Design and Synthesis of Angularly Annulated Spirocyclics via Enyne Metathesis and the Diels–Alder Reaction as Key Steps

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Abstract: We have developed a simple and an efficient route to a range of angularly fused spirocycles by the application of enyne metathesis and the Diels–Alder reaction as key steps. The enyne metathesis protocol has been further extended to the dibenzylation of indane-1,3-dione by using cross-enyne metathesis in the presence of hexa-1,5-diene with the aid of Grubbs' 1st generation catalyst followed by an aromatization sequence with DDQ.

Key words: active methylene compounds, cross-metathesis, Diels–Alder reaction, enyne metathesis, spirocyclic compounds

Since the development of ruthenium catalysts,[1] several metathesis protocols have opened up new and useful retrosynthetic strategies.[2] These advances have elevated organic synthesis to a higher level. The ring-closing enyne metathesis[3] (RCEM) protocol discovered by Katz in 1985 generate inner-outer 1,3-dienes, which are suitable for the Diels–Alder reaction. Generally, in the enyne metathesis sequence the alkylidene part migrates from the alkene to the alkyne carbon to deliver a conjugated diene and this skeletal reorganization is known as alkylidene migration reaction. Although ring-closing metathesis (RCM) is a useful route for the construction of carbon–carbon bonds, ring-closing enyne metathesis is unique and it is useful for the construction of conjugated 1,3-dienes containing polar functional groups in a single step. Over the last two decades, the metathesis sequence has been applied to generate challenging ring systems in natural products,[3k,4] in particular macrocyclic compounds and other biologically relevant substances. A number of selected bioactive natural products prepared by the enyne metathesis sequence are shown in Figure 1.[5] A simple access to dienes helps to expand the scope of the Diels–Alder reaction in preparative organic chemistry. It is worth noting that the Diels–Alder reaction is a powerful tool that enhances molecular diversity immensely in a single step.

Spirocyclics[2b,6] have attracted the attention of synthetic organic chemists because they constitute core structural units in several biologically important targets.[7] Molecules containing angularly fused aromatic systems with an extended π-framework are useful in designing electronic organic materials. These systems can create intricate molecular frameworks due to their unusual packing arrangement, which is difficult in linearly annulated structures. Although, a number of synthetic methods[8] are reported for the construction of linearly fused spirocyclics, only a limited number of strategies are available for the synthesis of angularly annulated spirocyclics. In our preliminary report,[9] we reported a simple synthetic strategy for the angularly annulation of indane-based spirocyclics starting with indane-1,3-dione (**5**) (Scheme 1, Figure 3).[10] Here, we report the full details of our preliminary work and also its extension to the generation of a library of angularly fused spirocyclics. We have assembled diverse spirocyclics by the sequential use of enyne metathesis and the Diels–Alder reaction which are atom-economic. We have also expanded the metathesis sequence to a dibenzylated product by employing a cross-enyne metathesis and aromatization sequence. The active methylene components and the Grubbs' catalysts used in our study are shown in Figure 2.

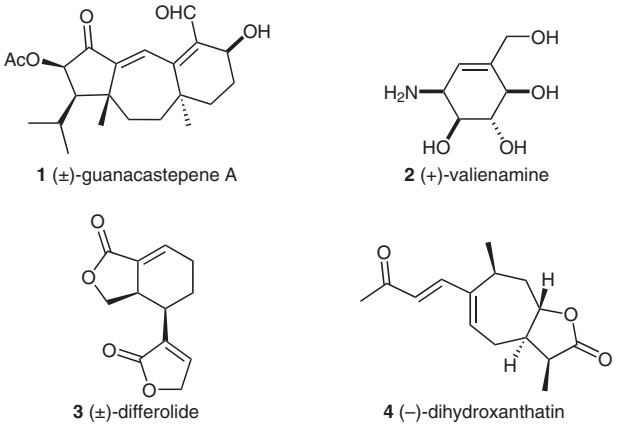

Figure 1 Some important natural products synthesized by the metathesis protocol

Our investigation started with the selective monoallylation of active methylene compounds. To achieve the monoallylation of **5**, different conditions were examined. However, our attempts clearly indicated that the formation of the diallylated compound is unavoidable (Scheme 1, Table 1). After extensive experimentation, we found that monoallylated product **7** was obtained in 34% yield along with a small amount of unidentified compound by using 20% aqueous potassium hydroxide and a catalytic amount of copper powder at room temperature (entry 2). We have also found an alternative route i.e. monopropargylation followed by allylation of indane-1,3-dione is a better route than the allylation followed propargylation to

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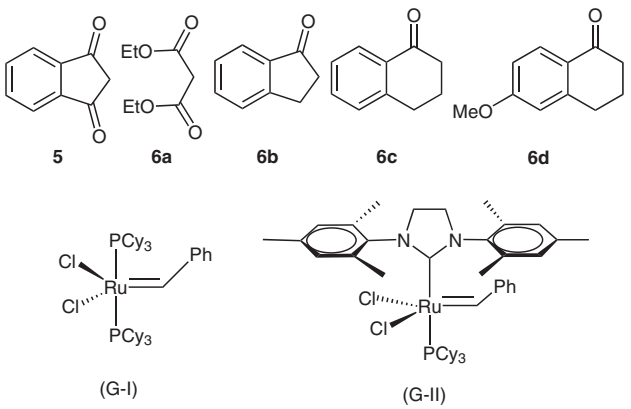


Figure 2 Active methylene components and the Grubbs' catalysts used in our strategy

generate the enyne building block **10**. Having the monoallylated compound **7** in hand, it was successfully converted into the enyne building block **10**. Later, different conditions were attempted to generate the diene building block **11** using a metathesis protocol in dry dichloromethane in the presence of Grubbs' 1st generation (G-I) or Grubbs' 2nd generation (G-II) catalyst. Since, the groups of Fürstner and Mori have reported the effects of titanium isopropoxide[11] and ethylene[12] in the facilitation of the metathesis sequence, we used a catalytic amount of titanium isopropoxide under ethylene atmosphere in dry dichloromethane in presence of Grubbs' 2nd generation catalyst, and the diene **11** was obtained in 48% yield (Table 2). The diene **11** was subjected to the Diels–Alder sequence with various dienophiles to generate cycloaddition products. During the Diels–Alder sequence a small amount of aromatized products was also obtained. Therefore, we did not isolated the Diels–Alder adducts and they were directly subjected to the aromatization sequence. Subsequent dehydrogenation with manganese(IV) oxide of these Diels–Alder adducts in refluxing 1,4-dioxane gave the corresponding aromatized products (Figure 3).

Table 1 Various Conditions Attempted for the Monoallylation of **5**

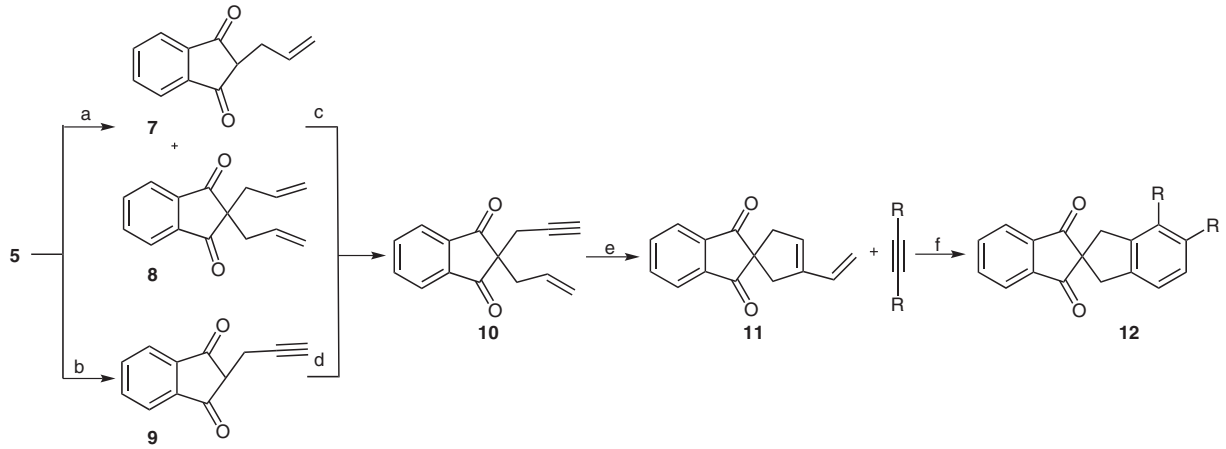
Entry	Reaction conditions	Yield[a] (%)	
		7	**8**
1	10% aq KOH, Cu powder, r.t., 8 h	20	–
2	20% aq KOH, Cu powder, r.t., 8 h	34	–
3	25% aq KOH, Cu powder, r.t., 8 h	30	–
4	KF-Celite, MeCN, reflux, 12 h	6	52
5	KF-Celite, MeCN, r.t., 12 h	15	43
6	NaH, THF, r.t., 2 h	18	59
7	NaH, THF, r.t., 0.5 h	24	40
8	K_2CO_3, TBAHS, MeCN, reflux, 4 h	8	51
9	K_2CO_3, TBAHS, MeCN, r.t., 12 h	13	63
10	K_2CO_3, TBAHS, MeCN, 0 °C, 8 h	9	55

[a] Isolated yields.

