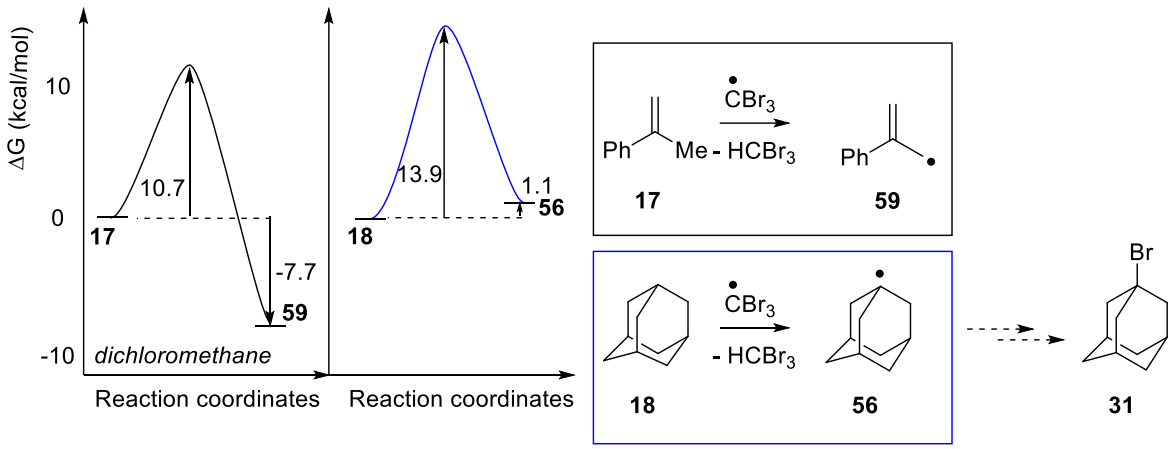
# KO$^t$Bu as a single electron donor? Revisiting the halogenation of alkanes with $CBr_4$ and $CCl_4$

**Katie J. Emery, Allan Young, J. Norman Arokianathar, Tell Tuttle, and John A. Murphy**

## SUPPORTING INFORMATION

### Computational analysis of the reactivity of methylstyrene 17 in dichloromethane.



**Computational modelling of single electron transfer from alkoxides, 14 and 29, to $CBr_4$ in dichloromethane or $CCl_4$ in tetrachloromethane.**

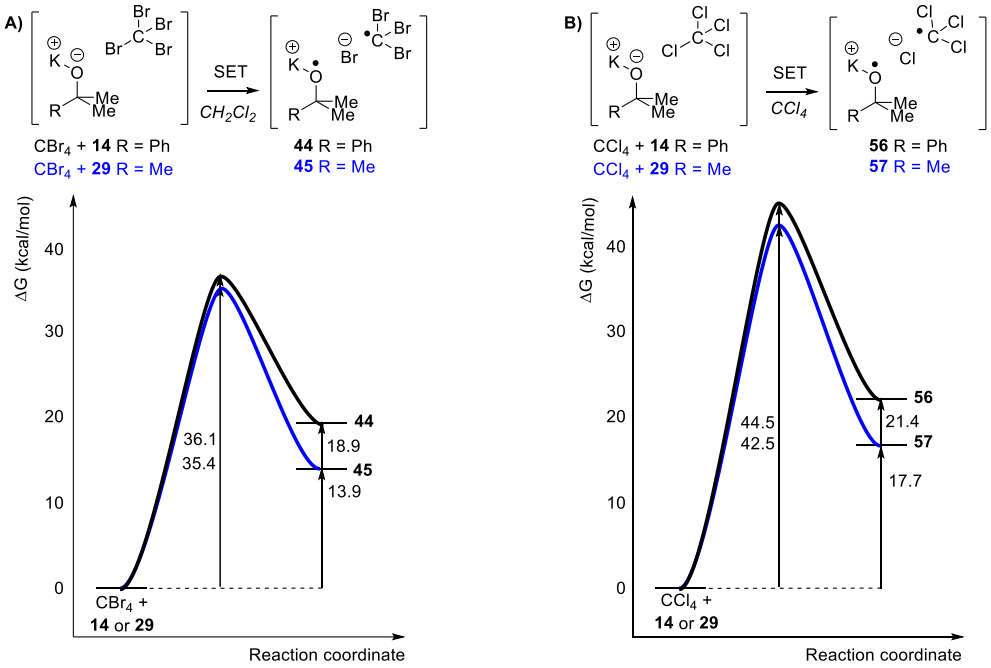
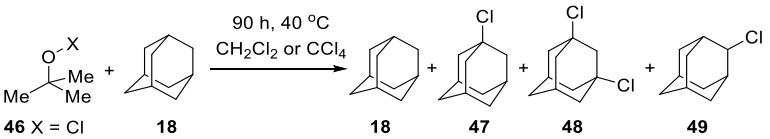



**Figure S1.** Energy profile for SET from potassium 2-phenylpropan-2-olate **14** (black line) or KO$^t$Bu **29** (blue line) to **A)** $CBr_4$ in dichloromethane (left) and **B)** $CCl_4$ in $CCl_4$ (right).

The energy barriers for SET from either KO$^t$Bu, **29**, or potassium 2-phenylpropan-2-olate **14** to a molecule of $CBr_4$ were calculated to be $\Delta G^{\ddagger}$ = 35.4 kcal/mol and 36.1 kcal/mol respectively (SET from KO$^t$Bu to $CCl_4$ in dichloromethane: $\Delta G^{\ddagger}$ = 38.8 kcal/mol and $\Delta G_{rxn}$ = 16.0 kcal/mol), and these barriers are not accessible for a reaction performed at 40 °C. When the reaction was performed in $CCl_4$ a similar energy profile was obtained for the SET from either of the two alkoxides to a molecule of $CCl_4$. The energy barriers calculated were $\Delta G^{\ddagger}$ = 42.5 kcal/mol and 44.5 kcal/mol for SET to $CCl_4$ from KO$^t$Bu **29** and potassium 2-phenylpropan-2-olate **14** respectively. From these computationally derived energy profiles for the SET step, it suggests that the initiation for this halogenation of adamantane **18** is not *via* SET from the alkoxide.

To reassure ourselves that our proposed pathway (Scheme 7) can occur experimentally under our conditions, *tert*-butyl hypochlorite **46** was prepared and subjected to our reaction conditions (Table S1).The *tert*-butyl hypochlorite **46** chlorinated adamantane **18**, in both dichloromethane and $CCl_4$ as the solvents, to give products: 1-chloroadamantane **47** (25% and 11% respectively), and 1,3-dichloroadamantane **48** (16% and 26% respectively) (Table S1, entry 1 and 2). 2-Chloroadamantane **49** (13%) was formed in dichloromethane, but not in $CCl_4$. We also explored whether an efficient chain reaction could be initiated by lower amounts of *tert*-butyl hypochlorite **46** when $CCl_4$ was added in stoichiometric quantities (Table S1, entries 3-5).

**Table S1.** The reaction of *tert*-butyl hypochlorite **46** in dichloromethane or carbon tetrachloride as solvent.

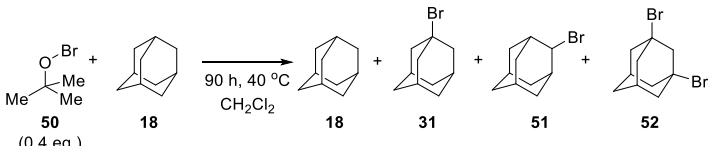



**46** X = Cl **18** **18** **47** **48** **49**

| Entry[a] | Substrate (mmol) | Additive (mmol) | Solvent (mL) | 18 (%) | 47 (%) | 48 (%) | 49 (%) |
|---|---|---|---|---|---|---|---|
| **1** | **46** (2) | **18** (0.5) | $CH_2Cl_2$ (3.13) | 10 | 25 | 16 | 13 |
| **2** | **46** (2) | **18** (0.5) | $CCl_4$ (3.13) | 2 | 11 | 26 | 0 |
| **3** | **46** (0.4) | **18** (0.5) $CCl_4$ (0.5) | $CH_2Cl_2$ (3.13) | 58 | 12 | 1 | 6 |
| **4** | **46** (0.1) | **18** (0.5) $CCl_4$ (0.5) | $CH_2Cl_2$ (3.13) | 66 | <1 | | |
| **5** | | **18** (0.5) $CCl_4$ (0.5) | $CH_2Cl_2$ (3.13) | 71 | | | |

[a] yields were determined by spiking with 1,3,5-trimethoxybenzene (internal standard, 8.4mg, 10mol%)

**Table S2.** *tert*-Butyl hypobromite **50 in** bromination of adamantane **18**.




**50** (0.4 eq.) **18** **18** **31** **51** **52**

(Yields based on adamantane **18** as the limiting reagent)

| Entry[a] | Substrate (mmol) | Additive (mmol) | Solvent (mL) | 18 (%) | 31 (%) | 51 (%) | 52 (%) |
|---|---|---|---|---|---|---|---|
| **1** | **50** (0.4) | **18** (0.5) | $CH_2Cl_2$ (3.13) | 70 | 16 | 4 | <1 |
| **2** | **50** (0.4) | **18** (0.5) $CBr_4$ (0.5) | $CH_2Cl_2$ (3.13) | 2 | 28 | 5 | 18 |
| **3** | **50** (0.1) | **18** (0.5) $CBr_4$ (0.5) | $CH_2Cl_2$ (3.13) | 29 | 35 | 14 | 11 |
| **4** | | **18** (0.5) $CBr_4$ (0.5) | $CH_2Cl_2$ (3.13) | 75 | | | |

[a] yields were determined by spiking with 1,3,5-trimethoxybenzene (internal standard, 8.4mg, 10mol%)

In addition, *tert*-butyl hypobromite **50** was synthesised and subjected to similar reaction conditions (Scheme 7), affording analogous bromoadamantanes - (adamantane **18** (70%), 1-bromooadamantane **31** (16%), 2-bromooadamantane **51** (4%), and 1,3-dibromoadamantane **48** (<1%). We also explored whether an efficient chain reaction could be initiated by lower amounts of *tert*-butyl hypbromite **46** when $CBr_4$ was added (Table S2, entries 2-4). In general, these conditions were not conducive to efficient halogenations.[1]

*Preparation of tert-butyl hypochlorite **46***

Throughout the experiment, all the equipment was covered in aluminium foil and the reaction mixture was always kept in the dark. NaOCl (0.6 M, 200 mL, 1.4 eq.) was added to a round-bottomed flask and the reaction mixture was stirred at 0 °C for 10 min. A mixture of *tert*-butanol (8 mL, 84 mmol) and acetic acid (5.3 mL, 92 mmol, 1.11 eq.) were added in one batch under vigorous stirring and the reaction mixture was stirred at 0 °C for 10 min. The reaction mixture phase-separated. The top yellow phase was separated from the reaction mixture, washed with saturated aqueous $NaHCO_3$ solution (50 mL) and water (50 mL), dried over $Na_2SO_4$ to give *tert*-butyl hypochlorite **46** [2,3] (0.82 mL, d = 1.128 g $mL^{-1}$, 34%) as a yellow oil $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.32 (9 H, s, 3 x C*H*$_3$); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 26.9 (3 x $CH_3$), 84.0 (C). These signals are consistent with the literature values. The *tert*-butyl hypochlorite **46** was used immediately.

*Reactions of tert-butyl hypochlorite 46 with adamantane **18:***

**Table S1, entry 1**

*tert*-Butyl hypochlorite **46** (0.19 mL, freshly prepared, 2 mmol, 4.0 eq.), adamantane **18** (68 mg, 0.5 mmol) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (10%), 1-chloroadamantane **47** (25%), 1,3-dichloroadamantane **48** (16%) and 2-chloroadamantane **49** (13%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.75 – 1.78 (12 H, m), 1.88 (4 H, br s) for adamantane **18**; δ 1.68 (6 H, s), 2.14 (9 H, s) for 1-chloroadamantane **47**;[4] δ 2.06 (8 H, d, *J* = 4 Hz), 2.47 (2 H, s) for 1,3-chloroadamantane **48**;[5] δ 4.40 (1 H, s) 2-chloroadamantane **49**;[6] $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 28.5, 37.9 for adamantane **18**; δ 31.9, 35.7, 47.9 for 1-chloroadamantane **47**;[4] δ 33.5, 33.8, 45.9, 56.6, 66.9 for 1,3-dichloroadamantane **48**;[5,6] δ 26.9, 27.5, 31.1, 35.9, 37.8, 38.3, 68.4 2-chloroadamantane **49**. Analysis of the crude material showed that the products were inseparable, hence the analysis of the product mixture was performed using experimental $^1$H-NMR and $^{13}$C-NMR values reported within the literature as a reference.

1-Chloroadamantane **47**[55] $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.68–1.69 (6 H, m, 6 x C*H*$_2$), 2.14 (9 H, s, 3 x C*H* and 3 x C*H*$_2$); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 31.9, 35.7, 47.9, 69.1.

1,3-Dichloroadamantane **48** [5,6] $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.63 (2 H, br s, C*H*$_2$), 2.06 (8 H, d, 4 x C*H*$_2$), 2.30 (2 H, br s, 2 x C*H*), 2.46 (2 H, s, C*H*$_2$); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 33.4 ($CH_2$), 33.7, (2 x CH), 45.7 (4 x $CH_2$), 56.5 ($CH_2$), 66.7 (2 x C).

2-Chloroadamantane **49**[6] $^1$H-NMR (500 MHz, $CDCl_3$) δ 1.56–1.59 (2 H, m, C*H*$_2$), 1.76–1.87 (6 H, m, 2 x C*H* and 2 x C*H*$_2$), 1.93–1.96 (2 H, m, C*H*$_2$), 2.08 (2 H, br s, 2 x C*H*), 2.26–2.29 (2 H, m, C*H*$_2$), 4.40 (1 H, s, C*H*); $^{13}$C-NMR (125 MHz, $CDCl_3$) δ 27.0, 27.6, 31.2, 36.0, 37.9, 38.3, 68.5.

**Table S1, entry 2**

*tert*-Butyl hypochlorite **46** (0.19 mL, freshly prepared, 2 mmol, 4.0 eq.), adamantane **18** (68 mg, 0.5 mmol) and $CCl_4$ (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (2%), 1-chloroadamantane **47** (11%) and 1,3-

dichloroadamantane **48** (26%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.75–1.78 (12 H, m), 1.88 (4 H, br s) for adamantane **18**; δ 1.68 (6 H, s), 2.14 (9 H, s) for 1-chloroadamantane **47**;[4] δ 2.06 (8 H, d, *J* = 4.0 Hz), 2.47 (2 H, s) for 1,3-chloroadamantane **48**;[5] $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 28.5, 37.9 for adamantane **18**; δ 31.9, 35.7, 47.9 for 1-chloroadamantane **47**;[7] δ 33.5, 33.8, 45.9, 56.6, 66.9 for 1,3-chloroadamantane **48**.[5] These signals are consistent with the literature values and reference samples.

**Table S1, entry 3**

*tert*-Butyl hypochlorite **46** (24 mg, freshly prepared, 0.22 mmol, 0.4 eq.), adamantane **18** (68 mg, 0.5 mmol), carbon tetrachloride (77 mg, 0.5 mmol, 1 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (58%), 1-chloroadamantane **47** (12%), 1,3-dichloroadamantane **48** (1%) and 2-chloroadamantane **49** (6%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.75 – 1.78 (12 H, m), 1.88 (4 H, br s) for adamantane **18**; δ 1.68 (6 H, s), 2.14 (9 H, s) for 1-chloroadamantane **47**;[7] δ 2.06 (8 H, d, *J* = 4 Hz), 2.47 (2 H, s) for 1,3-chloroadamantane **48**;[2] δ 4.40 (1 H, s) 2-chloroadamantane **49**.[9]

Analysis of the crude material showed that the products were inseparable, hence the analysis of the product mixture was performed using experimental $^1$H-NMR and $^{13}$C-NMR values reported within the literature as a reference.

