Visible Light-Enabled sp³-C–H Functionalization with Chloro- and Bromoalkynes: Chemoselective Route to Vinylchlorides or Alkynes

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1. General Information
Chemicals were purchased from commercial suppliers and used without any purification. Dry solvents were dispensed from the solvent purification system MB SPS-800. All reactions were carried out under nitrogen atmosphere. Deuterated solvents were bought from Euriso-Top and Sigma Aldrich. Unless otherwise stated, NMR spectra were recorded in room temperature on the following spectrometers; Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz), Bruker Avance III 600 (600 MHz) or Fourier 300 (300 MHz). Chemical shifts were referenced to residual solvent protons and reported in ppm and coupling constants in Hz. $^1$H and $^{13}$C spectra are calibrated in relation to the deuterated solvents, namely CDCl$_3$ (7.26 ppm; 77.16 ppm). The following abbreviations were used for $^1$H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). For Z/E-mixtures the minor isomers are incorporated in the listing in brackets. All $^{13}$C NMR spectra were measured with $^1$H decoupling. The multiplicities mentioned in these spectra [s (singlet, quaternary carbon), d (doublet, CH-group), t (triplet, CH$_2$-group), q (quartet, CH$_3$-group)] were determined by DEPT 135. HRMS were determined at the chemistry department of the University of Heidelberg. EI$^+$-spectra were measured on a JOEL JMS-700 spectrometer. IR spectra were recorded on a Bruker Vector 22, and the absorption maxima were given in wavelength in cm$^{-1}$ units. Flash Column Chromatography was accomplished using Silica gel 60 (0.04 – 0.063 mm / 230 – 400 mesh ASTM) purchased from Macherey-Nagel as the stationary phase. As eluents, the respectively mentioned proportions of petroleum ether (PE) and ethyl acetate (EA) were used. Thin-layer chromatography (TLC) was performed on pre-coated polyester sheets (POLYGRAM SIL G/UV254), and components were visualized by observation under UV light.
2. General procedures

2.1 General procedure for the synthesis of Chloroalkynes
Chloro, bromo, iodo alkynes were synthesized according to literature procedures.\(^1\)

2.2 General procedure for hydroalkylation of alkynes
An oven-dried pyrex tube was charged with a magnetic stirrer, alkyne (0.2 mmol, 1 equiv) and photocatalyst (15 mol%) in 0.05M solvent. The reaction mixture was degassed through the freeze-thaw cycle method three times at -78 °C under nitrogen, then placed it in front of two CFL bulbs at room temperature (temperature of the reaction was slightly increased due to close proximity of CFL light bulbs). After completion, the reaction was quenched with NH\(_4\)Cl solution and extracted with Et\(_2\)O, dried over Na\(_2\)SO\(_4\) and purified by silica-gel flash column chromatography using petroleum ether and ethyl acetate to give the desired product.

3. Optimization of reaction conditions

3.1 Screening of photocatalysts

\[
\begin{array}{cccc}
\text{Entry} & \text{Photocatalyst (x mol\%)} & \text{Time (h)} & \text{Yield (%) (Z:E)} \\
1 & 3a (15 mol\%) & 24 & 0 \\
2 & 3b (15 mol\%) & 24 & 0 \\
3 & 3c (15 mol\%) & 24 & 76 (3:1) \\
4 & 3d (15 mol\%) & 24 & 89 (3:1) \\
5 & 3e (15 mol\%) & 24 & 52 (2.8:1) \\
6 & 3f (15 mol\%) & 24 & 59 (2.9:1) \\
7 & 3d (10 mol\%) & 24 & 84 (3:1) \\
8 & 3d (20 mol\%) & 24 & 89 (3:1) \\
9 & 3f (15 mol\%) & 24 & 60 (2:1) \\
10 & Ru(bpy)\(_3\)Cl\(_2\) (5 mol\%) & 24 & 0 \\
11 & No catalyst & 24 & 0 \\
12 & No light & 24 & 0 \\
\end{array}
\]

**Reaction Conditions:** all reaction were carried out 2a (0.2 mmol), Photocatalyst (x mol\%) in THF (0.05M) under \(\text{N}_2\) under irradiation of 23W CFL white light. Yields were determined using 1,3,5-trimethoxy benzene as an internal standard.
### 3.2 Screening of light

| Entry | Photocatalyst | Light         | Time (h) | Yield (%) |
|-------|---------------|---------------|----------|-----------|
| 1     | 3d (15 mol%)  | 23W CFL       | 6        | 89        |
| 2     | 3d (15 mol%)  | 2 × 23W CFL   | 3        | 96        |
| 3     | 3d (15 mol%)  | Blue LED      | 24       | 42        |
| 4     | 3d (15 mol%)  | Sunlight      | 12       | 60        |

**Reaction Conditions:** All reactions were carried out with 2a (0.2 mmol), photocatalyst (15 mol%) in THF (0.05M) under N₂ under irradiation light. Yields were determined using 1,3,5-trimethoxy benzene as an internal standard.

### 2.3 Screening of Concentration

| Entry | Conc. (M) | Time (h) | Yield (%) |
|-------|-----------|----------|-----------|
| 1     | 0.2       | 24       | 61        |
| 2     | 0.05      | 3        | 96        |
| 3     | 0.025     | 24       | 83        |

**Reaction Conditions:** All reactions were carried out with 2a (0.2 mmol), photocatalyst (15 mol%) in THF under N₂ with irradiation of 2×23W CFL white light. Yields were determined using 1,3,5-trimethoxy benzene as an internal standard.

### 3.4 Screening of solvent

| Entry | Solvent            | Yield (%) |
|-------|--------------------|-----------|
| 1     | acetonitrile       | 56 (3:1)  |
| 2     | acetone            | 64 (3:1)  |
| 3     | dichloromethane    | 38 (3:1)  |
| 4     | water              | 71 (5:4)  |

**Reaction Conditions:** All reactions were carried out with 2a (0.2 mmol), photocatalyst (15 mol%), THF (4 mmol, 20 equiv) in solvent (0.1M) under N₂ with irradiation of 2×23W CFL white light. Yields were determined using 1,3,5-trimethoxy benzene as an internal standard.
4. Identification of desired products

Structure:

COSY: Correlation between \( H_a / H_b, H_b / H_c \)  
NOESY: Correlation between \( H_a / H_b \)
Isomer: \( Z \)

Structure:

COSY: No correlation between \( H_a / H_b, H_b / H_c \)  
NOESY: No correlation between \( H_a / H_b \)
Isomer: \( E \)

Structure:

\( J(H_{ab}) \): 11.6 Hz  
Isomer: \( Z \)

Structure:

\( J(H_{ab}) \): 15.9 Hz  
Isomer: \( E \)

5. Mechanistic study

5.1 Picture for reaction set up

Fig 1: A) mmol scale reaction, B) gram-scale reaction.
5.2 UV-VIS absorption spectra

The UV-visible absorption spectra for chloroalkyne (2a) and photocatalyst (3d) are shown above. The UV-vis absorption spectra for both compounds come below 400 nm in THF. The photocatalyst 3d showed a moderate instance $n \rightarrow \pi^*$ transition in the range of 320–380 nm. This indicates the reaction is indeed initiated by photoexcitation of 3d

5.3 Competitive kinetic study\(^2\)

\textbf{a) Kinetic study}

\[
\begin{align*}
\text{THF} & \quad + \quad \text{THF-d8} \\
\text{2a} & \quad \text{std. conditions} \quad \text{4a} \quad \text{4a'}
\end{align*}
\]

An oven-dried pyrex tube was charged with a magnetic stirrer, alkyne 2a (0.1 mmol, 1 equiv) and photocatalyst (15 mol\%) in THF (2mL) and THF-d\(_8\) (2mL) solvent. The reaction mixture was degassed through the freeze-thaw cycle method three times at -78 °C under nitrogen and then placed it in front of two CFL bulbs at room temperature. The crude residue was purified by PTLC using petroleum ether/EtOAc (30:1) as the eluent. The chloroalkene product ratio (4a and 4a') was analyzed by \(^1\)H NMR. The yield of 4a, $X_{4a}$, was determined by the integration of the H\(_a\) signal of 4a, which appeared as triplets (approximately 4.61 ppm). The total yield of 4a and 4a', $X_{total}$, was determined by integration of H\(_c\) of 4a and 4a', which appeared as doublets at the same chemical shift (7.63 ppm for both 4a and 4a'). The yield of 4a', $X_{4a'}$, could then be determined from the following formula: $X_{4a'} = X_{total} - X_{4a}$

So, $K_H/K_D = X_{4a}/X_{4a'} = 4.81$ (By NMR study) and 4.68 (by HRMS study)

The competitive kinetic study showed a high $K_H/K_D$ value which indicates that the hydrogen abstraction is the rate-determining step.
Crossover Experiment

\[
\frac{K_H}{K_D} = 4.8
\]
Fig: Mass spectroscopy of competitive kinetic study.

5.4 H/D Exchange experiment

To underline our proposal several control experiments were carried out. All H/D exchange reactions were performed under standard conditions noted around the arrow. Deuterium labelling experiment was conducted to elucidate the proton transfer to the vinylic position. A mixture of THF and THF-d8 as the coupling partner delivered both the THF and THF-d8 incorporated products. The competitive kinetic study showed a high $K_H/K_D$ value which indicates that the hydrogen abstraction is the rate-determining step. We could confirm that THF acts as the hydrogen source. In the case of THF-d8 as a coupling partner, greater than 99 % deuterium incorporated product was isolated. No exchange processes were detected if THF and D$_2$O (1:1; v/v) only minor traces of deuterium incorporated product was observed. This indicates that the vinyl radical
formed by the addition of a THF radical to the chloroalkyne may abstract the H-atom directly from THF only, not from the diarylalcohol intermediates that are formed by the photocatalyst (III, scheme 6). In this case, an H/D exchange to the alcoholic group would be likely.

5.5 Radical trapping experiment

A radical trapping experiment was carried out using 2a (0.1 mmol), 3d (15 mol%), TEMPO (0.2 M, 2.0 equiv) in 0.05 M degassed THF under irradiation of light for 30 minutes. The crude NMR showed 9% of THF-TEMPO adduct product (below fig.). No desired outcome was detected in GC-MS.
5.6 Reaction study by Generation of THF radical using DTBP

The reaction was carried out with 2a (0.1 mmol), DTBP (0.1 mmol) in 0.5 M THF for 12 hours under dark. No desired product was detected in GC-MS and $^1$H NMR.

5.7 Light ON-OFF experiment

The light ON-OFF investigation was carried out to examine the compact of light under alternative periods of irradiation and darkness. An oven-dried Pyrex tube was charged with a magnetic stirrer, alkyne (0.2 mmol, 1.0 equiv), and photocatalyst (15 mol%) in 0.05M THF. The reaction mixture was degassed through the freeze-thaw cycle method three times at -78 °C under nitrogen and then placed it in front of CFL bulbs at room temperature. At different time intervals, we took the GC yield using dodecane as an internal standard. The interruption of reaction progress resulted in the absence of light and recuperation of reaction progress on further irradiation under the light. These results demonstrated that light is necessary for the reaction.
5.8 Determination of Quantum yield by standard ferrioxalate actinometer

The quantum yield (φ) was determined by the ferrioxalate actinometry method. A ferrioxalate actinometry solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in the Handbook of Photochemistry. Owing to the UV/VIS absorption of diaryl ketone (3d) photocatalyst in the UV/VIS region, to determine the quantum yield, two 23W UVA CFL bulbs (purchased from Osram) were used. The irradiated light intensity was estimated to $2.56 \times 10^{-7}$ einstein S$^{-1}$ by using $\text{K}_3[\text{Fe(C}_2\text{O}_4)_3]$ as an actinometer.

