



RAPID COMMUNICATION

Lewis acid catalyst system for Diels–Alder reaction

RISHIR KALEPU and SATYENDRA MISHRA*

Medicinal Chemistry Laboratory, Department of Physical Sciences, Institute of Advanced Research, Koba Institutional Area, Gandhinagar, Gujarat 382426, India

E-mail: satyendramishra1@gmail.com; satyendra.mishra@iar.ac.in

MS received 23 November 2019; revised 10 January 2020; accepted 12 January 2020

Abstract. Ca(OTf)₂/Bu₄NPF₆ catalytic system has been illustrated for the synthesis of Diels–Alder adduct for the first time. This procedure tolerates substrate diversity and delivers high yield. Use of environmentally benign catalyst, high yields and substrate diversity are the highlight of the existing method.

Keywords. Diels–Alder reaction; Ca(OTf)₂; Dienophiles; Diene.

1. Introduction

The Diels–Alder reaction is a [4+2] cycloaddition reaction first described by Otto Diels and Kurt Alder.¹ It is a pericyclic reaction involving the addition of a conjugated diene to a substituted alkene/alkyne (the “dienophile”). The reaction is of great synthetic utility for forming new carbon-carbon σ -bonds resulting in a six-membered unsaturated ring adduct. It is well-established that the reaction proceeds *via* an aromatic transition state in a concerted mechanism.²

In the years following the discovery of the reaction, its potential utility in synthesis was widely acknowledged. In 1960, Yates and Eaton³ reported the first examples of Lewis-Acid catalysed Diels–Alder reactions using one molar equivalents of AlCl₃. Further development and optimisation followed, with other Lewis acids such as FeCl₃, BF₃, and SnCl₄ being used.⁴ With acidic catalysts, rates of reaction, the preference for endo stereoselectivity, and regioselectivity are increased.⁵ This is a consequence of lowering the LUMO of the dienophile by the increased electron deficiency caused by the Lewis acid, and changes in the orbital coefficients which cause stronger secondary orbital interactions and larger regiochemical preference. There are also downsides to adding Lewis or protic acids – undesired side reactions may also be accelerated.⁵

The landmark discovery of hydrophobic acceleration of Diels–Alder reactions was reported by Breslow

and co-workers in 1980.⁶ The effects of polarity,⁷ hydrophobicity,⁸ solute-solvent interactions,⁹ and internal pressure,¹⁰ have been extensively studied. As stated previously, the reactivity of a given diene with a dienophile is based on the energy gap. In the past decade, significant advances have been made in Diels–Alder reactions that form heterocyclic adducts, which proceed by the formation of C–X σ -bonds (X=O,N,S)—a variant known as the Hetero-Diels–Alder Reaction.^{11–14} The conditions used for these reactions tend to be substrate-dependent,¹⁵ and the scope of this work is limited to the normal electron-demand Diels–Alder reactions.

Unless a catalyst is used, the reaction tends to be endothermic and elevated temperatures are required to induce product formation.¹⁶ The presence of Lewis acid catalysts enhances the rate of the reaction, as well as regio- and stereoselectivity while allowing it to proceed at lower temperatures.¹⁷ Currently, traditionally used Lewis acids are being replaced for organic catalysts with newer classes of Lewis acidic salts. The AlCl₃/FeCl₃-catalysed procedure is also adopted for Diels–Alder reaction.¹⁸

Several catalysts have been reported that selectively result in the formation of a particular enantiomer or in a major product. Most notably, these are organocatalytic Diels–Alder reactions, which contain chiral centres as a common feature such as BINOL-derived catalysts, silicon organocomplexes, and N-Heterocyclic carbenes.^{19–21} There are far-reaching uses for this cycloaddition reaction.^{22–28} The testaments to its synthetic utility are the several dozens of natural products whose total syntheses involve the reaction as

*For correspondence

one of the steps. A few notable ones include: Morphine, Cortisol, and Gibberlic Acid.^{29–31}

Through herein, we aimed to improve the yield of the Diels–Alder reaction using calcium-based Lewis acids in catalytic amounts for various diene-dienophile combinations. Ca(II) based catalysts have known uses for activation of carbonyls, alcohols, and olefins. The Lewis acidity of Ca, when coordinated to bulky ligands, makes it a suitable candidate for the Diels–Alder reaction.³² Furthermore, it is more widely available and is hence a sustainable alternative to transition-metal catalysis.

