Supporting Information

Bench-Stable Solid Organozinc Reagents: Synthesis and Application

Sanjai R Yogaraj, Keerthika Selvam, Mohanavelu M Vijayan, Ramesh Rasappan*

School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, Vithura, Thiruvananthapuram, Kerala 695551, India.

E-mail: rr@iisertvm.ac.in (R. Rasappan)

Table of contents

1. **General consideration --S2**
2. **Optimization of direct synthesis of aryl and alkyl organozinc reagents --------S3**
3. **Organozinc reagents ---S6**
4. **Optimization for the application of reagents ---S18**
5. **Nickel catalysed cross-coupling employing solid organozinc reagents ----------S21**
6. **Crystallization of organozinc reagents --S29**
7. **Reaction profile ---S30**
8. **Effect of temperature on the stability of organozinc reagent ---------------------S32**
9. **X-ray crystallography data ---S34**
10. **References ---S46**
11. **NMR Data ---S49**

1. General consideration:

Reagents: Commercially purchased chemicals were taken to the reaction without any further purification. Bromobenzene (product code: 0102135), and other alkyl or aryl bromides and iodides were purchased from Spectrochem, $NiBr_2 \cdot 3H_2O$ (product code: 772243), $NiBr_2$·diglyme (product code: 459674) and 2,2'-Bipyridine(bpy) (product code: 289426) were purchased from Sigma Aldrich. Zn powder (product code: Z0015) was purchased from TCI. Anhydrous $NiBr_2$·bpy was prepared from $NiBr_2 \cdot 3H_2O$ according to the literature procedure[1].

Solvents: Anhydrous toluene, diethyl ether, tetrahydrofuran (THF) and 1,2-dimethoxy ethane (DME) were purchased from Spectrochem and dried using sodium wire. dimethylacetamide (DMA) was also purchased from Spectrochem, was degassed for 1 h and stored in 4Å molecular sieves for further use. N,N,N′,N′-Tetramethyl ethylenediamine (TMEDA) was also purchased from Spectrochem, was dried and distilled over CaH_2.

Analytical methods: All the NMR spectra were recorded in a 400 and 500 MHz Bruker Avance spectrometer at 23 °C with TMS as an internal standard. NMR spectra chemical shifts were reported in δ (ppm). ^1H NMR recorded in $CDCl_3$ was reported with reference at 7.26 ppm respectively, ^{13}C NMR in $CDCl_3$ at 77.16 ppm. $CDCl_3$ (Cat. No: 151823, 99.8 atom % D) were purchased from Sigma Aldrich and stored with 4Å molecular sieves. Progress of the reactions was analysed by GC-Agilent 7890B series (Mass detector G7077B series, EI-70 eV, quadrupole ion detector) with silica capillary column (9091S-433UI, HP-5MSUI, with 30 m x 0.25 mm dimension). Thin-layer chromatography (Cat. No. 1.05554), aluminium sheets with TLC Silica gel 60 (F254 coating) was purchased from Merck. TLC was visualized using shortwave UV-254 nm or the stain made out of phosphomolybdic acid or potassium permanganate then heating as the developer. Silica gel 230-400 mesh (purchased from FINAR, Product Code: 11457S5K25) was used for the column chromatography. FT-IR Alpha E (Bruker) spectrometer was used to record IR Spectra; solid and liquid compounds were measured in neat condition. The wave numbers are given in [cm^{-1}]. HRMS ESI-TOF (Waters Xevo G2-XS Q-TOF) was used for the high-resolution mass analysis. Crystals were layered with paratone oil before mounting on the X-ray diffractometer. X-ray diffraction data were collected on a Bruker Kappa Apex-II CCD diffractometer at 150 K, SHELXT and SHELXL-2014 were used for structure solution.

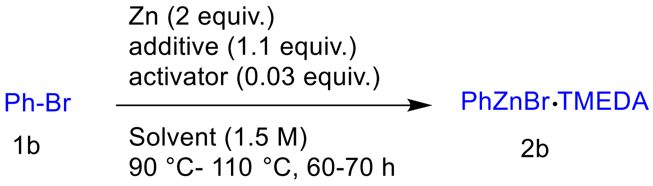
2. Optimization of direct synthesis of aryl and alkyl organozinc reagent

2.1. Optimization of organozinc reagent from corresponding bromides

General procedure for optimization

A flame dried Schlenk tube was evacuated and refilled with nitrogen three times. Zn powder (2 equiv., 3.06 mmol) was taken into the Schlenk tube from the glove box. It was heated with a heat gun for 5 min under vacuum, evacuated and refilled with nitrogen three times. The activator (0.03 equiv., 0.046 mmol) was added into the tube under nitrogen and stirred for 5-10 mins. Half the amount of solvent (1.5 M, 0.51 mL) was added. Then, bromobenzene (1 equiv., 1.53 mmol) was added dropwise followed by additive (1.1 equiv., 1.68 mmol) and remaining solvent (1.5 M, 0.51 mL). Then the tube was closed and heated to the temperature mentioned in table S1. The formation of organozinc reagent was confirmed by titration against iodine (Knochel's method)[2].

Table S1: Screening of activator

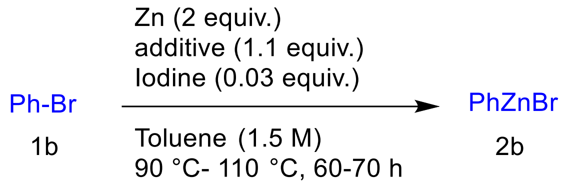


Entry	Activator	Additive, Solvent	2b (M)
1[a]	-	TMEDA (2 equiv.), toluene	0.1
2[a,b]	Iodine	TMEDA, toluene	0.41
3[a]	**Iodine**	**TMEDA, toluene**	**0.55[c]**
4[a,b]	DBE	TMEDA, toluene	0.44
5[a,b]	TMSCl	TMEDA, toluene	0.35
6[a,b]	Iodine	LiCl (1 equiv.), TMEDA, toluene	0.5
7[a,b]	DBE	LiCl (1 equiv.), TMEDA, toluene	0.3
8[a]	-	Zinc (3 equiv.), TMEDA, toluene	0.2
9[d]	DBE	TMEDA, benzene, 100 °C	0.17
10	Iodine	TMEDA, toluene, sonicate at rt	ND
11	Iodine	Zinc (1.5 equiv.), TMEDA, toluene, 70-90 °C, 60 h	0.33

---

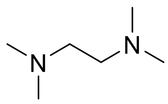
[a] 90 °C for 24 h then 120 °C for next 46 h. [b]0.01 equiv. of activator. [c] an average of 5-7 isolated runs. [d]0.1 equiv. of activator, 24 h. M: Molarity, TMEDA: N,N,N',N'-tetramethyl ethylenediamine, DBE: 1,2-dibromoethane, ND-not detected.

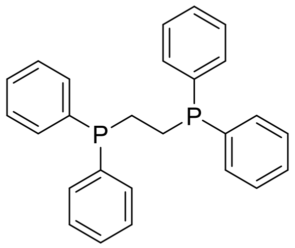
Table S2: Screening of additive

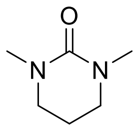


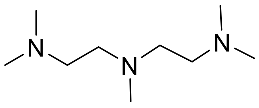
Entry	Additive	2b (M)
1	TMEDA	0.55
2	bpy	0.11
3	DPPE	0.21
4	DMPU	0.08
5	PDMT	0.22

TMEDA: N,N,N',N'-tetramethylethylenediamine, Bpy: 2,2′-Bipyridine, DPPE: 1,2-Bis(diphenylphosphino)ethane, DMPU: N,N'-dimethylpropyleneurea, PDMT: N,N,N′,N″,N″-Pentamethyldiethylenetriamine. M: Molarity.


TMEDA


DPPE


DMPU


PDMT

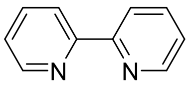
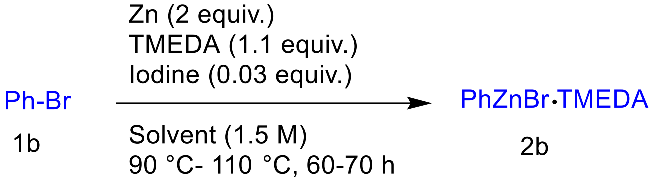

bpy

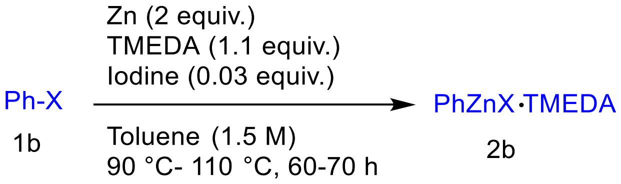
Table S3: Screening of solvents



Entry	Solvent	2b (M)
1[a]	Benzene	0.3
2	DMA	0.5
3	Toluene	0.55
4	DMF	0.2
5[b]	DME	0.02
6 [c]	Et_2O	ND
7[b]	THF	0.09
8[b]	Dioxane	0.07

[a]90 °C for 72 h. [b]50 °C for 72 h. [c]rt (25-30 °C) for 72 h. M: Molarity.

Table S4: Screening with different aryl halides



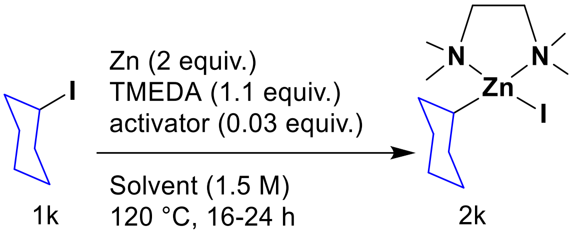
Entry	aryl halides	2b (M)
1	bromobenzene	0.55
2	iodobenzene	0.47
3	chlorobenzene	0.02

2.2.Optimization of organozinc reagents from corresponding iodides

General procedure for optimization

A flame dried Schlenk tube was evacuated and refilled with nitrogen three times. Zn powder (2 equiv., 3.82 mmol) was taken into the Schlenk tube from the glove box. It was heated with a heat gun for 5 min under vacuum, evacuated and refilled with nitrogen three times. The activator (0.03 equiv., 0.05 mmol) was added into the tube under nitrogen and stirred for 5-10 mins. Half of the amount of the solvent (1.5 M, 0.7 mL). Then, iodocyclohexane (1 equiv., 1.91 mmol) was added dropwise followed by the addition of TMEDA (1.1 equiv., 2.1 mmol) and the remaining solvent (1.5 M, 0.6 mL). Then the tube was closed and heated to the temperature mentioned in table S5. The formation of alkyl reagent was confirmed by titration against iodine (Knochel's method)[2].

Table S5: Optimization for synthesis of alkyl organozinc reagents from corresponding iodide

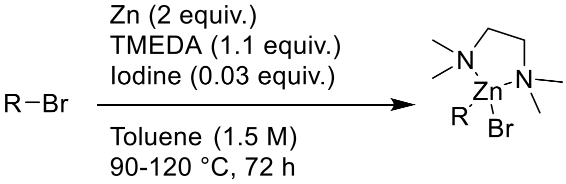


Entry	Activator	Solvent, Temperature	2k (M)
1	Iodine	zinc (1.5 equiv.), toluene	0.39
2	Iodine	THF, 90 °C	0.39
3	TMSCl	toluene	0.42
4	DBE	toluene	0.39
5	Iodine	benzene	0.27
6[a]	Iodine	toluene	0.55[b]
7[a]	DBE	toluene	0.6[b]
8	Iodine	Et_2O in rt	ND

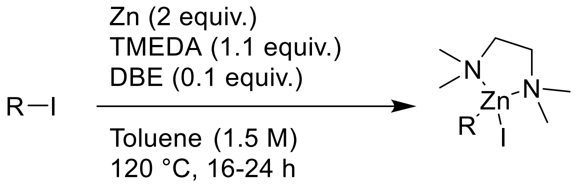
[a]0.1 equiv. of activator is used. [b]an average of 5-7 isolated runs. M: Molarity, DBE: 1,2-dibromoethane, TMEDA: N,N,N',N'-tetramethylethylenediamine, ND- not detected.

3. Organozinc reagents

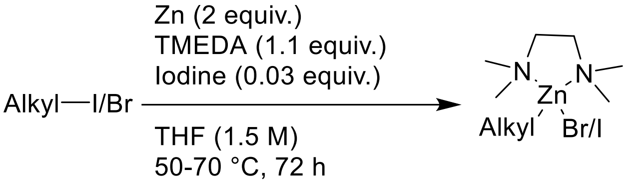
3.1.General procedure for the synthesis of organozinc reagents



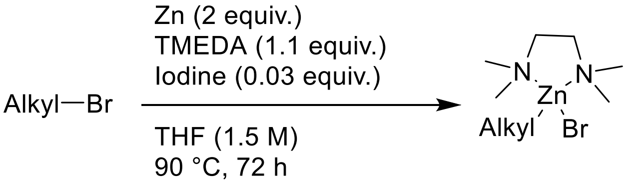
General procedure A: A flame dried Schlenk tube was evacuated and refilled with nitrogen three times. Zn powder (2 equiv., 76.5 mmol) was taken into the Schlenk tube from the glove box. It was heated with a heat gun for 5 min under vacuum, evacuated and refilled with nitrogen three times. Iodine (0.03 equiv., 1.15 mmol) was added into the tube under nitrogen flow and stirred for 5-10 mins. Half the amount of toluene (1.5 M, 12.7 mL) was added. Then, aryl/alkyl bromide (1 equiv., 38.2 mmol) was added dropwise followed by TMEDA (1.1 equiv., 42.1 mmol) and remaining toluene (1.5 M, 12.7 mL). Then the tube was closed and heated to the temperature of 90 °C for 24 h and then 120 °C for next 48 h. The formation of organozinc reagent was confirmed by titration against iodine (Knochel's method)[2]. For solidifying the reagent, the corresponding RZnBr·TMEDA in toluene was filtered and transferred into the Schlenk tube via filter paper tipped cannula under nitrogen atmosphere. Then toluene was removed under reduced pressure resulting in dense yellow/colourless oil with strong fishy smell. To this, sodium dried hexane was added and stirred for 30 minutes resulting in an off white solid. Then, the solvent was removed using syringe. The formed solid was washed with hexane three times and dried under reduced pressure to yield fine powder.



General procedure B: A flame dried Schlenk tube was evacuated and refilled with nitrogen three times. Zn powder (2 equiv., 76.5 mmol) was taken into the Schlenk tube from the glove box. It was heated with a heat gun for 5 min under vacuum, evacuated and refilled with nitrogen three times. Then, DBE (0.1 equiv., 3.82 mmol) was added into the tube under nitrogen and stirred for 5-10 mins. Half the amount of toluene (1.5 M, 12.7 mL) was added. Then, aryl/alkyl iodide (1 equiv., 38.2 mmol) was added dropwise followed by TMEDA (1.1 equiv., 42.1 mmol) and remaining toluene (1.5 M, 12.7 mL). Then the tube was closed and heated to the temperature of 120 °C for 16-24 h. The formation of organozinc reagent was confirmed by titration against iodine (Knochel's method)[2]. For solidifying the reagent, the corresponding RZnI·TMEDA in toluene was filtered and transferred into the Schlenk tube via filter paper tipped cannula under nitrogen atmosphere. Toluene was removed under reduced pressure resulting in dense yellow/colourless oil with strong fishy smell. To this, sodium dried hexane was added and stirred for 30 minutes resulting in an off white solid. Then, the solvent was removed using syringe. The formed solid was washed with hexane three times and dried under reduced pressure to yield fine powder.



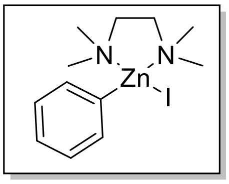
General procedure C: A flame dried Schlenk tube was evacuated and refilled with nitrogen three times. Zn powder (2 equiv., 76.5 mmol) was taken into the Schlenk tube from the glove box. It was heated with a heat gun for 5 min under vacuum, evacuated and refilled with nitrogen three times. Iodine (0.03 equiv., 1.15 mmol) was added into the tube under nitrogen and stirred for 5-10 mins. Half the amount of THF (1.5 M, 12.7 mL) was added. Then, alkyl bromide/iodide (1 equiv., 38.2 mmol) was added dropwise followed by TMEDA (1.1 equiv., 42.1 mmol), and remaining THF (1.5 M, 12.7 mL). Then the tube was closed and heated to the temperature of 50 °C for 10 h and then 70 °C for next 12 h. The formation of zinc reagent was confirmed by titration against iodine (Knochel's method)[2]. For solidifying the reagent, the corresponding RZnX·TMEDA in THF was filtered and transferred into the Schlenk tube via filter paper tipped cannula under nitrogen atmosphere. The THF was removed under reduced pressure resulting in dense yellow/colourless oil with strong fishy smell. To this, sodium dried hexane was added and stirred for 30 minutes resulting in an off white solid. Then, the solvent was removed using syringe. The formed solid was washed with hexane three times and dried under reduced pressure to yield fine powder.



General procedure D: A flame dried Schlenk tube was evacuated and refilled with nitrogen three times. Zn powder (2 equiv., 76.5 mmol) was taken into the Schlenk tube from the glove box. It was heated with a heat gun for 5 min under vacuum, evacuated and refilled with nitrogen three times. Iodine (0.03 equiv., 1.15 mmol) was added into the tube under nitrogen and stirred for 5-10 mins. Half the amount of THF (1.5 M, 12.7 mL) was added. Then, dropwise addition of alkyl bromide (1 equiv., 38.2 mmol) and TMEDA (1.1 equiv., 42.1 mmol), followed by the addition of remaining THF (1.5 M, 12.7 mL). Then the tube was closed and heated to the temperature of 90 °C for 72 h. The formation of zinc reagent was confirmed by titration against iodine (Knochel's method)[2]. For solidifying the reagent, the corresponding RZnBr·TMEDA in THF was filtered and transferred into the Schlenk tube via filter paper tipped cannula under nitrogen atmosphere. THF was removed under reduced pressure resulting in dense yellow/colourless oil with strong fishy smell. To this, sodium dried hexane was added and stirred for 30 minutes resulting in an off white solid. Then, the solvent was removed using a syringe. The formed solid was then washed with hexane three times and dried under reduced pressure to yield fine powder.

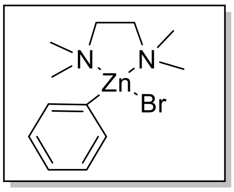
3.2. Scope of reagents

PhZnI·TMEDA (2a)



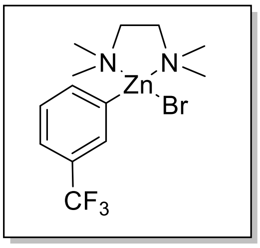
The title compound was prepared using iodobenzene (1 equiv., 7.8 g, 38.2 mmol), zinc powder (2 equiv., 5g, 76.5 mmol) and TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **B**. The formed PhZnI·TMEDA was titrated against iodine, with titre typically ranging **0.66 M**. Further solidification yielded pale yellow powder. **Melting Point:** 115 ºC. **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 7.68 – 7.55 (m, 2H, 2× Ar-C**H**), 7.25 – 7.19 (m, 2H, 2× Ar-C**H**), 7.19 – 7.11 (m, 1H, Ar-C**H**), 2.90 – 2.48 (m, 25H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (9H, uncomplexed or partially dissociated TMEDA)). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 154.8 (Ar**C**), 139.1 (2× Ar-**C**H),126.1 (Ar-**C**H), 57.3 (4× N-**C**H$_3$), 48.0 (2× N-**C**H$_2$). **FT-IR (neat, cm^{-1}) ν:** 3166, 1093, 1120, 1198, 1260, 1459, 795.

PhZnBr·TMEDA (2b)



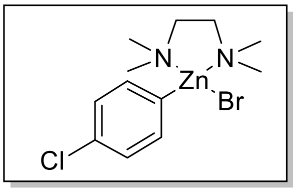
The title compound was prepared using bromobenzene (1 equiv., 6 g, 38.2 mmol), zinc powder (2 equiv., 5g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **A**. The formed PhZnBr·TMEDA was titrated against iodine, with titre typically ranging **0.55 M**. Further solidification yielded pale yellow to off white powder. **Melting Point:** 78 ºC. **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 7.56 – 7.48 (m, 2H, 2× Ar-C**H**), 7.18 – 7.10 (m, 2H, 2× Ar-C**H**), 7.10 – 7.03 (m, 1H, Ar-C**H**), 2.79 – 2.35 (m, 23H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (7H, uncomplexed or partially dissociated TMEDA)). **^{13}C NMR (126 MHz, $CDCl_3$) δ**: 153.3 (Ar**C**), 139.4 (2× Ar-**C**H), 127.0 (2× Ar-**C**H), 126.1 (Ar-**C**H), 57.4 (4× N-**C**H$_3$), 48.0 (2× N-**C**H$_2$). **FT-IR (neat, cm^{-1}) ν:** 3109, 1288, 1058, 1480, 864, 796. **HRMS-ESI-TOF *m/z*:** $[M]^+$ calcd for $C_{12}H_{21}N_2Zn$: 257.0996, observed: 257.0994.

m-CF_3PhZnBr·TMEDA (2c)



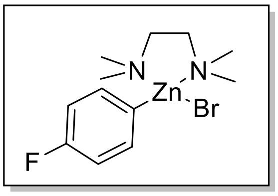
The title compound was prepared using 1-bromo-3-(trifluoromethyl)benzene (1 equiv., 8.6 g, 38.2 mmol), zinc powder (2 equiv., 5g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **A**. The formed m-CF_3PhZnBr·TMEDA was titrated against iodine, with titre typically ranging **0.4 M**. Further solidification yielded pale yellow powder. **Melting Point:** 96 ºC. **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 7.84 – 7.74 (m, 2H, 2× Ar-C**H**), 7.39 – 7.32 (m, 1H, Ar-C**H**), 7.32 – 7.27 (m, 1H, Ar-C**H**), 2.82 – 2.52 (m, 39H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (33H, uncomplexed or partially dissociated TMEDA)). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 154.6 (Ar**C**-Zn), 142.6 (Ar**C**H), 134.8 (q, J^3_{C-F} = 8.9Hz), 131.9 (Ar**C**H), 129.1 (q, J^2_{C-F} = 20.8 Hz) (Ar**C**-CF_3), 126.4 (q, J^3_{C-F} = 8.9Hz), 122.6 (d, J^1_{C-F} = 296.6 Hz), 57.3 (4× N-**C**H_3), 48.6 (2× N-**C**H_2). **^{19}F NMR (471 MHz, $CDCl_3$) δ**: -61.94. **FT-IR (neat, cm^{-1}) ν:** 1021, 1047, 1120, 1460, 1160, 1310, 797, 948. **HRMS-ESI-TOF m/z:** [M]$^+$ calcd for $C_{13}H_{20}F_3N_2Zn$: 325.0870, observed: 325.0882.

p-ClPhZnBr·TMEDA (2d)



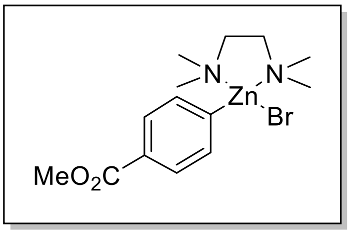
The title compound was prepared using 1-bromo-4-chlorobenzene (1 equiv., 7.32 g, 38.2 mmol), zinc powder (2 equiv., 5g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **A**. The formed p-ClPhZnBr·TMEDA was titrated against iodine, with titre typically ranging from **0.6 M**. Further solidification yielded pale yellow powder. **Melting Point:** 63 ºC. **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.57 – 7.47 (m, 2H, 2× Ar-C**H**), 7.21 – 7.11 (m, 2H, 2× Ar-C**H**), 2.85 – 2.43 (m, 30H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (14H, uncomplexed or partially dissociated TMEDA)).**^{13}C NMR (101 MHz, $CDCl_3$) δ**: 151.3 (1× Ar-**C**Zn), 140.3 (2× Ar-**C**H), 132.1 (1× Ar-**C**Cl), 126.8 (2× Ar-**C**H), 57.3 (4× N-**C**H_3), 48.8 (2× N-**C**H_2). **FT-IR (neat, cm^{-1}) ν:** 1287, 1235, 1160, 1122, 1088, 1047, 1010, 1555,1595, 3061, 3107, 790, 850. **HRMS-ESI-TOF m/z:** [M]$^+$ calcd for $C_{12}H_{20}ClN_2Zn$: 291.0606, observed: 291.0608.

p-FPhZnBr·TMEDA (2e)



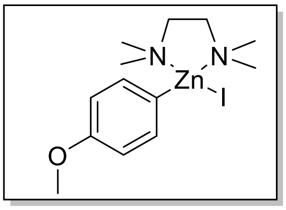
The title compound was prepared using 1-bromo-4-fluorobenzene (1 equiv., 6.69 g, 38.2 mmol), zinc powder (2 equiv., 5g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **A**. The formed p-FPhZnBr·TMEDA was titrated against iodine, with titre typically ranging **0.9 M**. Further solidification yielded pale yellow powder**.** **Melting Point:** 76 ºC. **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.63 – 7.48 (m, 2H 2× Ar-C**H**), 6.99 – 6.89 (m, 2H, 2× Ar-C**H**), 2.90 – 2.44 (m, 25H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (9H, uncomplexed or partially dissociated TMEDA)). **^{13}C NMR (126 MHz, $CDCl_3$) δ**: 162.5 (d, J^1_{C-F} = 239.4 Hz) (ArC**F**), 140.3 (d, J^3_{C-F} = 6.3 Hz) (2x ArC**H**), 115.4 (d, J^2_{C-F} = 25.2 Hz) (2x ArC**H**), 113.9 (d, J^4_{C-F} = 1.9 Hz) (Ar**C**Zn), 57.3 (4× N-**C**H$_3$), 48.6 (2×N-**C**H$_2$). **^{19}F NMR (471 MHz, $CDCl_3$) δ:** -113.10. **FT-IR (neat, cm^{-1}) ν:** 1567, 1214, 1288, 1018, 1161, 798. **HRMS-ESI-TOF m/z:** [M]$^+$ calcd for $C_{12}H_{20}FN_2Zn$: 275.0902, observed: 275.0910.

p-CO$_2$MePhZnBr·TMEDA (2f)



The title compound was prepared using methyl 4-bromobenzoate (1 equiv., 8.22 g, 38.2 mmol), zinc powder (2 equiv., 5g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **A**. The formed p-CO$_2$Me-PhZnBr·TMEDA was titrated against iodine, with titre typically ranging **0.8 M**. Further solidification yielded yellowish coloured semi solid. **^{1}H NMR (500 MHz, $CDCl_3$) δ**: 7.72 – 7.63 (m, 2H, 2× Ar-C**H**), 7.61 – 7.54 (m, 2H, 2× Ar-C**H**), 3.68 (s, 3H, CO$_2$C**H**$_3$), 2.65 – 2.32 (m, 23H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (7H, uncomplexed or partially dissociated TMEDA)). **^{13}C NMR (101 MHz, $CDCl_3$) δ**: 167.5 (**C**=O), 162.30 (**C**-Zn), 138.46 (2× Ar**C**H), 127.87 (2× Ar**C**H), 126.42 (Ar**C**H), 56.56 (4× N-**C**H$_3$), 51.14 (O**C**H$_3$), 47.8 (2× N-**C**H$_2$). **FT-IR (neat, cm^{-1}) ν:** 1745, 1195, 1202, 1058, 992, 769.

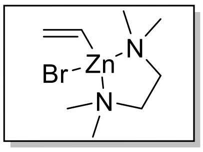
p-OMePhZnI·TMEDA (2g)



The title compound was prepared using 1-iodo-4-methoxybenzene (1 equiv., 8.95 g, 38.2 mmol), zinc powder (2 equiv., 5g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **B**. The formed p-OMePhZnI·TMEDA was titrated against iodine, with titre typically ranging **0.43 M**. Further solidification yielded pale yellow powder. **Melting Point:** 79 ºC. **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 7.59 – 7.51 (m, 2H, 2× Ar-C**H**), 6.87

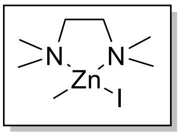
– 6.81 (m, 2H, 2× Ar-C**H**), 3.77 (s, 3H, O**C**H_3), 2.86 – 2.50 (m, 30H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (14H, uncomplexed or partially dissociated TMEDA)). **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 158.4 (Ar-**C**-OMe), 144.7 (Ar-**C**-Zn), 139.9 (2× Ar-**C**H), 112.9 (2× Ar-**C**H), 57.3 (4× N-**C**H$_3$), 54.9 (O-**C**H$_3$), 47.9 (2× N-**C**H$_2$). **FT-IR (neat, cm^1) ν:** 2951, 2994, 1039, 1179, 1240, 1291, 1497, 1599, 759, 791.

VinylZnBr·TMEDA (2h)



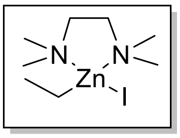
The title compound was prepared using bromoethene (1 equiv., 4.09 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **C**. The formed vinylZnBr·TMEDA was titrated against iodine, with titre typically ranging **0.3 M**. Further solidification yielded off-white powder. **Melting Point:** 130 ºC. ^{1}H ,^{13}C NMR contains unidentified byproduct in-conjunction with the expected peaks corresponding to the product **2h**, thus the spectra are not included. **FT-IR (neat, cm^{-1}) ν:** 1019, 1288, 1661, 3006, 761, 796, 947.

CH_3ZnI·TMEDA (2i)



The title compound was prepared using iodomethane (1 equiv., 5.43 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89 g, 42.1 mmol), by following the general procedure **C**. The formed CH_3ZnI·TMEDA was titrated against iodine, with titre typically ranging **0.57 M**. Further solidification yielded white powder. **Melting point:** 104 ºC. **^{1}H NMR (500 MHz, CDCl$_3$) δ**: 2.84 – 2.28 (m, 23H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (7H, uncomplexed or partially dissociated TMEDA)), -0.79 (s, 3H, C**H**$_3$). **^{13}C NMR (126 MHz, CDCl$_3$) δ**: 56.9 (4× N-**C**H$_3$), 49.7 (2× N-**C**H$_2$), -11.2 (H$_3$**C**-Zn). **FT-IR (neat, cm^{-1}) ν:** 1090, 1157, 1196, 1249, 1284, 1332, 2853, 2902, 1383. **HRMS-ESI-TOF *m/z*:** [M]$^+$ calcd for $C_7H_{19}N_2Zn$: 195.0840, observed: 195.0832.

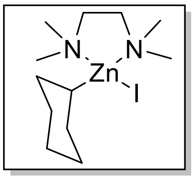
EthylZnI·TMEDA (2j)



The title compound was prepared using iodoethane (1 equiv., 4.17 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89 g, 42.1 mmol), by following the general procedure **C**. The formed ethylZnI·TMEDA was titrated against iodine, with titre typically ranging **0.7 M**. Further solidification yielded white powder. **Melting point:** 88 ºC. **^{1}H NMR (500 MHz, CDCl$_3$) δ**:

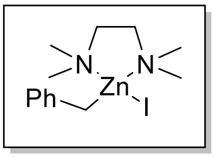
2.84 – 2.28 (m, 21H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (5H, uncomplexed or partially dissociated TMEDA)), 1.14 (t, *J* = 8.1 Hz, 3H, C**H**$_3$-CH$_2$), 0.06 (q, *J* = 8.0 Hz, 2H, CH$_3$-C**H**$_2$-Zn). **^{13}C NMR (126 MHz, CDCl$_3$) δ**: 57.0 (4× N-**C**H$_3$), 49.8 (2× N-**C**H$_2$), 13.2 (**C**H$_3$-CH$_2$), 1.8 (CH$_3$-**C**H$_2$-Zn). **FT-IR (neat, cm^{-1}) ν:** 1037, 2858, 1457**. HRMS-ESI-TOF m/z:** [M]$^+$ calcd for $C_8H_{21}N_2Zn$: 209.0992, observed: 209.0996.

CyclohexylZnI·TMEDA (2k)



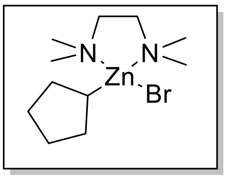
The title compound was prepared using iodocyclohexane (1 equiv., 8.03 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89 g, 42.1 mmol), by following the general procedure **B**. The formed cyclohexylZnI·TMEDA was titrated against iodine, with titre typically ranging **0.61 M**. Further solidification yielded pale yellow powder. **Melting Point:** 61 ºC. **^{1}H NMR (500 MHz, CDCl$_3$) δ**: 2.79 – 2.44 (m, 29H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (13H, uncomplexed or partially dissociated TMEDA)), 1.81 (dt, *J* = 12.6, 3.8 Hz, 2H, Cyhex-C**H$_2$**), 1.68 – 1.56 (m, 4H, Cyhex-(C**H$_2$**)$_2$), 1.42 – 1.31 (m, 2H, Cyhex-C**H$_2$**), 1.27 – 1.19 (m, 2H, Cyhex-C**H$_2$**), 0.71 (td, *J* = 9.8, 5.8 Hz, 1H, Cyhex-C**H**Zn). **^{13}C NMR (126 MHz, CDCl$_3$) δ**: 57.1 (4× N-**C**H$_3$), 49.7 (2× N-**C**H$_2$), 34.2 (2× Cyhex-**C**H$_2$), 30.3 (2× Cyhex-**C**H$_2$), 28.3 (Cyhex-**C**H$_2$), 27.8 (Cyhex-H**C**Zn**)**. **FT-IR (neat, cm^{-1}) ν:** 2901, 2929, 2854, 1458, 1019**. HRMS-ESI-TOF m/z:** [M]$^+$ calcd for $C_{12}H_{27}N_2Zn$: 263.1466, observed: 263.1468.

BenzylZnI·TMEDA (2l)



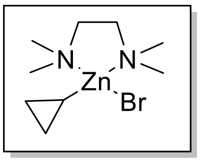
The title compound was prepared using (iodomethyl)benzene (1 equiv., 8.34 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **C**. The formed PhCH$_2$ZnI·TMEDA was titrated against iodine, with titre typically ranging **0.57 M**. Further solidification yielded yellowish white oily liquid. **^{1}H NMR (500 MHz, CDCl$_3$) δ:** 7.18 – 7.11 (m, 1H, Ar-C**H**), 7.09 – 7.02 (m, 1H, Ar-C**H**), 6.96 – 6.89 (m, 4H- (2×Ar-C**H**), **(**2H-protodemetallated reagent)), 6.66 – 6.59 (m, 1H, Ar-C**H**), 2.63 – 2.27 (m, 36H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H$_3$**), (20H, uncomplexed or partially dissociated TMEDA)), 1.72 (s, 2H, C**H$_2$**-Zn). ^{13}C NMR contains unidentified byproduct in-conjunction with the expected peaks corresponding to the product **2l**, thus the spectrum is not included. **FT-IR (neat, cm^{-1}) ν:** 1260, 1050, 1143, 3061, 775, 852.

CyclopentylZnBr·TMEDA (2m)



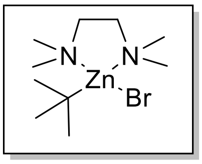
The title compound was prepared using bromocyclopentane (1 equiv., 5.7 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **A**. The formed cyclopentylZnBr·TMEDA was titrated against iodine, with titre typically ranging **0.66 M**. Further solidification yielded pale yellowish green colour powder. **Melting Point:** 50 ºC. **^{1}H NMR (500 MHz, $CDCl_3$) δ**: 2.78 – 2.43 (m, 23H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (7H, uncomplexed or partially dissociated TMEDA)), 1.93 – 1.80 (m, 2H, Cypent-C**H**$_2$), 1.58 – 1.38 (m, 4H, Cypent-(C**H**$_2$)$_2$), 1.28 (dd, *J* = 5.4, 2.7 Hz, 2H, Cypent-C**H**$_2$), 0.43 – 0.25 (m, 1H, (Cypent-**H**CZn)). **^{13}C NMR (126 MHz, $CDCl_3$) δ**: 57.1 (4× N-**C**H$_3$), 48.6 (2× N-**C**H$_2$), 32.9 (2× Cypent-**C**H$_2$), 26.4 (2× Cyhex-**C**H$_2$), 23.4 (Cypent-H**C**Zn). **FT-IR (neat, cm^{-1}) ν:** 2863, 2944, 1023, 1129, 1159, 1288, 1459.

CyclopropylZnBr·TMEDA (2n)



The title compound was prepared using bromocyclopropane (1 equiv., 4.63 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **A**. The formed cyclopropylZnBr·TMEDA was titrated against iodine, with titre typically ranging **0.73 M**. Further solidification yielded pale yellow powder. **Melting Point:** 85 ºC. **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 2.80 – 2.44 (m, 24H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (8H, uncomplexed or partially dissociated TMEDA)), 0.45 – 0.36 (m, 2H, Cyprop-C**H**$_2$), 0.22 – 0.14 (m, 2H, Cyprop-C**H**$_2$), -1.18 (tt, *J* = 10.2, 7.5 Hz, 1H, Cyprop-**H**CZn). **^{13}C NMR (126 MHz, $CDCl_3$) δ**: 57.1 (4× N-**C**H$_3$), 48.5 (2× N-**C**H$_2$), 1.1 (2× Cyprop-**C**H$_2$), -9.4 (Cyprop-H**C**Zn). **FT-IR (neat, cm^{-1}) ν:** 1020, 2927, 1456. **HRMS-ESI-TOF m/z:** $[M]^+$ calcd for $C_9H_{21}N_2Zn$: 221.0996, observed: 221.1003.

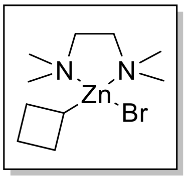
t-BuZnBr·TMEDA (2o)



The title compound was prepared using 2-bromo-2-methylpropane (1 equiv., 5.24 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89 g, 42.1 mmol), by following the general procedure **C**. The formed tertbutylZnBr·TMEDA was titrated against iodine, with titre typically ranging **0.8 M**. Further solidification yielded white powder. **Melting Point:** 130 ºC. **^{1}H NMR (500 MHz, $CDCl_3$) δ**: 2.78 – 2.42 (m, 28H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (12H, uncomplexed or partially dissociated TMEDA)), 1.05 (s, 9H, C(C**H**$_3$)$_3$). **^{13}C NMR (126**

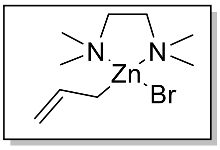
MHz, $CDCl_3$) δ: 57.3 (4× N-**C**H_3), 48.5 (2× N-**C**H_2), 33.4 (C(**C**H_3)$_3$), 22.1(**C**-Zn). **FT-IR (neat, cm^{-1}) ν:** 2890, 2963, 1444, 1405, 1087**. HRMS-ESI-TOF m/z:** $[M]^+$ calcd for $C_{10}H_{25}N_2Zn$: 237.1309, observed: 237.1302.

CyclobutylZnBr·TMEDA (2p)



The title compound was prepared using (bromomethyl)cyclopropane (1 equiv., 5.16 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89 g, 42.1 mmol), by following the general procedure **A**. The formed reagent was titrated against iodine, with titre typically ranging **0.43 M**, (cyclobutylZnBr·TMEDA: buteneZnBr·TMEDA= 76:24). Further solidification yielded white powder**. Melting Point:** 77 ºC. **^{1}H NMR (500 MHz, $CDCl_3$) δ**: 2.62 – 2.40 (m, 40H- (4H, 2× N-C**H**$_2$), (12H, 4× N-C**H**$_3$), (14H, uncomplexed or partially dissociated TMEDA)), 2.19 – 2.06 (m, 11H- (4H, Cybut-(C**H$_2$**)**$_2$**), 1.59 (q, *J* = 8.8 Hz, 2H, Cybut-C**H$_2$**), 0.19 – 0.05 (m, 1H, Cybut-**H**CZn). **^{13}C NMR (126 MHz, $CDCl_3$) δ**: 56.9 (4× N-**C**H_3), 48.5 (2× N-**C**H_2), 29.9 (2× Cybut -**C**H_2), 27.2 (Cybut -**C**H_2), 21.3 (Cybut-H**C**Zn)**. FT-IR (neat, cm^{-1}) ν:** 2850, 2897, 2919, 2977, 1462, 1019. **HRMS-ESI-TOF m/z:** $[M]^+$ calcd for $C_{10}H_{23}N_2Zn$: 235.1153, observed: 235.1153.

AllylZnBr·TMEDA (2q)



The title compound was prepared using 3-bromoprop-1-ene (1 equiv., 4.63 g, 38.2 mmol), zinc powder (2 equiv., 5 g, 76.5 mmol), TMEDA (1.1 equiv., 4.89g, 42.1 mmol), by following the general procedure **A**. The formed allylZnBr·TMEDA was titrated against iodine, with titre typically ranging from **0.48 M**. Further solidification yielded pale yellow powder. **Melting Point:** 92 ºC. ^{1}H ,^{13}C NMR contains unidentified byproduct in-conjunction with the expected peaks corresponding to the product **2q**, thus the spectra are not included. **FT-IR (neat, cm^{-1}) ν:** 1120, 1221, 837. **HRMS-ESI-TOF m/z:** $[M]^+$ calcd for $C_9H_{21}N_2Zn$: 221.0996, observed: 221.1004.

3.3.Large scale synthesis and photographs of solid reagents

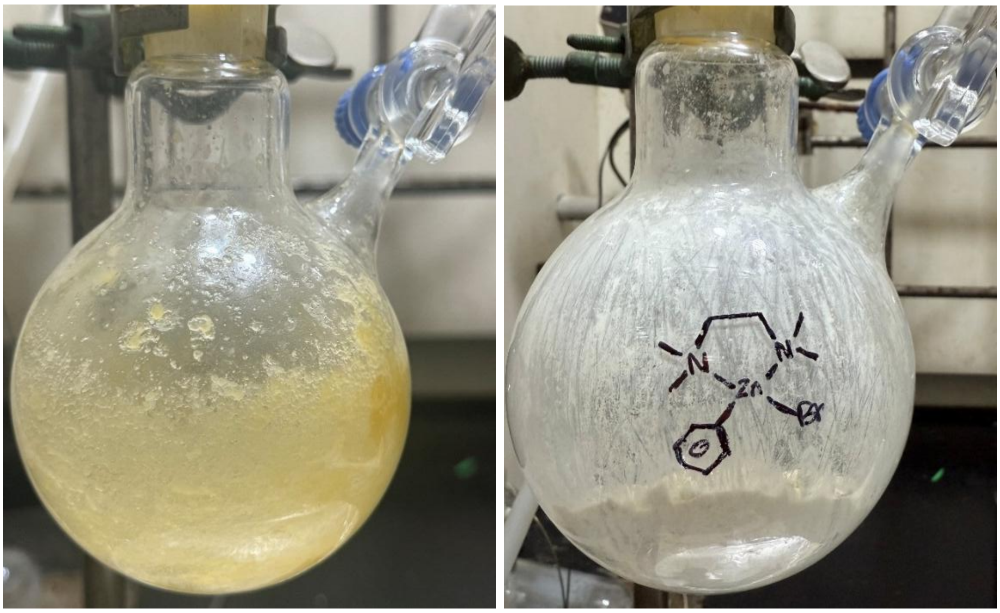
All reagents are amenable to large-scale preparation. The corresponding solid organozinc reagents were synthesized on up to a 100 mmol (1.0 equiv. of halides) scale and are suitable for further scale-up by following the corresponding general procedures, A–D.

PhZnBr·TMEDA (**2b)** was prepared using Zinc powder (13.1 g, 2 equiv., 200 mmol), Bromobenzene (10.7 mL,1 equiv., 100 mmol) and TMEDA (16.5 mL, 1.1 equiv., 110 mmol) by following the general procedure A. The formed reagent was titrated against iodine

(Knochel's method)[2], to afford PhZnBr·TMEDA reagent with titre typically ranging from **0.5-0.61 M**. The solid reagent exists without degradation for more than six months when it is stored at 4 °C.

