

Nazarov Cyclization and Tandem [4+2]-Cycloaddition Reactions of Donor-Acceptor Cyclopropanes

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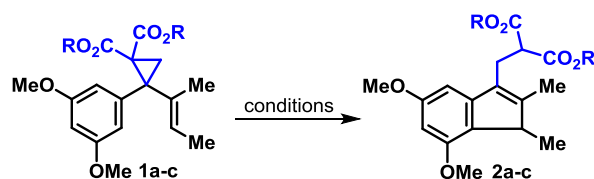
SUPPORTING INFORMATION

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1. General Table and Schemes

Optimization of reaction conditions:

We employed aryl vinyl DAC **1a** with several Lewis acids and Bronsted acid, trifluoroacetic acid (TFA). To our gratification, the reaction is found to afford the desired product in high yields. When 1M TiCl₄ in CH₂Cl₂ at -78 °C was used, the reaction gave the desired product **2a** in 93% yield (entry 1). Slightly improved yield (95%) was obtained with TFA (entry 2). When **1a** was subjected with 0.1 equiv of BF₃.OEt₂, the formation of **2a** was observed in almost quantitative yield (entry 3). Other Lewis acids such as FeCl₃, Cu(OTf)₂, and Sc(OTf)₃ also provided in very good yields (entries 4-6). With BF₃.Et₂O, dienyl DACs with different ester groups (**1b** and **1c**) were tested to verify the effect of the ester group in the conversion of the product. Obtaining **2b** in 96% and **2c** in 93% yield (comparable with a yield of **2a**) implies that there is no such profound effect of the ester group (entries 7 & 8).

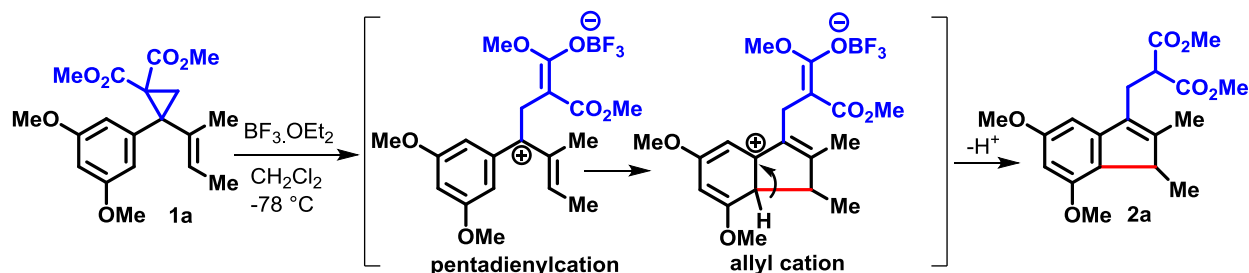


Entry ^a	Reagent ^b	1	Time (h)	(2) Yield ^c
1	TiCl ₄	1a (R = Me)	1.75	(2a) 93%
2	TFA	1a (R = Me)	1.75	(2a) 95%
3	BF₃.Et₂O	1a (R = Me)	1.5	(2a) 99%
4	FeCl ₃	1a (R = Me)	2.0	(2a) 88%
5	Cu(OTf) ₂	1a (R = Me)	1.5	(2a) 91%
6	Sc(OTf) ₃	1a (R = Me)	1.25	(2a) 90%
7	BF ₃ .Et ₂ O	1b (R = Et)	1.5	(2b) 96%
8	BF ₃ .Et ₂ O	1c (R = Bn)	1.5	(2c) 93%

^aReaction conditions: **1a** (0.1 mmol), CH₂Cl₂ (0.1 M) with respect to the aryl vinyl DAC **1** at -78 °C; ^b10 (mol%) acid; ^cIsolated product yield.

1a. Nazarov cyclization of Donor-Acceptor Aryl vinyl Cyclopropane and its plausible reaction mechanism

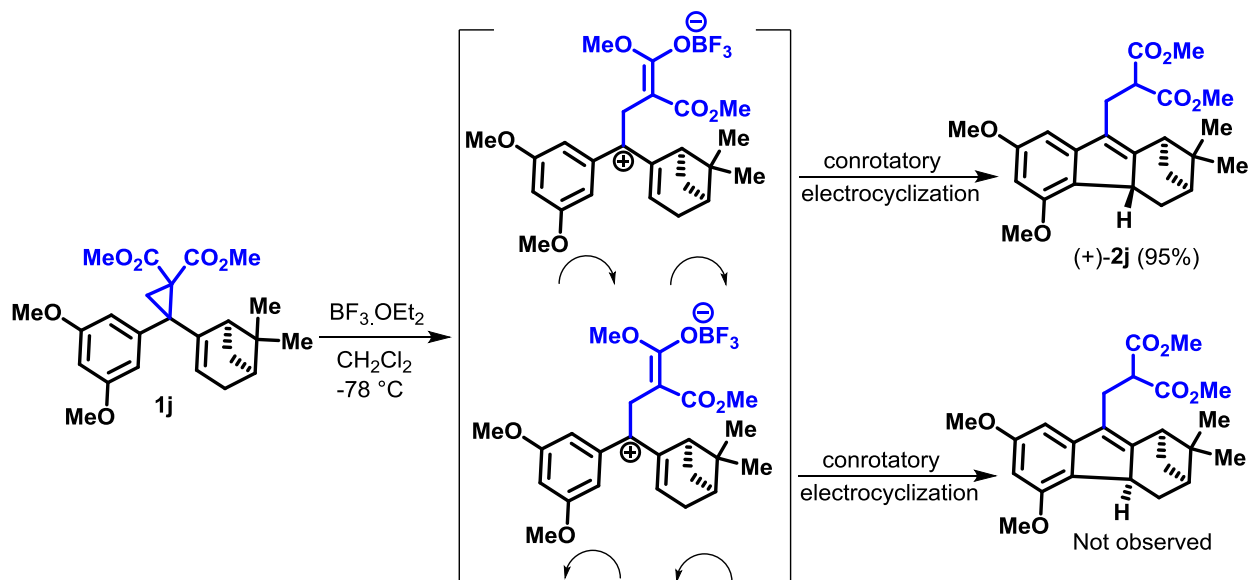
Under standard reaction conditions, compound **1a** would provide pentadienyl cation that undergoes 4π -electrocyclization to give cyclic allyl cation. Finally, loss of a proton leads to the formation of **2a** as shown in Scheme S1.



Scheme S1. Nazarov cyclization of Donor-Acceptor Aryl vinyl Cyclopropane

1b. Formation of **2j** from **1j**

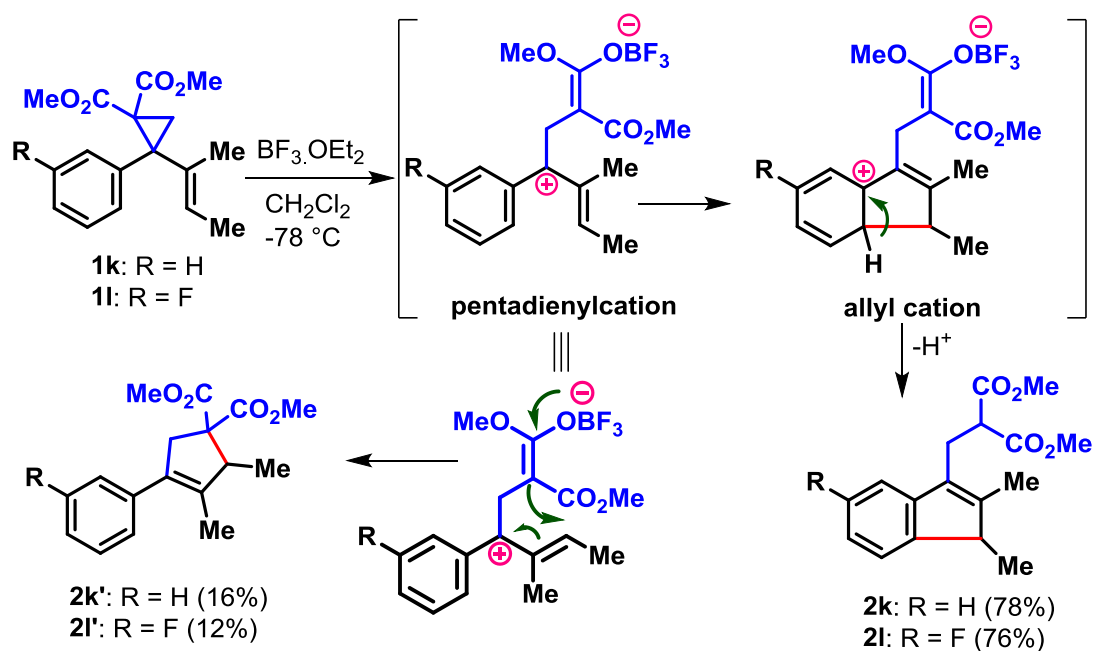
Under the standard reaction conditions, **1j** provided **2j**. The structure of **2j** was determined using 2D NMR (Figure S1 and Table S1). The formation of product (+)-**2j** selectively from **1j** may be explained from the torquoselective conrotatory electrocyclization of aryl vinyl cation because of sterically hindered geminal dimethyls as shown in Scheme S2.



Scheme S2. Proposed torquoselectivity for the formation of (+)-**2j** from **1j**

1c. Intramolecular cyclopent-annulation from Donor-Acceptor Aryl vinyl Cyclopropane and its plausible reaction mechanism

Under standard conditions, compounds **1k** and **1l** would provide pentadienyl cation that undergoes electrocyclization to form the cyclic allyl cation. Here, loss of a proton from the cyclic allyl cation would provide Nazarov cyclization products **2k** and **2l** as major. The formation of minor cyclopentene compounds **2k'** and **2l'** could be explained by the enolate addition to the carbon, which is β to the carbocation as shown in Scheme S3.

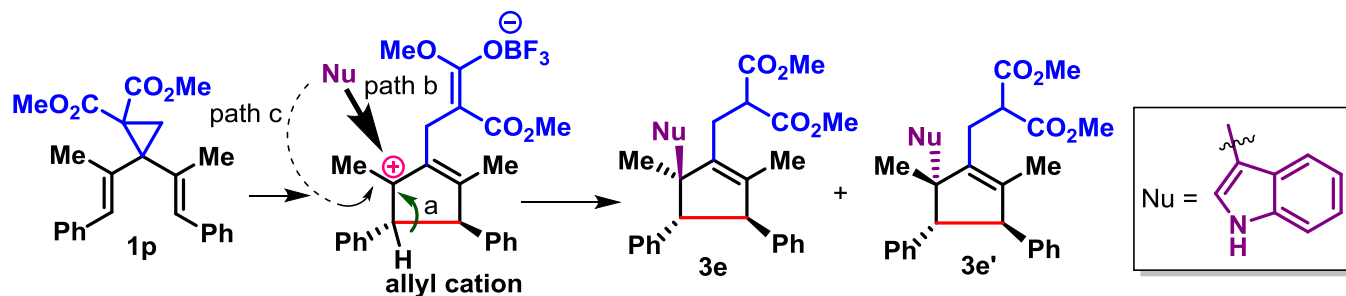


Scheme S3. Intramolecular cyclopent-annulation from Donor-Acceptor Aryl vinyl Cyclopropane

1d. Interrupted Nazarov cyclization and its plausible reaction mechanism

The addition of a nucleophile to carbocation could be from either below (path c) or above (path b) the plane, but its addition opposite side to phenyl group adjacent to carbocation (path b) is more favorable because of a less steric hindrance. This is apparent from the formation of **3e** as

major and **3e'** as minor, shown in Scheme S4. Structures of **3e** and **3e'** were fully characterized by using 2D NMR (Tables S2-S3 and Figures S2-S3).

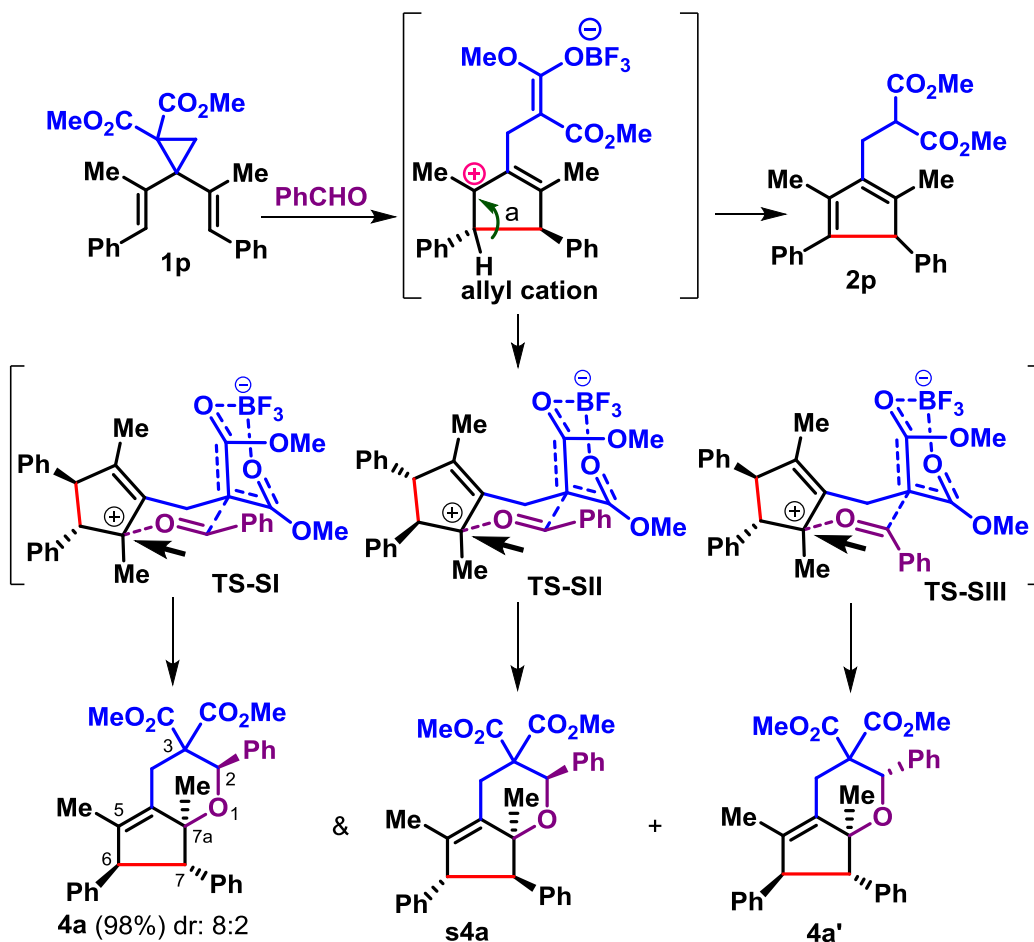


Scheme S4. Interrupted Nazarov cyclization

1e. Nazarov cyclization followed by [4+2]-cycloaddition and its plausible reaction mechanism

The addition of benzaldehyde to cyclic allyl cation provided separable **4a** and **4a'** in the ratio of 8:2 and with 98% combined yield. The major compound **4a** has a small amount of inseparable isomer **s4a**. Compounds **4a**, **s4a** and **4a'** have been characterized by using 2D NMR (Tables S4-S6 and Figures S4-S6). Based on the stereochemistry outcome, we propose the most probable six-membered cyclic transition states **TS-SI-SIII** (Scheme S5). The diastereoselectivity of major compound **4a** might be from **TS-SI**, in which upcoming alkyl/aryl group (dipolarophile) attacks from opposite side to the phenyl group (α to carbocation) and it attains a pseudo-equatorial position in the six-membered cyclic transition state. Formation of minor compound **4a'** could be from transition state **TS-SIII**, in which dipolarophile attacks from opposite side to the phenyl group (α to carbocation) but attaining a pseudo-axial position in the six-membered cyclic transition state. On the other hand, the formation of **s4a** could be from attacking dipolarophile

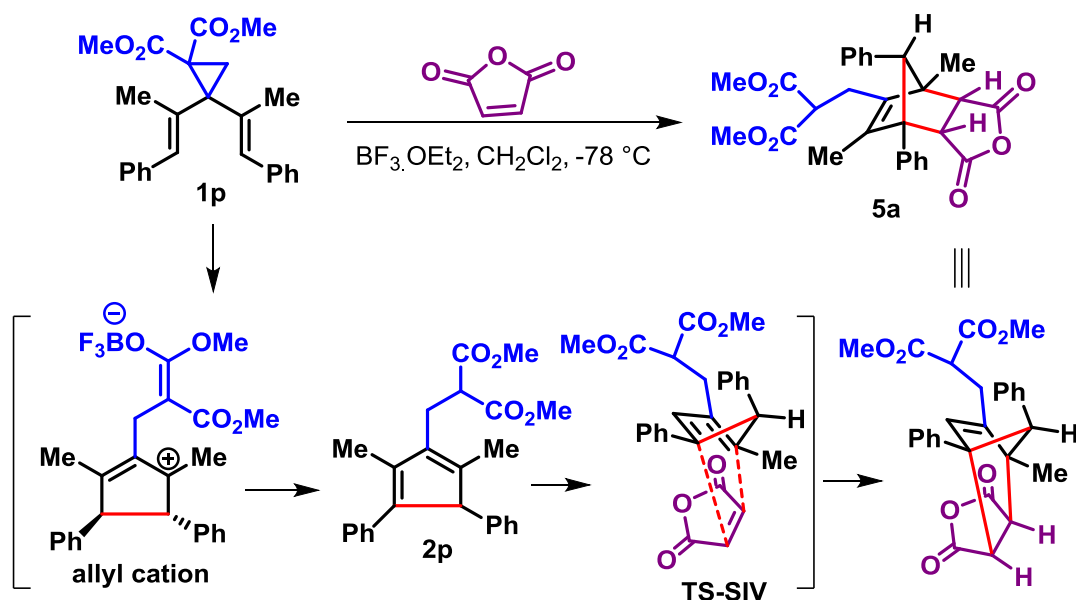
from the same side to the phenyl group (α to carbocation) and attaining a pseudo-equatorial position in the six-membered cyclic transition state (**TS-SII**).