2. Results and Discussion

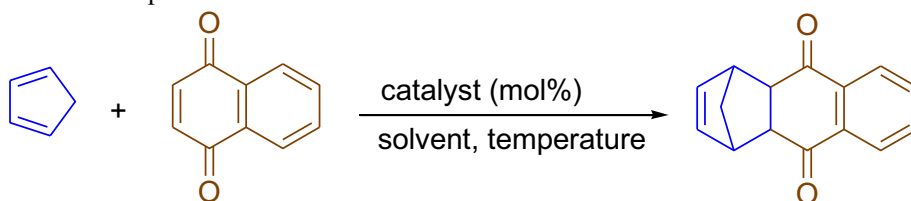
The aim of this work is to explore Ca (II) based Lewis acids as sustainable, efficient catalysts for the normal electron-demand Diels–Alder reaction at relatively milder conditions. Ca(OTf)₂ have been shown to be effective for the activation of carbonyls, alcohols, and alkenes. Moreover, when the reaction was performed with isoprene and anthracene, the desired product was not formed even in prolonged time and catalyst

(mol%). However, reactions proceed smoothly with cyclopentadiene as diene. Thus, cyclopentadiene (CPD) and 1,4-naphthoquinone was used as the model substrate for the optimization of reaction conditions. Our initial efforts in the development of this methodology began with screening various catalysts, solvents, loading of catalyst (mol%), temperature as well as additive as noted in Tables 1 and 2.

First, we examine the impact of catalysts on the Diels–Alder reaction. Initially, the model reaction was carried out using different catalyst AlCl₃, FeCl₃, Ca(OTf)₂, CaCl₂ and Bu₄NPF₆ (entries 1–5; Table 1) and we observed that Ca(OTf)₂ furnished the best yield of Diels–Alder adduct. Anhydrous CaCl₂ in high loadings also did not furnish product, whereas 20% yield was obtained in the case of FeCl₃ (entry 1; Table 1). Bu₄NPF₆ exhibited low yields of Diels–Alder product. Interestingly, no product formation was detected in the absence of catalyst Ca(OTf)₂ (entry 18; Table 1).

Next solvent screening was performed in order to get the best solvent system for Diels–Alder reaction. Various solvents such as acetonitrile, chloroform, dichloromethane (DCM), anhydrous dichloromethane,

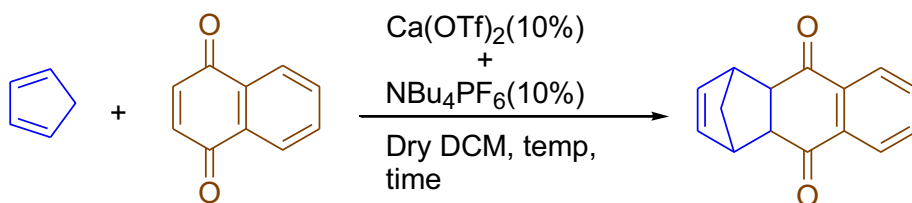
Table 1. Optimization of solvents for the Diels–Alder reaction^[a]



| Entry | Catalyst (mol%) | Solvent | Yield (%) ^[b] |
|-------|---|--------------|--------------------------|
| 1 | FeCl ₃ (5%) | DCM | 20 |
| 2 | AlCl ₃ (5%) | DCM | 5 |
| 3 | NBu ₄ PF ₆ (5%) | DCM | 10 |
| 4 | CaCl ₂ (5%) | DCM | nd |
| 5 | Ca(OTf) ₂ (5%) | DCM | 55 |
| 6 | Ca(OTf) ₂ (5%) | Acetonitrile | 35 |
| 7 | Ca(OTf) ₂ (5%) | Chloroform | 45 |
| 8 | Ca(OTf) ₂ (5%) | Dry DCM | 65 |
| 9 | Ca(OTf) ₂ (5%) | Toluene | 25 |
| 10 | Ca(OTf) ₂ (5%) | THF | 10 |
| 11 | Ca(OTf) ₂ (10%) | Dry DCM | 75 |
| 12 | Ca(OTf) ₂ (15%) | Dry DCM | 75 |
| 13 | Ca(OTf) ₂ (20%) | Dry DCM | 77 |
| 14 | Ca(OTf) ₂ (10%) + NBu ₄ PF ₆ (10%) | Dry DCM | 98 |
| 15 | Ca(OTf) ₂ (10%) + Proline (10%) | Dry DCM | 75 |
| 16 | Ca(OTf) ₂ (10%) + Bu ₄ NF (10%) | Dry DCM | 77 |
| 17 | Ca(OTf) ₂ (10%) + KPF ₆ (10%) | Dry DCM | 65 |
| 18 | No catalyst | Dry DCM | nd |

