# Electron Transfer Reactions: KO*t*Bu (but not NaO*t*Bu) Photoreduces Benzophenone, under Activation by Visible Light

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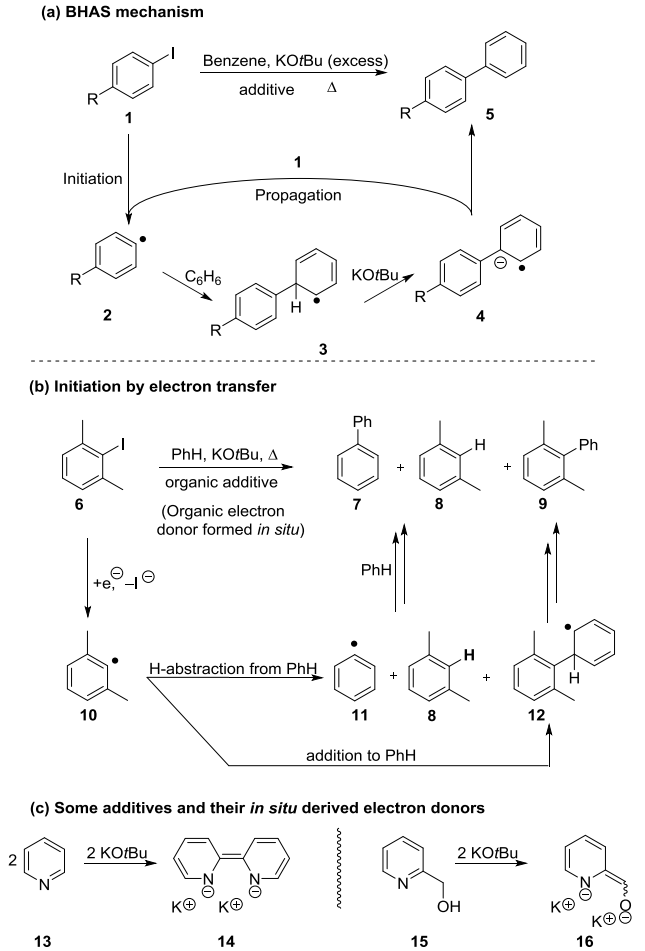
*Supporting Information Placeholder*

**ABSTRACT:** Long-standing controversial reports of electron transfer from KO*t*Bu to benzophenone have been investigated and resolved. The mismatch in the oxidation potential of KO*t*Bu (+0.10V *vs*. SCE in DMF) and the first reduction potential of benzophenone (of many values cited in the literature, the least negative value is −1.31 V *vs.* SCE in DMF), preclude direct electron transfer. Experimental and computational results now establish that a complex is formed between the two reagents, with the potassium ion providing the linkage, which markedly shifts the absorption spectrum to provide a tail in the visible light region. Photoactivation at room temperature by irradiation at defined wavelength (365nm or 400nm), or even by winter daylight, leads to the development of the blue color of the potassium salt of benzophenone ketyl, whereas no reaction is observed when the reaction mixture is maintained in darkness. So, no electron transfer occurs in the ground state. However, when photoexcited, electron transfer occurs within a complex formed from benzophenone and KOtBu. TDDFT studies match experimental findings and also define the electronic transition within the complex as n → π*, originating on the butoxide oxygen. Computation and experiment also align in showing that this reaction is selective for KO*t*Bu; no such effect occurs with NaO*t*Bu, providing the first case where such alkali metal ion selectivity is rationalized in detail. Chemical evidence is provided for the photoactivated electron transfer from KO*t*Bu to benzophenone: *tert*-butoxyl radicals are formed and undergo fragmentation to form (acetone and) methyl radicals, some of which are trapped by benzophenone. Likewise, when KOC(Et)$_3$ is used in place of KO*t*Bu, then ethylation of benzophenone is seen. Further evidence of electron transfer was seen when the reaction was conducted in benzene, in the presence of *p*-iodotoluene; this triggered BHAS coupling to form 4-methylbiphenyl in 74% yield.

## Introduction

Alkoxides of alkali metals are widely used in organic chemistry as powerful bases. In the past decade, however, these alkoxides have played a key role in an extremely wide range of reactions that involve, or are proposed to involve, single electron transfer - representative examples are cited here.[1-10] This is paradoxical, because alkoxides are very resistant to oxidation, due to electronegativity of oxygen and the consequent instability of alkoxyl radicals.



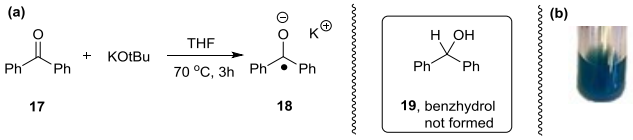

**Scheme 1**. (a) BHAS mechanism.[2] (b) Initiation by electron transfer.[5b] (c) Examples[5b,10] of additives and their proposed electron donors derived by reaction with KO*t*Bu.

Our interest in these alkoxides, and particularly KO*t*Bu, arose from our studies of the initiation of the Base-Promoted Homolytic Aromatic Substitution (BHAS) class of reactions,[10] (Scheme 1a), where KO*t*Bu[1-10] (sometimes NaO*t*Bu[1c,2c,3a]) promotes the coupling of aryl halides to arenes in the presence of a range of special organic additives. The reactions occur through the conversion of

aryl halides **1** to aryl radicals **2** by means of the chain reaction shown.

Some authors proposed that initial radical formation is the result of direct electron transfer from KO*t*Bu or a complex of KO*t*Bu with a ligand to the aryl halide, but our computational and experimental studies indicated[5b,f] that *in situ* chemical reaction between KO*t*Bu and a wide range of additives instead afforded very electron-rich compounds that behaved as powerful organic electron donors (*e.g.* **14**,[5b] **16**[7d,e] in Scheme 1c). These compounds are needed in vanishingly small amounts, as their role is simply to initiate radical formation; once initiated, conversion is amplified through the radical chain reaction shown.

BHAS reaction with substrate **6** (Scheme 1b), has been exploited by us as a very reliable and sensitive indicator of the formation of strong electron donors in solution. Substrate **6** does not react with KO*t*Bu; however, when KO*t*Bu reacts with a suitable additive to form a strong electron donor, electron transfer to **6** occurs, resulting in formation of aryl radical **10**, and an iodide ion. Radical **10** adds to benzene to form radical **12** and ultimately leads to biaryl **9**. But the *ortho*-methyl groups in **10** make the addition to benzene a challenging reaction, allowing a competing hydrogen atom abstraction from benzene to occur, thereby forming radical **11** together with xylene **8**, the latter as a volatile by-product. Radical **11** reacts with the solvent benzene, ultimately forming biphenyl **7**. The formation of **7** and **9** in a defined ratio of *ca*. 3:1 is a hallmark of the BHAS reaction on substrate **6**. Because of its hindered nature, the yields of coupled product from substrate **6** are not high, but the substrate gives a very clear differentiation between the presence of electron donors and their absence and, in this way, the mechanistic information that it provides is very valuable.[5b,5f]

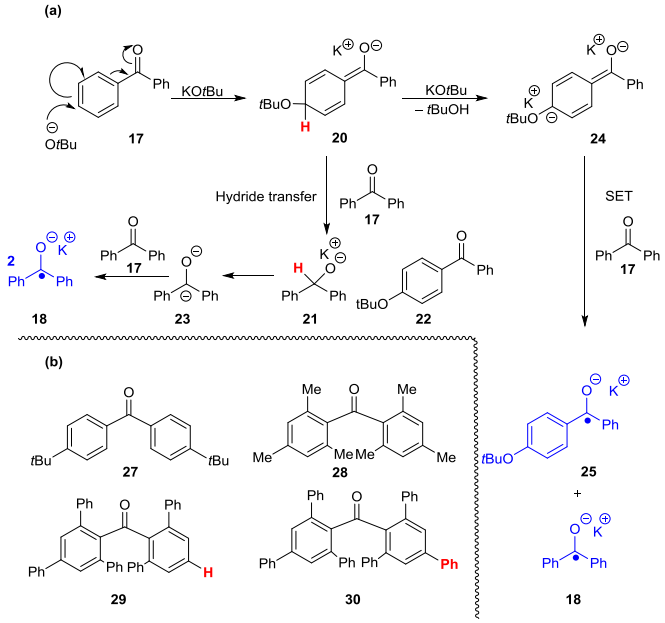



**Scheme 2** (a) Ketyl salt formation;[12] no benzhydrol **19** was formed. (b) Photograph shows blue ketyl salt of benzophenone in our repeat of Ashby experiment, but at 70 °C.

Discussion of electron transfer in reactions KO*t*Bu with benzophenone goes back to Russell *et al.* in 1962,[11a] who showed that radicals were generated when benzophenone and its dihydro derivative, benzhydrol, **19**, were mixed in the presence of KO*t*Bu in DMSO, although the paper did not discuss mechanism. In 1978, Screttas and Cazianis proposed[11b] electron transfer from lithium *s*-butoxide to fluorenones as a result of detection of ketyl radicals. The story was taken up in 1982 by Ashby *et al.*[12] who observed the blue color of the potassium ketyl of benzophenone on reaction of benzophenone with KO*t*Bu (Scheme 2). Ashby attributed the reaction to direct electron transfer from KO*t*Bu to benzophenone. Although not considered then, the reduction potential for benzophenone to its ketyl radical anion (cited values vary from –1.31 V *vs*. SCE in DMF to –2.2 V)[13a-c] and oxidation potential of KO*t*Bu, (+0.1 V in DMF, *vs*. SCE),[6e] indicate that this is not possible as a direct bimolecular electron transfer. With our background in the *in situ* formation of organic electron donors like **14** and **16**, we therefore explored whether formation of organic electron donors could explain the Ashby reactions.[14]

## Results and Discussion

Our first task was to validate the original observations of Ashby qualitatively. Adding sodium metal or potassium metal to a solution of benzophenone (**17**, BZP) (0.5 mmol) in THF (2.5 mL) afforded the blue color of the ketyl at ambient temperature. No color developed when KO*t*Bu (2 equiv) was instead added to benzophenone at room temperature, but heating to 70 °C produced the characteristic blue color after 3h [Scheme 2(b)], supporting Ashby's observation. Given sufficient time, the blue color decays, as reported. Work-up led to isolation of benzophenone, and no benzhydrol **19** was detected, again supporting Ashby's report. Interestingly, and in contrast to KO*t*Bu, NaO*t*Bu (2 equiv) showed no evidence of ketyl formation or other reaction under either set of conditions (see Fig S11 in S.I. file).



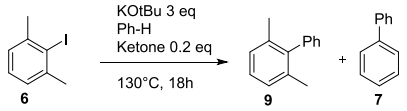

**Scheme 3** (a) A proposal for *in situ* formation of electron donors from KOtBu + $Ph_2CO$. (b) Diarylketones that were synthesized for this study.

We now proposed a number of ways in which organic electron donors[15] might arise in these reactions, one example of which is shown in Scheme 3 (see also S.I.) Attack by KO*t*Bu in the *para*-position of benzophenone **17** would afford anionic intermediate **20**. (Attack in the *ortho*-position should be a comparable alternative, and was considered, see S.I.). Two fates might await **20**: (a) hydride transfer to a molecule of benzophenone **17** would afford **21** and **22** (see ref[5f] for transfer of hydride from an alkoxide under BHAS conditions). As already stated, no benzhydrol **19** is formed in this reaction, so if **21** were formed, it would need to evolve in a different way; deprotonation would afford dianion **23** (see ref.[7d] for formation of dianions with KO*t*Bu under BHAS conditions) which would be a strong electron donor and could reduce benzophenone **17** to form two ketyl radical derivatives **18**. (b) a second possible fate of molecule **20** would involve deprotonation to afford dianion **24**, another candidate for donating an electron to benzophenone **17**. The result of the electron transfer would be two potassium ketyl species, **18** and **25**.

To explore this proposal, substituted benzophenones **27**-**30** were prepared (see SI for details). If addition of KO*t*Bu to the aryl rings of these substrates is valid, then at least some of these substrates, substituted in *ortho* and/or *para* positions, are likely to afford significantly diminished amounts of the potassium ketyl on comparison to **17**. In particular, a notable difference should be seen between closely related substrates like **29** (attack at the free *para*-position, followed by deprotonation is possible), and **30**, (where, even if addition of *tert*-butoxide occurs at the substituted *para* position, subsequent deprotonation is not possible, so that an electron donor should not be able to form). We recognized that the simple qualitative color test for ketyl formation could be compli-

cated with some of these substrates due to the extended chromophores of **29** and **30** and also to the likely variation in kinetics, compared to substrate **17**. So we deployed the BHAS reaction with substrate **6** as a sensitive test (Table 1). The experiments with **17** were repeated in triplicate, and the yields were repeatable.

**Table 1**. BHAS reactions of iodoarene **6**.




| Entry | Ketone | 9[a] (% yield) | 7[a] (% yield) |
|---|---|---|---|
| 1[c] | – | 0.2 | 0.4 |
| 2[c] | **17** | 1.2 | 3.5[b] |
| 3 | **27** | 1.0 | 3.2 |
| 4 | **28** | 0.7 | 1.8 |
| 5 | **29** | 0.8 | 2.4[b] |
| 6 | **30** | 0.4 | 1.2[b] |

[a] Yield calculated via NMR using 1,3,5-trimethoxybenzene as internal standard. [b] Yield deduced using the ratio 1:3 (**9**:**7**) calculated after isolation of the mixture of the coupled products.[c] Average of 3 runs.

As usual with substrate **6**, the yields of the biphenyl products, **7** and **9**, were not high, but they were at least three times higher than the yields from the non-zero yield in blank reactions.[16] The important point to note is that the BHAS reaction was not at 'blank' levels for any of the ketones, indicating that factors other than shown in Scheme 3 were at play. Moreover, we did not succeed in detecting or isolating any products arising from addition of *tert*-butoxide anion to any of the ketones. Coupled with computational studies which indicated unfavorable energy profiles for the proposals in Scheme 3 (see SI), this caused us to think afresh about these reactions.

While performing repeat experiments on the formation of the potassium salt of benzophenone ketyl through reaction with KOtBu on many different days, it was noticed that the time required for the development of the blue color varied by day. During a (rare) sunny day, we noticed that the switch to the blue color was much faster than usual. Performing parallel experiments when sunlight was present with (i) exposed and (ii) foil-covered reactions, showed the result to be strongly dependent on the irradiation.

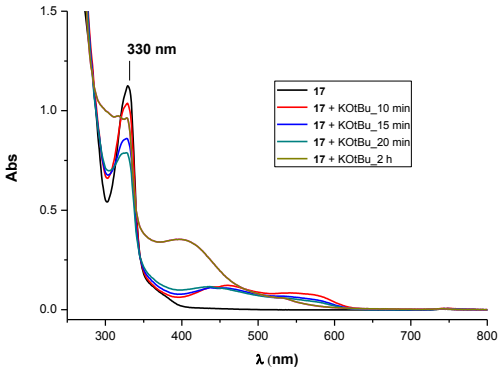



**Figure 1**. UV measurements of **17** (BZP) + KO*t*Bu with time in THF.

A preliminary study of the UV absorption of **17** and of mixtures of **17** with KO*t*Bu in THF was performed (Figure 1).

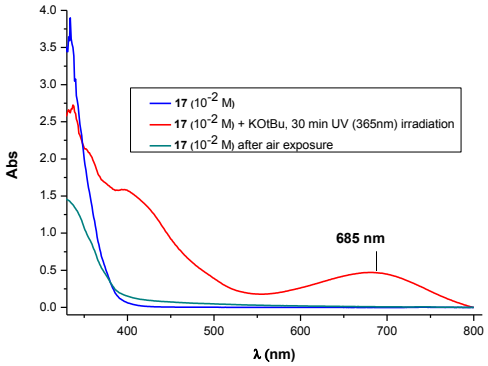



**Figure 2.** UV measurement of **17** ($10^{-2}$ M in THF) + KO*t*Bu pre- and post-irradiation.

Benzophenone does not absorb radiation at > 400 nm (black trace). When KO*t*Bu was added, a tail in the absorption in the range of 400-600 nm was detected; we attribute this to the formation of a transient complex or complexes. With time, the absorption profile changed with the appearance of a new maximum around 400 nm (See Figure 1, trace marked as: '**17** + KO*t*Bu_2 h'). This complex is discussed below, based on investigation through computational chemistry. Therefore we irradiated the mixture of KO*t*Bu and **17** in distilled THF with UV (365 nm, see Figure 2) and polychromatic visible light (see S.I.). In both cases, the blue coloration developed. Analysis via UV-vis spectrometry revealed the appearance of a broad band around $\lambda$=685 $\pm$ 30 nm, diagnostic of the ketyl radical anion of **17**[17] (Figure 2).

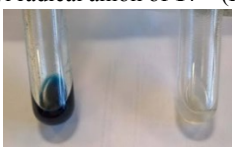


**Figure 3**. Reaction tubes containing KO*t*Bu and **17** in benzene (a) left: exposed to 400 nm light and (b) right: shielded from light by covering in foil.

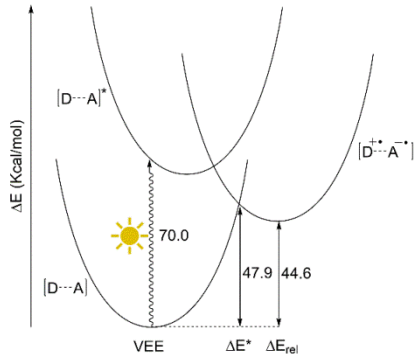
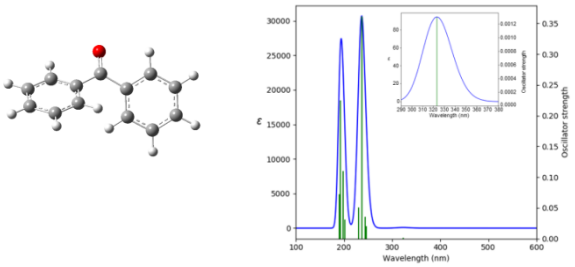


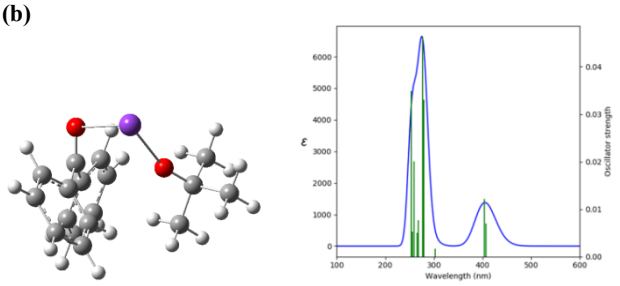

**Figure 4**. TD-DFT calculated vertical excitation energy (VEE) and DFT calculated single electron transfer energies (calculated using the complexation method)[18] for the complex of benzophenone **A** and KO*t*Bu (monomer) **D**. Geometries optimized using M06-2X/6-31++G(d,p) and subsequent single point energy or TD-DFT calculations carried out using CAM-B3LYP/6-31++G(d,p), all with CPCM solvation parameters for THF.

Given the absorption of the complex just above 400 nm, we also irradiated reaction tubes containing KO*t*Bu and benzophenone **17** in benzene with 400 nm LED light sources. Comparison was again made with a foil-covered reaction, conducted side-by-side and at the same time (see Figure 3). The Figure very clearly shows the effect of the LED light source on the reaction.

**(a)**




**(b)**




**(c)**

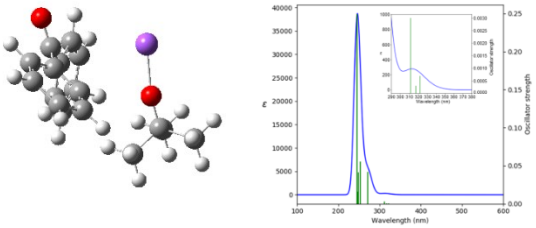
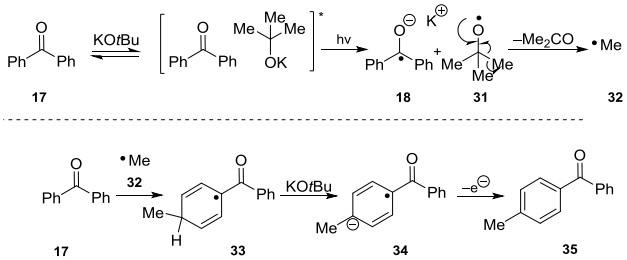



**Figure 5 (a)** Benzophenone **17** (left) and its computed absorption spectrum[19] (right) with expansion of weak n-π* at 332 nm inset. **(b)** complex of **17** with KO*t*Bu (left) and predicted spectrum showing the n-π* > 400 nm (right) **(c)** complex of **17** with NaO*t*-Bu (left) and predicted spectrum (right).

To understand the visible light promoted formation of the blue benzophenone ketyl radical anion, time-dependent density functional theory (TD-DFT) calculations were conducted. Initially, the first singlet excited state of benzophenone was calculated, which corresponds to an n-π* excitation occurring at 332 nm or 3.73 eV. It was therefore clear that no visible light excitation of benzophenone alone could be taking place. We therefore decided to study the complex between a monomer of KO$^t$Bu and benzophenone, which exhibits singlet excitations at 406 nm (3.05 eV or 70 Kcal/mol) and 404 nm (3.07eV) which correspond to CT from the [HOMO] and [HOMO-1], both residing on KO$^t$Bu, to the LUMO, residing on benzophenone. This suggests that it is indeed possible to photoexcite a complex of KOtBu and benzophenone using visible light. The complex between NaOtBu monomer and benzophenone however, does not exhibit any excitation in the visible region, with excitations occurring at 322 nm (3.85 eV) and 318 nm (3.90 eV) corresponding to CT from the [HOMO] and [HOMO-1], both residing on NaO*t*Bu, to the LUMO, residing on benzophenone. This lack of visible excitation (or indeed excitation around 365 nm) can explain why no ketyl radical anion is observed in reactions with NaO*t*Bu.

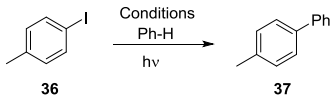
Marcus theory calculations for SET between ground-state KO$^t$Bu and benzophenone (Figure 4) predicts a relative electronic energy of 44.6 kcal/mol ($\Delta G_{rel}$ = 42.5 kcal/mol) with a calculated electronic activation energy of 47.9 kcal/mol ($\Delta G^*$ = 44.0 kcal/mol). These results indicate that ground state electron transfer between these reactants is not possible. In order to overcome the unfavorable energetics associated with ground state SET, visible light excitation of the reactant complex followed by charge separation would furnish the SET product complex.




**Scheme 4.** Fragmentation of *tert*-butoxyl radicals leading to formation of methylbenzophenone.

In reactions where electron transfer from *tert*-butoxide anions to benzophenone occurs, evidence ought to be available to support intermediacy of *tert*-butoxyl radicals and of the potassium ketyl of benzophenone. *tert*-Butoxyl radicals undergo fragmentation very rapidly to form acetone and methyl radicals (Scheme 4)[20] In our reactions with benzophenone in THF as solvent, methyl radicals can undergo hydrogen atom abstraction from the solvent, but they can also add to benzophenone to give methylbenzophenone. Whereas the formation of the ketyl occurs with irradiation at 365 nm, or 400 nm or daylight, it occurs most rapidly with excitation at 365 nm. Under these conditions, we looked for benzophenone-related products and detected and characterized the monomethylated analogue of benzophenone by GCMS. To confirm this result, we replaced KO*t*Bu, (*i.e.* KOCMe$_3$) by KOCEt$_3$, and characterized the monoethylated benzophenone GCMS.[21]

**Table 2**:




| Entry | Conditions[a] | Light (λ) | **37** (yield %) |
|---|---|---|---|
| 1 | **17**, 1 eq<br>KO*t*Bu 2 eq. | 365 nm | 74 |
| 2 | KO*t*Bu 2 eq, | 365 nm | 12 |

[a]The reactions were firstly put at RT under UV for 15 min and then placed in absence of irradiation at 130°C for 18h.

To look for further evidence of electron transfer, we examined the BHAS reaction in benzene with *p*-iodotoluene **36**, a substrate that is much less hindered than substrate **6**, and so the yield should be higher than for substrate **6**. As radical generation is simply part of the initiation process, we irradiated at 365 nm for 15 min and then turned off the irradiation and heated for 18h at 130°C. This afforded 4-methylbiphenyl (74%, Table 2); a blank experiment in which benzophenone was omitted gave 4-methylbiphenyl in 12% by comparison.

**Conclusions**. The historical observation by Ashby *et al*.[12] of formation of the potassium ketyl of benzophenone from reaction of benzophenone with KO*t*Bu was hitherto unexplained. The redox potentials of the two molecules are seriously mismatched, so that an outer sphere electron transfer can be discounted. Our studies show that mixing KO*t*Bu with benzophenone gives rise to a metastable complex with absorption just above 400 nm that can be excited in daylight or under activation with LED illumination at 400 nm or with UV illumination at 365 nm, resulting in electron transfer from the alkoxide to benzophenone **17**. The reaction seems very specific to KO*t*Bu; changing to NaO*t*Bu gave no reaction.[22] The important point to note is that while Ashby's observation of electron transfer is validated here, his conclusion that this reaction is a ground state reaction is wrong. KO*t*Bu can only transfer an electron to benzophenone upon photoactivation that is facilitated by a special complex formed between KOtBu and benzophenone.

Benzophenone plays a central role in pure and applied organic photochemistry.[23] Although benzophenone absorbs strictly in the UV, this paper reveals that formation of discrete complexes can lead to absorption in the visible region of the spectrum. This may be part of a much more general phenomenon allowing access to benzophenone photochemistry with visible light. In connection with that, two recent reports[24] highlighted 'excitations of benzophenone' with visible light sources, although no characterization of the absorbing species was carried out. Perhaps complexation also leads to species that absorb visible light. Potassium *tert*-butoxide is an unusual partner for electron transfer reactions. A recent paper highlighted KO*t*Bu as an electron donor to a highly oxidising iridium complex[25] and backed this with Stern-Volmer studies to show the involvement of the KO*t*Bu, but our paper now discloses the first characterized case of electron transfer to an organic substrate. It may be that further recently reported cases of the activity of KO*t*Bu as an electron donor actually constitute complexes that don't occur in the ground state but are photoactivated by sunlight.[6e] Placing this in context, the exploitation of organic molecular complexes absorbing visible light has been highlighted recently by Melchiorre and others as a growth area,[26,7e,8i] and adds to other recent developments[27] in chemical reactivity triggered by visible light.

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¥ These authors contributed equally to the research.

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(21) Unique peaks were detected and their elemental composition assigned in the methylation or ethylation experiments by HRMS (EI): (a) methylation experiment: methylbenzophenone $C_{14}H_{12}O$ (*m/z* 196.0893, calc. 196.0888); (b) ethylation experiment, ethylbenzophenone $C_{15}H_{14}O$ (*m/z* 210.1052, calc. 210.1045).

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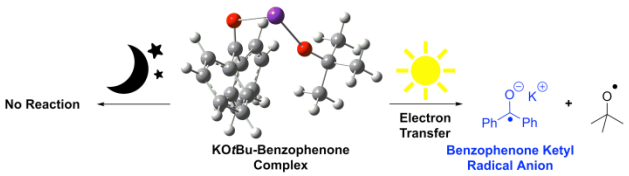
**TOC Graphic**


No Reaction
KO*t*Bu-Benzophenone Complex
Electron Transfer
Benzophenone Ketyl Radical Anion

**Supporting Information**

# Electron Transfer Reactions: KO*t*Bu (but not NaO*t*Bu) Photo-reduces Benzophenone, under Activation by Visible Light

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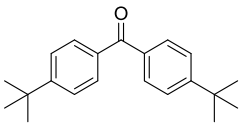
## General information

All reagents were purchased from commercial sources and used without further purification, except where stated. Anhydrous diethyl ether, tetrahydrofuran, dichloromethane and hexane were dried using a Pure-Solv 400 solvent purification system (Innovative Technology Inc., U.S.A.). Tetrahydrofuran was further distilled over sodium "wire" using benzophenone as indicator using a still. The distilled THF was used for all the ketyl radical development. Anhydrous benzene was purchased from Sigma Aldrich and dried over 3Å molecular sieves, previously activated by microwave heating. Thin layer chromatography analyses were carried out on silica gel pre-coated aluminum foil sheets and were visualized using UV light (254 nm). 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.

Where reactions were carried out in a glovebox, the atmosphere used was nitrogen and the glovebox was supplied by Innovative Technology Inc., USA. $^1$H-NMR, $^2$H-NMR and $^{13}$C-NMR spectra were recorded on spectrometers operating at 400 MHz, 61 MHz and 101 MHz, respectively. All spectral data were acquired at 295 K. Chemical shifts (δ) are quoted in parts per million (ppm). 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), qn (quintet), sextet (st), m (multiplet). Infrared (IR) spectra were recorded using an FTIR-ATR spectrometer. High resolution mass spectrometry was performed at the University of Swansea, in the EPSRC National Mass Spectrometry Centre. Accurate mass was obtained using a LTQ Orbitrap XL using Atmospheric Pressure Chemical Ionization (APCI) or High Resolution Nano-Electrospray (HNESP) using Electrospray Ionization (ESI). The mass spectra were recorded by gas-phase chromatography (GCMS) using electron ionization (EI). Low resolution GCMS data were recorded using an Agilent Technologies 7890A GC system coupled to a 5975C inert XL EI/CI MSD detector. Separation was performed using the DB5MS-UI column (30 m x 0.25 mm x 0.25 μm) at a temperature of 320 °C, using helium as the carrier gas.
All the UV reactions were carried out by using two focused UV lamps with filters (λ= 365 nm, each 100 watts) placed opposite to each other, around the reaction flask, at room temperature. All the Vis light reactions were carried out by using 60 LEDs in series (400 nm, 14.4 W total, SMD5050). The series internally lined a beaker and the reaction tubes were placed centrally in the beaker (2-3 cm of distance from the LEDs). When stated, the reactions were performed in direct sunlight. The 'dark' reactions were performed by covering the tube in foil to avoid any light exposure.
UV-visible absorption measurements were performed using a PerkinElmer Lambda 25 UV/VIS spectrophotometer.
Calculations of the yields of reactions using the internal standard 1,3,5-trimethoxybenzene ($^1$H-NMR internal standard) were performed as follows: 1,3,5-trimethoxybenzene (8.4 mg, 0.050 mmol, 10 mol%) was added as a solid to the reaction mixture. $CDCl_3$ (~1 mL) was added and the solution stirred for 5 min. A portion of the solution was taken and diluted for NMR analysis.

## Preparation of the substrates

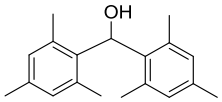
**4,4'-Di-*tert*-butylbenzophenone, 27**




4,4'-Di-tert-butylbenzophenone
Chemical Formula: $C_{21}H_{26}O$
Exact Mass: 294,1984

*p-tert*-Butylbenzoyl chloride (1.18 g, 1.17 ml, 6 mmol) was slowly added to *tert*-butylbenzene ( 1.93 mg, 2.22 mL, 14.4 mmol) and aluminium trichloride (2.22 g, 15.2 mmol) at RT. During the addition of *p-tert*-butylbenzoyl chloride, the reaction turned from a yellow suspension to a dark reddish brown solution. After the addition was complete, the reaction was warmed at 80 °C for 2.5 h. Vigorous bubbling was observed throughout the reaction. Afterwards, the hot reaction mixture was poured into crushed ice (30 g) and concentrated hydrochloric acid (10.5 mL). This yielded a tar-like substance which metamorphosed to a yellow solid after decomposition was complete (few minutes). This yellow solid was filtered, dissolved in toluene (15 mL), washed with water and 5% aqueous sodium hydroxide and dried over sodium sulfate. Recrystallisation from toluene produced a white powder which was washed with hexane to give **27** as a white solid (625 mg, 0.68 mmol, 35.5%).[1] Mp: 122-124 °C (lit: 123-124°C).[2] $\nu_{max}$ (neat, cm$^{-1}$) 2959, 2903, 2864, 1643, 1605, 1280, 1186, 1104, 932. $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.76 (4 H, d, *J* = 8.6, Ar*H*), 7.49 (4 H, d, *J* = 8.8, Ar*H*), 1.37 (18 H, s, C*H*$_3$) ppm. $^{13}$C-NMR (101 MHz, $CDCl_3$) δ 195.7, 155.4, 134.7, 129.5, 124.7, 34.6, 30.7 ppm. GC-MS (EI) *m/z* 294.1. Data were consistent with the literature.[1]

**Dimesitylmethanol**, **38**

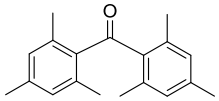



Dimesitylmethanol
Chemical Formula: $C_{19}H_{24}O$
Exact Mass: 268,1827

To a cooled (-78 °C) solution of mesityllithium, prepared by addition of *n*-butyllithium (2.2 mmol) to a solution of mesityl bromide (478 mg, 0.37 mL, 2.4 mmol) in 8 mL of THF, a solution of mesitylaldehyde (296 mg, 0.294 mL, 2.0 mmol) in 2 mL of THF. After 30 min, the solution was allowed to warm and was quenched with aqueous ammonium chloride. The product was extracted with diethyl ether, dried over sodium sulfate and concentrated. The crude was washed with pentane to give dimesitylmethanol **38** as a white solid (315 mg, 1.18

mol, 59%). Mp: 145-147 (lit: 149-150 °C)[3] IR $\nu_{max}$ (neat, $cm^{-1}$) 3472, 2908, 1608, 1476, 1420, 1375, 1126, 1045, 1003, 851, 694. $^1$H-NMR (400 MHz, $CDCl_3$) δ 6.82–6.78 (4 H, s, Ar*H*), 6.37–6.33 (1 H, s, C*H*OH), 2.27–2.24 (6 H, s, C$H_3$), 2.23–2.19 (12 H, s, C$H_3$), 1.73–1.68 (1 H, s, O*H*) ppm. $^{13}$C-NMR (101 MHz, $CDCl_3$) δ 136.7, 130.7, 73.5, 21.2, 20.8 ppm.[4] GC-MS (EI) *m/z* 268.1. Data were consistent with the literature. [4]

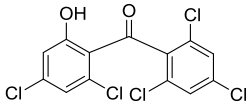
**Dimesitylmethanone, 28**



Dimesitylmethanone
Chemical Formula: $C_{19}H_{22}O$
Exact Mass: 266,1671

Pyridinium chlorochromate (2.53 g, 11.8 mmol) was added to a solution of dimesitylmethanol **38** (2.10 g, 7.8 mmol) in 35 mL of DCM and allowed to stir at RT for 3 h. The crude product was filtered on a celite pad, the solution concentrated and crystallised from methanol to give dimesitylmethanone, **28** as a white solid (1.4 g, 5.2 mmol, 67%). [4] Mp: 140-143 °C (lit: 138-140 °C)[4]. IR $\nu_{max}$ (neat, $cm^{-1}$) 2916, 1643, 1605, 1422, 1242, 887, 855, 696. $^1$H-NMR (400 MHz, $CDCl_3$) δ 6.84 (4 H, s, Ar*H*), 2.29 (6 H, s, C$H_3$), 2.12 (12 H, s, C$H_3$) ppm. $^{13}$C-NMR (101 MHz, $CDCl_3$) δ 202.8, 140.1, 138.6, 136.8, 129.9 21.3, 20.9 ppm. GC-MS (EI) *m/z* 266.1 ($M^+$).

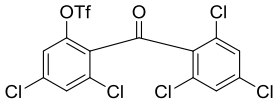
**(2,4-Dichloro-6-hydroxyphenyl)(2,4,6-trichlorophenyl)methanone, 39**



(2,4-dichloro-6-hydroxyphenyl)(2,4,6-trichlorophenyl)methanone
Chemical Formula: $C_{13}H_5Cl_5O_2$
Exact Mass: 367.8732

3,5-Dichloroanisole (2.8 mg, 16 mmol) and aluminium chloride (2.55 g, 19.2 mmol) were cooled to 0 °C in a flask under inert atmosphere. 2,4,6-Trichlorobenzoyl chloride (4.65 g, 19.2 mmol) was then added and the reaction mixture was stirred at 110 °C for 15 h. At the end of the reaction (monitored by TLC), water (15 mL) was added and the mixture stirred. The mixture was extracted with ethyl acetate, dried over sodium sulfate and concentrated *in vacuo*. Purification with silica gel chromatography (hexane) afforded (2,4-dichloro-6-hydroxyphenyl)(2,4,6-trichlorophenyl)methanone, **39** (1.7 g, 4.69 mmol, 58.6 %) as a white solid. Mp: 82-84 °C. IR $\nu_{max}$ (neat, $cm^{-1}$) 1626, 1543, 1386, 1365, 1298, 1224, 1184, 1089, 960, 916. $^1$H NMR (400 MHz $CDCl_3$) δ 12.58 (1 H, s, O*H*), 7.38 (2 H, s, Ar*H*), 7.06 (1 H, d, *J* = 2.1, Ar*H*), 6.96 (1 H, d, *J* = 2.1, Ar*H*) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 195.7, 165.9, 143.0, 137.8, 136.6, 136.44, 132.2, 128.5, 123.0, 118.4, 117.0 ppm. *m/z* (APCI) calcd. for $C_{13}H_6Cl_5O_2$ $[M+H]^+$: 368.8805, found: 368.8798.

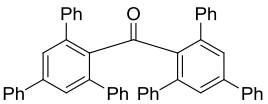
**3,5-Dichloro-2-(2,4,6-trichlorobenzoyl)phenyl trifluoromethanesulfonate**, **40**



3,5-dichloro-2-(2,4,6-trichlorobenzoyl)phenyl trifluoromethanesulfonate
Chemical Formula: $C_{14}H_4Cl_5F_3O_4S$
Exact Mass: 499.8225
Molecular Weight: 502.4872

Ketone **39** (1.61 g, 4,4 mmol), anhydrous DCM (8 mL) and pyridine (695.2 mg, 8,8 mmol) were added to a round-bottomed flask, under argon atmosphere. The mixture was cooled to 0° C in an ice bath, then was treated with dropwise addition of triflic anhydride (4.49 g, 5.28 mmol). The resulting mixture was allowed to warm up to RT and kept stirred for additional 4 h. The mixture was then filtered and concentrated *in vacuo*. The product was purified by chromatography (hexane), affording **40** (1.24 g, 2.48 mmol, 56.4 %). Mp: 110-112 °C. IR $\nu_{max}$ (neat, $cm^{-1}$) 1686, 1427, 1207, 1136, 1091, 953, 910, 798. $^1$H NMR (400 MHz $CDCl_3$) δ 7.46 (1 H, d, *J* = 1.9, Ar*H*), 7.40 – 7.36 (3 H, m, Ar*H*) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ ppm 185.8, 148.5, 138.8, 137.9, 134.9, 134.6, 134.5, 130.4, 129.3, 121.5, 118.5 (q, *J* = 320.6, *C*$F_3$) ppm. *m/z* (APCI) calcd. for $C_{14}H_5Cl_5F_3O_4S$ $[M+H]^+$: 500.8298, found: 500.8287.

**Bis(5'-phenyl-[1,1':3',1''-terphenyl]-2'-yl)methanone, 30**

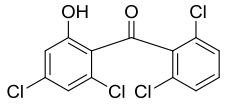


bis(5'-phenyl-[1,1':3',1''-terphenyl]-2'-yl)methanone
Chemical Formula: $C_{49}H_{34}O$
Exact Mass: 638.2610
Molecular Weight: 638.8100

Six different oven-dried microwave vials were charged, independently, with **40** (100,4 mg, 0,2 mmol), bis(acetonitrile)dichloropalladium(II) (2,6 mg, 0,01 mmol, 5%), Sphos (8,2 mg, 0,02 mmol, 10 %), phenylboric acid (292,8 mg, 2,4 mmol)

and $K_3PO_4$ (508,8 mg, 2,4 mmol). The mixture was then introduced into the glovebox and anhydrous toluene (10 mL) was added. The vial was then sealed inside the glovebox and transferred into the fumehood, where it was heated at 110 °C for 4 days. The six cooled reaction mixtures were then combined and diluted with water and extracted with toluene. The combined organic layers were combined, dried over sodium sulfate, filtered and concentrated *in vacuo*. The residue was purified by chromatography (hexane) affording a white solid which was recrystallised using a small amounts of toluene (very soluble) and hexane (almost insoluble) giving rise to ketone **30** (454 mg, 0.71 mmol, 59.3% combined yield from the 6 vials). The reaction was found to work better in a system under pressure such as a microwave vial. A bigger scale in a normal three-necked flask was tried, but only traces of product were detected.[5] Mp: 246-248 °C. IR $\nu_{max}$ (neat, $cm^{-1}$) 3053, 1665, 1590, 1491, 1229, 1074, 1029. $^1$H NMR (400 MHz $CDCl_3$) δ 7.52 – 7.48 (4 H, m, Ar*H*), 7.43 (4 H, t, *J* = 7.3, Ar*H*), 7.39 – 7.35 (2 H, m, Ar*H*), 7.33 – 7.26 (12 H, m, Ar*H*), 7.20 – 7.17 (8 H, m, Ar*H*), 7.09 (4 H, s, Ar*H*) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.7, 143.4, 141.2, 140.9, 139.4, 136.2, 129.8, 128.7, 128.3, 127.3, 126.7, 126.7, 126.2 ppm. *m/z* (APCI) calcd. for $C_{49}H_{35}O$ $[M+H]^+$: 639.2682, found: 639.2678.

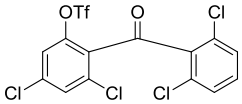
**(2,4-Dichloro-6-hydroxyphenyl)(2,6-dichlorophenyl)methanone, 41**




(2,4-dichloro-6-hydroxyphenyl)(2,6-dichlorophenyl)methanone
Chemical Formula: $C_{13}H_6Cl_4O_2$
Exact Mass: 333.9122
Molecular Weight: 335.9890

Aluminium chloride (1.8 g, 13.2 mmol) and 3,5-dichloroanisole (1.0 g, 6 mmol) were added to a flask under inert atmosphere and this was then cooled at 0 °C. 2,6-Dichlorobenzoyl chloride (1.5 g mg, 7.2 mmol) was then added. The reaction mixture was stirred at 110°C for 15 h. The mixture was extracted with ethyl acetate, dried over sodium sulfate and concentrated *in vacuo*. Purification with silica gel chromatography using pure hexane as eluent afforded **41** (1.91 g , 5.72 mmol, 72 % yield). Mp: 98-100 °C. IR $\nu_{max}$ (neat, $cm^{-1}$) 3080, 1618, 1593, 1545, 1425, 1396, 1296, 1223, 1175, 956, 912, 846, 804. $^1$H NMR (400 MHz $CDCl_3$) δ 12.70 (1 H, s, O*H*), 7.37 – 7.31 (3 H, m, Ar*H*), 7.05 (1 H, d, *J* = 2.0, Ar*H*), 6.94 (1 H, d, *J* = 2.1, Ar*H*) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 196.0, 165.3, 142.1, 138.5, 136.1, 131.2, 130.9, 130.5, 127.7, 122.3, 120.3, 117.6, 116.5 pm. *m/z* (APCI) calcd. for $C_{13}H_7Cl_4O_2$ $[M+H]^+$: 334.9200, found 334.9209. Analogous demethylation of anisole using $AlCl_3$ was previously reported in the literature.[6]

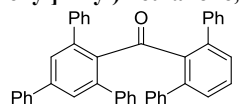
**3,5-Dichloro-2-(2,6-dichlorobenzoyl)phenyl trifluoromethanesulfonate, 42**




3,5-dichloro-2-(2,6-dichlorobenzoyl)phenyl
trifluoromethanesulfonate
Chemical Formula: $C_{14}H_5Cl_4F_3O_4S$
Exact Mass: 465.8615

Ketone **41** (1.6 g, 4.8 mmol), anhydrous DCM (8 mL) and pyridine (758.4 mg, 9.6 mmol) were added to a round-bottomed flask, under argon atmosphere. The solution was cooled to 0° C in an ice bath and then was treated with dropwise addition of triflic anhydride (1.62 g, 5.76 mmol). The resulting mixture was allowed to warm to RT and stirred for additional 4 h. At the end of the reaction (monitored by TLC), the mixture was filtered and concentrated *in vacuo*. The product was purified by chromatography (hexane), affording ketone **42** (2.0 g, 4.40 mmol, 92%) as a white solid. Mp: 95-97 °C. IR $\nu_{max}$ (neat, $cm^{-1}$) 1690, 1591, 1429, 1211, 1138, 955, 910, 868, 800, 781. $^1$H NMR (400 MHz $CDCl_3$) δ 7.46 (1 H, d, *J* = 1.8, Ar*H*), 7.38 (1 H, d, *J* = 1.8, Ar*H*), 7.36 – 7.34 (3 H, m, Ar*H*) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 186.0, 147.9, 137.9, 135.8, 134.0, 133.2, 131.7, 129.9, 129.7, 128.6, 120.7, 117.9 (q, *J* = 320 Hz, *C*$F_3$) ppm. *m/z* (APCI) calcd. for $C_{14}H_9Cl_4F_3NO_4S$ $[M+NH_4]^+$ : 483.8953, found 483.8950.

**[1,1':3',1''-Terphenyl]-2'-yl(5'-phenyl-[1,1':3',1''-terphenyl]-2'-yl)methanone, 29**

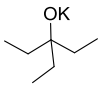



[1,1':3',1''-terphenyl]-2'-yl(5'-phenyl-[1,1':3',1''-terphenyl]-2'-yl)methanone
Chemical Formula: $C_{43}H_{30}O$
Exact Mass: 562.2297
Molecular Weight: 562.7120

Six oven-dried microwave vials were charged, independently, with ketone **42** (93.6 mg, 0.2 mmol), bis(acetonitrile)dichloropalladium(II) (2.59 mg, 0.01 mmol, 5%), Sphos (8.2 mg, 0.02 mmol, 10%) phenylboronic acid (244 mg, 2 mmol) and $K_3PO_4$ (424 mg, 2 mmol). The mixture was then introduced in the glovebox and anhydrous toluene (10 mL) was added. The vials were then closed, removed from the glovebox and placed in the fumehood, where they were heated at 110 °C for 5 days (monitored *via* NMR). The cooled reaction mixture was diluted with water and extracted with toluene. The combined organic layers were combined, dried over sodium sulfate, filtered and the filtrate was concentrated *in vacuo*. The mixture was purified *via* chromatography (hexane : ethyl acetate as 9.5 : 0.5), affording the product (420 mg, 0.75 mmol, 62 % combined yield) as a white powder. The reaction was found to work better in a system under pressure such as a microwave vial. A bigger scale in a normal three-necked flask was tried but only traces of product were detected. Reaction conditions were inspired by prior literature.[5] Mp: 90-93 °C. IR $\nu_{max}$ (neat/$cm^{-1}$) 3048, 1667, 1589, 1491, 1231, 926, 885, 756, 694. $^1$H NMR (400 MHz

$CDCl_3$) δ 7.51 – 7.47 (2 H, m), 7.45 – 7.39 (2 H, m), 7.39 – 7.33 (1 H, m), 7.33 – 7.23 (13 H, m), 7.18 – 7.13 (4 H, m), 7.13 – 7.09 (4 H, m), 7.06 (2 H, s), 6.87 (2 H, d, *J* = 7.6) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.9, 143.4, 142.6, 141.1, 140.9, 140.9, 139.4, 137.3, 135.8, 130.2, 129.8, 128.8, 128.6, 128.30, 127.3, 126.8, 126.7, 126.6, 126.2, 126.0 ppm. *m/z* (APCI) calcd. for $C_{43}H_{31}O$ $[M+H]^+$: 563.2375, found 563.2388.