Scheme S5. Nazarov cyclization followed by [4+2]-cycloaddition

1f. Nazarov cyclization followed by [4+2]-cycloaddition (Diels-Alder reaction) and its plausible reaction mechanism

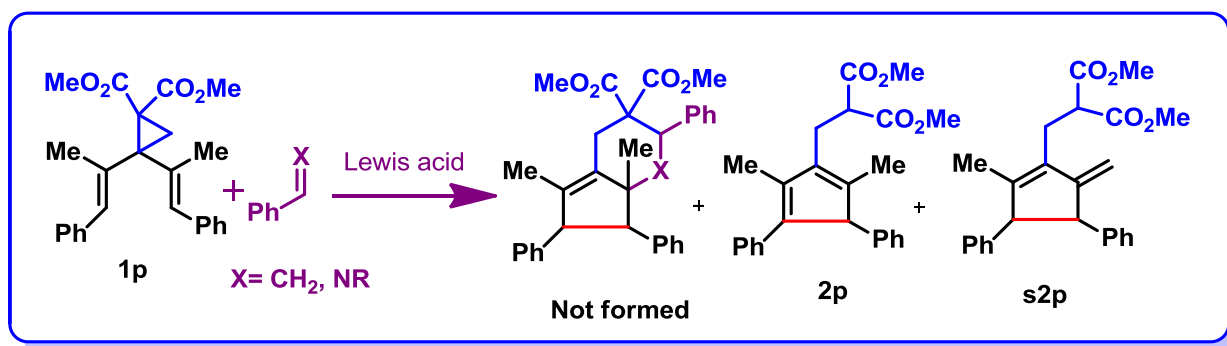
On the addition of maleic anhydride to dienyl donor-acceptor cyclopropane **1p** in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ in CH_2Cl_2 at -78°C afforded **5a** in 96% yield. The compound **5a** was fully characterized by using 2D NMR (Table S8 and Figure S8). We proposed that the initially formed cyclopentadiene **2p** would react with maleic anhydride to provide **5a**. This was further ascertained by treating preformed **2p** with maleic anhydride under a standard condition which afforded **5a** in 96% yield and complete endo-selectivity. Due to secondary orbital interactions as shown in the transition state (**TS-SIV**) could be favored to provide the complete endo-selectivity in product **5a** (Scheme S6).



Scheme S6. Nazarov cyclization followed by [4+2]-cycloaddition (Diels-Alder reaction)

1g. Attempts for [4+2]-cycloaddition with 1p and styrene & imines:

After achieving [4+2]-cycloaddition products from dienyI donor-acceptor cyclopropane and aldehydes, we have attempted with styrene and imines under various conditions but without success. However, in this process we have isolated **s2p** in the presence of Yb(OTf)₃ or Sc(OTf)₃ and majorly **2p** in other reaction conditions (table shown below). The compound **s2p** is characterized based on the ¹H NMR, ¹³C NMR, and HRMS.



Reaction conditions Table

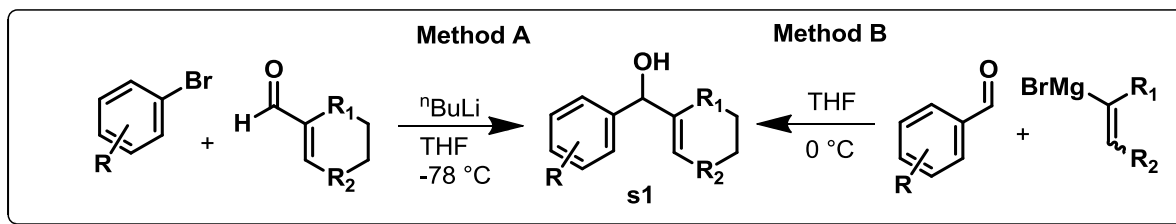
Entry	Reagent	Temperature	Solvent	Result & Yield (%)
1	BF ₃ .Et ₂ O	-78 °C	CH ₂ Cl ₂	2p (90)
2	Yb(OTf) ₃	-78 / -50 °C	CH ₂ Cl ₂	s2p (92)
3	SnCl ₄	-78 °C	CH ₂ Cl ₂	2p (85)
4	TiCl ₄	-78 °C	CH ₂ Cl ₂	2p (89)
5	TfOH	-78 °C	CH ₂ Cl ₂	2p (82)
6	Sc(OTf) ₃	-78 °C	CH ₂ Cl ₂	s2p (88)
7	TFA	-78 °C	CH ₂ Cl ₂	2p (90)

2. General Materials and Methods:

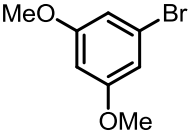
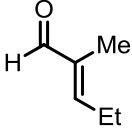
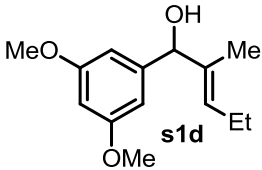
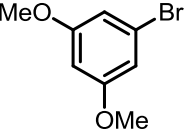
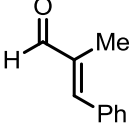
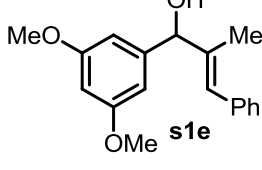
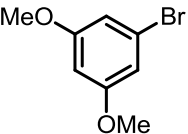
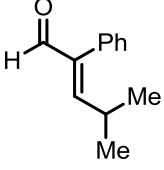
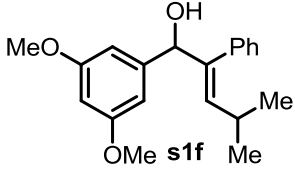
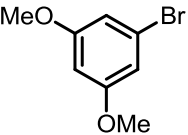
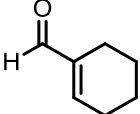
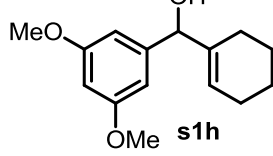
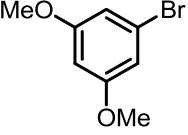
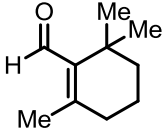
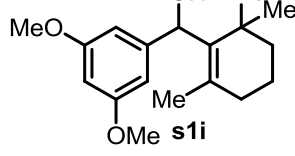
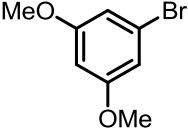
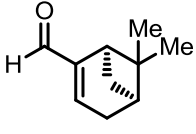
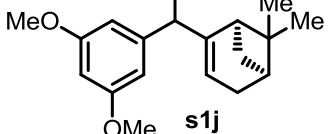
Anhydrous solvents were dried and distilled by standard methods before use. Commercially available reagents were used without further purification unless otherwise specified. All the reactions were performed under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring. Column chromatography was carried out using silica gel (60-120 or 100-200 or 230-400 mesh) and basic Al_2O_3 , and the column was eluted with ethyl acetate-petroleum ether or hexane. Visualization of the spots on TLC plates was achieved either by UV light or by staining in the plates in methanolic anisaldehyde-sulphuric acid-acetic acid or methanol-phosphomolybdic acid-sulphuric acid solution and charring on a hot plate. ^1H NMR, ^{13}C NMR were recorded in a CDCl_3 solvent on 500 MHz, 400MHz, 300MHz, and 75 MHz, 100 MHz, 125 MHz spectrometers, respectively at ambient temperature. Chemical shifts are as δ values relative to internal CHCl_3 δ 7.26 or TMS δ 0.0 for ^1H NMR and CHCl_3 δ 77.0 for ^{13}C NMR. ^1H NMR data is recorded as follows: chemical shift [multiplicity, coupling constant(s) J (Hz), relative integral] where multiplicity is defined as: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublet; dt = doublet of triplet; dq = doublet of quartet; tt = triplet of triplet; ddd = doublet of doublet of doublet; m = multiplet; brs = broad singlet; brd = broad doublet; qq = quartet of quartet. FTIR spectra were recorded as KBr thin films or neat. Mass spectra were recorded for ESI and are given in mass units (m/z). High resolution mass spectra (HRMS) [ESI+] were obtained using either a TOF or a double focusing spectrometer. Melting points were determined using Cintex melting point apparatus. Single crystal X-ray data for the compounds were collected on Bruker Smart Apex CCD diffractometer and Bruker D8 QUEST.

3. Synthesis of Starting Materials

3a. Dienyl alcohols



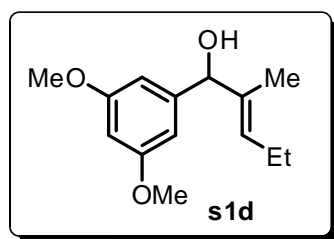
Method A

S.No	Aryl Bromide	Aldehyde	Product	Yield(%)
1.				95
2.				96
3.				92
4.				97
5.				90
6.				97

General procedure for the synthesis of dienyl alcohol:

Method A:^[1] In a flame-dried flask purged with argon, **1-bromo-3,5-dimethoxybenzene** (3.65 g, 16.83 mmol, 1.1 equiv) was dissolved in THF (35 mL) and cooled to -78 °C. n-Butyllithium solution (10.5 mL, 16.83 mmol, 1.1 equiv, 1.6M in hexanes) was added dropwise, and the reaction was stirred at -78 °C for 45 minutes. The desired aldehyde (1.5 g, 15.3 mmol, 1.0 equiv,) in THF (9 mL) was then added dropwise, and the reaction was stirred for an hour before it was allowed to warm slowly to 0 °C over an additional 2-3 hours. The reaction was quenched at 0 °C with a volume of saturated ammonium chloride solution equal to the volume of aryl bromide solution and diluted with an equivalent amount of water. The aqueous layer was extracted two times with EtOAc, and the combined layers were washed one time each with water and brine. The organic layer was then dried over Na₂SO₄, filtered and concentrated in *vacuo* to afford the crude product. Purification by using silica gel column chromatography with 10-20% EtOAc/hexanes solution furnished the desired product **s1** as shown in Scheme **s1**.

(*E*)-1-(3,5-Dimethoxyphenyl)-2-methylpent-2-en-1-ol (**s1d**):



Yield: 3.45 g, (95%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes);

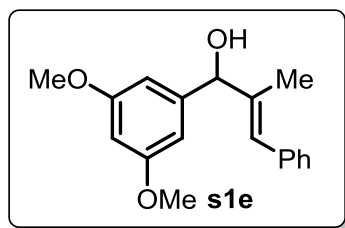
¹H NMR (500 MHz, CDCl₃): δ 6.53 (d, $J = 2.2$ Hz, 2H), 6.36 (t, $J = 2.2$ Hz, 1H), 5.62 (t, $J = 7.0$ Hz, 1H), 5.04 (s, 1H), 3.78 (s, 6H), 2.07 (m, 2H), 1.97 (brs, 1H), 1.49 (s, 3H), 1.00 (t, $J = 7.4$ Hz, 3H); **¹³C**

NMR (125 MHz, CDCl₃): δ 160.5, 145.0, 135.8, 129.0, 104.1, 99.0, 79.1, 55.2, 20.8, 13.9, 11.6;

IR (Neat): ν_{max} 3451, 2960, 2925, 1594, 1458, 1426, 1290, 1202, 1150, 1059, 1026, 826, 719;

HRMS (ESI): calcd for C₁₄H₁₉O₂ (M-OH)⁺ 219.1373, found 219.1379.

(E)-1-(3,5-Dimethoxyphenyl)-2-methyl-3-phenylprop-2-en-1-ol (s1e):

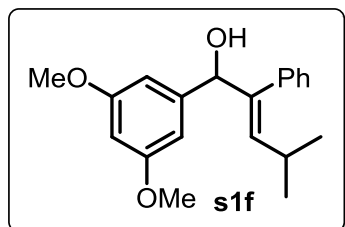


Yield: 2.05 g, (96%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes);

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.35-7.27 (m, 4H), 7.22 (m, 1H), 6.73 (s, 1H), 6.59 (d, $J = 2.2$ Hz, 2H), 6.38 (t, $J = 2.2$ Hz, 1H), 5.18 (s, 1H), 3.77 (s, 6H), 2.31 (brs, 1H), 1.74 (d, $J = 1.2$ Hz, 3H); ^{13}C

NMR (100 MHz, CDCl_3): δ 160.7, 144.6, 139.2, 137.3, 128.9, 128.0, 126.4, 126.1, 104.4, 99.3, 79.3, 55.2, 13.8; **IR** (Neat): ν_{max} 3414, 2922, 2852, 1593, 1458, 1427, 1344, 1291, 1201, 1150, 1058, 920, 833, 753, 726; **HRMS** (ESI): calcd for $\text{C}_{18}\text{H}_{19}\text{O}_2$ (M-OH) $^+$ 267.1374, found 267.1379.

(E)-1-(3,5-Dimethoxyphenyl)-4-methyl-2-phenylpent-2-en-1-ol (s1f):

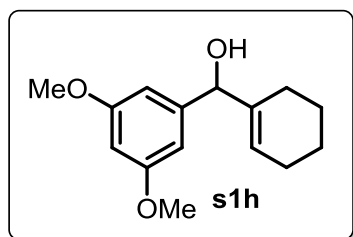


Yield: 1.81 g, (92%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.25-7.17 (m, 3H), 6.97-6.91 (m, 2H), 6.43 (d, $J = 2.2$ Hz, 2H), 6.34 (t, $J = 2.2$ Hz, 1H), 5.68 (d, $J = 0.9$ Hz, 0.5H), 5.66 (d, $J = 0.9$ Hz, 0.5H), 5.30 (s, 1H), 3.72 (s, 6H),

2.25 (m, 1H) 1.96 (brs, 1H), 0.97 (d, $J = 6.6$ Hz, 3H), 0.93 (d, $J = 6.6$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 160.4, 144.7, 140.1, 137.8, 136.5, 129.3, 127.8, 126.8, 104.5, 99.5, 78.4, 55.2, 27.7, 23.0; **IR** (Neat): ν_{max} 3478, 2955, 2837, 1595, 1461, 1427, 1341, 1292, 1202, 1152, 1059, 1032, 922, 840, 702; **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{25}\text{O}_3$ (M+H) $^+$ 313.1804, found 313.1803.

