Supporting Information

KO*t*Bu: a Privileged Reagent for Electron Transfer Reactions?

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(1) General Information

Except where stated, all reagents were purchased from commercial sources and used without further purification. Where used, anhydrous diethyl ether, tetrahydrofuran, dichloromethane and hexane were dried using a Pure-Solv 400 solvent purification system (Innovative Technology Inc., U.S.A.). Anhydrous benzene was purchased from Alfa Aesar and dried over 3Å molecular sieves which had been activated by microwave heating. Where reactions were carried out in a glovebox, the atmosphere used was either nitrogen or argon and the glovebox was supplied by Innovative Technology Inc., USA. ^{1}H NMR and ^{13}C NMR spectra were recorded on spectrometers operating at 400 MHz and 100 MHz, respectively. All spectral data were acquired at 295 K. Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peak, δ_H 7.27 and δ_C 77.0 for $CDCl_3$, δ_H 2.50 and δ_C 39.5 for d_6-DMSO, and δ_H 2.75 and 2.92 for d_7-DMF, was used as a reference. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The multiplicity abbreviations used are: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Signal assignment was achieved by analysis of DEPT, COSY, NOESY, HMBC and HSQC experiments where required. Infrared (IR) spectra were recorded using an FTIR-ATR spectrometer. High resolution mass spectrometry was performed at the University of Wales, Swansea, in the EPSRC National Mass Spectrometry Centre. Accurate mass was obtained using a LTQ Orbitrap XL using Atmospheric Pressure Chemical Ionisation (APCI) or High Resolution Nano-Electrospray (HNESP) using Electrospray Ionisation (ESI); masses observed are accurate to within 5 ppm. The melting points reported are uncorrected. Thin layer chromatography analyses were carried out on silica gel $60F_{254}$ pre-coated aluminum foil sheets and were visualised using UV light (254 nm) and stained with either basic aqueous potassium permanganate or phosphomolybdic acid, as appropriate. Flash column chromatography was carried out using slurry packed silica gel (SiO_2), 35-75 μm particle size, 60 Å pore size, under a light positive pressure, eluting with the specified solvent system. "Petrol" refers to petroleum ether 40–60 °C.

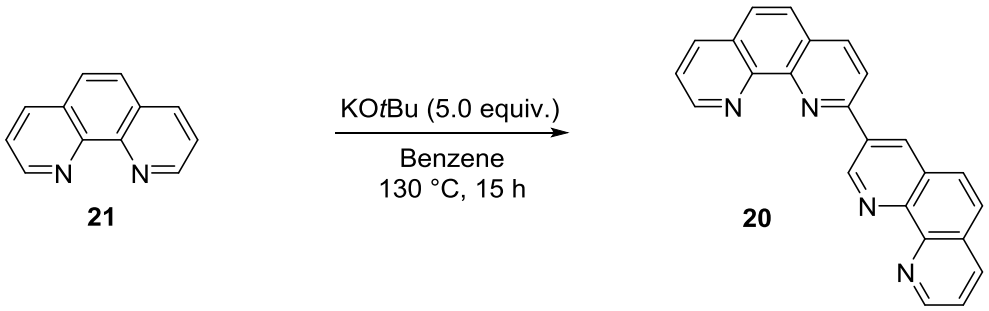
EPR data were processed using WinSIM Public EPR Software Tools (P.E.S.T.) software (MS-Windows 9x, NT, Version 0.98) from the National Institute of Environmental Health Sciences. Further details of EPR hardware is provided in section 2b.

UV-visible absorption measurements were performed using either a PerkinElmer Lambda 25 UV/VIS spectrophotometer.

(2) Transition metal-free coupling reactions

(2a) Cyclic Voltammetry

Synthesis of dimeric compound 20 used for cyclic voltammetry studies



In a glovebox, 1,10-phenanthroline (180 mg, 1.000 mmol) was added to an oven-dried pressure tube. Anhydrous benzene (10 mL) was added, followed by KO*t*Bu (561 mg, 5.000 mmol). The tube was sealed, removed from the glovebox, and stirred at 130 °C for 15 h. After cooling the pressure tube was returned to the glovebox and the blue/green precipitate was filtered and washed with benzene. The solids were transferred to an oven-dried pressure tube and DMF (8 mL) added. Iodine (254 mg, 1.000 mmol) was added and the tube was sealed and stirred at room temperature for 2 h. The reaction was quenched by the addition of water (150 mL) and the resultant light brown solids were filtered and washed with water (100 mL). This crude material was then purified by column chromatography (10% MeOH in MeCN) to give the dimeric compound **20** (83 mg, 23%) as a brown solid.

δ_H (400 MHz, $CDCl_3$): 9.88 (1 H, d, *J* = 2.1 Hz), 9.49 (1 H, d, *J* = 2.1 Hz), 9.30 (1 H, dd, *J* = 4.4, 1.8 Hz), 9.25 (1 H, dd, 4.4, 1.8 Hz), 8.47 (1 H, d, *J* = 8.3 Hz), 8.38 (1 H, d, *J* = 8.3 Hz), 8.32 (2 H, *app* td, *J* = 8.2, 1.6 Hz), 8.08 (1 H, d, *J* = 8.8 Hz), 7.91 (1 H, d, *J* = 8.8 Hz), 7.88 (1 H, d, *J* = 8.8 Hz), 7.87 (1 H, d, *J* = 8.8 Hz), 7.69 (1 H, dd, *J* = 8.0, 4.3 Hz), 7.66 (1 H, dd, *J* = 8.0, 4.3 Hz). These data were consistent with the literature.[1]

Cyclic Voltammetry

Cyclic voltammetry was conducted using a three-electrode setup consisting of a platinum wire working electrode (d = 1.0 mm), saturated calomel reference electrode and platinum gauze counter-electrode. Electrochemical measurements were carried out in a glovebox under N_2 using an Autolab®/PGSTAT302N potentiostat. Ferrocene and *n*-Bu_4NPF_6 were purchased commercially and used as supplied.

All solutions were prepared at 4 mM concentration (in 0.3 M Bu_4NBF_4/DMF) using ferrocene as an external standard to ensure consistency throughout the study and whose peak height (*ca*. 2.5 x 10^{-6} A) corresponds to a 1-electron oxidation. Anhydrous, degassed DMF was used throughout the study which was conducted within a glovebox under N_2 with 0.3 M Bu_4NBF_4/DMF as the electrolyte.

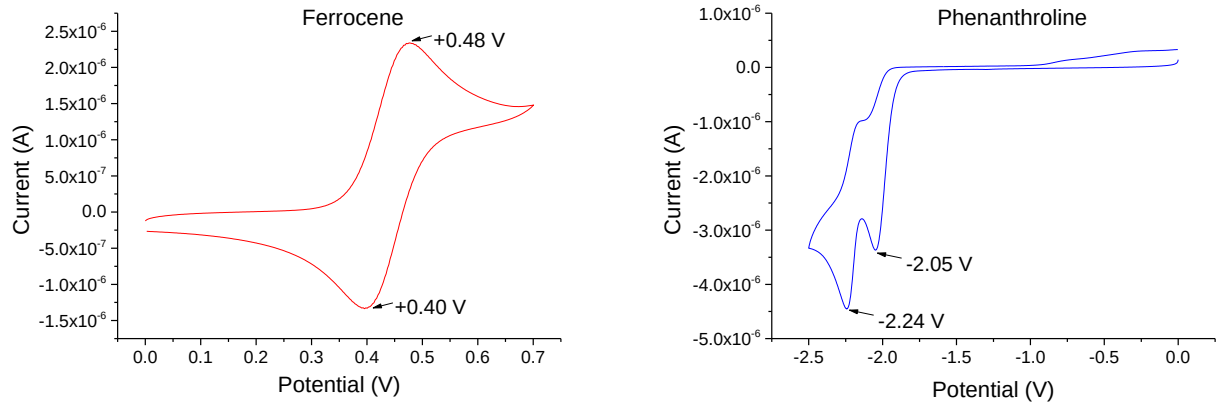


Figure S1: Left: Cyclic Voltammogram of ferrocene. Right: Cyclic Voltammogram of phenanthroline **21**.

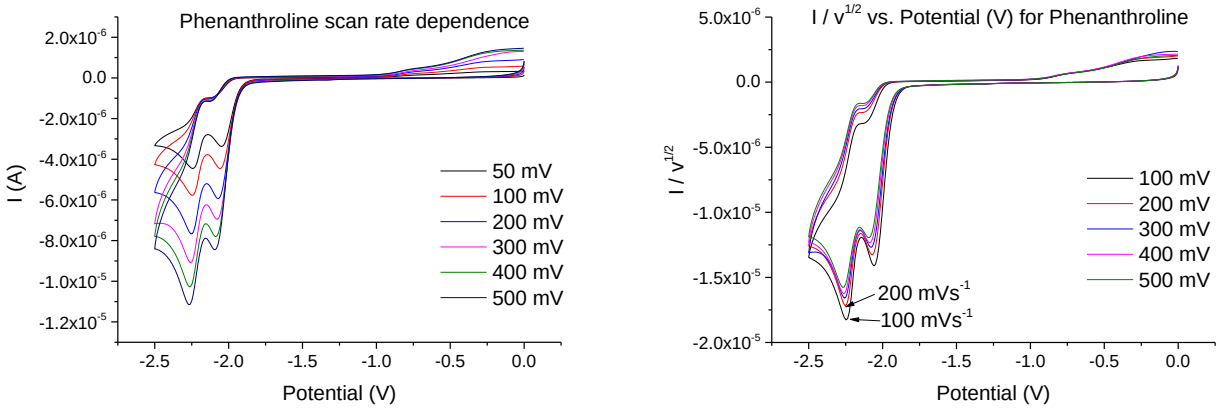


Figure S2: Left: Scan-rate dependence (mV s^{-1}) for phenanthroline **21**. Right: Plot of $\boldsymbol{I/v^{1/2}}$ *vs.* $\boldsymbol{V}$ for phenanthroline **21**.

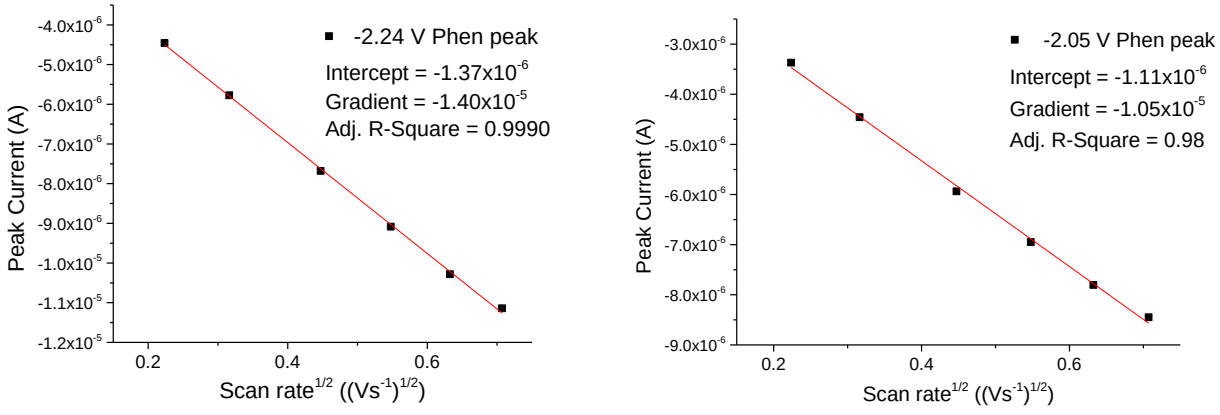


Figure S3: Randles-Sevcik plots[2,3] for phenanthroline **21** peak currents.

The CV for the phenanthroline substrate, at a scan rate of 50 mV s^{-1}, shows two reduction peaks at −2.05 V and −2.24 V *vs*. SCE and on the reverse scan, the oxidation peaks for both processes are observed (Figure S1 (right voltammogram). The cathodic-anodic peak separation for the second reduction, $\Delta E_{p\text{-}p}$ obtained was 90 mV (close to the value obtained for ferrocene at the same scan rate (80 mV *cf*. 59 mV/n for an ideal one-electron transfer), indicating a high degree of reversibility (and so rapid kinetics) for the electron transfer processes. By comparison with ferrocene, both these processes again appear to be single-electron transfer steps, in accordance with the low $\Delta E_{p\text{-}p}$ values. A scan rate dependence (over the range 50 mV s^{-1} to 500 mV s^{-1}) was carried out (Figure S2 (left plot)) and the Randles-Sevcik plots[2,3] obtained for the two peak currents were linear (Figure S3) and yielded a value for the diffusion coefficient $D = 9.36 \times 10^{-7}$ cm^2 s^{-1} for the phenanthroline species in the DMF medium. A normalised plot $I/v^{½}$ *vs*. *V* was also carried in order to examine whether the reduced product was involved in any chemical reaction prior to the reverse scan (Figure S2 (right spectrum)). The data show that this was not the case as the shape of the voltammogram remained unaltered over the scan rate range examined. It would have been expected from such a plot that all the scans should have superimposed but the contribution to the charging of the electrical double layer is not taken into account in the normalised plot.

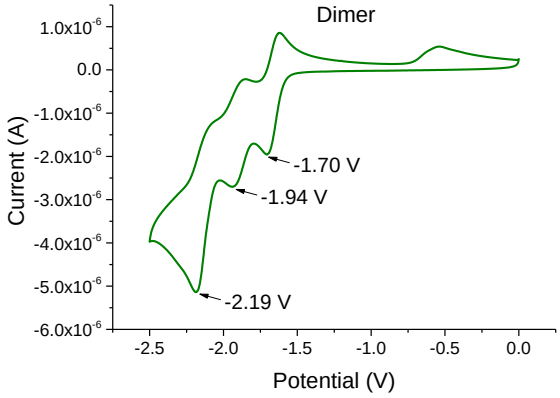


Figure S4: Cyclic voltammogram of phenanthroline dimer **20**.

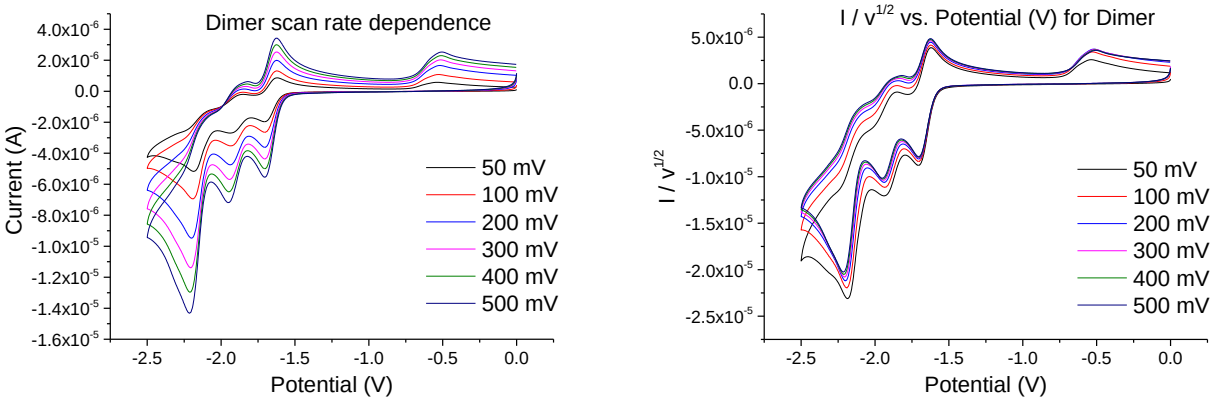


Figure S5: Scan-rate dependence (mV s^{-1}) for dimer **20**. Right: Plot of $\boldsymbol{I/v^{1/2}}$ *vs*. $\boldsymbol{V}$ for dimer **20**.

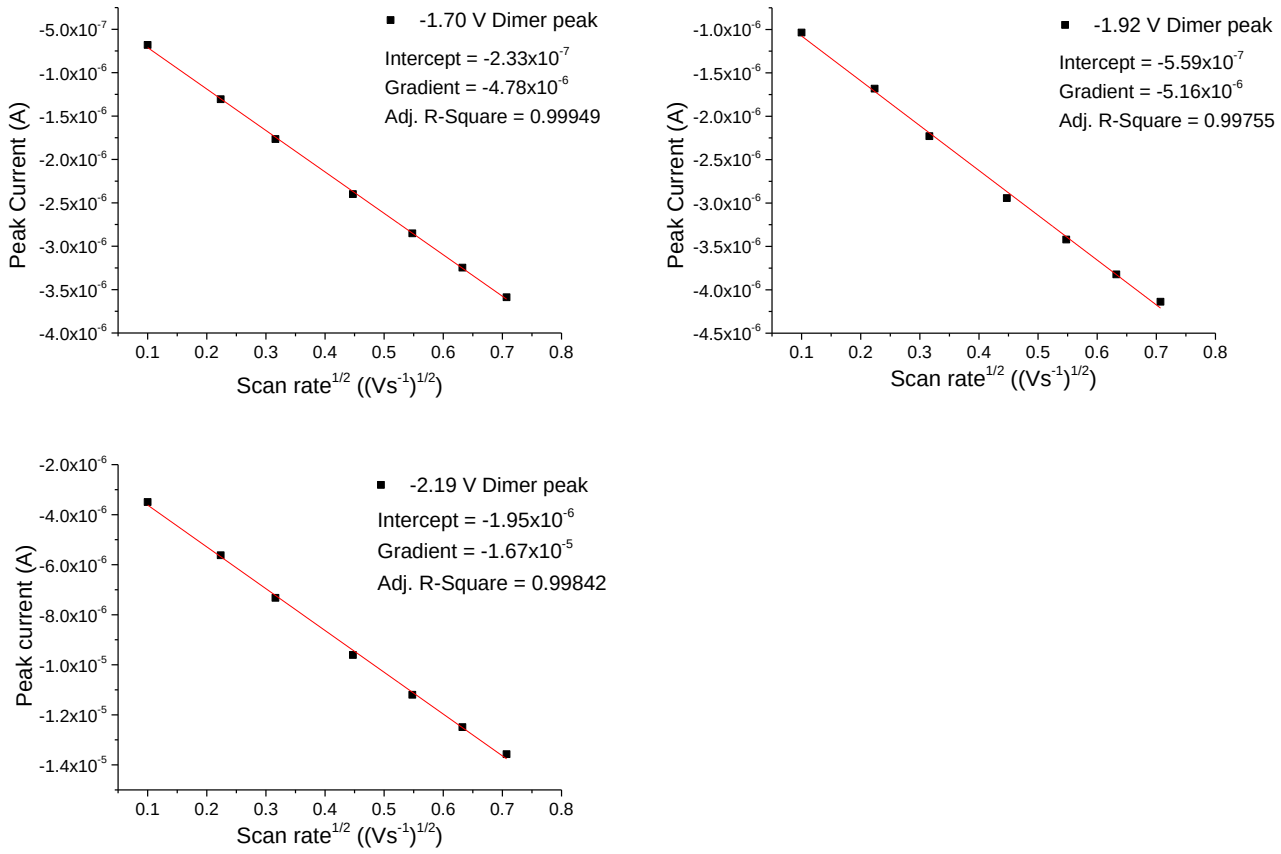


Figure S6: Randles-Sevcik plots for phenanthroline dimer peak currents.

For the phenanthroline dimer **20**, two single-electron transfer peaks (for the first reduction, $\Delta E_{p\text{-}p}$ obtained was 90 mV) were found at –1.70 V and –1.94 V *vs*. SCE, (Figure S4) corresponding to consecutive electron injections. Both of these potentials are less negative than those observed on the phenanthroline substrate **21**, consistent with enhanced electron delocalisation in the dimer. A scan rate dependence was similarly carried out here (Figure S5 (left plots)) and the Randles-Sevcik plots (Figure S6) yielded a value of $D = 4.36 \times 10^{-7}$ cm^2 s^{-1}, consistent with the larger size of the dimer and also for the lower peak currents obtained here. At more negative potentials, a third reduction process occurs giving a current peak at –2.19 V. Comparison with ferrocene indicates that this involves a 2-electron reduction step, leading to a tetra-anion **SI-3** (Figure S7). Overall then, this last process then appears as a two-electron transfer step. The normalised $I/v^{½}$ *vs*. V was also carried out here [Figure S5 (right spectrum)] and, as before, no significant change in the shape of the voltammograms was observed over the scan rates employed here.

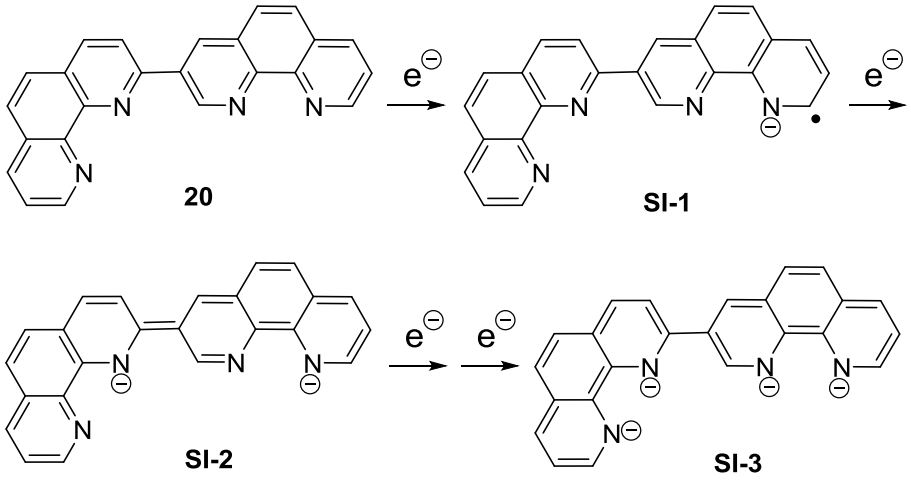


Figure S7: Sequential transfer of single electrons to dimer **20**.

(2b) EPR sample preparation and spectra

EPR Spectroscopy general details

EPR spectra were obtained with a Bruker EMX 10/12 spectrometer fitted with a rectangular ER4122 SP resonant cavity and operating at 9.5 GHz with 100 kHz modulation. Samples (0.2 cm^3), were prepared as described in the section below and placed in a 4 mm o.d. quartz tubes and positioned in the EPR resonant cavity. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker SimFonia and NIEHS Winsim2002 software packages. EPR signals were digitally filtered and double integrated using the Bruker WinEPR software and selected radical concentrations were calculated by reference to the double integral of the signal from a known concentration of the stable radical DPPH [1×10^{-3} M in PhMe], run under identical conditions. The majority of EPR spectra were recorded with 2.0 mW power, 0.8 G_{pp} modulation intensity and a gain of *ca.* 10^6.

EPR sample preparation and spectra

In a glovebox 1,10-phenanthroline (18.0 mg, 0.100 mmol) was added to an oven-dried pressure tube and DMF (2 mL) and KO*t*Bu (44.9 mg, 0.400 mmol) were added. The tube was sealed and stirred at 100 °C for 2 h. After being allowed to cool the tube was taken back into the glovebox and diluted with toluene (8 mL) to provide a 0.01 M solution (w.r.t. the starting 1,10-phenanthroline) which was used for EPR.

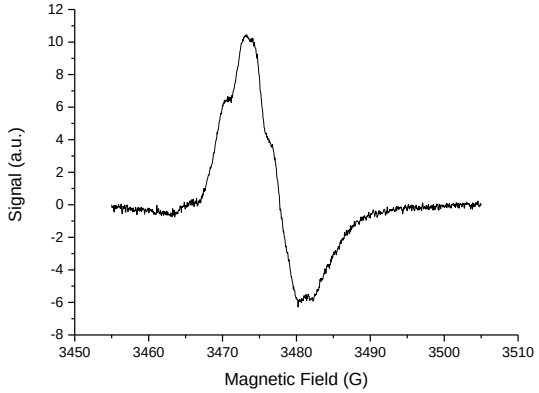


Figure S8. EPR spectrum of the reaction of 1,10-phenanthroline **21** and KO*t*Bu in DMF.

In a glovebox 1,10-phenanthroline (18.0 mg, 0.100 mmol) was added to an oven-dried pressure tube and toluene (2 mL) and KO*t*Bu (44.9 mg, 0.400 mmol) were added. The tube was sealed and stirred at 100 °C for 2 h. After being allowed to cool the tube was taken back into the glovebox and diluted with toluene (8 mL) to provide a 0.01 M solution (w.r.t. the starting 1,10-phenanthroline) which was used for EPR.

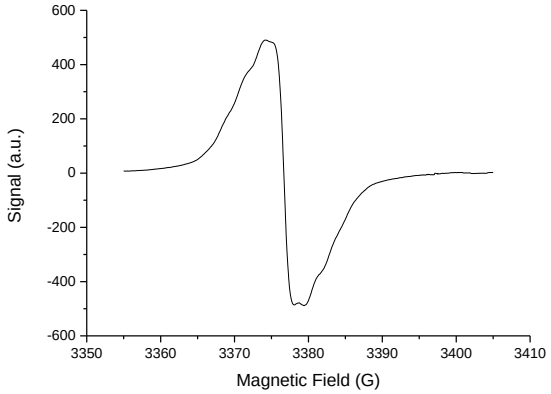


Figure S9. EPR spectrum of the reaction of 1,10-phenanthroline **21** and KO*t*Bu in toluene.

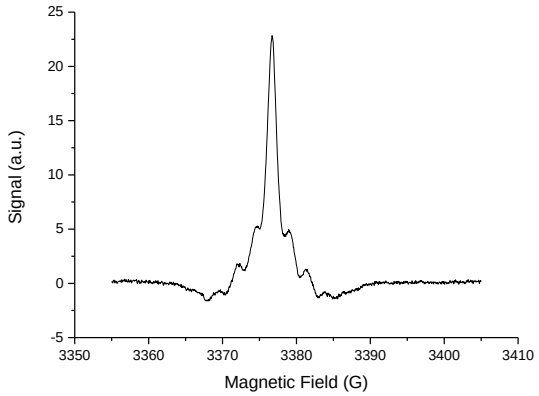


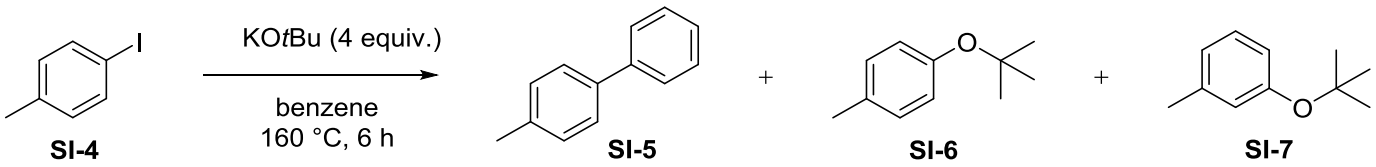
Figure S10. 2nd derivative of EPR spectrum of the reaction of 1,10-phenanthroline **21** and KO*t*Bu in toluene.

Spectra in Figures S8 and S9 show the presence of radical species in the relevant solutions. Figure S10, the 2nd derivative of Figure S9, shows that more than one radical species was present in the solution.

(2c) Evidence for the formation of benzynes under the conditions of Cuthbertson, J.; Gray, V. J.; Wilden, J. D. *Chem. Commun*., **2014**, *50*, 2575–2578.