**Potassium 3-ethylpentan-3-olate, 43**

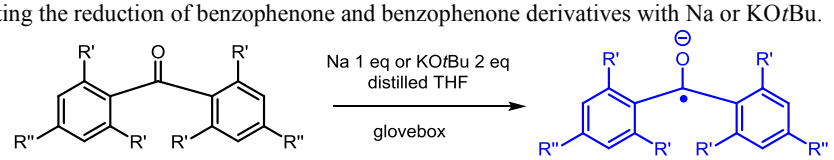



potassium 3-ethylpentan-3-olate
Chemical Formula: $C_7H_{15}KO$
Exact Mass: 154.0760

In the glovebox, previously washed potassium hydride (400 mg, 10 mmol) was added to a flame-dried three-necked flask, equipped with a vacuum tap. The flask was then sealed, removed from the glovebox and placed in a -78 °C bath in a fumehood. A solution of triethylcarbinol (1160 mg, 10 mmol) in anhydrous diethyl ether (20 mL) was added. The reaction mixture was stirred at -78 °C for 1 h, then at RT overnight. The solvent was removed on the house vacuum line and the crude material was dried for 3 h, put under an argon atmosphere and transferred into the glove box immediately giving rise to **43** (1.3 g, 8.4 mmol, 84 %). $^1$H NMR (400 MHz, $C_6D_6$) δ 1.22 (6 H, q, *J* = 7.5, $CH_2CH_3$), 0.85 (9 H, t, *J* = 7.5, $CH_2CH_3$) ppm. $^{13}$C NMR (101 MHz, $C_6D_6$) δ 71.8, 33.1, 8.1 ppm.

**Qualitative evaluation of formation of ketyl radicals of aromatic ketones**

General procedure for testing the reduction of benzophenone and benzophenone derivatives with Na or KO*t*Bu.




The aromatic ketone (1 eq, 0.77 mmol) was added to distilled THF (5 mL) into a pressure tube containing sodium (18 mg, 0.77 mmol) or KOIBu (172 mg 1.54 mmol) in the glovebox. The sealed pressure tube was then removed from the glovebox and placed on a stirrer hotplate in the fumehood. Where specified, the reaction was heated to 70°C behind a blast shield. The ketyl radical formation was detected through development of a blue coloration in the solution. The reaction was quenched with isopropyl alcohol and the blue coloration disappeared soon after the addition.

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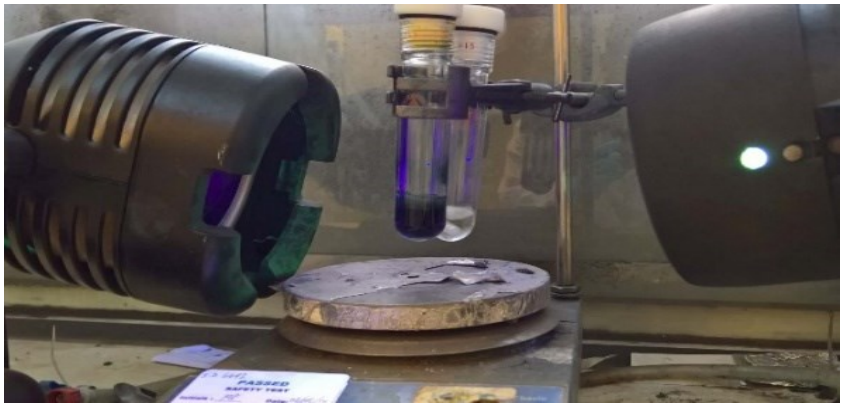

**Figure S1** Above is a typical example of reaction performed under UV lamps (365 nm, 100 W x 2) at RT.
Left: THF + **17** (0.5 mmol) + KO*t*Bu (2eq). Right: blank reaction THF + **17** (0.5 mmol). Picture taken after 30 min.

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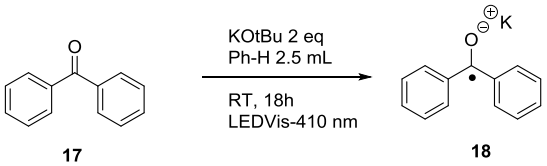


**17** **18**

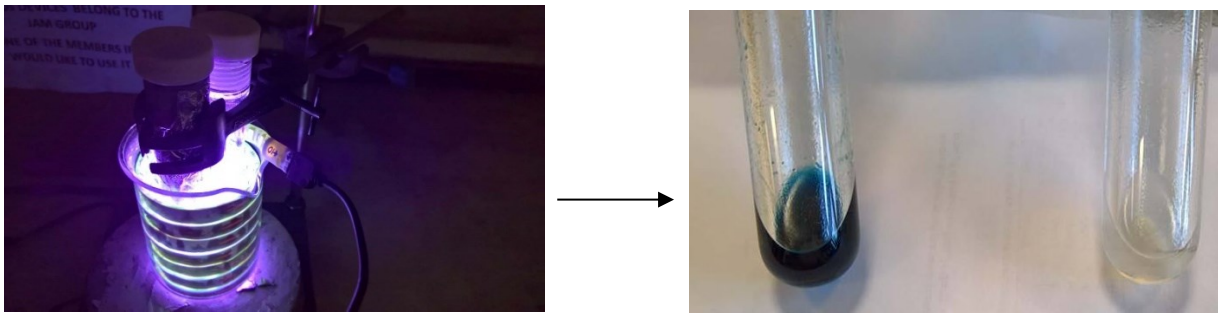

**Figure S2.** Above is a typical example of reaction **17** + KO*t*Bu 2 eq in benzene 2.5 mL performed under Vis LEDs light (400 nm, 14.4 W) at RT. Only the tube with a direct exposition to the light gives the typical blue coloration of the ketyl radical, afterwards confirmed by UV measurement.

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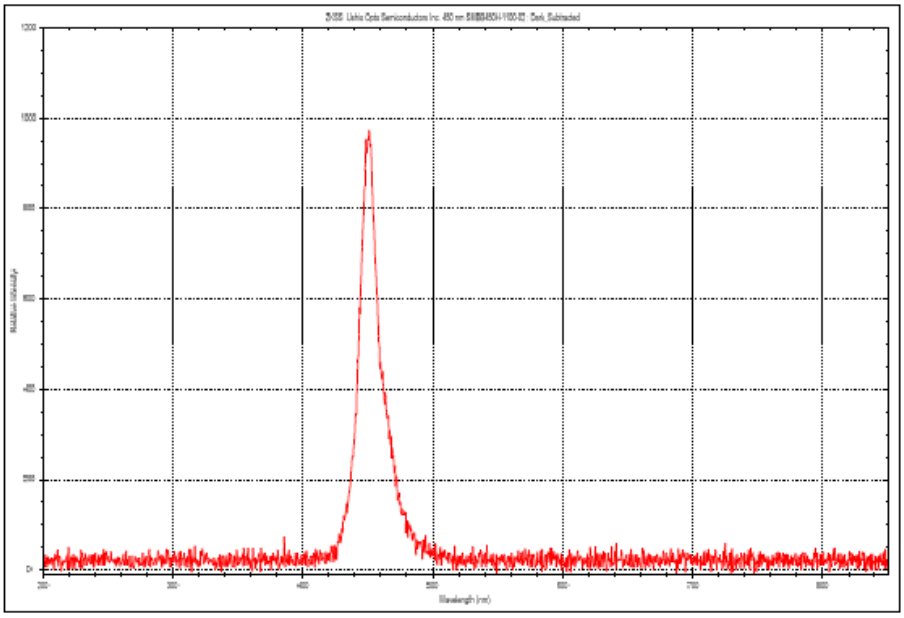
**LED Output Spectra**

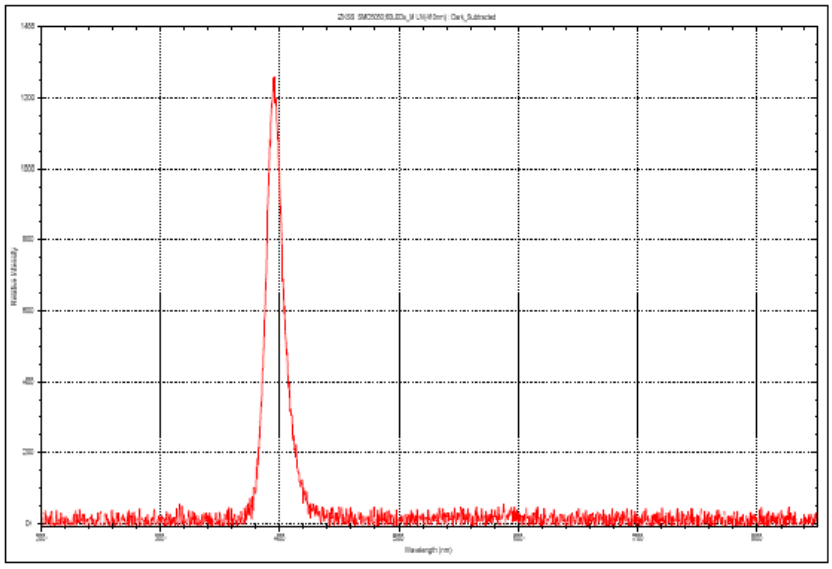
These spectra were produced using a BWTEK Inc, Exemplar LS (Low Straylight Smart CCD Spectrometer, http://bwtek.com/products/exemplar-ls/ )

(i) Reference spectrum taken of a Ushio Opto Semiconductors Inc. **450 nm:** SMBB450H-1100-02

(Full details in SI of https://doi.org/10.1002/cptc.201800082 page S10)



(ii) Spectrumof SMD5050;60LEDs/M; Color: UV(‘410nm’)



**Luminous flux measurements**

**Luminous flux**

Luminous flux measurements were taken with a Traceable® Dual-Display Light Meter (https://traceable.com/3252-traceable-dual-display-light-meter.html purchased from Fisher Scientific).

The Lux sensor was placed inside the coil of SMD5050;60LEDs Figure X, and the setup covered with tin foil to remove any external light.

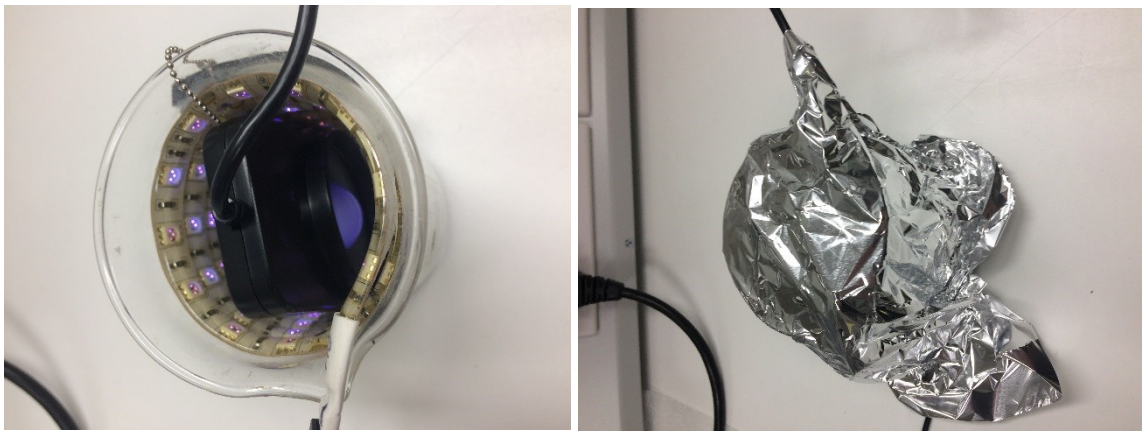


Figure X Lux measurement set up

Traceable® Dual-Display Light Meter was set to F= fluorescent mode, the LEDs where turned on a LUX reading taken, 39 LUX.

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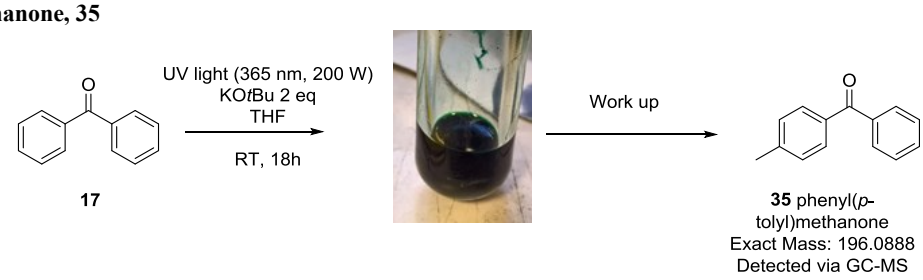
## Detection of methylated and ethylated benzophenone

**Phenyl(*p*-tolyl)methanone, 35**




Benzophenone **17** (91 mg, 0.5 mmol), KO*t*Bu (112 mg, 1 mmol) were loaded in a 15 mL pressure tube with THF (2.5 mL). The sealed tube was then moved out from the glovebox and placed under UV light for 18h. The dark green/blue colour gradually developed from the start of the reaction. After 18 h the tube was opened and water was added. The dark coloration disappear after few seconds of air exposure or water contact. The mixture was then extracted with ether, dried over sodium sulfate and concentrated *in vacuo*. The residue was analysed via TOF MS EI$^+$ (see spectrum below). The fragmentation pattern is consistent with the literature data for the ketone **35**. (lit: GCMS (EI) (%): 196 (M$^+$ , 43), 181(9), 165 (4), 152(4), 119(100), 105(32), 91(46), 77(43)).[7]

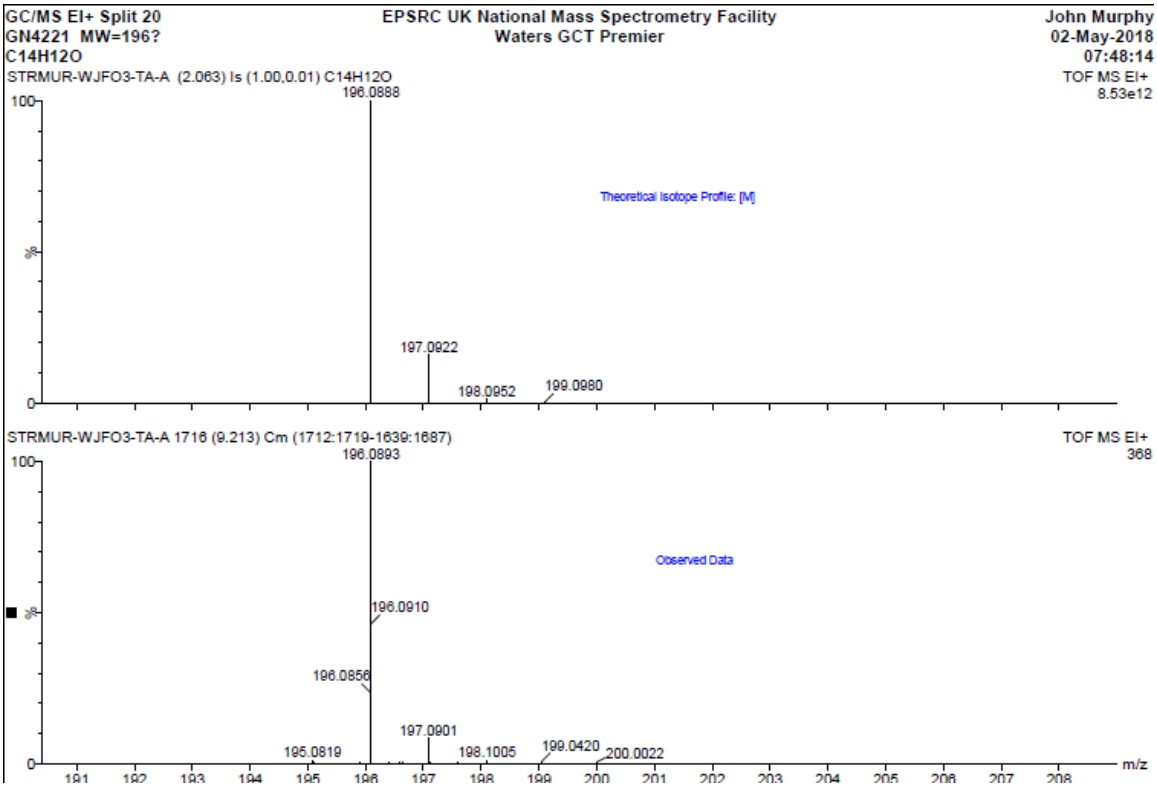



**Figure S3** Calculated and observed high resolution mass spectra of phenyl(*p*-tolyl)methanone **35**

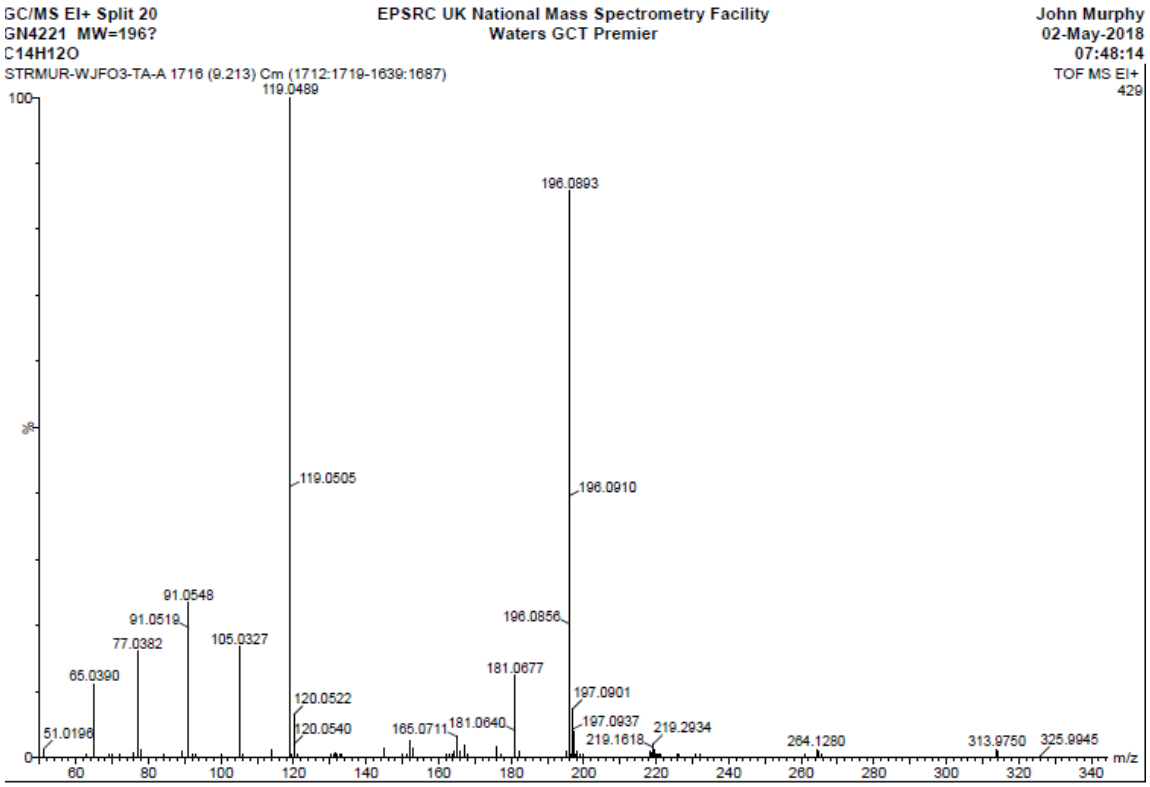
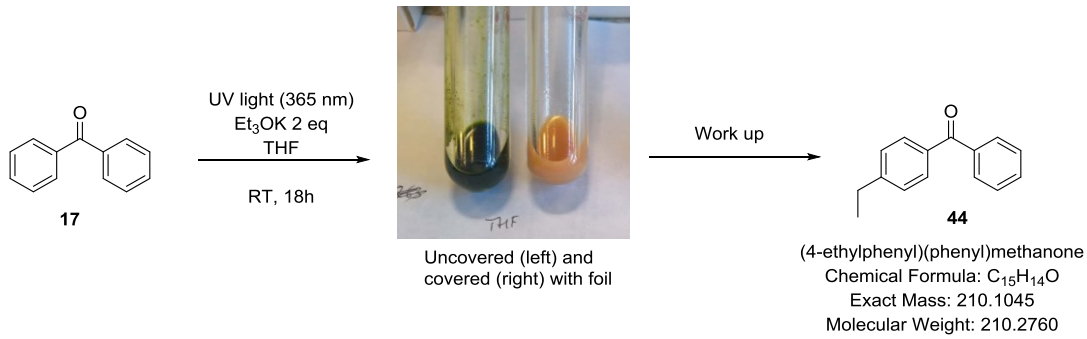



**Figure S4.** EI spectrum of phenyl(*p*-tolyl)methanone **35**

**(4-Ethylphenyl)(phenyl)methanone, 44**




Benzophenone **17** (91 mg, 0.5 mmol), $KOEt_3$ (154 mg, 1 mmol) were loaded in a 15 mL pressure tube with THF (2.5 mL). The sealed tube was then moved out from the glovebox and placed under UV light for 18h. The dark green/blue colour was gradually developed since the start of the reaction. The blank reaction (absence of any source of lights) does not give any blue/green colour throughout the entire course of the reaction. After 18 h the tube was opened and water was added. The dark coloration disappeared after few seconds of air exposure or water contact. The mixture was then extracted with ether, dried over sodium sulfate and concentrated *in vacuo*. The residue was analyzed via TOF MS $EI^+$ (see spectra below).

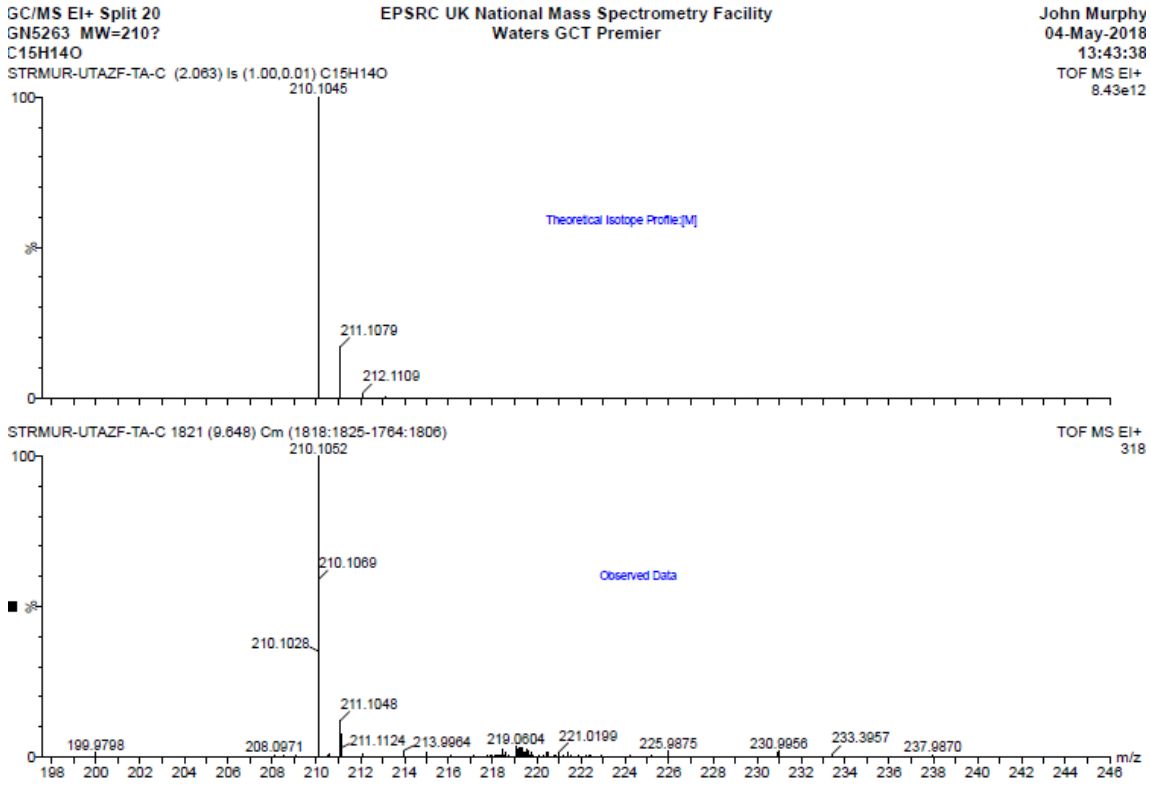



**Figure S5.** Calculated and observed high resolution mass spectra of of 4-ethylphenyl)(phenyl)methanone **44**

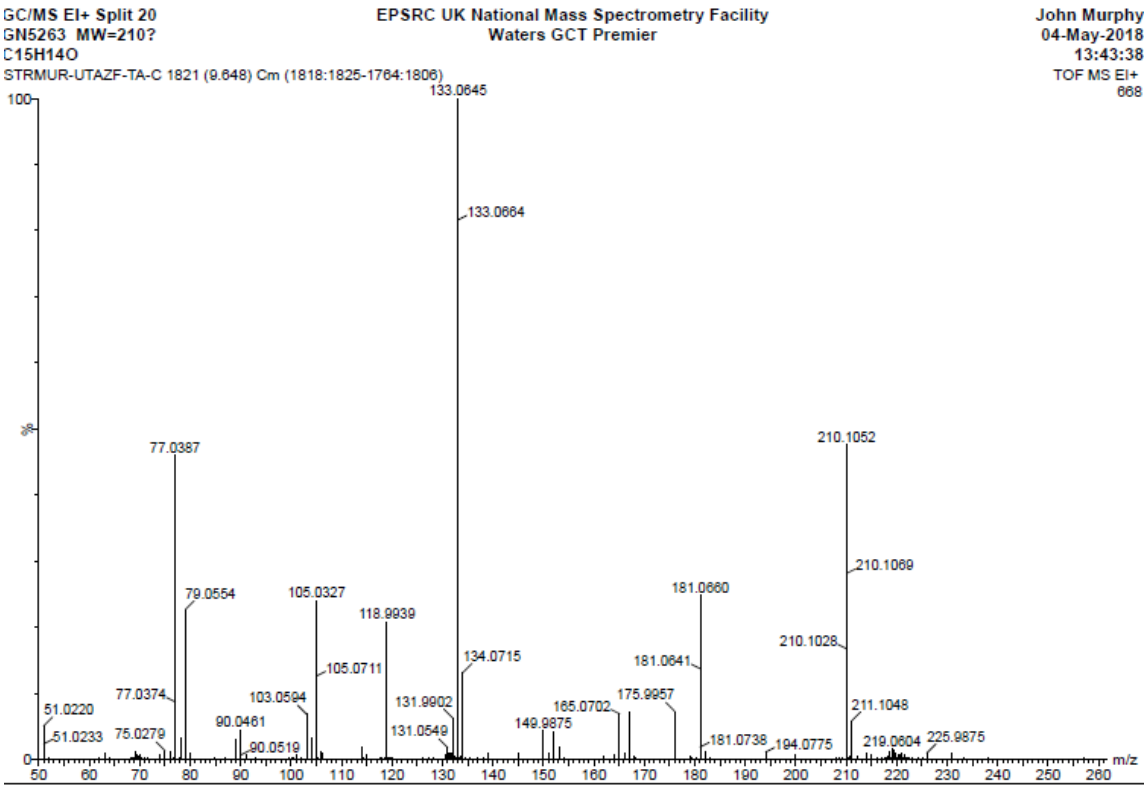



**Figure S6.** EI spectrum of 4-ethylphenyl)(phenyl)methanone **44**

## UV measurements

Every solution was prepared in the glovebox using distilled THF (3 mL) and a quartz standard cuvette.

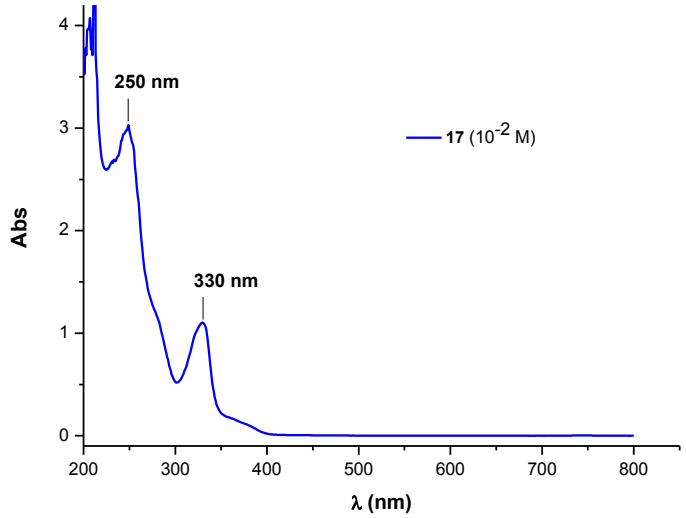



**Figure S7**. UV spectrum of benzophenone **17** ($10^{-2}$ **M**) in THF

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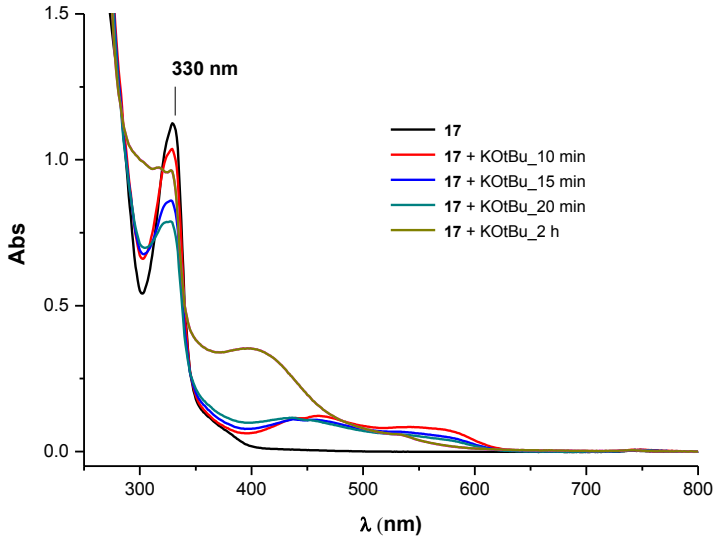


**Figure S8**. UV spectrum of benzophenone **17** ($10^{-2}$ **M**) in THF; In the presence of KO*t*Bu, a bathochromic expansion of the absorption occurs with the time.

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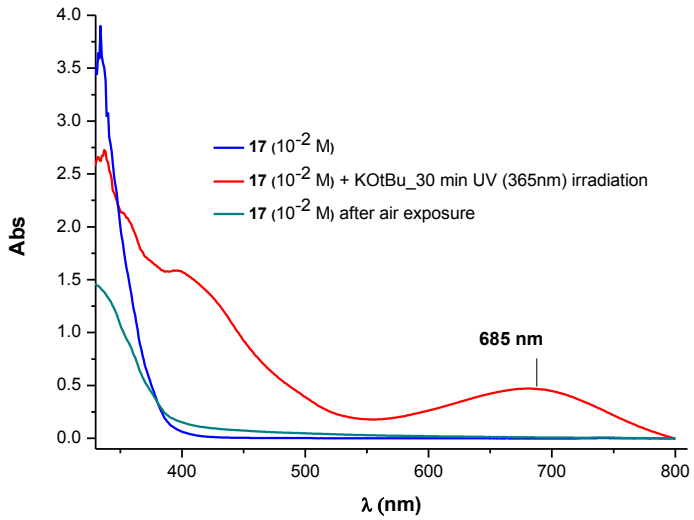


**Figure S9**. Formation of the ketyl radical **18** after irradiating the complex **17**+KO*t*Bu with UV light (365 nm, 100W x 2).

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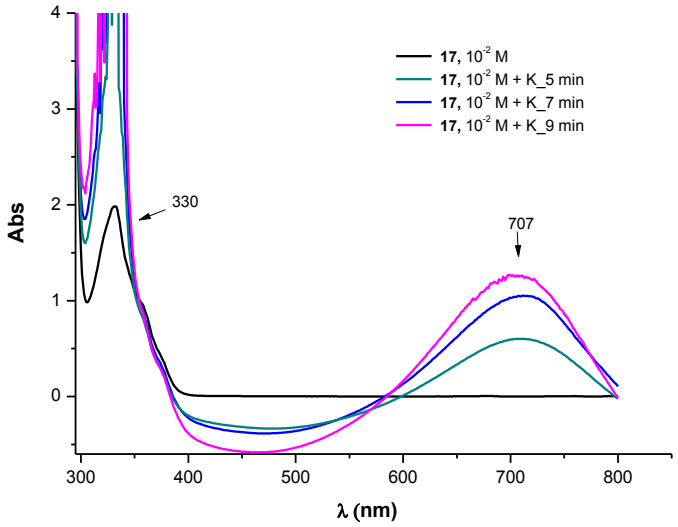


**Figure S10**. UV spectrum of **17** $10^{-2}$ **M** in presence of an excess of potassium metal. In the first 10 minutes formation of the ketyl radical peak around 700 nm was observed. The concentration of BZP used needs to be around $10^{-2}$-$10^{-3}$ **M** to make evident the development of the ketyl radical anion **18** peak. This spectrum is consistent with the literature.[8]

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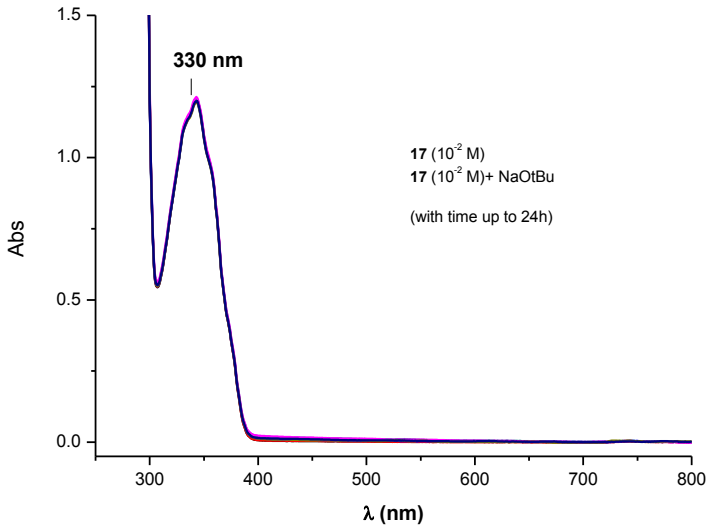


**Figure S 11**. UV measurements of **17** ($10^{-2}$ **M**) before and after adding NaO*t*Bu. The cuvette was agitated and measurements were taken every 10 min for 1h. The cuvette was then left overnight and no shift was observed the following day. No colour change in the cuvette was observed.

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**NMR tests throughout the reaction**

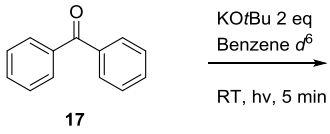
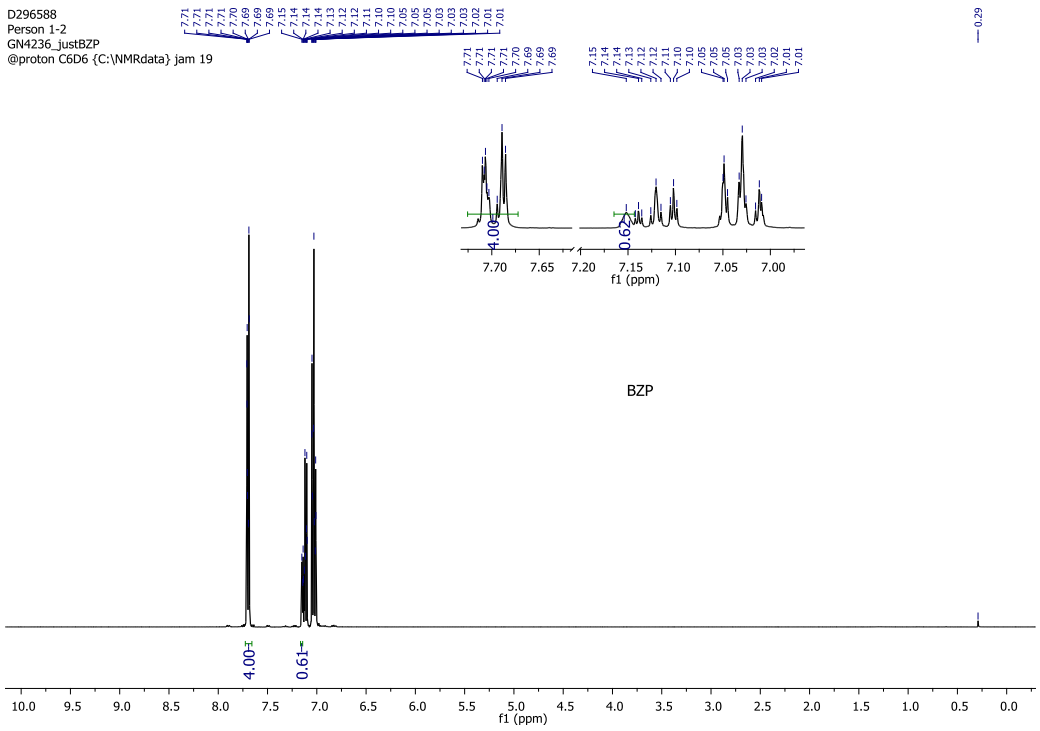



**Figure S 12.** The signals from structure **17** disappear just after 5 minutes UV exposure, indicating that radical species and macromolecular structures are formed in the reaction.[8]

$^{1}$H NMR spectrum of benzophenone **17**

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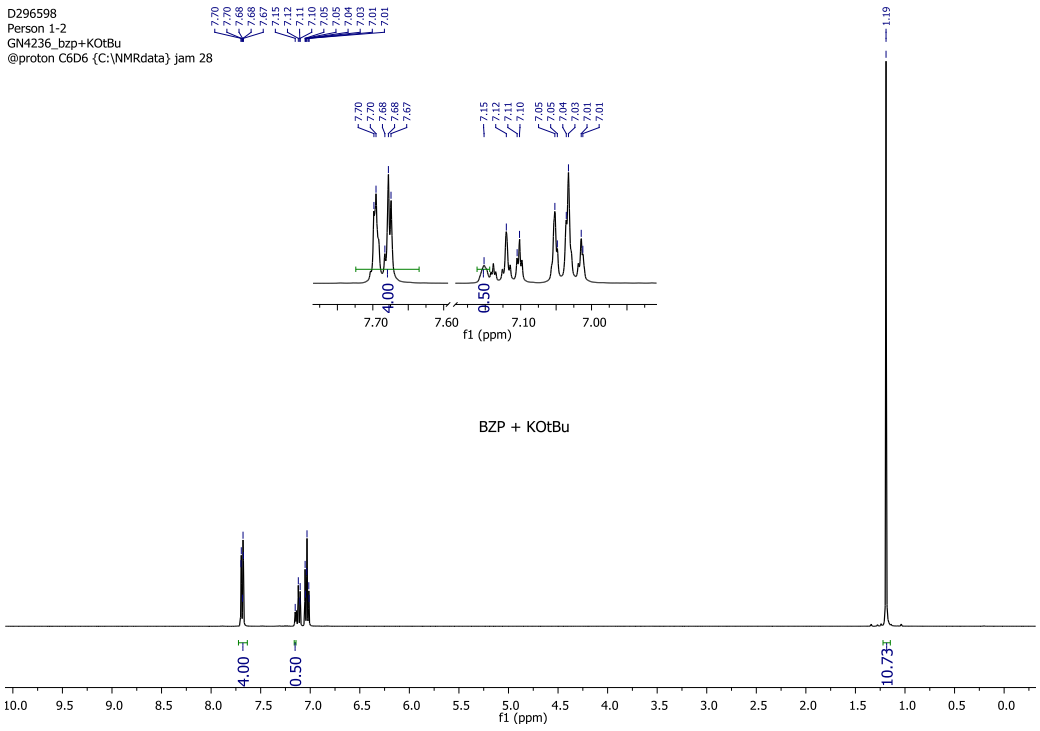
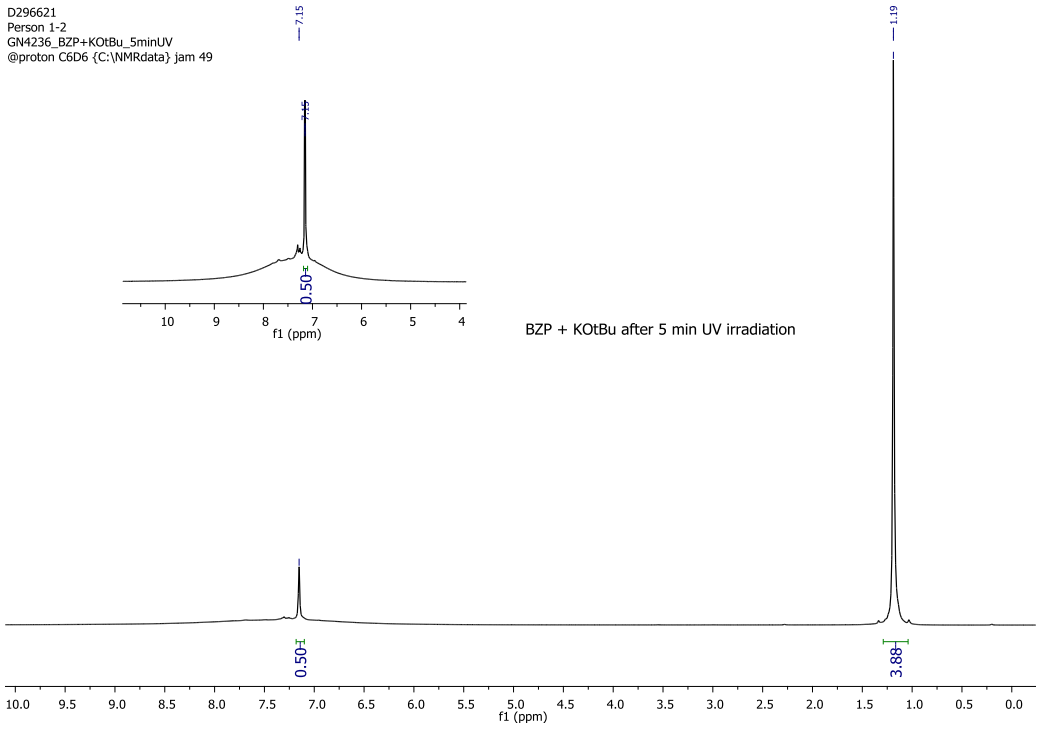
$^{1}$H NMR spectrum of benzophenone **17** + KO*t*Bu



$^1$H NMR spectrum of benzophenone **17** + KO*t*Bu after 5 min irradiation with UV (365 nm)

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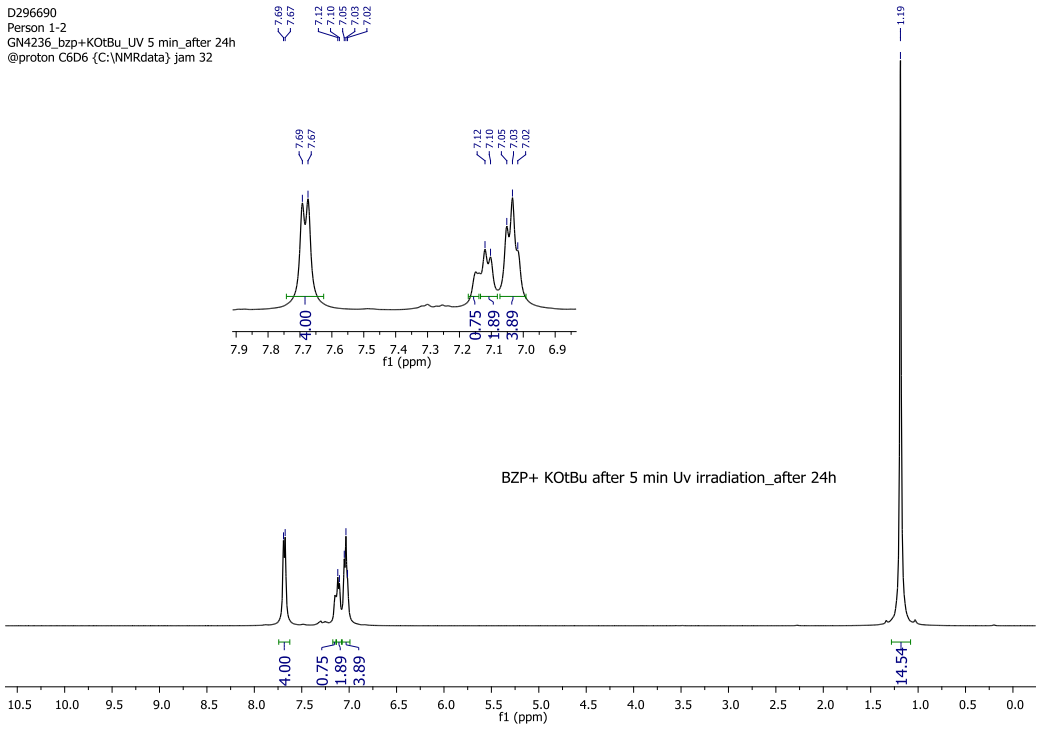
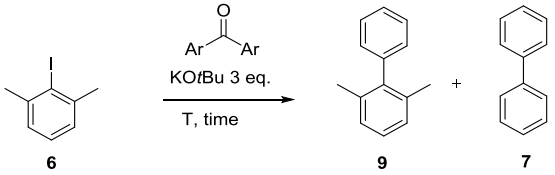
$^1$H NMR spectrum of benzophenone **17** + KO*t*Bu after 5 min irradiation with UV (365 nm), then standing for 24 h



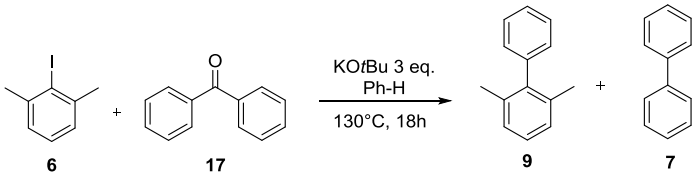
## General conditions and yield calculations for cross coupling reactions

Reactions with iodo-*m*-xylene using the aromatic ketones as additives.




A mixture of iodo-*m*-xylene **6** (0.5 mmol), KO*t*Bu (3.0 eq.) and the desired aromatic ketone (0.2 eq) in benzene (5 mL) was sealed in a 15 mL pressure tube in a glovebox. The tube was removed from the glovebox and heated at 130 ºC for 18 h behind a blast shield. After cooling to room temperature, the reaction was quenched by water (15 mL) and acidified with 1N hydrochloric acid until neutral p*H*. The mixture was extracted with diethyl ether (3 x 15 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to give rise to the residue. Since the coupled products **9** and **7** are inseparable, the yields were calculated from NMR spectra *via* internal standard. 1,3,5-trimethoxybenzene 8.4 mg, (0.050 mmol, 10 mol%) which was added as a solid to the reaction mixture, ~1 mL $CDCl_3$ was added to form a homogeneous solution and the solution stirred. A portion of the solution was taken and diluted for NMR analysis.

Cross coupling reaction using **17** as additive.




