

Abstract

Transition metal coordinated carbene intermediates are important in the formation of carbon-carbon bonds, a necessity for synthesizing many of the complex molecules we use today, including pharmaceuticals, polymers, and plastics.^{1,3} Analysis and isolation of the carbene intermediate proves challenging as the species is highly reactive and is difficult to isolate outside of low temperature and pressure systems, such as in interstellar space, where they are found in abundance. Sulfonium ylides provide an accessible route to forming carbene intermediates. From the purified sulfonium ylide, irradiation with light in the presence of a trapping allows for the formation of stable products that can be analyzed. Analysis of these carbene intermediates could provide useful information including new applications for these reactive intermediates.¹⁻³

Background

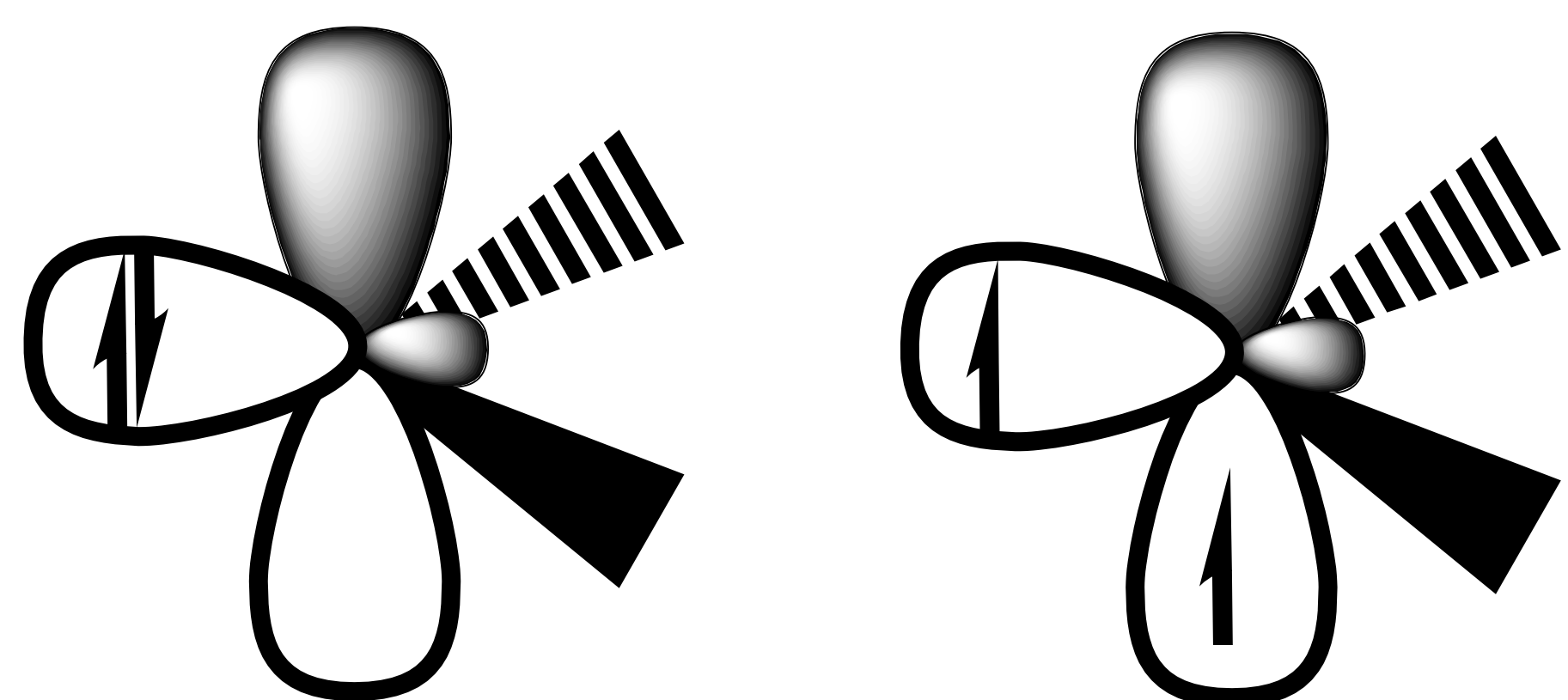
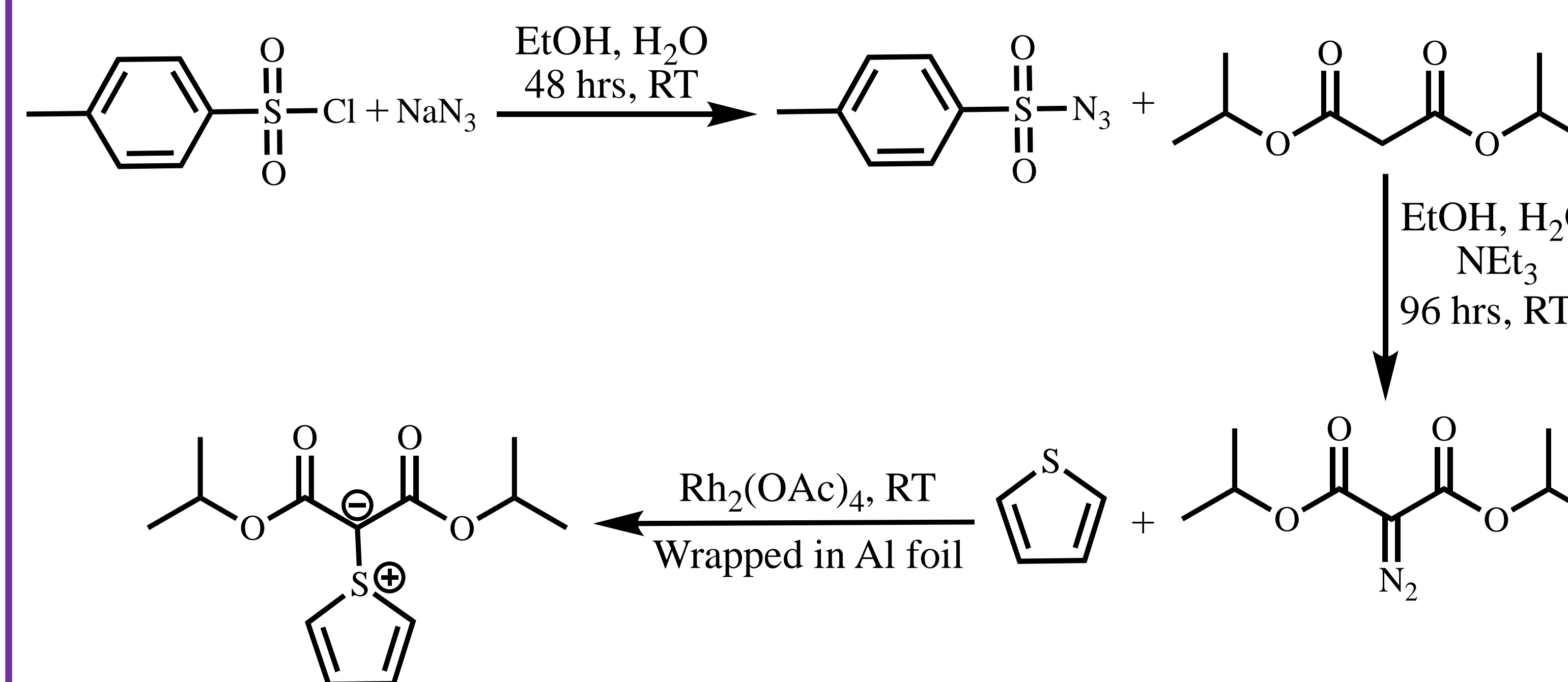


