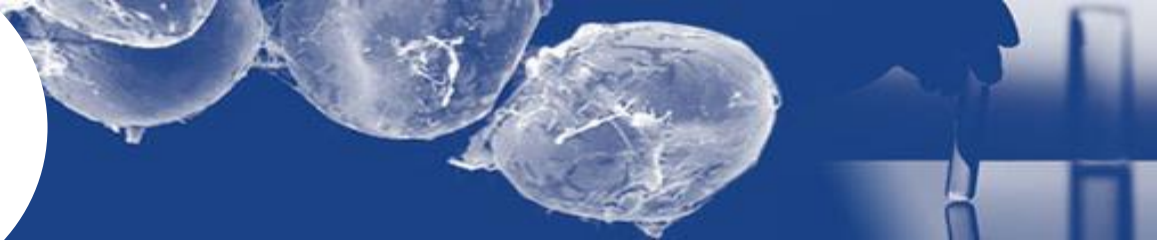


Towards Carbon-based Frustrated Lewis Pair Reactivity

Seminar talk presented by
Jama Ariai

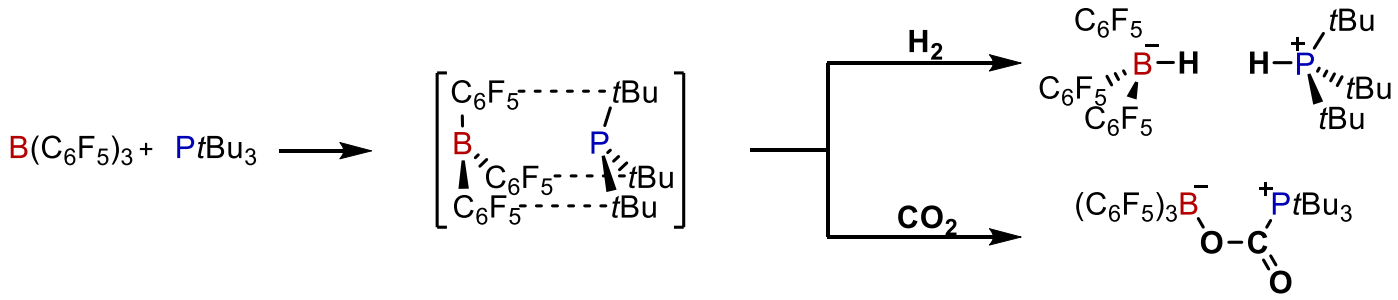
November 13th, 2020

Institute of Organic Chemistry
Justus-Liebig University Giessen

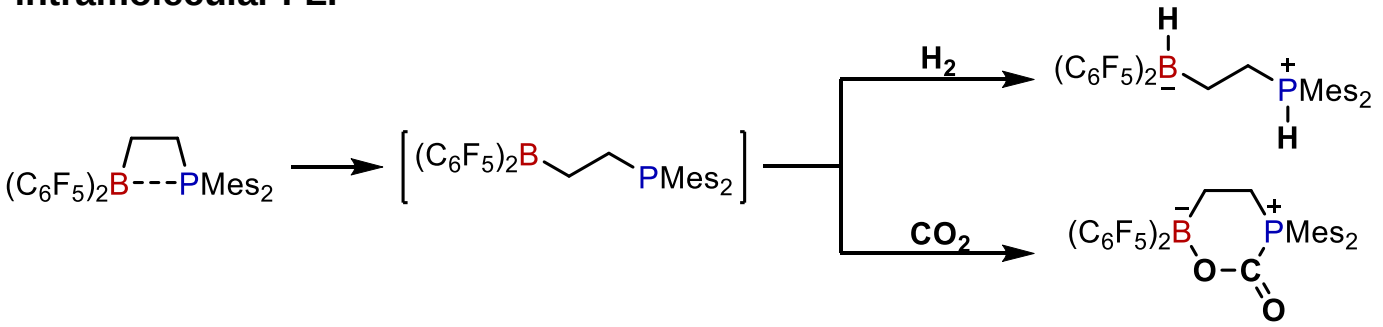
Introduction: Applications of FLPs

- FLPs split **H_2** and capture **CO_2** at ambient conditions (reversibly)

intermolecular FLP

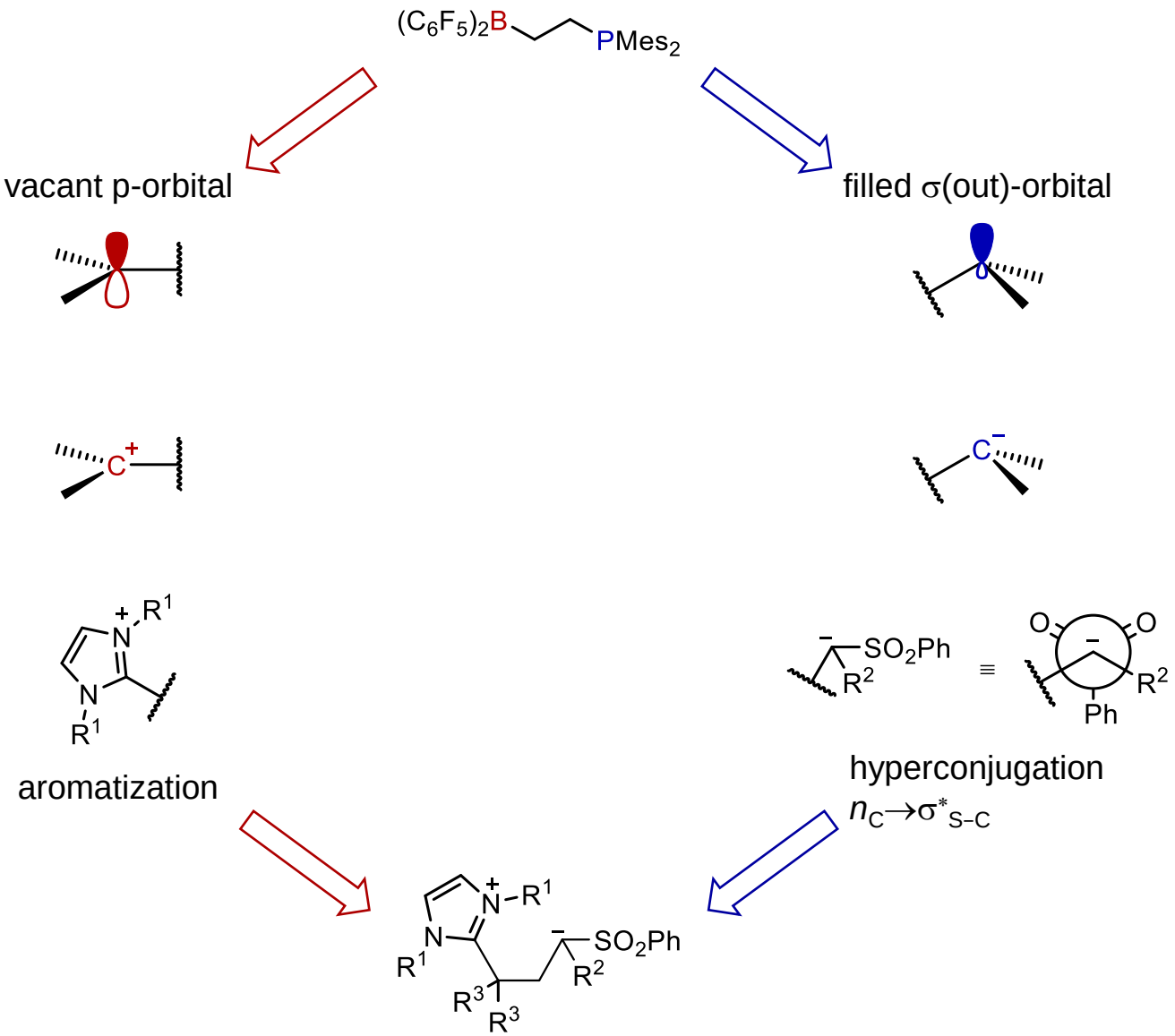


intramolecular FLP

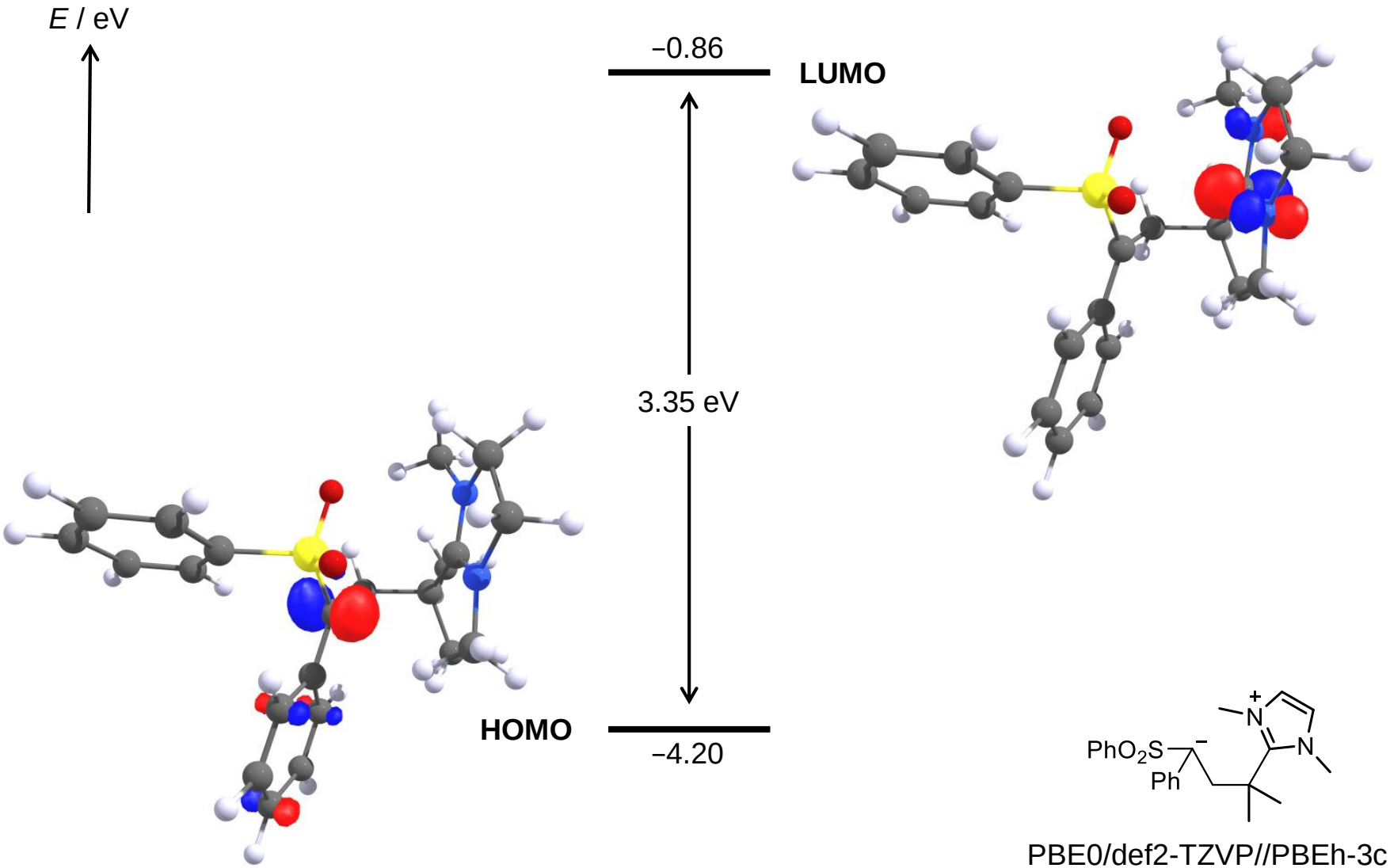


G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124-1126; G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880-1881; P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme, D. W. Stephan, *Chem. Commun.* **2007**, *0*, 5072-5074; D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400-6441; C. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2009**, *48*, 6643-6646; D. W. Stephan, G. Erker, *Chem. Sci.* **2014**, *5*, 2625-2641; T. A. Rokob, A. Hamza, I. Pápai, *J. Am. Chem. Soc.* **2009**, *131*, 10701-10710.