A mixture of 1-iodo-2,6-dimethylbenzene **6** (116 mg, 0.5 mmol), KO*t*Bu (168 mg, 1.5 mmol) and **17** (18.2 mg; 0.01 mmol) in benzene ( 5 mL) was sealed in a 15 mL pressure tube in a glovebox. The tube was removed from the glovebox and heated at 130 ºC for 18 h behind a blast shield. After cooling to room temperature, the reaction was quenched by water (15 mL) and acidified with 1N HCl until neutral pH. The mixture was extracted with diethyl ether (15 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to give the residue as a dark yellow oil. The yield was calculated using 1,3,5-trimethoxybenzene (10%) as internal standard. The quantity of each product was determined as following (also see annotated example spectrum below):

For the recovered starting material **6** the integration of methoxy signal of the internal standard in the $^1$H-NMR spectrum was set to 9 units. The integration of the methyl signal of **6** (2.50 ppm) was then measured and the following calculation gave the amount of **6** present:

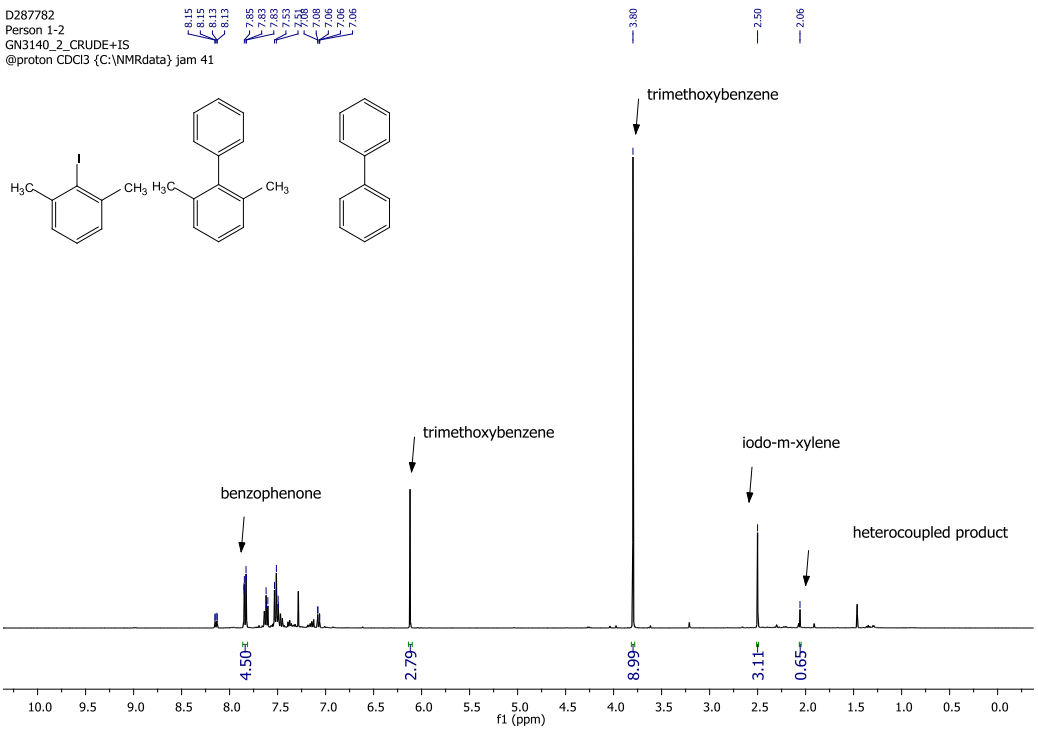
(3.11/6) × 10 = 5.2%

For the hetero-coupled product **9**, the integration of the methoxy signal of the internal standard in the $^1$H-NMR spectrum was set to 9 units. The integration of the methyl signal of **9** (2.04 ppm) was then measured and the following calculation gave the amount of **9** present:

(0.65/6) × 10 = 1.1%

For the biphenyl product **7** the integration of the aromatic signal of the internal standard was set to 3 units. The integration of the aromatic signals of **7** at 7.64–7.59 ppm (4 H) was then measured and the following calculation gave the amount of **7** present:

(int/4) × 10 = yield % but see text below the next spectrum**

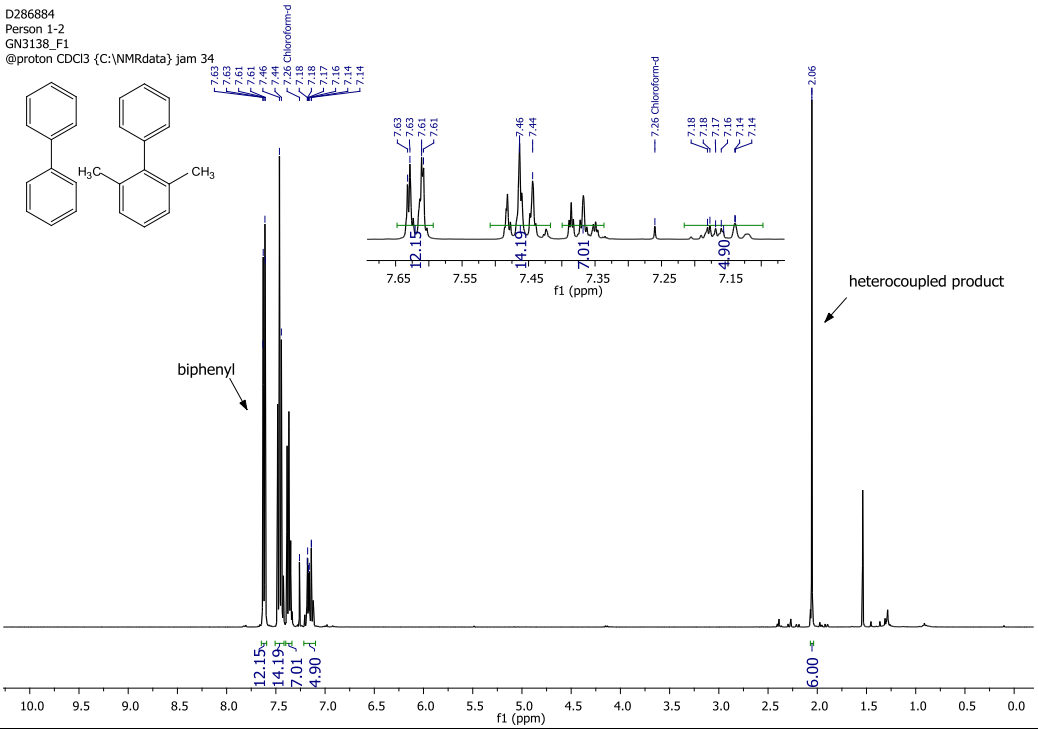



**In this particular case the diagnostic peak of biphenyl overlaps with one of the benzophenone peak. In the BHAS mediated mechanism the ratio between biphenyl and heterocoupled product is always 3:1. In fact, after purification by chromatography the inseparable mixture was indeed in 3:1 ratio. Integrating the methyl group (6H, 2.06 ppm) as 6 the ratio of biphenyl (4H, 7.62 ppm) is:

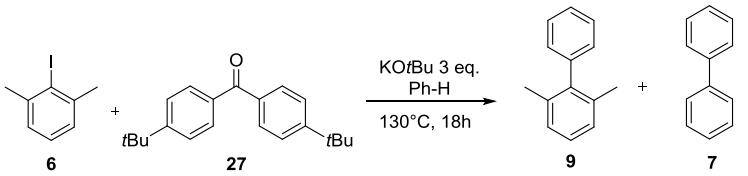
(12.15/4) = 3.0

Since the ratio was found to be 3:1, the tiled of biphenyl present in the mixture was 3.3%.
Number of runs: (a) Biphenyl 3.3 % ; 1,3-dimethylbiphenyl 1.1 %. (b) Biphenyl 3.6 % ; 1,3-dimethylbiphenyl 1.2%. (c) Biphenyl 3.6 % ; 1,3-dimethylbiphenyl 1.2%

Average of 3 runs: Biphenyl 3.5 % ; 1,3-dimethylbiphenyl 1.2%.



Cross coupling reaction using **27** as additive.




A mixture of 1-iodo-2,6-dimethylbenzene **6** (116 mg, 0.5 mmol), KO*t*Bu (168 mg, 1.5 mmol) and **27** (29.4 mg; 0.1 mmol) in benzene ( 5 mL) was sealed in a 15 mL pressure tube in a glovebox. The tube was removed from the glovebox and heated at 130 ºC for 18 h behind a blast shield. After cooling to room temperature, the reaction was quenched by water (15 mL) and acidified with 1N HCl until neutral pH. The mixture was extracted with diethyl ether (15 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to give the residue as a dark yellow oil which yielded 1.0 % of **9** and 3.2 % of **7**. The yield was calculated using 1,3,5-trimethoxybenzene (10%) as internal standard.

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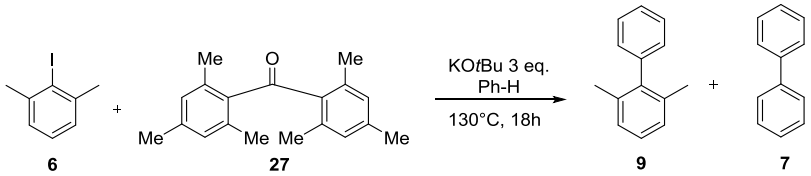
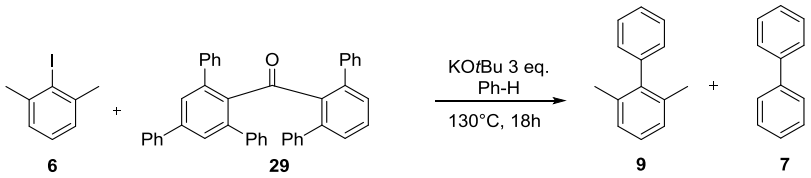
Cross coupling reaction using **28** as additive.




A mixture of 1-iodo-2,6-dimethylbenzene **6** (116 mg, 0.5 mmol), KO*t*Bu (168 mg, 1.5 mmol) and **28** (26.6 mg; 0.1 mmol) in benzene ( 5 mL) was sealed in a 15 mL pressure tube in a glovebox. The tube was removed from the glovebox and heated at 130 ºC for 18 h behind a blast shield. After cooling to room temperature, the reaction was quenched by water (15 mL) and acidified with 1N HCl until neutral pH. The mixture was extracted with diethyl ether (15 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to give the residue as a dark yellow oil which yielded 0.7 % of **9** and 1.8 % of **7**. The yield was calculated using 1,3,5-trimethoxybenzene (10%) as internal standard.

Cross coupling reaction using **29** as additive.




A mixture of 1-iodo-2,6-dimethylbenzene **6** (116 mg, 0.5 mmol), KO*t*Bu (168 mg, 1.5 mmol) and **28** (56.2 mg; 0.1 mmol) in benzene ( 5 mL) was sealed in a 15 mL pressure tube in a glovebox. The tube was removed from the glovebox and heated at 130 ºC for 18 h behind a blast shield. After cooling to room temperature, the reaction was quenched by water (15 mL) and acidified with 1N HCl until neutral pH. The mixture was extracted with diethyl ether (15 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to give the residue as a dark yellow oil which yielded 0.8 % of **9** and 2.4 % of **7**. The yield was calculated using 1,3,5-trimethoxybenzene (10%) as internal standard.

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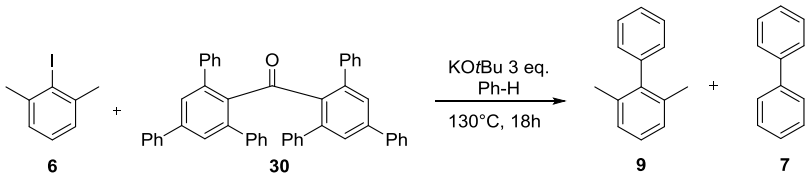
Cross coupling reaction using **30** as additive.




A mixture of 1-iodo-2,6-dimethylbenzene **6** (116 mg, 0.5 mmol), KO*t*Bu (168 mg, 1.5 mmol) and **28** (63.8 mg; 0.1 mmol) in benzene ( 5 mL) was sealed in a 15 mL pressure tube in a glovebox. The tube was removed from the glovebox and heated at 130 ºC for 18 h behind a blast shield. After cooling to room temperature, the reaction was quenched by water (15 mL) and acidified with 1N HCl until neutral pH. The mixture was extracted with diethyl ether (15 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to give the residue as a dark yellow oil which yielded 0.4 % of **9** and 1.2 % of **7**. The yield was calculated using 1,3,5-trimethoxybenzene (10%) as internal standard.

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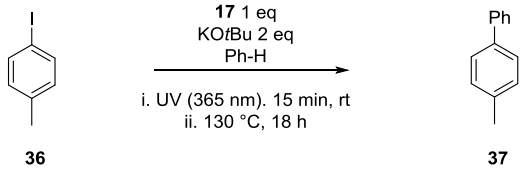
Reactions with iodo-*para*-toluene using **17** as additive

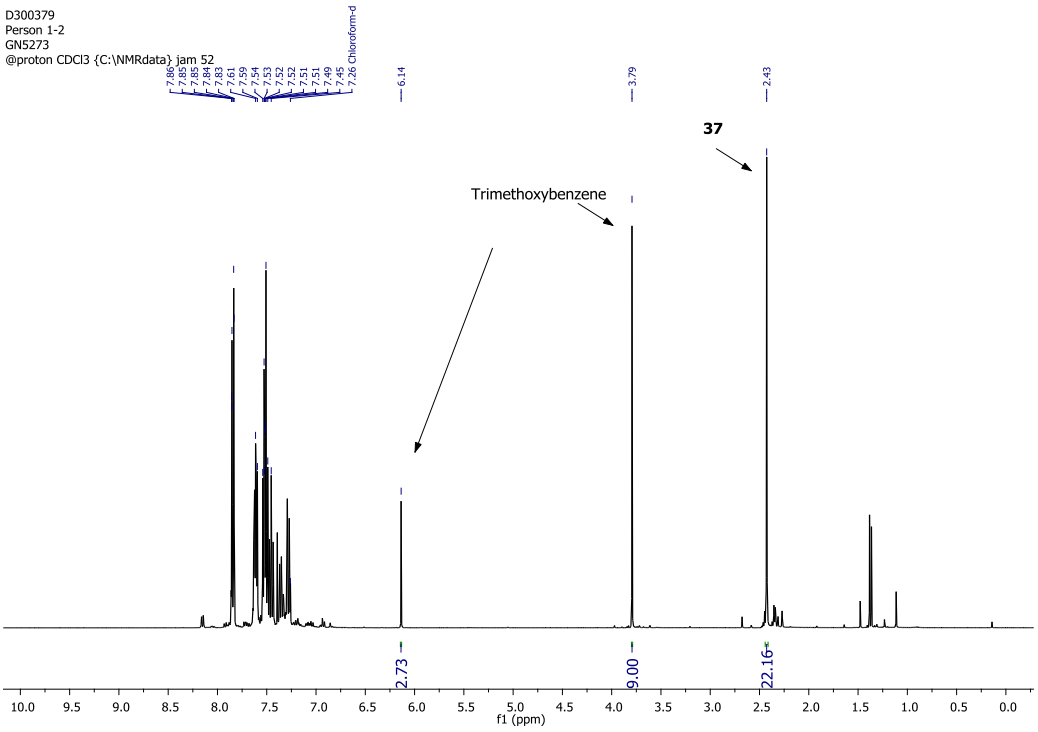



A mixture of iodo-*p*-toluene **36** (0.5 mmol), KO*t*Bu (112 mg, 1 mmol), **17** (91 mg, 0.5 mmol, if added) in benzene (2.5 mL) was sealed in a 15 mL pressure tube in glovebox. The tube was removed from the glovebox and placed RT for 15 min under UV (365 nm) irradiation and then transferred into an oil bath at 130 °C for 18h. After cooling to room temperature, the reaction was quenched by water (15 mL) and acidified with 1N HCl until neutral pH. The mixture was extracted with diethyl ether (3 x 15 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to give rise to the residue. 1,3,5-Trimethoxybenzene 8.4 mg, (0.050 mmol, 10 mol%) was added as a solid to the reaction mixture, ~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 product was determined as following. For the recovered starting material the integration of methoxy signal (3.81 ppm) of the internal standard in the $^1$H-NMR spectrum was set to 9 units. The integration of the methyl signal of **36** (3H, 2.33 ppm) was then measured and the following calculation gave the amount of **36** present:

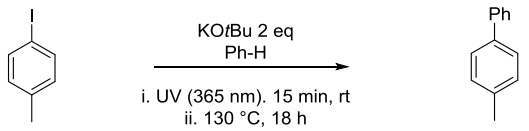
$(6.24/3) \times 10 = 21$ %

For the product **37** the integration of methoxy signal of the internal standard in the $^1$H-NMR spectrum was set to 9. The integration of the methyl signal of **37** (3H, 2.46 ppm) was then measured and the following calculation gave the amount of **37** present.

$(22.25/3) \times 10 = 74$ %




Reactions with iodo-*p*-toluene with no additive (blank reaction)



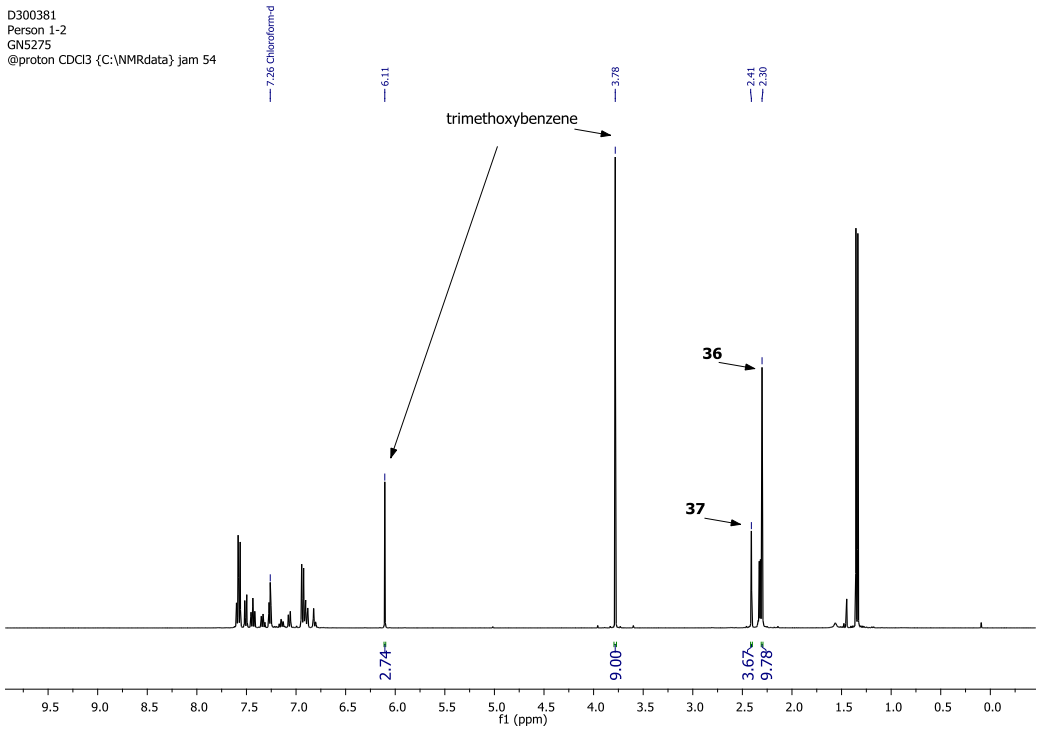

**36** **37**

A mixture of iodo-*p*-toluene **36** (0.5 mmol), KO*t*Bu (112 mg, 1 mmol) in benzene (2.5 mL) was sealed in a 15 mL pressure tube in glovebox. The tube was removed from the glovebox and placed RT for 15 min under UV (365 nm) irradiation and then transferred into an oil bath at 130 °C for 18h. After cooling to room temperature, the reaction was quenched by water (15 mL) and acidified with 1N HCl until neutral pH. The mixture was extracted with diethyl ether (3 x 15 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to give rise to the residue. 1,3,5-Trimethoxybenzene 8.4 mg, (0.050 mmol, 10 mol%) was added as a solid to the reaction mixture, ~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 product was determined as following. For the recovered starting material the integration of methoxy signal (3.81 ppm) of the internal standard in the $^1$H-NMR spectrum was set to 9 units. The integration of the methyl signal of **36** (3H, 2.33 ppm) was then measured and the following calculation gave the amount of **36** present:

(9.78/3) × 10 = 33 %

For the product **37** the integration of methoxy signal of the internal standard in the $^1$H-NMR spectrum was set to 9 units. The integration of the methyl signal of **37** (3H, 2.46 ppm) was then measured and the following calculation gave the amount of **37** present.

(3.68/3) × 10 = 12 %


D300381
Person 1-2
GN5275
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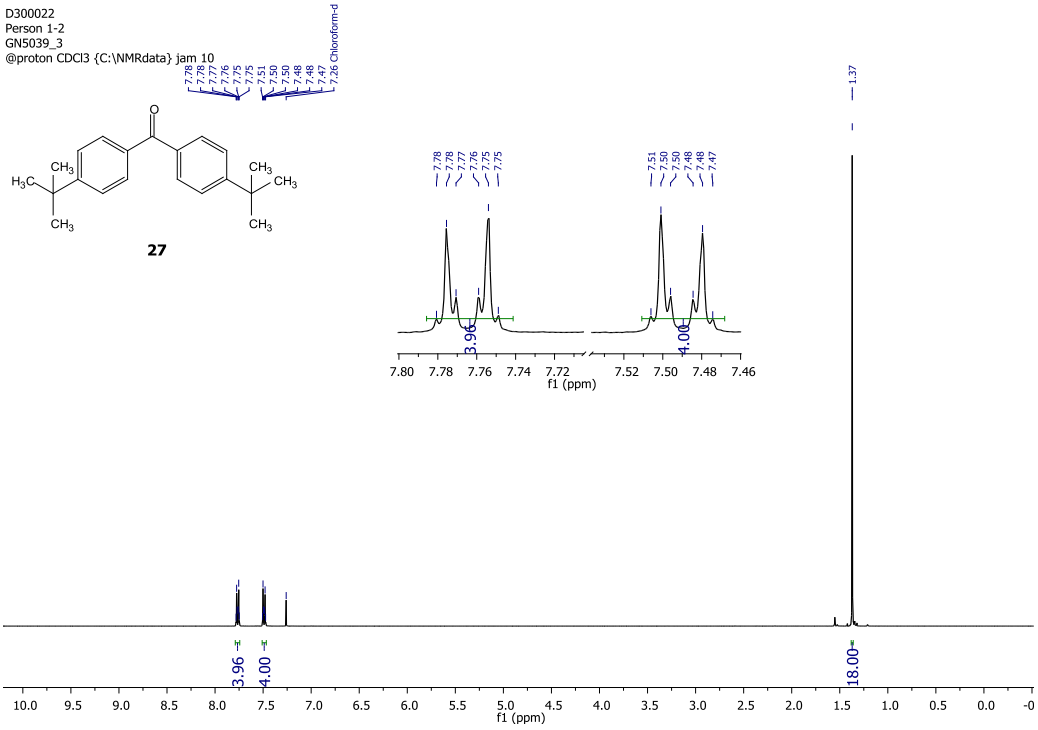
7.26 Chloroform-d
6.11
3.78
2.41
2.30
trimethoxybenzene
36
37
2.74
9.00
3.67
9.78
f1 (ppm)

**NMR Spectra:**


D300022
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GN5039_3
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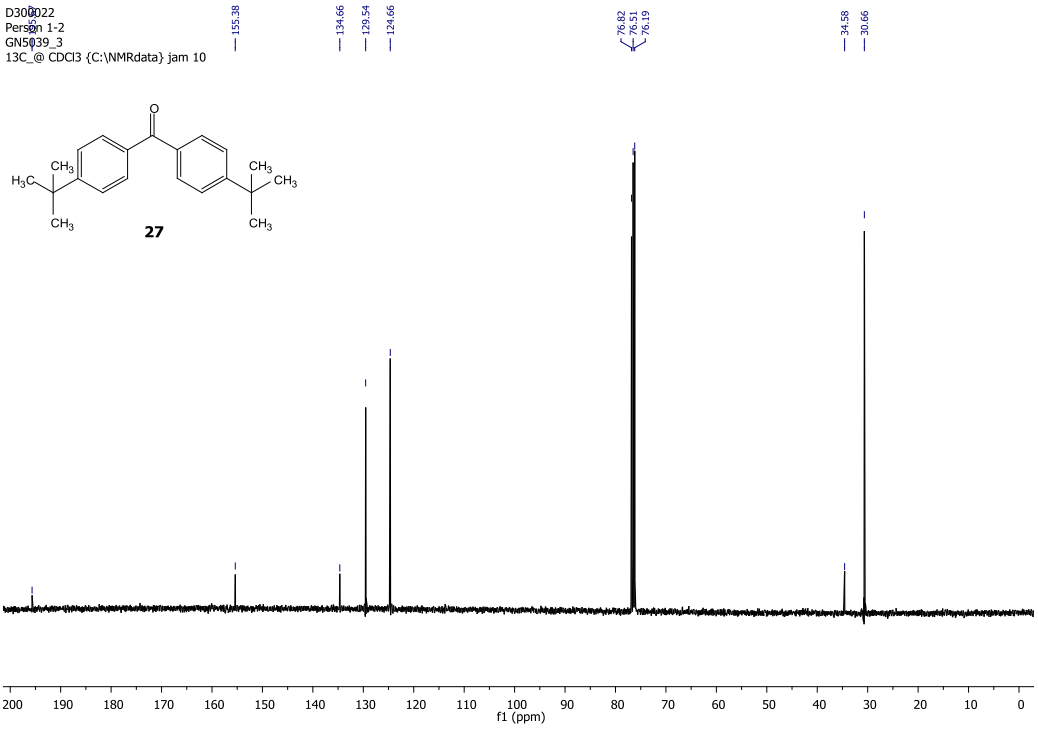
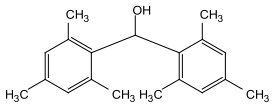
7.78
7.77
7.76
7.75
7.75
7.51
7.50
7.50
7.48
7.48
7.47
7.26 Chloroform-d
1.37
3.96
4.00
18.00
f1 (ppm)
27


D300022
Person 1-2
GN5039_3
13C_@ CDCl3 {C:\NMRdata} jam 10
77.00
155.38
134.66
129.54
124.66
76.82
76.51
76.19
34.58
30.66
f1 (ppm)
27

D261691
Person 1-2
GN2077
@proton CDCl3 {C:\NMRdata} jam 28



**38**




D261715
Person 1-2
GN2077
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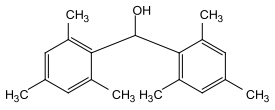
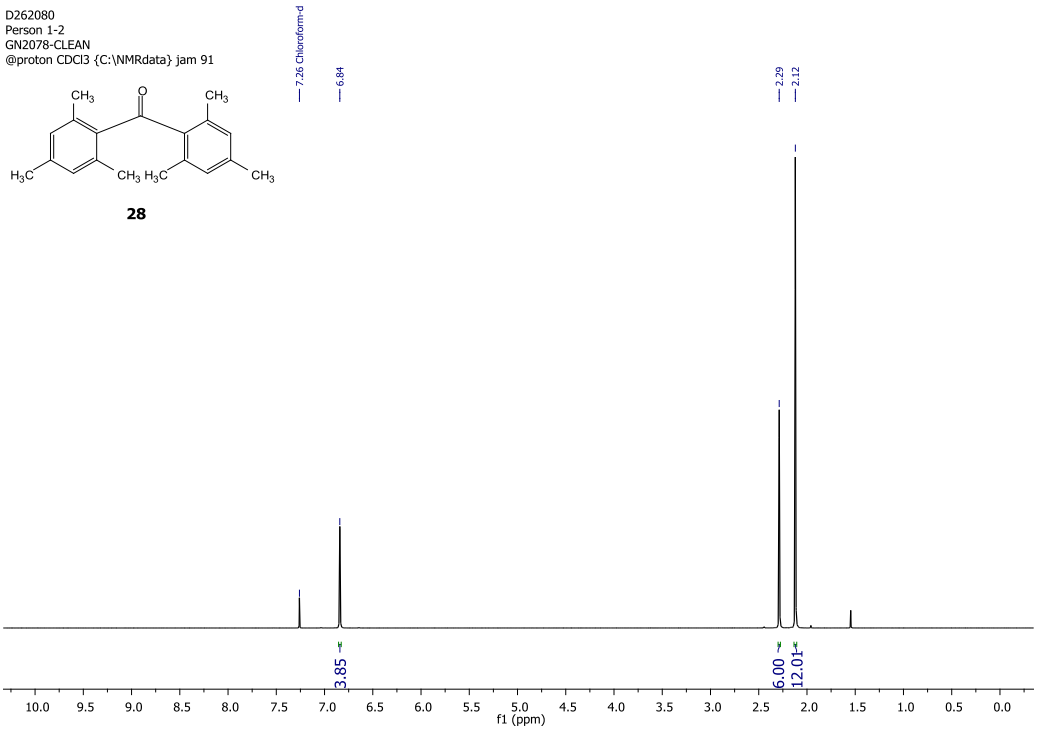
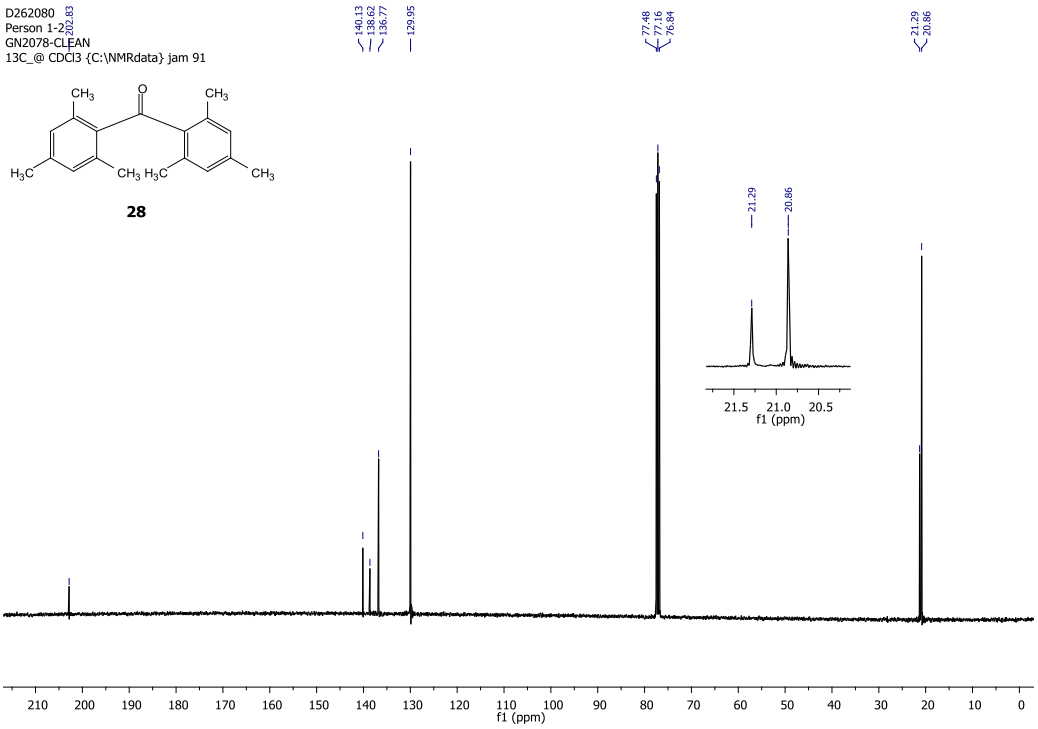


**38**


D262080
Person 1-2
GN2078-CLEAN
@proton CDCl3 {C:\NMRdata} jam 91
7.26 Chloroform-d
6.84
2.29
2.12
28
3.85
6.00
12.01
f1 (ppm)


D262080
Person 1-2
GN2078-CLEAN
13C_@ CDCl3 {C:\NMRdata} jam 91
202.83
140.13
138.62
136.77
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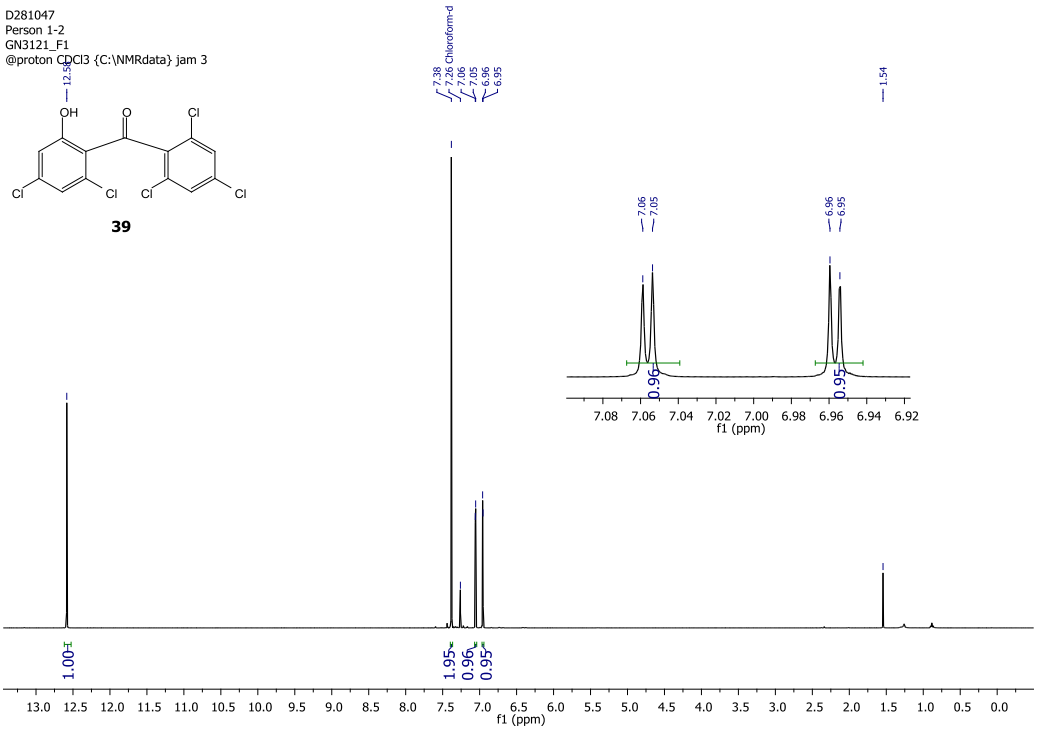
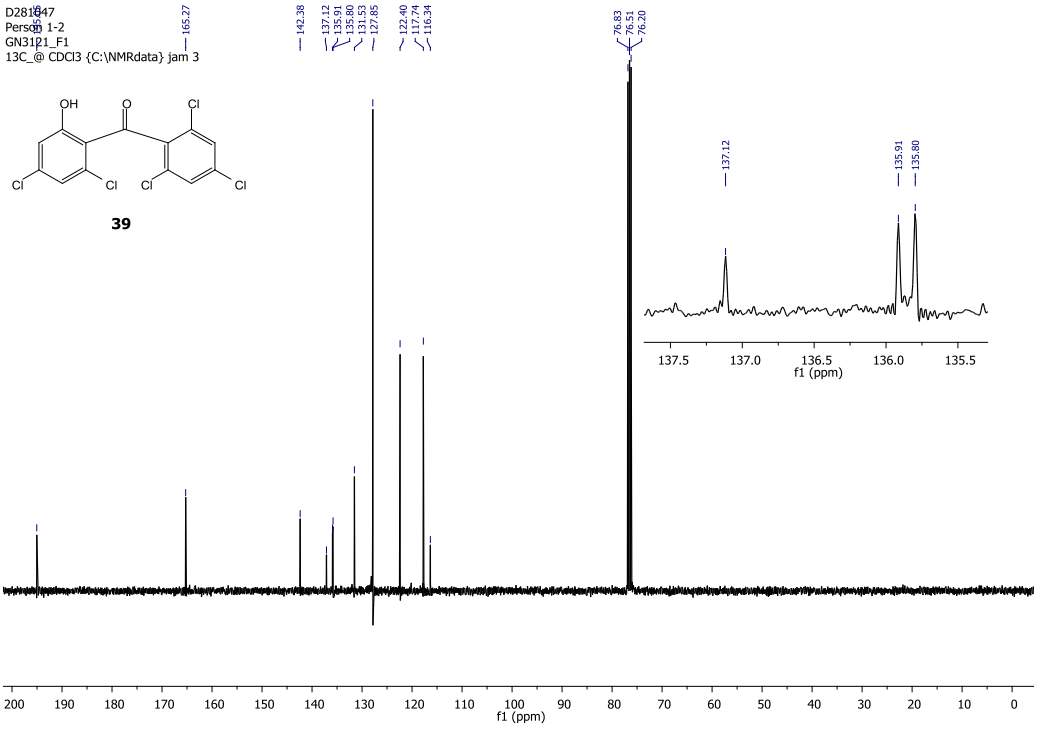
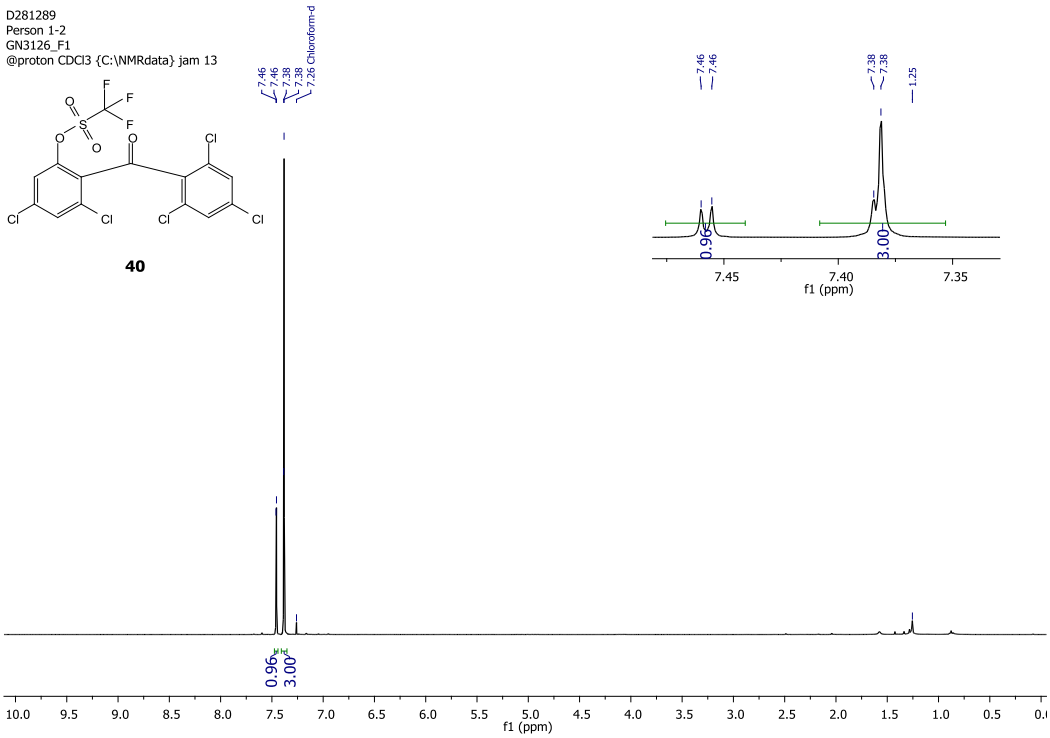
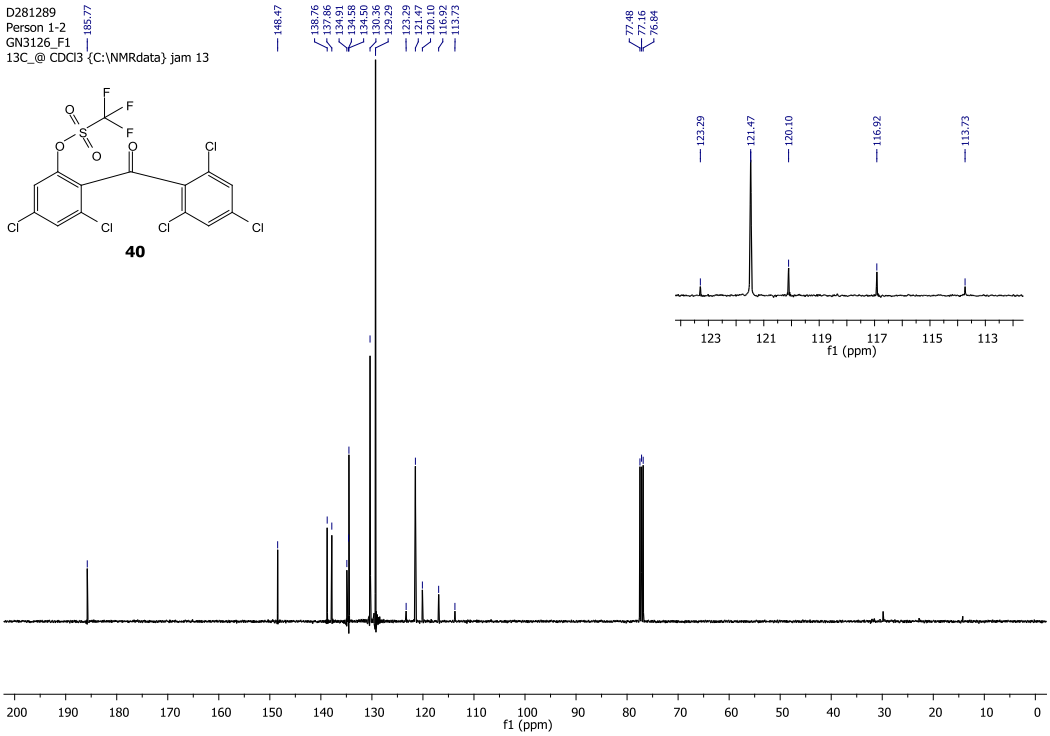
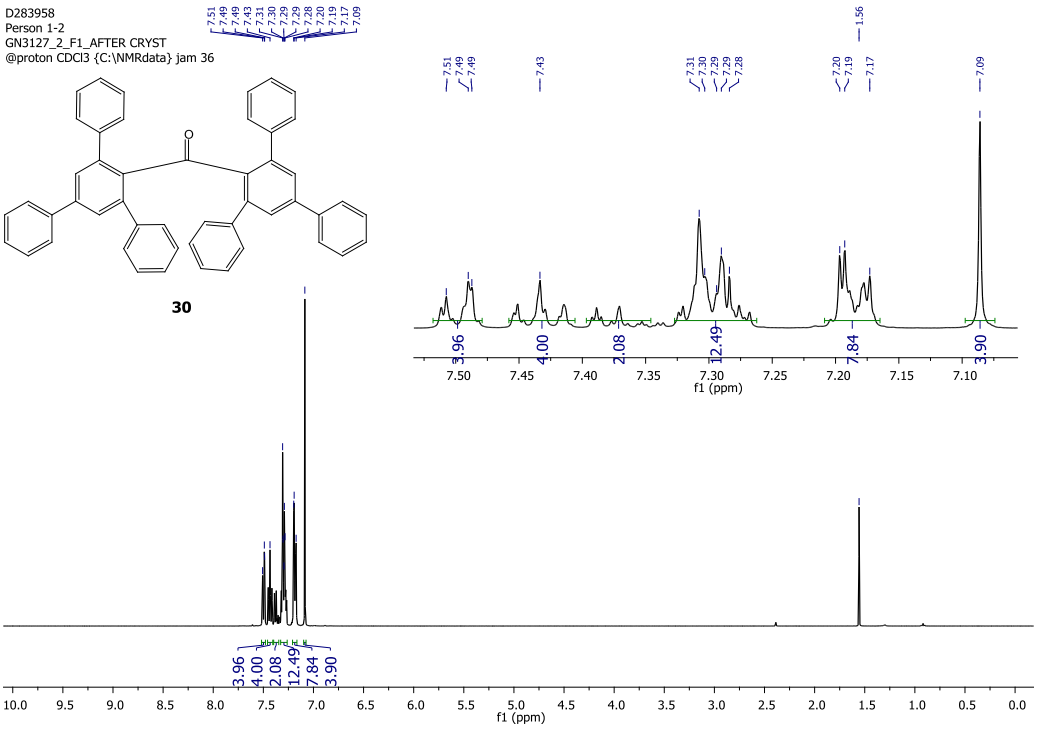
21.29
20.86
28
21.29
20.86
f1 (ppm)

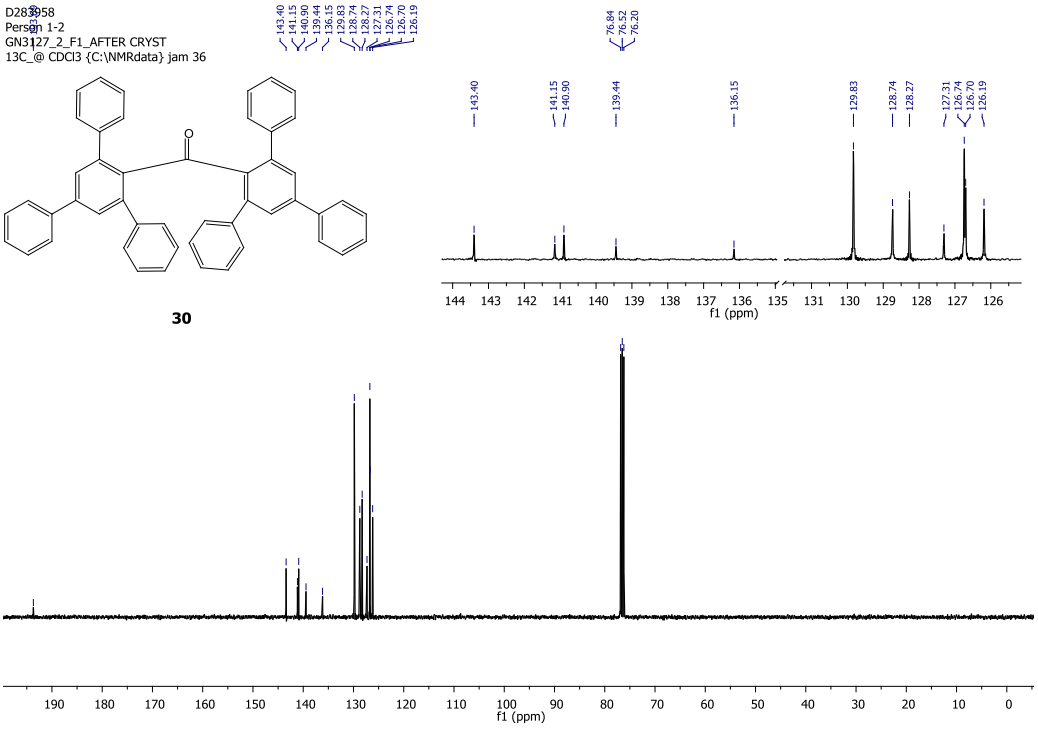

D281047
Person 1-2
GN3121_F1
@proton CDCl3 {C:\NMRdata} jam 3
12.56
7.38
7.26 Chloroform-d
7.06
7.05
6.96
6.95
1.54
OH
O
Cl
Cl
Cl
Cl
Cl
39
7.06
7.05
6.96
6.95
0.96
0.95
7.08 7.06 7.04 7.02 7.00 6.98 6.96 6.94 6.92
f1 (ppm)
1.00
1.95
0.96
0.95
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


D281047
Person 1-2
GN3121_F1
13C_@ CDCl3 {C:\NMRdata} jam 3
165.27
142.38
137.12
135.91
135.80
131.53
127.85
122.40
117.74
116.34
76.83
76.51
76.20
OH
O
Cl
Cl
Cl
Cl
Cl
39
137.12
135.91
135.80
137.5 137.0 136.5 136.0 135.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


