Article

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Diversity Oriented Synthesis of Tricyclic Compounds from Glycals Using the Ferrier and the Pauson−Khand Reactions

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Diversity oriented synthesis of tricyclic compounds was achieved using a combination of the Ferrier reaction and the Pauson−Khand reaction. Ferrier reaction was effected using $NbCl_5$, and the Pauson−Khand reaction was carried out using $Co_2(CO)_8$, acetonitrile-dimethoxyethane. Michael additions using various alkyl, aryl, and heterocyclic thiols were also performed successfully. The Ferrier, Pauson−Khand, and Michael addition reactions were found to be highly diastereoselective.

Introduction

Rapid identification of potent, selective, and specific small molecules to macromolecular receptor(s) having defined biological function is a major challenge in the post-genomic era.[1] For a long time, natural products are conceived to be of paramount importance in the identification of small molecule inhibitors.[2] Later on, the focus shifted to the combinatorial chemistry; however, the anticipated result in the identification of the small molecule probes was not observed, which was attributed partly to the clustering of small molecules in the three-dimensional chemical space.[3] In addition to this, a recent chemoinformatics data mining study revealed that, on average, natural products have higher molecular weights, incorporate fewer nitrogen atoms but more oxygen atoms, and are sterically more complex with number of rings and chiral centers than the corresponding congeners from combinatorial libraries.[4] Hence there exists a need to unravel the three-dimensional chemical space by the use of less explored templates to generate novel complex, chiral, and polycyclic compounds. Diversity oriented synthesis (DOS) of small molecules is a new algorithm that enables efficient synthesis of complex molecules.[5] Keeping these and our continued interest, we hypothesized that the carbohydrate precursors enable us to develop diversity oriented pathways for the synthesis of novel chemical scaffolds decorated with chiral centers and a number of oxygen atoms embedded to fused rings.[6] In this paper, we reveal one such study that was steered by complexity generating protocols such as the Ferrier and Pauson−Khand reactions on carbohydrate template.

A Lewis acid mediated S_N2' addition of alcohols to per-*O*-acetylated glycals is known as the Ferrier reaction,[7] and a $Co_2(CO)_8$ promoted 2+2+1 cyclization of an alkyne and an alkene is the Pauson-Khand reaction.[8] The Ferrier reaction was exploited[6b] for the synthesis of variety of designer molecules, but utility of the Pauson−Khand reaction using carbohydrate substrates has started recently.[9] An earlier DOS[10] using the Ferrier and Pauson−Khand reactions resulted in the development of a pathway wherein the Schreiber group treated suitably substituted per-*O*-acetyl glucal with various propargyl alcohols in the presence of $BF_3.Et_2O$ to obtain 2,3-unsaturated enynes, which were then subjected to 2+2+1 cyclization using $Co_2(CO)_8$ to obtain a library of tricyclic compounds (scaffold **A**, Figure 1). However, we envisaged that the Ferrier reaction can be effected using a variety of aglycones to obtain α-glycosides and then functional group interconversions should enable installation of a propargylic moiety at the C-4 position so that the Pauson−Khand reaction can be carried out stereoselectively to obtain tricyclic enones (scaffold **B**, Figure 1).

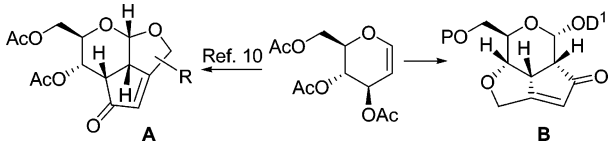

Figure 1. Structurally unique scaffolds from 3,4,6-tri-*O*-acetyl glucal.

We have recently observed that $NbCl_5$ effects the Ferrier reaction stereoselectively.[6b] To begin our investigation, 3,4,6-tri-*O*-acetyl D-glucal (**1**) was treated with benzyl alcohol for 1 h in the presence of $NbCl_5$ to obtain benzyl 4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-eno-α-D-glucopyranoside (**2**) in 97% yield. Compound **2** was then deacetylated under Zémplen conditions (NaOMe, MeOH), and the primary hydroxyl group was selectively blocked as its trityl ether (**3**). The remaining allylic hydroxyl group was converted to propargyl ether using propargyl bromide, NaH in DMF to afford the enyne **4** (Scheme 1).[11]

In the ^1H NMR spectrum of **4**, characteristic acetylenic methine proton was observed at δ 2.24 ppm as a triplet ($J = 2.4$ Hz), benzylic methylene group was identified at δ 4.78 ppm ($J = 11.8$ Hz) as an AB type quartet (ABq), and olefinic resonances were noticed at δ 5.81 (td, $J = 2.1$, 10.2 Hz) and δ 6.07 (d, $J = 10.3$ Hz) ppm with rest of the resonances in accordance with the assigned structure.[11] In

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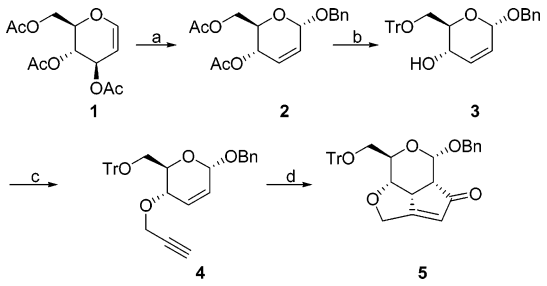
Scheme 1. Synthesis of Tricyclic Compounds via Ferrier and Pauson−Khand Reactions[a]



[a] Reagents. (a) BnOH, $NbCl_5$, acetonitrile, 1 h, 97%. (b) (i) NaOMe, MeOH, rt, 30 min, 95%; (ii) Ph_3CCl, pyridine, CH_2Cl_2, rt, 90%. (c) Propargyl bromide, NaH, DMF, nBu$_4$N$^+$I$^-$, 0 °C−rt, 3 h, 91%. (d) $Co_2(CO)_8$, CH_2Cl_2, rt, 1 h then acetonitrile−dimethoxyethane (1:1), 70 °C, 4 h, 92%.

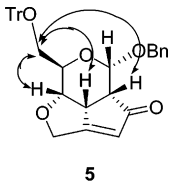


Figure 2. Some important NOE interactions in **5**.

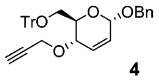
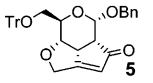
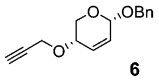
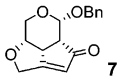
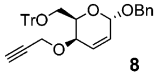
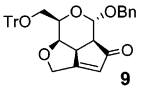
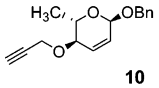
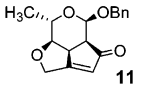
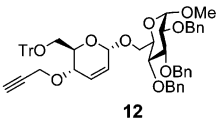
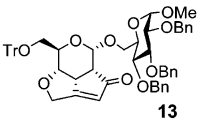
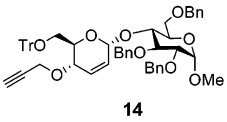
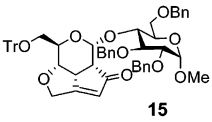
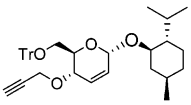
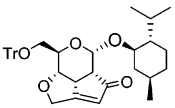
the ^{13}C NMR spectrum of **4,** resonances corresponding to the anomeric and acetylenic carbons were noticed at δ 93.3 and δ 74.4 ppm, respectively. Having the required enyne **4** in hand, we dwelt upon carrying out the Pauson−Khand reaction; accordingly, the enyne **4** was treated with $Co_2(CO)_8$ for 1 h under N_2 atmosphere and was passed through a pad of silica gel to obtain the $Co_2(CO)_6$−alkyne complex. At this stage, cleavage of the cobalt complex and insertion of the carbonyl group became an arduous task.

