Electronic Supplementary Material (ESI) for Chemical Science.

Structural and Reactivity Insights in Mg-Zn Hybrid Chemistry: Zn-I Exchange and Pd-Catalysed Cross-Coupling Applications of Aromatic Substrates

Tobias D. Bluemke,[a] William Clegg,[b] Pablo García-Alvarez,[c] Alan R. Kennedy,[a] Konrad Koszinowski,[d] Matthew McCall,[a] Luca Russo[b] and Eva Hevia*[a]

---

[a] WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL. UK. *eva.hevia@strath.ac.uk*.

[b] School of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK.

[c] Departamento de Química Orgánica e Inorgánica-IUQOEM, Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain.
[d] Institut für Organische und Biomolekulare Chemie, Georg-August Universität Göttingen, Tammannstraße 2, 37077 Göttingen, Germany

1 GENERAL CONSIDERATIONS

All reactions were carried out with magnetic stirring and under argon or nitrogen atmosphere in glassware dried with a heat gun. Syringes and needles which were used to transfer anhydrous solvents or reagents were purged three times with argon or nitrogen prior to use. High vacuum refers to a pressure of < 1 mbar. Indicated yields refer to isolated yields of compounds estimated to be of >95% purity as determined by ^{1}H-NMR spectroscopy or capillary GC, unless otherwise stated. Solvents were dried according to the standard procedures by distillation over drying agents and then stored under inert atmosphere (argon or nitrogen) over molecular sieves (4Å). THF and hexane were continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. All studies and reactions were performed in neat THF to avoid solvent effects which might lead to different aggregation of organometallics. The prepared organometallic solutions were strictly chloride containing to avoid additional complexity arising from halogen scrambling and thus giving rise to different organometallic species/aggregation.

1.1 Content Determination of Organometallic Reagents

Organozinc- and organomagnesium reagents were titrated against I_2 in THF.[1] The amount of organolithium reagents in solution was determined according to Parquette.[2]

1.2 Chromatography

Thin layer chromatography (TLC) was performed using aluminium plates coated with SiO_2 (MERCK 60, F-254). The spots were visualized either by UV light or by using one of the typical stains followed by heating with a heat gun if necessary.

- $KMnO_4$ (3.0 g), 5 drops of conc. H_2SO_4 in water (300 mL).
- Phosphomolybdic acid (5.0 g), $Ce(SO_4)_2$ (2.0 g) and conc. H_2SO_4 (12 mL) in water (230 mL).

Flash column chromatography was performed using silica gel 60 (0.040 – 0.063 mm, 230 – 400 mesh ASTM).

---

[1] A. Krasovskiy, P. Knochel, *Synthesis* **2006**, *5*, 890.

[2] H. S. Lin, L. A. Paquette, *Synth. Commun.* **1994**, *24*, 2503.

1.3 Analytical Data

^{1}H-NMR and **^{13}C-NMR** spectra were recorded on Bruker DPX 400 and AV 500 MHz spectrometers operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C. NMR spectra are referenced on residual solvent signals. Spectra were analysed using the software package JEOL Delta (v5.0.3) and/or TOPSPIN.

Mass spectrometry: Low resolution (MS) spectra were recorded on a FINNIGAN PolarisQ instrument. Electron ionization (EI) was conducted with an electron energy of 70 eV. For the combination of gas chromatography with mass spectrometric detection, a ThermoQuest Trace GC Ultra, equipped with an AS2000 autosampler, was used.

Infrared spectra (IR) were recorded from 4000 cm^{-1} to 650 cm^{-1} on an AGILENT 5500 Series FT-IR instrument.

Melting points (mp) were determined on a BÜCHI B-545 apparatus and are uncorrected.

X-ray Crystallography. Single crystal diffraction measurements were made with Oxford Diffraction instruments and with graphite monochromated Mo radiation. Refinement to convergence was with F^2 and against all unique reflections using programs from the SHELXL suit.[3] Selected crystallographic and refinement parameters are given in Table S1 and complete data have been supplied in cif format as CCDC 1000413-1000414.

---

[3] G. M. Sheldrick. *Acta Crystallogr. Sect A*, **2008**, 64, 112.

Table S1. Selected Crystallographic Data.

	4	**7**
empirical formula	$C_{70}H_{98}MgO_{13}Zn_2$	$C_{34}H_{48}MgN_2O_5Zn$
M_r	1302.53	816.77
crystal system	tetragonal	monoclinic
space group	$P\ 4_32_12$	$P\ 2_1/c$
a [Å]	12.1808(3)	16.1212(8)
b [Å]	12.1808(3)	9.5045(6)
c [Å]	44.474(2)	24.1563(14)
β [°]		98.132(5)
V [Å^3]	6598.7(4)	3664.1(4)
Temp. [K]	150(2)	123(2)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.311	1.481
reflns measured	11087	17865
2θ(max) [°]	50.5	54.0
unique reflns	4726	7990
observed reflns	3052	4799
R_{int}	0.0504	0.0444
GooF	1.001	0.815
R [on F, obs rflns only]	0.0667	0.0384
wR [on F^2, all data]	0.1841	0.0589
Largest diff. peak/hole [eÅ^{-3}]	0.573/-0.252	0.889/-0.726

Flack	0.032(10)	

2 EXPERIMENTAL PART

2.1 Typical Procedures

Typical Procedure for the Iodine/Zinc Exchange using the *in situ* prepared zincate (tBuMgCl/$ZnCl_2$, 3:1) and subsequent cross-coupling reaction (TP1)

A Schlenk flask was charged with freshly titrated tBuMgCl solution in THF (3 mmol) and a solution of $ZnCl_2$ in THF (1M, 1.0 mmol, 1.0 mL) was added via a syringe at 0 °C. The resulting clear solution was stirred for 5 min at 0 °C before the corresponding aryl iodide (0.9-1.0 equiv.) was added. The mixture was stirred for 30 min at 0 °C before the electrophile was added, followed by the Pd-catalyst (0.9-2.5 mol%). After stirring for 2 h at 20 °C the reaction was quenched by addition of aq. HCl (2M, 5 mL), the phases separated and the aqueous phase was extracted three times with ethyl acetate. The combined organic extracts were dried with $MgSO_4$ and the solvent was removed *in vacuo.* The crude product was subjected to column-chromatographical purification (SiO_2, hexane).

Typical Procedure for the Iodine/Zinc Exchange using the *in situ* prepared zincate (tBuMgCl/$ZnCl_2$, 3:1) under Barbier conditions and subsequent cross-coupling (TP2)

A Schlenk flask was charged with an aryl iodide (3 mmol, 702 mg) which was subsequently dissolved by addition of $ZnCl_2$ solution (1M in THF, 1.0 mmol, 1.0 mL). The solution was cooled to 0 °C and freshly titrated tBuMgCl (3 mmol) was added in one portion. The mixture was stirred for 30 min at 0 °C before the electrophile (0.9-1.0 equiv.) was added, followed by the Pd-catalyst (0.9-2.5 mol%). After stirring for 2 h at 20 °C the reaction was quenched by addition of aq. HCl (2M, 5 mL) and the aqueous phase was extracted three times with ethyl acetate. The combined organic extracts were dried with $MgSO_4$ and the solvent was removed *in vacuo.* The crude product was subjected to column-chromatographical purification (SiO_2, hexane).

Synthesis of compound 4 A solution of *tert*-butylmagnesium chloride (3 mL of a 1 M solution in THF, 3 mmol) was added to a solution of $ZnCl_2$ in THF (1M, 1.0 mmol, 1.0 mL) via a syringe at 0 °C. The resulting clear solution was stirred for 15 minutes at room temperature. 2-iodoanisole (**3b**) (0.39 mL, 3 mmol) was then introduced and the resulting pale yellow solution stirred for 30 minutes at room temperature. The volatiles (including ^tBuI) were then removed *in vacuo*, then THF (6 mL) was added and the resulting solution left to stand at room temperature overnight. After 48 hours a crop of colourless crystals of [$(THF)_4MgCl_2$] and **4** was isolated. Compound **4** could also be prepared using an alternative co-complexation route by reacting *t*BuMgCl (3 mL of a 1M solution in THF, 3 mmol) with

ZntBu$_2$ (0.18 g, 1 mmol) using THF as a solvent (3 ml), which allowed the isolation of pure **4** (0.360 g, 28%) as colourless crystals. ^{1}H NMR (400.13 MHz, 298K, d$_8$-THF) δ 7.49 (6H, d, CH_{meta}), 6.93 (6H, t, CH_{para}), 6.71 (6H, t, CH_{meta*}), 6.60 (6H, t, CH_{ortho*}), 3.70 (18H, s, OCH_3), 3.62 (24H, m, OCH_2, THF), 1.77 (24H, m, OCH_2, THF). ^{13}C{^{1}H} NMR (100.62 MHz, 298K, d$_8$-THF) δ 167.5 (MeO-C_{ipso}), 150.4 (Zn-C_{ortho}), 140.2 (C_{meta}), 126.6 (C$_{para}$), 121.2 (C_{meta}), 10.3 (C_{ortho*}) 68.5 (OCH$_2$, THF), 55.4 (OCH$_3$), 26.6 (CH$_2$, THF).

Synthesis of compound 7 Compound **7** was generated *in situ* by adding Zn^{t}Bu$_2$ (0.18 g, 1 mmol in 5 mL THF) to a solution of *tert*-butylmagnesium chloride (1 M solution in THF, 1 mL, 1 mmol), and the resulting solution stirred for 1 hour at room temperature. To this was added 2-iodobenzonitrile (**3i**) (0.687 g, 3 mmol) and the resulting deep red solution stirred for 24 hours at room temperature. The solvent and volatiles were removed *in vacuo*, THF (4 mL) added and the resulting red solution placed in the freezer (-30^{o}C) for four days, from which a crop of colourless crystals of **7** (0.124 g, 16% yield) were obtained. **^{1}H NMR (400**.13 MHz, 298K, d$_8$-THF) δ 8.08 (2H, d, CH_{meta}), 7.44 (2H, d, CH_{ortho*}), 7.34 (2H, t, CH_{para}), 7.09 (2H, t, CH_{meta*}), 3.62 (30H, m, OCH_2, THF), 1.77 (30H, m, OCH_2, THF). **^{13}C{^{1}H} NMR** (100.62 MHz, 298K, d$_8$-THF) δ 172.4 (Zn-C_{ipso}), 141.6 (C_{meta}), 132.1 (C_{ortho*}), 131.0 (C$_{para}$), 125.9 (C_{meta*}), 124.7 (C_{ipso}) 120.6 (C-Zn), 68.5 (OCH$_2$, THF), 26.6 (CH$_2$, THF).

3 PREPARATION AND NMR SPECTRA OF ORGANOMETALLICS AND SOLUTIONS

3.1 $ZnCl_2$ solution (1M IN THF)

The solution was prepared by drying $ZnCl_2$ (100 mmol, 136 g) in a *Schlenk*-flask under vacuum at 140 °C for 5 h (dry stirring). After cooling, 100 mL dry THF were added and stirring was continued until the salt was dissolved. If a suspension is obtained after 24 h of stirring, the $ZnCl_2$ contains ZnO and $Zn(OH)_2$. Such suspensions should not be used. Best results were obtained using $ZnCl_2$ from MERCK.

3.2 iPrMgCl in THF

iPrMgCl in THF was prepared in a dried Schlenk flask starting from iPrCl (20 mmol) and Mg (40 mmol) in THF (20 mL). The reaction was followed easily with no deuterium NMR spectroscopy. Spectra are referenced on the downfield THF resonance (3.62 ppm). The NMR spectra obtained for these mixtures are identical to commercially available iPrMgCl solutions in THF.

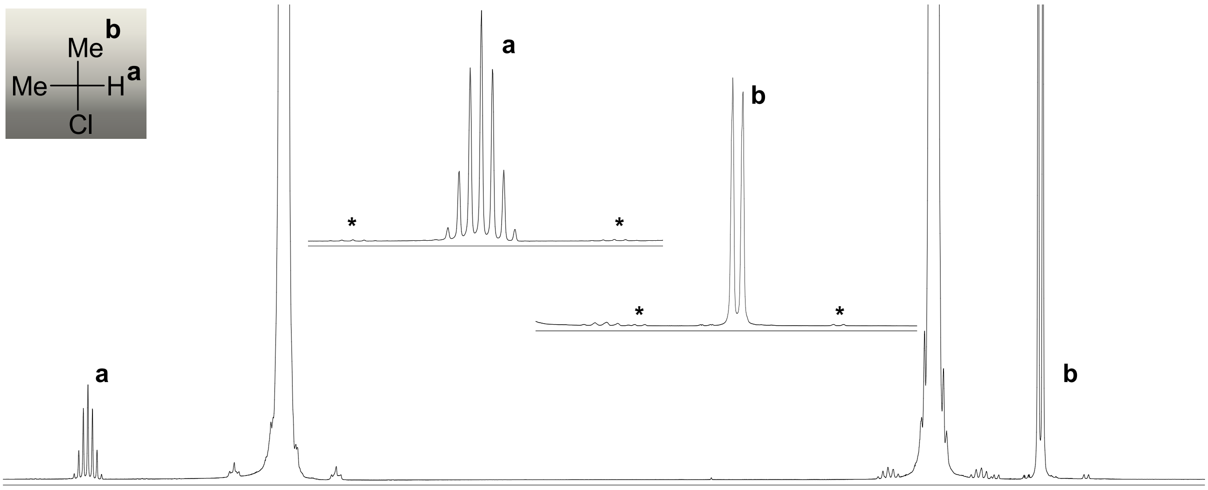


Figure S 1. No deuterium ^1H NMR (500 MHz) of iPrCl.

^{1}H NMR (500 MHz, THF, 27 °C) δ/ppm = 4.18 (sept, J_{HH} = 6.6 Hz, $^1J_{CH}$ = 151.4 Hz, 1H, **a**), 3.62 (THF), 1.78 (THF), 1.47 (d, J_{HH} = 6.6 Hz; J_{CH} = 127.8 Hz, 9H, **b**).

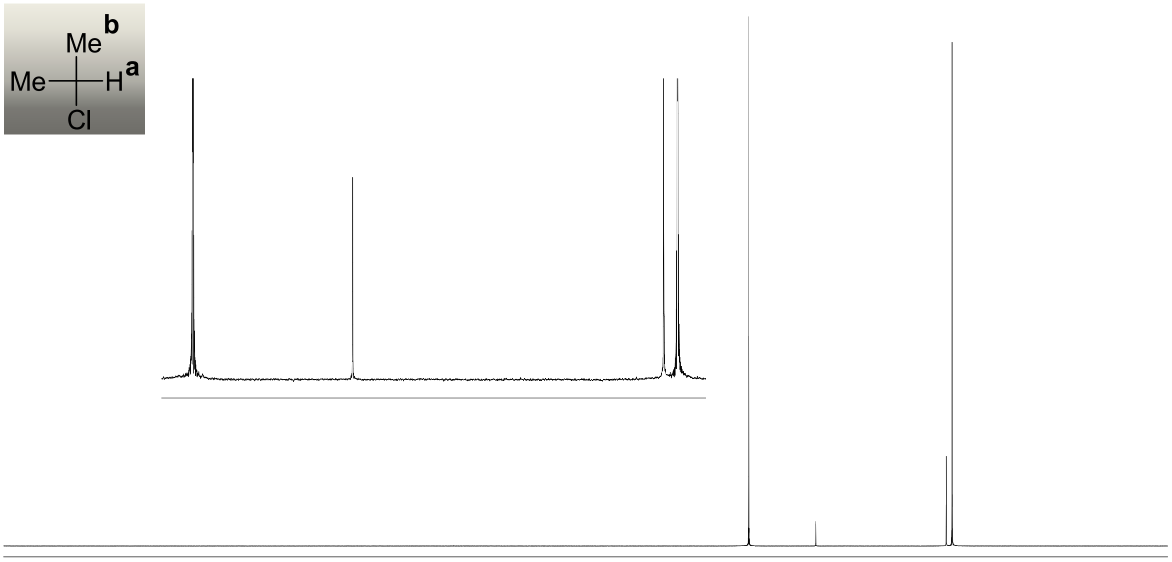


Figure S 2. No deuterium ^{13}C NMR (500 MHz) of iPrCl.

^{13}C NMR (500 MHz, THF, 27 °C) δ/ppm = 68.0 (THF), 54.3, 27.4, 26.2 (THF).

The ^{13}C-H coupling (J = 151 Hz) constant determined from the satellites observed in the ^{1}H NMR is in excellent agreement with prior determined values for iPrCl.[4]

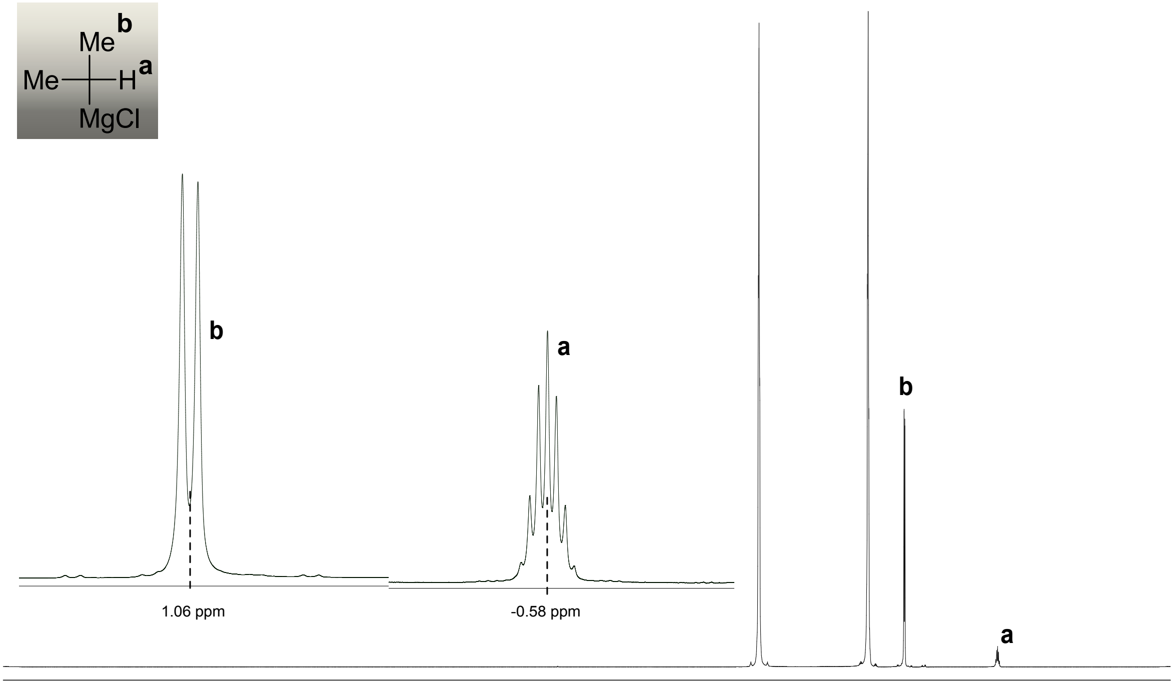


Figure S 3. No deuterium ^{1}H NMR of iPrMgCl in THF (c ≈ 1.75M).

^{1}H-NMR (500 MHz, THF, 27 °C): 3.62 (THF), 1.70 (THF), 1.06 (d, $^{3}J_{HH}$ = 7.8 Hz, $^{1}J_{CH}$ = 119.9 Hz, 6H, **b**), -0.58 (sept, $^{3}J_{HH}$ = 7.8 Hz, $^{1}J_{CH}$ = 107.1 Hz, 1H, **a**).

---

[4] E. R. Malinowski, *J. Am. Chem. Soc.* **1961**, *83*, 4479–4480.

Figure S 4. No deuterium ^{13}C NMR of iPrMgCl in THF (c ≈ 1.75M).

^{13}C-NMR (125 MHz, THF, 27 °C): 68.0 (THF), 25.3 (THF), 25.2 (CH_3, **b**), 8.28 (C-Mg, **a**).

3.3 ^{t}BuMgCl in THF

No deuterium ^1H and ^{13}C spectra of commercially available tBuMgCl (1M in THF) were recorded. Spectra are referenced on the downfield THF resonance (3.62/68.1) ppm. Two distinct species are detected in both NMR channels suggesting the presence of two different magnesium species, or aggregates, in solution.

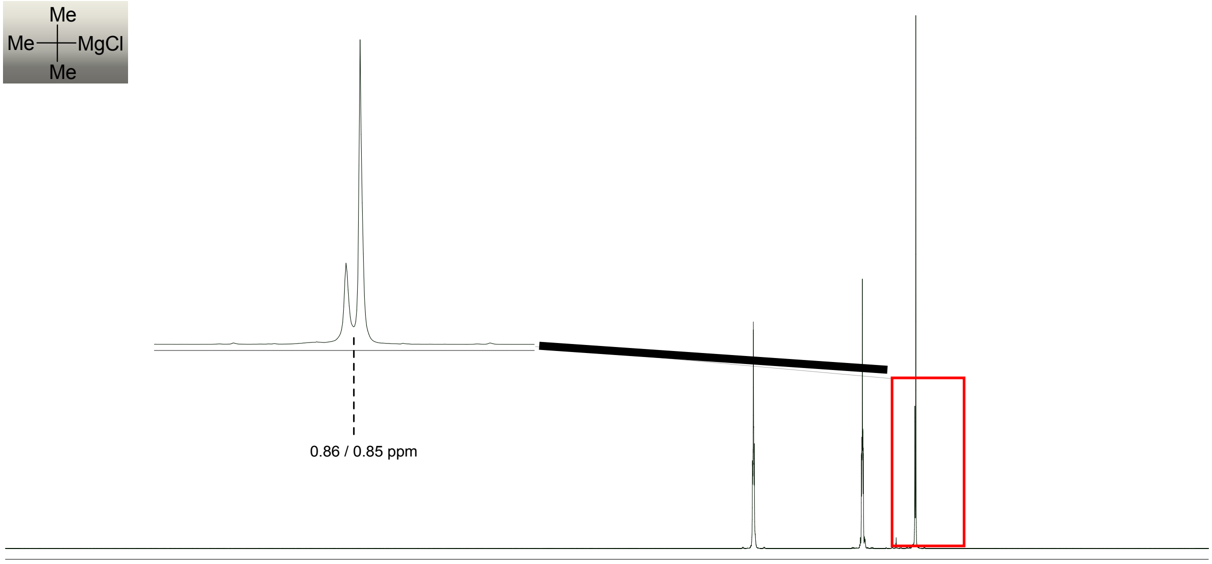


Figure S 5. ^1H NMR of commercially available tBuMgCl solution in THF/d^8-THF (c ≈ 0.75M) showing two different magnesium species or aggregates.