Cyclohexenyl(3, 5-dimethoxyphenyl)methanol (s1h):

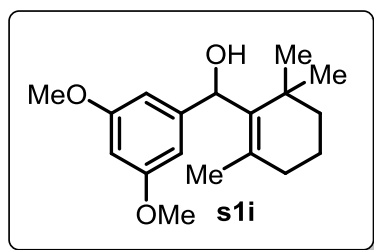


Yield: 3.3 g, (97%); colorless oil; $R_f = 0.4$ (15% EtOAc/hexanes);

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.52 (d, $J = 2.2$ Hz, 2H), 6.36 (t, $J = 2.2$ Hz, 1H), 5.85 (brs, 1H), 5.01 (s, 1H), 3.79 (s, 6H), 2.07 (brs,

2H), 1.99-1.72 (m, 3H), 1.68-1.48 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.5, 145.1, 139.3, 123.6, 104.2, 99.0, 78.1, 55.2, 24.9, 23.8, 22.4, 22.3; IR (Neat): ν_{max} 3432, 2924, 2836, 1594, 1459, 1427, 1341, 1292, 1202, 1151, 1058, 1023, 916, 837, 731, 692; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 271.1297, found 271.1304.

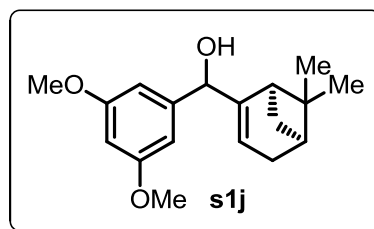
(3,5-Dimethoxyphenyl)(2,6,6-trimethylcyclohex-1-enyl)methanol (s1i):



Yield: 2.6 g, (90%); colorless oil; R_f = 0.4 (15% EtOAc/hexanes); ^1H NMR (500 MHz, CDCl_3): δ 6.61 (d, J = 2.2 Hz, 2H), 6.33 (t, J = 2.2 Hz, 1H), 5.31 (d, J = 4.7 Hz, 1H), 3.79 (s, 6H), 1.97 (t, J = 6.1 Hz, 2H), 1.82 (brs, 0.7H), 1.71-1.57 (m,

2H) 1.56-1.47 (m, 2H), 1.42 (s, 3H), 1.18 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 160.5, 147.6, 140.2, 133.9, 104.0, 97.8, 70.5, 55.1, 39.6, 34.7, 33.5, 28.7, 28.5, 21.4, 19.2; IR (Neat): ν_{max} 3506, 2996, 2952, 2928, 2865, 2835, 1594, 1456, 1425, 1338, 1287, 1247, 1202, 1149, 1060, 1039, 1013, 995, 921, 832, 732; HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{26}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 313.1770, found 313.1774.

(3,5-Dimethoxyphenyl)((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methanol (s1j):

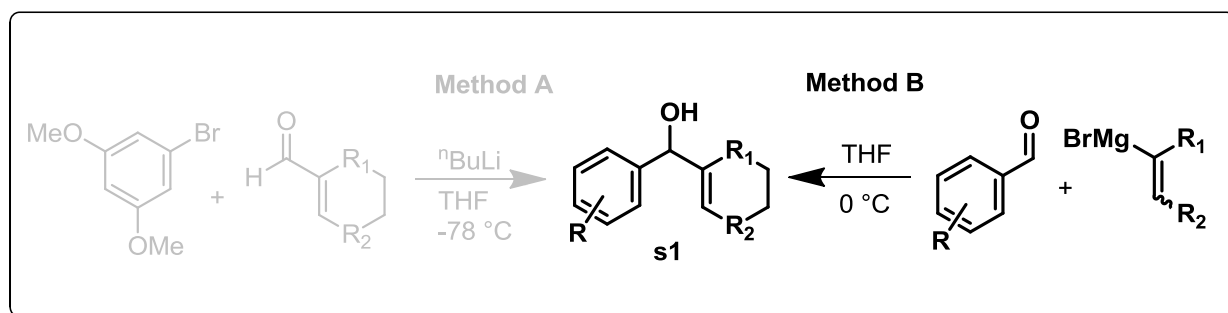


Yield: 1.85 g, (97%); *dr*: 7:3; colorless oil; R_f = 0.5 (15% EtOAc/hexanes); ^1H NMR (500 MHz, CDCl_3): δ 6.52 (d, J = 2.2 Hz, 1.3H), 6.50 (d, J = 2.2 Hz, 0.7H), 6.35 (m, 0.7H), 6.35 (m, 0.3H), 5.62 (brs, 0.7H), 5.62 (brs, 0.3H), 5.07 (s, 0.7H), 5.02

(s, 0.3H), 3.78 (s, 4H), 3.77 (s, 2H), 2.40-2.24 (m, 3.3H), 2.13-2.04 (m, 1.7H), 1.81 (brs, 0.7H), 1.60 (brs, 0.3H), 1.21 (s, 2H), 1.18 (s, 1H), 1.15 (d, J = 8.6 Hz, 0.3H), 1.10 (d, J = 8.6 Hz, 0.7H), 0.78 (s, 2H), 0.65 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 160.5, 149.1, 149.0, 144.2, 144.1,

119.3, 118.2, 104.6, 104.2, 99.5, 99.2, 76.5, 55.2, 42.2, 42.1, 40.7, 40.6, 37.7, 37.6, 32.0, 31.8, 31.2, 31.1, 26.0, 25.9, 21.2, 21.0; **IR** (Neat): ν_{\max} 3341, 2920, 2855, 1585, 1453, 1376, 1253, 1170, 1130, 1021, 964, 845, 813, 747; **HRMS** (ESI): calcd for $C_{18}H_{23}O_3$ (M-H)⁺ 287.1637, found 287.1641.

General procedure for the synthesis of dienyl alcohols from Method B:



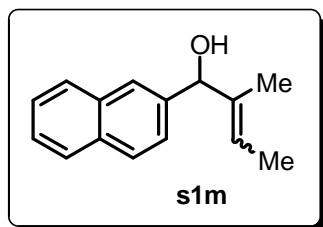
Method B:

S.No.	Aldehyde	RMgX	Product	Yield (%)
1.				93
2.				94

General Procedure for Method B:^[2] In a dry two-neck round bottom flask equipped with magnetic stirring bar, nitrogen inlet, reflux condenser, rubber septum, one iodine pinch and magnesium turnings (1.8 g, 77.0 mmol, 1.1 equiv) was stirred with dry THF (70 mL). (*E/Z*) or (*E*) **2-Bromo-2-butene** (7.1 mL, 70 mmol, 1.0 equiv) was added drop wise until exothermic

reaction began. On the completion of bromide reagent addition, the Grignard reagent was kept for reflux for 45 min and then stand for 3h at rt. This Grignard reagent (18.0 mL, 1.1 equiv) was added to ice cooled solution of the desired aldehyde (2.0 g, 16.12 mmol, 1.0 equiv) in dry THF (50 mL) at 0 °C and was stirred for 15 min. The reaction was monitored by TLC, after completion of the starting material, the reaction was quenched with aq NH₄Cl, and extracted with EtOAc. The organic layer was washed with aq NaCl, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/hexanes) to give dienol **s1**.

2-Methyl-1-(naphthalen-2-yl)but-2-en-1-ol (s1m):



Yield: 1.26 g, (93%); yellow oil; R_f = 0.4 (10% EtOAc/hexanes); ¹H

NMR (400 MHz, CDCl₃): δ 7.92-7.78 (m, 4H), 7.52-7.38 (m, 3H),

5.97 (s, 0.8H), 5.79 (q, J = 6.7 Hz, 0.2H), 5.53 (q, J = 6.9 Hz, 0.8H),

5.31 (s, 0.2H), 2.00 (brs, 1H), 1.88 (qd, J = 2.8, 1.3 Hz, 2.5H), 1.70

(d, J = 6.7 Hz, 0.5H), 1.62-1.59 (m, 2.5H), 1.52 (s, 0.5H); ¹³C **NMR** (125 MHz, CDCl₃): δ

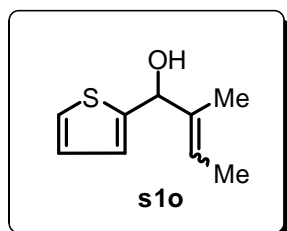
140.0, 137.4, 137.0, 133.2, 132.7, 132.6, 127.9, 127.8, 127.5, 125.9, 125.6, 124.6, 124.5, 124.0,

123.8, 122.8, 121.7, 79.4, 70.6, 17.4, 13.4, 13.2, 11.7; **IR** (Neat): ν_{max} 3376, 3054, 2968, 2920,

2856, 1632, 1601, 1508, 1452, 1439, 1375, 1269, 1157, 1119, 1056, 1015, 858, 820, 789, 757;

HRMS (ESI): calcd for C₁₅H₁₅ (M-OH)⁺ 195.1175, found 195.1170.

2-Methyl-1-(thiophen-2-yl)but-2-en-1-ol (s1o):



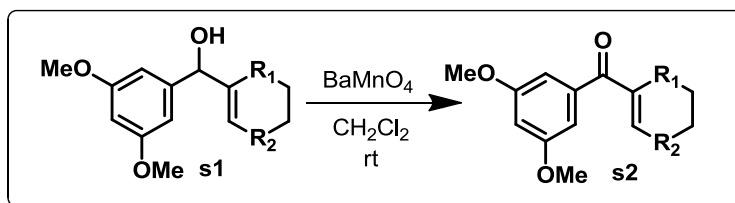
Yield: 2.83 g, (94%); yellow oil; R_f = 0.4 (10% EtOAc/hexanes); ¹H

NMR (400 MHz, CDCl₃): δ 7.19 (m, 0.6H), 7.01-6.82 (m, 2.4H), 5.89

(d, J = 3.7 Hz, 0.8H), 5.69 (q, J = 1.2 Hz, 0.2H), 5.43 (m, 0.8H), 5.30

(s, 0.2H), 2.54 (d, $J = 4.2$ Hz, 0.8H), 2.50 (d, $J = 3.6$ Hz, 0.2H) 1.80-1.68 (m, 5H), 1.65 (m, 0.5H), 1.58 (m, 0.5H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.0, 146.8, 137.0, 136.0, 126.6, 126.5, 124.5, 124.2, 123.9, 123.1, 122.4, 121.4, 75.6, 68.1, 17.4, 13.0, 11.6; **IR** (Neat): ν_{max} 3420, 2973, 2929, 2871, 1659, 1441, 1365, 1314, 1269, 1245, 1172, 1071, 1047, 965, 853, 819, 691; **HRMS** (ESI): calcd for $\text{C}_9\text{H}_{11}\text{OS}$ ($\text{M}-\text{H}$) $^+$ 167.0524, found 167.0525.

3b. Synthesis of dienyl ketones from dienyl alcohols

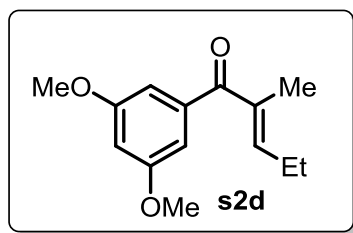


S.No.	Alcohol	Product	S.No.	Alcohol	Product
1.			4.		
2.			5.		
3.			6.		

General procedure for the synthesis of dienyl ketones **s2** from **s1**:^[2]

To the dienyl alcohol **(E)-1-(3,5-Dimethoxyphenyl)-2-methylpent-2-en-1-ol (s1d)** (1.40 g, 4.861 mmol, 1.0 equiv) in dry CH₂Cl₂ (25 mL) was added BaMnO₄ (2.50 g, 9.722 mmol, 2.0 equiv). The reaction mixture was stirred at rt. The reaction was monitored by TLC and after completion of the starting material, the reaction mixture was filtered through celite. The solvent was evaporated under reduced pressure, and the residue was purified by using silica gel column chromatography to afford dienone **s2d**.

(E)-1-(3,5-Dimethoxyphenyl)-2-methylpent-2-en-1-one (s2d):

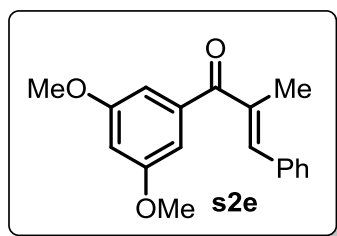


Yield: 2.8 g, (95%); colorless oil; R_f = 0.6 (10% EtOAc/hexanes);

¹H NMR (500 MHz, CDCl₃): δ 6.74 (d, J = 2.2 Hz, 2H), 6.57 (t, J = 2.2 Hz, 1H), 5.62 (tq, J = 7.3, 1.2 Hz, 1H), 3.79 (s, 6H), 2.31-2.23 (m, 2H), 1.93 (d, J = 1.2 Hz, 3H), 1.03 (t, J = 7.6 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 198.1, 160.0, 147.8, 140.4, 135.4, 106.8, 103.2, 55.1, 22.1, 12.7, 11.9; IR (Neat): ν_{max} 2964, 2925, 1646, 1588, 1454, 1423, 1343, 1321, 1203, 1152, 1061, 1038, 926, 842, 746; HRMS (ESI): calcd for C₁₄H₁₉O₃ (M+H)⁺ 235.13285, found 235.13287.

(E)-1-(3,5-Dimethoxyphenyl)-2-methyl-3-phenylprop-2-en-1-one (s2e):



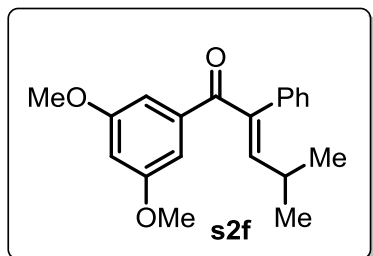
Yield: 1.62 g, (91%); white solid; m.p. 65-67 °C; R_f = 0.6 (10%

EtOAc/hexanes); ¹H NMR (500 MHz, CDCl₃): δ 7.45-7.30 (m, 5H), 7.23 (q, J = 1.3 Hz, 1H), 6.87 (d, J = 2.2 Hz, 2H), 6.63 (t, J = 2.2 Hz, 1H), 3.82 (s, 6H), 2.25 (d, J = 1.3 Hz, 3H); ¹³C NMR (100

MHz, CDCl₃): δ 198.9, 160.4, 142.1, 140.3, 136.5, 135.6, 129.6, 128.5, 128.3, 107.2, 103.8,

55.4, 14.3; **IR** (Neat): ν_{\max} 2922, 2851, 1644, 1588, 1453, 1423, 1321, 1203, 1152, 1062, 1022, 925, 837, 761, 691; **HRMS** (ESI): calcd for $\text{C}_{18}\text{H}_{19}\text{O}_3$ ($\text{M}+\text{H}$)⁺ 283.1329, found 283.31328.

(E)-1-(3,5-Dimethoxyphenyl)-4-methyl-2-phenylpent-2-en-1-one (s2f):

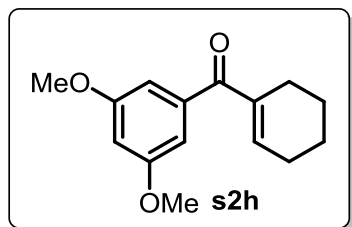


Yield: 1.1 g, (90%); colorless oil; R_f = 0.6 (10% EtOAc/hexanes);

¹H NMR (400 MHz, CDCl_3): δ 7.41-7.22 (m, 5H), 6.91 (d, J = 2.2 Hz, 2H), 6.60 (t, J = 2.2 Hz, 1H), 6.28 (d, J = 10.3 Hz, 1H), 3.80 (s, 6H), 2.64 (m, 1H) 1.04 (d, J = 6.6 Hz, 6H); **¹³C NMR**

(100 MHz, CDCl_3): δ 196.7, 160.3, 151.2, 140.1, 138.9, 136.2, 129.2, 128.1, 127.3, 107.4, 104.4, 55.4, 28.6, 22.3; **IR** (Neat): ν_{\max} 2960, 2933, 1657, 1590, 1455, 1424, 1347, 1294, 1204, 1154, 1063, 1042, 843, 763, 707; **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{23}\text{O}_3$ ($\text{M}+\text{H}$)⁺ 311.1638, found 311.1641.