Initially we used[12a] *N*-methyl morpholine *N*-oxide (NMO) in CH_2Cl_2 to effect cleavage of the cobalt complex, and we obtained **5** in 70% yield. However, to our surprise, the reaction was sluggish (3 days) and sensitive to the quality of NMO; hence, we sought alternate protocols.[12] Heating the $Co_2(CO)_6$−alkyne complex in the presence of other cleavage reagents such as cyclohexylamine[12b] or acetonitrile[12c] did not result in the formation of the **5** but led to the decomposition of the cobalt complex. Treatment of the $Co_2(CO)_6$−alkyne complex with H_2O_2 furnished the desired tricyclic enone **5** in 30% yield. Use of dimethoxyethane and acetonitrile at 70 °C as the $Co_2(CO)_6$−alkyne complex cleavage cocktail afforded the enone **5** in 92% yield.[12d]

^{1}H NMR spectrum of **5** showed no resonances corresponding to the enyne, and new resonances characteristic of olefinic proton associated with the enone were observed at δ 6.00 ppm as a singlet. Resonances due to the benzylic −CH_2 group were noticed at δ 4.67 ppm as an ABq (J = 12.2 Hz), and that of anomeric proton were evident at δ 5.22 ppm as a doublet (J = 7.8 Hz). It is pertinent to mention that the Pauson−Khand annulation occurred in a highly diastereoselective fashion; the NOESY spectrum showed NOE cross-peaks between H-2, H-3, H-4, and H-6 (Figure 2).[11,13]

Configuration at the C-4 position plays a predominant role in dictating the chirality of the Pauson−Khand annulation as the $Co_2(CO)_6$−alkyne will be below the plane. As a consequence, carbonyl insertion can take place from below only; hence, the observation of a single diastereomer.[13] Having identified a practical route to the synthesis of natural product-like tricyclic enones, we performed an initial survey of the substrate scope. As shown in Table 1, we could successfully extrapolate the current protocol to mono- and disaccharides derived from various glycals such as per-*O*-acetylated glucal, galactal, xylal, and rhamnal adopting our optimized aforementioned conditions.

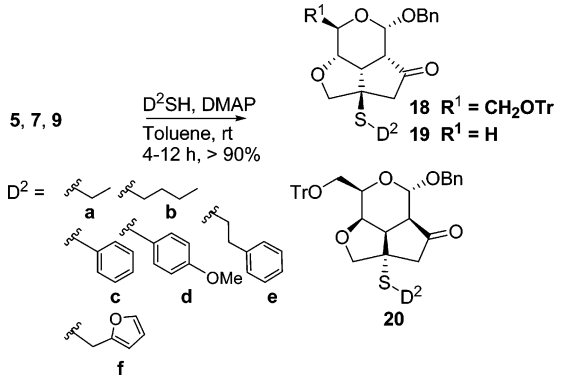
Table 1. Synthesis of Natural Product-like Tricyclic Enones

Entry Number	Substrate	Product	% Yield
1.	 **4**	 **5**	92
2.	 **6**	 **7**	87
3.	 **8**	 **9**	90
4.	 **10**	 **11**	83
5.	 **12**	 **13**	85
6.	 **14**	 **15**	88
7.	 **16**	 **17**	85

Furthermore, we envisioned that tricyclic enones can serve as a platform to carry out stereoselective conjugate thiolate additions using various thiols. Diversification through thiolates was chosen because of their propensity toward nucleophilic addition to enones under mild reaction conditions coupled with their ready availability and thiol-substituted compounds were found to be more potent than corresponding enones.[14] Although several thiols are available, six monothiols and three tricyclic enones synthesized vide supra were chosen for our studies (Scheme 2).

Accordingly, we performed the thiolate nucleophilic conjugate addition to enones and found that *N*,*N*-dimethylaminopyridine (DMAP) catalyzes thiolate addition very efficiently. In a typical experiment, a solution containing thiol was stirred with enone in the presence of a catalytic quantity of DMAP for 12 h to afford thiol incorporated tricyclic ketones. It is pertinent to mention that the conjugate addition favored a single diastereomer that can be rationalized based on the *bowl*-like conformation of enone; hence, the thiolate addition can take place from the least sterically demanding

Scheme 2. Nucleophilic Thiolate Conjugate Additions to Enones



phase only. A total of 25 tricyclic compounds were synthesized as a pilot library.

In conclusion, we have developed a practical protocol for the synthesis of natural product-like tricyclic compounds using the Ferrier and Pauson−Khand reactions. Conjugate thiolate addition to enones was performed under mild reaction conditions to afford a thiol-substituted library. It is pertinent to mention that the complexity generating reactions (viz., the Ferrier, Pauson−Khand, and Michael addition reactions) were highly diastereoselective thereby enabling chirally pure, oxygen-rich, tricyclic derivatives from easily accessible glycals. Our further efforts toward extrapolation of this pathway onto solid supports are currently underway and will be disclosed in time.

Experimental Section

General Experimental Techniques and Apparatus. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Unless otherwise reported, all reactions were performed under nitrogen atmosphere. Removal of solvent in vacuo refers to distillation using a Buchi or Heidolph rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. Analytical thin-layer chromatography was performed on precoated silica plates (Merck F_{254}, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 200 (200 MHz for ^{1}H and 50 MHz for ^{13}C NMR) or Bruker MSL300 (300 MHz for ^{1}H and 75 MHz for ^{13}C NMR) or Bruker DRX500 (500 MHz for ^{1}H and 125 MHz for ^{13}C NMR) spectrometers. Chemical shifts (δ_H) are quoted in ppm and are referenced to tetramethylsilane (internal). IR spectra were recorded on Schimadzu FT-IR spectrophotometer, and elemental analysis was carried out on Thermo Finnigan Flash EA 1112 series analyzer.

General Experimental Procedures. (a) Synthesis of 2,3-Unsaturated *O*-Glycosides. To a mixture of per-*O*-acetyl glycal (1 mmol) and alcohol (1.5 mmol) in acetonitrile (5 mL) was added $NbCl_5$ (0.01 mmol). The resulting solution was stirred at ambient temperature for 1 h. The reaction mixture was then diluted with water and extracted two times with ethyl acetate. The combined organic extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. The product was purified by silica gel column chromatography using ethyl acetate and light petroleum (60−80 °C).

(b) Deacetylation of 2,3-Unsaturated *O*-Glycosides. NaOMe (3 mmol) was added to the solution of 2,3-unsaturated *O*-glycoside in anhydrous methanol (5 mL). The resulting solution was stirred at room temperature until the reaction showed completion by TLC (takes about 30 min). The solvent was removed in vacuo, and the reaction mixture was diluted with water and extracted three times with ethyl acetate. The combined organic extracts were dried over anhydrous sodium sulfate and concentrated in vacuo to yield the diol, which was used without further purification in the next step.