^[a]Reagents and conditions: Cyclopentadiene (2 mmol), and 1,4-naphthoquinone (4 mmol), catalyst system, solvents, temp 0 °C to –20 °C.

^[b]Isolated yield.

Table 2. Optimization of temperature and time for the Diels–Alder reaction^[a]

| Entry | Temp (°C) | Time (h) | Yield (%) ^[b] |
|-------|--------------|----------|--------------------------|
| 1 | rt to 40 °C | 8 | nd |
| 2 | rt to 20 °C | 8 | nd |
| 3 | rt to 0 °C | 8 | 25 |
| 4 | rt to −20 °C | 8 | 96 |
| 5 | rt to −20 °C | 6 | 96 |
| 6 | rt to −20 °C | 4 | 96 |
| 7 | rt to −20 °C | 3 | 93 |

^[a]Reagents and conditions: Cyclopentadiene (2 mmol), and 1,4-naphthoquinone (4 mmol), $\text{Ca(OTf)}_2/\text{NBu}_4\text{PF}_6$ (10 mol%), anhydrous dichloromethane.

^[b]Isolated yield; nd: not detected.

toluene and tetrahydrofuran (THF) were used as solvents on the model reaction (entries 5–10; Table 1) in presence of Ca(OTf)_2 . In the presence of solvents dichloromethane and chloroform the products were formed in moderate amounts (entries 5, 7; Table 1). However, when the same reaction was conducted with anhydrous dichloromethane as a solvent, the corresponding product was obtained in appreciable yield (entry 8; Table 1). Thus anhydrous dichloromethane was used as an ideal solvent for all the reactions.

Subsequently, we screened the effect of loading of catalyst Ca(OTf)_2 from 5 to 20 mol% on the Diels–Alder reaction. The obtained results in Table 1 (entries 8, 11–13) reveal that 10 mol% of the catalyst accomplished best yields of Diels–Alder adduct (entry 12; Table 1). Further increase in the amount of catalyst loading up to 20 mol % (entry 11; Table 1) did not significantly affect the yields of Diels–Alder product. As a result, the optimum mole % of catalyst was conformed 10 mol% (entry 12; Table 1).

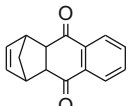
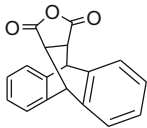
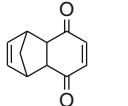
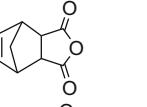
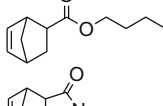
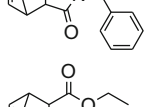
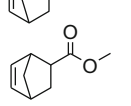
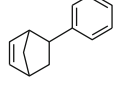
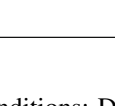
After securing the optimal reaction conditions, considering the importance of additives, we carried out the reaction with 10 mol% of catalyst Ca(OTf)_2 and various additives proline, Bu_4NF , KPF_6 and NBu_4PF_6 in 10 mol%. The reaction attempt between cyclopentadiene and 1,4-naphthoquinone using catalyst system Ca(OTf)_2 and L-proline, both in 10 mol% worked in a similar fashion (entry 15, Table 1), as it works alone with Ca(OTf)_2 . It is likely that L-Proline did not take part in the reaction catalytically and was present as a spectator ion. However, the yields of Diels–Alder

reaction of cyclopentadiene and 1,4-naphthoquinone were substantially enhanced with the catalytic system Ca(OTf)_2 (10 mol%) and NBu_4PF_6 (10 mol%) (entry 14; Table 1). We have since determined that the large rate enhancements seen in the Diels–Alder reaction are due to the presence of NBu_4PF_6 . Herein, the results infer that the presence of additive NBu_4PF_6 plays a key role in the catalytic system. Diels–Alder reaction of cyclopentadiene and 1,4-naphthoquinone using catalyst system Ca(OTf)_2 and NBu_4PF_6 (both in 10 mol%) furnished optimum yields.