D281289
Person 1-2
GN3126_F1
@proton CDCl3 {C:\NMRdata} jam 13
7.46
7.46
7.38
7.38
7.26 Chloroform-d
40
0.96
3.00
f1 (ppm)


D281289
Person 1-2
GN3126_F1
13C_@ CDCl3 {C:\NMRdata} jam 13
185.77
148.47
138.76
137.86
134.91
134.58
134.50
130.36
129.29
123.29
121.47
120.10
116.92
113.73
77.48
77.16
76.84
40
f1 (ppm)


D283958
Person 1-2
GN3127_2_F1_AFTER CRYST
@proton CDCl3 {C:\NMRdata} jam 36
30
f1 (ppm)


D283958
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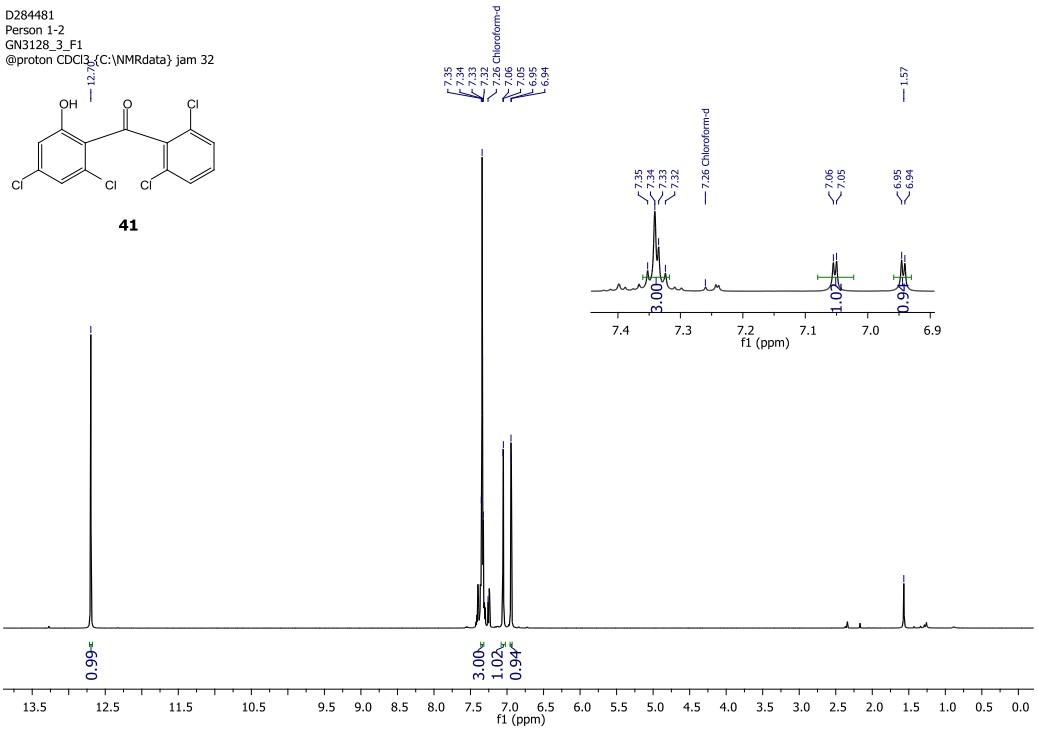
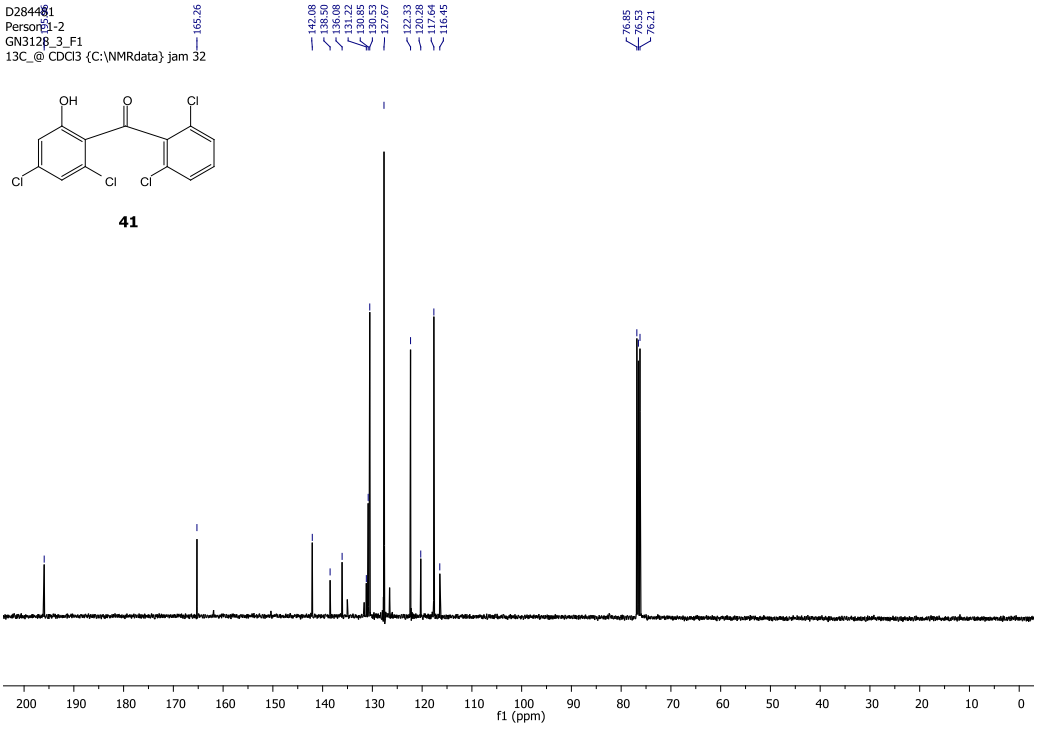
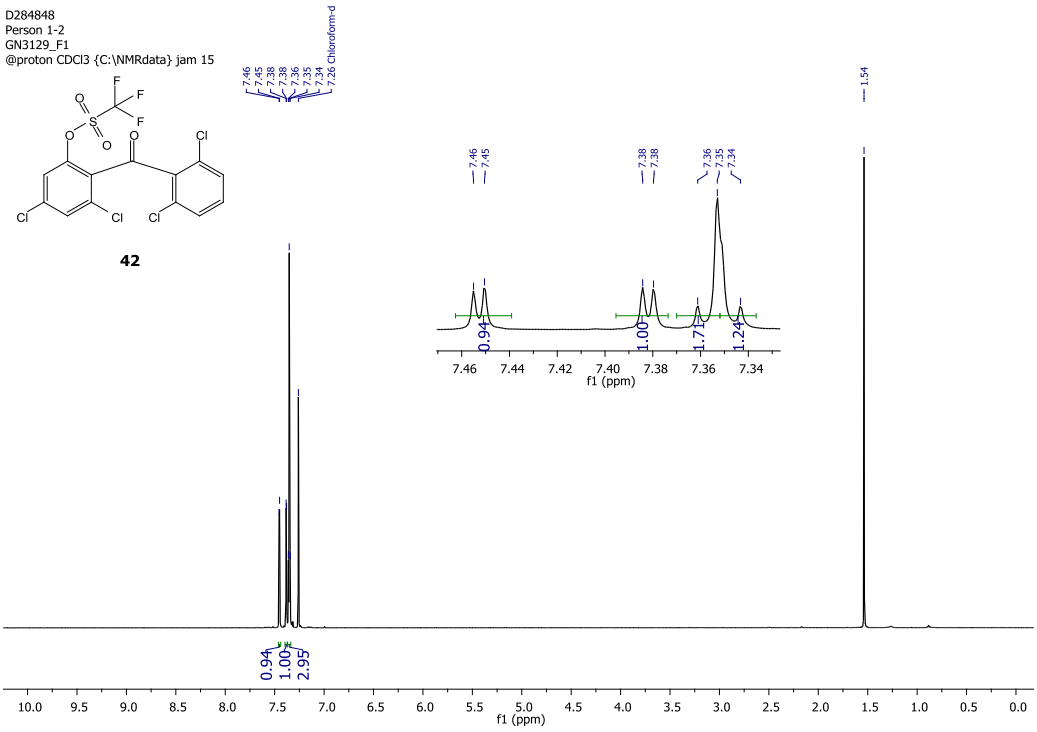
GN3127_2_F1_AFTER CRYST
13C_@ CDCl3 {C:\NMRdata} jam 36
30
f1 (ppm)


D284481
Person 1-2
GN3128_3_F1
@proton CDCl3 {C:\NMRdata} jam 32
OH
O
Cl
Cl
Cl
Cl
41
12.70
7.35
7.34
7.33
7.32
7.26 Chloroform-d
7.06
7.05
6.95
6.94
1.57
0.99
3.00
1.02
0.94
f1 (ppm)


D284481
Person 1-2
GN3128_3_F1
13C_@ CDCl3 {C:\NMRdata} jam 32
OH
O
Cl
Cl
Cl
Cl
41
165.26
142.08
138.50
136.08
131.22
130.65
130.53
127.67
122.33
120.28
117.64
116.45
76.85
76.53
76.21
f1 (ppm)


D284848
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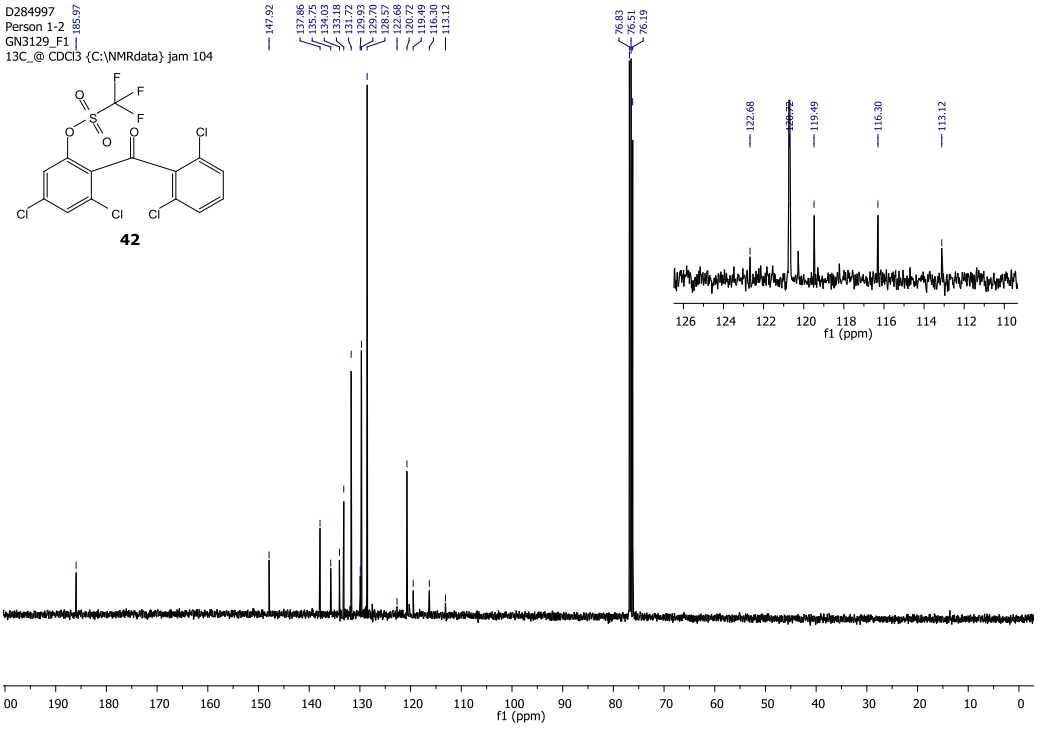
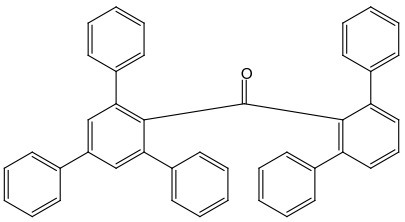
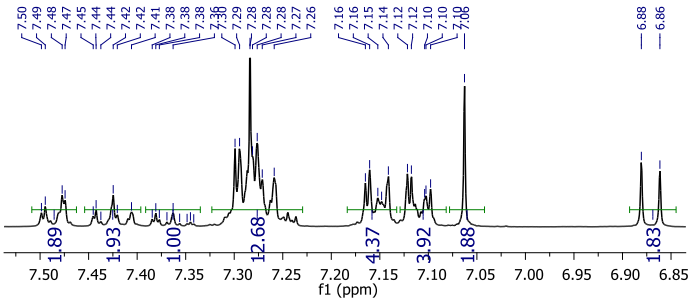
GN3129_F1
@proton CDCl3 {C:\NMRdata} jam 15
42
f1 (ppm)

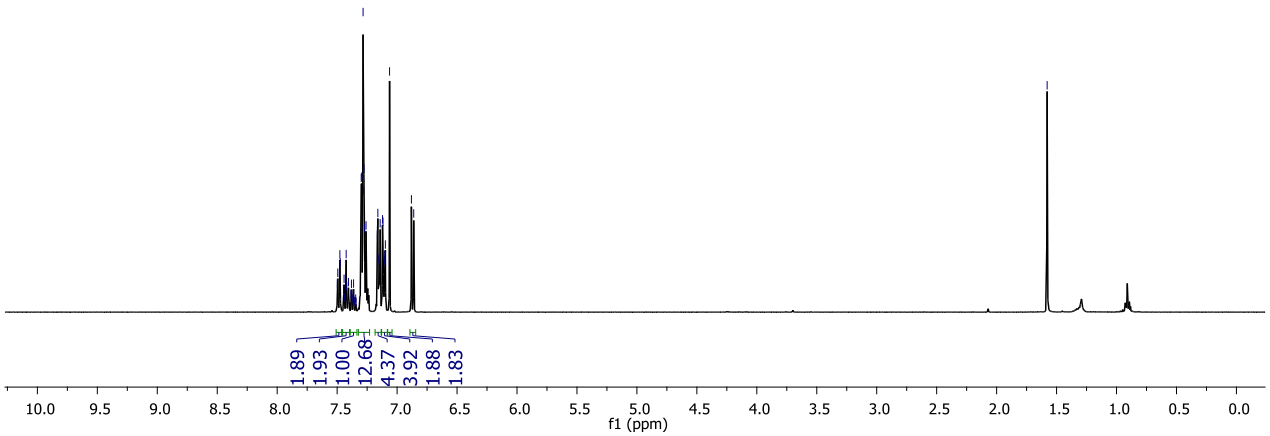

D284997
Person 1-2
GN3129_F1
13C_@ CDCl3 {C:\NMRdata} jam 104
42
f1 (ppm)

D285567
Person 1-2
GN3130_CLEAN
@proton CDCl3 {C:\NMRdata} jam 18

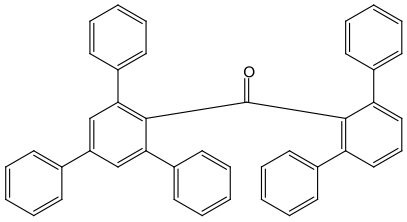


**29**



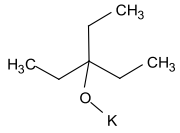




D285610
Person 1-2
GN3130_CLEANREP
13C_@ CDCl3 {C:\NMRdata} jam 59



**29**

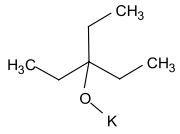
D299117
Person 1-2
GN4241_2
@proton C6D6 {C:\NMRdata} jam 68




**43**




D299117
Person 1-2
GN4241_2
13C_@ C6D6 {C:\NMRdata} jam 68




**43**

## Computational Results

Computational Methods

Density Functional Theory (DFT) was used for the geometry optimizations of all reactant complexes, transition states, intermediates and product complexes. The final optimized geometries were characterized as minima or transition states by performing frequency calculations, which also enabled calculation of the zero-point energies (ZPE), enthalpies (H), entropies (S) and Gibbs free energies (G) at 298 K. Geometry optimizations and frequency calculations were performed using the Gaussian 09[9] software package, using the M06-2X functional[10] and 6-31++G(d,p) basis set,[11] unless otherwise stated. Implicit solvation was modelled using the Conductor-Like Polarisable Continuum Model (CPCM)[12] with the associated parameters of THF solvent, unless otherwise stated. Gibbs free energy barriers and relative free energies were calculated between reactant complexes and transition states or reactant complexes and product complexes, respectively and are reported in kcal/mol throughout. Time dependent DFT (TD-DFT)[13] calculations were performed on the M06-2X/6-31++G(d,p) optimised geometries, with the CAM-B3LYP functional,[14] due to its good performance with intermolecular charge transfer (CT) excitations,[15] whilst maintaining the 6-31++G(d,p) basis set and CPCM solvent model.

Naked monomeric *tert*-butoxide anion is used throughout this work as a simple representation of tetrameric KO*t*Bu; see **Table S1** where it can be seen that the naked monomer is found to more closely reproduce the thermodynamics of the reaction utilising a KO*t*Bu tetramer, whilst underestimating the kinetics. This approach has also previously been utilised by Grubbs *et al*.,[16-17] after having shown that tetramer is the most stable structure in solution by DFT calculations.

Marcus Theory Calculations

In order to model a single electron transfer reaction computationally, Marcus-Hush Theory[18] is employed with the 4-point method of Nelsen et al.[19] or the complexation method of Anderson, Tuttle and co-workers[20] allowing calculation of the reorganisation energy ($\lambda$), $\Delta G_{rel}$ and $\Delta G^*$. The Nelsen 4-point method requires optimisation of the individual electron donor and acceptor species, before and after single electron transfer. Single point energy calculations are then performed on these optimised geometries using the charge and multiplicity of their other state in the electron transfer reaction. The complexation method requires optimisation of the electron donor and acceptor as a complex in both the reactant and product electronic states. Single point energy calculations are then performed on these optimized geometries with the alternative electronic configuration.

KO*t*Bu Representation

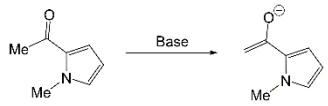



**Figure S15.** Deprotonation reaction studied using various forms of KO*t*Bu.

**Table S1.** Results of DFT Calculations for the reaction depicted in Figure S1, energies calculated relative to reactant and product complexes. (Computational Method: M06-2X/6-311++G(d,p), CPCM solvation method with parameters for benzene)

| Base | $\Delta G^*$ (Kcal/mol) | $\Delta G_{rel}$ (Kcal/mol) |
|---|---|---|
| O*t*Bu anion | 0.4 | -12.1 |
| KO*t*Bu monomer | 4.8 | -4.1 |
| KO*t*Bu dimer | 7.8 | -3.0 |
| KO*t*Bu tetramer | 3.9 | -14.5 |

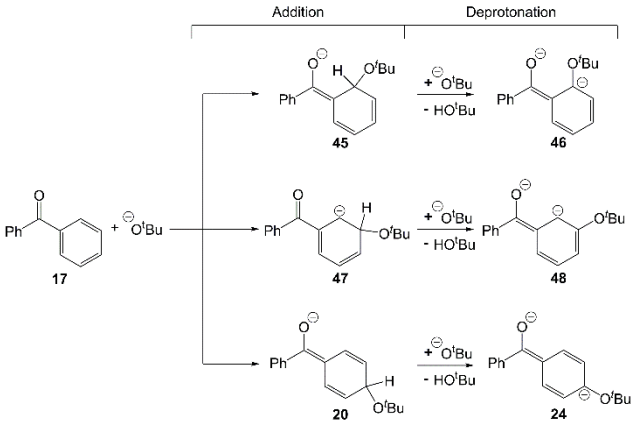
Feasibility of forming organic electron donors (**Scheme 3 (a)** main paper)

Given our group's previous evidence showing KO*t*Bu is a poor single electron donor, our initial investigations focused on the possible formation of *in situ* organic electron donor species resulting from reaction of KO*t*Bu with benzophenone (**17**). We proposed that *tert*-butoxide anion might add to the *ortho, meta* or *para* positions of a phenyl moiety in benzophenone generating anions **45, 47** and **20**, which could then be followed by a deprotonation, generating dianionic species **46, 48** and **24**. Dianions **46, 48** and **24** have the structural characteristics[21] to act as electron donors towards benzophenone, should they be accessible.

As shown in **Table S2**, addition in the *meta* position has an accessible free energy barrier (21.1 kcal/mol) but is highly endergonic (18.6 kcal/mol) thus disfavouring the addition reaction and we therefore disregarded any further reactivity through a *meta*-adduct. Addition in the *ortho* and *para* positions exhibits accessible free energy barriers at the reported

experimental conditions (room temperature),[22-25] whilst being endergonic by 5.8 and 5.0 kcal/mol, respectively. Subsequent deprotonation of *ortho* (**45**) and *para* (**20**) adducts to form dianions **46** and **24** respectively, occurs with accessible free energy barriers, with both reactions being endergonic (9.7 and 7.0 kcal/mol, calculated relative to reactant complex of **45** or **20** with *tert*-butoxide anion). Whilst bearing in mind the observation of 3% benzophenone ketyl radical anion **18**, by Ashby *et al.* these results suggest it is unlikely for even such a small amount of dianionic species such as **46** or **24** to be formed (<<1% of product would be formed in both addition and deprotonation steps).

**Table S2**. Calculated Gibbs free energies for addition and deprotonation.

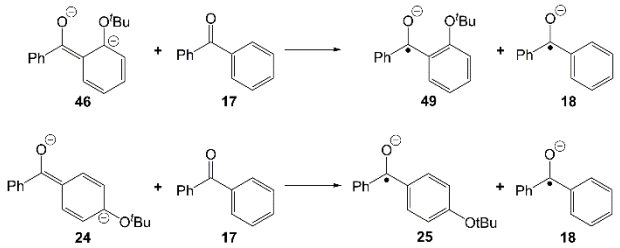



| | *ortho* (kcal/mol) | | *meta* (kcal/mol) | | *para* (kcal/mol) | |
|---|---|---|---|---|---|---|
| | **ΔG*** | **ΔG$_{rel}$** | **ΔG*** | **ΔG$_{rel}$** | **ΔG*** | **ΔG$_{rel}$** |
| ⊖O$^t$Bu Addition | 15.6 | 5.8 | 21.1 | 18.6 | 15.1 | 5.0 |
| Deprotonation by ⊖O$^t$Bu | 25.9 | 9.7 | - | - | 20.7 | 7.0 |

Despite the lack of possibility for forming dianions **46** and **24**, their ability to act as single electron donors to a molecule of neutral benzophenone was still examined. Marcus Theory calculations were performed to calculate the free energy of activation for SET, as well as the relative free energy, utilising the complexation method of Anderson *et al.*[20] and the Nelsen Four Point method.[19] Marcus Theory calculations utilising the method of Anderson *et al.* were carried out with and without potassium counter cations (see below for images of optimised complexes), and the results are presented in **Table S3**.

The calculated low activation energies and exergonic relative energies, from the complexation method, suggest that single electron transfer from a dianionic species such as **46** or **24** to benzophenone would occur readily. Results utilising the Nelsen 4-point method are also included and show similar overall exergonic SET reactions, however the predicted activation energy is higher for both **46** and **24**. Previous work in the group has shown the complexation method with counterions to be the most accurate for predicting SET energies,[20] (however, we include here the Nelsen 4-point results to allow comparison with results from later calculations which require the use of this methodology).

**Table S3.** Calculated Gibbs free energies for SET from dianions **46** and **24** to benzophenone (**17**).

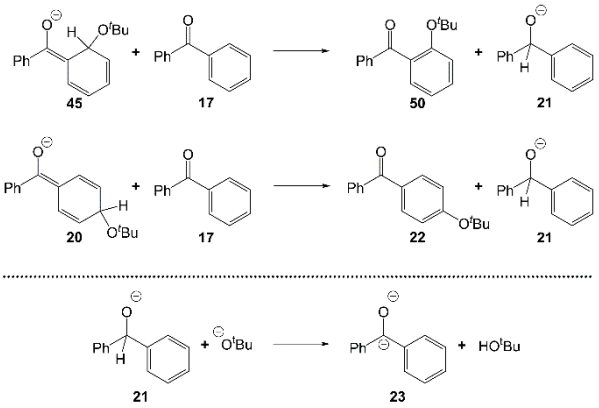



| **Complexation Method**[20] | **ΔG* (kcal/mol)** | **ΔG$_{rel}$ (kcal/mol)** |
|---|---|---|
| **46 + 17 → 49 + 18** | 0.3 | -20.3 |
| **46 + 17 → 49 + 18** (with 2 potassium cations) | 0.1 | -26.5 |
| **24 + 17 → 25 + 18** | 0.4 | -17.8 |
| **24 + 17 → 25 + 18** (with 2 potassium cations) | 3.3 | -7.9 |

| Nelsen 4-Point Method[19] | ΔG* (kcal/mol) | $\Delta G_{rel}$ (kcal/mol) |
|---|---|---|
| **46 + 17 → 49 + 18** | 9.1 | -36.7 |
| **24 + 17 → 25 + 18** | 8.3 | -32.9 |

With these results in hand, we wanted to probe alternative mechanisms that could be operating. We therefore investigated the possibility of a hydride transfer from either species **45** or **20** to benzophenone, forming **21**. Hydride transfer from anion **45** to benzophenone (**17**) exhibited an unfavourable free energy barrier of 34.3 kcal/mol and was slightly exergonic (0.7 kcal/mol), **Table S4**. On the other hand, anion **20** exhibited a comparable barrier to deprotonation (22.4 kcal/mol) and was exergonic by 3.8 kcal/mol; these results suggest hydride transfer from **20** would be possible. In order to achieve an electron donor species from **21** it would be necessary to deprotonate and access dianion **23** (SET from **23** to benzophenone (**17**) has an activation free energy of 6.9 kcal/mol and is exergonic by 31.6 kcal/mol, see **Figure S16** for results); this exhibits an accessible barrier of 23.0 kcal/mol whilst being endergonic by 10.2 kcal/mol. The combination of hydride transfer followed by deprotonation of **21** to form electron donor **23** can also be dismissed, on the basis of unfavourable kinetics.

**Table S4.** Calculated Gibbs free energies for hydride transfer from anions **45** and **20** to benzophenone (**17**) and deprotonation of product **21**.




| Reaction | ΔG* (kcal/mol) | $\Delta G_{rel}$ (kcal/mol) |
|---|---|---|
| **45 + 17 → 50 + 21** | 34.3 | -0.7 |
| **20 + 17 → 22 + 21** | 22.4 | -3.8 |
| **21 + ⊖O*t*Bu → 23 + HO*t*Bu** | 23.0 | 10.2 |

The above computational data indicates *tert*-butoxy substitution could not occur; similarly there has been no experimental evidence for formation of such *tert*-butoxy (or other alkoxy) substituted benzophenone products.

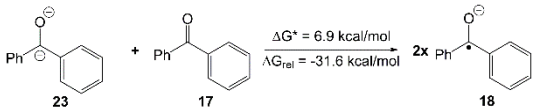
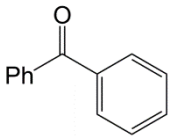


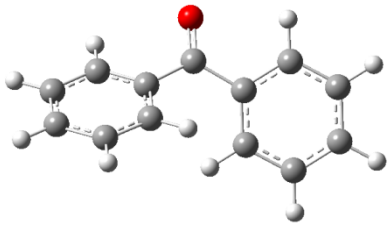

**Figure S16.** SET from 23 to 17 – Calculated using the Nelsen 4-point method

of this reaction and the ease of reverse reaction we decided not to further probe this as a route to potential electron donor species.

**XYZ Coordinates of Optimised Geometries**

Benzophenone (**17**)



24
-576.4217964

| | | | |
|---|---|---|---|
| C | -3.77491 | -0.91946 | 0.13834 |
| C | -2.66005 | -1.51373 | 0.72891 |
| C | -1.41870 | -0.88307 | 0.66828 |
| C | -1.29468 | 0.35659 | 0.03049 |
| C | -2.42112 | 0.95791 | -0.54344 |
| C | -3.65452 | 0.31666 | -0.50056 |
| H | -4.73880 | -1.41734 | 0.17881 |
| H | -2.75616 | -2.46854 | 1.23558 |
| H | -0.55385 | -1.34456 | 1.13523 |
| H | -2.31247 | 1.92559 | -1.02326 |
| H | -4.52237 | 0.77910 | -0.95960 |
| C | 0.00001 | 1.10670 | 0.00012 |
| C | 1.29469 | 0.35658 | -0.03038 |
| C | 1.41863 | -0.88309 | -0.66815 |
| C | 2.42119 | 0.95790 | 0.54342 |
| C | 2.65996 | -1.51377 | -0.72891 |
| H | 0.55373 | -1.34459 | -1.13500 |
| C | 3.65458 | 0.31663 | 0.50042 |
| H | 2.31261 | 1.92559 | 1.02323 |
| C | 3.77490 | -0.91950 | -0.13847 |
| H | 2.75601 | -2.46859 | -1.23556 |
| H | 4.52249 | 0.77908 | 0.95936 |
| H | 4.73877 | -1.41739 | -0.17902 |
| O | 0.00001 | 2.32919 | -0.00004 |

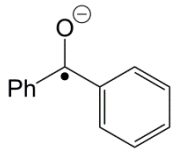
Single Point Radical Anion
using Optimised Geometry
**17**

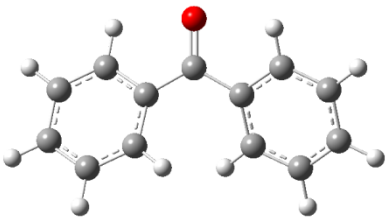
24
-576.4969276

| | | | |
|---|---|---|---|
| C | -3.77491100 | -0.91946000 | 0.13834000 |
| C | -2.66004800 | -1.51372800 | 0.72891100 |
| C | -1.41869800 | -0.88306600 | 0.66827600 |
| C | -1.29467500 | 0.35658600 | 0.03049100 |
| C | -2.42111600 | 0.95791000 | -0.54343500 |
| C | -3.65451800 | 0.31665800 | -0.50055600 |
| H | -4.73879700 | -1.41733800 | 0.17880600 |
| H | -2.75615900 | -2.46854300 | 1.23557600 |
| H | -0.55385200 | -1.34456400 | 1.13522700 |
| H | -2.31247100 | 1.92559200 | -1.02325800 |
| H | -4.52236900 | 0.77910400 | -0.95959900 |
| C | 0.00000900 | 1.10669700 | 0.00012000 |
| C | 1.29468600 | 0.35657700 | -0.03037700 |
| C | 1.41862700 | -0.88308900 | -0.66815100 |
| C | 2.42119400 | 0.95790000 | 0.54341800 |
| C | 2.65996300 | -1.51376800 | -0.72890500 |
| H | 0.55372600 | -1.34458800 | -1.13499700 |
| C | 3.65458400 | 0.31663200 | 0.50042000 |
| H | 2.31261200 | 1.92559200 | 1.02323500 |
| C | 3.77489600 | -0.91949800 | -0.13846700 |
| H | 2.75600900 | -2.46859300 | -1.23556100 |
| H | 4.52248800 | 0.77907700 | 0.95936400 |

| | | | |
|---|---|---|---|
| H | 4.73877200 | -1.41738800 | -0.17902500 |
| O | 0.00000900 | 2.32919400 | -0.00003600 |

Benzophenone Radical Anion (**18**)



24
-576.5066700

| | | | |
|---|---|---|---|
| C | 3.87258 | -0.87217 | -0.07837 |
| C | 2.74326 | -1.58592 | -0.49682 |
| C | 1.47967 | -1.00708 | -0.46971 |
| C | 1.28461 | 0.32117 | -0.01271 |
| C | 2.44758 | 1.03748 | 0.36951 |
| C | 3.70662 | 0.45123 | 0.34648 |
| H | 4.85658 | -1.33022 | -0.09921 |
| H | 2.85244 | -2.60291 | -0.86540 |
| H | 0.63747 | -1.57669 | -0.84842 |
| H | 2.32393 | 2.06687 | 0.68988 |
| H | 4.57160 | 1.03022 | 0.66107 |
| C | 0.00000 | 1.02918 | 0.00001 |
| C | -1.28461 | 0.32117 | 0.01272 |
| C | -1.47968 | -1.00708 | 0.46972 |
| C | -2.44758 | 1.03748 | -0.36951 |
| C | -2.74327 | -1.58592 | 0.49682 |
| H | -0.63748 | -1.57669 | 0.84844 |
| C | -3.70661 | 0.45123 | -0.34649 |
| H | -2.32392 | 2.06687 | -0.68988 |
| C | -3.87258 | -0.87216 | 0.07835 |
| H | -2.85245 | -2.60291 | 0.86540 |
| H | -4.57159 | 1.03023 | -0.66109 |
| H | -4.85658 | -1.33021 | 0.09919 |
| O | 0.00000 | 2.31424 | -0.00000 |

Single Point Singlet using
Optimised Geometry
Benzophenone Radical Anion

24
-576.4126038

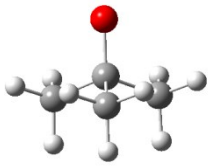
| | | | |
|---|---|---|---|
| C | 3.87257800 | -0.87216700 | -0.07836500 |
| C | 2.74326400 | -1.58592400 | -0.49682400 |
| C | 1.47967100 | -1.00708400 | -0.46970900 |
| C | 1.28460700 | 0.32116900 | -0.01271100 |
| C | 2.44758200 | 1.03748100 | 0.36951200 |
| C | 3.70661900 | 0.45122700 | 0.34647600 |
| H | 4.85658400 | -1.33021700 | -0.09921400 |
| H | 2.85244400 | -2.60290900 | -0.86539600 |
| H | 0.63747300 | -1.57669300 | -0.84842200 |
| H | 2.32392700 | 2.06687100 | 0.68988000 |
| H | 4.57159700 | 1.03022500 | 0.66106700 |
| C | 0.00000100 | 1.02918100 | 0.00001100 |
| C | -1.28460700 | 0.32116900 | 0.01272300 |
| C | -1.47967500 | -1.00708300 | 0.46972000 |
| C | -2.44757700 | 1.03748100 | -0.36951200 |
| C | -2.74326900 | -1.58592200 | 0.49682300 |
| H | -0.63748100 | -1.57669200 | 0.84844200 |
| C | -3.70661400 | 0.45122900 | -0.34648800 |
| H | -2.32391800 | 2.06687200 | -0.68988000 |
| C | -3.87257900 | -0.87216500 | 0.07835200 |
| H | -2.85245300 | -2.60290600 | 0.86539500 |
| H | -4.57158900 | 1.03022700 | -0.66108900 |
| H | -4.85658500 | -1.33021400 | 0.09919300 |
| O | 0.00000000 | 2.31423600 | -0.00000200 |

Single Point Dianion using
Optimised Geometry
Benzophenone Radical Anion

24
-576.5350689

| | | | |
|---|---|---|---|
| C | 3.87257800 | -0.87216700 | -0.07836500 |
| C | 2.74326400 | -1.58592400 | -0.49682400 |
| C | 1.47967100 | -1.00708400 | -0.46970900 |
| C | 1.28460700 | 0.32116900 | -0.01271100 |
| C | 2.44758200 | 1.03748100 | 0.36951200 |
| C | 3.70661900 | 0.45122700 | 0.34647600 |
| H | 4.85658400 | -1.33021700 | -0.09921400 |
| H | 2.85244400 | -2.60290900 | -0.86539600 |
| H | 0.63747300 | -1.57669300 | -0.84842200 |
| H | 2.32392700 | 2.06687100 | 0.68988000 |
| H | 4.57159700 | 1.03022500 | 0.66106700 |
| C | 0.00000100 | 1.02918100 | 0.00001100 |
| C | -1.28460700 | 0.32116900 | 0.01272300 |
| C | -1.47967500 | -1.00708300 | 0.46972000 |
| C | -2.44757700 | 1.03748100 | -0.36951200 |
| C | -2.74326900 | -1.58592200 | 0.49682300 |
| H | -0.63748100 | -1.57669200 | 0.84844200 |
| C | -3.70661400 | 0.45122900 | -0.34648800 |
| H | -2.32391800 | 2.06687200 | -0.68988000 |
| C | -3.87257900 | -0.87216500 | 0.07835200 |
| H | -2.85245300 | -2.60290600 | 0.86539500 |
| H | -4.57158900 | 1.03022700 | -0.66108900 |
| H | -4.85658500 | -1.33021400 | 0.09919300 |
| O | 0.00000000 | 2.31423600 | -0.00000200 |

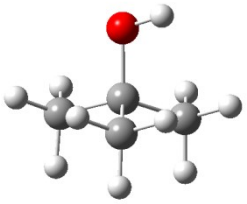
*tert*-Butoxide Anion

14
-233.0544325

| | | | |
|---|---|---|---|
| C | 1.44067 | -0.06139 | -0.43463 |
| C | 0.00048 | -0.00003 | 0.12965 |
| H | 2.01123 | 0.80195 | -0.07121 |
| H | 1.93541 | -0.97065 | -0.07217 |
| H | 1.47391 | -0.06232 | -1.53300 |
| C | -0.77523 | -1.21695 | -0.43101 |
| C | -0.66855 | 1.27897 | -0.43026 |
| H | -1.80900 | -1.19007 | -0.06549 |
| H | -0.79611 | -1.24637 | -1.52932 |
| H | -0.31234 | -2.14272 | -0.06828 |
| H | -0.68742 | 1.30985 | -1.52855 |
| H | -1.70061 | 1.34069 | -0.06418 |
| H | -0.12759 | 2.16163 | -0.06827 |
| O | 0.00353 | -0.00071 | 1.49975 |

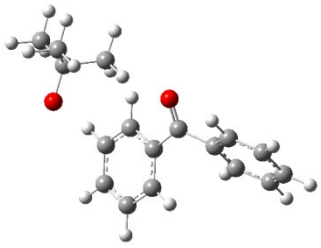
*tert*-Butanol (HO$^t$Bu)

15
-233.5806428

| | | | |
|---|---|---|---|
| C | -1.49270 | -0.00002 | -0.31732 |
| C | -0.00606 | 0.00000 | 0.01498 |
| H | -1.97347 | -0.88876 | 0.10226 |
| H | -1.97350 | 0.88872 | 0.10223 |
| H | -1.64200 | -0.00005 | -1.40068 |
| C | 0.67162 | 1.25791 | -0.52689 |
| C | 0.67166 | -1.25789 | -0.52689 |
| H | 1.73360 | 1.27098 | -0.25667 |
| H | 0.59949 | 1.29843 | -1.61812 |
| H | 0.19631 | 2.15130 | -0.11123 |
| H | 0.59956 | -1.29840 | -1.61812 |
| H | 1.73363 | -1.27094 | -0.25665 |
| H | 0.19636 | -2.15130 | -0.11124 |
| O | 0.05936 | 0.00000 | 1.44873 |
| H | 0.98799 | 0.00002 | 1.71513 |

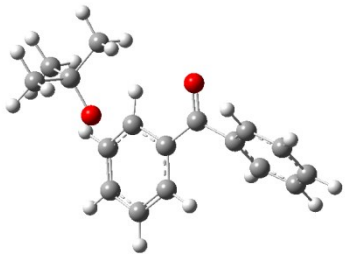
**Reactant Complex** for formation of **45** from **17** and **O*t*Bu anion**



38
-809.4818830

| | | | |
|---|---|---|---|
| C | 5.75012 | -0.43125 | 0.87668 |
| C | 4.74081 | 0.27793 | 1.52733 |
| C | 3.43543 | 0.24017 | 1.03985 |
| C | 3.13285 | -0.52599 | -0.09143 |
| C | 4.14609 | -1.25151 | -0.72891 |
| C | 5.45254 | -1.19473 | -0.25437 |
| H | 6.76811 | -0.39192 | 1.25185 |
| H | 4.96966 | 0.86115 | 2.41343 |
| H | 2.64934 | 0.78691 | 1.55171 |
| H | 3.89440 | -1.85102 | -1.59820 |
| H | 6.23842 | -1.74576 | -0.76103 |
| C | 1.73281 | -0.65782 | -0.60991 |
| C | 0.78155 | 0.48671 | -0.48134 |
| C | 1.21869 | 1.81657 | -0.52179 |
| C | -0.58800 | 0.20876 | -0.38002 |
| C | 0.28886 | 2.85304 | -0.46424 |
| H | 2.27664 | 2.04065 | -0.62171 |
| C | -1.52047 | 1.24045 | -0.29914 |
| H | -0.90924 | -0.82943 | -0.35637 |
| C | -1.07095 | 2.56398 | -0.34541 |
| H | 0.62718 | 3.88358 | -0.51076 |
| H | -2.59293 | 1.02871 | -0.19787 |
| H | -1.79138 | 3.37533 | -0.28890 |
| O | 1.37780 | -1.70367 | -1.13584 |
| O | -4.65328 | 0.80218 | 0.05679 |
| C | -4.81929 | -0.54029 | 0.28655 |
| C | -6.30695 | -0.89171 | 0.52227 |
| C | -4.32392 | -1.37679 | -0.91856 |
| C | -4.02291 | -0.99562 | 1.53466 |
| H | -6.68252 | -0.32872 | 1.38539 |
| H | -6.89410 | -0.59729 | -0.35615 |
| H | -6.47163 | -1.96222 | 0.70755 |
| H | -3.26540 | -1.15830 | -1.10670 |
| H | -4.43264 | -2.45923 | -0.76507 |
| H | -4.88899 | -1.09369 | -1.81492 |
| H | -4.13618 | -2.06713 | 1.74922 |
| H | -2.95657 | -0.78347 | 1.38792 |
| H | -4.36193 | -0.42757 | 2.40960 |

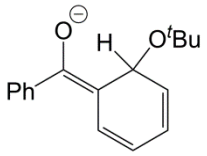
**Transition State** for formation of **45** from **17** and **O*t*Bu anion**

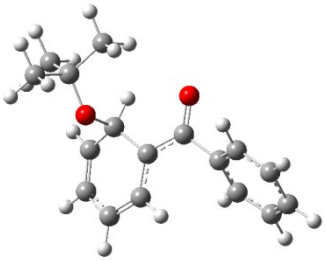


38
-809.4594074

| | | | |
|---|---|---|---|
| C | -5.10676 | -0.68944 | 0.37800 |
| C | -4.63181 | 0.47287 | -0.22909 |
| C | -3.27433 | 0.60620 | -0.51979 |
| C | -2.38391 | -0.43043 | -0.22151 |
| C | -2.87105 | -1.60334 | 0.36448 |
| C | -4.22292 | -1.72792 | 0.67640 |
| H | -6.16204 | -0.78810 | 0.61365 |
| H | -5.31740 | 1.27787 | -0.47566 |
| H | -2.90698 | 1.51233 | -0.99330 |
| H | -2.17865 | -2.41309 | 0.57628 |
| H | -4.58870 | -2.63593 | 1.14617 |
| C | -0.92247 | -0.36473 | -0.59182 |
| C | -0.12721 | 0.80604 | -0.22909 |
| C | -0.61645 | 1.83045 | 0.61240 |
| C | 1.21147 | 0.87633 | -0.70544 |
| C | 0.11949 | 2.97893 | 0.83758 |
| H | -1.59007 | 1.72199 | 1.08120 |
| C | 1.87747 | 2.13091 | -0.60911 |
| H | 1.50402 | 0.16378 | -1.46708 |
| C | 1.35775 | 3.13917 | 0.17336 |
| H | -0.26605 | 3.76395 | 1.47997 |
| H | 2.83408 | 2.26301 | -1.10580 |
| H | 1.90255 | 4.07475 | 0.27689 |
| O | -0.45147 | -1.32119 | -1.21422 |
| O | 2.25590 | -0.23500 | 0.68946 |
| C | 3.27430 | -1.06397 | 0.24335 |
| C | 4.09660 | -1.54901 | 1.45419 |
| C | 2.70977 | -2.30053 | -0.48538 |
| C | 4.23711 | -0.32453 | -0.71331 |
| H | 4.54504 | -0.69078 | 1.96782 |
| H | 3.43727 | -2.06467 | 2.16129 |
| H | 4.89978 | -2.23787 | 1.15997 |
| H | 2.07524 | -1.98863 | -1.32082 |
| H | 3.50411 | -2.95851 | -0.86174 |
| H | 2.08025 | -2.87568 | 0.20412 |
| H | 5.08348 | -0.95831 | -1.00675 |
| H | 3.71812 | -0.01269 | -1.62712 |
| H | 4.62820 | 0.57417 | -0.22244 |

**45**

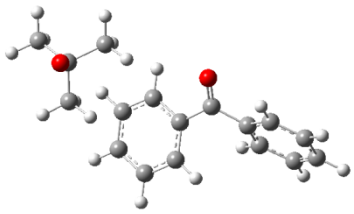


38
-809.4797478

| | | | |
|---|---|---|---|
| C | -5.12994 | -0.47372 | 0.29764 |
| C | -4.55389 | 0.63735 | -0.31762 |
| C | -3.17948 | 0.67168 | -0.55762 |
| C | -2.36537 | -0.40805 | -0.19792 |
| C | -2.95745 | -1.52718 | 0.39929 |
| C | -4.32617 | -1.55756 | 0.65770 |
| H | -6.19815 | -0.49805 | 0.49134 |
| H | -5.17387 | 1.47917 | -0.61182 |
| H | -2.73321 | 1.53784 | -1.03822 |
| H | -2.33063 | -2.37550 | 0.65958 |
| H | -4.76858 | -2.42711 | 1.13509 |
| C | -0.88442 | -0.44785 | -0.50926 |
| C | -0.05308 | 0.63349 | -0.12283 |
| C | -0.50295 | 1.73619 | 0.65971 |
| C | 1.39830 | 0.57215 | -0.49606 |
| C | 0.24269 | 2.88106 | 0.79872 |
| H | -1.47689 | 1.67738 | 1.14149 |
| C | 1.96422 | 1.95531 | -0.66761 |
| H | 1.50775 | -0.03059 | -1.40411 |
| C | 1.45213 | 3.00441 | 0.02430 |
| H | -0.11460 | 3.71477 | 1.39453 |
| H | 2.84830 | 2.08534 | -1.28761 |
| H | 1.93740 | 3.97758 | -0.04007 |
| O | -0.47819 | -1.46891 | -1.12563 |
| O | 2.13877 | -0.11883 | 0.57171 |
| C | 3.19686 | -1.00635 | 0.20197 |
| C | 3.91569 | -1.31213 | 1.51473 |
| C | 2.62805 | -2.29912 | -0.39045 |
| C | 4.18524 | -0.35931 | -0.77590 |
| H | 4.33732 | -0.39481 | 1.93763 |
| H | 3.21105 | -1.73590 | 2.23667 |
| H | 4.72592 | -2.03086 | 1.35353 |
| H | 2.01911 | -2.09661 | -1.27508 |
| H | 3.43918 | -2.98411 | -0.66131 |
| H | 1.98359 | -2.79061 | 0.34545 |
| H | 5.02217 | -1.04169 | -0.95806 |
| H | 3.71743 | -0.13960 | -1.74067 |
| H | 4.57943 | 0.57305 | -0.35974 |

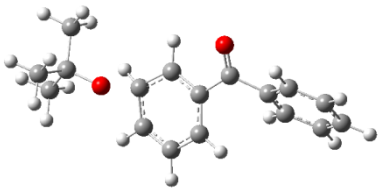
**Reactant Complex** for formation of **47** from **17** and **O*t*Bu anion**



