Asymmetric Synthesis of Tetrahydrobenzofurans and Annulated Dihydropyrans via Cooperative One-Pot Organo- and Silver-Catalysis

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In memory of Professor Jean Normant

Abstract A low catalyst loading of a squaramide (0.5 mol%) and a silver(I) salt (1 mol%) efficiently catalyzes a one-pot asymmetric Michael addition/hydroalkoxylation reaction between 1,3-diketones and alkynetethered nitroalkenes. Depending on the 1,3-dicarbonyl substrate this cooperative catalytic approach opens access to tetrahydrobenzofurans or annulated dihydropyrans in moderate to excellent yields and very good to excellent enantioselectivities.

Key words asymmetric synthesis, organocatalysis, one-pot synthesis, silver catalysis, annulation

Benzofuran and its partially hydrogenated analogues are important heterocyclic building blocks and very common structures in natural products with interesting biological and pharmaceutical properties. This is also true for structurally isomeric annulated dihydropyrans.1 Natural products such as the furanomonoterpene evodone (I), which has been isolated from Evodia hortensis, exhibits significant inhibitory activity on the seed germination of certain species.2 Curzerenone (II) and bisabolangelone (III) are other natural products with antibacterial and anti-inflammatory activities,3,4 respectively, whereas the diterpenoid maoecrystal V (IV) is a potent selective HeLa cell inhibitor.5 The dihydropyran-type natural product crolibulin (V) and the pharmaceutical HA14-1 (VI) show anticancer properties (Figure 1).6,7

Recently, much effort has been invested in the synthesis of tetrahydrobenzofuran and dihydropyran core structures.7 Singh and co-workers developed a silver-catalyzed interrupted Feist–Bény reaction between ynones and β-diketones to provide dihydrofurans in moderate to good yields and good to excellent enantioselectivities (Scheme 1).8 Feng and co-workers reported an asymmetric domino Michael addition/O-alkylation reaction between cyclohexane-1,3-dione derivatives and bromonitrostyrenes catalyzed by a bifunctional N,N′-dioxide organocatalyst to afford polysubstituted bicyclic dihydrofurans.9 Calter’s group published another interesting synthesis of highly substituted furanoids via an organocatalytic asymmetric aldol/oxa-Michael addition sequence between 2-ene-1,4-diketones and dimedone in the presence of a bis(cinchona alkaloid)-pyrimidine catalyst.10 The Schneider group developed an interesting enantioselective phosphoric acid-catalyzed syn-
thesis of 4-aryl-4H-chromenes via a conjugate addition of 1,3-diketones to in situ generated ortho-quinone methides followed by a cyclodehydration reaction.\(^{11}\)

In search of new methods for acquiring valuable bioactive heterocyclic compounds and our interest in the combination of organocatalysts and silver(I) salts,\(^{16}\) we investigated an asymmetric Michael addition/hydroalkoxylation sequence between 1,3-diketones and alkyne-tethered nitroalkenes catalyzed by a bifunctional squaramide\(^{17}\) and a silver(I) salt to provide the desired tetrahydrobenzofuranans. We began our investigation by choosing dimedone (1) and nitroalkene 2a as model substrates. To our delight, the one-pot reaction of 1 and 2a in CH\(_2\)Cl\(_2\) at room temperature catalyzed by squaramide A and Ag\(_2\)O afforded the desired 5-exo-dig cyclization product 3a in 98% yield and 94% enantiomeric excess (Scheme 2). Inspired by these excellent results, the reaction was carried out with different squaramide and thiourea catalysts A-I along with Ag\(_2\)O as silver(I) salt. All squaramide catalysts as well as thiourea catalysts provided the tetrahydrobenzofuran in high yields and moderate to very good enantioselectivities. The best result was obtained with squaramide A, which gave 98% yield and 94% ee.