^{1}H-NMR (500 MHz, THF-d^8, 27 °C): 3.62 (THF), 1.76 (THF), 0.86 (s, J_{CH} = 119.7 Hz), 0.85 (s, J_{CH} = 120.2 Hz).

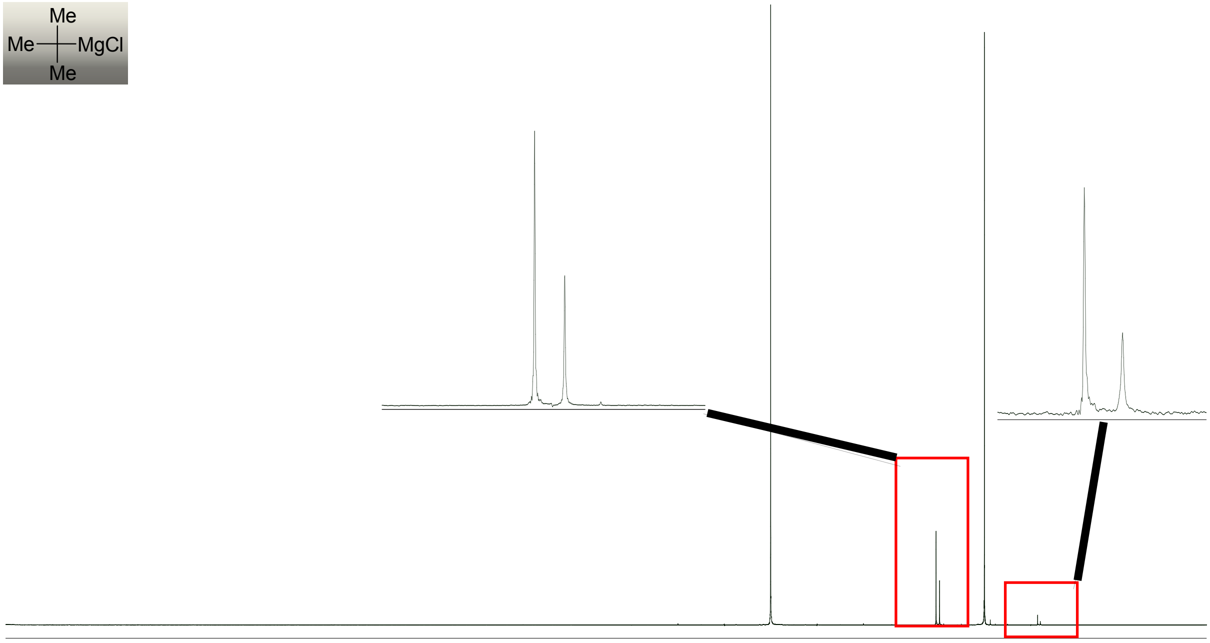


Figure S 6. No deuterium ^{13}C NMR of commercially available tBuMgCl solution in THF (c ≈ 0.75M) showing two different magnesium species or aggregates.

^{13}C-NMR (125 MHz, THF, 27 °C): 68.0 (THF) 35.5, 34.8, 26.0 (THF), 15.4 (C-Mg), 14.8 (C-Mg).

3.4 *t*Bu$_2$Zn in THF

Salt-free *t*Bu$_2$Zn was obtained by sublimation according to a modified literature procedure.[5] A dry Schlenk flask under argon atmosphere was charged with ZnCl$_2$ (2.05 g, 15 mmol) which was subsequently dissolved in diethyl ether (30 mL). Freshly titrated tBuLi (1.56M in hexane, 19.2 mL, 30 mmol) was added with a syringe at 0 °C. The resulting suspension was stirred for 30 min at 20 °C. The precipitated salts were filtered off and the filtrate was concentrated under vacuum. The concentrated ethereal solution was transferred to a sublimer with cooling finger and the remaining solvent was evaporated under vacuum. The solid residue was sublimed under high vacuum at 20 °C. The cooling finger temperature was kept at -50 °C (ethanol/dry ice) throughout the process. The freshly sublimed, salt free, tBu$_2$Zn (1.4 g, 53%) was collected in a glovebox and stored as 1M solution in THF under argon, in the dark. No deuterium ^{1}H and ^{13}C NMR spectra were recorded. Spectra are referenced on the downfield THF resonance (3.62 ppm for ^{1}H NMR and 68.03 ppm for ^{13}C NMR). The carbon-proton coupling ($^1J_{C-H}$) is estimated from the resolved ^{13}C satellites observed in the ^{1}H channel.

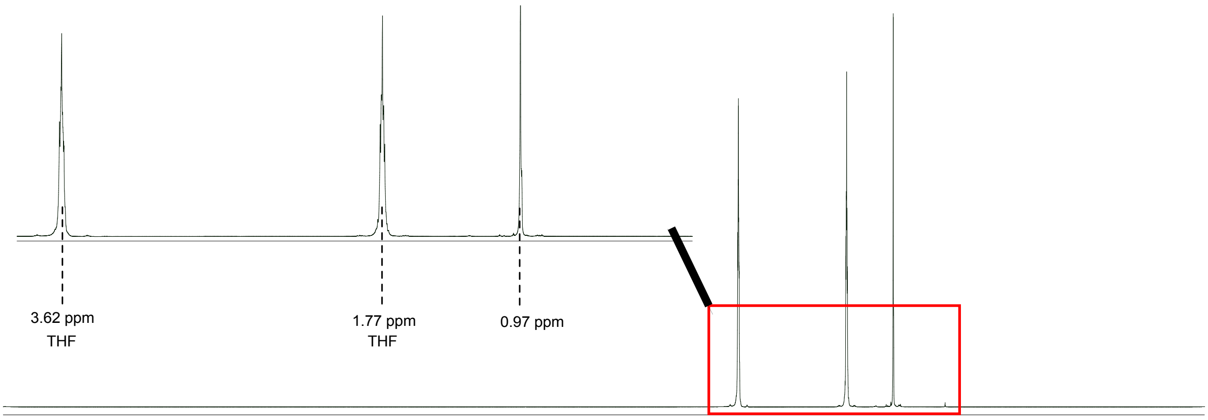


Figure S7. "No deuterium" 500 MHz ^{1}H-NMR of a ca. 1M solution of salt-free tBu$_2$Zn in THF. Impurity at 0.08 ppm is resulting from grease contamination.

---

[5] P. C. Andrikopoulos, D. R. Armstrong, H. R. L. Barley, W. Clegg, S. H. Dale, E. Hevia, G. W. Honeyman, A. R. Kennedy, R. E. Mulvey, *J. Am. Chem. Soc*, **2005**, *127*, 6184-6185.

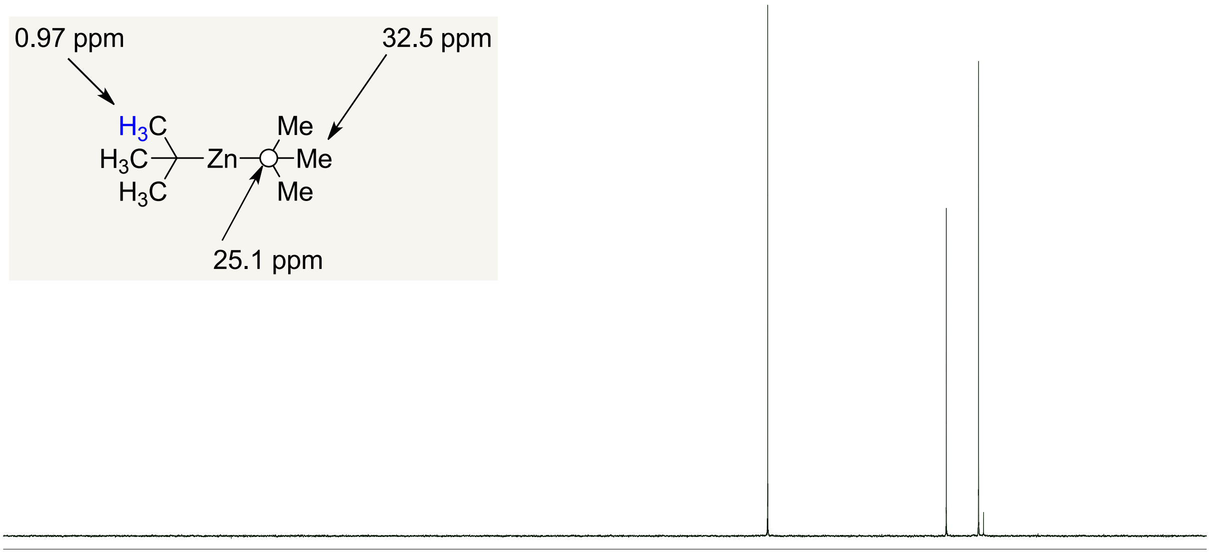


Figure S8. “No deuterium” ^{13}C NMR of salt free tBu_2Zn in THF (c ≈ 1M).

^{1}**H-NMR** (500 MHz, THF, 27 °C): 3.62 (THF), 1.77 (THF), 0.97 (tBu, $^1J_{C\text{-}H}$ = 122.1 Hz).

^{13}**C-NMR** (125 MHz, THF, 27 °C): 68.0 (THF), 32.5 (tBu), 26.1 (THF), 25.1 (C-Zn).

3.5 tBu$_2$Zn + 2 MgCl$_2$

A solution of *t*Bu$_2$Zn (1M in THF, 1 mmol, 1 mL) was combined with 2 molar equivalents of anhydrous MgCl$_2$ (2 mmol, 190 mg). The mixture was stirred (24 h, 20 °C) until the MgCl$_2$ had dissolved. This mixture did not show significant iodine/zinc exchange.

3.6 tBuMgCl + $ZnCl_2$ (1:1)

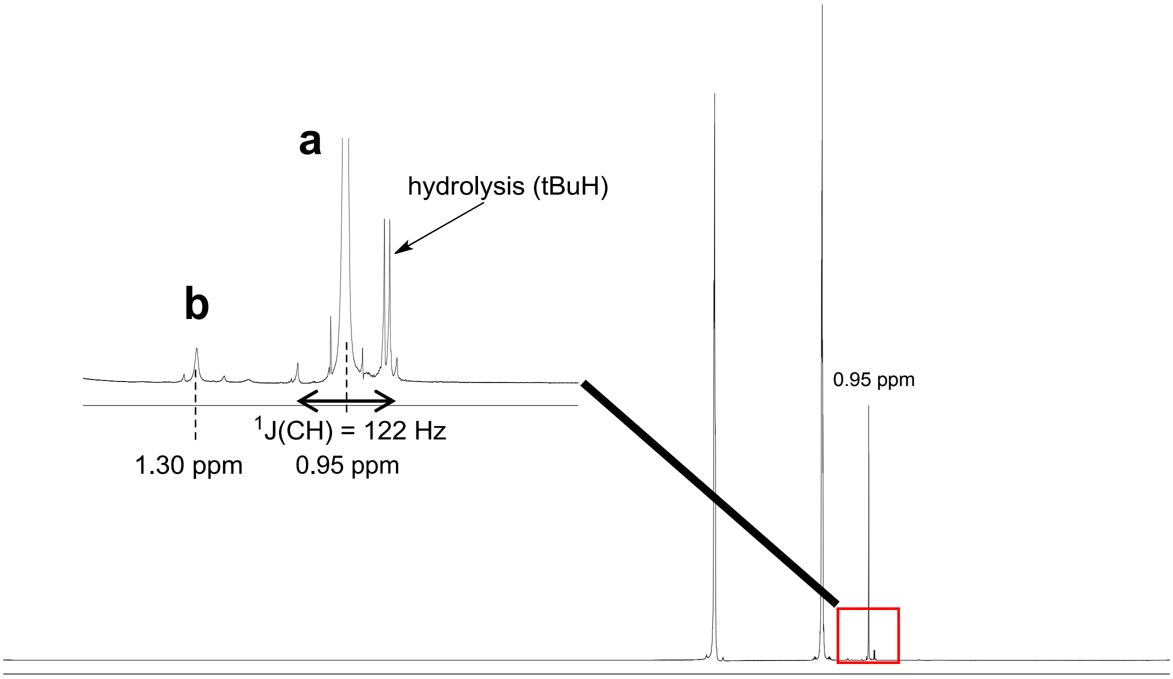


Figure S 9. “No deuterium” 500 MHz ^{1}H-NMR of a 1:1 mixture of tBuMgCl and $ZnCl_2$ in THF.

^{1}H-NMR (500 MHz, THF, 27 °C): 3.62 (THF), 1.73 (THF), 1.30 (b), 0.95 (tBu, $^1J_{C\text{-}H}$ = 122.1 Hz), 0.88 (d, $^3J_{HH}$ = 6.6 Hz, tBuH).

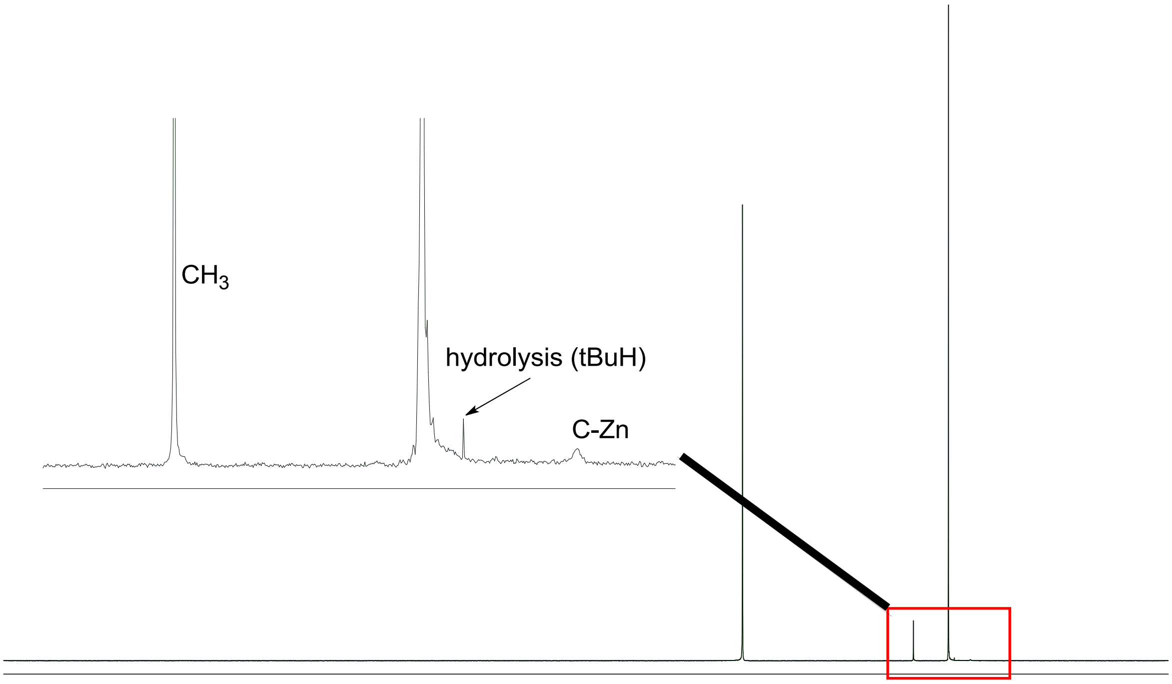


Figure S 10. “No deuterium” 500 MHz ^{13}C-NMR of a 1:1 mixture of tBuMgCl and $ZnCl_2$ in THF.

^{13}C-NMR (125 MHz, THF, 27 °C): 68.7 (THF), 33.5 (tBu), 26.3 (THF), 25.1 (tBuH), 21.8 (C-Zn).

3.7 *t*BuMgCl + $ZnCl_2$ (3:1)

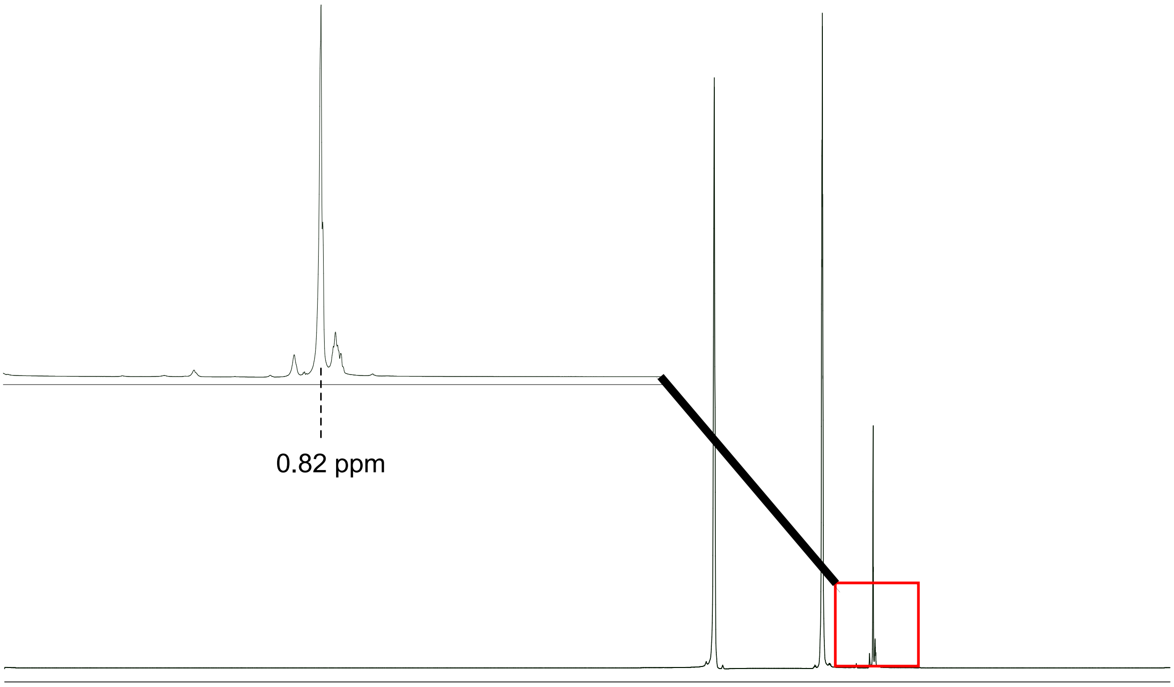


Figure S 11. “No deuterium” 500 MHz ^{1}H-NMR of a 3:1 mixture of tBuMgCl and $ZnCl_2$ in THF.

^{1}H-NMR (500 MHz, THF, 27 °C): 3.62 (THF), 1.71 (THF), 0.88, 0.82 ($^1J_{CH}$ = 119.9 Hz), 0.80.

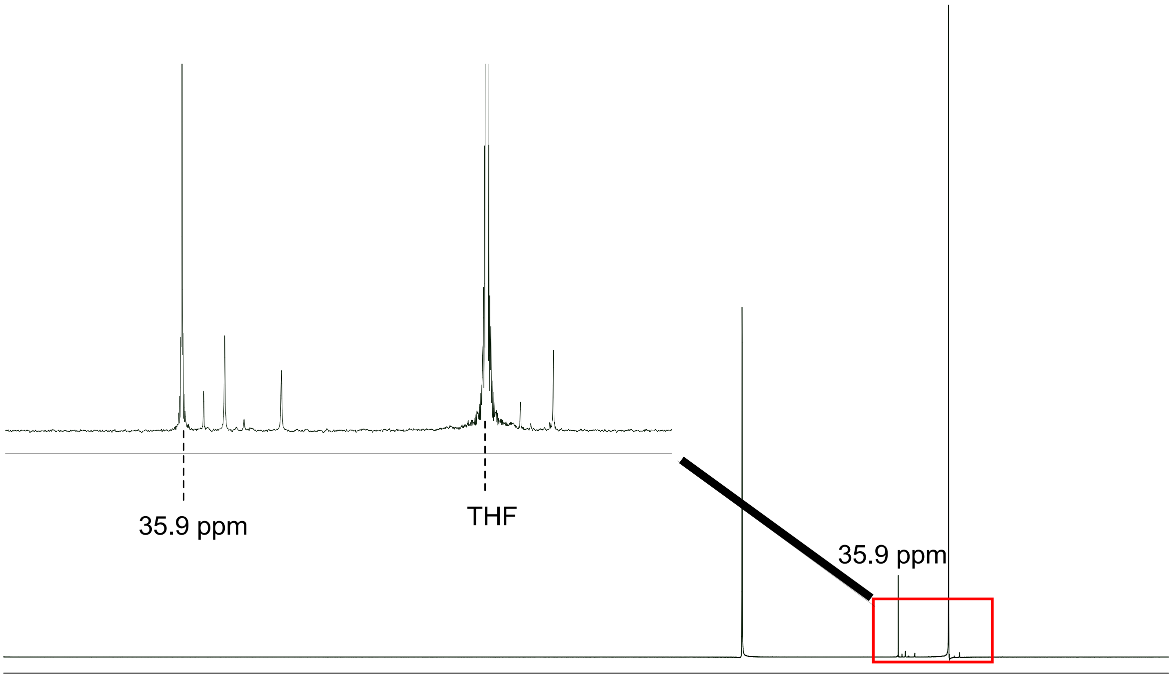


Figure S 12. “No deuterium” 500 MHz ^{13}C-NMR of a 3:1 mixture of *t*BuMgCl and $ZnCl_2$ in THF.

^{13}C-NMR (500 MHz, THF, 27 °C): 68.0 (THF), 35.9, 35.2 (RMg), 34.4 (RMg), 32.5, 25.6 (THF), 24.8, 23.4, 15.0 (C-Mg), 14.5 (C-Mg).