After optimizing the best catalyst system, our next focus was to investigate the effect of temperature on the catalytic activity in model reaction. The temperature of the reaction mixture gradually varied from room temperature to 40 °C and room temperature to −20 °C. It was found that a decrease in temperature down to −20 °C improve the yield of the product associated with room temperature (entry 4; Table 2). Furthermore, with the solvent, mol% of catalyst loading, and the temperature in hand, we have optimized the effect of time (entries 4–7; Table 2) on the Diels–Alder reaction. The result listed in Table 2 confirmed that the 4 h is the optimum time for the model reaction (entry 6; Table 2), moreover, increasing the time up to 8 h, found no adequate effect on the yield of products (entries 4–5; Table 2).

The summary of reactions with the novel Ca(II) based catalytic system is summarised in Table 3. The reactions were performed with 1:2 mole ratio of dienophile: diene and 10 mol% of $\text{Ca(OTf)}_2/\text{NBu}_4\text{PF}_6$ in

Table 3. Synthesis of Diels–Alder adducts with calcium catalysts^[a]

| Entry | Product | Yield ^[b] |
|-------|---|----------------------|
| 1 |  | 96% |
| 2 |  | 85% |
| 3 |  | 96% |
| 4 |  | 96% |
| 5 |  | 85% |
| 6 |  | 90% |
| 7 |  | trace |
| 8 |  | trace |
| 9 |  | trace |

^[a] Reagents and conditions: Dienophile (2 mmol), diene (4 mmol), $\text{Ca}(\text{OTf})_2/\text{Bu}_4\text{NPF}_6$ (10 mol%), anhydrous dichloromethane, temp 0 °C to –20 °C, 4 h.

^[b] Isolated yield.

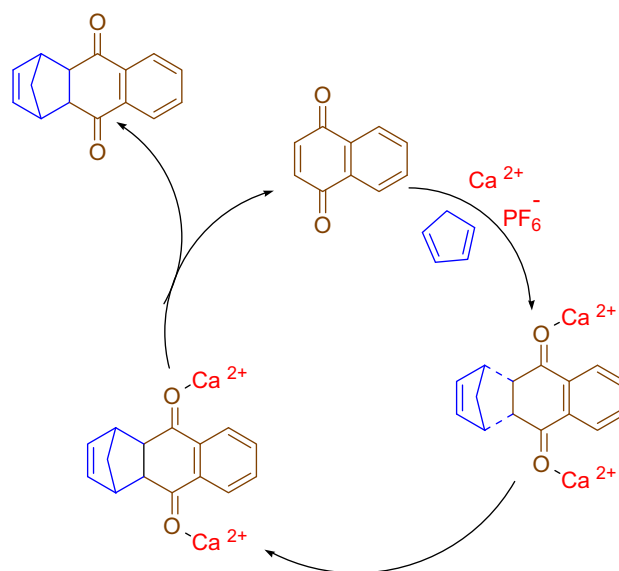
anhydrous DCM at –20 °C for 4 h, except where mentioned otherwise. Six products were synthesised in appreciable yields with the new catalyst combination, namely, Diels–Alder adduct. The reactions with methyl and ethyl acrylate as the dienophiles were unsuccessful (entry 7, 8; Table 3). However, reaction works well along with butyl acrylate (entry 5; Table 3). Further, reactions with benzoquinone and maleic anhydride also worked.