**Scheme 1** Approaches for the asymmetric synthesis of tetrahydrobenzofuranans and annulated dihydropyran derivatives

The activation of alkynes for subsequent transformations has become an important tool in organic chemistry to develop new and valuable reactions. Alkyne functionalization can be achieved in two crucial routes: \(\sigma\)-activation (\(\sigma\)-bond metathesis or \(\sigma\)-coordination) and \(\pi\)-activation (\(\pi\)-complex formation).\(^{12}\) The coinage metals (Cu, Ag and Au) are suitable candidates for alkyne functionalization due to their good alkynophilicity.\(^{13}\) Especially, silver(I) salts have emerged as powerful activators of alkynes. The advantages of stability, nontoxicity, low price, or catalyst compatibility with organocatalysts favor the choice of silver in C=C bond activation reactions such as alkynylation, cycloaddition, cycloisomerization, or hydrofunctionalization.\(^{14}\)

Merging organocatalysis and metal catalysis enables multiple unique transformations in one-pot and this catalytic approach has become a powerful strategy in asymmetric synthesis. Particularly cooperative, relay, synergistic, and dual catalysis variations, where all reactants and catalysts are present from the beginning, is challenging and require high compatibility of the combined catalysts.\(^{15}\) The reaction conditions were optimized further by varying the solvent (Table 1). The solvent screening indicated that the chlorinated solvents and Et\(_2\)O gave very good results. The best yields were obtained with CH\(_2\)Cl\(_2\) and CHCl\(_3\). We chose CH\(_2\)Cl\(_2\) over CHCl\(_3\) on the basis of its lower toxici-
ty. Further optimization studies were carried out by screening transition metal catalysts for the hydroalkoxylation reaction. Ag$_2$CO$_3$ provided the annulated product with 99% yield and 95% ee. The cost aspect led to our decision to use Ag$_2$O instead of Ag$_2$CO$_3$. After carrying out the reaction at different temperatures and catalyst loadings of the squaramide and the silver(I) salt, we determined the optimal reaction conditions, these being 0.5 mol% of the squaramide and the silver(I) salt, we determined the optimal reaction conditions, these being 0.5 mol% of the squaramide and Ag$_2$O, and CH$_2$Cl$_2$ as solvent at room temperature.

The cooperative catalysis condition to provide tetrahydrobenzofurans could be obtained in moderate yield and high enantioselectivity using 1,3-cyclopentanedione. The substrate scope of the cooperative catalytic reaction was extended further to 1,3-diketones bearing heteroatoms, which also provided dihydropyran derivatives in moderate to very good yields and enantiomeric excesses. An extended substrate scope was investigated using different cyclic 1,3-diketones based on five- and six-membered rings. The reaction with 1,3-cyclohexanedione led to the tetrahydrobenzofuran product in good yield and excellent enantioselectivity (Scheme 3, 5a).

The substrate scope of the cooperative organo- and silver-catalyzed asymmetric one-pot reaction was then explored for the reaction of dimedone with various alkyne-tethered nitroalkenes under optimal reaction conditions (Table 2). The nitroalkenes with electron-withdrawing and electron-donating groups worked smoothly under the cooperative catalysis condition to provide tetrahydrobenzofurans in excellent yields and very good enantioselectivities. The sterically encumbered 1-naphthyl- and 2-naphthyl-substituted nitroalkenes led to the formation of the desired tetrahydrobenzofurans in very good yields and excellent enantiomeric excesses (Table 2). Furthermore, the one-pot Michael addition/hydroalkoxylation sequence with heteroaryl-substituted nitroalkenes provided the desired annulated product in excellent yields and enantioselectivity.

An extended substrate scope was investigated using different cyclic 1,3-diketones based on five- and six-membered rings. The reaction with 1,3-cyclohexanedione led to the tetrahydrobenzofuran product in good yield and excellent enantioselectivity (Scheme 3, 5a). Interestingly, a dihydropyran derivative could be obtained in moderate yield and good enantiomeric excess using 1,3-cyclopentanedi-one. The substrate scope of the cooperative catalytic reaction was extended further to 1,3-diketones bearing heteroatoms, which also provided dihydropyran derivatives in moderate to very good yields and high enantiomeric selectivities (Scheme 3, 5c, d).

The developed one-pot asymmetric transformation was also conducted with various 5-substituted 1,3-cyclohexanediol led to the tetrahydrobenzofuran product in good yield and excellent enantioselectivity (Scheme 3, 5a). Interestingly, a dihydropyran derivative could be obtained in moderate yield and good enantiomeric excess using 1,3-cyclopentanedi-one. The substrate scope of the cooperative catalytic reaction was extended further to 1,3-diketones bearing heteroatoms, which also provided dihydropyran derivatives in moderate to very good yields and high enantiomeric selectivities (Scheme 3, 5c, d).