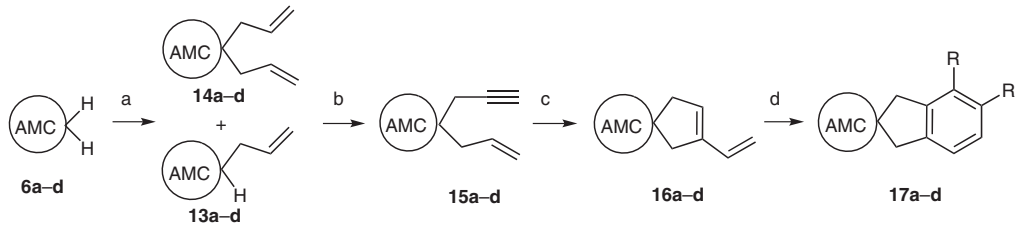
Table 2 Different Conditions Attempted for Enyne Metathesis of Building Block **10**

Entry	Reaction conditions	Yield[a] (%)
1	G-I (5 mol%), CH_2Cl_2, r.t., 15 h	19
2	G-I (5 mol%), Ti(O*i*-Pr)$_4$, CH_2Cl_2, r.t., 15 h	32
3	G-II (7.5 mol%), CH_2Cl_2, r.t., 16 h	27
4	G-II (7.5 mol%), Ti(O*i*-Pr)$_4$, CH_2Cl_2, r.t., 16 h	34
5	G-II (7.5 mol%), Ti(O*i*-Pr)$_4$, ethylene, CH_2Cl_2, r.t., 16 h	48

[a] Isolated yield along with some unidentified polymerized material.



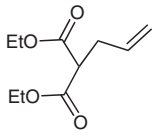
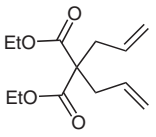
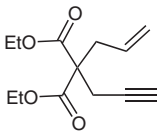
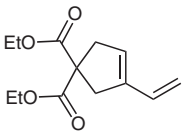
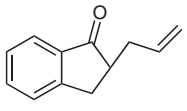
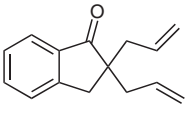
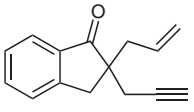
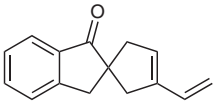
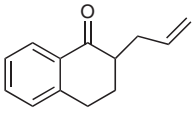
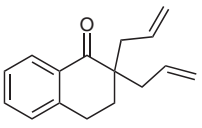
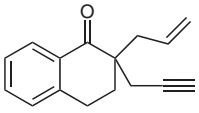
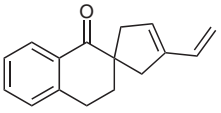
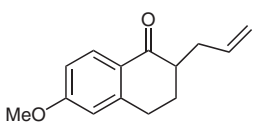
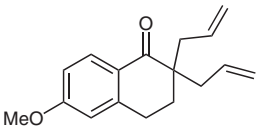
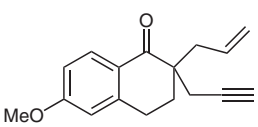
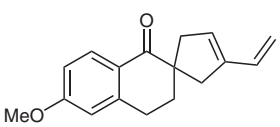
Scheme 1 Construction of angularly fused spirocyclics of **5**; *Reagents and conditions*: (a) conditions shown in Table 1; (b) 10% aq KOH, Cu powder, propargyl bromide, r.t., 72 h, 56%; (c) K_2CO_3, TBAHS, propargyl bromide, MeCN, r.t., 16 h, 75%; (d) K_2CO_3, TBAHS, allyl bromide, MeCN, r.t., 24 h, 68%; (e) conditions shown in Table 2 (f) 1. dienophiles, toluene, reflux, 12–24 h; 2. MnO_2, 1,4-dioxane, reflux, 24 h, 49–76%.



Scheme 2 Synthesis of spirocyclics of **6a–d**; *Reagents and conditions*: (a) NaH, allyl bromide, THF, r.t., 1.5–12 h, monoallyl product 39–63%, diallyl product 13–26%; (b) NaH, propargyl bromide, THF, r.t., 12–20 h, 61–79%; (c) G-II (7.5 mol%), Ti(O*i*-Pr)$_4$(20 mol%), ethylene, CH_2Cl_2, r.t., 5–16 h, 51–68%; (d) 1. dienophile, toluene, reflux, 8–24 h; 2. DDQ, toluene, reflux, 24 h, 59–75%.

To extend this strategy to other angularly fused spirocyclics, we prepared several dienes by varying the active methylene compound. In this regard, we used commercially available and inexpensive starting material such as diethyl malonate (**6a**). The monoallyl compound **13a** was obtained in 63% yield along with the diallylated product **14a** (24% yield) using sodium hydride and allyl bromide in tetrahydrofuran (Scheme 2, Table 3). Next, the monoallylated compound **13a** was successfully transformed into the enyne building block **15a** using sodium hydride and propargyl bromide in 79% yield. Subsequently, enyne metathesis in dry dichloromethane in the presence of Grubbs' 2nd generation catalyst gave the diene **16a** in 65% yield, which was further subjected to Diels–Alder reaction with various dienophiles followed by aromatization with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing toluene to afford the aromatized products (Figure 3). We also extended this strategy to other active methylene compounds with only one carbonyl group such as indan-1-one and 1-tetralones to deliver angularly fused spirocyclics. In case of 2,3-dihydro-1*H*-inden-1-one (**6b**), monoallylation gave **13b** in 39% yield under sodium hydride/allyl bromide conditions (Scheme 2, Table 3). Along similar lines, 3,4-dihydronaphthalen-1(2*H*)-one (**6c**) gave monoallylated compound **13c** in 54% yield using similar reaction conditions. In addition, we have also observed that, 6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (**6d**) delivered the monoallylated compound in 57% yield (Table 3). These monoallylated compounds **13b–d** were converted into the corresponding enyne building blocks **15b–d**; the propargylation of monoallylated compound **13b** gave a small amount of unexpected product **15b′** (Table 3, Scheme 3, the monoallylated compound **13b** was contaminated by a small amount of starting ma-

Table 3 Various Diene Building Blocks Prepared Using the Enyne Metathesis Sequence

13a–d (yield)	**14a–d** (yield)	Time (h)	**15a–d** (yield)	Time (h)	**16a–d** (yield)	Time (h)
		12		16		12
13a (63%)	**14a** (24%)		**15a** (79%)		**16a** (65%)	
		1.5		12		16
13b (39%)	**14b** (26%)		**15b** (61%) + **15b′** (6%)[a]		**16b** (51%)	
		3		15		8
13c (54%)	**14c** (18%)		**15c** (78%)		**16c** (68%)	
		6		20		5
13d (57%)	**14d** (13%)		**15d** (71%)		**16d** (58%)	

[a] Minor amount of unexpected product **15b′** isolated along with desired product

terial that could not be separated by column chromatography) which was also isolated and confirmed by ^{1}H and ^{13}C NMR spectral data and further supported by mass spectral data. Next, these enyne building blocks **15b–d** were subjected to ring-closing enyne metathesis to generate the inner-outer dienes **16b–d**. Treatment of these dienes **16b–d** with various dienophiles delivered the expected Diels–Alder adducts. Since these Diels–Alder adducts were contaminated with a minor amount of aromatized products, no effort was made to characterize these impure Diels–Alder adducts. Subsequently, these Diels–Alder adducts were subjected dehydrogenation with DDQ in refluxing toluene to deliver the corresponding aromatized products (Figure 3).