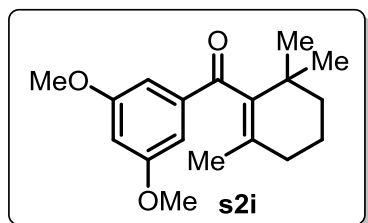
Cyclohexenyl(3,5-dimethoxyphenyl)methanone (s2h):



Yield: 3.2 g, (92%); colorless oil; R_f = 0.5 (10% EtOAc/hexanes);

¹H NMR (500 MHz, CDCl_3): δ 6.74 (d, J = 2.2 Hz, 2H), 6.62 (m, 1H), 6.56 (t, J = 2.2 Hz, 1H), 3.80 (s, 6H), 2.41-2.36 (m, 2H), 2.28-2.22 (m, 2H), 1.75-1.68 (m, 2H), 1.68-1.62 (m, 2H); **¹³C**

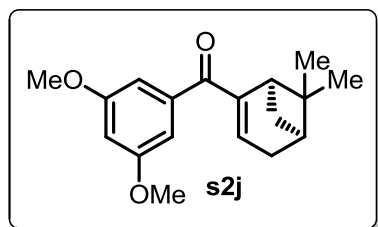
NMR (125 MHz, CDCl_3): δ 197.5, 160.2, 144.0, 140.5, 138.3, 106.8, 103.1, 55.3, 25.9, 23.7, 21.8, 21.5; **IR** (Neat): ν_{\max} 2932, 2857, 2839, 1643, 1587, 1453, 1422, 1294, 1202, 1152, 1061, 988, 916, 785, 745, 704, 683; **HRMS** (ESI): calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3$ ($\text{M}+\text{H}$)⁺ 247.1322, found 247.1328.



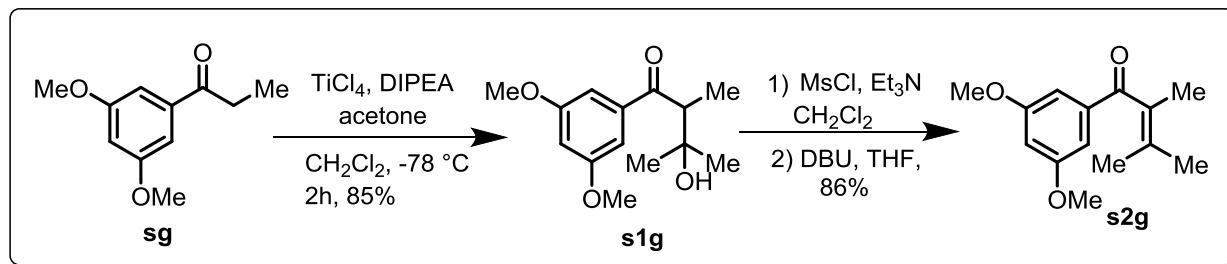
(3,5-Dimethoxyphenyl)(2,6,6-trimethylcyclohex-1-enyl)methanone (s2i):

Yield: 1.6 g, (92%); white solid; m.p. 97-99 °C; R_f = 0.5 (10% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.08 (d, J = 2.2 Hz, 2H), 6.63 (t, J = 2.2 Hz, 1H), 3.82 (s, 6H), 2.05 (t, J = 6.4 Hz, 2H), 1.80-1.68 (m, 2H), 1.55-1.50 (m, 2H), 1.44 (s, 3H) 1.03 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 200.7, 160.6, 139.9, 139.0, 131.3, 106.5, 104.8, 55.2, 38.5, 33.6, 30.9, 28.6, 21.4, 18.7; **IR** (Neat): ν_{max} 2955, 2930, 2866, 1662, 1590, 1457, 1426, 1349, 1295, 1204, 1154, 1064, 956, 845, 761, 727; **HRMS** (ESI): calcd for $\text{C}_{18}\text{H}_{25}\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 289.1792, found 289.1798.

(3,5-Dimethoxyphenyl)((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methanone (s2j):



Yield: 1.3 g, (93%); colorless oil; R_f = 0.5 (10% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.82 (d, J = 2.2 Hz, 2H), 6.59 (t, J = 2.2 Hz, 1H), 6.48 (m, 1H), 3.82 (s, 6H), 2.96 (t, J = 5.6 Hz, 1H) 2.60-2.40 (m, 3H) 2.18 (brs, 1H) 1.37 (s, 3H), 1.20 (d, J = 9.0 Hz, 1H) 0.86 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 195.0, 160.3, 148.3, 140.1, 140.0, 107.1, 103.5, 55.4, 41.4, 40.2, 37.6, 32.6, 31.2, 25.8, 20.8; **IR** (Neat): ν_{max} 2933, 2885, 2838, 1642, 1590, 1454, 1423, 1363, 1314, 1295, 1204, 1155, 1064, 1042, 926, 841, 791, 754, 722; **HRMS** (ESI): calcd for $\text{C}_{18}\text{H}_{23}\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 287.1656, found 287.1641.

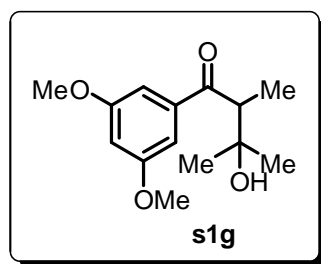


Scheme s3: Synthesis of s2g

Step 1: TiCl_4 (1M in CH_2Cl_2 , 12.5 mL, 12.37 mmol, 1.2 equiv) and diisopropylethylamine (DIPEA) (2.5 mL, 14.42 mmol, 1.4 equiv) were successively added to a stirred solution of **1-(3,**

5-dimethoxyphenyl) propan-1-one (sg)^[3] (2.0 g, 10.30 mmol, 1.0 equiv) in CH₂Cl₂ (45 mL) at -78 °C under an argon atm. After 30 min, acetone (1.15 mL, 15.45 mmol, 1.5 equiv) in CH₂Cl₂ (5 mL) was added to the reaction mixture, and stirred at -78 °C for 1h. The reaction mixture was quenched with H₂O at -78 °C and extracted twice with EtOAc. The organic phase was washed with H₂O, brine solution, dried over Na₂SO₄, filtered, and concentrated in *vacuo*. The obtained crude oil was purified by using silica gel column chromatography to give (**s1g**, 2.2 g, 85%) as a yellow oil.

1-(3,5-Dimethoxyphenyl)-3-hydroxy-2,3-dimethylbutan-1-one (s1g):

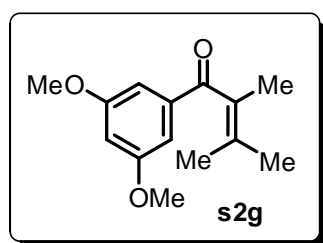


R_f = 0.4 (20% EtOAc/hexanes); ¹H NMR (500 MHz, CDCl₃): δ 7.08 (d, J = 2.2 Hz, 2H), 6.68 (t, J = 2.2 Hz, 1H), 3.84 (s, 6H), 3.42 (q, J = 7.2 Hz, 1H) 1.28 (d, J = 7.2 Hz, 3H) 1.26 (s, 3H), 1.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 206.9, 160.9, 138.7, 106.1, 105.5, 71.6, 55.5, 48.0, 29.4, 26.9, 13.3; IR (Neat): ν_{max} 3491, 2972, 2937, 2840, 1666, 1590, 1456, 1425, 1356, 1292, 1204, 1154, 1062, 1007, 948, 925, 843, 780, 715, 675; HRMS (ESI): calcd for C₁₄H₂₀O₄Na (M+Na)⁺ 275.1251, found 275.1253.

Step 2: A round-bottomed flask was charged with alcohol **s1g** (1.0 g, 3.968 mmol, 1.0 equiv) and CH₂Cl₂ (20 mL). The resulting solution was stirred and cooled to 0 °C. Then, sequentially Et₃N (5.5 mL, 39.68 mmol, 10.0 equiv) and methane sulfonyl chloride (1.25 mL, 15.872 mmol, 4.0 equiv) were added. The resulting solution was stirred at rt until TLC showed complete consumption of starting material. The resulting suspension was diluted with EtOAc (200 mL), quenched with saturated aq NaHCO₃, extracted with EtOAc and washed with saturated aq NaCl solution. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated in

vacuo. We proceeded to the next step without column purification. To the crude compound (1.1 g, 4.7 mmol, 1.0 equiv) in dry THF (25 mL), DBU (1.40 mL, 9.40 mmol, 2.0 equiv) was added at rt and stirred 65 °C for 8h. After completion of the starting material, the reaction mixture was quenched with H₂O, extracted with EtOAc and washed with aq NaCl solution. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated in *vacuo*. The obtained crude oil was purified by using silica gel column chromatography to give **s2g** (800 mg, 86%) as a white solid, m.p. 68-70 °C.

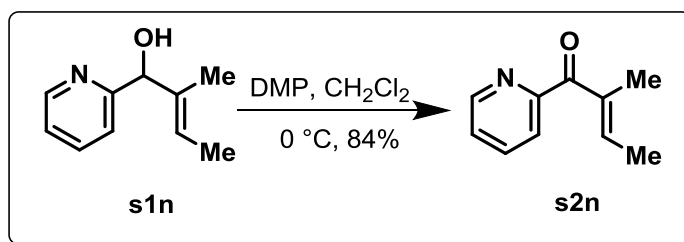
1-(3,5-Dimethoxyphenyl)-2,3-dimethylbut-2-en-1-one (s2g):



R_f = 0.6 (10% EtOAc/hexanes); ¹H NMR (500 MHz, CDCl₃): δ 7.02 (d, J = 2.2 Hz, 2H), 6.64 (t, J = 2.2 Hz, 1H), 3.83 (s, 6H), 1.86 (s, 3H), 1.81 (s, 3H) 1.61 (q, J = 1.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 201.2, 160.8, 138.7, 133.4, 129.5, 106.9, 105.1, 55.5, 22.3,

20.0, 16.5; **IR** (Neat): ν_{max} 2999, 2931, 2857, 2839, 1664, 1589, 1455, 1425, 1375, 1347, 1317, 1300, 1154, 1063, 1013, 925, 845, 773, 755, 679; **HRMS** (ESI): calcd for C₁₄H₁₈O₃Na (M+H)⁺ 257.1144, found 257.1148.

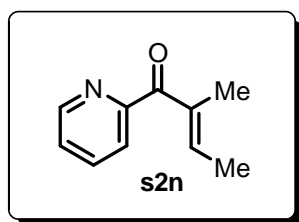
Modified procedure for Synthesis of ketone (s2n):



To an dienyl alcohol (*E*)-2-methyl-1-(pyridin-2-yl)but-2-en-1-ol (**s1n**)^[4] (1.5 g, 9.202 mmol, 1.0 equiv) solution in CH₂Cl₂ (45 mL) was cooled to 0 °C. Then Dess-Martin periodinane (DMP)

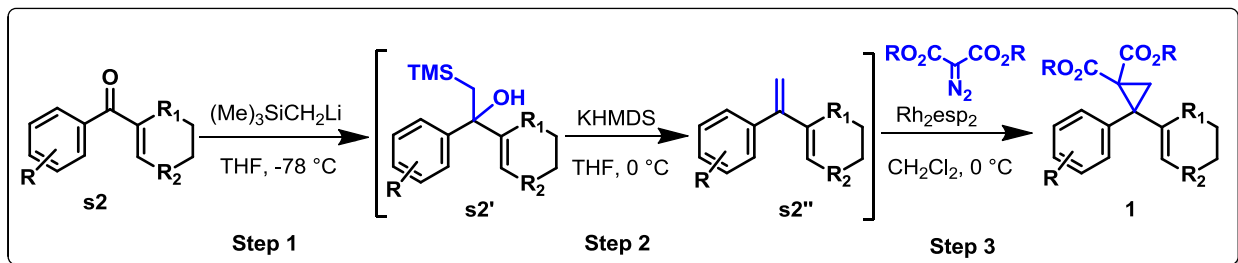
(4.3 g, 10.12 mmol, 1.2 equiv) was added portionwise. The reaction mixture was slowly warmed to rt. The reaction was monitored by TLC, and after completion of starting material, the reaction mixture was filtered through Celite. The organic solution was washed with aq NaHCO₃ solution, brine solution, dried over Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by using silica gel column chromatography to afford pure dienone.

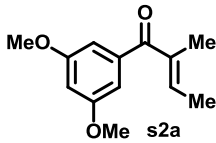
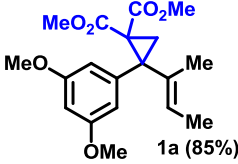
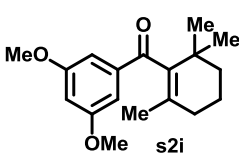
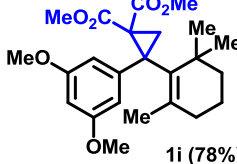
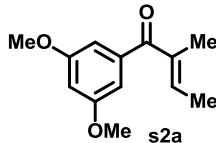
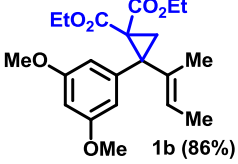
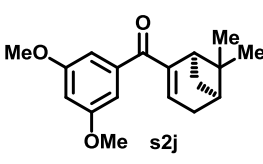
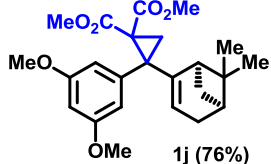
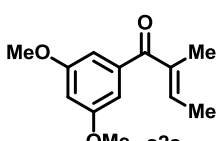
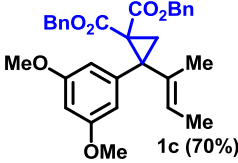
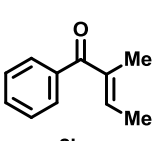
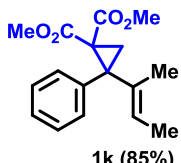
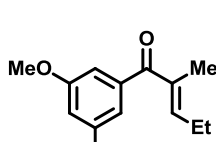
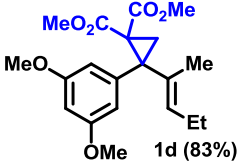
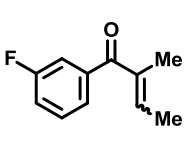
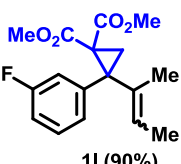
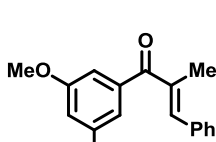
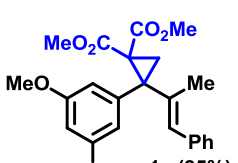
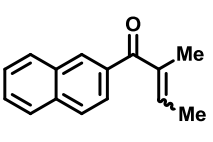
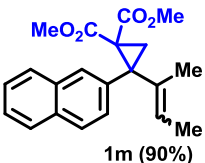
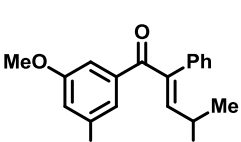
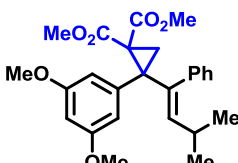
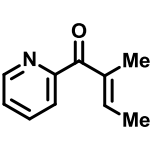
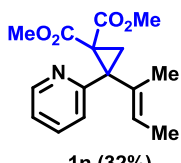
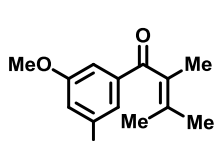
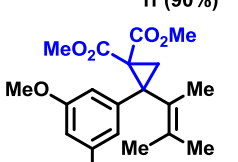
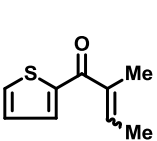
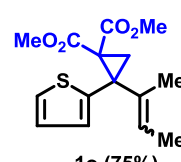
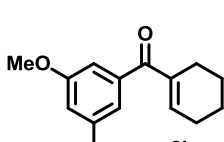
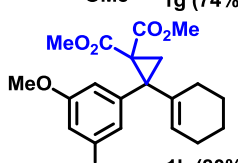
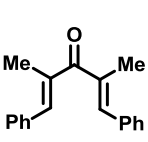
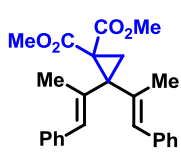
(E)-2-Methyl-1-(pyridin-2-yl)but-2-en-1-one (s2n):



Yield: 1.25 g, (84%); yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ¹H NMR (500 MHz, CDCl₃): δ 8.73 (dq, J = 1.5, 0.9 Hz, 1H), 8.00 (dt, J = 1.9, 0.9 Hz, 1H), 7.87 (tq, J = 7.6, 1.6 Hz, 1H), 7.46 (ddd, J = 5.9, 4.7, 1.2 Hz, 1H), 5.95 (qq, J = 3.0, 1.5 Hz, 1H), 2.05 (m, 3H), 1.58 (dq, J = 3.0, 1.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 198.5, 153.6, 148.6, 136.4, 135.7, 129.0, 126.0, 122.3, 20.3, 14.8; IR (Neat): ν_{max} 3052, 2921, 1652, 1581, 1567, 1458, 1434, 1351, 1271, 1235, 955, 886, 747, 706; HRMS (ESI): calcd for C₁₀H₁₂ON (M+H)⁺ 162.0921, found 162.0913.