Figure 1. Carbene intermediate singlet (left) and triplet states (right).



Scheme 1. Synthetic pathway to diisopropyl sulfonium ylide.

Results

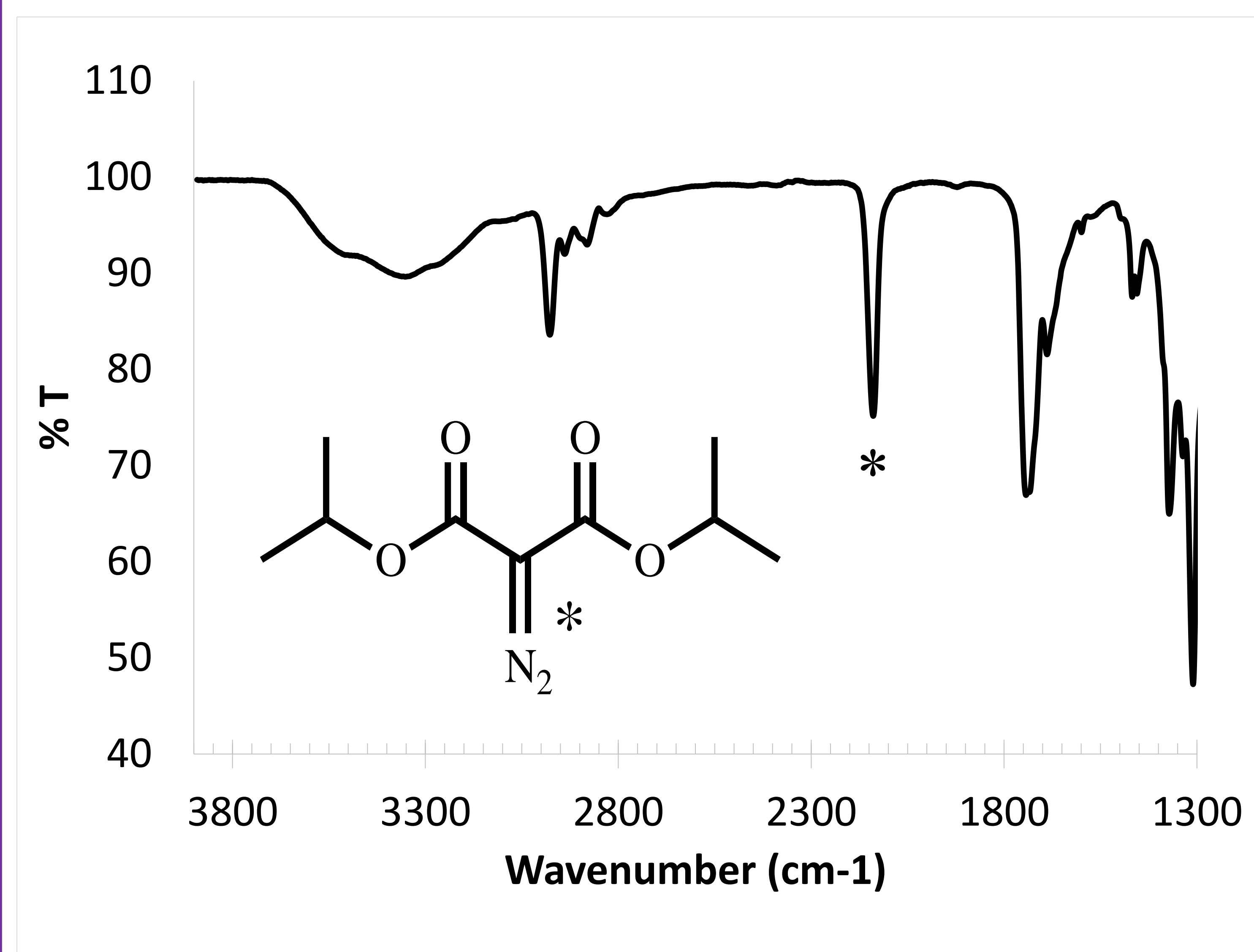


Figure 2. Infrared Spectroscopy of diisopropyl diazo malonate. The peak at 2100-2200 cm^{-1} (starred) indicates the presence of the diazo functional group.