PhZnBr·TMEDA in toluene after the reaction

PhZnBr·TMEDA in toluene filtered from Zinc and transferred to Schlenk flask using cannula



PhZnBr·TMEDA after evaporation of toluene

PhZnBr·TMEDA after multiple washes with hexane and resulted solid

Figure S1a: Solidification of PhZnBr·TMEDA

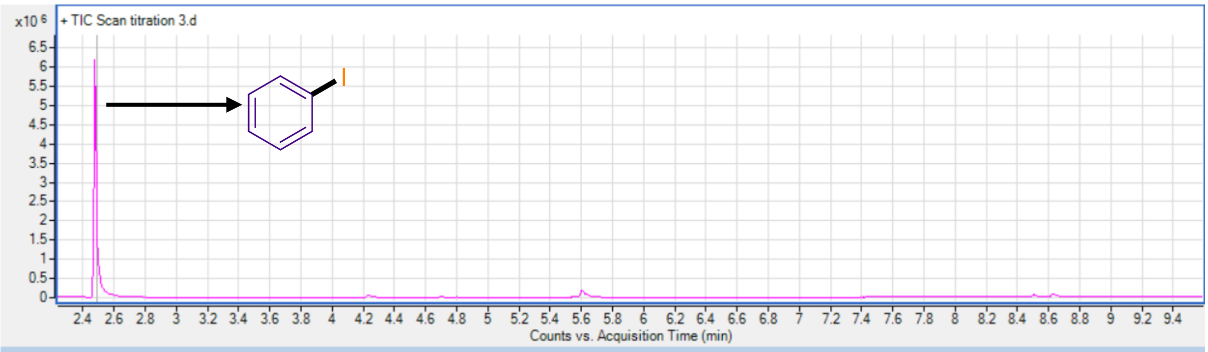


Figure S1b: GC-MS of titrated solid PhZnBr·TMEDA against iodine

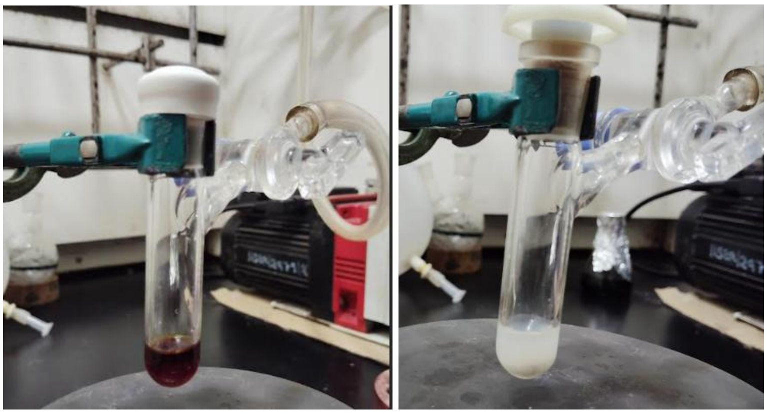
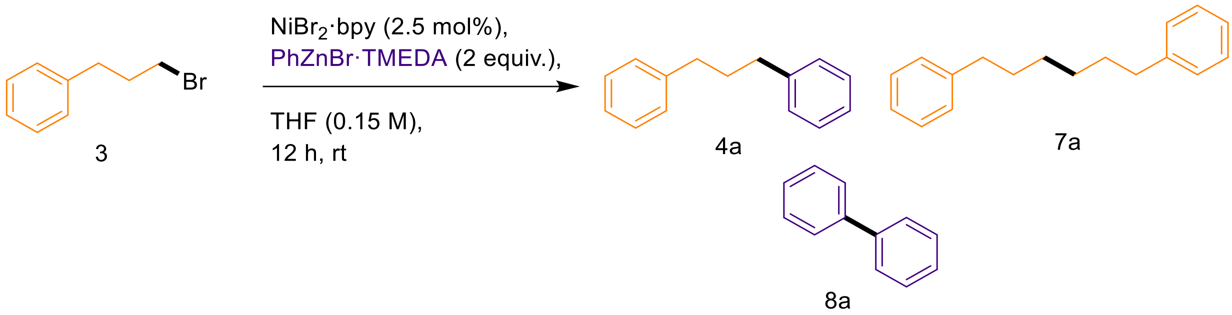


Figure S1c: Before Titration After Titration

Figure S1d: Photographs of all prepared solid organozinc reagents

4. Optimization for the Application of Reagents

4.1. General procedure for optimization of alkylation of organozinc reagents



Under an inert atmosphere, the oven dried Schlenk tube was charged with $NiBr_2$·bpy (1.41 mg, 0.00377 mmol), followed by the addition of THF (0.6 mL), (3-bromopropyl)benzene (30 mg, 0.151 mmol), and then addition of PhZnBr·TMEDA (102 mg, 0.301 mmol) and add remaining THF (0.4 mL). Then the reaction was stirred for overnight. 1,3,5-trimethoxy benzene (25.3 mg, 0.151 mmol) was added as an internal standard and diluted with ethyl acetate. An aliquot was taken from the reaction tube and analyzed using GC-MS.

Table S6: Optimization of alkylation of organozinc reagents

Entry	Deviation	4a %[a]	7a %[a]	8a %[a]
1	None	62	20	10
2	5 mol% $NiBr_2$·bpy	71	20	<5
3	20 mol% $NiBr_2$·bpy	82	15	<5
4	THF (0.2 M)	60	23	15
5	THF (1 M)	52	32	20
6	3 equiv. PhZnBr·TMEDA	73	18	12
7	Et_2O (0.15 M)	59	25	20
8	THF (0.05 M)	69	15	18
9	$NiBr_2$·DME (10 mol%), bpy (10 mol%)	69	17	9
10[b]	DME (0.15 M)	<5	ND	43
11[b]	ACN:THF (0.5:1)	23	30	12
12[b]	toluene	69	19	13
13	DMA:THF (0.5:1)	80	<5	<5
14	DMA:THF (1:1)	61	10	9
15	DMA:THF (0.5:1), 3 equiv. PhZnBr·TMEDA	92(85)[c]	<5	11

[a] GC yield, [b] Unreacted 3 is observed in small to medium amount. [c] Isolated yield.

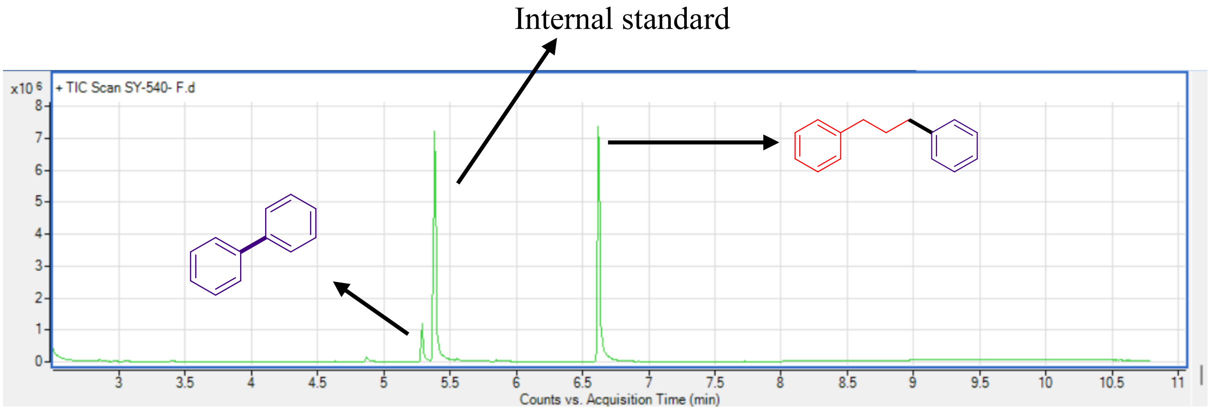
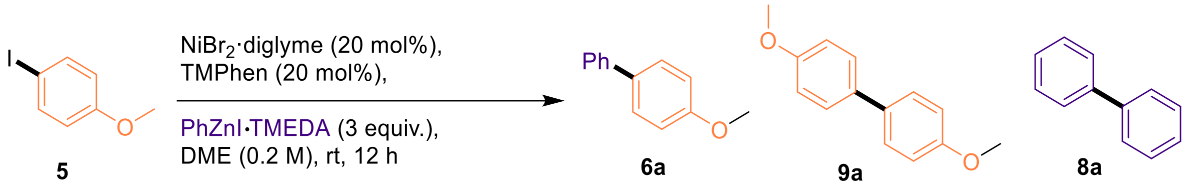


Figure S1e: GC-MS of entry 15

4.2.General procedure for optimization of arylation of organozinc reagents



Under an inert atmosphere, the oven dried Schlenk tube was charged with $NiBr_2$·diglyme (12.2.7 mg, 0.0342 mmol), TMPhen (8.08 mg, 0.0342 mmol) followed by the addition of 1,2-dimethoxyethane (0.5 ml), 1-iodo-4-methoxybenzene (40 mg, 0.171 mmol), and then addition of PhZnI·TMEDA (174 mg, 0.513 mmol) and remaining 1,2-dimethoxyethane (0.35 ml) was added. Then the reaction was stirred for overnight. 1,3,5-trimethoxy benzene (28.7 mg, 0.171 mmol) was added as an internal standard and diluted with ethyl acetate. An aliquot was taken from the reaction tube and analysed using GC-MS.

Table S7: Optimization of arylation of organozinc reagents

Entry	Deviations	6a%^{a}
1	None	85(70)^c
2^b	10 mol% bpy	30
3^b	10 mol% dtbbpy	38
4^b	4,4’-Dimethoxy bipyridine	49
5^b	4,4’-Dimethyl bipyridine	48
6^b	terpyridine	<5
7^b	neocuproine	59
8	DME (0.05 M)	69

9[b]	$NiBr_2$·dtbbpy (2.5 mol%)	33
10[b]	DMA	<5
11	Et_2O	42
12	THF	51
13	$NiBr_2$·bpy (15 mol%)	34
14[b]	DME:THF (1:1)	47

[a]GC yield calibrated using TMB. [b]Starting material was observed in medium amount. In all the reaction condition 9a and 8a was observed from small to medium amount. [c]Isolated yield.

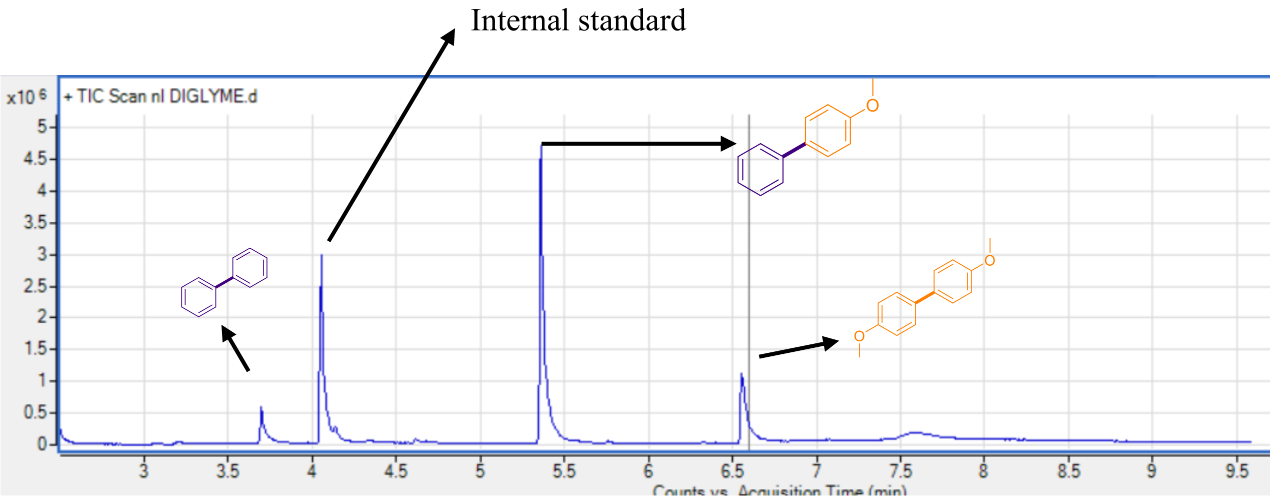
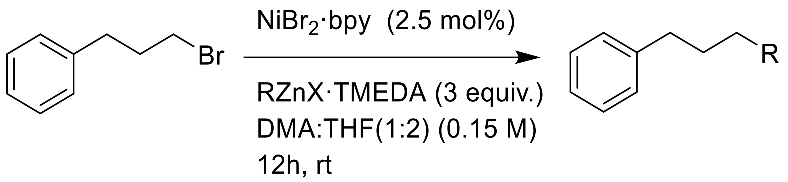


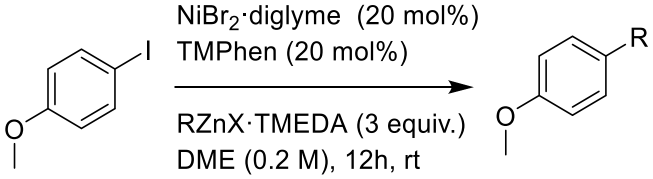
Figure S1f: GC-MS of entry 1

5. Nickel catalysed cross-coupling employing solid organozinc reagents

5.1. Application general procedure

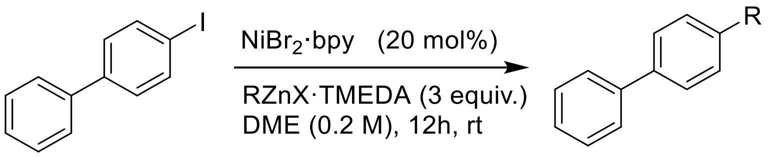


General procedure E: Under an inert atmosphere, the oven dried Schlenk tube was charged with $NiBr_2$·bpy (2.5 mol%), followed by the addition of DMA (ratio of 1 in 0.15 M), (3-bromopropyl) benzene (1 equiv.) and THF (ratio of 2 in 0.15 M, 95% of the solvent), addition of solid organozinc (3 equiv.) followed by remaining THF. Then, the reaction was stirred at room temperature for overnight or until the completion of reaction, monitored by TLC. After the reaction was completed, the mixture was filtered through a pad of silica, using ethyl acetate to remove metal salts in the filtrate. Then water was added and extracted with ethyl acetate, the organic layer was washed with brine and the solvent was evaporated under reduced pressure to obtain the crude reaction mixture. The crude was further subjected to flash column chromatography to obtain the pure product.



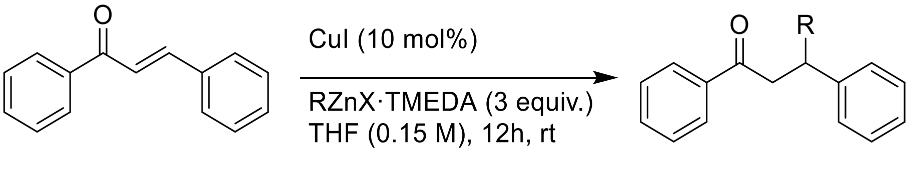
General procedure F: Under an inert atmosphere, the oven dried Schlenk tube was charged with $NiBr_2$·diglyme (20 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (20 mol%) followed by the addition of 1,2-dimethoxyethane (DME) (90% of solvent in 0.2 M), 1-iodo-4-methoxybenzene (1 equiv.), and then addition of solid organozinc reagent (3 equiv.) and remaining DME. Then the reaction was stirred at room temperature for overnight or until the completion of reaction, monitored by TLC. After the reaction was complete, the mixture was filtered through a pad of silica, using ethyl acetate to remove metal salts. The solvent was evaporated under reduced pressure to obtain the crude reaction mixture. The crude was further subjected to flash column chromatography to obtain the pure product.

Modified procedure for low boiling organozinc reagents

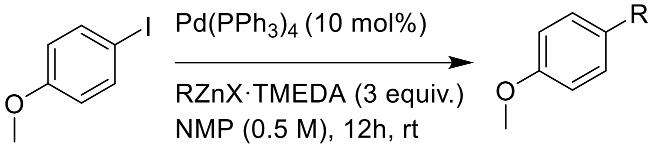


General procedure G: Under an inert atmosphere, the oven dried Schlenk tube was charged with $NiBr_2$·bpy (20 mol%), followed by the addition of 1,2-dimethoxyethane (DME, 95% of solvent in 0.2 M), 4-iodo-1,1'-biphenyl (1 equiv.), and, then addition of solid organozinc reagent (3 equiv.) and add remaining DME. Then the reaction was stirred at room temperature for overnight or until the completion of reaction, monitored by TLC. After the reaction was complete, the mixture was filtered through a pad of silica, using ethyl acetate to remove metal salts. The solvent was evaporated under reduced pressure to obtain the crude reaction mixture. The crude was further subjected to flash column chromatography to obtain the pure product.

Modified procedure for poor performing substrate



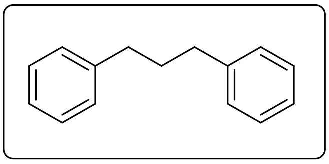
General procedure H: Under an inert atmosphere, the oven dried Schlenk tube was charged with Copper(I) iodide (10 mol%), followed by the addition of THF (95% of solvent in 0.15 M), (*E*)-chalcone (1 equiv.), and, then addition of solid organozinc reagent (3 equiv.) and remaining THF. Then the reaction was stirred at room temperature for overnight or until the completion of reaction, monitored by TLC. After the reaction was completed, the mixture was filtered through a pad of silica, using ethyl acetate to remove metal salts. The solvent was evaporated under reduced pressure to obtain the crude reaction mixture. The crude was further subjected to flash column chromatography to obtain the pure product.



General procedure I: Under an inert atmosphere, the oven dried Schlenk tube was charged with $Pd(PPh_3)_4$ (10 mol%) and followed by the addition of NMP (95% of solvent in 0.5 M), 1-iodo-4-methoxybenzene (1 equiv.), then addition of solid organozinc reagent (3 equiv.) and remaining solvent. Then the reaction was stirred at room temperature for overnight or until the completion of reaction, monitored by TLC. After the reaction was completed, the mixture was filtered through a pad of silica, using ethyl acetate to remove metal salts. The solvent was evaporated under reduced pressure to obtain the crude reaction mixture. The crude was further subjected to flash column chromatography to obtain the pure product.

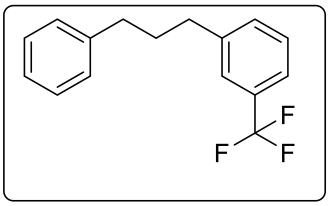
5.2.Scope employing solid organozinc reagents in cross-coupling reaction

1,3-diphenylpropane (4a)



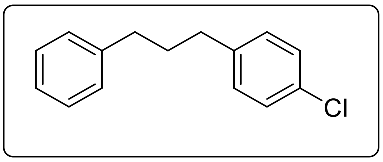
The title compound was prepared using (3-bromopropyl)benzene **3** (1 equiv., 0.15 ml, 1 mmol), PhZnBr·TMEDA **2b** (3 equiv., 1.02 g, 3.01 mmol) by following the general procedure **E**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, obtained as a colourless liquid **4a** (175 mg, 89%). **^{1}H NMR (500 MHz, $CDCl_3$) δ**: 7.32 – 7.26 (m, 5H, Ar-C**H**), 7.22 – 7.16 (m, 5H, Ar-C**H**), 2.66 (t, *J* = 7.8 Hz, 4H, Ar-C**H_2**), 2.01 – 1.93 (m, 2H, CH_2-C**H_2**-CH_2)· **^{13}C NMR (126 MHz, $CDCl_3$) δ**: 142.4 (2x Ar-**C**), 128.5 (4x Ar-**C**H), 128.4 (4x Ar-**C**H), 125.8 (2x Ar-**C**H), 35.5 (2x Ar-**C**H_2), 33.1 (1x Ar-CH_2-**C**H_2-CH_2-Ar). **FT-IR (neat, cm^{-1}) ν**: 1497, 1538, 1454, 3068, 3111, 878, 848. **EI-MS (*m/z*):** $[M]^+$ for $C_{15}H_{16}$ 196.12. Literature[3].

1-(3-phenylpropyl)-3-(trifluoromethyl)benzene (4b)



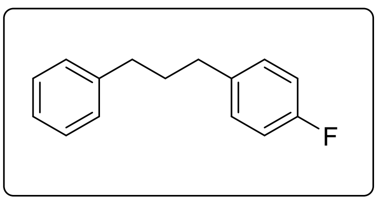
The title compound was prepared using (3-bromopropyl)benzene **3** (1 equiv., 0.15 ml, 1 mmol), m-CF_3PhZnBr·TMEDA **2c** (3 equiv., 1.23 g, 3.01 mmol) by following the general procedure **E**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether. Colourless liquid **4b** (190 mg, 72%). **^{1}H NMR (400 MHz, CDCl$_3$) δ**: 7.46 (m, 2H, Ar-C**H**), 7.43 – 7.35 (m, 2H, Ar-C**H**), 7.31 (m, 2H, Ar-C**H**), 7.22 (m, 3H, Ar-C**H**), 2.77 – 2.63 (m, 4H, Ar-CH$_2$-C**H$_2$**-C**H$_2$**-ArCF$_3$), 2.00 (dt, J = 9.4, 7.7 Hz, 2H, Ar-C**H$_2$**). **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 143.12 (1x Ar**C**), 141.81 (1x Ar**C**), 131.81 (1x ArC**H**), 130.59 (q, J^2_{C-F} = 24.2 Hz) (1x Ar**C**), 128.68 (2 xAr**C**H), 128.41 (2 xAr**C**H), 128.38 (q, J^3_{C-F} = 7.56 Hz) (1x Ar**C**H), 125.8 (q, J^3_{C-F} = 7.56 Hz) (1xAr**C**H), 124.47 (d, J^1_{C-F} = 273.42 Hz) (1x **C**F$_3$), 122.65 (q, J^4_{C-F} = 3.8 Hz) (1x Ar**C**H), 35.32 (1x Ar-**C**H$_2$), 35.16 (1x Ar-**C**H$_2$), 32.71 (1x Ar-CH$_2$-**C**H$_2$).**^{19}F NMR (471 MHz, CDCl$_3$) δ**: -62.56. **FT-IR (neat, cm^{-1}) ν**: 2929, 1599, 1451, 1329, 1265, 1075, 845. **EI-MS (*m/z*):** $[M]^+$ for $C_{16}H_{15}F_3$ 264.11. Literature[4].

1-chloro-4-(3-phenylpropyl)benzene (4c)



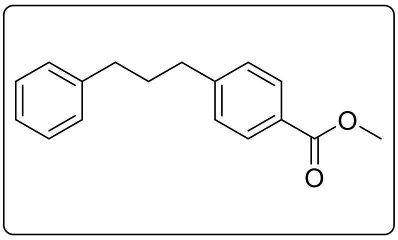
The title compound was prepared using (3-bromopropyl)benzene **3** (1 equiv., 0.15 mL, 1 mmol), p-ClPhZnBr·TMEDA **2d** (3 equiv., 1.12 g, 3.01 mmol) by following the general procedure **E**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether. Colourless liquid **4c** (173 mg, 75%). **^{1}H NMR (500 MHz, CDCl$_3$) δ**: 7.33 (m, 3H, ArC**H**), 7.23 (m, 4H, ArC**H**), 7.15 (m, 2H, ArC**H**), 2.71 – 2.61 (m, 4H, Ar-C**H$_2$**), 2.02 – 1.93 (m, 2H, CH$_2$-C**H$_2$**-CH$_2$). **^{13}C NMR (126 MHz, CDCl$_3$) δ:** 141.9 (1x Ar-**C**), 140.6 (1x Ar-**C**), 131.4 (1x Ar-**C**), 128.4 (1x Ar-**CH**), 128.37 (2x Ar-**CH**), 128.33 (2x Ar-**CH**), 128.2 (2x Ar-**CH**), 125.8 (2x Ar-**CH**), 35.2 (1x Ar-**C**H$_2$), 34.6 (1x Ar-**C**H$_2$), 32.8 (1x Ar-CH$_2$-**C**H$_2$). **FT-IR (neat, cm^{-1}) ν**: 2930, 2857, 1600, 1491, 1402, 769. **EI-MS (*m/z*):** $[M]^+$ for $C_{15}H_{15}Cl$ 230.08. Literature[5].

1-fluoro-4-(3-phenylpropyl)benzene (4d)



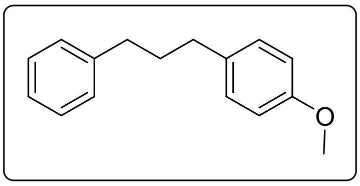
The title compound was prepared using (3-bromopropyl)benzene **3** (1 equiv., 0.15 mL, 1 mmol), p-FPhZnBr·TMEDA **2e** (3 equiv., 1.07 g, 3.01 mmol) by following the general procedure **E.** The reaction crude was purified through column chromatography. Isolated in 100% pet ether. Colourless liquid **4d** (182 mg, 85%). **^{1}H NMR (500 MHz, CDCl$_3$) δ**: 7.32 (m, 2H, Ar-**H**), 7.22 (m, 3H, Ar-**H**), 7.15 (m, 2H, Ar-**H**), 6.99 (m, 2H, Ar-**H**), 2.66 (dt, *J* = 10.3, 7.6 Hz, 4H, Ar-C**H$_2$**), 1.97 (p, *J* = 7.8 Hz, 2H, Ar-CH$_2$-C**H$_2$**). **^{13}C NMR (126 MHz, CDCl$_3$) δ:** 161.35 (d, J^1_{C-F} = 243.53 Hz) (1xAr**C**F), 142.24 (1x Ar**C**), 137.97 (d, J^4_{C-F} = 1.9 Hz) (1x Ar**C**), 129.84 (d, J^3_{C-F} = 7.5 Hz) (2x Ar**C**H),128.51 (d, J^2_{C-F} = 20.16 Hz) (2x Ar**C**H), 125.93 (2x Ar**C**H), 115.13 (2x ArC**H**), 114.8 (1x Ar**C**H), 35.44 (1x Ar-**C**H$_2$), 34.70 (1x Ar-**C**H$_2$), 33.21(1x Ar-CH$_2$-**C**H$_2$). **^{19}F NMR (471 MHz, CDCl$_3$) δ: -**117.96. **FT-IR (neat, cm^{-1}) ν**: 3111, 2933, 2850, 1509, 1224, 1097, 829. **EI-MS (*m/z*):** [M]$^+$ for $C_{15}H_{15}F$ 214.12. Literature[6].

methyl 4-(3-phenylpropyl)benzoate (4e)



The title compound was prepared using (3-bromopropyl)benzene **3** (1equiv., 0.15 ml, 1 mmol), p-methyl formate PhZnBr·TMEDA **2f** (3 equiv., 1.19 g, 0.151 mmol) by following the general procedure **E**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether. Colourless liquid **4e** (204 mg, 80%). **^{1}H NMR (400 MHz, CDCl$_3$) δ**: 8.00 – 7.93 (m, 2H, Ar-**H**), 7.29 (m, 3H, Ar-**H**), 7.24 (m, 1H, Ar-**H**), 7.20 (m, 3H, Ar-**H**), 3.91 (s, 3H, -OC**H$_3$**), 2.74 – 2.63 (m, 4H, Ar-C**H$_2$**), 2.03 – 1.94 (m, 2H, Ar-CH$_2$-C**H$_2$**). **^{13}C NMR (101 MHz, CDCl$_3$) δ**: 167.1 (1x **C**(O)), 147.8 (1x Ar-**C**), 141.9 (1x Ar-**C**), 129.7 (1x Ar-**C**), 128.49 (2x Ar-**C**H), 128.44 (2x Ar-**C**H), 128.39 (2x Ar-**C**H), 127.8 (2x Ar-**C**H), 125.8 (1x Ar-**C**H), 51.9 (1x -O**C**H$_3$), 35.44 (1x Ar-**C**H$_2$), 35.37 (1x Ar-**C**H$_2$), 32.6 (1x Ar-CH$_2$-**C**H$_2$) . **FT-IR (neat, cm^{-1}) ν**: 3050, 2930, 1730, 1250, 1150, and 830. **EI-MS (*m/z*):** [M]$^+$ for $C_{17}H_{18}O_2$ 254.13. Literature[8].

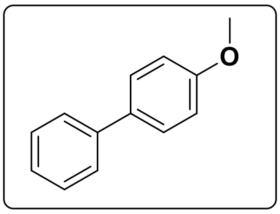
1-methoxy-4-(3-phenylpropyl)benzene (4f)



The title compound was prepared using (3-bromopropyl)benzene **3** (1 equiv., 0.15 ml, 1 mmol), p-OMePhZnI·TMEDA **2g** (3 equiv., 1.25 g, 3.01 mmol) by following the general procedure **E**. The reaction crude was purified through column chromatography. Isolated in: 100% pet ether. Colourless liquid **4f** (158 mg, 70%). **^{1}H NMR (500 MHz, CDCl$_3$) δ**: 7.30 (m, 2H, Ar-**H**), 7.24 – 7.18 (m, 3H, Ar-**H**), 7.15 – 7.10 (m, 2H, Ar-**H**), 6.86 (m, 2H, Ar-**H**), 3.81 (s, 3H, -OC**H$_3$**), 2.73 – 2.58 (m, 4H, Ar-C**H$_2$**), 2.01-1.91 (m, 2H, Ar-CH$_2$-C**H$_2$**). **^{13}C NMR (126 MHz, CDCl$_3$) δ:** 157.7 (1x Ar-**C**-OCH$_3$), 142.4 (1x Ar-**C**), 134.4 (1x Ar-**C**), 129.3 (2x Ar-**C**H), 128.4 (2x Ar-**C**H), 128.3 (2x Ar-**C**H), 125.7 (2x Ar-**C**H), 113.7 (1x Ar-**C**H), 55.2 (1x -O**C**H$_3$), 35.4 (1x Ar-**C**H$_2$), 34.5 (1x Ar-

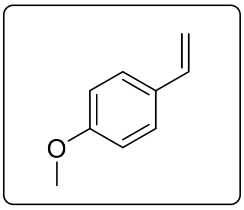
CH$_2$), 29.7 (1x Ar-CH$_2$-**C**H$_2$). **FT-IR (neat, cm^{-1}) ν**: 3131, 2945, 1518, 1251, 1184, 1042, 835. **EI-MS (*m/z*):** [M]$^+$ for $C_{16}H_{18}O$ 226.14. Literature[7].

4-methoxy-1,1'-biphenyl (6a)



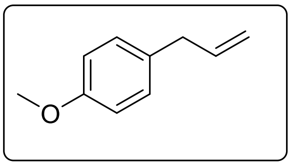
The title compound was prepared using 1-iodo-4-methoxybenzene **5** (1 equiv., 200 mg, 0.855 mmol), PhZnI·TMEDA **2a** (3 equiv., 989 mg, 2.56 mmol) by following the general procedure **F**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether. White solid **6a** (110 mg, 70%)**. ^{1}H NMR (500 MHz, CDCl$_3$) δ**: 7.58 – 7.50 (m, 4H, Ar-**H**), 7.44 – 7.39 (m, 2H, Ar-**H**), 7.33 – 7.28 (m, 1H, Ar-**H**), 7.00 – 6.95 (m, 2H, Ar-**H**), 3.86 (d, *J* = 1.2 Hz, 3H, -OC**H$_3$**). **^{13}C NMR (126 MHz, CDCl$_3$) δ**: 159.3 (1x Ar-**C**-OCH$_3$), 140.9 (1x Ar-**C**), 133.9 (1x Ar-**C**), 128.8 (2x Ar-**C**H), 128.3 (2x Ar-**C**H), 126.89 (2x Ar-**C**H), 126.80 (2x Ar-**C**H), 114.3 (1x Ar-**C**H), 55.5 (1x -O**C**H$_3$). **FT-IR (neat, cm^{-1}) ν**: 3146, 2923, 1520, 1486, 1378, 1249,1183, 1039, 834. **EI-MS (*m/z*):** [M]$^+$ for $C_{13}H_{12}O$ 184.1. Literature[9].

1-methoxy-4-vinylbenzene (6b)



The title compound was prepared using 1-iodo-4-methoxybenzene **5** (1 equiv., 200 mg, 0.855 mmol), vinylZnBr·TMEDA **2h** (3 equiv., 740 mg, 2.56 mmol) by following the general procedure **I**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, Colourless liquid **6b** (37.95 mg, 33%). **^{1}H NMR (500 MHz, CDCl$_3$) δ**: 7.39 (m, 2H, Ar-**H**), 6.91 (m, 2H, Ar-**H**), 6.71 (m, 1H, Ar-C**H**), 5.66 (d, *J* = 17.6 Hz, 1H, Ar-CH=C**H**$_2$), 5.18 (d, *J* = 10.9 Hz, 1H, Ar-CH=C**H$_2$**), 3.84 (d, *J* = 1.5 Hz, 3H, -OC**H**$_3$).**^{13}C NMR (126 MHz, CDCl$_3$) δ:** 159.3 (1x Ar-**C**-OCH$_3$), 136.1 (1x Ar-**C**-CH), 130.3 (1x Ar-**C**H=CH$_2$), 127.3 (2x Ar-**C**H), 113.8 (2x Ar-**C**H), 111.4 (1x Ar-CH=**C**H$_2$), 55.1 (1x -O**C**H$_3$). **FT-IR (neat, cm^{-1}) ν**: 3075, 3052, 1590, 1460, 1132, 1250, 830. **EI-MS (*m/z*):** [M]$^+$ for $C_9H_{10}O$ 134.1. Literature[16].

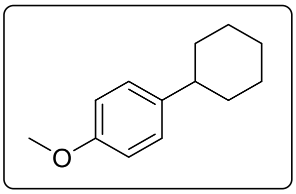
1-allyl-4-methoxybenzene (6c)



The title compound was prepared using 1-iodo-4-methoxybenzene **5** (1 equiv., 200 mg, 0.855 mmol), allylZnBr·TMEDA **2q** (3 equiv., 776 mg, 2.56 mmol) by following the general procedure **F**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, Colourless liquid **6c** (50.8 mg, 40%). **^{1}H NMR (500 MHz, CDCl$_3$) δ:** 7.20 – 7.10 (m, 2H, Ar-**H**), 6.93 – 6.86 (m, 2H, Ar-**H**), 6.01 (m, 1H, Ar-CH$_2$=C**H**), 5.15 – 5.06 (m, 2H, Ar-CH$_2$-CH=C**H$_2$**), 3.83 (s, 3H, -OC**H$_3$**), 3.38 (dd, *J* = 6.9, 1.8 Hz, 2H, Ar-C**H$_2$**). **^{13}C NMR (126 MHz, CDCl$_3$) δ**: 157.9

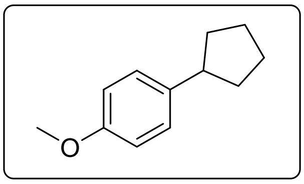
(1x Ar-**C**-OCH_3), 137.8 (1x Ar-**C**-CH_2), 132.0 (1x Ar-CH_2-**CH**), 129.4 (2x Ar-**C**), 115.3 (2x Ar-**C**H), 113.7 (1x Ar-CH_2-CH=**C**H_2), 55.1 (1x -O**C**H_3), 39.2 (1x Ar-**C**H_2). **FT-IR (neat, cm^{-1}) ν**: 3054, 2887, 1648, 1600, 1265, 1028, 980, 838. **EI-MS (*m/z*):** $[M]^+$ for $C_{10}H_{12}O$ 148.1. Literature[15].

1-cyclohexyl-4-methoxybenzene (6d)



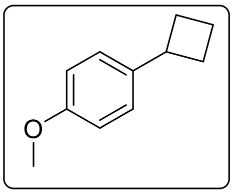
The title compound was prepared using 1-iodo-4-methoxybenzene **5** (1 equiv., 200 mg, 0.855 mmol), CyclohexylZnI·TMEDA **2k** (3 equiv., 1 g, 2.56 mmol) by following the general procedure **F**. The reaction crude was purified through column chromatography Isolated in 100% pet ether. White solid **6d** (102 mg, 63%). **^{1}H NMR (500 MHz, CDCl$_3$) δ**: 7.18 – 7.12 (m, 2H, Ar-C**H**), 6.88 – 6.83 (m, 2H, Ar-C**H**), 3.80 (s, 3H, -OC**H$_3$**), 2.46 (m, 1H, C**H** (Cy-hex)), 1.93 – 1.81 (m, 4H, C**H$_2$**(Cy-hex)), 1.76 (m, 1H, C**H**(Cy-hex)), 1.47 – 1.34 (m, 4H, C**H$_2$**(Cy-hex)), 1.26 (m,1H, C**H**(Cy-hex)). **^{13}C NMR (126 MHz, CDCl$_3$) δ:** 157.6 (1x Ar-**C**-OCH_3), 140.3 (2x Ar-**C**H), 127.5 (2x Ar-**C**H), 113.6 (1x Ar-**C**), 55.1 (1x -O**C**H_3), 43.6 (1x Ar-**C**H(Cy-hex)), 34.7 (2x **C**H_2(Cy-hex)), 26.93 (2x **C**H_2(Cy-hex)), 26.15 (1x **C**H_2(Cy-hex)). **FT-IR (neat, cm^{-1}) ν**: 3062, 2991,1514,1259, 1089, 1040. **EI-MS (*m/z*):** $[M]^+$ for $C_{13}H_{18}O$ 190.14. Literature[10].

1-cyclopentyl-4-methoxybenzene (6e)



The title compound was prepared using 1-iodo-4-methoxybenzene **5** (1 equiv., 200 mg, 0.855 mmol), CyclopentylZnBr·TMEDA **2m** (3 equiv., 848 mg, 2.56 mmol) by following the general procedure **F**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, Colourless liquid **6e** (83 mg, 55%). **^{1}H NMR (400 MHz, CDCl$_3$) δ**: 7.19 – 7.14 (m, 2H, Ar-C**H**), 6.86 – 6.81 (m, 2H, Ar-C**H**), 3.79 (s, 3H, -OC**H$_3$**), 2.94 (tt, *J* = 9.9, 7.4 Hz, 1H, C**H**(Cy-pent)), 2.09 – 1.99 (m, 2H, C**H$_2$**(Cy-Pent)), 1.84 – 1.74 (m, 2H, C**H$_2$**(Cy-pent)), 1.74 – 1.62 (m, 2H, C**H$_2$**(Cy-pent)), 1.60 – 1.53 (m, 2H, C**H$_2$**(Cy-pent)). **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 157.7 (1x Ar-**C**-OCH_3), 138.7 (2x Ar-**C**H), 128.0 (2x Ar-**C**H), 113.7 (1x Ar-**C**), 55.4 (1x -O**C**H_3), 45.2 (1x Ar-**C**H(Cy-pent)), 34.8 (2x **C**H_2(Cy-pent)), 25.5 (2x **C**H_2(Cy-pent)). **FT-IR (neat, cm^{-1}) ν**: 3153, 3092, 2947, 1518, 1298, 1035, 831, 785. **EI-MS (*m/z*):** $[M]^+$ for $C_{12}H_{16}O$ 176.12. Literature[12].

1-cyclobutyl-4-methoxybenzene (6f)



The title compound was prepared using 1-iodo-4-methoxybenzene **5** (1 equiv., 200 mg, 0.855 mmol), CyclobutylZnBr·TMEDA **2p** (3 equiv., 812 mg, 2.56 mmol) by following the general procedure **F**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, Colourless liquid **6f** (97.3 mg, 70%). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.19 – 7.09 (m, 2H, Ar-C**H**), 6.87 – 6.81 (m, 2H, Ar-C**H**), 3.79 (s, 3H, -OC**H_3**), 3.49 (p, *J* = 8.6 Hz, 1H, C**H**(Cy-but)), 2.31 (dtd, *J* = 10.5, 7.9, 2.4 Hz, 2H, C**H_2**(Cy-but)), 2.16 – 2.04 (m, 2H, C**H_2**(Cy-but)), 2.04 – 1.92 (m, 1H, C**H_2**(Cy-but)), 1.87 – 1.81 (m, 1H, C**H_2**(Cy-but)). **^{13}C NMR (101 MHz, $CDCl_3$) δ**: 157.8 (1x Ar-**C**-OCH_3), 138.6 (2x Ar-**C**H), 127.4 (2x Ar-**C**H), 113.7 (1x Ar-**C**), 55.4 (1x -OCH_3), 39.9 (1x Ar-CH(Cy-but)), 30.2 (2x **C**H_2(Cy-but)), 18.3 (1x **C**H_2(Cy-but). **FT-IR (neat, cm^{-1}) ν**: 3110, 2961, 1510, 1468, 1205, 792. **EI-MS (*m/z*):** $[M]^+$ for $C_{11}H_{14}O$ 162.1. Literature[11].

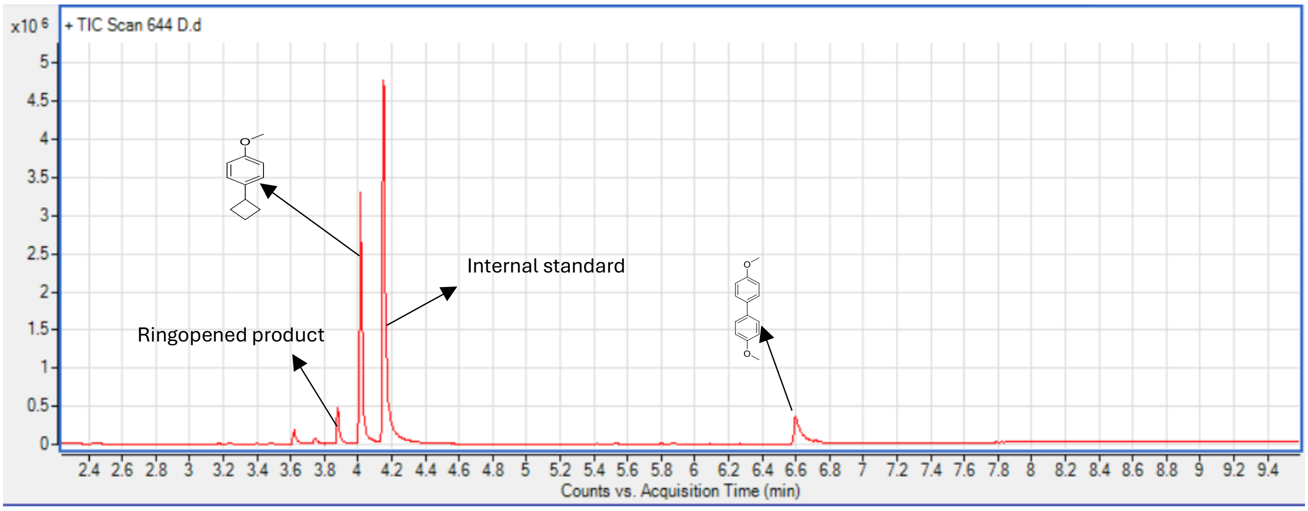
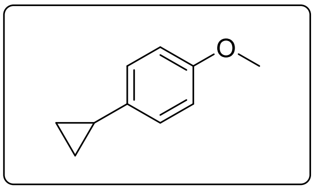


Figure S1g: Crude GC-MS of 6f with internal standard

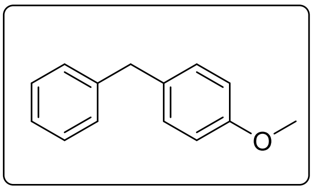
1-cyclopropyl-4-methoxybenzene (6g)



The title compound was prepared using 1-iodo-4-methoxybenzene **5** (1 equiv., 200 mg, 0.855 mmol), cyclopropylZnBr·TMEDA **2n** (3 equiv., 776 mg, 2.56 mmol) by following the general procedure **F**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, Colourless liquid **6g** (88 mg, 70%). **^{1}H NMR (500 MHz, $CDCl_3$) δ**: 7.10 – 7.00 (m, 2H, Ar-C**H**), 6.90 – 6.80 (m, 2H, Ar-C**H**), 3.81 (s, 3H, -OC**H_3**), 1.89 (tt, *J* = 8.5, 5.1 Hz, 1H, C**H**(Cy-prop)), 0.97 – 0.87 (m, 2H, C**H_2**(Cy-prop)), 0.69 – 0.61 (m, 2H, C**H_2**(Cy-prop)). **^{13}C NMR (101 MHz, $CDCl_3$) δ**: 157.5 (1x Ar-**C**-OCH_3), 135.8 (2x Ar-CH), 126.8 (2x Ar-CH), 113.7 (1x Ar-**C**), 55.2 (1x -OCH_3), 14.5 (1x Ar-**C**H(Cy-prop)), 8.4 (2x

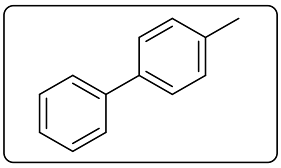
CH_2(Cy-prop)). **FT-IR (neat, cm^{-1}) ν**: 3081,3146, 2946, 1581, 1462, 1250, 1110, 825, 780. **EI-MS (*m/z*):** [M]$^+$ for $C_{10}H_{12}O$ 148.1. Literature[17].

1-benzyl-4-methoxybenzene (6h)



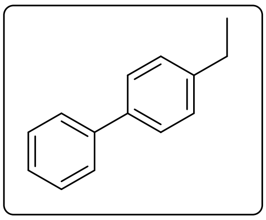
The title compound was prepared using 1-iodo-4-methoxybenzene **5** (1 equiv., 200 mg, 0.855 mmol), benzylZnI·TMEDA **2i** (3 equiv., 1.02 g, 2.56 mmol) by following the general procedure **F**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, colourless liquid **6j** (143.8 mg, 85%). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.20 (m, 2H, Ar-**H**), 7.14 – 7.07 (m, 3H, Ar-**H**), 7.05 – 7.01 (m, 2H, Ar-**H**), 6.78 – 6.73 (m, 2H, Ar-**H**), 3.85 (s, 2H, C**H_2**), 3.71 (s, 3H, OC**H_3**). **^{13}C NMR (101 MHz, $CDCl_3$) δ**: 133.2 (1x Ar-**C**-OCH_3), 129.8 (1x Ar-**C**), 128.8 (1x Ar-**C**), 128.4 (4x Ar-**C**H), 125.9 (2x Ar-**C**H), 116.3 (2x Ar-**C**H), 113.8 (1x Ar-**C**H), 55.2 (1x O**C**H_3), 41.0 (1x **C**H_2). **FT-IR (neat, cm^{-1}) ν**: 3133, 2895, 1504, 1455, 1220,1103, 1009, 830. **EI-MS (*m/z*):** [M]$^+$ for $C_{14}H_{14}O$ 198.1. Literature[18].

4-methyl-1,1'-biphenyl (6i)



The title compound was prepared using 4-iodo-1,1'-biphenyl **7** (1 equiv., 200 mg, 0.714 mmol), methylZnI·TMEDA **2f** (3 equiv., 693 mg, 2.14 mmol) by following the general procedure **G**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, white solid **6h** (108 mg, 90%). **^{1}H NMR (500 MHz, $CDCl_3$) δ**: 7.61 – 7.56 (m, 2H, Ar-C**H**), 7.50 (m, 2H, Ar-C**H**), 7.43 (m, 2H, Ar-C**H**), 7.33 (m, 1H, Ar-C**H**), 7.25 (m, 2H, Ar-C**H**), 2.40 (s, 3H, C**H_3**). **^{13}C NMR (126 MHz, $CDCl_3$) δ**: 141.3 (1x Ar-**C**), 138.5 (1x Ar-**C**H), 137.1 (2x Ar-**C**H), 129.6 (2x Ar-**C**H), 128.8 (1x Ar-**C**), 127.1 (2x Ar-**C**H), 127.1 (2x Ar-**C**H), 127.1 (1x Ar-**C**-CH_3), 21.2 (1x **C**H_3). **FT-IR (neat, cm^{-1}) ν**: 3066, 2988, 1489, 1379, 760. **EI-MS (*m/z*):** [M]$^+$ for $C_{13}H_{12}$ 168.1. Literature[13].