The reaction of the naphthoquinone and benzoquinone with cyclopentadiene gave excellent yields of the desired cycloadduct (entry 1, 3; Table 3). Encouraged by these results, we further checked the

scope of this methodology; it was observed that maleic anhydride and benzyl maleimide also provide good yields (entry 4, 6; Table 3). Further, we noticed that anthracene gave a modest yield of DA adduct with maleic anhydride (entry 2; Table 3). Whereas, under similar condition, in contrast to maleic anhydride, styrene does not provide any DA adduct with CPD (entry 9; Table 3). The experiment revealed that dienophiles *viz.*, acrolein, cinnamaldehyde, but-2-enoyl chloride, failed to produce desired products.

The proposed mechanism for the reaction is based on previously proposed mechanisms of Ca (II) based catalysts. In essence, the $\text{Ca}(\text{II})$ ions act in conjugation with the non-coordinating PF_6^- in order to activate the carbonyl groups (Figure 1). $\text{Ca}(\text{OTf})_2$ are expected to catalyze the reaction by activating the dienophile *via* reversible coordination to Ca (II), resulting in a favorable transition state for driving the reaction forward. The presence of bulky anions likely enhances the electrophilicity by leaving Ca(II) with unsaturated coordination sites.

The common feature among all the products obtained with Ca(II) is that they all contain a ketone group conjugated to the double bond, *i.e.*, they are labile to chelating activation by the calcium ions. Calcium triflate, $\text{Ca}(\text{OTf})_2/(n\text{-Bu})_4\text{NPF}_6$, has been shown as an effective Lewis acid catalyst for the normal electron-demand Diels–Alder reaction. The use of the additive is to enhance the Lewis acidity of Ca(II) ions in order to induce LUMO lowering of dienophiles. All products were obtained in excellent yields with no competing side-reactions taking place. The newly developed catalytic system is a sustainable alternative to existing methodologies.

**Figure 1.** Proposed mechanism for $\text{Ca}(\text{OTf})_2/\text{Bu}_4\text{NPF}_6$ Ca(II) catalysed Diels–Alder reaction.

Diels–Alder Reactions with calcium-based Lewis acids system Ca (OTf)₂ and Bu₄NPF₆: 10 mol% of the catalyst system (Ca (OTf)₂/Bu₄NPF₆) were taken in a flask containing DCM (2.5 mL per mmol of dienophile) and equipped with a magnetic bead. The vessel was purged with N₂ gas and was stirred for 30 min to 1 h until most of the solids dissolved. Following this, the dienophile (2 mmol; 1,4-naphthoquinone) was added and the stirring was continued for 30 more minutes. Upon thorough dissolution of the dienophile, the reaction vessel was cooled to –20 °C for 15 min. To this solution was added diene (4 mmol, 2 equivalents; cyclopentadiene) dropwise over 30 min *via* addition funnel at –20 °C. The mixture was stirred for 4 h at –20 °C and allowed to warm to 0 °C. The reaction was quenched at 0 °C by addition of cold aqueous citric acid solution (10 mL). The aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were washed with cold 50% saturated aqueous NaHCO₃ solution (20 mL) and cold saturated aqueous brine solution (100 mL). The organic layer concentrated *in vacuo*. This crude product was purified on column chromatography using EtOAc/hexanes.

Spectral data: *Entry 1*: ¹H NMR (400 MHz, CDCl₃): δ 8.04–8.00 (m, 2H), 7.71–7.67 (m, 2H), 5.98 (t, 2H, *J* = 1.6 Hz), 3.66 (d, 2H, *J* = 1.6 Hz), 3.46–3.45 (m, 2H), 1.74–1.52 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): 197.7, 135.5, 134.0, 126.8, 49.5, 49.2, 29.6; *entry 2*: ¹H NMR (400 MHz, CDCl₃): δ 7.34–7.31 (m, 4H), 7.25–7.17 (m, 4H), 4.82 (s, 2H), 3.51 (d, 2H, *J* = 1.2 Hz); ¹³C NMR (100 MHz, CDCl₃): 170.4, 140.6, 138.1, 127.7, 127.1, 125.2, 124.4, 48.0, 45.4. *entry 4*: ¹H NMR (400 MHz, CDCl₃): δ 6.31 (t, 2H, *J* = 2.0 Hz), 3.58–3.57 (m, 2H), 3.35–3.50 (m, 2H), 1.79–1.77 (m, 1H), 1.58–1.49 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 171.1, 135.5, 52.7, 47.1, 46.1; *entry 5*: ¹H NMR (400 MHz, CDCl₃): δ 6.09 (t, 2H, *J* = 1.6 Hz), 3.38 (t, 2H, *J* = 1.6 Hz), 3.32 (t, 2H, *J* = 3.2 Hz), 3.23–3.22 (m, 1H), 1.74–1.72 (m, 2H), 1.54–1.52 (m, 2H), 1.44–1.37 (m, 2H), 1.31–1.21 (m, 2H), 0.91–0.87 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 174.7, 137.7, 67.9, 46.5, 43.3, 39.2, 34.5, 26.6, 19.1, 14.6; *entry 6*: ¹H NMR (400 MHz, CDCl₃): δ 7.40–7.24 (m, 5H), 5.89 (t, 2H), 4.48 (s, 2H), 3.57 (t, 2H, *J* = 1.6 Hz), 3.24 (t, 2H, *J* = 1.6 Hz), 1.70–1.67 (m, 1H), 1.55–1.49 (m, 1H).