3.8 tBuMgCl + $ZnCl_2$ (4:1)

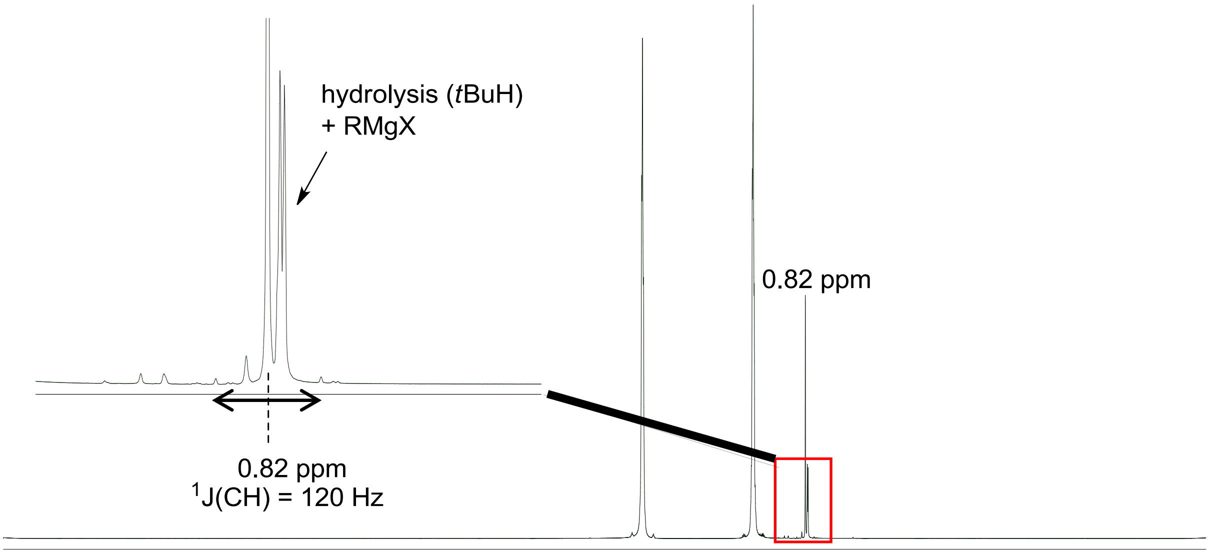


Figure S 13. "No deuterium" 500 MHz ^{1}H-NMR of a 4:1 mixture of *t*BuMgCl and $ZnCl_2$ in THF.

^{1}H-NMR (500 MHz, THF, 27 °C): 3.62 (THF), 1.72 (THF), 1.28, 1.18, 1.11, 0.88, 0.82 (*J* = 119.7 Hz), 0.79 (d, *J* = 6.6 Hz, tBuH).

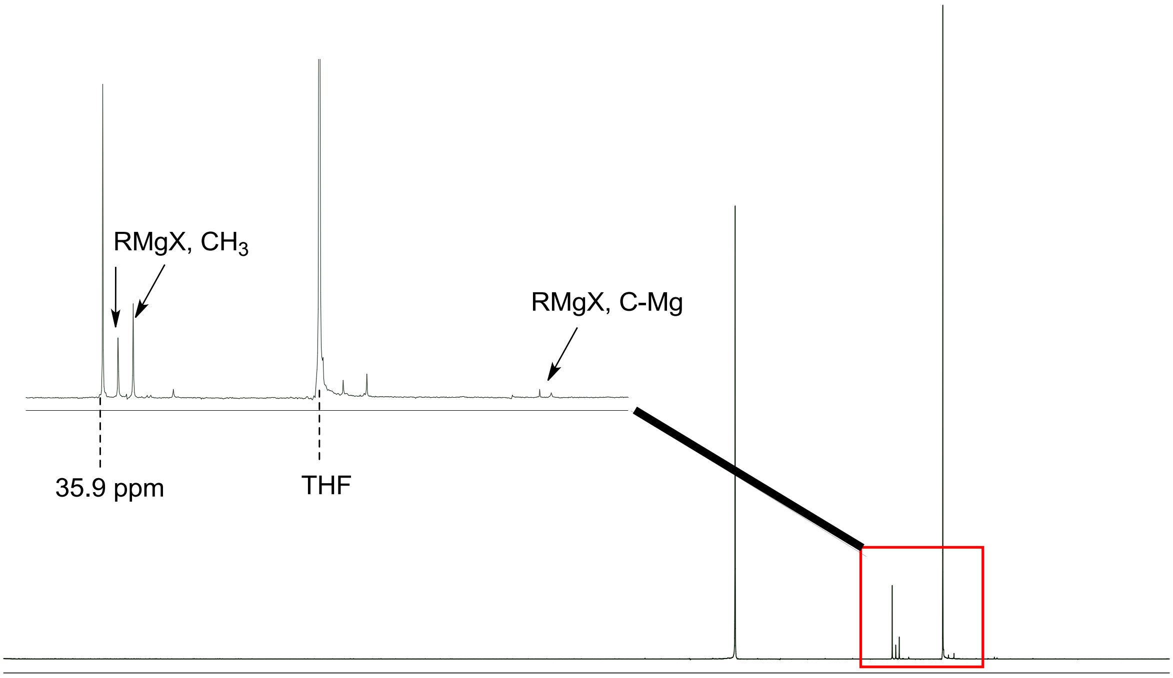


Figure S 14. "No deuterium" 500 MHz ^{13}C-NMR of a 4:1 mixture of *t*BuMgCl and $ZnCl_2$ in THF.

^{1}H-NMR (500 MHz, THF, 27 °C): 68.0 (THF), 35.9, 35.2, 34.5, 32.6, 25.6 (THF), 24.5, 23.3, 15.0 (C-Mg), 14.5 (C-Mg).

ESI MASS SPECTROMETRY

Sample solutions of $c \approx 25$ mm were continuously administered into the ESI source of an HCT quadrupole ion trap mass spectrometer (Bruker Daltonik) by a step motor-driven gas-tight syringe (flow rate: 0.5 mL h^{-1}). Similar to related previous experiments,[6] for the other reference, we do not use brackets the ESI source was operated with N_2 as sheath and drying gas (0.7 bar backing pressure and 5 L min^{-1} flow rate, respectively) at an ESI voltage of 3000 V. To minimize decomposition reactions during the ESI process, mild conditions similar to those reported previously were applied (60 °C drying gas temperature and low potential differences along the path of the ions).[5] The helium-filled quadrupole ion trap (estimated pressure p(He) ≈ 2 mTorr) was typically operated at a trap drive of 40. This medium value ensures that all ions of the probed mass range of $m/z = 50 - 1000$ were detected in good signal intensity. In gas-phase fragmentation (CID, collision-induced dissociation) experiments, the mass-selected ions (isolation widths of 1 – 8 amu) were subjected to excitation voltages with amplitudes of V_{exc} and allowed to collide with the He gas. Only fragment ions with m/z values above the instrument's cut-off (27% of the m/z ratios of the parent ion) could be efficiently detected. Peak assignments given are based on the measured m/z values, the observed isotope patterns, and the outcome of the gas-phase fragmentation reactions. Simulations of isotope patterns were performed with the CompassIsotopePattern software (Bruker Daltonik).

3.9 Comparison of *in situ* formed and crystalline zincate 2

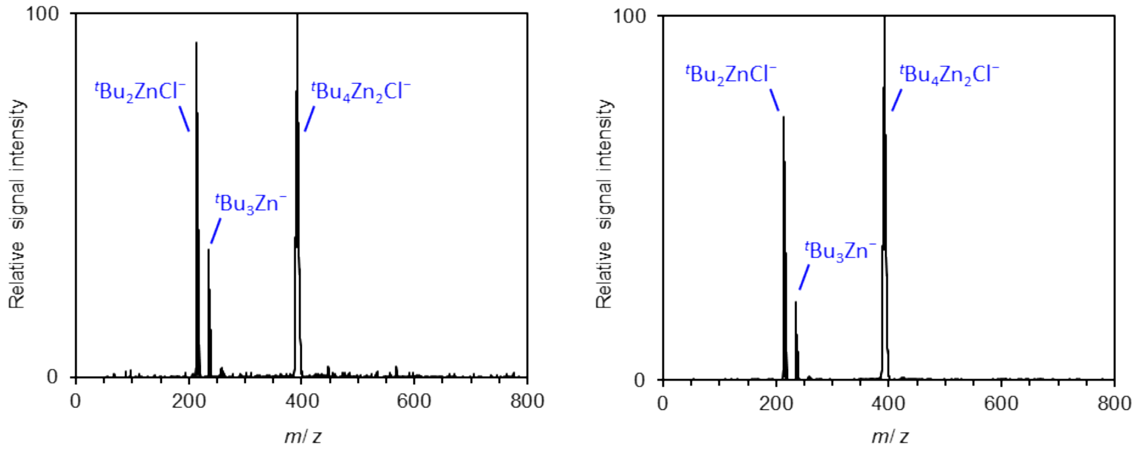


Figure S 15. Negative-ion mode ESI mass-spectrum of a mixture of left: in situ tBuMgCl/$ZnCl_2$ (3:1) and right: preformed [$\{Mg_2Cl_3(THF)_6\}^+\{Zn\textit{t}Bu_3\}^-$] (2) dissolved in THF ($c \approx 25$ mm).

---

[6] a) Koszinowski, K. *J. Am. Chem. Soc*. **2010**, *132*, 6032. b) Putau, A.; Koszinowski, K. *Organometallics* **2010**, *29*, 3593; addition/correction: *Organometallics* **2010**, *29*, 6841. c) Fleckenstein, J. E.; Koszinowski, K. *Organometallics* **2011**, *30*, 5018.

3.10 Equilibrium shift to {*t*Bu$_3$Zn$^-$} upon addition of a fourth eq. of *t*BuMgCl

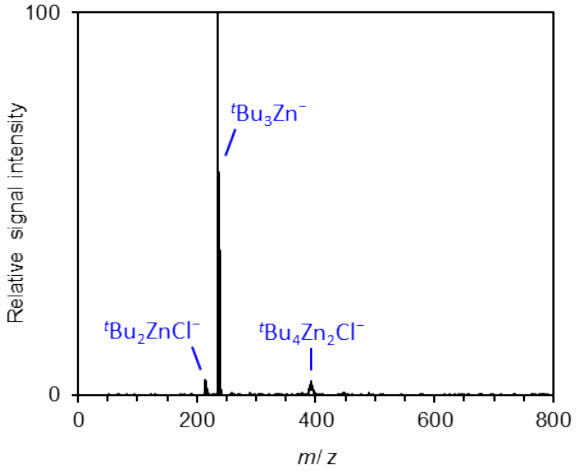


Figure S 16. Negative-ion mode ESI mass-spectrum of a 4:1 mixture of *t*BuMgCl and ZnCl$_2$ in THF (*c* ≈ 30 mm).

3.11 Measured and simulated isotope patterns for assigned zincate complexes

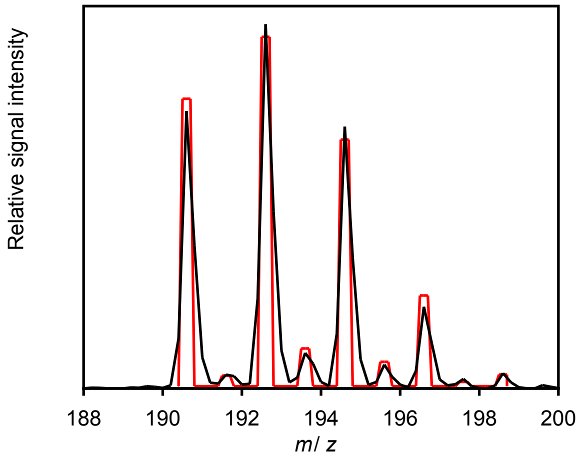


Figure S 17. Measured (black) and simulated (red) isotope pattern of *t*BuZnCl$_2^-$.

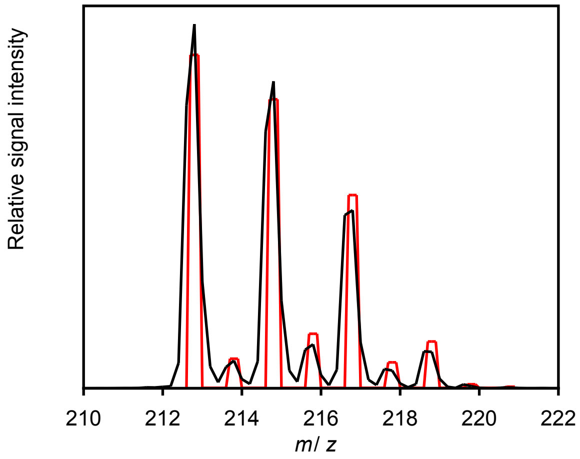


Figure S 18. Measured (black) and simulated (red) isotope pattern of *t*Bu$_2$ZnCl$^-$.

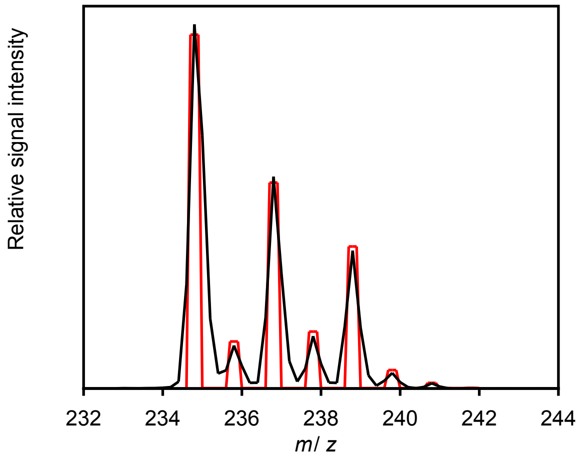


Figure S 19. Measured (black) and simulated (red) isotope pattern of *t*Bu$_3$Zn$^-$.

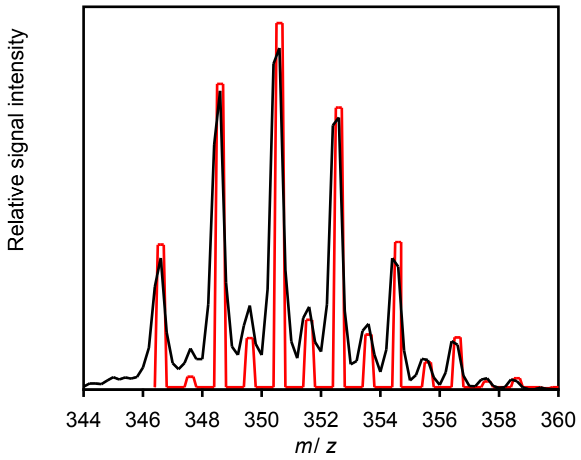


Figure S 20. Measured (black) and simulated (red) isotope pattern of $t\mathrm{Bu}_2\mathrm{Zn}_2\mathrm{Cl}_3^-$.

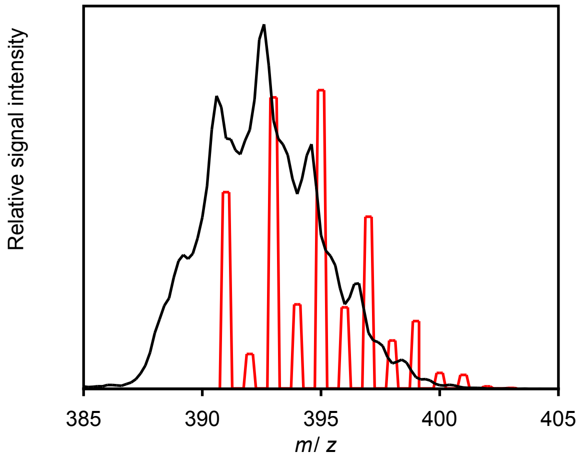


Figure S 21. Measured (black) and simulated (red) isotope pattern of $t\mathrm{Bu}_4\mathrm{Zn}_2\mathrm{Cl}^-$. The poor agreement between measured and simulated isotope pattern presumably results from a particularly low stability of $^t\mathrm{Bu}_4\mathrm{Zn}_2\mathrm{Cl}^-$ and its partial decomposition during the *m*/*z* scan. The poor resolution consistently observed only for this ion also points to its spontaneous decomposition. Although the analysis of the isotope pattern obviously does not suffice for the assignment of the ion, the CID experiments clearly prove its identity (see below).

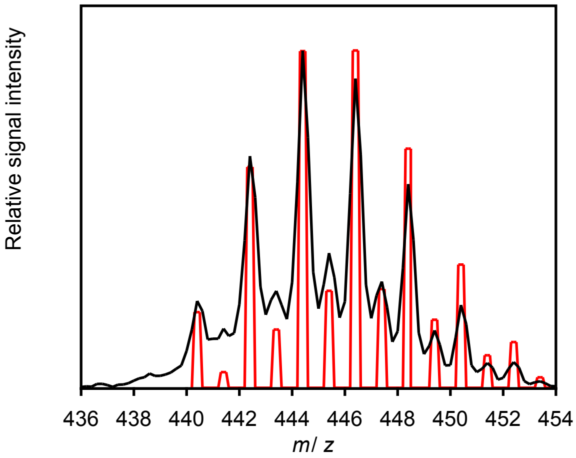


Figure S 22. Measured (black) and simulated (red) isotope pattern of $t\text{Bu}_2\text{MgZn}_2\text{Cl}_5^-$.

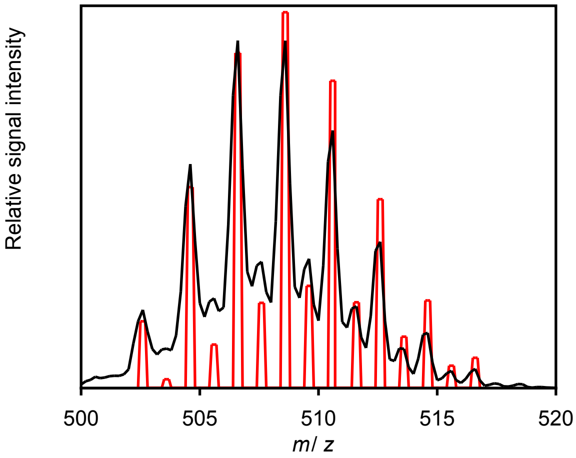


Figure S 23. Measured (black) and simulated (red) isotope pattern of $^t\text{Bu}_3\text{Zn}_3\text{Cl}_4^-$.

3.12 Mass selected zincate anions and their fragments produced during CID experiments

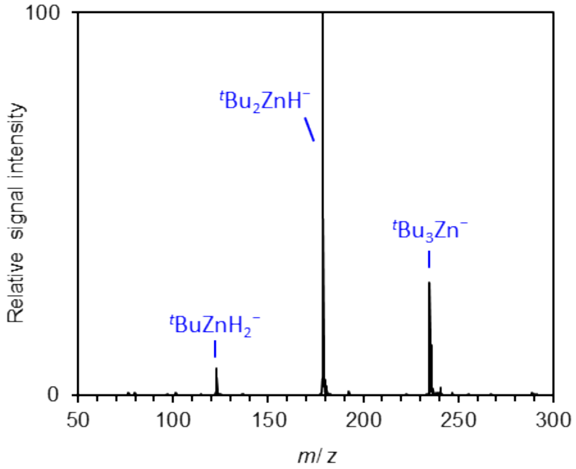


Figure S 24. Mass spectrum of mass-selected tBu$_3$Zn$^-$ and its fragment ions produced upon collision-induced dissociation (V_{exc} = 0.60 V).

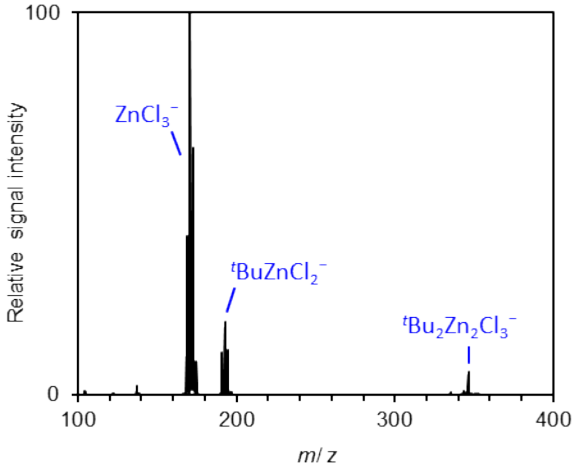


Figure S 25. Mass spectrum of mass-selected tBu$_2$Zn$_2$Cl$_3$$^-$ and its fragment ions produced upon collision-induced dissociation (V_{exc} = 0.40 V).

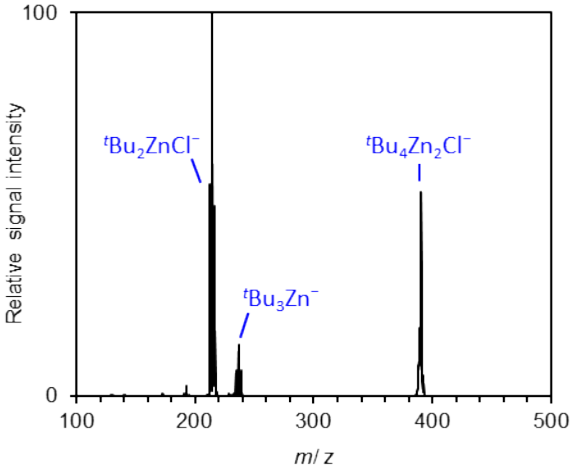


Figure S 26. Mass spectrum of mass-selected $t\mathrm{Bu}_4\mathrm{Zn}_2\mathrm{Cl}^-$ and its fragment ions produced upon collision-induced dissociation (V_{exc} = 0.50 V).

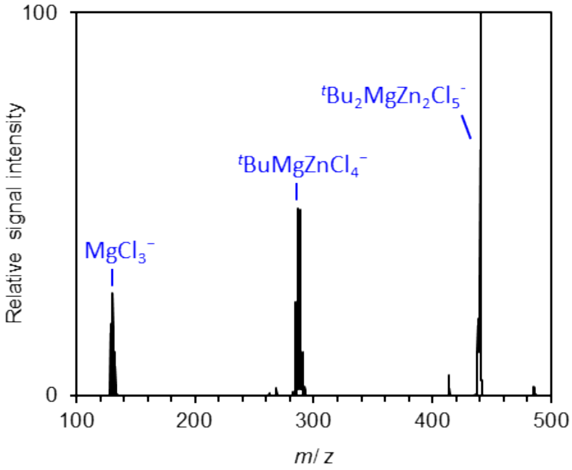


Figure S 27. Mass spectrum of mass-selected $t\mathrm{Bu}_2\mathrm{MgZn}_2\mathrm{Cl}_5^-$ and its fragment ions produced upon collision-induced dissociation (V_{exc} = 0.80 V).