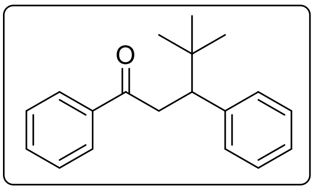
4-ethyl-1,1'-biphenyl (6j)



The title compound was prepared using 4-iodo-1,1'-biphenyl **7** (1 equiv., 200 mg, 0.714 mmol), ethylZnI·TMEDA **2j** (3 equiv., 622 mg, 2.14 mmol) by following the general procedure G. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, Colourless solid **6i** (109 mg, 84%). **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 7.63 – 7.57 (m, 2H, Ar-**H**), 7.56 – 7.50 (m, 2H, Ar-**H**), 7.48 – 7.40 (m, 2H, Ar-**H**), 7.38 –

7.27 (m, 3H, Ar-**H**), 2.71 (q, *J* = 7.6 Hz, 2H, C**H**$_2$), 1.33 – 1.24 (m, 3H, C**H**$_3$). **^{13}C NMR (101 MHz, CDCl$_3$) δ**: 143.3 (1x Ar-**C**H), 141.1 (2x Ar-**C**H), 138.5 (2x Ar-**C**H), 128.68 (1x Ar-**C**), 128.26 (1x Ar-**C**), 127.0 (2x Ar-**C**H), 126.99 (2x Ar-**C**H), 126.94 (1x Ar-**C**-CH$_2$), 28.4 (1x **C**H$_2$), 15.5 (1x **C**H$_3$). **FT-IR (neat, cm^{-1}) ν**: 3112, 3066, 2892, 1457, 1360, 779. **EI-MS (*m/z*):** [M]$^+$ for $C_{14}H_{14}$ 182.1. Literature[14].

4,4-dimethyl-1,3-diphenylpentan-1-one (6k)



The title compound was prepared by using (*E*)-chalcone (1 equiv., 200 mg, 0.96 mmol), t-ButylZnBr·TMEDA **2o** (3 equiv., 918 mg, 2.88 mmol) by following the general procedure **H**. The reaction crude was purified through column chromatography. Isolated in 100% pet ether, Colourless liquid **6k** (214 mg, 84%). **^{1}H NMR (500 MHz, CDCl$_3$) δ**: 7.90 – 7.87 (m, 2H, Ar-**H**), 7.56 – 7.52 (m, 1H, Ar-**H**), 7.46 – 7.41 (m, 2H, Ar-**H**), 7.26 – 7.14 (m, 5H, Ar-**H**), 3.54 (dd, *J* = 16.7, 10.0 Hz, 1H, C**H$_2$**), 3.36 (dd, *J* = 16.7, 3.8 Hz, 1H, C**H$_2$**), 3.28 (dd, *J* = 10.0, 3.8 Hz, 1H, C**H**), 0.97 (s, 9H,C**H$_3$**). **^{13}C NMR (101 MHz, CDCl$_3$) δ**: 199.5 (1x **C**(O)), 142.4 (1x Ar-**C**), 137.4 (1x Ar-**C**), 132.7 (2x Ar-**C**H), 129.4 (2x Ar-**C**H), 128.4 (2x Ar-**C**H), 127.9 (2x Ar-**C**H), 127.6 (1x Ar-**C**H), 126.1 (1x Ar-**C**H), 51.0 (1x **C**H-C(CH$_3$)), 39.8 (1x **C**H$_2$-CH), 33.9 (1x **C**(CH$_3$)), 28.1 (3x **C**H$_3$). **FT-IR (neat, cm^{-1}) ν**: 3052, 2942, 1687, 1620, 1452, 1382. **EI-MS (*m/z*):** [M]$^+$ for $C_{19}H_{22}O$ 266.17. Literature[19].

6. Crystallization of organozinc reagent

6.1.PhZnI·TMEDA (2a)

After completion of the reaction, the tube was left undisturbed for 1-3 days, and the growth of single crystal (X-ray quality) was observed on top of the zinc surface.

6.2. CyclobutaneZnBr·TMEDA (2p)

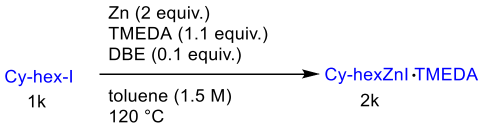
A flame dried Schlenk tube was evacuated and refilled with nitrogen. To this CyclobutaneZnBr·TMEDA (0.43 M in toluene, 1 mL) was added then the solvent was removed using slight vacuum, colourless crystals were obtained after few minutes (around 10-15 minutes).

7. Reaction profile

7.1. Iodides

Following the general procedure B, reaction profile was carried out for both alkyl (cyclohexyl) and aryl (phenyl) iodides with zinc (2 equiv., 7.65mmol), DBE (0.1 equiv., 0.382 mmol), alkyl/aryl iodide (1 equiv., 3.82 mmol), TMEDA (1.1 equiv., 4.21 mmol). Under the nitrogen flow, samples were taken periodically (see table: 8 and 9) and the formation of zinc reagent was confirmed by titration against iodine (Knochel's method)[2].

alkyl Iodide:



aryl Iodide:

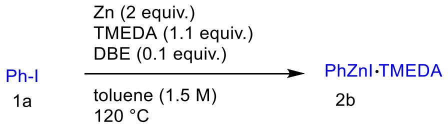


Table S8:

S.No.	Time	Molarity (M)
1	1 h	0.34
2	2 h	0.45
3	3 h	0.56
4	4 h	0.7
5	5 h	0.71
6	6 h	0.68

Table S9:

S.No.	Time	Molarity (M)
1	1 h	0.25
2	2 h	0.44
3	3 h	0.46
4	4 h	0.52
5	5 h	0.56
6	6 h	0.58

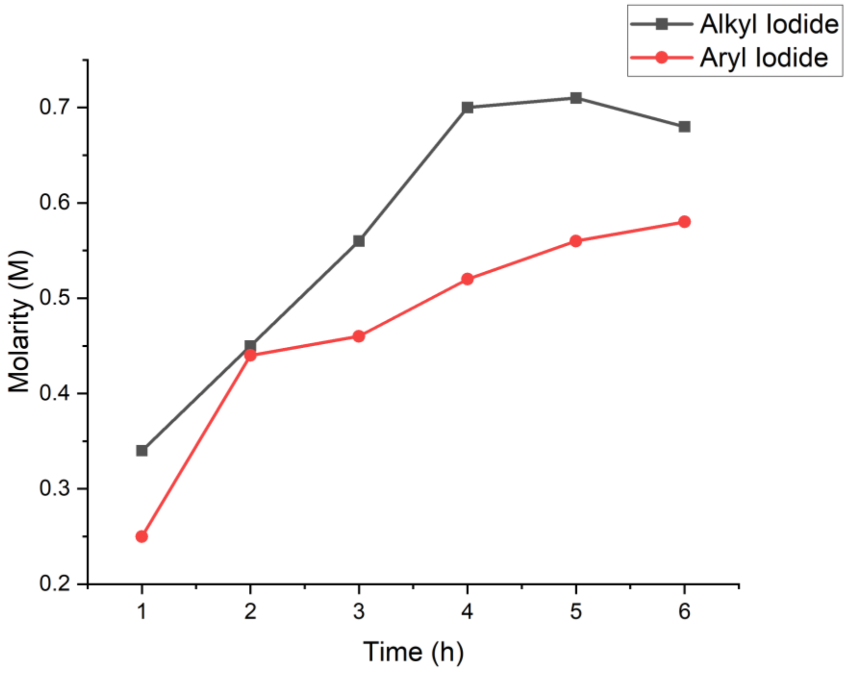
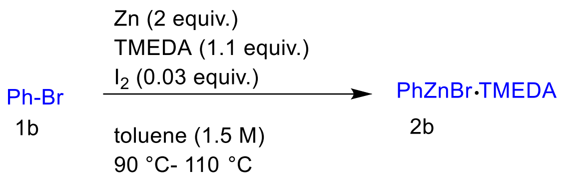


Figure S1h: Reaction profile of alkyl (cyclohexyl) and aryl (phenyl) iodide

7.2.Bromides

Following the general procedure A, reaction profile was carried out for both alkyl(cyclopropyl) and aryl(phenyl) bromides with zinc (2 equiv., 7.65mmol), iodine (0.03 equiv., 0.115 mmol), alkyl/ aryl bromide (1 equiv., 3.82 mmol), TMEDA (1.1 equiv., 4.21 mmol). Under nitrogen flow, samples were taken periodically (see table: S10 and S11) and the formation of zinc reagent was confirmed by titration against iodine (Knochel's method)[2].

aryl bromide:



alkyl bromide:

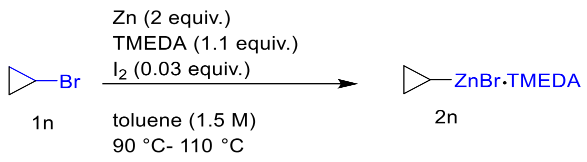


Table S10:

S.No.	Time	Molarity (M)
1	12 h	ND
2	24 h	0.09
3	36 h	0.2
4	48 h	0.31
5	60 h	0.44
6	70 h	0.55

Table S11:

S.No.	Time	Molarity (M)
1	12 h	0.13
2	24 h	0.22
3	36 h	0.31
4	48 h	0.57
5	60 h	0.65
6	70 h	0.78

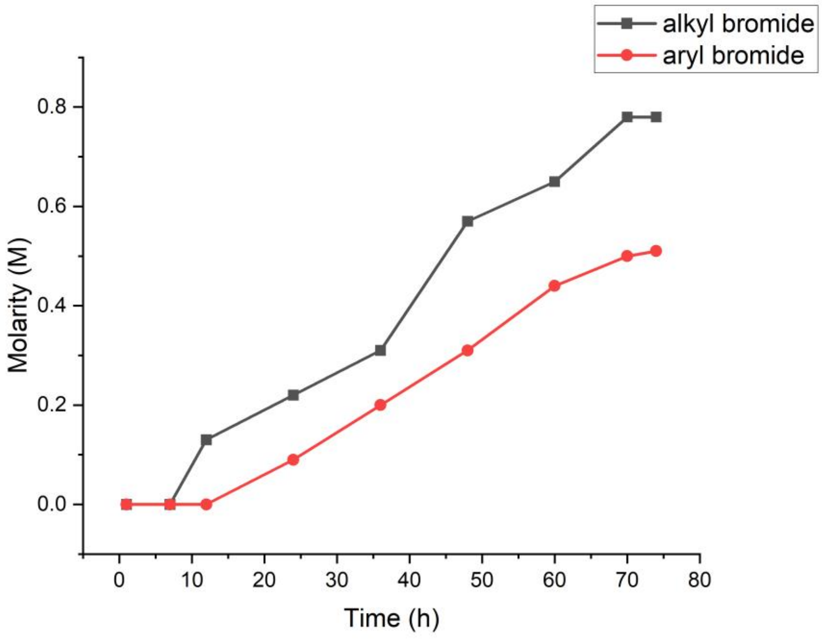


Figure S1i: Reaction profile of alkyl (cyclopropyl) and aryl (phenyl) bromide

8. Effect of temperature on the storage stability of organozinc reagent:

8.1.Storage stability of the reagent

The sample of solid organozinc reagents prepared were stored in a glovebox, at 4 °C, room temperature at two different locations (one is Stored in sealed vial and exposed to light and another is stored in sealed vial and covered with aluminium foil) to check whether it is light and bench stable. Also, the solid reagents were stored in a sealed vial at 4 °C for 6 months. The stability/reactivity of these reagents were analyzed through the alkylation reaction with (3-bromopropyl)benzene. $NiBr_2$·bpy (2.5 mol%, 0.00377 mmol, 1.41 mg), (3-bromopropyl)benzene (**3**, 1 equiv., 0.151 mmol, 30 mg) with PhZnBr·TMEDA **2a** (3 equiv., 153 mg, 0.452 mmol) by following the general procedure E gave 1,3-diphenylpropane **(4a)**. 1,3,5-trimethoxy benzene (27 mg, 0.16 mmol) was added as an internal standard and diluted with ethyl acetate. An aliquot was taken from the reaction tube and analyzed using GC-MS, see table S12.

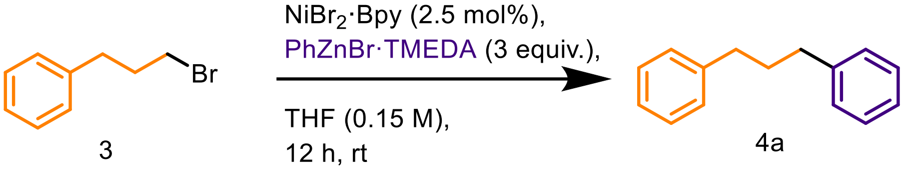


Table S12:

Condition (for month)	4a (Gc %Yield)
Stored at 4 °C	83
Stored at Glove Box	90
Stored in sealed vial and exposed to light	85
Stored in sealed vial and covered with aluminium foil	85
Stored at sealed vial 4 °C for 6 months	91

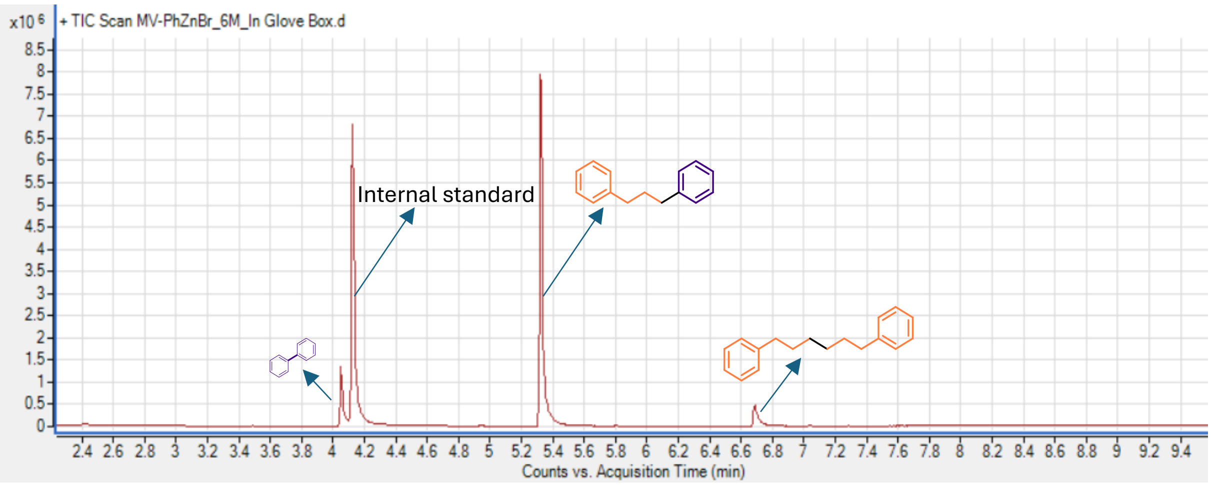


Figure S1j: standard reaction GC of reagent stored at sealed vial for 6 months

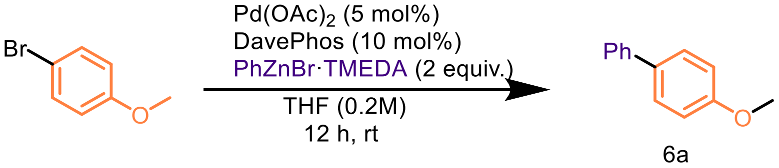
8.2.Thermal stability of the reagent

The sample of solid organozinc reagent prepared was evaluated by heating it at temperatures ranging from 40 to 80 °C for 30 min before adding catalyst and solvent. The stability of the reagent was analyzed through the alkylation reaction with (3-bromopropyl)benzene. $NiBr_2$·bpy (2.5 mol%, 0.00377 mmol, 1.41 mg), (3-bromopropyl)benzene (**3**, 1 equiv., 0.151 mmol, 30 mg) with PhZnBr·TMEDA **2a** (3 equiv., 153 mg, 0.452 mmol) by following the general procedure E. Complete consumption of the starting material was observed at its melting point (70 °C) upon melting. At 40, 50 and 80 °C, gives 45, 40 and 40% yield, see table S13.

Table S13:

PhZnBr·TMEDA in different temperature	4a (GC yield)
40 °C for 30 min	45
50 °C for 30 min	40
60 °C for 30 min	82
70 °C for 30 min	90
80 °C for 30 min	40

8.3.Open-air stability of the reagent



The sample of solid organozinc reagents prepared was evaluated by the reaction in open air using palladium catalyst[20]. To assess the influence of the reaction atmosphere, experiments were conducted in parallel under nitrogen and in air. Moreover, exposure of the PhZnBr·TMEDA reagent to air for 1 h prior to the reaction was also tested. The stability of the reagent was analysed through the arylation reaction with 1-iodo-4-methoxybenzene. $Pd(OAc)_2$ (5 mol%, 0.008 mmol, 1.8 mg), Davephos (10 mol%, 0.016 mmol, 6.31 mg), 1-bromo-4-methoxybenzene (1 equiv., 0.16 mmol, 30 mg) with PhZnBr·TMEDA (2 equiv., 109 mg, 0.321 mmol) in 0.2 M of THF (0.8 mL). Then the reaction was stirred for overnight. 1,3,5-trimethoxy benzene (27 mg, 0.16 mmol) was added as an internal standard and diluted with ethyl acetate. An aliquot was taken from the reaction tube and analyzed using GC-MS, see table S14.

Table S14:

Condition	6a (GC yield)
Under inert condition	94
open to air	95
Covered the opening with cotton	89
Reagent exposed to open air for 1 h	89
Reagent exposed to open air for 4 h	42
Reagent exposed to open air for 10 h	<5

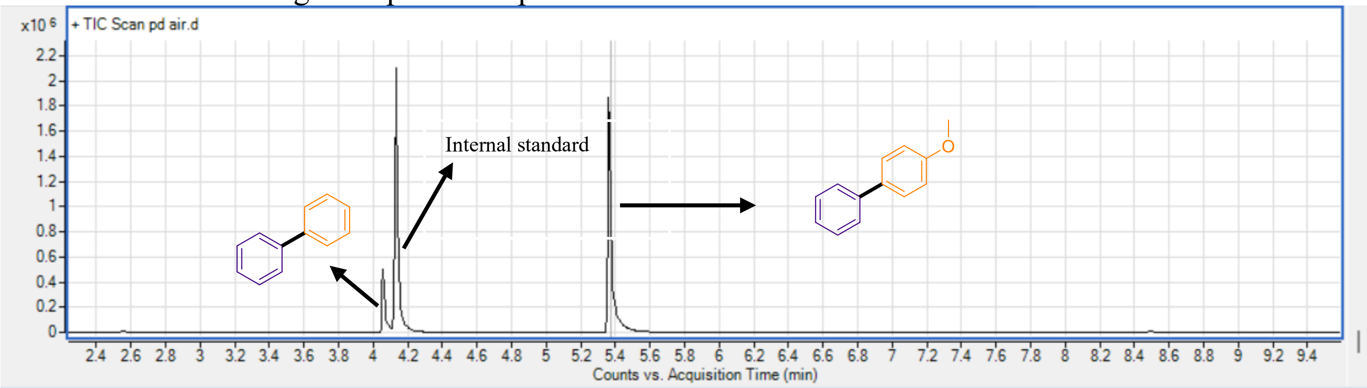


Figure S1k: Palladium catalyst reaction GC of reagent exposed to open air for 1 h

9. X-ray crystallography data

Table S15: Crystal data and structure refinement for PhZnI·TMEDA (2a)

CCDC number	**2513319**
Empirical formula	$C_{10}H_{17}IN_2Zn$
Formula weight	357.52
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	19.3518(8)
b [Å]	10.7938(4)
c [Å]	14.9233(6)
α [°]	90
β [°]	107.0290(10)
γ [°]	90
Volume [Å^3]	2980.5(2)
Z	8
ρ_{calc} [gcm^{-3}]	1.594
μ [mm^{-1}]	3.692
F(000)	1520
Crystal colour	clear colourless
Radiation	Mo K_α (λ=0.71073 Å)
2θ range [°]	4.40 to 56.54 (0.75 Å)

Index ranges	$-25 \le h \le 25$ $-14 \le k \le 12$ $-19 \le l \le 18$
Reflections collected	22049
Independent reflections	7266 $R_{\text{int}} = 0.0509$ $R_{\text{sigma}} = 0.0550$
Completeness to $\theta = 25.242°$	99.5
Data / Restraints / Parameters	7259 / 86 / 320
Goodness-of-fit on F^2	1.142
Final *R* indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0507$ $wR_2 = 0.1082$
Final *R* indexes [all data]	$R_1 = 0.0774$ $wR_2 = 0.1457$
Largest peak/hole [eÅ^{-3}]	2.72/−1.68

Table S16: Atomic coordinates and equivalent isotropic displacement parameters **PhZnI·TMEDA (2a).** U_{eq} [Å^2] is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	U_{eq}
I1	0.84770(2)	0.11480(4)	0.55735(3)	0.02086(12)
I2	0.62893(2)	0.10177(5)	0.15463(3)	0.02320(13)
Zn1	0.92927(4)	0.29445(8)	0.64834(5)	0.01618(18)
Zn2	0.55329(4)	0.28680(8)	0.18902(6)	0.02149(19)
N1	0.8986(3)	0.3234(6)	0.7723(4)	0.0188(12)
N2	0.8737(3)	0.4669(6)	0.6016(4)	0.0195(12)
N3	0.6114(5)	0.4509(9)	0.1760(6)	0.058(2)
N4	0.5910(4)	0.3226(7)	0.3353(5)	0.040(2)
C1	1.0371(4)	0.2907(6)	0.6555(5)	0.0157(13)
C2	1.0855(4)	0.3671(8)	0.7155(6)	0.0269(17)
H2	1.069274	0.424431	0.753307	0.032
C3	1.1586(4)	0.3611(8)	0.7214(6)	0.0310(18)
H3	1.192294	0.415000	0.762325	0.037
C4	1.1822(4)	0.2749(7)	0.6663(6)	0.0269(17)
H4	1.231900	0.269264	0.669633	0.032
C5	1.1325(4)	0.1994(7)	0.6078(5)	0.0217(15)
H5	1.147661	0.141432	0.569516	0.026
C6	1.0600(4)	0.2065(7)	0.6038(5)	0.0230(15)
H6	1.026207	0.151481	0.564210	0.028
C7	0.8420(4)	0.4204(8)	0.7461(5)	0.0270(17)

H7A	0.835946	0.458900	0.803567	0.032
H7B	0.795334	0.382110	0.711279	0.032
C8	0.8617(5)	0.5184(8)	0.6863(6)	0.0321(19)
H8A	0.822466	0.580589	0.668421	0.039
H8B	0.906188	0.561239	0.723288	0.039
C9	0.9197(5)	0.5482(8)	0.5642(7)	0.039(2)
H9A	0.926582	0.510914	0.507534	0.059
H9B	0.896407	0.629216	0.548786	0.059
H9C	0.966717	0.558495	0.611314	0.059
C10	0.9603(4)	0.3687(8)	0.8488(5)	0.0281(17)
H10A	0.980669	0.442436	0.827739	0.042
H10B	0.943907	0.389883	0.903094	0.042
H10C	0.997276	0.303932	0.866298	0.042
C11	0.8699(5)	0.2130(8)	0.8072(6)	0.0333(19)
H11A	0.828607	0.180474	0.757774	0.050
H11B	0.907686	0.149613	0.825060	0.050
H11C	0.854316	0.235564	0.861856	0.050
C12	0.8043(4)	0.4518(7)	0.5281(5)	0.0241(16)
H12A	0.813068	0.417232	0.471674	0.036
H12B	0.773133	0.395603	0.550334	0.036
H12C	0.780635	0.532650	0.513336	0.036
C13	0.4476(4)	0.2874(7)	0.1199(5)	0.0195(14)
C14	0.4209(4)	0.2086(6)	0.0441(5)	0.0218(15)
H14	0.452872	0.151102	0.028836	0.026
C15	0.3485(4)	0.2107(8)	−0.0107(6)	0.0295(17)
H15	0.331926	0.154813	−0.061622	0.035
C16	0.3015(4)	0.2941(7)	0.0096(5)	0.0220(15)
H16	0.252597	0.297335	−0.028202	0.026
C17	0.3260(4)	0.3738(8)	0.0858(5)	0.0271(17)
H17	0.293713	0.430468	0.101223	0.033
C18	0.3987(4)	0.3694(8)	0.1393(5)	0.0261(16)
H18	0.415064	0.424611	0.190768	0.031
C24	0.6376(5)	0.2250(8)	0.3906(6)	0.0341(19)
H24A	0.617109	0.143589	0.368783	0.051
H24B	0.686059	0.231547	0.382969	0.051
H24C	0.640630	0.235024	0.456935	0.051
C25	0.5261(8)	0.3046(18)	0.3776(12)	0.033(4)
H25A	0.487696	0.363702	0.348488	0.050
H25B	0.507458	0.219923	0.365208	0.050
H25C	0.542884	0.318851	0.445375	0.050
C26	0.6771(7)	0.4233(16)	0.1421(11)	0.023(3)
H26A	0.663169	0.366366	0.088671	0.034
H26B	0.695173	0.500687	0.122881	0.034

H26C	0.715137	0.385243	0.193032	0.034
C27	0.5615(7)	0.5069(15)	0.0779(11)	0.031(4)
H27A	0.560867	0.449120	0.026954	0.046
H27B	0.512198	0.518785	0.081406	0.046
H27C	0.581304	0.586621	0.065809	0.046
C28	0.6427(7)	0.4378(11)	0.3276(9)	0.018(3)
H28A	0.651792	0.487949	0.385419	0.022
H28B	0.689735	0.404153	0.325351	0.022
C29	0.6142(8)	0.5224(13)	0.2447(9)	0.030(3)
H29A	0.565691	0.554657	0.241792	0.036
H29B	0.647334	0.592801	0.246585	0.036
C29'	0.6566(8)	0.4649(17)	0.2895(9)	0.027(3)
H29C	0.699400	0.410197	0.301498	0.033
H29D	0.674953	0.550972	0.299109	0.033
C28'	0.6204(8)	0.4379(12)	0.3666(10)	0.021(3)
H28C	0.655976	0.433231	0.429558	0.025
H28D	0.582653	0.499666	0.367119	0.025
C27'	0.5693(8)	0.5664(13)	0.1776(11)	0.022(3)
H27D	0.533825	0.550840	0.211614	0.032
H27E	0.602274	0.632465	0.209122	0.032
H27F	0.544164	0.591796	0.113275	0.032
C26'	0.6626(10)	0.4595(19)	0.1309(14)	0.032(5)
H26D	0.687044	0.379423	0.133704	0.048
H26E	0.639851	0.482250	0.065339	0.048
H26F	0.697962	0.522919	0.161185	0.048
C25'	0.5341(8)	0.3751(16)	0.3624(11)	0.023(3)
H25D	0.494033	0.315787	0.350842	0.035
H25E	0.550705	0.395486	0.429280	0.035
H25F	0.517548	0.450623	0.326027	0.035

Table S17: Anisotropic displacement parameters (Å^2) for **PhZnI·TMEDA**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\,h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \dots + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	0.0203(2)	0.0232(2)	0.0188(2)	−0.00381(18)	0.00539(17)	−0.00442(18)
I2	0.0179(2)	0.0318(3)	0.0210(2)	0.00302(19)	0.00733(17)	0.00400(19)
Zn1	0.0120(4)	0.0209(4)	0.0150(4)	−0.0001(3)	0.0030(3)	0.0004(3)
Zn2	0.0116(4)	0.0232(4)	0.0275(4)	0.0058(3)	0.0023(3)	−0.0001(3)
N1	0.018(3)	0.023(3)	0.014(3)	−0.001(2)	0.003(2)	−0.001(2)
N2	0.014(3)	0.020(3)	0.020(3)	0.000(2)	−0.002(2)	0.002(2)
N3	0.057(3)	0.057(3)	0.060(3)	0.0014(10)	0.0171(12)	−0.0002(10)
N4	0.025(4)	0.037(4)	0.043(4)	−0.024(4)	−0.013(3)	0.010(3)
C1	0.0163(15)	0.0142(15)	0.0153(15)	0.0006(9)	0.0025(10)	0.0006(9)

C2	0.020(4)	0.030(4)	0.032(4)	−0.006(3)	0.009(3)	−0.001(3)
C3	0.015(4)	0.040(5)	0.036(4)	−0.006(4)	0.003(3)	−0.005(3)
C4	0.021(4)	0.022(4)	0.041(5)	−0.011(3)	0.013(3)	−0.002(3)
C5	0.017(3)	0.026(4)	0.022(4)	0.002(3)	0.006(3)	0.002(3)
C6	0.017(3)	0.032(4)	0.018(3)	0.006(3)	0.000(3)	0.001(3)
C7	0.025(4)	0.040(5)	0.016(3)	−0.007(3)	0.005(3)	0.008(3)
C8	0.039(5)	0.024(4)	0.026(4)	−0.005(3)	−0.001(3)	0.013(4)
C9	0.026(4)	0.031(5)	0.055(6)	0.020(4)	0.002(4)	−0.010(4)
C10	0.022(4)	0.042(5)	0.016(3)	−0.006(3)	0.001(3)	0.001(3)
C11	0.052(5)	0.031(5)	0.025(4)	0.001(3)	0.023(4)	−0.008(4)
C12	0.019(4)	0.024(4)	0.025(4)	−0.002(3)	0.000(3)	0.006(3)
C13	0.015(3)	0.023(4)	0.022(3)	0.007(3)	0.007(3)	0.002(3)
C14	0.020(3)	0.010(3)	0.035(4)	−0.007(3)	0.007(3)	−0.005(3)
C15	0.020(4)	0.028(4)	0.037(4)	−0.001(3)	0.004(3)	−0.008(3)
C16	0.016(3)	0.019(4)	0.033(4)	−0.003(3)	0.009(3)	−0.001(3)
C17	0.015(3)	0.039(5)	0.027(4)	0.001(3)	0.007(3)	0.003(3)
C18	0.019(4)	0.037(5)	0.023(4)	−0.005(3)	0.007(3)	0.003(3)
C24	0.042(5)	0.035(5)	0.023(4)	−0.004(3)	0.006(4)	0.003(4)
C25	0.033(4)	0.034(4)	0.032(4)	0.000(2)	0.009(2)	0.000(2)
C26	0.024(4)	0.022(4)	0.023(4)	0.0019(19)	0.006(2)	−0.0021(19)
C27	0.019(7)	0.025(8)	0.043(9)	0.021(7)	0.001(6)	−0.003(6)
C28	0.018(3)	0.018(3)	0.018(3)	−0.0009(10)	0.0049(12)	0.0005(10)
C29	0.024(7)	0.028(7)	0.036(7)	0.017(6)	0.006(6)	−0.006(6)
C29'	0.027(3)	0.027(3)	0.028(3)	−0.0002(10)	0.0081(13)	−0.0004(10)
C28'	0.021(3)	0.021(3)	0.021(3)	0.0003(10)	0.0061(13)	−0.0002(10)

Table S18: Bond lengths and angles for **PhZnI·TMEDA (2a)**

Atom–Atom	**Length [Å]**
I1–Zn1	2.6154(9)
I2–Zn2	2.6143(10)
Zn1–C1	2.058(7)
Zn1–N1	2.126(6)
Zn1–N2	2.161(6)
Zn2–C13	2.003(7)
Zn2–N4	2.125(7)
Zn2–N3	2.137(10)
N1–C11	1.471(10)
N1–C10	1.473(9)
N1–C7	1.483(10)
N2–C8	1.460(10)
N2–C9	1.472(10)
N2–C12	1.473(9)
N3–C29	1.272(14)

N3–C26'	1.353(14)
N3–C27'	1.494(13)
N3–C26	1.529(14)
N3–C27	1.616(13)
N3–C29'	1.670(14)
N4–C28'	1.391(13)
N4–C25'	1.400(13)
N4–C24	1.472(11)
N4–C25	1.573(14)
N4–C28	1.621(13)
C1–C6	1.349(10)
C1–C2	1.367(10)
C2–C3	1.394(11)
C3–C4	1.404(11)
C4–C5	1.363(11)
C5–C6	1.390(10)
C7–C8	1.504(12)
C13–C18	1.387(10)
C13–C14	1.389(10)
C14–C15	1.400(10)
C15–C16	1.374(11)
C16–C17	1.394(11)
C17–C18	1.400(10)
C28–C29	1.506(14)
C29'–C28'	1.541(15)

Atom–Atom–Atom	**Angle [°]**
C1–Zn1–N1	119.7(2)
C1–Zn1–N2	115.8(2)
N1–Zn1–N2	85.1(2)
C1–Zn1–I1	117.46(19)
N1–Zn1–I1	106.30(17)
N2–Zn1–I1	107.67(16)
C13–Zn2–N4	121.3(3)
C13–Zn2–N3	115.8(3)
N4–Zn2–N3	84.9(3)
C13–Zn2–I2	116.6(2)
N4–Zn2–I2	107.28(19)
N3–Zn2–I2	106.0(2)
C11–N1–C10	107.4(6)
C11–N1–C7	109.8(6)
C10–N1–C7	109.8(6)
C11–N1–Zn1	114.8(5)

C10–N1–Zn1	110.7(5)
C7–N1–Zn1	104.3(4)
C8–N2–C9	111.6(7)
C8–N2–C12	110.3(6)
C9–N2–C12	107.7(6)
C8–N2–Zn1	103.8(4)
C9–N2–Zn1	109.7(5)
C12–N2–Zn1	113.8(5)
C26'–N3–C27'	115.7(11)
C29–N3–C26	122.8(12)
C29–N3–C27	112.1(11)
C26–N3–C27	96.2(9)
C26'–N3–C29'	104.8(12)
C27'–N3–C29'	91.9(10)
C29–N3–Zn2	109.2(8)
C26'–N3–Zn2	125.7(10)
C27'–N3–Zn2	112.7(8)
C26–N3–Zn2	112.3(8)
C27–N3–Zn2	101.6(7)
C29'–N3–Zn2	96.7(7)
C28'–N4–C25'	79.6(10)
C28'–N4–C24	109.2(8)
C25'–N4–C24	122.2(10)
C24–N4–C25	96.7(9)
C24–N4–C28	107.4(7)
C25–N4–C28	134.8(10)
C28'–N4–Zn2	119.4(8)
C25'–N4–Zn2	107.9(7)
C24–N4–Zn2	114.6(5)
C25–N4–Zn2	108.4(7)
C28–N4–Zn2	95.7(6)
C6–C1–C2	120.3(7)
C6–C1–Zn1	118.8(5)
C2–C1–Zn1	120.8(5)
C1–C2–C3	120.1(7)

Table S19: Torsion angles for for **PhZnI·TMEDA (2a)**

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
C6–C1–C2–C3	2.1(12)
Zn1–C1–C2–C3	178.3(6)
C1–C2–C3–C4	−0.9(13)

C2–C3–C4–C5	0.4(13)
C3–C4–C5–C6	−0.9(12)
C2–C1–C6–C5	−2.6(11)
Zn1–C1–C6–C5	−178.9(5)
C4–C5–C6–C1	2.0(11)
C11–N1–C7–C8	−164.2(6)
C10–N1–C7–C8	77.9(7)
Zn1–N1–C7–C8	−40.7(7)
C9–N2–C8–C7	−157.1(7)
C12–N2–C8–C7	83.3(8)
Zn1–N2–C8–C7	−39.0(7)
N1–C7–C8–N2	57.3(8)
C18–C13–C14–C15	0.1(11)
Zn2–C13–C14–C15	−175.6(6)
C13–C14–C15–C16	0.7(12)
C14–C15–C16–C17	−1.5(12)
C15–C16–C17–C18	1.4(12)
C14–C13–C18–C17	−0.1(12)
Zn2–C13–C18–C17	175.4(6)
C16–C17–C18–C13	−0.6(12)
C24–N4–C28–C29	155.4(11)
C25–N4–C28–C29	−85.7(17)
Zn2–N4–C28–C29	37.4(12)
C26–N3–C29–C28	−82.9(14)
C27–N3–C29–C28	163.6(10)
Zn2–N3–C29–C28	51.8(12)
N4–C28–C29–N3	−64.1(15)
C26'–N3–C29'–C28'	−169.3(15)
C27'–N3–C29'–C28'	73.5(15)
Zn2–N3–C29'–C28'	−39.6(14)
C25'–N4–C28'–C29'	−139.1(12)
C24–N4–C28'–C29'	100.3(11)
Zn2–N4–C28'–C29'	−34.3(12)
N3–C29'–C28'–N4	50.1(16)

Table S20: Hydrogen bonds for **PhZnI·TMEDA (2a)**

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
C7–H7B···I2$^{\#1}$	0.99	3.09	3.952(8)	146.9
C11–H11A···I1	0.98	3.20	3.777(8)	119.4
C25^a–H25C^a···I2$^{\#1}$	0.98	3.20	4.154(17)	166.2
C26^a–H26A^a···I2	0.98	3.15	3.613(17)	110.3
C26'^b–H26D^b···I2	0.98	3.25	3.95(2)	129.9
C25'^b–H25E^b···I2$^{\#1}$	0.98	3.26	4.215(16)	165.4

Symmetry transformations used to generate equivalent atoms:
#1: +X, 0.5-Y, 0.5+Z;

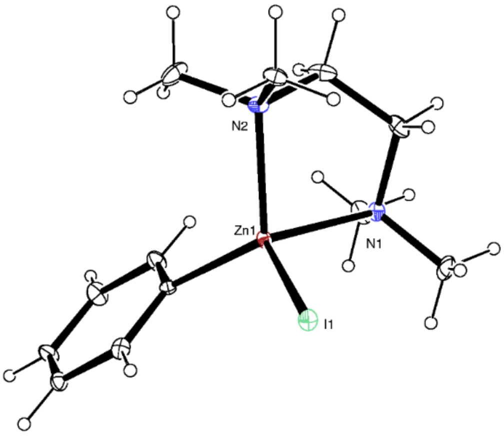


Figure S1l: OTREP diagram of **PhZnI·TMEDA (2a)**

Table S21: Crystal data and structure refinement for **CyclobutaneZnBr·TMEDA (2p)**

CCDC number	**2512822**
Empirical formula	$C_{10}H_{23}BrN_2Zn$
Formula weight	316.58
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	7.8878(3)
b [Å]	12.1726(4)
c [Å]	14.2124(6)
α [°]	90
β [°]	103.051(2)
γ [°]	90
Volume [Å^3]	1329.36(9)
Z	4
ρ_{calc} [gcm^{-3}]	1.582
μ [mm^{-1}]	4.823
F(000)	648
Crystal size [mm^3]	0.01×0.1×0.285
Crystal colour	clear colourless
Crystal shape	plate
Radiation	Mo K_α (λ=0.710
2θ range [°]	4.46 to 56.59 (0.
Index ranges	$-10 \leq h \leq 10$
	$-16 \leq k \leq 16$
	$-18 \leq l \leq 18$
Reflections collected	31874

Independent reflections	3308 $R_{\mathrm{int}} = 0.0401$ $R_{\mathrm{sigma}} = 0.0211$
Completeness to θ = 25.242°	100.0
Data / Restraints / Parameters	3308 / 0 / 131
Goodness-of-fit on F^2	0.745
Final *R* indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0296$ $wR_2 = 0.0835$
Final *R* indexes [all data]	$R_1 = 0.0398$ $wR_2 = 0.0945$
Largest peak/hole [eÅ^{-3}]	1.01/−0.43

Table S22: Atomic coordinates and equivalent isotropic displacement parameters **CyclobutaneZnBr·TMEDA (2p).** U_{eq} [Å^2] is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	***x***	***y***	***z***	***U*eq**
Br1	0.49137(4)	0.83844(2)	0.69634(2)	0.02688(10)
Zn1	0.65870(4)	0.66734(3)	0.72610(2)	0.02273(10)
N1	0.4753(3)	0.5537(2)	0.76254(17)	0.0246(5)
N2	0.7783(3)	0.66202(19)	0.87726(17)	0.0238(5)
C1	0.7993(4)	0.6255(2)	0.6294(2)	0.0248(6)
H1	0.889751	0.570731	0.659635	0.030
C2	0.8856(4)	0.7156(3)	0.5793(2)	0.0293(6)
H2A	1.011398	0.725616	0.607387	0.035
H2B	0.823364	0.786808	0.572325	0.035
C3	0.8450(4)	0.6435(3)	0.4866(2)	0.0304(6)
H3A	0.796242	0.684873	0.426655	0.036
H3B	0.942751	0.595931	0.478886	0.036
C4	0.7068(4)	0.5843(3)	0.5300(2)	0.0298(6)
H4A	0.587595	0.613833	0.507340	0.036
H4B	0.707907	0.503339	0.523429	0.036
C5	0.5099(4)	0.5553(3)	0.8692(2)	0.0296(6)
H5A	0.462957	0.487583	0.892370	0.036
H5B	0.449835	0.618961	0.890476	0.036
C6	0.7043(4)	0.5631(2)	0.9131(2)	0.0285(6)
H6A	0.724300	0.566467	0.984357	0.034
H6B	0.763349	0.496784	0.895908	0.034
C7	0.7403(4)	0.7613(3)	0.9294(2)	0.0302(6)
H7A	0.795261	0.754278	0.998176	0.045
H7B	0.614111	0.768906	0.921345	0.045
H7C	0.786282	0.826346	0.903000	0.045
C8	0.2904(4)	0.5797(3)	0.7212(3)	0.0333(7)
H8A	0.216439	0.524736	0.742637	0.050

H8B	0.268655	0.578962	0.650566	0.050
H8C	0.263416	0.652662	0.743111	0.050
C9	0.5128(4)	0.4434(2)	0.7285(2)	0.0300(6)
H9A	0.436918	0.389082	0.749217	0.045
H9B	0.634693	0.424470	0.755930	0.045
H9C	0.491472	0.443436	0.657861	0.045
C10	0.9693(4)	0.6494(3)	0.8926(2)	0.0303(6)
H10A	1.020247	0.639624	0.961607	0.045
H10B	1.018549	0.715173	0.869245	0.045
H10C	0.995476	0.584972	0.856971	0.045

Table S23: Anisotropic displacement parameters (Å^2) for **CyclobutaneZnBr·TMEDA (2p).** The anisotropic displacement factor exponent takes the form: $-2\pi^2[\,h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	0.03027(17)	0.01719(15)	0.02946(16)	0.00236(10)	−0.00106(12)	0.00256(10)
Zn1	0.02567(18)	0.02011(17)	0.02037(17)	0.00020(11)	0.00093(13)	0.00050(12)
N1	0.0228(12)	0.0212(11)	0.0271(12)	−0.0002(9)	−0.0005(9)	0.0004(9)
N2	0.0254(12)	0.0216(12)	0.0223(11)	−0.0007(8)	0.0009(9)	−0.0008(9)
C1	0.0196(13)	0.0197(13)	0.0355(15)	−0.0002(11)	0.0066(11)	0.0040(10)
C2	0.0252(14)	0.0272(15)	0.0323(15)	−0.0019(12)	0.0002(12)	−0.0024(11)
C3	0.0302(15)	0.0294(15)	0.0307(15)	0.0010(12)	0.0050(12)	−0.0032(12)
C4	0.0323(15)	0.0255(15)	0.0297(15)	0.0009(11)	0.0031(12)	−0.0040(12)
C5	0.0320(16)	0.0299(15)	0.0276(14)	−0.0016(11)	0.0083(12)	−0.0044(12)
C6	0.0365(16)	0.0266(14)	0.0206(13)	0.0029(11)	0.0022(11)	−0.0016(12)
C7	0.0345(16)	0.0275(15)	0.0260(14)	−0.0072(11)	0.0013(12)	0.0015(12)
C8	0.0223(14)	0.0308(16)	0.0438(18)	0.0020(13)	0.0014(12)	−0.0006(12)
C9	0.0322(15)	0.0218(14)	0.0323(15)	−0.0028(11)	−0.0008(12)	0.0014(11)
C10	0.0254(14)	0.0295(15)	0.0322(15)	−0.0024(12)	−0.0016(12)	0.0002(12)

Table S24: Bond lengths and angles for **CyclobutaneZnBr·TMEDA (2p).**

Atom–Atom	**Length [Å]**
Br1–Zn1	2.4509(4)
Zn1–C1	2.016(3)
Zn1–N2	2.143(2)
Zn1–N1	2.148(2)
N1–C8	1.479(4)
N1–C5	1.479(4)
N1–C9	1.480(4)
N2–C6	1.478(4)
N2–C10	1.481(4)
N2–C7	1.483(4)
C1–C4	1.521(4)
C1–C2	1.547(4)

C2–C3	1.554(4)
C3–C4	1.547(4)
C5–C6	1.522(4)

Atom–Atom–Atom	**Angle [°]**
C1–Zn1–N2	119.36(11)
C1–Zn1–N1	120.38(11)
N2–Zn1–N1	84.65(9)
C1–Zn1–Br1	117.04(8)
N2–Zn1–Br1	107.25(6)
N1–Zn1–Br1	102.90(7)
C8–N1–C5	109.9(2)
C8–N1–C9	108.4(2)
C5–N1–C9	110.1(2)
C8–N1–Zn1	115.09(19)
C5–N1–Zn1	105.09(17)
C9–N1–Zn1	108.11(18)
C6–N2–C10	109.4(2)
C6–N2–C7	110.6(2)
C10–N2–C7	109.0(2)
C6–N2–Zn1	104.56(17)
C10–N2–Zn1	110.68(19)
C7–N2–Zn1	112.52(18)
C4–C1–C2	88.6(2)
C4–C1–Zn1	119.6(2)
C2–C1–Zn1	120.1(2)
C1–C2–C3	87.8(2)
C4–C3–C2	87.4(2)
C1–C4–C3	89.0(2)
N1–C5–C6	110.9(2)
N2–C6–C5	110.4(2)

Table S25: Torsion angles for **CyclobutaneZnBr·TMEDA (2p).**

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
C4–C1–C2–C3	−20.2(2)
Zn1–C1–C2–C3	−144.0(2)
C1–C2–C3–C4	19.8(2)
C2–C1–C4–C3	20.3(2)
Zn1–C1–C4–C3	144.5(2)
C2–C3–C4–C1	−20.2(2)
C8–N1–C5–C6	−163.0(3)
C9–N1–C5–C6	77.6(3)
Zn1–N1–C5–C6	−38.6(3)
C10–N2–C6–C5	−160.9(2)
C7–N2–C6–C5	79.1(3)

Zn1–N2–C6–C5	−42.3(3)
N1–C5–C6–N2	57.4(3)

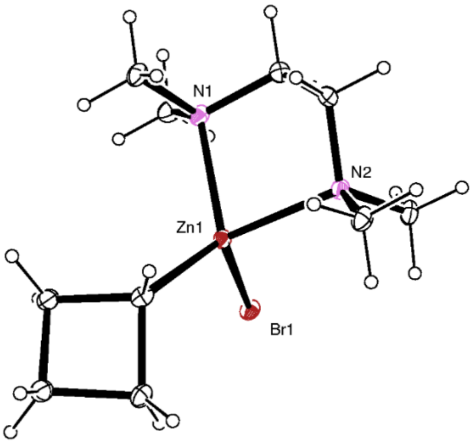


Figure S1m: OTREP diagram of **CyclobutaneZnBr·TMEDA (2p).**

10. References

[1] F. T. Pulikottil, R. Pilli, R. V. Suku, R. Rasappan, “Nickel-Catalyzed Cross-Coupling of Alkyl Carboxylic Acid Derivatives with Pyridinium Salts via C–N Bond Cleavage” *Org. Lett.* **2020**, *22*, 2902–2907.