Design of Carbon-based FLPs

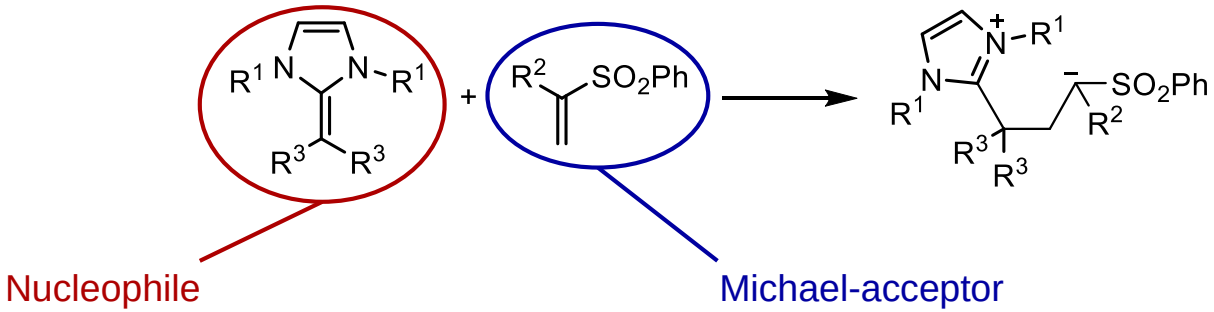


Molecular KS-Orbitals of a Carbon-based FLP

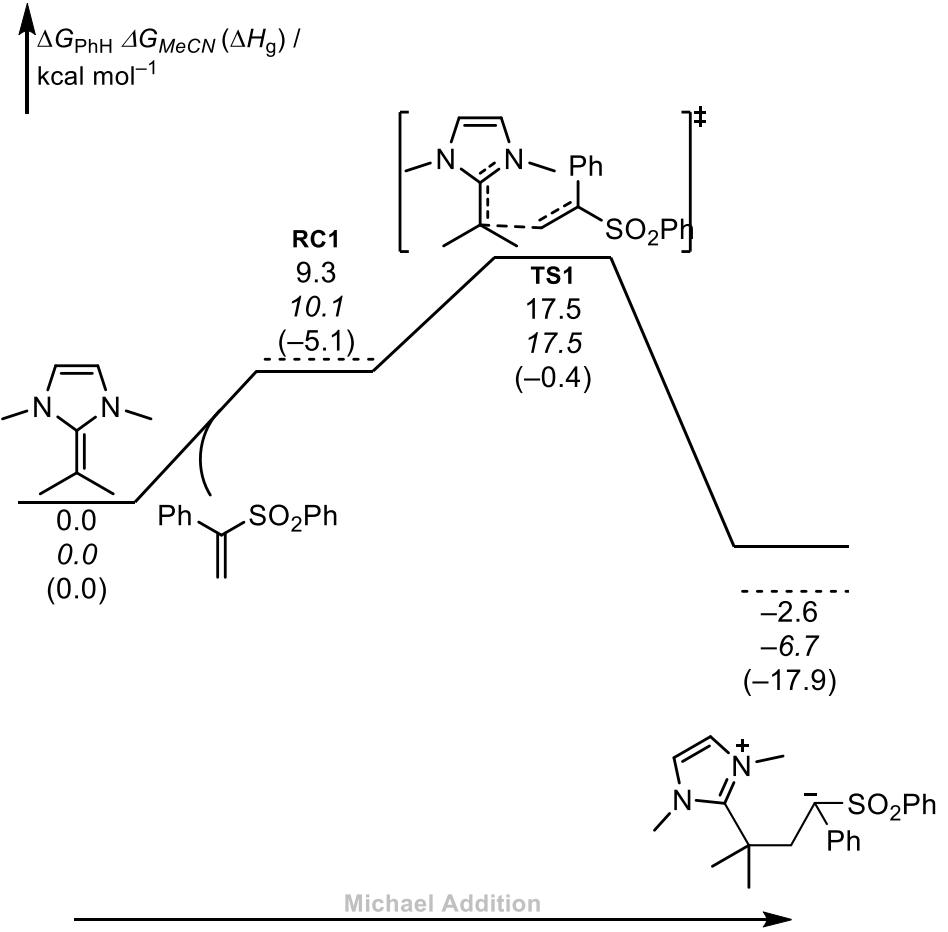


PBE0/def2-TZVP//PBEh-3c

Carbon-based FLP by Conjugate Addition

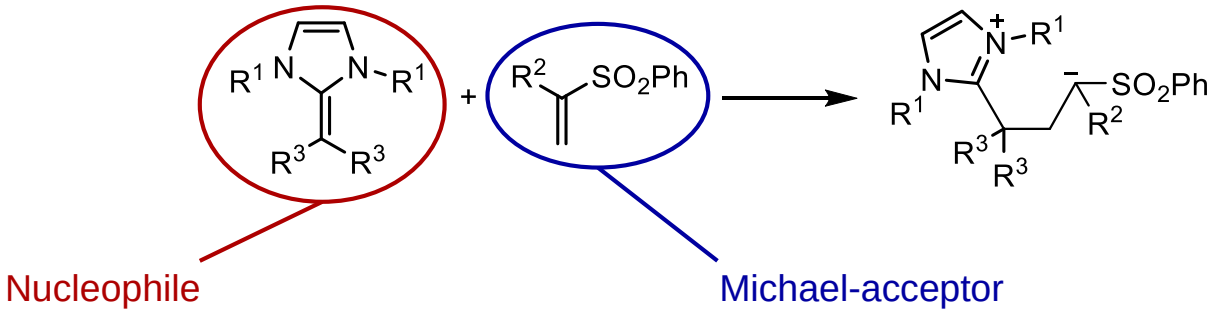


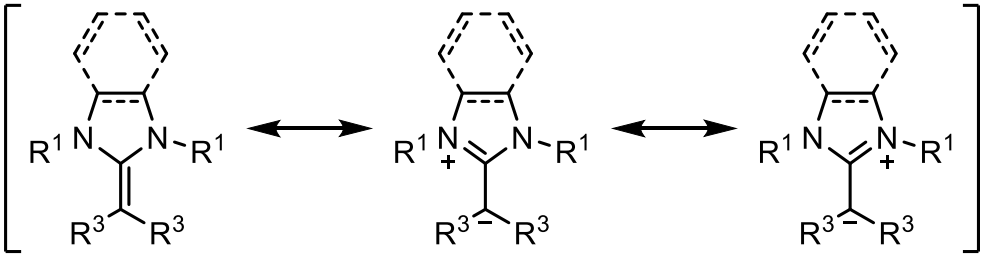
Potential Energy Surface: Carbon-based FLP Reactivity



revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c, SMD model for benzene (solid) and acetonitrile (dashed)

Carbon-based FLP by Conjugate Addition

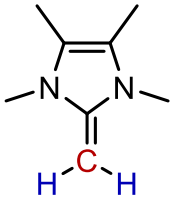


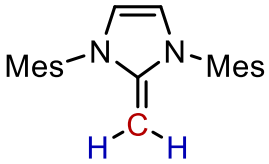


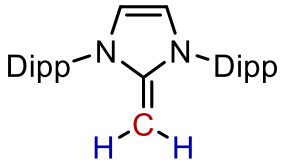
N-**H**eterocyclic **O**lefin (NHO)

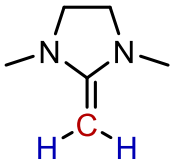
(ene-1,1-diamine, ketene aminals)

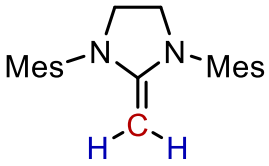
N-Heterocyclic Olefins: Overview & NMR Chemical Shifts

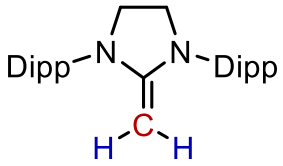








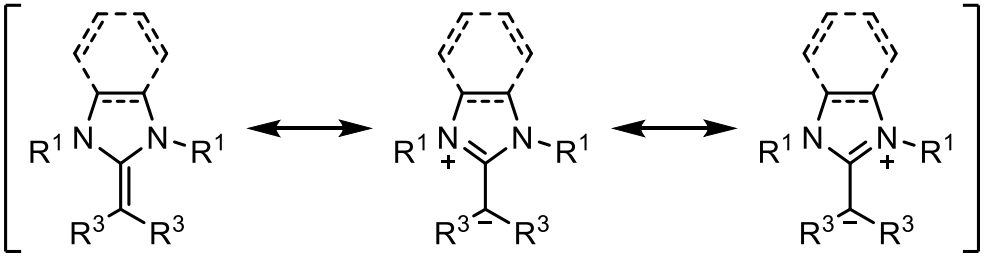


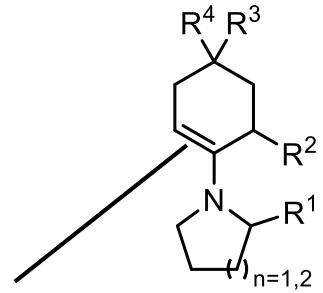


$\delta(C_6D_6)$ / ppm

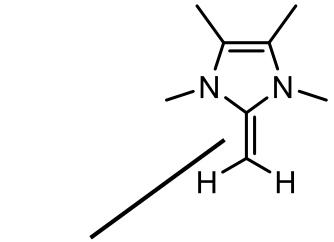
N. Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser. R. Boese, *J. Chem. Soc. Chem. Commun.* **1993**, 1136-1137; K. Powers, C. Hering-Junghans, R. McDonald, M. J. Ferguson, E. Rivard, *Polyhedron* **2016**, *108*, 8-14; S. Kronig, P. G. Jones, M. Tamm, *Eur. J. Inorg.* **2013**, *2013*, 2301-2314; A. J. Arduengo, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.* **1997**, *119*, 12742-12749; U. Gruseck, M. Heuschmann, *Chem. Ber.* **1987**, *120*, 2053-2064; D. Rottschäfer, M. K. Sharma, B. Neumann, H.-G. Stammler, D. M. Andrea, R. S. Ghadwal, *Chem. Eur. J.* **2019**, *25*, 8127-8134; S. Naumann, A. W. Thomas, A. P. Dove, *Angew. Chem. Int. Ed.* **2015**, *54*, 9550; H. Quast, M. Ach, M. K. Kindermann, P. Rademacher, M. Schindler, *Chem. Ber.* **1993**, *126*, 503-516; C. Reichardt, N. Kaufmann, *Chem. Ber.* **1985**, *118*, 3424-3427.

