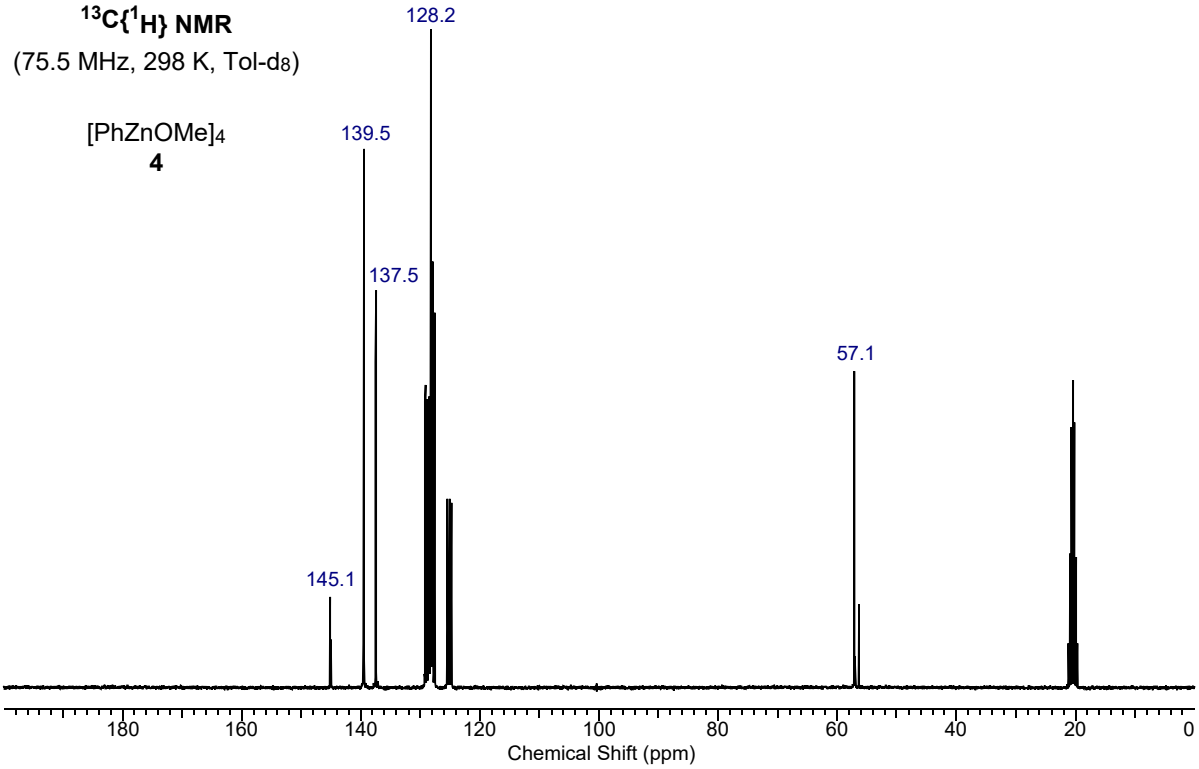


$^{13}C\{^{1}H\}$ NMR

(75.5 MHz, 298 K, Tol-d_8)