Our goal to generate the bis-diene **34** started with dipropargylation of 1*H*-indane-1,3(2*H*)-dione (**5**) under potassium carbonate/propargyl bromide conditions, the dialkyne building block **33** was obtained in 85% yield. The diyne **33** was treated with ethylene in the presence of Grubbs' 1st and 2nd generation catalysts in dry dichloromethane. To our surprise, **33** failed to deliver the bis-diene **34**. However, when compound **33** was treated with hexa-1,5-diene in the presence of Grubbs' 1st generation catalyst in dry dichloromethane, compound **35** was obtained in 59% yield. Surprisingly, treatment of compound **35** with various dienophiles such as dimethyl acetylenedicarboxylate, tetracyanoethylene, 1,4-benzoquinone, and 1,4-naphthoquinone did not afford the desired Diels–Alder

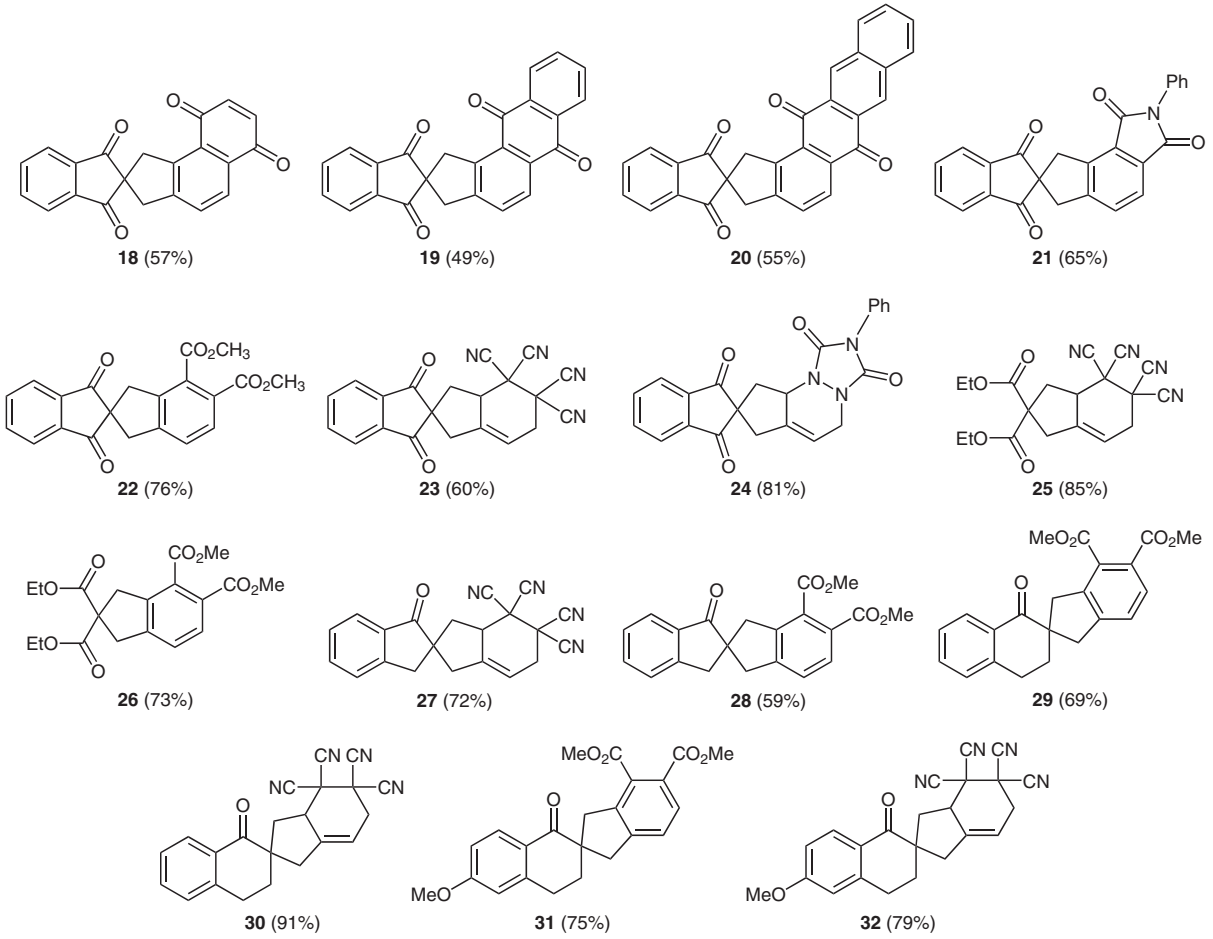
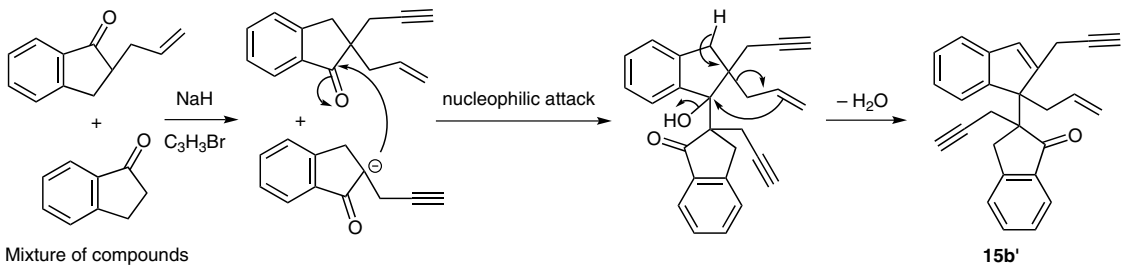
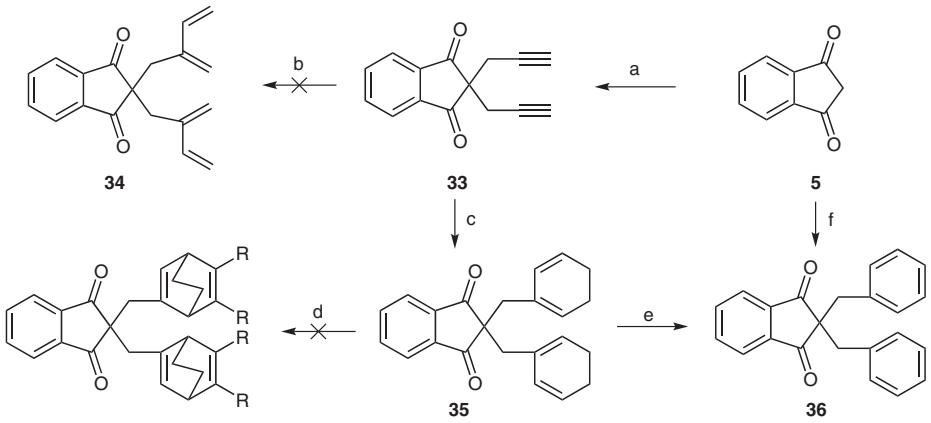


Figure 3 Diverse angularly fused spirocyclics assembled via enyne metathesis and Diels–Alder reaction



Scheme 3 Plausible mechanism for the formation of unexpected product **15b′**



Scheme 4 Dibenzylation of 1*H*-indene-1,3(2*H*)-dione (**5**) using cross enyne metathesis; *Reagents and conditions*: (a) K_2CO_3, TBAHS, propargyl bromide, MeCN, r.t., 7 h, 85%; (b) G-I/G-II (10 mol%), ethylene, CH_2Cl_2, r.t., 20 h; (c) G-I (10 mol%), hexa-1,5-diene, CH_2Cl_2, r.t., 6 h, 59%; (d) dienophiles (R = electron withdrawing group), toluene, reflux; (e) DDQ, toluene, reflux, 18 h, 94%; (f) K_2CO_3, TBAHS, BnBr, MeCN, r.t., 12 h, 79%.

adducts. On the other hand, dehydrogenation of compound **35** with DDQ in refluxing toluene gave the aromatized product **36** in 94% yield (Scheme 4). To establish the structure of compound **36**, an independent synthesis was undertaken by treating compound **5** with benzyl bromide using potassium carbonate as the base in acetonitrile to deliver **36** in 79% yield (Scheme 4). The spectral data of the dibenzylated compound obtained by this route was found to be identical to that of the compound obtained by the earlier route.

We have demonstrated a simple and useful method for the construction of angularly fused spirocyclics by the application of enyne metathesis and the Diels–Alder reaction as key steps. A variety of dienes were prepared by the enyne metathesis sequence and reacted with several dienophiles such as dimethyl acetylenedicarboxylate, tetracyanoethylene, 1,4-benzoquinone, 1,4-naphthoquinone, 1,4-anthraquinone, 4-phenyl-1,2,4-triazoline-3,5-dione, and *N*-phenylmaleimide to generate a library of angularly fused spirocyclic compounds. Further, the enyne metathesis sequence was expanded to generate dibenzylated product **36** involving cross enyne metathesis in the presence of hexa-1,5-diene with the aid of Grubbs 1st generation catalyst in dry dichloromethane. Advantageously, all the starting materials are simple, commercially available and the final products are found to be a key structural elements present in various biologically active substances. Our strategy may be applicable for the synthesis of highly functionalized spirocyclics of chemically and biologically interest in a diversity oriented fashion.[13]

Commercially available reagents were used without purification and reactions involving air sensitive reagents or catalysts were performed in degassed solvents. TBAHS = tetrabutylammonium hydrogensulfate Moisture sensitive materials were transferred using standard syringe-septum techniques and the reactions were maintained under a N_2 atmosphere. Analytical TLC was performed on (7.5 × 2.5 cm) glass plates coated with Acme silica gel GF 254 (containing 13% $CaSO_4$ as a binder) using EtOAc–petroleum ether (PE) for development. Column chromatography was performed using Acme silica gel (100–200 mesh) with EtOAc–PE. Yields refer to the isolated yields after column chromatography. Grubbs' catalysts were purchased from Sigma Aldrich. Infrared spectra were recorded on Nicolet Impact-400 FT IR spectrophotometer in KBr/(neat). ^{1}H NMR (400 MHz and 500 MHz) spectra and ^{13}C NMR (100 MHz and 125.8 MHz) spectra were recorded on a Bruker spectrometer. HRMS measurements were carried out by using electrospray ionization (ESI), (Q-ToF) spectrometer. Melting points were recorded on a Büchi B-545 melting point apparatus.