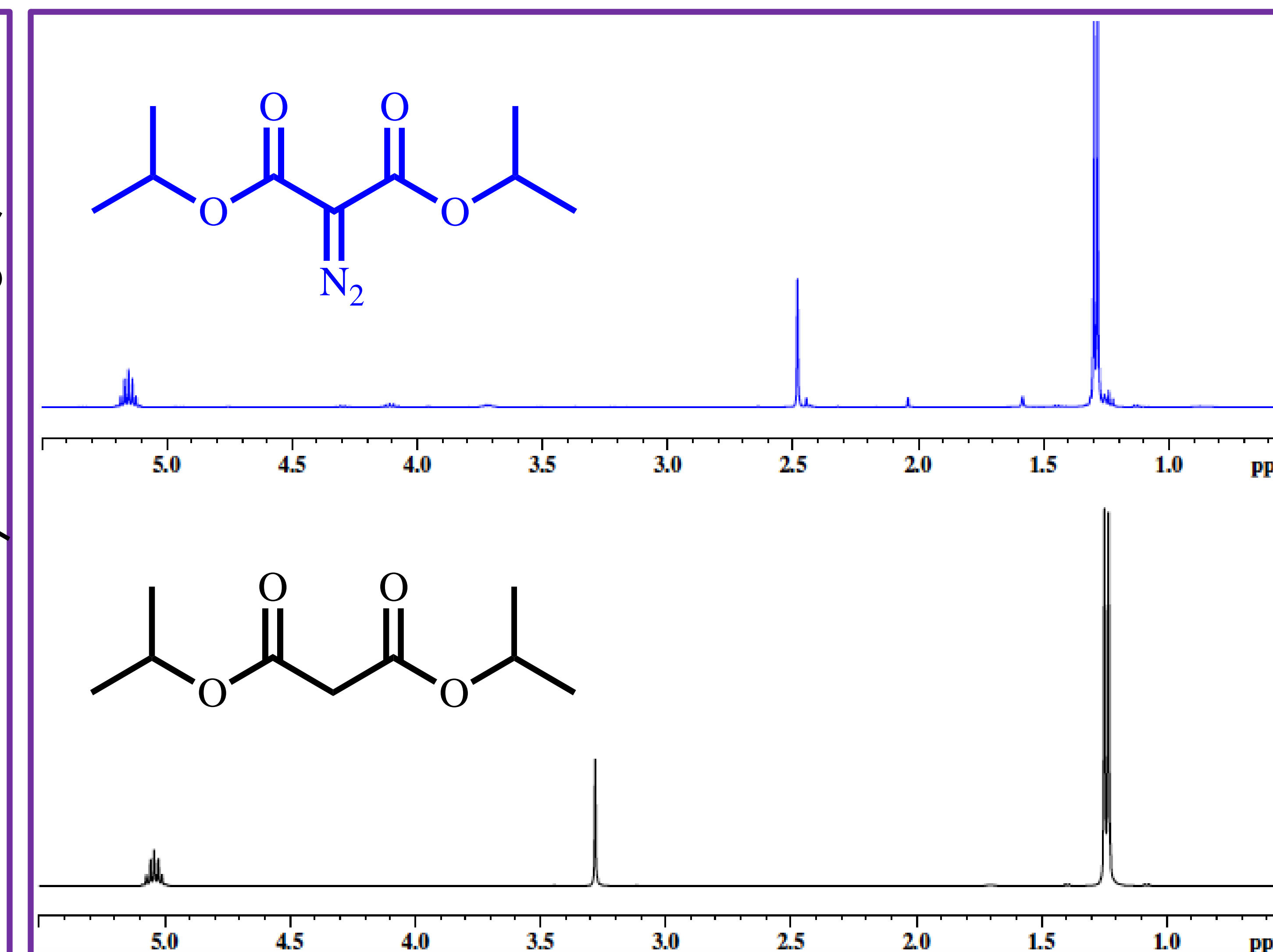


Figure 3. Stacked ^1H NMR (400 MHz, CDCl_3) of diisopropyl diazo malonate product (top) and diisopropyl malonate starting material (bottom).

Conclusion

- Diisopropyl diazo malonate precursor has been synthesized
- Optimizing of conditions for sulfonium ylide synthesis is underway
- Irradiation experiments will be carried out on sulfonium ylide product

Acknowledgements

Much thanks to Dr. Pharr for her many hours of guidance and research in organometallics and the E.L. Weigand Foundation for funding and resources

References

- (1) Xia, Y.; Qiu, D.; Wang, J. Transition-Metal-Catalyzed Cross-Couplings through Carbene Migratory Insertion. *Chem. Rev.* 2017, 117 (23), 13810–13889.
- (2) Stoffregen, S. A.; Heying, M.; Jenks, W. S. S,C - Sulfonium Ylides from Thiophenes: Potential Carbene Precursors. *Journal of the American Chemical Society* 2007, 129 (51), 15746–15747.
- (3) Jenks, W. S.; Heying, M. J.; Stoffregen, S. A.; Rockafellow, E. M. Reaction of Dicarbomethoxycarbene with Thiophene Derivatives. *The Journal of Organic Chemistry* 2009, 74 (7), 2765–2770.