**Model reaction solution:** 3d (15 mol%), Chloroalkyne 2a (0.1 mmol), THF (0.05 M) in five different Pyrex tubes degassed under nitrogen using the freeze-thaw method. Then, the reaction mixtures were irradiation with two 23W CFL bulbs for specified time intervals (15 min, 30 min, 45 min, 75 min, 90 min). The moles of products formed were determined by $^1$H NMR measurement with 1,3,5-trimethoxybenzene as a reference standard. The number of moles of products $\times 10^{-3}$ (y-axis) per unit time is related to the number of photons $\times 10^{-5}$ (x-axis, calculated from the light intensity). The slope gives the quantum yield (Φ) of the photoreaction is 3.87
6. Characterization of Products
2-(1-chloro-2-phenylvinyl)tetrahydrofuran (4a)

The Z-isomer of the title compound (4a) was carefully purified by preparative TLC using petroleum ether/ethyl acetate (50:1) and obtained as colourless liquid.

(Z)-Isomer
$^1$H NMR (301 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 7.3$ Hz, 2H), 7.34 (dd, $J = 16.0, 8.4$ Hz, 3H), 6.80 (s, 1H), 4.61 (t, $J = 6.2$ Hz, 1H), 4.07 (dd, $J = 13.9, 7.2$ Hz, 1H), 3.93 (dd, $J = 13.5, 7.6$ Hz, 1H), 2.31 – 1.86 (m, 4H).

The Z-configuration of the double bond was proved by NOESY and COSY NMR spectroscopy:

COSY
The Z/E mixture of compound (4a) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 93% yield as colourless liquid. (Z/E = 3:1)

(\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.63\) (d, \(J = 7.3\) Hz, 2H), 7.35 (ddd, \(J = 8.0, 6.6, 1.8\) Hz, 3H) \(7.24\)–7.15, 6.80 (s, 1H) \(6.90\) 4.61 (t, \(J = 6.2\) Hz, 1H) \(4.95\), 4.12–4.00 (m, 1H), 3.97–3.89 (m, 1H) \(3.88\)–3.80, 2.27–1.87 (m, 4H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 138.16, 135.18, 134.69, 134.64, 131.15, 129.38, 128.77, 128.58, 128.32, 127.95, 127.80, 123.73, 82.37, 75.96, 69.56, 31.27, 30.52, 26.98, 25.81. IR (Reflection): 3026, 2872, 1776, 1493, 1447, 1181, 1057, 923, 757, 696. HRMS (EI): Mass calculated for C\textsubscript{12}H\textsubscript{13}OCl: 208.0649; found: 208.0638

\textbf{2-(1-chloro-2-phenylvinyl)-1,4-dioxane (4b)}
The title compound (4b) was purified by silica gel flash column chromatography using hexane and ethyl acetate (40:1) in 68% yield as colourless liquid. \((Z/E = 1.4:1)\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.62 (d, J = 7.2 \text{ Hz}, 2\text{H}), 7.35 \text{ (dt, } J = 10.5, 5.3 \text{ Hz}, 3\text{H}) (7.29-7.19), 6.86 (s, 1\text{H}) (6.98), 4.28 (dd, J = 9.8, 2.5 \text{ Hz}, 1\text{H}) (4.66), \{Z: 4.10 \text{ (dd, } J = 11.4, 2.6 \text{ Hz}, 1\text{H}) \}, 3.90 \text{ (dt, } J = 11.5, 9.7 \text{ Hz}, 1\text{H}) 3.84 - 3.77 \text{ (m, } 1\text{H}), 3.75 \text{ (s, } 1\text{H}), 3.71 \text{ (dd, } J = 6.3, 4.1 \text{ Hz}, 1\text{H}), 3.54 \text{ (dt, } J = 11.4, 9.8 \text{ Hz}, 1\text{H}). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 133.47, 129.46, 128.81, 128.39, 126.12, 78.96, 73.43, 70.68, 69.07, 67.16, 66.78, 66.44, 66.19. \) IR (Reflection): 2960, 2855, 1731, 1448, 1256, 1119, 863, 697. HRMS (EI): Mass calculated for C\(_{12}\)H\(_{13}\)O\(_2\)Cl: 224.0598; found: 224.0602

2-(2-chloro-1-phenylvinyl)oxetane (4c)

The title compound (4c) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 72% yield as colourless liquid. \((Z/E = 2.2:1)\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.68 (d, J = 7.5 \text{ Hz}, 2\text{H}), 7.38 - 7.29 \text{ (m, } 3\text{H}), 6.92 \text{ (s, } 1\text{H}) (6.94), 5.34 \text{ (t, } 1\text{H}) (5.79), 4.70 - 4.64 \text{ (m, } 2\text{H}), 2.98 \text{ (m, } 1\text{H}), 2.78 - 2.61 \text{ (m, } 1\text{H}). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 137.86, 134.65, 134.12, 132.00, 129.44, 128.72, 128.64, 128.43, 128.29, 128.15, 124.26, 83.69, 68.65, 27.60, 26.34. \) IR (Reflection): 2957, 1589, 1493, 1100, 755, 696. HRMS (EI): Mass calculated for C\(_{11}\)H\(_{11}\)ClO: 194.0499; found: 194.0498

(2-chloro-3,4-dimethoxybut-1-en-1-yl)benzene (4d)

The title compound (4d) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 40% yield as colourless liquid. \((Z/E = 6.6:1)\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.41 - 7.27 \text{ (m, } 5\text{H}), 7.13 \text{ (s, } 1\text{H}), 4.55 \text{ (t, } J = 6.2 \text{ Hz}, 1\text{H}), 3.72 - 3.57 \text{ (m, } 2\text{H}), 3.43 \text{ (s, } 3\text{H}), 3.21 \text{ (s, } 3\text{H}). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 134.74, 134.70, 134.01, 128.83, 128.68, 128.03, 73.35, 59.64, 56.32. \) IR (ATR): 2928, 2826, 1730, 1492, 1190, 1115, 938, 762, 703 HRMS (EI): Mass calculated for C\(_{12}\)H\(_{15}\)O\(_2\)Cl: 226.0755, found: 226.0743

(2-chloro-3-(2-methoxyethoxy)prop-1-en-1-yl)benzene (4d’)

top The title compound (4d) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 40% yield as colourless liquid. \((Z/E = 6.6:1)\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.41 - 7.27 \text{ (m, } 5\text{H}), 7.13 \text{ (s, } 1\text{H}), 4.55 \text{ (t, } J = 6.2 \text{ Hz}, 1\text{H}), 3.72 - 3.57 \text{ (m, } 2\text{H}), 3.43 \text{ (s, } 3\text{H}), 3.21 \text{ (s, } 3\text{H}). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 134.74, 134.70, 134.01, 128.83, 128.68, 128.03, 73.35, 59.64, 56.32. \) IR (ATR): 2928, 2826, 1730, 1492, 1190, 1115, 938, 762, 703 HRMS (EI): Mass calculated for C\(_{12}\)H\(_{15}\)O\(_2\)Cl: 226.0755, found: 226.0743
The title compound (4d') was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 32% yield as colourless liquid. (Z/E = 10:1)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.68 (dd, \(J = 9.6, 2.4\) Hz, 1H), 7.40 – 7.31 (m, 2H), 7.23 – 7.13 (m, 2H), 6.79 (s, 1H (6.98)), 4.34 – 4.25 (m, 1H), 4.08 – 4.01 (m, 1H), 3.66 – 3.58 (m, 2H), 3.42 (d, \(J = 0.9\) Hz, 5H).

\(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 142.15, 133.64 (t), 129.99 (q), 128.34, 128.20, 128.04, 127.8126.07, 85.20, 74.03, 59.52, 57.09.

IR (ATR): 3434, 2928, 1491, 1190, 1095, 1013, 756, 694.

HRMS (EI): Mass calculated for C\(_{12}\)H\(_{15}\)O\(_2\)Cl: 226.0755, found: 226.0743

The title compound (4e) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 58% yield as colourless liquid. (Z/E = 2:1)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.67 (d, \(J = 7.4\) Hz, 2H (7.16)), 7.42 – 7.33 (m, 3H (7.32 – 7.29)), 6.72 (s, 1H (6.95)), 4.09 (q, \(J = 6.3\) Hz, 1H (4.54)), 3.68 – 3.53 (m, 1H), 3.51 – 3.36 (m, 1H (3.15)), 1.43 (dd, \(J = 6.3, 2.5\) Hz, 3H), 1.25 (dd, \(J = 8.7, 5.3\) Hz, 3H (1.12)).

\(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 139.41, 135.70, 135.12, 134.47, 130.74, 129.44, 128.62 (t), 127.78, 124.98, 79.94, 71.69, 64.25, 63.65, 20.66, 19.83, 15.44, 15.29. IR (Reflection): 2978, 2930, 1492, 1312, 1115, 757, 698.

HRMS (EI): Mass calculated for C\(_{12}\)H\(_{15}\)OCl: 210.0805, found 210.0793

The title compound (4f) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 75% yield as colourless liquid. (Z/E = 1.4:1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.65 – 7.61 (m, 2H), 7.39 – 7.28 (m, 3H), 6.82 (s, 1H (6.90)), 4.12 (d, \(J = 1.3\) Hz, 2H (4.15)), 1.29 (s, 9H (1.25)).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) δ 134.83 (t), 134.38 (t), 132.00, 131.72, 129.32, 128.67 (d), 128.28, 127.85 (d), 124.49, 74.48, 74.30, 66.94, 62.82, 27.77, 27.76. IR (Reflection): 3059, 2974, 1729, 1391, 1193, 1073, 761, 695.

HRMS (EI): Mass calculated for C\(_{13}\)H\(_{17}\)OCl: 224.0962, found: 224.0952

(Z)-2-chloro-3-phenylprop-2-en-1-ol (4g)

The title compound (4g) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (10:1) in 63% yield as colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.64 (dd, \(J = 5.1, 3.7\) Hz, 2H), 7.40 – 7.34 (m, 2H), 7.31 (dt, \(J = 4.6, 1.9\) Hz, 1H), 6.80 (s, 1H), 4.35 (s, 2H), 1.98 (s, 1H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) δ 134.28, 132.64, 129.33, 128.44, 128.28, 125.02, 67.97. IR (Reflection): 3374,
The title compound (4g') was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (10:1) in 25% yield as colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.30 (m, 4H), 7.24 (s, 1H), 6.91 (s, 1H), 4.41 (d, $J$ = 4.3 Hz, 2H), 2.00 (s, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 135.58, 134.84, 131.14, 128.76, 128.67, 128.13, 62.70. IR (ATR): 3366, 2918, 2849, 1729, 1492, 1446, 1098, 1015, 754, 694. HRMS (EI): Mass calculated for C$_9$H$_9$ClO: 168.0345, found: 168.0342

The title compound (4h) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (10:1) in 62% yield as colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 – 7.60 (m, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 6.79 (s, 1H), 4.53 (q, $J$ = 6.3 Hz, 1H), 1.49 (d, $J$ = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.27, 134.40, 129.42, 128.40, 128.19, 123.94, 72.67, 21.99. IR (reflection) 3379, 3016, 2942, 1721, 1446, 1133, 1027, 861, 756, 696. HRMS (EI): Mass calculated for C$_{10}$H$_{11}$ClO: 182.0498, found 182.0496