The purpose of these experiments was to investigate if, under these conditions, benzyne was produced. If so, this would be consistent with initiation of coupling reactions via a benzyne mechanism.[1]

Reaction of 4-iodotoluene SI-4 with benzene in the presence of KO*t*Bu



Inside a glovebox, 4-iodotoluene **SI-4** (218 mg, 1.000 mmol) was dissolved in benzene (10 mL) in an oven-dried pressure tube. KO*t*Bu (449 mg, 4.0 mmol, 4.0 eq.) was added, the tube sealed, removed from the glovebox, and the reaction stirred at 160 °C for 6 h. After being allowed to cool, the reaction was quenched with water (30 mL) and extracted with Et_2O (3 × 30 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material. 1,3,5-Trimethoxybenzene (17 mg, 0.101 mmol), selected to be an internal standard for NMR, was added as a solid. ~1 mL $CDCl_3$ was added and the solution stirred. A portion of the solution was taken and diluted for NMR analysis.

The quantity of each product was determined in the following way (also see annotated spectra in Figure S11 below): For the **coupled product SI-5** the integral of the methoxy signal of the internal standard was set to '9 units'. The integration of the methyl signal of **SI-5** (2.41 ppm, 3 H) was then measured and the following calculation gave the amount of coupled product **SI-5** present:

(9.1/3) × 10 = **30%**

For the 1-*tert*-butoxy-4-methylbenzene **SI-6** and 1-*tert*-butoxy-3-methylbenzene **SI-**7 (both arising from an intermediate benzyne) the methoxy signal of the internal standard was set to 9. The integration of the *t*-butoxy signals at 1.34 and 1.35 ppm (9 H) were then measured and the following calculation gave the amount of **SI-6** and **SI-7** present:

(18.4/9) × 10 = **20%** and (17.9/9) × 10 = **20%**

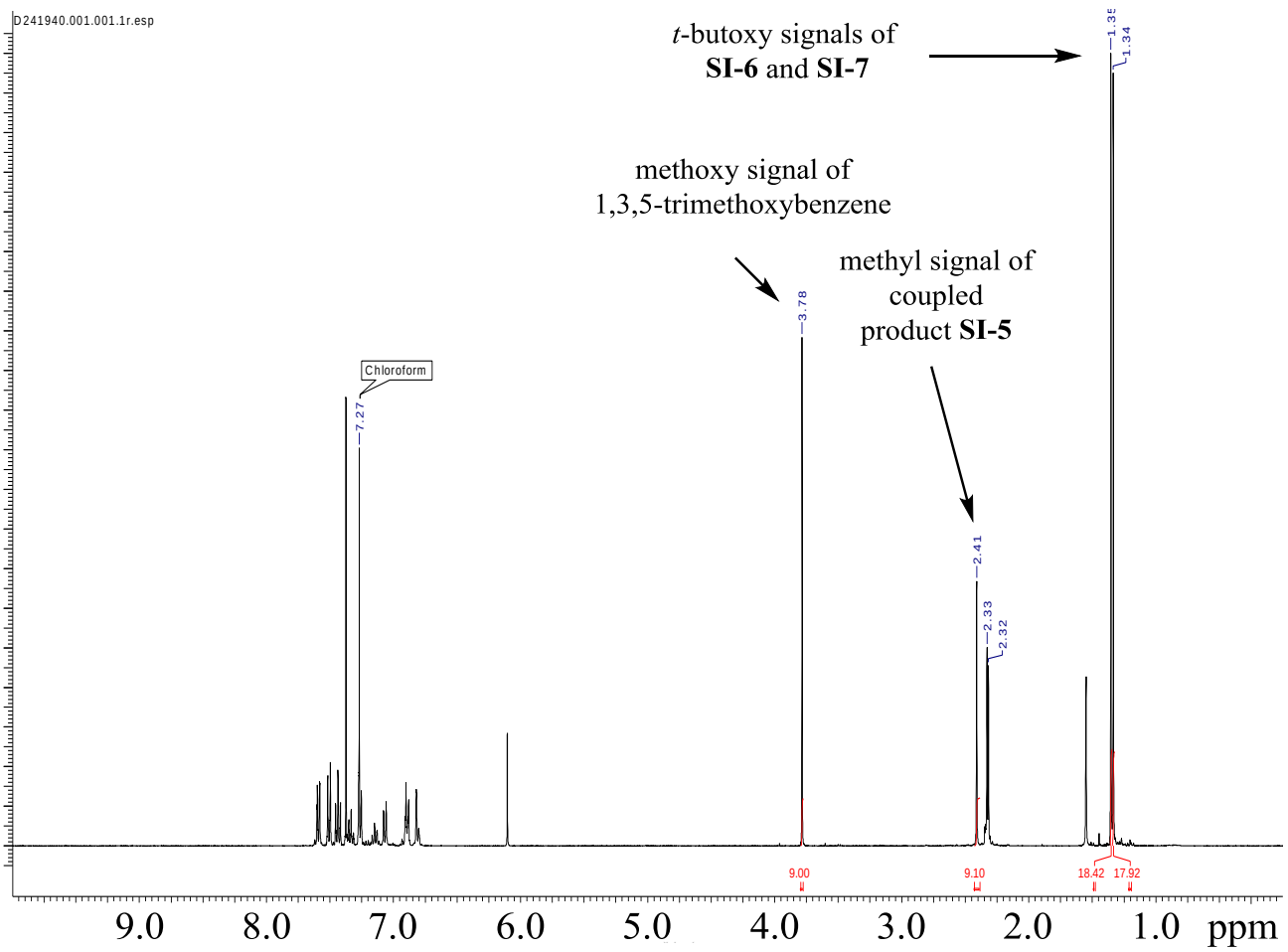
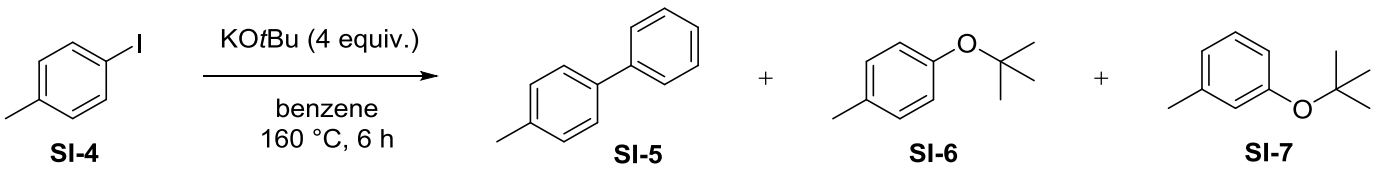


Figure S11. ^{1}H NMR spectrum of the crude material (with internal standard 1,3,5-trimethoxybenzene added) from the coupling reaction of 4-iodotoluene and benzene with KO*t*Bu.

Reaction of 4-iodotoluene with benzene in the presence of KO*t*Bu, with isolation of SI-6 and SI-7



Inside a glovebox 4-iodotoluene **SI-4** (218 mg, 1.000 mmol) was dissolved in benzene (10 mL) in an oven-dried pressure tube. KO*t*Bu (449 mg, 4.0 mmol, 4.0 eq.) was added, the tube sealed, removed from the glovebox, and the reaction stirred at 160 °C for 6 h. after being allowed to cool the reaction was quenched with water (30 mL) and extracted with Et_2O (3 × 30 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material. Purification by column chromatography (hexane as eluent) gave **SI-5** (45 mg, 27%) as a colourless solid and an inseparable mixture of **SI-6** and **SI-7** (65 mg, 40%) as a colourless oil.

Data for **SI-5**: [see Figure S12(a)]

Mp 45–47 °C [lit.,[4] 46–47 °C]; δ_H (400 MHz, $CDCl_3$) 7.59 (2 H, d, J = 8.4, 1.4 Hz), 7.51 (2 H, d, J = 8.0 Hz), 7.44 (2 H, t, J = 7.5 Hz), 7.36–7.30 (1 H, m), 7.28–7.24 (2 H, m) (note that this peak overlaps with residual chloroform), 2.41 (3 H, s). These data are consistent with the literature values.[5,6]

Data for inseparable mixture of **SI-6** and **SI-7** [see Figure S12(b)]:

δ_H (400 MHz, $CDCl_3$): 7.18–7.11 (1H, m), 7.07 (2 H, d, J = 8.5 Hz), 6.92–6.87 (1 H, m), 6.89 (2 H, d, J = 8.5 Hz), 6.84–6.78 (1 H, m), 6.82 (1 H, s), 2.33 (3 H, s), 2.32 (3H, s), 2.30 (3H, s), 1.35 (9H, s), 1.32 (9H, s). These data are consistent with the literature.[7]

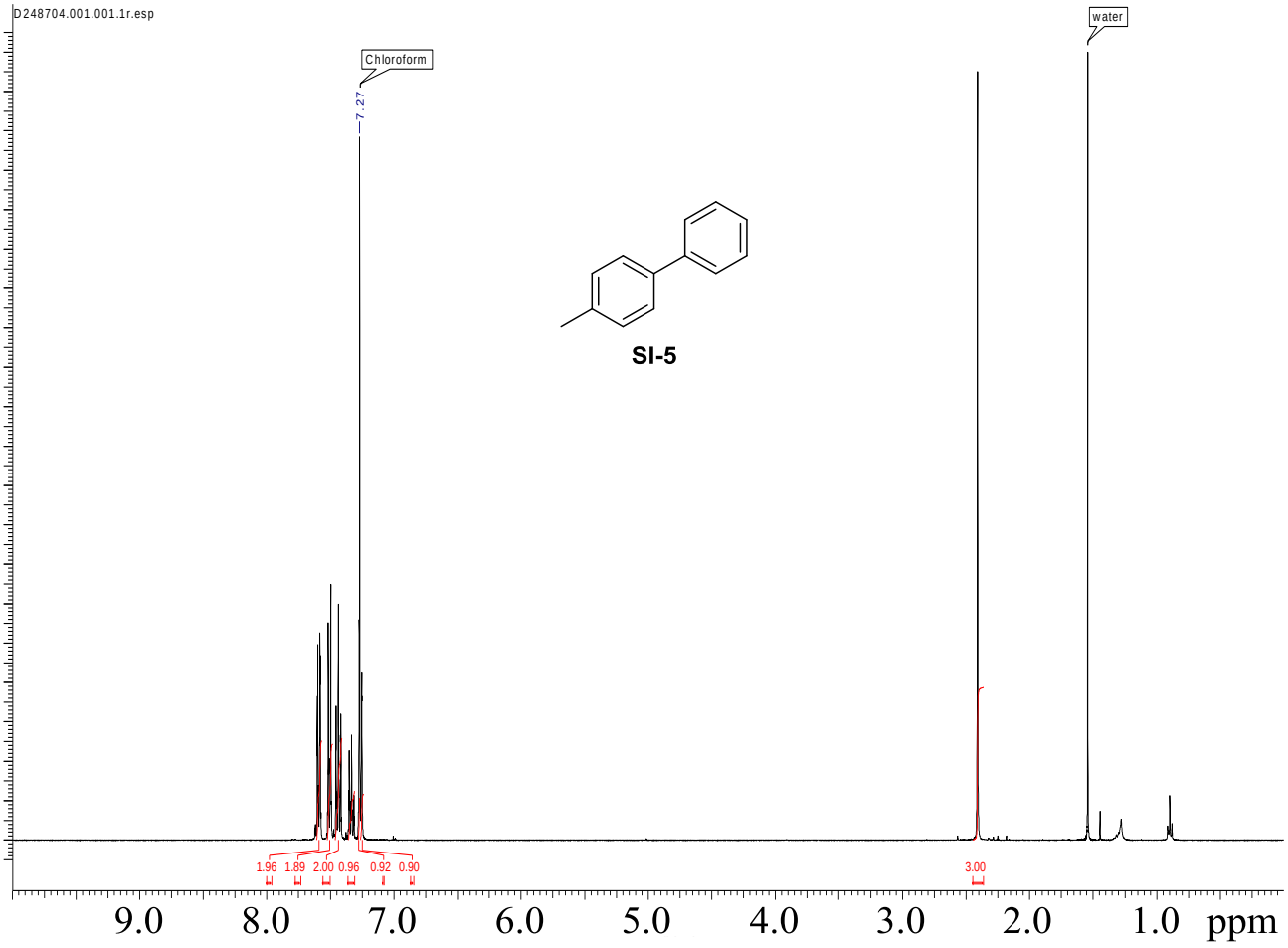


Figure S12(a) ^{1}H NMR spectrum of purified **SI-5**.

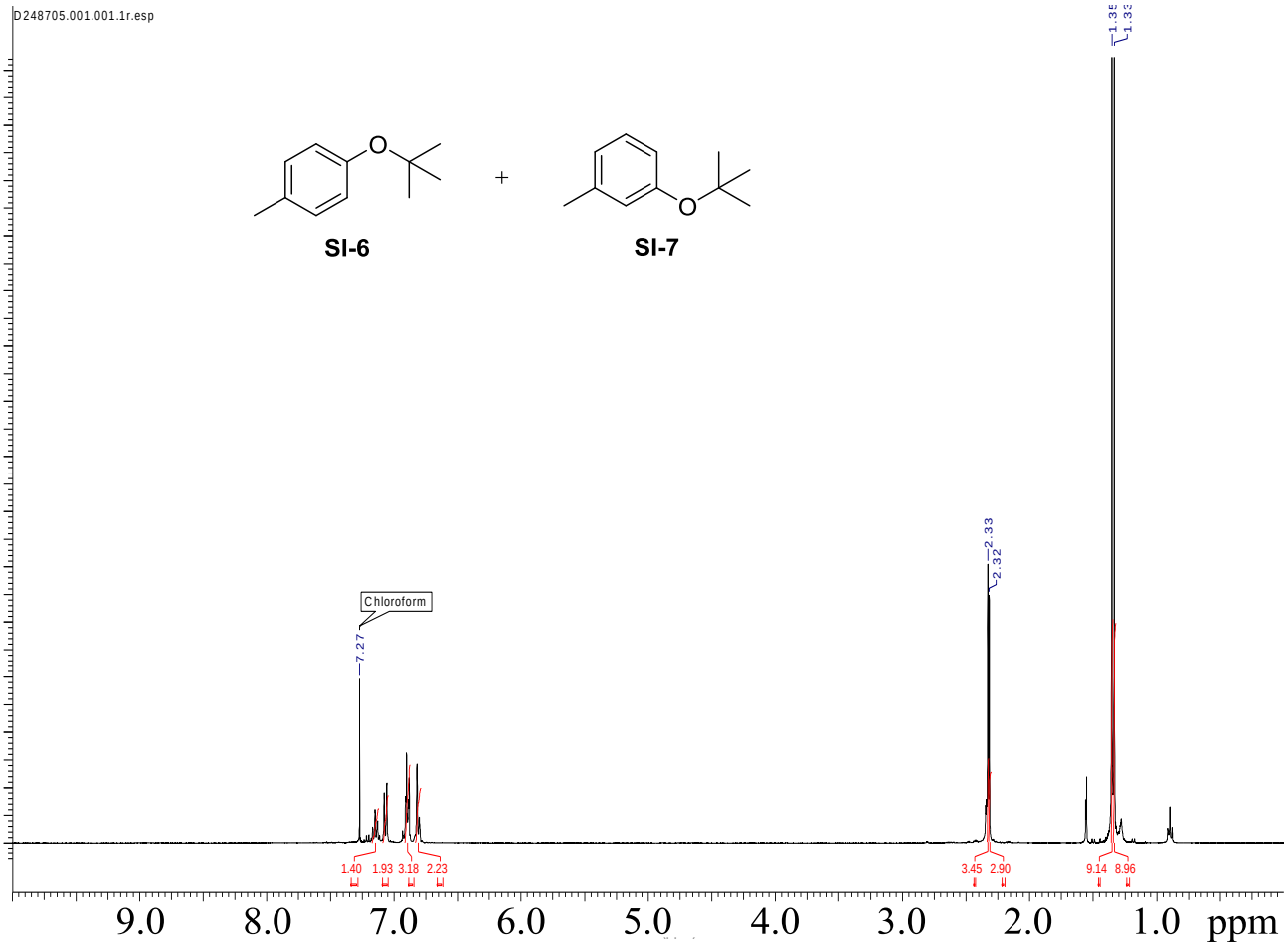
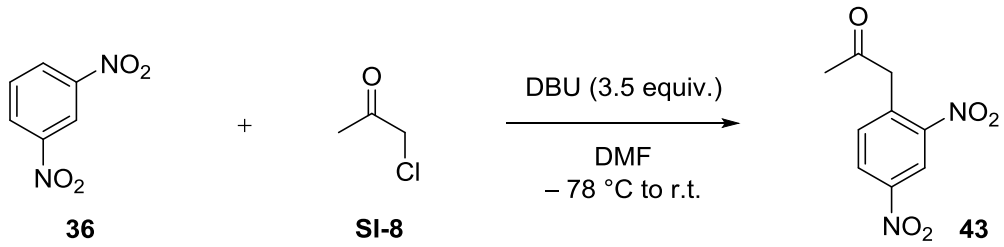


Figure S12(b) ^{1}H NMR spectrum of inseparable mixture of **SI-6** and **SI-7** after separation from **SI-5**.

(2d) Janovsky tests and UV-visible spectra

Synthesis of 1-(2,4-dinitrophenyl)propan-2-one (43)



A modified literature procedure was followed:[8] a solution of 1,3-dinitrobenzene **36** (1.68 g, 10.000 mmol) and chloroacetone **SI-8** (796 µL, 10.000 mmol) in DMF (25 mL) was cooled to −78 °C. DBU (5.23 mL, 35.000 mmol) was added slowly by syringe. The reaction was allowed to warm to room temperature and stirred for 3.5 h. The reaction was quenched with 1 M HCl (100 mL) and extracted with EtOAc (50 mL). The organic phase was washed with water (2 × 50 mL) before being dried (Na_2SO_4), filtered, and concentrated to give the crude product. Combination of the cleanest fractions obtained from purification

by column chromatography (CH_2Cl_2) gave ketone **43** (490 mg, 22%) as an orange oil which solidified on standing. Mp 59–63 °C [lit.,[9] 61–63 °C]; δ_H (400 MHz, $CDCl_3$) 8.97 (1 H, d, *J* = 2.5 Hz), 8.44 (1 H, dd, *J* = 8.5, 2.5 Hz), 7.51 (1 H, d, *J* = 8.5 Hz), 4.28 (2 H, s), 2.38 (3 H, s); HRMS (CI): calcd for $C_9H_9N_2O_5$ [MH+] 225.0506, found 225.0504. These data are consistent with the literature.[9]

Procedures for the Janovsky tests and discussion of the results

Our starting point for the investigation of the Janovsky test was to validate the literature.[10] Accordingly we measured the UV-visible spectra of the following mixtures and plotted the resulting UV-visible spectra (see Figure S13)

1) A 1:1 acetone/H_2O mixture (trace not shown) which, as expected, showed no absorption.

2) A 0.01 M aqueous solution of NaOH which, as expected, showed no absorption (Figure S13, black trace).

3) A 1:1 0.01 M 1,3-dinitrobenzene in acetone / H_2O mixture which showed no absorption in the visible part of the spectrum (red trace).

4) A 1:1 0.01 M 1,3-dinitrobenzene in acetone / 0.01 M NaOH mixture which showed an absorption at ~550 nm (green trace).

5) A re-run of mixture 4) after 2 mins. This showed an increase in intensity of the peak at ~550 nm (dark blue trace).

6) A re-run of mixture 5) after 2 further min. This showed a further increase in intensity of the peak at ~550 nm (light blue trace).

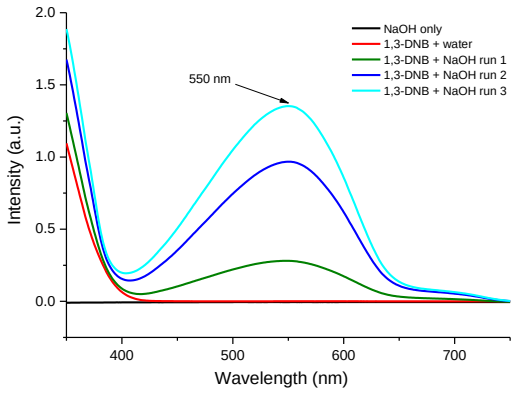


Figure S13. UV-visible spectrum of 1,3-dinitrobenzene in 1:1 acetone / 0.01 M NaOH.

These results were in accordance with the literature[10] which suggested that the peak at ~550 nm was due to adduct **41**.

Next we investigated the UV-visible spectra of the following mixtures (see Figure S14);

1) A THF blank which shows no absorption (trace not shown).

2) A 0.01 M solution of 1,3-dinitrobenzene in THF showed no absorption in the 350-750 nm window (trace not shown).

3) A 1:1 0.01 M 1,3-dinitrobenzene in THF / 0.01 M KO*t*Bu in THF mixture which showed an absorption at 558 nm (black trace).

4) A 1:1:1 0.01 M 1,3-dinitrobenzene in THF / 0.01 M KO*t*Bu in THF / 0.01 M acetone in THF showed an absorption at 552 nm (blue trace).

5) A 1:1:1 0.01 M 1,3-dinitrobenzene in THF / 0.01 M KO*t*Bu in THF / 0.01 M phenanthroline in THF showed an absorption at 554 nm (green trace).

6) A 1:1 0.01 M solution of ketone **43** in THF / 0.01 M KO*t*Bu in THF mixture which showed an absorption at 490 nm (red trace).

It was found that the order of addition of acetone, KO*t*Bu, and 1,3-DNB made no difference to the outcome. In each case a peak at ~550 nm resulted and no peak at ~490 nm was seen.

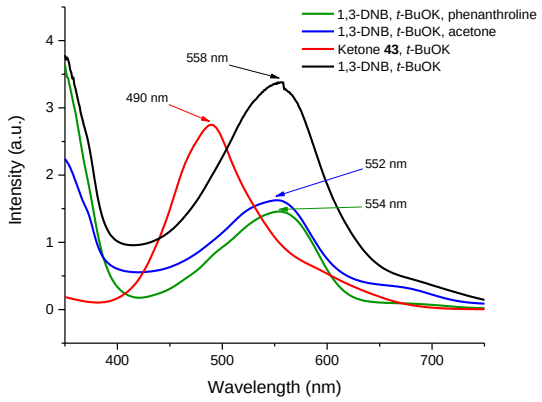


Figure S14. UV-visible spectra of THF solutions of 1,3-DNB/KO*t*Bu/phenanthroline, 1,3-DNB/KO*t*Bu/acetone, ketone **43**/KO*t*Bu, and 1,3-DNB/KO*t*Bu.

Next we investigated how the UV-visible spectrum of the 1:1 0.01 M 1,3-dinitrobenzene in acetone / 0.01 M NaOH mixture (see figure S15) changed over time. The UV-visible spectrum of a freshly prepared sample was run every 2 minutes for 60 mins. The 30 traces show an increase in the intensity of the peak at ~550 nm, but no peak at ~490 nm was detected which suggested that no transformation to the enolate **39** (enolate of ketone **43**) was occurring.

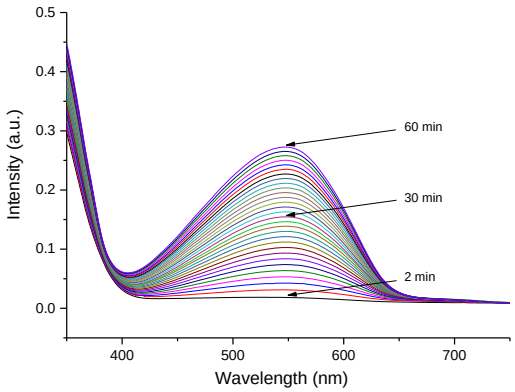


Figure S15. The changing UV-visible absorption of the 1:1 0.01 M 1,3-dinitrobenzene in acetone / 0.01 M NaOH mixture over time.

This sample was then left to age for 24 hours and then its UV-visible spectrum measured again (Figure S16). The previously discernible peak at ~550 nm had flattened out (black trace) and the sample had changed colour from purple to brown. No peak due to enolate **39** (at ~490 nm) was observed. A similar result was observed when the same sample was left for an extended period (up to 3 days, red trace).

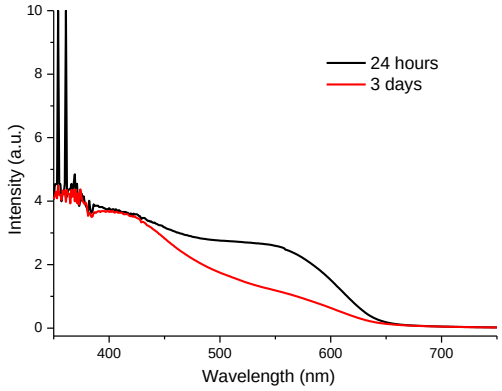


Figure S16. The UV-visible spectrum of a single sample of 1:1 0.01 M 1,3-dinitrobenzene in acetone / 0.01 M NaOH mixture which had been aged for 24 h and then for a further extended period (up to 3 days).

We investigated if the same UV-visible absorption at ~550 nm resulted when a 1,3-dinitrobenzene and acetone mixture were treated with NaOH in THF as opposed to NaOH in water. The following mixtures were prepared and their UV-visible spectra measured (see Figure S17):

1) An 8:1 THF / H_2O blank which shows no absorption (trace not shown).

2) A 1:1 0.01 M 1,3-dinitrobenzene in THF / 0.01 M NaOH in 4:1 THF/H_2O mixture with 100 eq. acetone added which showed an absorption at 550 nm (black trace).

3) A 1:1 0.01 M ketone **43** in THF / 0.01 M NaOH in 4:1 THF/H_2O mixture (red trace) which showed an intense absorption at ~490 nm which was attributed to the enolate of ketone **43**.

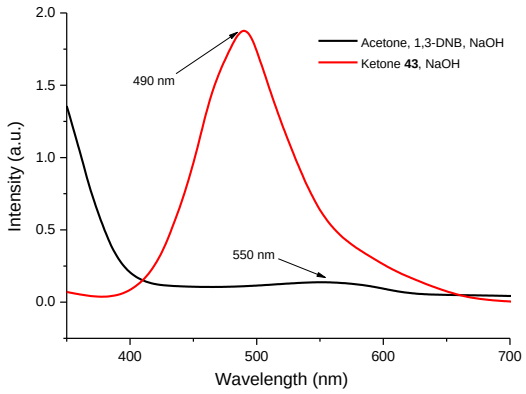


Figure S17. UV-visible spectra of 1,3-dinitrobenzene/acetone/NaOH in THF/H_2O and also of ketone **43**/NaOH in THF/H_2O.

(2e) ^{1}H NMR spectra of Janovsky adducts

Based on our UV-visible spectroscopy investigations of the Janovsky test we concluded that the purple coloration and absorption at ~550 nm was not resulting from enolate **39** (from ketone **43**), but depending on the compounds present in the mixture being analysed the adduct giving rise to this absorption would either be due to the addition of the enolate of acetone to 1,3-dinitrobenzene (to give adduct **41**) or due to the addition of the *t*-butoxide anion to 1,3-dinitrobenzene (to give adduct **44**). Because these two adducts would be expected to give similar UV-visible absorptions, we sought to distinguish between adducts by ^{1}H NMR. Fyfe and Foster have studied the addition of acetone to 1,3-dinitrobenzene under alkaline conditions.[11]

Initially we repeated Fyfe and Foster's study using the following procedure; 1,3-dinitrobenzene (16.8 mg, 0.10 mmol was dissolved in a 1:1 mixture of d_6-DMSO and acetone. NaOMe (5.4 mg, 0.10 mmol) was added as a solid and an intense purple colour resulted. The resulting spectrum (Figure S18) was consistent with that obtained by Fyfe and Foster[9] and showed the following signals; δ_H (600 MHz, 1:1 d_6-DMSO / acetone) 8.34 (1 H, d, J = 2.0 Hz), 6.61 (1 H, m), 5.37 (1 H, dd, J = 10.0, 5.0 Hz), 4.21 (1 H, dt, J = 8.7, 4.2 Hz), 3.19 (3 H, s), 2.83 (1 H, dd, J = 16.1, 3.5 Hz), 2.44 (1 H, dd, J = 16.1, 9.0 Hz). Note: The signal at 2.44 ppm shows an integration of greater than 1 due to the overlapping acetone signal.

