Cobalt Carbonyl-Catalyzed Tandem [2+2+1]/[4+2] Cycloaddition of Dienediyne to New Tetracycles

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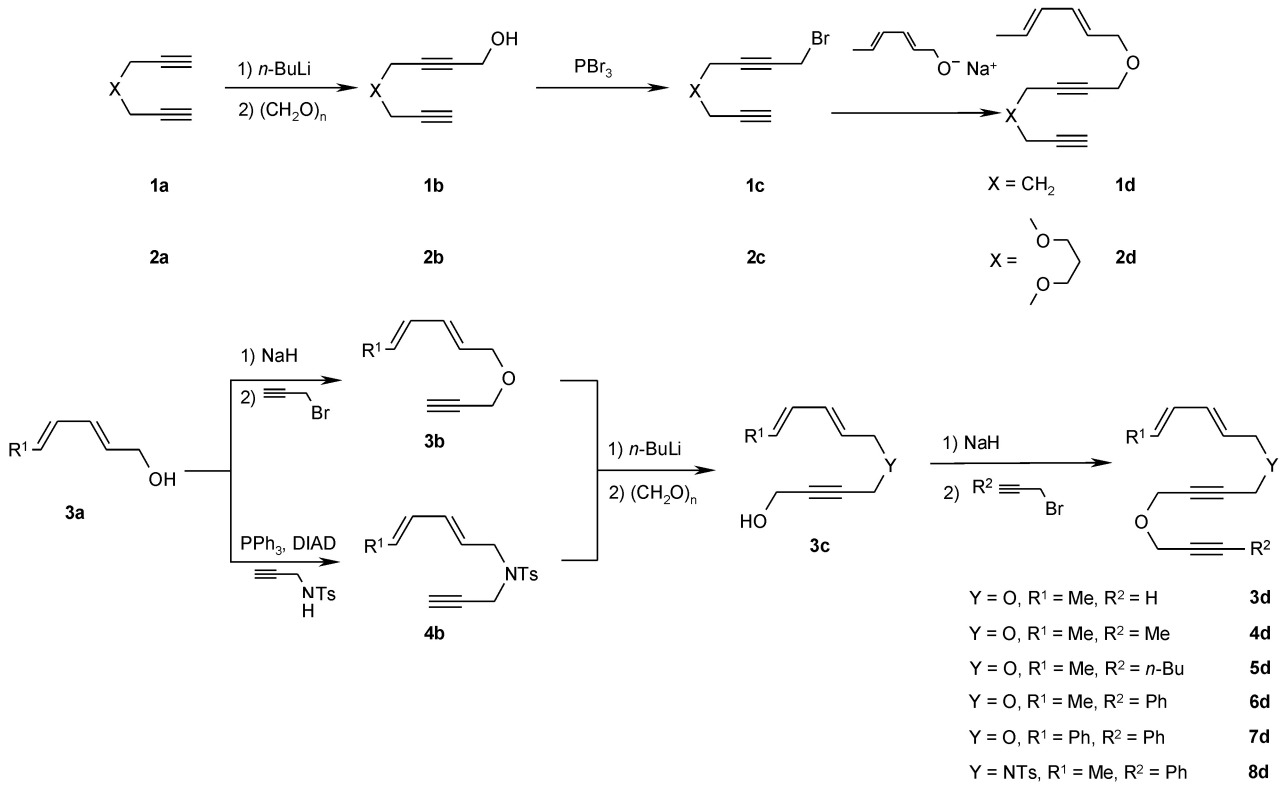
Abstract: A tandem reaction of dienediynes catalyzed by dicobalt octacarbonyl gives teracyclic compounds in a poor to high yield depending upon the substrate. The structural frame of the synthesized polycyclic compounds is disclosed for the first time in this study.

Key words: carbonylation, cyclization, enone, polycycle, tandem reaction

The last decade has witnessed a myriad of developments in cycloaddition reactions involving a combination of alkene–alkyne, diene–alkene, diene–alkyne, and so on.[1] Most of them are catalyzed by transition metal complexes.[2] Nowadays, much interest has been paid to transition-metal-catalyzed tandem reactions, in which multiple reactions are combined into one synthetic opearation.[3] Thus, multi-component cycloadditions involving three or more functional groups have been recently reported.[4]

Recently, we reported[5] an access to polycyclic compounds via a tandem intermolecular Pauson–Khand reaction (PKR) and Diels–Alder reaction (DAR) of cyclic alkenes, enynes, and dienophiles. The alkyne group of enynes participated in the PKR and the dienophile selectively participated in the DAR, resulted in high yields of the cyclic compounds. In other words, the combination of PKR and DAR was one of the best examples of the combination of two chemical reactions.