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The absolute configuration of the tetrahydrobenzofuran was determined by X-ray crystal structure analysis of compound 5a (Figure 2) in combination with a CD measurement and calculation (Figure 3).

The absolute configuration of the dihydropyran derivatives is based on an X-ray crystallographic analysis of compound 5d (Figure 4).

This one-pot Michael addition/hydroalkoxylation protocol is proposed to proceed via two catalytic cycles (Scheme 6). The first organocatalytic cycle involves the synergistic activation of the 1,3-diketone 1 and the nitroalkene 2 by the bifunctional squaramide A, where the squaramide moiety activates the nitroalkene 2 through the formation of hydrogen bonds to the nitro group and simultaneously the 1,3-diketone undergoes activation by the tertiary amine to promote the Michael addition from the Re-face. In the second catalytic cycle the silver forms a π-complex for the electrophilic activation of the internal alkyne to facilitate a 5-exo-dig or a 6-endo-dig annulation reaction leading to the vinylsilver intermediate. The latter undergoes a fast protodeargentation to provide the desired product 3, 5 and 7.

In conclusion, we have developed a one-pot asymmetric Michael addition/hydroalkoxylation protocol by merging a bifunctional squaramide and a silver(I) salt at a very low.
were measured on a PerkinElmer 241 polarimeter. Melting points were measured on a LLG MPM-HZ melting point instrument. Mass spectra were acquired on a Finnigan SSQ7000 (EI, 70 eV) spectrometer and on a ThermoFinnigan LCQ Deca XP plus (ESI) spectrometer and high-resolution ESI spectra on a ThermoFisher Scientific LTQ Orbitrap XL. Analytical HPLC was performed on a Agilent 1100, Agilent 1260, or Hewlett-Packard 1100 Series instrument using chiral stationary phases (Daicel Chiralpak IC, Daicel Chiralpak IA, Daicel Chiralpak AD, Daicel Chiralpak AS, Daicel Chiralpak IB columns). Analytical SFC was performed on a THAR-SFC MethodStation II with a WATERS 2998 Photodiode Array Detector using chiral stationary phases (Daicel Chiralcel OJ-H). Catalyst A and B, D, and the nitroalkenes 2 were prepared according to known procedures.

**Tetrahydrobenzofurans and Annulated Dihydropyrans; General Procedure**

A mixture of 1,3-diketones 1, 4, or 6 (0.25 mmol), nitroalkene 2 (0.275 mmol, 1.1 equiv), catalyst A (0.5 mol%), and Ag₂O (1 mol%) in CH₂Cl₂ (2.5 mL, 0.1 M) was stirred at r.t. until the intermediate Michael adduct was completely converted as indicated by TLC. The crude product was directly subjected to flash chromatography on silica (n-pentane/Et₂O or n-pentane(CH₂Cl₂) to afford the corresponding product 3, 5, or 7.

(R)-(Z)-2-Benzylidene-6,6-dimethyl-3-(nitromethyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3a)

**Scheme 6** Proposed mechanism of the one-pot Michael addition/ hydroalkoxylation reaction.

Catalyst loading. The combination of both catalytic systems enabled the formation of the desired tetrahydrobenzofurans and annulated dihydropyrans in moderate to excellent yields and good to excellent enantiomeric excesses.

Unless otherwise noted, all commercially available chemicals were used without purification. All solvents were distilled and purified according to standard procedures. Analytical TLC was performed using SIL G-25 UV254 from Macherey & Nagel (particle size 0.040–0.063 mm; 230–240 mesh, flash) and visualized with ultraviolet radiation at 254 nm. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded at ambient temperature on a Varian Innova 400 or Innova 600 spectrometer. Chemical shifts for ¹H NMR and ¹³C NMR spectra are reported in parts per million (ppm) and coupling constants in hertz (Hz). Standard abbreviations are used for the spin multiplicity (q = quintet). Optical rotations
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1H NMR (600 MHz, CDCl3): δ = 7.25 (m, 1 H, ArH), 7.11 (m, 2 H, ArH), 6.83–6.78 (m, 1 H, ArH), 5.71 (dd, J = 2.2 Hz, 1 H, OC=CH), 4.89 (dd, J = 13.3, 3.9 Hz, 1 H, CH\(_\text{NO2}\)), 4.73 (dd, J = 13.3, 7.1 Hz, 1 H, CH\(_\text{NO2}\)), 4.58–4.53 (m, 1 H, CH\(_\text{CH2}\)), 3.82 (s, 3 H, OCH\(_3\)), 2.54 (m, 2 H, CH\(_2\)), 2.31 (m, 2 H, CH\(_2\)), 1.17 (s, 3 H, CH\(_3\)), 1.16 (s, 3 H, CH\(_3\)).