2-Allyl-1*H*-indene-3(2*H*)-dione (7)

To 20% aq KOH solution were added **5** (3.5 g, 23.97 mmol) and Cu powder (1.2 g, 19.05 mmol), and the mixture was stirred at r.t. for 15 min. Allyl bromide (3 mL, 34.66 mmol) was added dropwise using a dropping funnel and stirring was continued at this temperature for 8 h. At the conclusion of the reaction (TLC monitoring), Cu powder was filtered through a sintered funnel, dil HCl was added at 0 °C (pH 2–3) to the mixture and the aqueous layer was extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, 5% EtOAc–PE) to afford **7** (1.5 g, 34%) as a yellow viscous liquid. ^{1}H and ^{13}C NMR spectra matched with the literature data.[14]

Monoallyl Products 13a–d; General Procedure

To a suspension of NaH (3 equiv) in anhyd THF (25–30 mL), **6a–d** was added and the mixture was stirred at r.t. for 10 min. Then allyl bromide (1.1–1.2 equiv) was added and stirring was continued for 1.5–12 h at this temperature. At the conclusion of the reaction (TLC monitoring), the mixture was diluted with EtOAc and the aqueous layer was extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the crude products were purified by column chromatography (silica gel, 1–2% EtOAc–PE) to afford the desired products **13a–d**.

Diethyl 2-Allylmalonate (13a) and Diethyl 2,2-Diallylmalonate (14a)

Following the general procedure gave **13a** (1.52 g, 63%) as a thick colorless liquid and **14a** (693 mg, 24%) also as a thick colorless liquid. The ^{1}H and ^{13}C NMR spectra matched with the literature data.[15]

2-Allyl-2,3-dihydro-1*H*-inden-1-one (13b) and 2,2-Diallyl-2,3-dihydro-1*H*-inden-1-one (14b)

Following the general procedure gave **13b** (353 mg, 39%) as a thick yellow liquid and **14b** (297 mg, 26%) also as a thick yellow liquid. The ^{1}H and ^{13}C NMR spectra matched with the literature data.[16]

2-Allyl-3,4-dihydronaphthalen-1(2*H*)-one (13c) and 2-Diallyl-3,4-dihydronaphthalen-1(2*H*)-one (14c)
Following the general procedure gave **13c** (624 mg, 54%) as a thick yellow liquid, **14c** (320 mg, 18%) also as a thick yellow liquid, and recovered starting material (290 mg). The ^{1}H and ^{13}C NMR spectra matched with the literature data.[17]

2-Allyl-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (13d) and 2-Diallyl-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (14d)
Following the general procedure gave **13d** (358 mg, 57%) as a thick yellow liquid, **14d** (96 mg, 13%) also as a thick yellow liquid, and recovered starting material (492 mg). The ^{1}H and ^{13}C NMR spectra matched with the literature data.[18]

2-Allyl-2-prop-2-ynyl-1*H*-inden-1,3(2*H*)-dione (10)
To a solution of **7** (480 mg, 2.58 mmol) in MeCN (20 mL) were added K_2CO_3 (750 mg, 5.43 mmol) and TBAHS (150 mg, 0.44 mmol) and the mixture was stirred at r.t. for 15 min. Propargyl bromide (0.6 mL, 6.73 mmol) was added and the stirring was continued at the this temperature for 16 h. At the conclusion of the reaction (TLC monitoring), excess K_2CO_3 was filtered off through a sintered funnel and the aqueous layer was extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, 4% EtOAc–PE) to afford **10** (435 mg, 75%) as a thick yellow liquid; mp 107–109 °C; R_f = 0.46 (PE–EtOAc, 80:20).

IR (KBr): 1597, 1706, 2923, 3001 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74 (t, J = 2.64 Hz, 1 H), 2.54 (d, J = 7.44 Hz, 2 H), 2.67 (d, J = 2.64 Hz, 2 H), 4.94 (dd, J_1 = 1.68 Hz, J_2 = 10.04 Hz, 1 H), 5.08 (dd, J_1 = 1.68 Hz, J_2 = 16.98 Hz, 1 H), 5.43–5.53 (m, 1 H), 7.84–7.89, (m, 2 H), 7.97–8.03 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.06, 38.57, 56.86, 71.53, 78.41, 120.17, 123.33, 130.96, 136.04, 142.39, 202.10.

HRMS (ESI, Q-ToF): m/z [M + H]$^+$ calcd for $C_{15}H_{13}O_2$: 225.0916; found: 225.0907.

Monoallyl-monopropargyl Products 15a–d; General Procedure
To a suspension of NaH (3 equiv) in anhyd THF (20 mL), **13a–d** was added and the mixture was stirred at r.t. for 15 min. Then propargyl bromide (2–3 equiv) was added and stirring was continued for 12–20 h at this temperature. At the conclusion of the reaction (TLC monitoring), the mixture was diluted with EtOAc and the aqueous layer was extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the crude products were purified by column chromatography (silica gel, 2–3% EtOAc–PE) to afford the desired enyne building blocks **15a–d**.

Diethyl 2-Allyl-2-prop-2-ynylmalonate (15a)
Following the general procedure gave **15a** (943 mg, 79%) as a yellow liquid. The ^{1}H and ^{13}C NMR spectra matched with the literature data.[19]

2-Allyl-2-prop-2-ynyl-2,3-dihydro-1*H*-inden-1-one (15b) and 2-(1-Allyl-2-propy-2-ynyl-1*H*-inden-1-yl)-2-prop-2-ynyl-2,3-dihydro-1*H*-inden-1-one (15b′)
To a suspension of NaH (280 mg, 8.72 mmol) in anhyd THF (20 mL), **13b** (500 mg, 2.91 mmol) was added and the mixture was stirred at r.t. for 15 min. Then, propargyl bromide (0.80 mL, 8.72 mmol) was added and stirring was continued for 12 h at this temperature. At the conclusion of the reaction (TLC monitoring), the mixture was diluted with EtOAc and the aqueous layer was extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, 3% EtOAc–PE) to afford **15b** as a thick yellow liquid (372 mg, 61%) along with unexpected compound **15b′** (63 mg, 6%) as a yellow solid.

Compound 15b
R_f = 0.53 (silica gel, 5% EtOAc–PE).

IR (neat): 1608, 1640, 1710, 2187, 2922, 3077, 3301 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88 (t, J = 2.64 Hz, 1 H), 2.38–2.50 (m, 4 H), 3.12, 3.25 (ABq, J = 17.41 Hz, 2 H), 4.98–5.13 (m, 2 H), 5.52–5.63 (m, 1 H), 7.35–7.39 (m, 1 H), 7.45–7.47 (m, 1 H), 7.59–7.63 (m, 1 H), 7.75 (d, J = 7.68 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.48, 36.87, 41.32, 51.67, 70.51, 80.56, 119.19, 124.27, 126.61, 127.64, 132.89, 135.32, 136.29, 153.15, 208.73.

HRMS (ESI, Q-ToF): m/z [M + H]$^+$ calcd for $C_{15}H_{15}O$: 211.1123; found: 211.1117.

Compound 15b′
Yellow solid; mp 122–124 °C; R_f = 0.48 (silica gel, 5% EtOAc–PE).

IR (neat): 1606, 1640, 1709, 2118, 2124, 2846, 3017, 3307 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (t, J = 2.60 Hz, 2 H), 2.54–2.70 (m, 4 H), 2.73–2.90 (m, 2 H), 3.41, 3.55 (ABq, J = 17.58 Hz, 2 H), 4.95 (dd, J_1 = 0.84 Hz, J_2 = 9.24 Hz, 1 H), 5.14 (dd, J_1 = 1.56 Hz, J_2 = 16.96 Hz, 1 H), 5.55–5.62 (m, 1 H), 6.47 (s, 1 H), 6.93–6.95 (m, 1 H), 7.12–7.19 (m, 2 H), 7.41–7.48 (m, 2 H), 7.61–7.66 (m, 2 H), 7.83 (d, J = 7.64 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.34, 25.40, 37.93, 41.39, 51.74, 53.62, 70.58, 70.75, 81.10, 119.05, 120.82, 122.80, 124.38, 125.56, 126.55, 127.55, 127.81, 132.84, 135.42, 136.72, 137.98, 141.90, 144.21, 149.52, 152.66, 207.12.

HRMS (ESI, Q-ToF): m/z [M + H]$^+$ calcd for $C_{27}H_{23}O$: 363.1749; found: 363.1753.

2-Allyl-2-prop-2-ynyl-3,4-dihydronaphthalen-1(2*H*)-one (15c)
Following the general procedure gave **15c** (479 mg, 78%) as a yellow liquid; R_f = 0.78 (silica gel, 5% EtOAc–PE).