In continuation of our ongoing study on the cobalt carbonyl [$Co_2(CO)_8$]-catalyzed cycloaddition reaction,[6] we have explored the tandem PKR and DAR of newly designed dienediyne substrates to generate new polycyclic compounds. The structural frame of the synthesized polycyclic compounds is disclosed for the first time in this study.



Scheme 1 Synthesis of dienediynes

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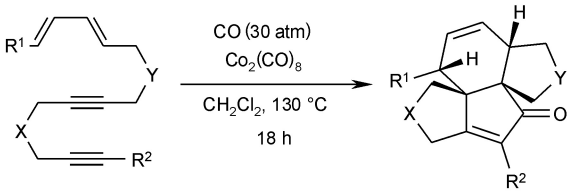
Both the structures of the dienediyne substrates (**1d**–**8d**) used in this study and of the cyclic compounds (**1**–**8**) prepared in this study are drawn in Scheme 1 and Equation 1. The dienediynes were synthesized by the methods shown in Scheme 1. Carbon- and oxygen-tethered dienediynes were prepared by different reaction routes. Reaction of the known diynes **1a** and **2a** with *n*-butyllithium followed by addition of *para*-formaldehyde furnished the diynols **1b** and **2b**. The bromo compounds **1c** and **2c** were prepared by reaction of PBr_3 with **1b** and **2b**. Reaction of **1c** and **2c** with an alkoxide generated by a reaction of 2,4-hexadien-1-ol with sodium hydride afforded the diynes **1d** and **2d** in high yields. Oxygen-tethered dienediynes **3d**–**8d** were prepared by the reaction of an alkoxide (generated by a reaction of **3c** with NaH) with substituted propargyl bromide.[7]

Tandem cycloaddition of the dienediynes was effected by using the reaction conditions [5 mol% of $Co_2(CO)_8$, 30 atm of CO, 18 h, CH_2Cl_2] that we have previously described.[6] Thus, treatment of dienediyne with dicobalt octacarbonyl in dichloromethane at 130 °C under 30 atm of CO for 18 hours yielded a tetracyclic compound in poor to high yield (Equation 1).[7]



1	23%
2	55%
3	19%
4	64%
5	57%
6	73%
7	52%
8	59%

Equation 1

The structure of one of the products **3** was characterized by an X-ray diffraction study (Figure 1).[8] The structural frame of the synthesized polycyclic compounds is disclosed for the first time in this study as far as we are aware.

There are two stereocenters in the molecule. The crystal structure shows that the termini of the diene of the dienediyne rotate in opposite directions and each proton on the 1- and 4-positions of diene moiety faces the same direction. Thus, the disrotatory mode is allowed, as expected from the thermal Diels–Alder reaction.

The yields were highly dependent upon the substrate itself. When the substrate was a terminal alkyne (**1d** and **3d**), the yield was rather poor, presumably due to side reactions, e.g. oligomerization of the substrate. A similar observation was reported by Inoue et al.[9] They attempted to use 1,6-diynes containing a terminal alkyne group in the palladium-catalyzed cycloaddition reaction of 1,6-diyne and carbon monoxide. Unfortunately, it was unsuccessful. In contrast to the internal 1,6-diynes, they were consumed by side reactions, e.g. oligomerization. Thus, an introduction of a bulky group will reduce the possibility of oligomerization of the substrates and will increase the yield of the reaction. As expected, internal alkynes (**4d**–**8d**) gave a much higher yield. Moreover, an introduction of the quaternary carbon center (**2d**) instead of a methylene group also promoted the yield to 55%, presumably due to the steric hindrance of the substituents on the quaternary carbon in the oligomerization.