N-Heterocyclic Olefins: Bond Lengths

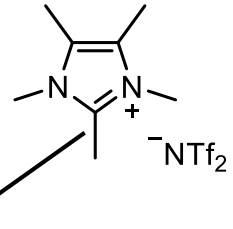




1.346(8) Å



1.363(3) Å



1.483(4) Å

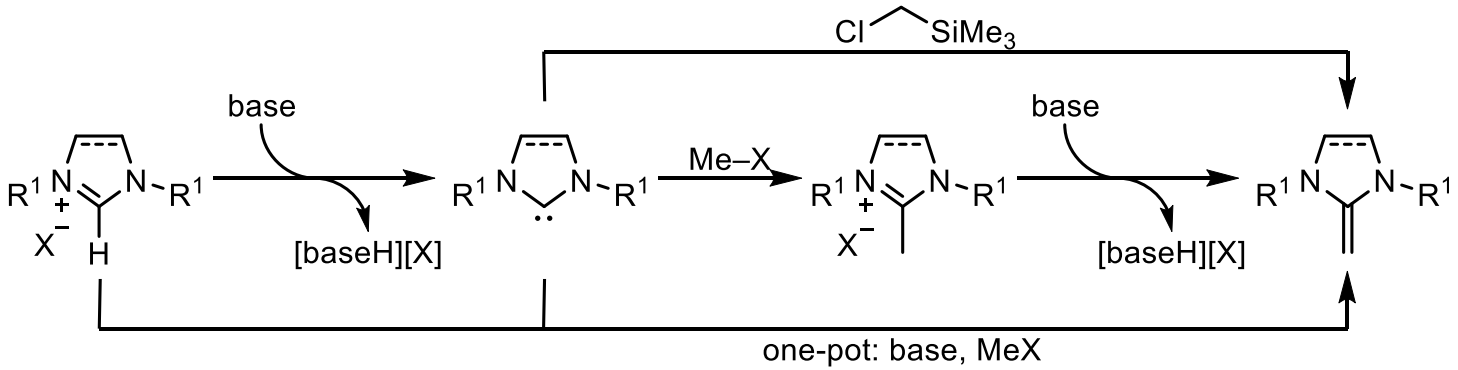
$H_2C=CH_2$
1.339 Å

Enamines: K. L. Brown, L. Damm, J. D. Dunitz, A. Eschenmoser, R. Hobi, C. Kratky, *Helv. Chim. Acta.* **1978**, *61*, 3108-3135.

Imidazolium: C. Roth, T. Peppel, K. Fumino, M. Köckerling, R. Ludwig, *Angew. Chem. Int. Ed.* **2010**, *49*, 10221-10224.

NHO: N. Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser. R. Boese, *J. Chem. Soc. Chem. Commun.* **1993**, 1136-1137.

N-Heterocyclic Olefins: Synthesis



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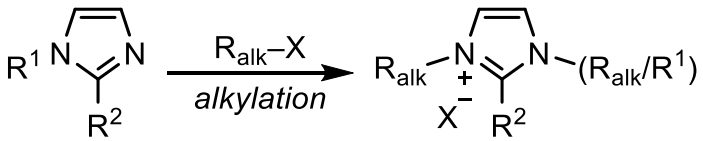
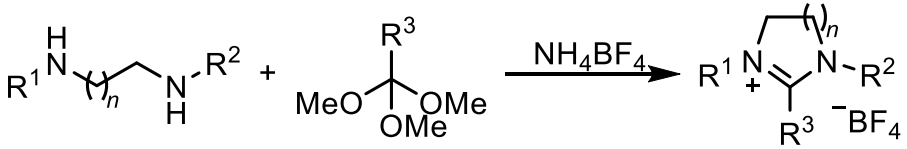
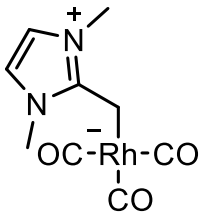


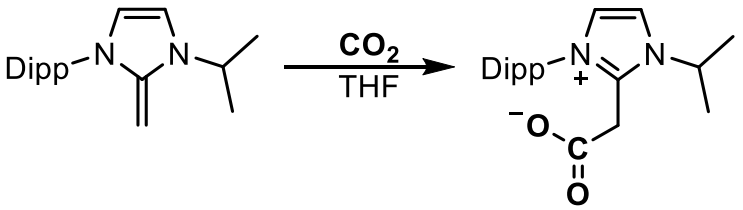


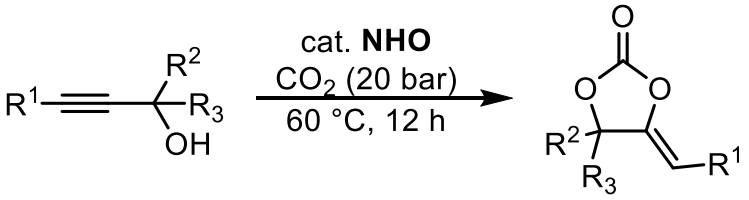
M. M. D. Roy, E. Rivard, *Acc. Chem. Res.* **2017**, *50*, 2017-2025; S. Naumann, *Chem. Commun.* **2019**, *55*, 11658-11670.

N-Heterocyclic Olefins: Applications

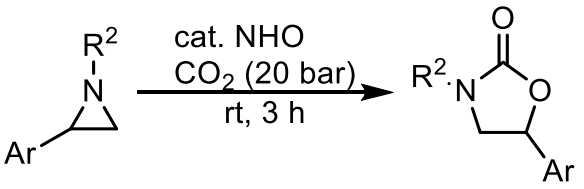


1966 cm^{-1}





- coordination chemistry
- polymerization (epoxides, lactones)
- bond activation
- …



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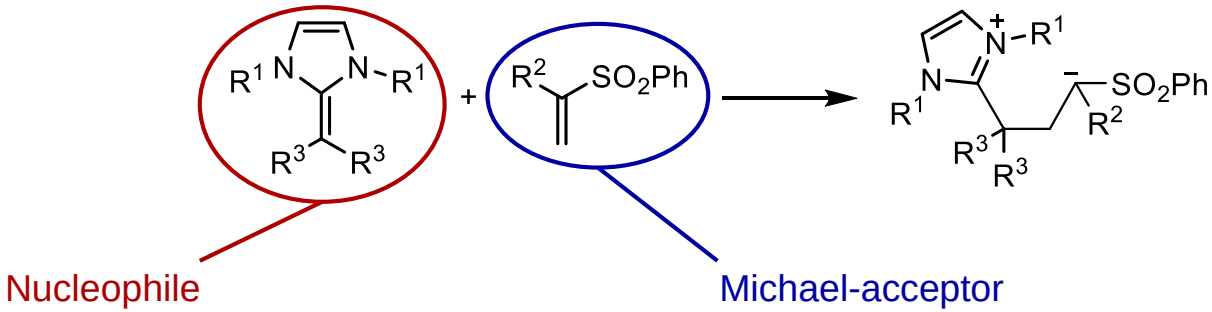
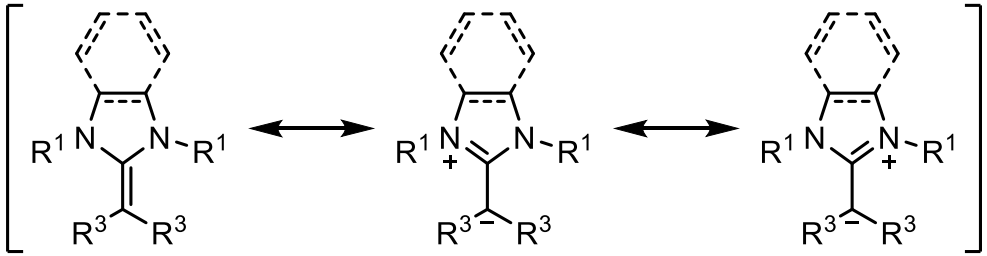
Carbon-based FLP by Conjugate Addition

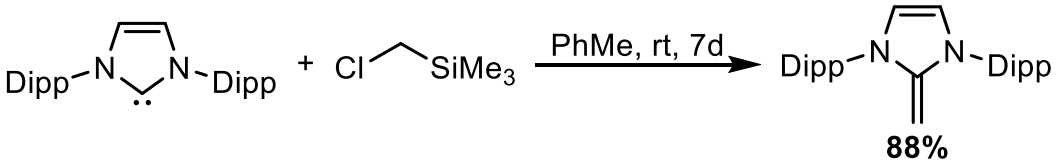


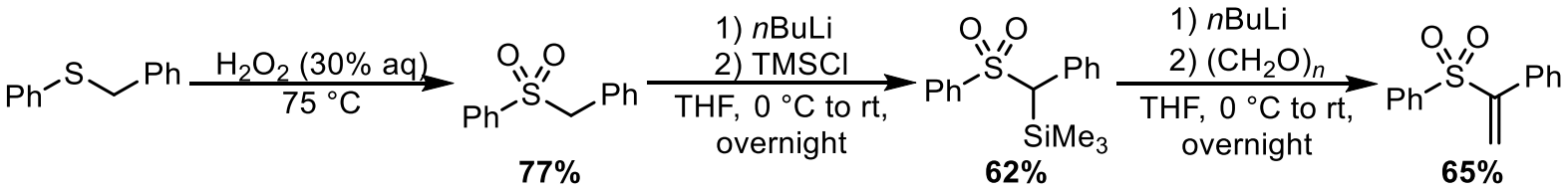


N-**H**eterocyclic **O**lefin (NHO)

(ene-1,1-diamine, ketene aminals)

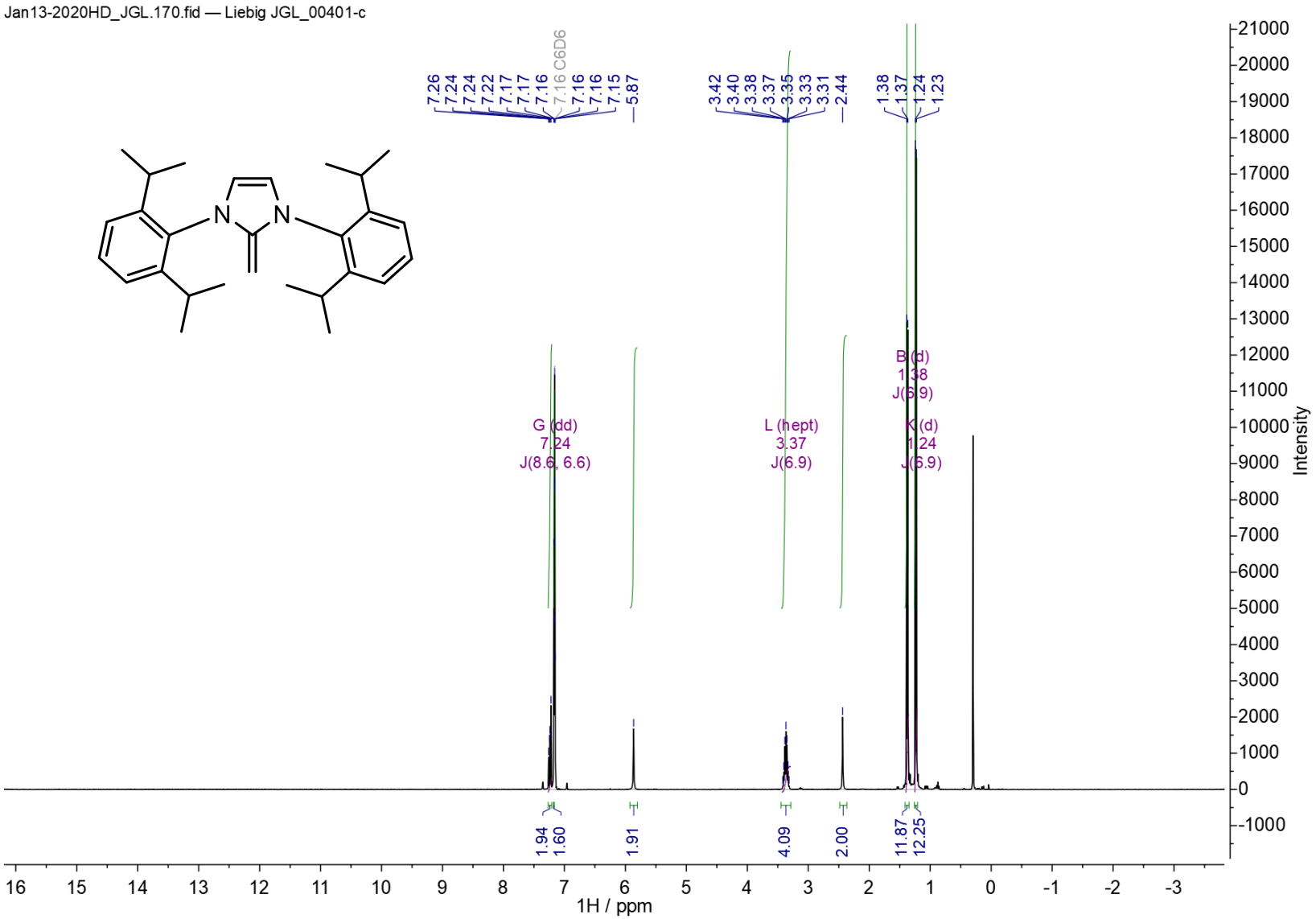
Carbon-based FLP by Conjugate Addition: I





M. Jereb, *Green. Chem.* **2012**, *14*, 3047-3052; D. J. Ager, *J. Chem. Soc. Perkin Trans. 1* **1986**, 195-204; D. J. Ager, *J. Chem. Soc. Perkin Trans. 1* **1986**, 183-194; X. Bantreil, S. P. Nolan, *Nat. Protoc.* **2011**, *6*, 69-77; K. Powers, C. Hering-Junghans, R. McDonald, M. J. Ferguson, E. Rivard, *Polyhedron* **2016**, *108*, 8-14.