Background and Applications

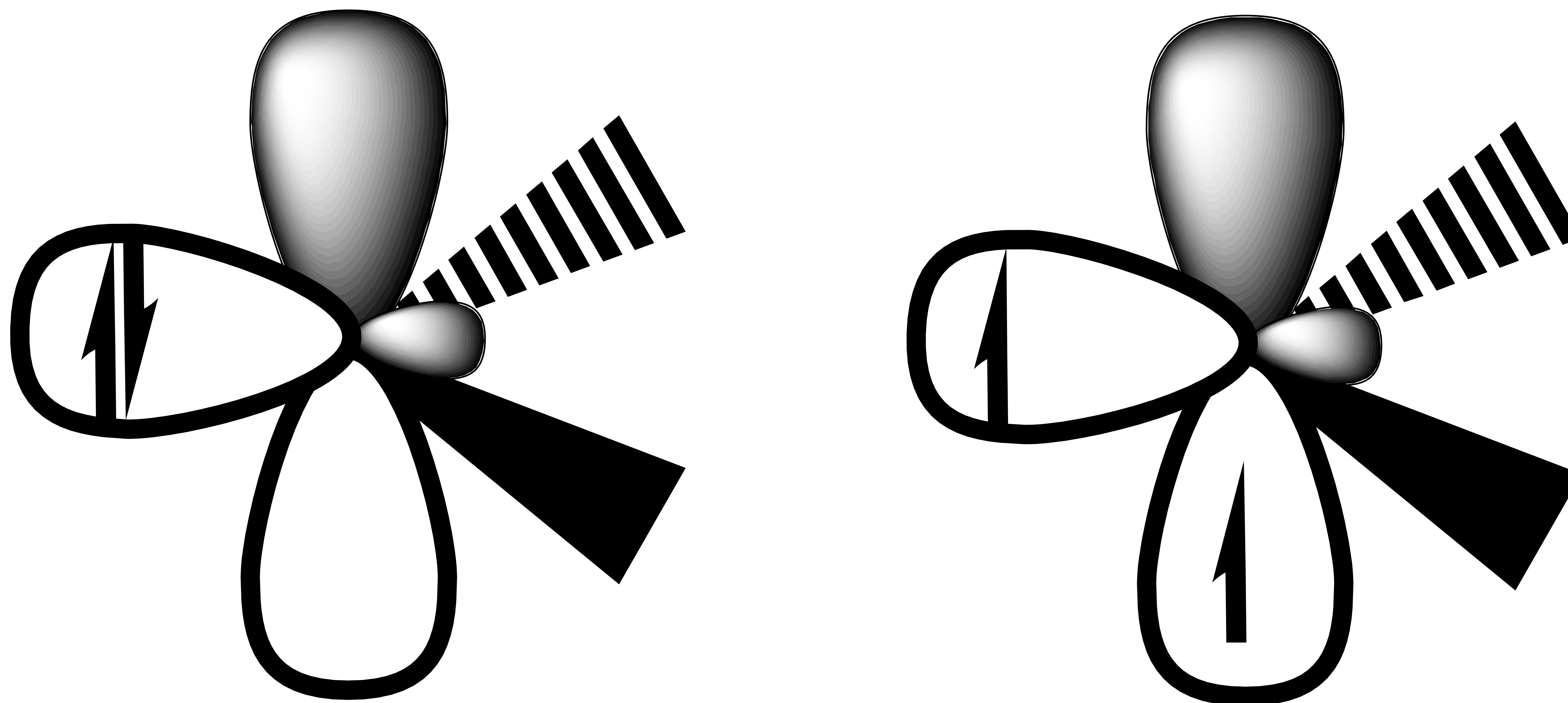


Figure 1. Carbene intermediate singlet (left) and triplet states (right).