(c) O-Tritylation of 2,3-Unsaturated *O*-Glycosides. The diol (1 mmol) prepared vide supra was dissolved in anhydrous pyridine (10 mL), and the solution was cooled to 0 °C. Trityl chloride (1.5 mmol) was added to the above solution, and the reaction mixture was brought to room temperature and allowed to stir for 24 h. The reaction mixture was poured into water and was extracted three times with ethyl acetate. The combined organic extracts washed with brine and dried over sodium sulfate. The solvent was removed under reduced pressure to yield the corresponding *O*-trityl derivative, which was purified by silica gel column chromatography using ethyl acetate and light petroleum (60−80 °C).

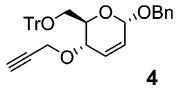
(d) O-Propargylation. To an ice-cooled solution of the trityl derivative of the glycal (1 mmol) in anhydrous DMF (5 mL) was added sodium hydride (1.5 equiv, 60% oil suspension) and stirred for 1 h at room temperature. Propargyl bromide (1.5 equiv) was introduced dropwise to the mixture at 0 °C and stirred at room temperature for 1 h. The resulting suspension was quenched with saturated ammonium chloride and extracted three times with ethyl acetate. The combined organic extracts were washed with brine solution and concentrated under reduced pressure to give the crude *O*-propargyl derivative that was purified by silica gel column chromatography using ethyl acetate and light petroleum (60−80 °C).

(e) Pauson−Khand Reaction. To an ice-cooled solution of alkyne in anhydrous dichloromethane was added $Co_2(CO)_8$ (1.2 equiv) and stirred at room temperature for 1 h. The reaction mixture was adsorbed on silica gel and was eluted with ethyl acetate and light petroleum to yield the cobalt−enyne complex as a thick red oil. Subsequently, the Co−alkyne complex was redissolved in anhydrous 1,2-dimethoxy ethane (5 mL) and anhydrous acetonitrile (20 mL) and was refluxed until the color of the solution changed from thick red to grayish black. The solution was filtered through a pad of silica gel and concentrated to give a light yellow oil, which was purified by silica gel column chromatography using ethyl acetate and light petroleum (60−80 °C).

(f) Thiolate Additions on Enones. The tricyclic enone (1 equiv) was dissolved in anhydrous toluene (10 mL/mmol), and the thiol (2 equiv) was added to it. The resulting solution was stirred in the presence of catalytic amount of DMAP until the reaction showed completion by TLC (typically takes about 12−24 h). Thereafter the solvent was removed in

vacuo, and the adduct was purified by silica gel column chromatography using ethyl acetate and light petroleum (60−80 °C).

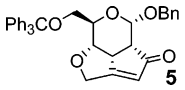
Compound **4**:



4

$[\alpha]_D$ ($CHCl_3$, *c* 0.7) = +33.6°. IR (cm^{-1}) = 3303. ^1H NMR (200 MHz, $CDCl_3$): δ 2.24 (t, 1 H, *J* = 2.39 Hz), 3.19 (dd, 1 H, *J* = 5.44, 10.31 Hz), 3.37 (dd, 1 H, *J* = 1.34, 10.23 Hz), 4.01 (m, 3 H), 4.23 (dd, 1 H, *J* = 1.18, 9.46 Hz), 4.78 (ABq, 2 H, *J* = 11.80 Hz), 5.15 (d, 1 H, *J* = 1.62 Hz), 5.81 (td, 1 H, *J* = 2.14, 10.22 Hz), 6.07 (d, 1 H, *J* = 10.28 Hz), 7.15−7.42 (m, 14 H), 7.47−7.54 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 56.6, 63.1, 69.4, 69.7, 70.1, 74.4, 79.7, 86.4, 93.3, 126.7−128.8, 131.0, 137.9, 144.1. Anal. Calcd for $C_{35}H_{32}O_4$: C, 81.37; H, 6.24. Found: C, 80.96; H, 6.21.

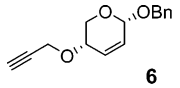
Compound **5**:



5

$[\alpha]_D$ ($CHCl_3$, *c* 0.9) = +177.9°. IR (cm^{-1}) = 1716, 1647. ^1H NMR (500 MHz, $CDCl_3$): δ 3.21−3.33 (m, 4 H), 3.59 (td, 1 H, *J* = 1.98, 7.34 Hz), 3.95 (t, 1 H, *J* = 9.13 Hz), 4.45 (m, 2 H), 4.67 (ABq, 2 H, *J* = 12.18 Hz), 5.22 (d, 1 H, *J* = 7.76 Hz), 6.00 (s, 1 H), 7.12−7.31 (m, 14 H), 7.33−7.45 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 45.5, 51.5, 64.0, 65.1, 65.7, 68.9, 71.2, 86.8, 94.3, 125.2, 126.8−128.7, 137.3, 143.9, 178.36, 206.7. Anal. Calcd for $C_{36}H_{32}O_5$: C, 79.39; H, 5.92. Found: C, 79.89; H, 6.20. MALDI-TOF: mol wt calcd 544.64; found 567.17 (M + 23 for Na).

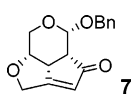
Compound **6**:



6

$[\alpha]_D$ ($CHCl_3$, *c* 1.0) = +69.4°. IR (cm^{-1}) = 3306. ^1H NMR (200 MHz, $CDCl_3$): δ 2.45 (t, 1 H, *J* = 2.28 Hz), 3.87 (m, 1 H), 3.96 (td, 1 H, *J* = 1.10, 12.81 Hz), 4.12 (dd, 1 H, *J* = 2.69, 4.12 Hz), 4.26 (d, 2 H, *J* = 2.41 Hz), 4.68 (ABq, 2 H, *J* = 11.77 Hz), 5.09 (d, 1 H, *J* = 2.35 Hz), 6.01 (dd, 1 H, *J* = 2.72, 10.23 Hz), 6.14 (td, 1 H, *J* = 1.12, 4.98 Hz), 7.25−7.38 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.5, 61.1, 66.6, 69.7, 74.7, 79.7, 92.2, 126.2, 127.7, 128.1, 128.4, 130.1, 137.6. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.69; H, 6.61.

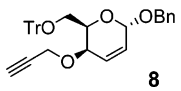
Compound **7**:



7

$[\alpha]_D$ ($CHCl_3$, *c* 1.5) = +52.2°. IR (cm^{-1}) = 1738, 1713. ^1H NMR (200 MHz, $CDCl_3$): δ 2.92 (d, 1 H, *J* = 6.78 Hz), 3.51 (m, 2 H), 4.03 (dd, 1 H, *J* = 5.30, 13.09 Hz), 4.38 (m, 1 H), 4.58 (ABq, 2 H, *J* = 11.50 Hz), 4.67 (t, 2 H, *J* = 14.29 Hz), 4.84 (s, 1 H), 6.10 (s, 1 H), 7.28−7.40 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 43.8, 51.5, 62.2, 65.2, 70.0, 70.1, 96.8, 124.6, 128.0, 128.5, 136.8, 183.5, 208.7. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.74; H, 6.29.