3. Conclusions

In summary, we have demonstrated the efficacy of complexes of calcium triflate, Ca(OTf)₂ in combination with *l*-(*n*-Bu)₄NPF₆, in catalyzing Diels–Alder reactions. The reactivity of Ca(OTf)₂/*l*-(*n*-Bu)₄NPF₆ has

allowed the synthesis of products that are either difficult to obtain through conventional Ca(OTf)₂ catalysis. Herein the reactions proceeded under reasonably mild conditions to give the Diels–Alder adduct in fair to good yields. We believe that this methodology will be amenable over the existing methods.

Acknowledgements

This work is generously supported by the Department of Science and Technology (DST- SERB/ ECR/2015/000363) India to SM.

Author Contributions S.M. and R.K. carried out the synthesis, purification, and characterization of the synthesized molecules. S.M. directed the synthetic work and wrote the paper based upon drafts written by R.K.

Compliance with ethical standards

Conflicts of interest The authors declare no conflict of interest.

References

- Diels O and Alder K 1928 Synthesen in der hydroaromatischen Reihe *Justus Liebigs Ann. Chem.* **460** 98
- Dewar M J S, Olivella S and Stewart J J P 1986 Mechanism of the Diels–Alder reaction: reactions of butadiene with ethylene and cyanoethylenes *J. Am. Chem. Soc.* **108** 5771
- Yates P and Eaton P 1960 Acceleration of the Diels–Alder reaction by aluminum chloride *J. Am. Chem. Soc.* **82** 4436
- Fray GI and Robinson R 1961 Catalysis of the Diels–Alder reaction *J. Am. Chem. Soc.* **83** 249
- Houk K N and Strozier R W 1973 Lewis acid catalysis of Diels–Alder reactions *J. Am. Chem. Soc.* **95** 4094
- Rideout DC and Breslow R 1980 Hydrophobic acceleration of Diels–Alder reactions *J. Am. Chem. Soc.* **102** 7816
- Ruiz-Lopez M F, Assfeld X, Garcia J I, Mayoral J A and Salvatella L 1993 Solvent effects on the mechanism and selectivities of asymmetric Diels–Alder reactions *J. Am. Chem. Soc.* **115** 8780
- Breslow R and Maitra U 1984 On the origin of product selectivity in aqueous Diels–Alder reactions *Tetrahedron Lett.* **25** 1239
- Blokzij W, Blandamer M J and Engberts J B F N 1991 Diels–Alder reactions in aqueous solutions. Enforced hydrophobic interactions between diene and dienophile *J. Am. Chem. Soc.* **113** 4241
- Kumar A 1994 Can internal pressure describes the effect of salt in aqueous Diels–Alder reactions? A possible explanation *J. Org. Chem.* **59** 230
- Jørgensen K A 2000 Catalytic Asymmetric Hetero-Diels–Alder Reactions of Carbonyl Compounds and Imines *Angew. Chem. Int. Ed.* **39** 3558