Background and Applications

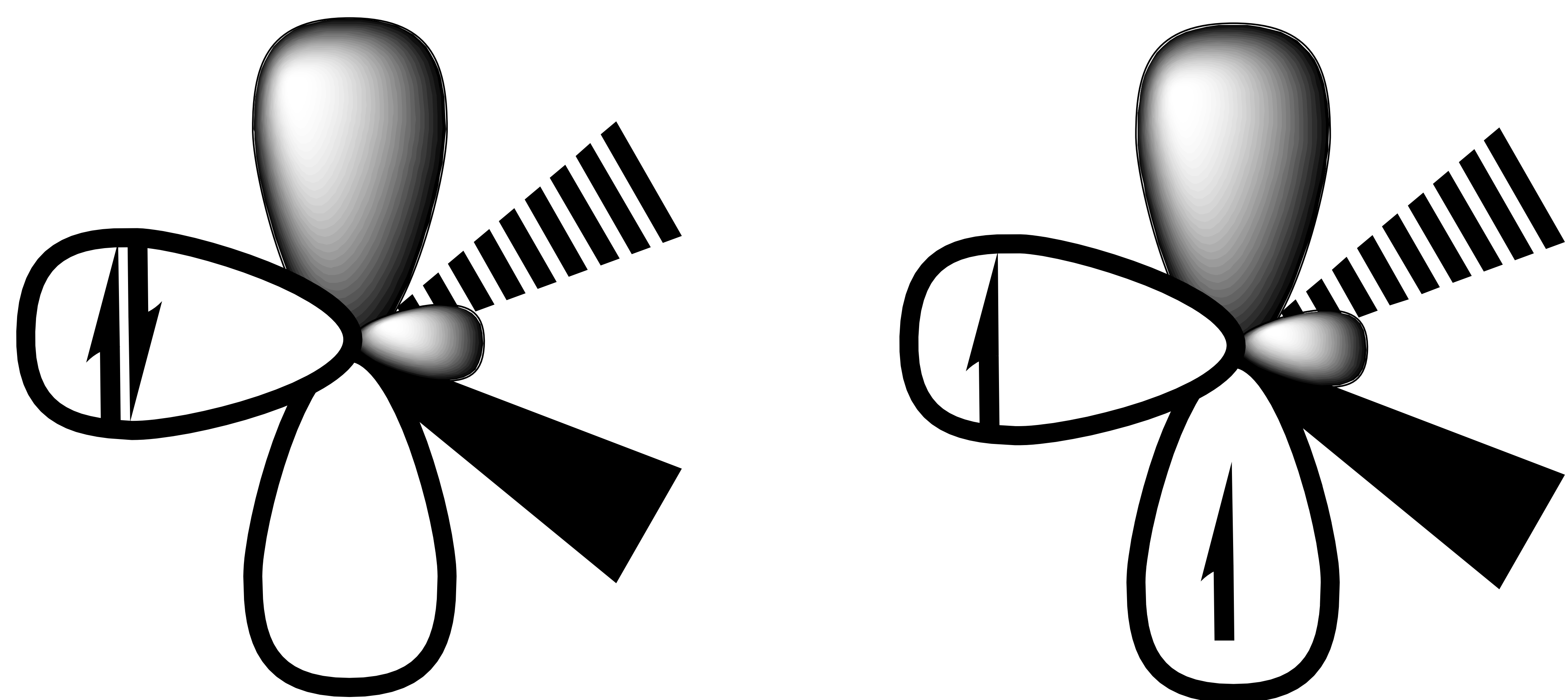
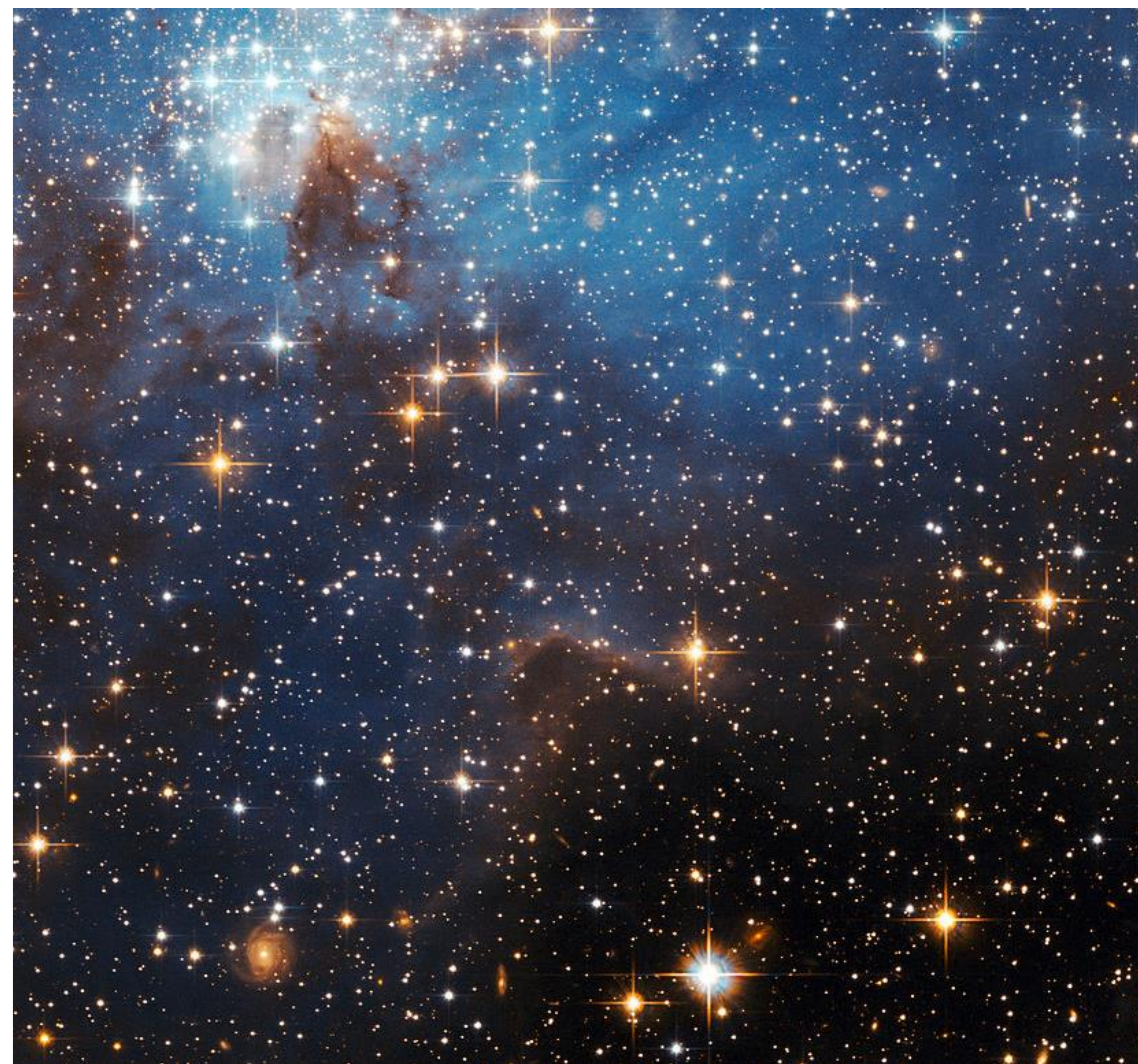