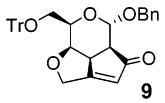
Compound **8**:



8

$[\alpha]_D$ ($CHCl_3$, *c* 2.82) = −80.4°. IR (cm^{-1}) = 3301, 1491, 1449. ^1H NMR (200 MHz, $CDCl_3$): δ 2.28 (t, 1 H, *J* = 2.28 Hz), 3.27 (dd,1 H, *J* = 5.47, 9.66 Hz), 3.54 (dd, 1 H, *J* = 7.10, 9.78 Hz), 3.85 (dd, 1 H, *J* = 2.54, 5.34 Hz), 4.09 (dd, 2 H, *J* = 1.52, 2.28 Hz), 4.35 (m, 1 H), 4.73 (ABq, 2 H, *J* = 11.63 Hz), 5.15 (d, 1 H, *J* = 2.98 Hz), 6.02 (dd, 1 H, *J* = 2.79, 9.99 Hz), 6.21 (ddd, 1 H, *J* = 0.77, 5.19, 9.90 Hz), 7.15−7.42 (m, 14 H), 7.45−7.55 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 56.2, 63.1, 67.0, 69.4, 69.8, 74.5, 79.8, 86.6, 92.9, 126.7−128.7, 129.9, 137.6, 143.9. Anal. Calcd for $C_{35}H_{32}O_4$: C, 81.37; H, 6.24. Found: C, 80.65; H, 6.58.

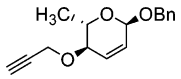
Compound **9**:



9

$[\alpha]_D$ ($CHCl_3$, *c* 0.8) = −130.9°. IR (cm^{-1}) = 1738, 1713. ^1H NMR (200 MHz, $CDCl_3$): δ 2.79 (d, 1 H, *J* = 6.39 Hz), 3.25 (dd, 1 H, *J* = 2.29, 10.53 Hz), 3.33 (m, 1 H), 3.43−3.64 (m, 1 H), 4.09 (dd, 1 H, *J* = 3.24, 9.62 Hz), 4.18 (dd, 1 H, *J* = 4.10, 7.79 Hz), 4.31 (ABq, 2 H, *J* = 14.75 Hz), 4.74 (ABq, 2 H, *J* = 11.45 Hz), 4.03 (d, 1 H, *J* = 11.85 Hz), 5.93 (s, 1 H), 7.12−7.38 (m, 14 H), 7.41−7.48 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 44.1, 51.7, 63.0, 65.8, 68.0, 69.3, 71.0, 86.9, 97.5, 124.0, 126.9−128.8, 137.0, 144.0, 183.6, 209.4. Anal. Calcd for $C_{36}H_{32}O_5$: C, 79.39; H, 5.92. Found: C, 79.61; H, 5.58.

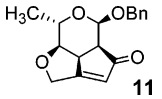
Compound **10**:



10

$[\alpha]_D$ ($CHCl_3$, *c* 1.7) = −96.4°. IR (cm^{-1}) = 3288. ^1H NMR (200 MHz, $CDCl_3$): δ 1.27 (d, 3 H, *J* = 5.78 Hz), 2.43 (t, 1 H, *J* = 2.39 Hz), 3.85 (m, 2 H), 4.23 (d, 2 H, *J* = 2.32 Hz), 4.68 (ABq, 2 H, *J* = 12.00 Hz), 5.03 (d, 1 H, *J* = 2.61 Hz), 5.79 (ddd, 1 H, *J* = 1.76, 2.65, 10.25 Hz), 6.07 (td, 1 H, *J* = 1.19, 10.37 Hz), 7.23−7.40 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.4, 56.7, 66.1, 70.3, 74.9, 76.5, 80.2, 94.1, 127.4−128.8, 130.65, 138.62. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 73.94; H, 6.58.

Compound **11**:

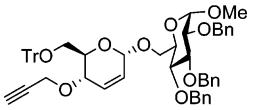


11

$[\alpha]_D$ ($CHCl_3$, *c* 1.2) = −268.2°. IR (cm^{-1}) = 1714, 1722. ^1H NMR (200 MHz, $CDCl_3$): δ 1.24 (d, 3 H, *J* = 6.13 Hz), 3.27−3.61 (m, 3 H), 3.93 (t, 1 H, *J* = 9.10 Hz), 4.50 (ABq,

2 H, J = 12.41 Hz), 4.62 (d, 2 H, J = 1.57 Hz), 5.16 (d, 1 H, J = 7.54 Hz), 6.05 (d, 1 H, J = 2.04 Hz), 7.22−7.40 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.1, 46.0, 51.9, 61.9, 85.6, 69.7, 78.0, 95.1, 125.3, 125.8−128.2, 137.6, 179.1, 207.3. Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.65; H, 6.71.

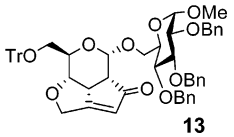
Compound **12**:



12

$[\alpha]_D$ ($CHCl_3$, c 1.06) = +31.2°. IR (cm^{-1}): 3205. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.25 (t, 1 H, J = 2.41 Hz), 2.98 (dd, 1 H, J = 3.92, 10.24 Hz), 3.25−3.42 (m, 4 H), 3.44−3.68 (m, 3 H), 3.70−3.85 (m, 3 H), 3.91−4.20 (m, 4 H), 4.31−4.42 (m, 1 H), 4.50−5.05 (m, 7 H), 5.75−5.90 (m, 1 H), 6.07 (m, 1 H), 7.05−7.55 (m, 30 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.1, 56.8, 62.5, 66.3, 66.7, 69.6, 70.0, 70.3, 73.3, 74.3, 75.0, 75.6, 79.9, 82.0, 86.3, 94.9, 98.1, 126.5−128.8, 131.1, 138.1, 138.9, 144.0. Anal. Calcd for $C_{56}H_{56}O_9$: C, 77.04; H, 6.47. Found: C, 77.45; H, 6.64.

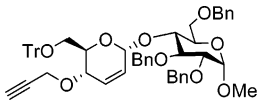
Compound **13**:



13

$[\alpha]_D$ ($CHCl_3$, c 1.0) = +85.0°. IR (cm^{-1}): 1720, 1649. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.25−3.49 (m, 8 H), 3.51−3.82 (m, 4 H), 3.85−4.13 (m, 3 H), 4.75−5.15 (m, 9 H), 5.31 (d, 1 H, J = 7.33 Hz), 5.97 (s, 1 H), 7.14−7.38 (m, 24 H), 7.39−7.40 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 29.7, 45.5, 51.5, 54.8, 64.0, 65.2, 65.5, 66.0, 70.2, 71.2, 73.4, 75.0, 75.6, 78.3, 80.1, 82.0, 86.8, 95.5, 97.8, 125.0, 127.0−128.8, 138.2, 138.3, 138.9, 143.9, 178.3, 206.3. Anal. Calcd for $C_{57}H_{56}O_{10}$: C, 75.98; H, 6.26. Found: C, 75.48; H, 5.90.