3c. Synthesis of Dienyl Donor-Acceptor Cyclopropanes from Dienyl ketones



S.No.	Ketone	Cyclopropane Diesters	S.No.	Ketone	Cyclopropane Diesters
1.	 s2a	 1a (85%)	9.	 s2i	 1i (78%)
2.	 s2a	 1b (86%)	10.	 s2j	 1j (76%)
3.	 s2a	 1c (70%)	11.	 s2k	 1k (85%)
4.	 s2d	 1d (83%)	12.	 s2l	 1l (90%)
5.	 s2e	 1e (85%)	13.	 s2m	 1m (90%)
6.	 s2f	 1f (90%)	14.	 s2n	 1n (32%)
7.	 s2g	 1g (74%)	15.	 s2o	 1o (75%)
8.	 s2h	 1h (80%)	16.	 s2p	 1p (92%)

General procedure for synthesis of 1:

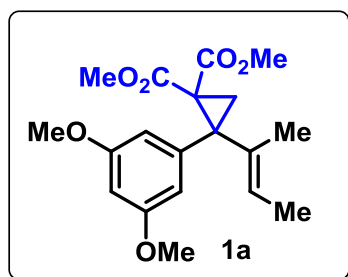
Compound **1** was synthesized from Step 1, Step 2 and Step 3 following reported procedures.^[5,6]

Step 1: To a stirred solution of (*E*)-1-(3,5-dimethoxyphenyl)-2-methylbut-2-en-1-one (**s2a**) (synthesized from the reported procedure)^[2] (3.60 g, 16.36 mmol, 1.0 equiv) in THF (82 mL) under argon at -78 °C was added (trimethylsilyl)methyl lithium solution (Me₃SiCH₂Li) (1M in pentane, 25.0 mL, 24.54 mmol, 1.5 equiv) drop wise. The reaction mixture turned to yellow color, and the reaction was monitored by using TLC. When the starting material completed, the reaction mixture was quenched with aqueous NH₄Cl (10 mL) at -78 °C, followed by the addition of water (10 mL) and hexanes (20 mL). The separated aqueous phase was extracted with hexanes (300 mL), and the combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The yellow color oil residue was enough to keep next reaction without further purification.

Step 2: To a stirred solution of alcohol **s2a'** (4.50 g, 14.61 mmol, 1 equiv) in THF (73 mL) under argon at 0 °C was added KHMDS (0.5 M in toluene, 58.5 mL, 29.22 mmol, 2.0 equiv) drop wise. The reaction mixture turned to dark color, and when the starting material was consumed completely (monitored by using TLC), it was quenched with aqueous NH₄Cl (30 mL), and hexanes (50 mL). The separated aqueous phase was extracted with hexanes (300 mL) and the combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The dark color residue was purified by flash column chromatography by using basic Al₂O₃, hexanes as an eluent (500 mL) to give olefin **s2a''** as a pale yellow oil. This purity is enough to proceed the next step.

Step 3: A solution of dimethyl 2-diazomalonate (2.93 g, 18.57 mmol, 1.5 equiv) in CH₂Cl₂ (20 mL) was added drop wise over 15-20 minutes to a green color solution of olefin **s2a''** (2.70 g, 12.38 mmol, 1.0 equiv) and bis[rhodium($\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-benzenedipropionic acid)] (19 mg, 24.7 μ mol, 0.2 mol%) in CH₂Cl₂ (40 mL) under argon at 0 °C. The reaction mixture was stirred up to 2-3h at same temperature and monitored by TLC, when the starting material was completed the solution was concentrated under the reduced pressure. The residue was purified by using silica gel column chromatography to afford dienyl cyclopropane-1,1-dicarboxylate **1a** as a yellow oil.

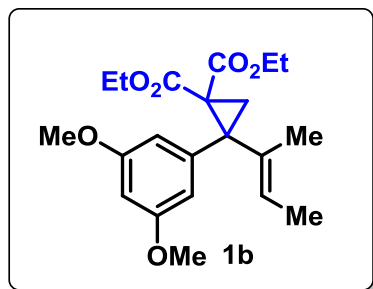
(E)-Dimethyl 2-(but-2-en-2-yl)-2-(3,5-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate(1a):



Yield: 3.7 g, (85%); yellow oil; R_f = 0.4 (20% EtOAc/hexanes); ¹H NMR (400 MHz, CDCl₃): δ 6.50 (d, J = 2.2 Hz, 2H), 6.32 (t, J = 2.2 Hz, 1H), 5.42 (q, J = 7.1 Hz, 1H), 3.75 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.44 (s, 3H), 2.34 (d, J = 5.1 Hz, 1H), 2.06 (d, J = 5.1 Hz, 1H), 1.81 (d, J = 7.1 Hz, 3H), 1.76 (s, 3H); ¹³C NMR (100

MHz, CDCl₃): δ 168.7, 167.5, 160.3, 141.0, 132.5, 125.0, 106.7, 99.1, 55.2, 52.5, 52.2, 44.7, 41.3, 25.2, 22.6, 14.9; IR (Neat): ν_{max} 2998, 2950, 2840, 1735, 1597, 1456, 1433, 1318, 1236, 1156, 1120, 1097, 1068, 830, 698; HRMS (ESI): calcd for C₁₉H₂₄O₆Na (M+Na)⁺ 371.1472, found 371.1465.

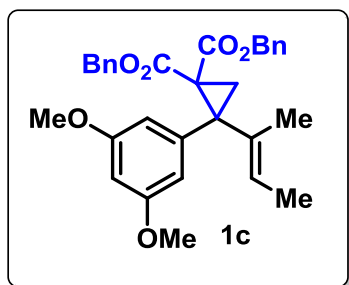
(E)-Diethyl 2-(but-2-en-2-yl)-2-(3,5-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate (1b):



Compound **1b** was synthesized from the ketone **s2a**^[2] by following the standard procedure. Yield: 450 mg, (86%); greenish oil; R_f = 0.4 (20% EtOAc/hexanes); ¹H NMR (500

MHz, CDCl₃): δ 6.52 (d, J = 2.2 Hz, 2H), 6.32 (t, J = 2.2 Hz, 1H), 5.42 (qq, J = 7.0, 1.3 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.97-3.82 (m, 2H), 3.75 (s, 6H), 2.32 (d, J = 5.0 Hz, 1H), 2.03 (d, J = 5.0 Hz, 1H) 1.82 (dq, J = 7.0, 1.3 Hz, 3H), 1.77 (m, 3H) 1.26 (t, J = 7.1 Hz, 3H), 0.99 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 168.3, 167.0, 160.3, 141.1, 132.6, 124.9, 106.9, 99.1, 61.4, 61.1, 55.2, 44.3, 41.5, 24.8, 22.7, 14.9, 13.9, 13.6; **IR** (Neat): ν_{\max} 2980, 2936, 1832, 1729, 1593, 1456, 1424, 1369, 1312, 1204, 1153, 1122, 1095, 1066, 1032, 832, 772; **HRMS** (ESI): calcd for C₂₁H₂₉O₆ (M+H)⁺ 377.1981, found 377.1958.

(E)-Dibenzyl

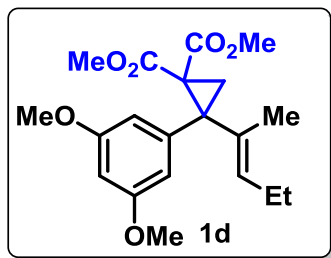


2-(but-2-en-2-yl)-2-(3,5-dimethoxyphenyl)cyclopropane-1,1-

dicarboxylate(1c): Compound **1c** was synthesized from the ketone **s2a**^[2] by following the standard procedure. Yield: 320 mg, (70%); yellow oil; R_f = 0.5 (20% EtOAc/hexanes); ¹H NMR (500 MHz, CDCl₃): δ 7.28-7.24 (m, 5H), 7.21-7.16 (m, 3H), 7.01-6.96 (m, 2H), 6.38 (d, J = 2.2 Hz, 2H), 6.21 (t, J = 2.2 Hz, 1H), 5.54 (q, J =

6.7 Hz, 1H), 5.08 (d, J = 12.3 Hz, 1H), 5.05 (d, J = 12.3 Hz, 1H), 4.80 (d, J = 12.3 Hz, 1H), 4.74 (d, J = 12.3 Hz, 1H), 3.63 (s, 6H), 2.13 (d, J = 5.1 Hz, 1H), 2.11 (d, J = 5.1 Hz, 1H) 1.50 (s, 3H), 1.37 (d, J = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.3, 167.1, 160.2, 135.3, 133.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 123.4, 107.4, 99.1, 67.2, 67.1, 55.2, 50.5, 41.0, 23.7, 15.1, 13.5; **IR** (Neat): ν_{\max} 2954, 2923, 2852, 1731, 1593, 1455, 1424, 1377, 1307, 1205, 1154, 1116, 1037, 966, 845, 750, 697; **HRMS** (ESI): calcd for C₃₁H₃₂O₆Na (M+Na)⁺ 523.2111, found 523.2091.

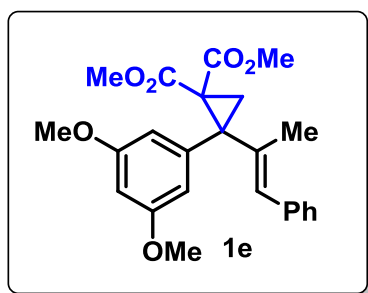
(E)-Dimethyl 2-(3,5-dimethoxyphenyl)-2-(pent-2-en-2-yl)cyclopropane-1,1-dicarboxylate



(1d): Compound **1d** was synthesized from the ketone **s2d** by following the standard procedure. Yield: 260 mg, (83%); colorless oil; $R_f = 0.4$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.46 (d, $J = 2.2$ Hz, 2H), 6.31 (t, $J = 2.2$ Hz, 1H), 5.55 (tq, $J = 7.0$, 1.3 Hz, 1H), 3.75 (s, 6H), 3.71 (s, 3H), 3.46 (s, 3H), 2.17 (d, $J = 5.0$ Hz, 1H), 2.14 (d, $J = 5.0$ Hz, 1H) 2.02-1.89 (m, 2H), 1.64 (s, 3H), 0.91 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.8, 167.7, 160.1, 141.7, 132.5, 130.7, 107.3, 99.1, 55.2, 52.3, 52.2, 50.0, 41.1, 23.2, 21.2, 15.1, 13.7; **IR** (Neat): ν_{max} 2953, 2923, 2852, 1732, 1593, 1456, 1432, 1323, 1223, 1203, 1153, 1109, 1066, 844, 701; **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{27}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 363.1795, found 363.1802.

(E)-Dimethyl

2-(3,5-dimethoxyphenyl)-2-(1-phenylprop-1-en-2-yl)cyclopropane-1,1-

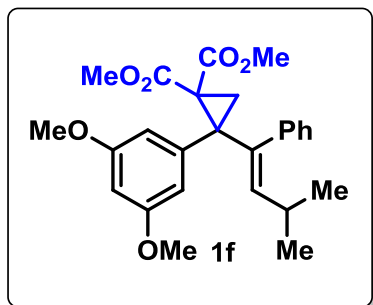


dicarboxylate (1e): Compound **1e** was synthesized from the ketone **s2e** by following the standard procedure. Yield: 260 mg, (85%); colorless oil; $R_f = 0.4$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.31-7.26 (m, 2H), 7.21-7.16 (m, 3H), 6.65 (s, 1H), 6.55 (d, $J = 2.2$ Hz, 2H), 6.34 (t, $J = 2.2$ Hz, 1H), 3.77 (s,

6H), 3.71 (s, 3H), 3.51 (s, 3H), 2.32 (d, $J = 5.2$ Hz, 1H), 2.27 (d, $J = 5.2$ Hz, 1H) 1.90 (d, $J = 1.3$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.7, 167.5, 160.2, 141.1, 137.2, 136.2, 128.7, 128.4, 127.9, 126.5, 107.4, 99.2, 55.2, 52.4, 52.3, 50.4, 41.1, 23.6, 16.9; **IR** (Neat): ν_{max} 3021, 2950, 2839, 1731, 1592, 1433, 1324, 1225, 1203, 1154, 1115, 748, 697; **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 411.17905, found 411.1802.

(E)-Dimethyl

2-(3,5-dimethoxyphenyl)-2-(3-methyl-1-phenylbut-1-enyl)cyclopropane-1,1-

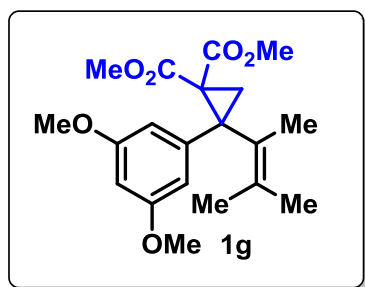


dicarboxylate (1f): Compound **1f** was synthesized from the

ketone **s2f** by following the standard procedure. Yield: 350 mg, (90%); colorless oil; $R_f = 0.4$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.25-7.18 (m, 3H), 6.91-6.87 (m, 2H), 6.43 (d, $J = 2.2$ Hz, 2H), 6.31 (t, $J = 2.2$ Hz, 1H), 5.70 (d, $J = 10$ Hz, 1H), 3.80 (s, 3H), 3.69 (s, 6H), 3.38 (s, 3H), 2.15 (d, $J = 5.6$ Hz, 1H), 2.14 (m, 1H), 2.04 (d, $J = 5.6$ Hz, 1H), 0.93 (d, $J = 6.7$ Hz, 3H), 0.85 (d, $J = 6.7$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 167.7, 166.9, 159.9, 141.3, 140.1, 139.6, 135.7, 128.5, 127.7, 126.6, 107.3, 99.5, 55.1, 52.3, 52.1, 48.2, 43.5, 28.2, 22.6, 22.4, 22.1; **IR** (Neat): ν_{max} 2953, 2926, 2864, 1736, 1595, 1458, 1433, 1327, 1223, 1204, 1155, 1103, 1070, 1039, 837, 703; **HRMS** (ESI): calcd for $\text{C}_{26}\text{H}_{30}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 461.1928, found 461.1934.