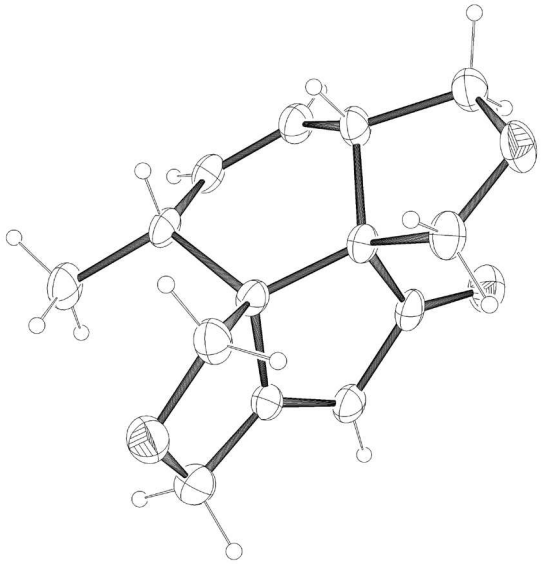
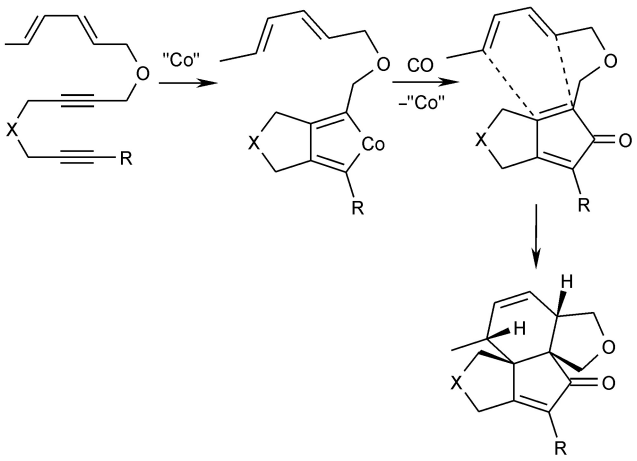


Figure 1 ORTEP drawing of **3**

A plausible mechanism is shown in Scheme 2. From the π-complexation of diyne with cobalt, the formation of cobaltacyclopentadiene, CO insertion, demetallation, and the Diels–Alder reaction follow.



Scheme 2 Proposed mechanism of tandem [2+2+1]/[4+2] cycloaddition of dienediyne

In conclusion, a cobalt carbonyl-catalyzed tandem [2+2+1]/[4+2] cycloaddition reaction of dienediyne has been developed, yielding new tetracycles. Further studies on the application of the new tetracycles as molecular scaffolds are underway.

General Procedure for [2+2+2] Cycloaddition

To a 100-mL high-pressure reactor were added **6d** (0.20 g, 0.71 mmol), 30 mL of CH_2Cl_2, and $Co_2(CO)_8$ (12 mg, 36 μmol). After the solution was flushed with CO gas in several seconds, the reactor was pressurized with 30 atm of CO. The reactor was heated at 130 °C for 18 h. After the reactor was cooled to r.t. and excess gas was relieved, the solution was transferred into a flask and then evaporated to dryness. The residue was chromatographed on a silica gel column eluting with hexane and EtOAc (v/v, 10:1).