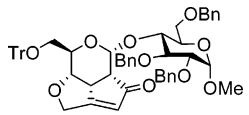
Compound **14**:



14

$[\alpha]_D$ ($CHCl_3$, c 1.08) = +35.34°. IR (cm^{-1}) = 3306. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.29 (t, 1 H, J = 2.40 Hz), δ 3.02 (dd, 1 H, J = 2.82, 10.22 Hz), δ 3.27 (d, 1 H, J = 9.84 Hz), δ 3.39 (s, 3 H), δ 3.44−3.71 (m, 5 H), δ 3.73−4.05 (m, 4 H), δ 4.17 (d, 1 H, J = 12.26 Hz), δ 4.32−4.44 (m, 2 H), δ 4.57−4.7 (m, 4 H), δ 5.04 (d, 1 H, J = 11.11 Hz), δ 5.45−5.6 (m, 2 H), δ 6.04 (d, 1 H, J = 9.82 Hz), δ 7.07−7.40 (m, 24 H), δ 7.45−7.5 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.1, 56.8, 61.9, 69.6, 70.0, 72.8, 73.2, 74.4, 75.6, 80.1, 81.9, 86.3, 96.0, 97.6, 126.1, 126.9−128.8, 131.3, 138.0, 138.1, 138.6, 143.9. Anal. Calcd for $C_{56}H_{56}O_9$: C, 77.04; H, 6.47. Found: C, 77.29; H, 6.25.

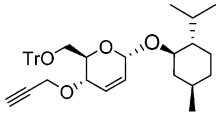
Compound **15**:



15

$[\alpha]_D$ ($CHCl_3$, c 0.9) = +113.88°. IR (cm^{-1}) = 1720. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.08−3.35 (m, 6 H); δ 3.38 (s, 3 H); δ 3.41−3.51 (m, 2 H); δ 3.58−3.72 (m, 2 H); δ 3.98 (dd, 1 H, J = 8.44, 9.22 Hz); δ 4.10 (m, 1 H); δ 4.17 (s, 1 H); δ 4.28 (t, 1 H, J = 8.59 Hz); δ 4.39−4.55 (m, 2 H); δ 4.56 (d, 1 H, J = 3.28 Hz); δ 4.67 (ABq, 2 H, J = 12.13 Hz); δ 5.04 (ABq, 2 H, J = 10.85 Hz); δ 5.81 (s, 1 H); δ 5.85 (s, 1 H); δ 7.07−7.36 (m, 22 H); δ 7.37−7.49 (m, 8 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 45.5, 51.1, 55.1, 62.9, 64.8, 65.5, 69.3, 69.5, 70.6, 72.9, 73.2, 74.8, 80.3, 81.9, 86.7, 94.6, 97.7, 125.0, 126.9−128.9, 138.0, 138.2, 139.1, 143.9, 177.9, 206.2. Anal. Calcd for $C_{57}H_{56}O_{10}$: C, 75.98; H, 6.26. Found: C, 75.88; H, 5.99.

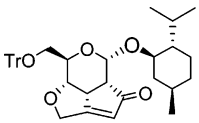
Compound **16**:



16

$[\alpha]_D$ ($CHCl_3$, c 1.6) = +8.76°. IR (cm^{-1}): 3216. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.72, 0.75, 0.79, 0.83, 0.89, 0.93 (6s, 9 H), 0.98−1.11 (m, 3 H), 1.19−1.70 (m, 4 H), 2.05−2.35 (m, 3 H), 3.23 (dd, 1 H, J = 4.04, 10.23 Hz), 3.38−3.58 (m, 2 H), 3.85−4.08 (m, 3 H), 4.24 (td, 1 H, J = 0.9, 9.23 Hz), 5.14 (s, 1 H), 5.73−6.10 (m, 2 H), 7.16−7.35 (m, 9 H), 7.40−7.56 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.2, 21.1, 22.2, 23.2, 25.6, 31.8, 34.4, 43.3, 48.8, 56.5, 63.1, 69.0, 70.5, 74.3, 79.8, 80.5, 86.4, 96.1, 126.8−128.8, 130.5, 143.9, 144.0. Anal. Calcd for $C_{38}H_{44}O_4$: C, 80.82; H, 7.85. Found: C, 80.49; H, 7.89.

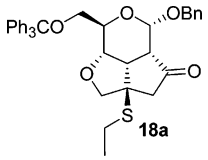
Compound **17**:



17

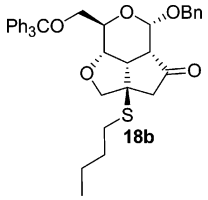
$[\alpha]_D$ ($CHCl_3$, c 1.0) = +147.5°. IR (cm^{-1}): 1749, 1454. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.60, 0.63 (2s, 3 H), 0.76, 0.79, 0.86, 0.92 (4s, 6 H), 0.83−0.97 (m, 3 H), 1.08−1.22 (m, 2 H), 1.58 (m, 3 H), 2.11 (m, 2 H), 3.24−4.45 (m, 5 H), 4.27 (dd, 1 H, J = 8.40, 9.61 Hz), 4.56 (bs, 2 H), 5.26 (d, 1 H, J = 7.59 Hz), 5.99 (d, 1 H, J = 1.51 Hz), 7.10−7.35 (m, 9 H), 7.42−7.53 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.8, 21.4, 22.2, 22.6, 24.7, 31.6, 34.2, 42.3, 45.7, 49.0, 52.2, 63.8, 65.2, 65.4, 71.3, 80.1, 86.8, 96.3, 125.0, 126.9−128.9, 144.0, 178.1, 206.7. Anal. Calcd for $C_{39}H_{44}O_5$: C, 79.02; H, 7.48. Found: C, 79.38; H, 6.96.

Compound **18a**:



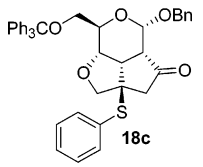
$[\alpha]_D$ (CH_2Cl_2, *c* 0.3) = +59.2°. IR (cm^{-1}): 1747. ^1H NMR (200 MHz, $CDCl_3$): 1.22 (t, 3 H, *J* = 7.31 Hz), 2.48−2.64 (m, 3 H), 2.70−2.83 (m, 2 H), 3.08 (m, 1 H), 3.32 (m, 2 H), 3.70 (m, 1 H), 3.86−4.02 (m, 3 H), 4.70 (ABq, 2 H, *J* = 12.56 Hz), 5.30 (d, 1 H, *J* = 7.44 Hz), 7.20 (m, 14 H), 7.42−7.53 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.6, 24.1, 29.7, 46.2, 48.6, 50.1, 52.2, 65.5, 69.0, 69.3, 73.2, 86.8, 93.9, 96.6, 127.0−128.8, 137.2, 144.0, 211.8. Anal. Calcd for $C_{38}H_{38}O_5S$: C, 75.22; H, 6.31; S, 5.28. Found: C, 75.59; H, 6.25; S, 5.34.