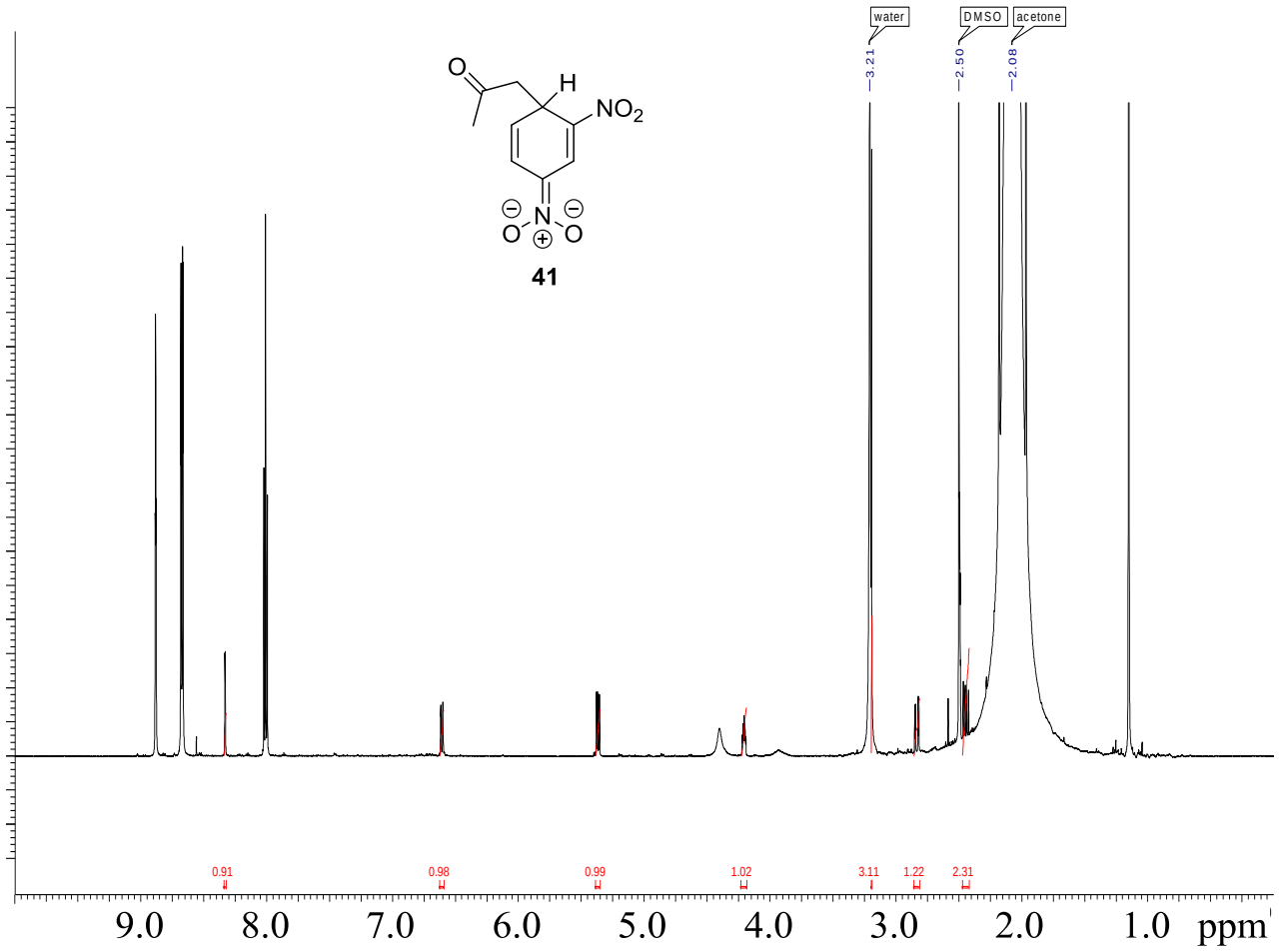


Figure S18. ^{1}H NMR of 1,3-dinitrobenzene and NaOMe in 1:1 d_6-DMSO / acetone.

When the above experiment was repeated using an identical amount of KO*t*Bu (11.2 mg, 0.10 mmol) in place of NaOMe an intense purple colour was observed and adduct **41** was again detected by ^{1}H NMR.

Subsequently we measured the spectra obtained when 1,3-dinitrobenzene was reacted with either NaOMe or KO*t*Bu in d_6-DMSO with acetone omitted. The use of KO*t*Bu gave rise to the same intense purple colour but a complex mixture was observed by ^{1}H NMR. We attempted to detect the alkoxide adduct of NaOMe and 1,3-dinitrobenzene in d_6-DMSO, but were hampered by DMSO and water signals overlapping with signals from the adduct and key assignments could not be made. Therefore d_7-DMF was selected as an appropriate alternative solvent.

Firstly we sought to detect the acetone adduct **41** when 1,3-dinitrobenzene (16.8 mg, 0.10 mmol) was dissolved in a 1:1 mixture of d_7-DMF and acetone. NaOMe (5.4 mg, 0.10 mmol) was added as a solid and an intense purple colour resulted, as was the case when d_6-DMSO was used. The following aromatic signals characteristic of the addition of acetone were observed (see Figure S19); δ_H (400 MHz, 1:1 d_7-DMF and acetone) 8.50 (1 H, dd, J = 2.0, 0.5 Hz), 6.75–6.68 (1 H, m), 5.44 (1 H, dd, J = 10.3, 5.0 Hz), 3.89 (1 H, *app* q, J = 5.3 Hz).

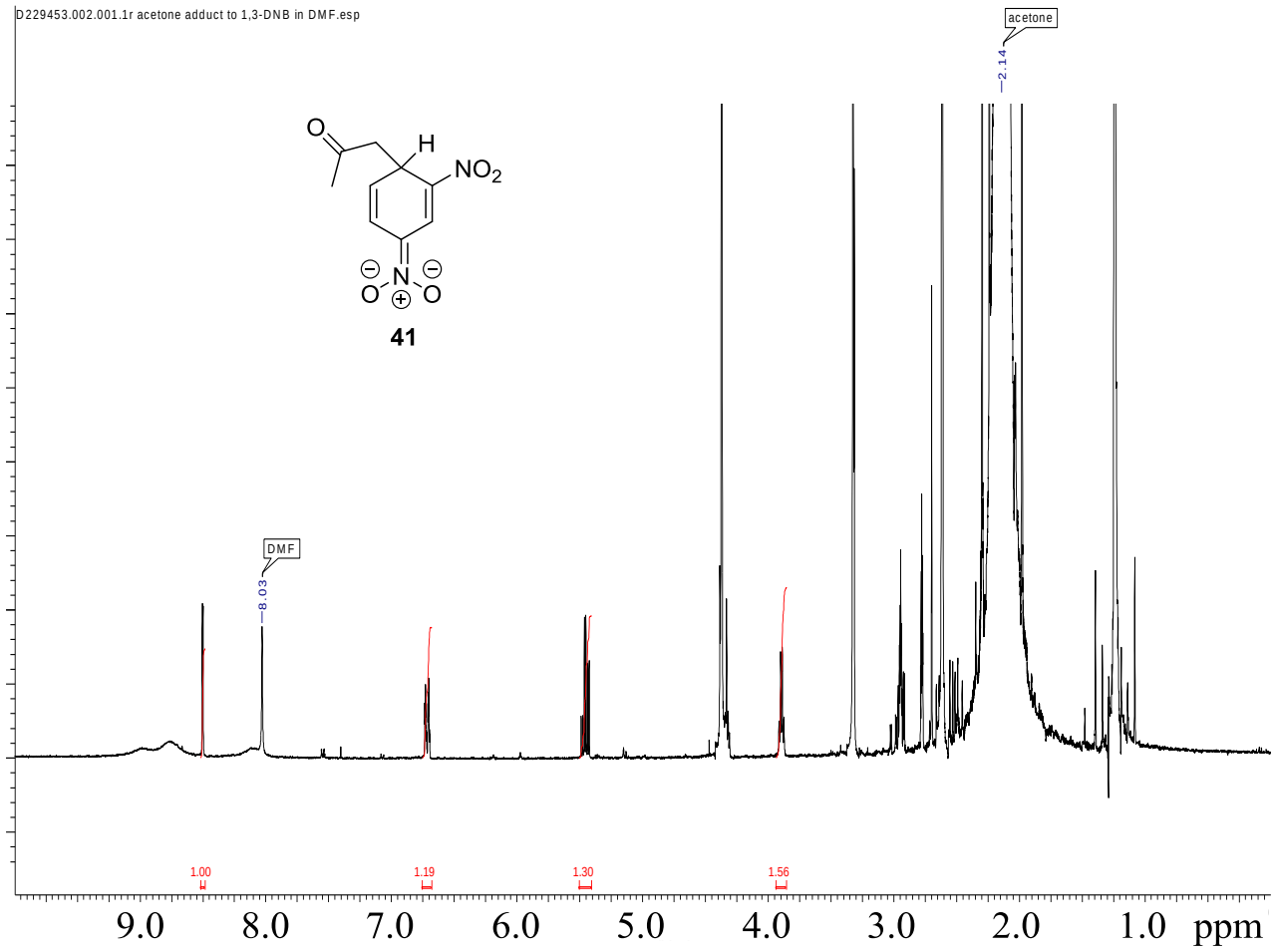


Figure S19. ^{1}H NMR of 1,3-dinitrobenzene and NaOMe in 1:1 d_7-DMF / acetone.

Subsequently we measured the spectrum obtained when 1,3-dinitrobenzene was reacted with NaOMe in d_7-DMF with acetone omitted (Figure S20). The sample was prepared as follows: 1,3-dinitrobenzene (16.8 mg, 0.10 mmol) was dissolved in d_7-DMF. NaOMe (5.4 mg, 0.10 mmol) was added as a solid and an intense purple colour again resulted. This time the spectra showed the following set of signals; δ_H (400 MHz, d_7-DMF) 8.65 (1 H, dd, *J* = 2.1, 1.1 Hz), 7.14 (1 H, dd, *J* = 9.4, 2.1 Hz), 5.65–5.50 (2 H, m), 3.03 (3 H, s).

The spectrum obtained (Figure S20) was clearly different than with acetone present. The absence of a quartet at ~3.9 ppm and presence of an additional signal at 5.65–5.50 ppm was indicative of a proton adjacent to a heteroatom, suggesting the addition of methoxide.

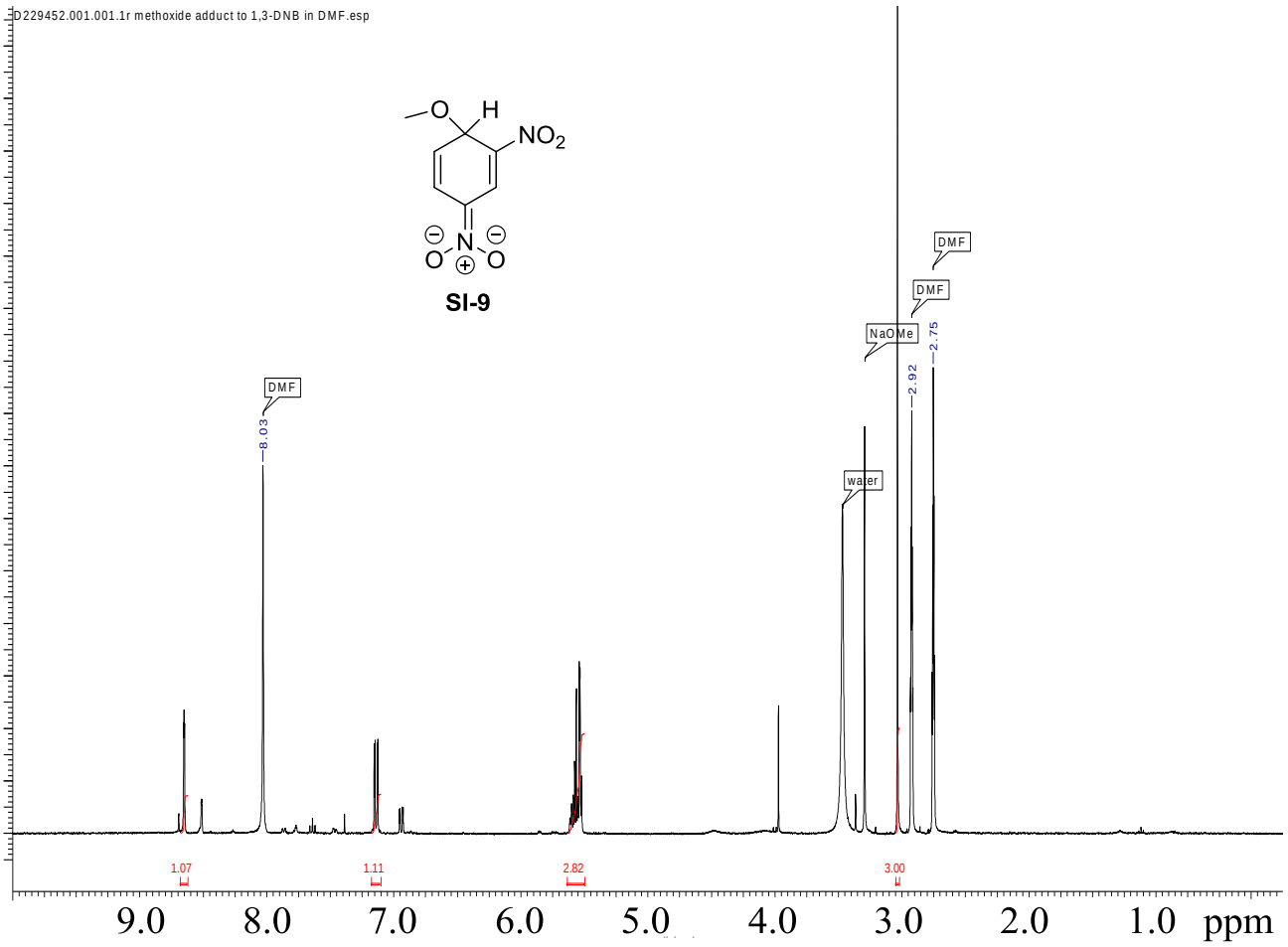
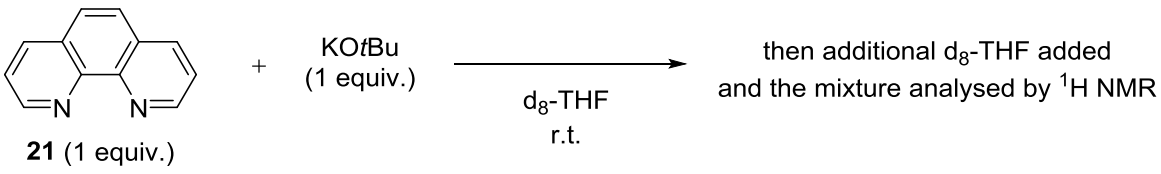


Figure S20. ^{1}H NMR of 1,3-dinitrobenzene and NaOMe in d_7-DMF.

(2f) NMR studies of KO*t*Bu and 1,10-phenanthroline mixtures

Sample preparation of a mixture of 1,10-phenanthroline 21 and KO*t*Bu in d_8-THF for ^{1}H NMR analysis in d_8-THF



21 (1 equiv.)

An oven-dried pressure tube was taken into a glovebox and 1,10-phenanthroline **21** (18.0 mg, 0.10 mmol) and KO*t*Bu (11.2 mg, 0.10 mmol) were added. d_8-THF (267 µL) was added and the pressure tube sealed. The reaction mixture was then stirred at room temperature for 2 h. The pressure tube was then opened and additional d_8-THF added in order to give an appropriate volume for NMR (~0.7 mL) which was then transferred to an NMR tube. The ^{1}H NMR spectrum of this mixture is shown below (Figure S21):

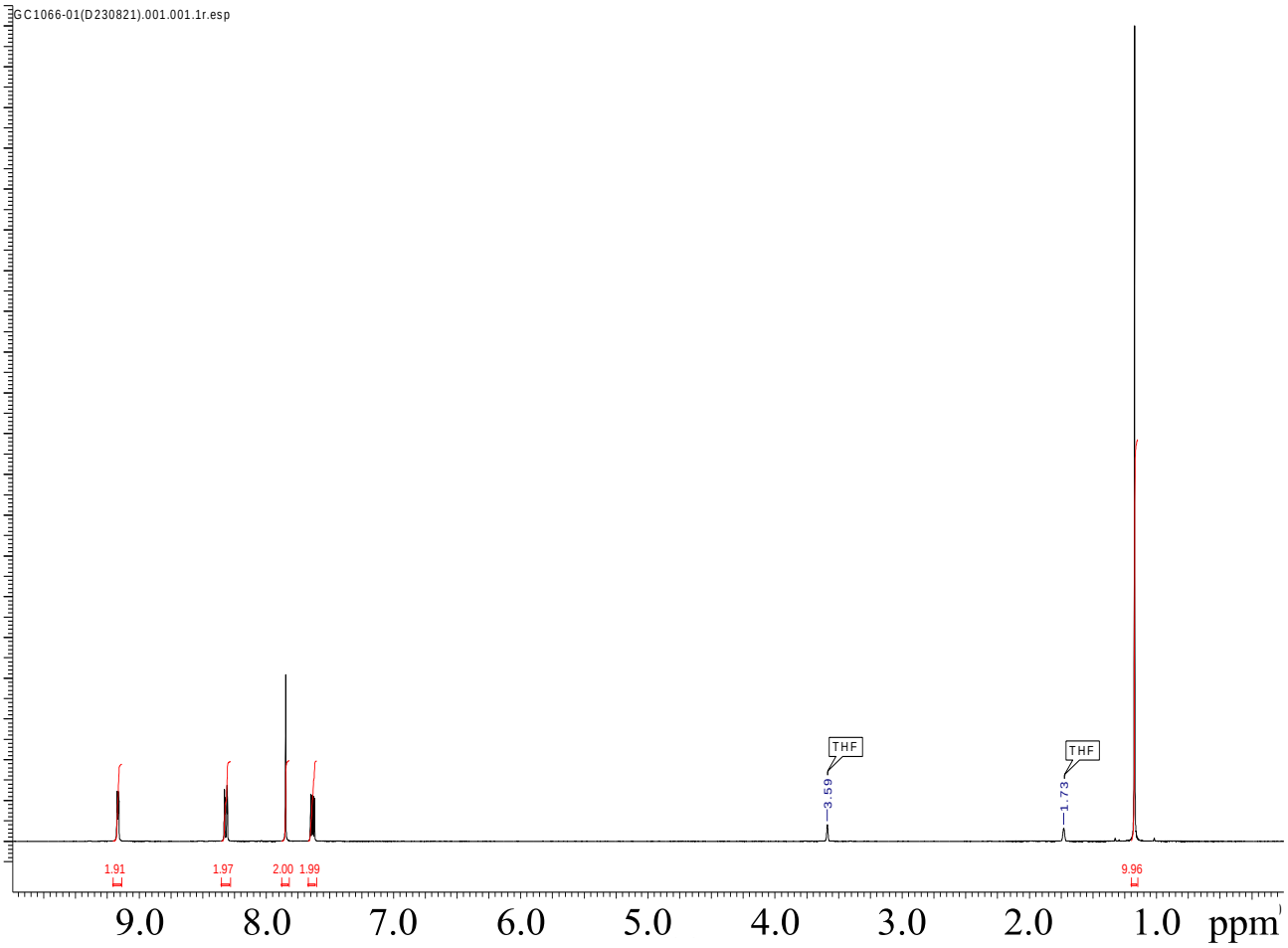
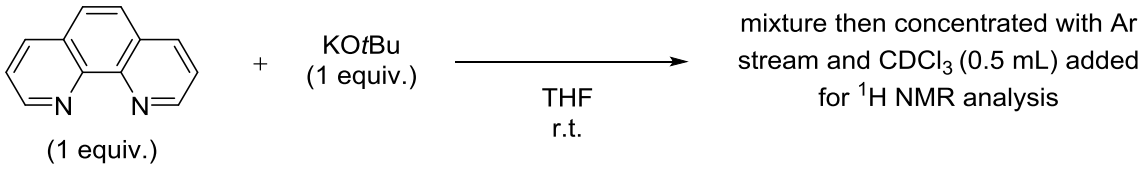


Figure S21. ^{1}H NMR spectrum of an equimolar mixture of 1,10-phenanthroline **21** and KO*t*Bu in d_8-THF after stirring at room temperature for 2 h.

Sample preparation of a mixture of 1,10-phenanthroline 21 and KO*t*Bu in THF for ^{1}H NMR analysis in $CDCl_3$



An oven-dried pressure tube was taken into a glovebox and 1,10-phenanthroline (18.0 mg, 0.10 mmol) and KO*t*Bu (11.2 mg, 0.10 mmol) were added. THF (267 µL) was added and the pressure tube sealed. The reaction mixture was then stirred at room temperature for 2 h. The pressure tube was then removed from the glovebox, opened, and the mixture concentrated with an argon stream. $CDCl_3$ (~0.5 mL) was added and the mixture analysed by ^{1}H NMR. The ^{1}H NMR spectrum of this mixture is shown below (Figure S22):

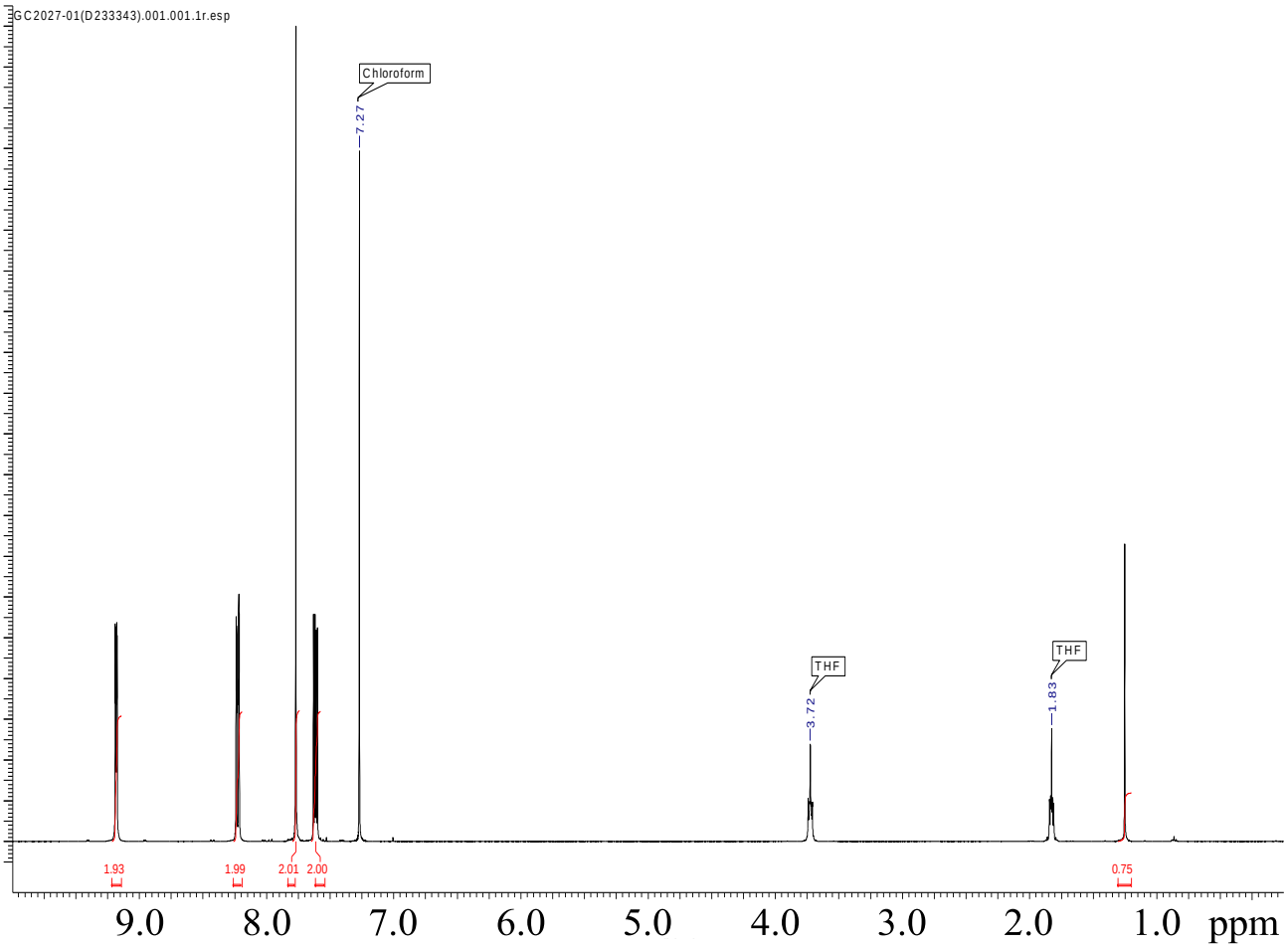
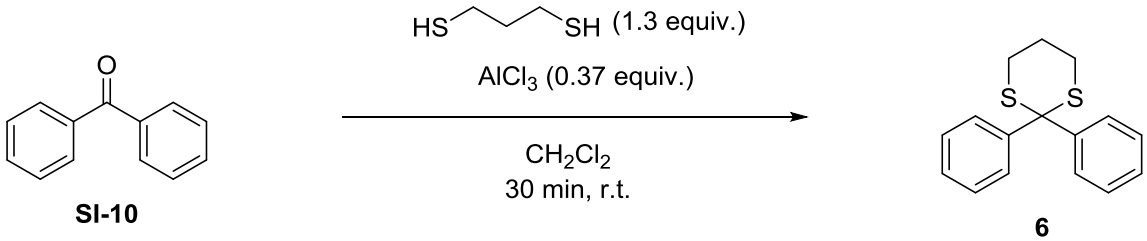


Figure S22. ^{1}H NMR spectrum of an equimolar mixture of 1,10-phenanthroline **21** and KO*t*Bu in THF to which $CDCl_3$ was added for NMR analysis. The collapse of the *t*-butyl group is attributed to a reaction between KO*t*Bu and $CDCl_3$.

(3) Reductive fragmentation of dithianes

Synthesis of 2,2-diphenyl-1,3-dithiane, 6



SI-10 **6**

Dithiane **6** was prepared according to a literature procedure;[12] benzophenone **SI-10** (0.94 g, 5.20 mmol, 1 eq.) and 1,3-propanedithiol (0.69 mL, 6.76 mmol, 1.3 eq.) were added to an oven-dried pressure tube and dissolved in CH_2Cl_2 (6 mL). $AlCl_3$ (0.26 g, 1.95 mmol, 0.37 eq.) was added and the pressure tube sealed and stirred for 30 min at room temperature. 2 M HCl (10 mL) was added and the organic phase isolated.

The aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL) and the combined organic phases dried (Na_2SO_4), filtered, and concentrated to give the crude material as a white solid. This was recrystallised from CH_2Cl_2/40-60 petroleum ether to give dithiane **6** (571 mg, 40%) (Figure S23), as a colourless microcrystalline solid. Mp 100–102 °C (from CH_2Cl_2/petrol) [lit.,[12] 104–105 °C (from CH_2Cl_2/petrol)]; ν_{max} (neat) 3059 - 2891 (C-H), 1593, 1481, 1442, 1281 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.71 (4 H, d, J = 7.6 Hz), 7.36 (4 H, t, J = 7.6 Hz), 7.28 (2H, m), 2.83–2.78 (4 H, m), 2.07–1.98 (2 H, m); δ_C (100 MHz, $CDCl_3$) 142.6 (2 x C), 129.3 (4 × CH), 128.4 (4 × CH), 127.5 (2 x CH), 62.8 (2 x C), 29.4 (2 × CH_2), 24.5 (CH_2); HRMS (ESI): calcd for $C_{16}H_{17}S_2$ [MH^+] 273.0766, found 273.0768. These data are consistent with the literature values.[12,13]

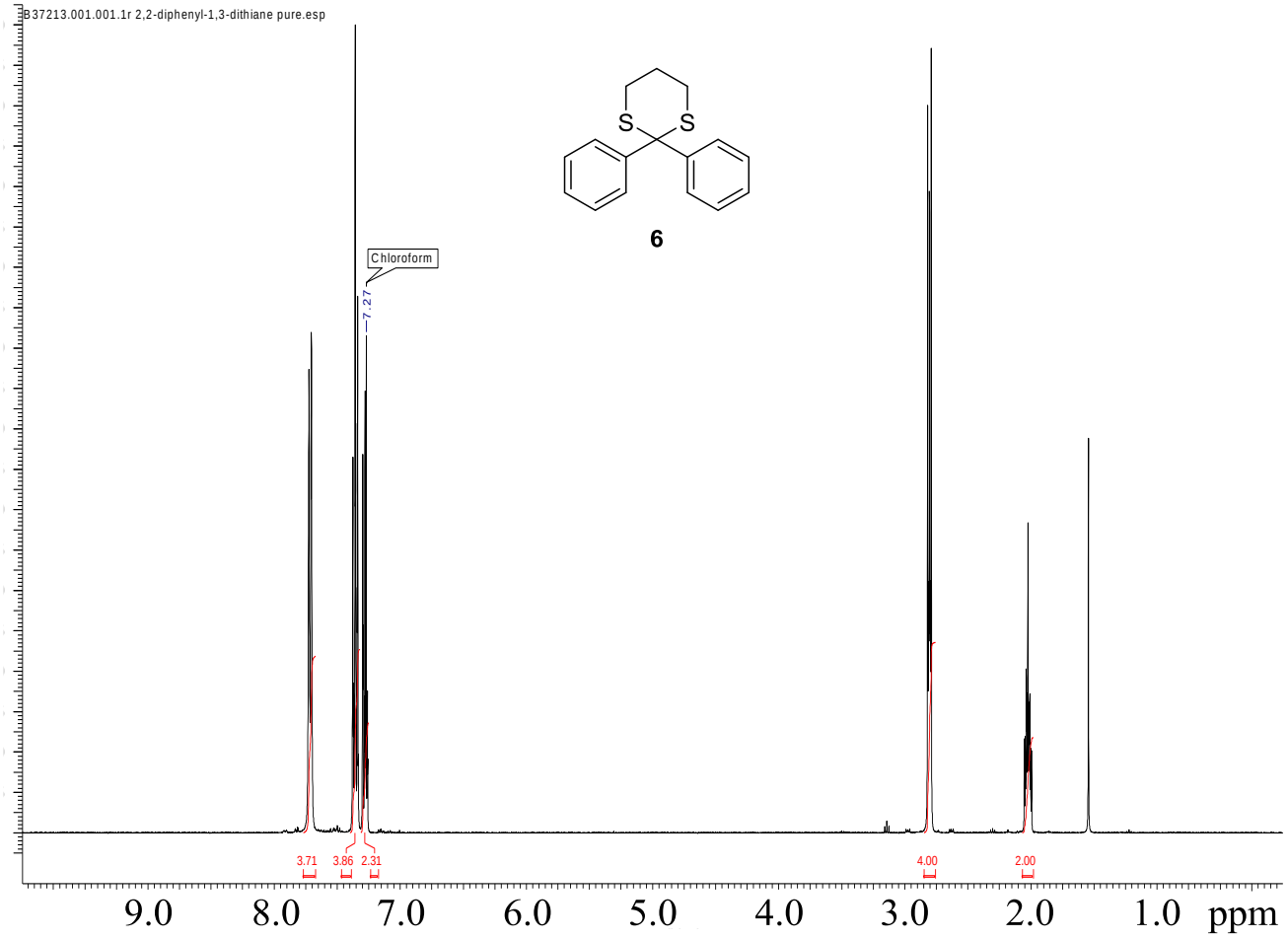


Figure S23a. ^1H NMR of dithiane **6** in $CDCl_3$.

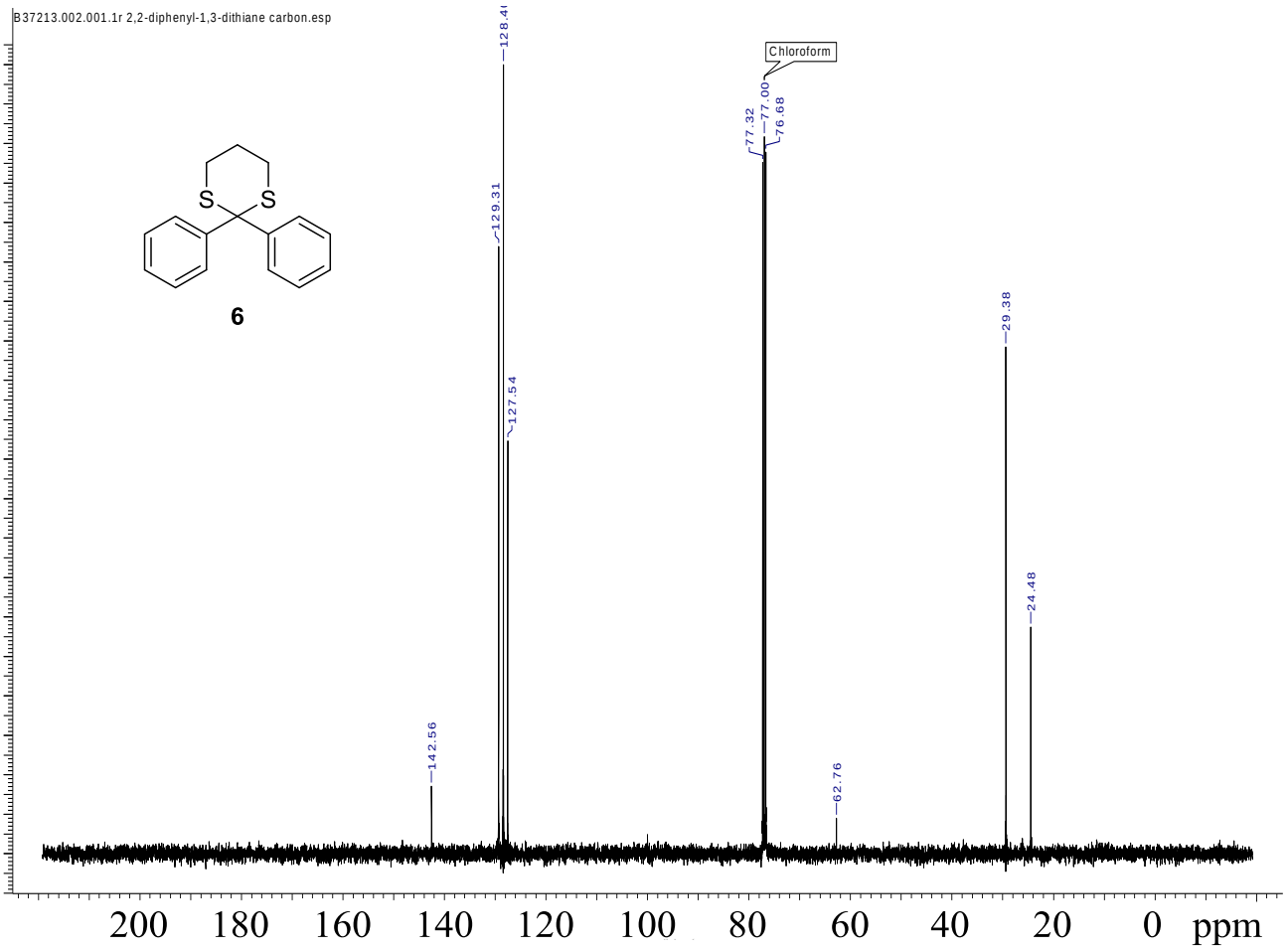
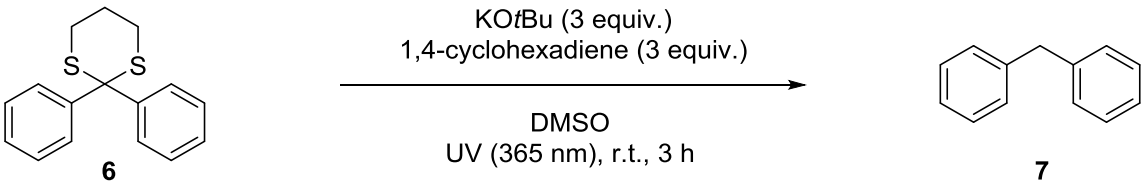


Figure S23b. ^{13}C NMR of dithiane **6** in $CDCl_3$

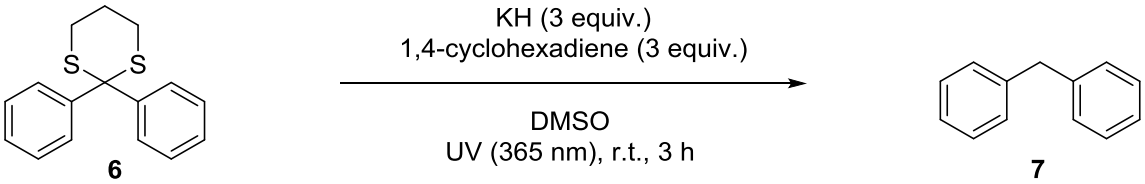
Synthesis of diphenylmethane 7 using KO*t*Bu / DMSO



Diphenylmethane **7** was prepared according to a literature procedure:[14] a flattened oven-dried glass vessel was equipped with a stirrer bar and KO*t*Bu (112 mg, 1.0 mmol), 2,2-diphenyl-1,3-dithiane **6** (91 mg, 0.33 mmol), 1,4-cyclohexadiene (81 mg, 1.0 mmol) and anhydrous, degassed DMSO (3.3 mL) were added in a glovebox. The reaction mixture appeared dark red in colour. The flask was sealed, removed from the glovebox, and irradiated with two UV-light (365 nm) lamps at a distance of *ca*. 10 cm for 3 h at rt. The reaction mixture was removed from the light and quenched with MeI (0.05 mL, 0.83 mmol) which changed the colour of the mixture from dark red to light yellow. Water (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude product as a brown oil. The crude material was dissolved in

CH_2Cl_2 (5 mL) and 1,3,5-trimethoxybenzene (56.2 mg, 0.33 mmol, 1 eq.) was added. The solution was stirred for 5 min at room temperature before being concentrated. This material was then analysed by ^{1}H NMR which showed the yield of diphenylmethane **7** to be 50% as judged by the internal standard. Purification by column chromatography (hexane) gave diphenylmethane 7 (25 mg, 45%) as a colourless residue. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.31 (4 H, *app*. t, J = 7.5 Hz), 7.24–7.20 (6 H, m), 4.01 (2 H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1 (2 × C), 128.9 (4 × CH_2), 128.4 (4 × CH_2), 126.1 (2 × CH), 41.9 (CH_2). These data are consistent with the literature.[15]

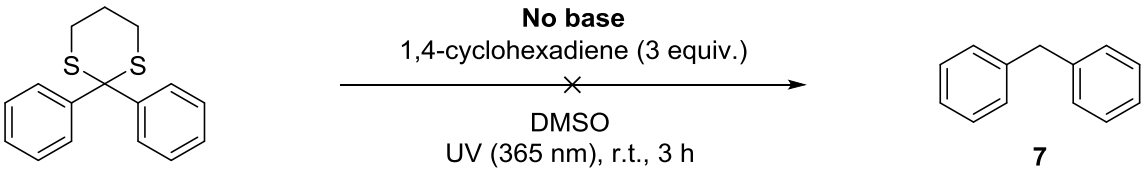
Synthesis of diphenylmethane 7 using KH / DMSO



6 **7**

The procedure followed was as described for the immediately preceeding example, but with the use of KH (40.1 mg, 1.00 mmol) in place of KO*t*Bu. On completion of the addition of all reagents, gas evolution was allowed to cease before the flask was sealed and irradiated. After work-up the use of 1,3,5-trimethoxybenzene as an internal standard showed a 16% yield of diphenylmethane **7**. Purification by column chromatography (hexane) gave diphenylmethane **7** (7 mg, 13%) as a film. The analytical data were as described for the previous entry.

Attempted formation of diphenylmethane 7 without the presence of a base



6 **7**

The reaction was carried out as in the above two procedures, but without the addition of any base. No coloration was observed during the reaction. After work-up, the use of 1,3,5-trimethoxybenzene as an internal standard showed a 69% yield of the starting material **6**, with no diphenylmethane detected. Purification by column chromatography (hexane) gave recovered starting dithiane **6** (56 mg, 62%) as a white solid. The analytical data were as described for dithiane **6** above.

Preparation of samples for UV-visible spectroscopy

The following samples were prepared and the UV-visible spectrum of the resulting mixture was measured.

1) 1.2×10^{-5} M dithiane **6** in DMSO (black trace on figure S24, cuvette A in figure S25)

2) 0.05 M KO*t*Bu in DMSO [UV-visible trace and appearance were the same as for 1)]

3) 1.2×10^{-5} M dithiane **6** / 0.05 M KO*t*Bu in DMSO (red trace on figure S23, cuvette B in figure S25)

4) 1.2×10^{-5} M dithiane **6** / 0.05 M KH in DMSO (blue trace on figure S23, cuvette C in figure S25)

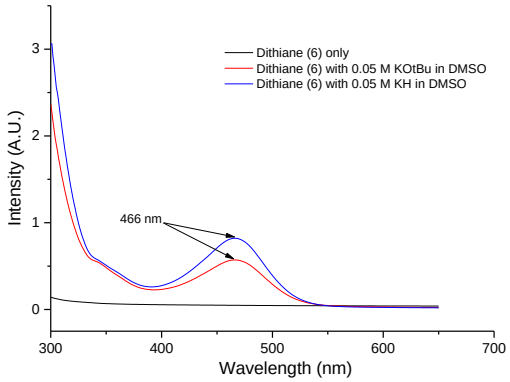


Figure S24. UV-visible spectra of dithiane **6** in DMSO, dithiane **6** in DMSO / KO*t*Bu, and dithiane **6** in DMSO / KH.

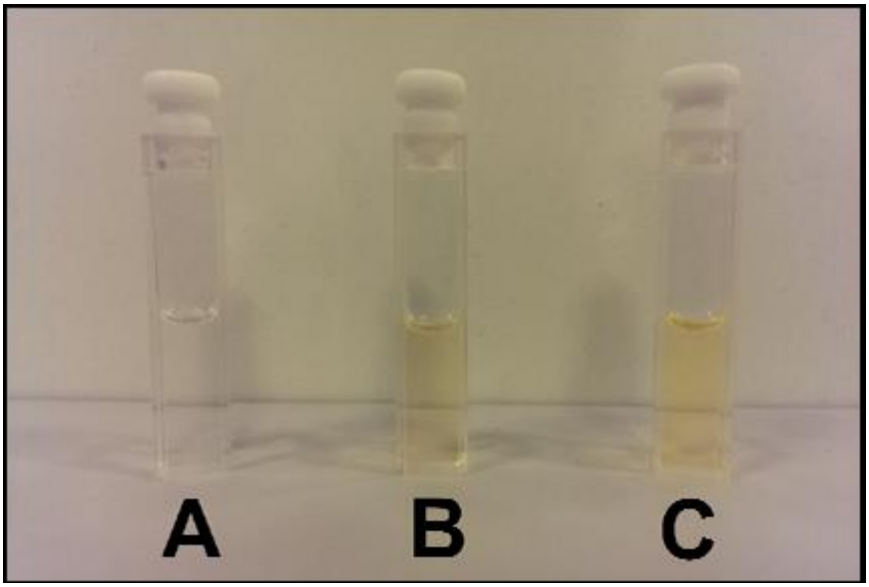


Figure S25. Photographs of dithiane **6** in DMSO (A), dithiane **6** in DMSO / KO*t*Bu (B), and dithiane **6** in DMSO / KH (C).

The observation that the mixture of dithiane **6** and KH in DMSO gives rise to a yellow coloration and a UV-visible absorption at 466 nm in the same way as dithiane **6** and KO*t*Bu in DMSO suggested to us that the yellow colour and UV-vis absorption might be arising from a charge transfer complex (CTC) between the dithiane **6** and the dimsyl anion (resulting from the deprotonation of DMSO by either KO*t*Bu and

DMSO or KH and DMSO) and not the dithiane **6** and KO*t*Bu. Further evidence for this was obtained when the following samples were prepared and their colour observed and UV-visible spectra measured.

1) DMF only (black trace on figure S26).

2) 1.2×10^{-5} M dithiane **6** in DMF (red trace on figure S26, cuvette A in figure S27).

3) 1.2×10^{-5} M dithiane **6** / 0.05 M KO*t*Bu in DMF (blue trace on figure S26, cuvette B in figure S27).

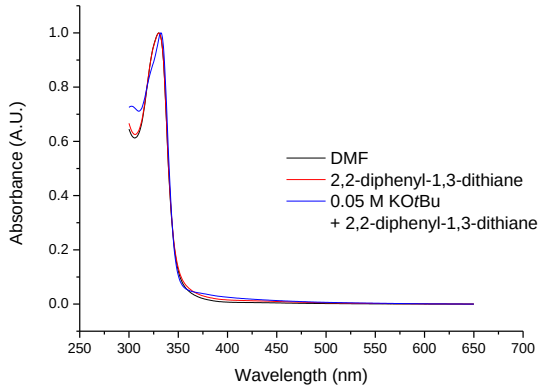


Figure S26. UV-visible spectra of DMF, dithiane **6** in DMF, and dithiane **6** and KO*t*Bu in DMF.

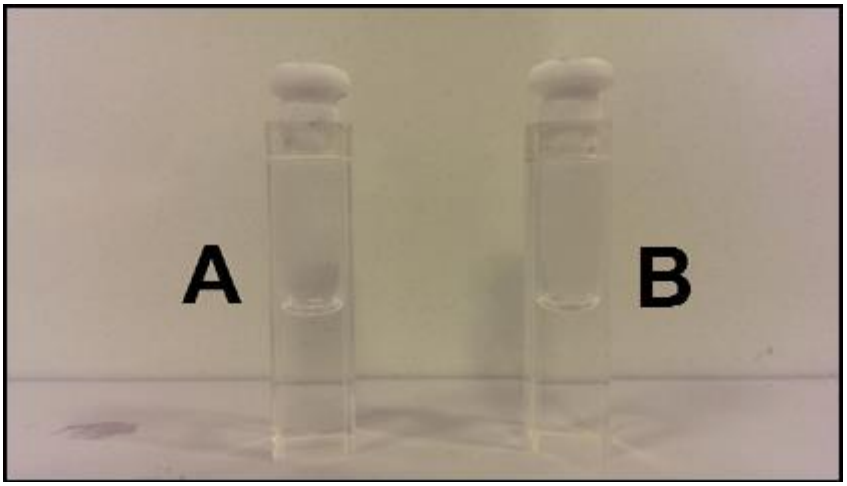
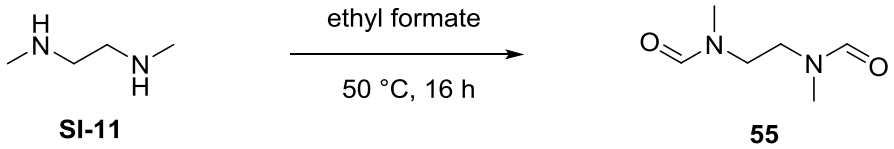


Figure S27. Pictures of dithiane **6** in DMF (A) and dithiane **6** / 0.05 M KO*t*Bu in DMF (B).

In these cases no coloration was seen and no UV-visible absorption observed at 466 nm. This shows that no charge transfer complex occurs between dithiane **6** and KO*t*Bu and that in the cases with DMSO as solvent it is deprotonation of DMSO that leads to the dimsyl anion which forms a charge transfer complex with the dithiane **6**.

(4) $S_{RN}1$ reactions in DMF

Procedures for the synthesis of the additives 55 and 58



SI-11 **55**

N,*N*'-Dimethylethylenediamine (1.00 g, 1.22 mL, 11.344 mmol) was dissolved in ethyl formate (10 mL) and the solution stirred at 50 °C for 16 h. The reaction was allowed to cool and then concentrated to give the crude product as an oil which solidified on standing. These solids were triturated with Et_2O which gave the diformamide **55** (1.49 g, 91%) as a white solid. Mp 80–83 °C [lit.,[16] 81–82 °C]; The ^1H NMR of this material clearly showed the presence of rotamers in a ratio which did not change upon trituration suggesting these peaks were indeed rotamers and not due to other compounds. δ_H (400 MHz, $CDCl_3$) 8.08–7.98 (2 H, 2 × HC=O), 3.56–3.40 (4 H, 2 × CH_2), 3.05–2.90 (2 × CH_3). Each of the regions listed contained a number of signals.

Rotamer 1: 8.02 (2 H, s), 3.55 (4 H, s), 3.01 (6 H, s).

Rotamer 2/3: 8.07 (2 H, s), 7.99 (2 H, s), 3.52–3.47 (4 H, m), 3.46–3.41 (4 H, m), 2.96 (6 H, s), 2.93 (6 H, s).

Rotamer 4: 8.00 (2 H, s), 3.41 (4 H, s), 2.91 (6 H, s).

See Figure S28a.

Variable temperature ^1H experiments in d_6-DMSO showed little coalescence of peaks at 70 °C.

δ_C (100 MHz, $CDCl_3$) (observed signals) 163.0, 162.8, 162.4, 47.4, 46.3, 42.4, 40.4, 35.2, 34.4, 29.9, 29.7

See Figure S28b

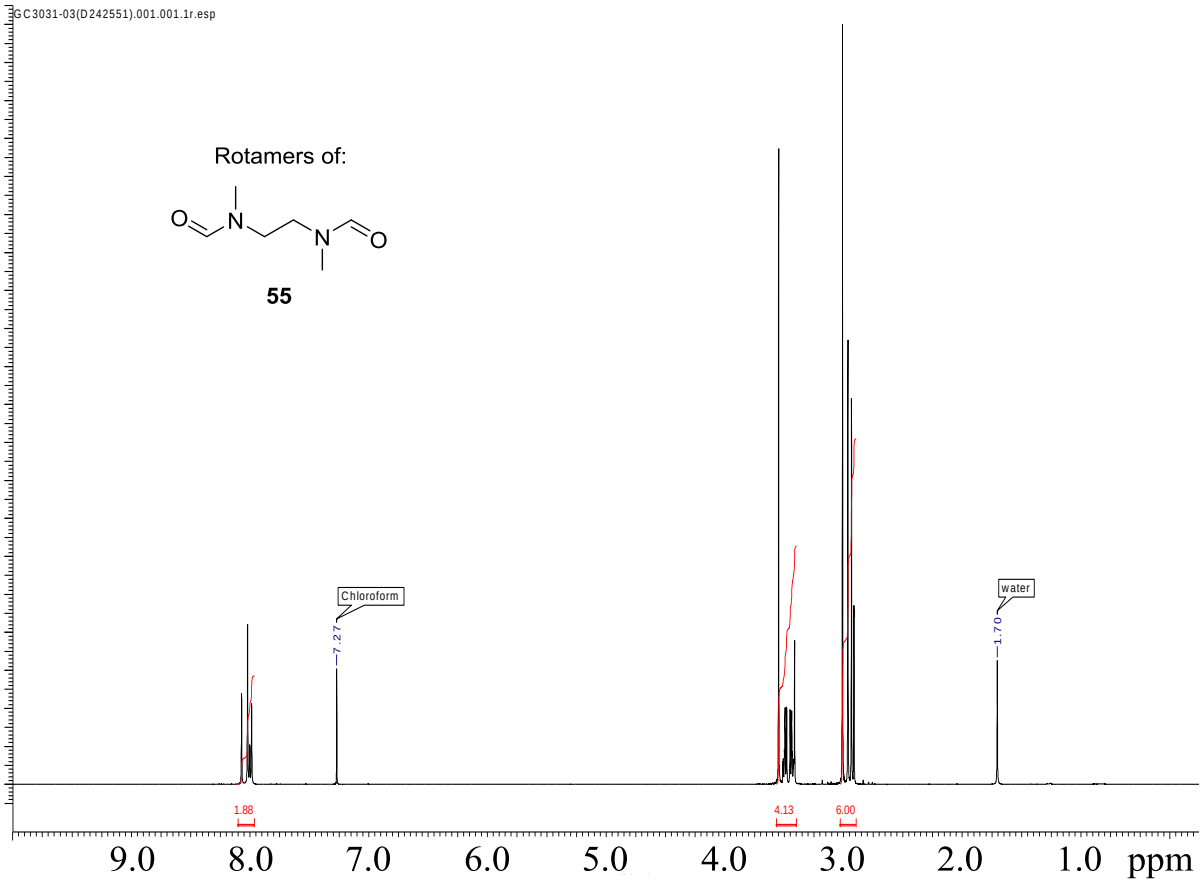


Figure S28 (a). ^{1}H NMR of diformamide **55** in $CDCl_3$.

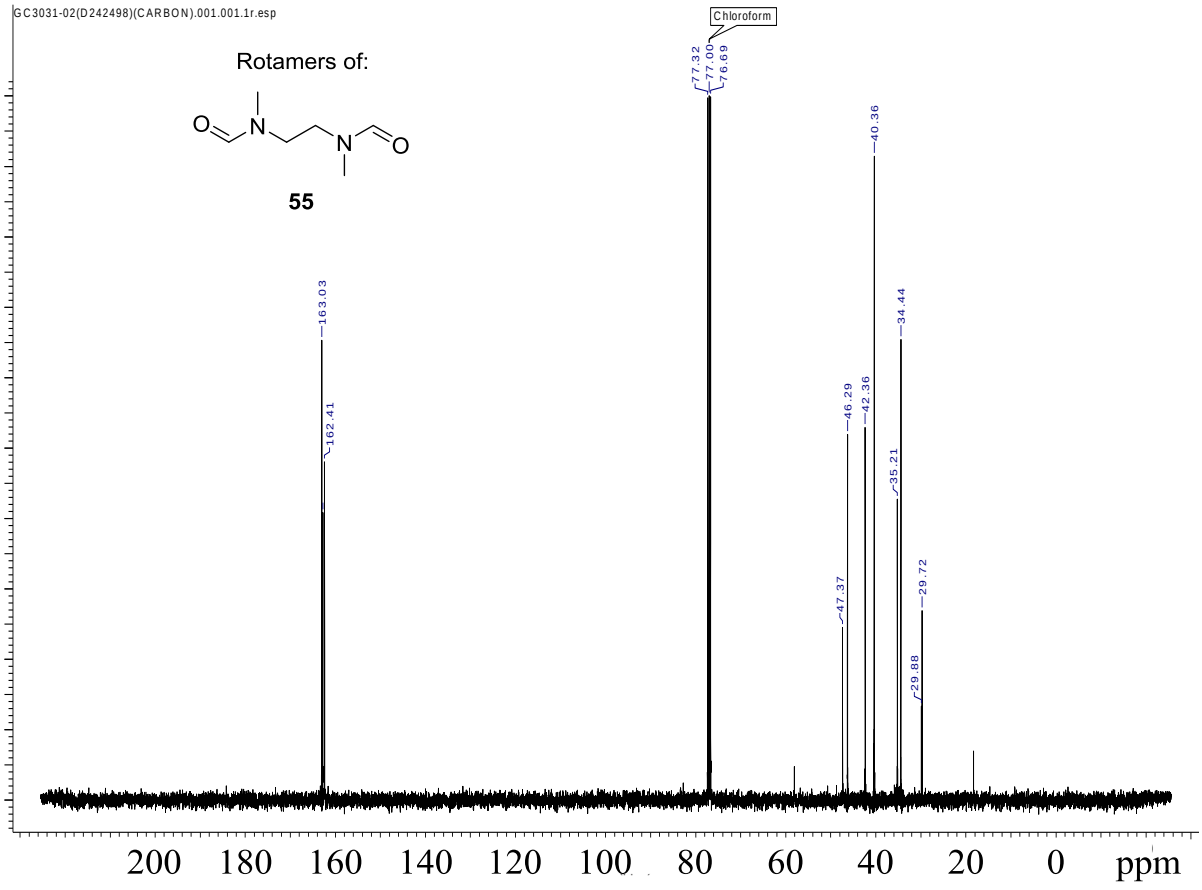
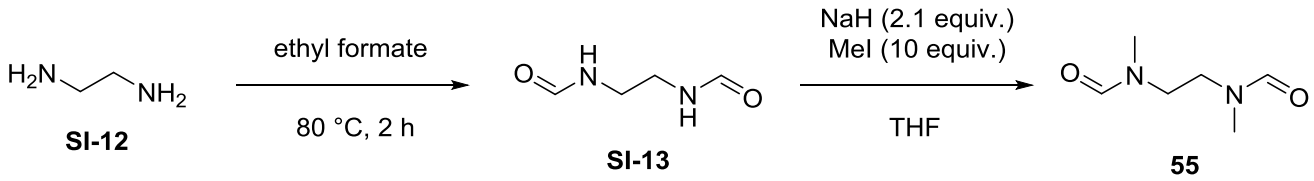


Figure S28 (b). ^{13}C NMR of diformamide **55** in $CDCl_3$.