$[PhZnOMe]_4$

4

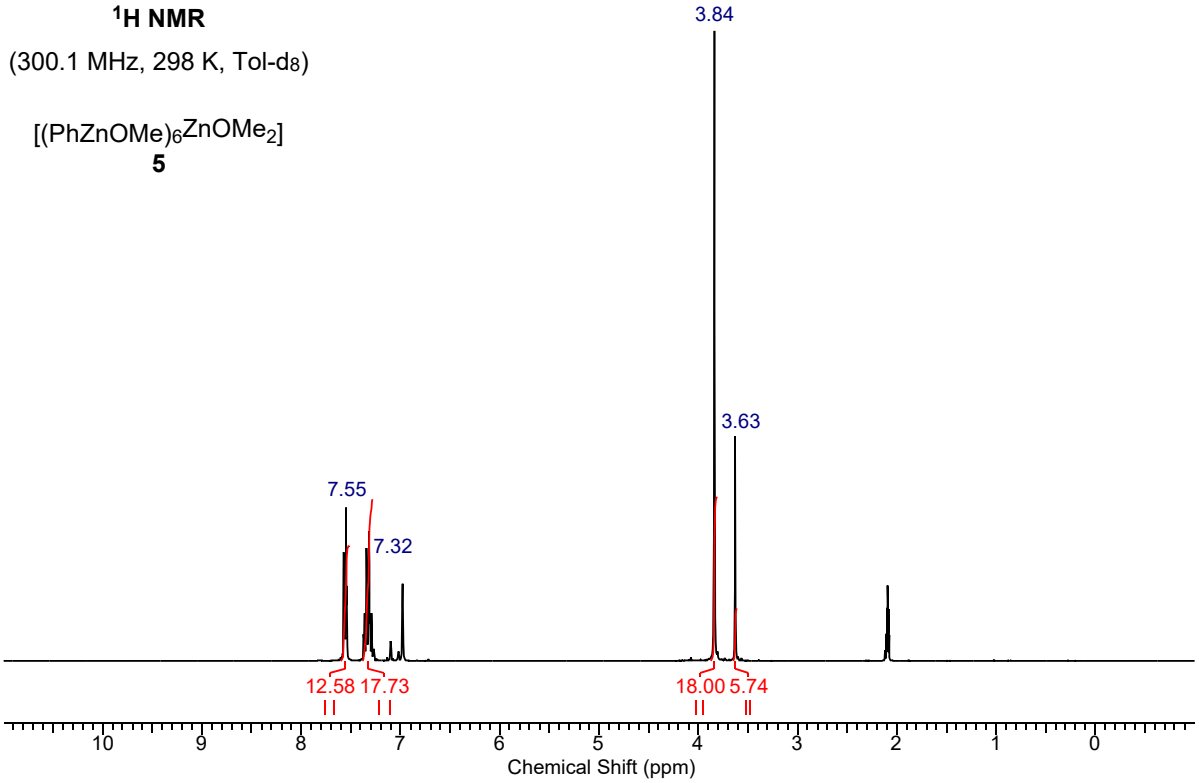


^{1}H NMR

(300.1 MHz, 298 K, Tol-d_8)