Dimethyl

2-(3,5-dimethoxyphenyl)-2-(3-methylbut-2-en-2-yl)cyclopropane-1,1-



dicarboxylate (1g): Compound **1g** was synthesized from the

ketone **s2g** by following the standard procedure. Yield: 300 mg,

(74%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $^1\text{H NMR}$

(400 MHz, CDCl_3): δ 6.48 (d, $J = 2.2$ Hz, 2H), 6.31 (t, $J = 2.2$ Hz,

1H), 3.75 (s, 6H), 3.71 (s, 3H), 3.42 (s, 3H), 2.39 (brs, 1H), 2.07

(brs, 1H), 1.84 (s, 3H), 1.75 (s, 3H), 1.65 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 168.7, 167.6,

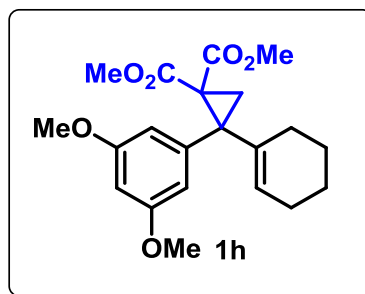
160.2, 141.6, 130.8, 125.0, 106.3, 98.8, 55.1, 52.4, 52.1, 47.5, 43.5, 21.7, 21.0, 18.8; **IR** (Neat):

ν_{max} 2999, 2949, 2923, 2854, 1731, 1594, 1455, 1433, 1331, 1267, 1227, 1205, 1156, 1117,

1068, 1040, 843, 769, 695; **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{27}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 363.1819, found

363.1815.

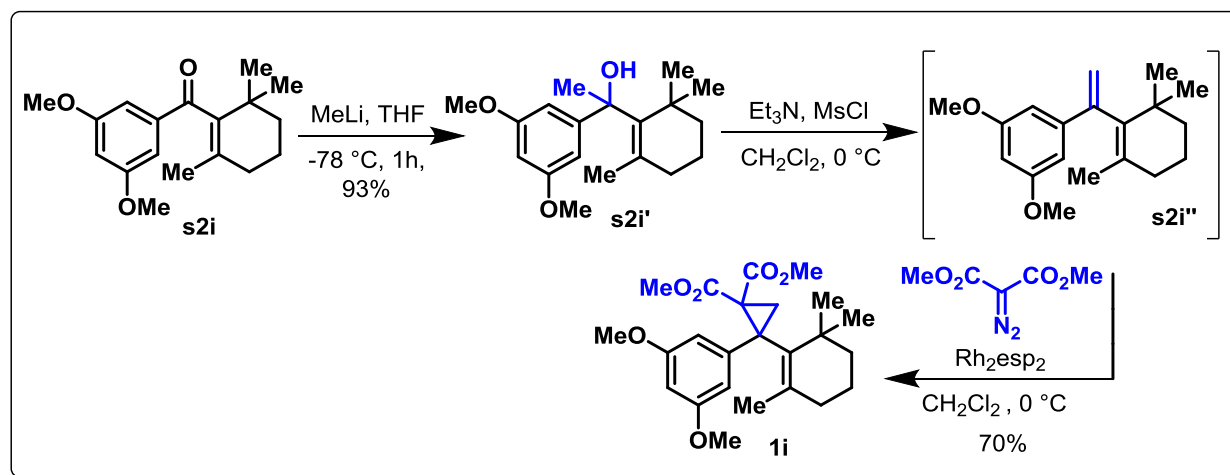
Dimethyl 2-cyclohexenyl-2-(3,5-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate (1h):



Compound **1h** was synthesized from the ketone **s2h** by following

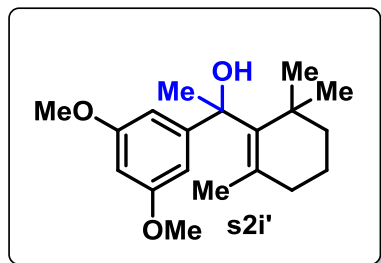
the standard procedure. Yield: 385 mg, (80%); colorless oil; $R_f = 0.4$ (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3): δ 6.41 (m, 2H), 6.29 (m, 1H), 5.76 (brs, 1H), 3.73 (s, 6H), 3.69 (s, 3H), 3.44 (s, 3H), 2.17 (d, $J = 5.1$ Hz, 1H), 2.08 (d, $J = 5.1$ Hz, 1H) 2.03 (m, 1H), 2.00-1.86 (m, 3H) 1.58 (m, 1H), 1.49 (m, 1H), 1.44-1.20 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.8, 167.8, 160.1, 141.7, 135.5, 125.4, 107.4, 99.0, 55.2, 52.4, 52.2, 49.1, 40.8, 27.2, 25.4, 22.7, 22.6, 22.0; IR (Neat): ν_{max} 2925, 2853, 1730, 1592, 1432, 1320, 1220, 1202, 1153, 1110, 1065, 1034, 892, 839, 701; HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{27}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 375.1795, found 375.1802.

Modified Procedure for Synthesis of (1i):



Step 1: Compound **s2i''** was prepared following a reported procedure.^[7] To a stirred solution of dienone **s2i** (1.0 g, 3.4722 mmol, 1 equiv) in dry THF (17 mL) at -78 °C was added MeLi (3.25 mL, 1.6M in hexanes, 1.5 equiv) drop wise and the reaction mixture was stirred for 1-2h at -78 °C. The reaction mixture was monitored by using TLC, and it was quenched with saturated aqueous NH_4Cl solution (5 mL) and extracted with EtOAc (100 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated in *vacuo*. The obtained crude oil was purified by using silica gel column chromatography to give alcohol **s2i'** as a white solid (980 mg, 93%).

1-(3,5-Dimethoxyphenyl)-1-(2,6,6-trimethylcyclohex-1-enyl)ethanol (s2i'):



$R_f = 0.4$ (10% EtOAc/hexanes); m.p. 102-104 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.65 (d, $J = 2.2$ Hz, 2H), 6.33 (t, $J = 2.2$ Hz, 1H), 3.86 (s, 0.7H), 3.78 (s, 6H), 2.0-1.83 (m, 3H), 1.81 (s, 3H), 1.70-1.46 (m, 3H), 1.43 (s, 3H), 1.42 (s, 3H), 1.08 (s, 3H); ^{13}C

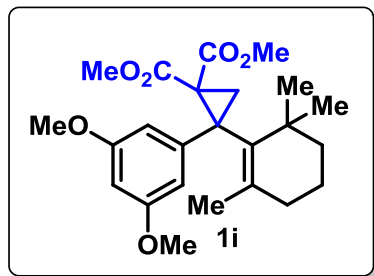
NMR (100 MHz, CDCl_3): δ 160.7, 153.3, 142.5, 129.2, 104.1, 97.8, 79.2, 55.2, 44.8, 35.9, 34.9, 29.9, 29.3, 28.3, 23.3, 19.2; **IR** (Neat): ν_{max} 3515, 2998, 2928, 2864, 1596, 1457, 1423, 1206, 1154, 1058, 1047, 850, 718; **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{27}\text{O}_2$ ($\text{M}-\text{OH}$) $^+$ 287.2003, found 287.2005.

Step 2: The resulting alcohol **s2i'** (1.0 g, 3.289 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (16.5 mL) and cooled to 0 °C with an ice/water bath. To this stirred solution was added Et_3N (2.3 mL, 16.4 mmol, 5 equiv) and methane sulfonyl chloride (0.65 mL, 8.223 mmol, 2.5 equiv) sequentially. The reaction mixture was monitored by using TLC, and it was quenched with H_2O , extracted with hexanes and washed with saturated aq NaCl solution. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated in *vacuo*. The crude oil was purified by using basic Al_2O_3 flash column chromatography (hexanes as an eluent) to give olefin **s2i''** as a colorless oil. This purity was good enough to proceed next step.

Step 3: Synthesis of cyclopropane-1,1-dicarboxylate **1i** was achieved from olefin **s2i''** following the standard procedure.^[6]

Dimethyl 2-(3,5-dimethoxyphenyl)-2-(2,6,6-trimethylcyclohex-1-enyl)cyclopropane-1,1-

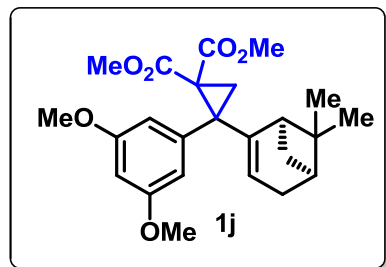
dicarboxylate (1i):



Yield: 285 mg, (78%); colorless oil; R_f = 0.4 (20% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.35 (d, J = 2.2 Hz, 2H), 6.29 (t, J = 2.2 Hz, 1H), 3.73 (s, 6H), 3.66 (s, 3H), 3.35

(s, 3H), 2.44 (d, J = 6.2 Hz, 1H), 2.40 (d, J = 6.2 Hz, 1H), 2.17-2.02 (m, 2H), 1.77 (s, 3H), 1.63 (m, 1H), 1.46-1.31 (m, 3H), 1.22 (s, 3H), 0.77 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 168.7, 167.7, 160.2, 141.9, 134.6, 132.1, 105.6, 98.5, 55.1, 52.3, 52.1, 44.7, 42.3, 41.9, 35.6, 32.4, 29.4, 28.9, 22.9, 21.9, 18.6; **IR** (Neat): ν_{max} 2928, 2866, 1736, 1596, 1458, 1434, 1320, 1299, 1204, 1155, 1042, 828; **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{32}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 439.2083, found 439.2091.

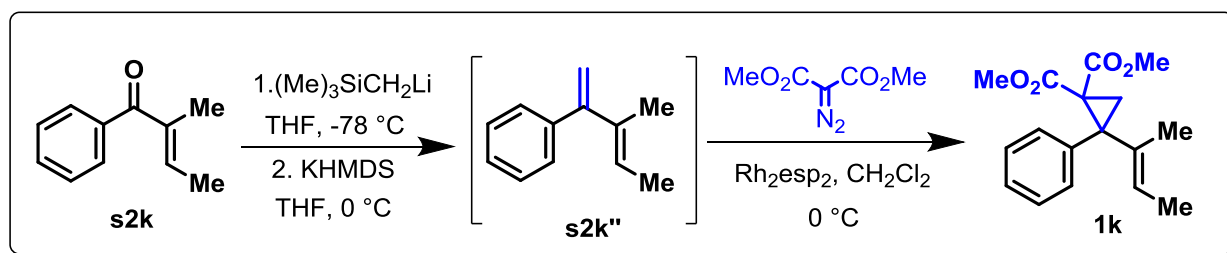
Dimethyl 2-(3,5-dimethoxyphenyl)-2-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)cyclopropane-1,1-dicarboxylate (1j): Major (Bottom)



Compound **1j** was synthesized from the ketone **s2j** by following the standard procedure. Yield: 196 mg, (66%); colorless oil; R_f = 0.5 (20% EtOAc/hexanes); $[\alpha]_{\text{D}}^{25} = -12.00$ (c = 0.03550, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.42 (d, J = 2.2 Hz,

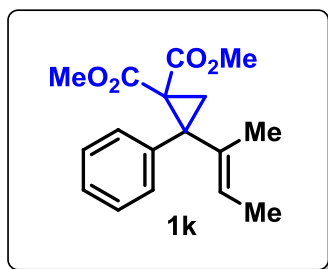
2H), 6.29 (t, J = 2.2 Hz, 1H), 5.51 (m, 1H), 3.75 (s, 6H), 3.73 (s, 3H), 3.43 (s, 3H), 2.30 (m, 1H), 2.23-2.10 (m, 3H), 2.10 (d, J = 5.0 Hz, 1H), 2.98 (d, J = 5.0 Hz, 1H), 1.97 (m, 1H), 1.17 (s, 3H), 0.99 (d, J = 8.5 Hz, 1H), 0.42 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.8, 167.6, 160.1, 145.4, 141.2, 121.7, 107.4, 99.1, 55.3, 52.4, 52.3, 47.8, 45.5, 41.4, 40.3, 37.7, 31.5, 31.3, 26.1, 21.7, 20.6; **IR** (Neat): ν_{max} 2948, 2921, 2853, 1735, 1593, 1457, 1431, 1323, 1299, 1203, 1153, 1110, 1065, 1037, 836, 752, 700; **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{30}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 437.1926, found 437.1934.

Minor (top) Yield: 28 mg, (10%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $[\alpha]_D^{31} = +51.25$ ($c = 0.0040$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.38 (d, $J = 2.2$ Hz, 2H), 6.28 (t, $J = 2.2$ Hz, 1H), 5.57 (m, 1H), 3.74 (s, 6H), 3.74 (s, 3H), 3.47 (s, 3H), 2.48 (m, 1H), 2.37-2.21 (m, 2H), 2.16 (d, $J = 4.8$ Hz, 1H), 2.13 (d, $J = 4.8$ Hz, 1H), 2.13-2.06 (m, 1H), 1.94 (m, 1H), 1.12 (s, 3H), 0.96 (d, $J = 8.5$ Hz, 1H), 0.19 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 168.0, 167.9, 160.1, 145.6, 140.5, 121.1, 107.3, 99.3, 55.3, 52.6, 52.3, 48.8, 45.2, 40.1, 40.0, 37.6, 32.0, 31.5, 25.8, 23.0, 20.2; **IR** (Neat): ν_{max} 2952, 2925, 2857, 1735, 1596, 1450, 1424, 1328, 1290, 1208, 1156, 1116, 1067, 1035, 839, 754, 703; **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{31}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 415.2120, found 415.2126.



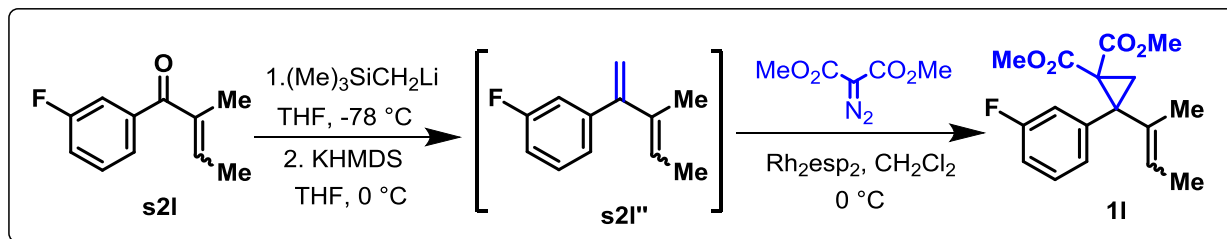
Compound **1k** was synthesized from the (*E*)-2-Methyl-1-phenylbut-2-en-1-one (**s2k**) (synthesized from the reported procedure)^[8] by following the standard procedure.

(*E*)-Dimethyl 2-(but-2-en-2-yl)-2-phenylcyclopropane-1,1-dicarboxylate (1k**):**



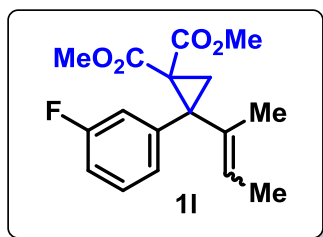
Yield: 325 mg, (85%); white solid; m.p. 62-64 °C; $R_f = 0.5$ (10% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.33-7.28 (m, 2H), 7.27-7.22 (m, 2H), 7.20 (m, 1H), 5.67 (qq, $J = 6.8, 1.3$ Hz, 1H), 3.72 (s, 3H), 3.39 (s, 3H), 2.20 (d, $J = 5.1$ Hz, 1H), 2.16 (d, $J = 5.1$ Hz, 1H), 1.64 (m, 3H), 1.55 (d, $J = 6.8$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 168.0, 167.7, 139.3, 134.0, 129.0, 127.8, 126.9, 122.9, 52.3, 52.1, 50.1, 40.7, 23.3, 14.8, 13.5; **IR** (Neat): ν_{max} 2950,

2922, 1733, 1434, 1329, 1310, 1236, 1167, 1118, 1099, 1064, 754, 702; **HRMS** (ESI): calcd for $C_{17}H_{20}O_4Na$ ($M+Na$)⁺ 311.12528, found 311.12779.



Compound **11** was synthesized from **1-(3-fluorophenyl)-2-methylbut-2-en-1-one** (**s2l**) (synthesized from the reported procedure)^[9] by following the standard procedure.