13C NMR (151 MHz, CDCl3): δ = 133.7 (C q), 132.4 (C q), 129.4 (Ar C), 121.3 (Ar C), 114.2 (Ar C), 112.8 (Ar C), 111.3 (C q), 106.7 (OC=CH), 75.7 (CH\(_3\NO2\)), 55.2 (OCH\(_3\)), 41.7 (CH\(_2\)), 37.2 (CH\(_2\)), 34.4 [C(\text{CH}_3)], 29.0 (CH\(_3\)), 28.3 (CH\(_3\)).

MS (EI, 70 eV): m/z (%): 343.3 (5, [M\(^+\)]), 297.3 (34, [M – NO\(_2\)]), 283.3 (12, [M – CH\(_2\NO2\)]).

HRMS (ESI\(^+\)): m/z [M + Na\(^+\)] calc for C\(_9\)H\(_9\)F\(_3\)NO\(_4\)Na: 404.1080; found: 404.1069.

**Compound 3c** was isolated after flash chromatography (n-pentane/EtO, 1:1); yield: 79 mg (97%); colorless solid; mp 138–140 °C; R\(_f\) = 0.26 (n-pentane/EtO, 1:1); [α]\(_D\)\(^{20}\) = 27.1 (c = 0.4, benzene).

HPLC: Daicel Chiralpak IB, n-heptane/i-PrOH (7:3), 0.7 mL/min, λ = 254 nm, t\(_{\text{R}}\) (minor) = 11.0 min, t\(_{\text{R}}\) (major) = 10.0 min; 95% ee.

1H NMR (600 MHz, CDCl3): δ = 7.37 (dd, J = 7.8, 1 H, H, ArH), 7.32 (s, 1 H, H, ArH), 7.23 (t, J = 7.7 Hz, 1 H, ArH), 7.06 (d, J = 7.5 Hz, 1 H, ArH), 7.07 (d, J = 2.2 Hz, 1 H, OC=CH), 4.89 (dd, J = 13.3, 3.9 Hz, 1 H, CH\(_\text{NO2}\)), 4.73 (dd, J = 13.3, 7.1 Hz, 1 H, CH\(_\text{NO2}\)), 4.55 (m, 1 H, CH\(_\text{CH2}\)), 2.55 (m, 2 H, CH\(_2\)), 2.35 (m, 3 H, CH\(_3\)), 2.32 (m, 2 H, CH\(_3\)), 1.17 (s, 3 H, CH\(_3\)), 1.16 (s, 3 H, CH\(_3\)).

13C NMR (151 MHz, CDCl3): δ = 130.8 (C q), 130.3 (C q), 128.8 (Ar C), 128.4 (Ar C), 128.4 (Ar C), 128.2 (Ar C), 125.7 (Ar C), 111.3 (C q), 106.9 (OC=CH), 75.7 (CH\(_3\NO2\)), 51.0 (CH\(_2\)), 41.7 (CH\(_2\)), 37.3 (CH\(_2\)), 34.4 [C(\text{CH}_3)], 29.0 (CH\(_3\)), 28.3 (CH\(_3\)), 21.5 (ArCH\(_2\)).

MS (EI, 70 eV): m/z (%): 327.2 (2, [M\(^+\)]), 328.2 (9, [M + H\(^+\)]), 281.3 (26, [M – NO\(_2\)]), 267.3 (17, [M – CH\(_2\NO2\)]).

HRMS (ESI\(^+\)): m/z [M + Na\(^+\)] calc for C\(_9\)H\(_9\)F\(_3\)NO\(_4\)Na: 350.1363; found: 350.1356.

1R (Z)-2-(Benzo[d][1,3]dioxol-5-ylmethylene)-6,6-dimethyl-3-(nitromethyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3f)

Compound 3f was isolated after flash chromatography (n-pentane/EtO, 1:2); yield: 87 mg (97%); colorless solid; mp 138–140 °C; R\(_f\) = 0.21 (n-pentane/EtO, 1:1); [α]\(_D\)\(^{20}\) = 47.2 (c = 0.4, benzene).