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(7) Compound **1d**: yield 59%. ^{1}H NMR ($CDCl_3$): δ = 6.22 (dd, *J* = 10.4, 15.1 Hz, 1 H), 6.06 (dd, 10.6, 14.9 Hz, 1 H), 5.70 (m, 1 H), 5.54 (m, 1 H), 4.10 (t, *J* = 2.1 Hz, 2 H), 4.04 (d, *J* = 6.4 Hz, 2 H), 2.36 (tt, *J* = 2.1, 7.0 Hz, 2 H), 2.30 (dd, *J* = 2.6, 7.0 Hz, 2 H), 1.97 (t, *J* = 2.6 Hz, 1 H), 1.75 (d, *J* = 6.6 Hz, 2 H), 1.73 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 134.0, 130.8, 130.3, 126.0, 85.6, 83.5, 76.8, 69.9, 69.0, 57.4, 27.5, 18.2, 17.8, 17.6. HRMS: *m/z* calcd for $C_{14}H_{18}O_1$: 202.1358; found: 202.1353.
Compound **2d**: yield 63%. ^{1}H NMR ($CDCl_3$): δ = 6.23 (dd, *J* = 10.4, 15.1 Hz, 1 H), 6.06 (dd, 10.6, 14.8 Hz, 1 H), 5.73 (m, 1 H), 5.61 (m, 1 H), 4.13 (t, *J* = 1.9 Hz, 2 H), 4.07 (d, *J* = 6.4 Hz, 2 H), 3.38–3.34 (m, 4 H), 3.35 (s, 3 H), 3.34 (s, 3 H), 2.39 (t, *J* = 1.9 Hz, 2 H), 2.33 (d, *J* = 2.6 Hz, 2 H), 1.98 (t, *J* = 2.6 Hz, 1 H), 1.76 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 134.0, 130.7, 130.3, 125.9, 83.0, 80.8, 78.2, 73.6, 70.4, 69.7, 59.4, 57.3, 41.8, 22.2, 21.9, 18.1. HRMS: *m/z* calcd for $C_{18}H_{26}O_3$: 290.1882; found: 290.1883.
Compound **3d**: yield 71%. ^{1}H NMR ($CDCl_3$): δ = 6.22 (dd, *J* = 10.4, 15.0 Hz, 1 H), 6.06 (m, 1 H), 5.74 (m, 1 H), 5.60 (m, 1 H), 4.31 (t, *J* = 1.7 Hz, 2 H), 4.25 (s, 2 H), 4.18 (t, *J* = 1.7 Hz, 2 H), 4.06 (d, *J* = 6.4 Hz, 2 H), 2.45 (m, 1 H), 1.75 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 134.3, 130.8, 130.6, 125.7, 83.3, 81.4, 79.0, 75.1, 70.2, 57.1, 56.9, 56.5, 18.2. HRMS: *m/z* calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1155.
Compound **4d**: yield 83%. ^{1}H NMR ($CDCl_3$): δ = 6.23 (dd, *J* = 10.5, 14.9 Hz, 1 H), 6.06 (m, 1 H), 5.74 (m, 1 H), 5.60 (m, 1 H), 4.28 (t, *J* = 1.7 Hz, 2 H), 4.22–4.18 (m, 2 H), 4.17 (d, *J* = 1.7 Hz, 2 H), 4.06 (d, *J* = 6.4 Hz, 2 H), 1.86 (m, 3 H), 1.76 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 134.2, 130.8, 130.5, 125.7, 83.2, 82.8, 81.8, 74.4, 70.1, 57.2, 57.1, 56.6, 18.2, 3.6. HRMS: *m/z* calcd for $C_{14}H_{18}O_2$: 218.1307; found: 218.1309.
Compound **5d**: yield 77%. ^{1}H NMR ($CDCl_3$): δ = 6.23 (dd, *J* = 10.5, 15.0 Hz, 1 H), 6.07 (dd, *J* = 10.5, 15.0 Hz, 1 H), 5.73 (m, 1 H), 5.61 (m, 1 H), 4.29 (s, 2 H), 4.23 (t, *J* = 1.7 Hz, 2 H), 4.18 (s, 2 H), 4.07 (d, *J* = 6.4 Hz, 2 H), 2.23 (t, *J* = 6.8 Hz, 2 H), 1.76 (d, *J* = 6.6 Hz, 3 H), 1.47 (m, 2 H), 1.42 (m, 2 H), 0.91 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 134.4, 130.8, 130.7, 125.8, 82.9, 81.9, 75.1, 70.2, 57.4, 57.2, 56.7, 31.8, 30.8, 22.1, 18.6, 18.3, 13.8. HRMS: *m/z* calcd for $C_{17}H_{24}O_2$: 260.1776; found: 260.1776.
Compound **6d**: yield 66%. ^{1}H NMR ($CDCl_3$): δ = 7.47–7.44 (m, 2 H), 7.33–7.30 (m, 3 H), 6.23 (dd, *J* = 10.4, 15.0 Hz, 1 H), 6.06 (m, 1 H), 5.73 (m, 1 H), 5.61 (m, 1 H), 4.48 (s, 2 H), 4.38 (t, *J* = 1.7 Hz, 2 H), 4.20 (t, *J* = 1.7 Hz, 2 H), 4.08 (d, *J* = 6.5 Hz, 2 H), 1.75 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 134.2, 131.8, 130.6, 130.5, 128.5, 128.3, 125.6, 122.4, 86.8, 84.2, 83.1, 81.5, 70.1, 57.3, 57.1, 56.9, 18.1. HRMS: *m/z* calcd for $C_{19}H_{20}O_2$: 280.1463; found: 280.1469.
Compound **7d**: yield 65%. ^{1}H NMR ($CDCl_3$): δ = 7.42–7.30 (m, 4 H), 7.30–7.09 (m, 6 H), 6.71 (dd, *J* = 10.5, 15.6 Hz, 1 H), 6.48 (d, *J* = 15.6 Hz, 1 H), 5.37 (dd, *J* = 10.5, 15.2 Hz, 1 H), 5.79 (dt, *J* = 6.3, 15.2 Hz, 1 H), 4.42 (s, 2 H), 4.31 (t, *J* = 1.7 Hz, 2 H), 4.16 (t, *J* = 1.7 Hz, 2 H), 4.09 (d, *J* = 6.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 137.2, 134.0, 133.3, 131.9, 129.1, 128.8, 128.7, 128.5, 128.2, 127.8, 126.6, 122.6, 87.0, 84.3, 83.1, 81.9, 70.1, 57.5, 57.4, 57.0. HRMS: *m/z* calcd for $C_{24}H_{22}O_2$: 342.1620; found: 342.1613.
Compound **8d**: yield 70%. ^{1}H NMR ($CDCl_3$): δ = 7.57 (d, *J* = 8.2 Hz, 2 H), 7.27–7.25 (m, 2 H), 7.17–7.09 (m, 3 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 5.99 (dd, *J* = 10.4, 15.0 Hz, 1 H), 5.84 (m, 1 H), 5.54 (m, 1 H), 5.25 (m, 1 H), 4.08 (s, 2 H), 3.96 (s, 2 H), 3.90 (s, 2 H), 3.66 (d, *J* = 6.9 Hz, 2 H), 2.22 (s, 3 H), 1.57 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 143.7, 136.3, 135.7, 131.9, 131.2, 130.5, 129.7, 128.9, 128.6, 128.0, 123.6, 122.6, 87.0, 84.2, 81.0, 80.0, 57.3, 56.7, 48.7, 36.2, 21.7, 18.2. HRMS: *m/z* calcd for $C_{26}H_{27}O_3N_1S_1$: 433.1712; found: 433.1715.
Compound **1**: yield 23%. ^{1}H NMR ($CDCl_3$): δ = 6.07 (dt, *J* = 3.3, 8.8 Hz, 1 H), 5.80 (s, 1 H), 5.48 (dt, *J* = 3.0, 8.8 Hz, 1 H), 4.49 (dd, *J* = 7.0, 11.4 Hz, 1 H), 4.20 (dd, *J* = 7.1, 9.0