38
-809.4818921

| | | | |
|---|---|---|---|
| C | -1.31648 | 1.76606 | -0.92637 |
| C | -0.03380 | 2.31452 | -0.89947 |
| C | 1.07756 | 1.48021 | -0.79390 |
| C | 0.90251 | 0.09195 | -0.73691 |
| C | -0.38965 | -0.44798 | -0.78282 |
| C | -1.50556 | 0.38170 | -0.86543 |
| H | -2.18186 | 2.41998 | -0.99649 |
| H | 0.10334 | 3.38983 | -0.95920 |
| H | 2.07665 | 1.90571 | -0.77991 |
| H | -0.50640 | -1.52750 | -0.74409 |
| H | -2.52188 | -0.03314 | -0.88081 |
| C | 2.06432 | -0.84605 | -0.69612 |
| C | 3.33468 | -0.43144 | -0.01781 |
| C | 3.33729 | 0.40958 | 1.10063 |
| C | 4.54132 | -0.96206 | -0.48896 |
| C | 4.53736 | 0.71449 | 1.74085 |
| H | 2.40226 | 0.80736 | 1.48330 |
| C | 5.74043 | -0.63909 | 0.13783 |
| H | 4.52346 | -1.62137 | -1.35119 |
| C | 5.73870 | 0.19825 | 1.25568 |
| H | 4.53369 | 1.35418 | 2.61743 |
| H | 6.67534 | -1.04031 | -0.24028 |
| H | 6.67335 | 0.44478 | 1.74993 |
| O | 1.98609 | -1.95243 | -1.21230 |
| O | -4.52486 | -0.58824 | -0.87041 |
| C | -4.97974 | -0.37810 | 0.40732 |
| C | -4.83469 | 1.10870 | 0.81535 |
| C | -6.47280 | -0.75910 | 0.54479 |
| C | -4.18087 | -1.22273 | 1.43026 |
| H | -3.77873 | 1.40068 | 0.76436 |
| H | -5.39521 | 1.73623 | 0.11157 |
| H | -5.20186 | 1.31198 | 1.83089 |
| H | -6.60596 | -1.81573 | 0.28234 |
| H | -6.86436 | -0.60142 | 1.55923 |
| H | -7.06879 | -0.15929 | -0.15382 |
| H | -4.51751 | -1.07363 | 2.46554 |
| H | -4.28124 | -2.28670 | 1.18351 |
| H | -3.11761 | -0.95969 | 1.36985 |

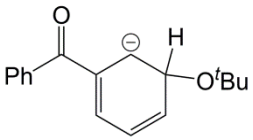
**Transition State** for formation of **47** from **17** and **O*t*Bu anion**

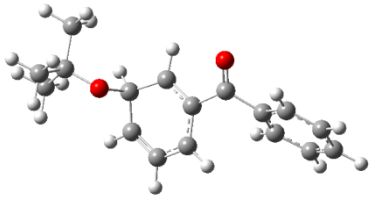


38
-809.4503761

| | | | |
|---|---|---|---|
| C | 1.57376 | 1.97195 | -0.10672 |
| C | 0.40222 | 2.22196 | 0.59235 |
| C | -0.64972 | 1.29731 | 0.61613 |
| C | -0.50268 | 0.11478 | -0.13691 |
| C | 0.67574 | -0.15339 | -0.83020 |
| C | 1.82982 | 0.68288 | -0.68696 |
| H | 2.35085 | 2.73146 | -0.15013 |
| H | 0.28245 | 3.17521 | 1.10364 |
| H | -1.55871 | 1.50100 | 1.17075 |
| H | 0.73568 | -1.05433 | -1.43445 |
| H | 2.57021 | 0.63363 | -1.47984 |
| C | -1.60210 | -0.88418 | -0.22392 |
| C | -3.03157 | -0.44581 | -0.06128 |
| C | -3.49191 | 0.78414 | -0.54450 |
| C | -3.93695 | -1.33773 | 0.52514 |
| C | -4.84213 | 1.11643 | -0.43828 |
| H | -2.79483 | 1.47165 | -1.01312 |
| C | -5.28012 | -0.99618 | 0.65143 |
| H | -3.57127 | -2.29560 | 0.88239 |
| C | -5.73480 | 0.23233 | 0.16699 |
| H | -5.19637 | 2.06625 | -0.82651 |
| H | -5.97391 | -1.68663 | 1.12096 |
| H | -6.78396 | 0.49705 | 0.25764 |
| O | -1.37855 | -2.07221 | -0.43576 |
| O | 2.91253 | -0.20338 | 0.52699 |
| C | 4.24769 | -0.41629 | 0.17342 |
| C | 4.96905 | 0.91068 | -0.14138 |
| C | 4.95597 | -1.07608 | 1.36721 |
| C | 4.36537 | -1.36281 | -1.03875 |
| H | 4.52435 | 1.41057 | -1.00867 |
| H | 4.88542 | 1.58632 | 0.71744 |
| H | 6.03252 | 0.74779 | -0.35500 |
| H | 4.46147 | -2.02167 | 1.61427 |
| H | 6.01264 | -1.28021 | 1.15112 |
| H | 4.89895 | -0.42013 | 2.24250 |
| H | 5.41299 | -1.57285 | -1.28705 |
| H | 3.86496 | -2.31068 | -0.81152 |
| H | 3.88901 | -0.93407 | -1.92689 |

**47**

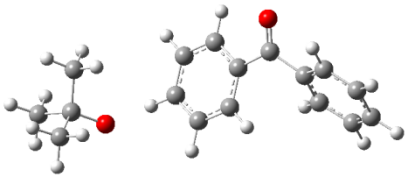


38
-809.4555653

| | | | |
|---|---|---|---|
| C | 1.61390 | 1.90790 | -0.10802 |
| C | 0.45450 | 2.16663 | 0.59449 |
| C | -0.59546 | 1.23259 | 0.69188 |
| C | -0.45718 | 0.03794 | -0.05718 |
| C | 0.70163 | -0.25512 | -0.75955 |
| C | 1.94230 | 0.53414 | -0.57169 |
| H | 2.36441 | 2.68717 | -0.22758 |
| H | 0.32333 | 3.15108 | 1.04453 |
| H | -1.50052 | 1.45464 | 1.24452 |
| H | 0.73321 | -1.14513 | -1.38372 |
| H | 2.54842 | 0.54320 | -1.48351 |
| C | -1.58237 | -0.93088 | -0.14808 |
| C | -3.00188 | -0.44084 | -0.04375 |
| C | -3.39821 | 0.79133 | -0.57520 |
| C | -3.96148 | -1.28320 | 0.52927 |
| C | -4.73861 | 1.17447 | -0.52987 |
| H | -2.65650 | 1.43992 | -1.03008 |
| C | -5.29534 | -0.89061 | 0.59581 |
| H | -3.64474 | -2.24464 | 0.92243 |
| C | -5.68574 | 0.33996 | 0.06285 |
| H | -5.04307 | 2.12580 | -0.95540 |
| H | -6.03097 | -1.54317 | 1.05596 |
| H | -6.72709 | 0.64491 | 0.10583 |
| O | -1.39886 | -2.13293 | -0.32434 |
| O | 2.81151 | -0.16256 | 0.44710 |
| C | 4.18080 | -0.37290 | 0.11834 |
| C | 4.89188 | 0.94380 | -0.22498 |
| C | 4.80495 | -0.96647 | 1.38065 |
| C | 4.32103 | -1.37697 | -1.03469 |
| H | 4.49315 | 1.39636 | -1.13818 |
| H | 4.76796 | 1.65937 | 0.59420 |
| H | 5.96237 | 0.76698 | -0.37765 |
| H | 4.29258 | -1.89510 | 1.65049 |
| H | 5.86717 | -1.18406 | 1.22497 |
| H | 4.70838 | -0.26266 | 2.21318 |
| H | 5.37707 | -1.59675 | -1.22694 |
| H | 3.81114 | -2.31028 | -0.77467 |
| H | 3.88414 | -0.99446 | -1.96206 |

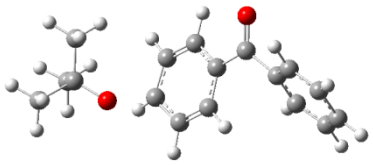
**Reactant Complex** for formation of **20** from **17** and **O*t*Bu anion**



38
-809.4824518

| | | | |
|---|---|---|---|
| C | 5.90193 | -1.42010 | 0.02160 |
| C | 4.79318 | -1.73406 | -0.76399 |
| C | 3.66907 | -0.90974 | -0.74735 |
| C | 3.65923 | 0.24456 | 0.04389 |
| C | 4.78326 | 0.56600 | 0.81397 |
| C | 5.89572 | -0.26930 | 0.81297 |
| H | 6.77226 | -2.06887 | 0.01567 |
| H | 4.80152 | -2.62126 | -1.38880 |
| H | 2.80972 | -1.15419 | -1.36418 |
| H | 4.76749 | 1.47110 | 1.41317 |
| H | 6.75856 | -0.02337 | 1.42362 |
| C | 2.50307 | 1.19815 | 0.04776 |
| C | 1.11253 | 0.68398 | -0.12574 |
| C | 0.73332 | -0.59745 | 0.29423 |
| C | 0.14899 | 1.54451 | -0.66902 |
| C | -0.59270 | -1.00795 | 0.16686 |
| H | 1.46582 | -1.26323 | 0.74098 |
| C | -1.16774 | 1.12001 | -0.80902 |
| H | 0.45199 | 2.53944 | -0.98113 |
| C | -1.55131 | -0.15970 | -0.39218 |
| H | -0.88248 | -1.99785 | 0.50725 |
| H | -1.90793 | 1.78775 | -1.24142 |
| O | 2.70894 | 2.39553 | 0.19672 |
| H | -2.59566 | -0.48531 | -0.49750 |
| O | -4.54872 | -1.03841 | -0.73092 |
| C | -5.37456 | -0.33290 | 0.10741 |
| C | -6.84924 | -0.41518 | -0.35246 |
| C | -5.29875 | -0.87962 | 1.55316 |
| C | -4.97885 | 1.16412 | 0.15015 |
| H | -6.93694 | -0.01654 | -1.37043 |
| H | -7.16895 | -1.46412 | -0.37135 |
| H | -7.53362 | 0.14473 | 0.29990 |
| H | -4.26500 | -0.81113 | 1.91369 |
| H | -5.94771 | -0.33615 | 2.25379 |
| H | -5.59002 | -1.93705 | 1.55871 |
| H | -5.63203 | 1.76183 | 0.80071 |
| H | -3.94814 | 1.26411 | 0.51111 |
| H | -5.02358 | 1.58126 | -0.86369 |

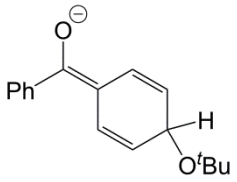
**Transition State** for formation of **20** from **17** and **O*t*Bu anion**

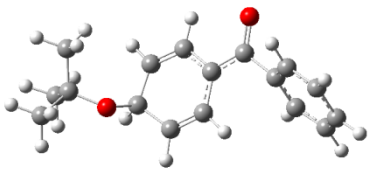


38
-809.4600997

| | | | |
|---|---|---|---|
| C | 5.54083 | -0.87473 | 0.67246 |
| C | 4.70913 | -1.43198 | -0.29855 |
| C | 3.49667 | -0.82040 | -0.61415 |
| C | 3.11460 | 0.36270 | 0.02706 |
| C | 3.96482 | 0.92910 | 0.98288 |
| C | 5.16588 | 0.30683 | 1.31482 |
| H | 6.48066 | -1.35642 | 0.92465 |
| H | 5.00346 | -2.34258 | -0.81114 |
| H | 2.85111 | -1.25270 | -1.37314 |
| H | 3.67065 | 1.85855 | 1.46169 |
| H | 5.81284 | 0.74436 | 2.06903 |
| C | 1.85371 | 1.09626 | -0.35089 |
| C | 0.62102 | 0.34939 | -0.58157 |
| C | 0.41122 | -0.96918 | -0.11147 |
| C | -0.42354 | 0.95545 | -1.31889 |
| C | -0.78423 | -1.62289 | -0.31925 |
| H | 1.20499 | -1.47992 | 0.42688 |
| C | -1.61291 | 0.30095 | -1.54958 |
| H | -0.24791 | 1.94090 | -1.74326 |
| C | -1.88447 | -0.95768 | -0.93565 |
| H | -0.91840 | -2.63474 | 0.05073 |
| H | -2.37668 | 0.77053 | -2.16339 |
| O | 1.91654 | 2.32615 | -0.46613 |
| H | -2.70292 | -1.55677 | -1.31458 |
| O | -3.02614 | -0.64814 | 0.70359 |
| C | -4.26385 | -0.02389 | 0.59785 |
| C | -5.12218 | -0.41166 | 1.81777 |
| C | -4.11003 | 1.51117 | 0.58044 |
| C | -5.02550 | -0.45663 | -0.67361 |
| H | -5.26698 | -1.49780 | 1.83918 |
| H | -4.60656 | -0.11668 | 2.73845 |
| H | -6.10752 | 0.07279 | 1.79911 |
| H | -3.50731 | 1.81781 | -0.28012 |
| H | -5.07922 | 2.02472 | 0.53059 |
| H | -3.59067 | 1.83540 | 1.48975 |
| H | -6.03563 | -0.03003 | -0.69919 |
| H | -4.50195 | -0.12898 | -1.57884 |
| H | -5.11221 | -1.54942 | -0.70414 |

**20**

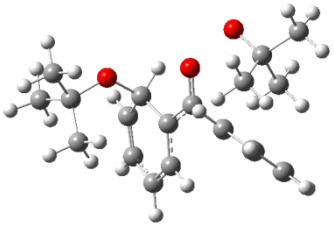


38
-809.4795644

| | | | |
|---|---|---|---|
| C | 5.43204 | -1.12117 | 0.51928 |
| C | 4.72102 | -1.30372 | -0.66650 |
| C | 3.54569 | -0.58682 | -0.89767 |
| C | 3.07364 | 0.32988 | 0.04798 |
| C | 3.80682 | 0.52124 | 1.22452 |
| C | 4.97006 | -0.20569 | 1.46723 |
| H | 6.34284 | -1.68347 | 0.70223 |
| H | 5.08192 | -2.00419 | -1.41407 |
| H | 2.99547 | -0.72991 | -1.82409 |
| H | 3.45228 | 1.24944 | 1.94865 |
| H | 5.51918 | -0.05602 | 2.39232 |
| C | 1.85189 | 1.19115 | -0.18644 |
| C | 0.61265 | 0.58761 | -0.51060 |
| C | 0.36875 | -0.83273 | -0.54524 |
| C | -0.50916 | 1.41761 | -0.86879 |
| C | -0.85493 | -1.36055 | -0.79822 |
| H | 1.19955 | -1.51501 | -0.37942 |
| C | -1.74431 | 0.92285 | -1.12673 |
| H | -0.32092 | 2.48341 | -0.98296 |
| C | -2.09349 | -0.52104 | -0.90262 |
| H | -0.98624 | -2.43947 | -0.83873 |
| H | -2.52909 | 1.59199 | -1.47339 |
| O | 2.02509 | 2.43361 | -0.05019 |
| H | -2.74414 | -0.89353 | -1.70586 |
| O | -2.82505 | -0.76348 | 0.34530 |
| C | -4.14885 | -0.24466 | 0.52930 |
| C | -4.79432 | -1.20422 | 1.53041 |
| C | -4.09057 | 1.15913 | 1.14439 |
| C | -4.97243 | -0.22886 | -0.76125 |
| H | -4.86294 | -2.20881 | 1.10176 |
| H | -4.18798 | -1.25561 | 2.44001 |
| H | -5.80003 | -0.86611 | 1.80037 |
| H | -3.66558 | 1.88407 | 0.44734 |
| H | -5.09577 | 1.49311 | 1.42530 |
| H | -3.46622 | 1.14060 | 2.04316 |
| H | -5.99919 | 0.06868 | -0.52567 |
| H | -4.57909 | 0.48289 | -1.49330 |
| H | -5.00134 | -1.22320 | -1.21880 |

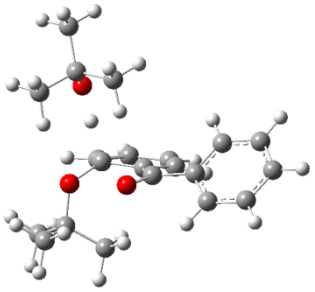
**Reactant Complex** for formation of **46** from **45** and **O*t*Bu anion**



52
-1042.5207433

| | | | |
|---|---|---|---|
| C | 1.07281 | 5.10002 | 0.36101 |
| C | 1.68861 | 3.98540 | 0.93030 |
| C | 1.23665 | 2.70132 | 0.62325 |
| C | 0.17238 | 2.51272 | -0.26521 |
| C | -0.42299 | 3.63716 | -0.84853 |
| C | 0.01229 | 4.92224 | -0.52979 |
| H | 1.41922 | 6.09989 | 0.60542 |
| H | 2.52172 | 4.11439 | 1.61530 |
| H | 1.71598 | 1.83406 | 1.06937 |
| H | -1.23300 | 3.49181 | -1.55827 |
| H | -0.47041 | 5.78514 | -0.97972 |
| C | -0.29778 | 1.13567 | -0.68885 |
| C | -0.68291 | 0.18653 | 0.28928 |
| C | -0.71291 | 0.49054 | 1.67968 |
| C | -0.99605 | -1.20924 | -0.19207 |
| C | -0.85428 | -0.47171 | 2.64813 |
| H | -0.61717 | 1.53019 | 1.98694 |
| C | -0.95642 | -2.20762 | 0.92822 |
| H | -0.25661 | -1.48103 | -0.95873 |
| C | -0.92092 | -1.85193 | 2.23437 |
| H | -0.86948 | -0.21203 | 3.70175 |
| H | -0.96816 | -3.25983 | 0.64851 |
| H | -0.91888 | -2.63041 | 2.99682 |
| O | -0.30219 | 0.92201 | -1.93067 |
| O | -2.20986 | -1.33190 | -1.01793 |
| C | -3.53968 | -1.30445 | -0.49775 |
| C | -4.39441 | -0.94070 | -1.71511 |
| C | -3.96176 | -2.69222 | 0.00739 |
| C | -3.75453 | -0.25994 | 0.59827 |
| H | -4.10082 | 0.04189 | -2.09758 |
| H | -4.25112 | -1.67882 | -2.51083 |
| H | -5.45678 | -0.91492 | -1.44955 |
| H | -3.43306 | -2.95731 | 0.92527 |
| H | -5.03948 | -2.71068 | 0.20812 |
| H | -3.73806 | -3.44585 | -0.75525 |
| H | -4.81339 | -0.25578 | 0.88240 |
| H | -3.15692 | -0.47942 | 1.48609 |
| H | -3.48241 | 0.73740 | 0.23934 |
| O | 3.40051 | -3.28512 | -0.99105 |
| C | 3.88156 | -2.12610 | -0.43806 |
| C | 2.73857 | -1.14255 | -0.09320 |
| C | 4.66464 | -2.41500 | 0.86680 |
| C | 4.84563 | -1.40351 | -1.41089 |
| H | 2.17864 | -0.88050 | -1.00003 |
| H | 2.03181 | -1.61457 | 0.60078 |
| H | 3.10172 | -0.21112 | 0.36481 |
| H | 5.49227 | -3.10173 | 0.64867 |
| H | 5.07740 | -1.50881 | 1.33184 |
| H | 4.00039 | -2.90402 | 1.58978 |
| H | 5.25244 | -0.46897 | -0.99977 |
| H | 5.68289 | -2.06836 | -1.65737 |
| H | 4.31267 | -1.17017 | -2.34048 |

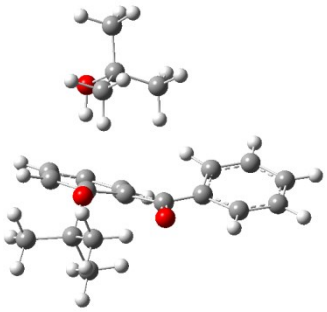
**Transition State** for formation of **46** from **45** and **O*t*Bu anion**



52
-1042.4790474

| | | | |
|---|---|---|---|
| C | -5.37397 | 0.13865 | -0.18284 |
| C | -4.54667 | 0.80351 | 0.72458 |
| C | -3.16229 | 0.64500 | 0.66699 |
| C | -2.55514 | -0.18413 | -0.29411 |
| C | -3.40535 | -0.81563 | -1.22026 |
| C | -4.78969 | -0.67198 | -1.16019 |
| H | -6.45229 | 0.26163 | -0.13906 |
| H | -4.98015 | 1.46138 | 1.47380 |
| H | -2.53238 | 1.18868 | 1.36620 |
| H | -2.94952 | -1.42352 | -1.99679 |
| H | -5.41783 | -1.19014 | -1.88081 |
| C | -1.06324 | -0.32483 | -0.46547 |
| C | -0.23878 | -0.46391 | 0.65471 |
| C | -0.79431 | -0.76309 | 1.96065 |
| C | 1.28272 | -0.35874 | 0.60340 |
| C | -0.05937 | -0.94428 | 3.09580 |
| H | -1.86645 | -0.93080 | 2.03297 |
| C | 1.98694 | -0.70780 | 1.83577 |
| H | 1.59283 | 1.03005 | 0.58765 |
| C | 1.39234 | -0.88904 | 3.04372 |
| H | -0.55935 | -1.20275 | 4.02686 |
| H | 3.07599 | -0.71482 | 1.76298 |
| H | 1.98059 | -1.01851 | 3.94955 |
| O | -0.66675 | -0.33243 | -1.70247 |
| O | 1.96121 | -0.84414 | -0.56368 |
| C | 2.05422 | -2.24805 | -0.84641 |
| C | 2.13176 | -2.31453 | -2.37125 |
| C | 3.33795 | -2.82143 | -0.23075 |
| C | 0.84841 | -3.05714 | -0.36653 |
| H | 1.21788 | -1.87238 | -2.77949 |
| H | 2.99499 | -1.74124 | -2.72850 |
| H | 2.23187 | -3.34909 | -2.71925 |
| H | 3.27342 | -2.83860 | 0.86106 |
| H | 3.50743 | -3.84692 | -0.58110 |
| H | 4.19916 | -2.20883 | -0.51947 |
| H | 0.99612 | -4.10928 | -0.63972 |
| H | 0.73334 | -2.98957 | 0.72024 |
| H | -0.06238 | -2.67916 | -0.83822 |
| O | 1.93276 | 2.20597 | 0.74563 |
| C | 1.63442 | 3.04320 | -0.33396 |
| C | 0.13173 | 2.98967 | -0.65760 |
| C | 2.01345 | 4.48271 | 0.04252 |
| C | 2.44658 | 2.62211 | -1.57193 |
| H | -0.16843 | 1.96337 | -0.89485 |
| H | -0.43952 | 3.31822 | 0.22011 |
| H | -0.12636 | 3.64276 | -1.50156 |
| H | 3.08126 | 4.53961 | 0.28285 |
| H | 1.80312 | 5.18473 | -0.77485 |
| H | 1.44594 | 4.79723 | 0.92570 |
| H | 2.20323 | 3.23144 | -2.45163 |
| H | 3.51768 | 2.72971 | -1.36111 |
| H | 2.25170 | 1.56989 | -1.80049 |

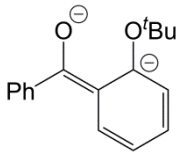
**Product Complex** of **46** and
**HO$^t$Bu**

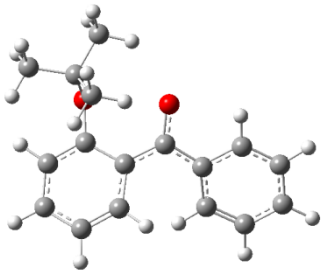


52
-1042.5068018

| | | | |
|---|---|---|---|
| C | -5.05918800 | -1.34905200 | -0.00939100 |
| C | -4.38141500 | -0.34867000 | 0.71092300 |
| C | -2.99614900 | -0.27772900 | 0.74411700 |
| C | -2.15624800 | -1.21411700 | 0.04601900 |
| C | -2.88548000 | -2.17942800 | -0.73318200 |
| C | -4.27158800 | -2.25087600 | -0.74113300 |
| H | -6.14356400 | -1.40435800 | -0.01725900 |
| H | -4.95197200 | 0.40676300 | 1.25004900 |
| H | -2.55223100 | 0.55562500 | 1.27622300 |
| H | -2.29723900 | -2.87065800 | -1.32609700 |
| H | -4.75472400 | -3.02528200 | -1.33671500 |
| C | -0.70863100 | -1.21775700 | -0.07930200 |
| C | 0.12580400 | -0.45412800 | 0.80250300 |
| C | -0.31116900 | 0.02650900 | 2.10004300 |
| C | 1.52528800 | -0.12723100 | 0.55037400 |
| C | 0.44222000 | 0.83522300 | 2.93312500 |
| H | -1.26982900 | -0.31410400 | 2.47309900 |
| C | 2.25682500 | 0.70335600 | 1.38587700 |
| H | 0.67576600 | 2.41094300 | 0.69156000 |
| C | 1.74356700 | 1.23778500 | 2.58402000 |
| H | 0.01441000 | 1.14300200 | 3.88673900 |
| H | 3.26749700 | 0.95014100 | 1.06574500 |
| H | 2.33460400 | 1.89923500 | 3.20827600 |
| O | -0.19708200 | -1.97709400 | -1.04903800 |
| O | 2.17370100 | -0.56027600 | -0.59764000 |
| C | 2.92431600 | -1.79654400 | -0.53190100 |
| C | 2.84133600 | -2.36823200 | -1.94296000 |
| C | 4.37273600 | -1.46693800 | -0.16054400 |
| C | 2.32926500 | -2.78432400 | 0.46946100 |
| H | 1.78893000 | -2.56909200 | -2.15959400 |
| H | 3.23072400 | -1.64146300 | -2.66512900 |
| H | 3.43187400 | -3.28762200 | -2.02386900 |
| H | 4.42556500 | -1.04541200 | 0.84831600 |
| H | 4.98893100 | -2.37281500 | -0.18576900 |
| H | 4.79033300 | -0.74033400 | -0.86608500 |
| H | 2.87601700 | -3.73191400 | 0.40278500 |
| H | 2.41781400 | -2.40687700 | 1.49404200 |
| H | 1.27513700 | -2.93226300 | 0.21505700 |
| O | 0.46961700 | 3.30050100 | 0.35630900 |
| C | -0.07679800 | 3.19688000 | -0.96365400 |
| C | -1.40681500 | 2.44755500 | -0.91058200 |
| C | -0.28060800 | 4.63423600 | -1.42888200 |
| C | 0.91000200 | 2.46457100 | -1.87326100 |
| H | -1.25406300 | 1.42533200 | -0.54356000 |
| H | -2.10324400 | 2.96316800 | -0.24033000 |
| H | -1.86098200 | 2.38955300 | -1.90625400 |
| H | 0.67481200 | 5.16866800 | -1.44478700 |
| H | -0.70882300 | 4.65360400 | -2.43572900 |
| H | -0.96167200 | 5.15797400 | -0.75027700 |
| H | 0.52421200 | 2.41107800 | -2.89709000 |
| H | 1.87046200 | 2.99161900 | -1.88838200 |
| H | 1.07776000 | 1.44390000 | -1.51203100 |

**46**



37
-808.9107073

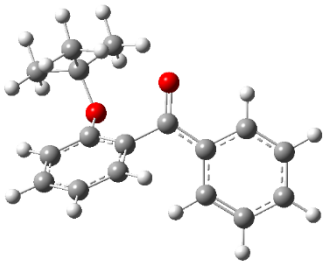
| | | | |
|---|---|---|---|
| C | -5.09273 | -0.40979 | -0.11715 |
| C | -4.36586 | 0.77381 | -0.36630 |
| C | -2.98319 | 0.81716 | -0.30598 |
| C | -2.18053 | -0.34127 | 0.01404 |
| C | -2.95579 | -1.54818 | 0.19609 |
| C | -4.34177 | -1.56767 | 0.14772 |
| H | -6.17765 | -0.42811 | -0.15316 |
| H | -4.90106 | 1.68619 | -0.62911 |
| H | -2.49893 | 1.75416 | -0.55951 |
| H | -2.40064 | -2.46135 | 0.38060 |
| H | -4.85764 | -2.51342 | 0.31667 |
| C | -0.74659 | -0.46026 | 0.03630 |
| C | 0.09885 | 0.71198 | 0.02797 |
| C | -0.33415 | 1.98764 | 0.54559 |
| C | 1.47571 | 0.74059 | -0.42306 |
| C | 0.41382 | 3.15243 | 0.48422 |
| H | -1.29254 | 2.02962 | 1.05221 |
| C | 2.20425 | 1.91917 | -0.50513 |
| C | 1.69919 | 3.15968 | -0.07928 |
| H | -0.00436 | 4.06722 | 0.90265 |
| H | 3.20258 | 1.85078 | -0.93248 |
| H | 2.28966 | 4.06697 | -0.15735 |
| O | -0.22876 | -1.69128 | 0.06450 |
| O | 2.09847 | -0.40260 | -0.90163 |
| C | 2.91605 | -1.17213 | 0.01309 |
| C | 2.79152 | -2.60737 | -0.48613 |
| C | 4.36247 | -0.68120 | -0.09312 |
| C | 2.42404 | -1.07492 | 1.45548 |
| H | 1.74084 | -2.89765 | -0.40297 |
| H | 3.10504 | -2.66740 | -1.53479 |
| H | 3.42389 | -3.28037 | 0.10349 |
| H | 4.44950 | 0.34781 | 0.26968 |
| H | 5.02376 | -1.31293 | 0.51069 |
| H | 4.70099 | -0.71585 | -1.13444 |
| H | 3.02221 | -1.74771 | 2.08072 |
| H | 2.53560 | -0.05638 | 1.84266 |
| H | 1.36937 | -1.36845 | 1.47553 |

Single Point Radical Anion
using Optimised Geometry
**46**

37
-808.8706291

| | | | |
|---|---|---|---|
| C | -5.09273100 | -0.40979100 | -0.11715000 |
| C | -4.36585900 | 0.77381000 | -0.36630500 |
| C | -2.98319200 | 0.81716000 | -0.30597700 |
| C | -2.18053100 | -0.34126600 | 0.01404400 |
| C | -2.95578500 | -1.54817800 | 0.19608700 |
| C | -4.34176800 | -1.56767000 | 0.14771600 |
| H | -6.17765200 | -0.42811000 | -0.15316300 |
| H | -4.90106100 | 1.68619100 | -0.62911300 |
| H | -2.49893200 | 1.75416200 | -0.55951500 |
| H | -2.40064000 | -2.46134800 | 0.38059500 |
| H | -4.85764100 | -2.51342200 | 0.31667100 |
| C | -0.74659400 | -0.46026300 | 0.03629600 |
| C | 0.09885300 | 0.71197600 | 0.02796500 |
| C | -0.33415200 | 1.98763800 | 0.54559200 |
| C | 1.47570900 | 0.74058600 | -0.42306000 |
| C | 0.41382500 | 3.15243300 | 0.48421600 |
| H | -1.29254200 | 2.02962200 | 1.05221200 |
| C | 2.20424600 | 1.91916700 | -0.50513000 |
| C | 1.69918900 | 3.15967600 | -0.07928100 |
| H | -0.00436100 | 4.06722000 | 0.90265500 |
| H | 3.20258300 | 1.85078400 | -0.93248100 |
| H | 2.28966200 | 4.06696900 | -0.15735400 |
| O | -0.22875800 | -1.69128000 | 0.06449700 |
| O | 2.09846900 | -0.40259600 | -0.90163000 |
| C | 2.91604600 | -1.17213500 | 0.01308800 |
| C | 2.79151900 | -2.60737400 | -0.48612900 |
| C | 4.36246900 | -0.68119800 | -0.09312000 |
| C | 2.42403600 | -1.07492500 | 1.45548100 |
| H | 1.74084000 | -2.89764900 | -0.40297300 |
| H | 3.10504100 | -2.66739600 | -1.53479200 |
| H | 3.42389100 | -3.28037300 | 0.10348900 |
| H | 4.44950100 | 0.34781400 | 0.26967800 |
| H | 5.02376100 | -1.31293000 | 0.51069300 |
| H | 4.70099300 | -0.71584700 | -1.13444500 |
| H | 3.02220900 | -1.74771000 | 2.08072100 |
| H | 2.53560000 | -0.05637700 | 1.84266200 |
| H | 1.36937300 | -1.36845300 | 1.47553300 |

**49**



37
-808.8808189

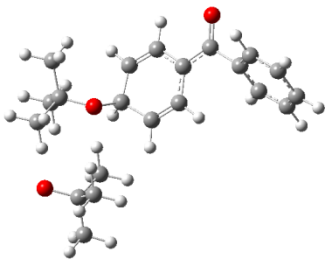
| | | | |
|---|---|---|---|
| C | -4.87949000 | -0.42050500 | -0.63585500 |
| C | -4.04384100 | 0.63688300 | -1.03822500 |
| C | -2.71673200 | 0.69602200 | -0.64534400 |
| C | -2.13944000 | -0.31170400 | 0.18834400 |
| C | -3.00330300 | -1.38500700 | 0.57242400 |
| C | -4.32935800 | -1.42858500 | 0.17128400 |
| H | -5.91823900 | -0.45902000 | -0.94804000 |
| H | -4.44040300 | 1.42271500 | -1.67747200 |
| H | -2.09965400 | 1.51890000 | -0.99476400 |
| H | -2.58828100 | -2.17165800 | 1.19452000 |
| H | -4.95281800 | -2.26164500 | 0.48971600 |
| C | -0.76400200 | -0.33218600 | 0.61315400 |
| C | 0.11345500 | 0.84941900 | 0.33623000 |
| C | -0.25291600 | 2.13361900 | 0.77352600 |
| C | 1.35792900 | 0.71827200 | -0.31305500 |
| C | 0.56972200 | 3.24199600 | 0.59024400 |
| H | -1.20829900 | 2.25054400 | 1.27979900 |
| C | 2.17770200 | 1.83077300 | -0.51814600 |
| C | 1.79583700 | 3.09073600 | -0.05944500 |
| H | 0.25641300 | 4.21671500 | 0.95243900 |
| H | 3.11088200 | 1.70057200 | -1.05765800 |
| H | 2.44568700 | 3.94567100 | -0.22073000 |
| O | -0.26809100 | -1.32522900 | 1.25366100 |
| O | 1.70715200 | -0.49604100 | -0.84827500 |
| C | 2.75596700 | -1.29979000 | -0.23306200 |
| C | 2.25650900 | -2.73285900 | -0.38164200 |
| C | 4.04916500 | -1.09201300 | -1.02039700 |
| C | 2.94716600 | -0.95676600 | 1.24069700 |
| H | 1.32098100 | -2.83808100 | 0.17436900 |
| H | 2.07483600 | -2.95816000 | -1.43767600 |
| H | 2.99908800 | -3.43952800 | 0.00230600 |
| H | 4.43118800 | -0.07468600 | -0.89482200 |
| H | 4.81834000 | -1.78716100 | -0.66788300 |
| H | 3.87657200 | -1.27432000 | -2.08555700 |
| H | 3.65718100 | -1.66631100 | 1.67713600 |
| H | 3.35217800 | 0.05142700 | 1.37168300 |
| H | 1.98563000 | -1.03564500 | 1.75515300 |

Single Point Dianion using
Optimised Geometry **49**

37
-808.9011778

| | | | |
|---|---|---|---|
| C | -4.87949000 | -0.42050500 | -0.63585500 |
| C | -4.04384100 | 0.63688300 | -1.03822500 |
| C | -2.71673200 | 0.69602200 | -0.64534400 |
| C | -2.13944000 | -0.31170400 | 0.18834400 |
| C | -3.00330300 | -1.38500700 | 0.57242400 |
| C | -4.32935800 | -1.42858500 | 0.17128400 |
| H | -5.91823900 | -0.45902000 | -0.94804000 |
| H | -4.44040300 | 1.42271500 | -1.67747200 |
| H | -2.09965400 | 1.51890000 | -0.99476400 |
| H | -2.58828100 | -2.17165800 | 1.19452000 |
| H | -4.95281800 | -2.26164500 | 0.48971600 |
| C | -0.76400200 | -0.33218600 | 0.61315400 |
| C | 0.11345500 | 0.84941900 | 0.33623000 |
| C | -0.25291600 | 2.13361900 | 0.77352600 |
| C | 1.35792900 | 0.71827200 | -0.31305500 |
| C | 0.56972200 | 3.24199600 | 0.59024400 |
| H | -1.20829900 | 2.25054400 | 1.27979900 |
| C | 2.17770200 | 1.83077300 | -0.51814600 |
| C | 1.79583700 | 3.09073600 | -0.05944500 |
| H | 0.25641300 | 4.21671500 | 0.95243900 |
| H | 3.11088200 | 1.70057200 | -1.05765800 |
| H | 2.44568700 | 3.94567100 | -0.22073000 |
| O | -0.26809100 | -1.32522900 | 1.25366100 |
| O | 1.70715200 | -0.49604100 | -0.84827500 |
| C | 2.75596700 | -1.29979000 | -0.23306200 |
| C | 2.25650900 | -2.73285900 | -0.38164200 |
| C | 4.04916500 | -1.09201300 | -1.02039700 |
| C | 2.94716600 | -0.95676600 | 1.24069700 |
| H | 1.32098100 | -2.83808100 | 0.17436900 |
| H | 2.07483600 | -2.95816000 | -1.43767600 |
| H | 2.99908800 | -3.43952800 | 0.00230600 |
| H | 4.43118800 | -0.07468600 | -0.89482200 |
| H | 4.81834000 | -1.78716100 | -0.66788300 |
| H | 3.87657200 | -1.27432000 | -2.08555700 |
| H | 3.65718100 | -1.66631100 | 1.67713600 |
| H | 3.35217800 | 0.05142700 | 1.37168300 |
| H | 1.98563000 | -1.03564500 | 1.75515300 |

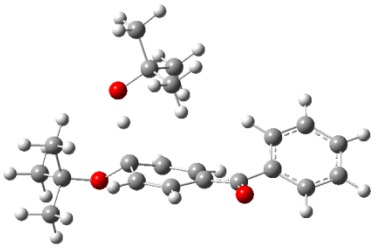
**Reactant Complex** for formation of **24** from **20** and **O*t*Bu anion**



52
-1042.5299146

| | | | |
|---|---|---|---|
| C | -6.20090 | 2.02091 | 0.95151 |
| C | -5.19761 | 2.46783 | 0.09198 |
| C | -4.28256 | 1.56288 | -0.44871 |
| C | -4.36398 | 0.19923 | -0.14634 |
| C | -5.38998 | -0.24139 | 0.69773 |
| C | -6.29448 | 0.66087 | 1.25402 |
| H | -6.90877 | 2.72568 | 1.37753 |
| H | -5.12643 | 3.52212 | -0.15948 |
| H | -3.50269 | 1.91441 | -1.11911 |
| H | -5.46938 | -1.30313 | 0.91434 |
| H | -7.07479 | 0.30444 | 1.92037 |
| C | -3.44191 | -0.82747 | -0.76705 |
| C | -2.04136 | -0.66037 | -0.67696 |
| C | -1.37771 | 0.37039 | 0.08652 |
| C | -1.16865 | -1.55071 | -1.40276 |
| C | -0.02888 | 0.45577 | 0.18812 |
| H | -1.98010 | 1.11828 | 0.59737 |
| C | 0.18263 | -1.49162 | -1.32579 |
| H | -1.63867 | -2.26372 | -2.07765 |
| C | 0.90073 | -0.58472 | -0.36468 |
| H | 0.42866 | 1.25979 | 0.76077 |
| H | 0.78485 | -2.14027 | -1.95880 |
| O | -4.01354 | -1.80342 | -1.33251 |
| H | 1.76196 | -0.10513 | -0.84957 |
| O | 1.43592 | -1.28049 | 0.80248 |
| C | 2.52872 | -2.20309 | 0.66497 |
| C | 3.26009 | -2.12434 | 2.00580 |
| C | 1.98152 | -3.62213 | 0.46637 |
| C | 3.50246 | -1.83778 | -0.45827 |
| H | 3.67462 | -1.12117 | 2.14607 |
| H | 2.56427 | -2.33586 | 2.82428 |
| H | 4.07780 | -2.85177 | 2.04539 |
| H | 1.47434 | -3.72085 | -0.49612 |
| H | 2.79579 | -4.35454 | 0.50723 |
| H | 1.26249 | -3.85544 | 1.25855 |
| H | 4.32616 | -2.56061 | -0.45066 |
| H | 3.03020 | -1.89102 | -1.44525 |
| H | 3.93604 | -0.84016 | -0.31397 |
| O | 5.58503 | 1.05348 | -0.00816 |
| C | 4.64513 | 2.04276 | -0.13615 |
| C | 3.52141 | 1.89341 | 0.91913 |
| C | 5.27489 | 3.44660 | 0.04408 |
| C | 3.98281 | 2.00556 | -1.53588 |
| H | 3.03578 | 0.91566 | 0.81142 |
| H | 3.95883 | 1.94288 | 1.92462 |
| H | 2.75033 | 2.67275 | 0.83733 |
| H | 6.06435 | 3.59104 | -0.70388 |
| H | 4.54455 | 4.26143 | -0.05983 |
| H | 5.73315 | 3.51698 | 1.03845 |
| H | 3.20385 | 2.77007 | -1.66479 |
| H | 4.74909 | 2.15586 | -2.30653 |
| H | 3.53006 | 1.02023 | -1.69831 |

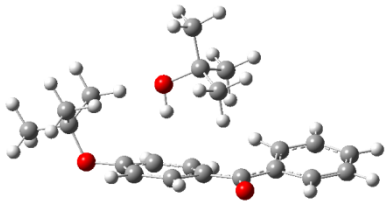
**Transition State** for formation of **24** from **20** and **O*t*Bu anion**



52
-1042.4942279

| | | | |
|---|---|---|---|
| C | 5.78637 | 0.41966 | -1.15973 |
| C | 4.56433 | 1.09537 | -1.12938 |
| C | 3.45989 | 0.52878 | -0.49443 |
| C | 3.54209 | -0.72998 | 0.12591 |
| C | 4.78754 | -1.37928 | 0.11420 |
| C | 5.89113 | -0.82260 | -0.52953 |
| H | 6.64696 | 0.86117 | -1.65393 |
| H | 4.47336 | 2.07521 | -1.59114 |
| H | 2.52083 | 1.07533 | -0.45775 |
| H | 4.87148 | -2.33317 | 0.62678 |
| H | 6.83861 | -1.35550 | -0.53509 |
| C | 2.40167 | -1.34314 | 0.89360 |
| C | 1.09680 | -1.21430 | 0.42137 |
| C | 0.69680 | -0.74582 | -0.90622 |
| C | -0.02799 | -1.65507 | 1.24430 |
| C | -0.60051 | -0.51529 | -1.22599 |
| H | 1.45891 | -0.60327 | -1.66954 |
| C | -1.32037 | -1.40514 | 0.91038 |
| H | 0.20836 | -2.16514 | 2.17533 |
| C | -1.71768 | -0.58995 | -0.26193 |
| H | -0.85226 | -0.19495 | -2.23840 |
| H | -2.10194 | -1.74913 | 1.58809 |
| O | 2.73043 | -1.95449 | 1.99021 |
| H | -1.95906 | 0.86199 | 0.04933 |
| O | -2.85772 | -1.13635 | -1.01053 |
| C | -4.17420 | -1.15363 | -0.46491 |
| C | -5.10196 | -0.84028 | -1.64300 |
| C | -4.48334 | -2.56798 | 0.04975 |
| C | -4.40909 | -0.12815 | 0.64475 |
| H | -4.90798 | 0.17237 | -2.01144 |
| H | -4.91907 | -1.54706 | -2.45926 |
| H | -6.15469 | -0.91260 | -1.34847 |
| H | -3.82996 | -2.83337 | 0.88502 |
| H | -5.52382 | -2.64088 | 0.38755 |
| H | -4.32648 | -3.29685 | -0.75223 |
| H | -5.46138 | -0.17348 | 0.94828 |
| H | -3.79028 | -0.33289 | 1.52296 |
| H | -4.17283 | 0.88118 | 0.30269 |
| O | -2.18940 | 2.00964 | 0.18741 |
| C | -1.05391 | 2.79682 | 0.43933 |
| C | -0.27656 | 3.06761 | -0.85974 |
| C | -1.52813 | 4.13292 | 1.02495 |
| C | -0.12562 | 2.10050 | 1.44538 |
| H | 0.06092 | 2.11871 | -1.28925 |
| H | -0.92741 | 3.56992 | -1.58522 |
| H | 0.59992 | 3.70365 | -0.68066 |
| H | -2.07412 | 3.95806 | 1.95870 |
| H | -0.68639 | 4.80463 | 1.23490 |
| H | -2.20363 | 4.63186 | 0.32062 |
| H | 0.74611 | 2.72357 | 1.68328 |
| H | -0.67109 | 1.89911 | 2.37540 |
| H | 0.22686 | 1.14490 | 1.04235 |

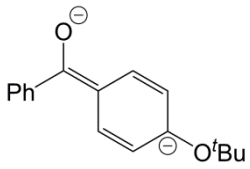
**Product Complex** of **24** and **HO$^t$Bu**

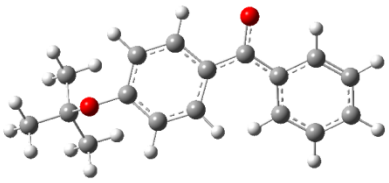


52
-1042.5214805

| | | | |
|---|---|---|---|
| C | 5.49302 | -0.79425 | -1.43145 |
| C | 4.20920 | -0.89572 | -1.99563 |
| C | 3.05680 | -0.89344 | -1.22192 |
| C | 3.09117 | -0.79258 | 0.21819 |
| C | 4.42263 | -0.62602 | 0.75421 |
| C | 5.56122 | -0.64100 | -0.03494 |
| H | 6.38653 | -0.80790 | -2.04793 |
| H | 4.10231 | -0.96489 | -3.07795 |
| H | 2.11436 | -0.91082 | -1.75274 |
| H | 4.50156 | -0.49598 | 1.82758 |
| H | 6.53317 | -0.52680 | 0.44514 |
| C | 1.99714 | -0.76605 | 1.14669 |
| C | 0.62852 | -1.03036 | 0.79838 |
| C | 0.10469 | -1.60502 | -0.41591 |
| C | -0.37866 | -0.78054 | 1.80242 |
| C | -1.25479 | -1.78303 | -0.63008 |
| H | 0.77325 | -1.98197 | -1.17803 |
| C | -1.73696 | -0.96430 | 1.57161 |
| H | -0.03239 | -0.42849 | 2.76729 |
| C | -2.20602 | -1.42824 | 0.33729 |
| H | -1.59857 | -2.22838 | -1.56239 |
| H | -2.45703 | -0.74471 | 2.35854 |
| O | 2.26235 | -0.46806 | 2.42553 |
| H | -0.90555 | 1.06098 | 0.42430 |
| O | -3.56237 | -1.65624 | 0.11620 |
| C | -4.34686 | -0.56858 | -0.42872 |
| C | -5.73157 | -1.17724 | -0.61933 |
| C | -4.40247 | 0.59667 | 0.55793 |
| C | -3.77347 | -0.10513 | -1.76664 |
| H | -5.68089 | -2.02227 | -1.31304 |
| H | -6.12096 | -1.53592 | 0.33863 |
| H | -6.42544 | -0.43372 | -1.02272 |
| H | -3.41176 | 1.03992 | 0.69266 |
| H | -5.07634 | 1.37210 | 0.17843 |
| H | -4.77642 | 0.25391 | 1.52850 |
| H | -4.42880 | 0.65413 | -2.20594 |
| H | -2.77958 | 0.33136 | -1.63162 |
| H | -3.70010 | -0.94768 | -2.46234 |
| O | -1.13420 | 1.94238 | 0.08095 |
| C | 0.07747 | 2.68807 | -0.09801 |
| C | 0.89043 | 2.06543 | -1.23180 |
| C | -0.36498 | 4.10152 | -0.45783 |
| C | 0.88604 | 2.67634 | 1.19923 |
| H | 1.16678 | 1.04069 | -0.96327 |
| H | 0.30232 | 2.05121 | -2.15609 |
| H | 1.81176 | 2.63134 | -1.41114 |
| H | -0.95763 | 4.53402 | 0.35488 |
| H | 0.50563 | 4.74093 | -0.63391 |
| H | -0.97615 | 4.08778 | -1.36633 |
| H | 1.79709 | 3.27542 | 1.08775 |
| H | 0.29105 | 3.10003 | 2.01607 |
| H | 1.18036 | 1.65198 | 1.46223 |