HPLC: Daicel Chiralpak IB, n-heptane/i-PrOH (7:3), 1.0 mL/min, λ = 254 nm, t\(_{\text{R}}\) (minor) = 9.8 min, t\(_{\text{R}}\) (major) = 13.8 min; 95% ee.

IR (ATR): 2957, 2290, 2086, 1644, 1547, 1474, 1403, 1238, 1280, 1214, 1171, 1039, 891, 846, 781, 697 cm\(^{-1}\).

1H NMR (600 MHz, CDCl3): δ = 7.42 (m, 1 H, ArH), 6.72 (m, 1 H, ArH), 6.64 (m, 1 H, ArH), 5.36 (dd, J = 2.1 Hz, 1 H, OC=CH), 5.27 (m, 2 H, OCH\(_2\O\)), 4.33 (dd, J = 12.9, 6.4 Hz, 1 H, CH\(_\text{NO2}\)), 4.18 (dd, J = 13.8, 3.0 Hz, 1 H, CH\(_\text{NO2}\)), 3.94 (s, 1 H, CH\(_\text{CH2}\)), 1.92 (d, J = 16.0 Hz, 1 H, CH\(_3\)), 1.56 (d, J = 17.9 Hz, 1 H, CH\(_3\)), 1.48 (d, J = 17.9 Hz, 1 H, CH\(_3\)), 0.63 (s, 3 H, CH\(_3\)), 0.57 (s, 3 H, CH\(_3\)).

13C NMR (151 MHz, CDCl3): δ = 191.7 (C q), 173.4 (C q), 151.9 (C q), 148.1 (C q), 146.8 (C q), 128.1 (C q), 123.1 (C q), 110.1 (C q), 108.6 (Ar C), 108.2 (Ar C), 106.0 (OC=CH), 100.8 (OCH\(_3\)), 75.4 (CH\(_3\NO2\)), 50.5 (CH\(_2\)), 41.8 (CH\(_2\)).

HRMS (ESI\(^+\)): m/z [M + Na\(^+\)] calc for C\(_9\)H\(_9\)F\(_3\)NO\(_4\)Na: 380.1105; found: 380.1094.
Compound 3g was isolated after flash chromatography (n-pentane/Et2O, 1:1 to 1:2); yield: 85 mg (94%); colorless solid; mp 135–137 °C; Rf = 0.14 (n-pentane/Et2O, 1:1); [α]D 24 +47.9 (c = 0.5, benzene).

HPLC: Daicel Chiralpak IB, n-heptane/i-PrOH (7:3); 0.7 mL/min, λ = 254 nm, tR (minor) = 11.1 min, tR (major) = 15.7 min; 96% ee.

IR (ATR): 3056, 2959, 1648, 1550, 1398, 1294, 1218, 1172, 1141, 1089, 1049, 1016, 989, 920, 884, 816, 747, 700, 671 cm–1.

Compound 5a was isolated after flash chromatography (n-pentane/Et2O, 1:2); yield: 56 mg (79%); colorless solid; mp 117–119 °C; Rf = 0.14 (n-pentane/Et2O, 1:1); [α]D 24 +74.9 (c = 0.5, benzene).

HPLC: Daicel Chiralpak AS, n-heptane/EOH (7:3); 0.5 mL/min, λ = 254 nm, tR (minor) = 13.3 min, tR (major) = 15.9 min; 98% ee.

IR (ATR): 3075, 2922, 2307, 1892, 1641, 1547, 1384, 1217, 1176, 1051, 974, 841, 696 cm–1.

IR (ATR): 3066, 2922, 2308, 2096, 1902, 1641, 1547, 1384, 1217, 1176, 1051, 974, 841, 696 cm–1.

Compound 3h was isolated after flash chromatography (n-pentane/Et2O, 1:1); yield: 82 mg (90%); colorless solid; mp 165–167 °C; Rf = 0.23 (n-pentane/Et2O, 1:1); [α]D 24 +110.1 (c = 0.4, benzene).

HPLC: Daicel Chiralpak IC, n-heptane/i-PrOH (7:3); 0.5 mL/min, λ = 230–240 °C, 1 H, CH2); 1.71 (d, J = 17.8 Hz, 1 H, CH3), 1.63 (d, J = 17.8 Hz, 1 H, CH3), 0.62 (s, 3 H, CH3), 0.57 (s, 3 H, CH3).