Hz, 1 H), 3.83 (d, *J* = 8.3 Hz, 1 H), 3.67 (d, *J* = 8.3 Hz, 1 H), 2.85 (m, 1 H), 2.28 (m, 1 H), 2.62 (d, *J* = 8.3 Hz, 2 H), 1.85 (m, 2 H), 1.75 (m, 2 H), 1.21 (d, *J* = 7.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 212.6, 189.8, 135.1, 130.2, 125.2, 69.7, 69.5, 68.5, 58.0, 44.9, 43.5, 31.0, 29.6, 25.2, 16.6. IR: 1694 (C=O) cm^{-1}. HRMS: *m/z* calcd for $C_{15}H_{18}O_2$: 230.1307; found: 230.1301.

Compound **2**: yield 55%. ^{1}H NMR ($CDCl_3$): δ = 5.98 (dt, *J* = 3.2, 8.8 Hz, 1 H), 5.74 (s, 1 H), 5.43 (dt, *J* = 2.9, 8.8 Hz, 1 H), 4.39 (dd, *J* = 7.0, 11.3 Hz, 1 H), 4.11 (dd, *J* = 7.2, 8.8 Hz, 1 H), 3.76 (d, *J* = 8.5 Hz, 1 H), 3.57 (d, *J* = 8.4 Hz, 1 H), 3.39 (d, *J* = 2.3 Hz, 2 H), 3.33 (s, 3 H), 3.17 (s, 3 H), 2.85 (dd, *J* = 9.0, 16.0, 2 H), 2.72 (m, 1 H), 2.60 (dd, *J* = 1.8, 15.6 Hz, 1 H), 2.37 (d, *J* = 15.6 Hz, 1 H), 2.16 (m, 1 H), 1.86 (d, *J* = 14.9 Hz, 1 H), 1.56 (d, *J* = 14.9 Hz, 1 H), 1.15 (d, *J* = 7.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 212.2, 188.4, 134.4, 130.6, 126.7, 76.1, 75.5, 69.7, 69.6, 69.5, 59.2, 59.0, 56.6, 48.5, 44.5, 44.4, 37.2, 35.2, 16.6. IR: 1698 (C=O) cm^{-1}. HRMS: *m/z* calcd for $C_{19}H_{26}O_4$: 318.1831; found: 318.1830.