**24**



37
-808.9229047

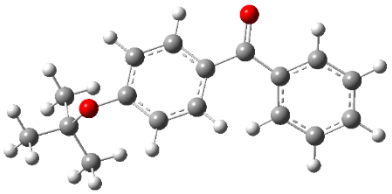
| | | | |
|---|---|---|---|
| C | -5.45312 | -1.52396 | 0.16393 |
| C | -4.14562 | -2.04807 | 0.18962 |
| C | -3.02194 | -1.23778 | 0.14052 |
| C | -3.10816 | 0.20324 | 0.04794 |
| C | -4.46341 | 0.70752 | 0.11245 |
| C | -5.57214 | -0.12124 | 0.14823 |
| H | -6.32499 | -2.17024 | 0.19022 |
| H | -4.00160 | -3.12561 | 0.27037 |
| H | -2.05665 | -1.71947 | 0.24091 |
| H | -4.58352 | 1.78516 | 0.11932 |
| H | -6.56393 | 0.33148 | 0.17049 |
| C | -2.04132 | 1.15131 | 0.00044 |
| C | -0.66494 | 0.79507 | -0.23020 |
| C | -0.15238 | -0.44020 | -0.76060 |
| C | 0.34119 | 1.80300 | -0.02021 |
| C | 1.20558 | -0.66735 | -0.94157 |
| H | -0.83434 | -1.20969 | -1.10126 |
| C | 1.69674 | 1.55944 | -0.19495 |
| H | -0.00109 | 2.78330 | 0.29223 |
| C | 2.15884 | 0.30900 | -0.62223 |
| H | 1.54398 | -1.61360 | -1.36116 |
| H | 2.42273 | 2.34918 | -0.00618 |
| O | -2.32538 | 2.44767 | 0.19524 |
| O | 3.51722 | 0.08234 | -0.84345 |
| C | 4.29390 | -0.46312 | 0.24760 |
| C | 5.70195 | -0.57785 | -0.32562 |
| C | 4.28068 | 0.48492 | 1.44587 |
| C | 3.76810 | -1.84055 | 0.64863 |
| H | 5.70008 | -1.23520 | -1.20055 |
| H | 6.06596 | 0.40772 | -0.63187 |
| H | 6.38874 | -0.98882 | 0.42031 |
| H | 3.27107 | 0.58597 | 1.85373 |
| H | 4.93602 | 0.09939 | 2.23356 |
| H | 4.63670 | 1.47685 | 1.14915 |
| H | 4.41575 | -2.27786 | 1.41535 |
| H | 2.75367 | -1.77041 | 1.05073 |
| H | 3.75300 | -2.50849 | -0.21887 |

Single Point Radical Anion
using Optimised Geometry
**24**

37
-808.8795541

| | | | |
|---|---|---|---|
| C | -5.45312300 | -1.52395700 | 0.16393200 |
| C | -4.14562400 | -2.04807000 | 0.18961700 |
| C | -3.02194000 | -1.23777500 | 0.14052100 |
| C | -3.10815800 | 0.20323700 | 0.04794100 |
| C | -4.46341400 | 0.70752300 | 0.11245500 |
| C | -5.57214000 | -0.12123600 | 0.14823300 |
| H | -6.32499400 | -2.17024000 | 0.19022300 |
| H | -4.00160300 | -3.12561300 | 0.27037100 |
| H | -2.05664600 | -1.71946800 | 0.24090800 |
| H | -4.58352000 | 1.78515800 | 0.11932000 |
| H | -6.56393000 | 0.33148000 | 0.17049200 |
| C | -2.04131600 | 1.15130600 | 0.00043700 |
| C | -0.66493800 | 0.79507300 | -0.23020100 |
| C | -0.15237800 | -0.44020200 | -0.76060000 |
| C | 0.34119000 | 1.80300400 | -0.02020800 |
| C | 1.20558300 | -0.66735400 | -0.94156900 |
| H | -0.83434000 | -1.20969200 | -1.10125900 |
| C | 1.69674500 | 1.55943900 | -0.19494600 |
| H | -0.00108600 | 2.78330500 | 0.29223300 |
| C | 2.15883800 | 0.30899900 | -0.62222600 |
| H | 1.54397900 | -1.61360500 | -1.36116000 |
| H | 2.42272800 | 2.34918400 | -0.00618200 |
| O | -2.32537900 | 2.44767000 | 0.19524300 |
| O | 3.51721500 | 0.08233500 | -0.84344800 |
| C | 4.29390000 | -0.46311900 | 0.24759600 |
| C | 5.70195200 | -0.57784900 | -0.32562000 |
| C | 4.28068300 | 0.48492200 | 1.44586800 |
| C | 3.76809600 | -1.84055500 | 0.64863000 |
| H | 5.70008300 | -1.23520100 | -1.20055400 |
| H | 6.06595800 | 0.40772000 | -0.63186500 |
| H | 6.38874400 | -0.98882400 | 0.42031400 |
| H | 3.27106600 | 0.58597100 | 1.85373100 |
| H | 4.93602000 | 0.09939500 | 2.23355800 |
| H | 4.63669800 | 1.47685100 | 1.14915000 |
| H | 4.41574600 | -2.27786000 | 1.41534800 |
| H | 2.75367300 | -1.77041300 | 1.05072700 |
| H | 3.75300200 | -2.50848700 | -0.21887200 |

**25**



37
-808.8876265

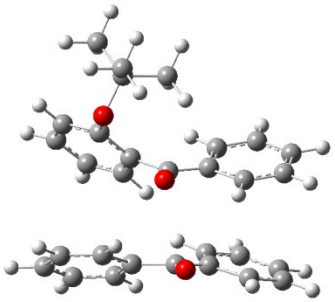
| | | | |
|---|---|---|---|
| C | -5.30743 | -1.62581 | 0.17207 |
| C | -3.99279 | -2.06245 | 0.37983 |
| C | -2.92481 | -1.17485 | 0.32528 |
| C | -3.12072 | 0.20545 | 0.05412 |
| C | -4.46551 | 0.63123 | -0.11331 |
| C | -5.52643 | -0.26318 | -0.06608 |
| H | -6.13713 | -2.32466 | 0.21071 |
| H | -3.79923 | -3.10925 | 0.60150 |
| H | -1.92848 | -1.54746 | 0.53913 |
| H | -4.64224 | 1.68750 | -0.28737 |
| H | -6.53949 | 0.10311 | -0.21541 |
| C | -2.06691 | 1.21913 | 0.02667 |
| C | -0.65164 | 0.87227 | -0.17069 |
| C | -0.18503 | -0.28980 | -0.83136 |
| C | 0.33238 | 1.80812 | 0.23030 |
| C | 1.17155 | -0.52334 | -1.02520 |
| H | -0.89504 | -0.99982 | -1.24217 |
| C | 1.68896 | 1.57348 | 0.04174 |
| H | -0.00343 | 2.73013 | 0.69363 |
| C | 2.12369 | 0.39390 | -0.56941 |
| H | 1.50662 | -1.41146 | -1.55445 |
| H | 2.42668 | 2.30495 | 0.36151 |
| O | -2.38155 | 2.45535 | 0.18532 |
| O | 3.46756 | 0.18562 | -0.81997 |
| C | 4.25410 | -0.50302 | 0.18762 |
| C | 5.64306 | -0.58312 | -0.43291 |
| C | 4.29070 | 0.30567 | 1.48268 |
| C | 3.69597 | -1.90172 | 0.44023 |
| H | 5.60734 | -1.14729 | -1.36953 |
| H | 6.02074 | 0.42176 | -0.64399 |
| H | 6.33625 | -1.08139 | 0.25094 |
| H | 3.29670 | 0.37913 | 1.93278 |
| H | 4.95647 | -0.18061 | 2.20230 |
| H | 4.66471 | 1.31627 | 1.29044 |
| H | 4.34861 | -2.43833 | 1.13560 |
| H | 2.69440 | -1.85476 | 0.87740 |
| H | 3.64378 | -2.46727 | -0.49542 |

Single Point Dianion using
Optimised Geometry **25**

37
-808.9145670

| | | | |
|---|---|---|---|
| C | -5.30742700 | -1.62580700 | 0.17206800 |
| C | -3.99279400 | -2.06244900 | 0.37983400 |
| C | -2.92480900 | -1.17485200 | 0.32528100 |
| C | -3.12072300 | 0.20545400 | 0.05411800 |
| C | -4.46550700 | 0.63122500 | -0.11330900 |
| C | -5.52643200 | -0.26318000 | -0.06607900 |
| H | -6.13712800 | -2.32465700 | 0.21071100 |
| H | -3.79923400 | -3.10924700 | 0.60150300 |
| H | -1.92847900 | -1.54745800 | 0.53912700 |
| H | -4.64224300 | 1.68750100 | -0.28737300 |
| H | -6.53948900 | 0.10310600 | -0.21541000 |
| C | -2.06691500 | 1.21912500 | 0.02667200 |
| C | -0.65163700 | 0.87226800 | -0.17069000 |
| C | -0.18503000 | -0.28979700 | -0.83135800 |
| C | 0.33237800 | 1.80811600 | 0.23030000 |
| C | 1.17154600 | -0.52334500 | -1.02519600 |
| H | -0.89503900 | -0.99982400 | -1.24217300 |
| C | 1.68895600 | 1.57348300 | 0.04174400 |
| H | -0.00342600 | 2.73012600 | 0.69363400 |
| C | 2.12368600 | 0.39389800 | -0.56941200 |
| H | 1.50662200 | -1.41145600 | -1.55444600 |
| H | 2.42668500 | 2.30494800 | 0.36151300 |
| O | -2.38155300 | 2.45535000 | 0.18532500 |
| O | 3.46755600 | 0.18561600 | -0.81997300 |
| C | 4.25409700 | -0.50301600 | 0.18762400 |
| C | 5.64306000 | -0.58312200 | -0.43290800 |
| C | 4.29069900 | 0.30567500 | 1.48267700 |
| C | 3.69596900 | -1.90172300 | 0.44023200 |
| H | 5.60733700 | -1.14728500 | -1.36953300 |
| H | 6.02073500 | 0.42176300 | -0.64399300 |
| H | 6.33625400 | -1.08139100 | 0.25094000 |
| H | 3.29669800 | 0.37913000 | 1.93278400 |
| H | 4.95646900 | -0.18060800 | 2.20229700 |
| H | 4.66471100 | 1.31626600 | 1.29044100 |
| H | 4.34861500 | -2.43833300 | 1.13560500 |
| H | 2.69439500 | -1.85475600 | 0.87739500 |
| H | 3.64377700 | -2.46727400 | -0.49542400 |

Singlet Complex between **46** and **17** (no counterions)



61
-1385.3661018

| | | | |
|---|---|---|---|
| C | 2.10253 | -3.76954 | 0.78342 |
| C | 1.39720 | -3.00080 | 1.72273 |
| C | 0.58367 | -1.94848 | 1.32329 |
| C | 0.42428 | -1.61693 | -0.05019 |
| C | 1.14512 | -2.40603 | -0.98594 |
| C | 1.96408 | -3.44836 | -0.57520 |
| H | 2.72950 | -4.59784 | 1.09980 |
| H | 1.47877 | -3.23342 | 2.78256 |
| H | 0.02522 | -1.40803 | 2.08153 |
| H | 1.03270 | -2.16232 | -2.03662 |
| H | 2.50757 | -4.02313 | -1.32283 |
| C | -0.54220 | -0.64943 | -0.56822 |
| C | -1.33043 | 0.18656 | 0.39015 |
| C | -0.69362 | 0.90351 | 1.41773 |
| C | -2.72927 | 0.35487 | 0.27123 |
| C | -1.37441 | 1.77149 | 2.26102 |
| H | 0.38173 | 0.79607 | 1.51077 |
| C | -3.41303 | 1.25139 | 1.09826 |
| C | -2.74772 | 1.96717 | 2.09105 |
| H | -0.82826 | 2.32412 | 3.02049 |
| H | -4.48245 | 1.36991 | 0.94749 |
| H | -3.29392 | 2.66292 | 2.72134 |
| O | -0.85046 | -0.63462 | -1.78819 |
| O | -3.47182 | -0.30979 | -0.68268 |
| C | -4.02768 | -1.60594 | -0.34906 |
| C | -4.73116 | -2.03086 | -1.63259 |
| C | -2.93220 | -2.60635 | 0.01316 |
| C | -5.03665 | -1.48084 | 0.79314 |
| H | -5.50158 | -1.30159 | -1.90179 |
| H | -4.00888 | -2.09630 | -2.45131 |
| H | -5.20366 | -3.00871 | -1.50055 |
| H | -2.39539 | -2.30264 | 0.91785 |
| H | -3.38481 | -3.58650 | 0.19637 |
| H | -2.20668 | -2.68921 | -0.80039 |
| H | -5.51561 | -2.44970 | 0.96600 |
| H | -4.54850 | -1.17105 | 1.72186 |
| H | -5.81166 | -0.74873 | 0.54353 |
| C | 5.07151 | -0.86219 | 0.95012 |
| C | 4.13341 | -0.07029 | 1.63389 |
| C | 3.09671 | 0.56066 | 0.95986 |
| C | 2.94245 | 0.45461 | -0.45052 |
| C | 3.88111 | -0.38842 | -1.11248 |
| C | 4.91927 | -1.01292 | -0.43371 |
| H | 5.88549 | -1.34689 | 1.48111 |
| H | 4.20139 | 0.03735 | 2.71461 |
| H | 2.37985 | 1.12279 | 1.54733 |
| H | 3.76668 | -0.51360 | -2.18370 |
| H | 5.61832 | -1.63657 | -0.98826 |
| C | 1.90285 | 1.06991 | -1.27272 |
| C | 1.13047 | 2.23977 | -0.82753 |
| C | 1.50163 | 3.12910 | 0.21229 |
| C | -0.02384 | 2.59422 | -1.57454 |

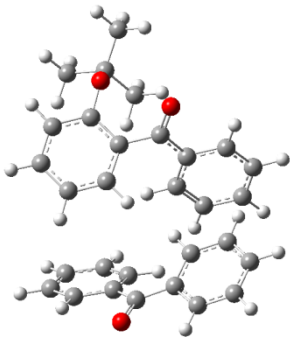
| | | | |
|---|---|---|---|
| C | 0.74713 | 4.26017 | 0.51103 |
| H | 2.42179 | 2.96797 | 0.76281 |
| C | -0.78115 | 3.71489 | -1.26184 |
| H | -0.31533 | 1.92808 | -2.37993 |
| C | -0.41194 | 4.56615 | -0.20943 |
| H | 1.07918 | 4.92107 | 1.30922 |
| H | -1.67474 | 3.93398 | -1.84338 |
| H | -0.99893 | 5.44877 | 0.02744 |
| O | 1.77896 | 0.69448 | -2.49333 |

Single Point Triplet, Using Singlet Complex (of **46** and **17**, no counterions) Optimised Geometry

61
-1385.3661697

| | | | |
|---|---|---|---|
| C | 2.10253 | -3.76954 | 0.78342 |
| C | 1.39720 | -3.00080 | 1.72273 |
| C | 0.58367 | -1.94848 | 1.32329 |
| C | 0.42428 | -1.61693 | -0.05019 |
| C | 1.14512 | -2.40603 | -0.98594 |
| C | 1.96408 | -3.44836 | -0.57520 |
| H | 2.72950 | -4.59784 | 1.09980 |
| H | 1.47877 | -3.23342 | 2.78256 |
| H | 0.02522 | -1.40803 | 2.08153 |
| H | 1.03270 | -2.16232 | -2.03662 |
| H | 2.50757 | -4.02313 | -1.32283 |
| C | -0.54220 | -0.64943 | -0.56822 |
| C | -1.33043 | 0.18656 | 0.39015 |
| C | -0.69362 | 0.90351 | 1.41773 |
| C | -2.72927 | 0.35487 | 0.27123 |
| C | -1.37441 | 1.77149 | 2.26102 |
| H | 0.38173 | 0.79607 | 1.51077 |
| C | -3.41303 | 1.25139 | 1.09826 |
| C | -2.74772 | 1.96717 | 2.09105 |
| H | -0.82826 | 2.32412 | 3.02049 |
| H | -4.48245 | 1.36991 | 0.94749 |
| H | -3.29392 | 2.66292 | 2.72134 |
| O | -0.85046 | -0.63462 | -1.78819 |
| O | -3.47182 | -0.30979 | -0.68268 |
| C | -4.02768 | -1.60594 | -0.34906 |
| C | -4.73116 | -2.03086 | -1.63259 |
| C | -2.93220 | -2.60635 | 0.01316 |
| C | -5.03665 | -1.48084 | 0.79314 |
| H | -5.50158 | -1.30159 | -1.90179 |
| H | -4.00888 | -2.09630 | -2.45131 |
| H | -5.20366 | -3.00871 | -1.50055 |
| H | -2.39539 | -2.30264 | 0.91785 |
| H | -3.38481 | -3.58650 | 0.19637 |
| H | -2.20668 | -2.68921 | -0.80039 |
| H | -5.51561 | -2.44970 | 0.96600 |
| H | -4.54850 | -1.17105 | 1.72186 |
| H | -5.81166 | -0.74873 | 0.54353 |
| C | 5.07151 | -0.86219 | 0.95012 |
| C | 4.13341 | -0.07029 | 1.63389 |
| C | 3.09671 | 0.56066 | 0.95986 |
| C | 2.94245 | 0.45461 | -0.45052 |
| C | 3.88111 | -0.38842 | -1.11248 |
| C | 4.91927 | -1.01292 | -0.43371 |
| H | 5.88549 | -1.34689 | 1.48111 |
| H | 4.20139 | 0.03735 | 2.71461 |
| H | 2.37985 | 1.12279 | 1.54733 |
| H | 3.76668 | -0.51360 | -2.18370 |
| H | 5.61832 | -1.63657 | -0.98826 |
| C | 1.90285 | 1.06991 | -1.27272 |
| C | 1.13047 | 2.23977 | -0.82753 |
| C | 1.50163 | 3.12910 | 0.21229 |
| C | -0.02384 | 2.59422 | -1.57454 |
| C | 0.74713 | 4.26017 | 0.51103 |
| H | 2.42179 | 2.96797 | 0.76281 |
| C | -0.78115 | 3.71489 | -1.26184 |
| H | -0.31533 | 1.92808 | -2.37993 |
| C | -0.41194 | 4.56615 | -0.20943 |
| H | 1.07918 | 4.92107 | 1.30922 |
| H | -1.67474 | 3.93398 | -1.84338 |
| H | -0.99893 | 5.44877 | 0.02744 |

| | | | |
|---|---|---|---|
| O | 1.77896 | 0.69448 | -2.49333 |



Triplet Complex between **46** and **17** (no counterions)

61
-1385.3909734

| | | | |
|---|---|---|---|
| C | -0.32054 | 3.28662 | 2.37139 |
| C | -0.21122 | 1.88413 | 2.36881 |
| C | 0.39681 | 1.21017 | 1.32235 |
| C | 0.92311 | 1.90722 | 0.19123 |
| C | 0.82347 | 3.33348 | 0.22639 |
| C | 0.21881 | 3.99367 | 1.28554 |
| H | -0.80278 | 3.80620 | 3.19335 |
| H | -0.61023 | 1.30982 | 3.20335 |
| H | 0.46433 | 0.12627 | 1.36772 |
| H | 1.23526 | 3.89132 | -0.60891 |
| H | 0.15728 | 5.08017 | 1.26766 |
| C | 1.60460 | 1.27876 | -0.91153 |
| C | 1.68977 | -0.21477 | -0.97196 |
| C | 0.52507 | -1.00170 | -0.93673 |
| C | 2.91599 | -0.89452 | -1.13417 |
| C | 0.55465 | -2.38759 | -1.06306 |
| H | -0.43464 | -0.50595 | -0.81708 |
| C | 2.94817 | -2.28208 | -1.29677 |
| C | 1.77543 | -3.03493 | -1.25676 |
| H | -0.37480 | -2.94828 | -1.01394 |
| H | 3.91111 | -2.76044 | -1.45031 |
| H | 1.81777 | -4.11354 | -1.37701 |
| O | 2.15890 | 1.96505 | -1.83958 |
| O | 4.10772 | -0.20402 | -1.19966 |
| C | 4.87802 | -0.01866 | 0.01465 |
| C | 6.04037 | 0.85665 | -0.43789 |
| C | 4.05891 | 0.69584 | 1.08674 |
| C | 5.39105 | -1.35991 | 0.53914 |
| H | 6.61915 | 0.34636 | -1.21391 |
| H | 5.65930 | 1.79716 | -0.84634 |
| H | 6.70095 | 1.07858 | 0.40540 |
| H | 3.18492 | 0.10576 | 1.38202 |
| H | 4.68180 | 0.85172 | 1.97370 |
| H | 3.70637 | 1.66420 | 0.72194 |
| H | 6.05863 | -1.18935 | 1.38962 |
| H | 4.56742 | -1.99607 | 0.87595 |
| H | 5.94849 | -1.88855 | -0.24073 |
| C | -4.01173 | 3.08433 | -1.04743 |
| C | -2.85430 | 2.49392 | -0.52758 |
| C | -2.79134 | 1.12157 | -0.31013 |
| C | -3.88740 | 0.27074 | -0.59621 |
| C | -5.03641 | 0.88767 | -1.15233 |
| C | -5.09821 | 2.26017 | -1.36384 |
| H | -4.06107 | 4.15610 | -1.21480 |
| H | -1.97805 | 3.09540 | -0.29241 |
| H | -1.85756 | 0.71881 | 0.06180 |
| H | -5.87739 | 0.25218 | -1.40981 |
| H | -6.00332 | 2.69515 | -1.78153 |
| C | -3.89504 | -1.19199 | -0.44141 |

| | | | |
|---|---|---|---|
| C | -2.95486 | -1.90242 | 0.43006 |
| C | -2.21782 | -1.32408 | 1.49677 |
| C | -2.82561 | -3.30787 | 0.26513 |
| C | -1.37371 | -2.08785 | 2.29391 |
| H | -2.32699 | -0.27031 | 1.72871 |
| C | -1.98050 | -4.06436 | 1.06663 |
| H | -3.40515 | -3.77845 | -0.52241 |
| C | -1.23025 | -3.46490 | 2.08523 |
| H | -0.82706 | -1.60059 | 3.09874 |
| H | -1.89836 | -5.13515 | 0.89356 |
| H | -0.56497 | -4.05538 | 2.70773 |
| O | -4.76940 | -1.87314 | -1.09315 |

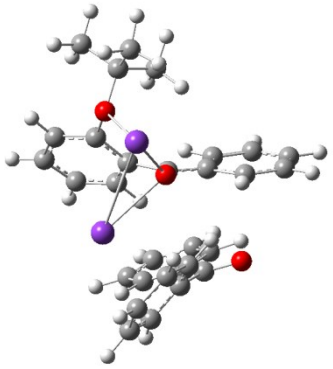
Single Point Singlet, Using Triplet Complex (of **46** and **17**, no counterions) Optimised Geometry

61
-1385.3505837

| | | | |
|---|---|---|---|
| C | -0.32054 | 3.28662 | 2.37139 |
| C | -0.21122 | 1.88413 | 2.36881 |
| C | 0.39681 | 1.21017 | 1.32235 |
| C | 0.92311 | 1.90722 | 0.19123 |
| C | 0.82347 | 3.33348 | 0.22639 |
| C | 0.21881 | 3.99367 | 1.28554 |
| H | -0.80278 | 3.80620 | 3.19335 |
| H | -0.61023 | 1.30982 | 3.20335 |
| H | 0.46433 | 0.12627 | 1.36772 |
| H | 1.23526 | 3.89132 | -0.60891 |
| H | 0.15728 | 5.08017 | 1.26766 |
| C | 1.60460 | 1.27876 | -0.91153 |
| C | 1.68977 | -0.21477 | -0.97196 |
| C | 0.52507 | -1.00170 | -0.93673 |
| C | 2.91599 | -0.89452 | -1.13417 |
| C | 0.55465 | -2.38759 | -1.06306 |
| H | -0.43464 | -0.50595 | -0.81708 |
| C | 2.94817 | -2.28208 | -1.29677 |
| C | 1.77543 | -3.03493 | -1.25676 |
| H | -0.37480 | -2.94828 | -1.01394 |
| H | 3.91111 | -2.76044 | -1.45031 |
| H | 1.81777 | -4.11354 | -1.37701 |
| O | 2.15890 | 1.96505 | -1.83958 |
| O | 4.10772 | -0.20402 | -1.19966 |
| C | 4.87802 | -0.01866 | 0.01465 |
| C | 6.04037 | 0.85665 | -0.43789 |
| C | 4.05891 | 0.69584 | 1.08674 |
| C | 5.39105 | -1.35991 | 0.53914 |
| H | 6.61915 | 0.34636 | -1.21391 |
| H | 5.65930 | 1.79716 | -0.84634 |
| H | 6.70095 | 1.07858 | 0.40540 |
| H | 3.18492 | 0.10576 | 1.38202 |
| H | 4.68180 | 0.85172 | 1.97370 |
| H | 3.70637 | 1.66420 | 0.72194 |
| H | 6.05863 | -1.18935 | 1.38962 |
| H | 4.56742 | -1.99607 | 0.87595 |
| H | 5.94849 | -1.88855 | -0.24073 |
| C | -4.01173 | 3.08433 | -1.04743 |
| C | -2.85430 | 2.49392 | -0.52758 |
| C | -2.79134 | 1.12157 | -0.31013 |
| C | -3.88740 | 0.27074 | -0.59621 |
| C | -5.03641 | 0.88767 | -1.15233 |
| C | -5.09821 | 2.26017 | -1.36384 |
| H | -4.06107 | 4.15610 | -1.21480 |
| H | -1.97805 | 3.09540 | -0.29241 |
| H | -1.85756 | 0.71881 | 0.06180 |
| H | -5.87739 | 0.25218 | -1.40981 |
| H | -6.00332 | 2.69515 | -1.78153 |
| C | -3.89504 | -1.19199 | -0.44141 |
| C | -2.95486 | -1.90242 | 0.43006 |
| C | -2.21782 | -1.32408 | 1.49677 |
| C | -2.82561 | -3.30787 | 0.26513 |
| C | -1.37371 | -2.08785 | 2.29391 |
| H | -2.32699 | -0.27031 | 1.72871 |
| C | -1.98050 | -4.06436 | 1.06663 |
| H | -3.40515 | -3.77845 | -0.52241 |
| C | -1.23025 | -3.46490 | 2.08523 |
| H | -0.82706 | -1.60059 | 3.09874 |
| H | -1.89836 | -5.13515 | 0.89356 |
| H | -0.56497 | -4.05538 | 2.70773 |

| | | | |
|---|---|---|---|
| O | -4.76940 | -1.87314 | -1.09315 |

Singlet Complex between **46** and **17** (counterions)



63
-2585.0745194

| | | | |
|---|---|---|---|
| C | 0.84795900 | -3.29825300 | -3.26774500 |
| C | 0.53231300 | -3.64211700 | -1.94275600 |
| C | 0.11927600 | -2.68372500 | -1.03084300 |
| C | -0.00776500 | -1.30897600 | -1.39430500 |
| C | 0.32516300 | -0.98573300 | -2.74259900 |
| C | 0.72775200 | -1.95809900 | -3.64906200 |
| H | 1.16959900 | -4.05471600 | -3.97717700 |
| H | 0.60425900 | -4.67898600 | -1.62069300 |
| H | -0.15424200 | -3.00602300 | -0.03094700 |
| H | 0.22719500 | 0.04712500 | -3.05826500 |
| H | 0.96615300 | -1.66527300 | -4.66968300 |
| C | -0.54563700 | -0.28369100 | -0.54555900 |
| C | -0.98688900 | -0.57553800 | 0.82709100 |
| C | -0.16853800 | -1.24201200 | 1.77087800 |
| C | -2.21947800 | -0.05441700 | 1.33195900 |
| C | -0.47472000 | -1.27824100 | 3.12826300 |
| H | 0.76111100 | -1.67785400 | 1.42422300 |
| C | -2.49964300 | -0.05477600 | 2.69481700 |
| C | -1.62647700 | -0.65061100 | 3.61227400 |
| H | 0.21376800 | -1.76853400 | 3.81188300 |
| H | -3.43550500 | 0.38649800 | 3.02764800 |
| H | -1.85587200 | -0.64080600 | 4.67279800 |
| O | -0.84456000 | 0.90260600 | -1.02369300 |
| O | -3.19201100 | 0.43687900 | 0.46729900 |
| C | -4.18303800 | -0.52993500 | -0.00412500 |
| C | -5.00347800 | 0.24401300 | -1.02947400 |
| C | -3.50988300 | -1.72790700 | -0.66849900 |
| C | -5.08052700 | -0.97928000 | 1.14740400 |
| H | -5.38824400 | 1.17301500 | -0.59471500 |
| H | -4.40635000 | 0.46540700 | -1.92032700 |
| H | -5.85773000 | -0.35529500 | -1.35489500 |
| H | -2.92351100 | -2.30722000 | 0.05108600 |
| H | -4.27879700 | -2.38205200 | -1.09141600 |
| H | -2.83795300 | -1.40058700 | -1.46728600 |
| H | -5.87329200 | -1.62500600 | 0.75809400 |
| H | -4.51766300 | -1.54588500 | 1.89326600 |
| H | -5.54358600 | -0.11515600 | 1.63472000 |
| C | 3.16934700 | -2.79780400 | 2.26519700 |
| C | 3.10285200 | -1.45203100 | 2.64281700 |
| C | 2.98854400 | -0.45040400 | 1.68605400 |
| C | 2.96587100 | -0.75369800 | 0.30232100 |
| C | 3.03834200 | -2.12033500 | -0.06020400 |
| C | 3.12931000 | -3.11733500 | 0.90312700 |
| H | 3.25026000 | -3.57848500 | 3.01522000 |
| H | 3.11491400 | -1.18063300 | 3.69511400 |
| H | 2.89779000 | 0.57007200 | 2.03803300 |
| H | 2.98918600 | -2.37117300 | -1.11418800 |
| H | 3.16159200 | -4.15796500 | 0.58967900 |
| C | 2.83845900 | 0.22276500 | -0.79799400 |
| C | 2.64539800 | 1.67569400 | -0.54236800 |

| | | | |
|---|---|---|---|
| C | 3.30126700 | 2.41416400 | 0.46651300 |
| C | 1.78955400 | 2.37505400 | -1.41902300 |
| C | 3.05268000 | 3.77460200 | 0.63446500 |
| H | 4.04192200 | 1.93545500 | 1.09773800 |
| C | 1.53549900 | 3.73295900 | -1.24081900 |
| H | 1.30154100 | 1.81714200 | -2.20891500 |
| C | 2.15176300 | 4.44145400 | -0.20409400 |
| H | 3.57739200 | 4.32109100 | 1.41255400 |
| H | 0.85278400 | 4.24369700 | -1.91486500 |
| H | 1.95604900 | 5.50020000 | -0.06701800 |
| O | 2.88215200 | -0.15624000 | -1.98904300 |
| K | -2.70145800 | 2.54503200 | -1.26602500 |
| K | 0.25361200 | 2.03240300 | 1.21810700 |

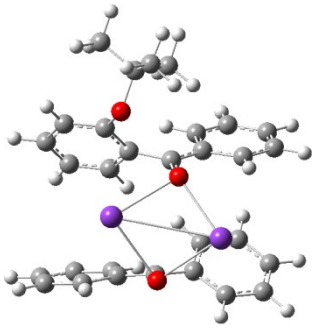
Single Point Triplet, Using Singlet Complex (of **46** and **17**, counterions) Optimised Geometry

63
-2585.0749126

| | | | |
|---|---|---|---|
| C | 0.84795900 | -3.29825300 | -3.26774500 |
| C | 0.53231300 | -3.64211700 | -1.94275600 |
| C | 0.11927600 | -2.68372500 | -1.03084300 |
| C | -0.00776500 | -1.30897600 | -1.39430500 |
| C | 0.32516300 | -0.98573300 | -2.74259900 |
| C | 0.72775200 | -1.95809900 | -3.64906200 |
| H | 1.16959900 | -4.05471600 | -3.97717700 |
| H | 0.60425900 | -4.67898600 | -1.62069300 |
| H | -0.15424200 | -3.00602300 | -0.03094700 |
| H | 0.22719500 | 0.04712500 | -3.05826500 |
| H | 0.96615300 | -1.66527300 | -4.66968300 |
| C | -0.54563700 | -0.28369100 | -0.54555900 |
| C | -0.98688900 | -0.57553800 | 0.82709100 |
| C | -0.16853800 | -1.24201200 | 1.77087800 |
| C | -2.21947800 | -0.05441700 | 1.33195900 |
| C | -0.47472000 | -1.27824100 | 3.12826300 |
| H | 0.76111100 | -1.67785400 | 1.42422300 |
| C | -2.49964300 | -0.05477600 | 2.69481700 |
| C | -1.62647700 | -0.65061100 | 3.61227400 |
| H | 0.21376800 | -1.76853400 | 3.81188300 |
| H | -3.43550500 | 0.38649800 | 3.02764800 |
| H | -1.85587200 | -0.64080600 | 4.67279800 |
| O | -0.84456000 | 0.90260600 | -1.02369300 |
| O | -3.19201100 | 0.43687900 | 0.46729900 |
| C | -4.18303800 | -0.52993500 | -0.00412500 |
| C | -5.00347800 | 0.24401300 | -1.02947400 |
| C | -3.50988300 | -1.72790700 | -0.66849900 |
| C | -5.08052700 | -0.97928000 | 1.14740400 |
| H | -5.38824400 | 1.17301500 | -0.59471500 |
| H | -4.40635000 | 0.46540700 | -1.92032700 |
| H | -5.85773000 | -0.35529500 | -1.35489500 |
| H | -2.92351100 | -2.30722000 | 0.05108600 |
| H | -4.27879700 | -2.38205200 | -1.09141600 |
| H | -2.83795300 | -1.40058700 | -1.46728600 |
| H | -5.87329200 | -1.62500600 | 0.75809400 |
| H | -4.51766300 | -1.54588500 | 1.89326600 |
| H | -5.54358600 | -0.11515600 | 1.63472000 |
| C | 3.16934700 | -2.79780400 | 2.26519700 |
| C | 3.10285200 | -1.45203100 | 2.64281700 |
| C | 2.98854400 | -0.45040400 | 1.68605400 |
| C | 2.96587100 | -0.75369800 | 0.30232100 |
| C | 3.03834200 | -2.12033500 | -0.06020400 |
| C | 3.12931000 | -3.11733500 | 0.90312700 |
| H | 3.25026000 | -3.57848500 | 3.01522000 |
| H | 3.11491400 | -1.18063300 | 3.69511400 |
| H | 2.89779000 | 0.57007200 | 2.03803300 |
| H | 2.98918600 | -2.37117300 | -1.11418800 |
| H | 3.16159200 | -4.15796500 | 0.58967900 |
| C | 2.83845900 | 0.22276500 | -0.79799400 |
| C | 2.64539800 | 1.67569400 | -0.54236800 |
| C | 3.30126700 | 2.41416400 | 0.46651300 |
| C | 1.78955400 | 2.37505400 | -1.41902300 |
| C | 3.05268000 | 3.77460200 | 0.63446500 |
| H | 4.04192200 | 1.93545500 | 1.09773800 |
| C | 1.53549900 | 3.73295900 | -1.24081900 |
| H | 1.30154100 | 1.81714200 | -2.20891500 |
| C | 2.15176300 | 4.44145400 | -0.20409400 |
| H | 3.57739200 | 4.32109100 | 1.41255400 |
| H | 0.85278400 | 4.24369700 | -1.91486500 |
| H | 1.95604900 | 5.50020000 | -0.06701800 |

| | | | |
|---|---|---|---|
| O | 2.88215200 | -0.15624000 | -1.98904300 |
| K | -2.70145800 | 2.54503200 | -1.26602500 |
| K | 0.25361200 | 2.03240300 | 1.21810700 |

Triplet Complex between **46** and **17** (counterions)



63
-2585.1100546

| | | | |
|---|---|---|---|
| C | -0.00789200 | 4.27420500 | -2.22961300 |
| C | -0.47176300 | 3.11282900 | -2.86804400 |
| C | -0.78548100 | 1.97159500 | -2.14556000 |
| C | -0.62693800 | 1.92397100 | -0.72995600 |
| C | -0.18540000 | 3.12361700 | -0.10134000 |
| C | 0.11424600 | 4.26231900 | -0.83471300 |
| H | 0.23528200 | 5.16331100 | -2.80221100 |
| H | -0.59710400 | 3.10501400 | -3.94806900 |
| H | -1.16137300 | 1.10048800 | -2.67455400 |
| H | -0.10962900 | 3.14464000 | 0.98085800 |
| H | 0.44939300 | 5.15675600 | -0.31433600 |
| C | -0.92076400 | 0.77163700 | 0.07370600 |
| C | -1.48707200 | -0.47045300 | -0.53914300 |
| C | -0.77228900 | -1.19743500 | -1.50802300 |
| C | -2.69427300 | -1.03677300 | -0.07018400 |
| C | -1.21140100 | -2.42956500 | -1.98644200 |
| H | 0.17403500 | -0.80086200 | -1.86441600 |
| C | -3.12466100 | -2.28436800 | -0.53209900 |
| C | -2.39211200 | -2.98252000 | -1.48975500 |
| H | -0.61287700 | -2.96710900 | -2.71591300 |
| H | -4.04065000 | -2.69889900 | -0.12249200 |
| H | -2.73678800 | -3.95183100 | -1.83590400 |
| O | -0.72149500 | 0.76699900 | 1.35523900 |
| O | -3.41730900 | -0.42351200 | 0.92619800 |
| C | -4.52085800 | 0.45417500 | 0.56212000 |
| C | -5.03655400 | 0.94439600 | 1.90884200 |
| C | -4.02540900 | 1.62338800 | -0.28330800 |
| C | -5.60623800 | -0.32487400 | -0.17791900 |
| H | -5.37672100 | 0.09989900 | 2.51558000 |
| H | -4.23999700 | 1.46642300 | 2.44680200 |
| H | -5.87392700 | 1.63306000 | 1.76536600 |
| H | -3.57859000 | 1.27665800 | -1.22107700 |
| H | -4.86918800 | 2.27623100 | -0.52795500 |
| H | -3.27235700 | 2.20223000 | 0.25870200 |
| H | -6.46930600 | 0.32604600 | -0.34659300 |
| H | -5.25277500 | -0.67675200 | -1.15142000 |
| H | -5.93200800 | -1.18661700 | 0.41302000 |
| C | 3.87552600 | 2.95228000 | -0.53037400 |
| C | 2.97627800 | 2.22818400 | -1.31470000 |
| C | 2.54826300 | 0.96581800 | -0.91544200 |
| C | 2.99773900 | 0.38586400 | 0.28520100 |
| C | 3.89315200 | 1.13945700 | 1.07325900 |
| C | 4.32998200 | 2.39922700 | 0.66964400 |
| H | 4.20395700 | 3.93957100 | -0.84021700 |
| H | 2.56917700 | 2.66229800 | -2.22398700 |
| H | 1.80314500 | 0.45493500 | -1.51460600 |
| H | 4.24950100 | 0.71096100 | 2.00709500 |
| H | 5.02966300 | 2.95054900 | 1.29187100 |
| C | 2.51863400 | -0.91761600 | 0.81032900 |
| C | 2.41340700 | -2.09702700 | -0.02462300 |
| C | 2.69141400 | -2.13652100 | -1.42175200 |

| | | | |
|---|---|---|---|
| C | 2.06698200 | -3.34034400 | 0.58085100 |
| C | 2.54477000 | -3.30314000 | -2.15525400 |
| H | 3.04108100 | -1.24534000 | -1.93045400 |
| C | 1.92364400 | -4.50352600 | -0.16586800 |
| H | 1.96273900 | -3.37889800 | 1.66148900 |
| C | 2.13764800 | -4.50056600 | -1.54746300 |
| H | 2.76046000 | -3.28549700 | -3.22059400 |
| H | 1.65652500 | -5.42877700 | 0.33877100 |
| H | 2.02018500 | -5.40784200 | -2.13101800 |
| O | 2.28697900 | -0.99744700 | 2.08591200 |
| K | 1.33593900 | 1.43415900 | 2.77617500 |
| K | -0.29345100 | -1.82670600 | 1.87715200 |

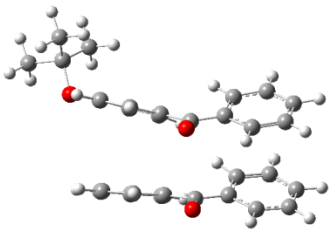
Single Point Singlet, Using Triplet Complex (of **46** and **17**, counterions) Optimised Geometry

63
-2585.0741665

| | | | |
|---|---|---|---|
| C | 0.00789200 | -4.27420500 | -2.22961300 |
| C | 0.47176300 | -3.11282900 | -2.86804400 |
| C | 0.78548100 | -1.97159500 | -2.14556000 |
| C | 0.62693800 | -1.92397100 | -0.72995600 |
| C | 0.18540000 | -3.12361700 | -0.10134000 |
| C | -0.11424600 | -4.26231900 | -0.83471300 |
| H | -0.23528200 | -5.16331100 | -2.80221100 |
| H | 0.59710400 | -3.10501400 | -3.94806900 |
| H | 1.16137300 | -1.10048800 | -2.67455400 |
| H | 0.10962900 | -3.14464000 | 0.98085800 |
| H | -0.44939300 | -5.15675600 | -0.31433600 |
| C | 0.92076400 | -0.77163700 | 0.07370600 |
| C | 1.48707200 | 0.47045300 | -0.53914300 |
| C | 0.77228900 | 1.19743500 | -1.50802300 |
| C | 2.69427300 | 1.03677300 | -0.07018400 |
| C | 1.21140100 | 2.42956500 | -1.98644200 |
| H | -0.17403500 | 0.80086200 | -1.86441600 |
| C | 3.12466100 | 2.28436800 | -0.53209900 |
| C | 2.39211200 | 2.98252000 | -1.48975500 |
| H | 0.61287700 | 2.96710900 | -2.71591300 |
| H | 4.04065000 | 2.69889900 | -0.12249200 |
| H | 2.73678800 | 3.95183100 | -1.83590400 |
| O | 0.72149500 | -0.76699900 | 1.35523900 |
| O | 3.41730900 | 0.42351200 | 0.92619800 |
| C | 4.52085800 | -0.45417500 | 0.56212000 |
| C | 5.03655400 | -0.94439600 | 1.90884200 |
| C | 4.02540900 | -1.62338800 | -0.28330800 |
| C | 5.60623800 | 0.32487400 | -0.17791900 |
| H | 5.37672100 | -0.09989900 | 2.51558000 |
| H | 4.23999700 | -1.46642300 | 2.44680200 |
| H | 5.87392700 | -1.63306000 | 1.76536600 |
| H | 3.57859000 | -1.27665800 | -1.22107700 |
| H | 4.86918800 | -2.27623100 | -0.52795500 |
| H | 3.27235700 | -2.20223000 | 0.25870200 |
| H | 6.46930600 | -0.32604600 | -0.34659300 |
| H | 5.25277500 | 0.67675200 | -1.15142000 |
| H | 5.93200800 | 1.18661700 | 0.41302000 |
| C | -3.87552600 | -2.95228000 | -0.53037400 |
| C | -2.97627800 | -2.22818400 | -1.31470000 |
| C | -2.54826300 | -0.96581800 | -0.91544200 |
| C | -2.99773900 | -0.38586400 | 0.28520100 |
| C | -3.89315200 | -1.13945700 | 1.07325900 |
| C | -4.32998200 | -2.39922700 | 0.66964400 |
| H | -4.20395700 | -3.93957100 | -0.84021700 |
| H | -2.56917700 | -2.66229800 | -2.22398700 |
| H | -1.80314500 | -0.45493500 | -1.51460600 |
| H | -4.24950100 | -0.71096100 | 2.00709500 |
| H | -5.02966300 | -2.95054900 | 1.29187100 |
| C | -2.51863400 | 0.91761600 | 0.81032900 |
| C | -2.41340700 | 2.09702700 | -0.02462300 |
| C | -2.69141400 | 2.13652100 | -1.42175200 |
| C | -2.06698200 | 3.34034400 | 0.58085100 |
| C | -2.54477000 | 3.30314000 | -2.15525400 |
| H | -3.04108100 | 1.24534000 | -1.93045400 |
| C | -1.92364400 | 4.50352600 | -0.16586800 |
| H | -1.96273900 | 3.37889800 | 1.66148900 |
| C | -2.13764800 | 4.50056600 | -1.54746300 |
| H | -2.76046000 | 3.28549700 | -3.22059400 |
| H | -1.65652500 | 5.42877700 | 0.33877100 |
| H | -2.02018500 | 5.40784200 | -2.13101800 |

| | | | |
|---|---|---|---|
| O | -2.28697900 | 0.99744700 | 2.08591200 |
| K | -1.33593900 | -1.43415900 | 2.77617500 |
| K | 0.29345100 | 1.82670600 | 1.87715200 |

Singlet Complex between **24** and **17** (no counterions)