The title compound (4i) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (10:1) in 25% yield as colourless liquid.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.36 (t, $J$ = 7.4 Hz, 1H), 7.31 (d, $J$ = 7.4 Hz, 1H), 7.21 (d, $J$ = 7.4 Hz, 1H), 6.81 (s, 1H), 1.88 (s, 1H), 1.44 (d, $J$ = 6.3 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 140.25, 134.83, 129.09, 128.73, 128.61, 127.94, 65.56, 21.97. IR (reflection) 3365, 3014, 2922, 1735, 1448, 1088, 755, 696. HRMS (EI): Mass calculated for C$_{10}$H$_{11}$ClO: 182.0498, found 182.0497
The title compound (4i) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (10:1) 61.5% yield as colourless liquid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.62 – 7.57 (m, 2H), 7.40 – 7.28 (m, 3H), 6.93 (s, 1H), 1.57 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.90, 134.99, 129.42, 128.32, 127.92, 122.16, 74.51, 66.00, 28.89. IR (ATR): 3396, 2979, 1738, 1492, 1200, 1013, 917, 796, 695. HRMS (EI) Mass calculated for C$_{11}$H$_{13}$ClO: 196.0654 found 196.0655

2-chloro-1,3-diphenylprop-2-en-1-ol (4j)

The title compound (4j) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (20:1) in 71% yield as colourless liquid. (Z/E = 3:1)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.66 (d, $J = 7.3$ Hz, 2H), 7.48 (t, $J = 8.0$ Hz, 3H), 7.44 – 7.29 (m, 5H), 7.00 (s, 1H), 5.45 (d, $J = 3.3$ Hz, 1H), 2.45 (s, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 147.92, 147.90, 140.36, 134.85, 134.26, 131.37, 129.49, 128.89, 128.73, 128.67, 128.51, 128.48, 128.43, 128.37, 128.26, 128.14, 127.14, 126.87, 126.23, 125.63, 78.28, 71.03. IR (Reflection): 3365, 3026, 2871, 1732, 1005, 814, 695. HRMS (EI): Mass calculated for C$_{15}$H$_{13}$ClO: 244.0655, found 244.0653

5-(1-chloro-2-phenylvinyl)pyrrolidin-2-one (4k)

The title compound (4k) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (10:1) 62% yield as colourless liquid. (Z/E = 3:1)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.62 (dd, $J = 7.3$ Hz, 2H), 7.42 – 7.29 (m, 3H), 6.71 (s, 1H), 5.76 (s, 1H), 4.49 (dd, $J = 7.7$, 4.3 Hz, 1H), 2.62 – 2.17 (m, 4H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 178.17, 134.26, 129.43, 128.59, 128.54, 128.26, 125.24, 60.79, 29.36, 26.54. IR (ATR): 3171, 2853, 1684, 1450, 1276, 920, 753, 689. HRMS (EI): Mass calculated for C$_{12}$H$_{12}$ClNO: 221.0610, found: 221.0608

N-(1-chloro-2-phenylallyl)-N-methylacetamide (4l)

The title compound (4l) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (10:1) in 68% yield as colourless liquid. (Z/E = 1:1:1)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.63 (d, $J = 7.3$ Hz, 2H), 7.44 – 7.27 (m, 3H), 6.61 (s, 1H), 6.57 (s, 1H), 4.37 (s, 1H), 4.20 (s, 1H), (3.06 (s, 1H), 2.99 (s, 1H), 2.20 (s, 3H), 2.18 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 171.12, 147.91, 133.81, 129.33, 128.59, 128.54, 128.40, 128.26, 126.86, 125.84, 59.69, 58.33, 54.64, 38.30, 35.74, 33.36, 31.39, 31.07, 22.01, 21.56. IR (Reflection): 3030, 2853, 1683, 1472, 1381, 1085, 753, 788. HRMS (EI): Mass calculated for C$_{12}$H$_{14}$ClNO: 223.0764, found: 223.0766
N-(1-chloro-2-phenylallyl)-N-methylformamide (4m)

The title compound (4m) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (10:1) in 58% yield as colourless liquid. (Z/E = 2:1)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (s, 1H) (8.19), 7.66 – 7.62 (m, 2H), 7.42 – 7.28 (m, 7H), 6.67 (s, 1H) (6.66), 4.31 (s, 1H) 4.11 (s, 2H), (3.01 (s, 1.5H)) 2.90 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.15, 162.79, 133.54, 129.21, 129.17, 128.66, 128.43, 128.31, 127.89, 127.61, 57.81, 51.77, 34.07, 29.14.

IR (Reflection): 2924, 2853, 1686, 1492, 1396, 1075, 764, 702.

HRMS (EI): Mass calculated for C$_{11}$H$_{12}$ClNO: 209.0607, found: 209.0606

2-(1-chloro-2-(p-tolyl)vinyl)tetrahydrofuran (5a)

The title compound (5a) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 95% yield as colourless liquid. (Z/E = 3.1:1)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.54 (d, $J = 8.1$ Hz, 2H), 7.21 – 7.12 (m, 3H), 6.76 (s, 1H) (6.86), 4.64 – 4.57 (m, 1H) (4.95), 4.06 (dd, $J = 14.4$, 6.8 Hz, 1H), 3.92 (dd, $J = 13.6$, 7.4 Hz, 1H) (3.80), 2.27 – 1.86 (m, 4H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 137.87, 133.78, 131.74, 131.16, 129.30, 129.26, 129.03, 128.67, 123.74, 82.44, 75.99, 69.52, 31.20, 30.46, 26.97, 25.84, 21.42.

IR (Reflection): 2977, 2872, 1728, 1645, 1512, 1182, 1057, 879, 757. HRMS (EI): Mass calculated for C$_{13}$H$_{15}$OCl: 222.08059, found: 222.08133

2-(1-chloro-2-(4-methoxyphenyl)vinyl)tetrahydrofuran (5b)

The title compound (5a) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 96% yield as colourless liquid. (Z/E = 3.1:1)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.61 (d, $J = 8.8$ Hz, 2H) (7.17), 6.88 (dd, $J = 8.9$, 3.1 Hz, 2H), 6.72 (s, 1H) (6.83), 4.59 (t, $J = 6.4$ Hz, 1H) (4.94), 4.06 (dd, $J = 14.4$, 6.4 Hz, 1H), 3.93 (dd, $J = 7.1$, 6.0 Hz, 1H), 3.81 (s, 3H), 2.23 – 1.88 (m, 4H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.28, 132.61, 130.87, 130.77, 130.05, 127.20, 123.38, 114.00, 113.74, 82.53, 76.00, 69.50, 69.47, 55.42, 55.39, 31.18, 30.42, 26.98, 25.88.

IR (Reflection): 2956, 2837, 2056, 1607, 1574, 1257, 1179, 1057, 879, 757. HRMS (EI): Mass calculated for C$_{13}$H$_{15}$OCl: 238.07551, found: 238.07648

2-(2-(4-(tert-butyl)phenyl)-1-chlorovinyl)tetrahydrofuran (5c)
The title compound (5a) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 91% yield as colourless liquid. \((Z/E = 3:1)\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.60 (d, \(J = 8.4\) Hz, 2H), 7.43 – 7.34 (m, 3H) (7.18), 6.77 (s, 1H) (6.87), 4.65 – 4.57 (m, 1H) (4.98), 4.35 (t, \(J = 7.0\) Hz, 1H), 4.13 – 4.01 (m, 1H), 3.93 (dd, \(J = 10.1, 4.0\) Hz, 1H), 3.87 – 3.79 (m, 1H), 2.25 – 1.89 (m, 4H), 1.31 (s, 9H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 151.07, 150.90, 147.81, 137.50, 133.83, 132.27, 131.73, 131.12, 129.14, 128.50, 125.50, 125.26, 123.59, 82.45, 69.53, 34.77, 31.38, 31.23, 30.48, 26.99, 25.81.

IR (Reflection): 2963, 2879, 1729, 1509, 1411, 1269.

HRMS (EI): Mass calculated for C\(_{16}\)H\(_{21}\)OCl: 264.1275; found: 264.1287

2-(1-chloro-2-(6-methoxynaphthalen-2-yl)vinyl)tetrahydrofuran (5d)

The title compound (5d) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 72% yield as colourless liquid. \((Z/E = 1.2:1)\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (s, 1H), 7.73 (ddd, \(J = 16.9, 9.0, 5.2\) Hz, 5H), 7.62 (s, 1H) (7.20 – 7.10), 6.91 (s, 1H) (7.01), 4.65 (t, \(J = 6.2\) Hz, 1H) (5.03), 4.08 (ddd, \(J = 13.0, 8.0, 6.6\) Hz, 1H), 3.99 – 3.95 (m, \(J = 4.6, 3.4\) Hz, 1H), 3.93 (s, 3H) (3.89 – 3.82), 2.28 – 1.88 (m, 4H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.92, 134.28, 134.20, 134.08, 131.43, 130.56, 130.10, 130.06, 130.04, 129.84, 128.90, 128.86, 128.80, 128.00, 127.77, 127.32, 127.14, 126.72, 124.01, 119.54, 119.27, 105.93, 105.89, 82.64, 76.24, 69.69, 55.61, 55.59, 31.41, 30.66, 27.10, 25.99. IR (ATR): 2923, 2855, 1627, 1598, 1503, 1481, 1372, 1356, 1239, 1198, 1056, 1027, 926, 854, 815. HRMS (EI): Mass calculated for C\(_{14}\)H\(_{17}\)ClOCl: 288.0917; found: 288.0918

2-(1-chloro-2-(4-fluorophenyl)vinyl)tetrahydrofuran (5e)

The title compound (5e) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 78% yield as colourless liquid. \((Z/E = 2.8:1)\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 – 7.58 (m, 2H) (7.24 – 7.18), 7.03 (dd, \(J = 12.1, 5.4\) Hz, 2H), 6.76 (s, 1H) (6.84), 4.65 – 4.55 (m, 1H) (4.87), 4.14 – 3.99 (m, 1H), 3.99 – 3.89 (m, 1H) (3.89 – 3.78), 2.27 – 1.87 (m, 4H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.54 (d, \(J = 13.3\) Hz), 161.08 (d, \(J = 13.5\) Hz), 142.21 (s), 138.22 (s), 134.52 (d, \(J = 1.8\) Hz), 133.63 (s), 132.93 (s), 131.12 (d, \(J = 8.0\) Hz), 130.70 (d, \(J = 3.3\) Hz), 130.49 (d, \(J = 8.1\) Hz), 130.11 (s), 130.01 (s), 127.85 (s), 122.60 (s), 115.59 (d, \(J = 21.6\) Hz), 115.29 (d, \(J = 21.4\) Hz), 82.29 (s), 75.88 (s), 69.58 (s), 31.27 (s), 30.46 (s), 26.96 (s), 25.81 (s). IR (Reflection): 3303, 2977, 2873, 1649, 1507, 1227, 1056, 825, 699. HRMS (EI): Mass calculated for C\(_{12}\)H\(_{12}\)OFCl: 226.055; found: 226.056
The title compound (5f) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 84% yield as colourless liquid. ($Z/E = 2.8:1$) 

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.52 – 7.45 (m, 2H), 7.28 – 7.22 (m, 2H), 7.11 (dt, $J = 9.0, 7.8$ Hz, 1H), 6.68 (s, 1H), 4.55 – 4.49 (m, 1H), 3.99 (dt, $J = 13.4, 6.7$ Hz, 1H), 3.91 – 3.81 (m, 1H), 2.20 – 2.07 (m, 1H), 2.02 – 1.83 (m, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 142.26, 135.47, 133.63, 133.08, 130.61, 130.06, 128.55, 122.50, 82.28, 82.23, 69.61, 33.96, 31.30, 25.79, 25.04. IR (Reflection): 3401, 2931, 1727, 1491, 1094, 1014, 793. HRMS (EI): Mass calculated for C$_{12}$H$_{12}$Cl$_2$O: 242.0265, found: 242.0271

The title compound (5g) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 80% yield as colourless liquid. ($Z/E = 2.9:1$) 

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.56 (d, $J = 8.5$ Hz, 1H), 7.48 (d, $J = 2.2$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.3$ Hz, 1H), 6.82 (d, $J = 6.8$ Hz), 6.74 (d, $J = 5.0$ Hz, 2H), 4.86 (t, $J = 6.7$ Hz), 4.59 (t, $J = 6.2$ Hz, 1H), 4.05 (dd, $J = 14.2, 7.1$ Hz, 1H), 3.99 – 3.88 (m, 1H) (3.83), 2.28 – 1.88 (m, 4H) (2.22). 