$[(PhZnOMe)_6ZnOMe_2]$

5

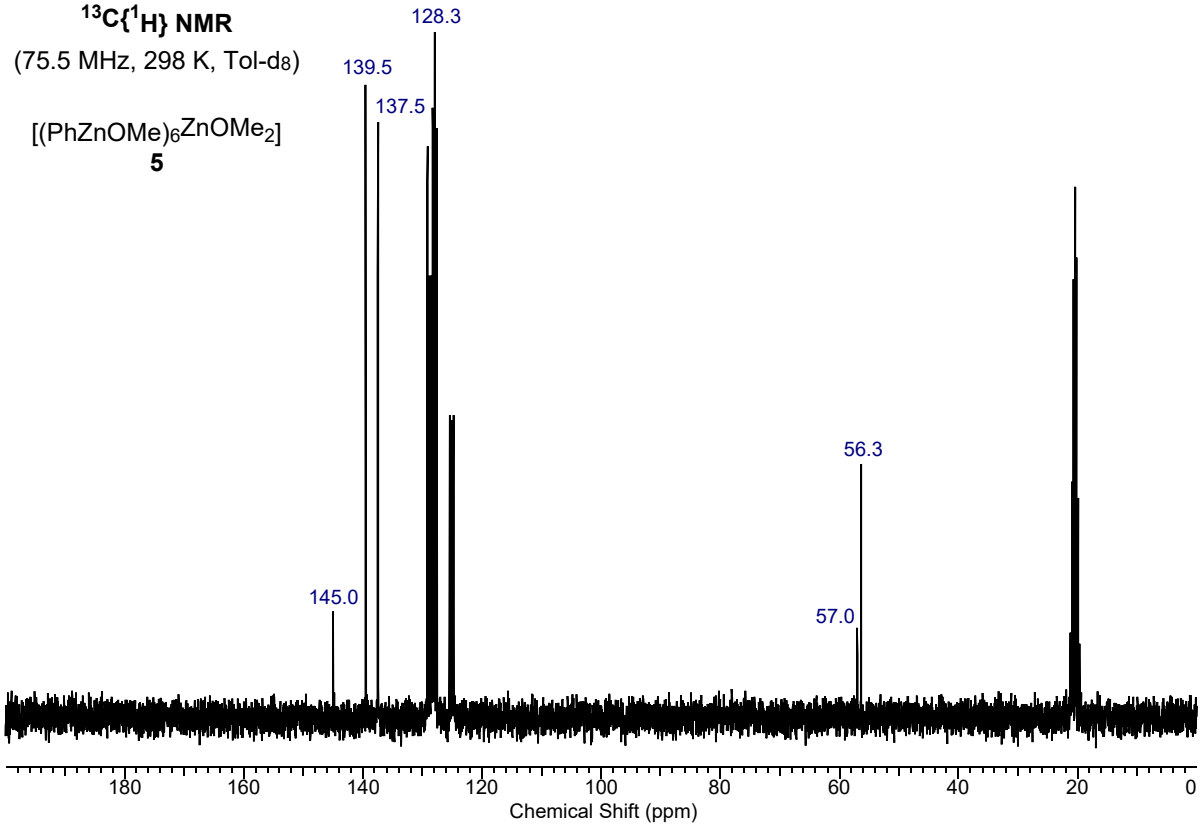


$^{13}C\{^{1}H\}$ NMR

(75.5 MHz, 298 K, Tol-d_8)

$[(PhZnOMe)_6ZnOMe_2]$

5

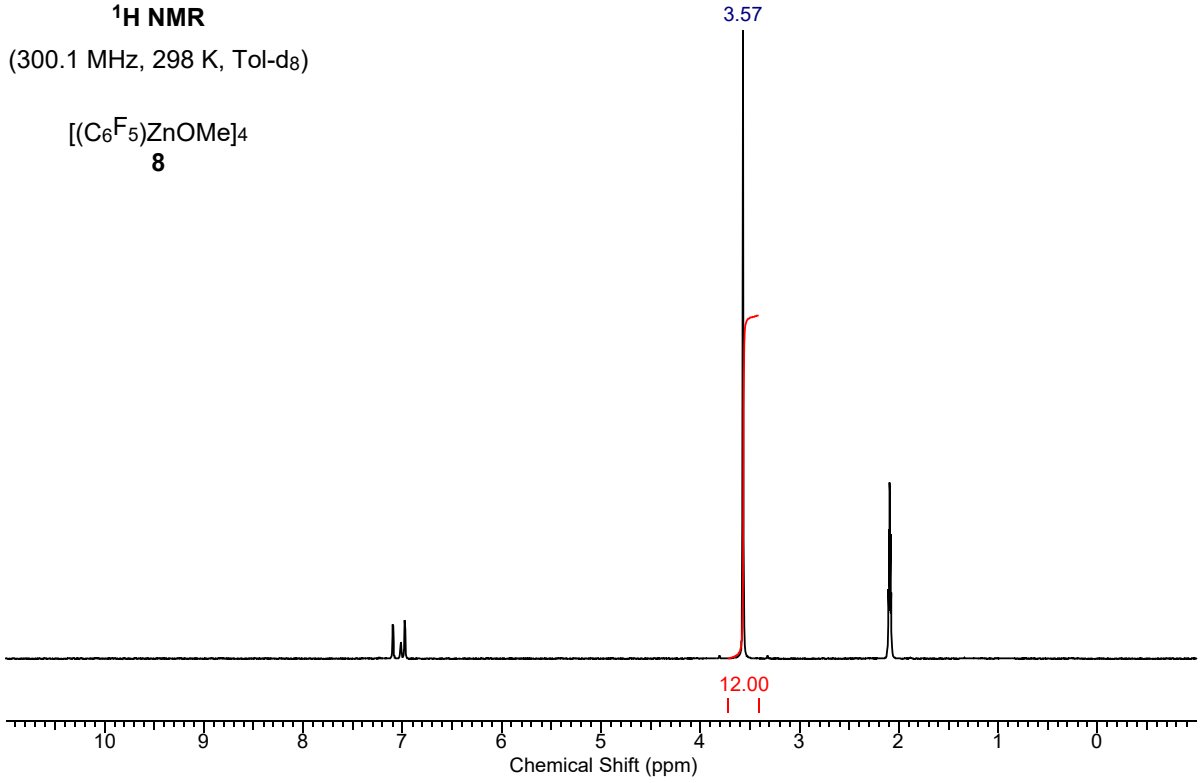


^{1}H NMR

(300.1 MHz, 298 K, Tol-d_8)