1-Chloroadamantane **47**[4] $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.68 – 1.69 (6 H, m, 6 x C*H*$_2$), 2.14 (9 H, s, 3 x C*H* and 3 x C*H*$_2$); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 31.9, 35.7, 47.9, 69.1.

1,3-Dichloroadamantane **48**[5,8] $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.63 (2 H, br s, C*H*$_2$), 2.06 (8 H, d, 4 x C*H*$_2$), 2.30 (2 H, br s, 2 x C*H*), 2.46 (2 H, s, C*H*$_2$); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 33.4 ($CH_2$), 33.7, (2 x CH), 45.7 (4 x $CH_2$), 56.5 ($CH_2$), 66.7 (2 x C).

2-Chloroadamantane **49**[9] $^1$H-NMR (500 MHz, $CDCl_3$) δ 1.56 – 1.59 (2 H, m, C*H*$_2$), 1.76 – 1.87 (6 H, m, 2 x C*H* and 2 x C*H*$_2$), 1.93 – 1.96 (2 H, m, C*H*$_2$), 2.08 (2 H, br s, 2 x C*H*), 2.26 – 2.29 (2 H, m, C*H*$_2$), 4.40 (1 H, s, C*H*); $^{13}$C-NMR (125 MHz, $CDCl_3$) δ 27.0, 27.6, 31.2, 36.0, 37.9, 38.3, 68.5.

**Table S1, entry 4**

*tert*-Butyl hypochlorite **46** (5.4 mg, freshly prepared, 0.05 mmol, 0.1 eq.), adamantane **18** (68 mg, 0.5 mmol), carbon tetrachloride (77 mg, 0.5 mmol, 1 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (66%) and 1-chloroadamantane **47** (<1%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.75 – 1.78 (12 H, m), 1.88 (4 H, br s) for adamantane **18**; δ 1.68 (6 H, s), 2.14 (9 H, s) for 1-chloroadamantane **47**;[4] $^{13}$C NMR (100MHz, $CDCl_3$) δ 28.5, 37.9 for adamantane **18**; δ 31.9, 35.7, 47.9 for 1-chloroadamantane **47**.[4]

Analysis of the crude material showed that the products were inseparable, hence the analysis of the product mixture was performed using experimental $^1$H-NMR and $^{13}$C-NMR values reported within the literature as a reference.

1-Chloroadamantane **47**[7] $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.68 – 1.69 (6 H, m, 6 x C*H*$_2$), 2.14 (9 H, s, 3 x C*H* and 3 x C*H*$_2$); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 31.9, 35.7, 47.9, 69.1.

**Table S1, entry 5, blank reaction**

Adamantane **18** (68 mg, 0.5 mmol), carbon tetrachloride (77 mg, 0.5 mmol, 1 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (71%) was determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The product was identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.75 – 1.78 (12 H, m), 1.88 (4 H, br s) for adamantane **18**. $^{13}$C NMR (100MHz, $CDCl_3$) δ 28.5, 37.9. These signals are consistent with the literature values and reference samples.

*Reaction of KO$^t$Bu with adamantane **18** in $CCl_4$*

KO$^t$Bu **29** (224 mg, 2 mmol, 4.0 eq.), adamantane **18** (68 mg, 0.5 mmol) and $CCl_4$ (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (64%) and 1-chloroadamantane **47**[4] (5%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.75–1.78 (12 H, m), 1.88 (4 H, br s) for adamantane **18**; δ 1.68 (6 H, s), 2.14 (9 H, s) for 1-chloroadamantane **47**;[4] $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 28.5, 37.9 for adamantane **18**; δ 31.7, 35.6, 47.8 for 1-chloroadamantane **47**.[4] These signals are consistent with the literature values and reference samples.

*Synthesis of tert-butyl hypobromite **50***

Throughout the experiment all the equipment was covered in aluminium foil and the reaction mixture was always kept in the dark. To a round-bottomed flask was added NaOCl (0.6 M, 200 mL, 1.4 eq.) and the reaction mixture was stirred at 0 °C for 10 min. NaBr (9.26 g, 90 mmol, 1.1 eq.) was added and the reaction mixture was stirred at 0 °C for 2 min. A mixture of *tert*-butanol (8 mL, 84 mmol) and acetic acid (5.3 mL, 92 mmol, 1.11 eq.) was added in one batch under vigorous stirring and the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was extracted with dichloromethane (10 mL), washed with water (100 mL), dried over $Na_2SO_4$ to give *tert*-butyl hypobromite **50**[57] as a dark red solution in dichloromethane $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.27 (9 H, s, 3 x C*H*$_3$); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 27.5 (3 x $CH_3$), 82.9 (C). The *tert*-butyl hypobromite **50** was used immediately.

To quantify the amount of *tert*-butyl hypobromite **50** formed, 0.2 mL of the *tert*-butyl hypobromite/dichloromethane solution was transferred to a small vial and a solution of 1,2-dibromoethane (internal standard) in dichloromethane (1 mL, 0.5 M, 0.5 mmol) was added. The concentration was determined from $^1$H-NMR: In 0.2 mL of the *tert*-butyl hypobromite / dichloromethane solution, there is 0.052 mmol of *tert*-butyl hypobromite **50**. The compound was used immediately in reactions. To ensure the *tert*-butyl hypobromite **50** had not decomposed prior to being used in the reactions, the *tert*-butyl hypobromite / dichloromethane solution was analysed in the same way immediately after being used, to determine the amount of *tert*-butyl hypobromite **50** present in the *tert*-butyl hypobromite/dichloromethane solution: the amount was determined from $^1$H-NMR: In 0.2 mL of the *tert*-butyl hypobromite/dichloromethane solution, there was 0.052 mmol of *tert*-butyl hypobromite **50**.

*Reaction of tert-butyl hypobromite **50** with adamantane **18**.*

*tert*-Butyl hypobromite **50** (0.87 mL, freshly prepared and used immediately, 0.22 mmol, 0.4 eq.), adamantane **18** (68 mg, 0.5 mmol) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (70%), 1-bromoadamantane **31** (16%), 2-bromoadamantane **51** (4%) and 1,3-

bromoadamantane **52** (< 1%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.74–1.76 (12 H, m), 1.88 (4 H, br s) for adamantane **18**; δ 1.72 (6 H, m), 2.10 (3 H, br s), 2.36 (6 H, m) for 1-bromoadamantane **31**;[19] δ 1.97–2.00 (2 H, m), 2.15 (2 H, br s), 2.33 (2 H, br s), 4.68 (1 H, br s) for 2-bromoadamantane **51**;[48] δ 1.70 (2 H, m), 2.25–2.30 (10 H, m), 2.87 (2 H, br s) for 1,3-dibromoadamantane **52**.[47] $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 28.5, 37.9 adamantane **18**; δ 32.8, 35.7, 49.5 for 1-bromoadamantane **31**. These signals are consistent with the literature values and reference samples.

*Reactions of KO$^t$Bu (**29**) with adamantane (**18**) and $CBr_4$*

**Table S2, entry 1**

KO$^t$Bu **29** (224 mg, 2 mmol, 4.0 eq.), adamantane **18** (68 mg, 0.5 mmol), $CBr_4$ (166 mg, 0.5 mmol, 1.0 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined and dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (84%) and 1-bromoadamantane **31** (4%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.74–1.76 (12 H, m), 1.88 (4 H, br s) for adamantane **18**; δ 1.72 (6 H, m), 2.10 (3 H, br s), 2.36 (6 H, m) for 1-bromoadamantane **31**; [11] $^{13}$C NMR (100 MHz, $CDCl_3$) δ 28.5, 37.9 adamantane **18**; δ 32.8, 35.7, 49.5 for 1-bromoadamantane **31**. These signals are consistent with the literature values and reference samples. [6, 11]

**Table S2, entry 2**

*tert*-Butyl hypobromite **50** (1.89 mL, freshly prepared and used immediately, 0.22 mmol**,** 0.4 eq.), adamantane **18** (68 mg, 0.5 mmol), carbon tetrabromide (166 mg, 0.5 mmol, 1 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (9%), 1-bromoadamantane **31** (28%), 2-bromoadamantane **51** (5%) and 1,3-bromoadamantane **52** (18%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.74 – 1.76 (12 H, m), 1.88 (4 H, br s) for adamantane **18**; δ 1.72 (6 H, m), 2.10 (3 H, br s), 2.36 (6 H, m) for 1-bromoadamantane **31**;[1] δ 1.97 – 2.00 (2 H, m), 2.15 (2 H, br s), 2.33 (2 H, br s), 4.68 (1 H, br s) for 2-bromoadamantane **51**;[6] δ 1.70 (2 H, m), 2.25 – 2.30 (10 H, m), 2.87 (2 H, br s) for 1,3-dibromoadamantane **52**.[11] $^{13}$C NMR (100MHz, $CDCl_3$) δ 28.5, 37.9 for adamantane **18**; δ 32.8, 35.7, 49.5 for 1-bromoadamantane **31**. These signals are consistent with the literature values and reference samples.

**Table S2, entry 3**

*tert*-Butyl hypobromite **50** (0.33 mL, freshly prepared and used immediately, 0.05 mmol**,** 0.1 eq.), adamantane **18** (68 mg, 0.5 mmol), carbon tetrabromide (166 mg, 0.5 mmol, 1 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (29%), 1-bromoadamantane **31** (35%), 2-bromoadamantane **51** (14%) and 1,3-bromoadamantane **52** (11%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.74 – 1.76 (12 H, m), 1.88 (4 H, br s) for adamantane **18**; δ 1.72 (6 H, m), 2.10 (3 H, br s), 2.36 (6 H, m) for 1-bromoadamantane **31**;[12] δ 1.97 – 2.00 (2 H, m), 2.15 (2 H, br s), 2.33 (2 H, br s), 4.68 (1 H, br s) for 2-bromoadamantane **51**;[45] δ 1.70 (2 H, m), 2.25 – 2.30 (10 H, m), 2.87 (2 H, br s) for 1,3-dibromoadamantane **52**.[13] $^{13}$C NMR (100MHz, $CDCl_3$) δ 28.5, 37.9 for adamantane **18**; δ 32.8, 35.7, 49.5 for 1-bromoadamantane **31**. These signals are consistent with the literature values and reference samples.

**Table S2, entry 4, blank reaction**

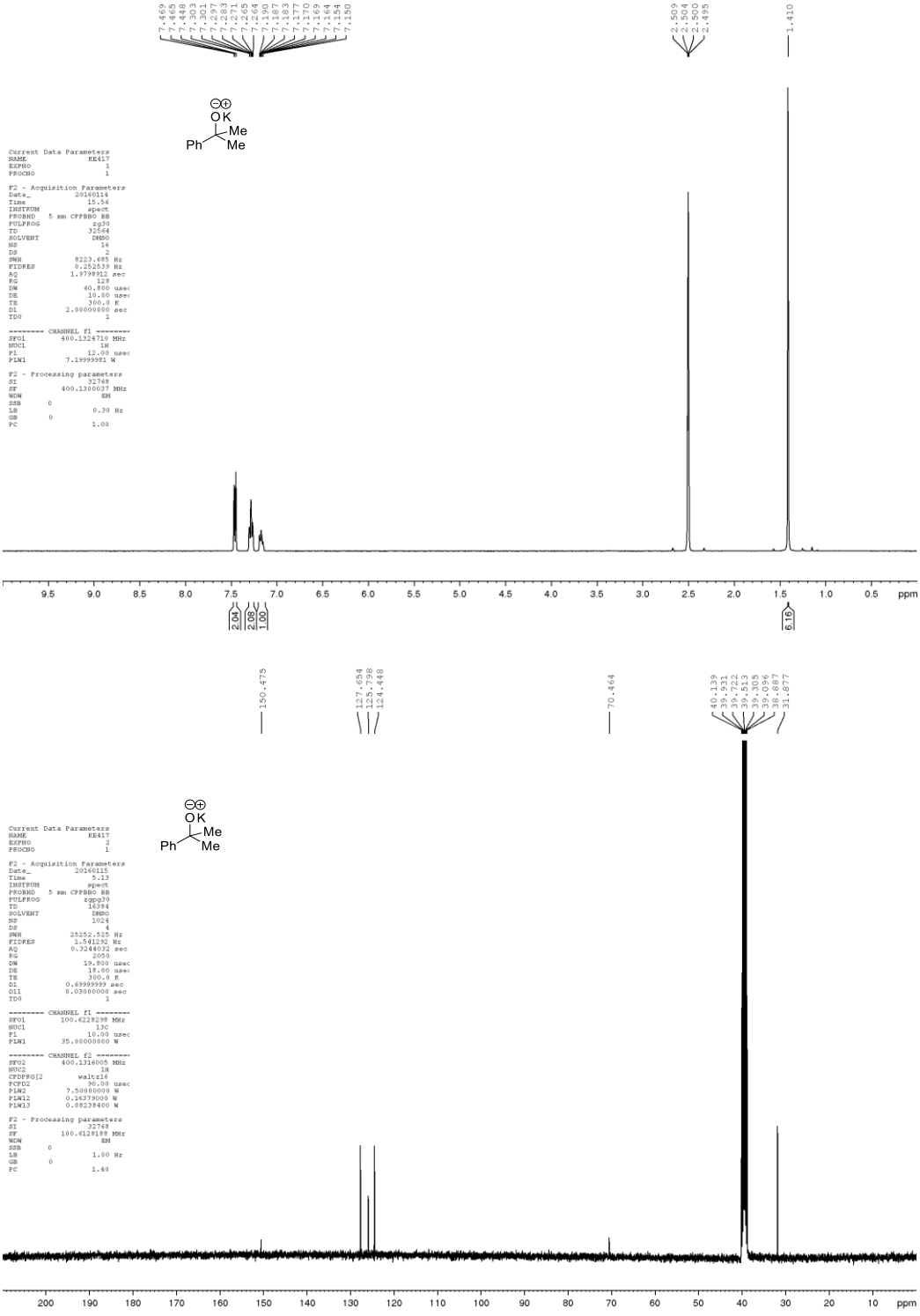
Adamantane **18** (68 mg, 0.5 mmol), carbon tetrabromide (166 mg, 0.5 mmol, 1 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (4 x 10 mL). The organic phases were combined, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The yield of adamantane **18** (75%) was determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The product was identified by the following characteristic signals; $^1$H-NMR (400 MHz, $CDCl_3$) δ 1.74 – 1.76 (12 H, m), 1.88 (4 H, br s) for adamantane **18**. $^{13}$C NMR (100MHz, $CDCl_3$) δ 28.5, 37.9. These signals are consistent with the literature values and reference samples.