[2] A. Krasovskiy, P. Knochel, “Convenient Titration Method for Organometallic Zinc, Magnesium, and Lanthanide Reagents” *Synthesis* **2006**, *2006*, 0890–0891.

[3] Z. Lu, Q. Zheng, S. Yang, C. Qian, Y. Shen, T. Tu, “NHC-Iridium-Catalyzed Deoxygenative Coupling of Primary Alcohols Producing Alkanes Directly: Synergistic Hydrogenation with Sodium Formate Generated in Situ” *ACS Catal.* **2021**, *11*, 10796–10801.

[4] P. Gao, J. Jiang, Y. Fukuzawa, S. Maeda, K. Kubota, H. Ito, “Direct arylation of alkyl fluorides using *in situ* mechanochemically generated calcium-based heavy Grignard reagents” *RSC Mechanochem.* **2024**, *1*, 486–491.

[5] D. J. Charboneau, H. Huang, E. L. Barth, A. P. Deziel, C. C. Germe, N. Hazari, X. Jia, S. Kim, S. Nahiyan, L. Birriel–Rodriguez, M. R. Uehling, “Homogeneous organic reductant based on 4,4′- Bu2-2,2′-bipyridine for cross-electrophile coupling” *Tetrahedron Letters* **2024**, *145*, 155159.

[6] B. K. Chi, J. K. Widness, M. M. Gilbert, D. C. Salgueiro, K. J. Garcia, D. J. Weix, "In-Situ Bromination Enables Formal Cross-Electrophile Coupling of Alcohols with Aryl and Alkenyl Halides" *ACS Catal.* **2022**, *12*, 580–586.

[7] N. R. Lee, R. T. H. Linstadt, D. J. Gloisten, F. Gallou, B. H. Lipshutz, "*B* -Alkyl sp^3 –sp^2 Suzuki–Miyaura Couplings under Mild Aqueous Micellar Conditions" *Org. Lett.* **2018**, *20*, 2902–2905.

[8] D. J. Charboneau, H. Huang, E. L. Barth, C. C. Germe, N. Hazari, B. Q. Mercado, M. R. Uehling, S. L. Zultanski, "Tunable and Practical Homogeneous Organic Reductants for Cross-Electrophile Coupling" *J. Am. Chem. Soc.* **2021**, *143*, 21024–21036.

[9] C. Wu, S. P. McCollom, Z. Zheng, J. Zhang, S.-C. Sha, M. Li, P. J. Walsh, N. C. Tomson, "Aryl Fluoride Activation through Palladium–Magnesium Bimetallic Cooperation: A Mechanistic and Computational Study" *ACS Catal.* **2020**, *10*, 7934–7944.

[10] D. Chen, C. Lepori, R. Guillot, R. Gil, S. Bezzenine, J. Hannedouche, "A Rationally Designed Iron(II) Catalyst for C(sp^3)−C(sp^2) and C(sp^3)−C(sp^3) Suzuki–Miyaura Cross-Coupling" *Angew Chem Int Ed* **2024**, *63*, e202408419.

[11] N. Sivendran, N. Pirkl, Z. Hu, A. Doppiu, L. J. Gooßen, "Halogen-Bridged Methylnaphthyl Palladium Dimers as Versatile Catalyst Precursors in Coupling Reactions" *Angew Chem Int Ed* **2021**, *60*, 25151–25160.

[12] G. Cahiez, V. Habiak, C. Duplais, A. Moyeux, "Iron-Catalyzed Alkylations of Aromatic Grignard Reagents" *Angew Chem Int Ed* **2007**, *46*, 4364–4366.

[13] L.-C. Liang, P.-S. Chien, J.-M. Lin, M.-H. Huang, Y.-L. Huang, J.-H. Liao, "Amido Pincer Complexes of Nickel(II): Synthesis, Structure, and Reactivity" *Organometallics* **2006**, *25*, 1399–1411.

[14] M. Espinal-Viguri, S. E. Neale, N. T. Coles, S. A. Macgregor, R. L. Webster, "Room Temperature Iron-Catalyzed Transfer Hydrogenation and Regioselective Deuteration of Carbon–Carbon Double Bonds" *J. Am. Chem. Soc.* **2019**, *141*, 572–582.

[15] N. Carrera, A. Salinas-Castillo, A. C. Albéniz, P. Espinet, R. Mallavia, "Fluorene-based stannylated polymers and their use as recyclable reagents in the Stille reaction" *Journal of Organometallic Chemistry* **2011**, *696*, 3316–3321.

[16] D. Gärtner, A. L. Stein, S. Grupe, J. Arp, A. Jacobi von Wangelin, "Iron-Catalyzed Cross-Coupling of Alkenyl Acetates" *Angew Chem Int Ed* **2015**, *54*, 10545–10549.

[17] D. Petzold, P. Singh, F. Almqvist, B. König, "Visible-Light-Mediated Synthesis of β-Chloro Ketones from Aryl Cyclopropanes" *Angew Chem Int Ed* **2019**, *58*, 8577–8580.

[18] N. H. Chan, J. J. Gair, M. Roy, Y. Qiu, D.-S. Wang, L. J. Durak, L. Chen, A. S. Filatov, J. C. Lewis, “Insight into the Scope and Mechanism for Transmetalation of Hydrocarbyl Ligands on Complexes Relevant to C–H Activation” *Organometallics* **2021**, *40*, 6–10.

[19] O. E. Okoromoba, T. Chen, E. S. Jang, C. L. McMullin, T. R. Cundari, T. H. Warren, “Copper-Catalyzed C(sp^3)−H α-Acetylation: Generation of Quaternary Centers” *Angew Chem Int Ed* **2025**, *64*, e202418692.

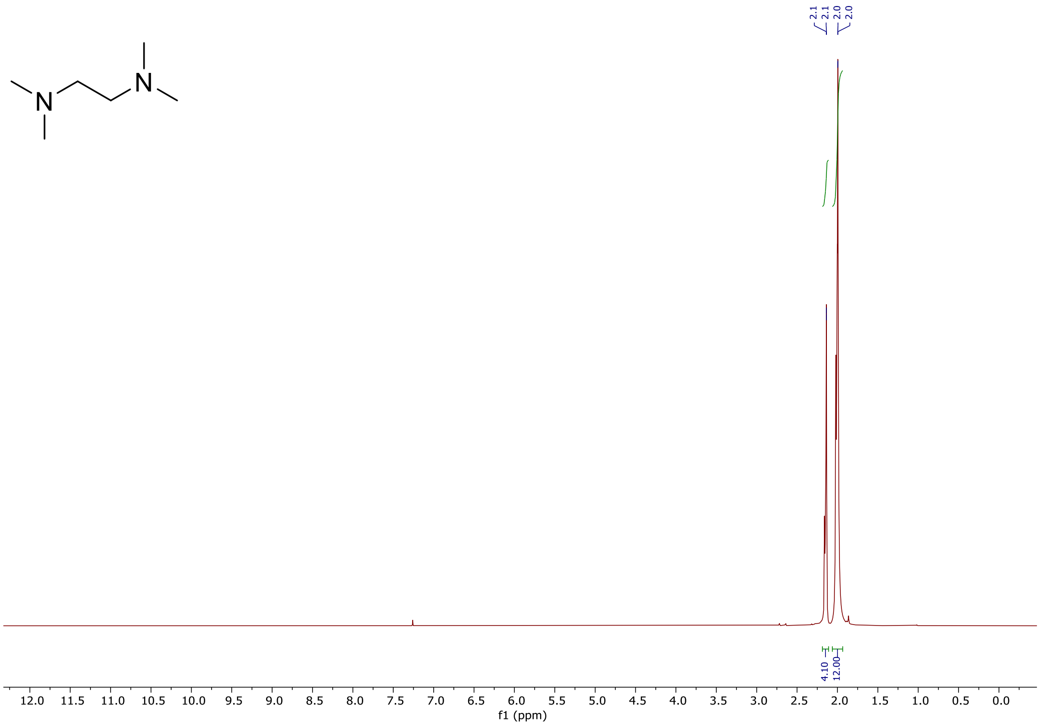
[20] A. Hernán-Gómez, E. Herd, E. Hevia, A. R. Kennedy, P. Knochel, K. Koszinowski, S. M. Manolikakes, R. E. Mulvey, C. Schnegelsberg, “Organozinc Pivalate Reagents: Segregation, Solubility, Stabilization, and Structural Insights” *Angewandte Chemie* **2014**, *126*, 2744–2748.

[21] D. E. Anderson, L. A. Malaspina, S. Grabowsky, E. Hevia, “Synthesis and Structure of Neopentyl Sodium: A Hydrocarbon-Soluble Reagent for Controlled Sodiation of Non-Activated Substrates” Angew Chem Int Ed **2025**, 64, e202511492.

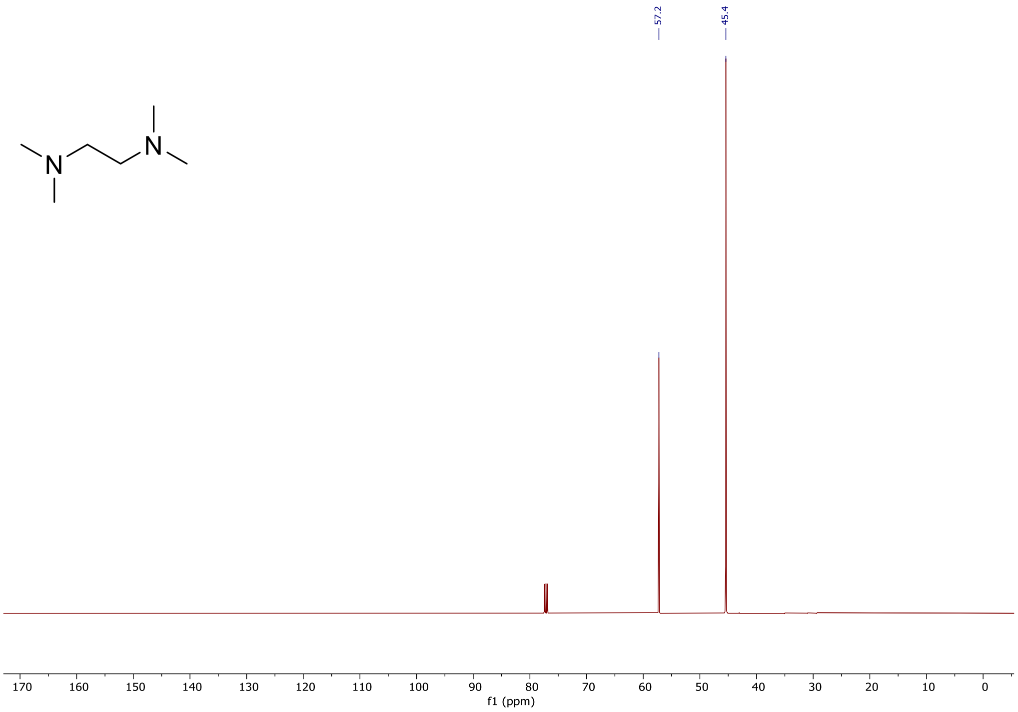
11. NMR data:

Based on comparison with the spectral data of TMEDA and $ZnBr_2$·TMEDA, the signals corresponding to uncomplexed or partially dissociated TMEDA were assigned in the reagent spectra.

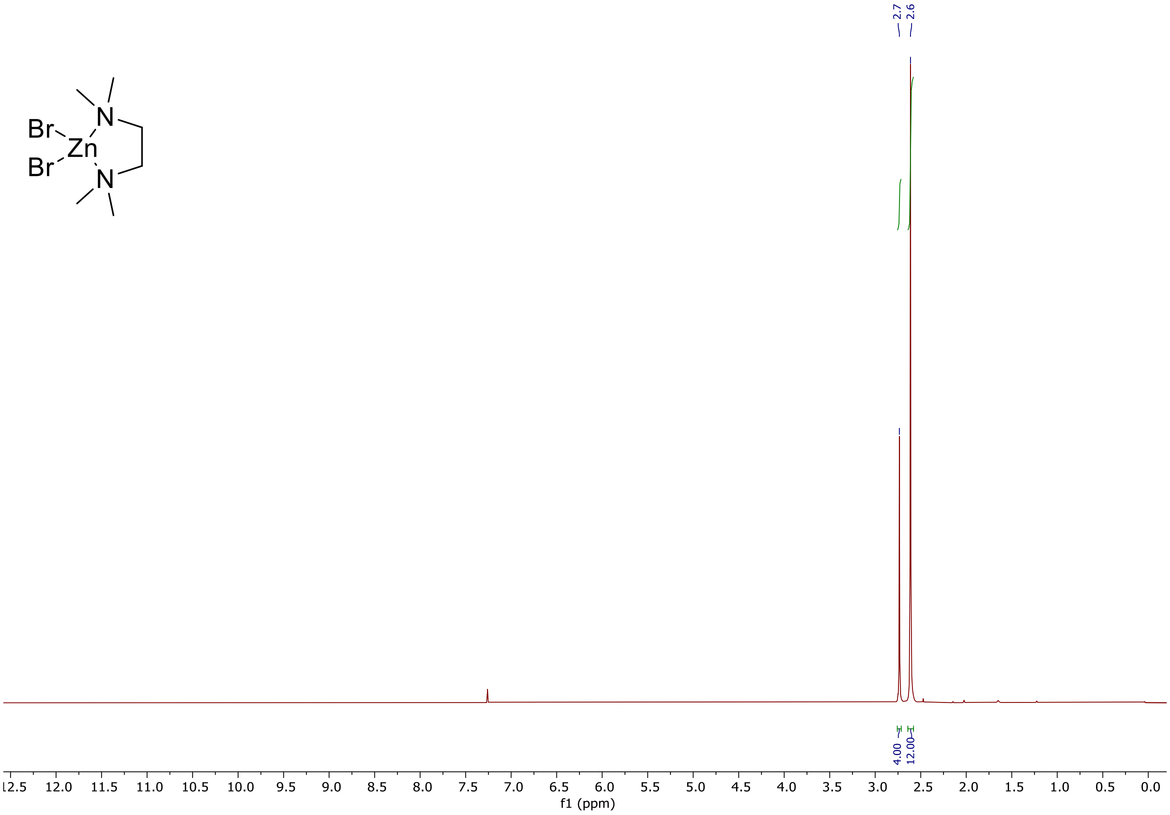
^{1}H NMR of TMEDA:



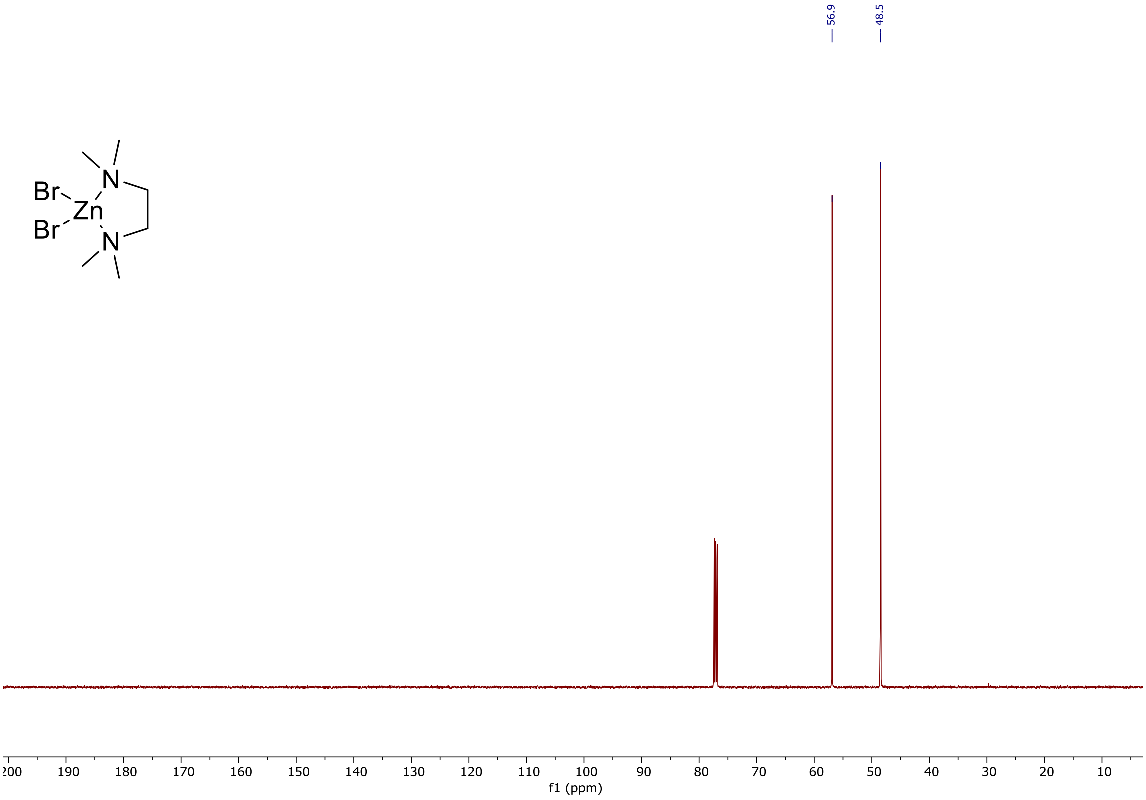
^{13}C NMR of TMEDA:



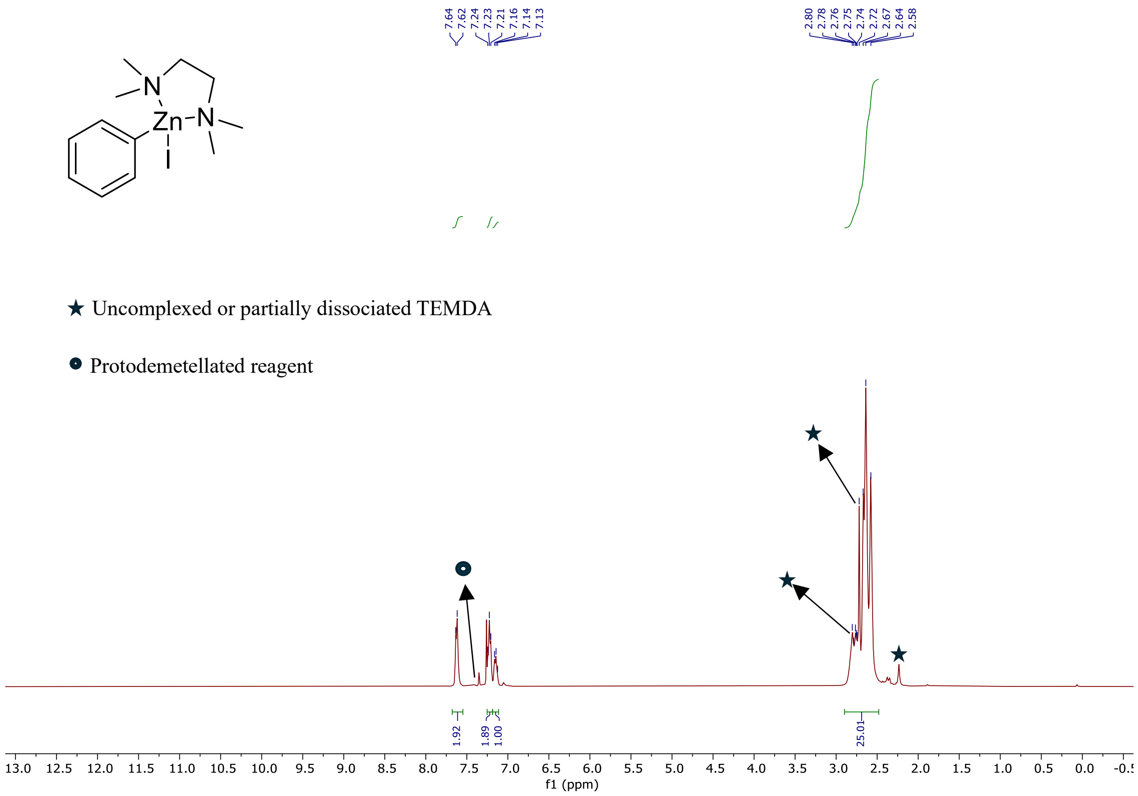
^{1}H NMR of $ZnBr_2 \cdot TMEDA$:



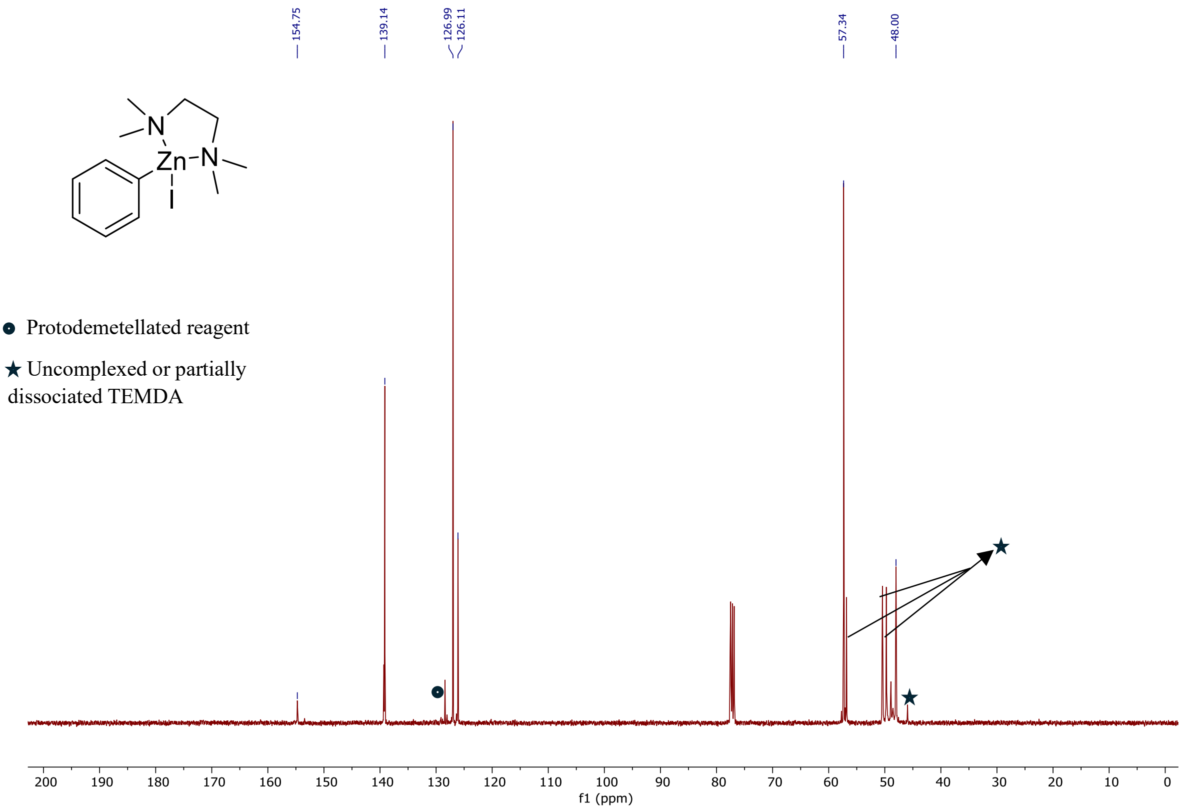
^{13}C NMR of $ZnBr_2 \cdot TMEDA$:



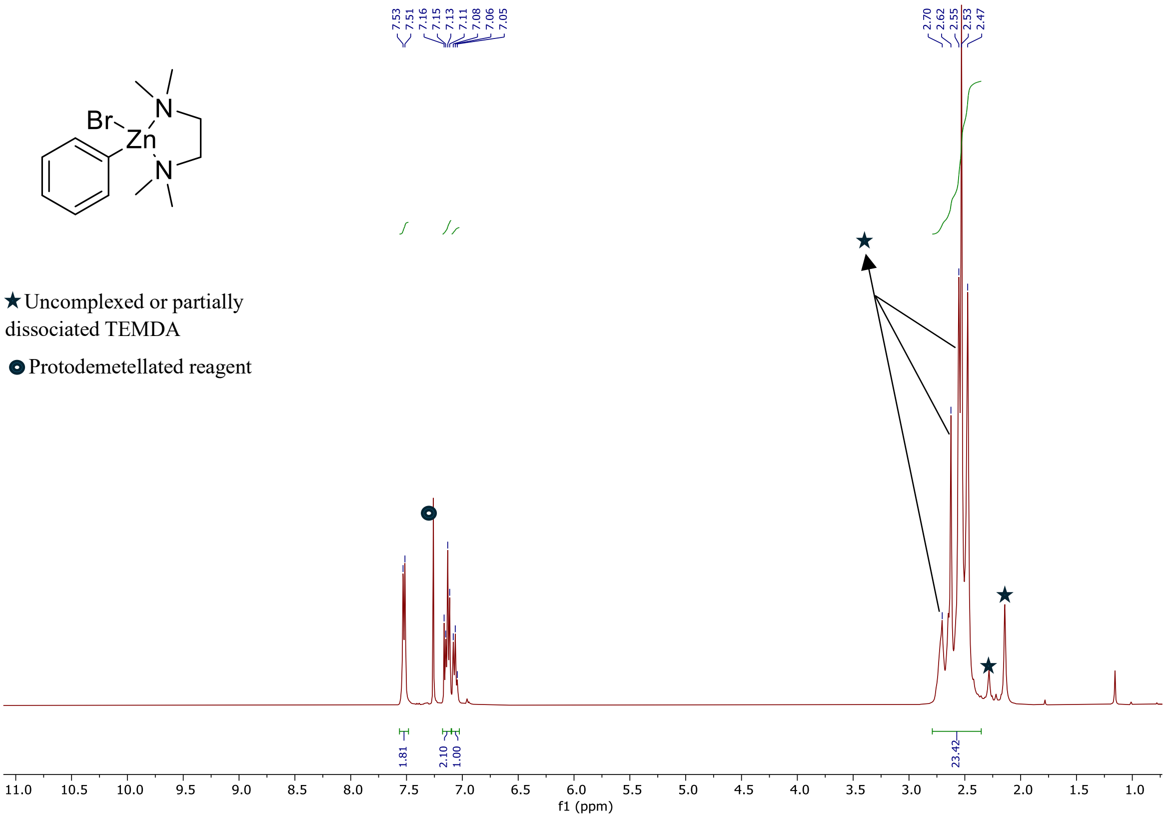
^{1}H NMR of PhZnI·TMEDA (2a)



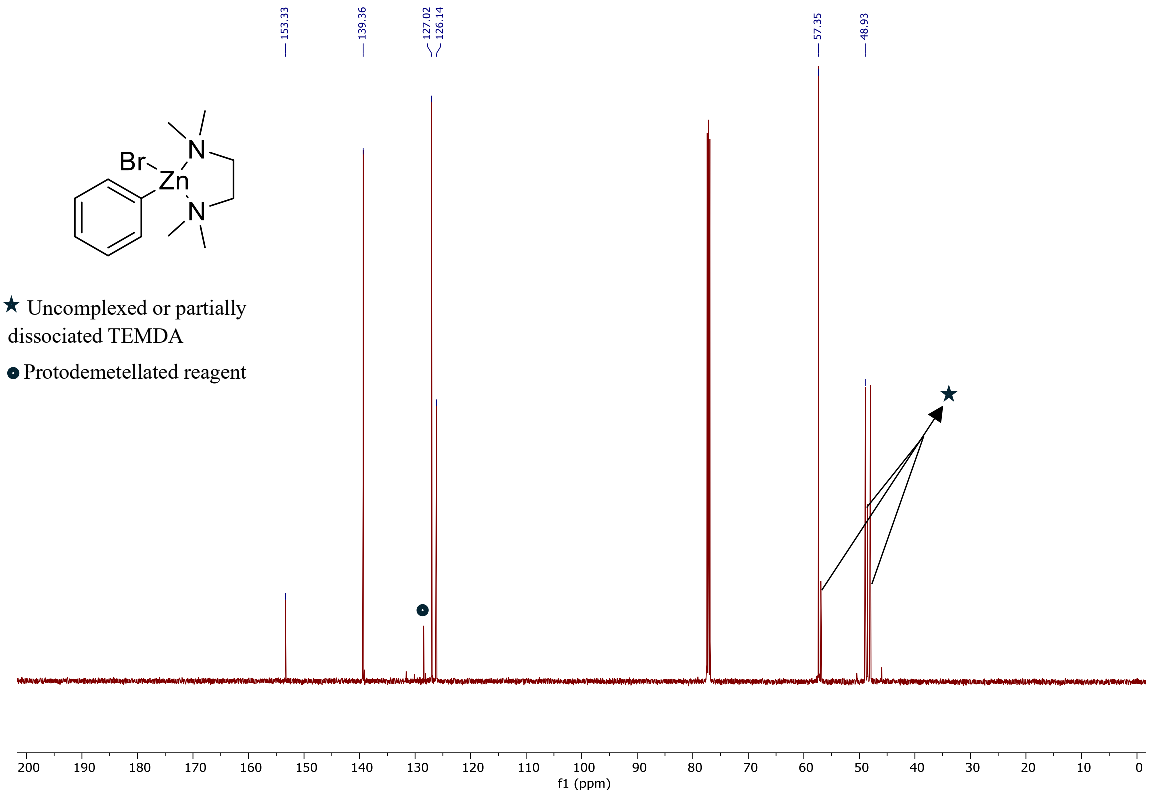
^{13}C NMR of 2a



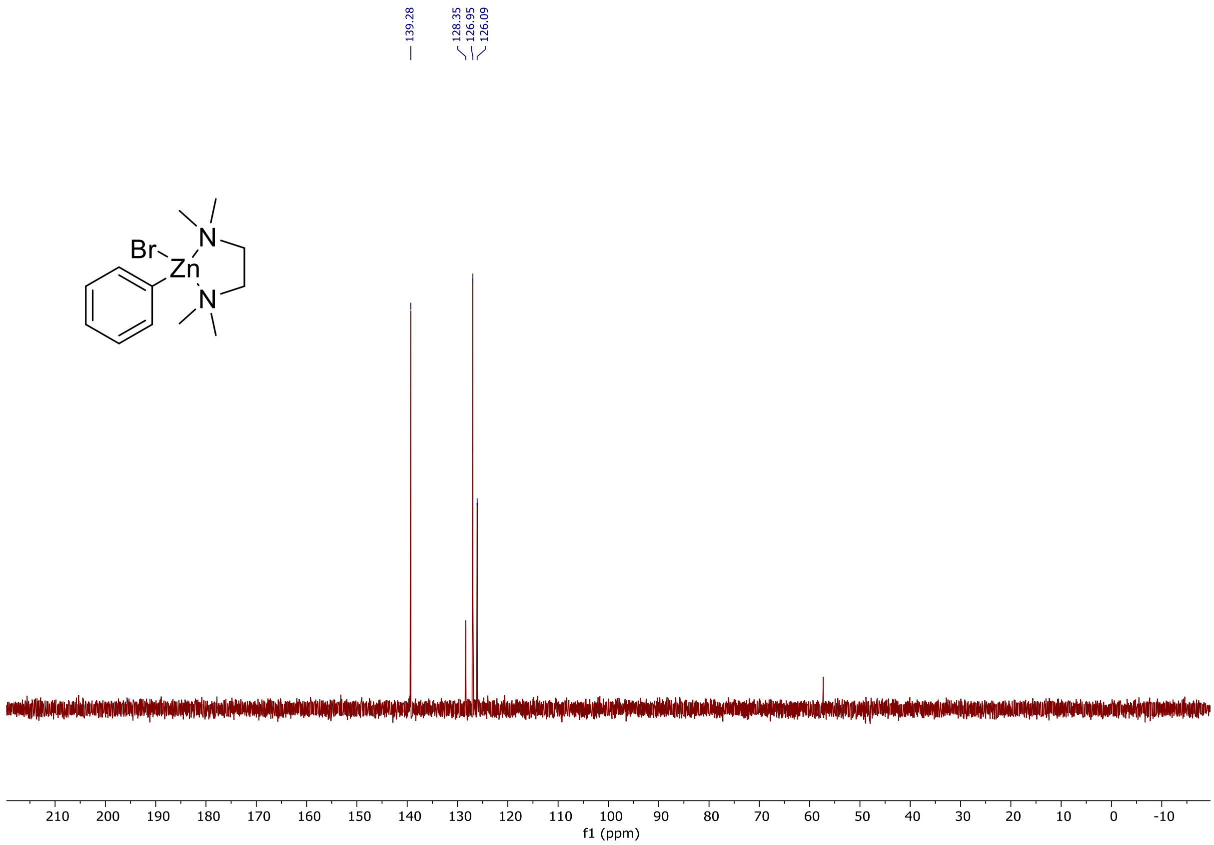
^{1}H NMR of PhZnBr·TMEDA (2b)



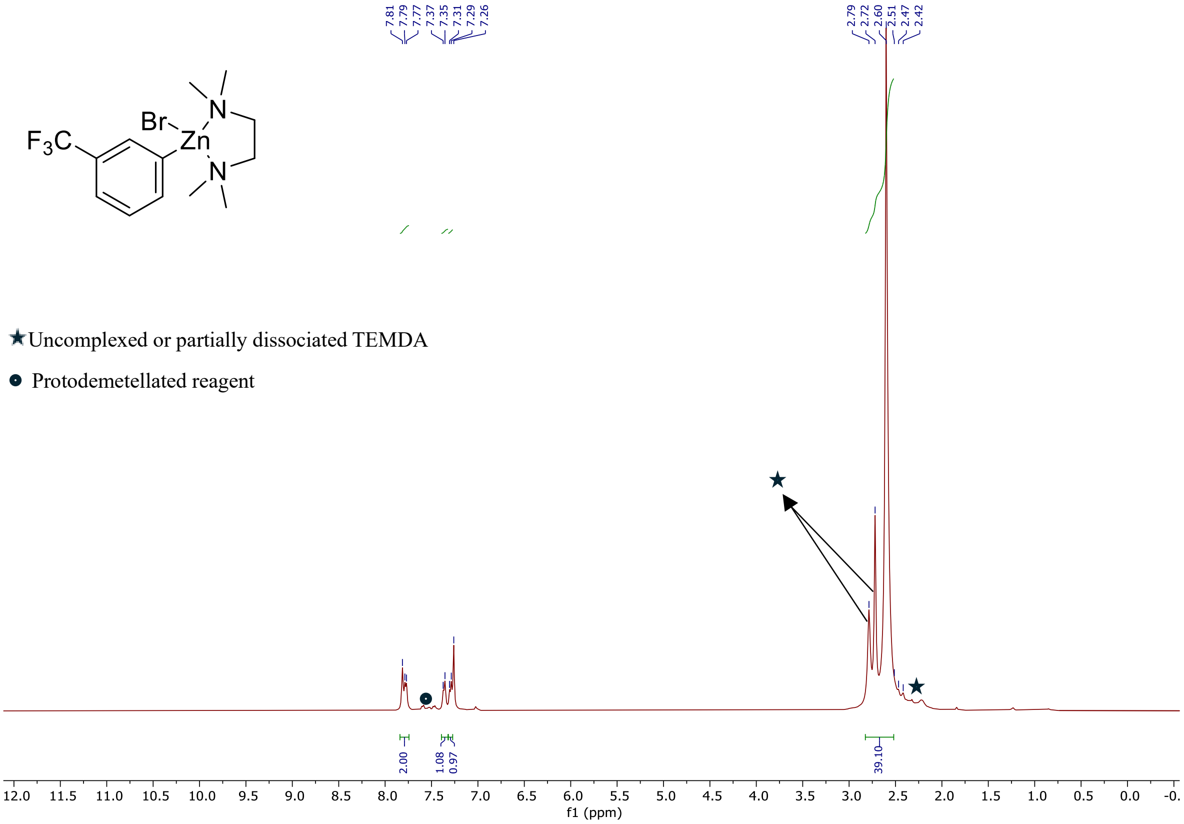
^{13}C NMR of 2b



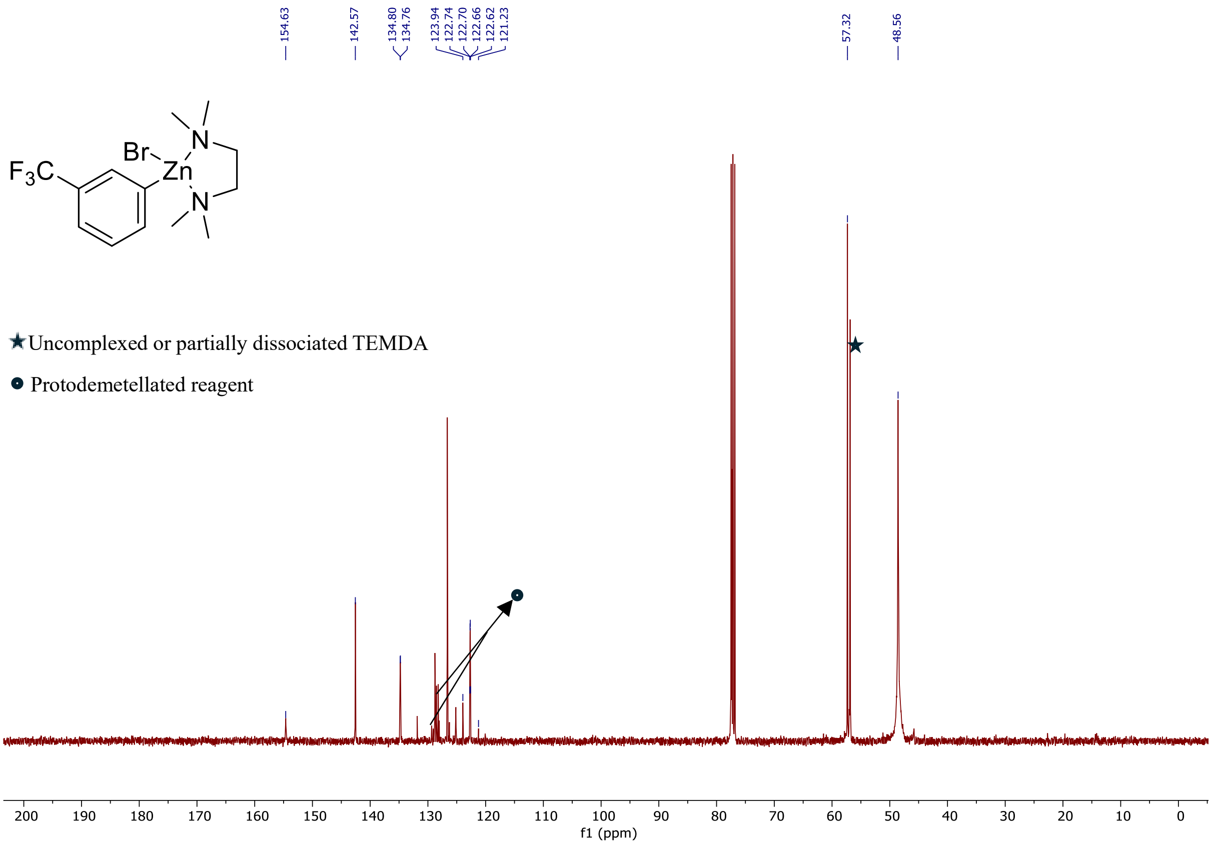
DEPT 90 of 2b (CH only)



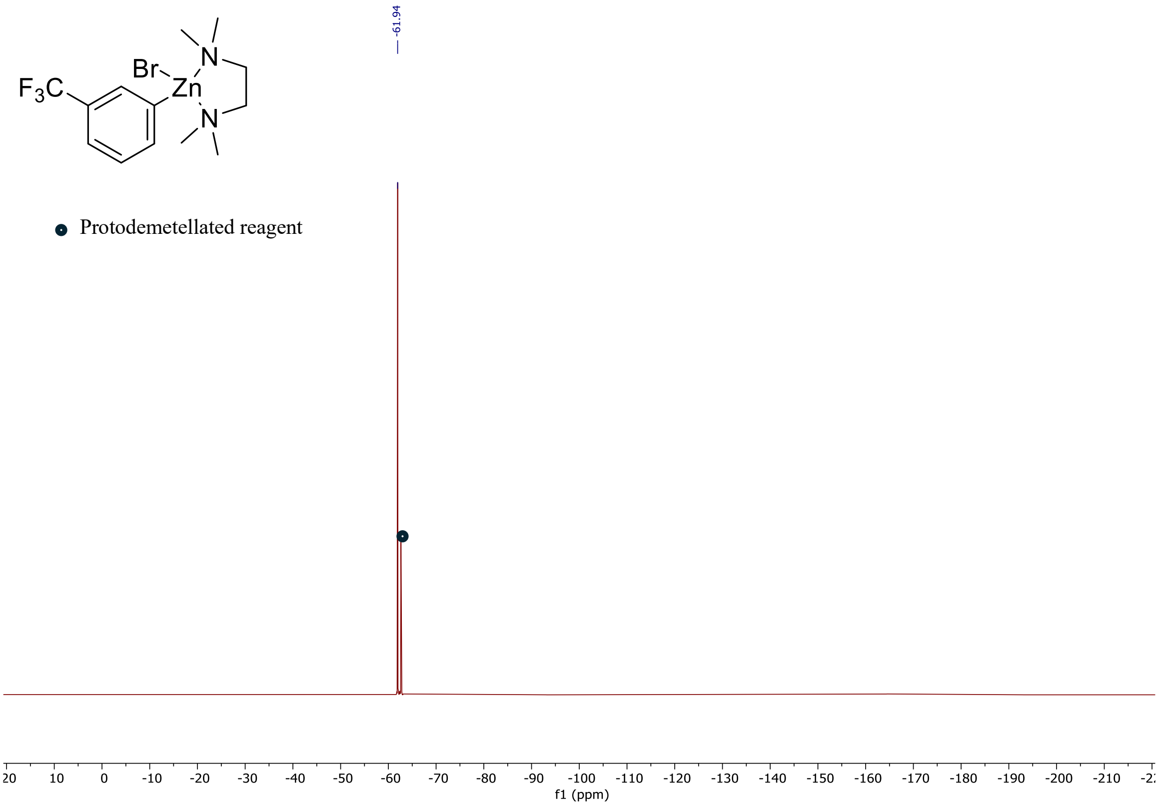
^{1}H NMR of m-CF_3PhZnBr·TMEDA (2c)