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 135.60, 135.46, 134.01, 133.63, 133.52, 133.06, 131.77, 131.49, 130.92, 130.64, 130.37, 130.08, 130.02, 129.99, 128.81, 128.53, 127.87, 122.52, 122.48, 121.85, 82.25, 75.88, 69.61, 69.59, 31.29, 30.49, 26.96, 25.79. IR (Reflection): 2976, 2872, 1728, 1588, 1401, 1265, 1181, 1075, 815. HRMS (EI): Mass calculated for C$_{13}$H$_{12}$OClBr: 285.9754 found: 285.9764

methyl (Z)-4-(2-chloro-2-(tetrahydrofuran-2-yl)vinyl)benzoate (5h)

The title compound (5h) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 71% yield as colourless liquid. ($Z/E = 2:1$) 

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.01 (d, $J = 8.3$ Hz, 1H), 7.68 (d, $J = 8.3$ Hz, 1H), 7.34 – 7.11 (m, 1H), (6.89 (s)), 6.84 (s, 1H), 4.88 (t, $J = 6.7$ Hz, 1H) (4.91), 4.65 – 4.57 (m, 1H), 4.06 (dt, $J = 13.4, 6.7$ Hz, 1H), 3.91 (s, 2H), (3.85 (dd, $J = 7.7, 4.1$ Hz), 2.14 – 1.89 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 207.09, 166.92, 166.79, 142.24, 139.93, 139.63, 139.17, 137.07, 133.55, 130.19, 130.02, 129.85, 129.57, 129.40, 129.25, 128.76, 127.80, 122.67, 82.19, 69.64, 52.24, 31.36, 31.05, 30.59, 26.95, 25.73. IR (Reflection): 3097, 2952, 2872, 1726, 1608, 1435, 1286, 1111, 1057, 819, 769, 701. HRMS (EI): Mass calculated for C$_{14}$H$_{15}$O$_3$Cl: 266.07042, found: 266.07089
2-(1-chloro-2-(4-(trifluoromethyl)phenyl)vinyl)tetrahydrofuran (5i)

The title compound (5i) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 77% yield as colourless liquid. ($Z/E = 1.5:1$)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.71 (d, $J = 8.5$ Hz, 2H), 7.62 – 7.58 (m, 2H), (7.36 (d, $J = 8.5$ Hz), 6.85 (s, 1H) (6.89), 4.64 – 4.59 (m, 1H) (4.85 (t, $J = 6.9$ Hz), 4.10 – 4.00 (m, 1H), 3.97 – 3.91 (m, 1H) (3.86 – 3.81 (m), 2.13 – 1.91 (m, 4H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.15 (s), 138.68 (s), 138.20 (d, $J = 1.3$ Hz), 137.21 (s), 129.76 (s), 129.54 (s), 129.08 (s), 125.56 (q, $J = 3.6$ Hz), 125.24 (q, $J = 3.8$ Hz), 122.24 (s), 82.12 (s), 75.88 (s), 69.66 (d, $J = 1.6$ Hz), 31.03 (s), 30.56 (s), 26.94 (s), 25.74 (s).

IR (reflection): 2979, 2876, 1730, 1617, 1460, 1327, 1126, 1068, 829. HRMS (EI): Mass calculated for C$_{16}$H$_{12}$OF$_3$Cl: 276.0523, found: 276.0513

2-(2-([1,1'-biphenyl]-4-yl)-1-chlorovinyl)tetrahydrofuran (5j)

The title compound (5j) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 79% yield as colourless liquid. ($Z/E = 2:1$)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.73 (d, $J = 8.2$ Hz, 2H), 7.60 (t, $J = 6.7$ Hz, 7H), 7.44 (t, $J = 7.4$ Hz, 4H), 7.34 (dd, $J = 13.0$, 7.6 Hz, 3H), 6.92 (s), 6.83 (s, 1H), 4.63 (t, $J = 6.4$ Hz, 1H), 4.08 (dd, $J = 14.2$, 7.1 Hz, 1H), 3.92 (dt, $J = 6.7$ Hz, 1H), 2.24 – 1.90 (m, 4H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.83, 134.64, 133.26, 129.83, 128.94, 127.17, 127.00, 123.33, 82.52, 69.60, 31.08, 25.69. IR (Reflection): 2953, 2874, 1590, 1487, 1305, 1013, 875, 761, 604. HRMS (EI): mass calculated for C$_{18}$H$_{17}$OCl : 284.09624; observed 284.09559

2-(1-chloro-2-(naphthalen-1-yl)vinyl)tetrahydrofuran (5k)

The title compound (5k) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 59% yield as colourless liquid. ($Z/E = 3:1$)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.96 – 7.92 (m, 1H) (7.95), 7.89 – 7.80 (m, 2H), 7.55 – 7.48 (m, 2H), 7.44 (d, $J = 8.1$ Hz, 1H) (7.36 (d, $J = 7.0$ Hz), 7.28 (s, 1H), 4.77 (t, $J = 7.0$ Hz, 1H), 4.02 (dd, $J = 14.4$, 7.3 Hz, 1H) (4.13), 3.79 (td, $J = 7.7$, 4.9 Hz, 1H), 2.21 – 1.87 (m, 4H) (1.77). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 147.84, 139.31, 133.60, 132.41, 131.75, 129.05, 128.53, 128.53, 126.90, 126.58, 126.35, 125.43, 125.06, 122.18, 82.01, 76.30, 69.58, 31.37, 30.54, 26.95, 25.85. IR (ATR): 2973, 2861, 1610, 1477, 1330, 1010, 875, 763, 612. HRMS (EI): Mass calculated for C$_{16}$H$_{14}$OCl: 258.0801, found: 258.0811
2-(1-chloro-2-(2-fluorophenyl)vinyl)tetrahydrofuran (5l)

The title compound (5l) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 70% yield as colourless liquid. \((Z/E = 3:1)\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (7.90 (td, \(J = 7.7, 1.6\) Hz), 7.30 – 7.23 (m, 1H), 7.17 – 7.10 (m, 1H), 7.09 – 7.02 (m, 1H), 6.93 (s, 1H) (6.81), 4.69 – 4.61 (m, 1H) (4.83), 4.14 – 4.00 (m, 1H), 3.98 – 3.89 (m, 1H) (3.87 – 3.81), 2.29 – 1.87 (m, 4H) (2.23).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.62 (s), 161.23 (s), 159.15 (s), 158.77 (s), 140.17 – 134.58 (m), 130.71 (d, \(J = 2.8\) Hz), 130.24 (d, \(J = 2.6\) Hz), 129.87 (s), 129.55 (d, \(J = 8.5\) Hz), 124.30 – 123.88 (m), 123.73 (d, \(J = 3.6\) Hz), 122.91 (d, \(J = 15.1\) Hz), 122.62 (d, \(J = 12.7\) Hz), 116.39 (d, \(J = 5.6\) Hz), 115.72 (d, \(J = 21.7\) Hz), 115.36 (d, \(J = 22.0\) Hz), 116.39 (d, \(J = 5.6\) Hz), 115.72 (d, \(J = 21.7\) Hz), 115.36 (d, \(J = 22.0\) Hz), 82.26 (s), 76.31 (s), 69.60 (s), 31.26 (s), 30.36 (s), 26.93 (s), 25.77 (s). IR (Reflection): 2927, 2873, 1727, 1455, 1365, 1236, 1059, 758.

HRMS (EI): Mass calculated for C\(_{15}\)H\(_{12}\)OFCl; 226.05552 found; 226.05161.

2-(1-chloro-2-(m-tolyl)vinyl)tetrahydrofuran (5m)

The title compound (5m) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 84% yield as colourless liquid. \((Z/E = 3.8:1)\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.50 – 7.42 (m, 2H), 7.25 (dt, \(J = 11.2, 4.0\) Hz, 1H), 7.11 (d, \(J = 7.5\) Hz, 1H), 7.06 (s, 1H), 6.78 (s, 1H) (6.88), 4.68 – 4.57 (m, 1H) (4.96 (t, \(J = 6.8\) Hz)), 4.08 (dt, \(J = 13.5, 6.7\) Hz, 1H) (3.85), 4.00 – 3.91 (m, 1H) (3.89 – 3.82), 2.28 – 1.87 (m, 4H) (2.25).

\(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 138.22, 137.96, 137.86, 135.10, 134.53, 134.43, 131.22, 130.08, 129.41, 128.73, 128.56, 128.45, 128.21, 126.42, 125.80, 123.84, 82.38, 75.96, 69.54, 31.24, 30.51, 26.97, 25.80, 21.58, 21.53.

IR (Reflection): 2977, 2871, 1646, 1486, 1273, 1058, 786, 696. HRMS (EI): Mass calculated for C\(_{13}\)H\(_{12}\)OCl: 222.08059 found 222.08161.

2-(2-(3,5-bis(trifluoromethyl)phenyl)-1-chlorovinyl)tetrahydrofuran (5n)

The title compound (5n) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 72% yield as colourless liquid. \((Z/E = 4:1)\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (s, 1.5H), 7.82 – 7.69 (m, 1.5H) (7.71), 6.90 (s, 1H), 4.66 – 4.60 (m, 1H) (4.75), 4.07 (tt, \(J = 4.7, 4.0\) Hz, 1H), (4.01 – 3.92 (m)), 2.33 – 1.94 (m, 4H) (3.87 – 3.81). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 141.80 (s), 138.99 (s), 137.08 (s), 136.71 (s), 131.73 (q, \(J = 33.2\) Hz), 129.25 (s), 128.03 (s), 124.79 (s), 121.83 – 121.10 (m), 120.60 (s), 81.86 (s), 75.92 (s), 69.74 (d, \(J = 4.9\) Hz), 31.50 (s), 30.72 (s), 26.83.
(s), 25.67 (s). **IR** (Reflection): 2957, 2849, 1732, 1463, 1378, 1278, 1133, 899. **HRMS** (EI): Mass calculated for C$_{14}$H$_{11}$OF$_6$Cl: 344.03971 found: 344.03914

**(E)-2-(1,2-diphenylvinyl)tetrahydrofuran (5o)**

![Chemical Structure](image)

The title compound (5o) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 50% yield as colourless liquid.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.28 (m, 3H), 7.22 – 7.17 (m, 2H), 7.07 (dt, $J$ = 7.2, 2.3 Hz, 3H), 6.96 – 6.91 (m, 2H), 6.69 (s, 1H), 4.69 (td, $J$ = 7.0, 1.2 Hz, 1H), 3.98 (dd, $J$ = 8.1, 6.7 Hz, 1H), 3.89 (dd, $J$ = 14.0, 7.5 Hz, 1H), 1.98 (dt, $J$ = 11.8, 6.3 Hz, 1H), 1.86 (ddt, $J$ = 10.1, 7.0, 3.7 Hz, 2H), 1.70 (ddd, $J$ = 14.8, 11.8, 7.4 Hz, 1H). **$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 143.22, 139.14, 136.93, 129.46, 129.39, 128.70, 127.96, 127.31, 126.64, 125.93, 83.70, 68.84, 53.56, 31.28, 25.95. **IR** (reflection): 3056, 2926, 2856, 1599, 1493, 1446, 1050, 768, 700. **HRMS** (EI): Mass calculate for C$_{18}$H$_{18}$O: found