## References

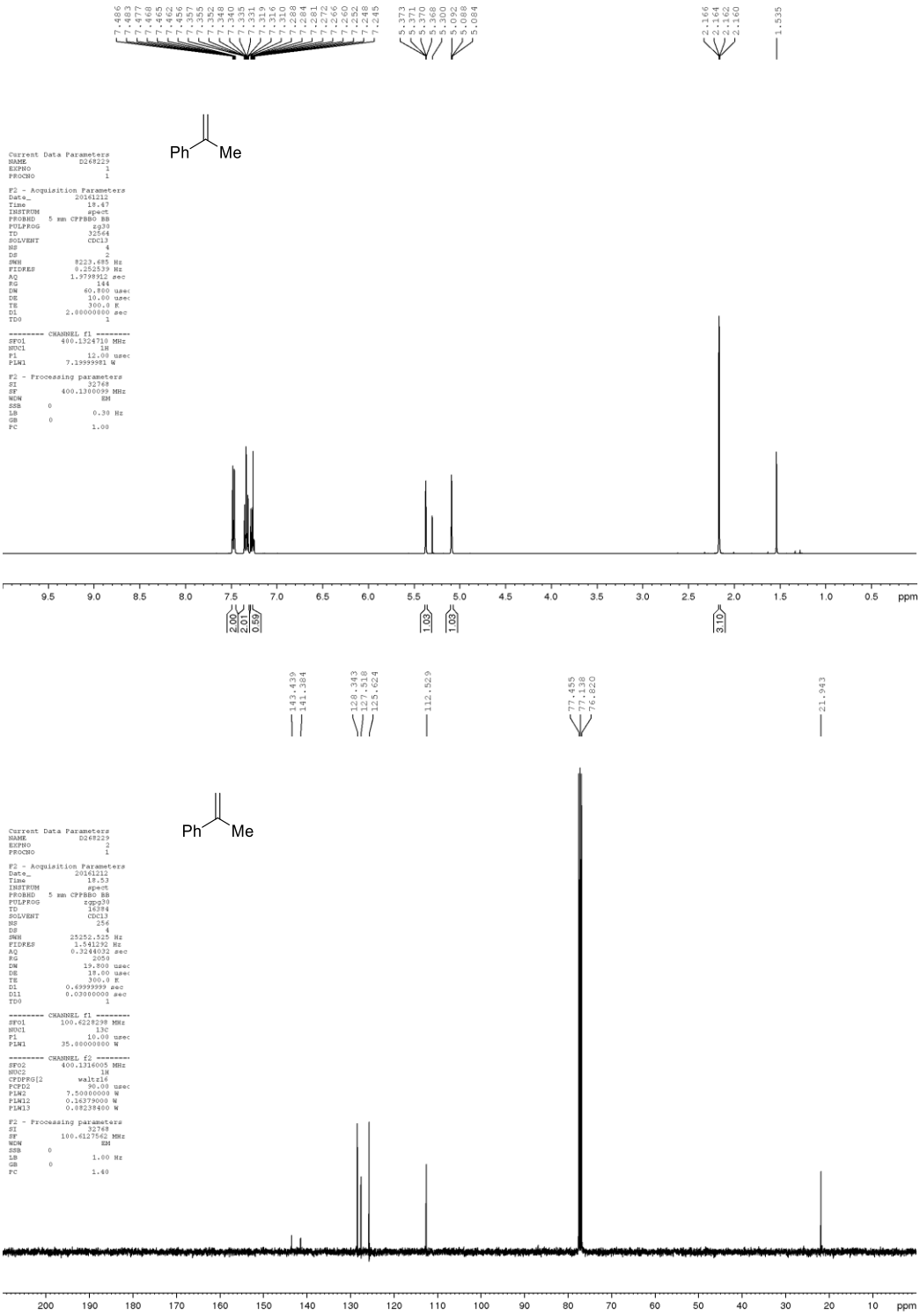
1. For efficient halogenation of alkanes with hypohalites, seeR. Montoro and T. Wirth, *Synthesis*, 2005, 1473−1478.
2. G. Bentzinger, W. De Souza, C. Mullié, P. Agnamey, A. Dassonville-Klimpt, P. Sonnet, *Tetrahedron: Asymmetry*, 2016, **27**, 1−11.
3. F. Kleinbeck, G. J. Fettes, L. D. Fader, E. M. Carreira, *Chem. Eur. J.*, 2012, **18**, 3598−3610.
4. L. Candish, E. A. Standley, A. Gómez-Suárez, S. Mukherjee, F. Glorius, *Chem. Eur. J.*, 2016, **22**, 9971−9974.
5. J. Y. Becker, S. Yatziv, *J. Org. Chem.*, 1988, **53**, 1744−1748.
6. Y. Liu, Y. Xu, S. H. Jung, J. Chae, *Synlett*, 2012, **23**, 2692−2698.
7. Y. Sato, T. Aoyama, T. Takido, M. Kodomari, *Tetrahedron*, 2012, **68**, 7077−7081.
8. R. I. Khusnutdinov, N. A. Shchadneva, A. R. Bayguzina, T. Oshnyakova, Y. Y. Mayakova, U. M. Dzhemilev, *Russ. J. Org.Chem.*, 2013, **49**, 1557−1566.
9. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009
10. C. Walling, J. A. McGuinness, *J. Am. Chem. Soc.*, 1969, **91**, 2053−2058.
11. S. E. Denmark, B. R. Henke, *J. Am. Chem. Soc.*, 1991, **113**, 2177−2194
12. A. A. Fokin and P. R. Schreiner, *Adv. Synth. Catal.*, 2003, **345**, 1035−1052.
13. 44. M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.*, 2003, **24**, 669−681

# $^{1}$H and $^{13}$C-NMR Spectra

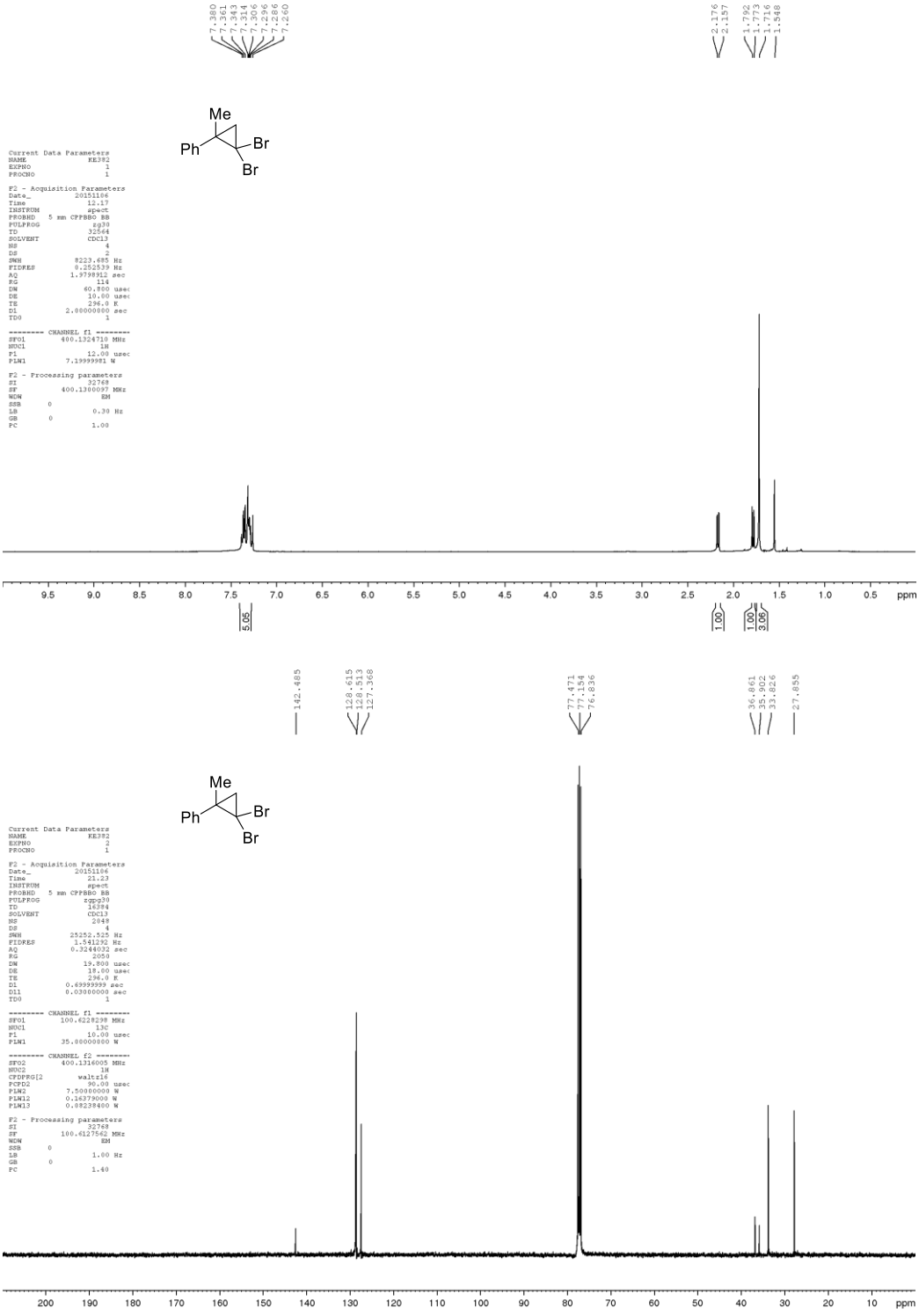
## $^{1}$H-NMR and $^{13}$C-NMR 14



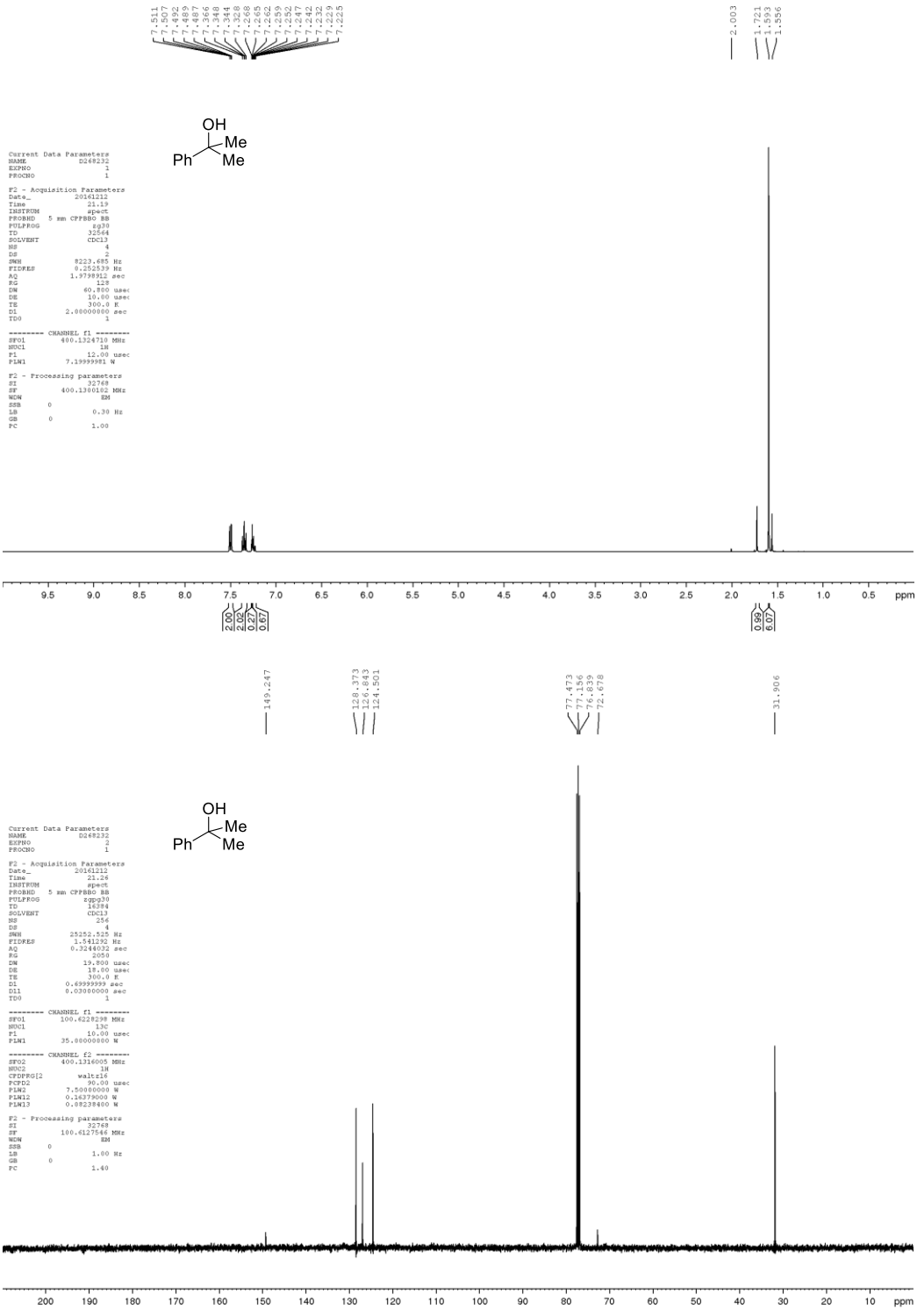
## $^{1}$H-NMR and $^{13}$C-NMR 17 (Commercial sample used as a reference)