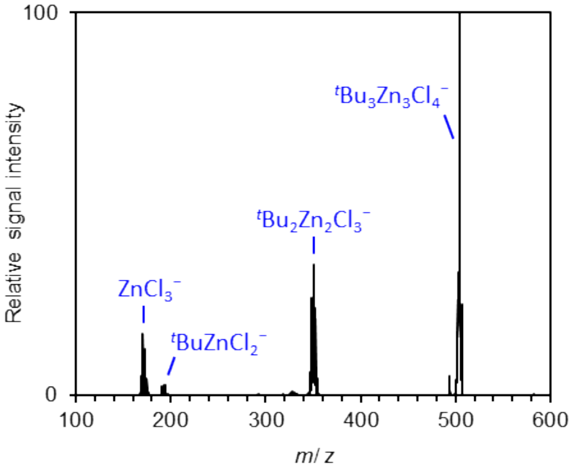


Figure S 28. Mass spectrum of mass-selected $t\mathrm{Bu}_3\mathrm{Zn}_3\mathrm{Cl}_7^-$ and its fragment ions produced upon collision-induced dissociation (V_{exc} = 0.70 V).

4 ^{1}H NMR MONITORING OF IODINE/ZINC EXCHANGE REACTIONS USING 2 IODOBENZONITRILE (3I) AS SUBSTRATE

NMR monitoring of an exchange reaction using **2** and 2-iodobenzonitrile (**3i**) revealed that only two *t*Bu moieties are active in the exchange reaction. The initially formed Ar-Zn species (a, blue) is slowly converted to another Ar-Zn species (b, red) over time. The ^{1}H NMR resonances observed of Ar-Zn(b) are identical to those of isolated crystals of $[(THF)_4MgCl\{NC\text{-}o\text{-}C_6H_4\}ZnI(o\text{-}C_6H_4CN)(THF)]]$ (**7**).

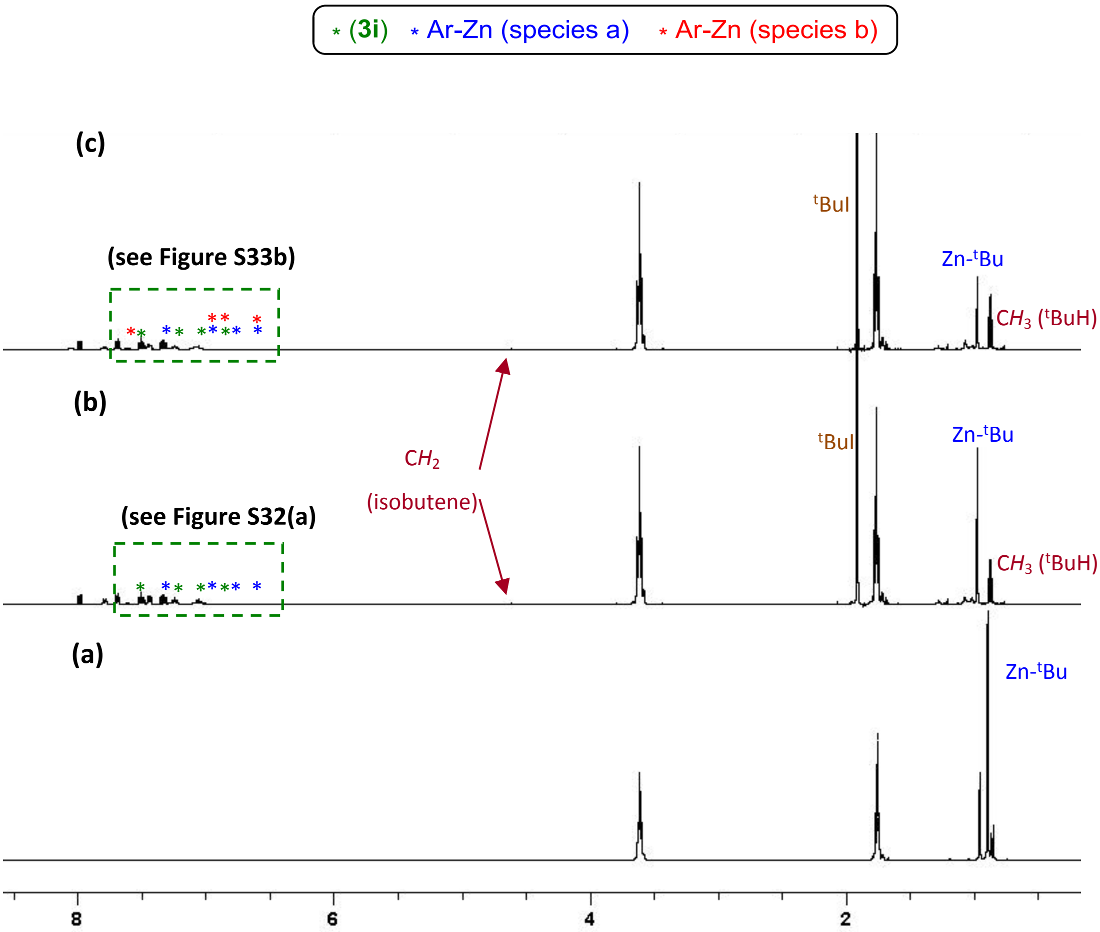


Figure S 31. ^{1}**H NMR spectra for the reaction of 1 with three equivalents of 2-iodobenzonitrile (a) before the addition of Ar-I, (b) 15 minutes after addition and (c) 2 hours after addition.**

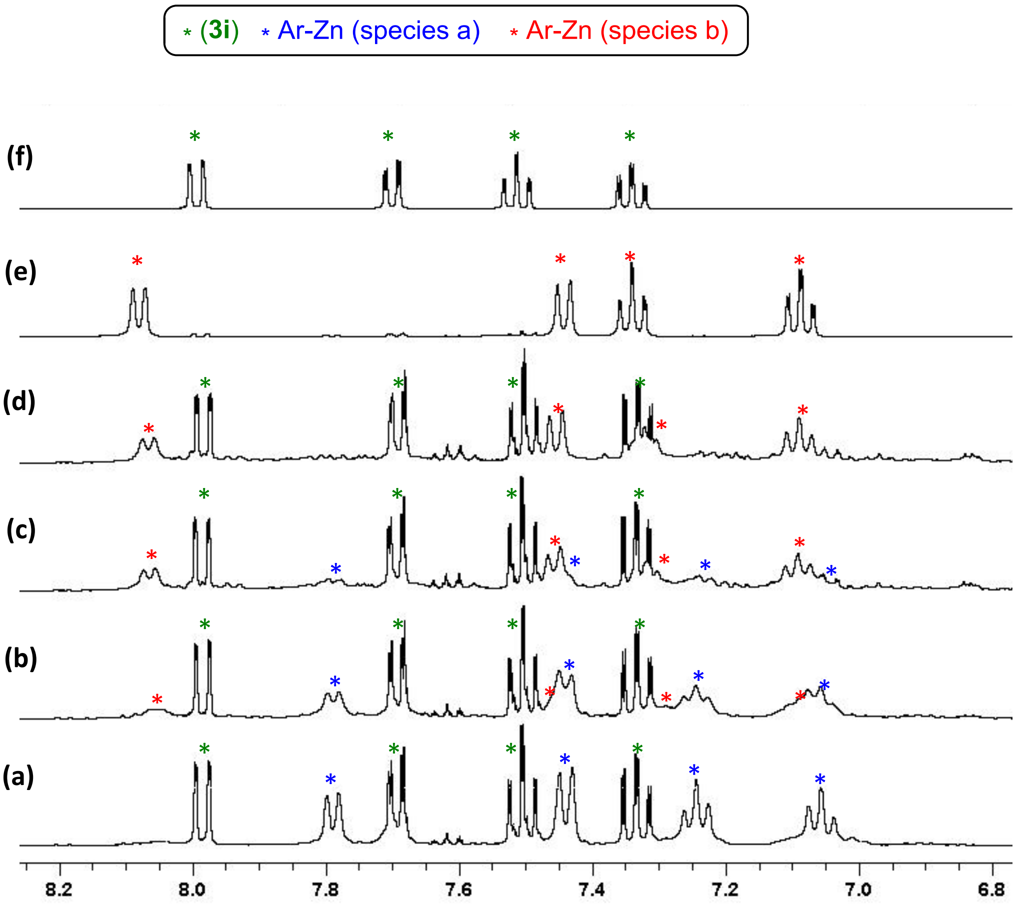
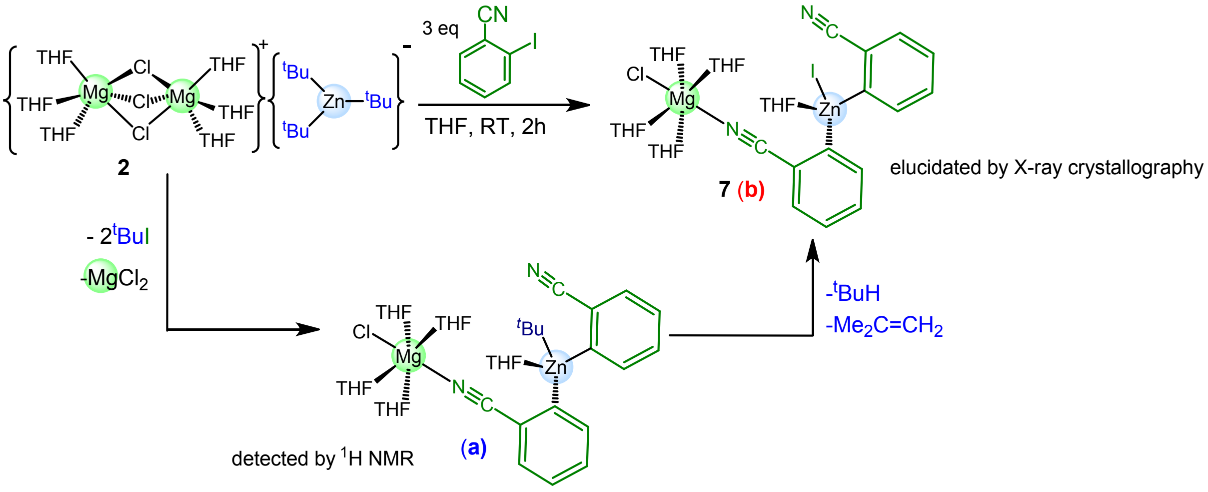


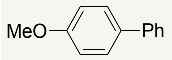
Figure S 32. Aromatic region of the ^1H NMR spectra for the reaction of 1 with three equivalents of 2-iodobenzonitrile (a) 15 minutes after addition, (b) 2 hours after addition, (c) 9 hours after addition, (d) 20 hours after addition, (e) [(THF)$_4$MgCl{NC-o-C$_6$H$_4$}ZnI(o-C$_6$H$_4$CN)(THF)]) and (f) 2-Iodobenzonitrile in d^8-THF.



Scheme S1: Proposed reaction of **2** with three molar equivalents of **3i**, to form the putative intermediate a, which undergoes subsequent reaction with ^{t}BuI to form **7** (species **b** in Figures S31 and S32)

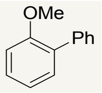
5 PREPARATION AND NMR DATA OF CROSS-COUPLING PRODUCTS (TABLE 3)

5.1 4-Methoxy-1,1'-biphenyl (6a)



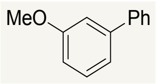
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 4-iodoanisol (**3a**, 702 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (1.0 M, 3.0 mL). Cross-coupling using iodobenzene (**5a**, 612 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification **6a** as white solid (434 mg, 79%). **Mp.**: 91-92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 27 °C): δ = 7.59-7.52 (m, 4H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$, 27 °C): δ = 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3. **GC-MS** (EI, 70 eV): *m/z* (%) = 50 (1), 63 (2), 87 (1), 89 (4), 113 (2), 115 (39), 116 (3), 126 (1), 139 (10), 140 (3), 141 (59), 142 (7), 151 (2), 152 (5), 153 (2), 154 (1), 169 (70), 170 (9), 184 (100), 185 (15); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3067, 3033, 2836, 1603, 1582, 1519, 1464, 1450, 1438, 1286, 1269, 1248, 1200, 1184, 1119, 993, 986, 833.

5.1 2-Methoxy-1,1'-biphenyl (6b)



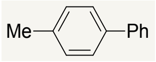
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 2-iodoanisol (**3b**, 702 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (1.0 M, 3.0 mL). Cross-coupling using iodobenzene (**5a**, 612 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification **6b** as reddish liquid (422 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$, 27 °C): δ = 7.58-7.54 (m, 2H), 7.46-7.41 (m, 2H), 7.38-7.33 (m, 3H), 7.06 (dt, *J* = 7.2 Hz, 0.9 Hz, 1H), 7.03-7.01 (m, 1H), 3.84 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$, 27 °C): δ = 156.5, 138.5, 130.8, 130.9, 129.5, 128.6, 128.0, 126.9, 120.8, 111.2, 55.6; **GC-MS** (EI, 70 eV): *m/z* (%) = 186 (2), 185 (20), 184 (100), 183 (21), 170 (7), 169 (32), 168 (4), 167 (4), 166 (2), 165 (6), 155 (3), 153 (3), 142 (6), 141 (20), 139 (5), 116 (3), 115 (10), 91 (2); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3057, 2952, 2832, 1595, 1583, 1503, 1481, 1462, 1453, 1258, 1233, 1178, 1161, 1122, 1073, 1055, 994, 912, 849, 799.

5.2 3-Methoxy-1,1'-biphenyl (6c)



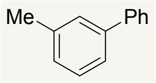
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 3-iodoanisol (**3c**, 702 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (1.0 M, 3.0 mL). Cross-coupling using iodobenzene (**5a**, 612 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification **6c** as colorless liquid (423 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$, 27 °C): δ = 7.64-7.60 (m, 2H), 7.49-7.44 (m, 2H), 7.40-7.36 (m, 2H), 7.23-7.19 (m, 1H), 7.17-7.19 (m, 1H), 6.93 (dd, *J* = 5.7 Hz, 2.5 Hz, 1H), 3.89 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$, 27 °C): δ = 159.9, 142.8, 141.1, 129.7, 128.7, 127.4, 127.2, 119.7, 112.9, 112.7, 55.3; **GC-MS** (EI, 70 eV): *m/z* (%) = 186 (2), 185 (21), 184 (100), 165 (1), 156 (2), 155 (14), 154 (16), 153 (17), 152 (5), 151 (2), 150 (1), 142 (3), 141 (11), 140 (2), 139 (5), 116 (4), 115 (16), 89 (2), 63 (1); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3029, 2952, 2832, 1611, 1597, 1572, 1477, 1453, 1420, 1310, 1219, 1168, 1113, 1018, 992, 967, 872.

5.3 4-Methyl-1,1'-biphenyl (6d)



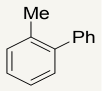
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 4-iodotoluene (**3d**, 654 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (1.0 M, 3.0 mL). Cross-coupling using iodobenzene (**5a**, 612 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification **6d** as white solid (330 mg, 65 %). **Mp**.: 45-46 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 27 °C): δ = 7.62-7.59 (m, 2H), 7.53-7.48 (m, 2H), 7.46-7.42 (m, 2H), 7.37-7.32 (m, 1H), 7.29-7.24 (m, 2H), 2.43 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$, 27 °C): δ = 141.2, 138.4, 136.9, 129.5, 128.7, 126.9, 126.8, 21.0; **GC-MS** (EI, 70 eV): *m/z* (%) = 169 (14), 168 (100), 167 (88), 166 (14), 165 (43), 164 (7), 163 (3), 154 (4), 153 (32), 152 (32), 151 (8), 150 (2), 141 (3), 139 (3), 128 (2), 115 (6), 89 (2), 83 (5), 82 (6), 63 (3); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3031, 2916, 2855, 1600, 1477, 1463, 1446, 1403, 1377, 1128, 1112, 1076, 1038, 1022, 1006, 823, 804, 754, 698.

5.4 3-Methyl-1,1'-biphenyl (6e)



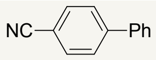
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 3-iodotoluene (**3e**, 654 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (1.0 M, 3.0 mL). Cross-coupling using iodobenzene (**5a**, 612 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification **6e** as colorless liquid (360 mg, 65 %). **^{1}H NMR** (400 MHz, $CDCl_3$, 27 °C) δ = 7.65-7.61 (m, 2H), 7.50-7.42 (m, 4H), 7.40-7.35 (m, 2H), 7.23-7.18 (m, 1H), 2.47 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$, 27 °C): δ = 141.4, 141.2, 138.3, 128.7, 128.6, 128.0, 127.2, 124.3, 21.5; **GC-MS** (EI, 70 eV): *m/z* (%) = 169 (13), 168 (100), 167 (64), 166 (17), 165 (24), 164 (2), 163 (2), 155 (1), 154 (6), 153 (23), 152 (16), 151 (1), 141 (1), 139 (1), 115 (3), 89 (1); **FT-IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3028, 1599, 1575, 1480, 1167, 1091, 1074, 1052, 1038, 898, 791, 773.

5.5 2-Methyl-1,1'-biphenyl (6f)



The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 2-iodotoluene (**3f**, 654 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (1.0 M, 3.0 mL). Cross-coupling using iodobenzene (**5a**, 612 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification **6f** as colorless liquid (303 mg, 60 %). The compound is obtained in 90% purity containing 2,2'-dimethylbiphenyl as inseparable mixture. **^{1}H NMR** (400 MHz, $CDCl_3$, 27 °C) δ = 7.49-7.44 (m, 2H), 7.43-7.36 (m, 3H), 7.35-7.27 (m, 4H), 2.34 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$, 27 °C): δ = 142.0, 141.9, 135.4, 130.3, 129.8, 129.2, 128.1, 127.3, 126.8, 125.8, 20.3; **GC-MS** (EI, 70 eV): *m/z* (%) = 169 (14), 168 (100), 167 (91), 166 (25), 165 (38), 164 (4), 163 (3), 155 (2), 154 (8), 153 (47), 152 (27), 150 (1), 141 (2), 139 (2), 128 (1), 115 (4), 89 (1); **FT-IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3057, 3018, 2949, 2922, 1598, 1478, 1457, 1452, 1380, 1156, 1009, 997, 942, 773, 745, 715.

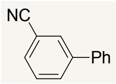
5.6 [1,1'-Biphenyl]-4-carbonitrile (6g)



The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 4-iodobenzonitrile (**3g**, 687 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (1.0 M, 3.0 mL). Cross-coupling using iodobenzene (**5a**, 612 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification **6g** as white solid (381 mg, 71 %).

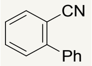
Mp.: 89-90°C; **^{1}H NMR** (400 MHz, $CDCl_3$, 27 °C): *δ* = 7.75-7.67 (m, 4H), 7.61-7.57 (m, 2H), 7.51-7.46 (m, 2H), 7.45-7.40 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$, 27 °C): δ = 145.7, 139.2, 132.6, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9; **GC-MS** (EI, 70 eV): *m/z* (%) = 181 (2), 180 (17), 179 (100), 178 (33), 177 (11), 176 (2), 153 (7), 152 (11), 151 (24), 150 (10), 149 (2), 126 (3), 125 (2), 87 (2), 85 (2), 76 (4), 75 (3), 74 (2), 63 (3), 50 (3); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3062, 2226, 1605, 1483, 1396, 1312, 1178, 1129, 1113, 1077, 1022, 923, 848, 836, 767.

5.7 [1,1'-Biphenyl]-3-carbonitrile (6h)



The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 3-iodobenzonitrile (**3h**, 687 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (1.0 M, 3.0 mL). Cross-coupling using iodobenzene (**5a**, 612 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification **6h** as white solid (404 mg, 75 %). **Mp**.: 45-46 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 27 °C): *δ* = 7.87 (t, *J* = 1.3 Hz, 1H), 7.82 (dt, *J* = 7.9 Hz, 0.9 Hz, 1H), 7.63 (dt, *J* = 7.9 Hz, 0.9 Hz, 1H), 7.58-7.53 (m, 3H), 7.50-7.45 (m, 2H), 7.44-7.39 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$, 27 °C): δ = 142.5, 138.9, 131.5, 130.7, 130.6, 129.6, 129.1, 128.4, 127.1, 118.8, 112.9; **GC-MS** (EI, 70 eV): *m/z* (%) = 180 (16), 179 (100), 178 (27), 177 (7), 154 (1), 153 (5), 152 (11), 151 (16), 150 (5), 127 (1), 126 (2), 87 (1), 76 (2), 75 (2), 74 (1), 63 (2), 50 (1); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3029, 2224, 1597, 1581, 1571, 1475, 1450, 1410, 1268, 1172, 1157, 1097, 1078, 1025, 894, 802, 758, 698.

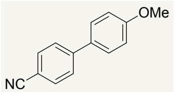
5.8 [1,1'-Biphenyl]-2-carbonitrile (6i)



The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 3-iodobenzonitrile (**3h**, 687 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (1.0 M, 3.0 mL). Cross-coupling using iodobenzene (**5a**, 612 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification **6h** as yellow oil (404 mg, 31 %). **^{1}H NMR** (400 MHz, $CDCl_3$, 27 °C) *δ* = 7.77 (dd, *J* = 7.6 Hz, *J* = 1.0 Hz, 1H), 7.65 (td, *J* = 7.6 Hz, *J* = 1.5 Hz, 1H), 7.59-7.41 (m, 7H); **^{13}C-NMR** (100 MHz, $CDCl_3$, 27 °C) δ = 145.4, 138.1, 133.7, 132.7, 130.0, 128.7, 127.5, 118.6, 111.2; **GC-MS** (EI, 70 eV): *m/z* (%) = 180 (19), 179 (100), 178 (29), 177 (6), 154 (2), 153 (8), 152 (15), 151 (10), 150 (6), 126 (2), 87 (1), 76 (2), 75 (1), 63 (2); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1}

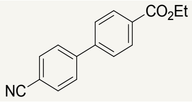
= 3062, 2223, 1595, 1582, 1561, 1477, 1451, 1434, 1267, 1188, 1164, 1108, 1076, 1049, 1009, 992, 956, 918, 777, 756, 733, 698.