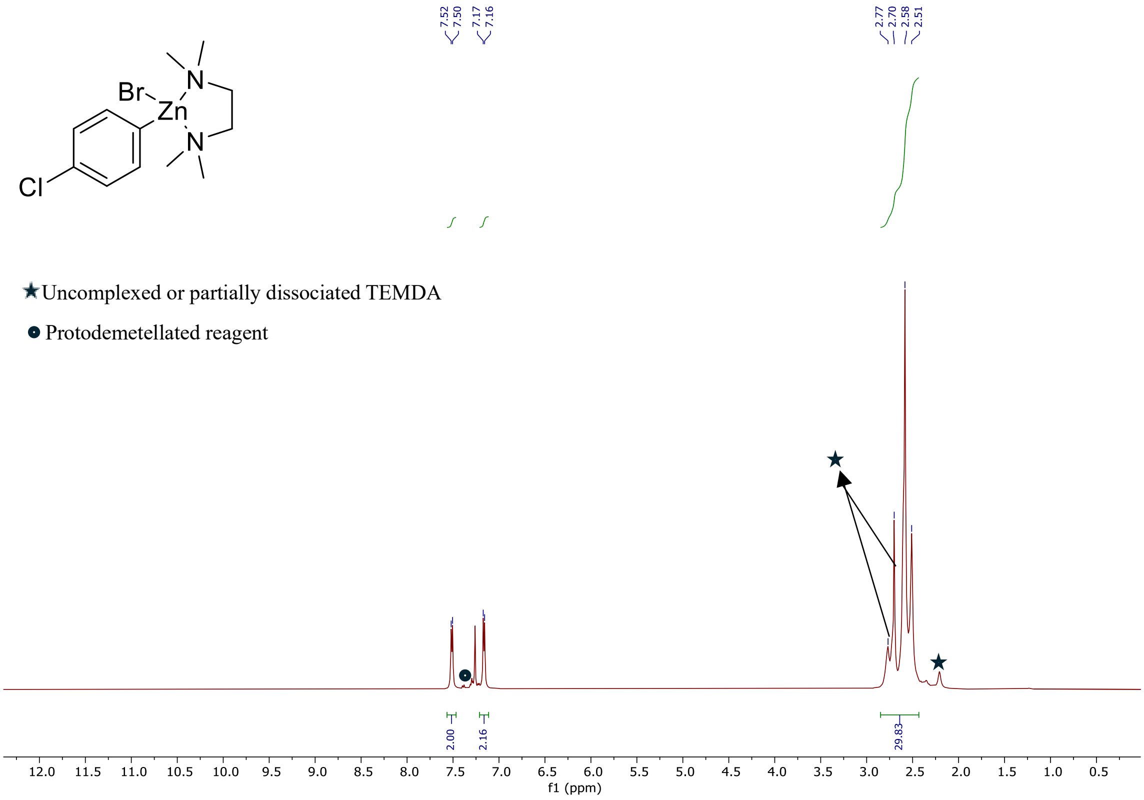
^{13}C NMR of 2c



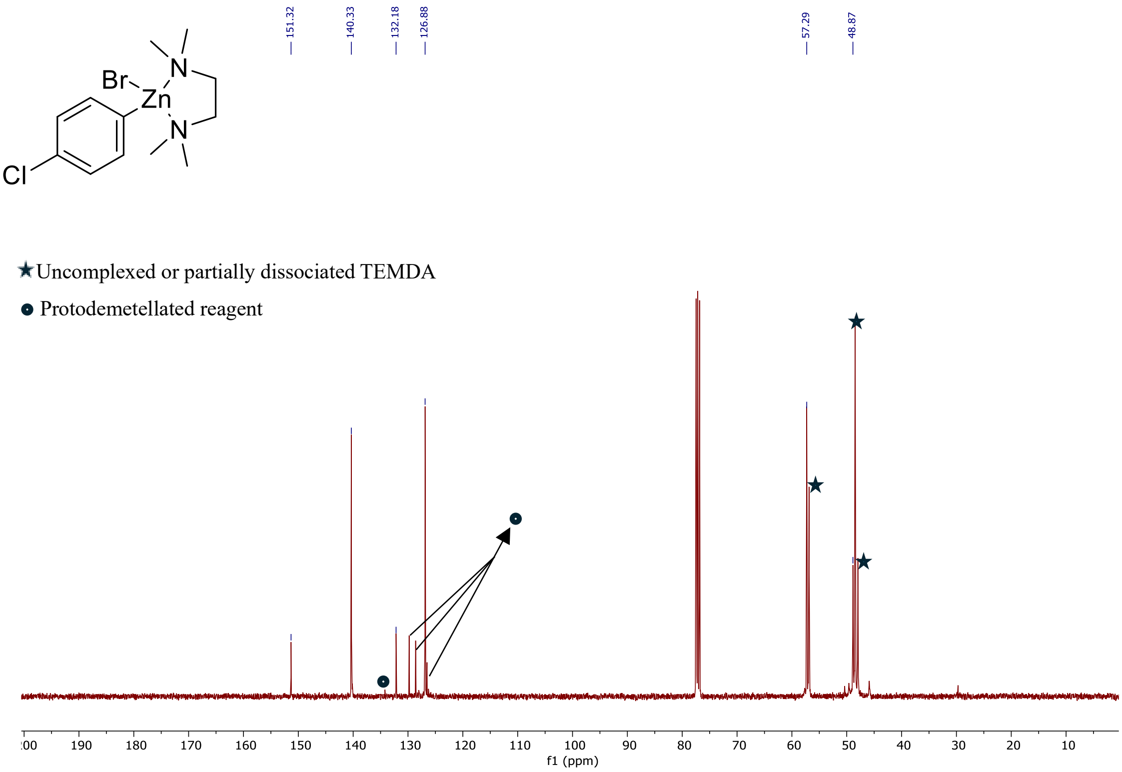
^{19}F NMR of 2c



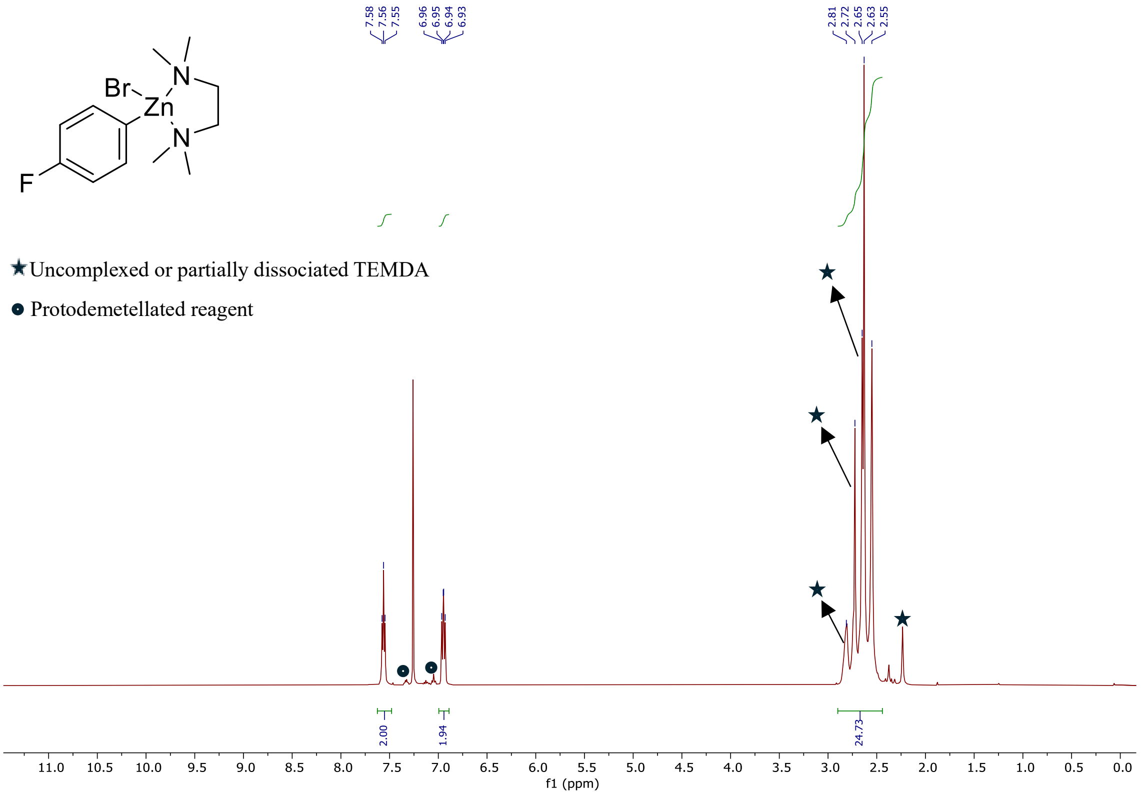
^{1}H NMR of p-ClPhZnBr·TMEDA (2d)



^{13}C NMR of 2d



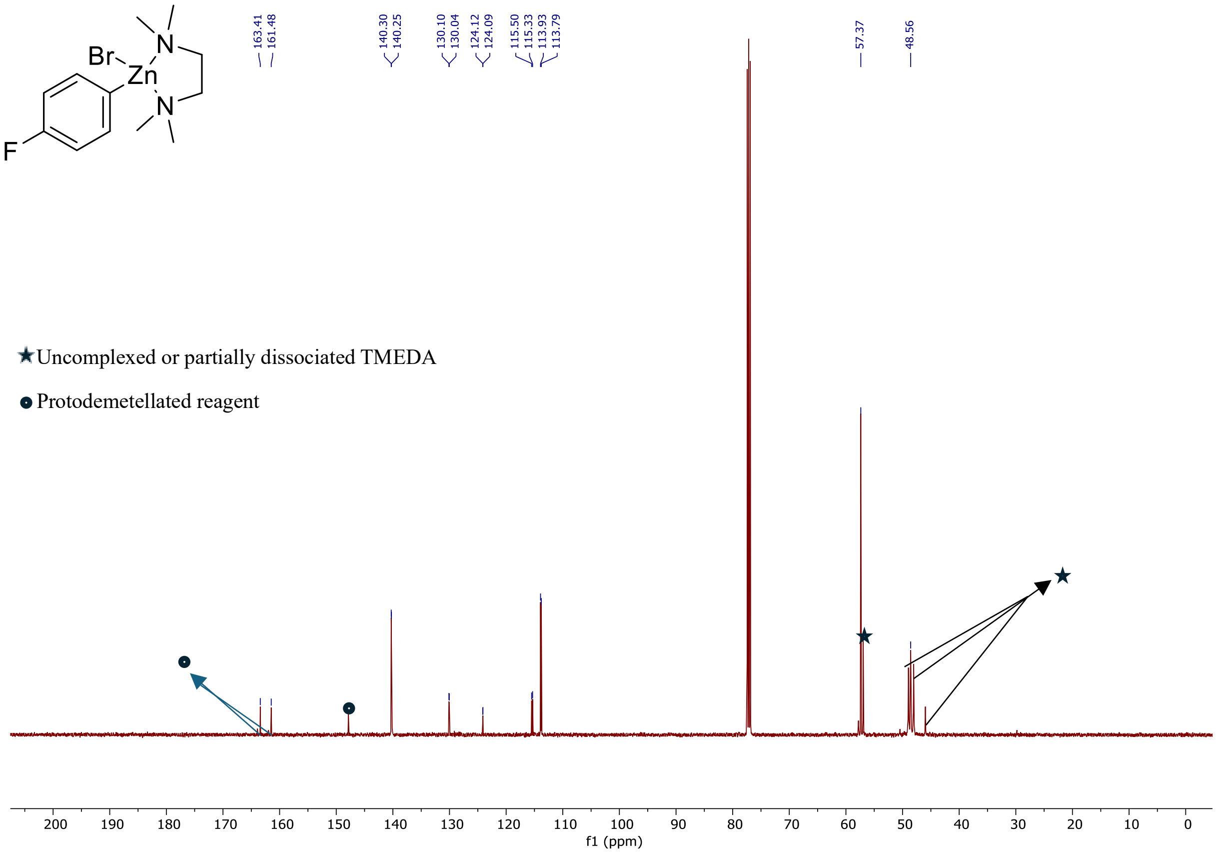
^{1}H NMR of p-FPhZnBr·TMEDA (2e)



★Uncomplexed or partially dissociated TEMDA

● Protodemetellated reagent

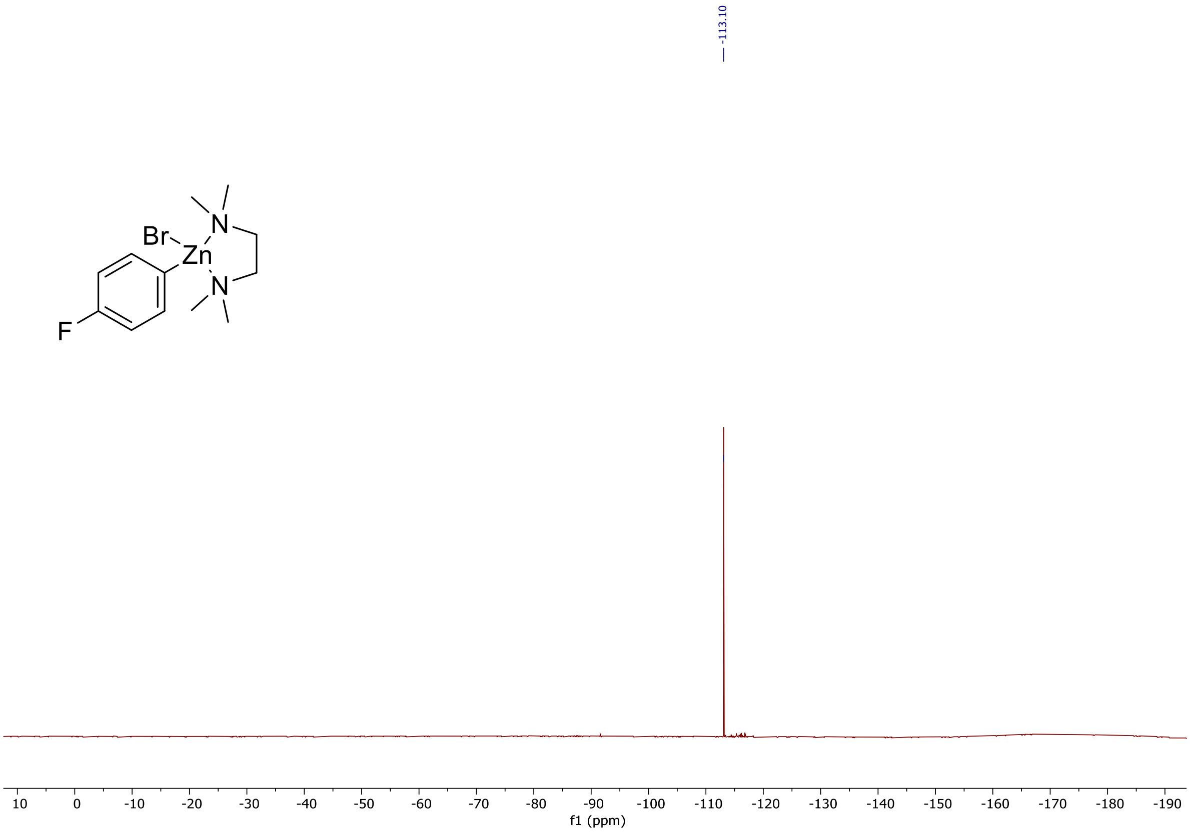
^{13}C NMR of 2e



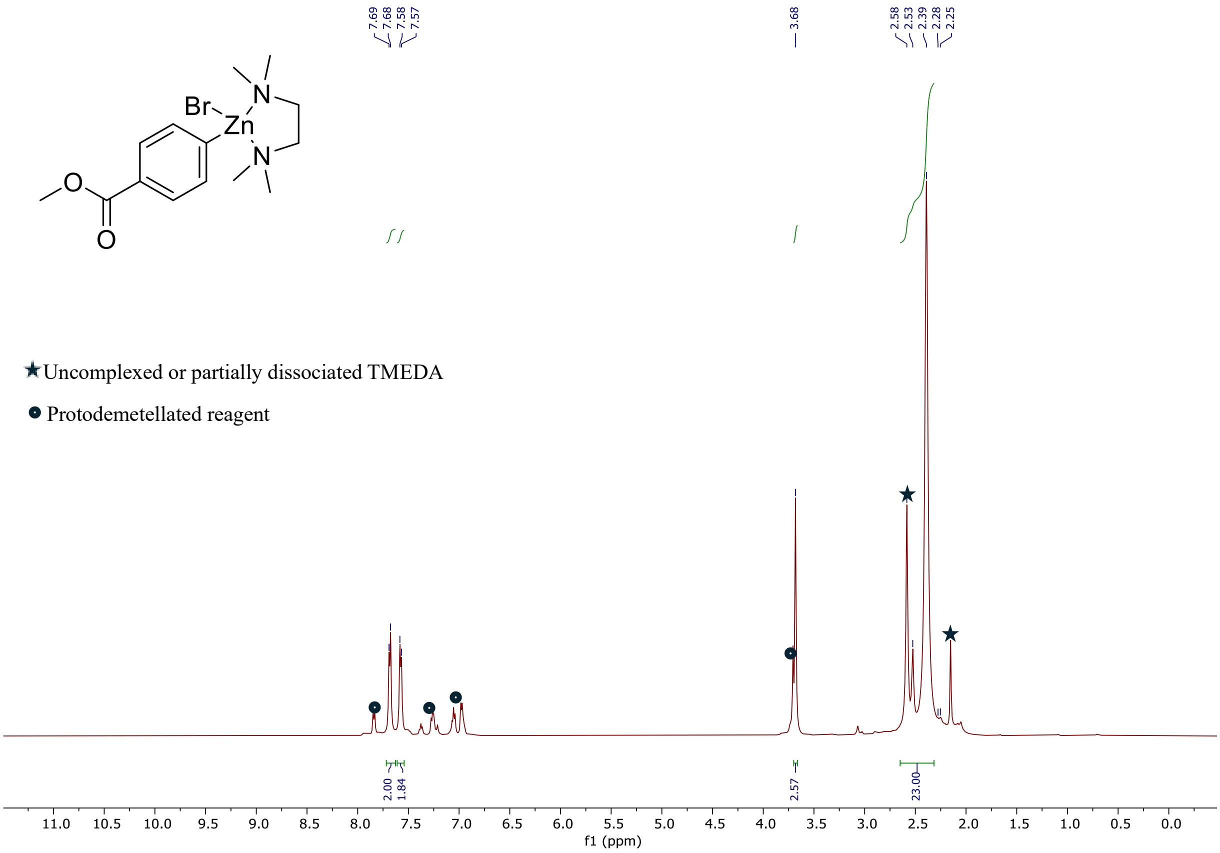
★Uncomplexed or partially dissociated TMEDA

● Protodemetellated reagent

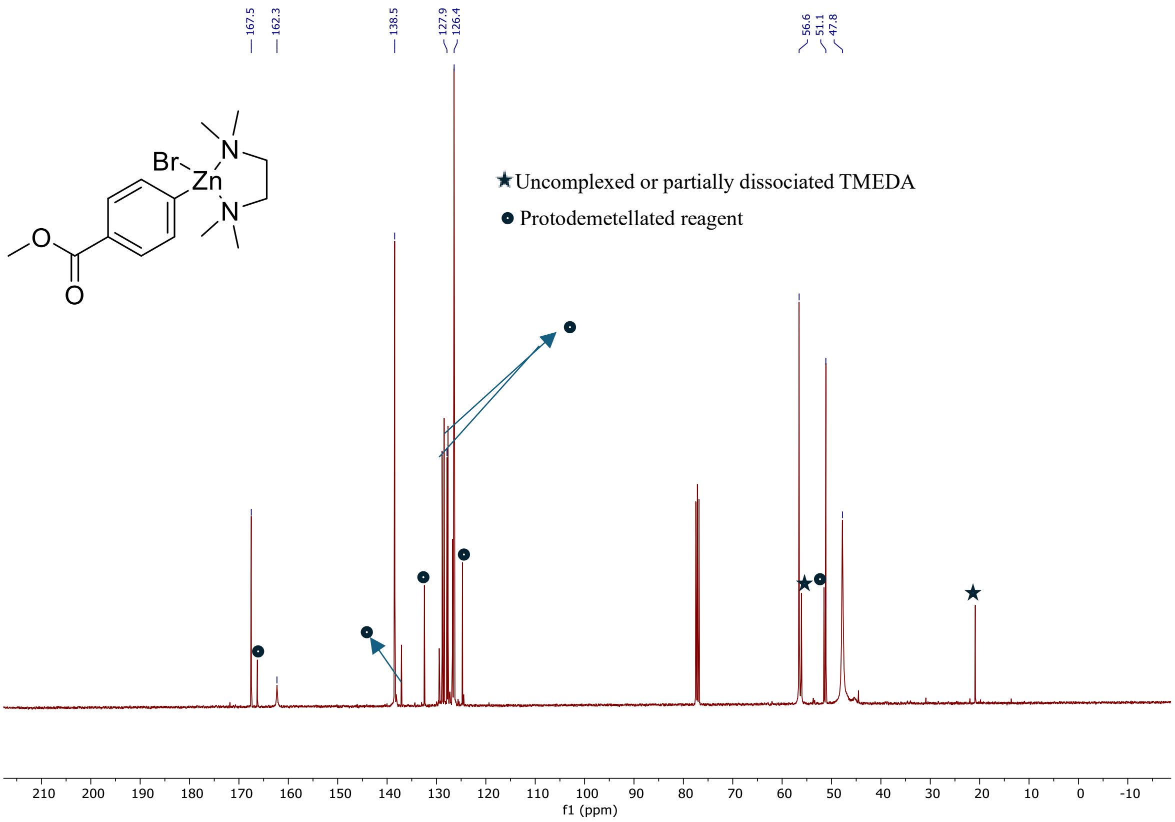
^{19}F NMR of 2e



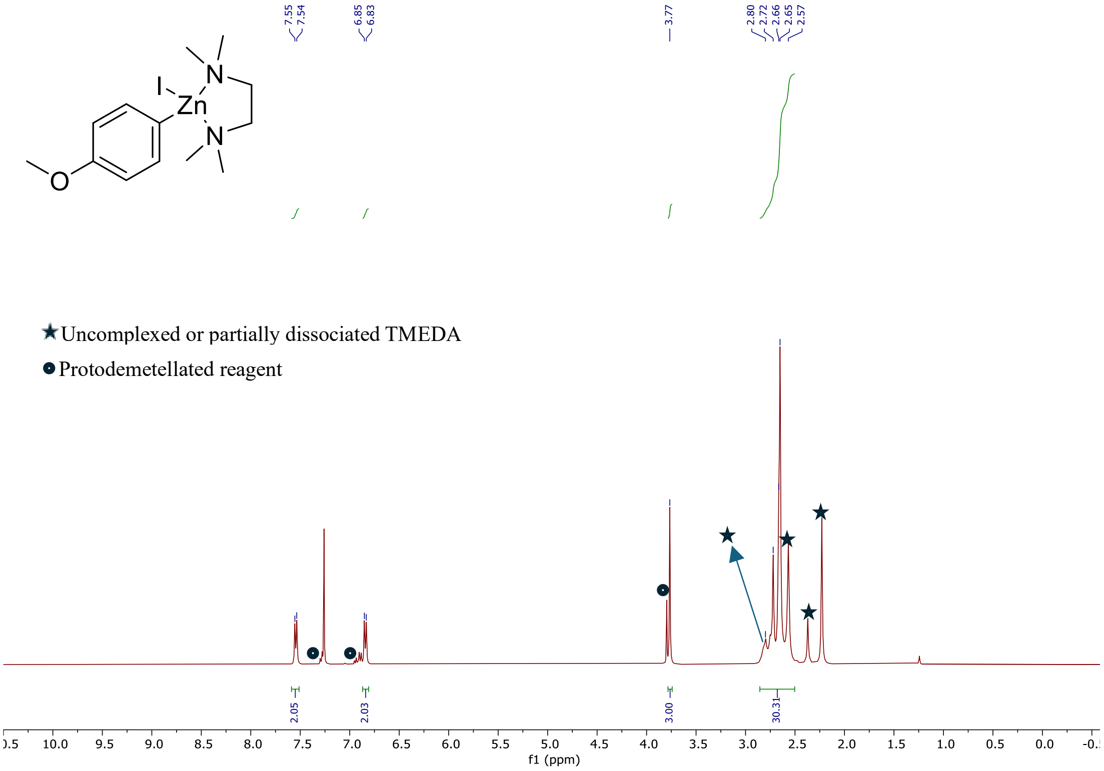
^{1}H NMR of p-CO$_2$Me-PhZnBr·TMEDA (2f)



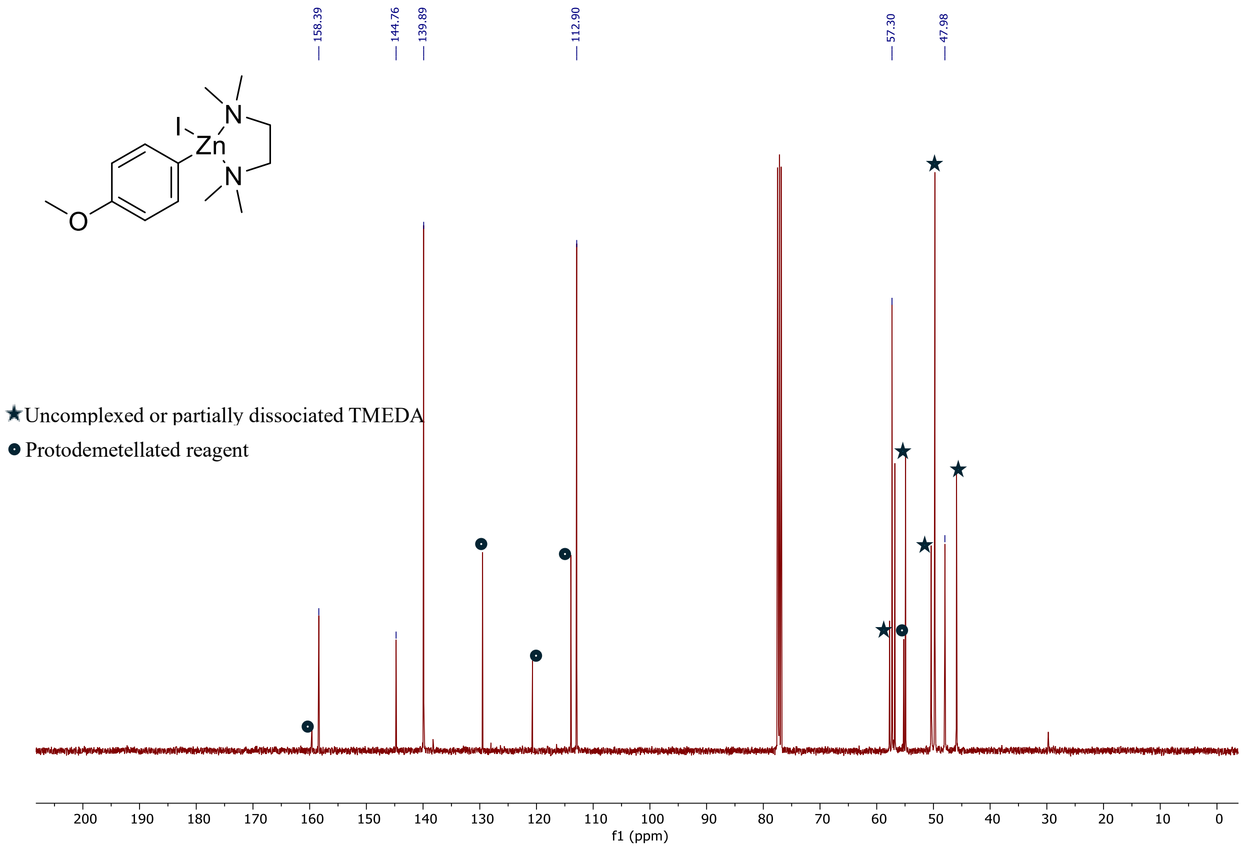
^{13}C NMR of 2f



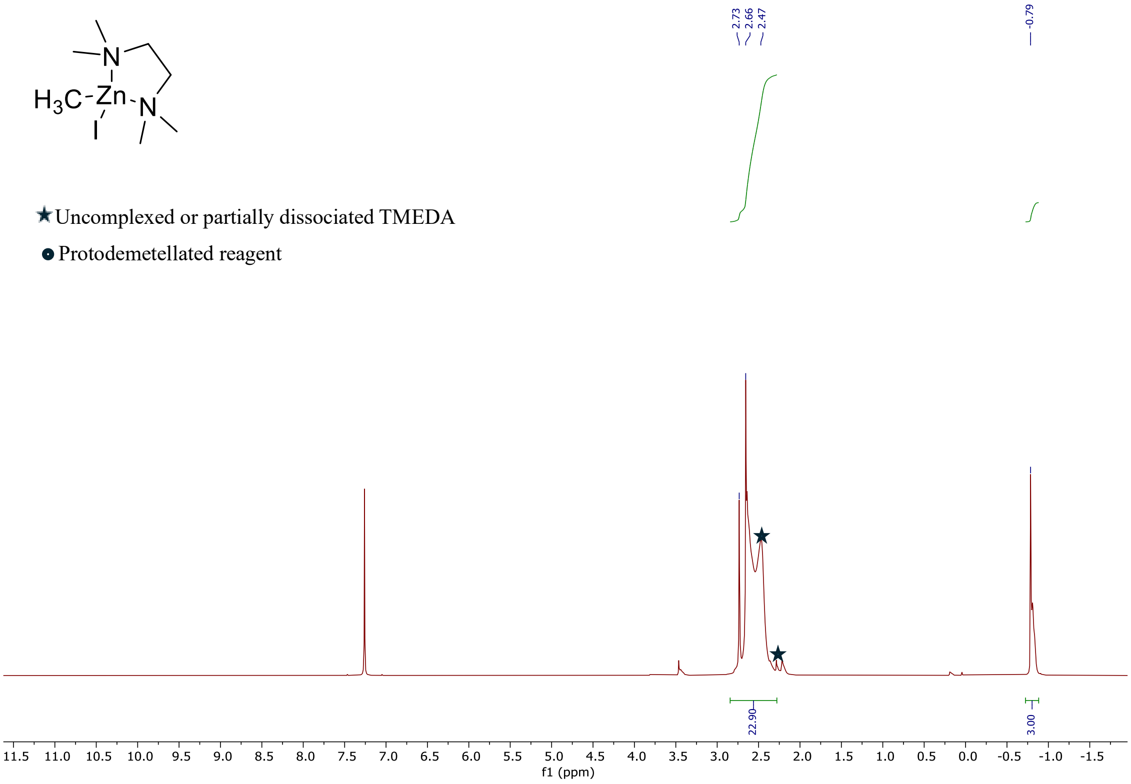
^{1}H NMR of p-OMePhZnI·TMEDA (2g)



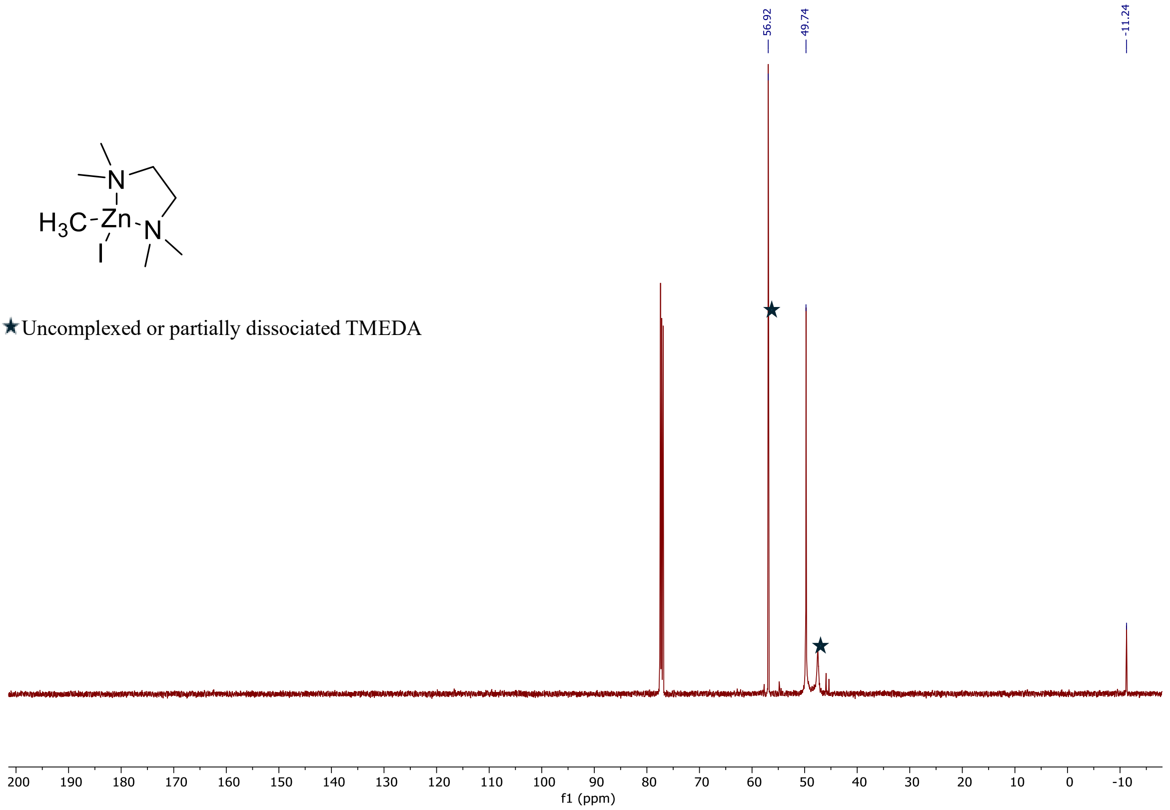
^{13}C NMR of 2g



^{1}H NMR of $CH_3ZnI \cdot TMEDA$ (2i)

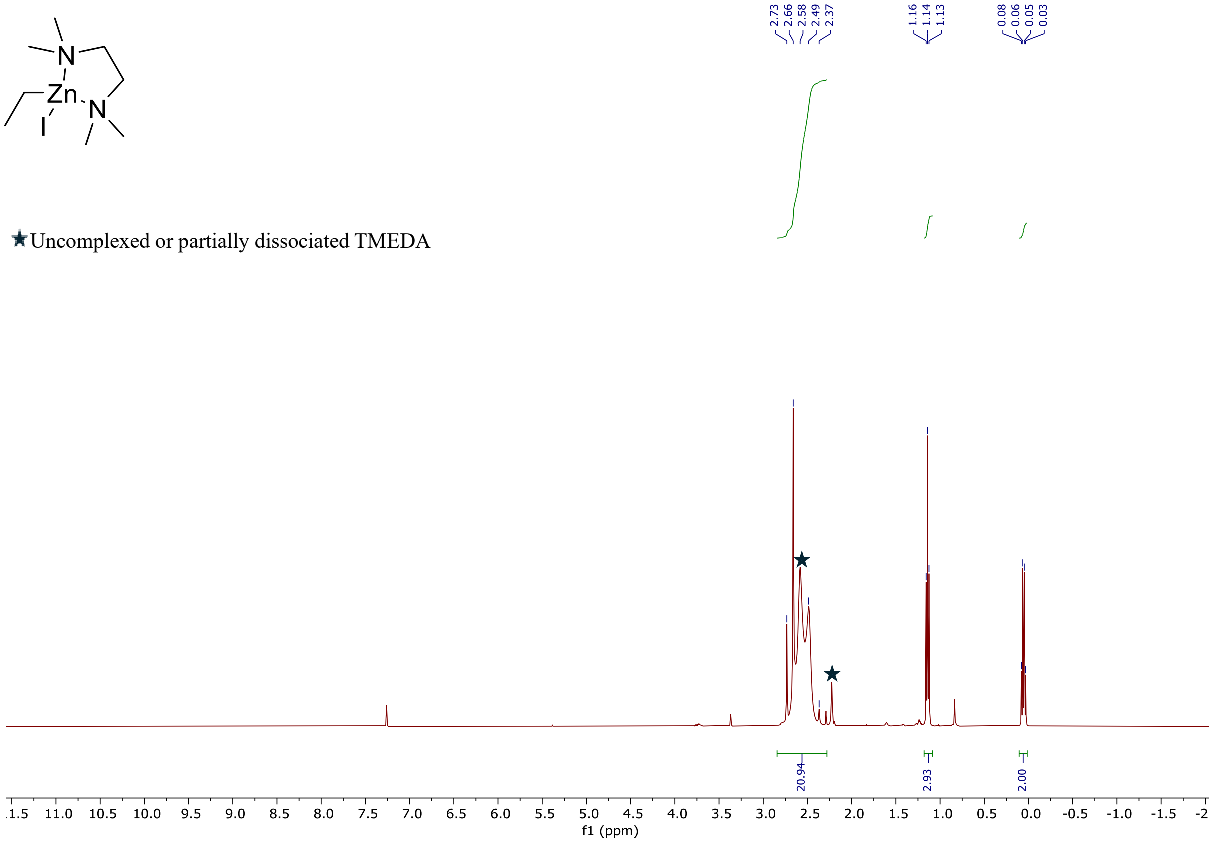


^{13}C NMR of 2i



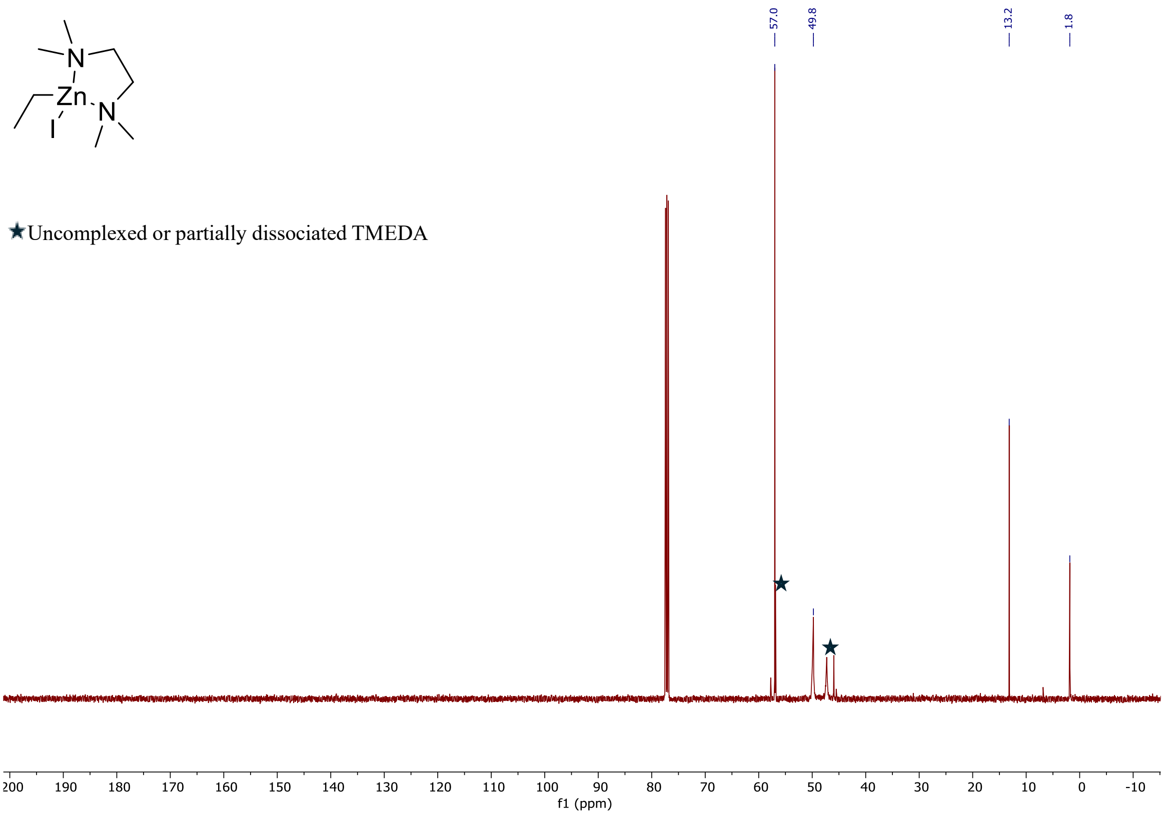
★Uncomplexed or partially dissociated TMEDA

^{1}H NMR of EthylZnBr·TMEDA (2j)



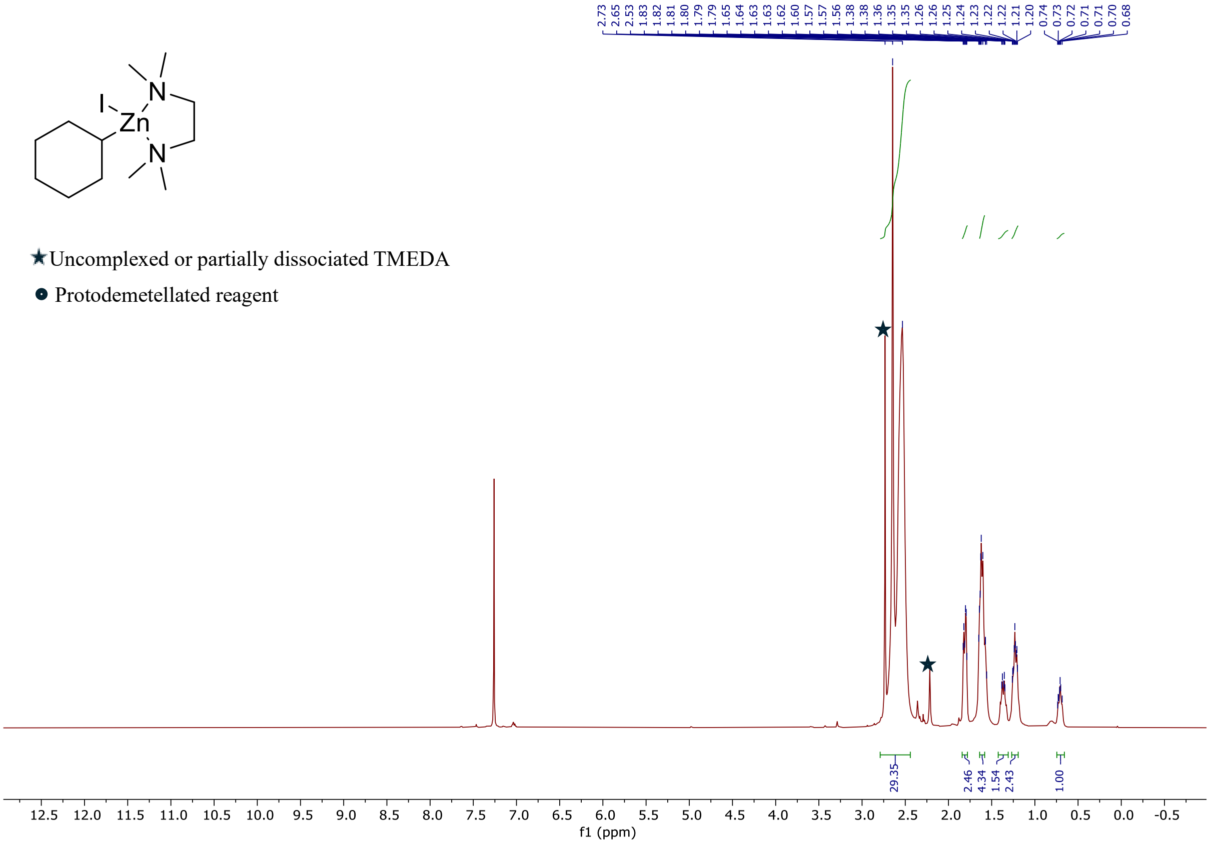
★Uncomplexed or partially dissociated TMEDA

^{13}C NMR of 2j



★Uncomplexed or partially dissociated TMEDA

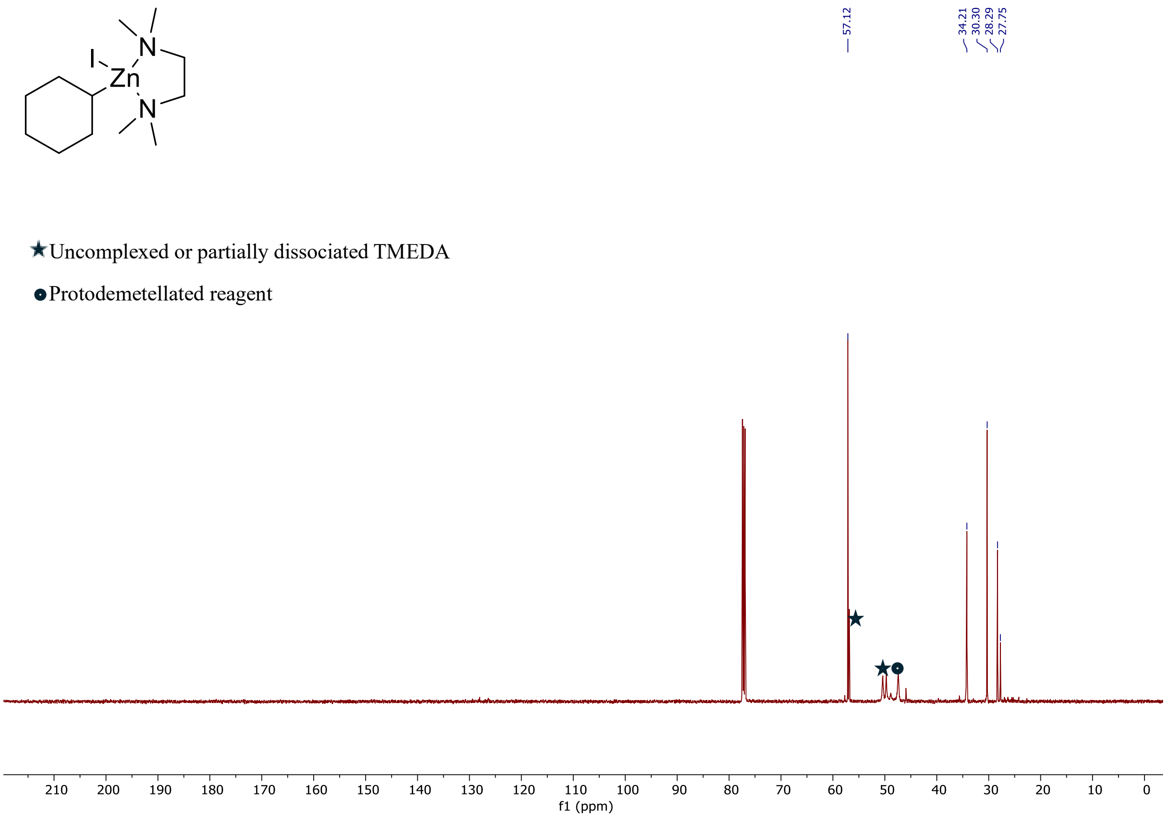
^{1}H NMR of CyclohexylZnI·TMEDA (2k)