Given the presence of rotamers of diformamide **55** it was also synthesised by an alternative route in order to demonstrate that the ^{1}H NMR spectrum of the material obtained from the alternative route was the same as that obtained from the synthesis outlined above.

***N,N*'-ethane-1,2-diyldiformamide, SI-13 and *N,N*'-dimethyl-ethane-1,2-diyldiformamide**



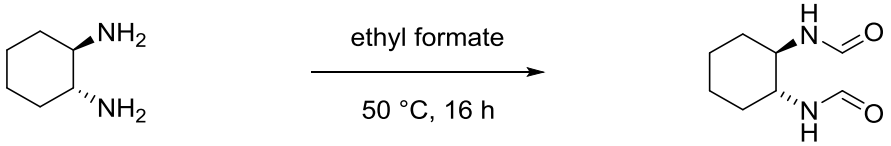
SI-12 **SI-13** **55**

Ethyl formate (5 mL) was cooled to 0 °C and ethylenediamine (500 mg, 556 µL, 8.319 mmol) added dropwise. The reaction mixture was stirred at 80 °C for 2 h and then allowed to cool to room temperature. The reaction mixture was concentrated to give the diformamide **SI-13** (820 mg, 85%) as a pale yellow solid. Mp 102–104 °C [lit.,[17] 108–110 °C]; δ_H (400 MHz, d_6-DMSO) 8.04–8.00 (2 H) 3.18–3.10 (4 H, m).

The diformamide **SI-13** (250 mg, 2.153 mmol, 1 eq.) was added to an oven-dried flask under argon and anhydrous THF (5 mL) added (Note: the material does not dissolve). NaH (60% dispersion in oil) (180.0 mg, 4.521 mmol, 2.1 eq.) was added as a solid (not washed of oil). The mixture was stirred at reflux for 1 h before being allowed to cool to room temperature. MeI (3.06 g, 1.34 mL, 10 eq.) was added by syringe and the reaction stirred at reflux for 1 h before being allowed to cool to room temperature. The reaction was carefully quenched with water (20 mL) and then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the diformamide **55** (99 mg, 32%) as a yellow oil which solidified over time.

The ^{1}H NMR of this material in $CDCl_3$ showed the same ratio of rotamers as **55** synthesised directly from *N,N*'-dimethylethylenediamine.

***N,N*'-[(±)-trans-cyclohexane-1,2-diyl]diformamide, SI-15**



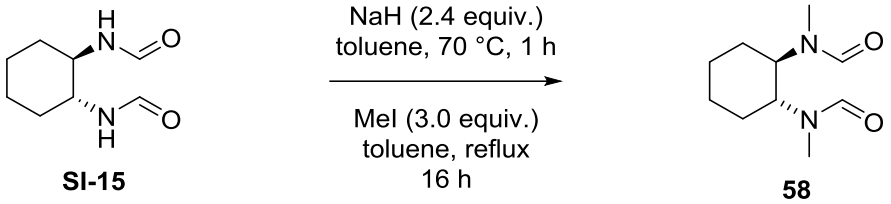
SI-14 **SI-15**

A solution of (±)-*trans*-1,2-diaminocyclohexane **SI-15** (0.36 mL; 3 mmol) in ethyl formate (1.45 mL; 18 mmol) was heated at 50 °C overnight. The mixture was concentrated at 35 °C to remove most of the ethanol and unreacted ethyl formate, and left under vacuum for 30 min to afford a white solid. The solid

was washed with ethyl acetate and filtered to give the diformamide **SI-15** (1.28 g, 84%) as a white solid. Mp 162–165 °C [lit.,[18] 187–188 °C (from ethanol)]; ν_{max} (neat) 3261, 3064, 2931, 2854, 1625, 1550, 1386, 1251, 1231, 723 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.17 (2 H, s), 6.00 (2 H, br. s), 3.88–3.71 (2 H, m), 2.14–2.02 (2 H, m), 1.86–1.75 (2 H, m), 1.41–1.23 (4 H, m); δ_C (100 MHz, $CDCl_3$) 161.2 (2 × C=O), 51.8 (2 × CH), 31.8 (2 × CH_2), 24.1 (2 × CH_2).

These data are consistent with the literature.[19]

***N*,*N*'-(±)-trans-cyclohexane-1,2-diyl)bis(*N*-methylformamide), 58**

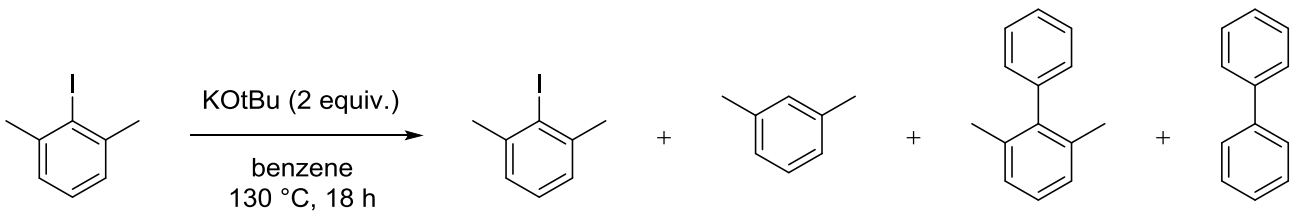


SI-15 **58**

A solution of *N*,*N*'-(±)-trans-cyclohexane-1,2-diyl)diformamide (340 mg, 2.00 mmol) in toluene (5 mL) was added to a suspension of sodium hydride (oil-free) (115 mg, 4.80 mmol) and toluene (20 mL) under argon. The resulting mixture was stirred at 70 °C for 1 h. The mixture was allowed to cool to room temperature and iodomethane (852 mg, 6.0 mmol) was added. The mixture was refluxed for 16 h before being allowed to cool to room temperature. The mixture was poured into sat. aq. NaCl (10 mL) and extracted with dichloromethane (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated to give diformamide **58** (330 mg, 83%) as a colourless oil which solidified on standing. Mp 93–96 °C; ν_{max} (neat) 2933, 2860, 1672, 1653, 1427, 1408, 1065, 725 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.08–7.98 (2 H, singlets are seen at 8.05, 8.04, 8.00 due to rotamers), 4.55–4.34 (1 H, m), 3.59–3.29 (1 H, m), 2.88–2.75 (6 H, singlets are seen at 2.84, 2.80, 2.78, 2.76 due to rotamers), 1.94–1.72 (6 H, m), 1.47–1.30 (2 H, m); δ_C (100 MHz, $CDCl_3$) 162.5 (C=O), 161.9 (C=O), 57.5, 57.0, 49.8, 30.2, 28.4, 25.4, 25.1, 24.3.

Procedures for the coupling reactions of 1-iodo-2,6-dimethylbenzene using either no additive or DMF, linear diformamide 55, or cyclic diformamide 58 as additives.

No additive (Table 2, entry 1)



35 **35** **SI-16** **50** **51**

In a glovebox 1-iodo-2,6-dimethylbenzene (116.0 mg, 0.500 mmol) contained in a vial was dissolved in benzene (5 mL) and added to an oven-dried pressure tube. KO*t*Bu (112.2 mg, 1.000 mmol) was added as a solid. The pressure tube was sealed, removed from the glovebox, and stirred at 130 °C for 18 h. After the reaction had cooled to room temperature it was quenched with 1 M HCl (10 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material (~95 mg). 1,3,5-Trimethoxybenzene (NMR internal standard, 8.4 mg, 0.050 mmol, 10 mol%) was added as a solid. ~1 mL $CDCl_3$ was added and the solution stirred. A portion of the solution was taken and diluted for NMR analysis (Figure S29).

The quantity of each product was determined in the following way (also see annotated spectra below):
For the **recovered starting material 35** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal of **35** (2.50 ppm) was then measured and the following calculation gave the amount of **35** present:

(38.53/6) × 10 = **64.2%**

For the **hetero-coupled product 50** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal of **50** (2.05 ppm) was then measured and the following calculation gave the amount of **50** present:

(0.05/6) × 10 = **0.1%**

For the **biphenyl product 51** the aromatic signal of the internal standard was set to 3. The integration of the aromatic signals of **51** at 7.64–7.59 ppm (4 H) was then measured and the following calculation gave the amount of **51** present:

(0.14/4) × 10 = **0.4%**

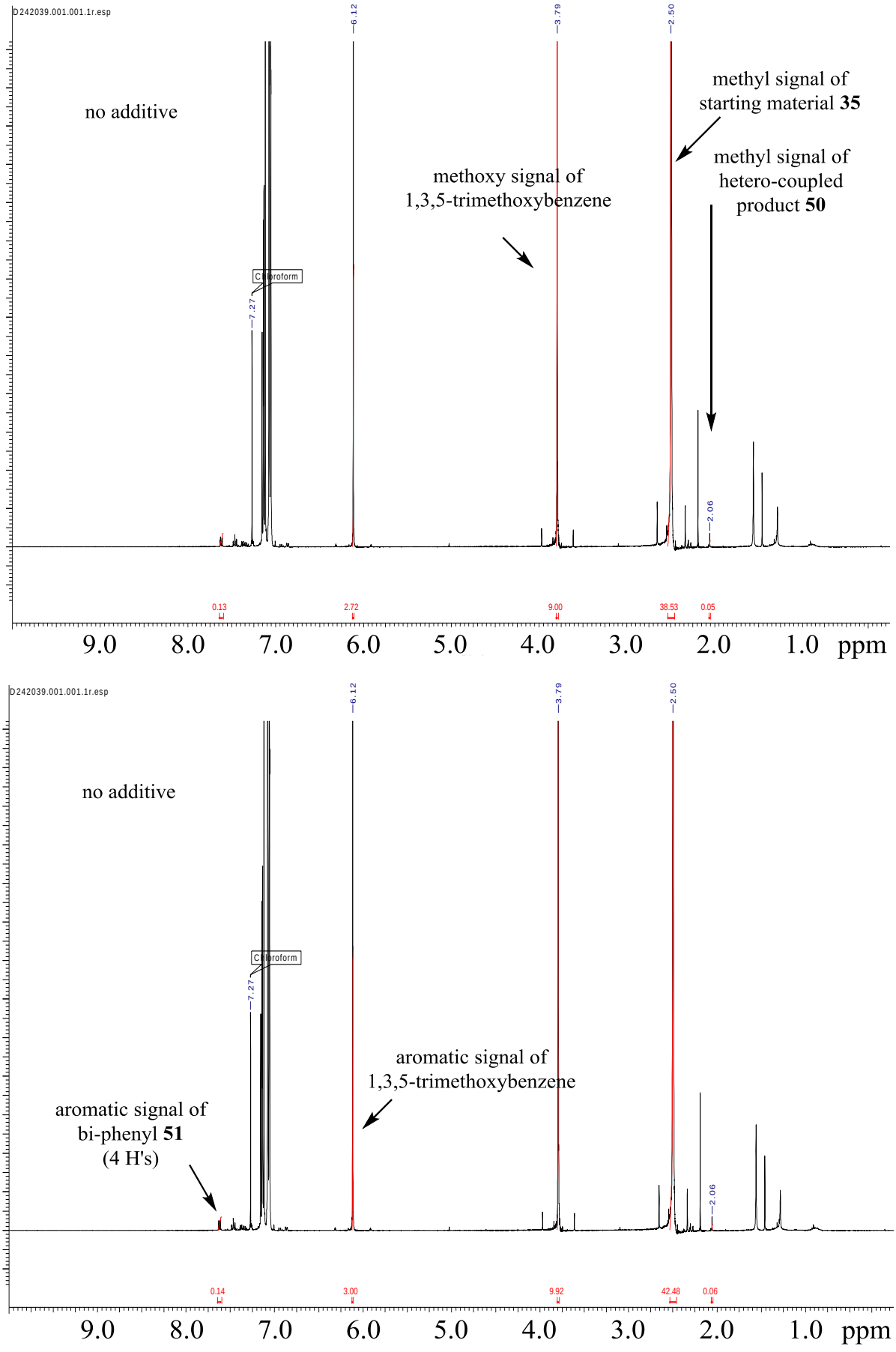
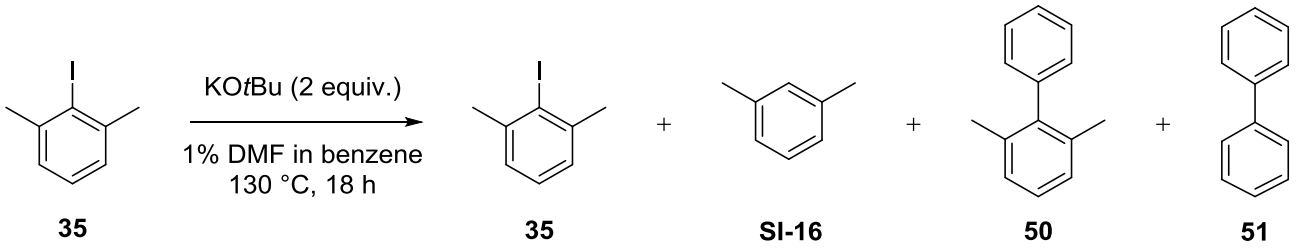


Figure S29 ^{1}H NMR spectrum of coupling of substrate **35**, in absence of any additive (Table 2, entry 1).

DMF as an additive (1%, Table 2, entry 2)



In a glovebox, 1-iodo-2,6-dimethylbenzene (116.0 mg, 0.500 mmol) contained in a vial was dissolved in 1% DMF in benzene (5 mL) and added to an oven-dried pressure tube. KO*t*Bu was added as a solid. The pressure tube was sealed, removed from the glovebox, and stirred at 130 °C for 18 h. After the reaction had cooled to room temperature it was quenched with 1 M HCL (10 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material (~95 mg). 1,3,5-Trimethoxybenzene (8.4 mg, 0.050 mmol, 10 mol%) was added as a solid. ~1 mL $CDCl_3$ was added and the solution stirred. A portion of the solution was taken and diluted for NMR analysis (see Figure S30).

The quantity of each product was determined in the following way (also see annotated spectra below):
For the recovered **starting material 35** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal of **35** (2.49 ppm) was then measured and the following calculation gave the amount of **35** present:

(50.46/6) × 10 = **84.1%**

For the **hetero-coupled product 50** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal of **50** (2.05 ppm) was then measured and the following calculation gave the amount of **50** present:

(0.36/6) × 10 = **0.6%**

For the **biphenyl product 51** the aromatic signal of the internal standard was set to 3. The integration of the aromatic signals of **51** at 7.64–7.59 ppm (4 H's) was then measured and the following calculation gave the amount of **51** present:

(0.79/4) × 10 = **2.0%**

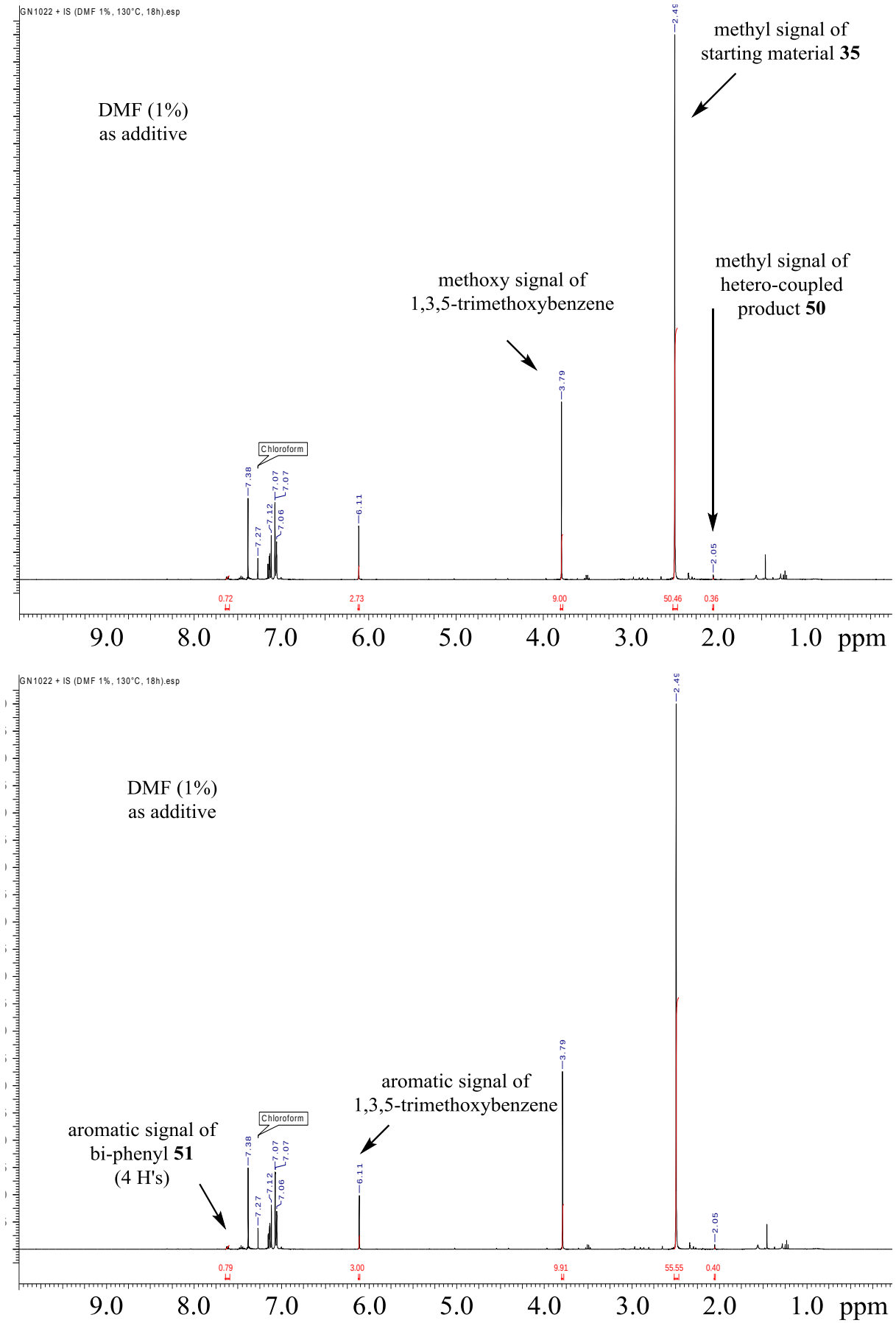
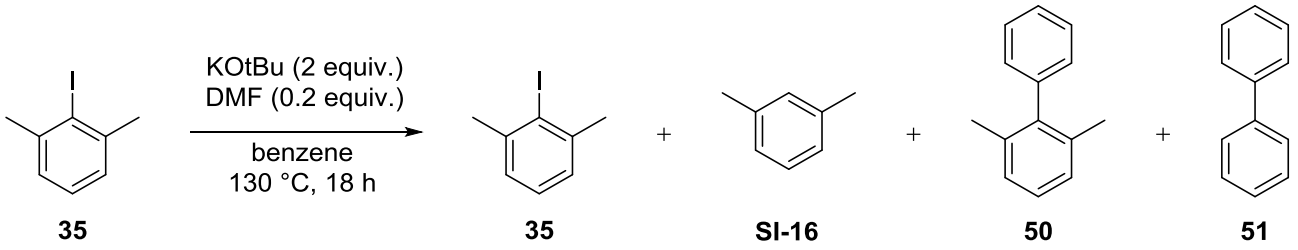


Figure S30 ^{1}H NMR spectrum of coupling of substrate **35**, [1% DMF as additive (Table 2, entry 2)].

DMF as an additive (0.2 eq., Table 2, entry 3)



A stock solution of DMF in benzene was made in the following way: DMF (77.4 µL) was added by syringe to a 10 mL volumetric flask containing a few mL of benzene. Benzene was then added to make the solution up to the 10 mL mark. 1 mL of this solution therefore contained the required amount of DMF (7.3 mg, 7.7 µL, 0.100 mmol) to be used as the additive.

In a glovebox 1-iodo-2,6-dimethylbenzene (116.0 mg, 0.500 mmol) contained in a vial was dissolved in benzene (4 mL) and added to an oven-dried pressure tube. KOtBu was added as a solid and then 1mL of the DMF in benzene stock solution added (containing 7.3 mg, 7.7 µL, 0.100 mmol, 0.2 eq. of DMF). The pressure tube was sealed, removed from the glovebox, and stirred at 130 °C for 18 h. After the reaction had cooled to room temperature it was quenched with 1 M HCL (10 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material (~95 mg). 1,3,5-Trimethoxybenzene (8.4 mg, 0.050 mmol, 10 mol%) was added as a solid. ~1 mL $CDCl_3$ was added and the solution stirred. A portion of the solution was taken and diluted for NMR analysis (see Figure S31).

The quantity of each product was determined in the following way (also see annotated spectra below):

For the recovered **starting material 35** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal of **35** (2.49 ppm) was then measured and the following calculation gave the amount of **35** present:

(56.06/6) × 10 = **93.5%**

For the **hetero-coupled product 50** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal of **50** was then measured and the following calculation gave the amount of **50** present:

(0.08/6) × 10 = **0.1%**

For the **biphenyl product 51** the aromatic signal of the internal standard was set to 3. The integration of the aromatic signals of **51** at 7.64–7.59 ppm (4 H) was then measured and the following calculation gave the amount of **51** present:

(0.21/4) × 10 = **0.5%**

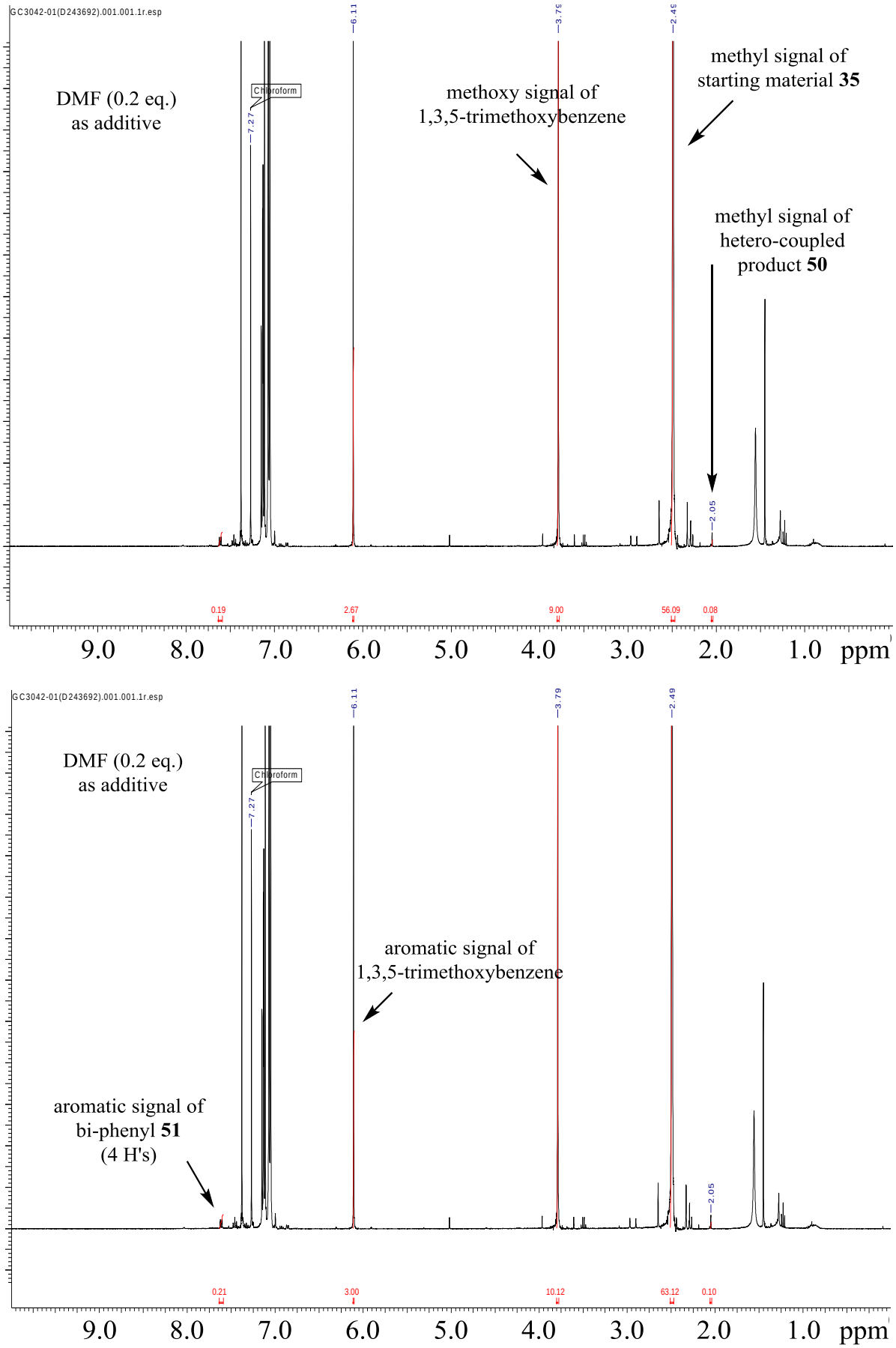
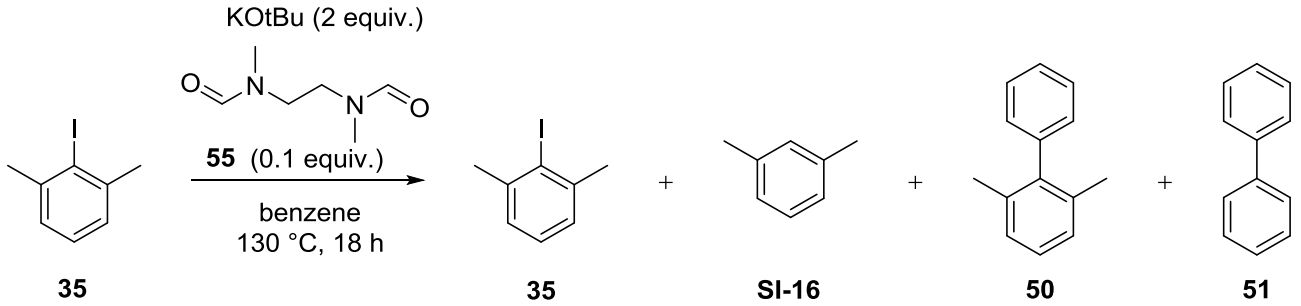


Figure S31 ^{1}H NMR spectrum of coupling of substrate **35** [0.2 equiv. = 0.1 mmol DMF as additive (Table 2, entry 3)]

Linear di-formamide 55 as an additive:



In a glovebox, 1-iodo-2,6-dimethylbenzene (116.0 mg, 0.500 mmol) contained in a vial was dissolved in benzene (5 mL) and added to an oven-dried pressure tube. KO*t*Bu (112.2 mg, 1.000 mmol) was added as a solid and then linear diformamide **55** (7.2 mg, 0.050 mmol, 0.1 eq.). The pressure tube was sealed, removed from the glovebox, and stirred at 130 °C for 18 h. After the reaction had cooled to room temperature it was quenched with 1 M HCL (10 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material (~95 mg). 1,3,5-Trimethoxybenzene (8.4 mg, 0.050 mmol, 10 mol%) was added as a solid. ~1 mL $CDCl_3$ was added and the solution stirred. A portion of the solution was taken and diluted for NMR analysis (see Figure S32).