IR (neat): 1601, 1639, 1680, 2118, 2931, 3074, 3301 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (t, J = 2.68 Hz, 1 H), 2.16–2.32 (m, 2 H), 2.36–2.42 (m, 1 H), 2.49–2.60 (m, 3 H), 2.94–3.13 (m, 2 H), 5.06–5.11 (m, 2 H), 5.67–5.78 (m, 1 H), 7.24 (d, J = 7.72 Hz, 1 H), 7.32 (t, J = 7.44 Hz, 1 H), 7.48 (dt, J_1 = 1.40 Hz, J_2 = 8.84 Hz, 1 H), 8.04 (dd, J_1 = 1.16 Hz, J_2 = 7.88 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.06, 25.20, 30.99, 38.27, 47.70, 71.19, 81.01, 119.05, 126.95, 128.26, 128.93, 131.64, 133.09, 133.57, 143.23, 199.93.

HRMS (ESI, Q-ToF): m/z [M + Na]$^+$ calcd for $C_{16}H_{16}NaO$: 247.1093; found: 247.1093.

2-Allyl-6-methoxy-2-prop-2-ynyl-3,4-dihydronaphthalen-1(2*H*)-one (15d)
Following the general procedure gave **15d** (582 mg, 71%) as a yellow liquid; R_f = 0.77 (silica gel, 5% EtOAc–PE).

IR (neat): 1600, 1673, 1728, 2117, 2939, 3007, 3075, 3296 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (t, J = 2.60 Hz, 1 H), 2.13–2.30 (m, 2 H), 2.34–2.40 (m, 1 H), 2.47–2.59 (m, 3 H), 2.89–3.05 (m, 2 H), 3.86 (s, 3 H), 5.07–5.10 (m, 2 H), 5.68–5.76 (m, 1 H), 6.68 (d, J = 2.20 Hz, 1 H), 6.83 (dd, J_1 = 2.40 Hz, J_2 = 8.76 Hz, 1 H), 8.01 (d, J = 8.76 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.21, 25.64, 31.04, 38.57, 47.41, 55.63, 71.10, 81.20, 112.55, 113.63, 118.88, 125.27, 130.73, 133.33, 145.75, 163.76, 198.71.

HRMS (ESI, Q-ToF): m/z [M + Na]$^+$ calcd for $C_{17}H_{18}NaO_2$: 277.1199; found: 277.1193.

Enyne Metathesis of 10 and 15a–d; General Procedure
The solution of enynes **10** and **15a–d** in CH_2Cl_2 (20 mL) was degassed with N_2 for 10 min, after that, G-II (7.5 mol%) and Ti(O*i*-Pr)$_4$ (20 mol%) were added and the reaction vessel was kept under ethylene pressure (balloon pressure). The mixture was stirred at r.t. for 5–16 h. At the conclusion of the reaction (TLC monitor-

ing), the solvent was removed under reduced pressure and the crude products were purified by column chromatography (silica gel, 3–5% EtOAc–PE) to afford the desired dienes **11** and **16a–d**.

3-Vinylspiro[cyclopent-3-ene-1,2′-indene]-1′,3′-dione (11)
Following the general procedure gave **11** (67 mg, 48%) as a white solid; mp 123–124 °C; R_f = 0.41 (PE–EtOAc, 80:20).

IR (KBr): 1597, 1742, 2854 , 2923, 3011 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.85–2.87 (m, 4 H), 5.03 (d, J = 17.52 Hz, 1 H), 5.12 (d, J = 10.72 Hz, 1 H), 5.72–5.73 (br, 1 H), 6.54–6.62 (m, 1 H), 7.86–7.88 (m, 2 H), 8.01–8.03 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.70, 41.56, 57.77, 115.51, 123.78, 127.58, 132.34, 135.96, 140.68, 141.76, 203.50.

HRMS (ESI, Q-ToF): m/z [M + H]$^+$ calcd for $C_{15}H_{13}O_2$: 225.0916; found: 225.0912.

Diethyl 3-Vinylcyclopent-3-ene-1,1-dicarboxylate (16a)
Following the general procedure gave **16a** (130 mg, 65%) as a thick colorless liquid. The ^{1}H and ^{13}C NMR spectra matched with the literature reported spectral data.[20]

3-Vinylspiro[cyclopent-3-ene-1,2′-inden]-1′(3′*H*)-one (16b)
Following the general procedure gave **16b** (178 mg, 51%) as a yellow liquid; R_f = 0.47 (silica gel, 10% EtOAc–PE).

IR (neat): 1608, 1640, 1701, 2926, 3017 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38–2.48 (m, 2 H), 2.98 (d, J = 14.40 Hz, 2 H), 3.19 (s, 2 H), 5.04 (dd, J_1 = 10.64, Hz, J_2 = 18.16 Hz, 2 H), 5.71(s, 1 H), 6.56 (dd, J_1 = 10.60, Hz, J_2 = 17.41 Hz, 1 H), 7.37–7.45 (m, 2 H), 7.58–7.62 (m, 1 H), 7.79 (d, J = 7.64 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.58, 45.50, 45.55, 55.62, 114.81, 124.40, 126.62, 127.65, 128.35, 133.09, 134.98, 136.25, 141.17, 152.81, 210.15.

HRMS (ESI, Q-ToF): m/z [M + K]$^+$ calcd for $C_{15}H_{14}KO$: 249.0676; found: 249.0688.

3-Vinyl-3′,4′-dihydrospiro[cyclopent-3-ene-1,2′-naphthalen]-1′-one (16c)
Following the general procedure gave **16c** (54 mg, 68%) as a yellow liquid; R_f = 0.76 (silica gel, 5% EtOAc–PE).

IR (neat): 1601, 1681, 2931, 3019 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16–2.22 (m, 2 H), 2.43–2.55 (m, 2 H), 2.95–3.06 (m, 4 H), 5.01–5.10 (m, 2 H), 5.63 (s, 1 H), 6.49–6.57 (m, 1 H), 7.21–7.36 (m, 2 H), 7.43–7.47 (m, 1 H), 8.06 (dd, J_1 = 1.04, J_2 = 7.80 Hz, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 26.17, 35.10, 39.98, 41.84, 52.02, 114.43, 126.85, 127.95, 128.44, 128.83, 131.69, 133.31, 133.38, 140.41, 143.59, 201.03.

HRMS (ESI, Q-ToF): m/z [M + Na]$^+$ calcd for $C_{16}H_{16}NaO$: 247.1093; found: 247.1091.

6′-Methoxy-3-vinyl-3′,4′-dihydrospiro[cyclopent-3-ene-1,2′-naphthalen]-1′-one (16d)
Following the general procedure gave **16d** (69 mg, 58%) as a yellow liquid; R_f = 0.74 (silica gel, 50% EtOAc–PE).

IR (neat): 1609, 1640, 1710, 2843, 2922, 3077 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15–2.20 (m, 2 H), 2.46–2.59 (m, 2 H), 2.95–3.05 (m, 4 H), 3.86 (s, 3 H), 5.00–5.30 (m, 2 H), 5.64 (s, 1 H), 6.50–6.58 (m, 1 H), 6.68 (d, J = 2.24 Hz, 1 H), 66.83 (dd, J_1 = 1.56, J_2 = 8.76 Hz, 1 H), 8.04 (d, J = 8.80 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.42, 35.12, 40.07, 41.94, 51.59, 55.49, 112.35, 113.35, 114.23, 125.09, 127.91, 130.66, 133.30, 140.31, 145.96, 163.45, 199.91.

HRMS (ESI, Q-ToF): m/z [M + H]$^+$ calcd for $C_{17}H_{19}O_2$: 255.1380; found: 255.1379.

Diels–Alder Reaction of 11, 16a–d and Subsequent Aromatization; General Procedure
To a solution of diene **11**, **16a–d** in toluene, dienophile (1.5 equiv) was added and the mixture was refluxed for 8–24 h. At the conclusion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude products were purified by column chromatography (silica gel, EtOAc–PE) to afford the Diels–Alder adducts. Aromatization of the Diels–Alder adducts was carried out with activated MnO_2 (10 equiv, 100% conversion) in 1,4-dioxane or DDQ (4 equiv, 100% conversion) in toluene at reflux temperature for 20–24 h. Then, the solvent was removed under reduced pressure and the crude products were purified by column chromatography (silica gel, EtOAc–PE) to deliver aromatized products.

Compound 18
Following the general procedure using MnO_2 gave **18** (21 mg, 57%) as a yellow solid; mp 168–170 °C; R_f = 0.40 (silica gel, 40% EtOAc–PE).