Compound **18b**:



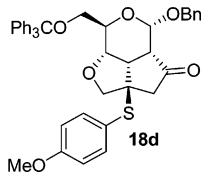
$[\alpha]_D$ ($CHCl_3$, *c* 1.16) = +67.51°. IR (cm^{-1}): 1747. ^1H NMR (200 MHz, $CDCl_3$): 0.80 (t, 3 H, *J* = 7.04 Hz), 1.25−1.53 (m, 4 H), 2.45−2.90 (m, 5 H), 3.02−3.13 (m, 1 H), 3.32 (m, 2 H), 3.73−3.99 (m, 4 H), 4.72 (ABq, 2 H, *J* = 11.99 Hz), 5.30 (d, 1 H, *J* = 7.50 Hz), 7.15−7.36 (m, 14 H), 7.41−7.52 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.6, 22.1, 29.7, 31.5, 46.0, 48.5, 50.0, 55.0, 65.4, 68.8, 69.1, 73.0, 77.3, 86.7, 93.8, 127.0−128.9, 137.1, 143.9, 212.0. Anal. Calcd for $C_{40}H_{42}O_5S$: C, 75.68; H, 6.67; S, 5.05. Found: C, 75.01; H, 6.34; S, 5.23.

Compound **18c**:



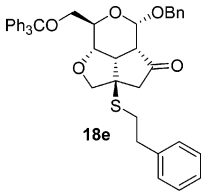
$[\alpha]_D$($CHCl_3$, *c* 0.44) = +84.14°. IR (cm^{-1}): 1747. ^1H NMR (200 MHz, $CDCl_3$): δ 2.62 (m, 2 H), 2.85 (m, 1 H), 3.06 (m, 1 H), 3.28 (m, 2 H), 3.83−3.95 (m, 4 H), 4.70 (ABq, 2 H, *J* = 12.36 Hz), 5.30 (d, 1 H, *J* = 7.75 Hz), 7.20−7.36 (m, 18 H), 7.41−7.49 (m, 7 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.7, 45.4, 48.5, 50.0, 58.1, 65.5, 69.3, 73.4, 77.0,86.8, 94.0, 127.0−129.3, 131.5, 135.9, 137.2, 144.0, 211.4. Anal. Calcd for $C_{42}H_{38}O_5S$: C, 77.04; H, 5.85; S, 4.90. Found: C, 77.11; H, 5.99; S, 5.01.

Compound **18d**:



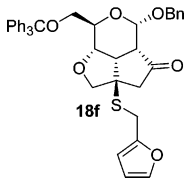
$[\alpha]_D$ ($CHCl_3$, *c* 0.98) = +84.92°. IR (cm^{-1}): 1747. ^1H NMR (200 MHz, $CDCl_3$): δ 2.54−2.74 (m, 2 H), 2.83 (dd, 1 H, *J* = 8.72, 10.89 Hz), 3.05 (ddd, 1 H, *J* = 1.39, 7.58, 10.72 Hz), 3.21 (dd, 1 H, *J* = 5.93, 9.92 Hz), 3.35 (dd, 1 H, *J* = 2.57, 9.98 Hz), 3.73−3.95 (m, 4 H), 3.76 (s, 3 H), 4.69 (ABq, 2 H, *J* = 12.36 Hz), 5.29 (d, 1 H, *J* = 7.49 Hz), 6.75−6.81 (m, 2 H), 7.20−7.48 (m, 22 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 45.0, 48.6, 50.0, 55.4, 58.2, 65.5, 69.3, 73.6, 76.8, 86.7, 94.0, 114.8, 116.1, 121.7, 127.1−128.6, 137.2, 138.3, 144.0, 160.9, 212.1. Anal. Calcd for $C_{43}H_{40}O_6S$: C, 75.41; H, 5.89; S, 4.68. Found: C, 75.21; H, 5.65; S, 4.49.

Compound **18e**:



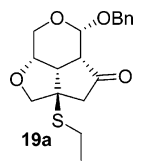
$[\alpha]_D$ ($CHCl_3$, *c* 1.16) = +76.38°. IR (cm^{-1}): 1747. ^1H NMR (200 MHz, $CDCl_3$): δ 2.56 (dd, 1 H, *J* = 1.01, 17.50 Hz), 2.68−2.91 (m, 6 H), 3.06 (ddd, 1 H, *J* = 1.50, 7.77, 10.78 Hz), 3.22−3.37 (m, 2 H), 3.81 (ABq, 2 H, *J* = 9.40 Hz), 3.94 (m, 2 H), 4.71 (ABq, 2 H, *J* = 12.27 Hz), 5.28 (d, 1 H, *J* = 7.56 Hz), 7.10−7.39 (m, 19 H), 7.41−7.50 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.7, 35.9, 46.1, 48.6, 50.1, 55.4, 65.5, 68.8, 69.3, 73.2, 77.4, 86.8, 93.8, 126.6−128.9, 137.2, 139.9, 143.9, 212.0. Anal. Calcd for $C_{44}H_{42}O_5S$: C, 77.39; H, 6.20; S, 4.70. Found: C, 77.12; H, 6.55; S, 4.94.

Compound **18f**:



$[\alpha]_D$ ($CHCl_3$, *c* 0.9) = +53.85°. IR (cm^{-1}): 1748. ^1H NMR (200 MHz, $CDCl_3$): δ 1.16 (dd, 1 H, *J* = 1.16, 17.82 Hz), 2.65−2.82 (m, 2 H), 3.05 (ddd, 1 H, *J* = 1.38, 7.81, 10.82 Hz), 3.25−3.39 (m, 2 H), 3.67 (ABq, 2 H, *J* = 9.58 Hz), 3.77 (m, 2 H), 3.90−3.98 (m, 2 H), 4.70 (ABq, 2 H, *J* = 12.22 Hz), 5.28 (d, 1 H, *J* = 7.54 Hz), 6.14 (d, 1 H, *J* = 3.12 Hz), 6.28 (dd, 1 H, *J* = 2.01, 3.17 Hz), 7.15−7.39 (m, 15 H), 7.40−7.52 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 27.1, 46.0, 48.4, 49.4, 55.3, 65.4, 68.8, 69.2, 72.7, 77.1, 86.7, 91.0, 93.8, 107.9, 110.8, 127.0−128.7, 137.1, 142.1 143.9, 150.7, 211.9. Anal. Calcd for $C_{41}H_{38}O_6S$: C, 74.75; H, 5.81; S, 4.87. Found: C, 74.89; H, 5.86; S, 4.78.

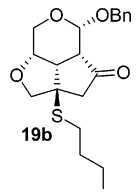
Compound **19a**:



$[\alpha]_D$ (CH_2Cl_2, *c* 3.5) = −95.9°. IR (cm^{-1}): 1749. ^1H NMR (200 MHz, $CDCl_3$): δ 7.48 (t, 3 H, *J* = 7.48 Hz), 2.55−2.78 (m, 4 H), 2.85 (dd, 1 H, *J* = 1.77, 18.77 Hz), 3.00 (dd,

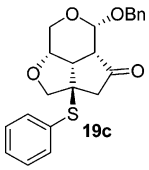
1 H, J = 7.27, 10.70 Hz), 3.70−4.13 (m, 5 H), 4.60 (ABq, 2 H, J = 11.60 Hz), 5.26 (s, 1 H), 7.30 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.7, 23.8, 44.1, 48.4, 51.2, 53.7, 58.2, 69.4, 73.3, 80.3, 94.8, 128.0, 128.5, 137.1, 211.3. Anal. Calcd for $C_{18}H_{22}O_4S$: C, 64.65; H, 6.63; S, 9.59. Found: C, 64.72; H, 6.58; S, 9.37.