Carbon-based FLP by Conjugate Addition: I



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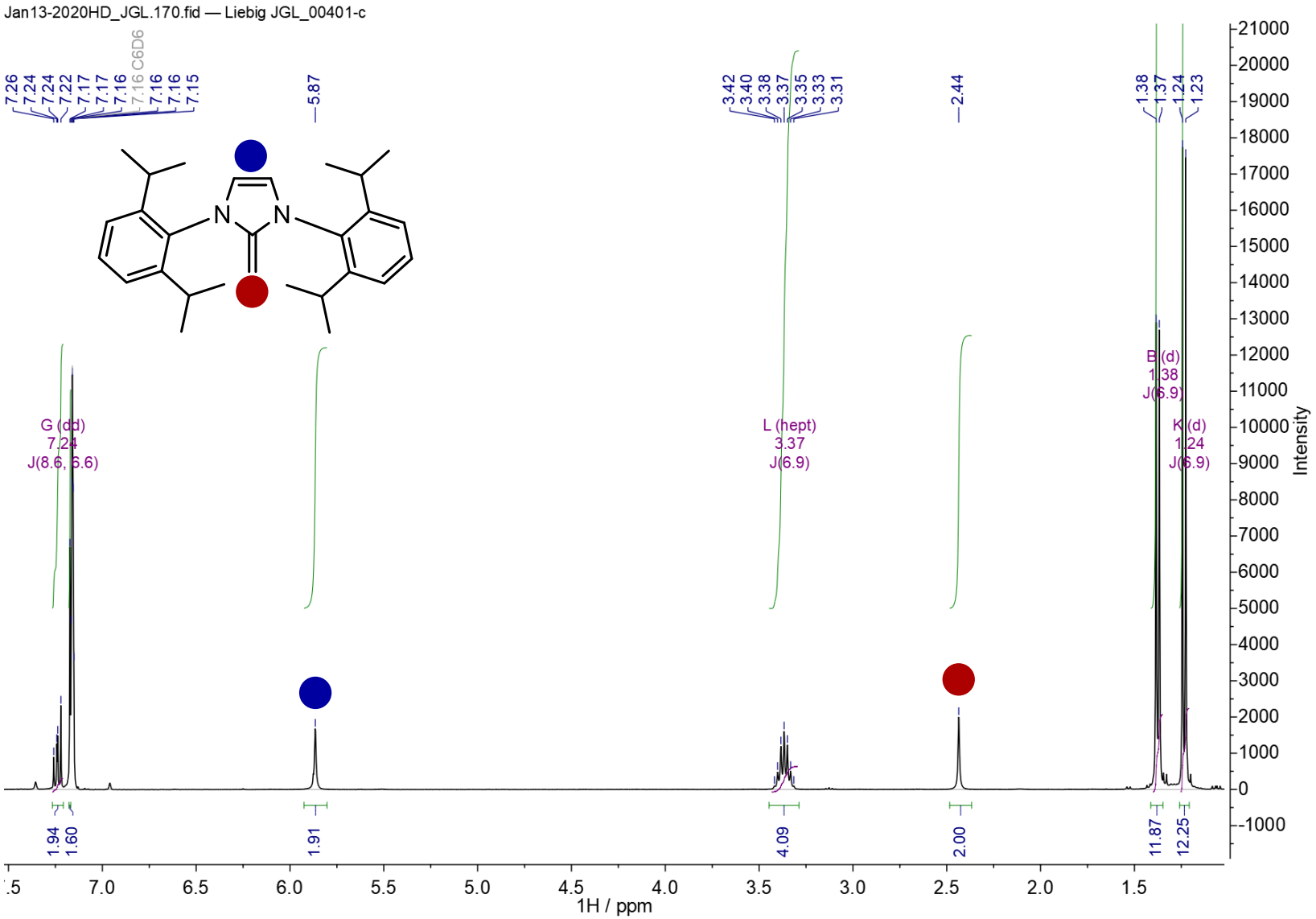
Carbon-based FLP by Conjugate Addition: I



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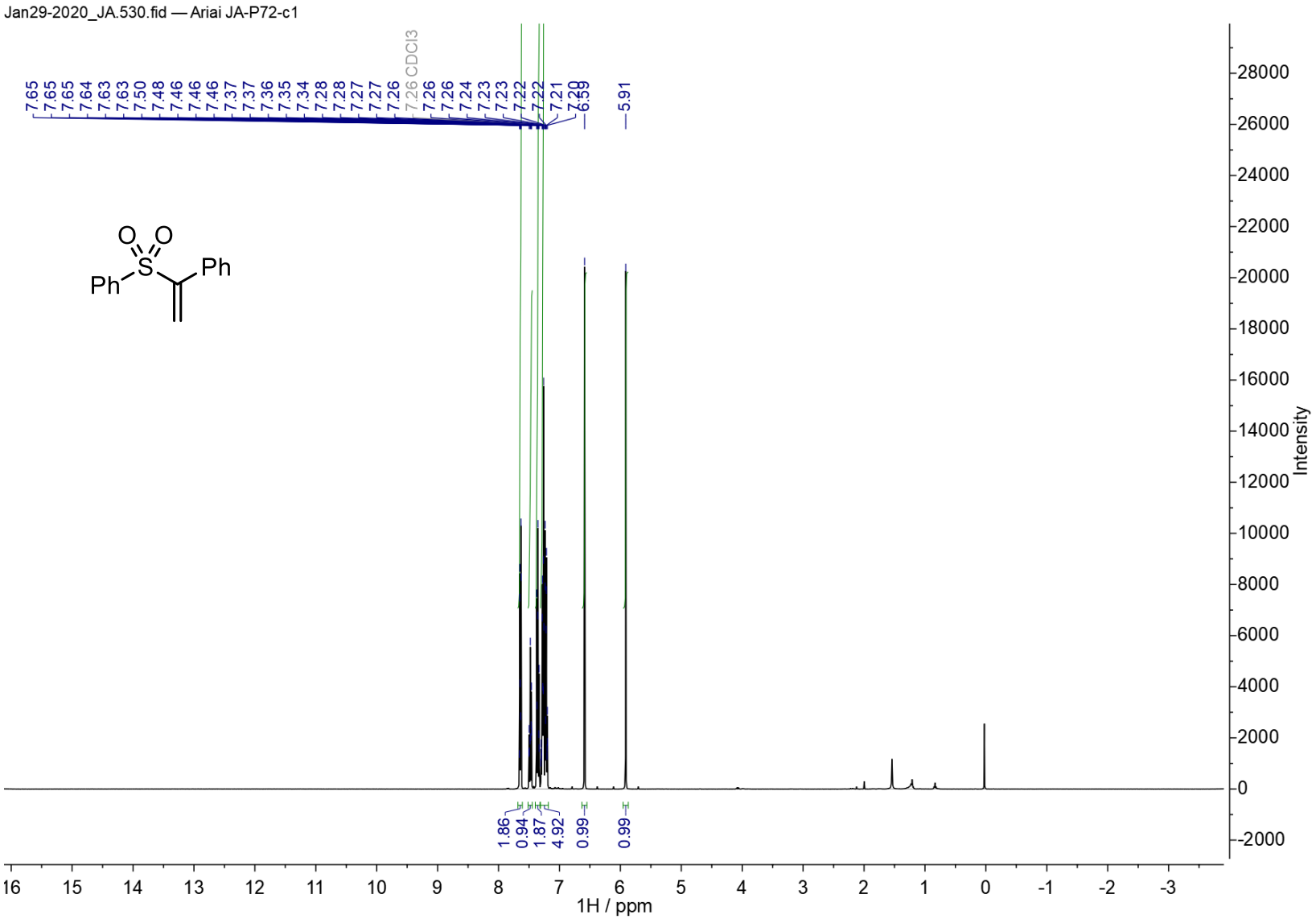
Carbon-based FLP by Conjugate Addition: I



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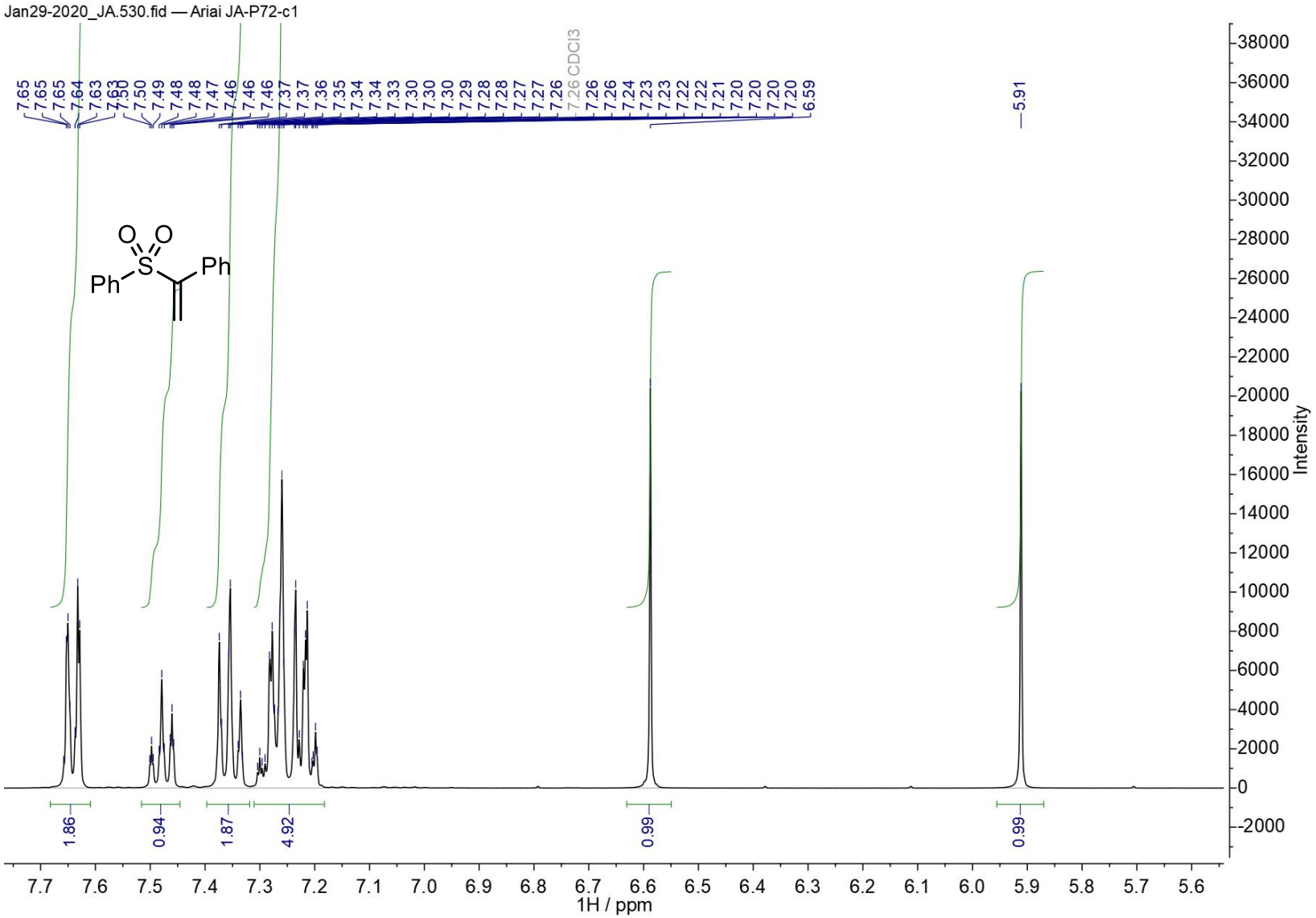
Carbon-based FLP by Conjugate Addition: I