IR (KBr): 1593, 1664, 1710, 1745, 2929, 3056 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (s, 2 H), 3.79 (s, 2 H), 6.88 (d, J = 10.28 Hz, 1 H), 6.95 (d, J = 10.32 Hz, 1 H), 7.61 (d, J = 7.85 Hz, 1 H), 7.91–7.94 (m, 2 H), 8.02–8.07 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.35, 42.51, 59.11, 124.01, 127.21, 127.93, 129.39, 131.90, 136.35, 138.49, 139.07, 141.62, 142.33, 149.74, 185.01, 186.55, 202.50.

HRMS (ESI, Q-ToF): m/z [M + H]$^+$ calcd for $C_{21}H_{13}O_4$: 329.0814; found: 329.0813.

Compound 19
Following the general procedure using MnO_2 gave **19** (18 mg, 49%) as a yellow solid; mp 174–176°C; R_f = 0.44 (silica gel, 40% EtOAc–PE).

IR (KBr): 1593, 1671, 1700, 1742, 2917, 3066 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 2 H), 3.93 (s, 2 H), 7.66 (d, J = 7.88 Hz, 1 H), 7.72–7.76 (m, 2 H), 7.90–7.94 (m, 2 H), 8.02–8.07 (m, 2 H), 8.20–8.22 (m, 1 H), 8.28–8.31 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.31, 43.28, 59.26, 124.01, 127.18, 127.25, 128.08, 129.59, 129.64, 133.47, 133.57, 133.97, 134.11, 134.19, 136.31, 141.67, 143.00, 149.91, 183.19, 184.55, 202.59.

HRMS (ESI, Q-ToF): m/z [M + H]$^+$ calcd for $C_{25}H_{15}O_4$: 379.0970; found: 379.0980.

Compound 20
Following the general procedure using MnO_2 gave **20** (21 mg, 55%) as a yellow solid; mp 171–173 °C; R_f = 0.50 (silica gel, 40% EtOAc–PE).

IR (KBr): 1618, 1672, 1706, 1739, 2846, 2920, 3055 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.47 (s, 2 H), 3.97 (s, 2 H), 7.64–7.68 (m, 3 H), 7.90–7.94 (m, 2 H), 8.05–8.09 (m, 4 H), 8.36 (d, J = 7.88 Hz, 1 H), 8.82 (s, 1 H), 8.72 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.37, 43.47, 59.29, 124.02, 128.35, 129.46, 129.53, 129.68, 129.80, 130.27, 130.32, 130.61, 134.57, 135.26, 135.33, 136.31, 141.71, 143.19, 149.90, 183.05, 184.36, 202.68.

HRMS (ESI, Q-ToF): m/z [M + H]$^+$ calcd for $C_{29}H_{17}O_4$: 429.1127; found: 429.1138.

Compound 21
Following the general procedure using MnO_2 gave **21** (29 mg, 65%) as a yellow solid; mp 108–110 °C; R_f = 0.42 (silica gel, 40% EtOAc–PE).

IR (KBr): 1593, 1714, 1742, 2925, 3055 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 2 H), 3.71 (s, 2 H), 7.37–7.43 (m, 3 H), 7.48–7.52 (m, 2 H), 7.63 (d, *J* = 7.57 Hz, 1 H), 7.85 (d, *J* = 7.56 Hz, 1 H), 7.91–7.94 (m, 2 H), 8.03–8.06 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.01, 40.03, 59.36, 123.47, 124.11, 126.82, 127.30, 128.22, 129.28, 129.70, 131.33, 131.92, 136.50, 139.26, 141.53, 149.85, 167.51, 202.05.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{16}NO_4$: 394.1079; found: 394.1088.

Compound 22

Following the general procedure using MnO_2 gave **22** (62 mg, 76%) as a yellow solid; mp 119–120°C; R_f = 0.42 (silica gel, 50% EtOAc–PE).

IR (KBr): 1597, 1709, 1722, 2923, 3049 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (s, 2 H), 3.43, (s, 2 H), 3.86, (s, 3 H), 3.89, (s, 3 H), 7.35–7.37 (m, 1 H), 7.77 (d, *J* = 7.89 Hz, 1 H), 7.89–7.52 (m, 2 H), 8.01–8.05 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.04, 40.27, 52.65, 52.71, 58.54, 123.98, 125.95, 129.17, 129.36, 130.10, 136.31, 140.03, 141.52, 146.08, 167.28, 168.39, 202.21.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{17}O_6$: 365.1025; found: 365.1024.

Compound 23

Following the general procedure gave **23** (19 mg, 60%) as a yellow solid; mp 148–149 °C; R_f = 0.41 (silica gel, 40% EtOAc–PE).

IR (KBr): 1597, 1742, 2925, 3060 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (t, *J* = 12.7 Hz, 1 H), 2.48–2.53 (m, 1 H), 2.80–2.93 (m, 2 H), 3.19–3.32 (m, 2 H), 3.98–3.99 (br, 1 H), 5.74–5.75 (m, 1 H), 7.91–7.96 (m, 2 H), 8.02–8.08 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.61, 36.42, 36.99, 38.36, 42.33, 44.16, 55.48, 108.16, 110.29, 110.54, 111.08, 113.69, 123.92, 124.19, 136.67, 136.71, 137.33, 140.60, 141.40, 200.07, 201.90.

HRMS (ESI, Q-ToF): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{12}N_4O_2Na$: 375.0858; found: 375.0862.

Compound 24

Following the general procedure gave **24** (38 mg, 81%) as a white solid; mp 245–247 °C; R_f = 0.5 (silica gel, 50% EtOAc–PE).

IR (KBr): 1599, 1742, 1772, 2920, 3060 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (t, *J* = 11.8 Hz, 1 H), 2.86–2.96 (m, 3 H), 4.18 (d, *J* = 16.6 Hz, 1 H), 4.53 (d, *J* = 16.7 Hz, 1 H), 4.79 (br, 1 H), 5.89 (br, 1 H), 7.44–7.60 (m, 5 H), 7.99–8.00 (m, 2 H), 8.10–8.12 (br, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.22, 39.26, 43.02, 56.78, 57.69, 113.54, 123.86, 124.09, 125.72, 128.36, 129.33, 131.24, 136.37, 136.47, 137.52, 141.11, 141.70, 151.73, 153.90, 202.00, 202.98.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{18}N_3O_4$: 400.1297; found: 400.1280.

Compound 25

Following the general procedure gave **25** (110 mg, 85%) as a thick colorless liquid; R_f = 0.52 (silica gel, 25% EtOAc–PE).

IR (neat): 1655, 1730, 2984, 3020 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (dt, J_1 = 4.12 Hz, J_2 = 7.16 Hz, 6 H), 2.25–2.32 (m, 1 H), 2.99–3.08 (m, 1 H), 3.12–3.25 (m, 4 H), 3.45–3.49 (br, 1 H), 4.19–4.32 (m, 4 H), 5.68 (t, *J* = 2.24 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.04, 14.07, 33.48, 36.17, 37.83, 38.40, 42.35, 43.73, 57.18, 62.60, 62.76, 108.43, 110.48, 110.64, 111.19, 113.69, 136.89, 169.61, 170.61.

HRMS (ESI, Q-ToF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{18}N_4NaO_4$: 389.1220; found: 389.1226.

Compound 26

Following the general procedure using DDQ gave **26** (146 mg, 73%) as a thick colorless liquid; R_f = 0.44 (silica gel, 25% EtOAc–PE).

IR (neat): 1591, 1730, 2854, 2926, 3019 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.12 Hz, 6 H), 3.63 (s, 2 H), 3.66, (s, 2 H), 3.87, (s, 3 H), 3.93, (s, 3 H), (q, J_1 = 7.08 Hz, J_2 = 14.20 Hz, 4 H), 7.32 (d, *J* = 7.88 Hz, 1 H), 7.43 (d, *J* = 7.88 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.07, 39.34, 40.43, 52.59, 52.69, 60.07, 62.10, 125.75, 128.37, 129.02, 130.40, 139.44, 145.61, 166.99, 168.56, 171.07.

HRMS (ESI, Q-ToF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{22}NaO_8$: 401.1207; found: 401.1209.

Compound 27

Following the general procedure gave **27** (58 mg, 72%) as a white solid; mp 126–127 °C; R_f = 0.77 (silica gel, 50% EtOAc–PE).

IR (neat): 1643, 1708, 2254, 2944, 3165 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96–2.07 (m, 1 H), 2.51 (d, *J* = 16.6 Hz, 1 H), 2.72 (dd, J_1 = 8.44, Hz, J_2 = 13.04 Hz, 1 H), 2.93 (d, *J* = 16.61 Hz, 1 H), 3.16–3.32 (m, 4 H), 3.95–3.99 (br, 1 H), 5.68–5.70 (br, 1 H), 7.42–7.47 (m, 2 H), 7.66 (dt, J_1 = 1.16 Hz, J_2 = 7.60 Hz, 1 H), 7.79 (d, *J* = 7.64 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.76, 38.53, 38.71, 42.04, 42.79, 43.64, 52.91, 109.23, 110.53, 110.84, 111.45, 112.93, 124.92, 126.57, 128.35, 134.68, 135.91, 139.20, 152.01, 208.19.