Compound **3**: yield 19%. ^{1}H NMR ($CDCl_3$): δ = 6.11 (dt, *J* = 3.3, 8.8 Hz, 1 H), 5.95 (s, 1 H), 5.50 (dt, *J* = 3.0, 8.8 Hz, 1 H), 4.68 (dd, *J* = 2.0, 16.4 Hz, 1 H), 4.52 (d, *J* = 16.4 Hz, 1 H), 4.48 (dd, *J* = 7.2, 11.4 Hz, 1 H), 4.19 (dd, *J* = 7.2, 8.8 Hz, 1 H), 4.04 (d, *J* = 8.8 Hz, 1 H), 3.77 (d, *J* = 8.4 Hz, 1 H), 3.73 (d, *J* = 8.4 Hz, 1 H), 3.71 (d, *J* = 8.8 Hz, 1 H), 2.89 (m, 1 H), 2.52 (m, 1 H), 1.33 (d, *J* = 7.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 210.7, 183.1, 135.0, 130.1, 124.8, 74.1, 68.9, 68.5, 67.3, 66.9, 58.4, 45.3, 42.1, 15.9. IR: 1706 (C=O) cm^{-1}. HRMS: *m/z* calcd for $C_{14}H_{16}O_3$: 232.1099; found: 232.1098.

Compound **4**: yield 64%. ^{1}H NMR ($CDCl_3$): δ = 6.08 (dt, *J* = 3.2, 8.8 Hz, 1 H), 5.47 (dt, *J* = 3.0, 8.8 Hz, 1 H), 4.62 (d, *J* = 15.8 Hz, 1 H), 4.51 (t, *J* = 11.4 Hz, 1 H), 4.50 (d, *J* = 11.6 Hz, 1 H), 4.20 (dd, *J* = 7.1, 8.8 Hz, 1 H), 4.03 (d, *J* = 8.5 Hz, 1 H), 3.76 (d, *J* = 8.3 Hz, 1 H), 3.66 (d, *J* = 8.6 Hz, 2 H), 2.90 (m, 1 H), 2.49 (m, 1 H), 1.70 (s, 3 H), 1.32 (d, *J* = 7.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 210.8, 175.5, 135.4, 133.3, 129.9, 74.3, 69.1, 68.8, 66.8, 66.4, 56.4, 45.7, 42.3, 16.0, 9.4. IR: 1707 (C=O) cm^{-1}. HRMS: *m/z* calcd for $C_{15}H_{18}O_3$: 246.1256; found: 246.1258.

Compound **5**: yield 57%. ^{1}H NMR ($CDCl_3$): δ = 6.08 (dt, *J* = 3.2, 8.8 Hz, 1 H), 5.46 (dt, *J* = 3.0, 8.8 Hz, 1 H), 4.62 (d, *J* = 15.9 Hz, 1 H), 4.53 (t, *J* = 3.5 Hz, 1 H), 4.49 (d, *J* = 7.3 Hz, 1 H), 4.20 (dd, *J* = 7.1, 8.8 Hz, 1 H), 4.02 (d, *J* = 8.8 Hz, 1 H), 3.77 (d, *J* = 8.3 Hz, 1 H), 3.65 (d, *J* = 8.3 Hz, 2 H), 2.88 (m, 1 H), 2.48 (m, 1 H), 2.25 (m, 1 H), 2.03 (m, 1 H), 1.36 (m, 2 H), 1.32 (d, *J* = 7.3 Hz, 3 H), 1.27 (m, 2 H), 0.89 (t, *J* = 3.5 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 210.7, 175.4, 137.7, 135.3, 130.3, 74.4, 69.2, 68.8, 67.0, 66.5, 56.5, 45.7, 42.4, 30.1, 24.2, 22.6, 16.2, 14.0. IR: 1708 (C=O) cm^{-1}. HRMS: *m/z* calcd for $C_{18}H_{24}O_3$: 288.1725; found: 288.1723.