61
-1385.3732444

| | | | |
|---|---|---|---|
| C | -5.10017 | 0.10807 | -1.78301 |
| C | -3.76676 | 0.02184 | -2.21120 |
| C | -2.73692 | 0.57166 | -1.46555 |
| C | -2.98117 | 1.25385 | -0.24409 |
| C | -4.33016 | 1.27894 | 0.19597 |
| C | -5.36184 | 0.73713 | -0.56205 |
| H | -5.90346 | -0.32088 | -2.37523 |
| H | -3.52580 | -0.52089 | -3.12278 |
| H | -1.71899 | 0.41086 | -1.80230 |
| H | -4.53687 | 1.75243 | 1.15040 |
| H | -6.38324 | 0.79465 | -0.19061 |
| C | -1.96905 | 1.85084 | 0.63146 |
| C | -0.64410 | 2.26220 | 0.14329 |
| C | -0.28313 | 2.45291 | -1.21365 |
| C | 0.33815 | 2.61285 | 1.10695 |
| C | 0.97589 | 2.92314 | -1.57549 |
| H | -1.01203 | 2.28629 | -1.99862 |
| C | 1.59841 | 3.06167 | 0.73998 |
| H | 0.07742 | 2.50569 | 2.15480 |
| C | 1.94118 | 3.22136 | -0.60815 |
| H | 1.20241 | 3.06709 | -2.62992 |
| H | 2.33019 | 3.28548 | 1.51370 |
| H | 2.92740 | 3.57442 | -0.89550 |
| O | -2.29962 | 2.16431 | 1.82861 |
| C | -3.90161 | -3.09579 | -0.56226 |
| C | -2.60549 | -3.07430 | -1.08985 |
| C | -1.58218 | -2.37755 | -0.45570 |
| C | -1.80414 | -1.67092 | 0.75355 |
| C | -3.11929 | -1.73718 | 1.28822 |
| C | -4.13827 | -2.41630 | 0.63972 |
| H | -4.69982 | -3.63426 | -1.06498 |
| H | -2.38472 | -3.61527 | -2.00771 |
| H | -0.58568 | -2.43308 | -0.87966 |
| H | -3.30901 | -1.22314 | 2.22497 |
| H | -5.13775 | -2.41244 | 1.07023 |
| C | -0.77718 | -0.99086 | 1.54770 |
| C | 0.57383 | -0.72137 | 1.01895 |
| C | 0.89696 | -0.52239 | -0.34298 |
| C | 1.62604 | -0.55506 | 1.94589 |
| C | 2.19377 | -0.25619 | -0.75409 |
| H | 0.10644 | -0.50421 | -1.08494 |
| C | 2.93156 | -0.29645 | 1.53748 |
| H | 1.39098 | -0.64142 | 3.00193 |
| C | 3.23064 | -0.16716 | 0.18172 |
| H | 2.41038 | -0.06828 | -1.80251 |
| H | 3.72869 | -0.18154 | 2.26794 |
| O | -0.99641 | -0.77195 | 2.78427 |
| O | 4.51887 | 0.14295 | -0.22581 |
| C | 5.41036 | -0.95125 | -0.55668 |
| C | 6.71110 | -0.25486 | -0.93742 |
| C | 5.62259 | -1.85762 | 0.65446 |
| C | 4.86605 | -1.75178 | -1.73842 |
| H | 6.54752 | 0.41004 | -1.79080 |
| H | 7.08034 | 0.33965 | -0.09642 |
| H | 7.47270 | -0.99227 | -1.20752 |

| | | | |
|---|---|---|---|
| H | 4.69266 | -2.35546 | 0.94392 |
| H | 6.36369 | -2.62667 | 0.41511 |
| H | 5.98640 | -1.27568 | 1.50731 |
| H | 5.59255 | -2.51558 | -2.03318 |
| H | 3.92875 | -2.25181 | -1.47912 |
| H | 4.68559 | -1.09284 | -2.59372 |

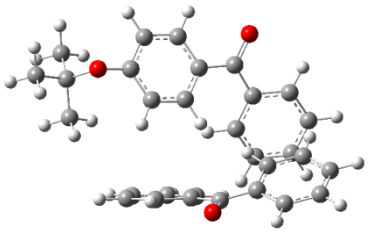
Single Point Triplet, Using Singlet Complex (of **24** and **17**, no counterions) Optimised Geometry

61
-1385.3745736

| | | | |
|---|---|---|---|
| C | -5.10016900 | 0.10807000 | -1.78300600 |
| C | -3.76676100 | 0.02184000 | -2.21120200 |
| C | -2.73691900 | 0.57166000 | -1.46554700 |
| C | -2.98116900 | 1.25384800 | -0.24408700 |
| C | -4.33016200 | 1.27893900 | 0.19597200 |
| C | -5.36183500 | 0.73712800 | -0.56204600 |
| H | -5.90346300 | -0.32088200 | -2.37522800 |
| H | -3.52579900 | -0.52089200 | -3.12278300 |
| H | -1.71898600 | 0.41086400 | -1.80230200 |
| H | -4.53687400 | 1.75243200 | 1.15039700 |
| H | -6.38323800 | 0.79464800 | -0.19061300 |
| C | -1.96905300 | 1.85083600 | 0.63146300 |
| C | -0.64409600 | 2.26219800 | 0.14329100 |
| C | -0.28312700 | 2.45290600 | -1.21364600 |
| C | 0.33815300 | 2.61285400 | 1.10695300 |
| C | 0.97589500 | 2.92314400 | -1.57549000 |
| H | -1.01203300 | 2.28629400 | -1.99861500 |
| C | 1.59841000 | 3.06166700 | 0.73997900 |
| H | 0.07741700 | 2.50569000 | 2.15479900 |
| C | 1.94117600 | 3.22136300 | -0.60815100 |
| H | 1.20240600 | 3.06709200 | -2.62991500 |
| H | 2.33018500 | 3.28548500 | 1.51369600 |
| H | 2.92739700 | 3.57442400 | -0.89550200 |
| O | -2.29962500 | 2.16431100 | 1.82861300 |
| C | -3.90160600 | -3.09578900 | -0.56225800 |
| C | -2.60548900 | -3.07429500 | -1.08984700 |
| C | -1.58218300 | -2.37754700 | -0.45569800 |
| C | -1.80413600 | -1.67091700 | 0.75355500 |
| C | -3.11928900 | -1.73717900 | 1.28821800 |
| C | -4.13826600 | -2.41629700 | 0.63972500 |
| H | -4.69981900 | -3.63426100 | -1.06497600 |
| H | -2.38472200 | -3.61526900 | -2.00770500 |
| H | -0.58567900 | -2.43308300 | -0.87966200 |
| H | -3.30901400 | -1.22313600 | 2.22497200 |
| H | -5.13774800 | -2.41244400 | 1.07022800 |
| C | -0.77717600 | -0.99086500 | 1.54770300 |
| C | 0.57383100 | -0.72136800 | 1.01894900 |
| C | 0.89696400 | -0.52239300 | -0.34297700 |
| C | 1.62604300 | -0.55505700 | 1.94588500 |
| C | 2.19377100 | -0.25618800 | -0.75409500 |
| H | 0.10643600 | -0.50421300 | -1.08493700 |
| C | 2.93156300 | -0.29645200 | 1.53748100 |
| H | 1.39098500 | -0.64142000 | 3.00192700 |
| C | 3.23064000 | -0.16715900 | 0.18171800 |
| H | 2.41038400 | -0.06827600 | -1.80251200 |
| H | 3.72868800 | -0.18154300 | 2.26794300 |
| O | -0.99641100 | -0.77195300 | 2.78427000 |
| O | 4.51886800 | 0.14294900 | -0.22581200 |
| C | 5.41035600 | -0.95124500 | -0.55667900 |
| C | 6.71109800 | -0.25485600 | -0.93742300 |
| C | 5.62259100 | -1.85761900 | 0.65445900 |
| C | 4.86605000 | -1.75178300 | -1.73842300 |
| H | 6.54751600 | 0.41004400 | -1.79080000 |
| H | 7.08034300 | 0.33965200 | -0.09642500 |
| H | 7.47270300 | -0.99227200 | -1.20752200 |
| H | 4.69266200 | -2.35546400 | 0.94391600 |
| H | 6.36368800 | -2.62667300 | 0.41511200 |
| H | 5.98640200 | -1.27568000 | 1.50730600 |
| H | 5.59254500 | -2.51558200 | -2.03318000 |
| H | 3.92874600 | -2.25181000 | -1.47912300 |

| | | | |
|---|---|---|---|
| H | 4.68559100 | -1.09283700 | -2.59371600 |

Triplet Complex between **24** and **17** (no counterions)



61
-1385.3969055

| | | | |
|---|---|---|---|
| C | -5.18824500 | -0.51908900 | -1.54246600 |
| C | -4.06327300 | 0.06402900 | -0.94806600 |
| C | -2.96486300 | -0.71104200 | -0.59161900 |
| C | -2.94200600 | -2.11075800 | -0.80562900 |
| C | -4.07861300 | -2.67333100 | -1.43751500 |
| C | -5.17712500 | -1.89676100 | -1.78860500 |
| H | -6.04617200 | 0.08651400 | -1.81862800 |
| H | -4.02590200 | 1.13550600 | -0.76201700 |
| H | -2.10498400 | -0.20374200 | -0.16970800 |
| H | -4.07005500 | -3.73958700 | -1.63950200 |
| H | -6.03542900 | -2.36869700 | -2.26117900 |
| C | -1.80497300 | -2.99490200 | -0.50637800 |
| C | -0.78170800 | -2.65136000 | 0.48241000 |
| C | -0.93801500 | -1.70815100 | 1.53194900 |
| C | 0.43825100 | -3.38012200 | 0.46460000 |
| C | 0.07292500 | -1.48052000 | 2.45830200 |
| H | -1.87148900 | -1.16578300 | 1.64174400 |
| C | 1.44197800 | -3.14854100 | 1.39538600 |
| H | 0.56712500 | -4.12911900 | -0.30988100 |
| C | 1.28123300 | -2.18590700 | 2.40003500 |
| H | -0.08770600 | -0.74601500 | 3.24501300 |
| H | 2.36593400 | -3.71982900 | 1.33745200 |
| H | 2.07057700 | -1.99781200 | 3.12156600 |
| O | -1.71610100 | -4.11542800 | -1.13051400 |
| C | -3.64670400 | 2.36329500 | 2.21569500 |
| C | -2.43072100 | 1.68621800 | 2.38093100 |
| C | -1.37236400 | 1.88417400 | 1.50429300 |
| C | -1.47981400 | 2.76876200 | 0.39583400 |
| C | -2.70995300 | 3.47311600 | 0.27093900 |
| C | -3.76254000 | 3.26841800 | 1.15283500 |
| H | -4.47236100 | 2.19785300 | 2.90071200 |
| H | -2.30271000 | 0.99827300 | 3.21447400 |
| H | -0.43879200 | 1.36685600 | 1.69848000 |
| H | -2.80768700 | 4.17830800 | -0.54804000 |
| H | -4.69182700 | 3.81549400 | 1.00916000 |
| C | -0.40755100 | 3.07059500 | -0.54713300 |
| C | 0.78378700 | 2.21087800 | -0.68046100 |
| C | 0.82183600 | 0.82805900 | -0.38847700 |
| C | 1.96297900 | 2.77354900 | -1.22190300 |
| C | 1.97271500 | 0.06945600 | -0.56993800 |
| H | -0.06762500 | 0.31341900 | -0.04424300 |
| C | 3.11819900 | 2.02057300 | -1.39985700 |
| H | 1.94670700 | 3.82291900 | -1.49825400 |
| C | 3.13957000 | 0.66598100 | -1.05621300 |
| H | 1.95967700 | -0.99405300 | -0.34086500 |
| H | 4.01798500 | 2.47295300 | -1.80916100 |
| O | -0.48044700 | 4.13198500 | -1.26896900 |
| O | 4.27575900 | -0.08917000 | -1.28713500 |
| C | 5.21309700 | -0.26131100 | -0.19241000 |
| C | 6.32828300 | -1.10129900 | -0.80256600 |
| C | 5.75037600 | 1.09295200 | 0.26696400 |
| C | 4.55534700 | -1.00388800 | 0.96817900 |
| H | 5.93079600 | -2.05784400 | -1.15455200 |

| | | | |
|---|---|---|---|
| H | 6.77742800 | -0.57569800 | -1.65058900 |
| H | 7.10634900 | -1.29660500 | -0.05892500 |
| H | 4.95601000 | 1.70797600 | 0.69990800 |
| H | 6.52185500 | 0.94521000 | 1.02891600 |
| H | 6.19184300 | 1.63405000 | -0.57606800 |
| H | 5.30007200 | -1.20540200 | 1.74486200 |
| H | 3.74623500 | -0.41663900 | 1.41183700 |
| H | 4.13783100 | -1.95604400 | 0.62573800 |

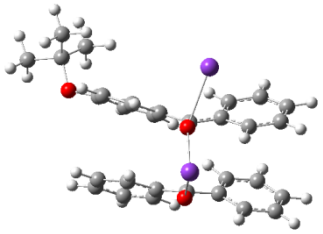
Single Point Singlet, Using Triplet Complex (of **24** and **17**, no counterions) Optimised Geometry

61
-1385.3571770

| | | | |
|---|---|---|---|
| C | -5.18824500 | -0.51908900 | -1.54246600 |
| C | -4.06327300 | 0.06402900 | -0.94806600 |
| C | -2.96486300 | -0.71104200 | -0.59161900 |
| C | -2.94200600 | -2.11075800 | -0.80562900 |
| C | -4.07861300 | -2.67333100 | -1.43751500 |
| C | -5.17712500 | -1.89676100 | -1.78860500 |
| H | -6.04617200 | 0.08651400 | -1.81862800 |
| H | -4.02590200 | 1.13550600 | -0.76201700 |
| H | -2.10498400 | -0.20374200 | -0.16970800 |
| H | -4.07005500 | -3.73958700 | -1.63950200 |
| H | -6.03542900 | -2.36869700 | -2.26117900 |
| C | -1.80497300 | -2.99490200 | -0.50637800 |
| C | -0.78170800 | -2.65136000 | 0.48241000 |
| C | -0.93801500 | -1.70815100 | 1.53194900 |
| C | 0.43825100 | -3.38012200 | 0.46460000 |
| C | 0.07292500 | -1.48052000 | 2.45830200 |
| H | -1.87148900 | -1.16578300 | 1.64174400 |
| C | 1.44197800 | -3.14854100 | 1.39538600 |
| H | 0.56712500 | -4.12911900 | -0.30988100 |
| C | 1.28123300 | -2.18590700 | 2.40003500 |
| H | -0.08770600 | -0.74601500 | 3.24501300 |
| H | 2.36593400 | -3.71982900 | 1.33745200 |
| H | 2.07057700 | -1.99781200 | 3.12156600 |
| O | -1.71610100 | -4.11542800 | -1.13051400 |
| C | -3.64670400 | 2.36329500 | 2.21569500 |
| C | -2.43072100 | 1.68621800 | 2.38093100 |
| C | -1.37236400 | 1.88417400 | 1.50429300 |
| C | -1.47981400 | 2.76876200 | 0.39583400 |
| C | -2.70995300 | 3.47311600 | 0.27093900 |
| C | -3.76254000 | 3.26841800 | 1.15283500 |
| H | -4.47236100 | 2.19785300 | 2.90071200 |
| H | -2.30271000 | 0.99827300 | 3.21447400 |
| H | -0.43879200 | 1.36685600 | 1.69848000 |
| H | -2.80768700 | 4.17830800 | -0.54804000 |
| H | -4.69182700 | 3.81549400 | 1.00916000 |
| C | -0.40755100 | 3.07059500 | -0.54713300 |
| C | 0.78378700 | 2.21087800 | -0.68046100 |
| C | 0.82183600 | 0.82805900 | -0.38847700 |
| C | 1.96297900 | 2.77354900 | -1.22190300 |
| C | 1.97271500 | 0.06945600 | -0.56993800 |
| H | -0.06762500 | 0.31341900 | -0.04424300 |
| C | 3.11819900 | 2.02057300 | -1.39985700 |
| H | 1.94670700 | 3.82291900 | -1.49825400 |
| C | 3.13957000 | 0.66598100 | -1.05621300 |
| H | 1.95967700 | -0.99405300 | -0.34086500 |
| H | 4.01798500 | 2.47295300 | -1.80916100 |
| O | -0.48044700 | 4.13198500 | -1.26896900 |
| O | 4.27575900 | -0.08917000 | -1.28713500 |
| C | 5.21309700 | -0.26131100 | -0.19241000 |
| C | 6.32828300 | -1.10129900 | -0.80256600 |
| C | 5.75037600 | 1.09295200 | 0.26696400 |
| C | 4.55534700 | -1.00388800 | 0.96817900 |
| H | 5.93079600 | -2.05784400 | -1.15455200 |
| H | 6.77742800 | -0.57569800 | -1.65058900 |
| H | 7.10634900 | -1.29660500 | -0.05892500 |
| H | 4.95601000 | 1.70797600 | 0.69990800 |
| H | 6.52185500 | 0.94521000 | 1.02891600 |
| H | 6.19184300 | 1.63405000 | -0.57606800 |
| H | 5.30007200 | -1.20540200 | 1.74486200 |
| H | 3.74623500 | -0.41663900 | 1.41183700 |

| | | | |
|---|---|---|---|
| H | 4.13783100 | -1.95604400 | 0.62573800 |

Singlet Complex between **24** and **17** (counterions)



63
-2585.0928644

| | | | |
|---|---|---|---|
| C | -4.73708400 | 1.40014600 | -2.21282300 |
| C | -3.39034100 | 1.39343500 | -2.59219900 |
| C | -2.38698500 | 1.51316500 | -1.64156800 |
| C | -2.69281300 | 1.64917600 | -0.27261000 |
| C | -4.05103800 | 1.61541600 | 0.09634100 |
| C | -5.05841400 | 1.50649100 | -0.85917300 |
| H | -5.51901500 | 1.30872200 | -2.96091000 |
| H | -3.12166600 | 1.26196800 | -3.63685500 |
| H | -1.35175300 | 1.44189800 | -1.95786100 |
| H | -4.29806000 | 1.69274600 | 1.15077600 |
| H | -6.09902800 | 1.49874200 | -0.54522000 |
| C | -1.68316700 | 1.75116300 | 0.80379600 |
| C | -0.34491400 | 2.34876500 | 0.56987400 |
| C | -0.02348800 | 3.17589200 | -0.52115500 |
| C | 0.64245400 | 2.15361900 | 1.55528700 |
| C | 1.23955800 | 3.75606700 | -0.63345500 |
| H | -0.77246200 | 3.40447800 | -1.27165500 |
| C | 1.90529200 | 2.71748000 | 1.43412700 |
| H | 0.39629000 | 1.52449100 | 2.40393400 |
| C | 2.21644900 | 3.52319700 | 0.33535000 |
| H | 1.45730900 | 4.40013500 | -1.48110800 |
| H | 2.65717500 | 2.52347400 | 2.19451400 |
| H | 3.20323600 | 3.96663900 | 0.23908000 |
| O | -2.03314700 | 1.51475700 | 1.99187000 |
| C | -3.54913600 | -2.21212900 | -2.53144000 |
| C | -2.22524300 | -1.93009200 | -2.89647100 |
| C | -1.28912300 | -1.50001100 | -1.96583900 |
| C | -1.61680700 | -1.32794200 | -0.58581300 |
| C | -2.96540900 | -1.65989600 | -0.23804000 |
| C | -3.89445500 | -2.07345800 | -1.18237700 |
| H | -4.27643300 | -2.54140000 | -3.26690200 |
| H | -1.91233200 | -2.05579400 | -3.93109300 |
| H | -0.27314800 | -1.34150000 | -2.30782200 |
| H | -3.25943700 | -1.56435000 | 0.80255200 |
| H | -4.91277300 | -2.28731300 | -0.86227800 |
| C | -0.70350700 | -0.97468700 | 0.47928700 |
| C | 0.70747400 | -0.66421200 | 0.24783800 |
| C | 1.22856600 | 0.00038100 | -0.89262300 |
| C | 1.63924700 | -0.94267200 | 1.27686200 |
| C | 2.57401600 | 0.31119200 | -1.01107600 |
| H | 0.55442700 | 0.35550200 | -1.66401200 |
| C | 2.99479300 | -0.64593400 | 1.15273500 |
| H | 1.26461800 | -1.39009500 | 2.19208700 |
| C | 3.47874100 | -0.02844100 | 0.00139500 |
| H | 2.93376300 | 0.86212400 | -1.87642600 |
| H | 3.68708800 | -0.87268500 | 1.96032600 |
| O | -1.06086300 | -1.27052800 | 1.71778400 |
| O | 4.80780500 | 0.34876800 | -0.09109300 |
| C | 5.74151400 | -0.57455100 | -0.70839000 |
| C | 7.07041900 | 0.16889500 | -0.65679900 |
| C | 5.81904800 | -1.87057300 | 0.09595500 |
| C | 5.34328300 | -0.86060600 | -2.15478500 |
| H | 6.99915700 | 1.10863000 | -1.21249100 |
| H | 7.33599800 | 0.39546100 | 0.38002200 |
| H | 7.86524800 | -0.43944000 | -1.09775100 |

| | | | |
|---|---|---|---|
| H | 4.86453300 | -2.40457300 | 0.07640300 |
| H | 6.58650700 | -2.52502400 | -0.32854400 |
| H | 6.07990700 | -1.65684300 | 1.13728500 |
| H | 6.10647000 | -1.48532300 | -2.62907800 |
| H | 4.38757000 | -1.39003900 | -2.20634100 |
| H | 5.25750500 | 0.07292700 | -2.71973400 |
| K | -0.86901500 | -3.79725000 | 0.94225600 |
| K | -2.36701700 | -0.35660300 | 3.66392100 |

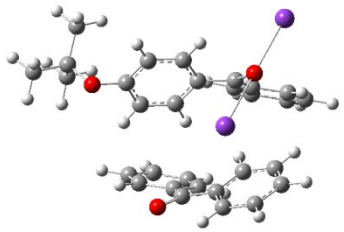
Single Point Triplet, Using Singlet Complex (of **24** and **17**, counterions) Optimised Geometry

63
-2585.0809371

| | | | |
|---|---|---|---|
| C | -4.73708400 | 1.40014600 | -2.21282300 |
| C | -3.39034100 | 1.39343500 | -2.59219900 |
| C | -2.38698500 | 1.51316500 | -1.64156800 |
| C | -2.69281300 | 1.64917600 | -0.27261000 |
| C | -4.05103800 | 1.61541600 | 0.09634100 |
| C | -5.05841400 | 1.50649100 | -0.85917300 |
| H | -5.51901500 | 1.30872200 | -2.96091000 |
| H | -3.12166600 | 1.26196800 | -3.63685500 |
| H | -1.35175300 | 1.44189800 | -1.95786100 |
| H | -4.29806000 | 1.69274600 | 1.15077600 |
| H | -6.09902800 | 1.49874200 | -0.54522000 |
| C | -1.68316700 | 1.75116300 | 0.80379600 |
| C | -0.34491400 | 2.34876500 | 0.56987400 |
| C | -0.02348800 | 3.17589200 | -0.52115500 |
| C | 0.64245400 | 2.15361900 | 1.55528700 |
| C | 1.23955800 | 3.75606700 | -0.63345500 |
| H | -0.77246200 | 3.40447800 | -1.27165500 |
| C | 1.90529200 | 2.71748000 | 1.43412700 |
| H | 0.39629000 | 1.52449100 | 2.40393400 |
| C | 2.21644900 | 3.52319700 | 0.33535000 |
| H | 1.45730900 | 4.40013500 | -1.48110800 |
| H | 2.65717500 | 2.52347400 | 2.19451400 |
| H | 3.20323600 | 3.96663900 | 0.23908000 |
| O | -2.03314700 | 1.51475700 | 1.99187000 |
| C | -3.54913600 | -2.21212900 | -2.53144000 |
| C | -2.22524300 | -1.93009200 | -2.89647100 |
| C | -1.28912300 | -1.50001100 | -1.96583900 |
| C | -1.61680700 | -1.32794200 | -0.58581300 |
| C | -2.96540900 | -1.65989600 | -0.23804000 |
| C | -3.89445500 | -2.07345800 | -1.18237700 |
| H | -4.27643300 | -2.54140000 | -3.26690200 |
| H | -1.91233200 | -2.05579400 | -3.93109300 |
| H | -0.27314800 | -1.34150000 | -2.30782200 |
| H | -3.25943700 | -1.56435000 | 0.80255200 |
| H | -4.91277300 | -2.28731300 | -0.86227800 |
| C | -0.70350700 | -0.97468700 | 0.47928700 |
| C | 0.70747400 | -0.66421200 | 0.24783800 |
| C | 1.22856600 | 0.00038100 | -0.89262300 |
| C | 1.63924700 | -0.94267200 | 1.27686200 |
| C | 2.57401600 | 0.31119200 | -1.01107600 |
| H | 0.55442700 | 0.35550200 | -1.66401200 |
| C | 2.99479300 | -0.64593400 | 1.15273500 |
| H | 1.26461800 | -1.39009500 | 2.19208700 |
| C | 3.47874100 | -0.02844100 | 0.00139500 |
| H | 2.93376300 | 0.86212400 | -1.87642600 |
| H | 3.68708800 | -0.87268500 | 1.96032600 |
| O | -1.06086300 | -1.27052800 | 1.71778400 |
| O | 4.80780500 | 0.34876800 | -0.09109300 |
| C | 5.74151400 | -0.57455100 | -0.70839000 |
| C | 7.07041900 | 0.16889500 | -0.65679900 |
| C | 5.81904800 | -1.87057300 | 0.09595500 |
| C | 5.34328300 | -0.86060600 | -2.15478500 |
| H | 6.99915700 | 1.10863000 | -1.21249100 |
| H | 7.33599800 | 0.39546100 | 0.38002200 |
| H | 7.86524800 | -0.43944000 | -1.09775100 |
| H | 4.86453300 | -2.40457300 | 0.07640300 |
| H | 6.58650700 | -2.52502400 | -0.32854400 |
| H | 6.07990700 | -1.65684300 | 1.13728500 |
| H | 6.10647000 | -1.48532300 | -2.62907800 |
| H | 4.38757000 | -1.39003900 | -2.20634100 |

| | | | |
|---|---|---|---|
| H | 5.25750500 | 0.07292700 | -2.71973400 |
| K | -0.86901500 | -3.79725000 | 0.94225600 |
| K | -2.36701700 | -0.35660300 | 3.66392100 |

Triplet Complex between **24** and **17** (counterions)



63
-2585.0997061

| | | | |
|---|---|---|---|
| C | -3.60714300 | -1.40758700 | -2.73856900 |
| C | -3.33312300 | -1.13632800 | -1.38890600 |
| C | -2.19402800 | -1.63499300 | -0.76767500 |
| C | -1.26500400 | -2.45774500 | -1.46841800 |
| C | -1.54481100 | -2.68628200 | -2.84860000 |
| C | -2.68759100 | -2.18487800 | -3.45851200 |
| H | -4.50295400 | -1.02002500 | -3.21248200 |
| H | -4.00434500 | -0.50468300 | -0.81380100 |
| H | -2.00187700 | -1.33697900 | 0.25824400 |
| H | -0.83555200 | -3.28167900 | -3.41323300 |
| H | -2.86853800 | -2.40057300 | -4.50870600 |
| C | -0.02336500 | -3.00173200 | -0.92958200 |
| C | 0.23808700 | -3.09935500 | 0.52019900 |
| C | -0.75061500 | -3.12748300 | 1.52975900 |
| C | 1.58192800 | -3.23186500 | 0.93881800 |
| C | -0.40660500 | -3.20651000 | 2.87670200 |
| H | -1.80161200 | -3.12240700 | 1.26228800 |
| C | 1.92282600 | -3.30220100 | 2.28431000 |
| H | 2.34945900 | -3.26620300 | 0.17189300 |
| C | 0.93235700 | -3.27418400 | 3.27150700 |
| H | -1.19491400 | -3.22513200 | 3.62499500 |
| H | 2.96934900 | -3.38081200 | 2.56840600 |
| H | 1.19649200 | -3.32607800 | 4.32317600 |
| O | 0.88225900 | -3.40504600 | -1.74160800 |
| C | -3.63633400 | 0.51136500 | 3.36572800 |
| C | -2.23763700 | 0.48017400 | 3.45143500 |
| C | -1.44403900 | 0.86384900 | 2.37965400 |
| C | -2.01904300 | 1.29076900 | 1.15153100 |
| C | -3.43922400 | 1.34022300 | 1.09669900 |
| C | -4.22410400 | 0.95483600 | 2.17721900 |
| H | -4.24889000 | 0.20591000 | 4.20755500 |
| H | -1.76007800 | 0.15816900 | 4.37318800 |
| H | -0.36577000 | 0.85592900 | 2.49815800 |
| H | -3.90763400 | 1.65503000 | 0.16822200 |
| H | -5.30695400 | 0.99042500 | 2.08844400 |
| C | -1.25868500 | 1.71741100 | -0.00874500 |
| C | 0.18717100 | 1.46324000 | -0.15501000 |
| C | 0.83423600 | 0.30249900 | 0.32030100 |
| C | 0.95570800 | 2.35910400 | -0.93092400 |
| C | 2.18261200 | 0.07487500 | 0.06947800 |
| H | 0.26912200 | -0.46192100 | 0.84710000 |
| C | 2.30834500 | 2.13942800 | -1.17020300 |
| H | 0.46795300 | 3.23776700 | -1.34291600 |
| C | 2.93544100 | 1.00153000 | -0.65711100 |
| H | 2.64918200 | -0.84341200 | 0.41187300 |
| H | 2.89122300 | 2.84111900 | -1.76026700 |
| O | -1.85761900 | 2.35885000 | -0.97254000 |
| O | 4.25433000 | 0.75163100 | -0.96054000 |
| C | 5.27120000 | 1.14359300 | 0.00412000 |
| C | 6.57744500 | 0.77711400 | -0.68757100 |
| C | 5.19893800 | 2.64574900 | 0.26499600 |
| C | 5.11175900 | 0.35764200 | 1.30348100 |
| H | 6.60425800 | -0.29562700 | -0.89941100 |
| H | 6.67214600 | 1.32304400 | -1.63067700 |
| H | 7.42787900 | 1.02987300 | -0.04841600 |

| | | | |
|---|---|---|---|
| H | 4.25789200 | 2.91946400 | 0.75167900 |
| H | 6.02148800 | 2.94474500 | 0.92130000 |
| H | 5.28367400 | 3.20081000 | -0.67450700 |
| H | 5.94709500 | 0.58600000 | 1.97219900 |
| H | 4.18342800 | 0.61925600 | 1.81932200 |
| H | 5.11135400 | -0.71818900 | 1.10201200 |
| K | -2.70453200 | 4.39399100 | 0.43847800 |
| K | -1.01835400 | 0.49754200 | -2.77767800 |

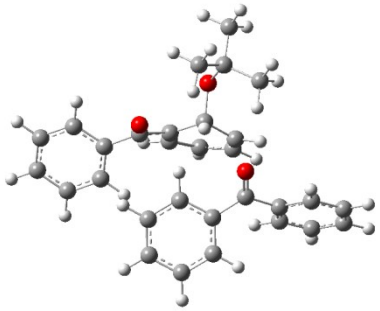
Single Point Singlet, Using Triplet Complex (of **24** and **17**, counterions) Optimised Geometry

63
-2585.0715682

| | | | |
|---|---|---|---|
| C | -3.60714300 | -1.40758700 | -2.73856900 |
| C | -3.33312300 | -1.13632800 | -1.38890600 |
| C | -2.19402800 | -1.63499300 | -0.76767500 |
| C | -1.26500400 | -2.45774500 | -1.46841800 |
| C | -1.54481100 | -2.68628200 | -2.84860000 |
| C | -2.68759100 | -2.18487800 | -3.45851200 |
| H | -4.50295400 | -1.02002500 | -3.21248200 |
| H | -4.00434500 | -0.50468300 | -0.81380100 |
| H | -2.00187700 | -1.33697900 | 0.25824400 |
| H | -0.83555200 | -3.28167900 | -3.41323300 |
| H | -2.86853800 | -2.40057300 | -4.50870600 |
| C | -0.02336500 | -3.00173200 | -0.92958200 |
| C | 0.23808700 | -3.09935500 | 0.52019900 |
| C | -0.75061500 | -3.12748300 | 1.52975900 |
| C | 1.58192800 | -3.23186500 | 0.93881800 |
| C | -0.40660500 | -3.20651000 | 2.87670200 |
| H | -1.80161200 | -3.12240700 | 1.26228800 |
| C | 1.92282600 | -3.30220100 | 2.28431000 |
| H | 2.34945900 | -3.26620300 | 0.17189300 |
| C | 0.93235700 | -3.27418400 | 3.27150700 |
| H | -1.19491400 | -3.22513200 | 3.62499500 |
| H | 2.96934900 | -3.38081200 | 2.56840600 |
| H | 1.19649200 | -3.32607800 | 4.32317600 |
| O | 0.88225900 | -3.40504600 | -1.74160800 |
| C | -3.63633400 | 0.51136500 | 3.36572800 |
| C | -2.23763700 | 0.48017400 | 3.45143500 |
| C | -1.44403900 | 0.86384900 | 2.37965400 |
| C | -2.01904300 | 1.29076900 | 1.15153100 |
| C | -3.43922400 | 1.34022300 | 1.09669900 |
| C | -4.22410400 | 0.95483600 | 2.17721900 |
| H | -4.24889000 | 0.20591000 | 4.20755500 |
| H | -1.76007800 | 0.15816900 | 4.37318800 |
| H | -0.36577000 | 0.85592900 | 2.49815800 |
| H | -3.90763400 | 1.65503000 | 0.16822200 |
| H | -5.30695400 | 0.99042500 | 2.08844400 |
| C | -1.25868500 | 1.71741100 | -0.00874500 |
| C | 0.18717100 | 1.46324000 | -0.15501000 |
| C | 0.83423600 | 0.30249900 | 0.32030100 |
| C | 0.95570800 | 2.35910400 | -0.93092400 |
| C | 2.18261200 | 0.07487500 | 0.06947800 |
| H | 0.26912200 | -0.46192100 | 0.84710000 |
| C | 2.30834500 | 2.13942800 | -1.17020300 |
| H | 0.46795300 | 3.23776700 | -1.34291600 |
| C | 2.93544100 | 1.00153000 | -0.65711100 |
| H | 2.64918200 | -0.84341200 | 0.41187300 |
| H | 2.89122300 | 2.84111900 | -1.76026700 |
| O | -1.85761900 | 2.35885000 | -0.97254000 |
| O | 4.25433000 | 0.75163100 | -0.96054000 |
| C | 5.27120000 | 1.14359300 | 0.00412000 |
| C | 6.57744500 | 0.77711400 | -0.68757100 |
| C | 5.19893800 | 2.64574900 | 0.26499600 |
| C | 5.11175900 | 0.35764200 | 1.30348100 |
| H | 6.60425800 | -0.29562700 | -0.89941100 |
| H | 6.67214600 | 1.32304400 | -1.63067700 |
| H | 7.42787900 | 1.02987300 | -0.04841600 |
| H | 4.25789200 | 2.91946400 | 0.75167900 |
| H | 6.02148800 | 2.94474500 | 0.92130000 |
| H | 5.28367400 | 3.20081000 | -0.67450700 |
| H | 5.94709500 | 0.58600000 | 1.97219900 |
| H | 4.18342800 | 0.61925600 | 1.81932200 |

| | | | |
|---|---|---|---|
| H | 5.11135400 | -0.71818900 | 1.10201200 |
| K | -2.70453200 | 4.39399100 | 0.43847800 |
| K | -1.01835400 | 0.49754200 | -2.77767800 |

**Reactant Complex** for formation of **50** and **21** from **45** and **17**

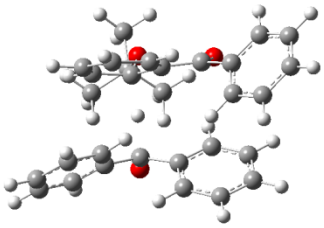


62
-1385.9139884

| | | | |
|---|---|---|---|
| C | 0.86878 | -3.78018 | -1.19840 |
| C | -0.42615 | -4.16450 | -0.84843 |
| C | -1.44850 | -3.21782 | -0.81251 |
| C | -1.18074 | -1.88340 | -1.14343 |
| C | 0.11634 | -1.50752 | -1.51285 |
| C | 1.13858 | -2.45061 | -1.52912 |
| H | 1.66733 | -4.51631 | -1.21387 |
| H | -0.64083 | -5.19968 | -0.60257 |
| H | -2.45612 | -3.52239 | -0.54676 |
| H | 0.33284 | -0.47311 | -1.76423 |
| H | 2.14656 | -2.14061 | -1.78958 |
| C | -2.25407 | -0.84279 | -1.17875 |
| C | -3.46490 | -0.98529 | -0.30734 |
| C | -3.39445 | -1.54138 | 0.97482 |
| C | -4.68062 | -0.47524 | -0.77530 |
| C | -4.53191 | -1.58753 | 1.77814 |
| H | -2.44404 | -1.90202 | 1.35670 |
| C | -5.82133 | -0.54128 | 0.02022 |
| H | -4.71833 | -0.03194 | -1.76577 |
| C | -5.74699 | -1.09589 | 1.29902 |
| H | -4.46793 | -2.00292 | 2.77886 |
| H | -6.76512 | -0.15648 | -0.35299 |
| H | -6.63392 | -1.13886 | 1.92367 |
| O | -2.15847 | 0.11797 | -1.93011 |
| C | 5.97406 | -1.62733 | 0.58832 |
| C | 4.74793 | -2.14881 | 1.00079 |
| C | 3.57041 | -1.43439 | 0.77608 |
| C | 3.60034 | -0.19533 | 0.12548 |
| C | 4.83421 | 0.30717 | -0.30449 |
| C | 6.01432 | -0.39388 | -0.06509 |
| H | 6.89140 | -2.17959 | 0.76953 |
| H | 4.70608 | -3.11417 | 1.49716 |
| H | 2.61560 | -1.84712 | 1.09061 |
| H | 4.85616 | 1.25639 | -0.83260 |
| H | 6.96477 | 0.01704 | -0.39315 |
| C | 2.34422 | 0.57543 | -0.21963 |
| C | 1.36077 | 0.81369 | 0.77125 |
| C | 1.52335 | 0.46217 | 2.14394 |
| C | 0.10078 | 1.51725 | 0.35673 |
| C | 0.46758 | 0.43982 | 3.02104 |
| H | 2.51113 | 0.17847 | 2.50096 |
| C | -1.05364 | 1.10480 | 1.22809 |
| H | -0.10419 | 1.30732 | -0.69854 |
| C | -0.85579 | 0.67524 | 2.49922 |
| H | 0.60737 | 0.16300 | 4.06101 |
| H | -2.06367 | 1.23008 | 0.84484 |
| H | -1.71724 | 0.46154 | 3.13167 |
| O | 2.23926 | 0.94471 | -1.42120 |
| O | 0.30083 | 2.96856 | 0.46853 |
| C | -0.29047 | 3.80634 | -0.52930 |
| C | -0.10122 | 5.22450 | 0.00556 |
| C | 0.44300 | 3.65551 | -1.86570 |

| | | | |
|---|---|---|---|
| C | -1.78645 | 3.52293 | -0.71186 |
| H | -0.62155 | 5.33980 | 0.96159 |
| H | 0.96270 | 5.42751 | 0.16253 |
| H | -0.49694 | 5.96066 | -0.70172 |
| H | 0.37585 | 2.63273 | -2.24527 |
| H | 0.01683 | 4.33899 | -2.60846 |
| H | 1.50422 | 3.88998 | -1.73735 |
| H | -2.21294 | 4.24545 | -1.41616 |
| H | -1.96235 | 2.51846 | -1.11101 |
| H | -2.31124 | 3.61771 | 0.24440 |

**Transition State** for formation of **50** and **21** from **45** and **17**

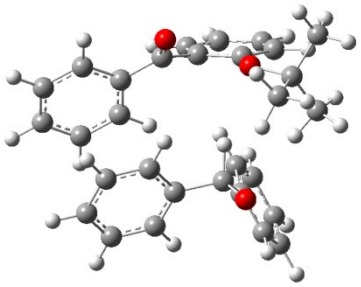


62
-1385.8589518

| | | | |
|---|---|---|---|
| C | 2.45915000 | -2.09826200 | -2.49545400 |
| C | 1.53473500 | -2.98577500 | -1.94950100 |
| C | 0.29762000 | -2.52224100 | -1.49212100 |
| C | -0.03656300 | -1.16606600 | -1.58088400 |
| C | 0.90204200 | -0.28651300 | -2.13301700 |
| C | 2.13825700 | -0.74176700 | -2.58042000 |
| H | 3.42322900 | -2.45669300 | -2.84421800 |
| H | 1.76820200 | -4.04473300 | -1.88321200 |
| H | -0.41797100 | -3.23329000 | -1.09083300 |
| H | 0.65489000 | 0.76887100 | -2.19715600 |
| H | 2.85735000 | -0.03517600 | -2.98566200 |
| C | -1.44632800 | -0.63863200 | -1.30801300 |
| C | -2.30644500 | -1.45850000 | -0.36824000 |
| C | -1.79394500 | -2.09017100 | 0.76773300 |
| C | -3.67690400 | -1.55895900 | -0.63118100 |
| C | -2.62259000 | -2.83389400 | 1.60490900 |
| H | -0.74094900 | -1.97704400 | 1.01752300 |
| C | -4.51319500 | -2.29269700 | 0.20959800 |
| H | -4.06478200 | -1.05804800 | -1.51300900 |
| C | -3.98578300 | -2.94132300 | 1.32770500 |
| H | -2.20479500 | -3.31314200 | 2.48622100 |
| H | -5.57455600 | -2.36497700 | -0.01070600 |
| H | -4.63257400 | -3.51958200 | 1.98114500 |
| O | -2.02501400 | -0.12339200 | -2.32980700 |
| C | 5.55160700 | -0.66090500 | 0.85989100 |
| C | 4.41034300 | -1.43896900 | 0.66049100 |
| C | 3.15881400 | -0.83333200 | 0.56267600 |
| C | 3.03931400 | 0.55723700 | 0.64539000 |
| C | 4.18900300 | 1.33319400 | 0.81699100 |
| C | 5.43902000 | 0.72807000 | 0.93899700 |
| H | 6.52535600 | -1.13377700 | 0.94645500 |
| H | 4.49432600 | -2.51864100 | 0.57469800 |
| H | 2.26940200 | -1.43622700 | 0.38799400 |
| H | 4.09395500 | 2.41483800 | 0.85496900 |
| H | 6.32455400 | 1.33828000 | 1.09030700 |
| C | 1.71166600 | 1.25621500 | 0.43706400 |
| C | 0.55592800 | 0.80285700 | 1.20600300 |
| C | 0.76665800 | 0.00854900 | 2.35775400 |
| C | -0.80943900 | 1.19416700 | 0.84583100 |
| C | -0.24389200 | -0.35784000 | 3.22306300 |
| H | 1.78573400 | -0.26977000 | 2.60595300 |
| C | -1.83197900 | 0.82534100 | 1.81924400 |
| H | -1.11702900 | 0.37889700 | -0.33478100 |
| C | -1.55743600 | 0.08413900 | 2.93562500 |
| H | -0.02891300 | -0.92855000 | 4.11975000 |
| H | -2.83874800 | 1.18989400 | 1.65301600 |
| H | -2.36812100 | -0.14510800 | 3.62388400 |
| O | 1.69896200 | 2.17506900 | -0.38907900 |
| O | -0.90626500 | 2.50612700 | 0.37805600 |
| C | -1.81659900 | 3.02382500 | -0.61283500 |
| C | -1.92298400 | 4.50281800 | -0.24135400 |
| C | -1.18045600 | 2.88084200 | -1.99485000 |
| C | -3.20129800 | 2.37944200 | -0.58348000 |
| H | -2.33354400 | 4.61620800 | 0.76670000 |
| H | -0.93374400 | 4.97018200 | -0.27203800 |

| | | | |
|---|---|---|---|
| H | -2.57673700 | 5.02299700 | -0.94827600 |
| H | -1.21855100 | 1.83993000 | -2.32468400 |
| H | -1.73388200 | 3.48987600 | -2.71949700 |
| H | -0.14304000 | 3.22317400 | -1.95095200 |
| H | -3.79124100 | 2.79431500 | -1.40779400 |
| H | -3.14327400 | 1.29815600 | -0.73570700 |
| H | -3.72594600 | 2.60159800 | 0.35085400 |

**Product Complex** for formation of **50** and **21** from **45** and **17**

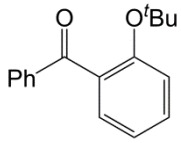


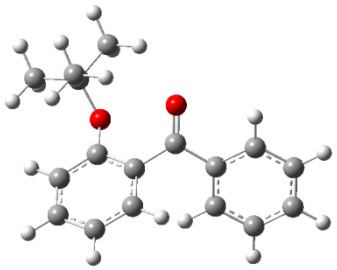
62
-1385.9151685

| | | | |
|---|---|---|---|
| C | -4.11678 | 1.54675 | -1.24331 |
| C | -3.49056 | 2.54731 | -0.50260 |
| C | -2.09579 | 2.58914 | -0.41347 |
| C | -1.30488 | 1.63799 | -1.06364 |
| C | -1.95056 | 0.63811 | -1.80280 |
| C | -3.33833 | 0.58721 | -1.89575 |
| H | -5.20084 | 1.50537 | -1.30320 |
| H | -4.08690 | 3.29488 | 0.01440 |
| H | -1.61894 | 3.37172 | 0.17252 |
| H | -1.34255 | -0.11404 | -2.30493 |
| H | -3.81694 | -0.20733 | -2.46262 |
| C | 0.23418 | 1.69117 | -1.11272 |
| C | 0.78802 | 2.36661 | 0.15399 |
| C | 0.95410 | 1.66295 | 1.35234 |
| C | 1.15720 | 3.71371 | 0.12303 |
| C | 1.45868 | 2.28750 | 2.49360 |
| H | 0.71077 | 0.60176 | 1.38491 |
| C | 1.65533 | 4.34973 | 1.26164 |
| H | 1.05533 | 4.24130 | -0.82127 |
| C | 1.80704 | 3.63937 | 2.45380 |
| H | 1.58971 | 1.71694 | 3.40974 |
| H | 1.93354 | 5.39967 | 1.21895 |
| H | 2.20346 | 4.12916 | 3.33859 |
| O | 0.65855 | 2.26451 | -2.27077 |
| C | -4.54212 | -1.22490 | 1.08090 |
| C | -3.46337 | -0.45419 | 1.51391 |
| C | -2.16289 | -0.82974 | 1.18817 |
| C | -1.93595 | -1.96861 | 0.40742 |
| C | -3.02303 | -2.72611 | -0.04096 |
| C | -4.32165 | -2.36305 | 0.30397 |
| H | -5.55556 | -0.93273 | 1.33999 |
| H | -3.63451 | 0.44699 | 2.09422 |
| H | -1.32835 | -0.21569 | 1.51271 |
| H | -2.83353 | -3.60032 | -0.65638 |
| H | -5.16114 | -2.96243 | -0.03467 |
| C | -0.56221 | -2.38299 | -0.03195 |
| C | 0.60638 | -2.05841 | 0.84603 |
| C | 0.46239 | -2.18140 | 2.23195 |
| C | 1.87233 | -1.71964 | 0.30302 |
| C | 1.53878 | -1.99883 | 3.09459 |
| H | -0.51202 | -2.44212 | 2.63470 |
| C | 2.95762 | -1.56326 | 1.17611 |
| H | 0.54516 | 0.61728 | -1.01589 |
| C | 2.78507 | -1.69695 | 2.55173 |
| H | 1.40854 | -2.10268 | 4.16616 |
| H | 3.94186 | -1.33767 | 0.79419 |
| H | 3.64466 | -1.56296 | 3.20185 |
| O | -0.42545 | -3.02485 | -1.06261 |
| O | 1.91556 | -1.55853 | -1.02871 |
| C | 3.02181 | -1.00598 | -1.79549 |
| C | 4.09912 | -2.07592 | -1.95973 |
| C | 2.34958 | -0.70006 | -3.13283 |
| C | 3.57043 | 0.30218 | -1.21867 |

| | | | |
|---|---|---|---|
| H | 4.53438 | -2.37546 | -1.00265 |
| H | 3.67573 | -2.96235 | -2.44109 |
| H | 4.90410 | -1.68753 | -2.59092 |
| H | 1.63553 | 0.12377 | -3.00577 |
| H | 3.10464 | -0.40211 | -3.86680 |
| H | 1.83116 | -1.58993 | -3.50268 |
| H | 4.08167 | 0.83430 | -2.02656 |
| H | 2.75019 | 0.93709 | -0.87271 |
| H | 4.29184 | 0.16797 | -0.41191 |