HRMS (ESI, Q-ToF): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{14}N_4NaO$: 361.1060; found: 361.1063.

Compound 28

Following the general procedure using DDQ gave **28** (39 mg, 59%) as a white solid; mp 110–112 °C; R_f = 0.64 (silica gel, 50% EtOAc–PE).

IR (neat): 1639, 1730, 2944, 3004 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.90–2.99 (m, 2 H), 3.14–3.24 (m, 2 H), 3.48–3.57 (m, 2 H), 3.88 (s, 3 H), 3.89 (s, 3 H), 7.35 (d, *J* = 7.80 Hz, 1 H), 7.38–7.46 (m, 2 H), 7.62–7.66 (m, 1 H), 7.81 (dd, J_1 = 7.64, Hz J_2 = 14.88 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.71, 43.76, 43.86, 44.57, 52.64, 57.37, 124.63, 125.89, 126.81, 127.96, 128.15, 129.07, 130.87, 135.41, 136.02, 140.88, 147.35, 152.43, 167.11, 168.85, 208.21.

HRMS (ESI, Q-ToF): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{18}NaO_5$: 373.1046; found: 373.1046.

Compound 29

Following the general procedure using DDQ gave **29** (11 mg, 69%) as a white semi solid; R_f = 0.72 (silica gel, 50% EtOAc–PE).

IR (neat): 1650, 1719, 2987, 3054 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (t, *J* = 6.52 Hz, 2 H), 2.96–3.13 (m, 4 H), 3.45 (d, *J* = 16.76 Hz, 1 H), 3.61 (d, *J* = 16,73 Hz, 1 H), 3.88 (s, 6 H), 7.31–7.35 (m, 3 H), 7.51 (t, *J* = 7.40 Hz, 1 H), 7.75 (d, *J* = 7.88 Hz, 1 H), 8.04 (d, *J* = 7.84 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.17, 34.10, 40.05, 41.71, 52.60, 52.67, 53.57, 126.10, 127.08, 128.09, 128.51, 128.97, 128.99, 130.98, 131.48, 133.70, 140.45, 143.41, 147.30, 167.21, 169.04, 199.88.

HRMS (ESI, Q-ToF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{20}NaO_5$: 387.1203; found: 387.1202.

Synthesis of Compound 30
To a solution of diene **16c** (50 mg, 0.22 mmol) in toluene (20 mL), tetracyanoethylene (43 mg, 0.33 mmol) was added and the mixture was refluxed for 12 h. At the conclusion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, 40% EtOAc–PE) to furnish **30** (71 mg, 91%) as a white semisolid; R_f = 0.73 (silica gel, 50% EtOAc–PE).

IR (neat): 1601, 1678, 2255, 2929, 3020 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.81 (t, *J* = 11.96 Hz, 1 H), 2.22 (t, *J* = 6.20 Hz, 2 H), 2.47 (d, *J* = 17.45 Hz, 1 H), 2.72–2.77 (m, 1 H), 3.01–3.25 (m, 5 H), 3.71 (br, 1 H), 5.63 (s, 1 H), 7.27 (d, *J* = 7.28 Hz, 1 H), 7.35 (t, *J* = 7.52 Hz, 1 H), 7.53 (t, *J* = 6.96 Hz, 1 H), 8.06 (d, *J* = 7.72 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.45, 33.73, 35.47, 38.17, 38.46, 39.14, 42.82, 43.88, 50.59, 109.04, 110.56, 110.89, 111.51, 112.85, 127.33, 128.62, 128.93, 130.35, 134.23, 138.97, 143.17, 199.93.

HRMS (ESI, Q-ToF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{16}NaN_4O$: 375.1216; found: 375.1214.

Compound 31
Following the general procedure using DDQ gave **31** (47 mg, 75%) as a white solid; mp 130–132 °C; R_f = 0.36 (silica gel, 40% EtOAc–PE).

IR (neat): 1671, 1725, 2952, 3020 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.18 (t, *J* = 6.40 Hz, 2 H), 2.93–3.10 (m, 4 H), 3.44 (d, *J* = 16.75 Hz, 1 H), 3.59 (d, *J* = 16.70 Hz, 1 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 3.88 (s, 3 H), 6.70 (s, 1 H), 6.85 (dd, J_1 = 1.85 Hz, J_2 = 8.65 Hz, 1 H), 7.31 (d, *J* = 7.80 Hz, 1 H), 7.74 (d, *J* = 7.85 Hz, 1 H), 8.02 (d, *J* = 8.75 Hz, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 26.50, 34.13, 40.19, 41.82, 52.58, 52.64, 53.27, 55.63, 112.58, 113.70, 124.96, 126.04, 127.86, 128.89, 130.88, 130.93, 140.52, 145.88, 147.46, 163.85, 167.17, 169.08, 198.74.

HRMS (ESI, Q-ToF): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{22}NaO_6$: 417.1309; found: 417.1308.

Compound 32
Following the general procedure gave **32** (54 mg, 79%) as a white semi solid; R_f = 0.37 (silica gel, 40% EtOAc–PE).

IR (neat): 1599, 1667, 2240, 2926, 3020 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.79 (t, *J* = 11.90 Hz, 1 H), 2.18 (t, *J* = 6.00 Hz, 2 H), 2.43 (d, *J* = 17.40 Hz, 1 H), 2.71–2.75 (m, 1 H), 2.95–3.2 (m, 5 H), 3.73–3.75 (br, 1 H), 3.88 (s, 3 H), 5.62 (s, 1 H), 6.70 (d, *J* = 1.65 Hz, 1 H), 6.87 (dd, J_1 = 2.15 Hz, J_2 = 8.75 Hz, 1 H), 8.04 (d, *J* = 8.75 Hz, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 26.92, 33.84, 35.73, 38.43, 38.45, 39.45, 42.87, 43.95, 50.33, 55.72, 109.14, 110.56, 110.90, 111.54, 112.64, 112.70, 113.98, 123.89, 131.21, 139.33, 145.68, 164.29, 198.73.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{19}N_4O_2$: 383.1503; found: 383.1507.

2,2-Diprop-2-ynyl-1*H*-indene-3(2*H*)-dione (33)
Brown solid; mp 81–82 °C. The ^1H and ^{13}C NMR spectra matched with the literature data.[21]

2,2-Bis[(cyclohexa-1,5-dienyl)methyl]-1*H*-indene-3(2*H*)-dione (35)
The solution of **33** (100 mg, 0.45 mmol) and hexa-1,5-diene (0.4mL, 3.15 mmol) in CH_2Cl_2 (20 mL) was degassed with N_2 for 15 min. After that, G-I (37 mg, 10 mol%) was added and the mixture was stirred at r.t. for 6 h. At the conclusion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, 5% EtOAc–PE) to deliver **35** (87 mg, 59%) as a white solid; mp 138–139 °C; R_f = 0.73 (silica gel, 5% EtOAc–PE).

IR (neat): 1596, 1705, 1741, 2936, 3017 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.49–1.54 (m, 4 H), 1.76–1.81 (m, 4 H), 2.58 (s, 4 H), 5.30–5.54 (m, 6 H), 7.73 (dd, J_1 = 2.64 Hz, J_2 = 5.72 Hz, 2 H), 7.85 (dd, J_1 = 3.08 Hz, J_2 = 5.64 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.78, 22.24, 41.55, 60.55, 122.62, 125.84, 126.99, 127.79, 130.87, 135.19, 143.52, 204.22.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}O_2$: 331.1693; found: 331.1694.

2,2-Dibenzyl-1*H*-indene-1,3(2*H*)-dione (36)
The solution of **35** (50 mg, 0.15 mmol) and DDQ (50 mg, 0.15 mmol) in toluene (20 mL) was refluxed for 18 h. At the conclusion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, 4% EtOAc–PE) to furnish **36** (46 mg, 94%) as a white solid. The ^1H and ^{13}C NMR spectra matched with the literature data.[22]

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References

(1) (a) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117. (b) Fürstner, A. *Angew. Chem. Int. Ed.* **2000**, *39*, 3013. (c) Deiters, A.; Martin, S. F. *Chem. Rev.* **2004**, *104*, 2199.

(2) (a) Holt, D. J.; Barker, W. D.; Jenkins, P. R.; Davies, D. L.; Garratt, S.; Fawcett, J.; Russell, D. R.; Ghosh, S. *Angew. Chem. Int. Ed.* **1998**, *37*, 3298. (b) Kotha, S.; Manivannan, E.; Sreenivasachary, N.; Ganesh, T.; Deb, A. C. *Synlett* **1999**, 1618. (c) Giessert, A. J.; Diver, S. T. *Chem. Rev.* **2004**, *104*, 1317. (d) Maifeld, S. V.; Lee, D. *Chem.–Eur. J.* **2005**, *11*, 6118. (e) Mori, M. *Adv. Synth. Catal.* **2007**, *349*, 121. (f) Kotha, S.; Mandal, K. *Chem. Asian J.* **2009**, *4*, 354. (g) Kotha, S.; Dipak, M. K. *Tetrahedron* **2012**, *68*, 397. (h) Kotha, S.; Lahiri, K. *Synlett* **2007**, 2767. (i) Kotha, S.; Sreenivasachary, N. *Indian J. Chem., Sect. B* **2001**, *40*, 763. (j) Ruprah, P. K.; Cros, J.-P.; Pease, J. E.; Whittingham, W. G.; Williams, J. M. J. *Eur. J. Org. Chem.* **2002**, 3145. (k) Lee, H.-Y.; Kim, B. G.; Snapper, M. L. *Org. Lett.* **2003**, *5*, 1855.