Compound **6**. yield 73%. ^{1}H NMR ($CDCl_3$): δ = 7.50–7.47 (m, 2 H), 7.40–7.34 (m, 3 H), 6.11 (dt, *J* = 3.3, 8.8 Hz, 1 H), 5.51 (dt, *J* = 3.0, 8.8 Hz, 1 H), 4.97 (d, *J* = 16.7 Hz, 1 H), 4.61 (t, *J* = 3.5 Hz, 1 H), 4.56 (d, *J* = 7.4 Hz, 1 H), 4.25 (dd, *J* = 7.1, 9.1 Hz, 1 H), 4.09 (d, *J* = 8.8 Hz, 1 H), 3.82 (d, *J* = 4.0 Hz, 2 H), 3.68 (d, *J* = 8.8 Hz, 1 H), 2.96 (m, 1 H), 2.59 (m, 1 H), 1.42 (d, *J* = 7.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ = 208.4, 176.6, 135.1, 134.8, 130.4, 130.2, 128.8, 128.5, 128.2, 73.7, 69.1, 68.5, 68.1, 67.8, 56.2, 45.5, 42.6, 16.0. IR: 1706 (C=O) cm^{-1}. HRMS: *m/z* calcd for $C_{20}H_{20}O_3$: 308.1412; found: 308.1413.

Compound **7**: yeld 52%. ^{1}H NMR ($CDCl_3$): δ = 7.46–7.34 (m, 4 H), 7.33–7.25 (m, 6 H), 6.63 (d, *J* = 16.2 Hz, 1 H), 6.17 (dd, *J* = 6.7, 16.2 Hz, 1 H), 4.98–4.85 (m, 2 H), 4.85 (d, *J* = 7.4 Hz, 1 H), 4.37 (dd, *J* = 7.2, 9.1 Hz, 1 H), 4.09 (d, *J* = 9.0 Hz, 1 H), 4.06 (d, *J* = 8.8 Hz, 2 H), 3.92 (d, *J* = 8.8 Hz, 1 H), 3.09 (m, 1 H), 2.68 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ = 207.9, 176.5, 135.2, 135.0, 130.3, 129.0, 128.8, 128.6, 128.5, 128.4, 128.2, 128.0, 127.8, 73.3, 69.0, 68.5, 67.9, 67.8, 56.1, 45.5, 42.4. IR: 1705 (C=O) cm^{-1}. HRMS: *m/z* calcd for $C_{25}H_{22}O_3$: 370.1569; found: 370.1564.

Compound **8**: yield 59%, ^{1}H NMR ($CDCl_3$): δ = 7.70 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.26–7.23 (m, 3 H), 7.07–7.01 (m, 2 H), 5.89 (dt, *J* = 3.2, 8.9 Hz, 1 H), 5.33 (dt, *J* = 2.9, 8.9 Hz, 1 H), 4.83 (d, *J* = 16.8 Hz, 1 H), 4.43 (d, *J* = 16.8 Hz, 1 H), 4.01 (dd, *J* = 7.1, 8.9 Hz, 1 H), 3.98 (d, *J* = 8.9 Hz, 1 H), 3.61 (s, 2 H), 3.41 (d, *J* = 10.6 Hz, 1 H), 3.14 (d, *J* = 10.6 Hz, 1 H), 2.73 (m, 1 H), 2.44 (s, 3 H), 2.40 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ = 207.2, 176.3, 143.3, 135.0, 134.9, 134.5, 130.6, 130.0, 129.6, 128.9, 128.5, 128.2, 127.6, 73.7, 68.1, 67.1, 65.2, 56.8, 49.3, 43.6, 41.9, 21.6, 16.0. IR: 1706 (C=O) cm^{-1}. HRMS: *m/z* calcd for $C_{27}H_{27}O_4N_1S_1$: 461.1661; found: 461.1664.

(8) Compound **3**: $C_{14}H_{16}O_3$, *M* = 232.27, monoclinic, space group *P*2 (1)/c, *a* = 8.223 (2) Å, *b* = 8.552 (3) Å, *c* = 16.543 (3) Å, *β* = 91.633 (19), *V* = 1163.0(5) Å^3, *Z* = 4, D_c = 1.327 mg m^{-3}, $\mu(MoK_\alpha)$ = 0.092 mm^{-1}, *F*(000) = 496. No. of data collected: 2769, no. of unique data: 949, *R* = 0.0641, R_w = 0.1749. A single crystal was placed on an Enraf-Nonius CCD single crystal X-ray diffractometer. The structures were solved by direct methods (SHELXS-97) and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. Data collected at 293 (2) K with MoK_α radiation: $\lambda(K_\alpha)$ = 0.7107 Å), $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]^2]]^{1/2}$ with $F_o > 2.0\sigma(I)$. CCDC reference number 272770.

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