Compound **19b**:



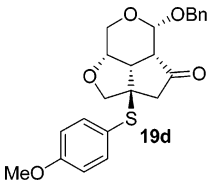
$[\alpha]_D$ ($CHCl_3$, c 1.5) = −97.7°. IR (cm^{-1}): 1749. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.92 (t, 3 H, J = 6.80 Hz), 1.32−1.65 (m, 4 H), 2.54−2.76 (m, 4 H), 2.84 (dd, 1 H, J = 1.74, 18.68 Hz), 3.01 (dd, 1 H, J = 7.29, 10.77 Hz), 3.70−4.13 (m, 5 H), 5.01 (ABq, 2 H, J = 11.50 Hz), 5.26 (s, 1 H), 7.35 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.6, 22.1, 29.5, 31.7, 44.1, 48.5, 51.3, 53.7, 58.2, 69.5, 73.4, 80.3, 94.9, 128.0, 128.5, 137.1, 211.4. Anal. Calcd for $C_{20}H_{26}O_4S$: C, 66.27; H, 7.23; S, 8.85. Found: C, 66.03; H, 7.31; S, 8.98.

Compound **19c**:



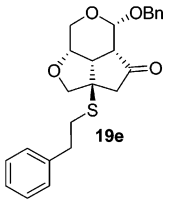
$[\alpha]_D$ (CH_2Cl_2, c 1.2) = −97.29°. IR (cm^{-1}): 1749. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.52 (d, 1 H, J = 18.93 Hz), 2.63 (ddd, 1 H, J = 0.75, 1.75, 10.86 Hz), 2.79 (dd, 1 H, J = 1.88, 18.93 Hz), 3.10 (dd, 1 H, J = 10.73, 7.33 Hz), 3.68−4.09 (m, 5 H), 4.59 (ABq, 2 H, J = 11.62 Hz), 5.22 (s, 1 H), 7.30−7.42 (m, 8 H), 7.48−7.56 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 43.9, 48.5, 50.7, 56.8, 58.3, 69.5, 73.3, 79.8, 94.9, 128.1−129.5, 131.0, 136.0, 137.1, 211.4. Anal. Calcd for $C_{22}H_{22}O_4S$: C, 69.09; H, 5.80; S, 8.38. Found: C, 68.58; H, 6.01; S, 8.48.

Compound **19d**:



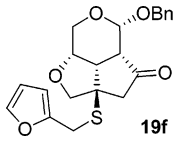
$[\alpha]_D$ ($CHCl_3$, c 0.8) = +64.4°. IR (cm^{-1}): 1749. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.56−2.75 (m, 3 H), 2.88 (dd,1 H, J = 8.65, 10.14 Hz), 3.72−3.95 (m, 5 H), 3.81 (s, 3 H), 4.66 (d, 1 H, J = 5.06 Hz), 4.71 (ABq, 2 H, J = 12.18 Hz), 6.84, 6.88 (2s, 2 H), 7.30 (m, 5 H), 7.38, 7.42 (2s, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 46.1, 47.5, 50.3, 55.3, 57.7, 65.7, 69.7, 72.7, 77.3, 97.3, 114.8, 121.2, 127.7−128.4, 137.0, 138.1, 160.8, 210.5. Anal. Calcd for $C_{23}H_{24}O_5S$: C, 66.97; H, 5.86; S, 7.77. Found: C, 66.73; H, 5.99; S, 7.94.

Compound **19e**:



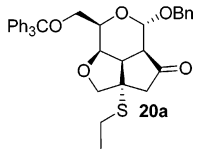
$[\alpha]_D$ ($CHCl_3$, c 0.9) = +68.23°. IR (cm^{-1}): 1747. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.64 (ddd, 1 H, J = 1.01, 2.23, 17.4 Hz), 2.73−2.91 (m, 7 H), 3.69 (d, 1 H, J = 9.09 Hz), 3.79 (dd, 1 H, J = 4.83, 12.88 Hz), 3.92−4.03 (m, 2 H), 4.14 (dd, 1 H, J = 2.03, 13.03 Hz), 4.51 (d, 1 H, J = 4.51 Hz), 4.71 (ABq, 2 H, J = 12.31 Hz), 7.13−7.38 (m, 10 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.3, 35.9, 46.9, 47.4, 50.6, 54.8, 65.4, 69.7, 72.5, 77.8, 97.1, 126.6−128.4, 136.9, 139.7, 210.5. Anal. Calcd for $C_{24}H_{26}O_4S$: C, 70.22; H, 6.38; S, 7.81. Found: C, 69.87; H, 6.15; S, 7.46.

Compound **19f**:



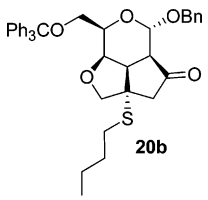
$[\alpha]_D$ ($CHCl_3$, c 0.82) = +24.14°. IR (cm^{-1}): 1746. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.61−2.85 (m, 4 H), 3.56 (d, 1 H, J = 9.17 Hz), 3.70−3.98 (m, 5 H), 4.14 (dd,1 H, J = 1.87, 12.86 Hz), 4.33 (d, 1 H, J = 4.33 Hz), 4.71 (ABq, 2 H, J = 12.45 Hz), 6.31 (dd, 1 H, J = 1.98, 3.21 Hz); 6.13 (ddd, 1 H, J = 0.54, 1.08, 3.16 Hz), 7.25−7.38 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.8, 47.0, 47.3, 50.0, 54.7, 65.3, 69.8, 72.2, 77.8, 97.1, 107.9, 110.8, 127.7−128.4, 136.9, 142.2, 150.8, 210.4. Anal. Calcd for $C_{21}H_{22}O_5S$: C, 65.27; H, 5.74; S, 8.30. Found: C, 65.43; H, 5.97; S, 8.99.

Compound **20a**:



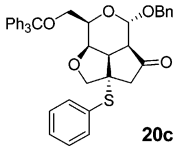
$[\alpha]_D$ ($CHCl_3$, c 0.48) = +10.04°. IR (cm^{-1}): 1747. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.24 (t, 3 H, J = 7.42 Hz), 2.50−2.89 (m, 5 H), 3.04 (dd, 1 H, J = 6.95, 10.97 Hz), 3.27 (dd, 1 H, J = 4.03, 9.99 Hz), 3.45 (dd, 1 H, J = 7.57, 9.97 Hz), 3.70 (dd, 1 H, J = 2.14, 6.84 Hz), 3.77 (ABq, 2 H, J = 9.10 Hz), 4.24 (m, 1 H), 4.74 (ABq, 2 H, J = 11.47 Hz), 5.36 (s, 1 H), 7.10−7.52 (m, 20 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.7, 23.9, 45.9, 48.3, 51.3, 53.2, 64.0, 66.3, 69.0, 74.2, 80.9, 86.7, 95.5, 127.0−128.7, 137.2, 144.0, 211.1. Anal. Calcd for $C_{38}H_{38}O_5S$: C, 75.22; H, 6.31; S, 5.28. Found: C, 75.45; H, 6.13; S, 5.34.