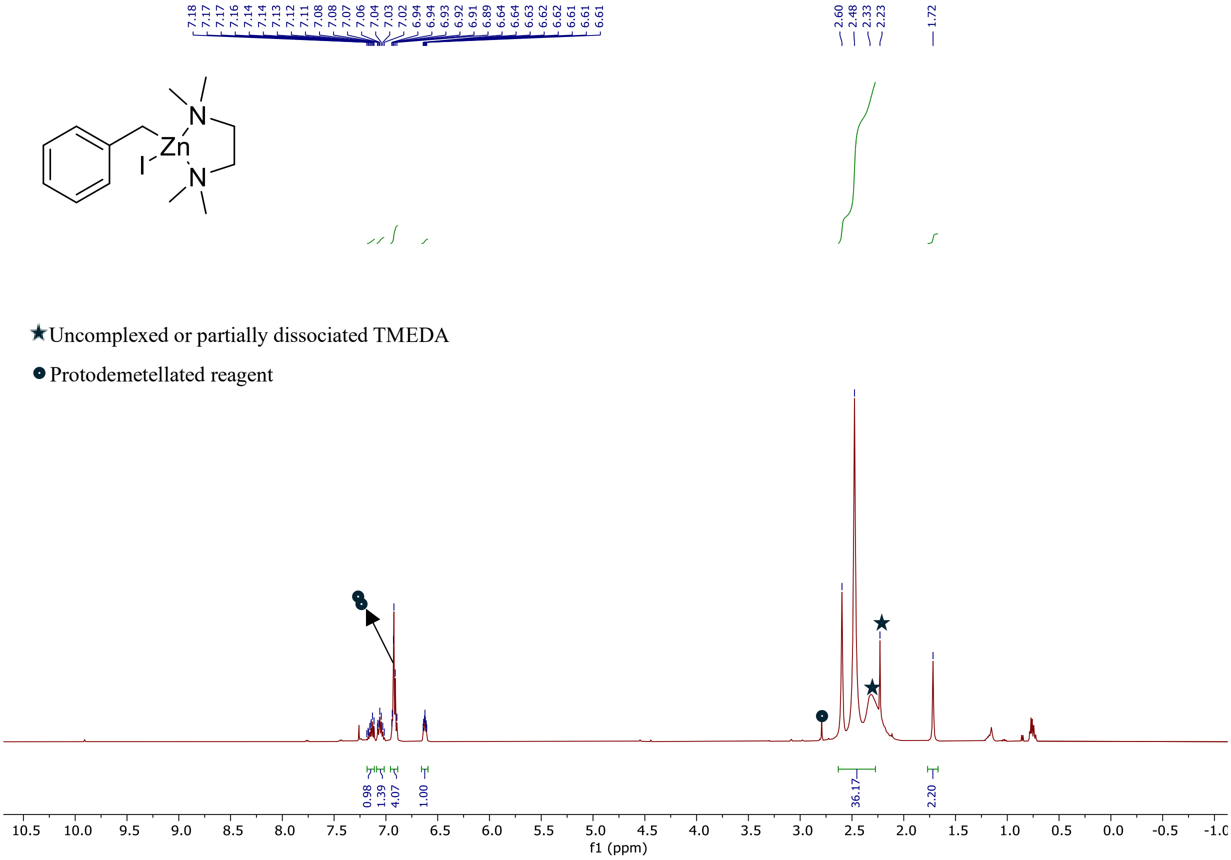
★Uncomplexed or partially dissociated TMEDA

● Protodemetellated reagent

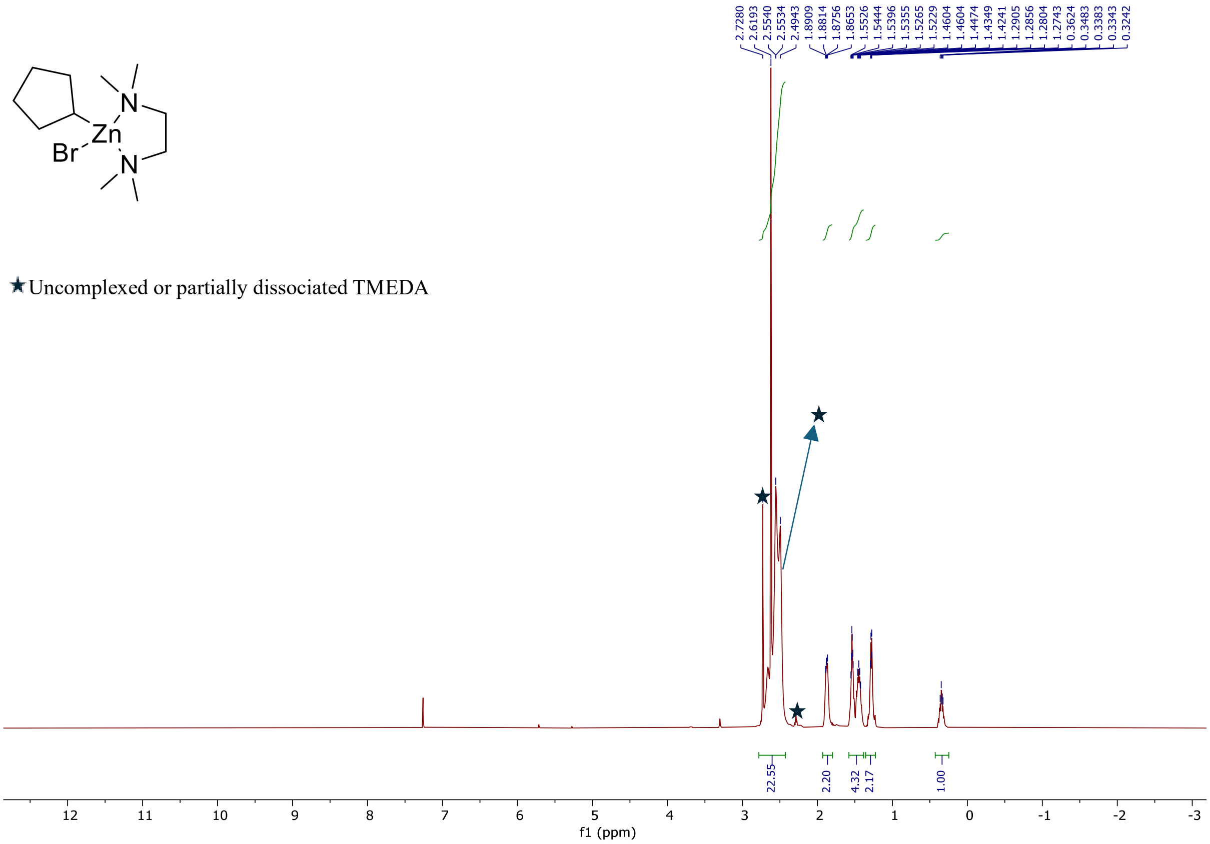
^{13}C NMR of 2k



^{1}H NMR of benzylZnI·TMEDA (2l)

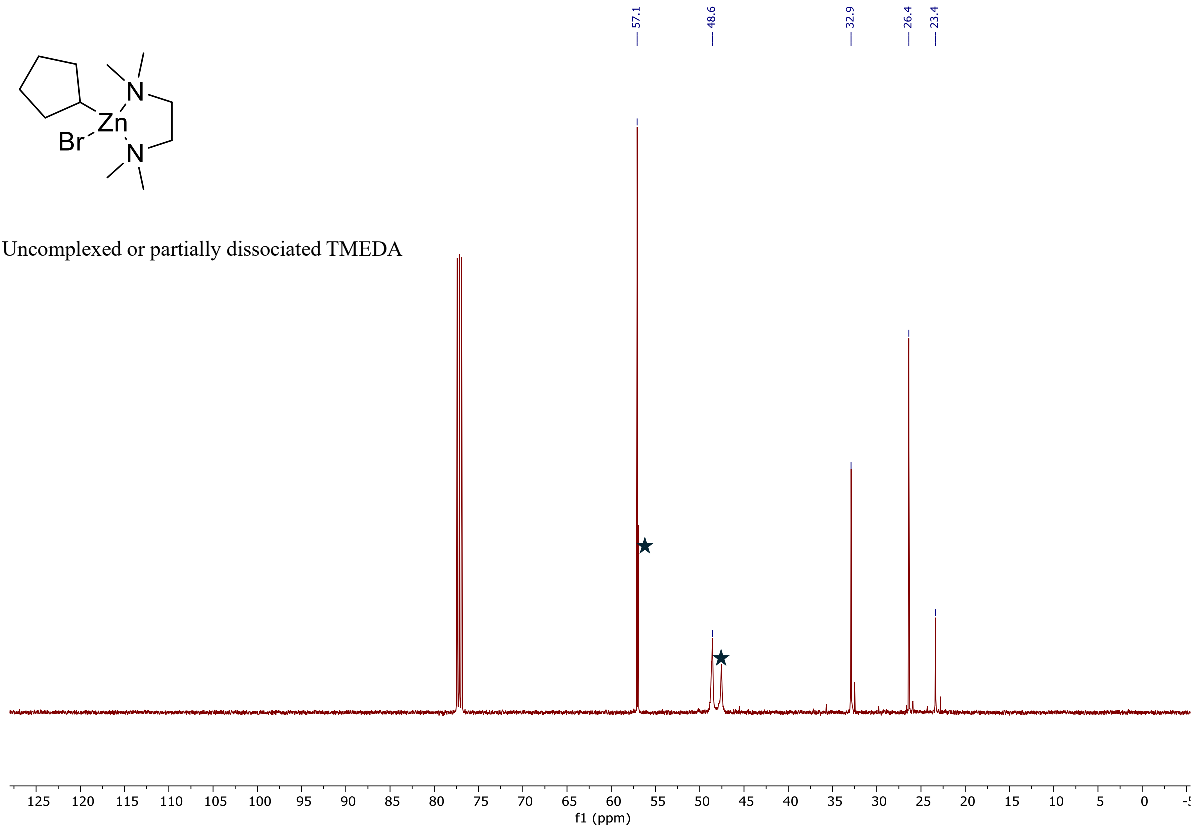


^{1}H NMR of CyclopentylZnBr·TMEDA (2m)



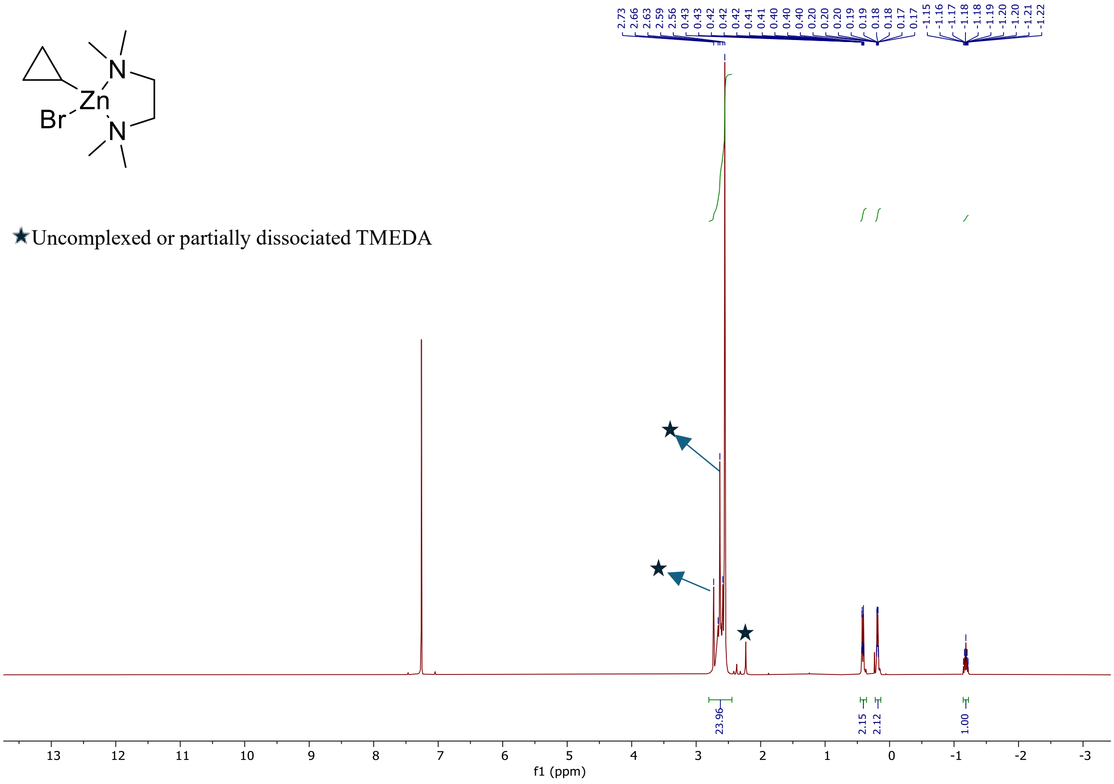
★Uncomplexed or partially dissociated TMEDA

^{13}C NMR of 2m

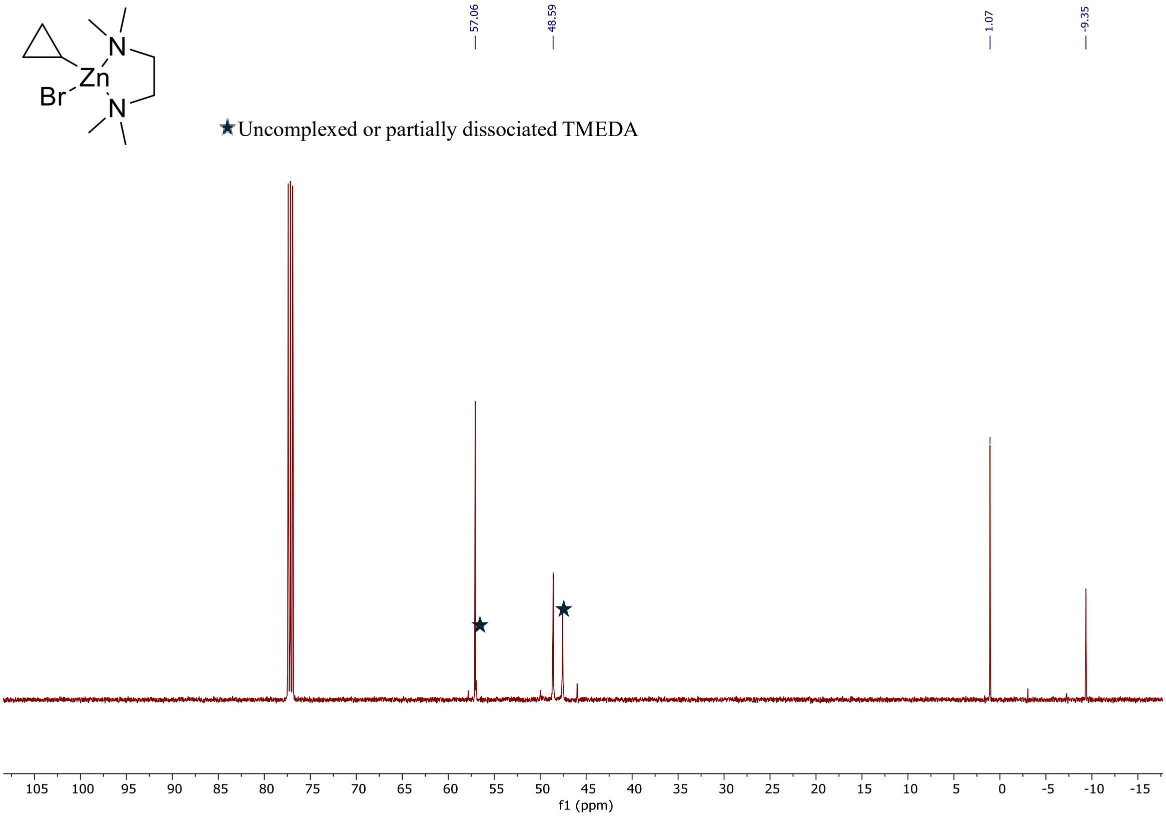


★Uncomplexed or partially dissociated TMEDA

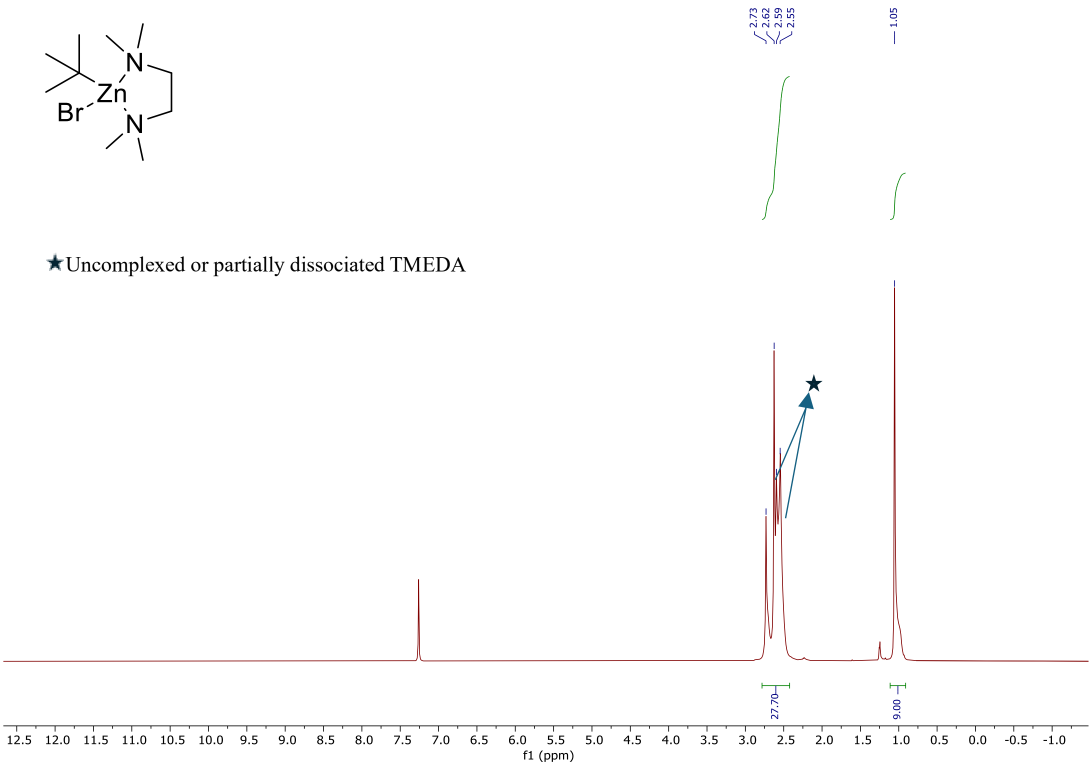
^{1}H NMR of CyclopropylZnBr·TMEDA (2n)



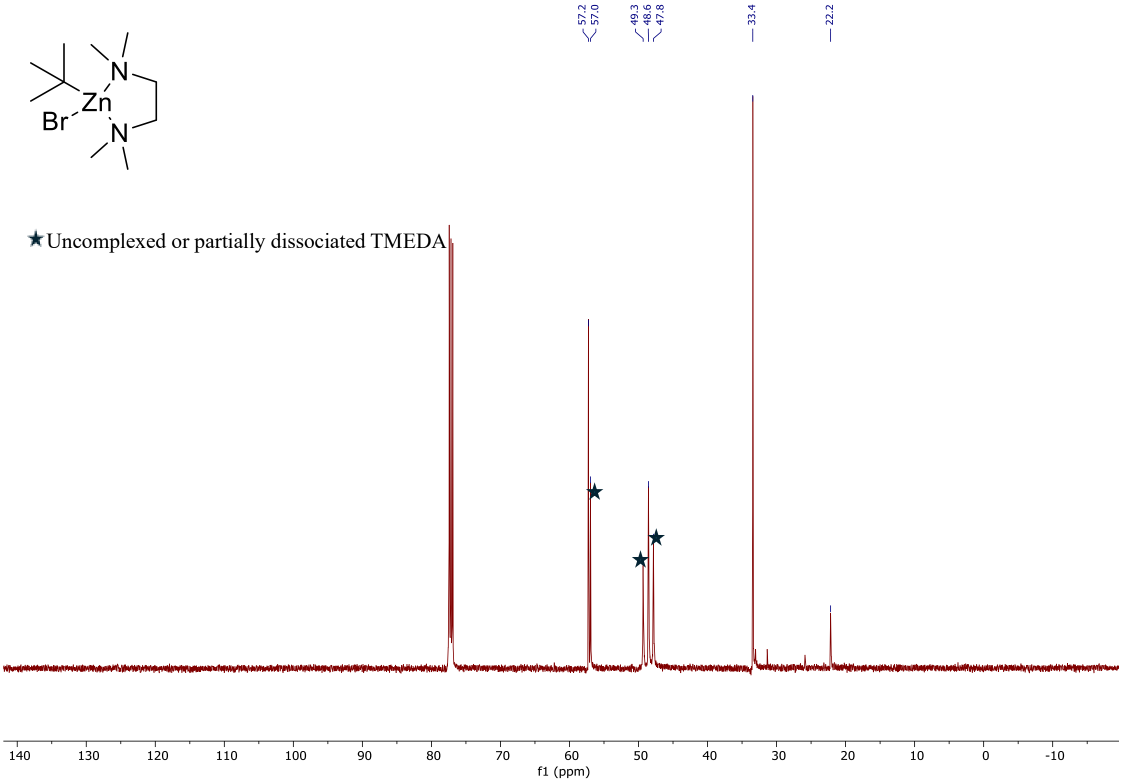
^{13}C NMR of 2n



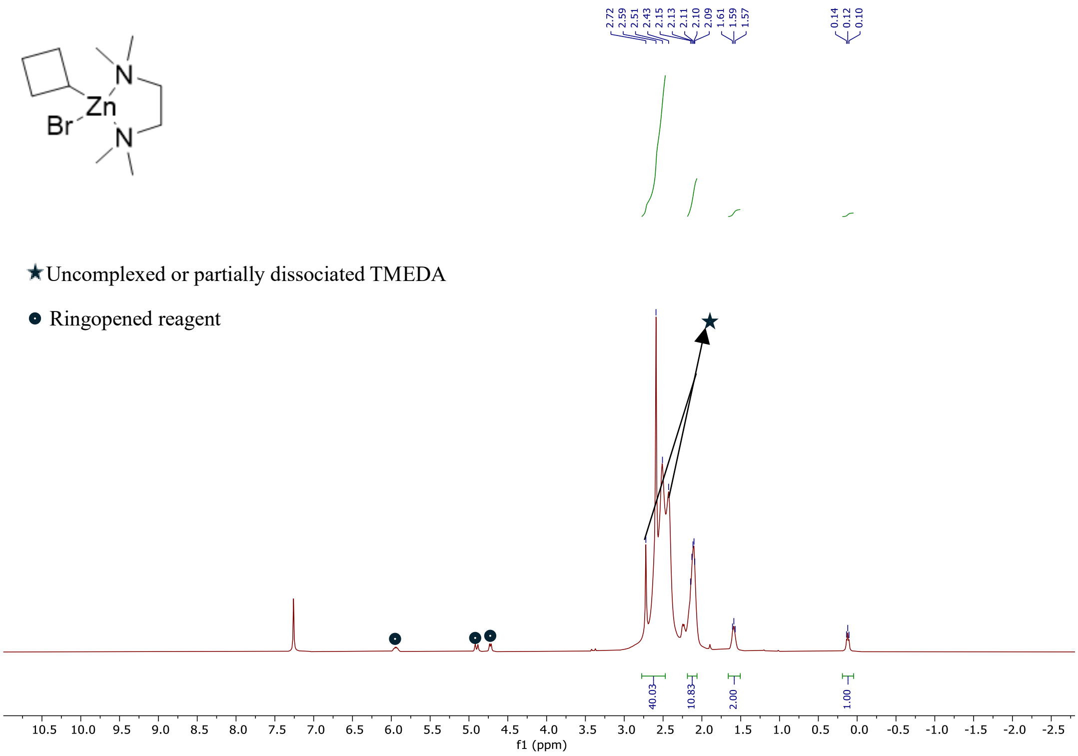
^{1}H NMR of t-BuZnBr·TMEDA (2o)



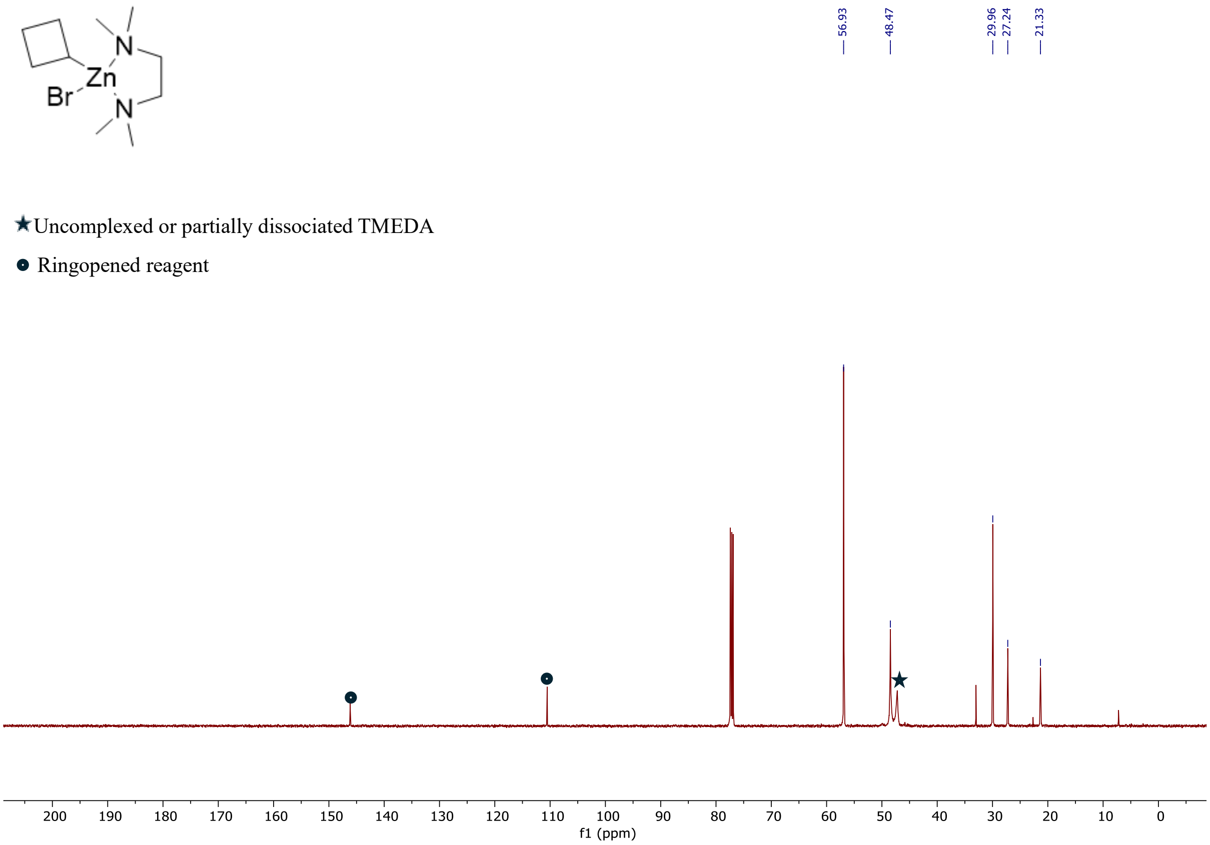
^{13}CNMR of 2o



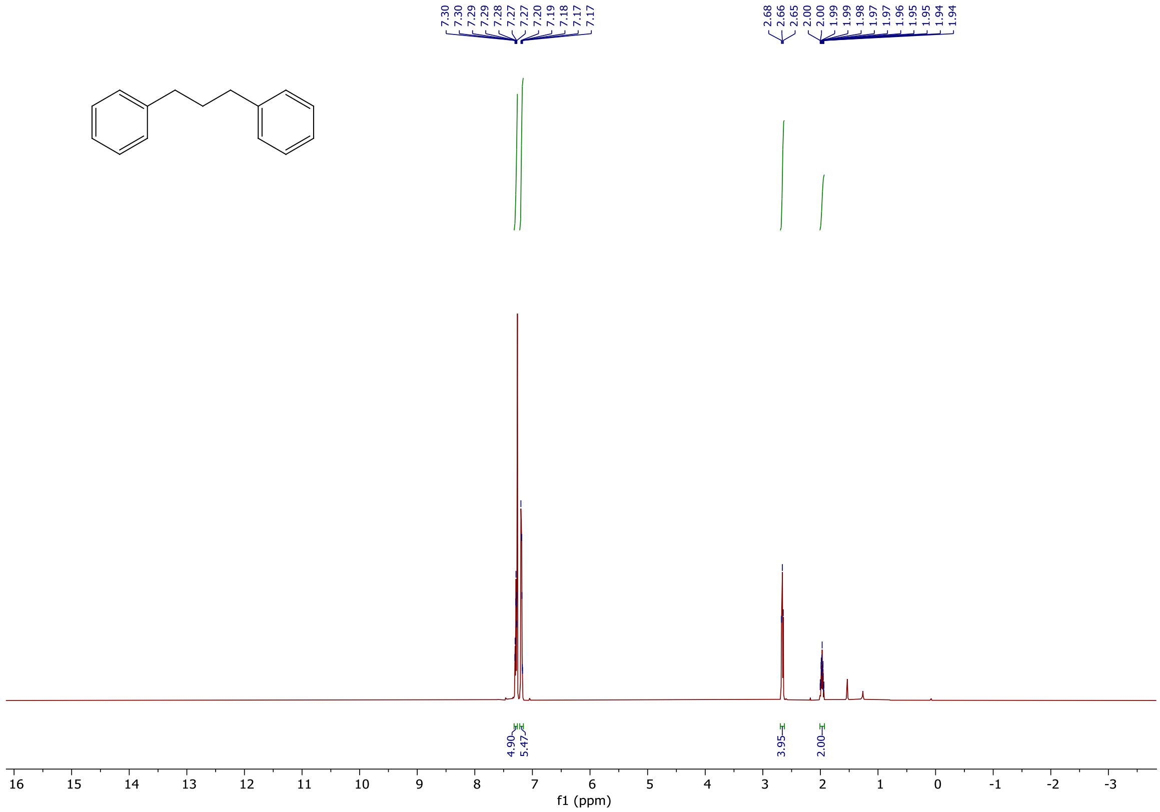
^{1}H NMR of CyclobutylZnBr·TMEDA (2p)



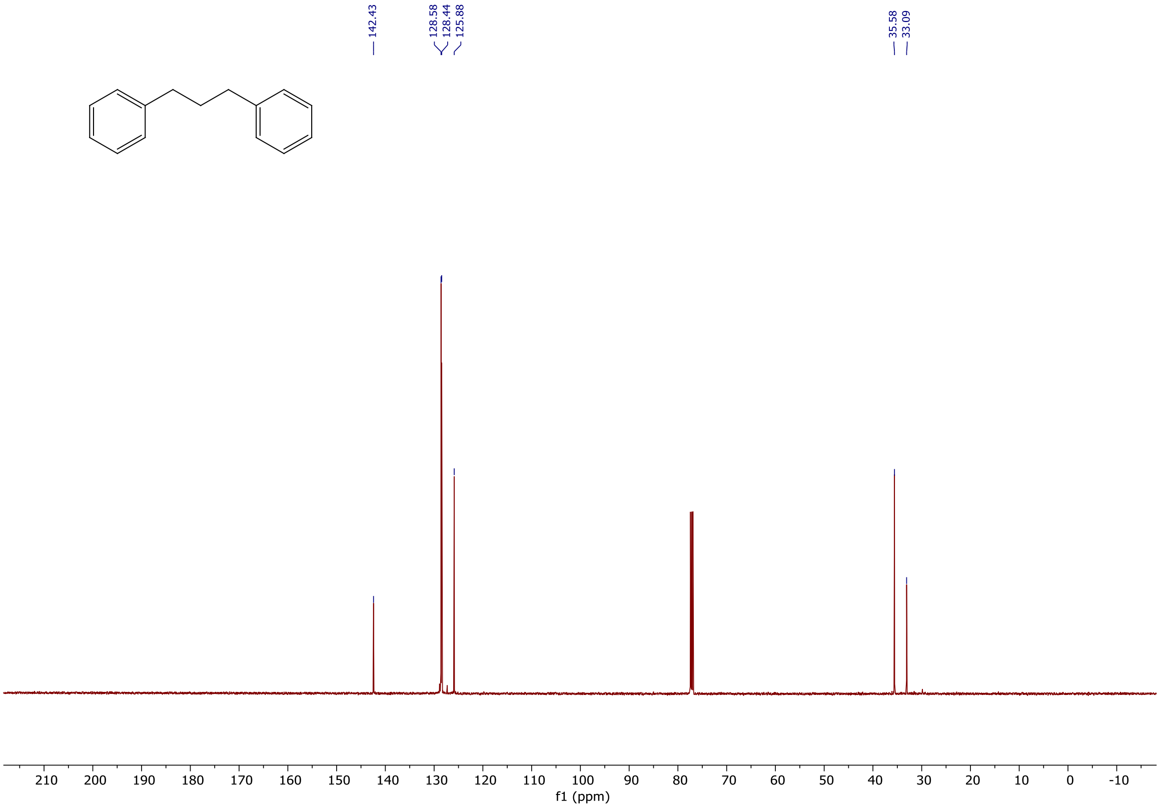
^{13}C NMR of 2p



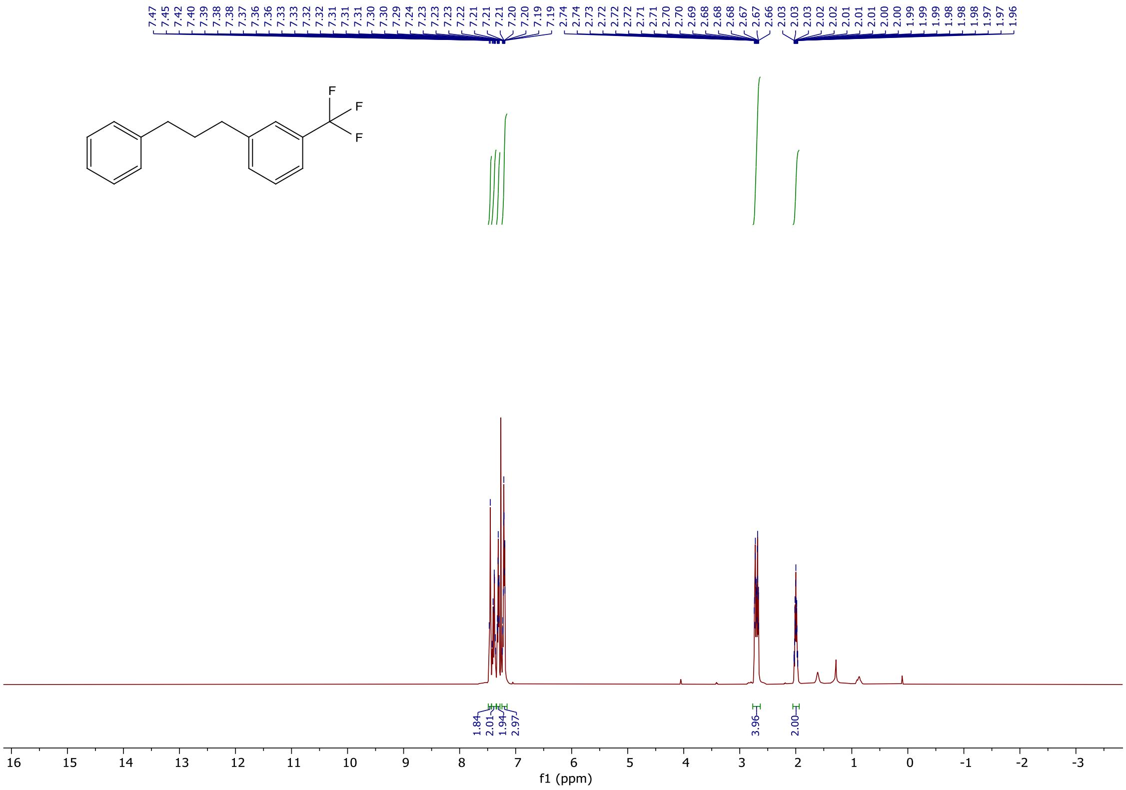
^{1}H NMR of 1,3-diphenylpropane (4a)



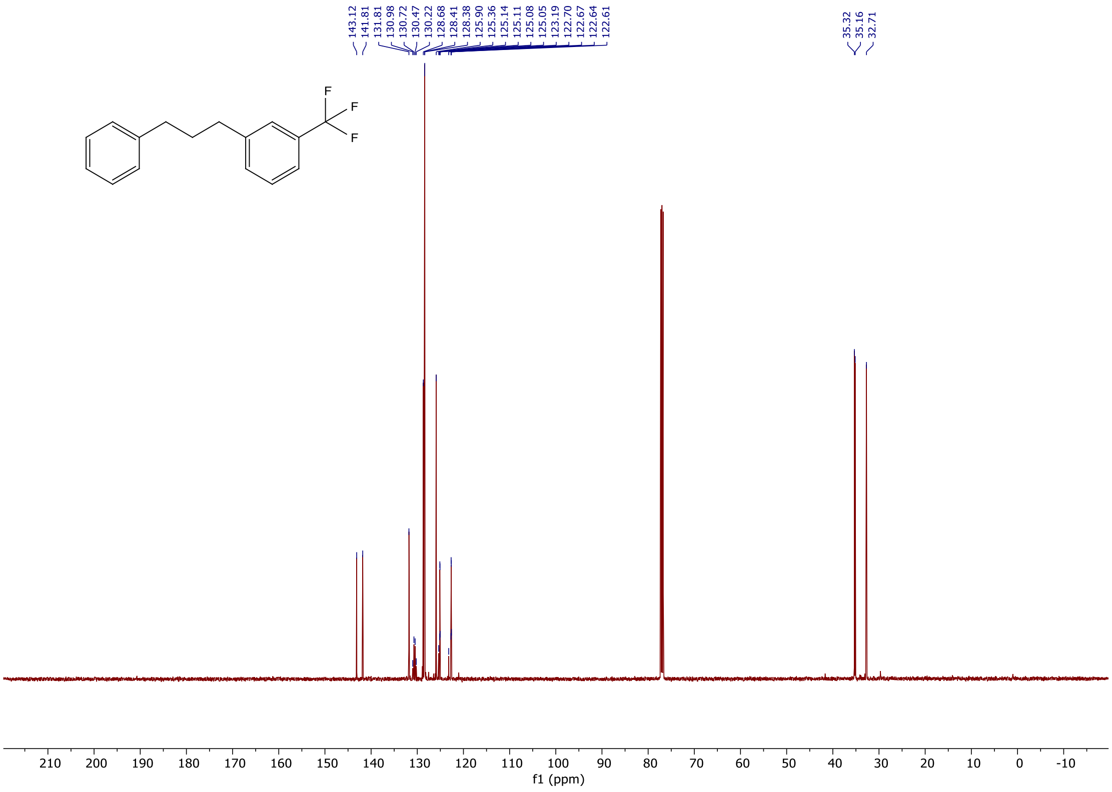
^{13}C NMR of 4a



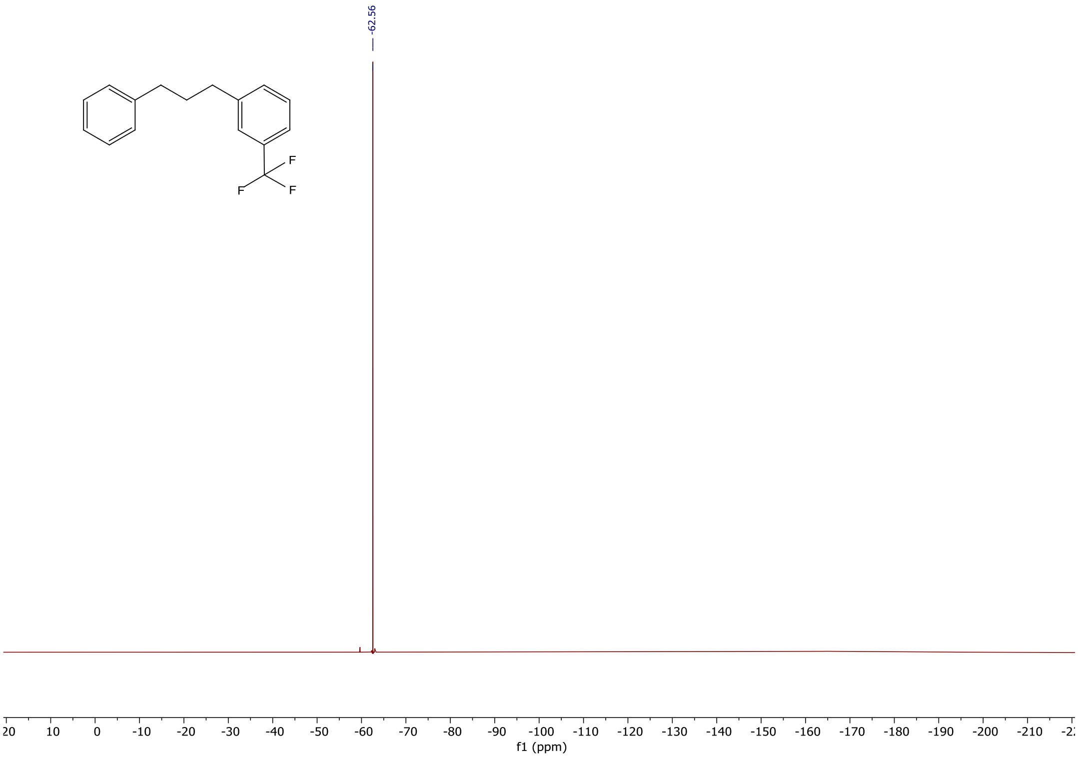
^{1}H NMR of 1-(3-phenylpropyl)-3-(trifluoromethyl)benzene (4b)