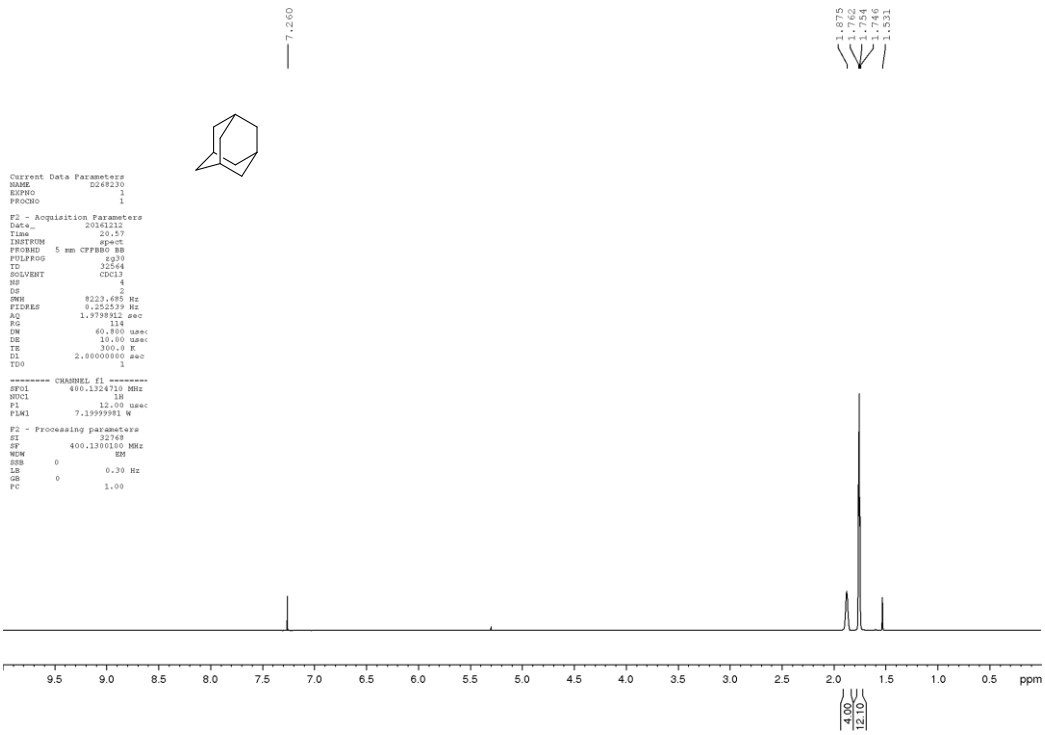
## $^{1}$H-NMR and $^{13}$C-NMR 16

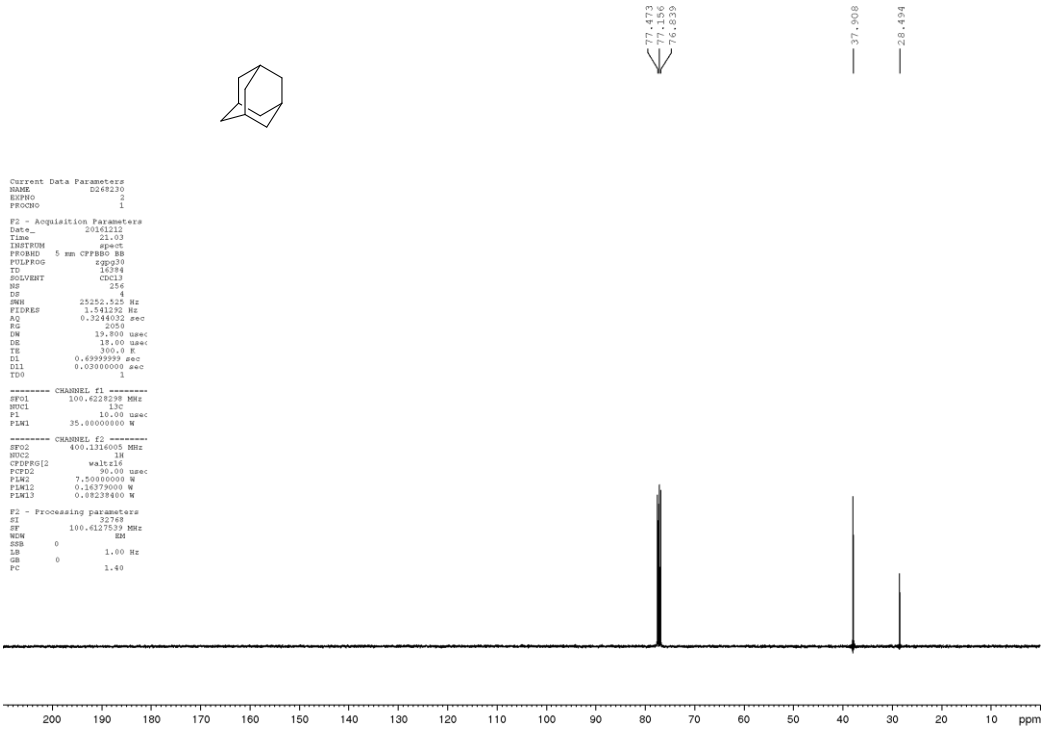


## $^{1}$H-NMR and $^{13}$C-NMR 15

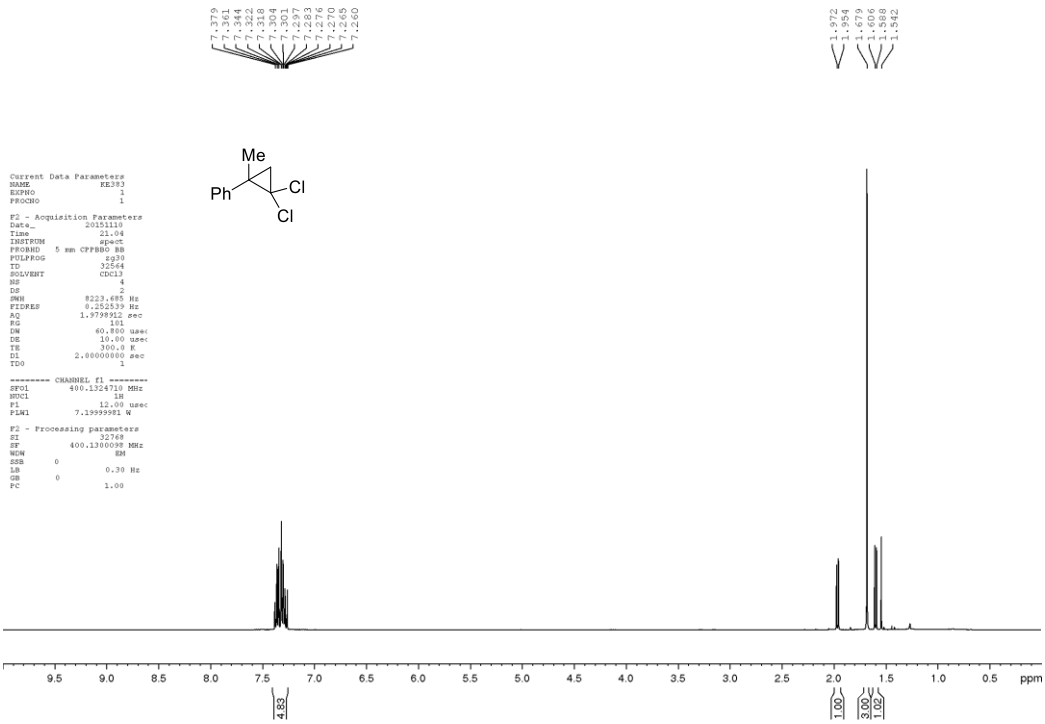


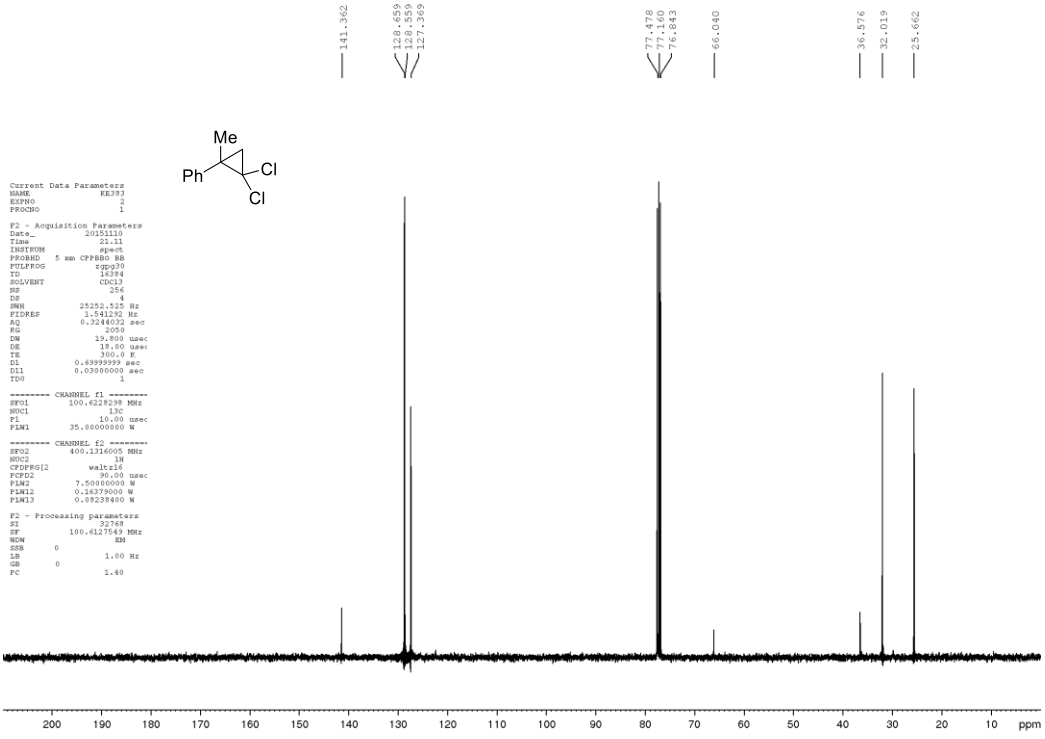
## $^{1}$H-NMR and $^{13}$C-NMR 18



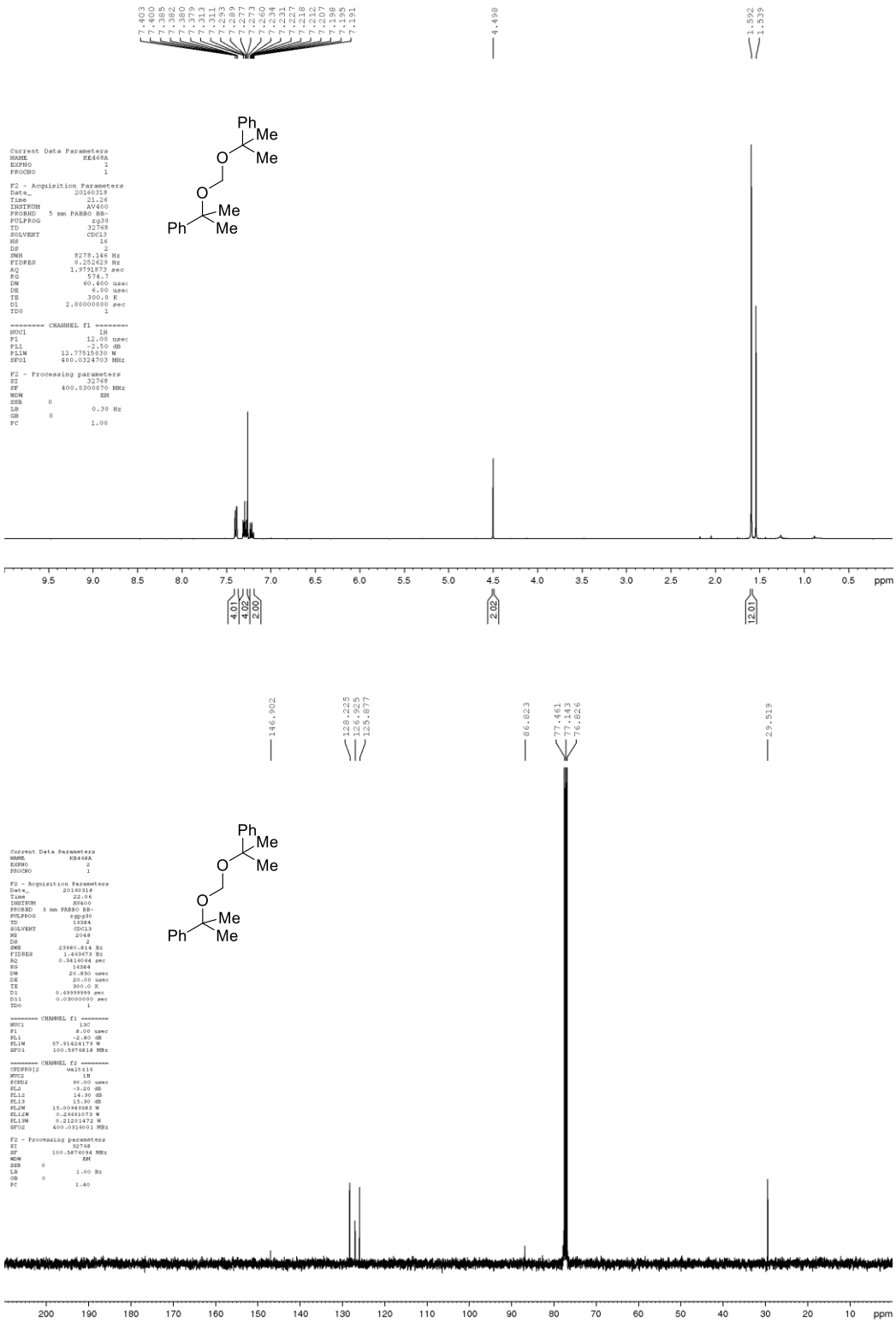



## $^{1}$H-NMR and $^{13}$C-NMR 19

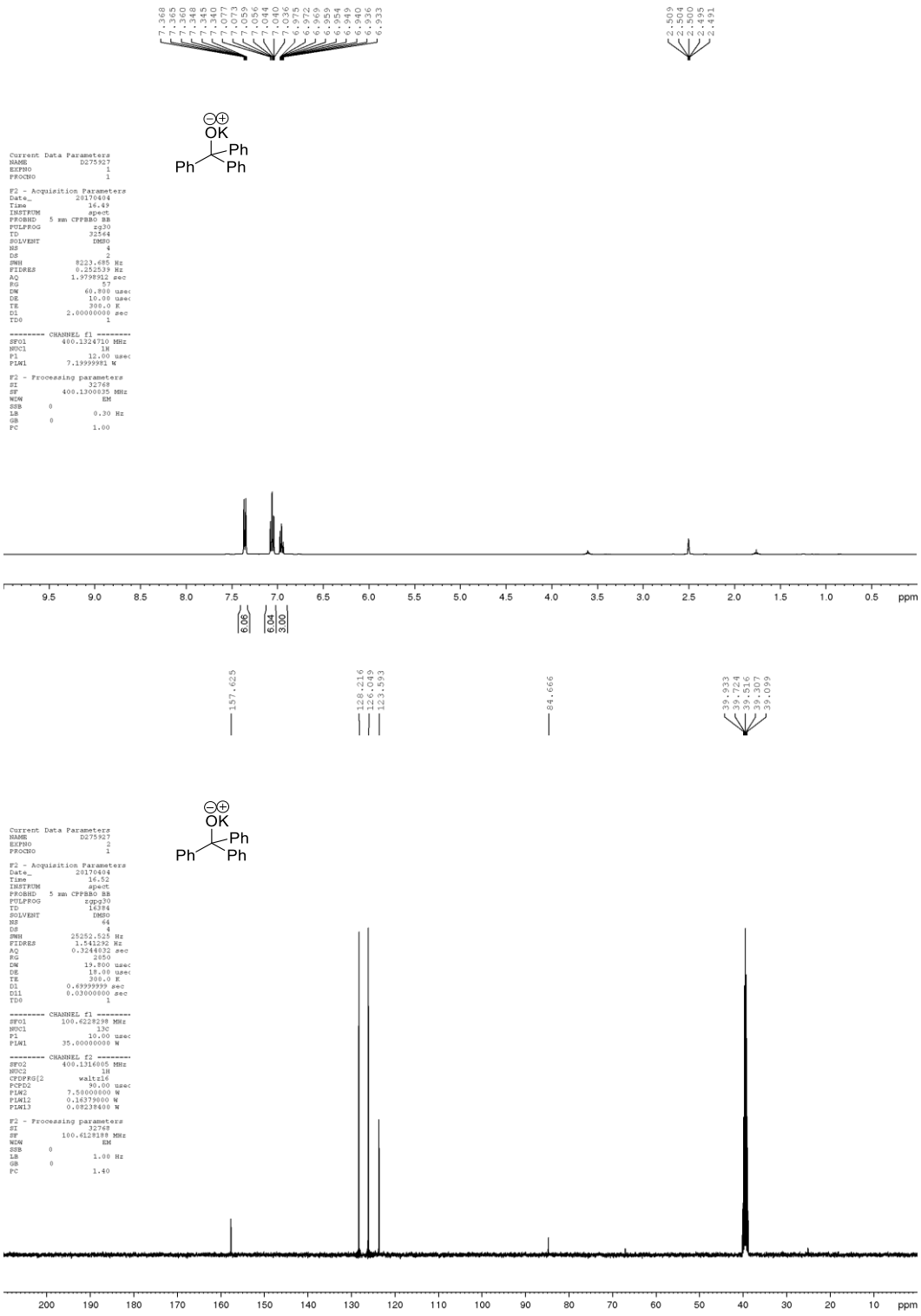




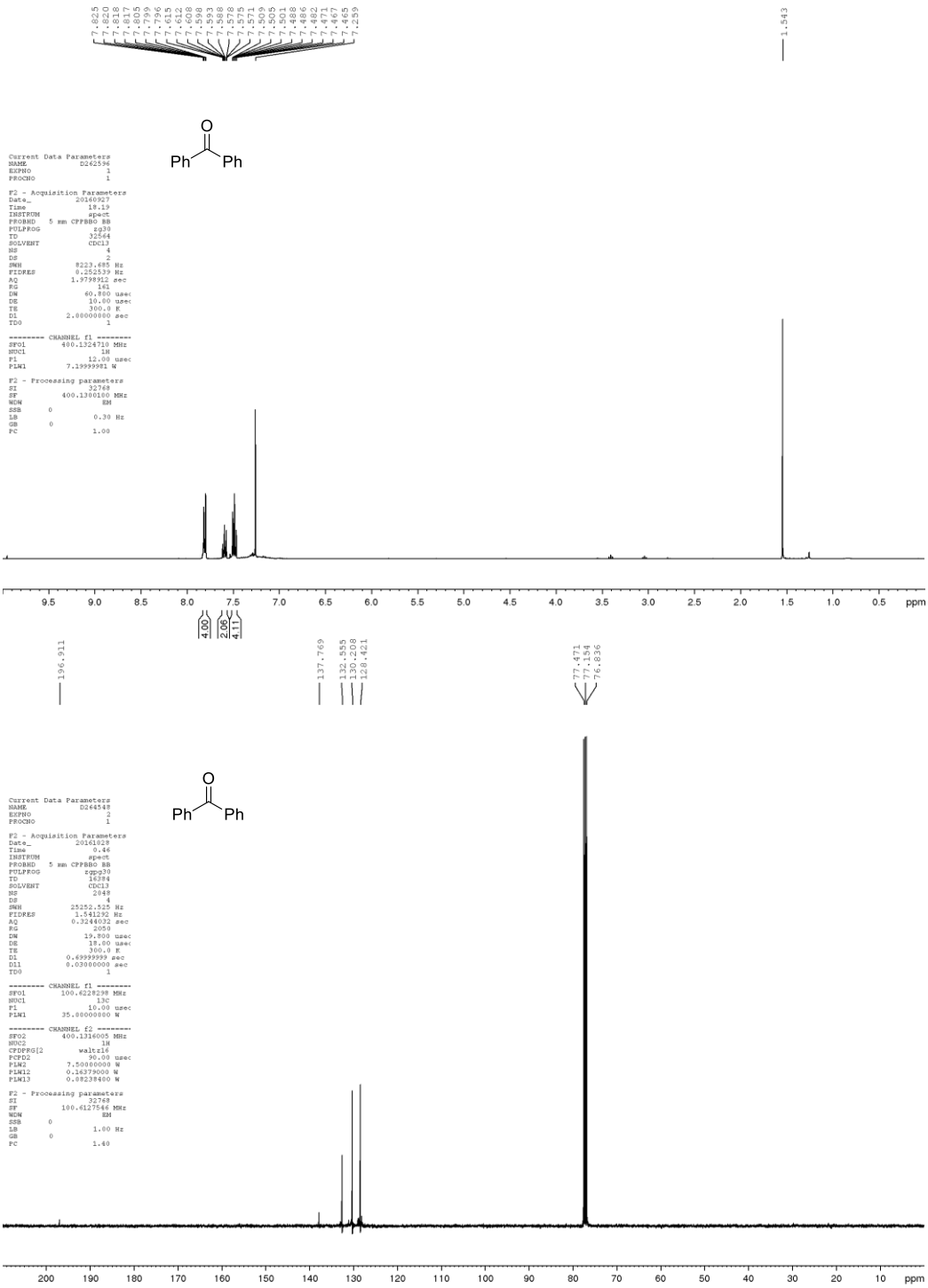

**$^{1}$H-NMR and $^{13}$C-NMR 20**



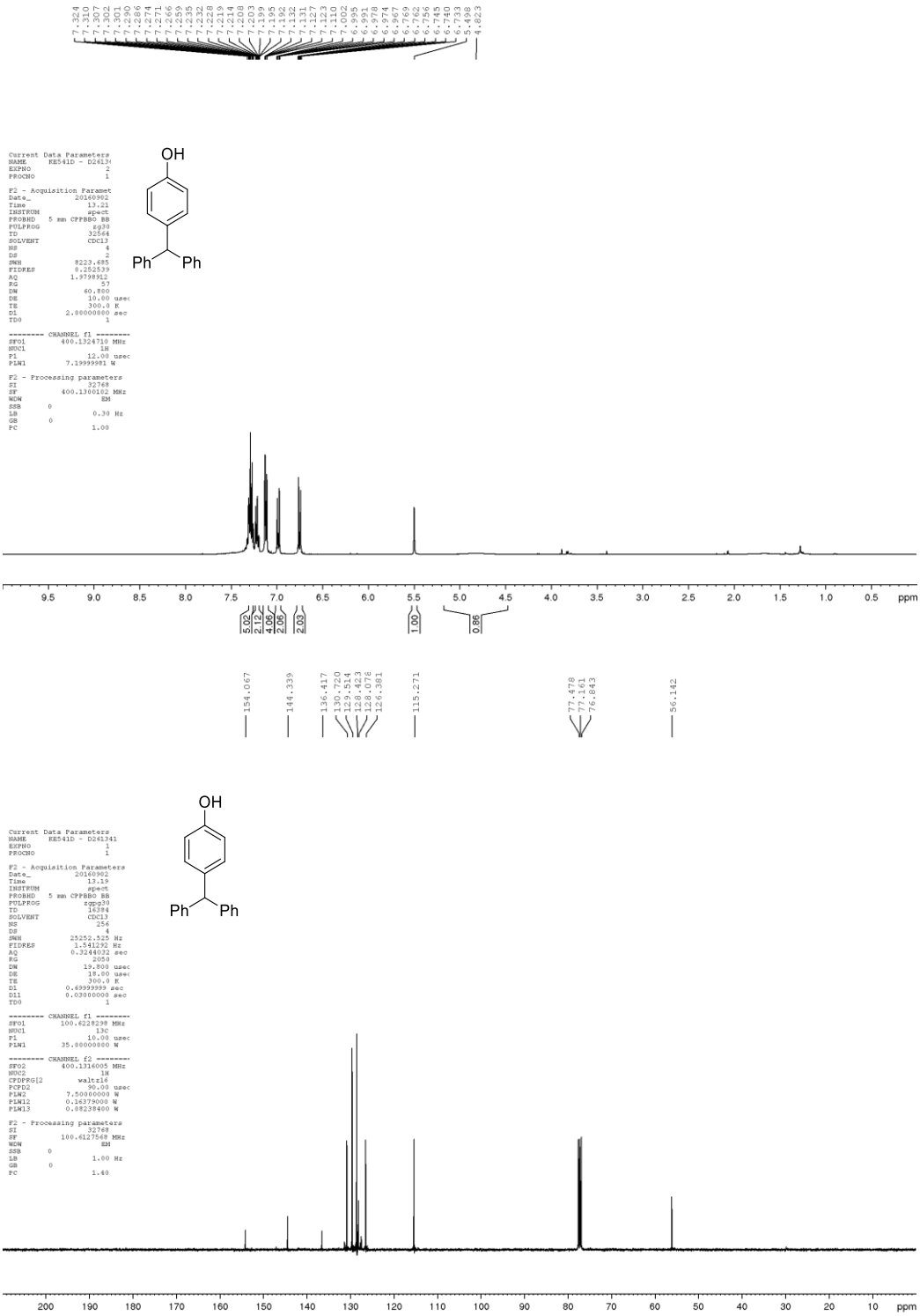

**$^{1}$H-NMR and $^{13}$C-NMR 30**



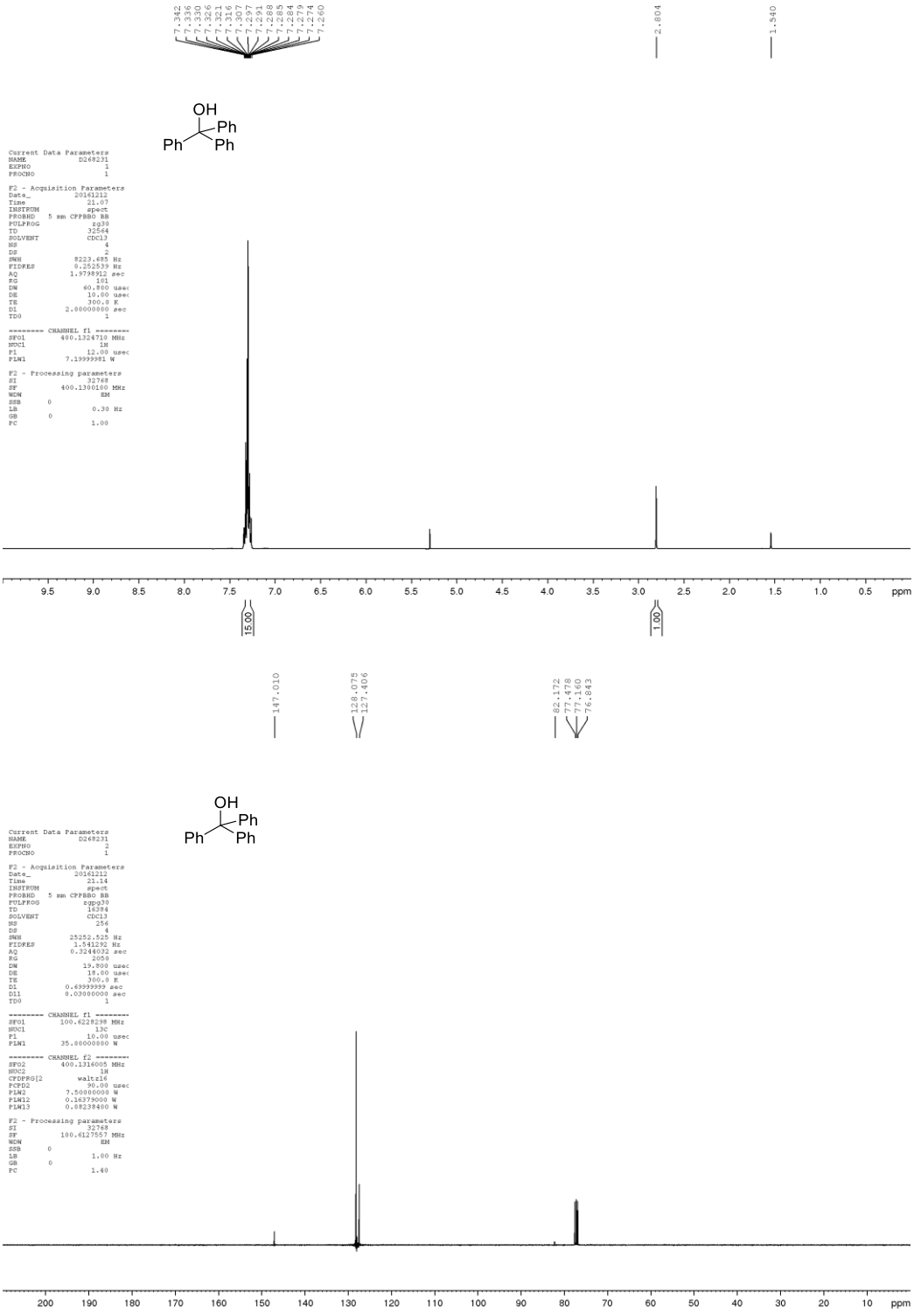

**$^{1}$H-NMR and $^{13}$C-NMR 33**


7.625
7.620
7.618
7.617
7.605
7.799
7.796
7.615
7.612
7.608
7.598
7.593
7.588
7.578
7.575
7.571
7.503
7.505
7.501
7.488
7.486
7.482
7.471
7.467
7.465
7.259
1.543
O
Ph
Ph
Current Data Parameters
NAME D262596
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160927
Time 18.19
INSTRUM spect
PROBHD 5 mm CPFBBO BB
PULPROG zg30
TD 32564
SOLVENT CDCl3
NS 4
DS 2
SWH 8223.685 Hz
FIDRES 0.252539 Hz
AQ 1.9798912 sec
RG 161
DW 60.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
PLW1 7.19999981 W
F2 - Processing parameters
SI 32768
SF 400.1300180 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
4.00
2.06
4.11
196.911
137.769
132.555
130.208
128.421
77.471
77.154
76.836
O
Ph
Ph
Current Data Parameters
NAME D264548
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20161028
Time 0.46
INSTRUM spect
PROBHD 5 mm CPFBBO BB
PULPROG zgpg30
TD 16384
SOLVENT CDCl3
NS 2048
DS 4
SWH 25252.525 Hz
FIDRES 1.541292 Hz
AQ 0.3244032 sec
RG 2050
DW 19.800 usec
DE 18.00 usec
TE 300.0 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
PLW1 35.00000000 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 7.50000000 W
PLW12 0.16379000 W
PLW13 0.08238400 W
F2 - Processing parameters
SI 32768
SF 100.6127546 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