**(Z)-2-(1,2-diphenylvinyl)tetrahydrofuran (5o’)**

![Chemical Structure](image)

The title compound (5o’) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 40% yield as colourless liquid.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.54 – 7.48 (m, 2H), 7.39 – 7.28 (m, 8H), 6.74 (s, 1H), 4.98 (dd, $J$ = 8.4, 6.8 Hz, 1H), 3.94 – 3.84 (m, 1H), 3.77 (t, $J$ = 13.1, 6.5 Hz, 1H), 1.98 – 1.88 (m, 1H), 1.86 – 1.75 (m, 2H), 1.70 – 1.64 (m, 1H). **$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 142.60, 141.49, 137.13, 133.19, 129.21, 128.96, 128.31, 127.99, 127.16, 127.15, 68.47, 53.56, 30.78, 29.85, 26.80. **IR** (Reflection): 3056, 2926, 2871, 1712, 1493, 1446, 1050, 768, 700. **HRMS** (EI): Mass calculate for C$_{18}$H$_{18}$O: found

**2-(1-bromo-2-phenylvinyl)tetrahydrofuran (5p)**

![Chemical Structure](image)

The title compound (5p) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 39% yield as colourless liquid.
$^1$H NMR (300 MHz, CDCl$_3$) δ 7.57 (t, $J = 9.2$ Hz, 2H), 7.43 (dd, $J = 17.3$, 8.2 Hz, 2H), 7.18 (q, $J = 8.9$ Hz, 1H), 6.67 – 6.55 (m, 1H), 4.56 (ddd, $J = 16.3$, 11.0, 6.9 Hz, 1H), 4.03 – 3.91 (m, 1H), 3.90 – 3.71 (m, 1H), 2.21 – 2.06 (m, 1H), 2.04 – 1.88 (m, 2H), 1.77 – 1.61 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.40, 135.04, 133.51, 130.40, 130.00, 129.20, 128.98, 127.87, 126.73, 125.65, 125.60, 125.29, 125.23, 79.40, 68.47, 68.34, 33.05, 32.48, 26.53, 26.03.

IR (reflection): 3029, 2865, 1752, 1480, 1451, 1183, 1057, 923, 757, 696.

HRMS (EI): Mass calculated for C$_{12}$H$_{13}$OBr: 252.0156, found: 252.0147

ethyl-3-phenyl-2-(tetrahydrofuran-2-yl)acrylate (5q)

The title compound (5q) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (20:1) in 91% yield as colourless liquid. ($Z/E = 1.3:1$) $^1$H NMR (300 MHz, CDCl$_3$) δ (7.72 (s)), 7.39 – 7.13 (m, 10H), 6.88 (s, 1H), (4.93 – 4.83 (m)), 4.78 – 4.68 (m, 1H), (4.28 (q, $J = 7.1$ Hz)), 4.14 (q, $J = 7.1$ Hz, 2H), 4.07 – 3.94 (m, 2H), (3.93 – 3.73 (m)), (2.39 – 2.18 (m)), 2.13 – 1.85 (m, 8H), (1.35 (t, $J = 7.1$ Hz)), 1.12 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 168.61, 142.19, 141.44, 135.89, 135.15, 133.85, 133.64, 131.64, 130.00, 129.33, 128.61, 128.50, 128.44, 128.23, 128.00, 127.87, 82.65, 79.71, 68.87, 65.99, 60.84, 31.88, 31.32, 27.38, 25.76, 15.42, 14.40, 13.93. IR (reflection): 2976, 2870, 1710, 1642, 1485, 1452, 1296, 1206, 1027, 870, 696. HRMS (EI): calculated mass for C$_{15}$H$_{18}$O$_3$ 246.1255, found: 246.1256

2-styryltetrahydrofuran (5s)

The title compound (5s) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 81% yield as colourless liquid. ($Z/E = 1.4:1$) $^1$H NMR (300 MHz, CDCl$_3$) δ 7.41 – 7.27 (m, 5H), (7.23 (dd, $J = 6.0$, 2.6 Hz, 1H)), (6.61 (s, 0.86H)), 6.57 (d, $J = 4.0$ Hz, 1H), 5.71 (dd, $J = 11.6$, 8.9 Hz, 1H), 4.67 (dd, $J = 15.5$, 7.7 Hz, 1H), (4.48 (dd, $J = 15.8$, 6.6 Hz (q, $J = 6.9$ Hz, 0.78H)), 3.97 (ddd, $J = 14.6$, 7.1, 4.1 Hz, 1H), 3.90 – 3.73 (m, 1H), 2.22 – 2.08 (m, 1H), 2.05 – 1.88 (m, 2H), 1.80 – 1.62 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 168.61, 142.19, 141.44, 135.89, 135.15, 133.85, 133.64, 130.00, 129.33, 128.61, 128.50, 128.44, 128.23, 128.00, 127.87, 82.65, 79.71, 68.87, 65.99, 60.84, 31.88, 31.32, 27.38, 25.76, 15.42, 14.40, 13.93. IR (reflection): 2979, 2870, 1710, 1642, 1485, 1452, 1296, 1206, 1027, 870, 696. HRMS (EI): calculated mass for C$_{15}$H$_{18}$O$_3$ 246.1255, found: 246.1256

2-(4-methylstyril)tetrahydrofuran (5t)

The title compound (5t) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (20:1) in 80% yield as colourless liquid. ($Z/E = 1.4:1$) $^1$H NMR (300 MHz, CDCl$_3$) δ 7.31 – 7.07 (m, 4H), (6.58 (s, 1H)), 6.53 (d, $J = 3.6$ Hz, 1H), (6.15 (dd, $J = 15.8$, 6.7 Hz, 1H)), 5.66 (dd, $J = 11.6$, 8.9 Hz, 1H), 4.67 (dd, $J =$
15.7, 7.4 Hz, 1H), (4.46 (q, J = 6.9 Hz, 1H)), 4.04 – 3.91 (m, 1H), 3.90 – 3.72 (m, 1H), 2.34 (s, 3H), 2.14 (dd, J = 14.1, 9.7, 5.7 Hz, 1H), 2.05 – 1.88 (m, 2H), 1.76 – 1.63 (m, 1H). \( ^{13}C\) NMR (75 MHz, CDCl\(_3\)) δ 137.44, 137.04, 134.23, 134.00, 132.34, 131.57, 130.59, 129.60, 129.02, 128.92, 79.95, 75.31, 68.28, 68.18, 33.08, 32.56, 26.53, 26.08, 21.33. IR (ATR): 2972, 2868, 1489, 1051, 966, 826. HRMS (EI): Mass calculated for C\(_{13}\)H\(_{16}\)O: 188.1223, found: 188.1211.

2-(4-chlorostyryl)tetrahydrofuran (5u)

The title compound (5t) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 84% yield as colourless liquid. (Z/E = 2:1) \( ^{1}H\) NMR (300 MHz, CDCl\(_3\)) δ 7.29 (t, J = 6.1 Hz, 4H), (7.23 (d, J = 8.6 Hz, 2H), (6.56 (d, J = 3.8 Hz, 0.8H)), 6.51 (s, 1H), (6.18 (dd, J = 15.9, 6.5 Hz, 1H), 5.72 (dd, J = 11.6, 8.9 Hz, 1H), 4.59 (dd, J = 15.4, 7.7 Hz, 1H), (4.46 (q, J = 6.5 Hz, 0.69H), 4.01 – 3.91 (m, 1H), 3.89 – 3.74 (m, 1H), 2.19 – 2.06 (m, 1H), 2.03 – 1.89 (m, 2H), 1.77 – 1.62 (m, 1H). \( ^{13}C\) NMR (75 MHz, CDCl\(_3\)) δ 135.25, 133.64, 133.15, 131.40, 130.58, 130.28, 129.31, 128.81, 128.50, 127.81, 126.46, 79.62, 75.01, 68.38, 68.27, 33.04, 32.50, 26.53, 26.06. IR (Reflection): 3016, 2869, 1729, 1490, 1091, 1052, 843. HRMS (EI): Mass calculated for C\(_{12}\)H\(_{13}\)OCl: 208.0649, found: 208.0667.

1-(4-((tetrahydrofuran-2-yl)vinyl)phenyl)ethan-1-one (5v)

The title compound (5u) was purified by silica gel flash column chromatography using petroleum ether and ethyl acetate (30:1) in 63% yield as colourless liquid. (Z/E = 2:1) \( ^{1}H\) NMR (300 MHz, CDCl\(_3\)) δ 7.98 (t, J = 8.4 Hz, 1H), (7.91 (q, J = 8.4 Hz, 1H), 7.18 (d, J = 11.6, 8.9 Hz, 1H), (6.56 (d, J = 3.8 Hz, 1H), 6.61 (dd, J = 13.8, 6.4 Hz, 1H), (6.05 (d, J = 8.8 Hz, 1H)), 6.33 (dd, J = 15.9, 6.3 Hz, 1H), (6.36), 5.80 (dd, J = 15.9, 6.3 Hz, 1H), 4.62 (dd, J = 15.5, 7.7 Hz, 1H), (4.50 (d, J = 6.8 Hz, 1H)), 3.97 (dd, J = 10.5, 4.3 Hz, 1H), 3.91 (d, J = 3.0 Hz, 1H), 3.87 – 3.73 (m, 1H), 2.15 – 1.87 (m, 2H), 1.80 – 1.64 (m, 1H). \( ^{13}C\) NMR (75 MHz, CDCl\(_3\)) δ 207.10, 167.05, 141.55, 141.48, 134.99, 133.53, 130.67, 130.03, 129.62, 129.40, 128.93, 128.84, 127.83, 126.46, 79.47, 75.04, 68.44, 68.32, 52.23, 33.04, 32.47, 31.06, 26.52, 26.04. IR (Reflection): 3427, 2952, 1730, 1436, 1369, 1329, 1291, 1180, 1131, 869, 774 HRMS (EI): Mass calculated for C\(_{14}\)H\(_{16}\)O: 216.1156, found: 216.1148.

(2-chloro-2-cyclohexylvinyl)benzene (6a)

The title compound (6a) was purified by silica gel flash column chromatography using hexane as eluent with 53% yield as colourless liquid. (Z/E = 1.4:1)
1H NMR (300 MHz, CDCl₃) δ 7.58 (d, J = 7.5 Hz, 1.84H), 7.34 (ddd, J = 7.6, 6.5, 4.6 Hz, 5H), 7.18 (d, J = 7.5 Hz, 2H), 6.64 (s, 1H), (6.47 (s, 0.8H)), 2.87 (dt, J = 9.8, 8.4 Hz, 1H), (2.40 – 2.28 (m, 0.93H)), 1.94 (d, J = 12.6 Hz, 2H), 1.88 – 1.60 (m, 12H), 1.49 – 1.30 (m, 6H). 13C NMR (75 MHz, CDCl₃) δ 144.01, 136.35, 135.54, 128.54, 128.04, 126.68, 48.61, 41.35, 31.71, 30.89, 25.79. IR (Reflection): 2932, 2854, 1628, 1494, 1157, 964, 801, 694. HRMS (EI): Mass calculated for C₁₄H₁₇Cl: 220.1022, found: 220.1020

1-(2-chloro-3,3-diethylpent-1-en-1-yl)-4-methylbenzene (6b)

The title compound (6b) was purified by silica gel flash column chromatography using hexane as eluent with 56% yield as colourless liquid. (Z/E = 4:1) (C₃:C₂ = 15:1)

1H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.43 (s, 1H), 2.35 (s, 3H), 1.58 – 1.52 (q, 6H), 0.79 (t, J = 7.4 Hz, 9H). 13C NMR (101 MHz, CDCl₃) δ 141.80, 137.11, 133.39, 129.34, 128.85, 126.17, 125.48, 117.82, 116.85, 48.94, 26.39, 21.37, 8.15. IR (Reflection): 2965, 2926, 1613, 1458, 869, 804, 780. HRMS (EI): Mass calculated for C₁₆H₂₃Cl: 250.1489, found: 250.1492

2-((4-methoxyphenyl)ethynyl)tetrahydrofuran (7a)

The title compound (7a) was purified by silica gel flash column chromatography using hexane as eluent with 71% yield as colourless liquid.