5.9 4'-Methoxy-[1,1'-biphenyl]-4-carbonitrile (6j)



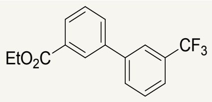
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from 4-iodoanisol (**3a**, 702 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (0.96 M in THF, 3.12 mL, 3 mmol)). Cross-coupling using 4-bromobenzonitrile (**5b**, 546 mg, 3 mmol) and $PdCl_2$dppf (54 mg, 0.074 mmol) furnished after workup and column chromatographical purification (silica, hexane/EtOAc = 6:1) **6j** as off white solid (505 mg, 81%). **Mp.**: 104-105 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$, 27 °C): $\delta =$ 7.73-7.60 (m, 4H), 7.56-7.50 (m, 2H), 7.04-6.97 (m, 2H), 3.86 (s, J_{CH} = 144.1 Hz, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$, 27 °C): 160.1, 145.1, 132.4, 131.4, 128.2, 127.0, 119.0, 114.5, 110.0, 55.3; **GC-MS** (EI, 70 eV): *m/z* (%) = 211 (2), 210 (15), 209 (100) [M^+], 195 (9), 194 (61), 179 (3), 177 (2), 167 (9), 166 (59), 164 (6), 151 (2), 150 (2), 141 (4), 140 (28), 139 (11), 138 (2), 115 (2), 114 (2), 113 (4), 63 (2); **FT-IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 2963, 2842, 2223, 1605, 1515, 1493, 1463, 1447, 1396, 1295, 1266, 1241, 1177, 1110, 1021, 1015, 960, 955, 853.

5.10 Ethyl 4'-cyano-[1,1'-biphenyl]-4-carboxylate (6k)



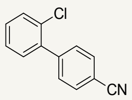
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from ethyl 4-iodobenzoate (**3j**, 773 mg, 2.8 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (0.96 M in THF, 3.12 mL, 3 mmol)). Cross-coupling using 4-bromobenzonitrile (**5b**, 491 mg, 2.7 mmol) and PEPPSi-*i*Pr (19 mg, 0.028 mmol) furnished after workup and column chromatographical purification (silica, hexane/EtOAc = 20:1) **6k** as brown solid (519 mg, 76%).**Mp.**: 119-120 °C; **^{1}H-NMR** (500 MHz, C_6D_6, 27 °C): 8.19-8.13 (m, 2H), 7.16-7.06 (m, 4H), 6.95-6.90 (m, 2H), 4.18 (q, J_{HH} = 7.2 Hz, J_{CH} = 147.5 Hz, 2H), 1.07 (t, J_{HH} = 7.2 Hz, J_{CH} = 127.2 Hz, 3H); **^{13}C-NMR** (125 MHz, C_6D_6, 27 °C): 165.8, 143.8, 143.3, 132.5, 131.0, 130.4, 127.7, 127.3, 118.7, 112.2, 61.1, 14.3; **GC-MS** (EI, 70 eV): *m/z* (%) = 252 (5), 251 (27) [M^+], 250 (3), 224 (13), 223 (74), 208 (2), 207 (18), 206 (100), 192 (3), 179 (5), 178 (30), 177 (17), 176 (3), 152 (7), 151 (36), 150 (12), 149 (4), 125 (2), 75 (3), 74 (2); **FT-IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 2993, 2223, 1703, 1606, 1472, 1446, 1396, 1363, 1311, 1277, 1266, 1178, 1101, 1021, 937, 915, 872, 854.

5.11 Ethyl 3'-(trifluoromethyl)-[1,1'-biphenyl]-3-carboxylate (6l)



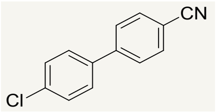
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP1** from ethyl 3-iodobenzoate (**3k**, 828 mg, 3 mmol), $ZnCl_2$ (1M in THF, 1.0 mL, 1 mmol) and tBuMgCl (0.96 M in THF, 3.12 mL, 3 mmol). Cross-coupling using 3-bromobenzotrifluoride (**5c**, 608 mg, 2.7 mmol) and PEPPSi-*i*Pr (19 mg, 0.028 mmol) furnished after workup and column chromatographical purification (silica, hexane/EtOAc = 10:1) **6l** as yellow liquid (683 mg, 86%). **^{1}H-NMR** (500 MHz, C_6D_6, 27 °C): δ = 8.29 (t, *J* = 1.7 Hz, 1H), 8.07 (dt, *J* = 7.5 Hz, 1.3 Hz, 1H), 7.69 (s, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.24 (dt, *J* = 8.5 Hz, 1.3 Hz, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.98 (t, *J* = 7.9 Hz, 1H), 4.18 (q, J_{HH} = 7.2 Hz, J_{CH} = 147.6 Hz, 2H), 1.09 (t, J_{HH} = 7.2 Hz, J_{CH} = 127.2 Hz, 3H); **^{13}C-NMR** (125 MHz, C_6D_6, 27 °C): δ = 165.7, 141.3, 140.1, 131.9, 131.5, 131.3 (q, J_{CF} = 22 Hz), 130.7, 129.6, 129.23, 129.18, 128.5, 124.8 (q, J_{CF} = 272 Hz), 124.4 (q, J_{CF} = 4 Hz), 124.0 (q, J_{CF} = 4 Hz), 61.1, 14.3; **GC-MS** (EI, 70 eV): *m/z* (%) =295 (22), 294 (91) [M$^+$], 276 (6), 275 (10), 267 (7), 266 (35), 250 (20), 249 (100), 248 (4), 222 (8), 221 (25), 220 (5), 219 (5), 202 (11), 201 (60), 181 (5), 170 (4), 153 (8), 152 (35), 151 (7); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 2981, 1715, 1593, 1457¸1410, 1368, 1283, 1265, 1164, 1108, 1049, 1002, 924, 895.

5.12 2'-Chloro-[1,1'-biphenyl]-4-carbonitrile (6m)



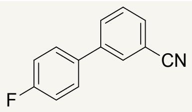
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP2** from 1-chloro-2-iodobenzene (**3l**, 715 mg, 3 mmol), $ZnCl_2$ (1 M in THF, 1.0 mL, 1 mmol) and tBuMgCl (0.84 M in THF, 3.55 mL, 2.98 mmol). Cross-coupling using 4-bromobenzonitrile (**5b**, 491 mg, 2.7 mmol) and PEPPSi-*i*Pr (19 mg, 0.028 mmol) furnished after workup and column chromatographical purification (silica, hexane/EtOAc = 10:1) **6m** as off-white solid (514 mg, 89%). **Mp**.: 95-97 °C; **^{1}H-NMR** (500 MHz, C_6D_6, 27 °C): δ = 7.22 (dd, *J* = 7.9 Hz, 1.3 Hz, 1H), 7.11-6.96 (m, 4H), 6.94 (dd, *J* = 7.5 Hz, 1.6 Hz, 1H), 6.92-6.88 (m, 1H), 6.87-6.84 (m, 1H); **^{13}C-NMR** (125 MHz, C_6D_6, 27 °C): δ = 143.5, 139.0, 132.3, 131.8, 131.2, 130.3, 130.2, 129.7, 127.2, 118.7, 111.9; **GC-MS** (EI, 70 eV): *m/z* (%) = 216 (6), 215 (33), 214 (15), 213 (100) [M$^+$], 179 (4), 178 (24), 177 (18), 176 (3), 175 (2), 152 (6), 151 (28), 150 (12), 149 (4), 125 (2), 123 (2), 99 (2), 98 (1), 89 (2), 75 (5), 74 (3); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3062, 2228, 1608, 1508, 1468, 1446, 1431, 1411, 1398, 1282, 1182, 1110, 1068, 977, 948; **HRMS** (ESI): calculated for $C_{13}H_9ClN$: 214.0418; found: 214.0416.

5.13 4'-Chloro-[1,1'-biphenyl]-4-carbonitrile (6n)



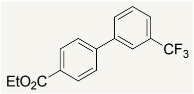
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP2** from 1-chloro-4-iodobenzene (**3m**, 668 mg, 2.8 mmol), $ZnCl_2$ (1 M in THF, 1.0 mL, 1 mmol) and tBuMgCl (0.84 M in THF, 3.55 mL, 2.98 mmol). Cross-coupling using 4-bromobenzonitrile (**5b**, 491 mg, 2.7 mmol) and PEPPSi-*i*Pr (19 mg, 0.028 mmol) furnished after workup and column chromatographical purification (silica, hexane/EtOAc = 10:1) **6n** as off-white solid (494 mg, 86%). **Mp.**: 134-135 °C; **^{1}H-NMR** (500 MHz, C_6D_6, 27 °C): δ = 7.13-7.09 (m, 2H), 7.09-7.05 (m, 2H), 6.88-6.83 (m, 4H); **^{13}C-NMR** (125 MHz, C_6D_6, 27 °C): δ= 143.7, 137.7, 134.9, 132.5, 129.3, 128.6, 127.3, 118.7, 111.7; **GC-MS** (EI, 70 eV): *m/z* (%) = 216 (4), 215 (31), 214 (16), 213 (100) [M^+], 179 (3), 178 (19), 177 (16), 176 (3), 152 (7), 151 (30), 150 (10), 149 (3), 125 (2), 99 (1), 98 (1), 88 (2), 75 (5), 74 (2), 62 (1), 50 (2); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3071, 3034, 2226, 1607, 1483, 1418, 1391, 1184, 1090, 1041, 957, 940, 838.

5.14 4'-Fluoro-[1,1'-biphenyl]-3-carbonitrile (6p)



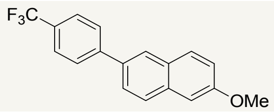
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP2** from 1-fluoro-4-iodobenzene (**3o**, 666 mg, 3 mmol), $ZnCl_2$ (1 M in THF, 1.0 mL, 1 mmol) and tBuMgCl (0.84 M in THF, 3.55 mL, 2.98 mmol). Cross-coupling using 3-bromobenzonitrile (**5d**, 491 mg, 2.7 mmol) and PEPPSi-*i*Pr (19 mg, 0.028 mmol) furnished after workup and column chromatographical purification (silica, hexane/EtOAc = 10:1) **6p** as white solid (412 mg, 75%). **Mp.**: 66-67 °C; **^{1}H-NMR** (500 MHz, C_6D_6, 27 °C): δ = 7.25 (s, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.88-6.74 (m, 5H); **^{13}C-NMR** (125 MHz, C_6D_6, 27 °C): δ = 163.3 (d, *J* = 250 Hz), 141.1, 135.0, 130.7, 130.5 (d, *J* = 7 Hz), 129.4, 128.9 (d, *J* = 7 Hz), 118.7, 116.0, 115.9, 113.5; **GC-MS** (EI, 70 eV): *m/z* (%) = 199 (2), 198 (16), 197 (100) [M^+], 196 (22), 195 (6), 178 (2), 177 (5), 176 (5), 171 (6), 170 (10), 169 (10), 168 (5), 151 (2), 150 (3), 149 (2), 144 (1), 85 (2), 75 (2), 74 (2), **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3069, 3047, 2231, 1610, 1514, 1478, 1433, 1397, 1262, 1224, 1160, 1133, 1010, 971, 906.

5.15 Ethyl 3'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (6q)



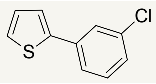
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP2** from 3-iodobenzotrifluoride (**3o**, 789 mg, 2.9 mmol), $ZnCl_2$ (1 M in THF, 1.0 mL, 1 mmol) and tBuMgCl (0.84 M in THF, 3.55 mL, 2.98 mmol). Cross-coupling using ethyl 4-iodobenzoate (**2j**, 773 mg, 2.8 mmol) and PEPPSi-*i*Pr (19 mg, 0.028 mmol) furnished after workup and column chromatographical purification (silica, hexane/EtOAc = 10:1) **5o** as white solid (658 mg, 80%). **Mp.**: 84-85 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$, 27 °C): $\delta =$ 8.31-8.18 (m, 2H), 7.79 (s, 1H), 7.51-7.31 (m, 2H), 7.30-7.23 (m, 2H), 7.14-7.02 (m, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR** (125 MHz, C_6D_6, 27 °C): $\delta =$ 165.9, 143.7, 141.1, 131.4 (q, *J* = 33 Hz), 130.7, 130.6, 130.5, 129.5, 127.3, 124.8 (q, *J* = 274 Hz), 124.7 (br), 124.2 (br), 61.0, 14.3; **GC-MS** (EI, 70 eV): *m/z* (%) = 295 (22), 294 (85) [M^+], 293 (2), 275 (7), 267 (4), 266 (25), 250 (20), 249 (100), 222 (4), 221 (13), 220 (3), 219 (4), 202 (10), 201 (47), 181 (3), 170 (4), 153 (6), 152 (25), 151 (5), 150 (2); **FT-IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 2983, 1704, 1609, 1476, 1440, 1402, 1368, 1332, 1309, 1301, 1274,1157, 1119, 1099, 1076, 1017, 962, 929, 876, 853; **HRMS** (ESI): calculated for $C_{16}H_{14}O_2F_3$: 295.0939; found: 295.0940.

5.16 Ethyl 3'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (6r)



The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP2** from 4-iodobenzotrifluoride (**3p**, 816 mg, 3 mmol), $ZnCl_2$ (1 M in THF, 1.0 mL, 1 mmol) and tBuMgCl (0.82 M in THF, 3.78 mL, 3.1 mmol). Cross-coupling using 2-bromo-6-methoxynaphthalene (**5e**, 640 mg, 2.7 mmol) and PEPPSi-*i*Pr (19 mg, 0.028 mmol) furnished after workup and column chromatographical purification (silica, hexane) **6r** as brown solid (323 mg, 78%). **Mp.**: 172-173 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$, 27 °C): $\delta =$ 7.22 (s, 1H), 7.87-7.68 (m, 7H), 7.25-7.15 (m, 2H); **^{13}C-NMR** (125 MHz, C_6D_6, 27 °C): $\delta =$ 158.2, 144.7, 134.8, 134.2, 129.8, 129.0 (q, *J* = 32 Hz), 129.0, 127.5, 127.3, 126.1, 125.7, 125.6, 124.4 (q, *J* = 269 Hz), 119.5, 105.6, 55.3; **GC-MS** (EI, 70 eV): *m/z* (%) = 304 (2), 303 (21), 302 (100) [M^+], 288 (3), 287 (17), 283 (4), 272 (2), 261 (2), 260 (15), 259 (87), 240 (3), 239 (2), 238 (5), 233 (9), 207 (2), 202 (4), 190 (7), 189 (23), 188 (2), 183 (2), **FT-IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3033, 1627, 1613, 1603, 1581, 1574, 1568, 1502, 1485, 1328, 1278, 1262, 1253, 1206, 1163, 1124, 1111, 1073, 1032, 1023, 1012, 970, 962, 914, 893; **CHN**: expected C: 71.52%, H: 4.33%; found: C: 69.89, H: 4.07%.

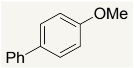
5.1 2-(3-Chlorophenyl)thiophene (6s)

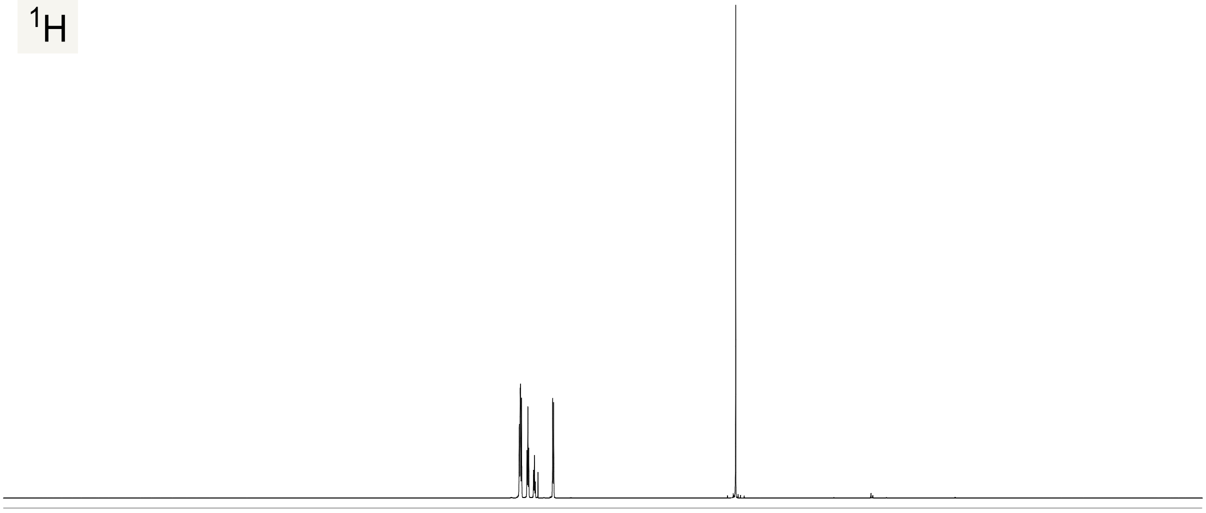


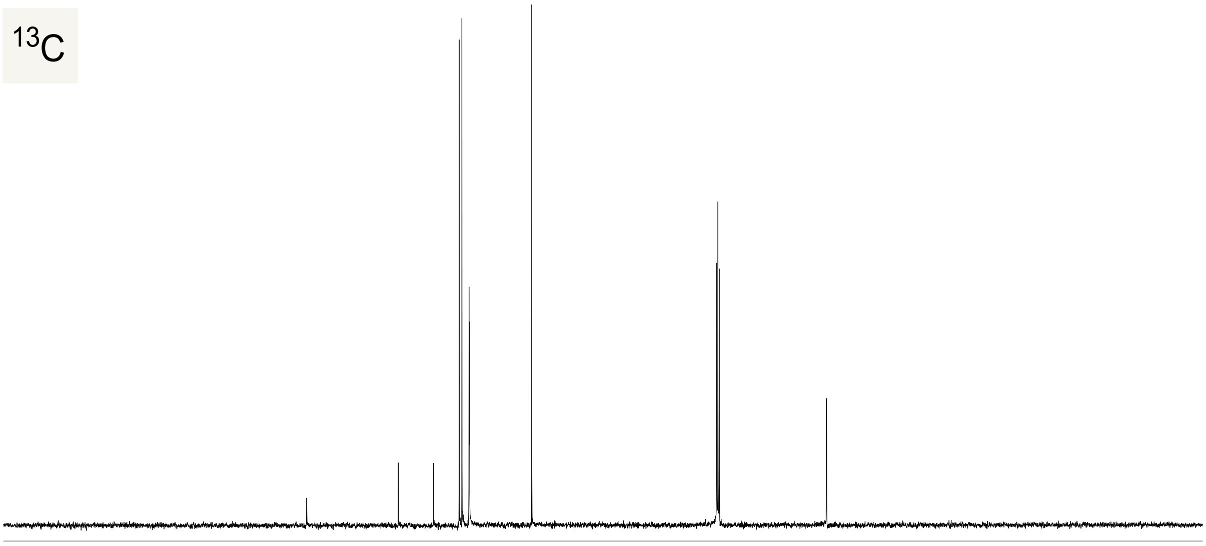
The zincate reagent was prepared by iodine/zinc exchange *in situ* according to **TP2** from 2-iodo thiophene (**3q**, 630 mg, 3 mmol), $ZnCl_2$ (1 M in THF, 1.0 mL, 1 mmol) and tBuMgCl (0.84 M in THF, 3.55 mL, 2.98 mmol). Cross-coupling using 1-chloro-3-iodobenzene (**5f**, 644 mg, 2.7 mmol) and PEPPSi-*i*Pr (19 mg, 0.028 mmol) furnished after workup and column chromatographical purification (silica, hexane) **6s** as colorless liquid (323 mg, 61%). **^{1}H-NMR** (500 MHz, $CDCl_3$, 27 °C): $\delta = 7.65$ (t, *J* = 1.9 Hz, 1H), 7.29-7.26 (m, 1H), 7.09-7.06 (m, 1H), 6.98 (dd, *J* = 3.8 Hz, 1.3 Hz, 1H), 6.92 (dd, *J* = 5.0 Hz, 0.9 Hz, 1H), 6.88 (t, *J* = 7.9 Hz, 1H), 6.80 (dd, J = 5.0 Hz, 3.7 Hz, 1H) ; **^{13}C-NMR** (125 MHz, C_6D_6, 27 °C): $\delta = 142.8$, 136.5, 135.1, 130.3, 127.4, 126.0, 125.6, 124.2; **GC-MS** (EI, 70 eV): *m/z* (%) = 197 (5), 196 (38), 195 (14), 194 (100), 162 (6), 160 (3), 159 (22), 158 (7), 155 (3), 151 (3), 150 (2), 149 (14), 136 (3), 116 (6), 115 (43), 114 (9), 113 (5), 89 (3), 75 (3), 74 (3); **FT**-**IR** (neat, Diamond ATR): $\tilde{\nu}$/cm^{-1} = 3105, 3087, 3077, 3066, 1590, 1583, 1530, 1480, 1467, 1431, 1418, 1393, 1353, 1346, 1257, 1216, 1198, 1170, 1097, 1093, 1085, 1078, 1056, 994, 979, 967, 875, 852, 836, 825.