Compound **20b**:



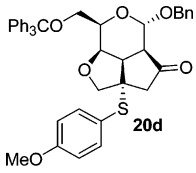
$[\alpha]_D$ ($CHCl_3$, *c* 1.4) = +10.96°. IR (cm^{-1}): 1743. ^1H NMR (200 MHz, $CDCl_3$): δ 0.91 (m, 3 H), 1.32−1.63 (m, 4 H), 2.50−2.85 (m, 5 H), 3.03 (dd, 1 H, *J* = 6.94, 11.02 Hz), 3.26 (dd, 1 H, *J* = 3.94, 9.87 Hz), 3.50 (dd, 1 H, *J* = 7.58, 9.85 Hz), 3.70 (dd, 1 H, *J* = 2.02, 6.96 Hz), 3.76 (ABq, 2 H, *J* = 9.04 Hz), 4.25 (m, 1 H), 4.74 (ABq, 2 H, *J* = 11.49 Hz), 5.36 (s, 1 H), 7.11−7.52 (m, 20 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.6, 22.1, 29.5, 31.7, 45.9, 48.3, 51.4, 53.2, 64.1, 66.3, 69.0, 74.2, 80.8, 86.8, 95.5, 127.0−128.8, 137.3, 144.0, 211.1. Anal. Calcd for $C_{40}H_{42}O_5S$: C, 75.68; H, 6.67; S, 5.05. Found: C, 75.34; H, 6.76; S, 5.33.

Compound **20c**:



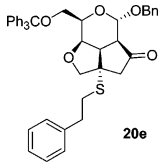
$[\alpha]_D$ ($CHCl_3$, *c* 1.0) = +14.37°. IR (cm^{-1}): 1747. ^1H NMR (200 MHz, $CDCl_3$): δ 2.43 (d, 1 H, *J* = 18.79 Hz), 2.61 (dd, 1 H, *J* = 1.52, 10.89 Hz), 2.75 (dd, 1 H, *J* = 1.51, 18.71 Hz), 3.09−3.27 (m, 2 H), 3.48 (dd, 1 H, *J* = 7.83, 9.96 Hz), 3.61 (dd, 1 H, *J* = 2.03, 9.23 Hz), 3.76 (ABq, 2 H, *J* = 9.23 Hz), 4.22 (m, 1 H), 4.74 (ABq, 2 H, *J* = 11.51 Hz), 5.33 (s, 1 H), 7.15−7.53 (m, 25 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 45.6, 48.2, 50.7, 56.3, 64.0, 66.2, 69.0, 74.1, 80.1, 86.7, 95.5, 126.9−129.4, 131.0, 136.0, 137.2, 144.0, 211.0. Anal. Calcd for $C_{42}H_{38}O_5S$: C, 77.04; H, 5.85; S, 4.90. Found: C, 77.57; H, 5.95; S, 4.99.

Compound **20d**:



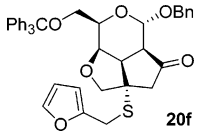
$[\alpha]_D$ ($CHCl_3$, *c* 0.78) = +19.46°. IR (cm^{-1}): 1747. ^1H NMR (200 MHz, $CDCl_3$): δ 2.42 (d, 1 H, *J* = 18.83 Hz), 2.58 (dd, 1 H, *J* = 1.56, 11.00 Hz), 2.73 (dd, 1 H, *J* = 1.49, 18.69 Hz), 3.06−3.25 (m, 2 H), 3.48 (dd, 1 H, *J* = 7.95, 9.97 Hz), 3.57 (dd, 1 H, *J* = 1.90, 6.95 Hz), 3.71 (ABq, 2 H, *J* = 9.26 Hz), 3.80 (s, 3 H), 4.21 (m, 1 H), 4.69 (ABq, 2 H, *J* = 11.53 Hz), 5.32 (s, 1 H), 6.84, 6.88 (2s, 2 H), 7.17−7.51 (m, 22 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 45.5, 48.3, 50.6, 55.4, 56.5, 64.1, 66.3, 69.1, 74.3, 79.8, 86.8, 95.6, 114.9, 121.5, 127.0−128.8, 137.3, 138.2, 144.1, 160.9, 211.3. Anal. Calcd. for $C_{43}H_{40}O_6S$: C, 75.41; H, 5.89; S, 4.68. Found: C, 75.88; H, 5.98; S, 4.94.

Compound **20e**:



$[\alpha]_D$ ($CHCl_3$, *c* 0.9) = +68.23°. IR (cm^{-1}): 1747. ^1H NMR (200 MHz, $CDCl_3$): δ 2.46−2.74 (m, 3 H), 2.82 (m, 4 H), 3.00 (dd, 1 H, *J* = 6.96, 11.01 Hz), 3.25 (dd, 1 H, *J* = 4.06, 9.97 Hz), 3.53 (dd, 1 H, *J* = 7.58, 9.96 Hz), 3.67 (dd, 1 H, *J* = 2.31, 6.74 Hz), 3.71 (ABq, 2 H, *J* = 9.12 Hz), 4.22 (m, 1 H), 4.73 (ABq, 2 H, *J* = 11.56 Hz), 5.35 (s, 1 H), 7.11−7.45 (m, 25 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.4, 35.8, 45.7, 48.2, 51.3, 53.3, 64.0, 66.2, 69.0, 74.2, 80.6, 86.7, 95.4, 126.7−128.7, 137.2, 139.7, 144.0, 210.8. Anal. Calcd for $C_{44}H_{42}O_5S$: C, 77.39; H, 6.20; S, 4.70. Found: C, 77.89; H, 5.99; S, 4.49.

Compound **20f**:



$[\alpha]_D$ ($CHCl_3$, *c* 0.82) = +24.14°. IR (cm^{-1}): 1747. ^1H NMR (200 MHz, $CDCl_3$): δ 2.49 (d, 1 H, *J* = 18.69 Hz), 2.67 (dd, 1 H, *J* = 1.10, 11.14 Hz), 2.79 (dd, 1 H, *J* = 1.52, 18.66 Hz), 2.97 (dd, 1 H, *J* = 6.85, 10.98 Hz), 3.24 (dd, 1 H, *J* = 4.16, 9.98 Hz), 3.48 (dd, 1 H, *J* = 7.69, 9.09 Hz), 3.61 (ABq, 2 H, *J* = 9.26 Hz), 3.66 (dd, 1 H, *J* = 2.l5, 6.86 Hz), 3.80 (m, 2 H), 4.21 (m, 1 H), 4.67 (ABq, 2 H, *J* = 11.71 Hz), 5.35 (s, 1 H), 6.16 (dd, 1 H, *J* = 0.63, 3.27 Hz), 6.31 (dd, 1 H, *J* = 1.89, 3.16 Hz), 7.15−7.48 (m, 21 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 27.1, 46.0, 48.1, 50.9, 53.2, 64.1, 66.3, 69.0, 73.9, 81.1, 86.8, 95.5, 108.0, 111.0, 127.0−128.8, 137.3, 142.3, 144.1, 150.9, 210.9. Anal. Calcd for $C_{41}H_{38}O_6S$: C, 74.75; H, 5.81; S, 4.87. Found: C, 74.39; H, 5.45; S, 4.60.

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Supporting Information Available. General experimental procedures and ^1H, ^{13}C, and DEPT NMR spectra of some of enynes, enones, and thiolate addition products. This material is available free of charge via Internet at http://pubs.acs.org.

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