1H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 8.9 Hz, 1H), 6.82 (d, J = 8.9 Hz, 1H), 4.82 – 4.77 (m, 1H), 4.01 (dt, J = 10.4, 7.1 Hz, 1H), 3.89 – 3.83 (m, 1H), 3.80 (s, 2H), 2.11 – 2.04 (m, 1H), 1.99 – 1.92 (m, 1H). 13C NMR (101 MHz, CDCl₃) δ 159.73, 133.32, 113.99, 113.72, 87.76, 84.54, 82.65, 68.85, 68.02, 55.41, 33.62, 25.66. IR (Reflection): 2935, 2843, 2223, 1626, 1291, 1050, 836. HRMS (EI): Mass calculated for C₁₃H₁₄O₂: 202.0961, found: 202.097

2-((4-bromophenyl)ethynyl)tetrahydrofuran (7b)

The title compound (7b) was purified by silica gel flash column chromatography using hexane as eluent with 66% yield as colourless liquid.

1H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.6 Hz, 1H), 7.28 (d, J = 8.6 Hz, 1H), 4.79 (dd, J = 7.2, 5.0 Hz, 1H), 4.03 – 3.96 (m, 1H), 3.90 – 3.82 (m, 1H), 2.26 – 2.18 (m, 1H), 2.08 (ddd, J = 6.8, 4.3, 1.0 Hz, 1H), 2.00 – 1.93 (m, 1H). 13C NMR (101 MHz, CDCl₃) δ 133.16, 131.49, 122.51, 121.80, 90.29, 83.43, 83.36, 68.54, 68.02, 33.33, 25.51. IR (ATR): 2967, 2928, 2854, 2221, 1460, 1377, 1161, 1054, 820. HRMS (EI): Mass calculated for C₁₂H₁₁BrO: 249.2011, found: 202.2009

2-((2-chlorophenyl)ethynyl)tetrahydrofuran (7c)
The title compound (7c) was purified by silica gel flash column chromatography using hexane as eluent with 64% yield as colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.44 (dd, 1H), 7.40 – 7.36 (dd, 1H), 7.21 (dd, $J$ = 3.2, 1.9 Hz, 1H), 4.88 (dd, $J$ = 7.3, 4.5 Hz, 1H), 4.04 (dd, $J$ = 14.3, 7.9 Hz, 1H), 3.92 – 3.85 (m, 1H), 2.29 – 2.21 (m, 1H), 2.14 (ddd, $J$ = 6.6, 4.6, 2.7 Hz, 2H), 1.99 – 1.93 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 136.21, 133.56, 129.44, 129.34, 126.50, 122.92, 94.72, 81.39, 68.76, 68.09, 33.56, 25.51. IR (Reflection): 2962, 2930, 2232, 1453, 1176, 768.

HRMS (EI): Mass calculated for C$_{12}$H$_{11}$ClO: 206.0498, found: 206.0489

(cyclohexylethynyl)benzene (7d)

The title compound (7d) was purified by silica gel flash column chromatography using hexane as eluent to give 61% yield as colourless liquid

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.37 (m, 2H), 7.29 – 7.22 (m, 3H), 2.63 – 2.55 (m, 1H), 1.88 (dd, $J$ = 10.1, 3.7 Hz, 2H), 1.76 (dd, $J$ = 9.6, 3.8 Hz, 2H), 1.54 (m, 3H), 1.40 – 1.30 (m, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 131.73, 128.29, 127.54, 124.31, 94.62, 80.67, 32.89, 29.83, 26.10, 25.07. IR (Reflection): 2929, 2853, 2232, 1453, 1176, 768. HRMS (EI): Mass calculated for C$_{14}$H$_{16}$: 184.1251, found: 184.1254

(3,3-diethylpent-1-yn-1-yl)benzene (7e)

The title compound (7e) was purified by silica gel flash column chromatography using hexane as eluent to give 59% yield as colourless liquid. (C3:C2 = 10:1)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 – 7.48 (m, 2H), 7.42 – 7.33 (m, 3H), 1.53 (dd, $J$ = 14.1, 6.7 Hz, 6H), 0.95 (dt, $J$ = 14.9, 7.4 Hz, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 131.74, 131.68, 128.28, 128.25, 127.48, 127.40, 124.53, 96.20, 82.43, 46.35, 29.97, 8.94. IR (Reflection): 2953, 2929, 2870, 2222, 1612, 1488, 1365, 754, 690. HRMS (EI): Mass calculated for C$_{15}$H$_{20}$: 200.1561; found 200.1559

1-(2-chloro-1-phenylvinyl)-4-methylbenzene ()
The title compound (XX) was purified by silica gel flash column chromatography using petroleum ether as eluent to give 59% yield as colourless liquid. (Z/E = 1:1.5)

$^1$H NMR (301 MHz, CDCl$_3$) $\delta$ 7.37 (ddd, $J$ = 12.3, 5.2, 4.3 Hz, 5.76H), 7.30 (s, 1.43H), 7.15 (s, 1.93H), 6.60 (s, 0.45H), 6.60 (s, 1H), 2.43 (s, 3H), 2.38 (s, 1.5H).

2,2,6,6-tetramethyl-1-((tetrahydrofuran-2-yl)oxy)piperidine

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.36 (dd, $J$ = 5.2, 2.0 Hz, 1H), 3.92-3.80 (m, 2H), 2.03-1.89 (m, 3H), 1.82-1.73 (m, 1H), 1.53-1.43 (m, 5H), 1.34-1.29 (m, 1H), 1.21 (s, 3H), 1.11 (s, 3H), 1.06 (s, 3H), 1.04 (s, 3H);

7. Computational Study

Geometries as well as frequencies were calculated on the PBE0-DE/pceseg-2 level of theory within the Q-Chem software package. Furthermore, CPCM was utilized to implicitly model the solvation effects of the THF solvent. Using time-dependent density functional theory calculations with the range-separated wB97X-D3 functional, the electronic absorptions spectra were simulated. Furthermore, a non-equilibrium CPCM formalism (ptSS & ptLR) to properly calculate the energetic shifts of the excited states due to solvent effects. Spin-orbit coupling elements between excited states were estimated via the one-electron Breit-Pauli Hamiltonian. Electron/hole densities were calculated using the libwfa library.

Geometries

V – Transition State

|   |   |   |   |   |
|---|---|---|---|---|
| C | -2.4712759 | -0.8628321 | 1.6334816 |
| C | -2.0331794 | -2.0570780 | 0.7765343 |
| C | -1.3908800 | 0.1628879 | 1.3389689 |
| H | -2.4537623 | -1.1323362 | 2.6968362 |
| H | -3.4737536 | -0.4966468 | 1.3901067 |
| O | -0.2009385 | -0.6144509 | 1.1373294 |
| H | -1.1893281 | 0.8647647 | 2.1529686 |
| H | -1.5999943 | 0.7295116 | 0.4208284 |
| C | -0.5637756 | -1.8231088 | 1.8637580 |
| H | -2.5377415 | -2.0505576 | -0.2030144 |
| H | -2.2619472 | -3.0249112 | 1.2412772 |
| C | -0.2684779 | -1.3287151 | -1.8637580 |
| C | -0.0063816 | -0.1369172 | -1.8814313 |
| Cl | -0.5549600 | -2.8680247 | -2.4173060 |
| C | 0.2584764 | 1.2338887 | -1.6306924 |
### V – (E) Product

| Element | X (Å) | Y (Å) | Z (Å) |
|---------|-------|-------|-------|
| C       | 4.1569188495 | 0.8951137727 | 0.3454655703 |
| C       | 2.7305505540  | 1.4284586517 | 0.3425062453 |
| C       | 3.9471863712  | -0.5158939103 | -0.1720144253 |
| H       | 4.5600412463  | 0.8709337042 | 1.3605507545 |
| H       | 4.8325492398  | 1.4770094630 | -0.281443960 |
| O       | 2.6997862977  | -0.9383240474 | 0.3753288413 |
| H       | 4.7130822924  | -1.2225023592 | 0.1499265740 |
| H       | 3.8938401950  | -0.5311294864 | -1.2670616252 |
| C       | 1.9158919935  | 0.1947925301 | 0.7389115302 |
| H       | 2.4533989079  | 1.7605293016 | -0.6596307106 |
| H       | 2.564864408   | 2.2529559700 | 1.0353348885 |
| C       | -0.5674910498 | 0.1108875214 | 0.8552158718 |
| C       | 0.5497084427  | 0.1175977299 | 0.1267657011 |
| Cl      | 0.5506478381  | 0.0004704891 | -1.6091804150 |
| C       | -1.9754121815 | 0.0755149996 | 0.4597386989 |
| C       | -4.2253721525 | -0.6467898196 | 1.0026392516 |
| C       | -4.7087965558 | -0.0451266466 | -0.1519926899 |
| C       | -3.8306411244 | 0.6305658551 | -0.9893469086 |
| C       | -2.4780482121 | 0.6904364965 | -0.6907296553 |
| C       | -2.8763264050 | -0.5755766747 | 1.309663814 |
| H       | -2.5062790785 | -1.038684192 | 2.2174996224 |
| H       | -4.9017162334 | -1.1681098066 | 1.6694624455 |
| H       | -5.7639807616 | -0.0936263365 | -0.3924858685 |
| H       | -4.2015842232 | 1.1210263338 | -1.8815185729 |
| H       | -1.8142599360 | 1.2362468192 | -1.3462505016 |
| H       | 1.7692185244  | 0.1750245341 | 1.8243123487 |
| H       | -0.3945892918 | 0.0937937076 | 1.9280406435 |

### V – (Z) Product

| Element | X (Å) | Y (Å) | Z (Å) |
|---------|-------|-------|-------|
| C       | 4.1147743105 | 0.5451350125 | 0.6019546749 |
| C       | 2.8277157536  | 1.2275235881 | 0.1549257190 |
| C       | 3.7917270671  | -0.9123465853 | 0.3366135830 |
| H       | 4.2895533071  | 0.7076631645 | 1.6679358412 |
| H       | 4.9915023253  | 0.8869912276 | 0.0519256045 |
| O       | 2.4035207000  | -1.0566699264 | 0.6364053956 |
| H       | 4.3469668305  | -1.6078559496 | 0.9672880744 |
| H       | 3.9685003468  | -1.1735727547 | -0.7132230666 |
| C       | 1.7615788221  | 0.2178541609 | 0.5853994030 |
| H       | 2.8243200405  | 1.3594254149 | -0.9278308000 |
| H       | 2.6616461252  | 2.1983992751 | 0.6198539379 |
| C       | -0.7203198317 | 0.3304599866 | 0.0815985663 |
| C       | 0.5488860299  | 0.1554052345 | -0.2865677273 |
| Cl      | 0.8827165883  | -0.1605549735 | -1.9741648801 |
| Atom | x    | y    | z    |
|------|------|------|------|
| C    | -1.2285969727 | 0.5164209549 | 1.4472275648 |
| C    | -1.3173516803 | -0.058593757 | 3.7940613266 |
| C    | -2.3003981481 | 0.8995949559 | 4.004321507  |
| C    | -2.7645244716 | 1.652162818 | 2.9331226723 |
| C    | -2.2402424752 | 1.4554097229 | 1.6652962160 |
| C    | -0.7884347506 | -0.2532605653 | 2.5272139512 |
| H    | -0.047379397 | 4 | -1.0271358590 | 2.3687083237 |
| H    | -0.9674280095 | -0.6676258926 | 4.6189263576 |
| H    | -2.7133383271 | 1.0482452462 | 4.9945838378 |
| H    | -3.5417694694 | 2.3920963527 | 3.0839579728 |
| H    | -2.6103845450 | 2.0390885063 | 0.8298951864 |
| H    | 1.4160398123 | 0.4695710577 | 1.5905129337 |
| H    | -1.4711799806 | 0.3564313945 | -0.7020945746 |