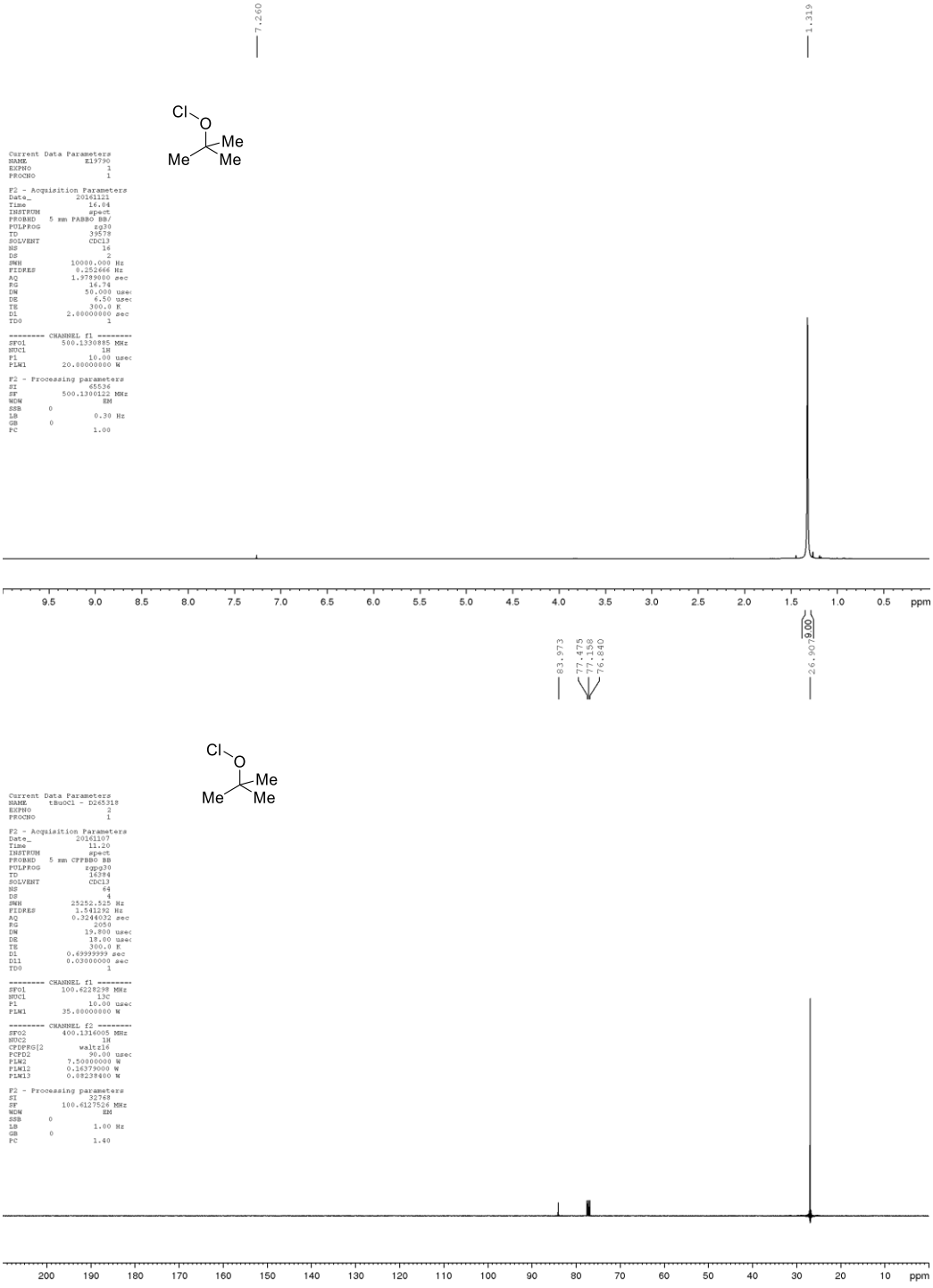
# $^{1}$H-NMR and $^{13}$C-NMR 34



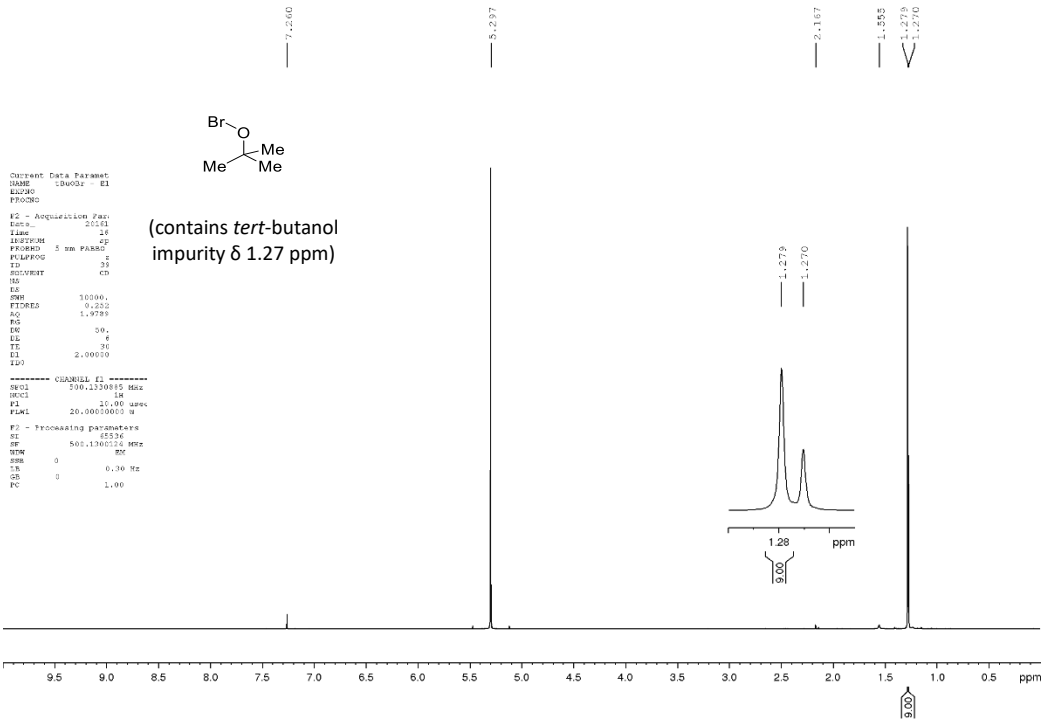
## $^{1}$H-NMR and $^{13}$C-NMR 32



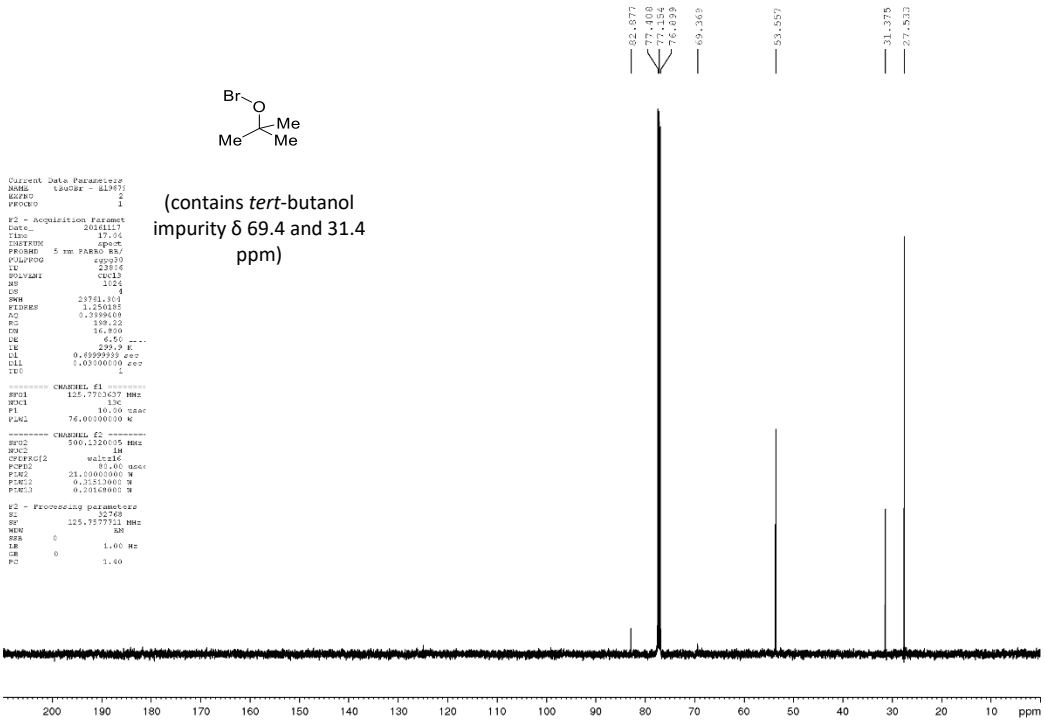
## $^{1}$H-NMR and $^{13}$C-NMR 46



## $^{1}$H-NMR and $^{13}$C-NMR *tert*-butyl hypobromite 50

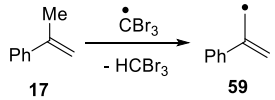



(contains *tert*-butanol impurity δ 1.27 ppm)




(contains *tert*-butanol impurity δ 69.4 and 31.4 ppm)

# 1.5 XYZ coordinates for computational optimisation




**H atom abstraction in 17 /$CBr_3$ radical – starting species 17 and $CBr_3$ radical in benzene**

23

-426.9051125

| | | | |
|---|---|---|---|
| C | -3.90491 | -0.96580 | -0.22621 |
| C | -3.75423 | 0.22028 | -0.93490 |
| C | -2.81466 | 1.16321 | -0.53024 |
| C | -2.01249 | 0.94800 | 0.59521 |
| C | -2.18151 | -0.24924 | 1.30281 |
| C | -3.11299 | -1.19521 | 0.89682 |
| H | -4.62615 | -1.70798 | -0.54756 |
| H | -4.36334 | 0.41279 | -1.81055 |
| H | -2.70514 | 2.07400 | -1.10586 |
| H | -1.55768 | -0.45941 | 2.16292 |
| H | -3.21328 | -2.12069 | 1.45215 |
| C | -0.98211 | 1.94772 | 0.98847 |
| C | -0.47340 | 2.00075 | 2.22312 |
| H | -0.80937 | 1.34756 | 3.01932 |
| H | 0.29386 | 2.72463 | 2.47338 |
| C | -0.53525 | 2.92369 | -0.07065 |
| H | -0.28316 | 2.40786 | -1.00190 |
| H | -1.32946 | 3.64039 | -0.29914 |
| H | 0.33765 | 3.48289 | 0.26573 |
| C | 0.98108 | -0.25076 | -0.12691 |
| Br | 0.07561 | -0.85567 | -1.68954 |
| Br | 1.21401 | -1.53394 | 1.26330 |
| Br | 2.45321 | 0.93081 | -0.41129 |

**H atom abstraction from 17/$CBr_3$ radical – transition state in benzene**

23

-426.8834349

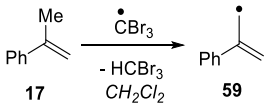
| | | | |
|---|---|---|---|
| C | 4.17606 | -1.13666 | -0.53288 |
| C | 3.82027 | -1.28025 | 0.80551 |
| C | 2.92644 | -0.39085 | 1.38987 |
| C | 2.38639 | 0.66507 | 0.65015 |
| C | 2.75495 | 0.80453 | -0.69065 |
| C | 3.64219 | -0.09082 | -1.27887 |
| H | 4.86504 | -1.83688 | -0.99040 |
| H | 4.23815 | -2.08797 | 1.39485 |
| H | 2.65968 | -0.51158 | 2.43379 |
| H | 2.31817 | 1.60298 | -1.27986 |
| H | 3.90778 | 0.02362 | -2.32324 |
| C | 1.40737 | 1.60667 | 1.26104 |
| C | 1.48234 | 2.93075 | 1.04236 |
| H | 2.29363 | 3.36218 | 0.46779 |
| H | 0.73944 | 3.60649 | 1.45056 |
| C | 0.29768 | 1.01752 | 2.02100 |
| H | 0.53096 | 0.13828 | 2.62011 |
| H | -0.34978 | 1.72754 | 2.53226 |
| H | -0.44283 | 0.49086 | 1.12809 |
| C | -1.17109 | -0.08734 | 0.05548 |
| Br | -0.29117 | -1.76801 | -0.34876 |
| Br | -1.03658 | 1.20776 | -1.37934 |
| Br | -2.98928 | -0.31824 | 0.70604 |

**H atom abstraction from 17 – products 59 and $HCBr_3$ in benzene**

23

-426.9178080

| | | | |
|---|---|---|---|
| C | -3.43817 | -1.67132 | -0.27794 |
| C | -3.64023 | -0.56709 | -1.10143 |
| C | -3.10845 | 0.66920 | -0.75541 |
| C | -2.37730 | 0.82307 | 0.42482 |
| C | -2.19771 | -0.28572 | 1.25574 |
| C | -2.71640 | -1.52726 | 0.90250 |
| H | -3.84107 | -2.63822 | -0.55513 |
| H | -4.20963 | -0.66968 | -2.01787 |
| H | -3.26482 | 1.52608 | -1.40150 |
| H | -1.62590 | -0.18269 | 2.17282 |
| H | -2.54776 | -2.38216 | 1.54689 |
| C | -1.75329 | 2.13504 | 0.76979 |
| C | -1.82435 | 2.60181 | 2.07395 |
| H | -2.37191 | 2.06320 | 2.83593 |
| H | -1.34882 | 3.53447 | 2.35094 |
| C | -1.08500 | 2.83989 | -0.22445 |
| H | -1.00182 | 2.45018 | -1.23132 |
| H | -0.62342 | 3.79539 | -0.00779 |
| C | 1.01894 | -0.02651 | 0.04643 |
| Br | 0.18676 | -0.65225 | -1.59916 |
| Br | 1.41858 | -1.50066 | 1.26207 |
| Br | 2.60186 | 1.06525 | -0.31788 |
| H | 0.31481 | 0.62475 | 0.54665 |




**H atom abstraction from 17 – starting species 17 and $CBr_3$ radical in dichloromethane**

23

-426.9068042

| | | | |
|---|---|---|---|
| C | -0.59175 | 3.06143 | 0.44122 |
| C | -1.02673 | 2.66498 | -0.82260 |
| C | -1.80766 | 1.52723 | -0.96838 |
| C | -2.18557 | 0.76412 | 0.14608 |
| C | -1.73160 | 1.16674 | 1.40583 |

| | | | |
|---|---|---|---|
| C | -0.94354 | 2.30540 | 1.55306 |
| H | 0.03010 | 3.94199 | 0.55238 |
| H | -0.73792 | 3.23400 | -1.69904 |
| H | -2.10703 | 1.20768 | -1.96006 |
| H | -1.99174 | 0.58985 | 2.28556 |
| H | -0.60309 | 2.59794 | 2.53975 |
| C | -3.03071 | -0.45118 | -0.00387 |
| C | -2.86318 | -1.54062 | 1.02446 |
| C | -3.91791 | -0.56892 | -0.99594 |
| H | -4.08513 | 0.22324 | -1.71640 |
| H | -4.51586 | -1.46719 | -1.10062 |
| C | 0.89088 | -0.29981 | -0.06697 |
| Br | 1.20544 | -0.97081 | 1.69270 |
| Br | 2.20482 | 0.90390 | -0.74481 |
| Br | 0.18166 | -1.55165 | -1.32107 |
| H | -3.41533 | -2.43363 | 0.73161 |
| H | -3.23589 | -1.21965 | 2.00120 |
| H | -1.80850 | -1.80068 | 1.14977 |

**H atom abstraction from 17 – transition state in dichloromethane**

23

-426.8841066

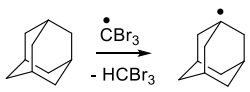
| | | | |
|---|---|---|---|
| C | -4.93425 | -0.93960 | 0.31081 |
| C | -4.45968 | -1.10433 | -0.98683 |
| C | -3.35036 | -0.38621 | -1.42252 |
| C | -2.70425 | 0.51624 | -0.57224 |
| C | -3.18871 | 0.67134 | 0.73140 |
| C | -4.29340 | -0.04975 | 1.16937 |
| H | -5.79446 | -1.50352 | 0.65184 |
| H | -4.95357 | -1.79168 | -1.66365 |
| H | -3.00198 | -0.51388 | -2.44109 |
| H | -2.67823 | 1.34348 | 1.41216 |
| H | -4.64978 | 0.07666 | 2.18501 |
| C | -1.53952 | 1.31267 | -1.05076 |
| C | -1.39905 | 2.60647 | -0.70624 |
| H | -2.13987 | 3.11551 | -0.10122 |
| H | -0.54483 | 3.18284 | -1.04387 |
| C | -0.51527 | 0.64293 | -1.86737 |
| H | -0.82085 | -0.25558 | -2.39869 |
| H | 0.10015 | 1.30802 | -2.47133 |
| H | 0.32769 | 0.19521 | -1.04441 |
| C | 1.31070 | -0.12675 | -0.04838 |
| Br | 0.28971 | -0.44313 | 1.56750 |
| Br | 2.43186 | 1.45424 | 0.06253 |
| Br | 2.26696 | -1.69725 | -0.67083 |

**H atom abstraction of 17 $CBr_3$ radical – products X and $HCBr_3$ in dichloromethane**

23

-426.9183180

| | | | |
|---|---|---|---|
| C | 4.11587 | 0.97577 | -0.96558 |
| C | 4.15326 | -0.41515 | -1.02216 |
| C | 3.34429 | -1.17143 | -0.18125 |
| C | 2.48362 | -0.55089 | 0.72891 |
| C | 2.46284 | 0.84529 | 0.78609 |
| C | 3.26953 | 1.60346 | -0.05627 |
| H | 4.74458 | 1.56573 | -1.62210 |
| H | 4.81842 | -0.91153 | -1.71908 |
| H | 3.39178 | -2.25371 | -0.22384 |
| H | 1.78713 | 1.34464 | 1.47062 |
| H | 3.22978 | 2.68531 | -0.00560 |
| C | 1.59060 | -1.36238 | 1.60902 |
| C | 1.28807 | -0.91016 | 2.88641 |
| H | 1.72996 | -0.00937 | 3.29075 |
| H | 0.61904 | -1.47671 | 3.52222 |
| C | 1.05011 | -2.55022 | 1.12671 |
| H | 1.23036 | -2.88931 | 0.11532 |
| H | 0.41636 | -3.15755 | 1.76138 |
| C | -1.19716 | -0.04895 | 0.03483 |
| Br | -0.29426 | -0.28200 | -1.67931 |
| Br | -1.15922 | 1.80871 | 0.63442 |
| Br | -3.02314 | -0.74819 | -0.01312 |
| H | -0.65202 | -0.63812 | 0.76026 |




**18** **56**

H **atom abstraction from 18 – starting species 18 in dichloromethane**

26

-390.6458290

| | | | |
|---|---|---|---|
| C | -1.10154 | 0.02223 | -1.38950 |
| H | -0.87252 | -0.32352 | -2.40376 |
| H | -2.13602 | 0.38348 | -1.39153 |
| C | -0.14894 | 1.16304 | -0.99714 |
| H | -0.25448 | 1.98966 | -1.70645 |
| C | -0.95480 | -1.14017 | -0.39527 |
| H | -1.63379 | -1.95113 | -0.67608 |
| C | 0.49445 | -1.65081 | -0.41808 |
| H | 0.74433 | -2.02000 | -1.41905 |
| H | 0.60526 | -2.48969 | 0.27824 |
| C | 1.29871 | 0.64722 | -1.01915 |
| H | 1.98763 | 1.45755 | -0.75565 |
| H | 1.55958 | 0.30977 | -2.02852 |
| C | 1.45112 | -0.51376 | -0.02418 |
| H | 2.48252 | -0.87897 | -0.04101 |
| C | 1.10161 | -0.02221 | 1.38921 |
| H | 1.22124 | -0.83941 | 2.10939 |
| H | 1.78726 | 0.77959 | 1.68541 |
| C | -0.49477 | 1.65065 | 0.41869 |
| H | -1.52101 | 2.03405 | 0.44120 |
| H | 0.17003 | 2.47435 | 0.70211 |
| C | -1.29900 | -0.64750 | 1.01887 |
| H | -2.33607 | -0.29479 | 1.04870 |
| H | -1.21276 | -1.47342 | 1.73385 |
| C | -0.34658 | 0.49150 | 1.41647 |
| H | -0.59276 | 0.84140 | 2.42368 |