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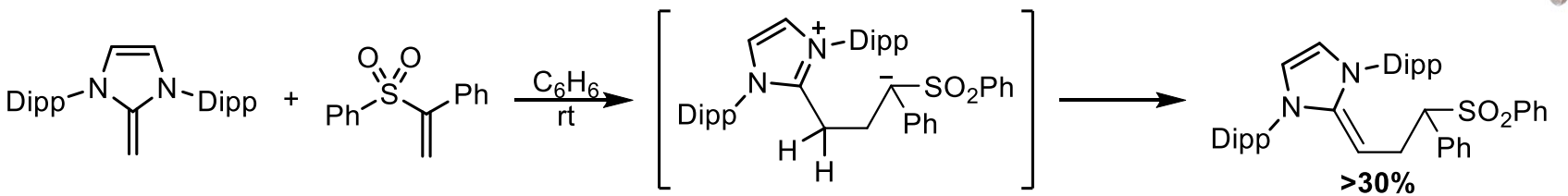
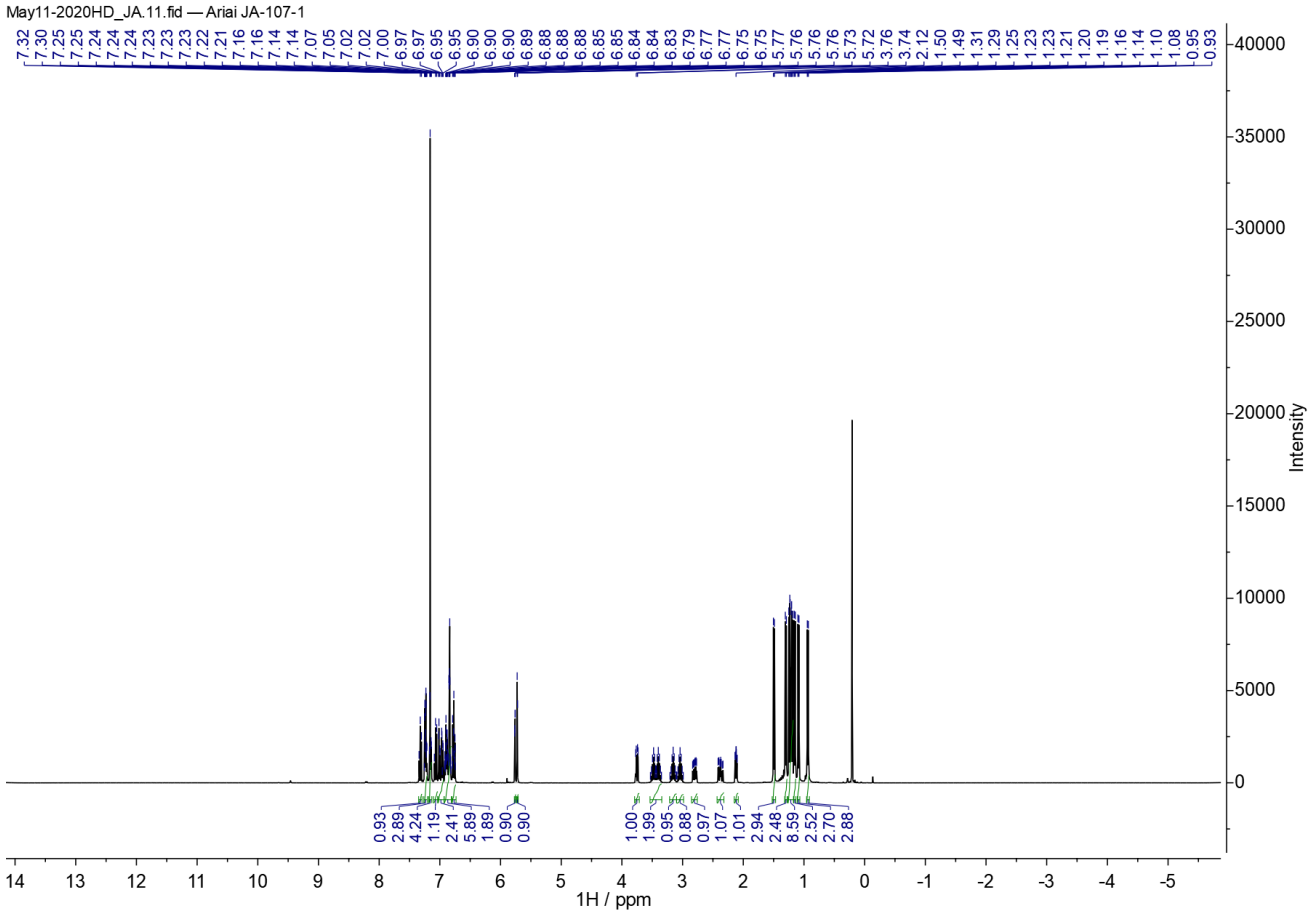
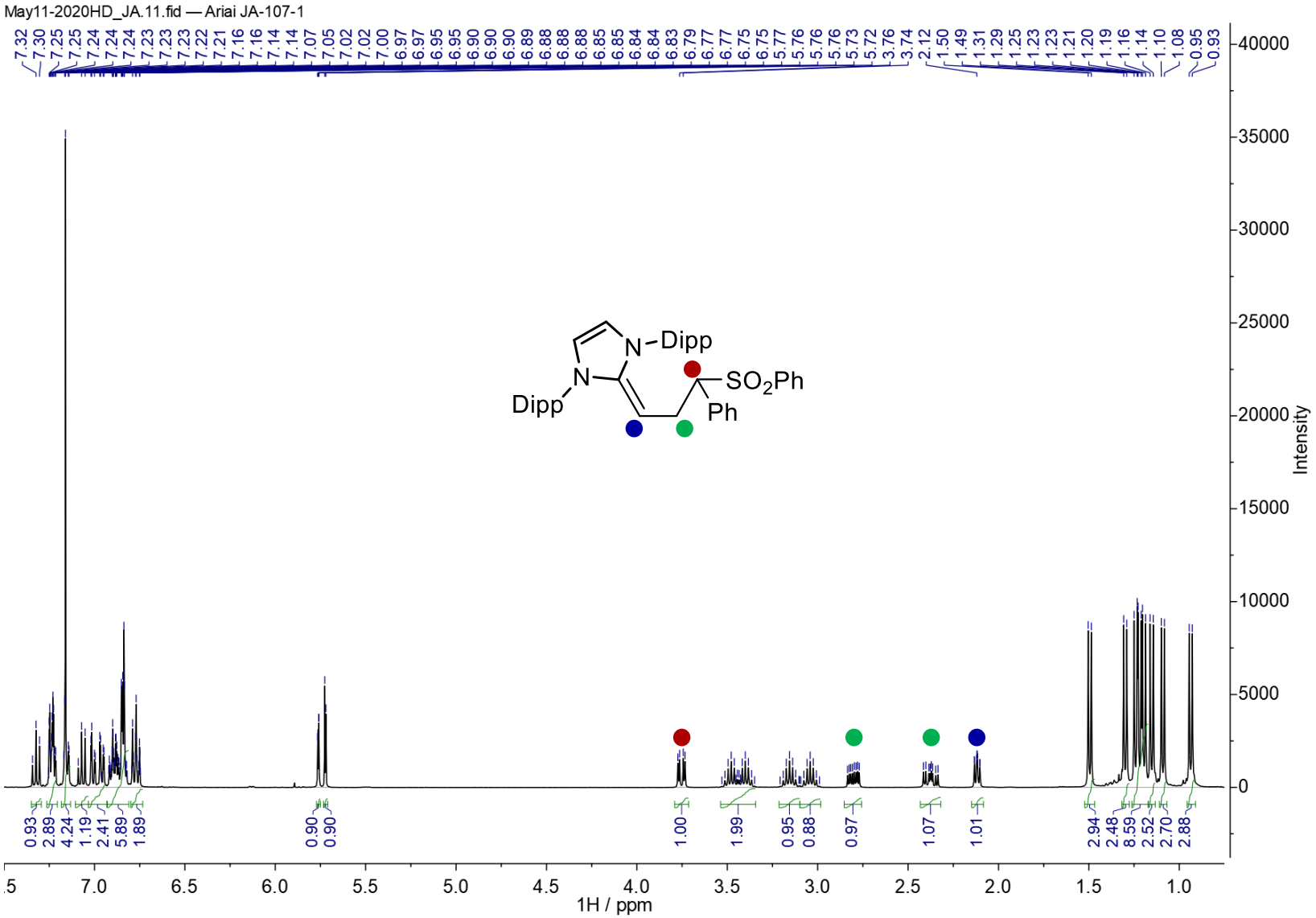
Carbon-based FLP by Conjugate Addition: I