6 NMR SPECTRA OF PRODUCTS (TABLE 5)

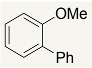
6.1 4-Methoxy-1,1'-biphenyl (6a)

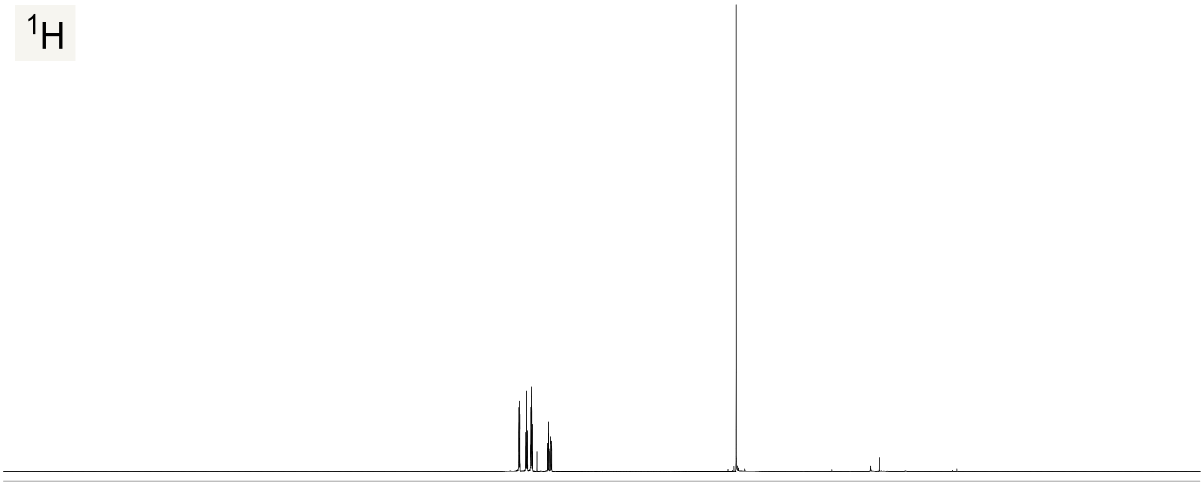


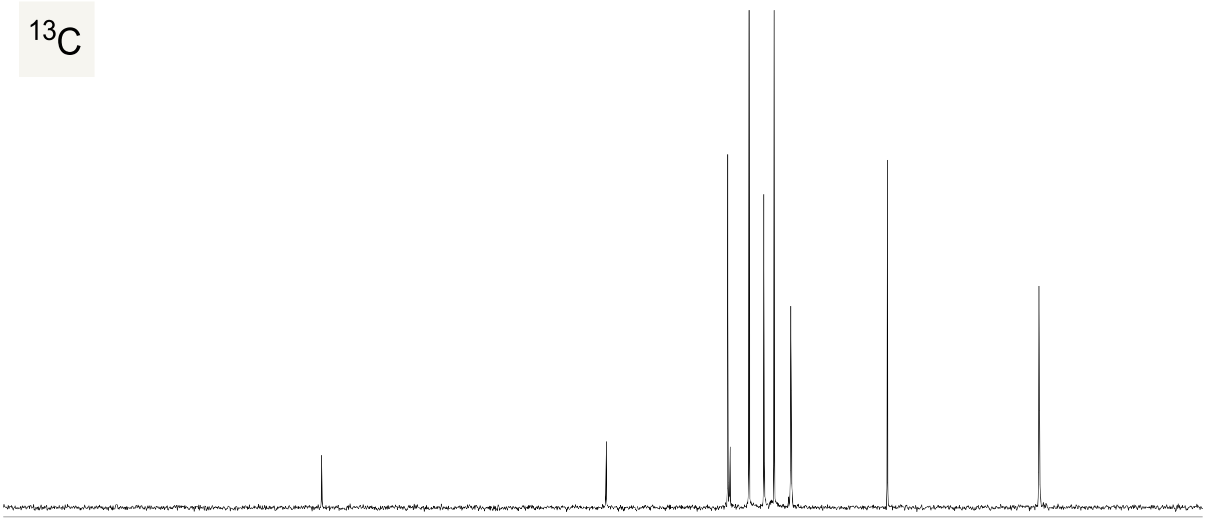




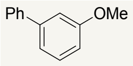
6.2 2-Methoxy-1,1'-biphenyl (6b)

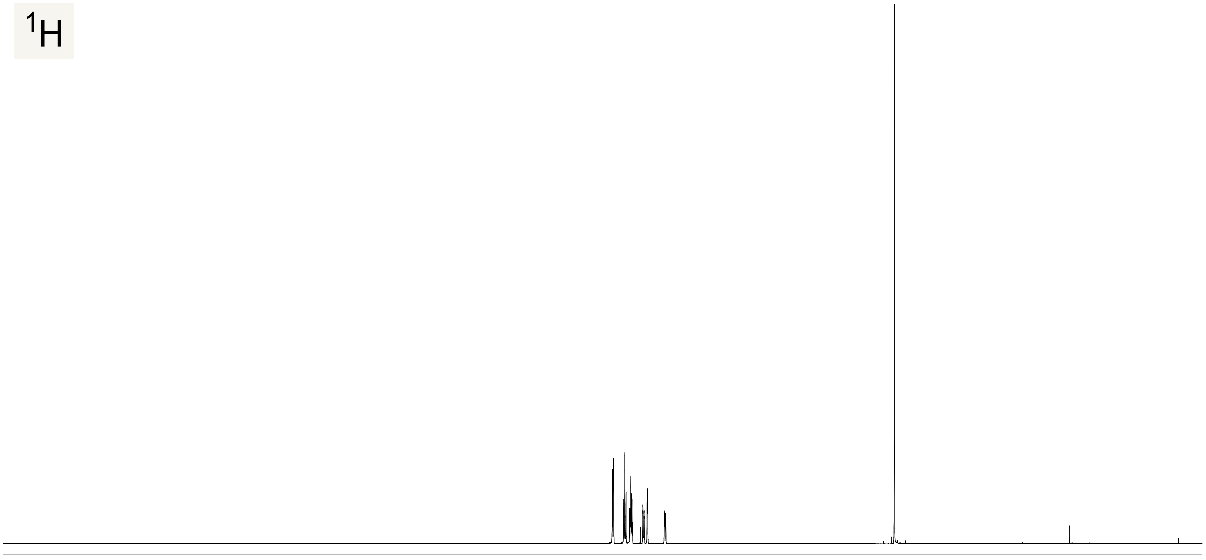


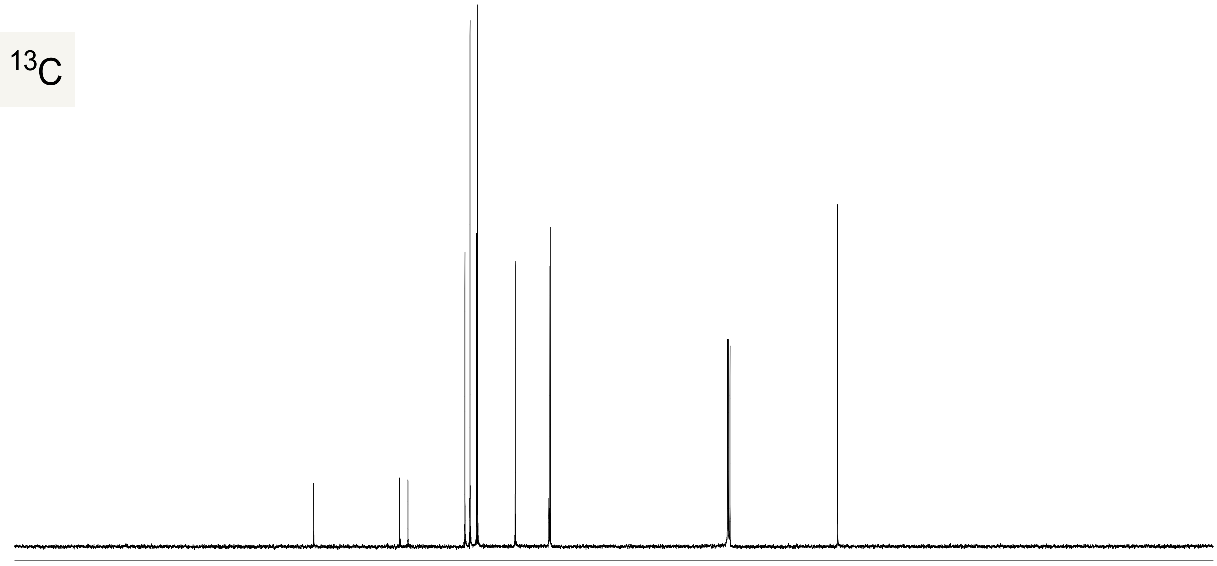




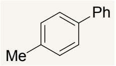
6.3 3-Methoxy-1,1'-biphenyl (6c)

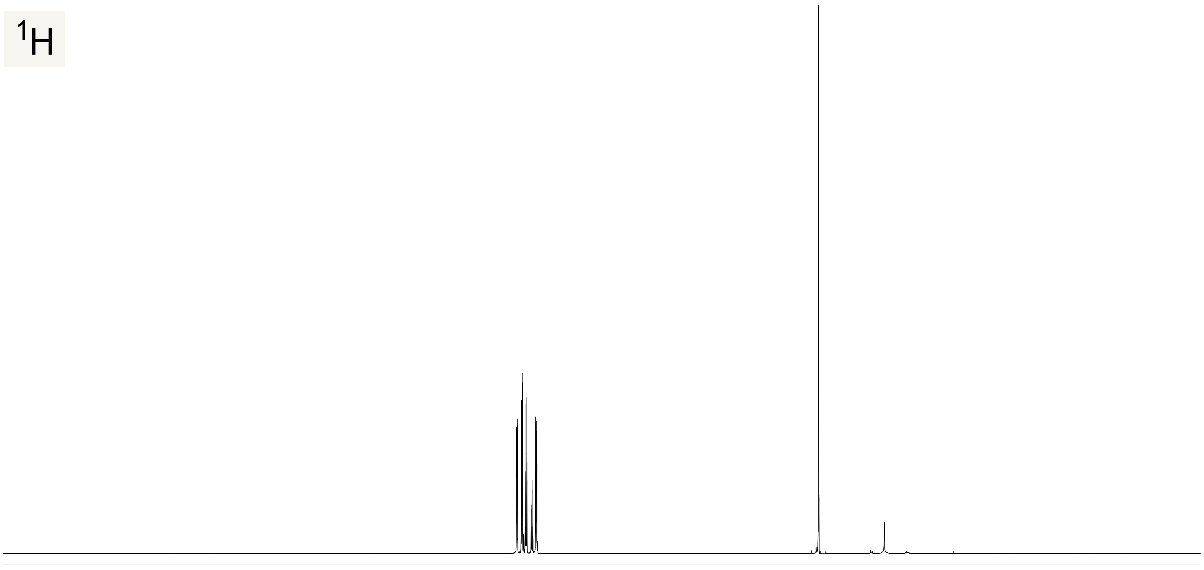


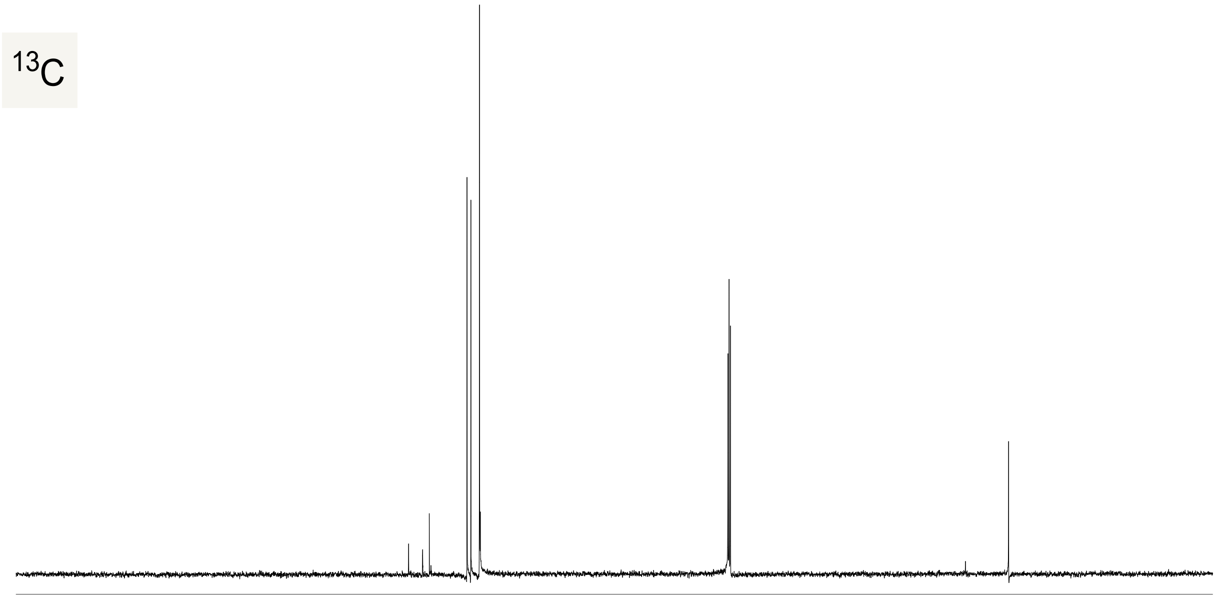




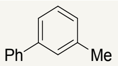
6.4 4-Methyl-1,1'-biphenyl (6d)



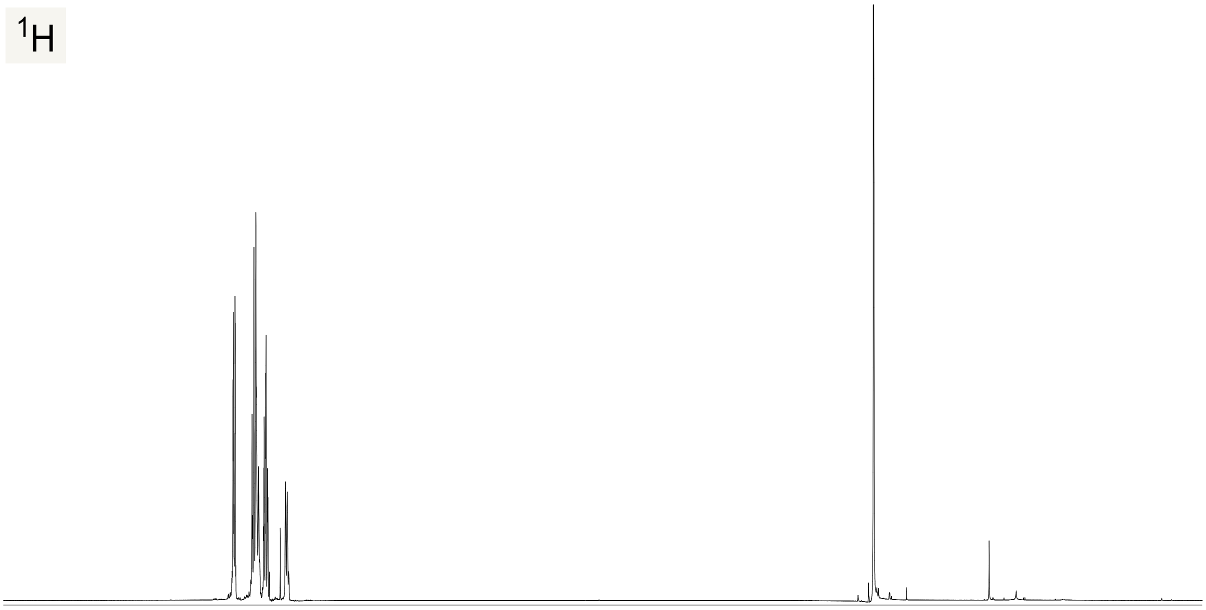




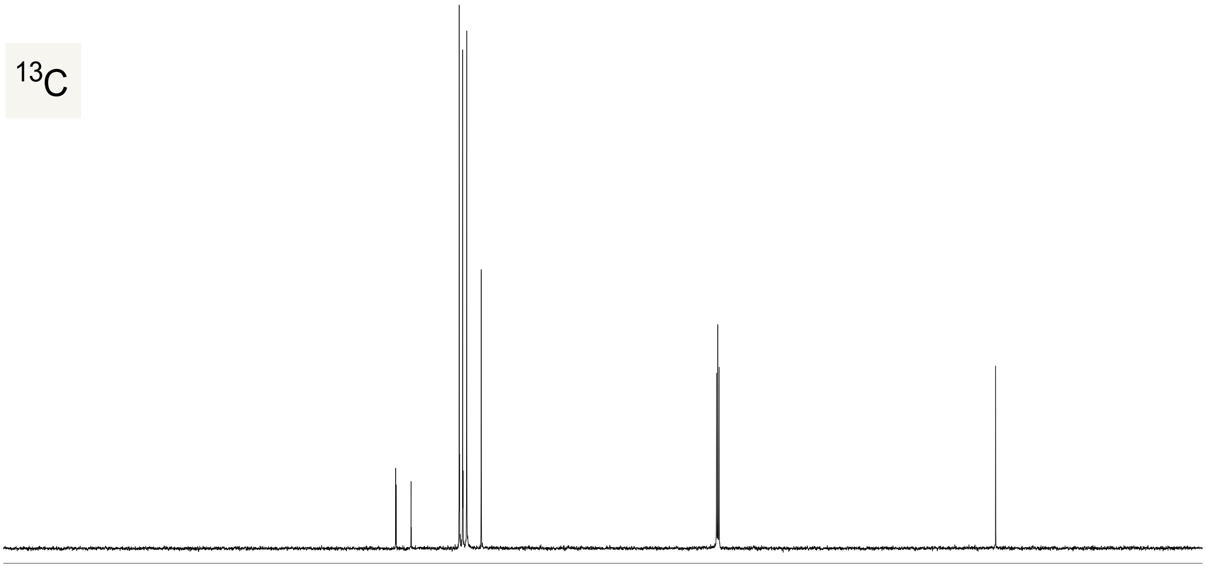
6.5 3-Methyl-1,1'-biphenyl (6e)



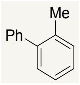
^{1}H

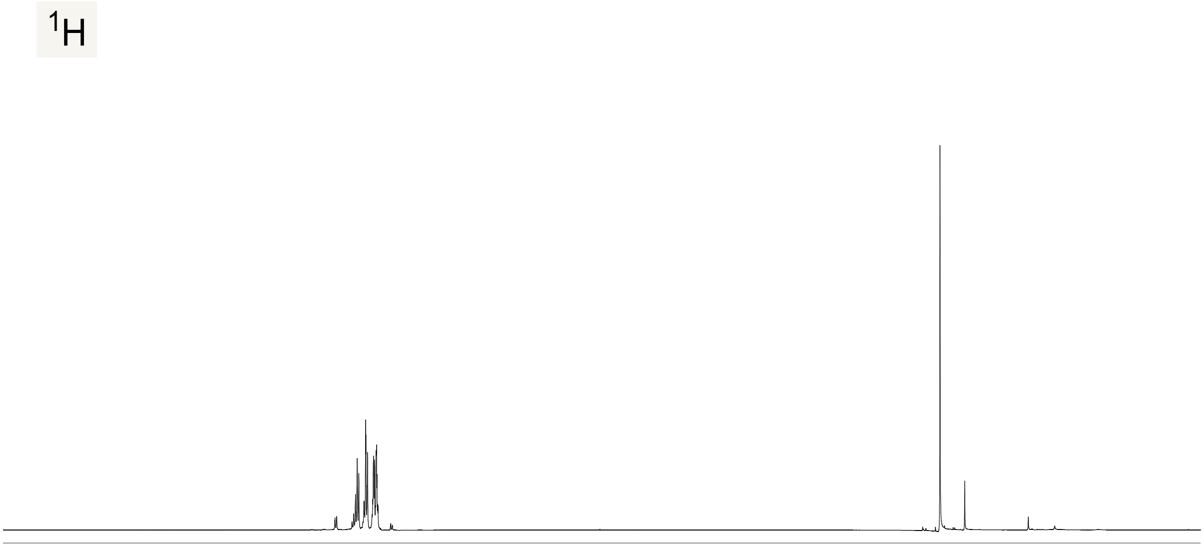


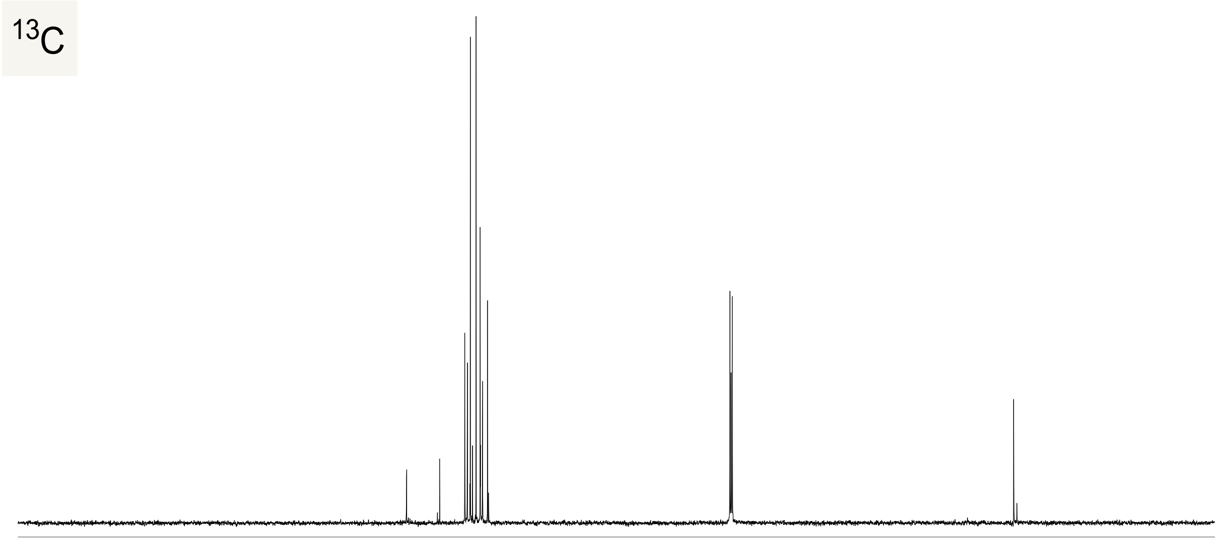
^{13}C



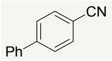
6.6 2-Methyl-1,1'-biphenyl (6f)