$[(C_6F_5)ZnOMe]_4$

8

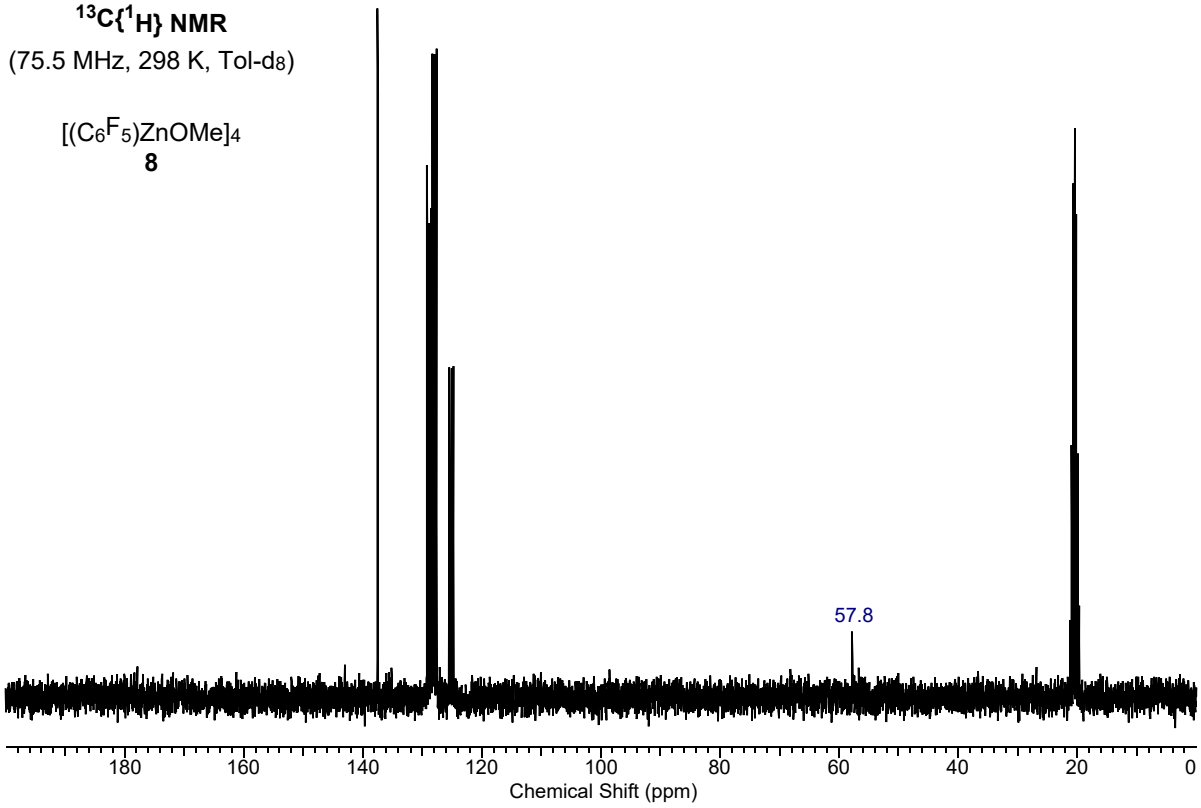


$^{13}C\{^{1}H\}$ NMR

(75.5 MHz, 298 K, Tol-d_8)