**V’ – Transition State**

| Atom | x    | y    | z    |
|------|------|------|------|
| C    | -2.7014281030 | -0.1504606933 | 0.9770444213 |
| C    | -2.0382454138 | -1.1835614208 | 0.0579104036 |
| C    | -1.5111187283 | 0.6444909552 | 1.4844949189 |
| H    | -3.2034451136 | -0.6520725128 | 1.8136615318 |
| H    | -3.4352467350 | 0.4789734984 | 0.4634642899 |
| O    | -0.445418939 | -0.3169729543 | 1.5645989029 |
| H    | -1.6377682700 | 1.0735100565 | 2.4824370606 |
| H    | -1.2174255556 | 1.4374378513 | 0.7837449144 |
| C    | -0.6541144401 | -1.2721573781 | 0.6163017172 |
| H    | -2.0288805771 | -0.8317705309 | -0.9861599903 |
| H    | -2.5514769403 | -2.1536413387 | 0.0592715844 |
| C    | 1.0868448276 | -1.9251802089 | -1.8470954654 |
| C    | 0.7570784322 | -0.8414508380 | -1.3833789595 |
| Cl   | 1.2292186255 | -3.5626631971 | -2.0158458236 |
| C    | 0.5856819052 | 0.5681874506 | -1.2108223639 |
| C    | 1.1635901156 | 2.6312563249 | -0.0908670908 |
| C    | 0.1955498564 | 3.3102968499 | -0.8291605629 |
| C    | -0.5697339290 | 2.6211411522 | -1.7667934796 |
| C    | -0.3785815725 | 1.2587777950 | -1.9610520875 |
| C    | 1.3603604761 | 1.2698960453 | -0.2756287858 |
| H    | 2.1047639853 | 0.7343337354 | 0.3083930885 |
| H    | 1.7668252312 | 3.1674195457 | 0.6397119598 |
| H    | 0.0416709490 | 4.3771034846 | -0.6764216224 |
| H    | -1.3217923364 | 3.1478215535 | -2.3517203904 |
| Atom | x         | y          | z          |
|------|-----------|------------|------------|
| H    | -0.9719844005 | 0.7172889702 | -2.6948584486 |
| H    | -0.1030467239 | -2.1911994731 | 0.7996883465 |

\( V' - (Z) \)

| Atom | x         | y          | z          |
|------|-----------|------------|------------|
| C    | 1.4158115975 | 2.7890977677 | 0.9358271148 |
| C    | 1.1991284834 | 1.3305911624 | 1.3167481145 |
| C    | 0.7794336229 | 2.8283622045 | -0.4403842619 |
| H    | 2.4816665024 | 3.0203558089 | 0.8707919596 |
| H    | 0.9559804720 | 3.4892474590 | 1.6336563822 |
| O    | 1.0611075381 | 1.5668495399 | -1.0307543087 |
| H    | 1.1859341005 | 3.6024406634 | -1.0928921324 |
| H    | -0.3062141192 | 2.9713380713 | -0.3652796963 |
| C    | 1.3762509076 | 0.6114313674 | -0.0239492228 |
| H    | 0.1821783562 | 1.1800493407 | 2.0688902161 |
| H    | 1.8933239531 | 0.9574224910 | 1.390255178 |
| C    | 1.0477575691 | -1.8310842150 | -0.2018707819 |
| C    | 0.5103879930 | -0.6297676780 | -0.1390255178 |
| Cl   | 2.6009569146 | -2.435468352 | -0.2438418856 |
| C    | -0.9676156078 | -0.5133557106 | -0.0849141801 |
| C    | -3.0438491825 | 0.4318645389 | -0.874923283 |
| C    | -3.7565652283 | -0.3330640047 | 0.0375527310 |
| C    | -3.075407271 | -1.193875276 | 0.8860880030 |
| C    | -1.693321569 | -1.2801727526 | 0.8269549698 |
| C    | -1.6619246890 | 0.3430650728 | -0.9401948576 |
| H    | -1.1111379089 | 0.9216921953 | -1.6680080011 |
| H    | -3.5681303315 | 1.0965417516 | -1.5507531257 |
| H    | -4.864228884 | -0.2623233034 | 0.083535465 |
| H    | -3.6211250136 | -1.7977805215 | 1.6006429789 |
| H    | -1.1607120069 | -1.9448472685 | 1.4962758349 |
| H    | 2.4193355413 | 0.3123518669 | -0.1622067724 |

\( V' - (E) \)

| Atom | x         | y          | z          |
|------|-----------|------------|------------|
| C    | -3.3982391771 | 0.1095350164 | -0.8122571932 |
| C    | -2.0580012966 | -0.4336490208 | -1.2902835525 |
| C    | -3.0389847989 | 0.5607357154 | 0.5916026797 |
| H    | -4.1505726153 | -0.6821741306 | -0.7782130813 |
| H    | -3.7803473161 | 0.9202379371 | -1.4330275296 |
| O    | -2.1069327407 | -0.3956051751 | 1.0730366649 |
| H    | -3.8846018025 | 0.5841201976 | 1.2805310390 |
| H    | -2.5766292068 | 1.5562904128 | 0.5712891292 |
| C    | -1.4850692432 | -1.0696477802 | -0.0201714141 |
| H    | -1.4156792933 | 0.3876384782 | -1.6161670050 |
| H    | -2.1324435627 | -1.1533486240 | -2.1045038424 |
| C    | 0.7193064318 | -2.0864956796 | 0.1481941716 |
Sk – Radical Intermediate

C  -2.8401219800  0.9110563768  -0.6047090746
C  -3.4737525886  -0.4534353273  -0.8589573495
C  -2.5986399418  0.9081465360  0.9039042621
O  -2.7138875219  -0.4506799282  1.3452358014
C  -2.8414856028  -1.3078379359  0.2365143115
C  -0.3351151893  -1.5048417088  0.2763705091
C  -1.4894034615  -1.8667443599  -0.1616680386
Cl  -1.6207828253  -3.1674297660  -1.3745617507
C  0.8739881217  -1.1036657984  0.7506824832
C  2.8504171669  0.3796695907  0.6379731815
C  3.3456005946  -0.2414271134  1.8132037830
C  2.6419270937  -1.2597982272  2.4221930178
C  1.4252075580  -1.6935072945  1.9111765687
C  1.6174213910  -0.0470750920  0.0853996913
C  3.5640266584  1.4130236278  -0.0058693368
C  1.1504057515  0.5556172140  -1.0912341753
C  1.8656660253  1.5590022405  -1.7011616170
C  3.0812611282  1.9936738111  -1.1519925294
H  -1.8982351990  1.0053821188  -1.145884751
H  -3.4844675333  1.7333458551  -0.9139415083
H  -3.2893836736  -0.8377328955  -1.8609102677
H  -4.5527076361  -0.4210679522  -0.6968910192
H  -3.3468149643  1.4916930384  1.4446869448
H  -1.6070419473  1.2870139877  1.1620827560
H  -3.4778107753  -2.1485893245  0.5252571017
H  4.2915861823  0.0927035105  2.2219495100
H  3.0370707316  -1.7307847006  3.3141206544
H  0.8753200769  -2.4870613186  2.4004554681
H  4.5060596034  1.7373262551  0.4217765260
H  0.2162942278  0.2167363060  -1.5230260221
5k – (Z) Product

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | -3.3065951112 | 0.5067312584 | -0.9977694746 |
| C       | -3.4836957847  | -0.9806399501  | -0.7225734020 |
| C       | -3.5797558002  | 1.1097744825  | 0.3680972930 |
| O       | -3.1817179762  | 0.1232449210  | 1.3279334404 |
| C       | -2.9020218448  | -1.1065305087 | 0.6893152346 |
| C       | -0.4820519519  | -0.4782527178 | 0.9876507072 |
| C       | -1.4151609928  | -1.3716357612 | 0.6796147812 |
| Cl      | -1.0387847747  | -2.9890532239 | 0.1618637068 |
| O       | 0.9748973595   | -0.6427931980 | 0.9946506675 |
| C       | 3.2023264129   | 0.1686433689  | 0.3449284889 |
| C       | 3.7750499182   | -0.8841285866 | 1.0938712910 |
| C       | 2.9773338001   | -1.7770285887 | 1.7552693588 |
| C       | 1.5774975054   | -1.6543898308 | 1.705392014 |
| C       | 1.7855455247   | 0.2950899318  | 0.288962954 |
| C       | 4.0026635898   | 1.0924321770  | -0.3653562676 |
| C       | 1.2288029151   | 1.3335943901  | -0.4924588400 |
| C       | 2.0312136512   | 2.2116281678  | -1.171064408 |
| C       | 3.4329546461   | 2.0930645995  | -1.105138974 |
| C       | 2.2837220206   | 0.7173928496  | -1.317073941 |
| C       | -3.9867190972  | 0.8829000462  | -1.7613790705 |
| C       | -2.9844477565  | -1.6243870062 | -1.4448236205 |
| C       | -4.5422187230  | -1.2473550752 | -0.6996390814 |
| C       | -4.6448121124  | 1.3203550505  | 0.5075182050 |
| C       | -3.0156849288  | 2.0246823769  | 0.5587253439 |
| C       | -3.3881313622  | -1.9102146358 | 1.2525800029 |
| C       | -0.8722557395  | 0.4982203764  | 1.2572513890 |
| C       | 4.8548212969   | -0.9721918044 | 1.1321004950 |
| C       | 3.4182080590   | -2.5828724098 | 2.3294928739 |
| C       | 0.9627231860   | -2.3590677896 | 2.2509557192 |
| C       | 5.0808306508   | 0.9885657210  | -0.3167803673 |
| C       | 0.1516885732   | 1.4226188770  | -0.563465292 |
| C       | 1.5867905262   | 2.9989751746  | -1.7680114246 |
| C       | 4.0575166227   | 2.7926344175  | -1.6473646359 |

5k – (E) Product

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | 2.0372157275 | -0.9668614796 | 0.3661125475 |
| C       | 1.9824120239  | -0.4576572008 | -1.0736001659 |
| C       | 2.8933753432  | 0.0822769047  | 1.0487926056 |
| O       | 2.5576074777  | 1.3100127215  | 0.4187236634 |
| C       | 2.2459124391  | 1.0619218356  | -0.9439099885 |
| C       | -0.1331845245 | 1.9914236909  | -0.8575064327 |
The text contains a table with coordinates for various atoms, including carbon (C), chlorine (Cl), hydrogen (H), and oxygen (O). The table is followed by a section labeled "5j – Radical Intermediate," which also includes coordinates for these atoms.