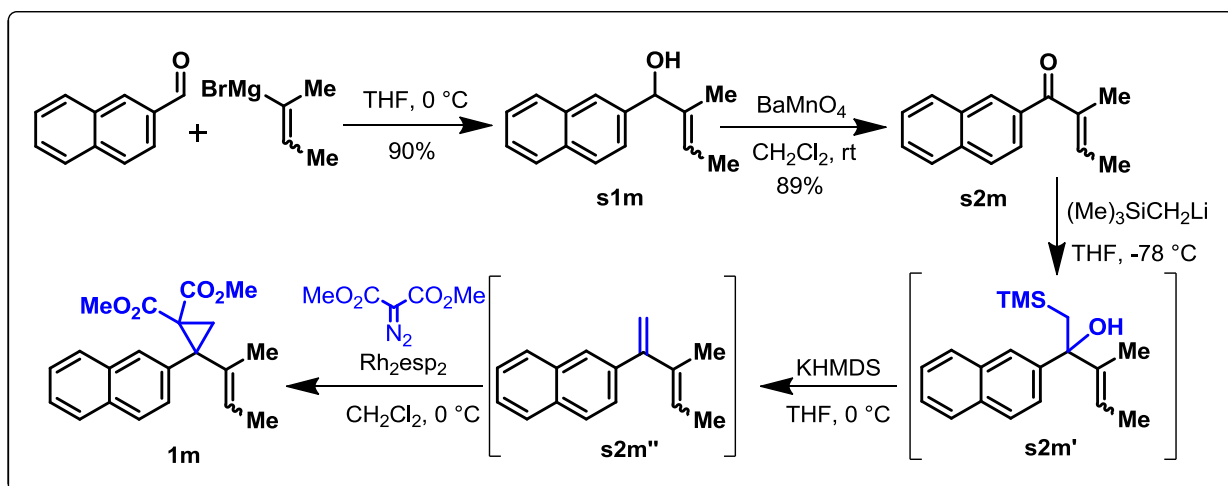
Dimethyl 2-(but-2-en-2-yl)-2-(3-fluorophenyl)cyclopropane-1,1-dicarboxylate (11**): (*E*+*Z*)**



Yield: 220 mg, (90%); colorless oil; R_f = 0.5 (10% EtOAc/hexanes);

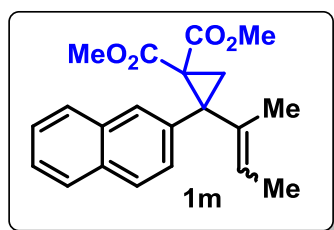
¹H NMR (400 MHz, CDCl₃): δ 7.22 (m, 1H), 7.13-6.98 (m, 2H), 6.92 (m, 1H), 5.67 (q, J = 6.8 Hz, 0.4H), 5.46 (q, J = 7.1 Hz, 0.6H), 3.74 (s, 1.8H), 3.72 (s, 1.2H), 3.45 (s, 1.2H), 3.41 (s, 1.8H), 2.34 (d,

J = 5.3 Hz, 0.6H), 2.20 (d, J = 5.2 Hz, 0.4H), 2.13 (d, J = 5.2 Hz, 0.4H), 2.09 (d, J = 5.3 Hz, 0.6H), 1.80 (d, J = 7.1 Hz, 1.8H), 1.75 (s, 1.8H), 1.63 (s, 1.2H), 1.56 (d, J = 6.8 Hz, 1.2H); ¹³C NMR (125 MHz, CDCl₃): δ 168.45, 167.7, 167.6, 167.2, 163.3 (d, J = 20.8 Hz), 161.3 (d, J = 20.8 Hz), 141.9 (d, J = 7.2 Hz), 141.2 (d, J = 7.2 Hz), 135.0, 132.0, 129.4 (d, J = 9.1 Hz), 129.2 (d, J = 8.1 Hz), 125.4, 124.6 (d, J = 2.7 Hz), 123.8 (d, J = 2.7 Hz), 123.6, 116.1 (d, J = 21.8 Hz), 115.5 (d, J = 21.8 Hz), 114.2 (d, J = 20.8 Hz), 114.0 (d, J = 20.8 Hz), 52.5, 52.4, 52.3, 52.2, 49.4, 43.7, 41.6, 40.9, 24.7, 23.3, 22.4, 14.8, 13.5; **IR** (Neat): ν_{max} 2951, 2858, 1733, 1613, 1486, 1435, 1321, 1202, 1153, 1116, 884, 827, 700; **HRMS** (ESI): calcd for $C_{17}H_{19}O_4FNa$ ($M+Na$)⁺ 329.1155, found 329.1159.



Compound **1m** was synthesized from **2-methyl-1-(naphthalen-2-yl)but-2-en-1-one (s2m)** (synthesized from the reported procedure)^[10] by following the standard procedure.

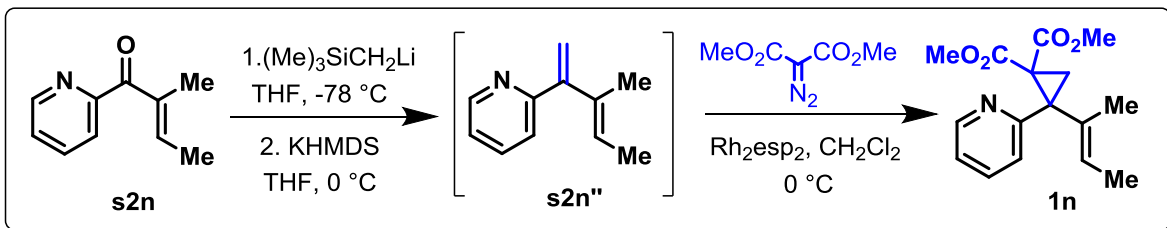
Dimethyl 2-(but-2-en-2-yl)-2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate (1m): (*E*+*Z*)



Yield: 670 mg, (90%); colorless oil; $R_f = 0.5$ (10% EtOAc/hexanes);

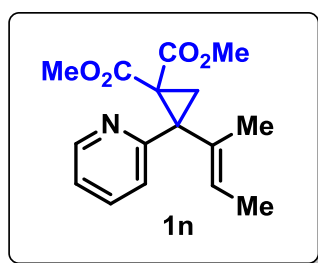
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.81-7.70 (m, 4H), 7.52-7.40 (m, 3H), 5.75 (qq, $J = 6.8, 1.3$ Hz, 0.2H), 5.45 (qq, $J = 7.0, 1.3$ Hz, 0.8H), 3.76 (s, 2.4H), 3.75 (s, 0.6H), 3.35 (s, 0.6H), 3.29 (s, 2.4H),

2.51 (d, $J = 5.2$ Hz, 0.8H), 2.29 (d, $J = 5.1$ Hz, 0.2H), 2.27 (d, $J = 5.1$ Hz, 0.2H), 2.17 (d, $J = 5.2$ Hz, 0.8H), 1.88 (dq, $J = 7.0, 1.3$ Hz, 2.4H), 1.80 (m, 2.4H), 1.67 (m, 0.6H), 1.56 (dq, $J = 6.8, 1.3$ Hz, 0.6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 168.6, 168.0, 167.7, 167.4, 136.8, 136.2, 134.0, 132.9, 132.5, 132.4, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2, 126.4, 126.0, 125.9, 125.8, 124.9, 123.1, 52.5, 52.4, 52.1, 50.1, 44.6, 41.5, 40.9, 24.9, 23.4, 22.5, 14.9, 14.8, 13.5; **IR** (Neat): ν_{max} 3054, 2933, 2949, 2920, 2860, 1731, 1504, 1434, 1318, 1232, 1193, 1114, 893, 859, 821, 802, 747; **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 361.1407, found 361.1410.



Compound **1n** was synthesized from the ketone **s2n** by following the standard procedure.

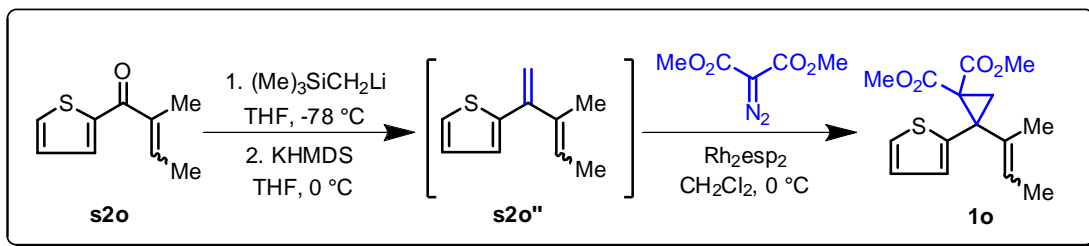
(E)-Dimethyl 2-(but-2-en-2-yl)-2-(pyridin-2-yl)cyclopropane-1,1-dicarboxylate (1n):



Yield: 45 mg, (32 %, brsm); yellow oil; $R_f = 0.5$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.45 (d, $J = 4.7$ Hz, 1H), 7.58 (dt, $J = 7.7, 1.8$ Hz, 1H), 7.33 (td, $J = 7.7, 0.9$ Hz, 1H), 7.08 (ddd, $J = 7.7, 4.7, 0.9$ Hz, 1H), 5.70 (qq, $J = 6.7, 1.3$ Hz, 1H),

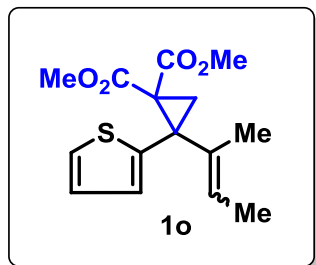
3.71 (s, 3H), 3.46 (s, 3H), 2.39 (d, $J = 4.7$ Hz, 1H), 2.20 (d, $J = 4.7$ Hz, 1H), 1.69 (m, 3H), 1.63 (qd, $J = 6.7, 1.1$ Hz, 3H); $^{13}\text{C NMR}$ (500 MHz, CDCl_3): δ 168.1, 168.0, 158.5, 148.4, 136.0, 132.0, 125.7, 123.4, 121.5, 52.5, 52.2, 49.2, 42.3, 24.3, 15.3, 13.6; **IR** (Neat): ν_{max} 2950, 2921, 2853, 1735, 1586, 1568, 1467, 1434, 1347, 1308, 1236, 1192, 1107, 1057, 992, 895, 767, 749;

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{19}\text{O}_4\text{NNa}$ ($\text{M}+\text{Na}$) $^+$ 312.1219, found 312.1206.



Compound **1o** was synthesized from **2-Methyl-1-(thiophen-2-yl)but-2-en-1-one (s2o)** (synthesized from the reported procedure)^[10] by following the standard procedure.

Dimethyl 2-(but-2-en-2-yl)-2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate (1o**): (*E*+*Z*)**

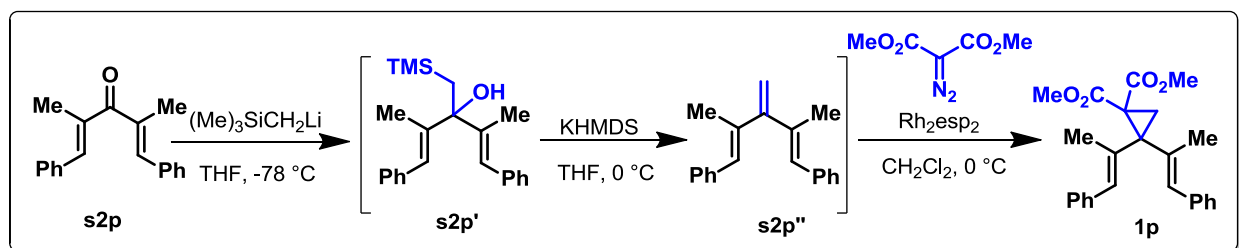


Yield: 235 mg, (75%); yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ^1H

NMR (500 MHz, CDCl_3): δ 7.15-7.13 (m, 1H), 6.88-6.83 (m, 1H), 6.79 (m, 1H), 5.68 (dq, J = 6.8, 1.3 Hz, 0.2H), 5.50 (q, J = 6.8 Hz, 0.8H), 3.71 (s, 2.4H), 3.70 (s, 0.6H), 3.46 (s, 2.4H), 3.45 (s, 0.6H),

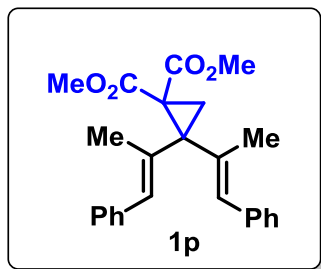
2.28 (d, J = 5.5 Hz, 0.8H), 2.25 (d, J = 5.5 Hz, 0.2H), 2.21 (d, J = 5.5 Hz, 0.2H), 2.10 (d, J = 5.5 Hz, 0.8H), 1.79 (d, J = 6.8 Hz, 2.4H), 1.79 (s, 2.4H), 1.72 (s, 0.6H), 1.60 (d, J = 6.8 Hz, 0.6H);

^{13}C **NMR** (100 MHz, CDCl_3): δ 168.1, 167.6, 167.1, 166.9, 143.6, 143.3, 133.4, 132.7, 126.3, 126.2, 125.7, 125.6, 125.1, 125.0, 124.6, 52.5, 52.3, 44.3, 43.2, 39.3, 25.4, 24.3, 22.3, 15.1, 14.8, 13.5; **IR** (Neat): ν_{max} 2950, 2922, 2853, 1733, 1434, 1316, 1298, 1239, 1217, 1158, 1115, 894, 855, 828, 772, 702; **HRMS** (ESI): calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4\text{NaS}$ ($\text{M}+\text{Na}$) $^+$ 317.0814, found 317.0818.



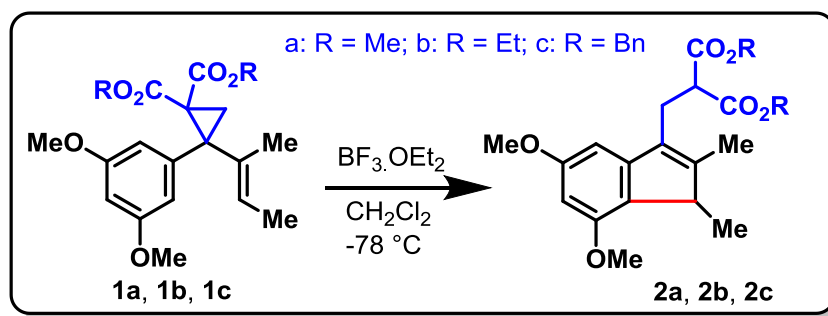
Compound **1p** was synthesized from (*1E,4E*)-2,4-dimethyl-1,5-diphenylpenta-1,4-dien-3-one (**s2p**) (which was synthesized from the reported procedure)^[11] by following the standard procedure.

Dimethyl 2,2-bis((*E*)-1-phenylprop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (1p):



Yield: 8.95 g, (92%); green solid; recrystallization from EtOH yielded in a crystalline form m.p. 74-76 °C; $R_f = 0.5$ (10% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.37-7.31 (m, 4H), 7.28-7.20 (m, 6H), 6.59 (s, 2H), 3.72 (s, 6H), 2.16 (s, 2H), 1.98 (d, $J = 1.3$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.9, 137.4, 134.2, 129.6, 128.7, 128.0, 126.5, 53.3, 52.4, 41.8, 23.1, 16.7; **IR** (Neat): ν_{max} 3023, 2951, 2923, 2853, 1735, 1599, 1492, 1435, 1378, 1322, 1235, 1149, 1115, 1067, 770, 748, 699; **HRMS** (ESI): calcd for $\text{C}_{25}\text{H}_{27}\text{O}_4$ ($\text{M}+\text{H}$) $^+$ 391.1905, found 391.1904

4. Nazarov Cyclization of dienyl Donor-Acceptor Cyclopropanes (DACs)

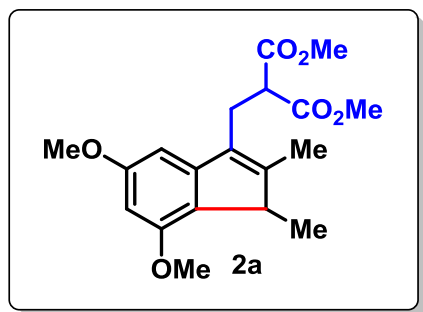


S.No.	Cyclopropane Diesters	Product	S.No.	Cyclopropane Diesters	Product
1.			9.		
2.			10.		
3.			11.		
4.			12.		
5.			13.		
6.			14.		
7.			15.		
8.			16.		