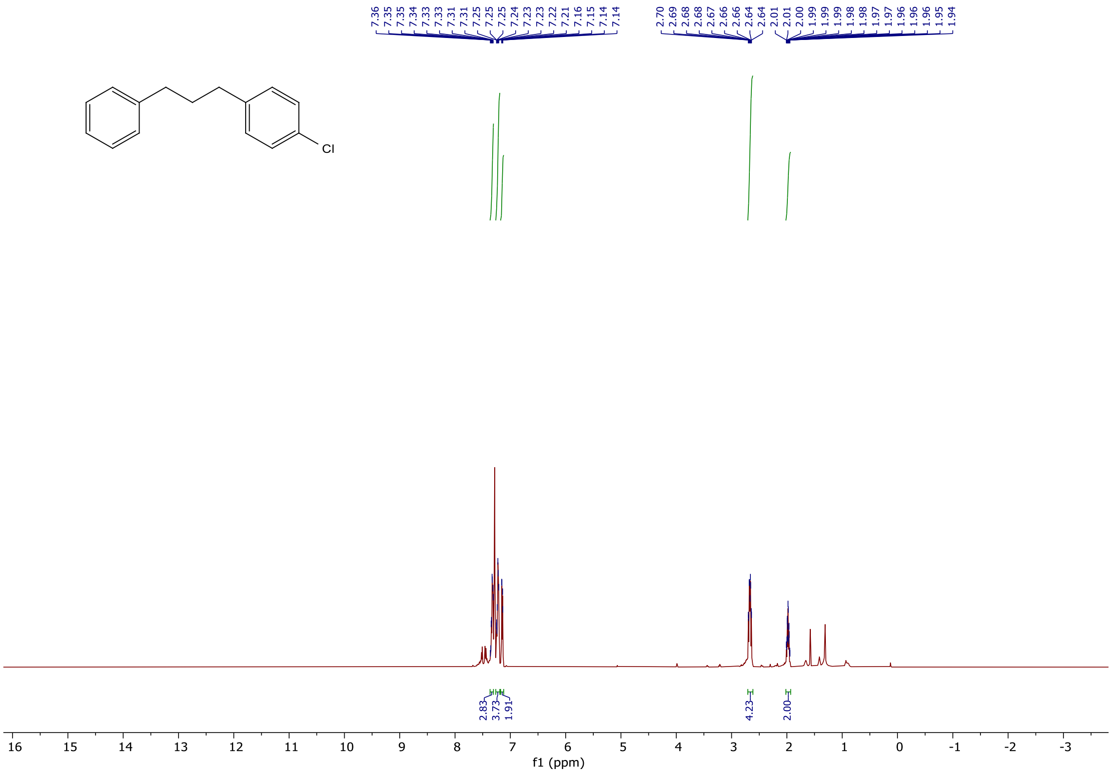
^{13}C NMR of 4b



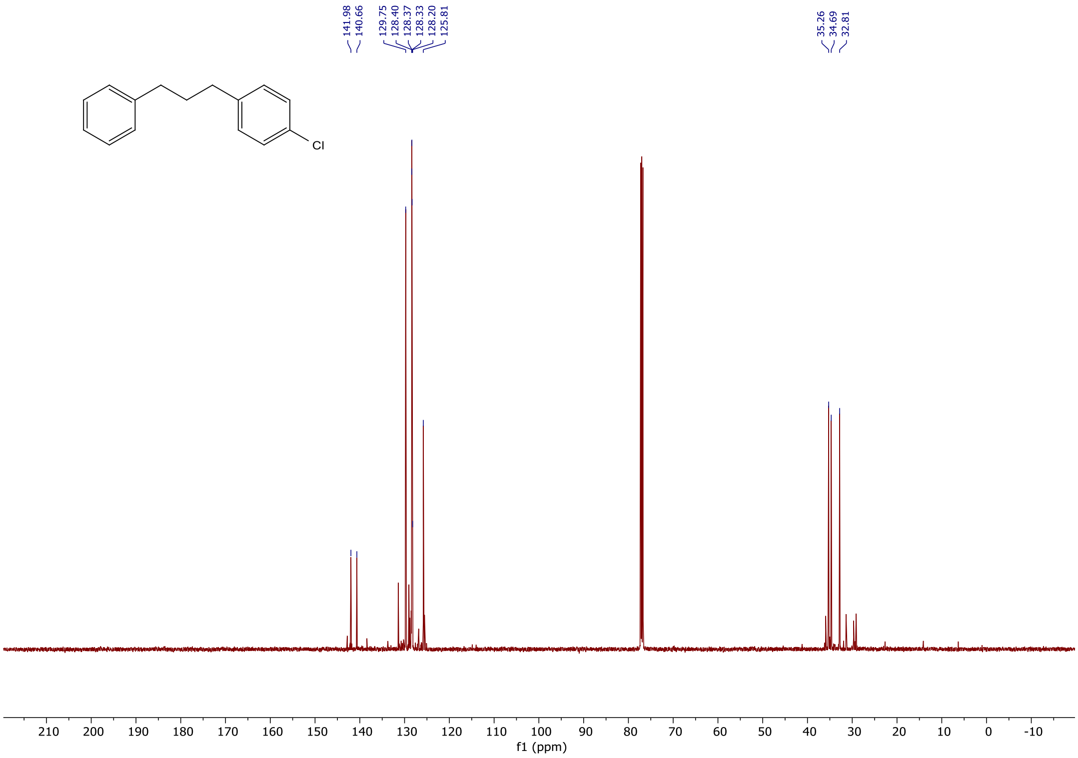
^{19}F NMR of 4b



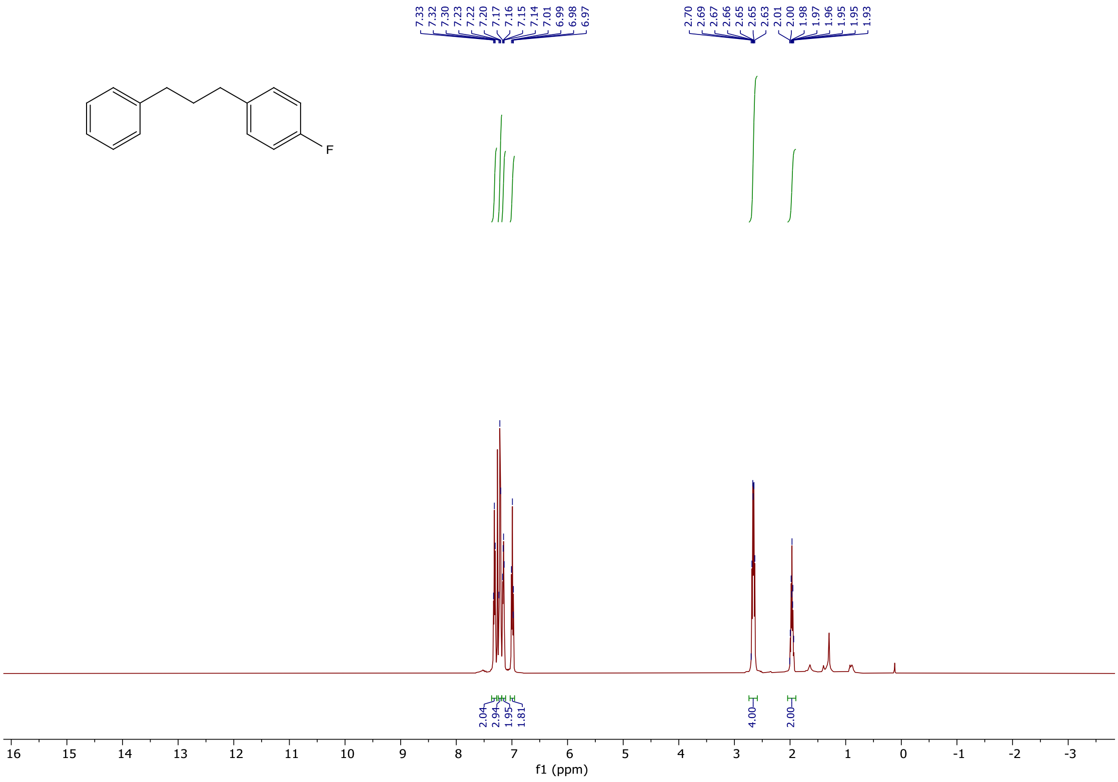
^{1}H NMR of 1-chloro-4-(3-phenylpropyl)benzene (4c)



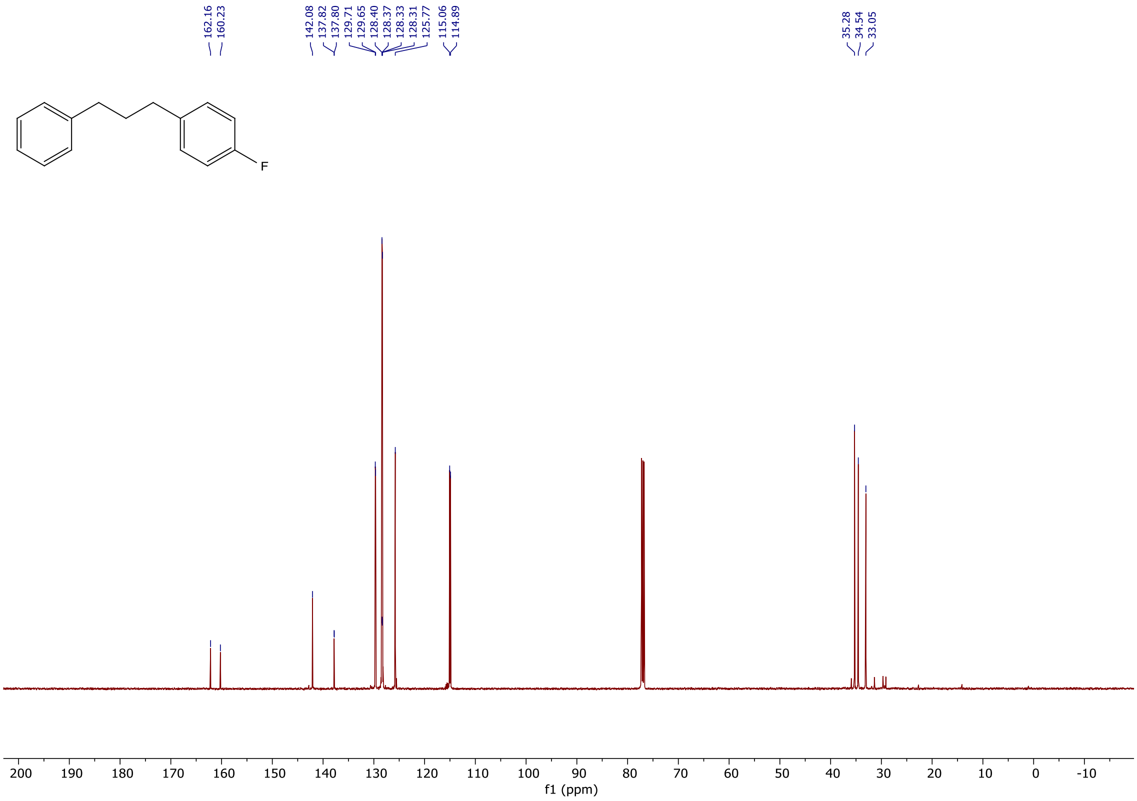
^{13}C NMR of 4c



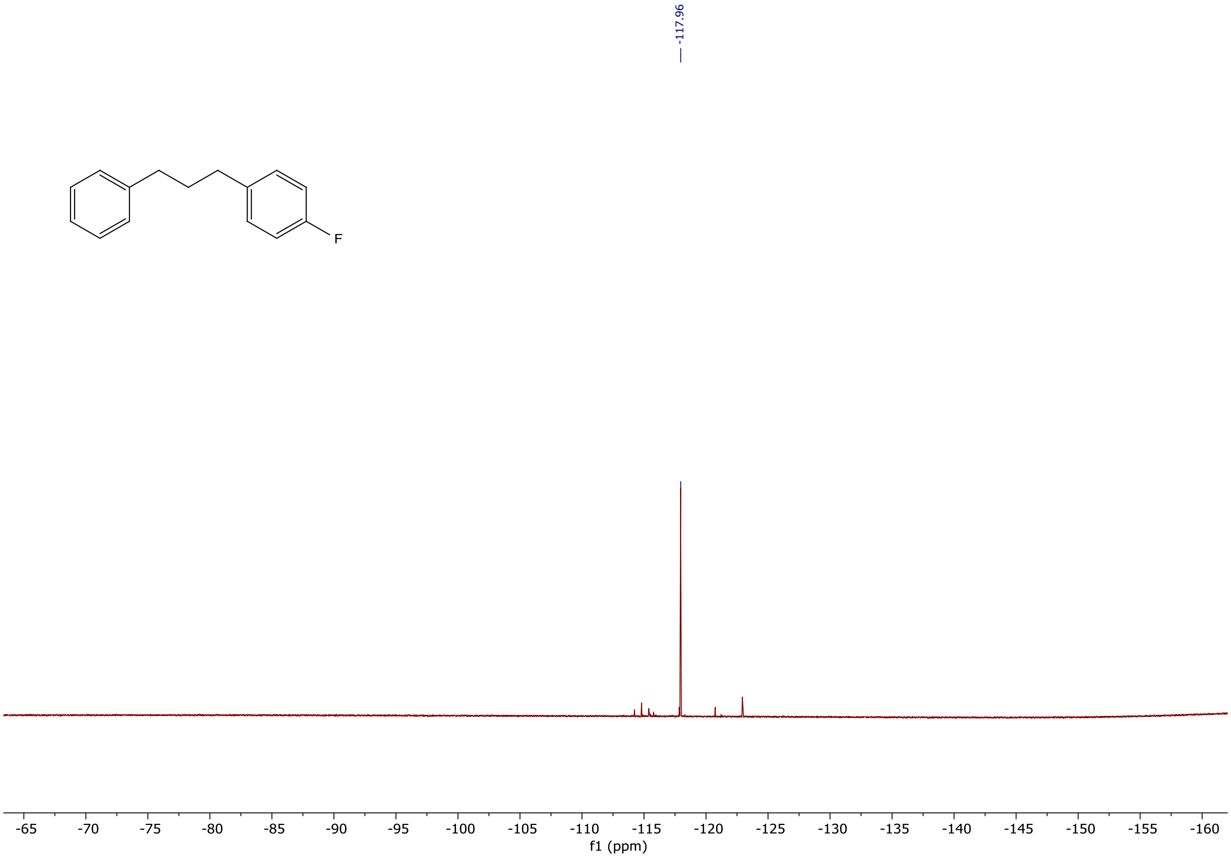
^{1}H NMR of 1-fluoro-4-(3-phenylpropyl)benzene (4d)



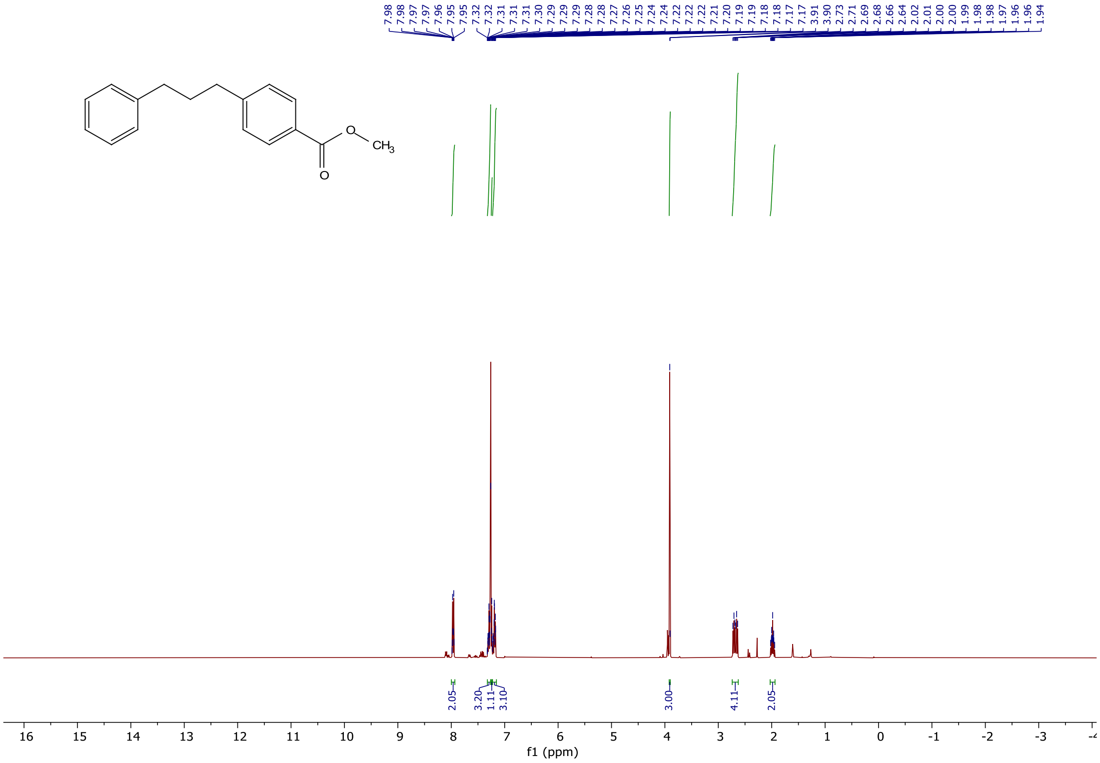
^{13}C NMR of 4d



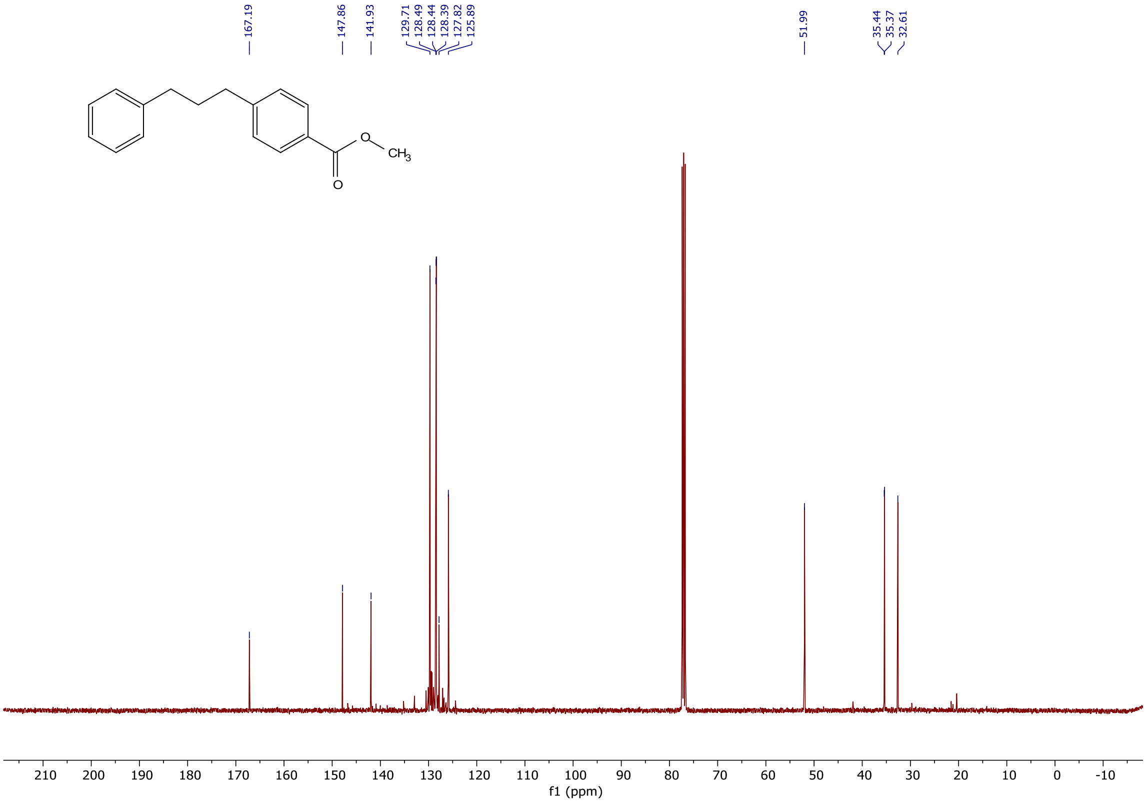
^{19}F NMR of 4d



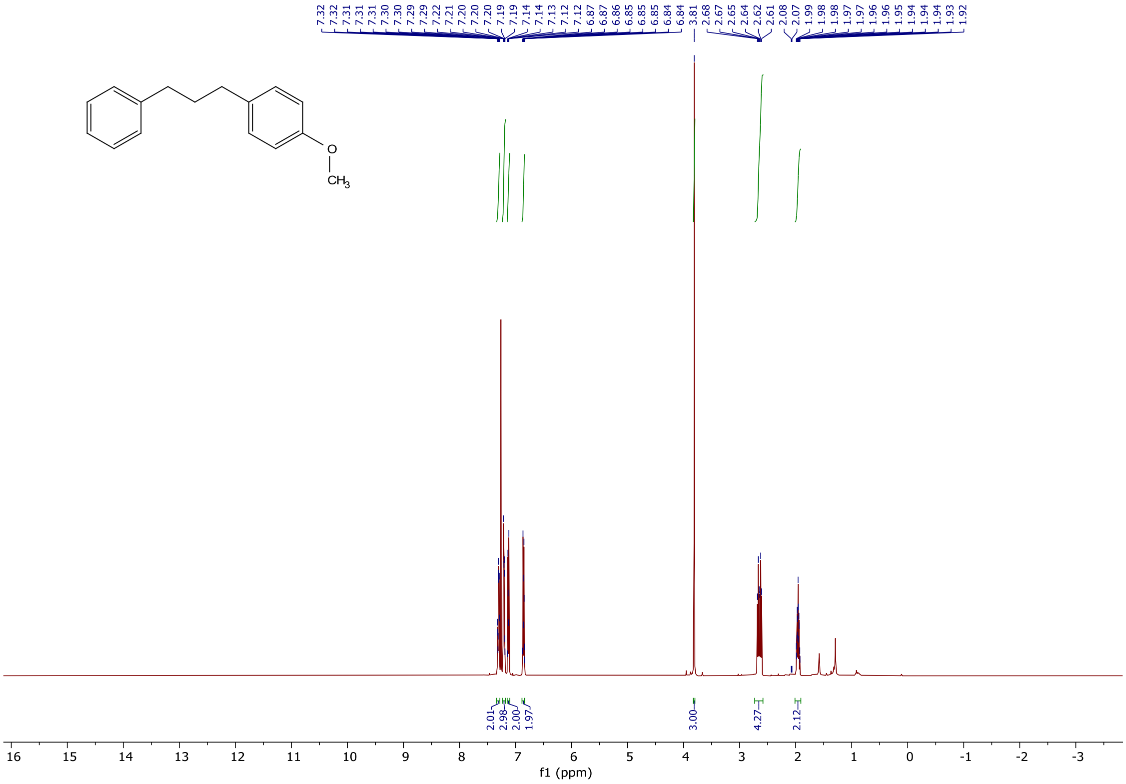
^{1}H NMR of methyl 4-(3-phenylpropyl)benzoate (4e)



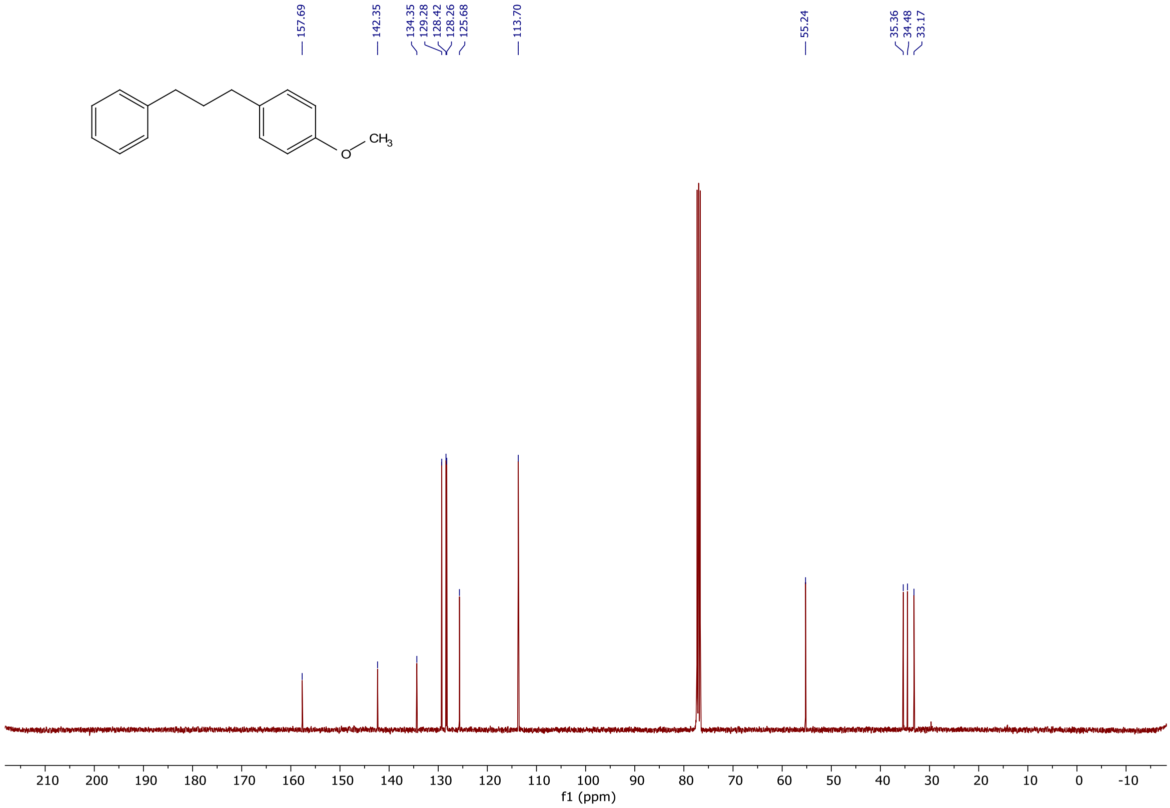
^{13}C NMR of 4e



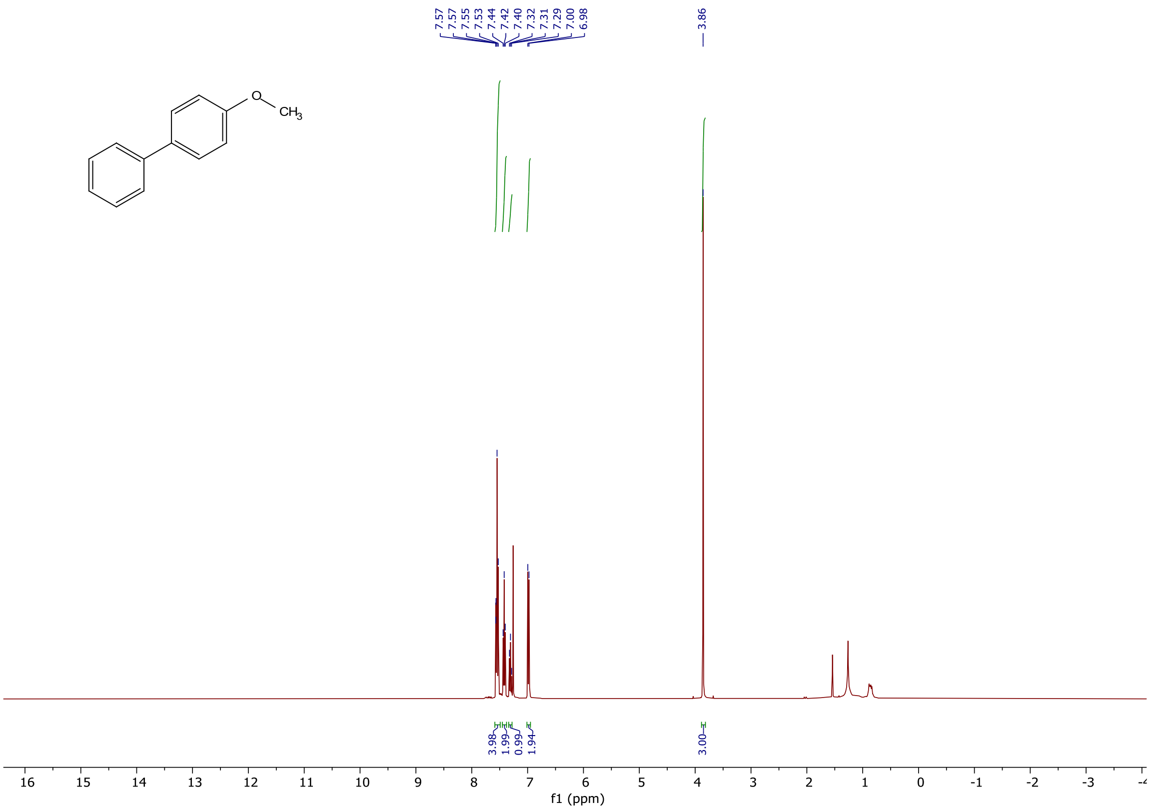
^{1}H NMR of 1-methoxy-4-(3-phenylpropyl)benzene(4f)



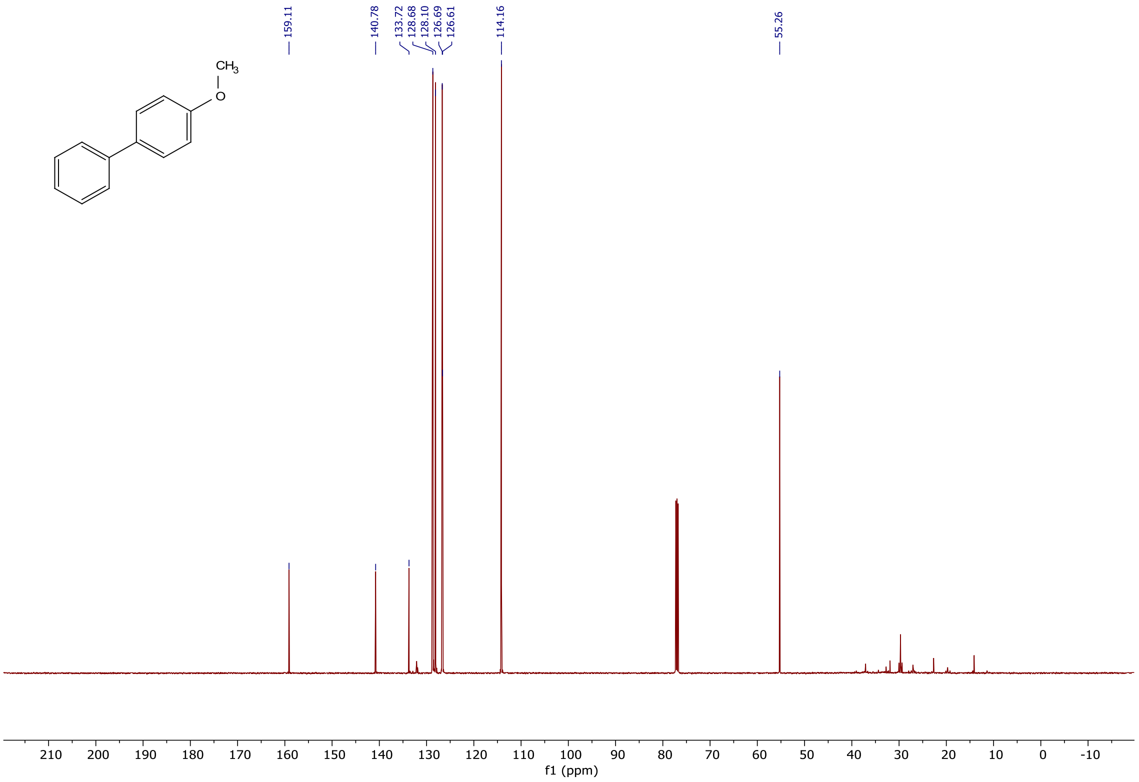
^{13}C NMR of 4f



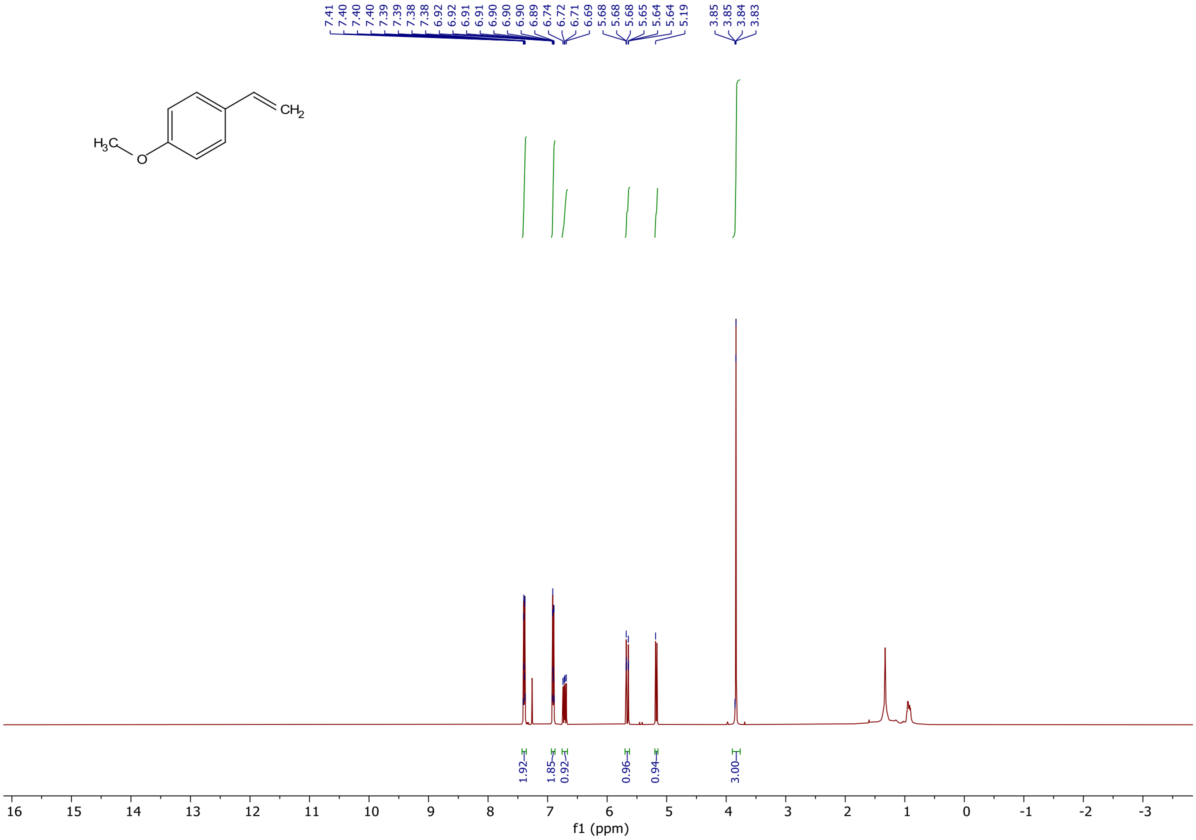
^{1}H NMR of 4-methoxy-1,1'-biphenyl (6a)



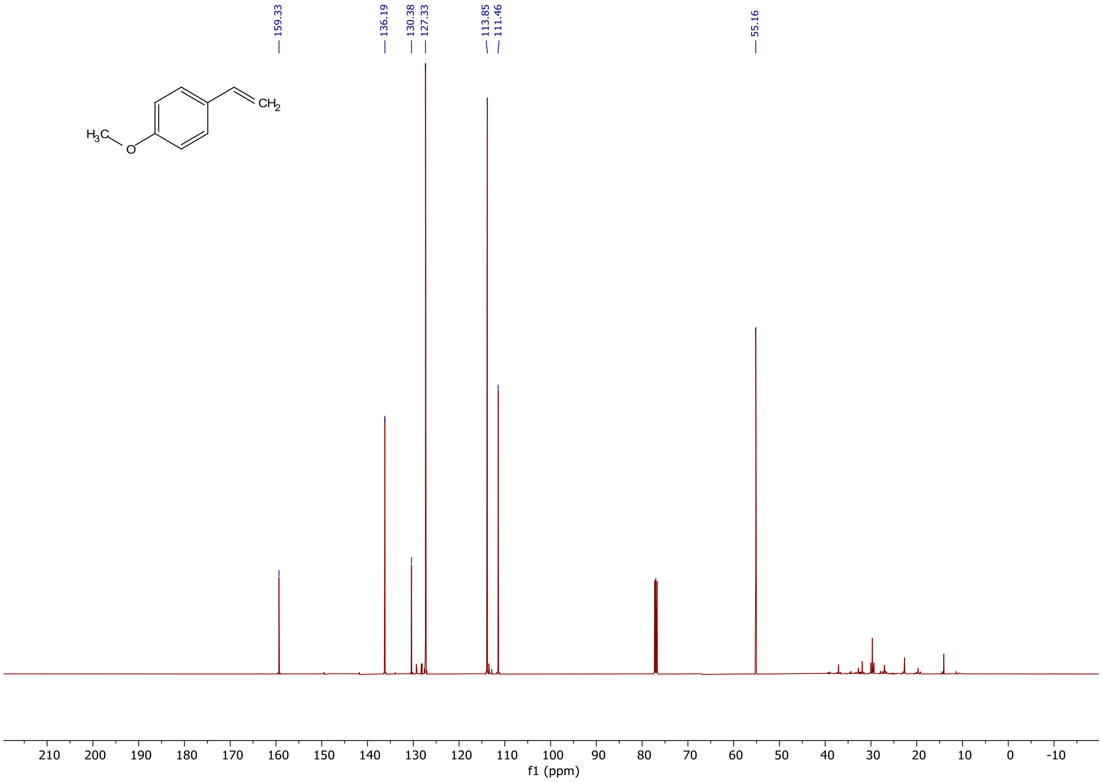
^{13}C NMR of 6a



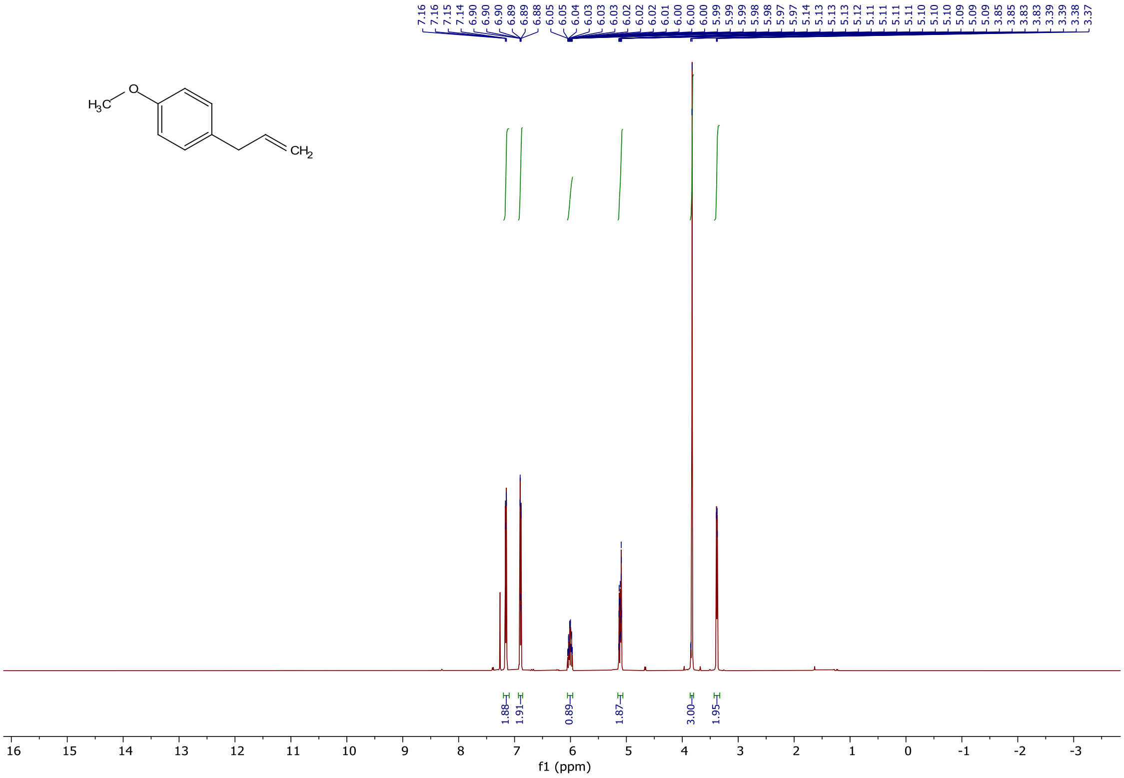
^{1}H NMR of Vinylanisole (6b)



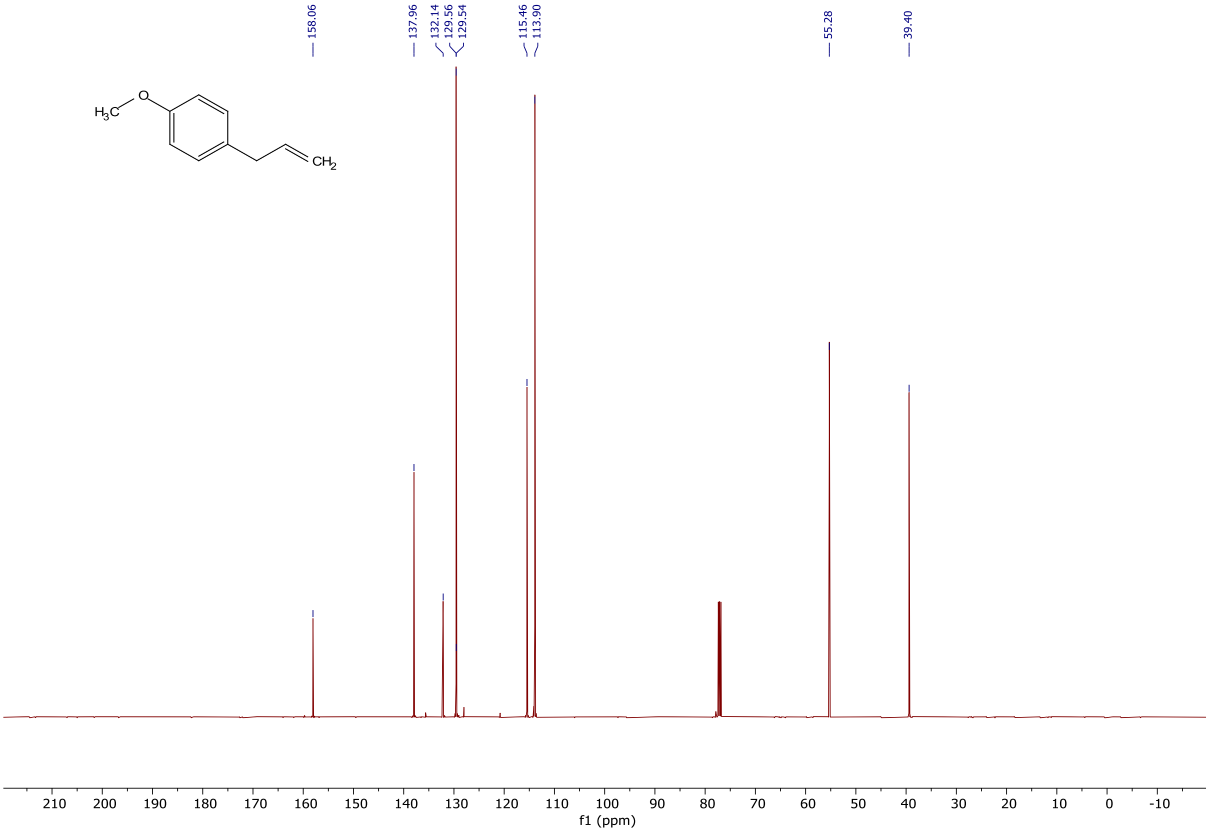
^{13}C NMR of 6b



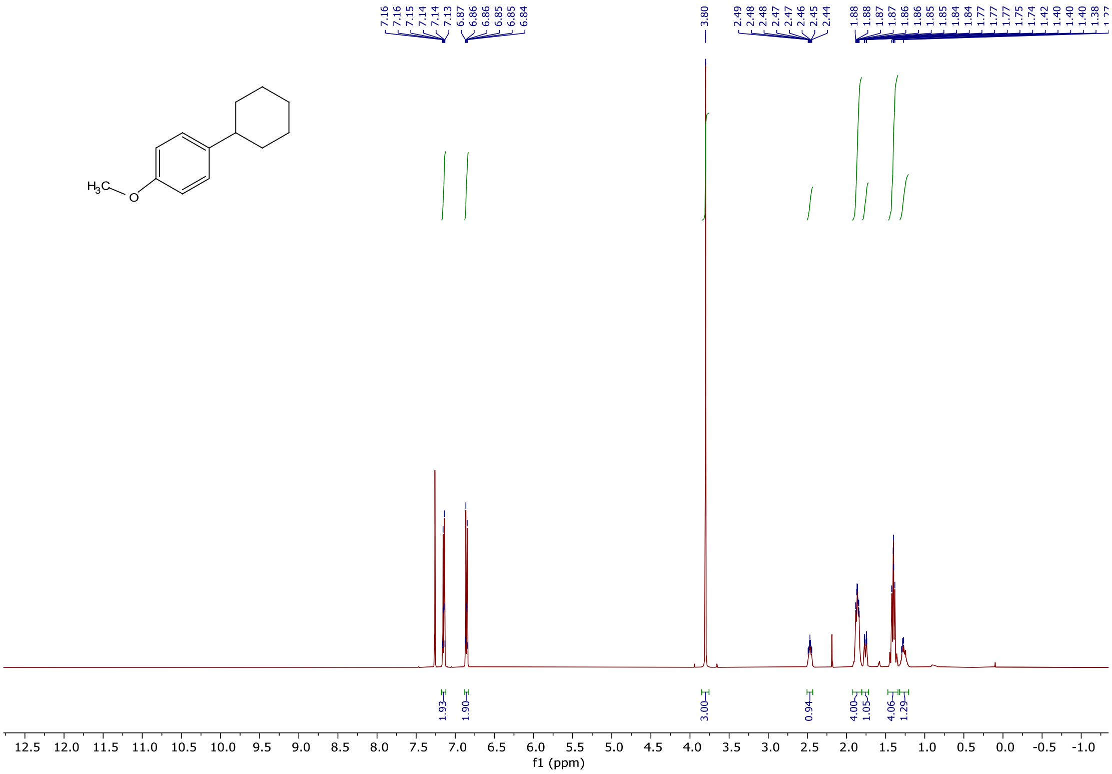
^{1}H NMR of Allylanisole (6c)