The quantity of each product was determined in the following way (also see annotated spectra below):
For the recovered **starting material 35** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal of **35** (2.49 ppm) was then measured and the following calculation gave the amount of **35** present:

(35.62/6) × 10 = **59.4%**

For the **hetero-coupled product 50** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal of **50** (2.05 ppm) was then measured and the following calculation gave the amount of **50** present:

(0.77/6) × 10 = **1.3%**

For the **biphenyl product 51** the aromatic signal of the internal standard was set to 3. The integration of the aromatic signals of **51** at 7.64–7.59 ppm (4 H) was then measured and the following calculation gave the amount of **51** present:

(2.69/4) × 10 = **6.7%**

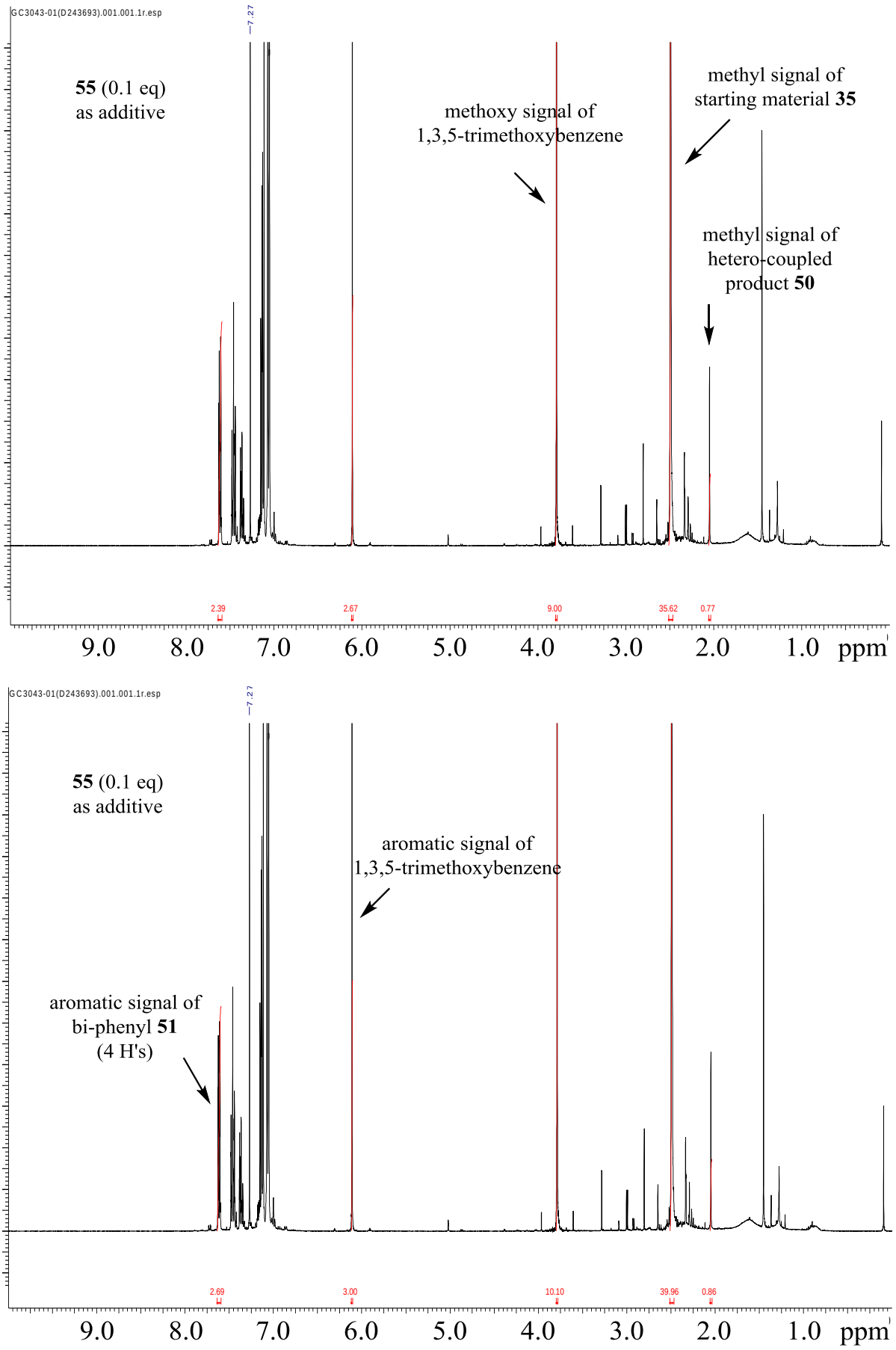
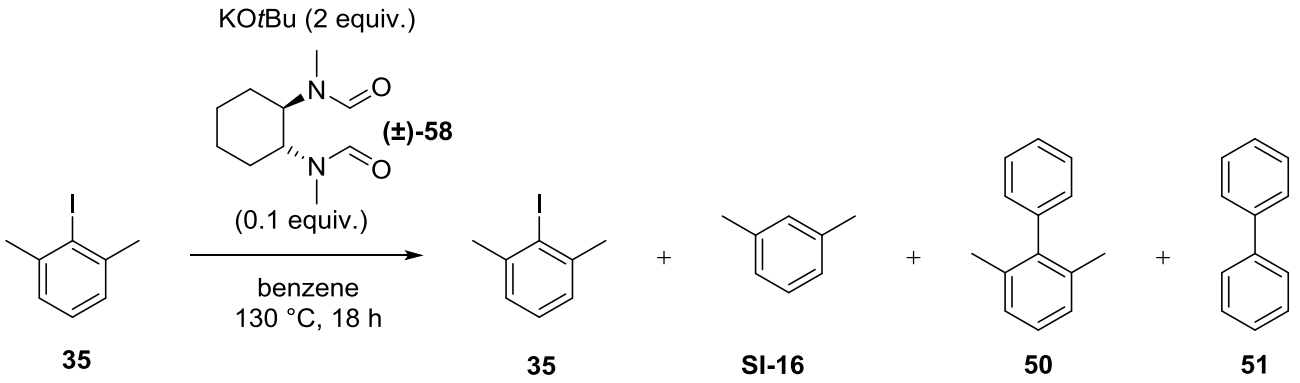


Figure S32 ^{1}H NMR spectrum of coupling of substrate **35**, [with linear diformamide **55** (0.1 equiv.) as additive (Table 2, entry 4)].

Cyclic diformamide (±)-58 as an additive



In a glovebox 1-iodo-2,6-dimethylbenzene (116.0 mg, 0.500 mmol) contained in a vial was dissolved in benzene (5 mL) and added to an oven-dried pressure tube. KO*t*Bu (112.2 mg, 1.000 mmol) was added as a solid and then cyclic diformamide **(±)-58** (9.9 mg, 0.050 mmol, 0.1 equiv.). The pressure tube was sealed, removed from the glovebox, and stirred at 130 °C for 18 h. After the reaction had cooled to room temperature it was quenched with 1 M HCL (10 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material (~95 mg). 1,3,5-Trimethoxybenzene (8.4 mg, 0.050 mmol, 10 mol%) was added as a solid. ~1 mL $CDCl_3$ was added and the solution stirred. A portion of the solution was taken and diluted for NMR analysis (See Figure S33).

The quantity of each product was determined in the following way (also see annotated spectra below):
For the recovered **starting material 35** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal of **35** (2.49 ppm) was then measured and the following calculation gave the amount of **35** present:
(33.18/6) × 10 = **55.3%**
For the **hetero-coupled product 50** the methoxy signal of the internal standard was set to 9. The integration of the methyl signal (2.05 ppm) of **50** was then measured and the following calculation gave the amount of **50** present:
(1.96/6) × 10 = **3.3%**
For the **biphenyl product 51** the aromatic signal of the internal standard was set to 3. The integration of the aromatic signals of **51** at 7.64–7.59 ppm (4 H) was then measured and the following calculation gave the amount of **51** present:
(5.13/4) × 10 = **12.8%**

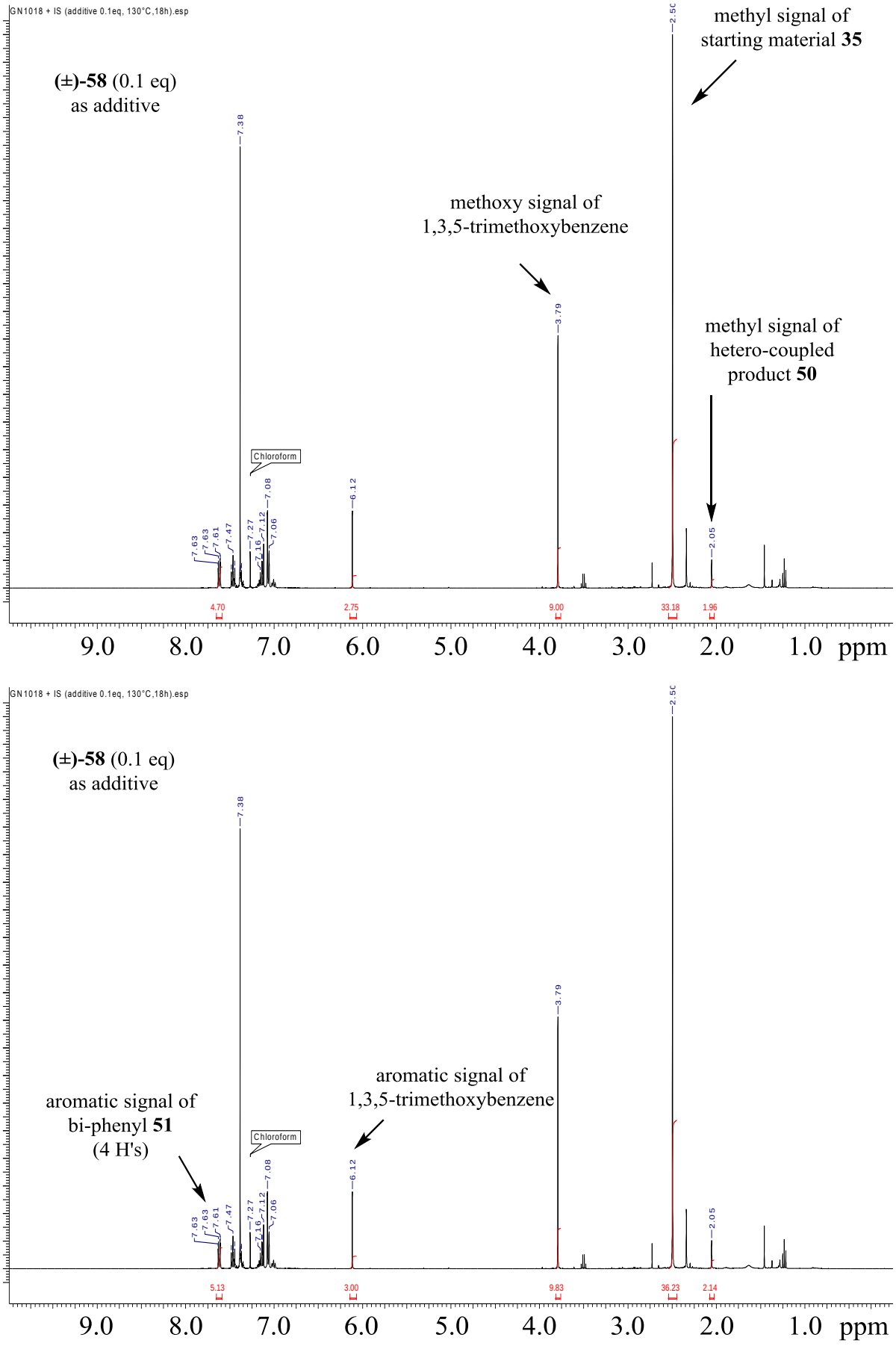
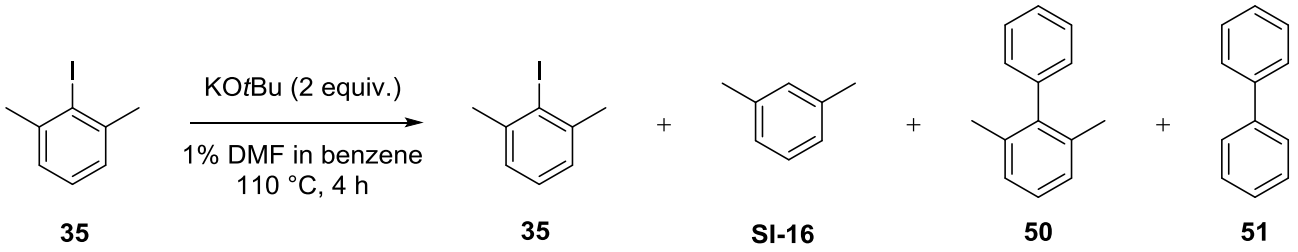


Figure S33 ^{1}H NMR spectrum of coupling of substrate **35**, [with diamide **58** (0.1 equiv) as additive (Table 2, entry 5)

DMF as an additive (1%, 110 °C, 4 h, Table 2, entry 6)



The procedure used was the same as that for a previous example (Table 2, entry 2), but the reaction was run for 4 h at 110 °C. Work-up and analysis as described for entries 1-5 gave a measured combined yield of **0.4%** for bi-aryls **50** and **51**.

The 0.5% amount of additive **55** or **58** used in the following examples is based on the number of moles of DMF used in the 1% DMF in benzene solution. The mass of DMF that 0.05 mL corresponds to is:

Mass = 0.05 (Vol) × 0.944 (Density)

= 0.0472

= 47.2 mg

The number of moles this corresponds to is;

Number of moles = 0.0472 / 73.09

= 0.000645

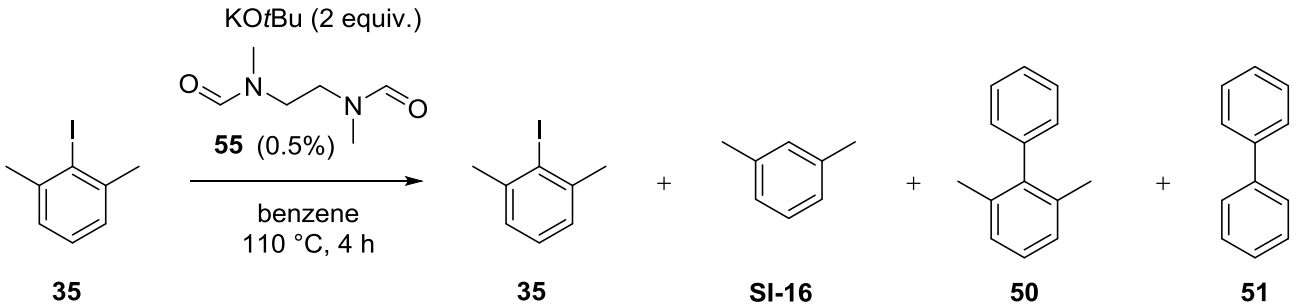
= 0.646 mmol

Therefore for 0.5% of **55** and **58** the number of mmol used was 0.646 / 2 = 0.323 mmol

And the amount of **55** used was 0.323 mmol × 144.17 = **46.6 mg**

And the amount of **58** used was 0.323 mmol × 198.27 = **64.0 mg**

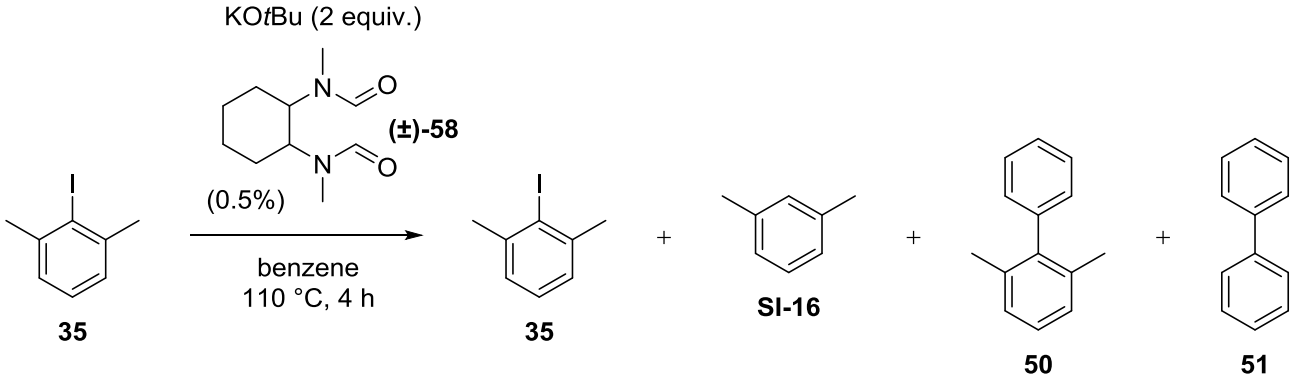
Linear diformamide 55 as an additive (0.5%, 110 °C, 4 h, Table 2, entry 7)



In a glovebox 1-iodo-2,6-dimethylbenzene (116.0 mg, 0.500 mmol) contained in a vial was dissolved in benzene (5 mL) and added to an oven-dried pressure tube. KO*t*Bu (112.2 mg, 1.000 mmol) was added as

a solid and then linear diformamide **55** (46.6 mg, 0.323 mmol). The pressure tube was sealed, removed from the glovebox, and stirred at 110 °C for 4 h. After the reaction had cooled to room temperature it was quenched with 1 M HCl (10 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material (~95 mg). 1,3,5-Trimethoxybenzene (8.4 mg, 0.050 mmol, 10 mol%) was added as a solid. ~1 mL $CDCl_3$ was added and the solution stirred. A portion of the solution was taken and diluted for NMR analysis. Analysis, as described for entries 1-5, gave a combined yield of **19.6%** of **50** and **51**.

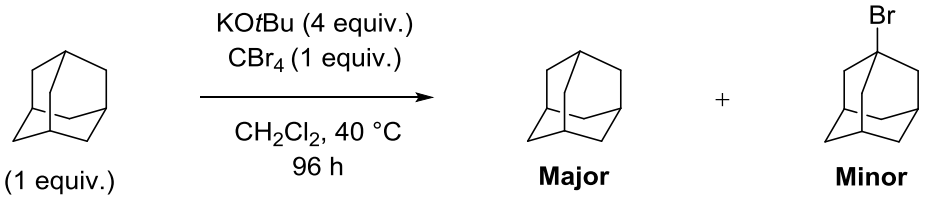
Cyclic diformamide (±)-58 as an additive (0.5%, 110 °C, 4 h, Table 2, entry 8)



The procedure used was the same that used for the previous example above (entry 7), but with cyclic di-formamide **(±)-58** (64.0 mg, 0.323 mmol) as the additive. Work-up and analysis as described for entries 1-5 gave a measured combined yield of **31.6%** for bi-aryls **50** and **51**.

(5) Can KO*t*Bu ever act as a direct electron donor?

Detection of bromoadamantane



Adamantane (68.1 mg, 0.500 mmol), tetrabromomethane (165.8 mg, 0.500 mmol), and KO*t*Bu (224.4 mg, 2.00 mmol) were added to a pressure tube followed by CH_2Cl_2 (3.13 mL). The reaction mixture was stirred at 40 °C for 96 h. After the mixture had cooled 1 M HCl (10 mL) was added and the mixture was extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material. The following characteristic signals were seen; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 2.38 (6 H, m), 2.11 (3 H, br. s). (See Figure 34a)

These signals are consistent with the literature values,[20] but the reported peak at 1.72 ppm is likely obscured by adamantane signals. The peaks at 1.88 and 1.76 are from unreacted adamantane.

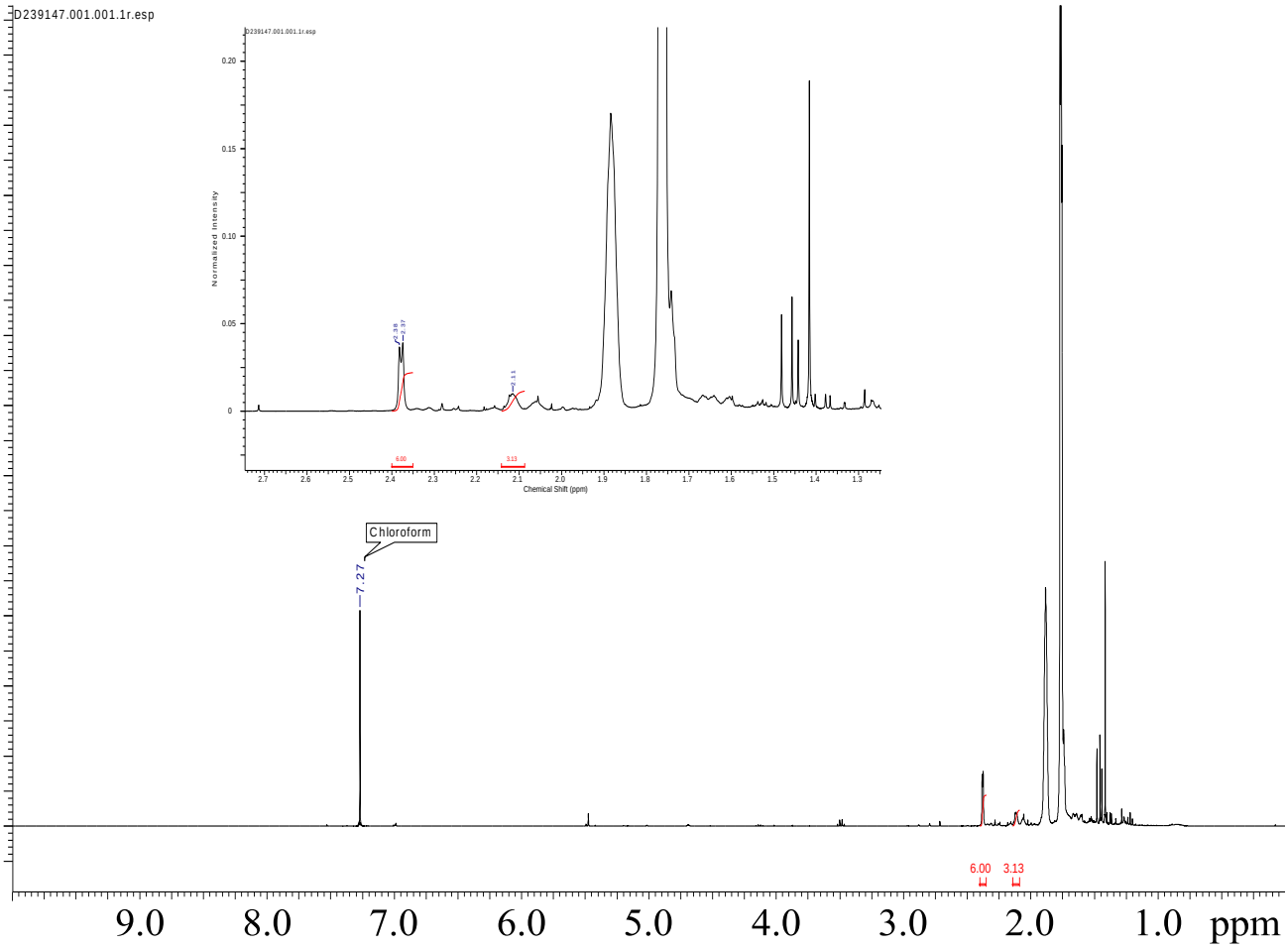


Figure S34a ^{1}H NMR spectrum from bromination of adamantane.

Further confirmation of the presence of adamantane was obtained from ^{13}C NMR analysis (see Figure 34b).

The following signals were observed; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 49.3, 35.5, 32.6. These signals are consistent with the literature.[20] The signals at 37.7 and 28.3 are from unreacted adamantane.

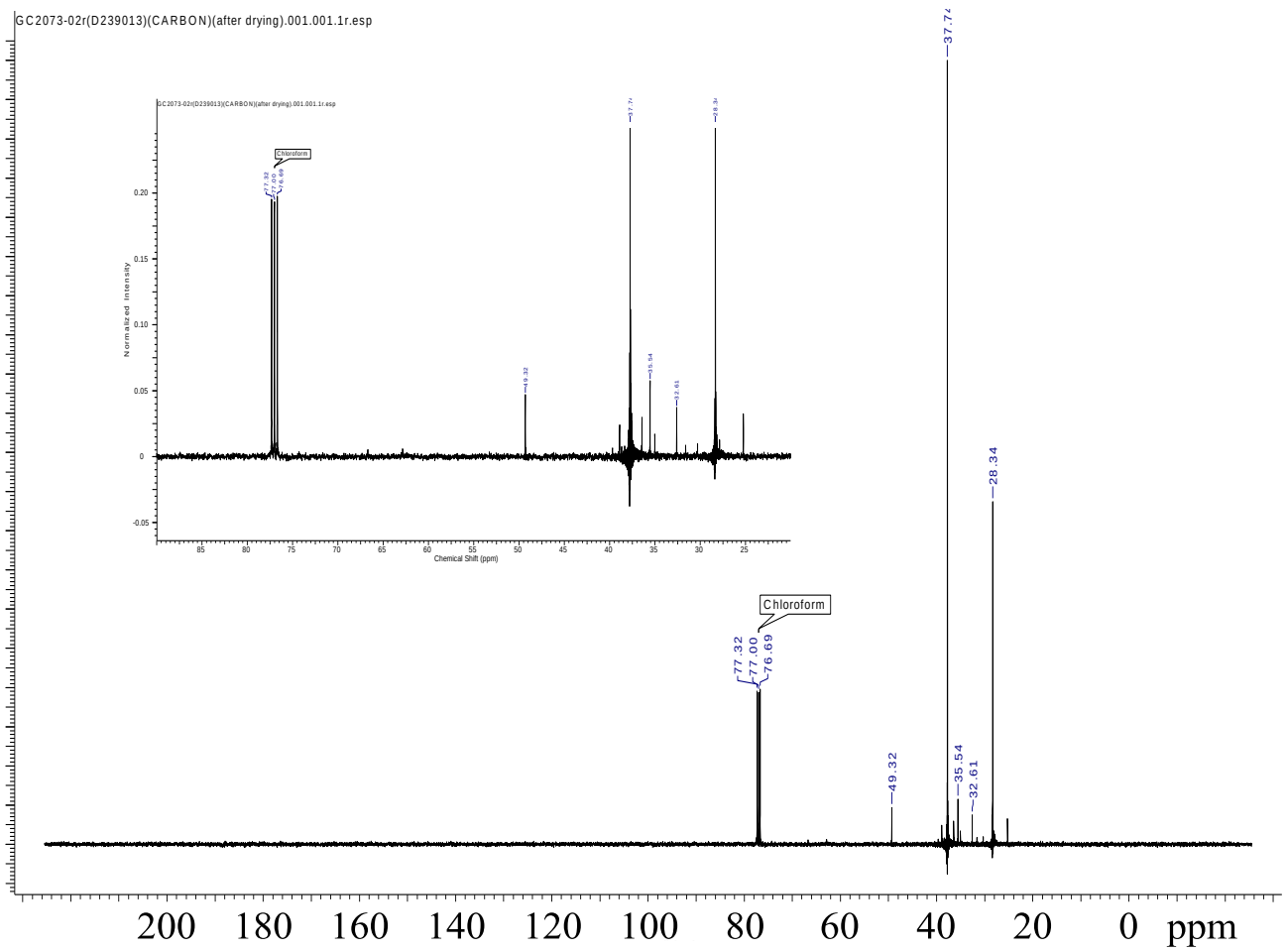
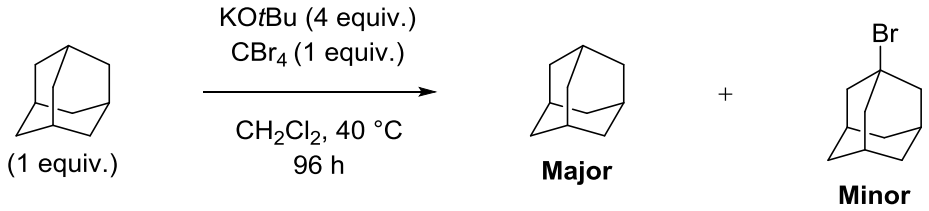


Figure S34b ^{13}C NMR spectrum from bromination of adamantane.