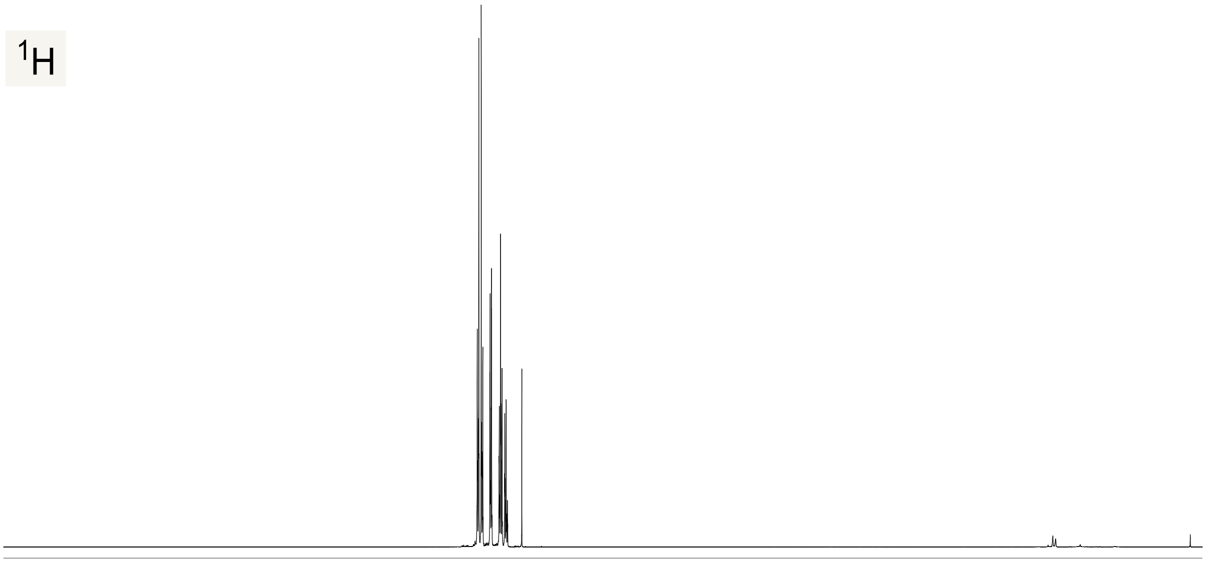


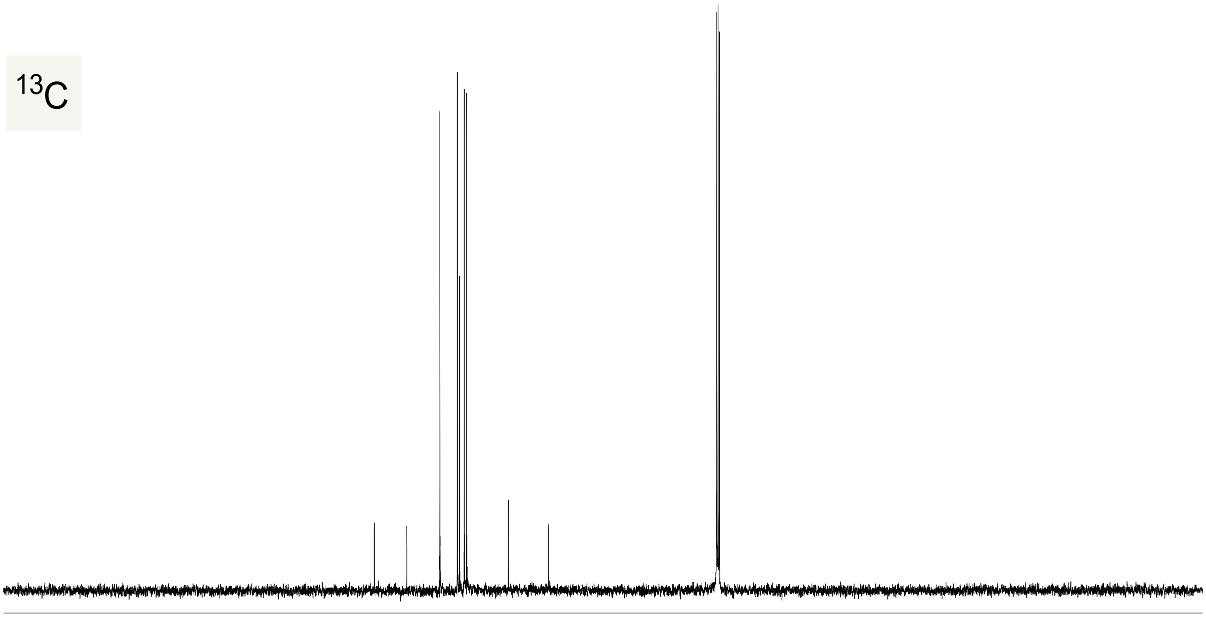




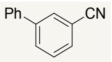
6.7 [1,1'-Biphenyl]-4-carbonitrile (6g)



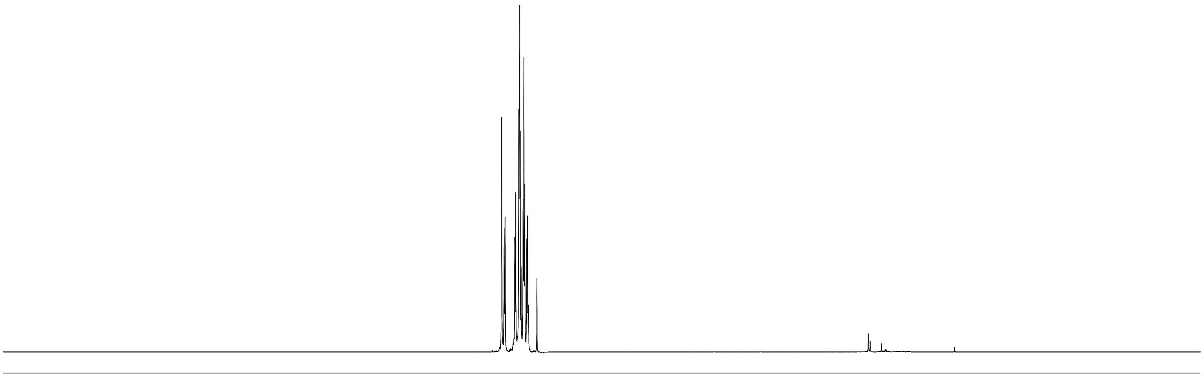




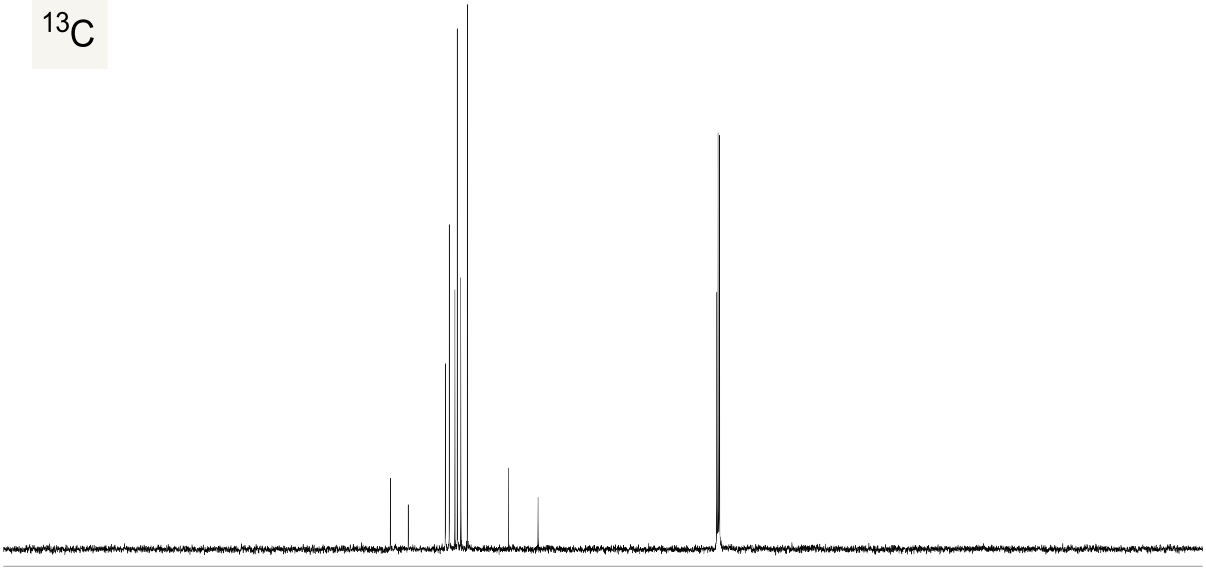
6.8 [1,1'-Biphenyl]-3-carbonitrile (6h)



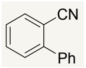
^1H

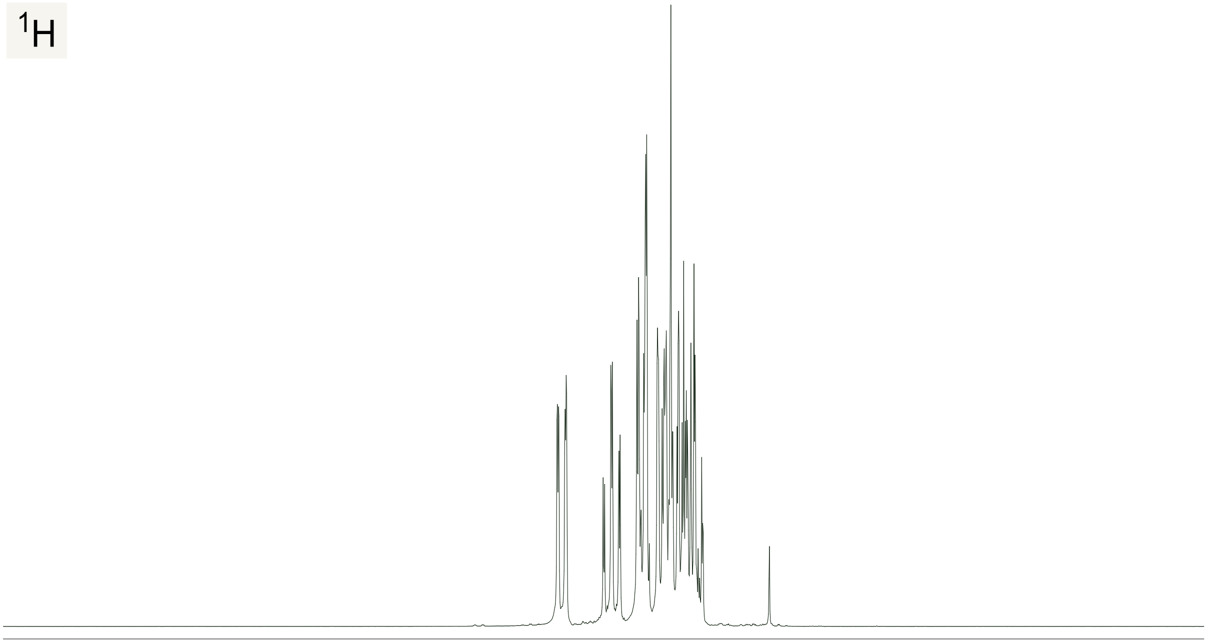


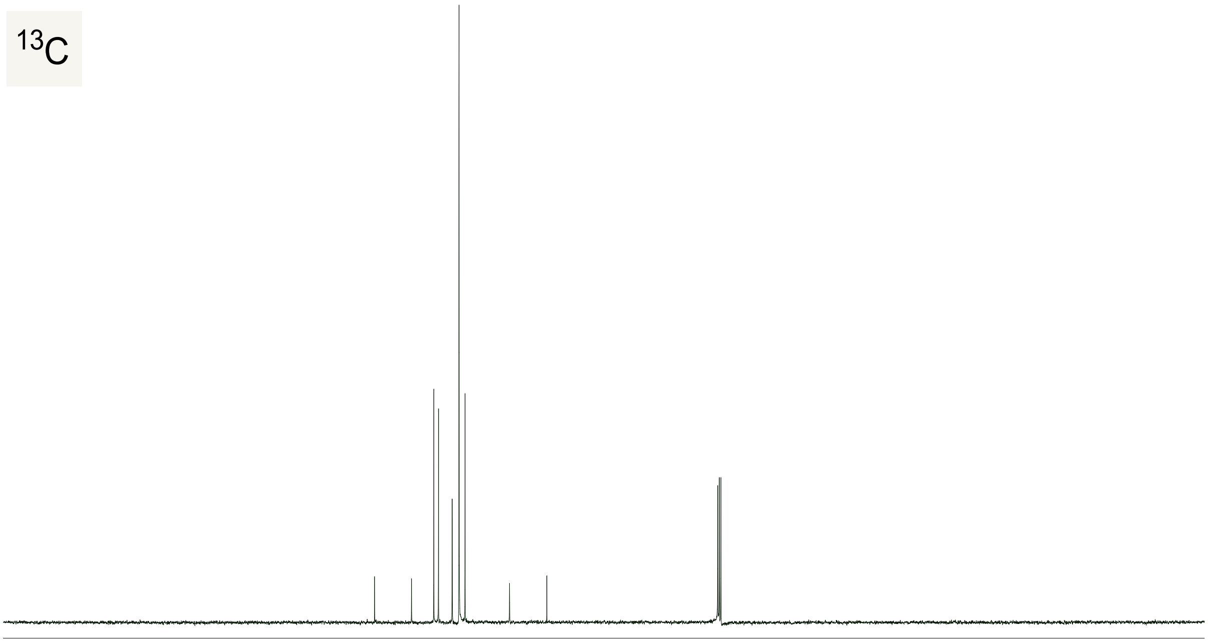
^{13}C



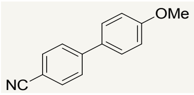
6.9 [1,1'-Biphenyl]-3-carbonitrile (6i)



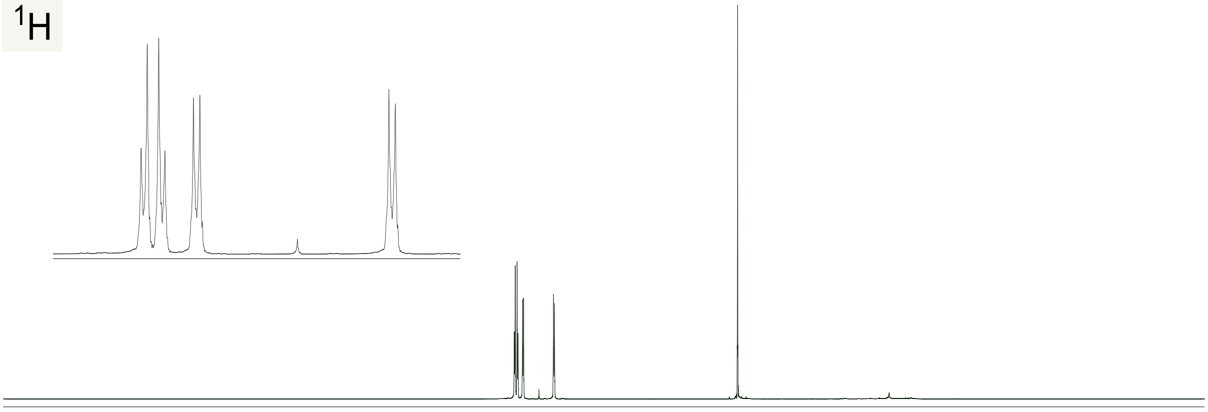




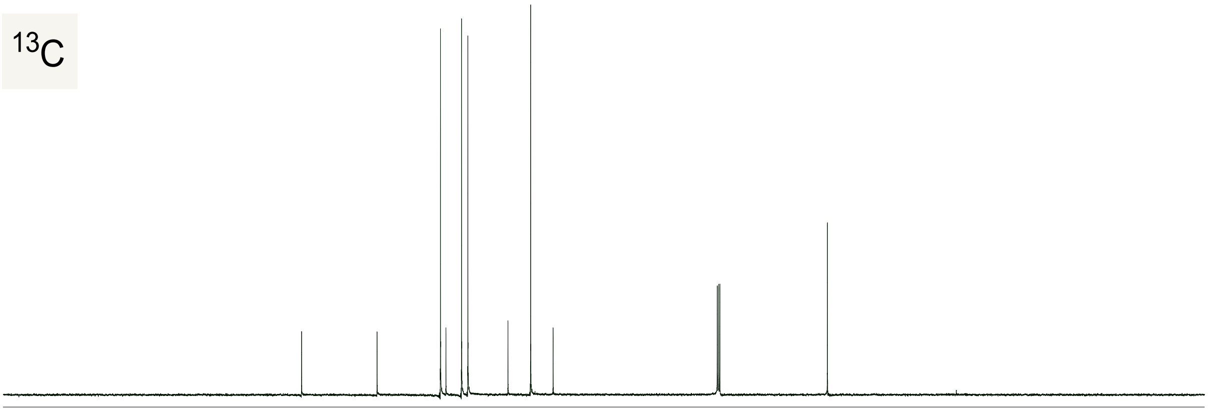
6.10 4'-Methoxy-[1,1'-biphenyl]-4-carbonitrile (6j)



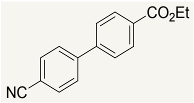
^{1}H



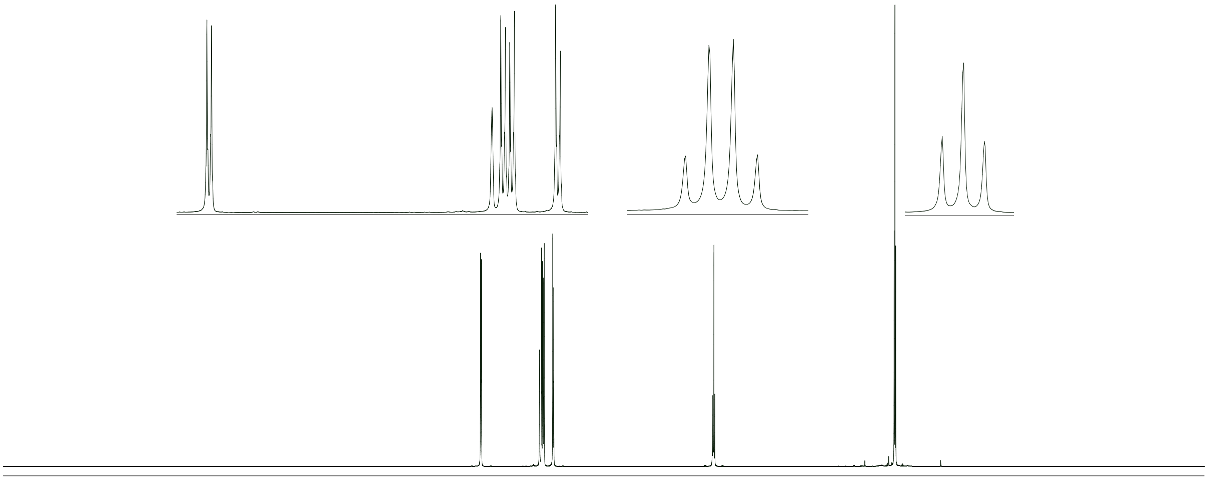
^{13}C



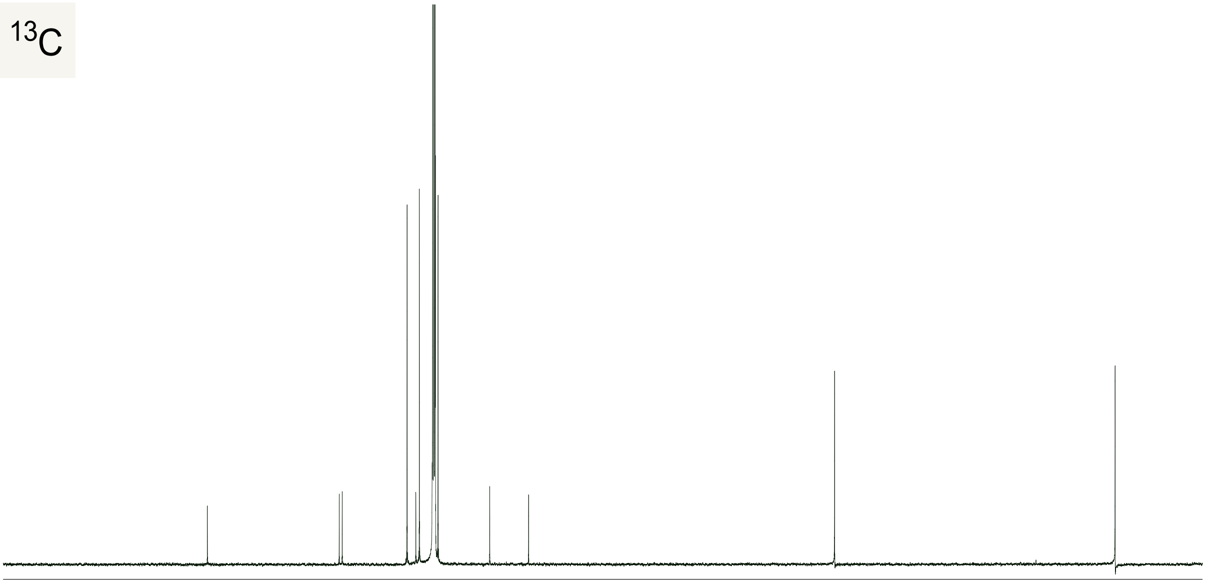
6.11 Ethyl 4'-cyano-[1,1'-biphenyl]-4-carboxylate (6k)