**50**

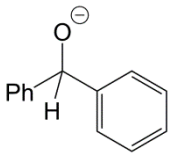


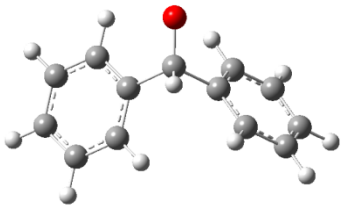



37
-808.7992613

| | | | |
|---|---|---|---|
| C | -4.86776 | -0.41049 | -0.62905 |
| C | -3.99293 | 0.51453 | -1.19720 |
| C | -2.65544 | 0.54093 | -0.80544 |
| C | -2.18694 | -0.36987 | 0.14844 |
| C | -3.06787 | -1.30496 | 0.70652 |
| C | -4.40471 | -1.32032 | 0.32511 |
| H | -5.91089 | -0.42490 | -0.92954 |
| H | -4.35116 | 1.21556 | -1.94399 |
| H | -1.97460 | 1.25867 | -1.25243 |
| H | -2.68843 | -2.00890 | 1.44032 |
| H | -5.08748 | -2.03906 | 0.76667 |
| C | -0.74922 | -0.41085 | 0.56538 |
| C | 0.09460 | 0.80873 | 0.33964 |
| C | -0.35465 | 2.05514 | 0.79162 |
| C | 1.34508 | 0.71075 | -0.29143 |
| C | 0.43543 | 3.19110 | 0.64976 |
| H | -1.32773 | 2.12635 | 1.27053 |
| C | 2.11583 | 1.86214 | -0.47485 |
| C | 1.67039 | 3.09009 | 0.00769 |
| H | 0.08488 | 4.14802 | 1.02109 |
| H | 3.05647 | 1.78948 | -1.00923 |
| H | 2.28448 | 3.97414 | -0.13380 |
| O | -0.28676 | -1.40700 | 1.09710 |
| O | 1.72581 | -0.49265 | -0.80881 |
| C | 2.84571 | -1.23020 | -0.22039 |
| C | 2.99364 | -0.92671 | 1.26669 |
| C | 2.46376 | -2.68941 | -0.43602 |
| C | 4.12182 | -0.88977 | -0.98687 |
| H | 3.30212 | 0.10864 | 1.44016 |
| H | 2.04948 | -1.11245 | 1.78515 |
| H | 3.76383 | -1.58197 | 1.68376 |
| H | 2.30426 | -2.88256 | -1.50120 |
| H | 3.26215 | -3.34595 | -0.07827 |
| H | 1.54229 | -2.91432 | 0.10699 |
| H | 4.93112 | -1.55521 | -0.67041 |
| H | 3.96323 | -1.02140 | -2.06117 |
| H | 4.44317 | 0.13809 | -0.79853 |

**21**

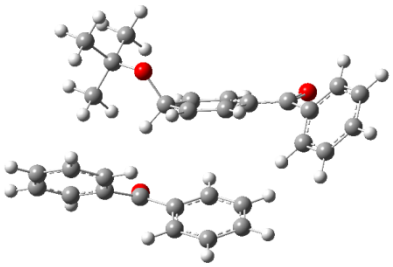


25
-577.1054866

| | | | |
|---|---|---|---|
| C | 3.47966 | -1.04717 | 0.60152 |
| C | 2.59326 | -1.70582 | -0.25566 |
| C | 1.48398 | -1.03222 | -0.76370 |
| C | 1.23797 | 0.30637 | -0.43256 |
| C | 2.13210 | 0.95578 | 0.41825 |
| C | 3.24405 | 0.28613 | 0.93617 |
| H | 4.34569 | -1.56867 | 0.99906 |
| H | 2.77060 | -2.74328 | -0.52675 |
| H | 0.79519 | -1.55130 | -1.42924 |
| H | 1.93106 | 1.99761 | 0.65045 |
| H | 3.93092 | 0.80718 | 1.59844 |
| C | 0.00695 | 1.06832 | -0.98244 |
| C | -1.23648 | 0.38687 | -0.37454 |
| C | -1.59424 | 0.66649 | 0.94976 |
| C | -2.03258 | -0.49984 | -1.10202 |
| C | -2.70770 | 0.06886 | 1.53418 |
| H | -0.98334 | 1.37057 | 1.50958 |
| C | -3.15487 | -1.10272 | -0.52457 |
| H | -1.77602 | -0.71805 | -2.13735 |
| C | -3.49535 | -0.82211 | 0.79713 |
| H | -2.96745 | 0.29586 | 2.56490 |
| H | -3.76504 | -1.78471 | -1.11080 |
| H | -4.36693 | -1.28601 | 1.24959 |
| O | 0.04618 | 2.40220 | -0.76372 |
| H | -0.02470 | 0.78953 | -2.06733 |

**Reactant Complex** for formation of **22** and **21** from **20** and **17**

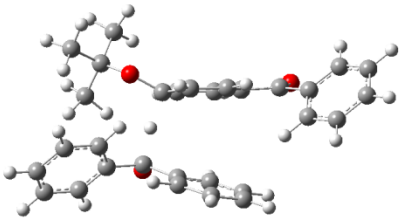


62
-1385.9144795

| | | | |
|---|---|---|---|
| C | -6.46454 | -0.56985 | -1.69885 |
| C | -5.30953 | -1.29211 | -1.39933 |
| C | -4.32036 | -0.72919 | -0.59210 |
| C | -4.47476 | 0.55828 | -0.06552 |
| C | -5.64935 | 1.26405 | -0.35177 |
| C | -6.63128 | 0.71305 | -1.17248 |
| H | -7.23180 | -1.00443 | -2.33268 |
| H | -5.17811 | -2.29619 | -1.79273 |
| H | -3.42252 | -1.29432 | -0.35726 |
| H | -5.78238 | 2.25219 | 0.07966 |
| H | -7.52951 | 1.28020 | -1.39887 |
| C | -3.46540 | 1.17460 | 0.87828 |
| C | -2.09106 | 1.17147 | 0.54095 |
| C | -1.55147 | 0.75794 | -0.73099 |
| C | -1.11878 | 1.59763 | 1.51559 |
| C | -0.22534 | 0.77634 | -1.00947 |
| H | -2.23261 | 0.41947 | -1.50834 |
| C | 0.21477 | 1.62300 | 1.27868 |
| H | -1.49209 | 1.85889 | 2.50415 |
| C | 0.81308 | 1.29405 | -0.05944 |
| H | 0.13079 | 0.44849 | -1.98461 |
| H | 0.89751 | 1.87019 | 2.08935 |
| O | -3.93884 | 1.66770 | 1.94111 |
| H | 1.62116 | 0.55831 | 0.05483 |
| O | 1.42558 | 2.43833 | -0.73226 |
| C | 2.65093 | 3.00336 | -0.24451 |
| C | 3.32006 | 3.58270 | -1.49209 |
| C | 2.35194 | 4.13847 | 0.74228 |
| C | 3.58308 | 1.96964 | 0.39249 |
| H | 3.55240 | 2.78051 | -2.20007 |
| H | 2.64579 | 4.29276 | -1.98107 |
| H | 4.24732 | 4.10338 | -1.23200 |
| H | 1.90557 | 3.76070 | 1.66460 |
| H | 3.27336 | 4.67306 | 0.99853 |
| H | 1.65325 | 4.84762 | 0.28754 |
| H | 4.52335 | 2.46087 | 0.66364 |
| H | 3.16094 | 1.53025 | 1.30271 |
| H | 3.81035 | 1.16096 | -0.31099 |
| C | 5.23823 | -1.15398 | -1.81266 |
| C | 3.89354 | -1.17497 | -2.18376 |
| C | 2.90849 | -1.40003 | -1.22400 |
| C | 3.26510 | -1.58644 | 0.11681 |
| C | 4.61447 | -1.55010 | 0.48509 |
| C | 5.59882 | -1.34626 | -0.47737 |
| H | 6.00457 | -0.98330 | -2.56246 |
| H | 3.61046 | -1.00922 | -3.21835 |
| H | 1.86088 | -1.38921 | -1.51141 |
| H | 4.87589 | -1.67513 | 1.53135 |
| H | 6.64469 | -1.32748 | -0.18765 |
| C | 2.23681 | -1.70206 | 1.20173 |
| C | 0.89312 | -2.28310 | 0.90087 |
| C | 0.71319 | -3.28382 | -0.06201 |
| C | -0.20257 | -1.82822 | 1.64379 |
| C | -0.55454 | -3.81879 | -0.28186 |

| | | | |
|---|---|---|---|
| H | 1.56280 | -3.65889 | -0.62486 |
| C | -1.47091 | -2.34825 | 1.40753 |
| H | -0.05275 | -1.04447 | 2.37815 |
| C | -1.64702 | -3.34468 | 0.44512 |
| H | -0.68949 | -4.60215 | -1.02068 |
| H | -2.32258 | -1.97009 | 1.96536 |
| H | -2.63690 | -3.75392 | 0.26288 |
| O | 2.49792 | -1.30172 | 2.32807 |

**Transition State** for formation of **22** and **21** from **20** and **17**

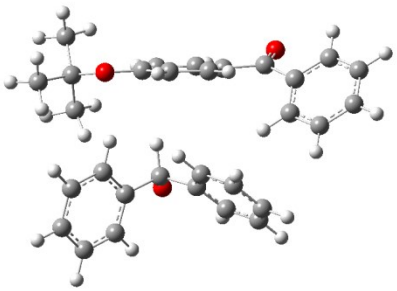


62
-1385.8777800

| | | | |
|---|---|---|---|
| C | -6.58335800 | -0.72169400 | -1.34930600 |
| C | -5.38328800 | -1.39153200 | -1.11275800 |
| C | -4.34502500 | -0.75194500 | -0.43513000 |
| C | -4.50276800 | 0.55969300 | 0.02545000 |
| C | -5.71930600 | 1.21622700 | -0.19495400 |
| C | -6.74893600 | 0.58643600 | -0.88980900 |
| H | -7.38845900 | -1.21790500 | -1.88273700 |
| H | -5.25325900 | -2.41450000 | -1.45369200 |
| H | -3.41521200 | -1.27972200 | -0.24503100 |
| H | -5.84498800 | 2.22541700 | 0.18599800 |
| H | -7.68268100 | 1.11113000 | -1.06828300 |
| C | -3.44474200 | 1.27204700 | 0.83140600 |
| C | -2.05581700 | 1.20072200 | 0.43594400 |
| C | -1.59694900 | 0.69744000 | -0.81446900 |
| C | -1.06827300 | 1.74230700 | 1.29908300 |
| C | -0.27392800 | 0.71587700 | -1.15541000 |
| H | -2.31136600 | 0.33539200 | -1.54837600 |
| C | 0.26432500 | 1.79562000 | 0.98112000 |
| H | -1.39986200 | 2.15032100 | 2.25063300 |
| C | 0.75846600 | 1.20774900 | -0.25428600 |
| H | 0.05352600 | 0.36349500 | -2.12985500 |
| H | 0.96269400 | 2.20679300 | 1.69813600 |
| O | -3.83047100 | 1.91667000 | 1.82363900 |
| H | 1.37658400 | 0.08215100 | 0.23094700 |
| O | 1.82005500 | 1.73650500 | -0.99417800 |
| C | 2.82242900 | 2.62885900 | -0.46580200 |
| C | 3.78547700 | 2.78143900 | -1.64250300 |
| C | 2.21290100 | 3.99808100 | -0.14120600 |
| C | 3.57211600 | 2.02929400 | 0.72629800 |
| H | 4.15534000 | 1.79666800 | -1.94413000 |
| H | 3.28115500 | 3.24837900 | -2.49419500 |
| H | 4.63718700 | 3.40452800 | -1.35336500 |
| H | 1.61314400 | 3.99442700 | 0.76931600 |
| H | 3.01922700 | 4.72735800 | -0.01252200 |
| H | 1.58076300 | 4.32559200 | -0.97242400 |
| H | 4.17665400 | 2.81064100 | 1.19917900 |
| H | 2.90407000 | 1.59760400 | 1.47667700 |
| H | 4.24131800 | 1.23205300 | 0.38994700 |
| C | 5.63616600 | -1.60899000 | -0.94659100 |
| C | 4.52376100 | -1.24800400 | -1.70983900 |
| C | 3.28898400 | -1.04654800 | -1.09569500 |
| C | 3.14483600 | -1.20367000 | 0.28746300 |
| C | 4.26499400 | -1.55914900 | 1.04450600 |
| C | 5.50189200 | -1.76565600 | 0.43347800 |
| H | 6.60020100 | -1.75963000 | -1.42322000 |
| H | 4.62217100 | -1.10797000 | -2.78270500 |
| H | 2.43726200 | -0.72225600 | -1.68865000 |
| H | 4.15209300 | -1.64969800 | 2.12082300 |
| H | 6.36354800 | -2.04111600 | 1.03491600 |
| C | 1.83566300 | -0.94037200 | 1.01533000 |
| C | 0.66977900 | -1.85877000 | 0.67276400 |
| C | 0.64358600 | -2.72832400 | -0.42366300 |
| C | -0.46101600 | -1.78505300 | 1.49588900 |
| C | -0.48813500 | -3.50161700 | -0.69248900 |
| H | 1.50906300 | -2.81940700 | -1.07175700 |

| | | | |
|---|---|---|---|
| C | -1.58930600 | -2.55419400 | 1.22969800 |
| H | -0.43255500 | -1.10698900 | 2.34210800 |
| C | -1.60984200 | -3.41588700 | 0.12984800 |
| H | -0.48808700 | -4.17392000 | -1.54564600 |
| H | -2.45938500 | -2.47873600 | 1.87698100 |
| H | -2.49178400 | -4.01404000 | -0.08230400 |
| O | 1.90460500 | -0.51922400 | 2.22266700 |

**Product Complex** for formation of **22** and **21** from **20** and **17**

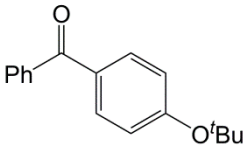


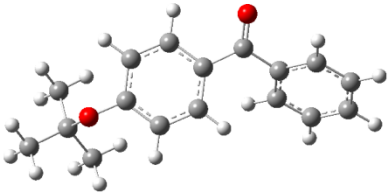
62
-1385.9218525

| | | | |
|---|---|---|---|
| C | 5.95010 | 0.77914 | -1.00308 |
| C | 4.64208 | 1.21209 | -0.78994 |
| C | 3.68860 | 0.34245 | -0.26061 |
| C | 4.05525 | -0.96734 | 0.07071 |
| C | 5.37518 | -1.39134 | -0.12476 |
| C | 6.31788 | -0.52633 | -0.67103 |
| H | 6.68363 | 1.46006 | -1.42393 |
| H | 4.35746 | 2.22984 | -1.03407 |
| H | 2.67299 | 0.69598 | -0.08887 |
| H | 5.64620 | -2.40571 | 0.15169 |
| H | 7.33590 | -0.86587 | -0.83424 |
| C | 3.09771 | -1.93392 | 0.69871 |
| C | 1.67646 | -1.96645 | 0.26529 |
| C | 1.24570 | -1.51159 | -0.99164 |
| C | 0.73839 | -2.56143 | 1.11480 |
| C | -0.07893 | -1.64668 | -1.36983 |
| H | 1.95145 | -1.06618 | -1.68613 |
| C | -0.59646 | -2.68913 | 0.75406 |
| H | 1.06927 | -2.92595 | 2.08225 |
| C | -1.02166 | -2.21778 | -0.49724 |
| H | -0.42266 | -1.29491 | -2.33736 |
| H | -1.28397 | -3.14040 | 1.45308 |
| O | 3.50619 | -2.70841 | 1.55701 |
| H | -1.07133 | 0.17644 | 0.52593 |
| O | -2.28106 | -2.24582 | -0.98271 |
| C | -3.45740 | -2.67544 | -0.24523 |
| C | -4.58709 | -2.32630 | -1.21171 |
| C | -3.41940 | -4.18649 | -0.02187 |
| C | -3.64173 | -1.87753 | 1.04748 |
| H | -4.62846 | -1.24370 | -1.36560 |
| H | -4.42439 | -2.81579 | -2.17610 |
| H | -5.54451 | -2.66065 | -0.80347 |
| H | -2.60209 | -4.49900 | 0.63029 |
| H | -4.35860 | -4.50422 | 0.44056 |
| H | -3.31423 | -4.70143 | -0.98136 |
| H | -4.67328 | -2.00447 | 1.38949 |
| H | -2.98656 | -2.19213 | 1.86040 |
| H | -3.47091 | -0.81359 | 0.85698 |
| C | -4.74981 | 2.92631 | -0.76349 |
| C | -4.14499 | 1.82096 | -1.36080 |
| C | -3.00419 | 1.25268 | -0.78748 |
| C | -2.45007 | 1.77419 | 0.38585 |
| C | -3.07359 | 2.87548 | 0.98213 |
| C | -4.20841 | 3.45152 | 0.41375 |
| H | -5.63778 | 3.37003 | -1.20421 |
| H | -4.56466 | 1.39595 | -2.26921 |
| H | -2.54677 | 0.37588 | -1.24670 |
| H | -2.65687 | 3.26291 | 1.90854 |
| H | -4.67795 | 4.30888 | 0.88884 |
| C | -1.18677 | 1.16507 | 1.03110 |
| C | 0.01271 | 1.99802 | 0.51186 |
| C | 0.30932 | 2.10106 | -0.85479 |
| C | 0.81857 | 2.68703 | 1.41865 |

| | | | |
|---|---|---|---|
| C | 1.35871 | 2.90009 | -1.30488 |
| H | -0.29795 | 1.55508 | -1.57483 |
| C | 1.87311 | 3.49113 | 0.97512 |
| H | 0.58841 | 2.57530 | 2.47431 |
| C | 2.13864 | 3.61154 | -0.38795 |
| H | 1.56997 | 2.97100 | -2.36887 |
| H | 2.48583 | 4.02786 | 1.69499 |
| H | 2.94981 | 4.24600 | -0.73476 |
| O | -1.25206 | 1.08132 | 2.37987 |

**22**

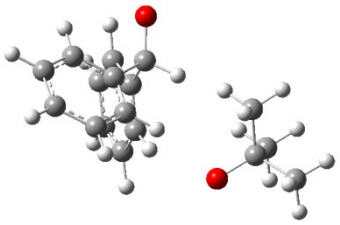


37
-808.8042505

| | | | |
|---|---|---|---|
| C | -5.12732 | -1.71741 | 0.14505 |
| C | -3.85453 | -2.02500 | 0.62451 |
| C | -2.84443 | -1.06537 | 0.58859 |
| C | -3.11192 | 0.21369 | 0.08763 |
| C | -4.39700 | 0.52341 | -0.37266 |
| C | -5.39819 | -0.44222 | -0.35537 |
| H | -5.90995 | -2.46966 | 0.16485 |
| H | -3.64782 | -3.01149 | 1.02689 |
| H | -1.85694 | -1.30524 | 0.97139 |
| H | -4.59371 | 1.52318 | -0.74744 |
| H | -6.38912 | -0.20279 | -0.72771 |
| C | -2.08051 | 1.29930 | 0.08730 |
| C | -0.64158 | 0.95759 | -0.11928 |
| C | -0.23732 | -0.14893 | -0.87643 |
| C | 0.32901 | 1.82256 | 0.40201 |
| C | 1.11436 | -0.39340 | -1.09637 |
| H | -0.97752 | -0.80832 | -1.31892 |
| C | 1.68006 | 1.57389 | 0.19888 |
| H | 0.00928 | 2.69203 | 0.96771 |
| C | 2.07628 | 0.45632 | -0.54458 |
| H | 1.43726 | -1.23528 | -1.69986 |
| H | 2.43658 | 2.24170 | 0.59759 |
| O | -2.42057 | 2.46247 | 0.25412 |
| O | 3.40163 | 0.24156 | -0.81192 |
| C | 4.18985 | -0.54608 | 0.13244 |
| C | 5.55449 | -0.63359 | -0.53621 |
| C | 4.28721 | 0.17725 | 1.47232 |
| C | 3.57881 | -1.93378 | 0.30347 |
| H | 5.46855 | -1.12827 | -1.50782 |
| H | 5.96780 | 0.36767 | -0.68676 |
| H | 6.24312 | -1.20689 | 0.09041 |
| H | 3.31053 | 0.25320 | 1.95913 |
| H | 4.95317 | -0.37923 | 2.13837 |
| H | 4.69474 | 1.18343 | 1.33520 |
| H | 4.23188 | -2.54288 | 0.93488 |
| H | 2.59666 | -1.88321 | 0.78300 |
| H | 3.47332 | -2.42937 | -0.66638 |

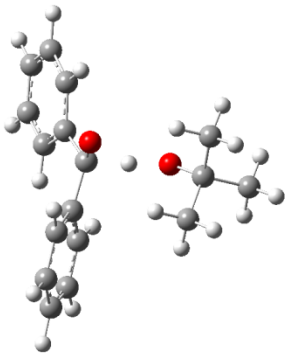
**Reactant Complex** for formation of **23** and **HO$^t$Bu** from **21** and **O$^t$Bu anion**



39
-810.1530973

| | | | |
|---|---|---|---|
| C | 0.79226 | 3.75659 | -1.07679 |
| C | -0.26555 | 2.85112 | -1.15924 |
| C | -0.24264 | 1.66189 | -0.42304 |
| C | 0.84350 | 1.36498 | 0.40881 |
| C | 1.89558 | 2.28386 | 0.49314 |
| C | 1.87702 | 3.46695 | -0.24387 |
| H | 0.77098 | 4.68055 | -1.64813 |
| H | -1.12077 | 3.07048 | -1.79422 |
| H | -1.08963 | 0.97471 | -0.50194 |
| H | 2.72420 | 2.05641 | 1.15931 |
| H | 2.70461 | 4.16803 | -0.16783 |
| C | 0.91269 | 0.06144 | 1.23394 |
| C | 1.70065 | -0.96116 | 0.37797 |
| C | 1.20028 | -1.45244 | -0.83571 |
| C | 2.94456 | -1.41753 | 0.81577 |
| C | 1.92711 | -2.36922 | -1.59343 |
| H | 0.22748 | -1.11171 | -1.18756 |
| C | 3.68201 | -2.33175 | 0.05831 |
| H | 3.30620 | -1.04234 | 1.76898 |
| C | 3.17729 | -2.81160 | -1.15012 |
| H | 1.51975 | -2.74221 | -2.52956 |
| H | 4.65007 | -2.67534 | 0.41464 |
| H | 3.74587 | -3.52586 | -1.73901 |
| O | 1.41894 | 0.23330 | 2.47841 |
| H | -0.13505 | -0.32907 | 1.22354 |
| O | -3.09021 | -0.10940 | -1.13593 |
| C | -3.63866 | -0.67787 | -0.01520 |
| C | -3.44313 | 0.22523 | 1.22696 |
| C | -5.15979 | -0.91057 | -0.19015 |
| C | -2.98813 | -2.04847 | 0.29664 |
| H | -2.37264 | 0.38524 | 1.40148 |
| H | -3.90533 | 1.20343 | 1.04314 |
| H | -3.88301 | -0.20079 | 2.13956 |
| H | -5.33215 | -1.56598 | -1.05294 |
| H | -5.63040 | -1.36665 | 0.69221 |
| H | -5.65363 | 0.04864 | -0.38947 |
| H | -3.40858 | -2.52871 | 1.19138 |
| H | -3.12865 | -2.72289 | -0.55734 |
| H | -1.90957 | -1.91573 | 0.45002 |

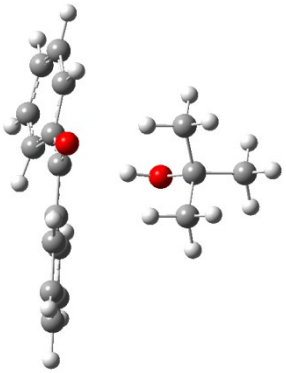
**Transition State** for formation of **23** and **HO*t*Bu** from **21** and **O*t*Bu anion**



39
-810.1171016

| | | | |
|---|---|---|---|
| C | 2.45006 | -3.33827 | -0.37560 |
| C | 1.74524 | -2.63590 | -1.36125 |
| C | 0.83272 | -1.64369 | -1.01452 |
| C | 0.56171 | -1.31193 | 0.33497 |
| C | 1.31259 | -2.00875 | 1.30656 |
| C | 2.22684 | -3.00411 | 0.96231 |
| H | 3.16774 | -4.10741 | -0.64707 |
| H | 1.92720 | -2.84994 | -2.41244 |
| H | 0.35810 | -1.06934 | -1.80508 |
| H | 1.15741 | -1.72466 | 2.34241 |
| H | 2.77529 | -3.52242 | 1.74691 |
| C | -0.32282 | -0.18568 | 0.75624 |
| C | -1.73069 | -0.23462 | 0.27966 |
| C | -2.23227 | -0.96422 | -0.82969 |
| C | -2.68280 | 0.56855 | 0.96076 |
| C | -3.55724 | -0.86196 | -1.24474 |
| H | -1.58341 | -1.64562 | -1.36867 |
| C | -4.00524 | 0.67509 | 0.53739 |
| H | -2.33663 | 1.10544 | 1.83800 |
| C | -4.46485 | -0.03048 | -0.57886 |
| H | -3.88857 | -1.45161 | -2.09766 |
| H | -4.69083 | 1.31410 | 1.09147 |
| H | -5.49616 | 0.05009 | -0.90987 |
| O | -0.16335 | 0.21862 | 2.05690 |
| H | 0.09301 | 0.80810 | -0.08321 |
| O | 0.46724 | 1.79918 | -0.85988 |
| C | 1.60256 | 2.42403 | -0.34244 |
| C | 2.66572 | 1.37890 | 0.04528 |
| C | 2.18833 | 3.36655 | -1.40392 |
| C | 1.23453 | 3.23144 | 0.91511 |
| H | 2.25666 | 0.71613 | 0.81557 |
| H | 2.92106 | 0.76622 | -0.82823 |
| H | 3.58160 | 1.85200 | 0.42384 |
| H | 1.44272 | 4.11837 | -1.68828 |
| H | 3.08504 | 3.88635 | -1.04099 |
| H | 2.45733 | 2.79533 | -2.30014 |
| H | 2.10961 | 3.71622 | 1.36884 |
| H | 0.50354 | 4.00798 | 0.65701 |
| H | 0.78180 | 2.54251 | 1.63794 |

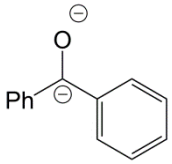
**Product Complex** for formation of **23** and **HO$^t$Bu** from **21** and **O$^t$Bu anion**

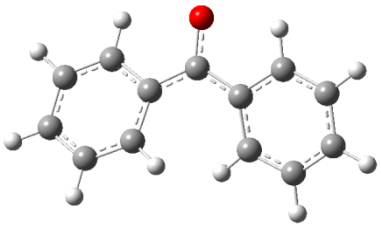


39
-810.1414320

| | | | |
|---|---|---|---|
| C | 3.90670 | -1.50900 | -0.66151 |
| C | 2.78043 | -1.46925 | -1.50330 |
| C | 1.49937 | -1.27112 | -1.00955 |
| C | 1.23461 | -1.09289 | 0.39383 |
| C | 2.41468 | -1.08113 | 1.21856 |
| C | 3.68709 | -1.29462 | 0.70921 |
| H | 4.90363 | -1.67282 | -1.05904 |
| H | 2.91055 | -1.57667 | -2.57964 |
| H | 0.69797 | -1.17516 | -1.73281 |
| H | 2.26949 | -0.89402 | 2.27689 |
| H | 4.53519 | -1.28956 | 1.39360 |
| C | -0.03128 | -0.82710 | 1.02674 |
| C | -1.30076 | -1.05212 | 0.39255 |
| C | -1.56893 | -1.79970 | -0.81205 |
| C | -2.48864 | -0.58337 | 1.06507 |
| C | -2.85182 | -1.96517 | -1.31275 |
| H | -0.76305 | -2.31094 | -1.32447 |
| C | -3.76041 | -0.74641 | 0.54034 |
| H | -2.34617 | -0.07146 | 2.01044 |
| C | -3.98072 | -1.42224 | -0.67337 |
| H | -2.98020 | -2.55235 | -2.22179 |
| H | -4.61050 | -0.34356 | 1.09107 |
| H | -4.97867 | -1.54927 | -1.08130 |
| O | -0.02326 | -0.40095 | 2.29593 |
| H | -0.32754 | 0.81138 | -0.62721 |
| O | -0.36025 | 1.63671 | -1.15173 |
| C | 0.07129 | 2.69408 | -0.29127 |
| C | 1.54649 | 2.49225 | 0.06176 |
| C | -0.12454 | 3.98122 | -1.08356 |
| C | -0.78028 | 2.68970 | 0.97897 |
| H | 1.67479 | 1.54357 | 0.59493 |
| H | 2.15026 | 2.46012 | -0.85223 |
| H | 1.91188 | 3.30833 | 0.69525 |
| H | -1.17897 | 4.10400 | -1.35202 |
| H | 0.18797 | 4.84797 | -0.49245 |
| H | 0.46812 | 3.95553 | -2.00413 |
| H | -0.47183 | 3.49709 | 1.65356 |
| H | -1.83580 | 2.83545 | 0.72155 |
| H | -0.66880 | 1.72756 | 1.49811 |

**23**



24
-576.5430630

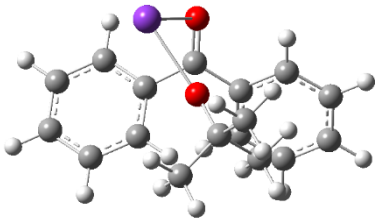
| | | | |
|---|---|---|---|
| C | 3.93409 | -0.84781 | -0.02633 |
| C | 2.79551 | -1.61869 | -0.33036 |
| C | 1.51843 | -1.07963 | -0.32629 |
| C | 1.26328 | 0.30324 | -0.00469 |
| C | 2.45815 | 1.07902 | 0.22642 |
| C | 3.72613 | 0.51879 | 0.23161 |
| H | 4.92888 | -1.28262 | -0.02361 |
| H | 2.91443 | -2.66815 | -0.59902 |
| H | 0.70416 | -1.72072 | -0.64286 |
| H | 2.32613 | 2.14010 | 0.40878 |
| H | 4.58259 | 1.16105 | 0.43767 |
| C | 0.00001 | 0.98227 | 0.00018 |
| C | -1.26319 | 0.30325 | 0.00508 |
| C | -1.51856 | -1.07953 | 0.32690 |
| C | -2.45813 | 1.07912 | -0.22641 |
| C | -2.79571 | -1.61860 | 0.33027 |
| H | -0.70468 | -1.72063 | 0.64433 |
| C | -3.72602 | 0.51893 | -0.23204 |
| H | -2.32593 | 2.14023 | -0.40850 |
| C | -3.93412 | -0.84784 | 0.02560 |
| H | -2.91455 | -2.66807 | 0.59896 |
| H | -4.58245 | 1.16119 | -0.43816 |
| H | -4.92902 | -1.28243 | 0.02271 |
| O | 0.00016 | 2.32310 | 0.00001 |

Single Point Radical Anion
using Optimised Geometry
**23**

24
-576.4988415

| | | | |
|---|---|---|---|
| C | 0.06673400 | 2.46635100 | 1.08064200 |
| C | -0.08552000 | 1.26026900 | 0.30293700 |
| C | -0.41975100 | 1.49579300 | -1.08046400 |
| C | -0.49679400 | 2.77062600 | -1.61962100 |
| C | -0.26265800 | 3.92476600 | -0.84791600 |
| C | 0.00000000 | 3.73242900 | 0.52022600 |
| H | 0.25336500 | 2.34506100 | 2.14221700 |
| H | -0.68576700 | 0.66372800 | -1.72182000 |
| H | -0.76913400 | 2.87357200 | -2.66984700 |
| H | -0.31816800 | 4.91798700 | -1.28284000 |
| H | 0.15032900 | 4.59960000 | 1.16364400 |
| C | 0.00000000 | 0.00000000 | 0.98163000 |
| C | 0.08552000 | -1.26026900 | 0.30293700 |
| C | 0.41975100 | -1.49579300 | -1.08046400 |
| C | -0.06673400 | -2.46635100 | 1.08064200 |
| C | 0.49679400 | -2.77062600 | -1.61962100 |
| H | 0.68576700 | -0.66372800 | -1.72182000 |
| C | 0.00000000 | -3.73242900 | 0.52022600 |
| H | -0.25336500 | -2.34506100 | 2.14221700 |
| C | 0.26265800 | -3.92476600 | -0.84791600 |
| H | 0.76913400 | -2.87357200 | -2.66984700 |
| H | -0.15032900 | -4.59960000 | 1.16364400 |
| H | 0.31816800 | -4.91798700 | -1.28284000 |
| O | 0.00000000 | 0.00000000 | 2.32223400 |

Singlet Complex KO$^t$Bu + Benzophenone



39
-1409.2932637

| | | | |
|---|---|---|---|
| C | 3.56791700 | -1.28791300 | -1.59990700 |
| C | 2.37991400 | -0.72238500 | -2.06753500 |
| C | 1.25181200 | -0.69279900 | -1.25195800 |
| C | 1.31337600 | -1.21906600 | 0.04243400 |
| C | 2.51048800 | -1.76844600 | 0.51559100 |
| C | 3.63351200 | -1.81196700 | -0.30847600 |
| H | 4.44420900 | -1.31428500 | -2.24015600 |
| H | 2.33476800 | -0.29657600 | -3.06508000 |
| H | 0.33720400 | -0.21548000 | -1.58723500 |
| H | 2.54864400 | -2.16558900 | 1.52597400 |
| H | 4.55657200 | -2.25122300 | 0.05616400 |
| C | 0.14690100 | -1.15169200 | 0.97677400 |
| C | -1.23124500 | -1.42876900 | 0.48090900 |
| C | -1.46852700 | -2.15435600 | -0.69164100 |
| C | -2.31240900 | -0.98445500 | 1.25121300 |
| C | -2.77623500 | -2.41532200 | -1.09767400 |
| H | -0.63731600 | -2.52790100 | -1.28113200 |
| C | -3.61545400 | -1.23857300 | 0.84186700 |
| H | -2.11074900 | -0.42225800 | 2.15759400 |
| C | -3.84863200 | -1.95111900 | -0.33709900 |
| H | -2.95706000 | -2.98072000 | -2.00618300 |
| H | -4.45093600 | -0.87778200 | 1.43339500 |
| H | -4.86666000 | -2.14822500 | -0.65908300 |
| O | 0.34485800 | -0.91198800 | 2.16459100 |
| C | -0.73007700 | 2.57544700 | -0.63723600 |
| C | 0.08225100 | 2.90717200 | -1.90974700 |
| H | 0.95072300 | 3.52032400 | -1.63983200 |
| H | 0.45284000 | 1.98152500 | -2.36601700 |
| H | -0.50633400 | 3.45079700 | -2.66045200 |
| C | -1.25231200 | 3.90618200 | -0.05016500 |
| H | -1.88416500 | 4.46484900 | -0.75334600 |
| H | -1.83763600 | 3.69930100 | 0.85397400 |
| H | -0.40405900 | 4.54148200 | 0.23248700 |
| C | -1.95665400 | 1.73479700 | -1.05600600 |
| H | -1.63305200 | 0.77473300 | -1.47700200 |
| H | -2.57197900 | 1.51395700 | -0.17636700 |
| H | -2.58043700 | 2.24794000 | -1.79990700 |
| O | 0.04823300 | 1.90833600 | 0.28024700 |
| K | 1.76331200 | 1.43441800 | 1.96239100 |

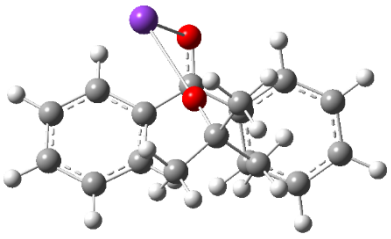
Single Point Triplet using Optimised Geometry of Singlet Complex KO*t*Bu + Benzophenone

39
-1409.2035039

| | | | |
|---|---|---|---|
| C | 3.56791700 | -1.28791300 | -1.59990700 |
| C | 2.37991400 | -0.72238500 | -2.06753500 |
| C | 1.25181200 | -0.69279900 | -1.25195800 |
| C | 1.31337600 | -1.21906600 | 0.04243400 |
| C | 2.51048800 | -1.76844600 | 0.51559100 |
| C | 3.63351200 | -1.81196700 | -0.30847600 |
| H | 4.44420900 | -1.31428500 | -2.24015600 |
| H | 2.33476800 | -0.29657600 | -3.06508000 |

| | | | |
|---|---|---|---|
| H | 0.33720400 | -0.21548000 | -1.58723500 |
| H | 2.54864400 | -2.16558900 | 1.52597400 |
| H | 4.55657200 | -2.25122300 | 0.05616400 |
| C | 0.14690100 | -1.15169200 | 0.97677400 |
| C | -1.23124500 | -1.42876900 | 0.48090900 |
| C | -1.46852700 | -2.15435600 | -0.69164100 |
| C | -2.31240900 | -0.98445500 | 1.25121300 |
| C | -2.77623500 | -2.41532200 | -1.09767400 |
| H | -0.63731600 | -2.52790100 | -1.28113200 |
| C | -3.61545400 | -1.23857300 | 0.84186700 |
| H | -2.11074900 | -0.42225800 | 2.15759400 |
| C | -3.84863200 | -1.95111900 | -0.33709900 |
| H | -2.95706000 | -2.98072000 | -2.00618300 |
| H | -4.45093600 | -0.87778200 | 1.43339500 |
| H | -4.86666000 | -2.14822500 | -0.65908300 |
| O | 0.34485800 | -0.91198800 | 2.16459100 |
| C | -0.73007700 | 2.57544700 | -0.63723600 |
| C | 0.08225100 | 2.90717200 | -1.90974700 |
| H | 0.95072300 | 3.52032400 | -1.63983200 |
| H | 0.45284000 | 1.98152500 | -2.36601700 |
| H | -0.50633400 | 3.45079700 | -2.66045200 |
| C | -1.25231200 | 3.90618200 | -0.05016500 |
| H | -1.88416500 | 4.46484900 | -0.75334600 |
| H | -1.83763600 | 3.69930100 | 0.85397400 |
| H | -0.40405900 | 4.54148200 | 0.23248700 |
| C | -1.95665400 | 1.73479700 | -1.05600600 |
| H | -1.63305200 | 0.77473300 | -1.47700200 |
| H | -2.57197900 | 1.51395700 | -0.17636700 |
| H | -2.58043700 | 2.24794000 | -1.79990700 |
| O | 0.04823300 | 1.90833600 | 0.28024700 |
| K | 1.76331200 | 1.43441800 | 1.96239100 |

Triplet Complex KO*t*Bu + Benzophenone



39

-1409.2222485

| | | | |
|---|---|---|---|
| C | 3.63296200 | -0.45756700 | -1.77428500 |
| C | 2.34970700 | -0.07100200 | -2.18334200 |
| C | 1.22615500 | -0.42428800 | -1.44769900 |
| C | 1.33001100 | -1.19261300 | -0.25680500 |
| C | 2.64404800 | -1.55249400 | 0.15084500 |
| C | 3.76273500 | -1.19774400 | -0.59444100 |
| H | 4.50647600 | -0.18073400 | -2.35543400 |
| H | 2.22689600 | 0.52723400 | -3.08300500 |
| H | 0.25398900 | -0.07304300 | -1.77642900 |
| H | 2.75438100 | -2.13583600 | 1.06054100 |
| H | 4.74815500 | -1.50784700 | -0.25598600 |
| C | 0.21217900 | -1.52023000 | 0.62335000 |
| C | -1.18173800 | -1.51550100 | 0.16200800 |
| C | -1.58022300 | -1.73491100 | -1.17567500 |
| C | -2.20720000 | -1.34821100 | 1.12057400 |
| C | -2.92268700 | -1.72526200 | -1.53895300 |
| H | -0.83192900 | -1.94260600 | -1.93427900 |
| C | -3.54785600 | -1.33680700 | 0.75357400 |
| H | -1.91886300 | -1.21691100 | 2.15868600 |
| C | -3.92082100 | -1.51134100 | -0.58277900 |
| H | -3.19463900 | -1.90041600 | -2.57653100 |
| H | -4.31074500 | -1.18916000 | 1.51360300 |
| H | -4.96752400 | -1.50173200 | -0.87070200 |

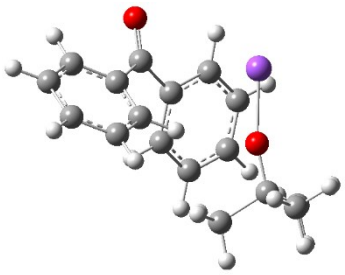
| | | | |
|---|---|---|---|
| O | 0.45664400 | -1.76516200 | 1.86940600 |
| C | -0.74974500 | 2.57995100 | -0.25854800 |
| C | 0.15573100 | 3.25602300 | -1.28973600 |
| H | 0.96802700 | 3.79135700 | -0.79015100 |
| H | 0.58940900 | 2.50260400 | -1.95432300 |
| H | -0.41807500 | 3.96451600 | -1.89442700 |
| C | -1.28439300 | 3.62538100 | 0.75910200 |
| H | -1.86284400 | 4.36399300 | 0.19742000 |
| H | -1.93210900 | 3.14491400 | 1.49554900 |
| H | -0.45818200 | 4.12838200 | 1.26640900 |
| C | -1.92290000 | 1.84412500 | -0.91174200 |
| H | -1.56172500 | 1.13209800 | -1.65881300 |
| H | -2.49169000 | 1.28547500 | -0.16244900 |
| H | -2.58147800 | 2.56176100 | -1.41046700 |
| O | -0.01759300 | 1.73108200 | 0.55644000 |
| K | 1.63127800 | 0.53755500 | 2.33112300 |

Single Point Singlet using Optimised Geometry of Triplet Complex KO*t*Bu + Benzophenone

39
-1409.2708159

| | | | |
|---|---|---|---|
| C | 3.63296200 | -0.45756800 | -1.77428500 |
| C | 2.34970700 | -0.07100200 | -2.18334200 |
| C | 1.22615500 | -0.42428800 | -1.44769900 |
| C | 1.33001100 | -1.19261300 | -0.25680500 |
| C | 2.64404800 | -1.55249500 | 0.15084500 |
| C | 3.76273500 | -1.19774500 | -0.59444100 |
| H | 4.50647600 | -0.18073500 | -2.35543400 |
| H | 2.22689600 | 0.52723400 | -3.08300500 |
| H | 0.25398900 | -0.07304300 | -1.77642900 |
| H | 2.75438100 | -2.13583700 | 1.06054100 |
| H | 4.74815500 | -1.50784800 | -0.25598600 |
| C | 0.21217900 | -1.52023000 | 0.62335000 |
| C | -1.18173800 | -1.51550100 | 0.16200800 |
| C | -1.58022300 | -1.73491100 | -1.17567500 |
| C | -2.20720000 | -1.34821100 | 1.12057400 |
| C | -2.92268700 | -1.72526200 | -1.53895300 |
| H | -0.83192900 | -1.94260600 | -1.93427900 |
| C | -3.54785600 | -1.33680600 | 0.75357400 |
| H | -1.91886300 | -1.21691100 | 2.15868600 |
| C | -3.92082100 | -1.51134000 | -0.58277900 |
| H | -3.19463900 | -1.90041500 | -2.57653100 |
| H | -4.31074500 | -1.18915900 | 1.51360300 |
| H | -4.96752400 | -1.50173100 | -0.87070200 |
| O | 0.45664400 | -1.76516200 | 1.86940600 |
| C | -0.74974500 | 2.57995100 | -0.25854800 |
| C | 0.15573100 | 3.25602300 | -1.28973600 |
| H | 0.96802800 | 3.79135700 | -0.79015100 |
| H | 0.58940900 | 2.50260400 | -1.95432300 |
| H | -0.41807400 | 3.96451600 | -1.89442700 |
| C | -1.28439200 | 3.62538100 | 0.75910200 |
| H | -1.86284300 | 4.36399300 | 0.19742000 |
| H | -1.93210900 | 3.14491400 | 1.49554900 |
| H | -0.45818100 | 4.12838200 | 1.26640900 |
| C | -1.92290000 | 1.84412500 | -0.91174200 |
| H | -1.56172500 | 1.13209800 | -1.65881300 |
| H | -2.49169000 | 1.28547500 | -0.16244900 |
| H | -2.58147800 | 2.56176100 | -1.41046700 |
| O | -0.01759300 | 1.73108200 | 0.55644000 |
| K | 1.63127800 | 0.53755500 | 2.33112300 |

Benzophenone complex with NaO*t*Bu



39
-971.7183487

| | | | |
|---|---|---|---|
| C | 1.75878 | 3.01639 | -1.07029 |
| C | 1.04574 | 2.10808 | -1.85180 |
| C | -0.12554 | 1.53527 | -1.36098 |
| C | -0.59872 | 1.88760 | -0.09223 |
| C | 0.10943 | 2.81591 | 0.68025 |
| C | 1.29221 | 3.36836 | 0.19807 |
| H | 2.68089 | 3.44779 | -1.44761 |
| H | 1.40675 | 1.83618 | -2.83869 |
| H | -0.67616 | 0.82272 | -1.96775 |
| H | -0.27567 | 3.09088 | 1.65782 |
| H | 1.84947 | 4.07383 | 0.80611 |
| C | -1.87998 | 1.33464 | 0.44584 |
| C | -2.31700 | -0.03488 | 0.03283 |
| C | -1.39267 | -1.07007 | -0.16243 |
| C | -3.68875 | -0.28193 | -0.10037 |
| C | -1.85437 | -2.34562 | -0.48891 |
| H | -0.32059 | -0.90834 | -0.02255 |
| C | -4.13824 | -1.55008 | -0.45425 |
| H | -4.39067 | 0.52989 | 0.06523 |
| C | -3.21929 | -2.58443 | -0.64698 |
| H | -1.14129 | -3.15381 | -0.62131 |
| H | -5.20067 | -1.73494 | -0.57717 |
| H | -3.56913 | -3.57617 | -0.91713 |
| O | -2.56374 | 1.99739 | 1.21437 |
| O | 1.73406 | -1.13754 | 0.93557 |
| C | 2.65690 | -1.56193 | 0.00418 |
| C | 3.72705 | -0.47802 | -0.23993 |
| C | 3.36609 | -2.84330 | 0.48772 |
| C | 1.96886 | -1.86779 | -1.34288 |
| H | 3.24383 | 0.44005 | -0.59543 |
| H | 4.24375 | -0.25101 | 0.70030 |
| H | 4.47633 | -0.78615 | -0.98056 |
| H | 2.62509 | -3.63425 | 0.65293 |
| H | 4.11037 | -3.21063 | -0.23034 |
| H | 3.87206 | -2.64606 | 1.44034 |
| H | 2.67877 | -2.20545 | -2.10860 |
| H | 1.21336 | -2.65065 | -1.20438 |
| H | 1.46257 | -0.96728 | -1.71207 |
| Na | 0.73503 | -0.37133 | 2.58857 |

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