**H atom abstraction from 18 – starting species $CBr_3$ radical in dichloromethane**

4

-78.0020647

| | | | |
|---|---|---|---|
| C | 0.00044 | -0.00044 | 0.33966 |
| Br | 1.85239 | -0.26784 | -0.01942 |
| Br | -1.15836 | -1.46920 | -0.01941 |
| Br | -0.69410 | 1.73712 | -0.01940 |

**H atom abstraction of 18 – transition state in dichloromethane**

30

-468.6412626

| | | | |
|---|---|---|---|
| C | -1.69951 | 0.40968 | -1.37350 |
| H | -1.35970 | -0.26981 | -2.16298 |
| H | -1.26297 | 1.39556 | -1.56598 |
| C | -1.27870 | -0.11942 | -0.01398 |
| H | -0.01580 | -0.12510 | -0.00522 |
| C | -3.24812 | 0.48677 | -1.37206 |
| H | -3.58923 | 0.88147 | -2.33389 |
| C | -3.81937 | -0.91892 | -1.13979 |
| H | -3.51459 | -1.58326 | -1.95483 |
| H | -4.91350 | -0.87447 | -1.13991 |
| C | -1.77575 | -1.53624 | 0.19124 |
| H | -1.39852 | -1.96322 | 1.12699 |
| H | -1.45054 | -2.17692 | -0.63501 |
| C | -3.32356 | -1.47091 | 0.21180 |
| H | -3.72308 | -2.47631 | 0.36899 |
| C | -3.79325 | -0.53614 | 1.33668 |
| H | -4.88798 | -0.50047 | 1.33763 |
| H | -3.47812 | -0.92654 | 2.31069 |
| C | -1.68675 | 0.80869 | 1.11071 |
| H | -1.28831 | 1.81234 | 0.92686 |
| H | -1.29891 | 0.46045 | 2.07465 |
| C | -3.71027 | 1.41610 | -0.24248 |
| H | -3.32890 | 2.43104 | -0.39422 |
| H | -4.80407 | 1.47528 | -0.24405 |
| C | -3.23091 | 0.87094 | 1.11601 |
| H | -3.55531 | 1.52897 | 1.92712 |
| C | 1.37627 | -0.02003 | -0.01850 |
| Br | 1.72052 | 1.87164 | -0.36574 |
| Br | 2.14090 | -1.19722 | -1.37614 |
| Br | 1.91769 | -0.54391 | 1.78549 |

**H atom abstraction from 18 – product 56 in dichloromethane**

25

-389.9798509

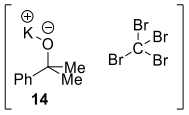
| | | | |
|---|---|---|---|
| C | -0.90747 | -1.12797 | 1.07358 |
| H | -1.92515 | -0.97635 | 1.44813 |
| H | -0.54442 | -2.09287 | 1.44230 |
| C | 0.00178 | -0.00498 | 1.48362 |
| C | -0.91612 | -1.13082 | -0.48126 |
| H | -1.56639 | -1.93233 | -0.84494 |
| C | -1.43462 | 0.22863 | -0.97862 |
| H | -2.45908 | 0.39005 | -0.62550 |
| H | -1.46100 | 0.23602 | -2.07377 |
| C | -0.51662 | 1.34640 | 1.08041 |
| H | 0.12724 | 2.14995 | 1.45289 |
| H | -1.53112 | 1.51522 | 1.45616 |
| C | -0.52385 | 1.36006 | -0.47432 |
| H | -0.89524 | 2.32476 | -0.83336 |
| C | 0.90989 | 1.13046 | -0.98045 |
| H | 0.92292 | 1.14984 | -2.07578 |
| H | 1.56426 | 1.93703 | -0.63197 |
| C | 1.42982 | -0.22903 | 1.07371 |
| H | 1.80724 | -1.18921 | 1.44059 |
| H | 2.08563 | 0.56422 | 1.44743 |
| C | 0.51992 | -1.34927 | -0.98734 |
| H | 0.89383 | -2.31972 | -0.64288 |
| H | 0.52654 | -1.36656 | -2.08268 |
| C | 1.43704 | -0.22444 | -0.48103 |
| H | 2.45613 | -0.38419 | -0.84639 |

**H atom abstraction from 18 – product $HCBr_3$ in dichloromethane**

5

-78.6661292

| | | | |
|---|---|---|---|
| C | 0.00056 | -0.00040 | 0.53201 |
| Br | 1.75864 | -0.62524 | -0.04580 |
| Br | -1.42110 | -1.20979 | -0.04575 |
| Br | -0.33767 | 1.83511 | -0.04573 |
| H | 0.00105 | -0.00068 | 1.61262 |




**14**

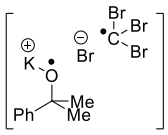
**Neutral complex of 14 and $CBr_4$ in dichloromethane**

27

-1116.1116760

| | | | |
|---|---|---|---|
| C | 3.10600 | 0.93009 | 0.61016 |
| C | 2.68297 | 0.81112 | 2.08946 |
| H | 3.50789 | 0.50312 | 2.73667 |
| H | 2.32364 | 1.78662 | 2.42866 |
| H | 1.87227 | 0.08711 | 2.19661 |
| C | 4.31261 | 1.88956 | 0.52154 |
| H | 4.62136 | 1.99333 | -0.52192 |
| H | 4.01315 | 2.87211 | 0.89887 |
| H | 5.16877 | 1.53943 | 1.10545 |
| O | 2.07777 | 1.45022 | -0.15433 |
| C | 3.56206 | -0.44960 | 0.10293 |
| C | 3.03091 | -0.98119 | -1.07248 |
| C | 4.53174 | -1.19650 | 0.78308 |
| C | 3.44692 | -2.22296 | -1.55210 |
| H | 2.28262 | -0.40565 | -1.60253 |
| C | 4.95150 | -2.43506 | 0.30863 |
| H | 4.97143 | -0.80792 | 1.69593 |
| C | 4.40798 | -2.95647 | -0.86405 |
| H | 3.01802 | -2.61808 | -2.46680 |
| H | 5.70410 | -2.99399 | 0.85377 |
| H | 4.73220 | -3.92206 | -1.23477 |
| Br | -0.06633 | 0.46111 | -0.01173 |

| | | | |
|---|---|---|---|
| C | -1.95735 | -0.26662 | 0.04902 |
| Br | -3.14756 | 0.82699 | -1.09293 |
| Br | -2.64399 | -0.22230 | 1.90371 |
| Br | -1.99814 | -2.13452 | -0.59663 |
| K | 1.24586 | 3.63343 | -0.93669 |

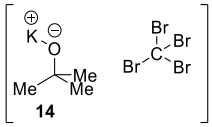


**Triplet complex 44 in dichloromethane**

27

-1116.0776501

| | | | |
|---|---|---|---|
| C | 2.30193 | -1.04484 | 0.70234 |
| C | 1.46279 | -1.77821 | -0.35183 |
| H | 2.01937 | -2.61793 | -0.77089 |
| H | 0.54809 | -2.15406 | 0.11012 |
| H | 1.19767 | -1.08111 | -1.14787 |
| C | 2.57293 | -1.99402 | 1.90724 |
| H | 3.15012 | -1.47761 | 2.67451 |
| H | 1.62566 | -2.33948 | 2.32256 |
| H | 3.14293 | -2.85097 | 1.54593 |
| O | 1.56608 | -0.03774 | 1.28604 |
| C | 3.62712 | -0.54028 | 0.13215 |
| C | 3.95004 | 0.81504 | 0.16401 |
| C | 4.53801 | -1.43677 | -0.43376 |
| C | 5.16100 | 1.26634 | -0.35685 |
| H | 3.23946 | 1.51694 | 0.58047 |
| C | 5.74696 | -0.98756 | -0.95468 |
| H | 4.30882 | -2.49665 | -0.47177 |
| C | 6.06335 | 0.36839 | -0.91725 |
| H | 5.39506 | 2.32445 | -0.32957 |
| H | 6.44147 | -1.69666 | -1.38991 |
| H | 7.00381 | 0.72032 | -1.32460 |
| Br | 0.49425 | 1.83738 | -1.00419 |
| C | -2.22121 | -0.32519 | -0.17504 |
| Br | -2.02620 | -1.20291 | 1.51587 |
| Br | -2.12953 | -1.44307 | -1.71261 |
| Br | -3.51162 | 1.07993 | -0.23179 |
| K | 0.06526 | 1.94213 | 2.09261 |

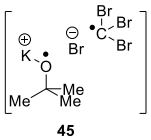


**Neutral complex of 14 and $CBr_4$ in dichloromethane**

20

-924.4005342

| | | | |
|---|---|---|---|
| C | 3.68603 | -0.95755 | -0.00045 |
| C | 3.38994 | -1.79739 | 1.25294 |
| H | 4.00014 | -2.70535 | 1.28365 |
| H | 3.59906 | -1.20742 | 2.15015 |
| H | 2.33679 | -2.08982 | 1.27196 |
| C | 5.17655 | -0.58026 | -0.00169 |
| H | 5.40793 | 0.01591 | -0.88910 |
| H | 5.40934 | 0.01548 | 0.88565 |
| H | 5.81889 | -1.46676 | -0.00236 |
| O | 2.93691 | 0.21790 | 0.00033 |
| C | 3.38738 | -1.79711 | -1.25348 |
| C | -1.41957 | -0.05845 | -0.00013 |
| K | 2.83217 | 2.66403 | 0.00262 |
| H | 3.99700 | -2.70543 | -1.28527 |
| H | 2.33392 | -2.08900 | -1.27099 |
| H | 3.59542 | -1.20717 | -2.15097 |
| Br | -2.07517 | -1.39505 | -1.30191 |
| Br | -2.09604 | -0.54006 | 1.79686 |
| Br | -2.14752 | 1.71745 | -0.49499 |
| Br | 0.62939 | -0.00450 | -0.00076 |

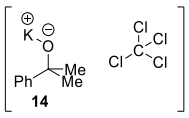


**Triplet complex 45 in dichloromethane**

20

-924.3685022

| | | | |
|---|---|---|---|
| C | 4.70433 | -0.31992 | 0.25852 |
| C | 4.59623 | -1.79140 | 0.66061 |
| H | 5.48883 | -2.33459 | 0.34233 |
| H | 4.49407 | -1.87981 | 1.74398 |
| H | 3.71962 | -2.23312 | 0.18318 |
| C | 5.90609 | 0.34368 | 0.98065 |
| H | 5.96968 | 1.40266 | 0.72715 |
| H | 5.81279 | 0.23106 | 2.06114 |
| H | 6.81402 | -0.15968 | 0.64270 |
| O | 3.62317 | 0.39507 | 0.75021 |
| C | 4.83439 | -0.14945 | -1.25482 |
| C | -2.06866 | -0.03608 | 0.11930 |
| K | 1.78092 | 2.04832 | -0.29321 |
| H | 5.71972 | -0.67292 | -1.62259 |
| H | 3.94853 | -0.56239 | -1.74140 |
| H | 4.92257 | 0.90922 | -1.51111 |
| Br | -3.15680 | -1.15085 | -0.97859 |
| Br | -2.04671 | -0.44498 | 1.98252 |
| Br | -2.06619 | 1.82747 | -0.32393 |
| Br | 1.05408 | -0.94765 | -0.84691 |



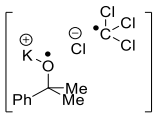
**Neutral complex of 14 and $CCl_4$ in carbon tetrachloride**

27

-2903.5754123

| | | | |
|---|---|---|---|
| C | 2.29240 | 1.12884 | 0.64758 |
| C | 1.95731 | 0.99349 | 2.15010 |
| H | 2.78116 | 0.58595 | 2.74215 |
| H | 1.71297 | 1.98667 | 2.53662 |
| H | 1.08514 | 0.34798 | 2.27901 |
| C | 3.56417 | 1.99612 | 0.50483 |

| | | | |
|---|---|---|---|
| H | 3.80938 | 2.10474 | -0.55511 |
| H | 3.36302 | 2.98780 | 0.92066 |
| H | 4.42902 | 1.56777 | 1.02040 |
| O | 1.24533 | 1.71555 | -0.01778 |
| C | 2.62482 | -0.26963 | 0.08274 |
| C | 2.00048 | -0.72218 | -1.07906 |
| C | 3.56668 | -1.11112 | 0.68725 |
| C | 2.29093 | -1.97510 | -1.61611 |
| H | 1.27553 | -0.07034 | -1.54943 |
| C | 3.86206 | -2.36313 | 0.15710 |
| H | 4.08170 | -0.78798 | 1.58596 |
| C | 3.22166 | -2.80411 | -0.99896 |
| H | 1.78737 | -2.30502 | -2.51865 |
| H | 4.59301 | -2.99670 | 0.64743 |
| H | 3.44763 | -3.78058 | -1.41161 |
| C | -2.55237 | -0.56021 | 0.18435 |
| K | -0.27510 | 3.08460 | -1.15816 |
| Cl | -3.75660 | 0.46765 | -0.64398 |
| Cl | -0.98260 | 0.27978 | 0.21369 |
| Cl | -3.10512 | -0.88079 | 1.84009 |
| Cl | -2.39511 | -2.09310 | -0.69620 |



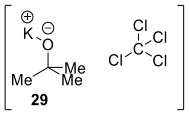
**60**

**Triplet complex of 60 in carbon tetrachloride**

27

-2903.5364951

| | | | |
|---|---|---|---|
| C | -1.80480 | 1.60632 | -0.46437 |
| C | -2.30812 | 1.27837 | -1.87784 |
| H | -3.35447 | 0.97347 | -1.85532 |
| H | -2.21206 | 2.16235 | -2.50998 |
| H | -1.71792 | 0.46443 | -2.30189 |
| C | -2.66274 | 2.76194 | 0.14295 |
| H | -2.28228 | 3.03372 | 1.12724 |
| H | -2.65176 | 3.62725 | -0.51988 |
| H | -3.68247 | 2.38795 | 0.24419 |
| O | -0.55857 | 2.18283 | -0.53988 |
| C | -1.83634 | 0.40052 | 0.47379 |
| C | -0.72678 | 0.06598 | 1.24467 |
| C | -2.98897 | -0.38387 | 0.57314 |
| C | -0.75446 | -1.04480 | 2.08541 |
| H | 0.18814 | 0.64186 | 1.19501 |
| C | -3.02018 | -1.48943 | 1.41537 |
| H | -3.87150 | -0.13999 | -0.00853 |
| C | -1.89894 | -1.82777 | 2.17097 |
| H | 0.13462 | -1.28744 | 2.65710 |
| H | -3.92019 | -2.08997 | 1.47852 |
| H | -1.92202 | -2.69508 | 2.82015 |
| C | 0.82704 | -1.51652 | -0.84676 |
| K | 2.02323 | 2.65420 | -0.00182 |
| Cl | 2.79126 | 0.59266 | 1.80325 |
| Cl | 1.19342 | -0.13550 | -1.82774 |
| Cl | 2.15241 | -2.43336 | -0.29053 |
| Cl | -0.58621 | -2.38118 | -1.30128 |