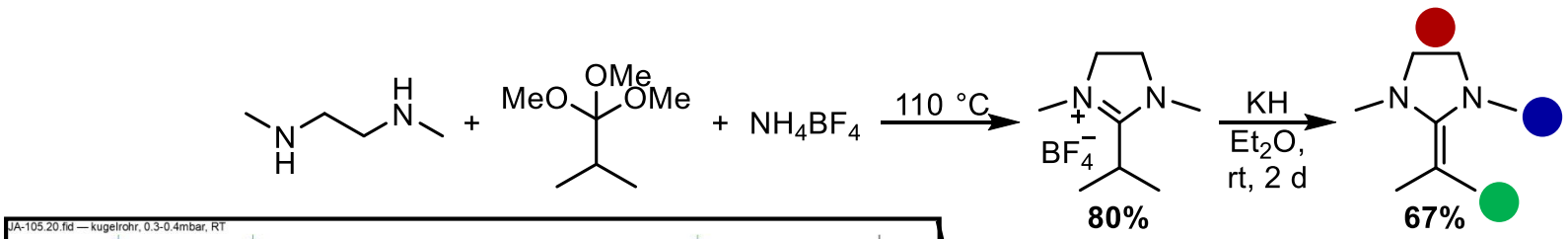


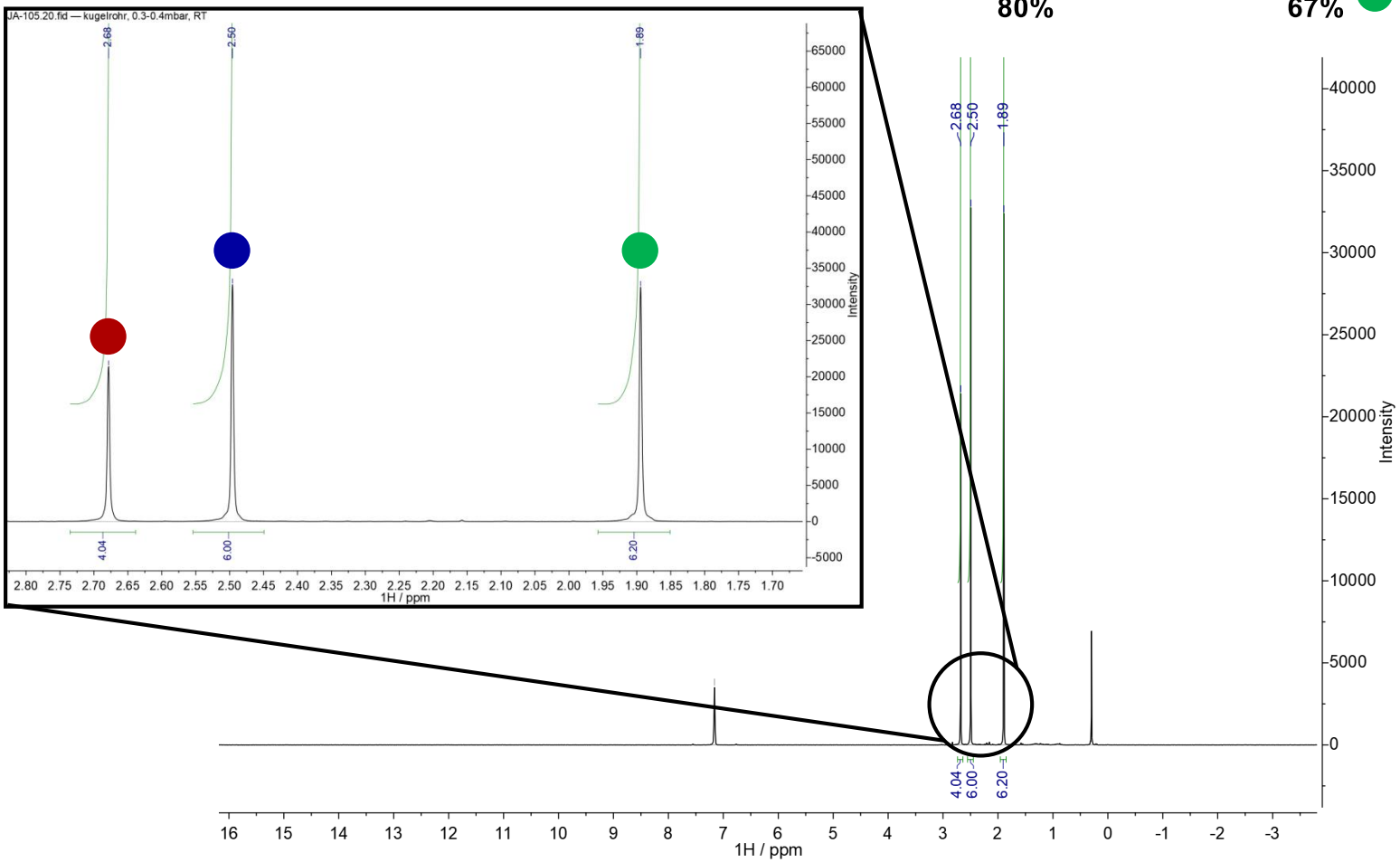


Carbon-based FLP by Conjugate Addition: I



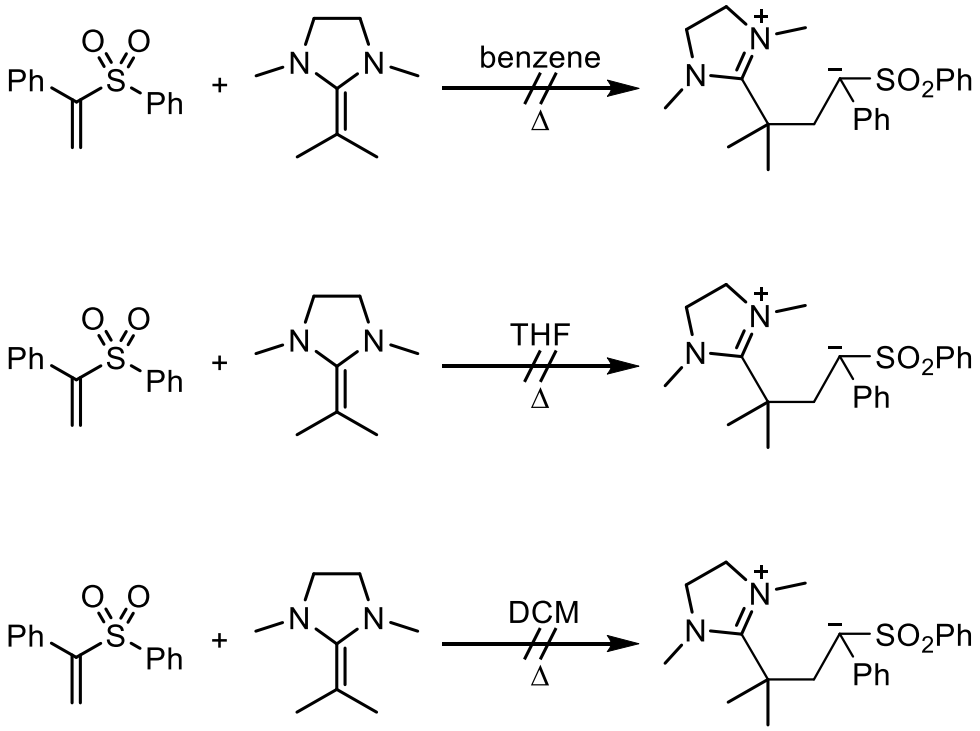
Carbon-based FLP by Conjugate Addition: II



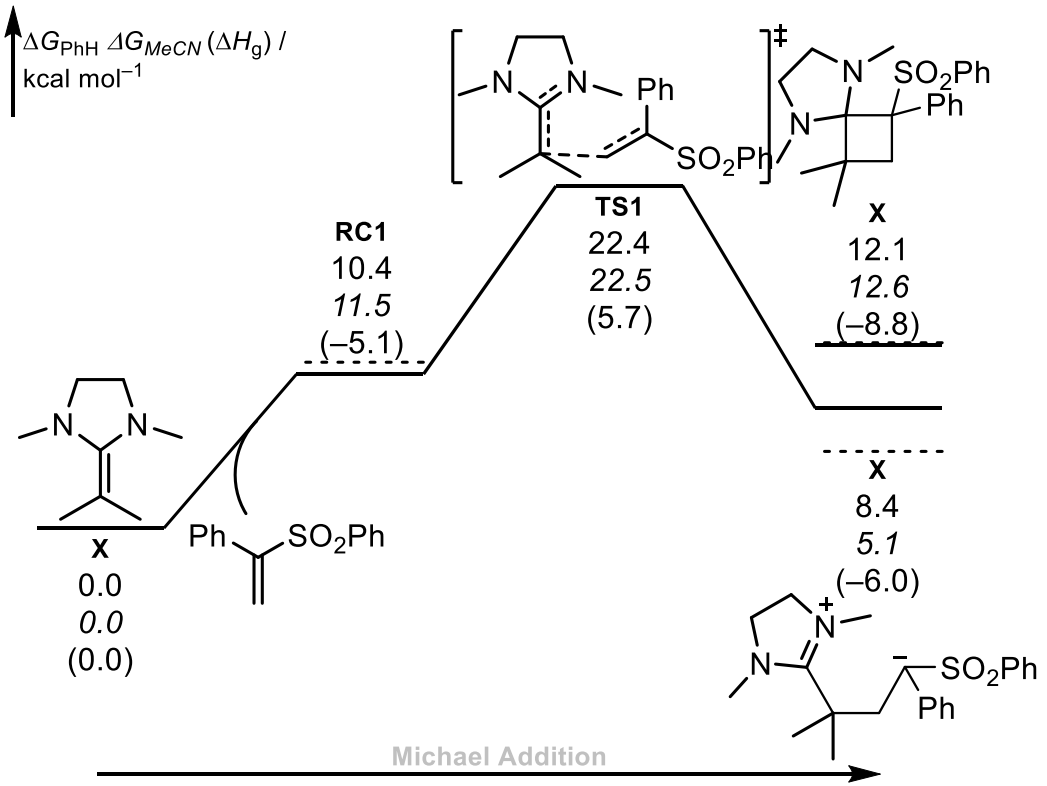


S. Naumann, A. W. Thomas, A. P. Dove, *ACS Macro Lett.* **2016**, *5*, 134-138.

Carbon-based FLP by Conjugate Addition: II

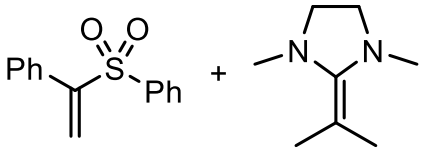


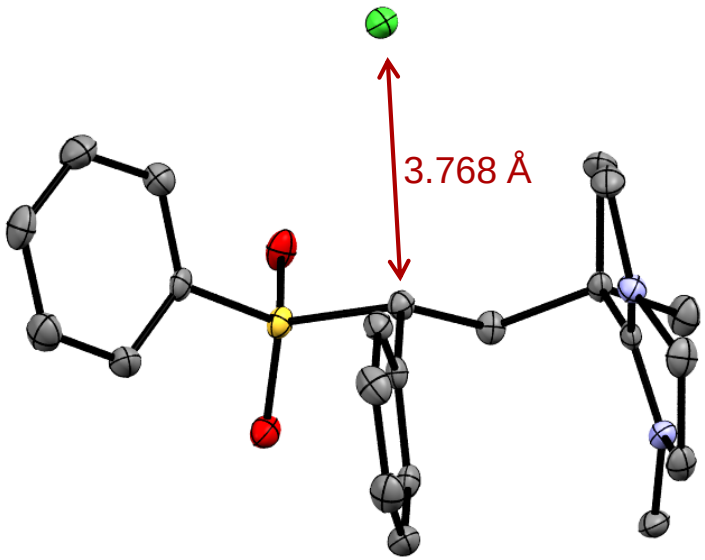
Carbon-based FLP by Conjugate Addition: II

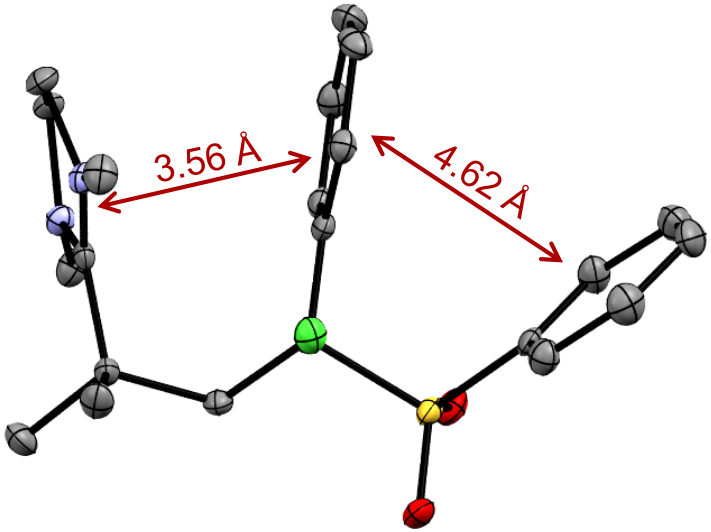


revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c, SMD model for benzene (solid) and acetonitrile (dashed)

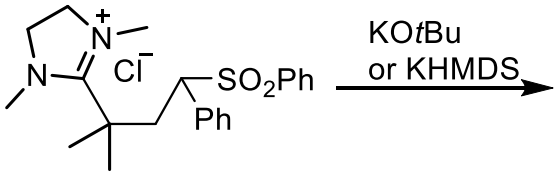
Carbon-based FLP by Conjugate Addition: II