Compound 5b was isolated after flash chromatography (n-pentane/Et2O, 1:2); yield: 43 mg (63%); colorless solid; mp 153–155 °C; Rf = 0.24 (benzene).

HPLC: Daicel Chiralpak AS, n-heptane/EOH (7:3); 0.5 mL/min, λ = 254 nm, tR (major) = 15.9 min; 95% ee.

IR (ATR): 3065, 2959, 1648, 1530, 1294, 1218, 1172, 1141, 1089, 1019, 975, 815, 838, 780, 699 cm–1.


Compound 7c was isolated after flash chromatography (n-pentane/EtO, 1:1); yield: 86 mg (98%); colorless solid; mp 143–145 °C; 1H NMR (600 MHz, C6D6): δ = 7.51 (m, 4 H, ArH, ArH Diast.), 7.19 (m, 4 H, ArH, ArH Diast.), 7.04 (m, 8 H, ArH, ArH Diast.), 6.72 (m, 4 H, ArH, ArH Diast.); 13C NMR (151 MHz, C6D6): δ = 190.1 (C, ArC Diast.), 137.9 (C, ArC Diast.), 137.0 (C, ArC Diast.), 130.5 (C, ArC Diast.), 128.5 (4 C, ArC, ArC Diast.), 128.6 (4 C, ArC, ArC Diast.), 127.0 (2 C, ArC, ArC Diast.), 126.1 (4 C, ArC, ArC Diast.), 119.1 (4 C, ArC, ArC Diast.), 112.9 (6 C, ArC, ArC Diast.), 106.8 (OC=CH), 106.6 (OC=CH2), 75.7 (CH2NO2), 75.0 (CH2NO2), 43.7 (CH3), 43.6 (CH3 Diast.), 41.9 (CHC3H2 Diast.), 41.8 (CHC3H2 Diast.), 39.7 (CHF2), 39.6 (CHF2), 30.1 (CH3 Diast.), 30.0 (CH3 Diast.). HRMS (ESI+): m/z [M + Na]+ calcld for C27H19NO4Na: 384.1206; found: 384.1207.

**Synthesis**

(R)-(Z)-2-Benzylidene-6-(furan-2-yl)-3-(nitromethyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (7d)

Compound 7d was isolated after flash chromatography (n-pentane/EtO, 1:1); yield: 86 mg (98%); colorless solid; mp 143–145 °C; 1H NMR (600 MHz, C6D6): δ = 7.51 (m, 4 H, ArH, ArH Diast.), 7.19 (m, 4 H, ArH, ArH Diast.), 7.04 (m, 8 H, ArH, ArH Diast.), 6.72 (m, 4 H, ArH, ArH Diast.); 13C NMR (151 MHz, C6D6): δ = 190.1 (C, ArC Diast.), 137.9 (C, ArC Diast.), 137.0 (C, ArC Diast.), 130.5 (C, ArC Diast.), 128.5 (4 C, ArC, ArC Diast.), 128.6 (4 C, ArC, ArC Diast.), 127.0 (2 C, ArC, ArC Diast.), 126.1 (4 C, ArC, ArC Diast.), 119.1 (4 C, ArC, ArC Diast.), 112.9 (6 C, ArC, ArC Diast.), 106.8 (OC=CH), 106.6 (OC=CH2), 75.7 (CH2NO2), 75.0 (CH2NO2), 43.7 (CH3), 43.6 (CH3 Diast.), 41.9 (CHC3H2 Diast.), 41.8 (CHC3H2 Diast.), 39.7 (CHF2), 39.6 (CHF2), 30.1 (CH3 Diast.), 30.0 (CH3 Diast.). HRMS (ESI+): m/z [M + Na]+ calcld for C27H19NO4Na: 384.1206; found: 384.1207.


**Acknowledgment**

Financial support from the European Research Council (ERC Advanced Grant 320493 ‘DOMINOCAT’) is gratefully acknowledged. We thank Prof. Englert, Institute of Inorganic Chemistry for his help with the X-ray crystal structure determination of 5a.

**Supporting Information**

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561468.

**References**


(18) CCDC 1474771 (5a) and CCDC 1474975 (5d) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.