### Table of Atomic Coordinates

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | 1.0886448738 | 1.9343970442 | -1.3737418290 |
| Cl   | 1.4433874233  | 2.9233407746  | -2.7731255100 |
| C    | -0.6089305122 | 1.1890667952  | 0.2883703459  |
| C    | -1.9433778057 | -0.6763710712 | 1.1650399900  |
| C    | -1.5624597607 | -0.298938812  | 2.4718363247  |
| C    | -0.7490478402 | 0.7825043827  | 2.6707471023  |
| C    | -0.2738160359 | 1.5268179645  | 0.0545286481  |
| C    | -2.7782811104 | -1.7937854665 | 0.9312988324  |
| C    | -1.8437457557 | -0.3278689154 | 1.2478139957  |
| C    | -2.6539769028 | -1.415093864  | -1.4410283071 |
| C    | -3.1282732967 | -2.1563776262 | -0.341069006  |
| H    | 1.0414172496  | -0.9864558906| 0.809749852  |
| H    | 2.4663552590  | -1.9661675328 | 0.4404555224 |
| H    | 1.0308566677  | -0.6709128894 | -1.5572975353 |
| H    | 2.7715815226  | -0.9082340332 | -1.6762482946 |
| H    | 2.6887585603  | 0.1936767482  | 2.1139049938  |
| H    | 3.9623112433  | -0.1294718238 | 0.9152731729  |
| C    | 4.1608200631  | 0.9600413384  | 0.2434016621  |
| C    | 2.7474760315  | 1.2745667884  | -0.2342584310 |
| C    | 4.0436624005  | -0.5179513829 | 0.5607077780  |
| H    | 4.4005620520  | 1.5237383262  | 1.7458361976  |
| H    | -3.1342451823 | -2.3618698474 | 1.7835016954  |
| H    | -1.4743525510 | 0.290606320  | -2.1006121757 |
| H    | -2.9304979182 | -1.712614773 | -2.445311760 |
| H    | -3.7665219427 | -3.015896404  | -0.5074260490 |

**5j – Radical Intermediate**

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | 4.1608200631 | 0.9600413384 | 0.2434016621 |
| C    | 2.7474760315 | 1.2745667884 | -0.2342584310 |
| C    | 4.0436624005 | -0.5179513829 | 0.5607077780 |
| H    | 4.4005620520 | 1.5237383262 | 1.7458361976 |
| H    | 4.9212664622 | 1.1706900609 | -0.5085340415 |
| O    | 2.7408122753 | -0.6757112340 | 1.1188026930 |
| H    | 4.7656557630 | -0.873916240 | 1.2963406669 |
| H    | 4.1354164540 | -1.1248708177 | -0.3473780620 |
| C    | 1.8858805721 | 0.3555321070 | 0.6401154242 |
| H    | 2.6370438589 | 1.0100306878 | -1.2870533177 |
| H    | 2.4617690910 | 2.3181568907 | -0.1110496560 |
| C    | -0.5513527473 | 0.0051141824 | 0.1901373053 |
| C    | 0.6915738142 | -0.2233891583 | -0.0677242859 |
| Cl   | 1.1100495070 | -1.3287975846 | -1.4115147543 |
| C    | -1.9256912308 | 0.0439504143 | 0.1903598601 |
| C    | -4.0562332959 | -0.8126424129 | 0.9731315906 |
| C    | -4.7558020854 | 0.1355998630 | 0.2094870918 |
\begin{verbatim}
C  -4.0066351494  1.0425619304 -0.5574735828
C  -2.6332439201  1.0114932550 0.5694636148
C  -2.6836927889 -0.8669010614  0.9712330839
H   -2.1652558199 -1.6165960779  1.5551513536
H   -4.6080005514 -1.5390750684  1.5572839714
H   -4.5182932776  1.7988089344 -1.1403141114
H   -2.0753765892  1.7267758290 -1.1601187661
H    1.4943375846  0.9009288221  1.5036287962
H   -2.2261857609  0.1725537157  0.2075941375
C   -6.9569125866 -0.1857076668  0.2075941375
H   -6.4348807502 -0.4728247483  2.2505275765
C   -8.3420796512 -0.1510089796  1.5421495601
H   -8.8868202237 -0.4237619934  2.2381411616
C   -9.0306699820  0.2388585303  0.2005354333
H  -10.1136559931  0.2647415248  0.1979387609
H   -8.3190706020  0.5949021769 -0.9379073849
H   -8.8458428245  0.8920770457 -1.8369117699
C   -6.9335415549  0.5636629034 -0.9343765100
H   -6.3946444486  0.8232767301 -1.8374673515

Sj – (Z) Product

C   4.2162269091  0.8162410957  0.1318989058
C   2.8260455105  1.4139051761  0.3149266136
C   3.8819818485 -0.5131390063  0.5149772139
H    4.7001276356  0.6583116092  1.0985425438
H    4.8691413955  1.4328830755 -0.4852183599
O    2.6713446384 -0.9401901419  0.1052657628
H    4.6336808084 -1.2863039063 -0.3519299353
H    3.7257501204 -0.3962451664  1.5936973558
C    1.9777262935  0.1821956993  0.6459865922
H    2.4838226319  1.8679424114 -0.6168559858
H    2.7658764487  2.1617687312  1.1044287888
C   -0.4941035133  0.1882455410  0.9392990126
C    0.5691184141  0.2245402327  0.1319871696
Cl   0.4581485180  0.2788281058 -1.6025384740
C   -1.9299487910  0.2187879807  0.6830915375
C   -4.1435871474 -0.3170811325  1.5253184816
C   -4.7431784434  0.1683537366  0.3610476535
C   -3.9087184847  0.7017692349 -0.6235688159
C   -2.5344662623  0.7285156392 -0.4714728010
C   -2.7713100696 -0.2833303014  1.6836095732
H   -2.3316251757 -0.6721196691  2.5953738760
H   -4.7565771122 -0.7458221105  2.3088026353
H   -4.3446567094  1.1239807547 -1.5212193831
H   -1.9337470787  1.1691110954 -1.2528642465
C    1.9105243904  0.0518045680  1.7311470604

\end{verbatim}
C  -6.2064600268  0.1201526629  0.1761343179
C  -7.0741734135  0.2993278765  1.2566122436
H  -6.669682256  0.5020119495  2.2410780336
C  -8.4485920998  0.2458274565  1.0818003403
H  -9.1030279825  0.3951817918  1.9324115000
C  -8.9858770854  0.0102731586  0.1770343642
H  -10.0597051825  0.0335033796  0.3131753471
C  -8.1350444790  0.1687034898  1.2600409759
H  -9.1030279825  0.3951817918  1.9324115000
C  -8.9858770854  0.0102731586  0.1770343642
H  -10.0597051825  0.0335033796  0.3131753471
C  -8.1350444790  0.1687034898  1.2600409759
H  -9.1030279825  0.3951817918  1.9324115000
C  -8.9858770854  0.0102731586  0.1770343642
H  -10.0597051825  0.0335033796  0.3131753471

5j – (E) Product

C  3.6494085297  1.5623492566  0.3848201207
C  2.2444449203  1.5321590689  0.2050514475
C  3.8804900244  0.0938668913  0.6832192535
H  3.6693785115  2.1453415462  1.3082721445
H  4.3901402605  1.9740196939  0.307397015
O  2.6162860391  -0.4072821997  1.1096190705
H  4.5989331974  -0.0864845894  1.4835892360
H  4.2113527399  -0.4435991279  0.2131944756
C  1.5694000795  0.4134058838  0.5965508180
H  2.2814451438  1.2718099107  -1.2647785642
H  1.7057585919  2.4739991031  0.1051282964
C  -0.7213733265  -0.5124075324  0.0164114073
C  0.5988323316  -0.4197073305  -0.1825461119
Cl  1.3490101404  1.4122089579  1.4084737080
C  -1.5479766830  0.2353420754  0.9336281655
C  -3.4121790112  0.2257402206  2.4784541307
C  -3.2216337642  1.5785766998  2.7723938250
C  -2.1904387657  2.492738896  2.1127339806
C  -1.3720668691  1.5932994465  1.2087528550
C  -2.6015071768  -0.4281383528  1.5706074907
H  -2.7817426228  1.4741923039  1.3498582333
H  -4.2257369819  -0.316356556  2.9456321002
H  -2.0193896265  3.3004864632  2.3112605913
H  0.6057165938  2.1547437447  0.6899933360
H  1.0275201694  0.8276262650  1.4508026290
C  -4.1041983692  2.2762431754  3.7269877772
C  -4.6011023813  1.6189787104  4.8551618873
H  -4.3121171601  0.5923713518  5.0463075848
C  -5.4399083224  2.2706017831  5.7462508546
H  -5.8081733843  1.7437898935  6.6185308792
C  -5.8003323623  3.5939060202  5.5274933561
H  -6.4564983946  4.1033891714  6.2227091846
3d – Photocatalyst

| Element | X Position | Y Position | Z Position |
|---------|------------|------------|------------|
| H       | 0.8502752554 | -1.1255593781 | 2.1512560493 |
| C       | 0.4314807868 | -0.6634661487 | 1.2675314885 |
| C       | -0.8362782961 | -0.1033280985 | 1.3043278141 |
| Cl      | -1.7365191443 | -0.1358416441 | 2.7828661590 |
| C       | -1.4040731491 | 0.4796724112  | 0.1789210759 |
| H       | -2.3942885319 | 0.9125648686  | 0.2297093999 |
| C       | -0.6874399966 | 0.4900297772  | -1.0024558629 |
| H       | -1.1194488299 | 0.9271894925  | -1.8938173856 |
| C       | 0.5964477668  | -0.0514982087 | -1.0618766259 |
| C       | 1.3036537862  | -0.689918069  | -2.3700720991 |
| C       | 1.1474775831  | -0.6249950363 | 0.0827033532 |
| H       | 2.1323599408  | -1.0725635148 | 0.0492558716 |
| O       | 0.6730161049  | -0.1341366679 | -3.4102826391 |
| C       | 2.7897544947  | -0.0140557382 | -2.3945891279 |
| C       | 3.5183641340  | 0.7055949188  | -1.4494094910 |
| H       | 3.0085181065  | 1.2306451354  | -0.6518606305 |
| C       | 4.8982379008  | 0.7866942746  | -1.5357894270 |
| H       | 5.4643713510  | 1.3567327119  | -0.8114714908 |
| C       | 5.5462525846  | 0.1228548709  | -2.5660848105 |
| Cl      | 7.2728481572  | 0.2006506662  | -2.6695979529 |
| C       | 4.8420044132  | -0.6011321119 | -3.5192274880 |
| H       | 5.3688366960  | -1.1115922247 | -4.3143171399 |
| C       | 3.4635116832  | -0.6539590479 | -3.4342224864 |
| H       | 2.8958772028  | -1.2039195007 | -4.1740365540 |

Excited States

3d – Excitation Energies (ptLR/ptSS)

| State | Exc. Energy [nm] | Osc. Strength |
|-------|-----------------|---------------|
| T1    | 362.02          | 0.0000        |
| T2    | 325.62          | 0.0000        |
| T3    | 324.02          | 0.0000        |
| S1    | 313.63          | 0.0020        |
| S2    | 241.64          | 0.0202        |
| S3    | 238.77          | 0.0039        |

3d – SOC Elements
Total SOC elements between the S1 state and excited triplet states:

| State | Value               |
|-------|---------------------|
| T1    | 15.045037 cm⁻¹     |
| T2    | 10.465331 cm⁻¹     |
| T3    | 22.094881 cm⁻¹     |

3d – Electron/Hole Densities of S1

8. References:

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(2) M. Ye, G.-L. Gao, A. J. F. Edmunds, P. A. Worthington, J. A. Morris, J.-Q. Yu, *J. Am. Chem. Soc.* 2011, 133, 19090–19093.

(3) Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng *et al.*, *Mol. Phys.* 2015, 113, 184–215.
9. NMR Spectra

pure isomer (Z)