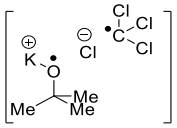
**29**

**Neutral complex of 29 and $CCl_4$ in carbon tetrachloride**

20

-2711.8636814

| | | | |
|---|---|---|---|
| C | -3.02634 | -0.76219 | 0.00198 |
| C | -2.69791 | -1.61317 | -1.24061 |
| H | -3.28973 | -2.53383 | -1.28056 |
| H | -2.89900 | -1.03050 | -2.14476 |
| H | -1.63798 | -1.88314 | -1.23742 |
| C | -4.52907 | -0.42322 | -0.02676 |
| H | -4.78689 | 0.17543 | 0.85221 |
| H | -4.75553 | 0.16477 | -0.92150 |
| H | -5.15837 | -1.31976 | -0.03256 |
| O | -2.27628 | 0.39675 | 0.01073 |
| C | -2.74169 | -1.60166 | 1.26262 |
| C | 2.09086 | -0.20150 | 0.00142 |
| K | -1.49979 | 2.60659 | -0.00004 |
| Cl | 2.78925 | 1.37273 | -0.46841 |
| Cl | 0.31288 | -0.07798 | 0.02300 |
| Cl | 2.59502 | -1.43469 | -1.17262 |
| Cl | 2.69393 | -0.63997 | 1.61483 |
| H | -3.33004 | -2.52506 | 1.28827 |
| H | -1.68088 | -1.86538 | 1.29983 |
| H | -2.97875 | -1.01277 | 2.15387 |



**61**

**Triplet complex 61 in carbon tetrachloride 61**

**2**0

-2711.8260835

| | | | |
|---|---|---|---|
| C | -2.83443 | -0.68658 | -0.00449 |
| C | -2.28839 | -1.77393 | -0.93147 |
| H | -2.61761 | -2.75876 | -0.59371 |
| H | -2.65334 | -1.61892 | -1.94951 |
| H | -1.19800 | -1.74960 | -0.93819 |
| C | -4.36360 | -0.70193 | 0.07124 |
| H | -4.71590 | 0.08841 | 0.73563 |
| H | -4.79215 | -0.54819 | -0.92155 |
| H | -4.70979 | -1.66542 | 0.45062 |
| O | -2.38719 | 0.55854 | -0.39227 |
| C | -2.22821 | -0.84550 | 1.42033 |
| C | 1.95988 | -0.55890 | -0.13473 |
| K | -0.64093 | 2.50685 | -0.67527 |
| Cl | 0.56444 | 1.52425 | 1.71236 |
| Cl | 1.23764 | -0.16704 | -1.66020 |
| Cl | 3.60471 | -0.12491 | 0.05089 |
| Cl | 1.46236 | -2.04237 | 0.56768 |
| H | -2.51259 | -1.83854 | 1.77564 |
| H | -1.14322 | -0.74953 | 1.39094 |

| | | | |
|---|---|---|---|
| H | -2.62952 | -0.08559 | 2.09070 |
| H | -1.45529 | 0.42553 | 0.48601 |


**Cl abstraction from 46 – starting species 54 and 46 in dichloromethane**

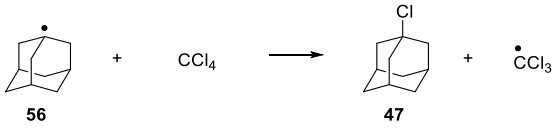
25
-389.9787578

| | | | |
|---|---|---|---|
| C | 1.25958 | -1.21146 | 0.30720 |
| H | 2.15841 | -1.04459 | 0.91215 |
| H | 1.28647 | -2.24614 | -0.04961 |
| C | 1.25632 | -0.23910 | -0.89902 |
| H | 2.14286 | -0.41326 | -1.51406 |
| C | 0.00009 | -0.97690 | 1.15805 |
| H | 0.00017 | -1.66874 | 2.00589 |
| C | -0.00057 | 0.46994 | 1.67516 |
| H | 0.88261 | 0.64453 | 2.29962 |
| H | -0.88417 | 0.64393 | 2.29922 |
| C | 1.25596 | 1.20874 | -0.36549 |
| H | 1.27791 | 1.91142 | -1.20471 |
| H | 2.15506 | 1.38132 | 0.23669 |
| C | -0.00056 | 1.44414 | 0.48793 |
| H | -0.00097 | 2.47407 | 0.85759 |
| C | -1.25657 | 1.20799 | -0.36601 |
| H | -2.15600 | 1.37998 | 0.23582 |
| H | -1.27862 | 1.91067 | -1.20523 |
| C | 0.00046 | -0.47349 | -1.68393 |
| H | 0.00080 | -1.13093 | -2.54645 |
| C | -1.25886 | -1.21235 | 0.30669 |
| H | -1.28476 | -2.24705 | -0.05013 |
| H | -2.15805 | -1.04622 | 0.91131 |
| C | -1.25581 | -0.23990 | -0.89946 |
| H | -2.14201 | -0.41466 | -1.51482 |

**Cl abstraction of 46 – products 47 and 62 in dichloromethane**

40
-1083.2201766

| | | | |
|---|---|---|---|
| C | 0.94175 | -0.08291 | -0.69188 |
| H | 0.69362 | -0.04390 | -1.75329 |
| C | 1.84639 | -1.28100 | -0.39802 |
| C | 1.60627 | 1.22181 | -0.24969 |
| H | 1.33285 | -2.20030 | -0.69102 |
| C | 2.22126 | -1.32695 | 1.09047 |
| C | 3.12301 | -1.10026 | -1.24206 |
| H | 0.92436 | 2.05478 | -0.43929 |
| C | 1.98202 | 1.16360 | 1.23822 |
| C | 2.88324 | 1.38683 | -1.09495 |
| H | 2.88377 | -2.18078 | 1.26578 |
| H | 1.32648 | -1.47550 | 1.70167 |
| C | 2.92680 | -0.02191 | 1.48884 |
| H | 2.87115 | -1.08284 | -2.30775 |
| H | 3.78515 | -1.95571 | -1.07511 |
| C | 3.82963 | 0.20358 | -0.84352 |
| H | 1.08185 | 1.06805 | 1.85182 |
| H | 2.47286 | 2.10097 | 1.51904 |
| H | 2.62682 | 1.44438 | -2.15822 |
| H | 3.37239 | 2.32789 | -0.82438 |
| H | 3.18992 | -0.05924 | 2.54977 |
| C | 4.19948 | 0.15078 | 0.64661 |
| H | 4.73479 | 0.32603 | -1.44510 |
| H | 4.71722 | 1.07208 | 0.93487 |
| H | 4.88589 | -0.68295 | 0.83041 |
| Cl | -0.68541 | -0.28519 | 0.11879 |
| O | -3.61021 | -0.08282 | 1.13598 |
| C | -4.38060 | 0.04668 | -0.00738 |
| C | -5.81978 | 0.13303 | 0.56072 |
| H | -5.92173 | 1.00112 | 1.21269 |
| H | -6.50483 | 0.23494 | -0.28326 |
| H | -6.06721 | -0.77216 | 1.11603 |
| C | -4.23705 | -1.18738 | -0.90021 |
| H | -3.20748 | -1.27182 | -1.25421 |
| H | -4.49292 | -2.08870 | -0.34001 |
| H | -4.89770 | -1.10934 | -1.76650 |
| C | -4.03019 | 1.33601 | -0.75350 |
| H | -4.14041 | 2.19677 | -0.09135 |
| H | -2.99778 | 1.29134 | -1.10652 |
| H | -4.68870 | 1.46423 | -1.61544 |




**Cl abstraction from $CCl_4$ – starting species $CCl_4$ and 56 in dichloromethane**

30
-2268.8442784

| | | | |
|---|---|---|---|
| C | -1.70633 | -0.00075 | -1.27199 |
| H | -1.40594 | -0.00053 | -2.31553 |
| C | -2.24373 | 1.25671 | -0.65558 |
| C | -2.24679 | -1.25755 | -0.65693 |
| H | -1.79936 | 2.14176 | -1.11831 |
| C | -1.96852 | 1.25352 | 0.86154 |
| C | -3.77896 | 1.26152 | -0.87995 |
| H | -1.80459 | -2.14320 | -1.12059 |
| C | -1.97155 | -1.25665 | 0.86019 |
| C | -3.78204 | -1.25842 | -0.88131 |
| H | -2.39911 | 2.15341 | 1.31423 |
| H | -0.88967 | 1.27464 | 1.04467 |
| C | -2.58623 | -0.00117 | 1.49782 |
| H | -3.99726 | 1.28780 | -1.95241 |
| H | -4.21512 | 2.16047 | -0.42961 |
| C | -4.39177 | 0.00194 | -0.24566 |
| H | -0.89275 | -1.28065 | 1.04327 |
| H | -2.40434 | -2.15598 | 1.31191 |
| H | -4.00039 | -1.28303 | -1.95379 |
| H | -4.22037 | -2.15679 | -0.43191 |

| | | | |
|---|---|---|---|
| H | -2.38096 | -0.00199 | 2.57264 |
| C | -4.10454 | 0.00077 | 1.26299 |
| H | -5.47318 | 0.00335 | -0.41315 |
| H | -4.55593 | -0.88223 | 1.72865 |
| H | -4.55381 | 0.88434 | 1.72961 |
| Cl | 1.28256 | -0.00112 | -0.64777 |
| C | 2.94381 | 0.00002 | -0.00840 |
| Cl | 3.18743 | 1.44949 | 0.98816 |
| Cl | 4.10668 | -0.00022 | -1.34805 |
| Cl | 3.18880 | -1.44820 | 0.98967 |

**Cl abstraction from $CCl_4$ – transition state in dichloromethane**

30

-2268.836283

| | | | |
|---|---|---|---|
| C | -1.34484 | 1.06143 | 0.36895 |
| H | -1.12708 | 2.07691 | 0.69060 |
| C | -1.96806 | 0.15035 | 1.38463 |
| C | -1.89261 | 0.89363 | -1.01778 |
| H | -1.49563 | 0.27987 | 2.36136 |
| C | -1.88831 | -1.31663 | 0.92899 |
| C | -3.46247 | 0.57336 | 1.46451 |
| H | -1.36567 | 1.54247 | -1.72134 |
| C | -1.81621 | -0.57624 | -1.46737 |
| C | -3.38721 | 1.31471 | -0.93036 |
| H | -2.40032 | -1.94852 | 1.66187 |
| H | -0.84412 | -1.63818 | 0.88741 |
| C | -2.54445 | -1.46880 | -0.45134 |
| H | -3.54024 | 1.61056 | 1.80511 |
| H | -3.96817 | -0.05780 | 2.20282 |
| C | -4.11315 | 0.41589 | 0.08191 |
| H | -0.77245 | -0.88812 | -1.56227 |
| H | -2.28164 | -0.67155 | -2.45372 |
| H | -3.46321 | 2.36394 | -0.62825 |
| H | -3.83906 | 1.22165 | -1.92348 |
| H | -2.47712 | -2.51259 | -0.77127 |
| C | -4.01830 | -1.04944 | -0.36764 |
| H | -5.16329 | 0.71670 | 0.14163 |
| H | -4.49743 | -1.16969 | -1.34530 |
| H | -4.55218 | -1.69095 | 0.34169 |
| Cl | 0.87696 | 0.48822 | 0.22435 |
| C | 2.79197 | -0.00719 | -0.00477 |
| Cl | 3.69291 | 1.45240 | -0.39512 |
| Cl | 2.88347 | -1.17837 | -1.31744 |
| Cl | 3.34957 | -0.71407 | 1.51027 |

**Cl abstraction from $CCl_4$ – products 47 and $CCl_3$ radical in dichloromethane**

30

-2268.8829758

| | | | |
|---|---|---|---|
| C | -1.58604 | -1.46703 | 0.00019 |
| H | -2.21505 | -2.35788 | 0.00028 |
| C | -1.83404 | -0.63474 | -1.25885 |
| C | -1.83402 | -0.63445 | 1.25903 |
| H | -1.61769 | -1.24319 | -2.14078 |
| C | -0.96150 | 0.62779 | -1.25309 |
| C | -3.32163 | -0.23217 | -1.25070 |
| H | -1.61771 | -1.24271 | 2.14110 |
| C | -0.96148 | 0.62805 | 1.25306 |
| C | -3.32161 | -0.23182 | 1.25079 |
| H | -1.16916 | 1.21111 | -2.15594 |
| H | 0.09560 | 0.34834 | -1.27951 |
| C | -1.26408 | 1.46426 | -0.00013 |
| H | -3.95438 | -1.12586 | -1.26913 |
| H | -3.54069 | 0.34311 | -2.15577 |
| C | -3.62563 | 0.60597 | -0.00007 |
| H | 0.09574 | 0.34882 | 1.27958 |
| H | -1.16921 | 1.21159 | 2.15575 |
| H | -3.95437 | -1.12548 | 1.26961 |
| H | -3.54060 | 0.34378 | 2.15568 |
| H | -0.63892 | 2.36138 | -0.00026 |
| C | -2.74716 | 1.86611 | -0.00020 |
| H | -4.68150 | 0.89140 | -0.00010 |
| H | -2.97002 | 2.47461 | 0.88295 |
| H | -2.97000 | 2.47439 | -0.88351 |
| Cl | 0.11380 | -2.14257 | 0.00013 |
| C | 2.54831 | 0.26743 | -0.00006 |
| Cl | 3.07425 | -0.46121 | 1.46149 |
| Cl | 2.40267 | 1.97875 | -0.00008 |
| Cl | 3.07406 | -0.46143 | -1.46152 |

**$BrO^tBu$ Homolysis - $BrO^tBu$ Optimised Geometry in dichloromethane**

15

-246.3067183

| | | | |
|---|---|---|---|
| C | -1.27184 | 0.00002 | 0.03466 |
| C | -1.29606 | 1.26315 | 0.88399 |
| H | -0.47035 | 1.27354 | 1.59818 |
| H | -1.22662 | 2.14805 | 0.24799 |
| H | -2.23046 | 1.30891 | 1.44693 |
| C | -1.29667 | -1.26185 | 0.88579 |
| H | -2.23005 | -1.30539 | 1.45059 |
| H | -1.22963 | -2.14780 | 0.25101 |
| H | -0.46966 | -1.27236 | 1.59849 |
| C | -2.41975 | -0.00035 | -0.97642 |
| H | -2.37324 | 0.88876 | -1.60696 |
| H | -2.37279 | -0.88956 | -1.60682 |
| H | -3.36878 | -0.00058 | -0.43652 |
| O | -0.13765 | -0.00115 | -0.86009 |
| Br | 1.56511 | -0.00001 | -0.02944 |

**$BrO^tBu$ Homolysis - Br Radical Optimised Geometry in dichloromethane**

1

-13.2872674

| | | | |
|---|---|---|---|
| Br | 0.00000 | 0.00000 | 0.00000 |

**$BrO^tBu$ Homolysis - $O^tBu$ Radical Optimised Geometry in dichloromethane**

14

-232.9600216

| | | | |
|---|---|---|---|
| C | 0.00013 | -0.02598 | 0.07633 |
| C | -1.26562 | -0.79290 | -0.31355 |
| H | -1.29097 | -1.75801 | 0.19702 |
| H | -2.15303 | -0.22279 | -0.03306 |
| H | -1.28435 | -0.97201 | -1.39063 |
| C | 1.27237 | -0.78234 | -0.31324 |
| H | 1.29295 | -0.96129 | -1.39032 |
| H | 2.15486 | -0.20482 | -0.03242 |
| H | 1.30554 | -1.74719 | 0.19736 |
| C | -0.00569 | 1.38003 | -0.57554 |
| H | -0.89906 | 1.93341 | -0.28471 |
| H | 0.88274 | 1.94106 | -0.28425 |
| H | -0.00486 | 1.24269 | -1.65861 |
| O | -0.00136 | 0.25952 | 1.42945 |