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Background and Applications

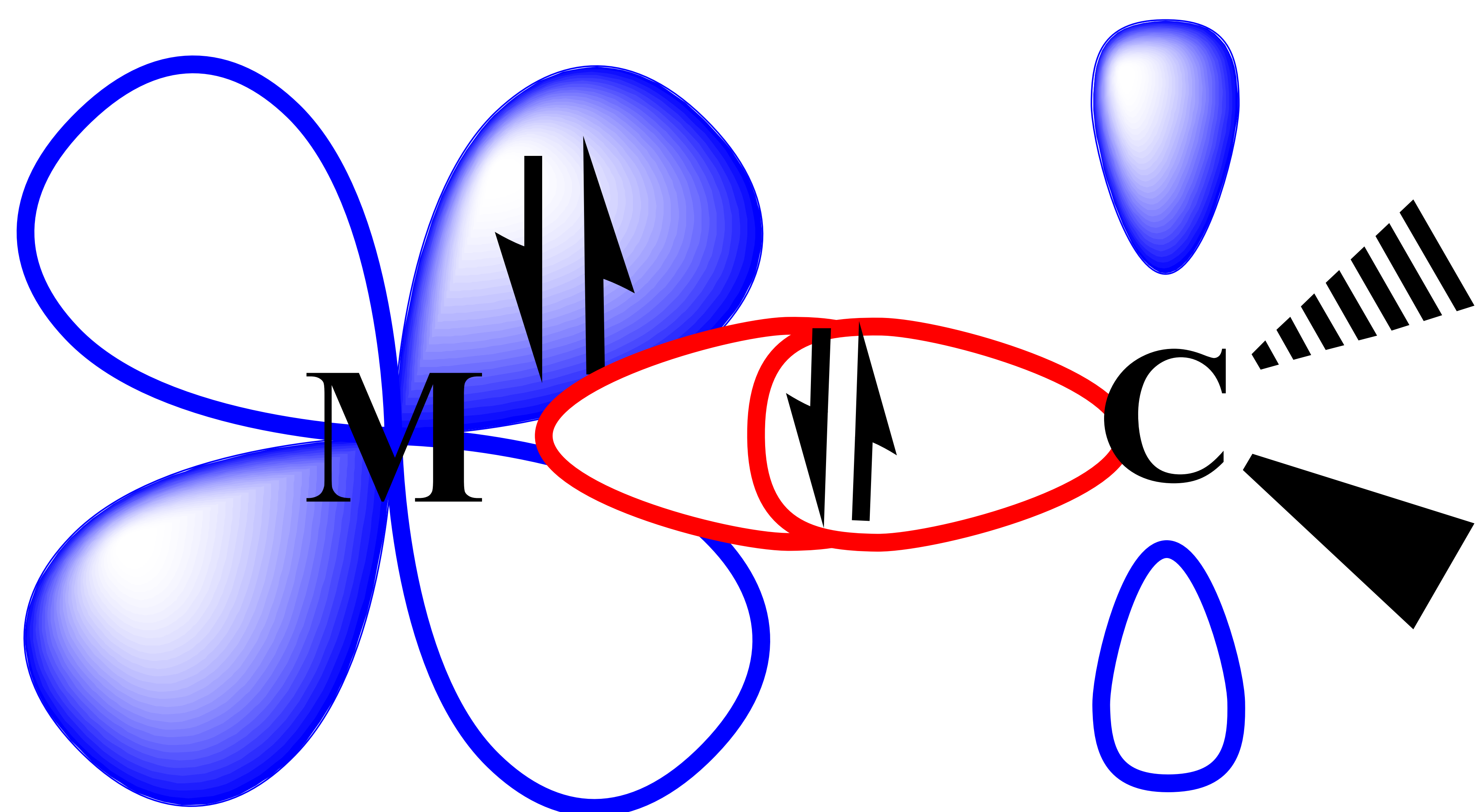
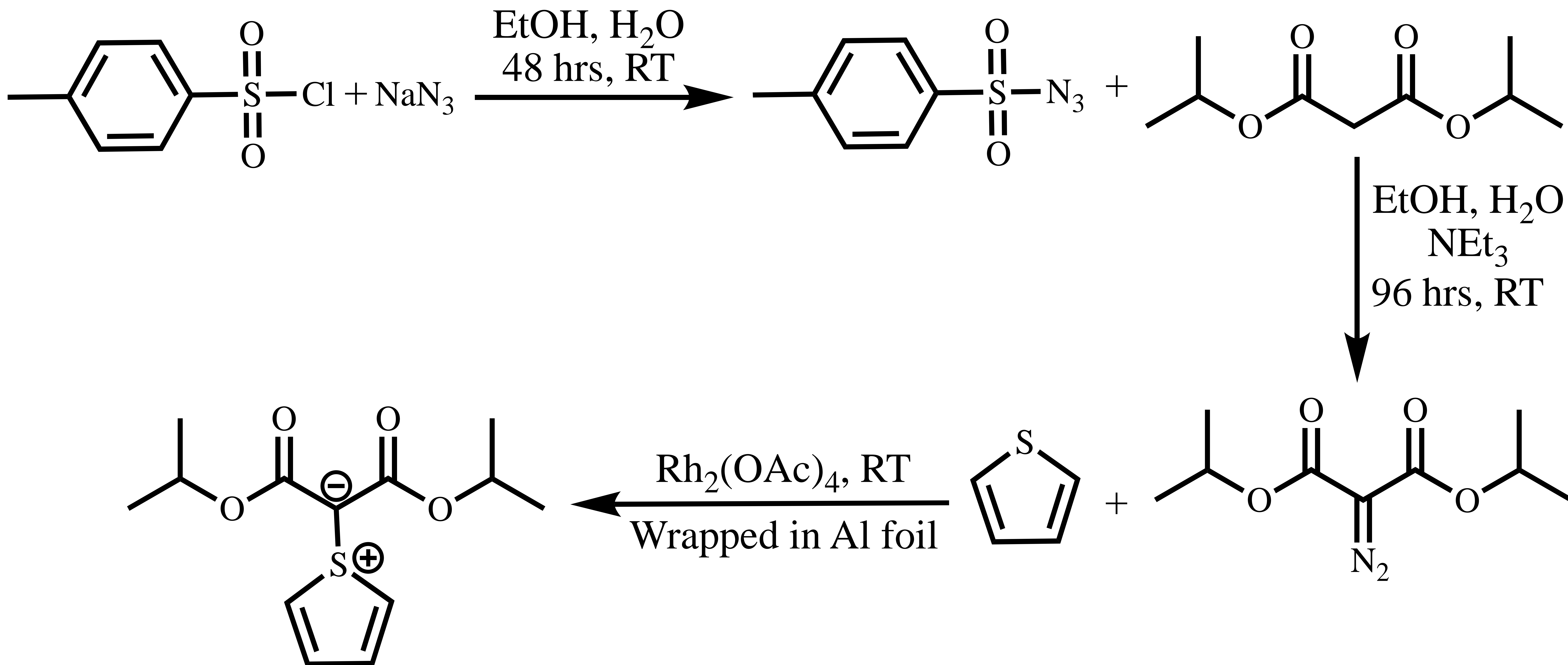