(3) (a) Katz, T. J.; McGinnis, J. *J. Am. Chem. Soc.* **1975**, *97*, 1592. (b) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. (c) Sivavec, T. M.; Katz, T. J.; Chiang, M. Y.; Yang, G. X.-Q. *Organometallics* **1989**, *8*, 1620. (d) Katz, T. J.; Yang, G. X.-Q. *Tetrahedron Lett.* **1991**, *32*, 5895. (e) Kotha, S.; Meshram, S.; Tiwari, A. *Chem. Soc. Rev.* **2009**, *38*, 2065. (f) Kurhade, S. E.; Sanchawala, A. I.; Ravikumar, V.; Bhuniya, D.; Reddy, D. S. *Org. Lett.* **2011**, *13*, 3690. (g) For one-pot metathesis/Diels–Alder reaction see: Lee, H.-Y.; Kim, H. Y.; Tae, H.; Kim, B. G.; Lee, J. *Org. Lett.* **2003**, *5*, 3439. (h) Bentz, D.; Laschat, S. *Synthesis* **2000**, 1766. (i) Banti, D.; North, M. *Tetrahedron Lett.* **2002**, *43*, 1561. (j) Guo, H.; Madhushaw, R. J.; Shen, F.-M.; Liu,

R.-S. *Tetrahedron* **2002**, *58*, 5627. (k) Hoye, T. R.; Donaldson, S. M.; Vos, T. J. *Org. Lett.* **1999**, *1*, 277.
(4) For the total synthesis of natural products by metathesis, see ref 3k and: (a) Boyer, F.-D.; Hanna, I.; Ricard, L. *Org. Lett.* **2004**, *6*, 1817. (b) Kinoshita, A.; Mori, M. *J. Org. Chem.* **1996**, *61*, 8356. (c) Kummer, D. A.; Brenneman, J. B.; Martin, S. F. *Org. Lett.* **2005**, *7*, 4621. (d) Mori, M.; Tonogaki, K.; Nishiguchi, N. *J. Org. Chem.* **2002**, *67*, 224.
(5) For all the four compounds shown in Figure 1, see: Mori, M. *Materials* **2010**, *3*, 2087.
(6) (a) Sannigrahi, M. *Tetrahedron* **1999**, *55*, 9007. (b) Holt, D. J.; Barker, W. D.; Jenkins, P. R.; Panda, J.; Ghosh, S. *J. Org. Chem.* **2000**, *65*, 482. (c) Kotha, S. *Acc. Chem. Res.* **2003**, *36*, 342. (d) Kotha, S.; Mandal, K. *Tetrahedron Lett.* **2004**, *45*, 1391. (e) Kotha, S.; Deb, A. C.; Chattopadhyay, S. *Lett. Org. Chem.* **2006**, *3*, 128. (f) Kotha, S.; Deb, A. C.; Lahiri, L.; Manivannan, E. *Synthesis* **2009**, 165. (g) Kotha, S.; Dipak, M. K.; Mobin, S. M. *Tetrahedron* **2011**, *67*, 4616. (h) Kotha, S.; Deb, A. C. *Indian J. Chem., Sect. B* **2008**, *47*, 1120. (i) Kotha, S.; Manivannan, E. *ARKIVOC* **2003**, *iii*, 67; http://www.arkat-usa.org/home. (j) Kotha, S.; Deb, A. C.; Kumar, R. V. *Bioorg. Med. Chem.* **2005**, *15*, 1039. (k) Singh, P.; Paul, K. *J. Heterocycl. Chem.* **2006**, *43*, 607. (l) Basavaiah, D.; Badsara, S. S.; Veeraraghavaiah, G. *Tetrahedron* **2013**, *69*, 7995. (m) Basavaiah, D.; Reddy, K. R. *Org. Lett.* **2007**, *9*, 57. (n) Kozhushkov, S. I.; de Meijere, A.; Haumann, T.; Boese, R. *Angew. Chem. Int. Ed.* **1993**, *32*, 401.
(7) (a) Mehta, G.; Subrahmanyam, D. *Tetrahedron* **1987**, *28*, 479. (b) Kelly, T. R.; Ohashi, N. *J. Am. Chem. Soc.* **1986**, *108*, 7100. (c) Keese, R. *Chem. Rev.* **2006**, *106*, 4787. (d) Kuck, D.; Bögge, H. *J. Am. Chem. Soc.* **1986**, *108*, 8107.
(8) (a) Naik, S. N.; Pandey, B.; Ayyangar, N. R. *Synth. Commun.* **1988**, 633. (b) Sakata, Y.; Goto, S.; Tatemitsu, H.; Misumi, S. *J. Am. Chem. Soc.* **1989**, *111*, 8979. (c) Norris, D. J.; Corrigan, J. F.; Sun, Y.; Taylor, N. J.; Collins, S. *Can. J. Chem.* **1993**, *71*, 1029. (d) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1991**, *113*, 701. (e) Evans, P. A.; Brandt, T. A. *Tetrahedron Lett.* **1996**, *37*, 1367. (f) Bach, R. D.; Klix, R. C. *Tetrahedron Lett.* **1986**, *27*, 1983. (g) Kuroda, C.; Hirono, H. *Tetrahedron Lett.* **1994**, *35*, 6895.
(9) Kotha, S.; Ali, R.; Tiwari, A. *Synlett* **2013**, *24*, 1921.
(10) Swager, T. M. *Synfacts* **2013**, *9*, 1172.
(11) (a) Fürstner, A.; Langemann, K. *J. Am. Chem. Soc.* **1997**, *119*, 9130. (b) Buschmann, N.; Ruckert, N. A.; Blechert, S. *J. Org. Chem.* **2002**, *67*, 4325. (c) Davis, F. A.; Yang, B. J. *J. Am. Chem. Soc.* **2005**, *127*, 8398.
(12) (a) Mori, M.; Sakakibara, N.; Kinoshita, A. *J. Org. Chem.* **1998**, *63*, 6082. (b) Kitamura, T.; Mori, M. *Org. Lett.* **2001**, *3*, 1161.
(13) (a) Kotha, S.; Khedkar, P. *Eur. J. Org. Chem.* **2009**, 730. (b) Kotha, S.; Vittal, S. *Synlett* **2011**, 2329. (c) Kotha, S.; Wagule, G. T. *J. Org. Chem.* **2012**, *77*, 6314. (d) Comer, E.; Rohan, E.; Deng, L.; Porco, J. A. *Org. Lett.* **2007**, *9*, 2123. (e) Zhou, A.; Rayabarapu, D.; Hanson, P. R. *Org. Lett.* **2009**, *11*, 531. (f) Kotha, S.; Goyal, D.; Chavan, A. S. *J. Org. Chem.* **2013**, *78*, 12288.
(14) (a) Okada, T.; Takeuchi, D.; Osakada, K. *Macromolecules* **2010**, *43*, 9998. (b) Ou, J.; Wong, W.-T.; Chiu, P. *Org. Biomol. Chem.* **2012**, *10*, 5971.
(15) Duttagupta, I.; Goswami, K.; Sinha, S. *Tetrahedron* **2012**, *68*, 8347.
(16) Jose, M. C.; Juan, L. R.; Andres, A. T. *Tetrahedron Lett.* **2004**, *45*, 1133.
(17) (a) Kitamura, M.; Shintaku, Y.; Kudo, D.; Okauchi, T. *Tetrahedron Lett.* **2010**, *51*, 4890. (b) Konkol, L. C.; Jones, B. T.; Thomson, R. J. *Org. Lett.* **2009**, *11*, 5550.
(18) Claraz, A.; Leroy, J.; Oudeyer, S.; Levacher, V. *J. Org. Chem.* **2011**, *76*, 6457.
(19) (a) Sylvester, K. T.; Chirik, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 8772. (b) Oh, C. H.; Piao, L.; Kim, J. H. *Synthesis* **2013**, *45*, 174.
(20) Grotevendt, G. D.; Lummiss, J. A. M.; Mastronardi, M. L.; Fogg, D. E. *J. Am. Chem. Soc.* **2011**, *133*, 15918.
(21) Kotha, S.; Manivannan, E. *J. Chem. Soc., Perkin Trans 1* **2001**, 2543.
(22) Paisdor, B.; Kuck, D. *J. Org. Chem.* **1991**, *56*, 4753.