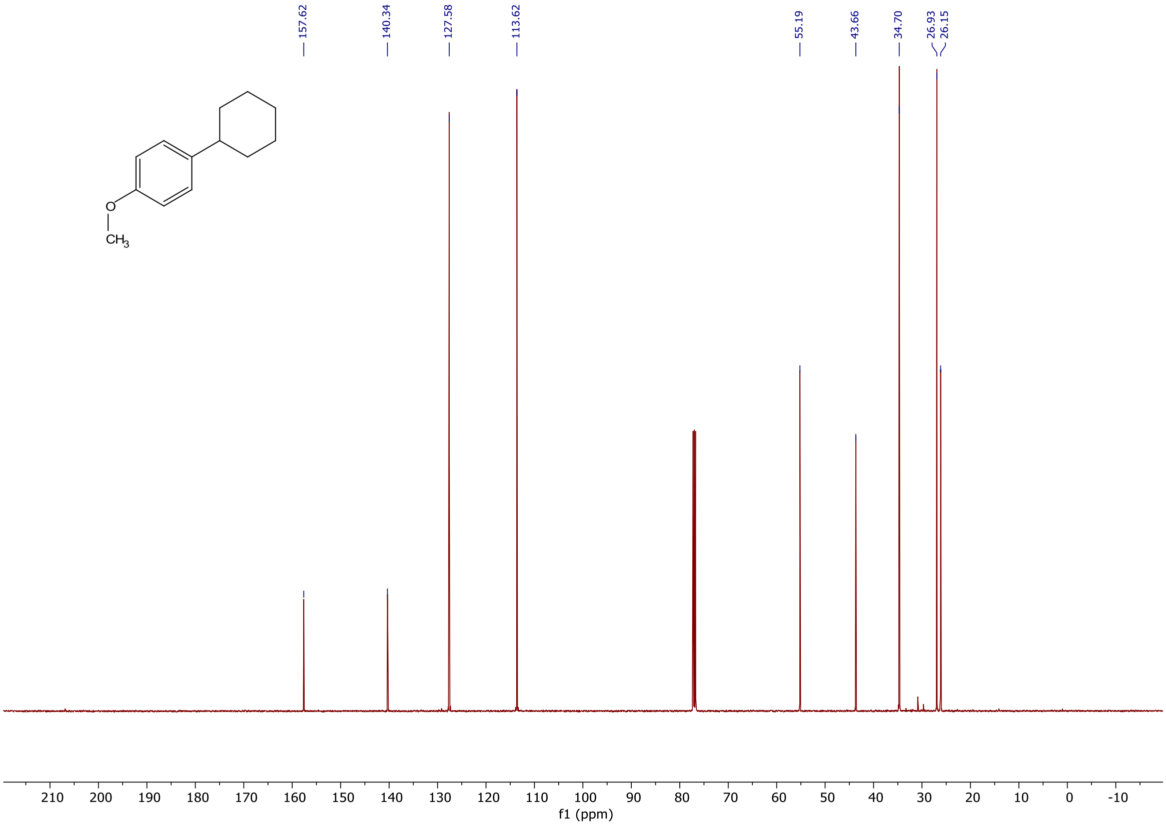
^{13}C NMR of 6c



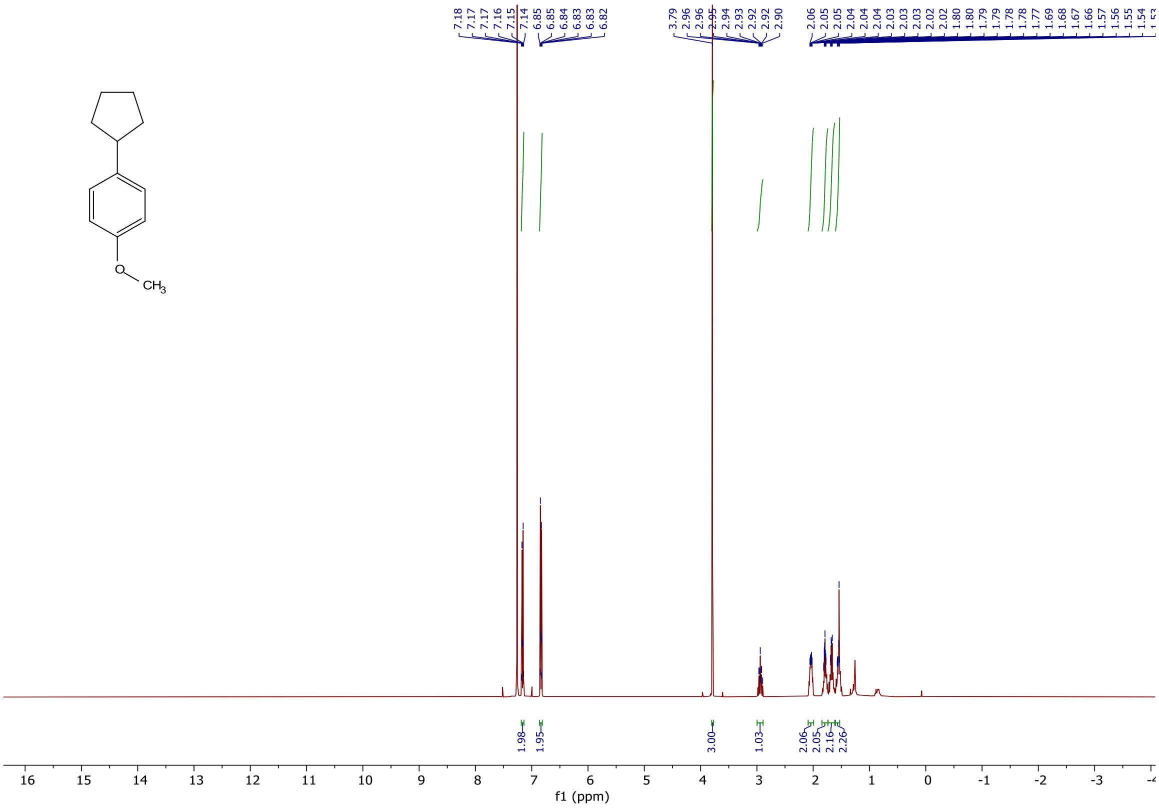
^{1}H NMR of 1-cyclohexyl-4-methoxybenzene (6d)



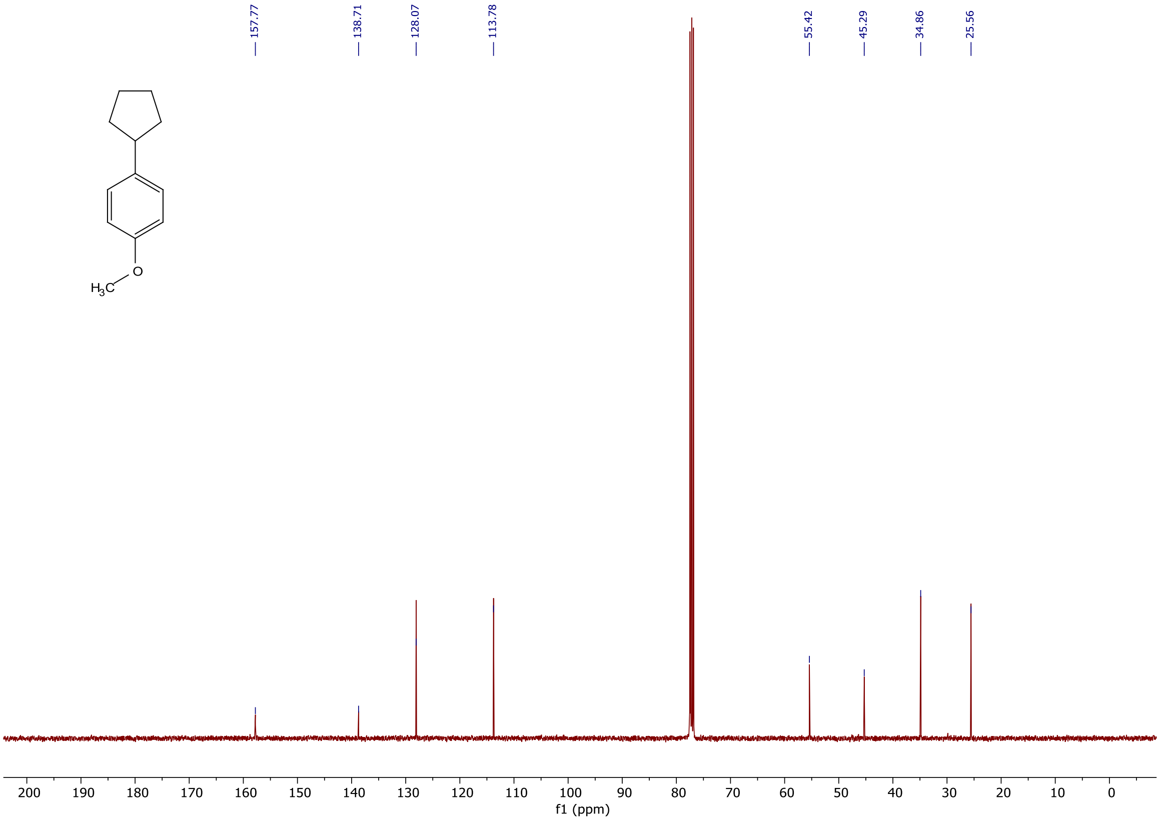
^{13}C NMR of 6d



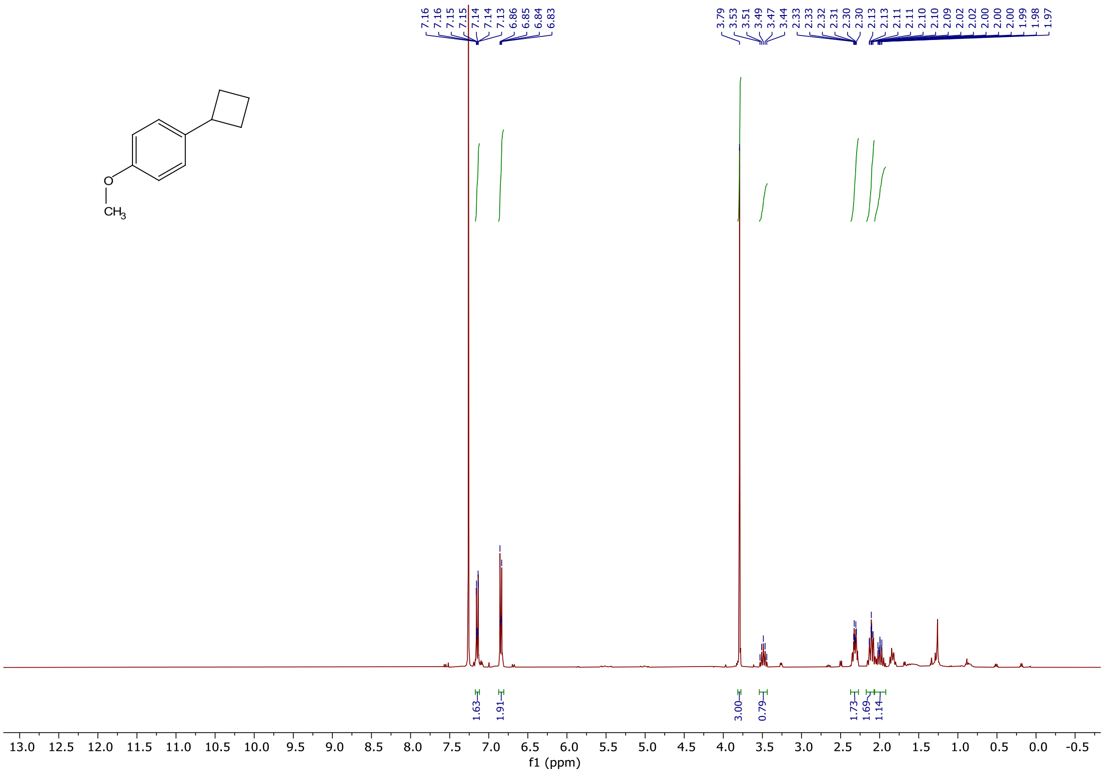
^{1}H NMR of 1-cyclopentyl-4-methoxybenzene (6e)



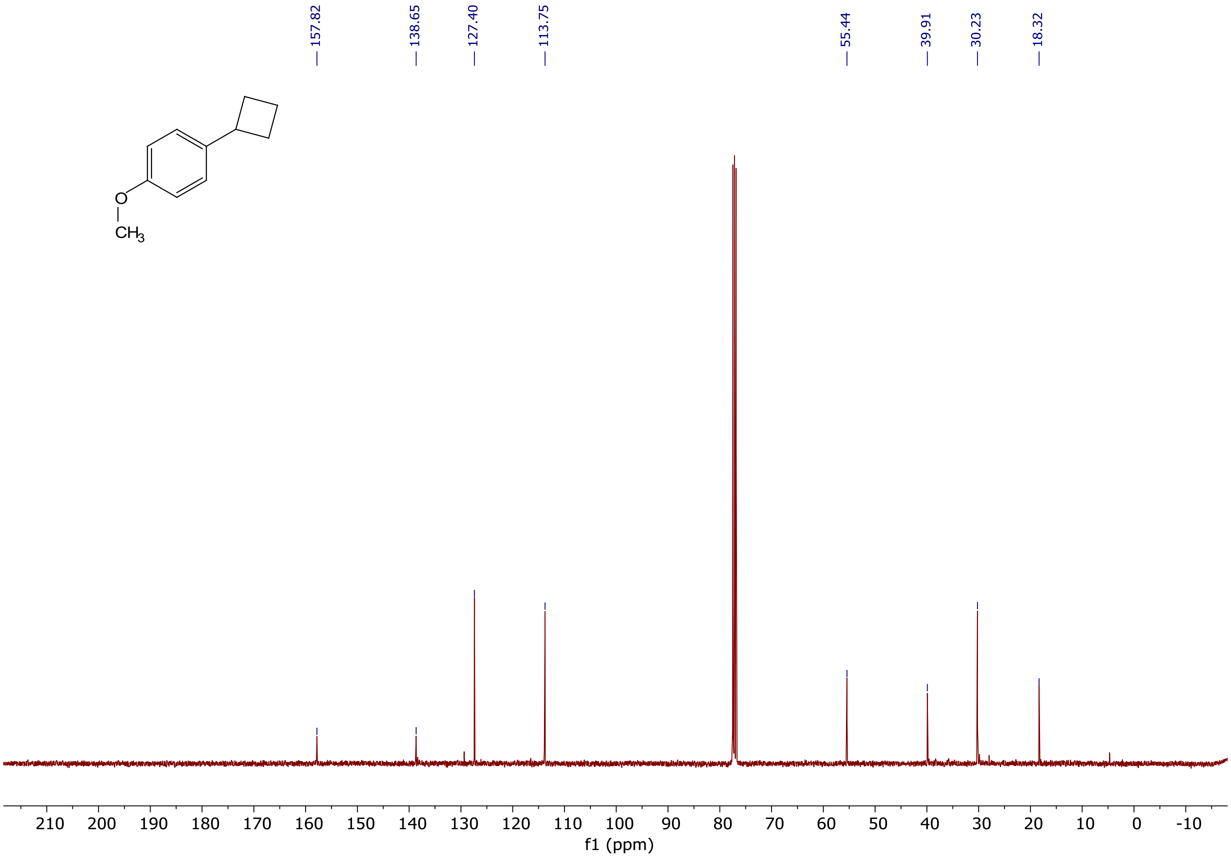
^{13}C NMR of 6e



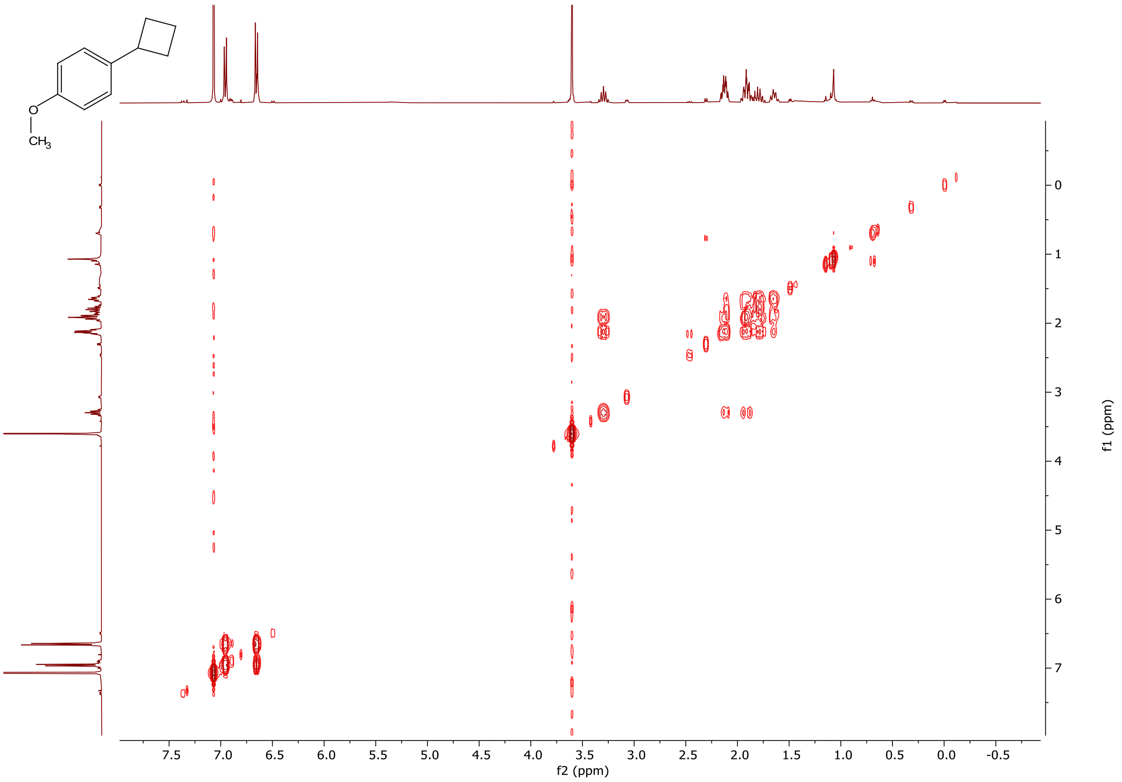
^{1}H NMR of 1-cyclobutyl-4-methoxybenzene (6f)



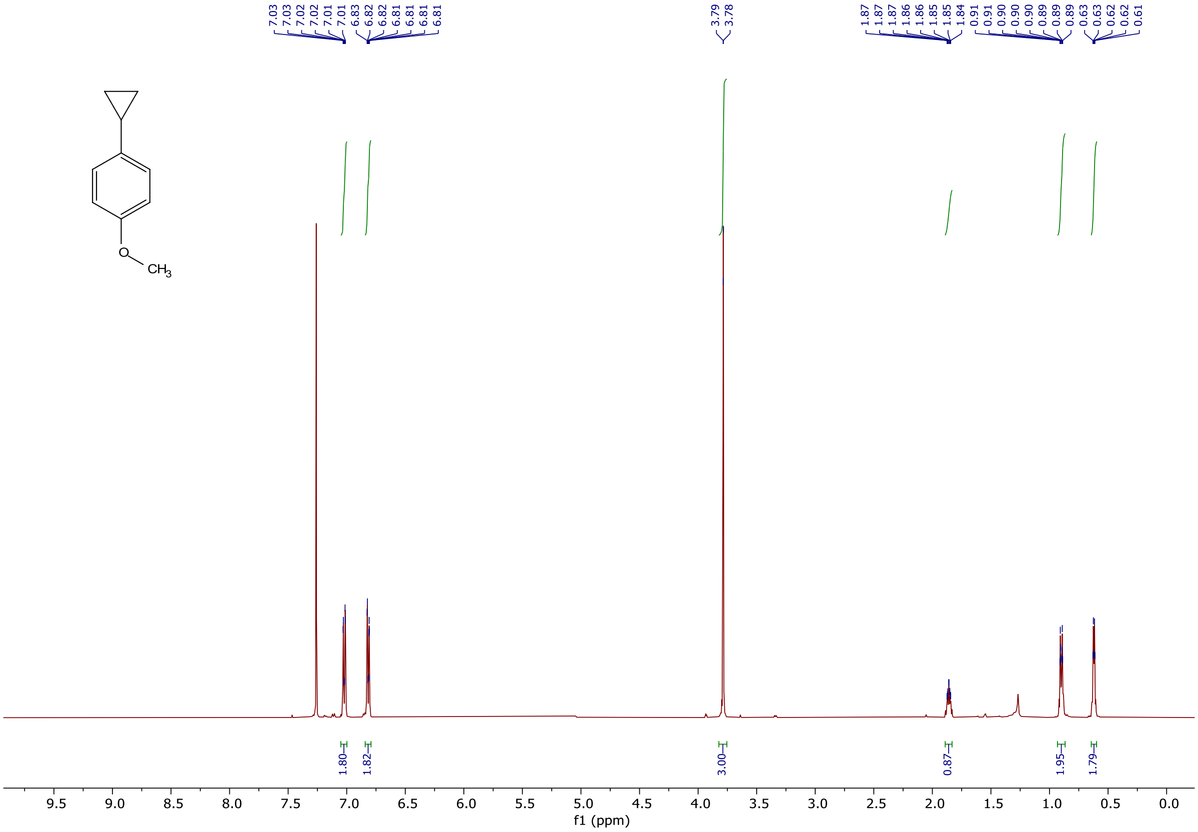
^{13}C NMR of 6f



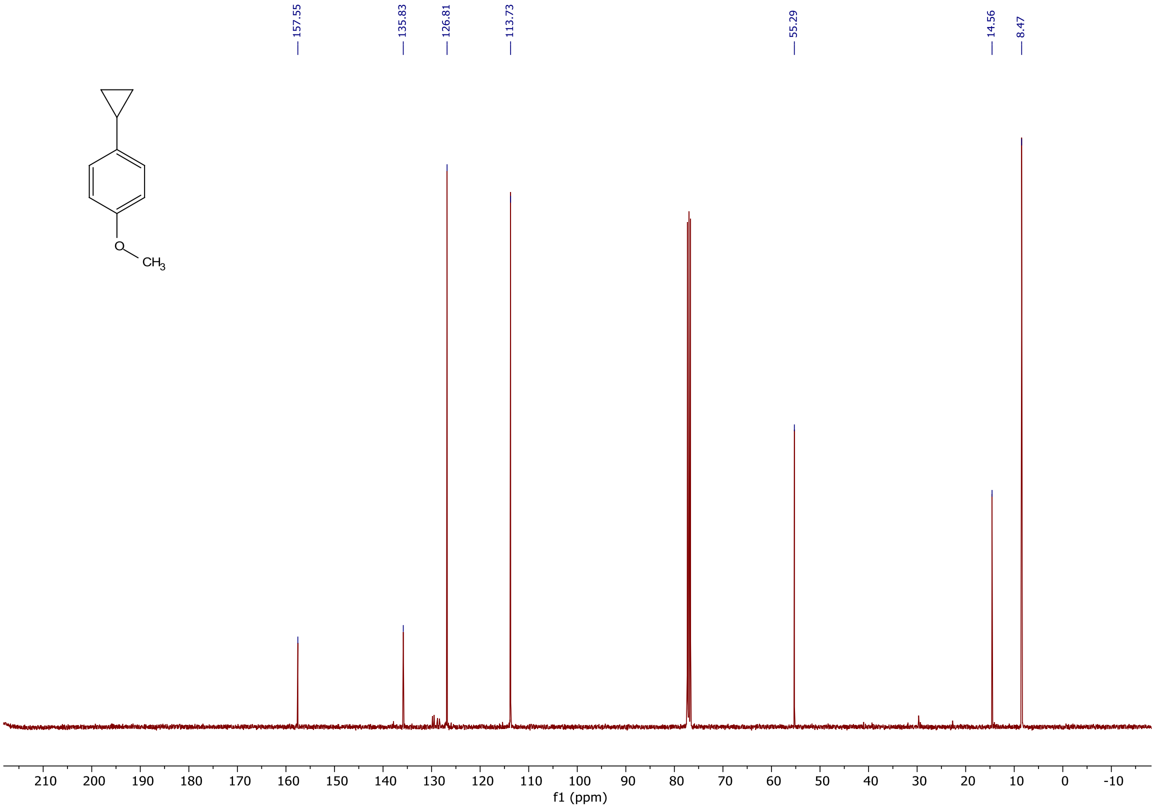
COSY of 6f



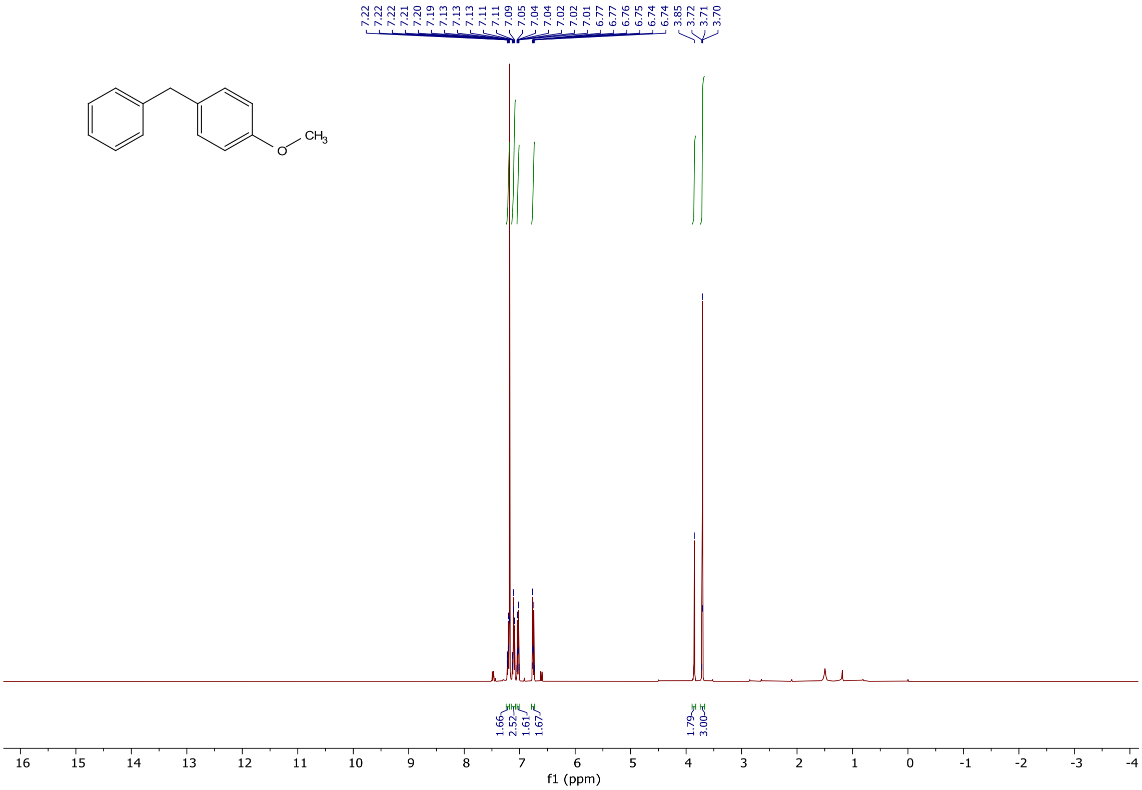
^{1}H NMR of 1-cyclopropyl-4-methoxybenzene (6g)



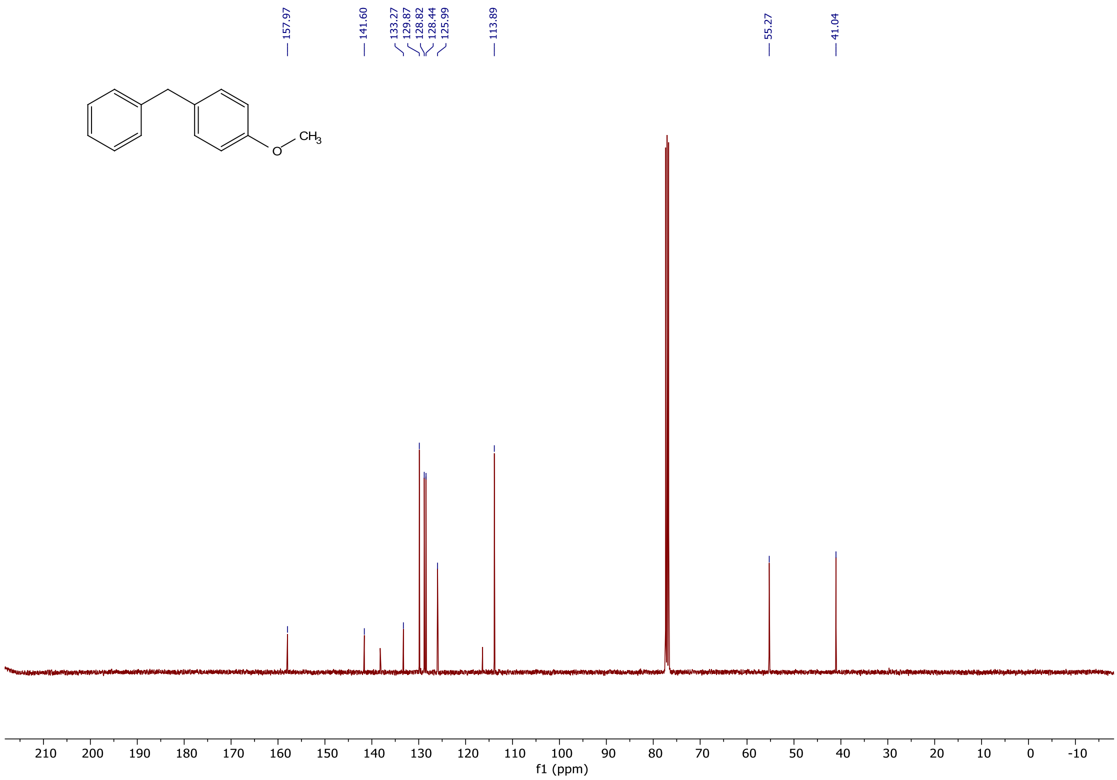
^{13}C NMR of 6g



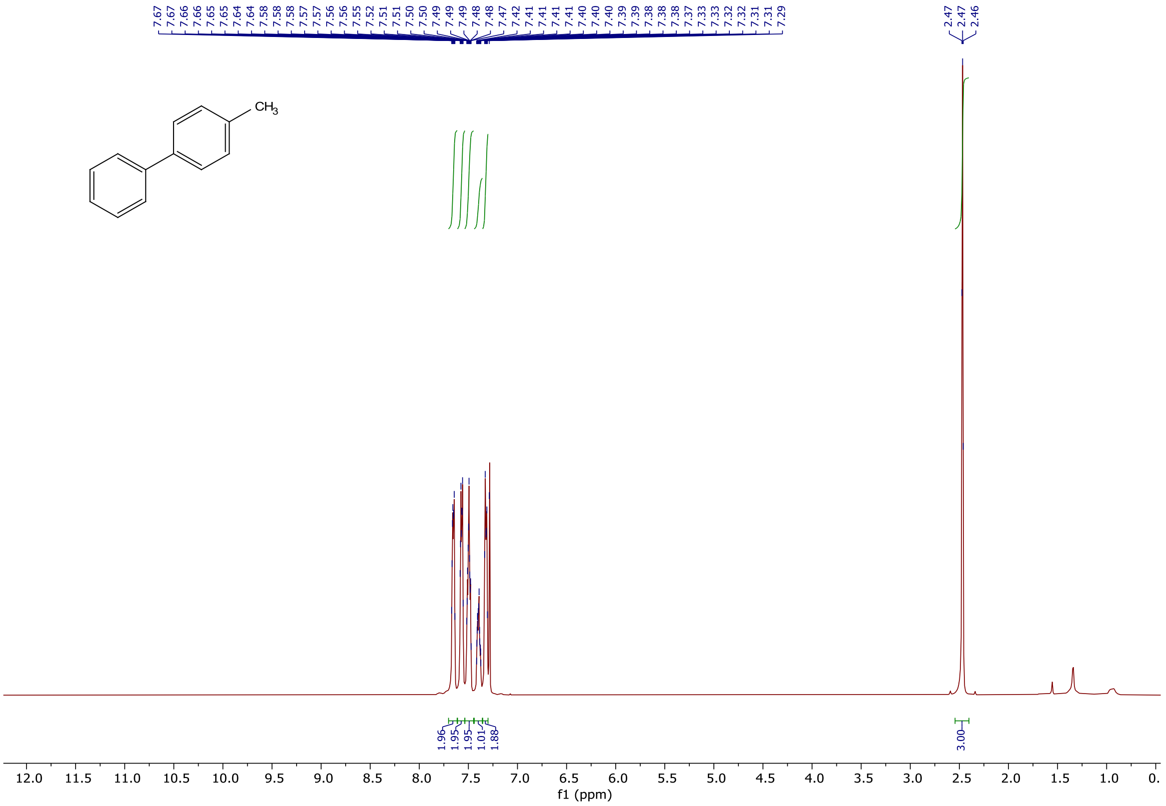
^{1}H NMR of 1-benzyl-4-methoxybenzene (6h)



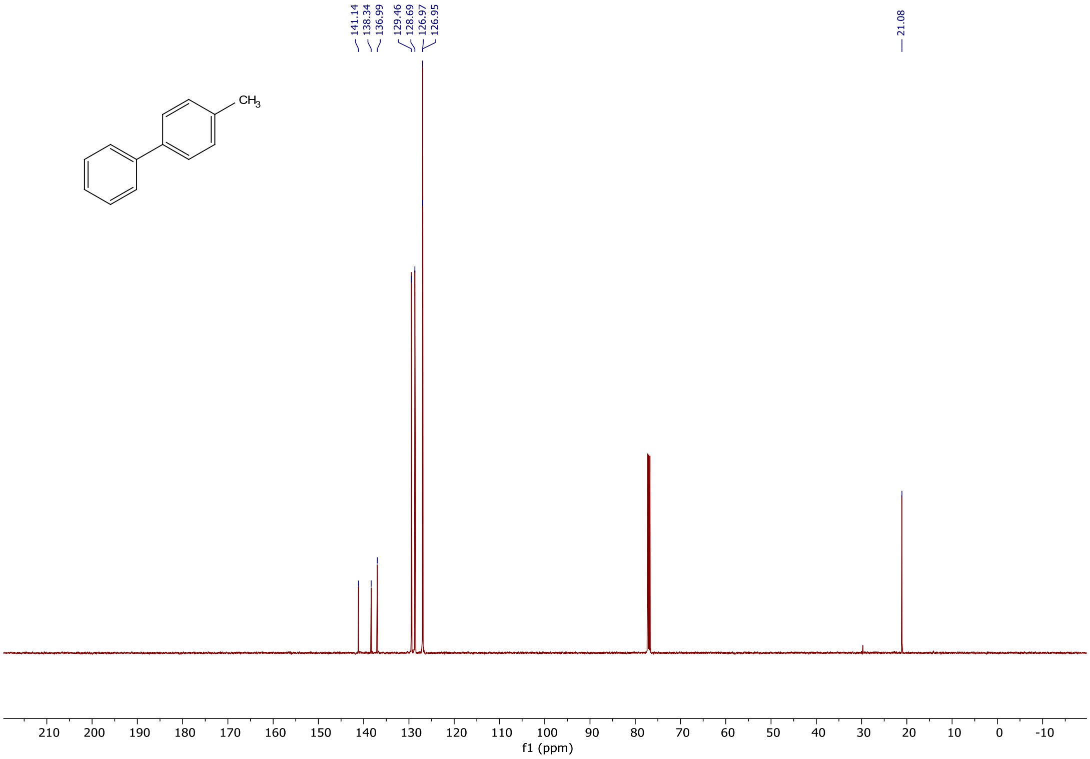
^{13}C NMR of 6h



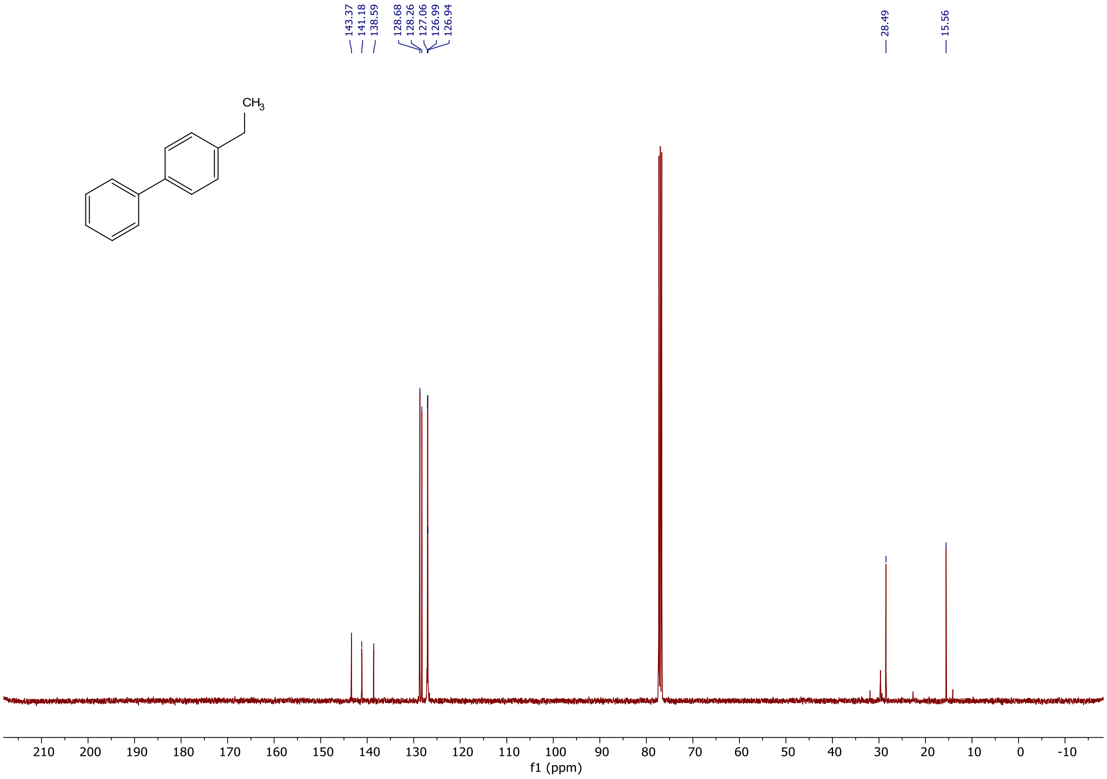
^{1}H NMR of Biphenylmethyl (6i)



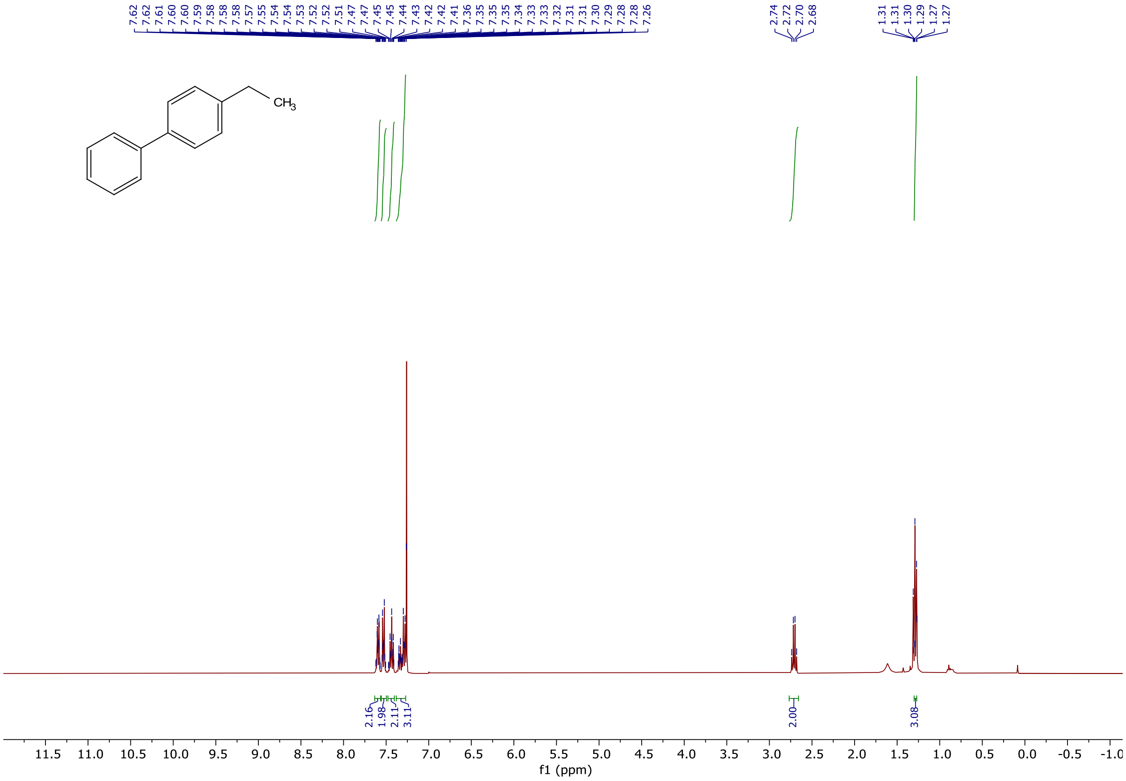
^{13}C NMR of 6i



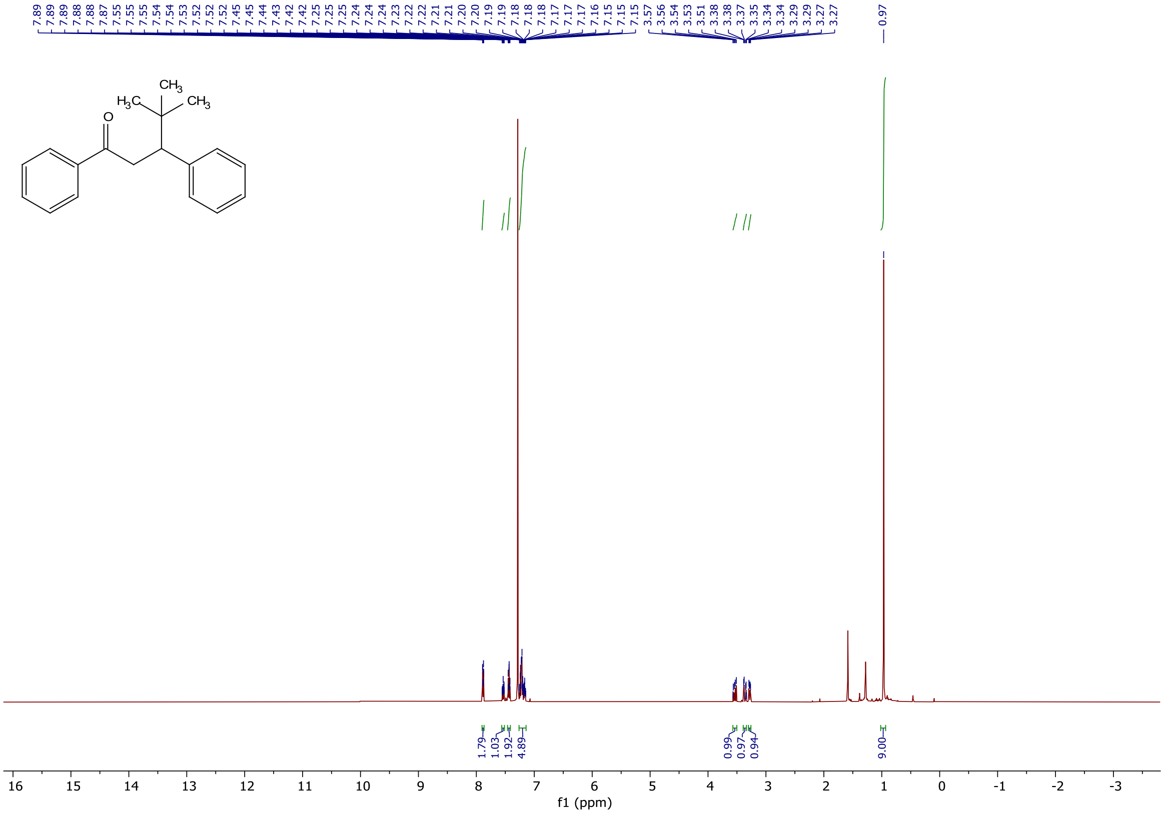
^{1}H NMR of 4-ethyl-1,1'-biphenyl (6j)



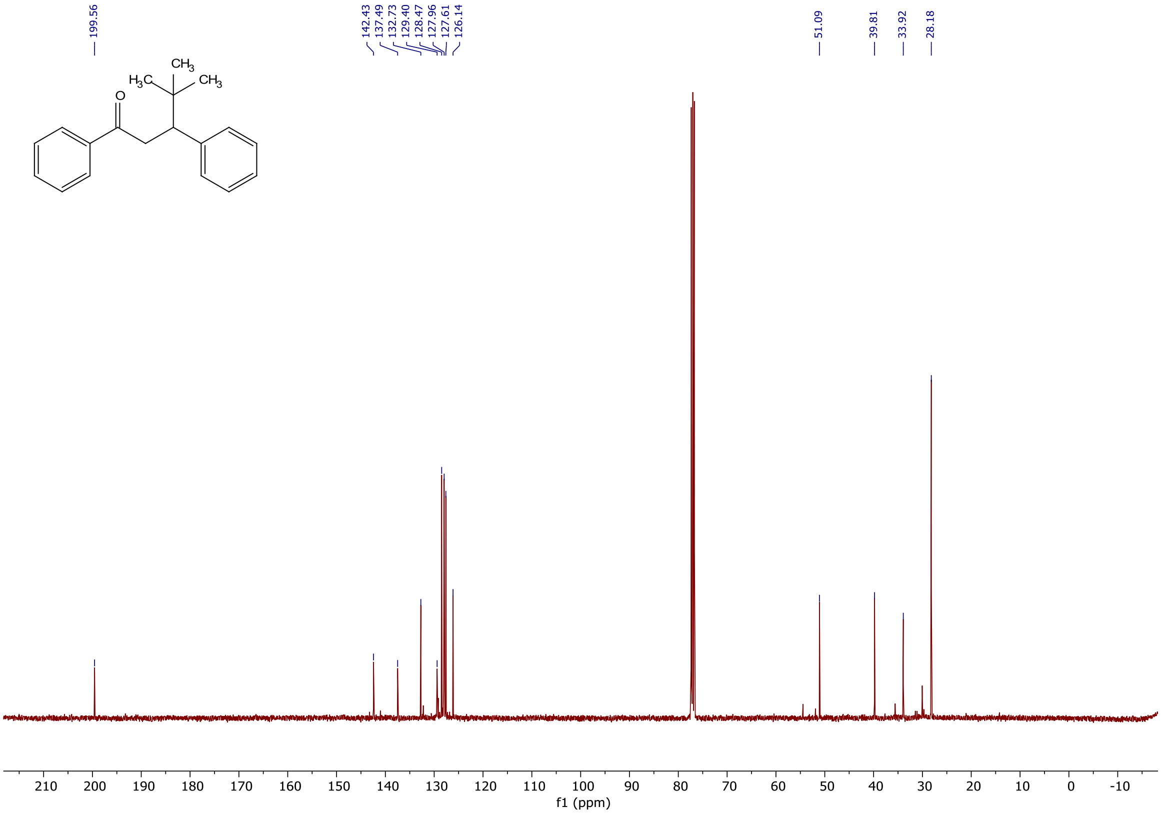
^{13}C NMR of 6j



^{1}H NMR of 4,4-dimethyl-1,3-diphenylpentan-1-one (6k)



^{13}C NMR of 6k


199.56
142.43
137.49
132.73
129.40
128.47
127.96
127.61
126.14
51.09
39.81
33.92
28.18
CH3
H3C
CH3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

COSY of 6k:


9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)