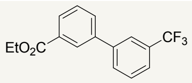
^{1}H

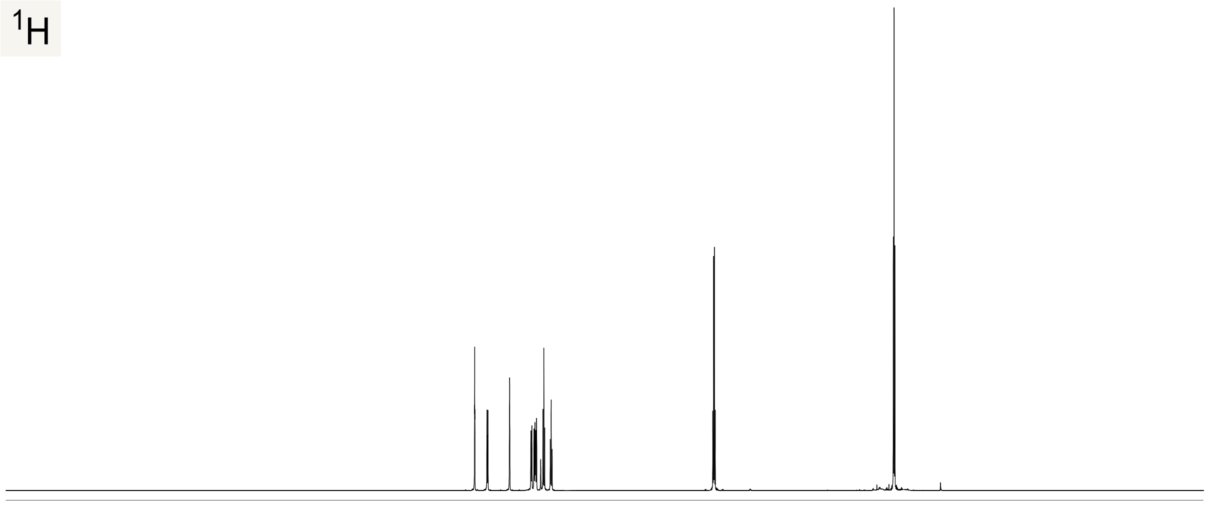


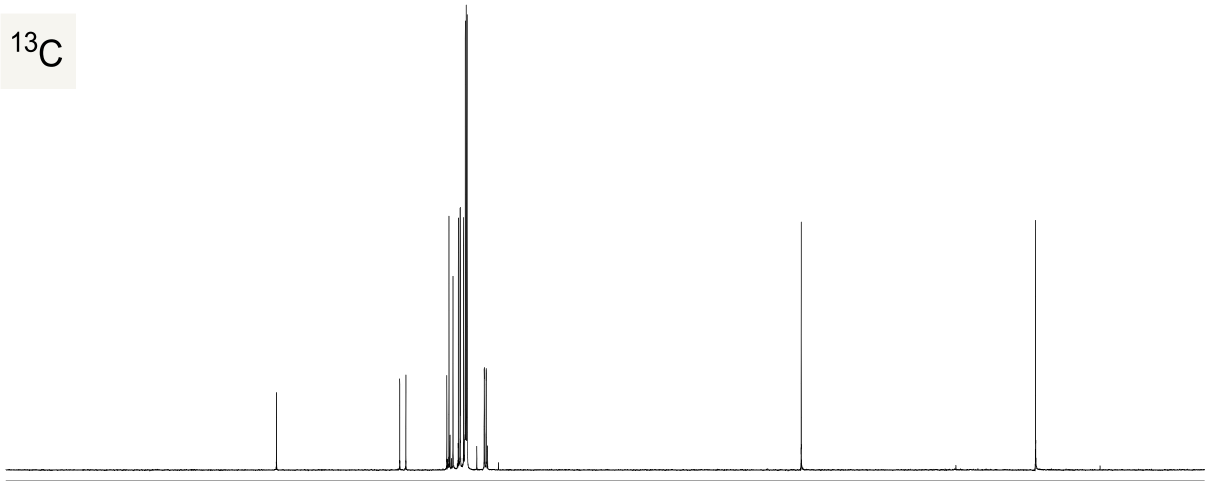
^{13}C



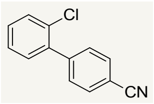
6.12 Ethyl 3'-(trifluoromethyl)-[1,1'-biphenyl]-3-carboxylate (6l)

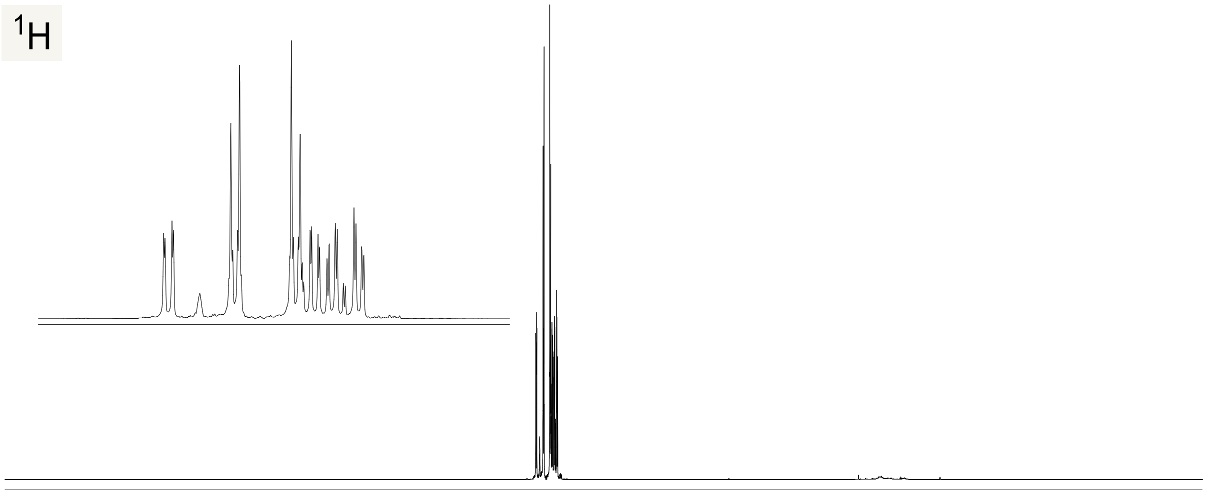


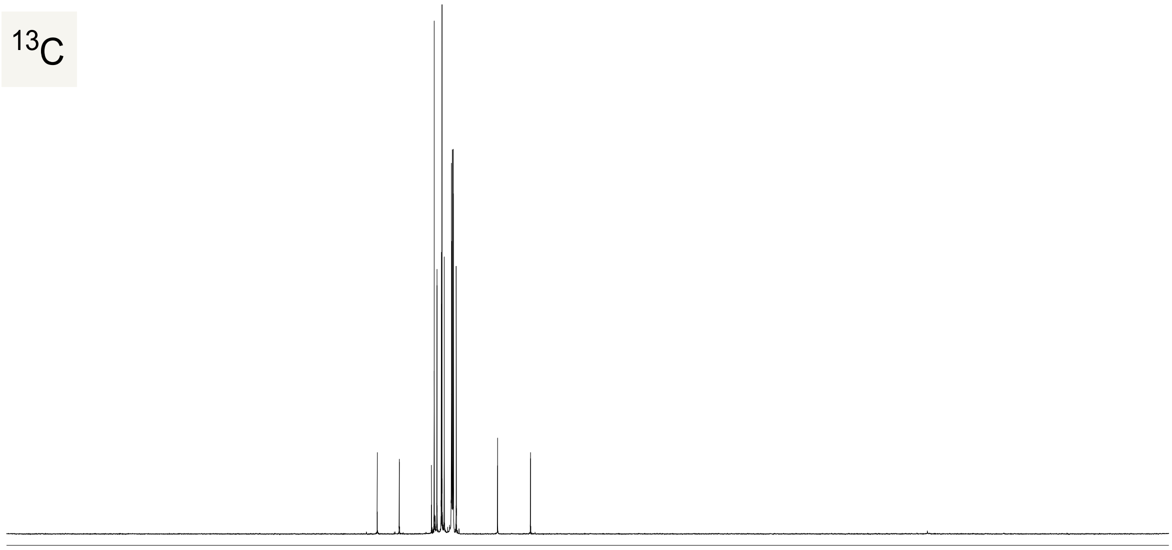




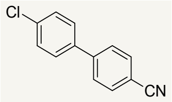
6.13 2'-Chloro-[1,1'-biphenyl]-4-carbonitrile (6m)

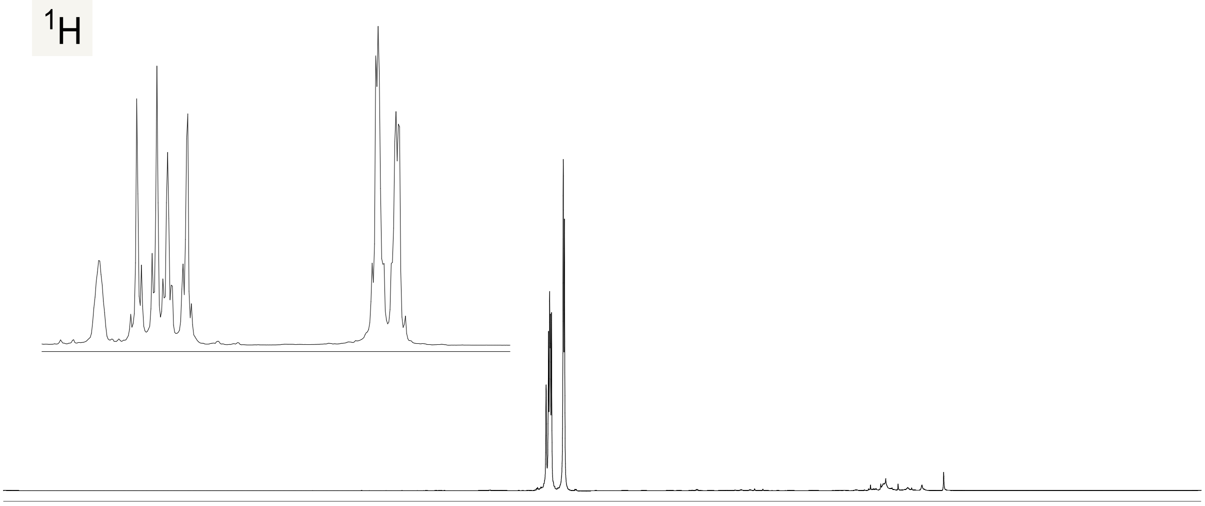


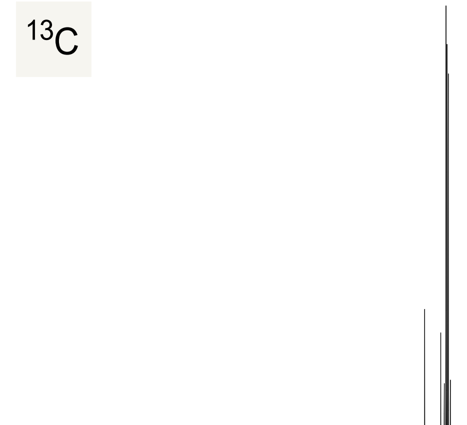




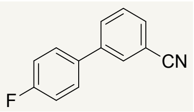
6.14 2'-Chloro-[1,1'-biphenyl]-4-carbonitrile (6n)



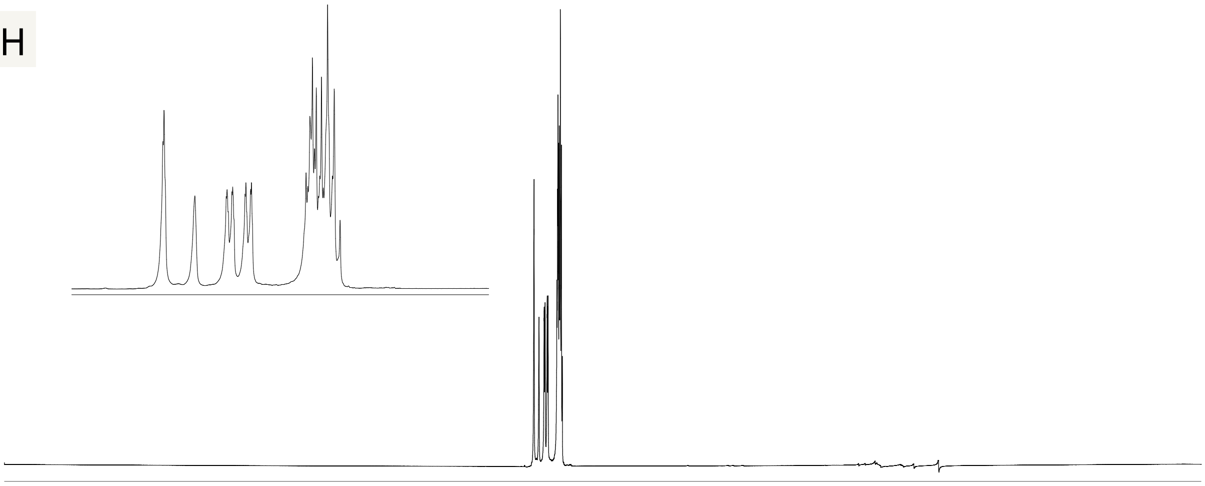




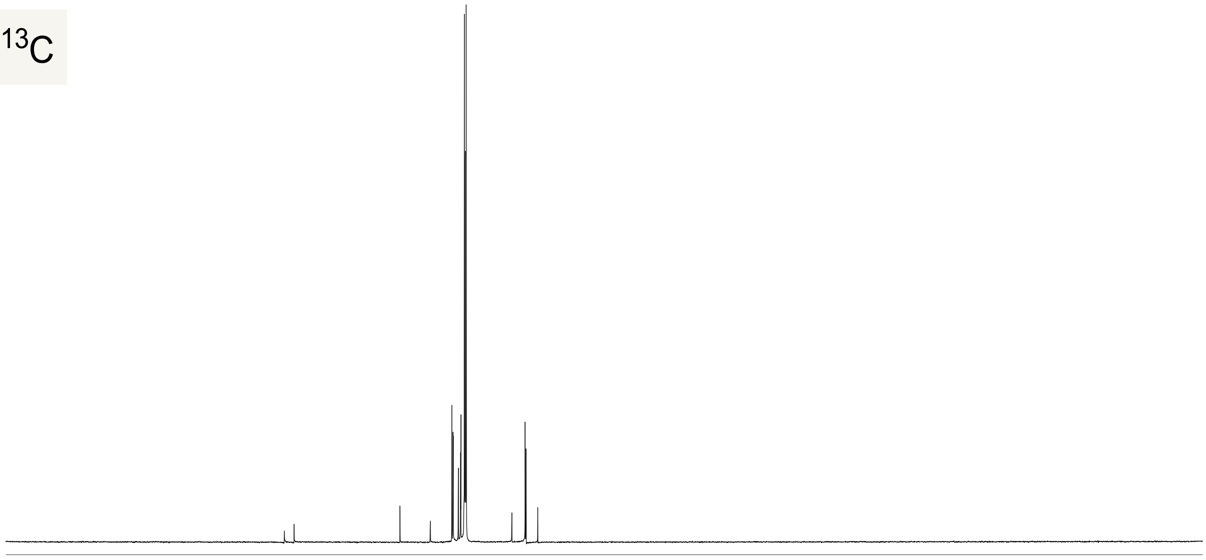
6.15 4'-Fluoro-[1,1'-biphenyl]-3-carbonitrile (6p)



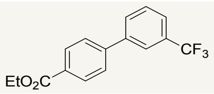
^{1}H

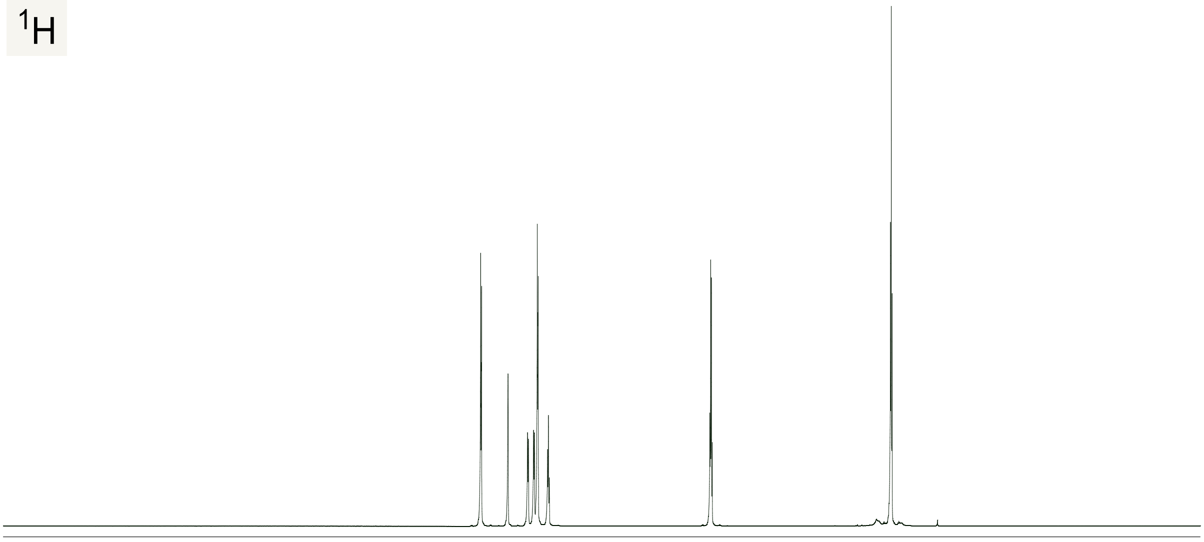


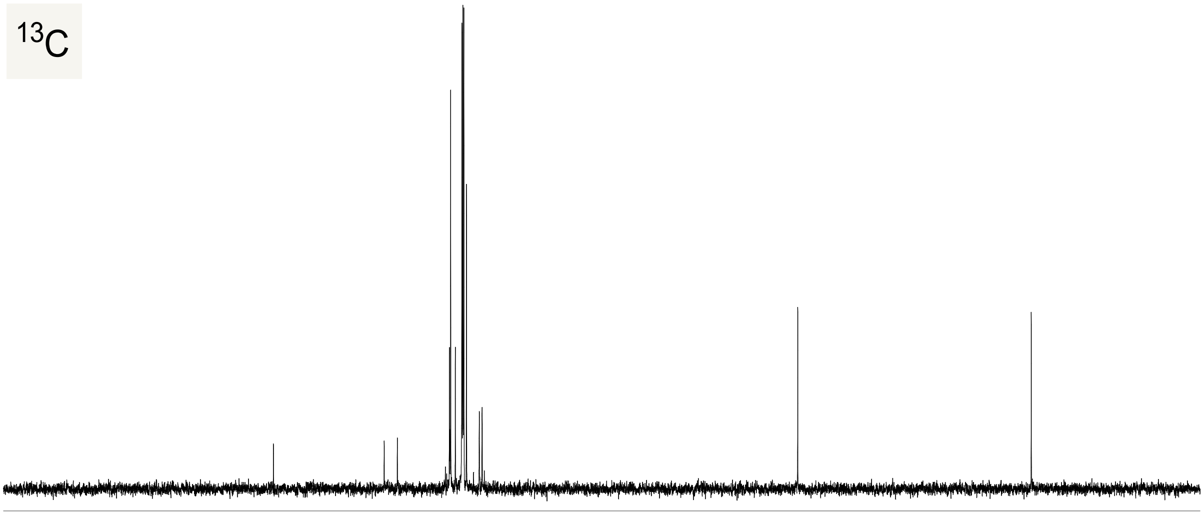
^{13}C



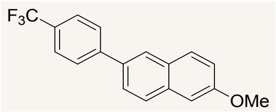
6.16 Ethyl 3'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (6q)



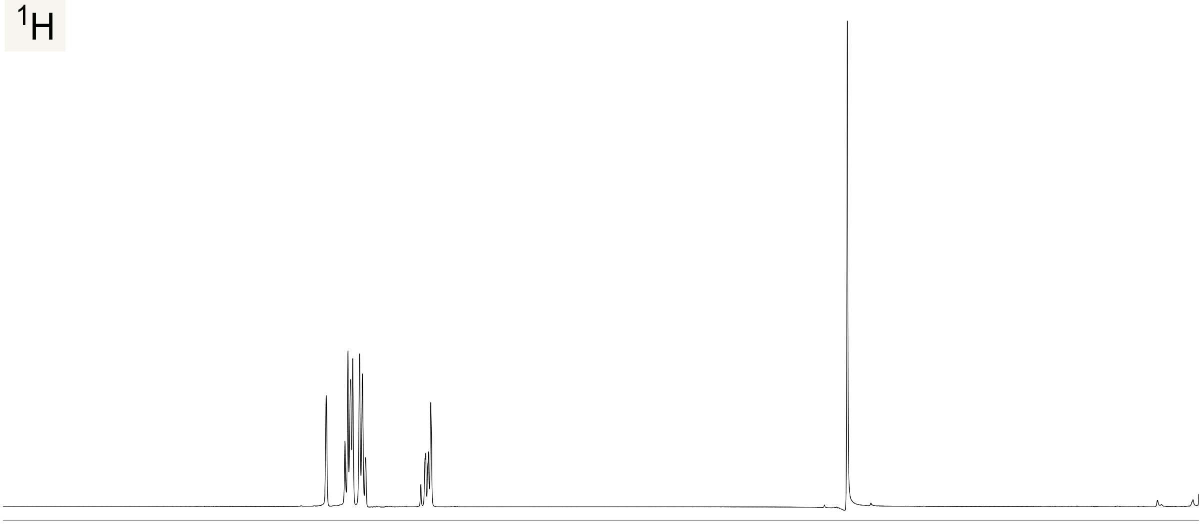




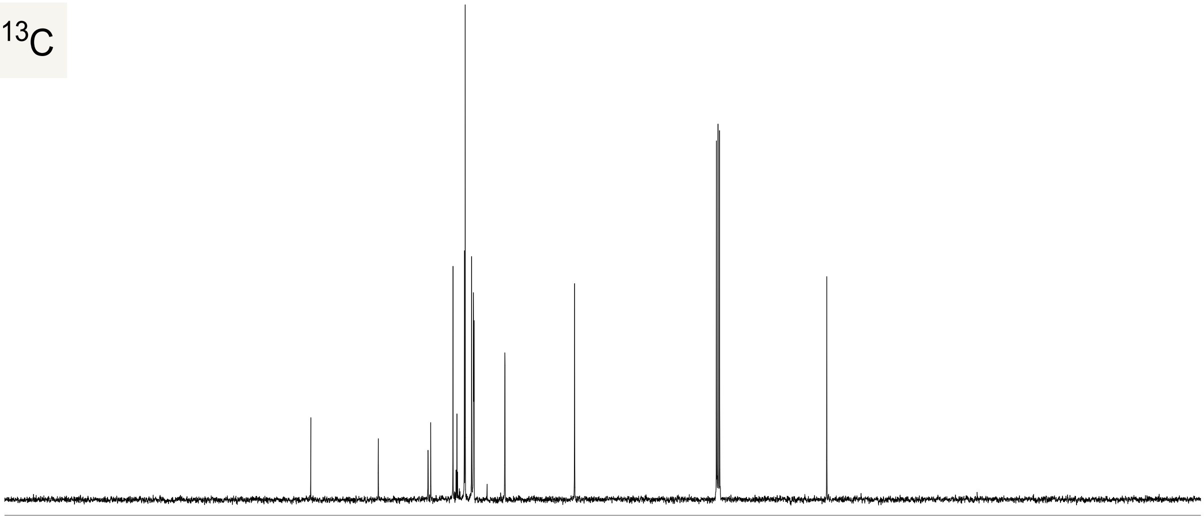
6.17 2-Methoxy-6-(4-(trifluoromethyl)phenyl)naphthalene (6r)



^{1}H



^{13}C



6.18 2-(3-chlorophenyl)thiophene (6s)