$[(C_6F_5)ZnOMe]_4$

8

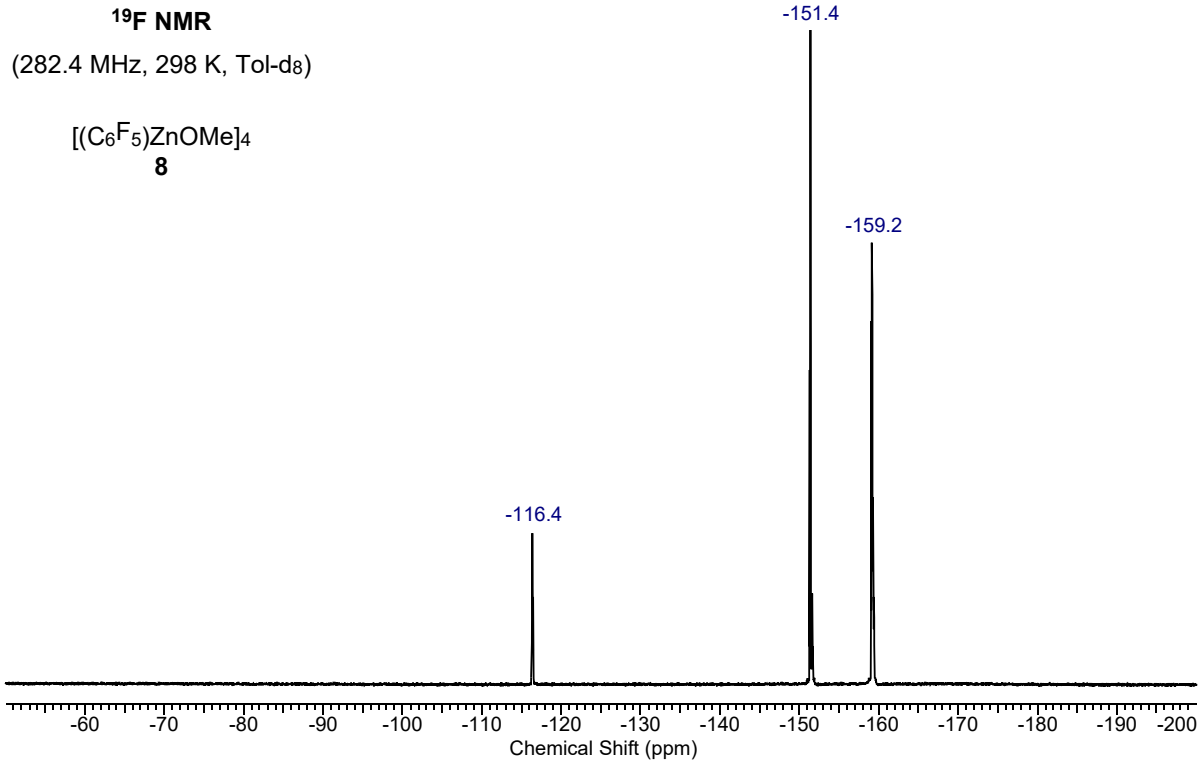


^{19}F NMR

(282.4 MHz, 298 K, Tol-d_8)

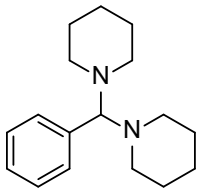
$[(C_6F_5)ZnOMe]_4$

8



^{1}H NMR

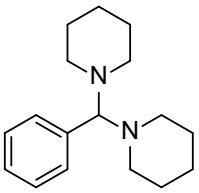
(300.1 MHz, 298 K, Tol-d_8)



6

^{13}C{^{1}H} NMR

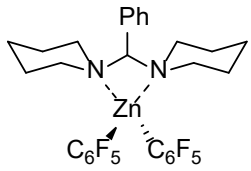
(75.5 MHz, 298 K, Tol-d_8)



6

^{1}H NMR

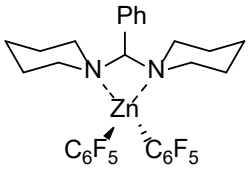
(300.1 MHz, 298 K, Tol-d$_8$)



7

^{13}C{^{1}H} NMR

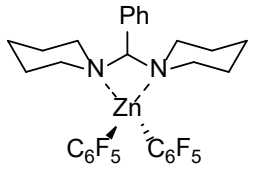
(75.5 MHz, 298 K, Tol-d$_8$)



7

^{19}F NMR

(282.4 MHz, 298 K, Tol-d_8)



7

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