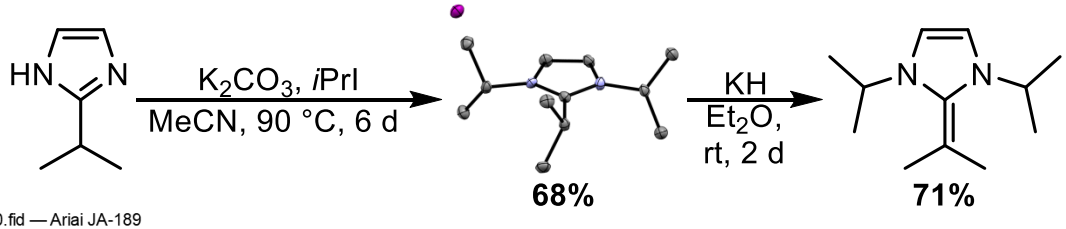


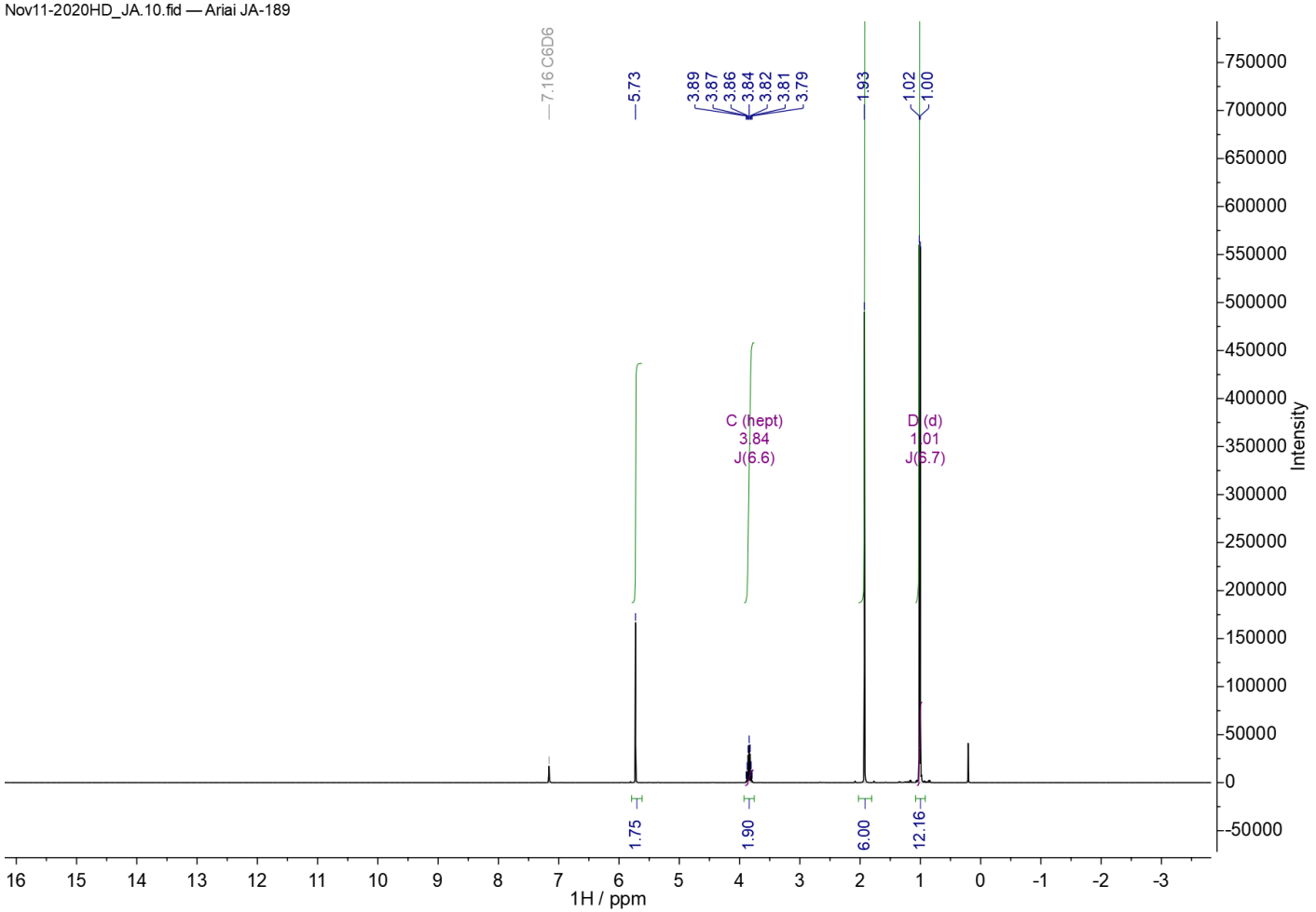


Carbon-based FLP by Conjugate Addition: II

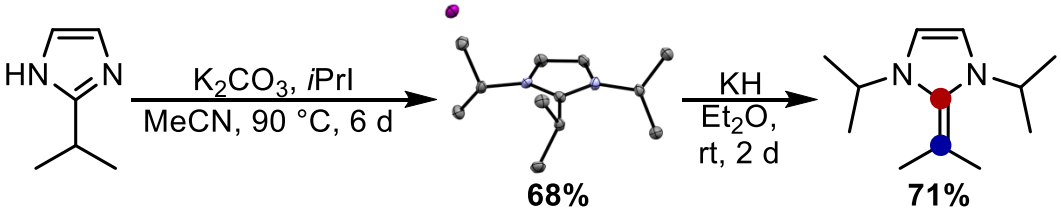


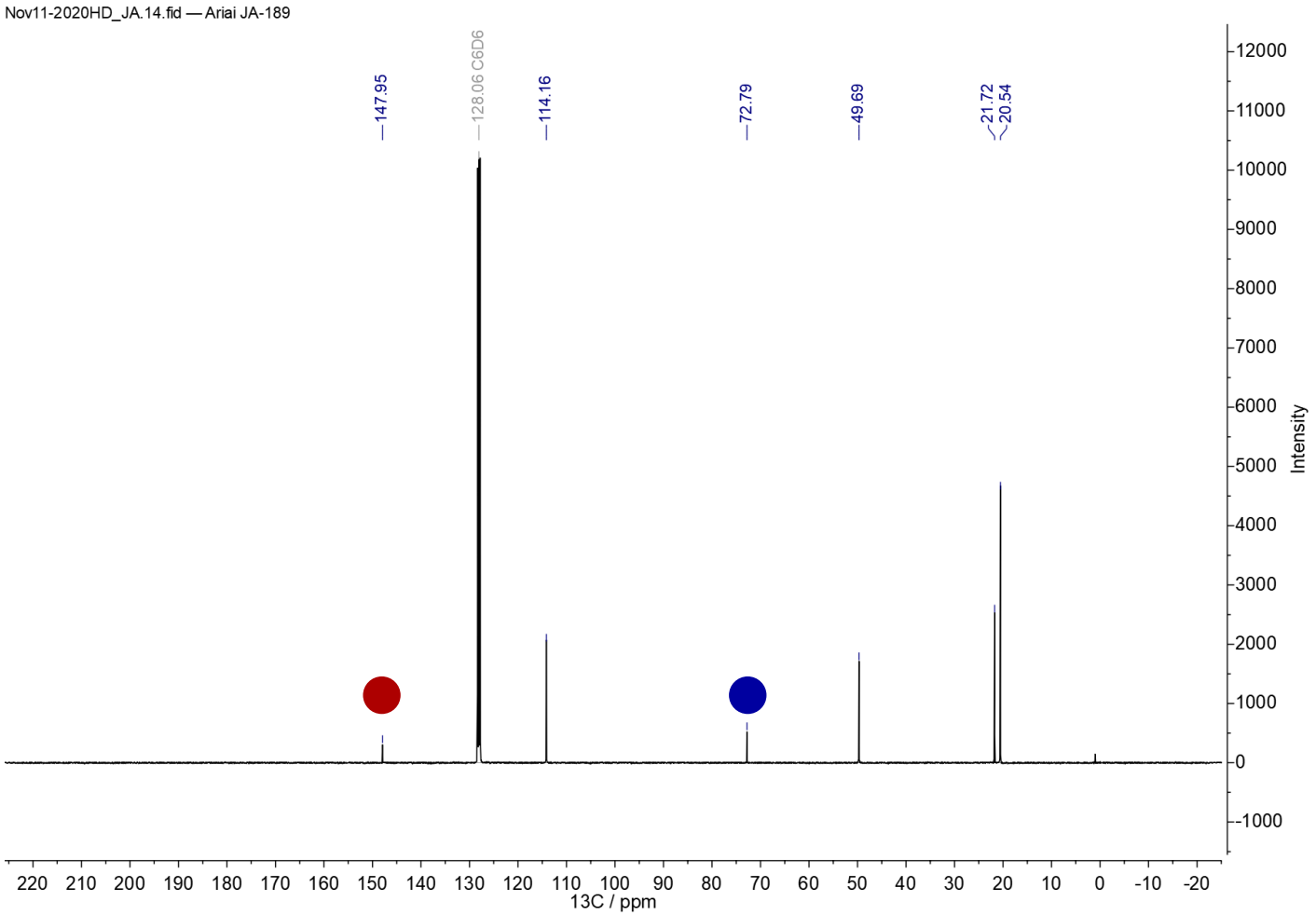
Carbon-based FLP by Conjugate Addition: III





Carbon-based FLP by Conjugate Addition: III





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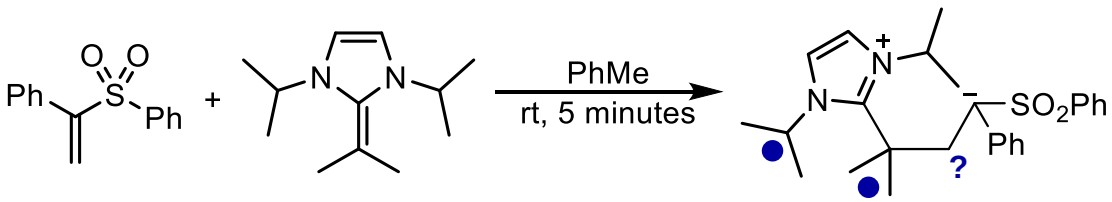
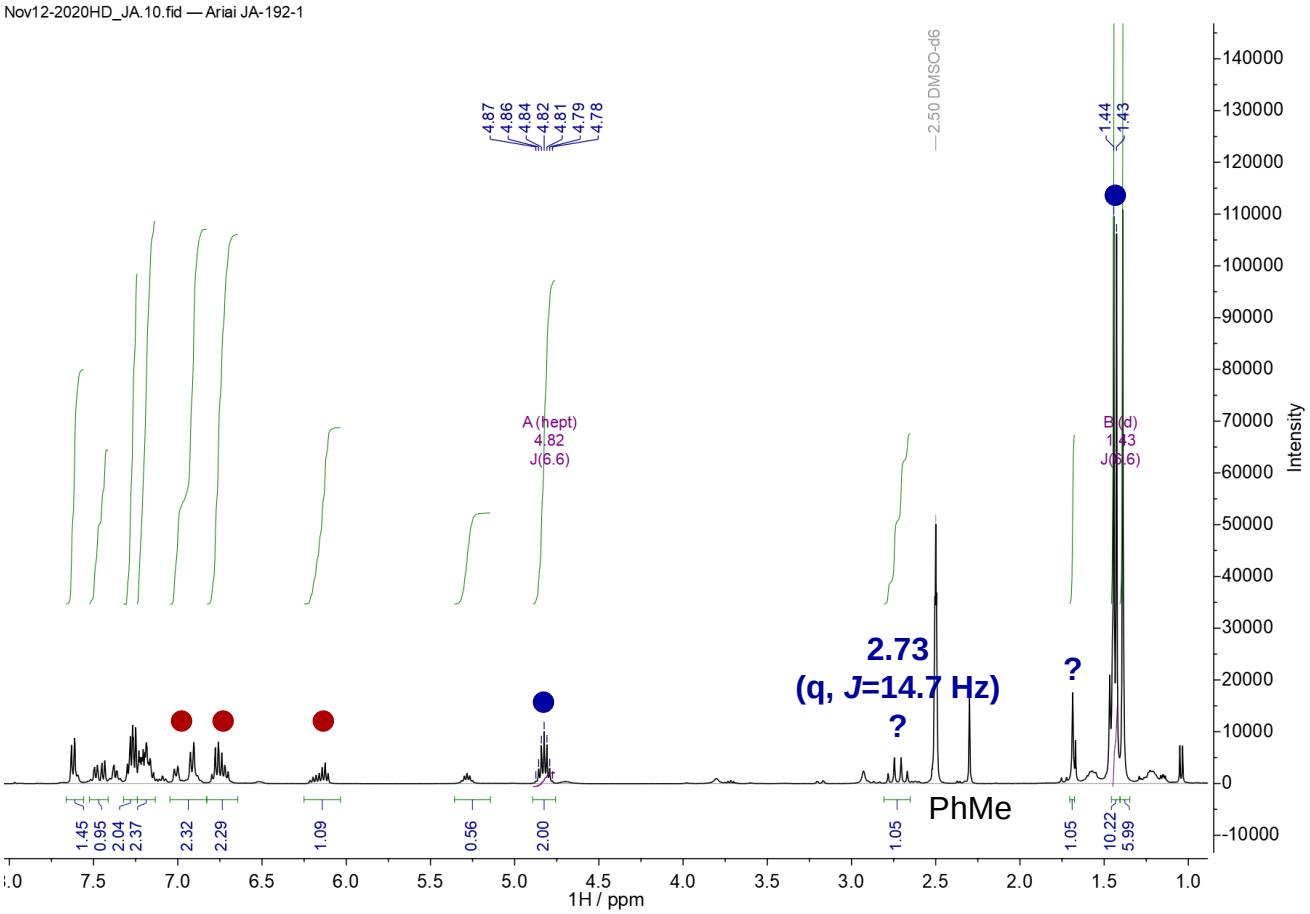
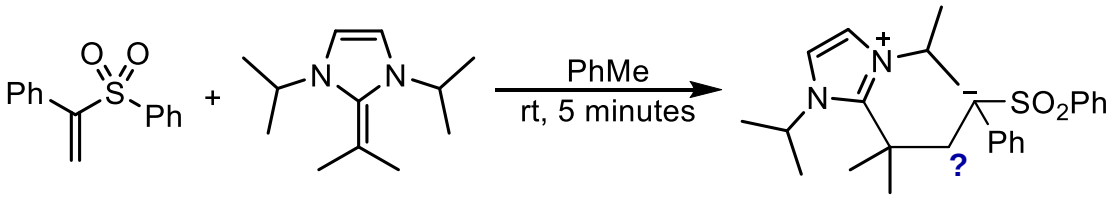