Detection of bromoadamantane, reaction with light excluded



Adamantane (68.1 mg, 0.500 mmol), tetrabromomethane (165.8 mg, 0.500 mmol), and KO*t*Bu (224.4 mg, 2.00 mmol) were added to a pressure tube followed by CH_2Cl_2 (3.13 mL). The pressure tube was covered with foil and then stirred at 40 °C for 96 h. After the mixture had cooled 1 M HCl (10 mL) was added and the mixture was extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material.

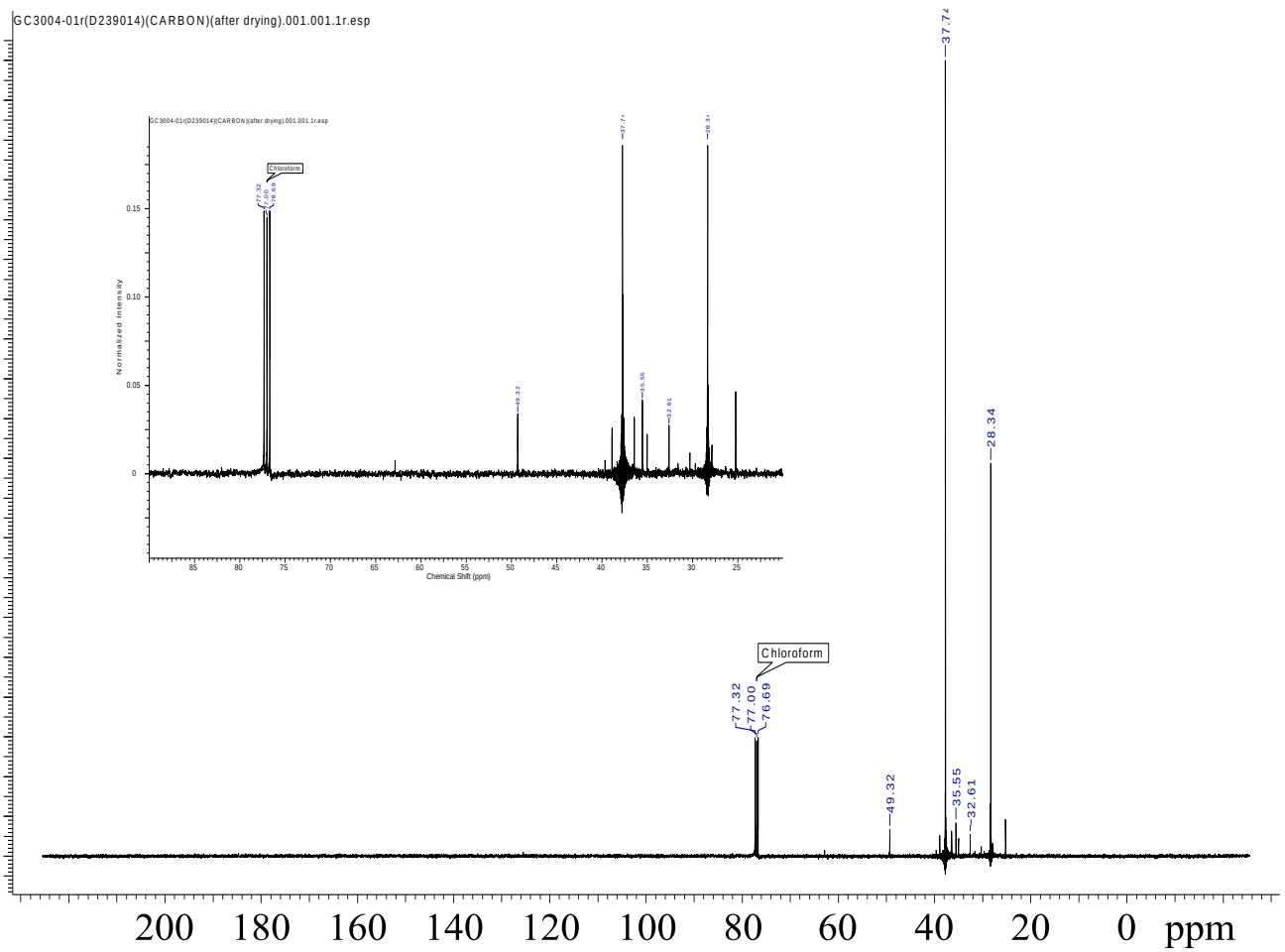
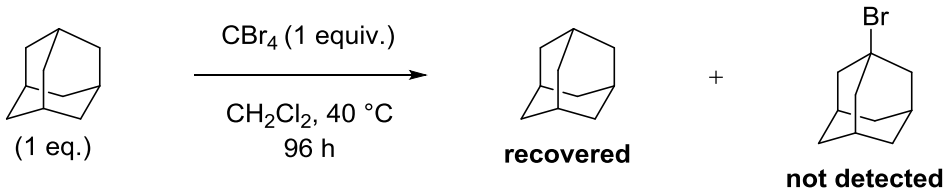


Figure S35 ^{13}C NMR spectrum from bromination of adamantane (with light excluded).

Control reaction with omission of KO*t*Bu



Adamantane (68.1 mg, 0.500 mmol) and tetrabromomethane (165.8 mg, 0.500 mmol) were added to a pressure tube followed by CH_2Cl_2 (3.13 mL). The pressure tube was sealed and then stirred at 40 °C for 96 h. After the mixture had cooled 1 M HCl (10 mL) was added and the mixture was extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material (see Figure S36).

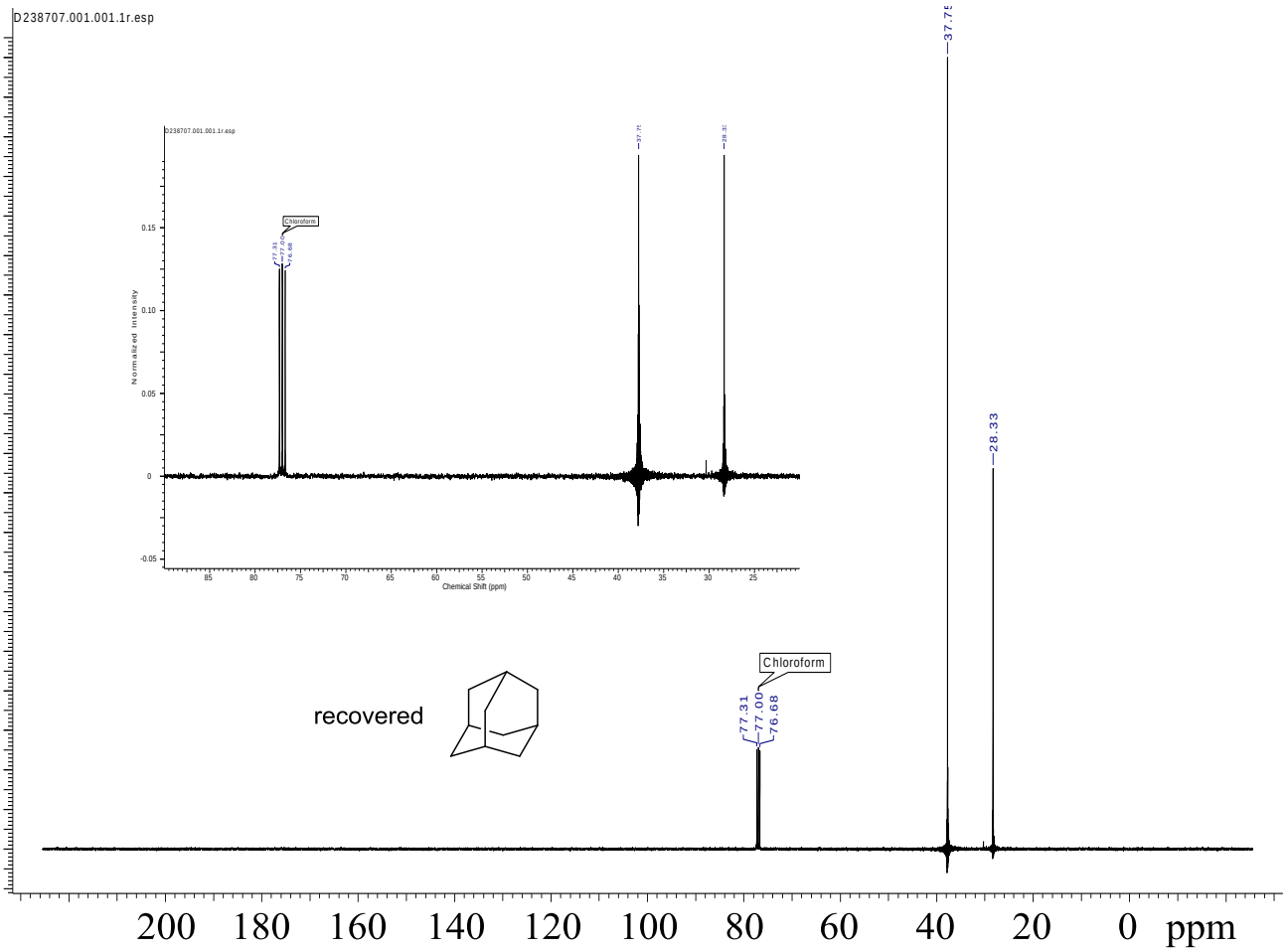
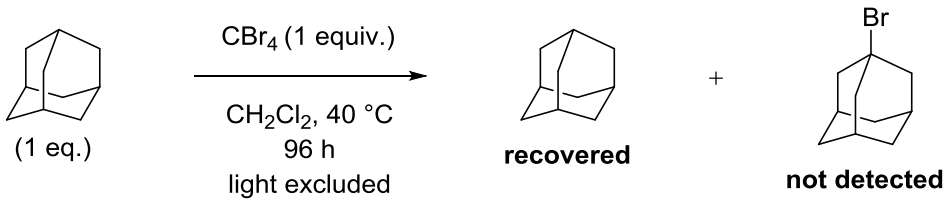


Figure S36 ^{13}C NMR spectrum from bromination of adamantane (with KO*t*Bu omitted from the reaction mixture).

Control reaction with omission of KO*t*Bu and exclusion of light



Adamantane (68.1 mg, 0.500 mmol) and tetrabromomethane (165.8 mg, 0.500 mmol) were added to a pressure tube followed by CH_2Cl_2 (3.13 mL). The pressure tube was sealed, covered in foil and then stirred at 40 °C for 96 h. After the mixture had cooled 1 M HCl (10 mL) was added and the mixture was extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated to give the crude material. (See Figure S37).

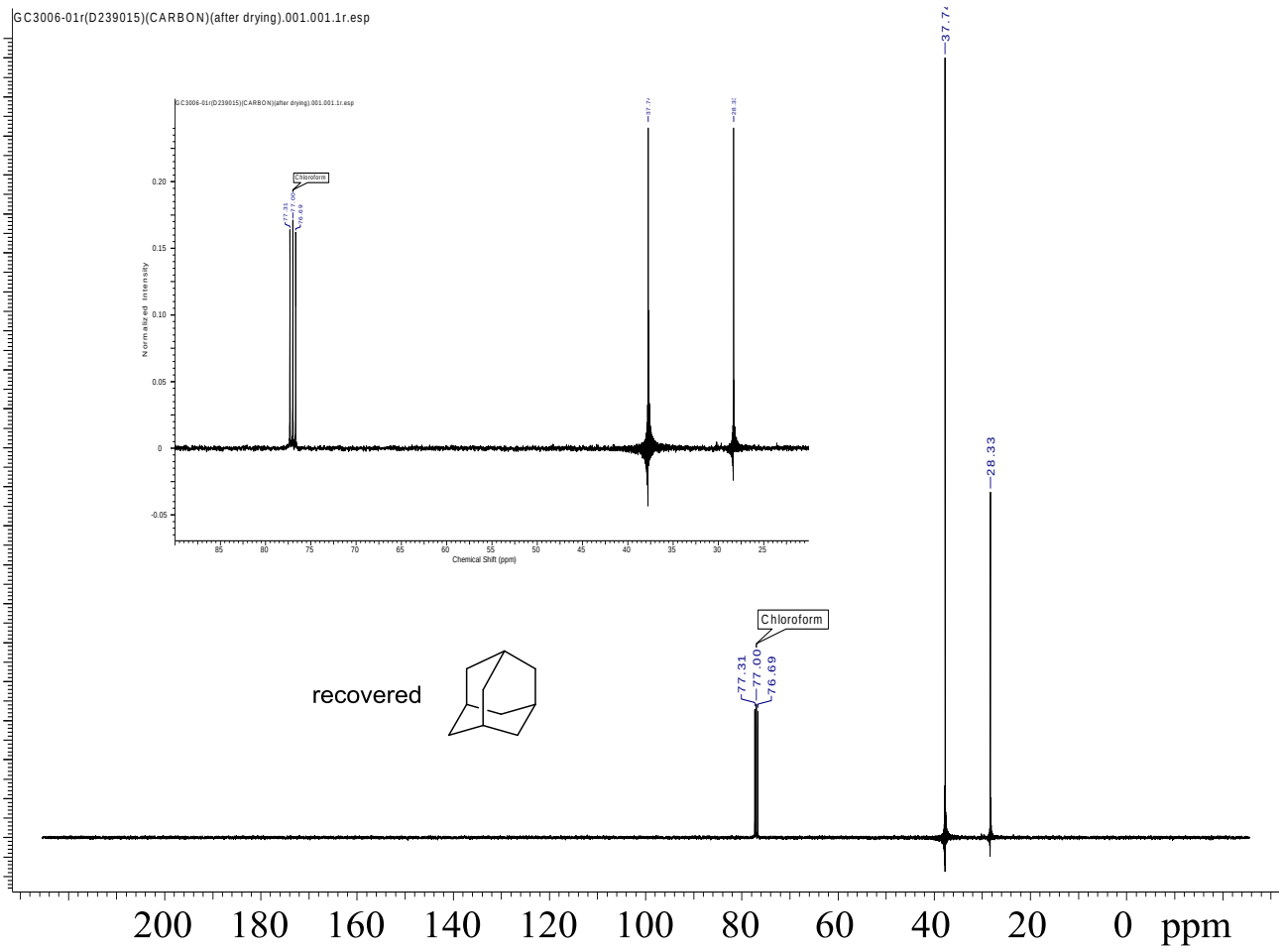


Figure S37 ^{13}C NMR spectrum from bromination of adamantane (light excluded and with KO*t*Bu omitted from the reaction mixture).

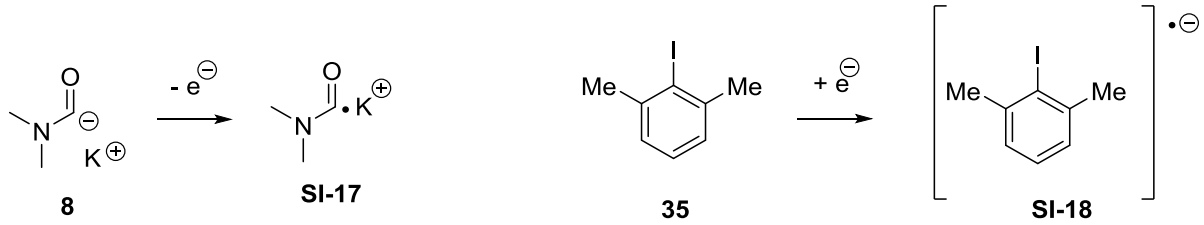
Reduction potentials of CBr_4 in DMF have been reported in the literature.[21,22]

$E_{1/2} = -0.31$ V (vs. SCE)

$E^0 = -0.36$ V (vs. SCE)

(6) Computational results relating to sections C and D

Computational details for section C ($S_{RN}1$ reactions in DMF)



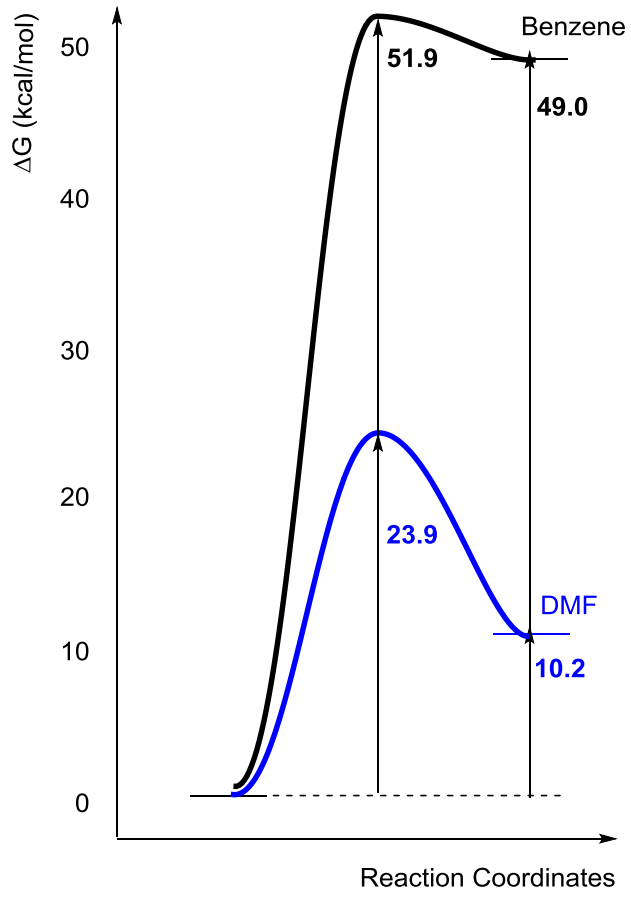
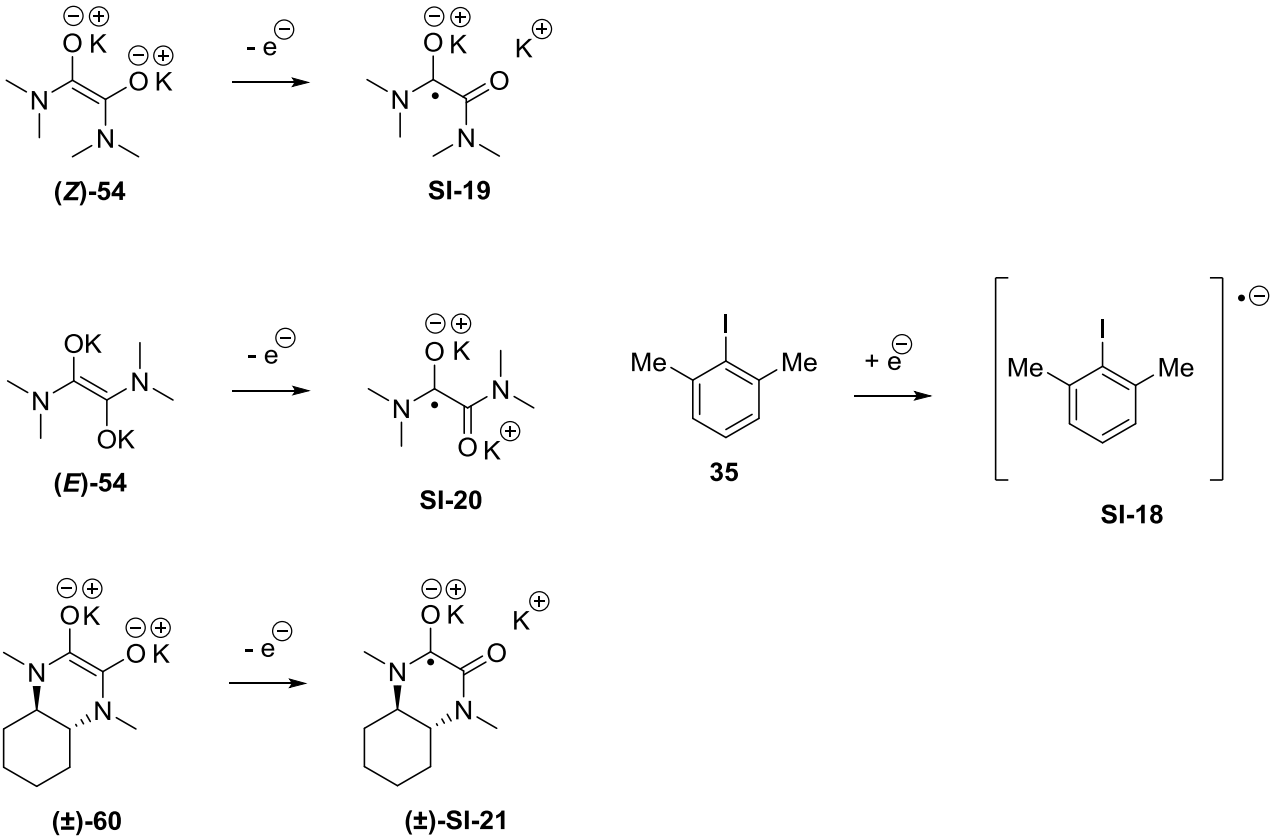


Figure S38. The calculated energetics for single electron transfer (SET) from carbamoyl anion **8** to 2-iodo-1,3-dimethylbenzene **35** using the Nelson four-point method.[23,24]



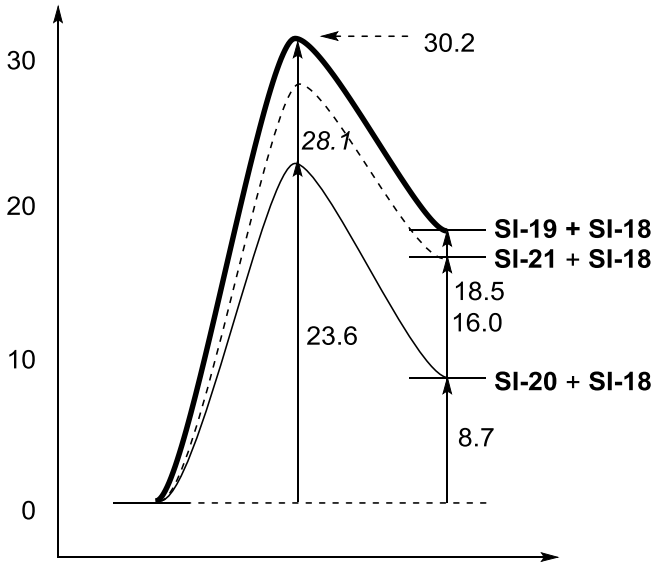


Figure S39. The calculated energetics for SET from the electron donors (*E*)-**54**, (*Z*)-**54**, and **60** to 1-iodo-2,6-dimethylbenzene **35**, using the Nelson four-point method, in benzene. [23,24]

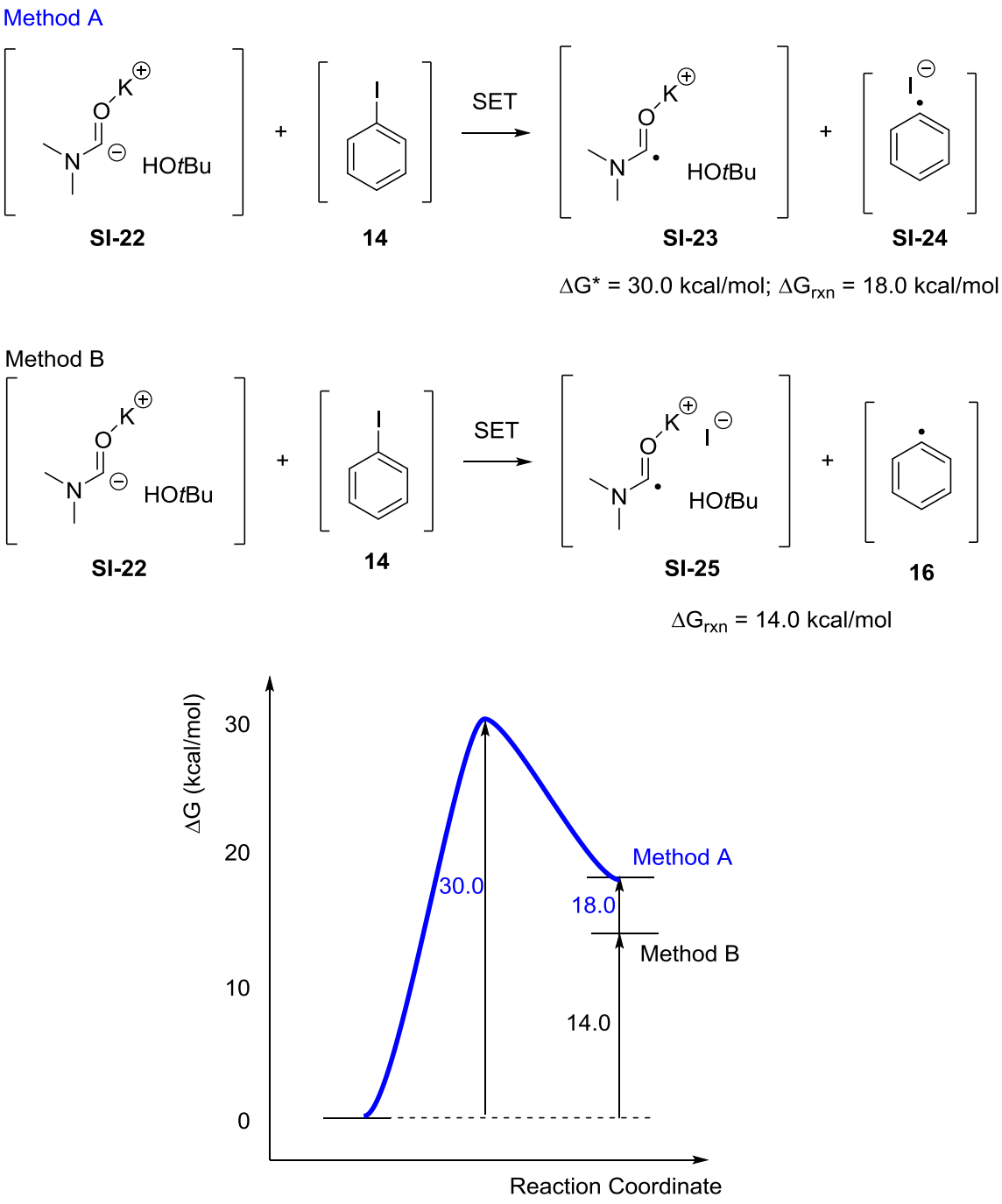


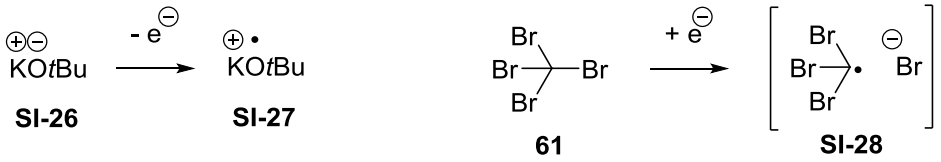
Figure S40. The calculated energetics for SET between **SI-22** and iodobenzene **14** in DMF, to provide a comparison of the relative energies obtained from the Nelson four-point method (Method A) and the direct method of subtracting the combined energies of the products **SI-25** and **16**, from that of the starting materials **SI-22** and **14** (Method B) [23,24,25]

Method A: Employed Marcus theory[23,24]; The M062X functional[26,27] was used with the 6-311++G(d,p) basis set[28,29,30,31,32] on all atoms, except for the iodine. Iodine was modelled with the MWB46 relativistic pseudo potential and associated basis set was used.[33] All calculations were carried out using the C-PCM implicit solvent model[34,35] as implemented in Gaussian09.[36]

Method B: Calculated the relative energies of the Starting material and Product: The M062X functional[26,27] was used with the 6-311++G(d,p) basis set[28,29,30,31,32] on all atoms, except for the iodine. Iodine was modelled with the MWB46 relativistic pseudo potential and associated basis set was used.[33] All calculations were carried out using the C-PCM implicit solvent model[34,35] as implemented in Gaussian09.[36]

These ΔG_{rxn} values compare with the energies calculated by Taillefer *et al.*[25] who reported ΔG_{rxn} = 15.6 kcal/mol.