Figure 1.1 Illustration of a generic metal bound carbene



https://i.guim.co.uk/img/media/65d68c03a1e035d0670711a642f7a272d3e660eb/0_1216_3063_1838/master/3063.jpg?width=1200&height=1200&quality=85&auto=format&fit=crop&s=3056330a3a98cf23d2dfcbe60ba711ad (accessed Apr 15, 2021).



Scheme 1. Synthetic pathway to diisopropyl sulfonium ylide.

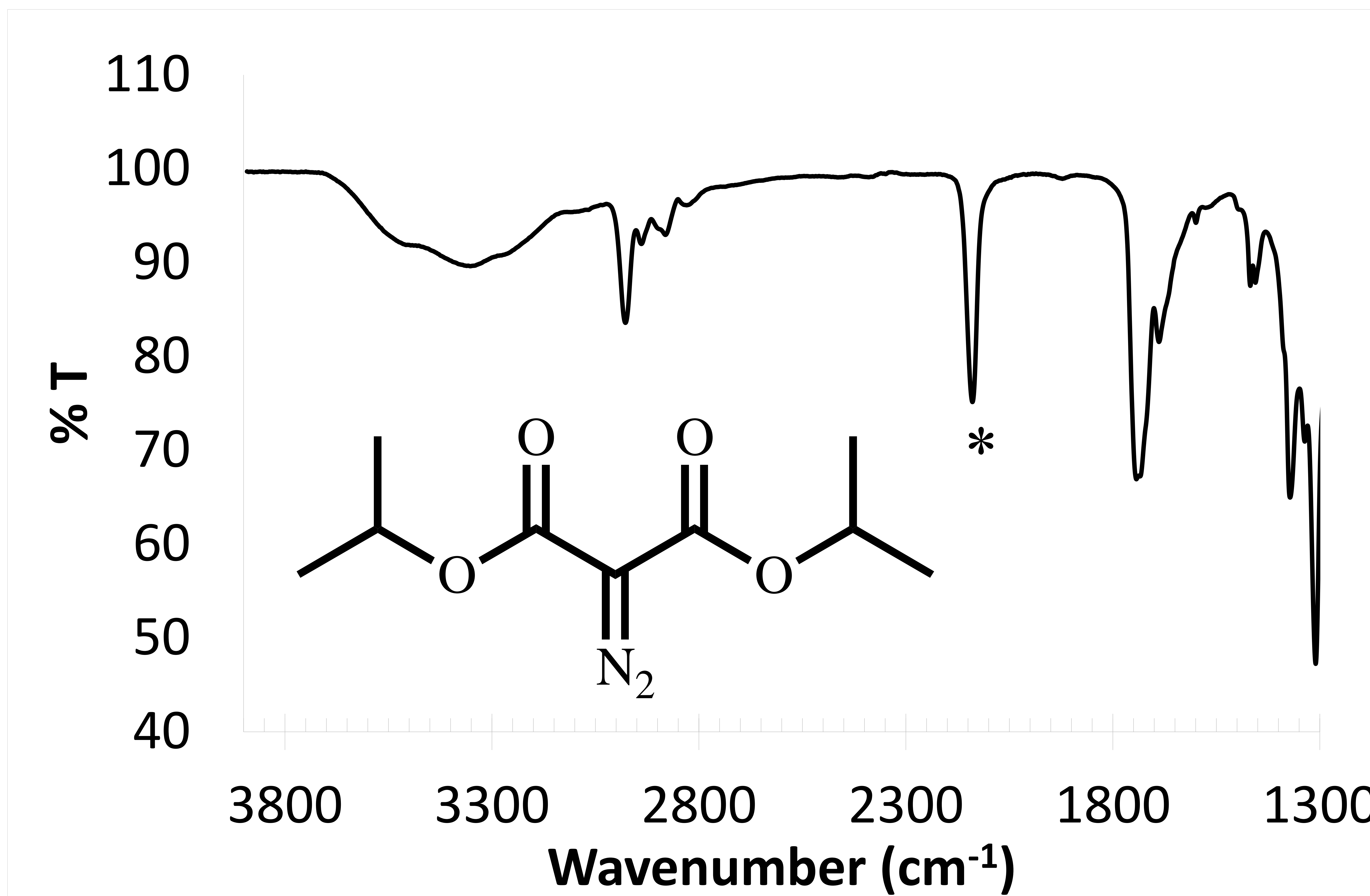


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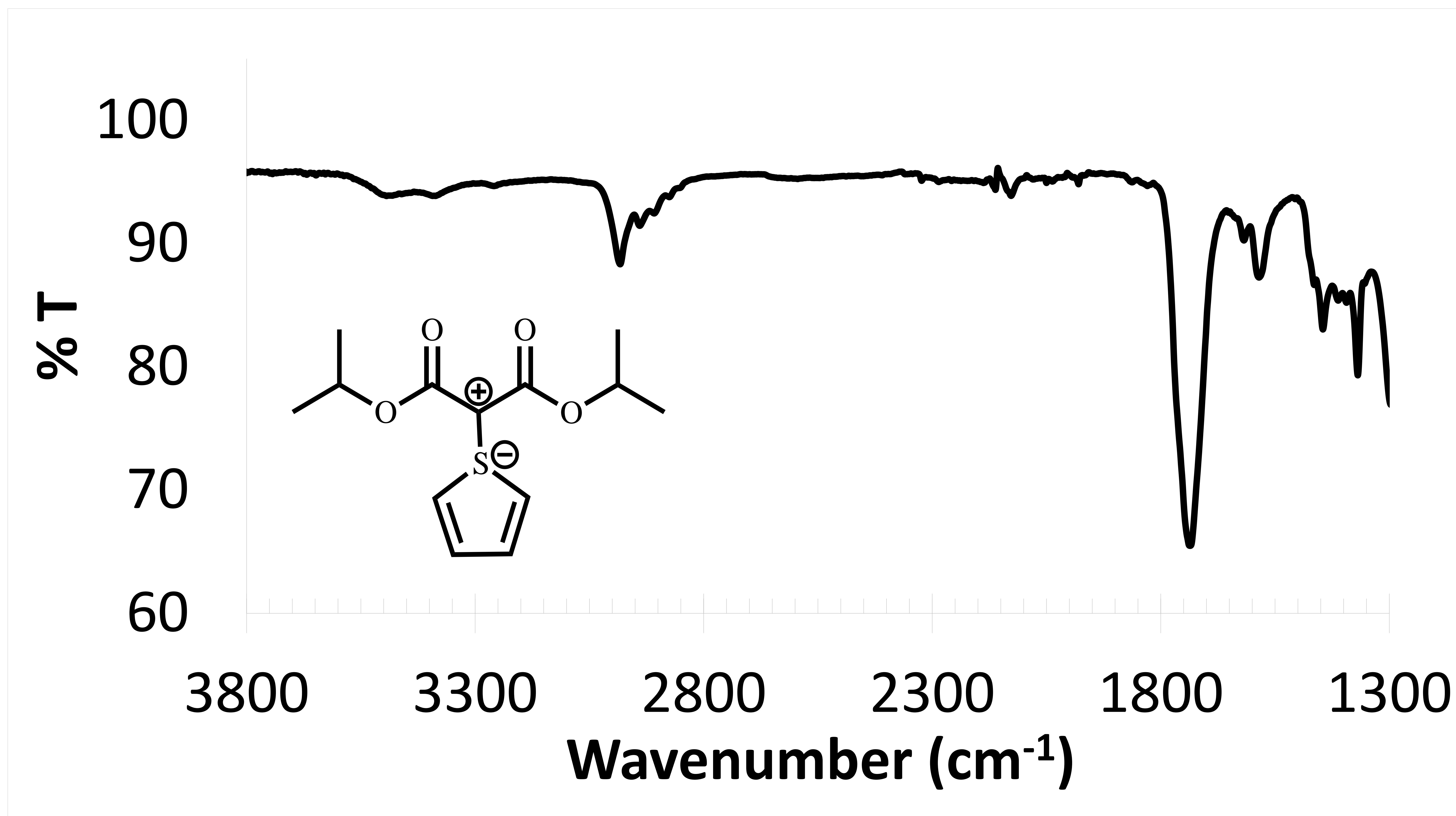


Figure 3. Infrared spectroscopy of diisopropyl malonate sulfonium ylide. The absence of the peak between 2100-2200 cm⁻¹ illustrates production of ylide and removal of the diazo substrate.

Conclusion

- Diisopropyl diazo malonate precursor has been synthesized
- Optimizing of conditions for sulfonium ylide synthesis is underway
- Future work on the sulfonium ylide to produce the carbene intermediate

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Much thanks to Dr. Pharr for her many hours of guidance and research in organometallics and the E.L. Weigand Foundation for funding and resources