MS ✓
NMR ?



COSY contact

Carbon-based FLP by Conjugate Addition: III



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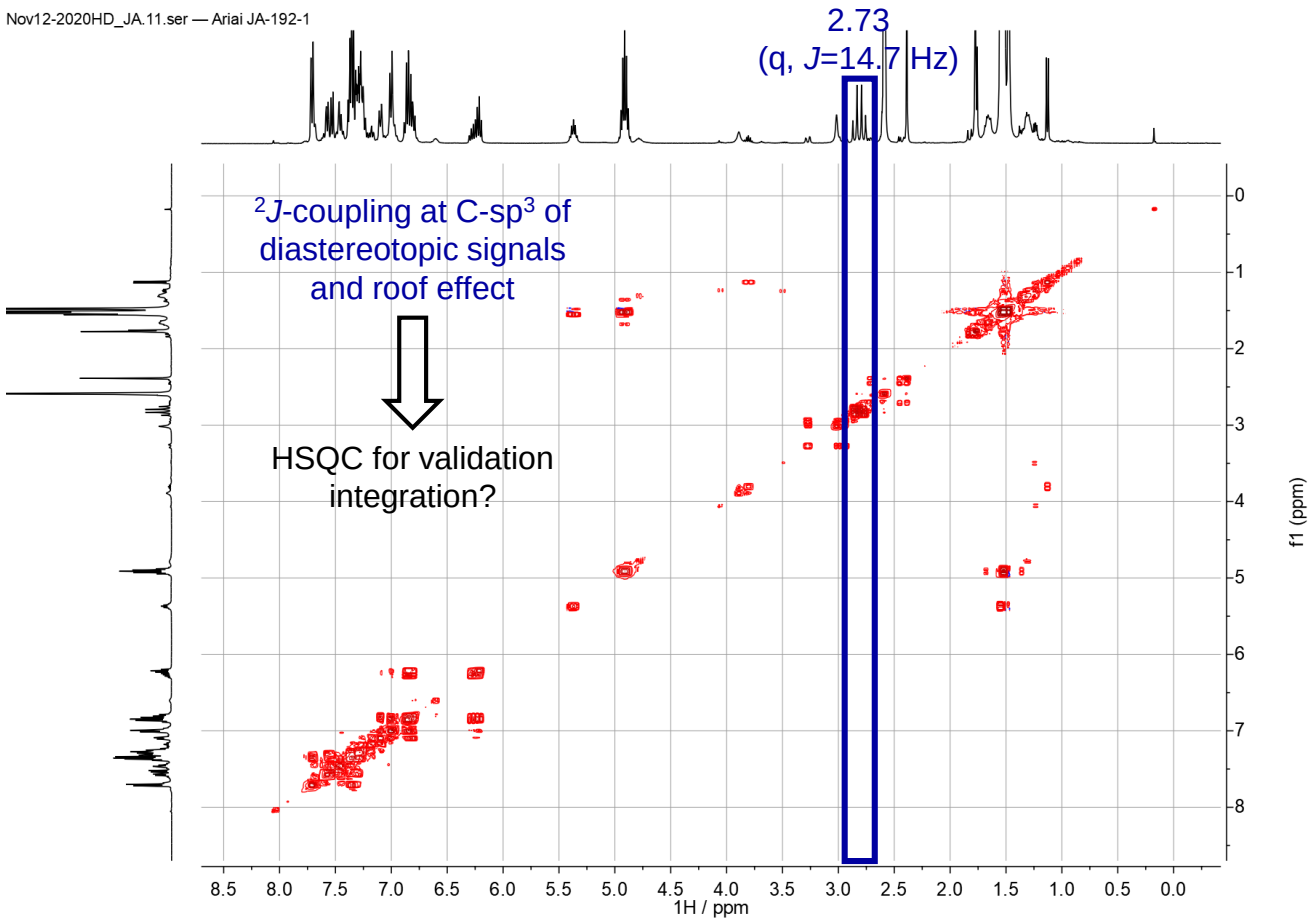
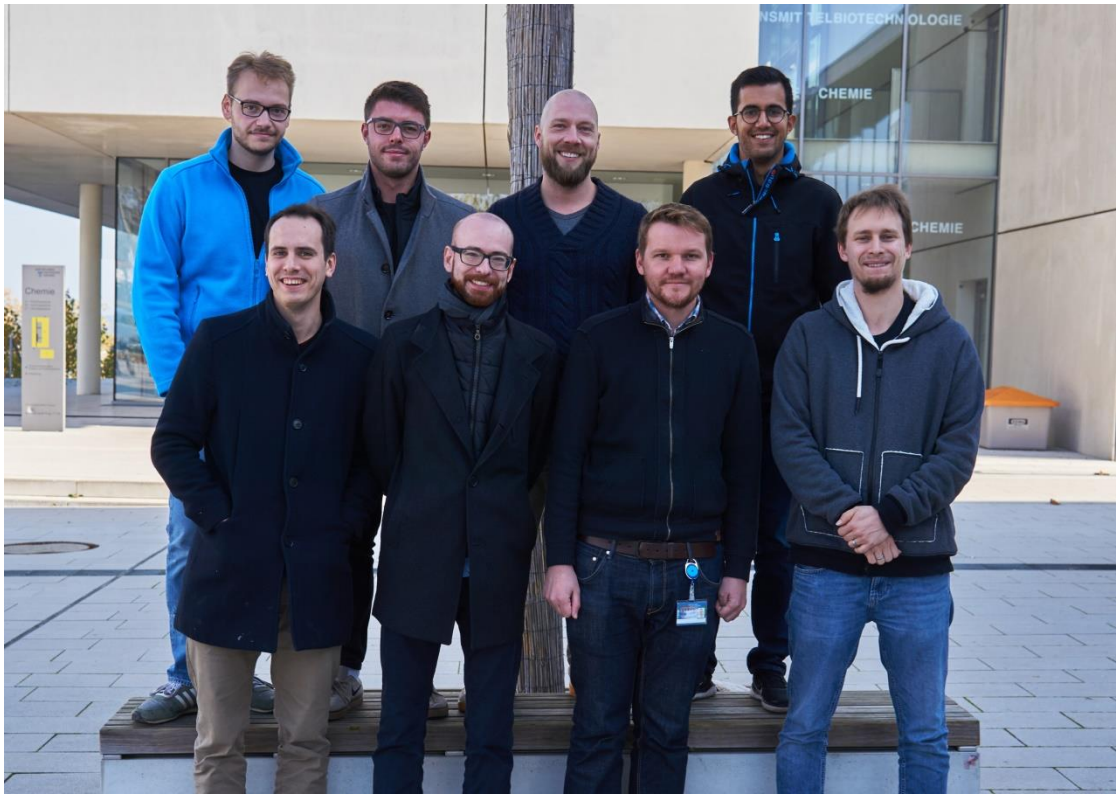


Thank you …

- Dr. Urs Gellrich
- John
- Tizian, Max, Sebastian, Felix, Arthur, Michael
- Dr. Dennis Gerbig
- Dr. Jonathan Becker
- Dr. Heike Hausmann, OC-Analytics
- Schreiner, Göttlich, and Wegner Group



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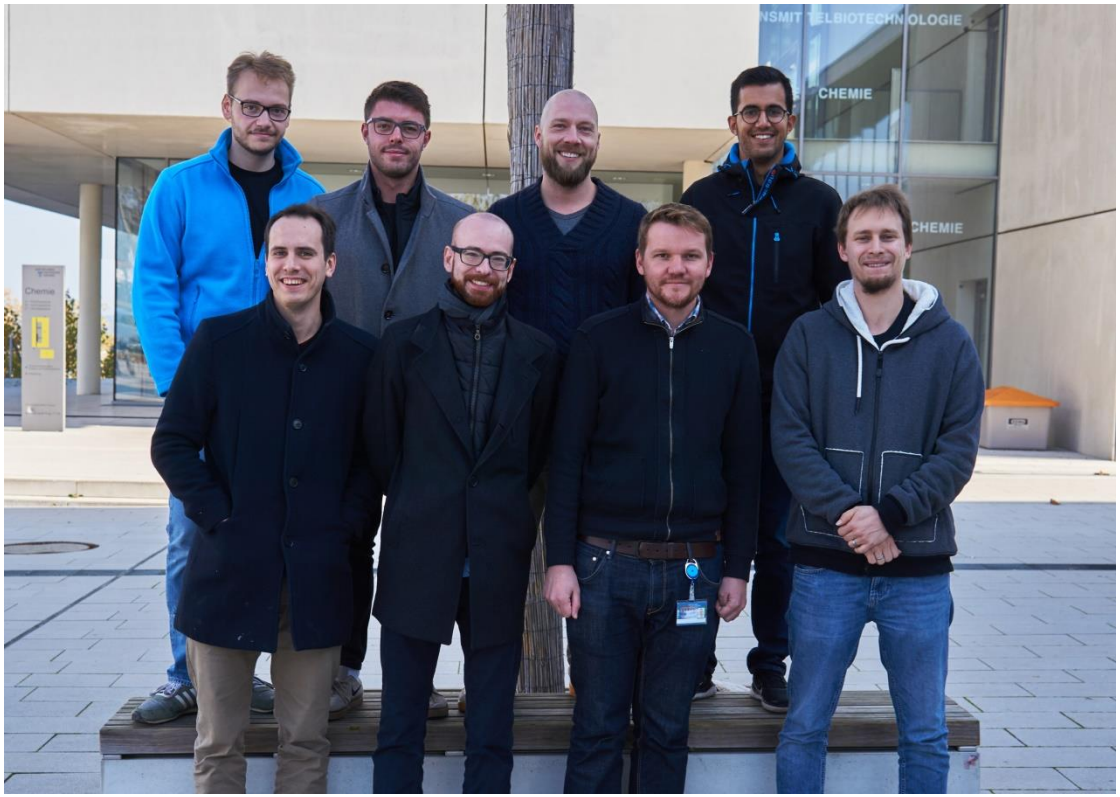

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