Computational details for section D (Can KO*t*Bu ever act as a direct electron donor?)



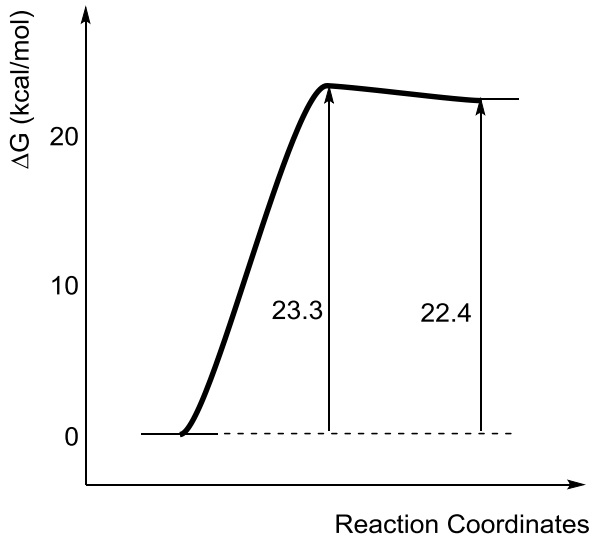
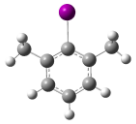


Figure S41. The calculated energetics for SET from KO*t*Bu to CBr_4 using the Nelson four-point method, in CH_2Cl_2.[23,24]

Computational Section - XYZ coordinates

XYZ for section C ($S_{RN}1$ reactions in DMF)

1-iodo-2,6-dimethylbenzene **35**, solvent = benzene

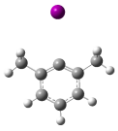


Charge = 0; Multiplicity = 1

18
-321.5822882

C	0.52163	0.00000	-0.00009
C	1.18619	1.23039	-0.00016
C	2.58326	1.20094	-0.00027
C	3.27814	-0.00004	-0.00030
C	2.58322	-1.20099	-0.00023
C	1.18615	-1.23041	-0.00013
H	3.12416	2.14061	-0.00032
H	3.12409	-2.14069	-0.00026
I	-1.62203	0.00001	0.00017
H	4.36154	-0.00006	-0.00038
C	0.46943	-2.55353	-0.00003
H	-0.17097	-2.65388	0.87959
H	-0.17135	-2.65381	-0.87937
H	1.18832	-3.37237	-0.00021
C	0.46952	2.55355	-0.00012
H	-0.17124	2.65383	-0.87947
H	-0.17088	2.65396	0.87949
H	1.18845	3.37236	-0.00032

SI-18, solvent = benzene



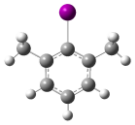
Charge = -1; Multiplicity = 2

18
-321.6512155

C	-1.22916	0.00000	0.00041
C	-1.84778	1.23177	0.00021
C	-3.24941	1.21087	-0.00025
C	-3.93896	-0.00001	-0.00048
C	-3.24939	-1.21088	-0.00025
C	-1.84777	-1.23177	0.00020
H	-3.79763	2.14848	-0.00044
H	-3.79761	-2.14850	-0.00044
I	2.31147	0.00000	-0.00011
H	-5.02321	-0.00002	-0.00085
C	-1.05531	-2.51333	0.00044
H	-0.40433	-2.55788	-0.87502
H	-0.40491	-2.55792	0.87633
H	-1.71604	-3.38220	0.00021

C	-1.05534	2.51333	0.00044
H	-0.40493	2.55793	0.87633
H	-0.40436	2.55789	-0.87502
H	-1.71607	3.38220	0.00021

1-iodo-2,6-dimethylbenzene **35**, solvent = DMF



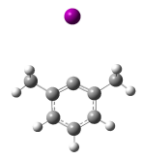
Charge = 0; Multiplicity = 1

18

-321.5839116

C	-0.52196	0.00000	-0.00003
C	-1.18646	-1.23113	-0.00011
C	-2.58397	-1.20163	-0.00023
C	-3.27899	-0.00006	-0.00027
C	-2.58403	1.20154	-0.00020
C	-1.18651	1.23111	-0.00007
H	-3.12477	-2.14143	-0.00030
H	-3.12487	2.14132	-0.00025
I	1.62302	0.00002	0.00013
H	-4.36237	-0.00009	-0.00036
C	-0.47108	2.55512	-0.00001
H	0.16894	2.65672	0.87980
H	0.16940	2.65658	-0.87949
H	-1.19082	3.37299	-0.00025
C	-0.47093	-2.55509	-0.00010
H	0.16953	-2.65648	-0.87960
H	0.16912	-2.65668	0.87969
H	-1.19062	-3.37301	-0.00035

SI-18, solvent = DMF



Charge = -1; Multiplicity = 2

18

-321.6911747

C	-1.44230	0.00003	0.00255
C	-2.05384	1.23534	0.00142
C	-3.45611	1.21120	-0.00151
C	-4.14426	-0.00011	-0.00314
C	-3.45598	-1.21134	-0.00186
C	-2.05370	-1.23534	0.00108
H	-4.00345	2.14861	-0.00249
H	-4.00322	-2.14881	-0.00319
I	2.53795	0.00002	-0.00061
H	-5.22809	-0.00017	-0.00541

C	-1.27069	-2.52344	0.00286
H	-0.62204	-2.58276	-0.87374
H	-0.63151	-2.58605	0.88620
H	-1.94071	-3.38369	-0.00223
C	-1.27095	2.52352	0.00269
H	-0.62407	2.58195	0.88065
H	-0.63000	2.58715	-0.87930
H	-1.94106	3.38369	0.00731

8, solvent = benzene

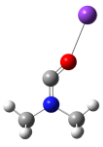
Charge = 0; Multiplicity = 1

12

-847.8092022

C	2.31448	-1.04962	0.00001
H	2.95872	-1.06478	0.88671
H	1.67797	-1.93236	-0.00018
H	2.95907	-1.06463	-0.88643
N	1.46424	0.12692	-0.00008
C	2.15033	1.39549	0.00002
H	1.40471	2.19040	-0.00013
H	2.78811	1.50266	0.88649
H	2.78844	1.50262	-0.88621
C	0.08919	0.07947	-0.00001
O	-0.42840	-1.07772	0.00002
K	-2.56440	0.21302	0.00000

SI-17, solvent = benzene



Charge = 1; Multiplicity = 2

12

-847.6540273

C	2.02134	1.39114	-0.00003
H	2.58925	1.66749	-0.88976
H	1.06322	1.90516	0.00014
H	2.58911	1.66687	0.89020
N	1.78973	-0.05715	-0.00030
C	2.96910	-0.91821	-0.00001
H	2.65074	-1.95845	0.00041
H	3.56842	-0.71798	-0.88972
H	3.56814	-0.71729	0.88995
C	0.58103	-0.56502	-0.00002
O	-0.51101	-0.04417	0.00026

K	-3.04725	-0.02841	-0.00005

8, solvent = DMF

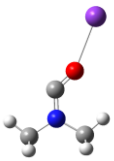
Charge = 0; Multiplicity = 1

12

-847.8270968

C	-2.35118	-1.04804	0.00072
H	-2.99633	-1.06194	-0.88501
H	-1.72104	-1.93503	0.00136
H	-2.99624	-1.06057	0.88653
N	-1.49728	0.12757	-0.00017
C	-2.19262	1.39335	-0.00005
H	-1.45543	2.19606	-0.00024
H	-2.83178	1.49541	-0.88563
H	-2.83134	1.49541	0.88585
C	-0.11807	0.08708	-0.00083
O	0.40272	-1.06869	-0.00087
K	2.63487	0.20699	0.00033

SI-17, solvent = DMF



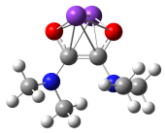
Charge = 1; Multiplicity = 2

12

-847.6944711

C	-2.04509	1.39006	0.00057
H	-2.61048	1.66828	0.89159
H	-1.08533	1.90119	-0.00120
H	-2.61378	1.66838	-0.88831
N	-1.81689	-0.05775	-0.00004
C	-2.99587	-0.91572	0.00178
H	-2.67877	-1.95642	0.00081
H	-3.59429	-0.71538	0.89250
H	-3.59753	-0.71466	-0.88657
C	-0.60484	-0.56746	-0.00221
O	0.48221	-0.04552	-0.00403
K	3.10082	-0.02759	0.00120

(*Z*)-**54**, solvent = benzene



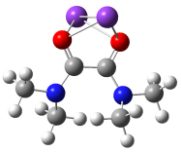
Charge = 0; Multiplicity = 1

24

-1695.6764854

C	-1.60786	-1.47029	1.79228
H	-0.86120	-2.18728	2.17032
H	-1.52840	-0.54338	2.36684
H	-2.60406	-1.89099	1.96251
N	-1.43251	-1.17706	0.37657
C	-1.61620	-2.39170	-0.40582
H	-1.50867	-2.15766	-1.46893
H	-0.88615	-3.17386	-0.14790
H	-2.62329	-2.78828	-0.24393
C	-0.14486	-0.56817	0.12344
O	0.94133	-1.32373	0.35211
K	1.72299	0.52347	1.89091
C	-0.04649	0.73704	-0.31710
N	-1.15117	1.57046	-0.71166
C	-1.34886	2.69815	0.17737
H	-0.38037	3.13895	0.41562
H	-1.96731	3.45999	-0.30788
H	-1.85157	2.40137	1.11740
C	-2.40705	1.00074	-1.15082
H	-3.05283	0.66220	-0.32913
H	-2.94497	1.76205	-1.72896
H	-2.21754	0.14107	-1.79509
O	1.14057	1.33257	-0.42405
K	1.79727	-0.61206	-1.91227

SI-19, solvent = benzene



Charge = 1; Multiplicity = 2

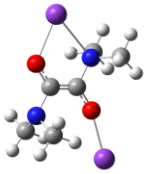
24

-1695.5680071

C	-2.36450	1.47638	-0.65763
H	-2.07325	2.22727	-1.40549
H	-2.45692	0.50850	-1.14432
H	-3.33707	1.75992	-0.25020
N	-1.38742	1.41937	0.42584
C	-1.23699	2.68977	1.11831
H	-0.62858	2.55998	2.01065
H	-0.76219	3.45148	0.48598
H	-2.22814	3.04371	1.40562

C	-0.21793	0.68077	0.25650
O	0.90647	1.18917	0.60887
K	1.94389	0.87826	-1.81096
C	-0.21850	-0.68036	-0.25716
N	-1.38859	-1.41784	-0.42684
C	-1.23933	-2.68827	-1.11950
H	-0.63030	-2.55903	-2.01149
H	-0.76578	-3.45069	-0.48707
H	-2.23076	-3.04097	-1.40737
C	-2.36631	-1.47381	0.65608
H	-3.33922	-1.75525	0.24799
H	-2.07681	-2.22577	1.40354
H	-2.45720	-0.50609	1.14339
O	0.90554	-1.18989	-0.60903
K	1.93946	-0.88062	1.81292

(*E*)-**54**, solvent = benzene



Charge = 0; Multiplicity = 1

24

-1695.6446141

C	-1.19138	-2.00409	1.19210
H	-0.29618	-2.64169	1.23616
H	-1.20463	-1.37078	2.08268
H	-2.07545	-2.65277	1.20630
N	-1.20497	-1.16015	0.00006
C	-1.19125	-2.00417	-1.19192
H	-1.20421	-1.37094	-2.08255
H	-0.29611	-2.64189	-1.23567
H	-2.07538	-2.65276	-1.20627
C	-0.05325	-0.24219	0.00010
O	1.14632	-0.82384	-0.00004
C	-0.32550	1.09718	0.00011
N	0.81715	2.01607	0.00051
C	1.61374	1.96847	-1.20595
H	0.96540	2.11918	-2.07223
H	2.35712	2.77452	-1.19599
H	2.13772	1.00593	-1.34398
C	1.61432	1.96719	1.20653
H	2.13829	1.00449	1.34340
H	2.35776	2.77318	1.19690
H	0.96645	2.11714	2.07329
O	-1.50970	1.67644	-0.00047
K	3.44596	-1.14781	-0.00035
K	-3.49591	0.30727	-0.00006

SI-20, solvent = benzene

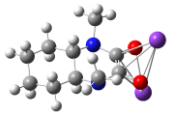
Charge = 1; Multiplicity = 2

24

-1695.5545210

C	2.36318	2.31770	-0.20612
H	2.83659	2.17645	0.77572
H	2.86867	1.68237	-0.93164
H	2.49050	3.35941	-0.50317
N	0.94354	2.01845	-0.17903
C	0.14999	3.04093	0.49323
H	-0.90456	2.79353	0.43662
H	0.45410	3.13876	1.54463
H	0.31113	4.00099	-0.00058
C	0.60006	0.67699	-0.08530
O	1.52235	-0.19384	-0.02241
C	-0.78685	0.29385	-0.15065
N	-1.14189	-1.08252	0.15019
C	-0.58929	-1.64698	1.37733
H	-0.68198	-0.92073	2.18677
H	-1.15959	-2.54084	1.64704
H	0.46744	-1.92094	1.27851
C	-0.93650	-1.97486	-0.99127
H	0.13120	-2.15109	-1.18129
H	-1.42139	-2.93715	-0.80157
H	-1.37842	-1.53241	-1.88660
O	-1.72739	1.04992	-0.54578
K	3.51796	-1.57653	-0.03268
K	-3.82261	-0.25475	0.00950

60, solvent = benzene



Charge = 0; Multiplicity = 1

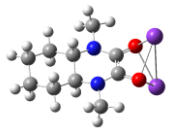
32

-1850.5184598

C	1.55960	0.73821	-0.19207
H	1.59278	0.80024	-1.29979
N	0.35785	1.39650	0.31015
C	0.18050	2.71625	-0.27849
H	-0.74435	3.14607	0.09778
H	1.00869	3.37406	-0.01382
H	0.11966	2.65902	-1.38353
C	-0.86244	0.62139	0.21291

O	-1.97390	1.25845	0.57280
K	-2.36122	-0.67408	2.18317
C	-0.87096	-0.70907	-0.15005
N	0.35259	-1.43266	-0.36720
C	1.51644	-0.74852	0.18968
H	1.40094	-0.77864	1.28362
C	0.47073	-1.89293	-1.74504
H	0.76362	-1.08826	-2.44245
H	1.18910	-2.71075	-1.83445
H	-0.50811	-2.26930	-2.04285
O	-1.99810	-1.42160	-0.22132
K	-3.00446	0.43791	-1.59748
C	2.81647	1.41045	0.37931
H	2.88439	2.44470	0.03508
H	2.70354	1.44256	1.46980
C	2.81849	-1.46510	-0.16683
H	2.73735	-2.51356	0.13593
H	2.96055	-1.45341	-1.25321
C	4.02620	-0.79004	0.47765
H	3.93384	-0.82642	1.56987
H	4.94202	-1.32642	0.21457
C	4.10303	0.66620	0.02365
H	4.95951	1.17006	0.48022
H	4.25896	0.69462	-1.06182

SI-21, solvent = benzene



Charge = 1; Multiplicity = 2

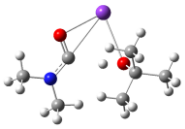
32

-1850.4142970

C	1.63771	0.74463	-0.17942
H	1.63014	0.82128	-1.28175
N	0.43178	1.37642	0.35761
C	0.37927	2.83151	0.31296
H	-0.62078	3.14899	0.59187
H	1.09592	3.26098	1.01195
H	0.60470	3.20603	-0.69556
C	-0.76744	0.70030	0.17445
O	-1.88969	1.30226	0.33324
K	-2.92290	-0.47773	1.93891
C	-0.76748	-0.70009	-0.17512
N	0.43174	-1.37609	-0.35898
C	1.63752	-0.74458	0.17879
H	1.62928	-0.82129	1.28112
C	0.37904	-2.83117	-0.31527
H	1.09696	-3.26020	-1.01319
H	0.60246	-3.20646	0.69343
H	-0.62049	-3.14845	-0.59627

O	-1.88977	-1.30219	-0.33314
K	-2.92526	0.47741	-1.93721
C	2.90291	1.42593	0.34591
H	2.90891	2.47519	0.04679
H	2.88617	1.39953	1.44245
C	2.90298	-1.42593	-0.34582
H	2.90878	-2.47521	-0.04676
H	2.88701	-1.39931	-1.44236
C	4.16306	-0.74131	0.17923
H	4.20898	-0.85242	1.26888
H	5.04703	-1.23668	-0.22813
C	4.16315	0.74115	-0.17851
H	5.04708	1.23640	0.22908
H	4.20948	0.85219	-1.26816

SI-22, solvent = DMF



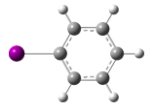
Charge = 0; Multiplicity = 1

27

-1081.4834832

C	-3.63144	-0.50075	0.58763
H	-3.75586	-1.33954	1.28111
H	-3.64035	0.43296	1.14585
H	-4.47457	-0.51220	-0.11182
N	-2.36875	-0.60556	-0.12223
C	-2.19095	-1.80740	-0.90571
H	-1.22679	-1.75784	-1.41173
H	-2.21320	-2.70255	-0.27220
H	-2.98284	-1.90709	-1.65705
C	-1.38343	0.35336	-0.08887
H	0.25372	-0.01403	-0.64607
O	-1.62055	1.38981	0.59744
O	1.26562	-0.05435	-0.86717
C	1.93565	-0.83173	0.12040
C	3.35716	-1.06084	-0.38051
H	3.85352	-0.10253	-0.55335
H	3.93993	-1.62809	0.34981
H	3.34027	-1.61716	-1.32094
C	1.95881	-0.06420	1.44679
H	0.93733	0.16627	1.76423
H	2.44180	-0.64775	2.23495
H	2.51397	0.87185	1.33277
C	1.21809	-2.17123	0.30749
H	1.15011	-2.69674	-0.64882
H	1.75869	-2.80461	1.01585
H	0.20489	-2.01191	0.68649
K	0.51246	2.54331	-0.35258

Iodobenzene **14**, solvent = DMF



Charge = 0; Multiplicity = 1

12
-242.9682233

C	2.64531	-1.20411	0.00000
C	1.25223	-1.21321	-0.00001
C	0.57437	-0.00002	0.00000
C	1.25222	1.21321	0.00000
C	2.64527	1.20413	-0.00001
C	3.34252	0.00001	0.00001
H	3.18144	-2.14575	0.00000
H	0.71162	-2.15110	-0.00000
H	0.71156	2.15107	0.00001
H	3.18142	2.14576	-0.00001
H	4.42555	0.00004	0.00002
I	-1.55628	0.00000	0.00000

SI-23, solvent = DMF

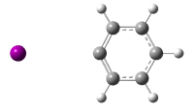
Charge = 1; Multiplicity = 2

27
-1081.3428081

C	-3.76359	0.09866	0.77174
H	-3.80707	-0.51501	1.67320
H	-3.55731	1.13248	1.03861
H	-4.71713	0.03596	0.24507
N	-2.69286	-0.39313	-0.10095
C	-2.80009	-1.76712	-0.57718
H	-1.95294	-1.98869	-1.22399
H	-2.80261	-2.45303	0.27245
H	-3.72805	-1.88898	-1.13847
C	-1.66189	0.35764	-0.41662
H	0.59821	-0.24458	-1.12871
O	-1.36650	1.49106	-0.13437
O	1.43198	0.01958	-0.71844
C	1.88987	-1.07217	0.10499
C	3.20594	-0.60335	0.70782
H	3.04909	0.27414	1.33993
H	3.64136	-1.39402	1.32167
H	3.91341	-0.34614	-0.08332
C	0.85736	-1.34912	1.19561
H	-0.07969	-1.70948	0.76017
H	1.22474	-2.11326	1.88444
H	0.65090	-0.43715	1.76160
C	2.09596	-2.30251	-0.77246

H	2.83446	-2.09584	-1.54995
H	2.44392	-3.14701	-0.17349
H	1.15532	-2.59088	-1.25141
K	1.07991	2.63032	-0.12116

SI-24, solvent = DMF



Charge = -1; Multiplicity = 2

12

-243.0754418

C	3.64561	-1.21088	-0.00014
C	2.24659	-1.22152	0.00032
C	1.61468	0.00002	0.00052
C	2.24663	1.22155	0.00032
C	3.64564	1.21087	-0.00014
C	4.33623	-0.00002	-0.00036
H	4.19115	-2.14790	-0.00032
H	1.69441	-2.15461	0.00049
H	1.69446	2.15464	0.00049
H	4.19122	2.14786	-0.00032
H	5.41963	-0.00003	-0.00072
I	-2.33213	0.00000	-0.00005

SI-25, solvent = DMF

Charge = 0; Multiplicity = 2

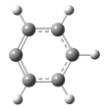
28

-1092.9131822

C	-2.81033	2.85784	-0.33002
H	-3.27667	2.36903	-1.18899
H	-3.33023	2.57135	0.58158
H	-2.86277	3.94028	-0.45987
N	-1.40942	2.44292	-0.23547
C	-0.54704	2.75523	-1.36852
H	0.44402	2.34185	-1.18711
H	-0.96359	2.31361	-2.27737
H	-0.48474	3.83775	-1.49750
C	-0.95905	1.76641	0.79998
H	-0.04916	-1.03740	-0.39833
O	-1.49564	1.39572	1.81467
O	-0.70550	-1.47161	0.16964
C	-1.84419	-1.86038	-0.61424
C	-2.71486	-2.69398	0.31468
H	-2.99797	-2.10597	1.19125

H	-3.62378	-3.01195	-0.20000
H	-2.17161	-3.58128	0.64717
C	-2.58741	-0.60832	-1.07407
H	-1.93215	0.01973	-1.68647
H	-3.46344	-0.87525	-1.67010
H	-2.91539	-0.03005	-0.20669
C	-1.37094	-2.68153	-1.81032
H	-0.81964	-3.56125	-1.47094
H	-2.22174	-3.01029	-2.41146
H	-0.71393	-2.08202	-2.44799
K	0.31561	-0.59836	2.43781
I	2.45027	-0.00819	-0.40314

16, solvent = DMF



Charge = 0; Multiplicity = 2

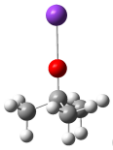
11

-231.5160855

C	1.21101	0.63045	0.00000
C	1.22267	-0.76846	0.00000
C	0.00000	-1.39689	-0.00000
C	-1.22267	-0.76845	0.00000
C	-1.21101	0.63045	0.00000
C	0.00000	1.32045	0.00000
H	2.14820	1.17539	0.00000
H	2.15590	-1.31991	0.00000
H	-2.15589	-1.31992	0.00000
H	-2.14820	1.17539	0.00000
H	-0.00001	2.40379	0.00000

XYZ coordinates for section D (Can KO*t*Bu ever act as a direct electron donor?)

SI-26, solvent = CH_2Cl_2

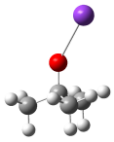


Charge = 0; Multiplicity = 1

15
-833.0085306

C	-1.10588	0.00013	-0.00116
C	-1.65914	-1.15698	-0.85936
H	-1.28403	-2.10960	-0.47279
H	-2.75406	-1.19099	-0.86108
H	-1.31573	-1.04931	-1.89263
C	-1.65626	1.32530	-0.56967
H	-2.75155	1.35474	-0.57788
H	-1.29217	2.16063	0.03602
H	-1.29904	1.46534	-1.59460
C	-1.65460	-0.16731	1.43138
H	-1.31307	-1.11954	1.84950
H	-1.27215	0.63664	2.06766
H	-2.74923	-0.14436	1.46654
O	0.26965	-0.00089	-0.00354
K	2.64890	-0.00017	0.00003

SI-27, solvent = CH_2Cl_2

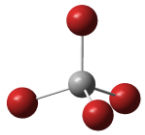


Charge = 1; Multiplicity = 2

15
-832.8230302

C	1.18659	0.02769	0.01772
C	1.53782	-1.25001	-0.79445
H	0.79647	-1.42450	-1.57450
H	2.51258	-1.07999	-1.25566
H	1.59494	-2.11756	-0.13735
C	2.21527	0.24267	1.12944
H	3.20121	0.42307	0.69679
H	1.93888	1.10946	1.73325
H	2.26423	-0.63670	1.77342
C	1.07763	1.23419	-0.91580
H	0.33991	1.04437	-1.69814
H	0.77697	2.11924	-0.35087
H	2.04241	1.43732	-1.38464
O	-0.04560	-0.28863	0.55866
K	-2.69509	-0.00489	0.05826

61, solvent = CH_2Cl_2

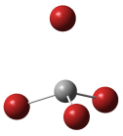


Charge = 0; Multiplicity = 1

5
-91.3749874

C	-0.00010	0.00000	-0.00027
Br	0.94937	1.60555	-0.62222
Br	0.94937	-1.60555	-0.62222
Br	-1.82999	0.00000	-0.71935
Br	-0.06873	0.00000	1.96384

SI-28, solvent = CH_2Cl_2



Charge = -1; Multiplicity = 2

5
-91.5190674

C	-0.20502	0.00037	-0.00076
Br	-0.82167	1.80750	-0.47417
Br	2.45366	0.01316	-0.00241
Br	-0.79744	-1.32182	-1.33051
Br	-0.79941	-0.49890	1.80722

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