12. Schaus S E, Brånalt J and Jacobsen E N 1998 Asymmetric Hetero-Diels–Alder Reactions Catalyzed by Chiral (Salen)Chromium(III) Complexes *J. Org. Chem.* **63** 403
13. Deguin B and Vogel P 1992 Hetero-Diels–Alder addition of sulfur dioxide to 1,3-dienes. Suprafaciality, regioselectivity, and stereoselectivity *J. Am. Chem. Soc.* **114** 9210
14. Streith J and Defoin A 1994 Hetero Diels–Alder Reactions with Nitroso Dienophiles: Application to the Synthesis of Natural Product Derivatives *Synth.* **11** 1107
15. Waldmann H 1994 Asymmetric Hetero Diels–Alder Reactions *Synth.* **6** 535
16. Houk K N, Lin Y T and Brown F K 1986 Evidence for the concerted mechanism of the Diels–Alder reaction of butadiene with ethylene *J. Am. Chem. Soc.* **108** 554
17. Kagan H B and Riant O 1992 Catalytic asymmetric Diels–Alder reactions *Chem. Rev.* **92** 1007
18. Nicolaou K C, Snyder S A, Montagnon T and Vassilikogiannakis G 2002 The Diels–Alder reaction in total synthesis *Angew. Chem. Int. Ed Engl.* **41** 1668
19. Du H, Long J, Hu J, Li X and Ding K 2002 3,3'-Br₂-BINOL-Zn Complex: A Highly Efficient Catalyst for the Enantioselective Hetero-Diels–Alder Reaction *Org. Lett.* **42** 4349
20. Hara K, Akiyama R and Sawamura M 2005 Strong Counteranion Effects on the Catalytic Activity of Cationic Silicon Lewis Acids in Mukaiyama Aldol and Diels–Alder Reactions *Org. Lett.* **25** 5621
21. Fang X, Chen X and Chi YC 2011 Enantioselective Diels–Alder Reactions of Enals and Alkylidene Diketones Catalyzed by N-Heterocyclic Carbenes *Org. Lett.* **13** 4708
22. Funel J A and Abele S 2013 Industrial Applications of the Diels–Alder Reaction *Angew. Chem. Int. Ed.* **52** 3822
23. Goussé C and Gandini A 1999 Diels–Alder polymerization of difurans with bismaleimides *Polym. Int.* **48** 723
24. Gacal B, Durmaz H, Tasdelen MA, Hizal G, Tunca U, Yagci Y and Demirel A L 2006 Anthracene–Maleimide-Based Diels–Alder “Click Chemistry” as a Novel Route to Graft Copolymers *Macromolecules* **39** 5330
25. Plass T, Milles S, Koehler C, Szymański J, Mueller R, Wiessler M, Schultz C and Lemke EA 2012 Amino acids for Diels–Alder reactions in living cells *Angew. Chem. Int. Ed. Engl.* **51** 4166
26. Liu Y-L and Chuoa T-W 2013 Self-healing polymers based on thermally reversible Diels–Alder chemistry *Polym. Chem.* **4** 2194
27. Shi Z, Hau S, Luo J, Kim T D, Tucker N M, Ka J W and Jen A K Y 2007 Highly Efficient Diels–Alder Crosslinkable Electro-Optic Dendrimers for Electric-Field Sensors *Adv. Func. Mat.* **17** 2557
28. Sarkar S, Bekyarova E and Haddon R C 2012 Chemistry at the Dirac Point: Diels–Alder Reactivity of Graphene *Acc. Chem. Res.* **45** 673
29. Gates M and Tschudi G 1952 The synthesis of morphine *J. Am. Chem. Soc.* **74** 1109
30. Woodward R B, Sondheimer F, Taub D, Heusler K and McLamore W M 1952 The Total Synthesis of Steroids *J. Am. Chem. Soc.* **74** 4223
31. Corey E J, Guzman-Perez A and Loh T-P 1994 Demonstration of the Synthetic Power of Oxazaborolidine-Catalyzed Enantioselective Diels–Alder Reactions by Very Efficient Routes to Cassiol and Gibberellic Acid *J. Am. Chem. Soc.* **116** 3611
32. Begouin J-M and Niggemann M 2013 Based Lewis Acid Catalysts *Chem. Eur. J.* **19** 8030