Standard procedure for Nazarov cyclization:

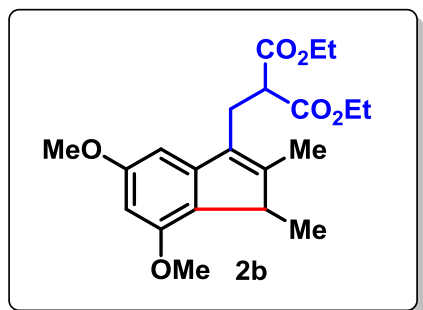
Dienyl donor-acceptor cyclopropane 1,1-dicarboxylates **1a** (400 mg, 1.149 mmol, 1 equiv) was dissolved in CH₂Cl₂ (12 mL) under argon and cooled to -78 °C. To this, boron trifluoride diethyl etherate (BF₃.Et₂O) (0.12 mL, 0.1149 mmol, 0.1 equiv) was added drop wise. The orange color reaction mixture was stirred at -78 °C for 30 mins and brought to 0 °C over 1h. The reaction mixture was quenched with the saturated aqueous NaHCO₃ (5 mL) at 0 °C. The aqueous phase was extracted with EtOAc, and the combined organic layers were washed with brine solution (5 mL), dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by using silica gel column chromatography to afford the desired product as colorless oil (**2a**).

Dimethyl 2-((5,7-dimethoxy-1,2-dimethyl-1*H*-inden-3-yl)methyl)malonate (**2a**):



Yield: 397 mg, (99%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); ¹H NMR (500 MHz, CDCl₃): δ 6.43 (d, $J = 1.9$ Hz, 1H), 6.29 (d, $J = 1.9$ Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.69 (s, 3H), 3.69 (t, $J = 7.9$ Hz, 1H), 3.68 (s, 3H), 3.23 (q, $J = 7.4$ Hz, 1H), 3.11 (dd, $J = 17.5, 7.9$ Hz, 1H), 3.07 (dd, $J = 17.5, 7.9$ Hz, 1H), 1.95 (s, 3H), 1.25 (d, $J = 7.4$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 169.5, 169.4, 160.6, 155.6, 148.6, 46.3, 130.5, 126.8, 96.1, 94.7, 55.5, 55.1, 52.4, 52.3, 50.4, 45.5, 24.8, 14.5, 12.0; IR (Neat): ν_{max} 2955, 2849, 1737, 1591, 1484, 1435, 1341, 1290, 1230, 1204, 1140, 1092, 1038, 825; HRMS (ESI): calcd for C₁₉H₂₅O₆ (M+H)⁺ 349.1655, found 349.1645.

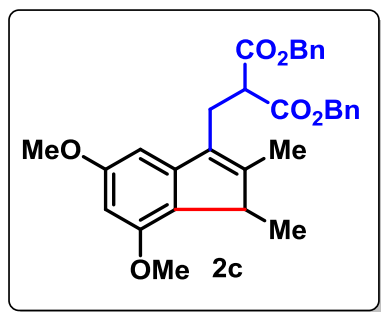
Diethyl 2-((5,7-dimethoxy-1,2-dimethyl-1*H*-inden-3-yl)methyl)malonate (2b): Compound **2b**



was synthesized from the **1b** by following the standard procedure. Yield: 82 mg, (96%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.45 (d, $J = 1.8$ Hz, 1H), 6.29 (d, $J = 1.8$ Hz, 1H), 4.16 (q, $J = 6.4$ Hz, 2H), 4.14 (q, $J = 6.4$ Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.65

(t, $J = 7.5$ Hz, 1H), 3.22 (q, $J = 7.3$ Hz, 1H), 3.08 (d, $J = 7.5$ Hz, 2H), 1.96 (s, 3H), 1.27-1.18 (m, 9H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 169.1, 160.5, 155.6, 148.3, 146.5, 130.8, 126.8, 96.2, 94.7, 61.3, 55.5, 55.1, 50.8, 45.5, 24.7, 14.5, 14.0, 13.9, 12.1; **IR** (Neat): ν_{max} 2979, 2961, 2930, 2853, 1733, 1592, 1484, 1464, 1368, 1333, 1270, 1226, 1141, 1094, 1039, 934, 830, 772; **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{29}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 377.1983, found 377.1958.

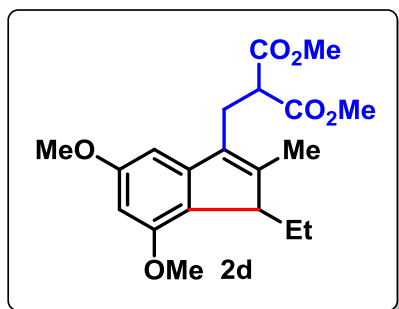
Dibenzyl 2-((5,7-dimethoxy-1,2-dimethyl-1*H*-inden-3-yl)methyl)malonate (2c): Compound **2c**



was synthesized from **1c** by following the standard procedure. Yield: 99 mg, (93%); colorless oil; $R_f = 0.6$ (15% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.33-7.26 (m, 6H), 7.24-7.16 (m, 4H), 6.43 (d, $J = 1.8$ Hz, 1H), 6.28 (d, $J = 1.8$ Hz, 1H), 5.13-5.06 (m, 4H), 3.84 (s, 3H), 3.78 (t, $J = 7.6$ Hz,

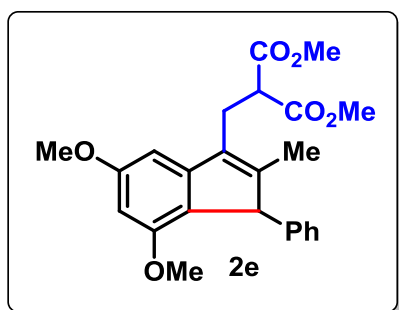
1H), 3.76 (s, 3H), 3.17 (q, $J = 7.4$ Hz, 1H), 3.13 (d, $J = 7.6$ Hz, 2H), 1.89 (s, 3H), 1.20 (d, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 168.9, 168.8, 160.6, 155.7, 148.6, 146.4, 135.2, 130.6, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 126.8, 96.0, 94.9, 67.1, 55.5, 55.1, 50.8, 45.6, 24.8, 14.4, 12.1; **IR** (Neat): ν_{max} 2958, 2925, 2853, 1785, 1735, 1591, 1483, 1455, 1205, 1142, 1037, 772, 750, 697; **HRMS** (ESI): calcd for $\text{C}_{31}\text{H}_{33}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 501.2292, found 501.2271.

Dimethyl 2-((1-ethyl-5,7-dimethoxy-2-methyl-1*H*-inden-3-yl)methyl)malonate (2d):



Compound **2d** was synthesized from **1d** by following the standard procedure. Yield: 58 mg, (98%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.42 (d, $J = 1.9$ Hz, 1H), 6.28 (d, $J = 1.9$ Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.71 (dd, $J = 8.4, 6.9$ Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.36 (t, $J = 4.2$ Hz, 1H), 3.16 (dd, $J = 14.1, 8.4$ Hz, 1H), 3.06 (dd, $J = 14.1, 6.9$ Hz, 1H), 2.29 (m, 1H), 1.93 (s, 3H), 1.79 (m, 1H), 0.27 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 169.4, 160.4, 155.6, 147.4, 146.1, 132.2, 124.1, 95.9, 94.5, 55.4, 55.0, 52.4, 52.3, 50.9, 50.4, 24.9, 20.1, 12.1, 6.9; **IR** (Neat): ν_{max} 2956, 2923, 2852, 1734, 1589, 1454, 1433, 1359, 1204, 1138, 1037, 933, 823; **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{27}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 363.1798, found 363.1802.

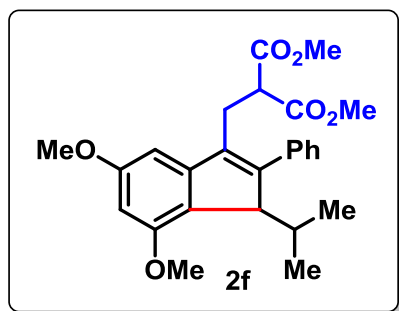
Dimethyl 2-((5,7-dimethoxy-2-methyl-1-phenyl-1*H*-inden-3-yl)methyl)malonate (2e):



Compound **2e** was synthesized from **1e** by following the standard procedure. Yield: 120 mg, (96%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.23-7.13 (m, 3H), 6.98-6.93 (m, 2H), 6.49 (d, $J = 1.9$ Hz, 1H), 6.24 (d, $J = 1.9$ Hz, 1H), 4.27 (s, 1H), 3.85 (s, 3H), 3.78 (dd, $J = 8.5, 7.0$ Hz, 1H), 3.73 (s, 3H), 3.64 (s, 3H), 3.58 (s, 3H), 3.19 (dd, $J = 14.1, 8.5$ Hz, 1H), 3.12 (dd, $J = 14.1, 7.0$ Hz, 1H), 1.77 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 169.4, 161.6, 155.6, 147.8, 147.1, 139.6, 132.0, 128.1, 127.9, 126.5, 126.1, 96.4, 95.5, 56.9, 55.5, 55.4, 52.6, 52.5, 50.4, 25.0, 12.5; **IR** (Neat): ν_{max} 2922, 2851, 1735, 1591, 1434, 1271, 1204, 1151, 1037, 827, 755, 700; **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 411.1794, found 411.1802.

Dimethyl 2-((1-isopropyl-5,7-dimethoxy-2-phenyl-1*H*-inden-3-yl)methyl)malonate (2f):

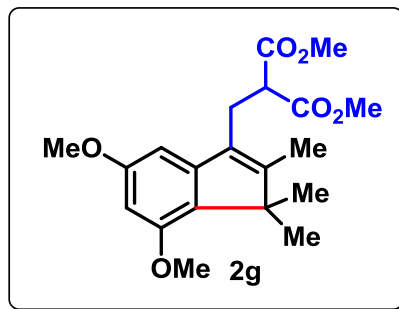
Compound **2f** was synthesized from **1f** by following the standard procedure. Yield: 142 mg,



(94%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.39 (t, , $J = 7.6$ Hz, 2H), 7.32-7.27 (m, 3H), 6.53 (d, $J = 1.9$ Hz, 1H), 6.37 (d, $J = 1.9$ Hz, 1H), 3.94 (d, $J = 2.5$ Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.65 (dd, $J = 8.5$, 6.5 Hz, 1H), 3.65 (s, 3H), 3.42 (s, 3H), 3.34 (dd, $J = 14.3$, 8.5

Hz, 1H), 3.13 (dd, $J = 14.3$, 6.5 Hz, 1H), 2.51 (m, 1H), 0.66 (d, $J = 7.0$ Hz, 3H), 0.51 (d, $J = 7.0$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 169.4, 169.1, 160.5, 155.8, 149.5, 146.9, 137.7, 134.2, 128.9, 128.2, 126.9, 125.1, 96.8, 95.8, 56.8, 55.5, 55.0, 52.4, 52.3, 50.7, 28.5, 24.8, 20.0, 18.2; **IR** (Neat): ν_{max} 2953, 2925, 2853, 1736, 1601, 1586, 1462, 1436, 1334, 1206, 1151, 1046, 827, 703; **HRMS** (ESI): calcd for $\text{C}_{26}\text{H}_{31}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 439.2130, found 439.2115.

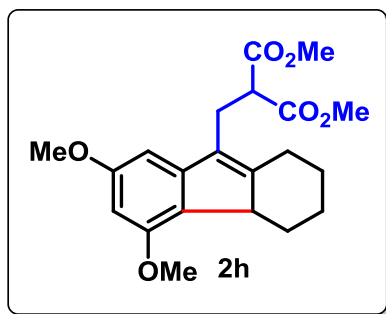
Dimethyl 2-((5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)methyl)malonate (2g):



Compound **2g** was synthesized from **1g** by following the standard procedure. Yield: 132 mg, (97%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.41 (d, $J = 1.8$ Hz, 1H), 6.28 (d, $J = 1.8$ Hz, 1H), 3.83 (s, 6H), 3.70 (t, $J = 7.7$ Hz, 1H), 3.67 (s, 6H), 3.08 (d, $J = 7.7$ Hz, 2H),

1.83 (s, 3H), 1.23 (s, 6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 169.5, 160.4, 155.6, 153.1, 144.8, 131.0, 128.5, 96.0, 94.8, 55.5, 55.0, 52.3, 52.3, 50.3, 49.9, 24.8, 21.3, 21.3, 9.4; **IR** (Neat): ν_{max} 2955, 2929, 2840, 1736, 1590, 1484, 1433, 1353, 1341, 1283, 1228, 1205, 1150, 1091, 1038, 933, 825, 677; **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{26}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 385.1622, found 385.1621.

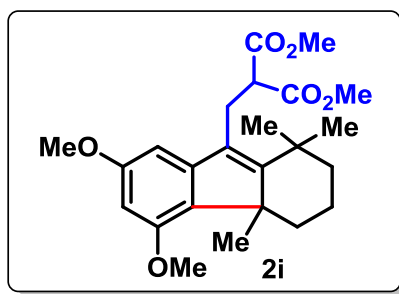
Dimethyl 2-((5,7-dimethoxy-2,3,4,4a-tetrahydro-1H-fluoren-9-yl)methyl)malonate (2h):



Compound **2h** was synthesized from **1h** by following the standard procedure. Yield: 118 mg, (96%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.47 (d, $J = 1.9$ Hz, 1H), 6.29 (d, $J = 1.9$ Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.70 (t, $J = 7.7$ Hz, 1H), 3.69 (s, 3H), 3.69 (s, 3H), 3.11

(d, $J = 7.7$ Hz, 2H), 3.06 (dd, $J = 12.2, 5.4$ Hz, 1H), 2.85 (d, $J = 13.5$ Hz, 1H), 2.73 (m, 1H), 2.15 (td, $J = 13.4, 5.1$ Hz, 1H), 1.98 (d, $J = 12.8$ Hz, 1H), 1.79 (d, $J = 13.5$ Hz, 1H), 1.52 (qt, $J = 13.2, 3.3$ Hz, 1H), 1.14 (qt, $J = 13.1, 3.9$ Hz, 1H), 0.74 (qd, $J = 12.8, 3.2$ Hz, 1H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 169.4, 160.5, 155.9, 150.7, 146.7, 127.5, 125.8, 96.3, 94.6, 55.5, 55.1, 52.4, 52.3, 50.8, 48.4, 31.8, 28.1, 26.6, 25.4, 24.4; **IR** (Neat): ν_{max} 2925, 2852, 1734, 1603, 1588, 1481, 1433, 1327, 1272, 1202, 1139, 1036, 933, 827; **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{27}\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 375.1797, found 375.1802.

Dimethyl 2-((5,7-dimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydro-1H-fluoren-9-

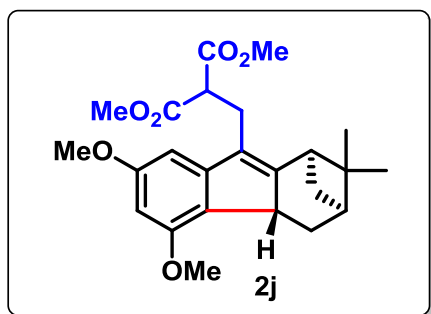


yl)methyl)malonate (2i): Compound **2i** was synthesized from **1i** by following the standard procedure. Yield: 109 mg, (97%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.44 (d, $J = 1.9$ Hz, 1H), 6.28 (d, $J = 1.9$ Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.72 (dd, $J = 9.1, 6.1$ Hz, 1H),

3.68 (s, 3H), 3.64 (s, 3H), 3.12 (dd, $J = 14.1, 6.1$ Hz, 1H), 2.51 (m, 1H), 1.85 (m, 1H), 1.60-1.52 (m, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.26 (s, 3H), 1.22 (m, 1H), 1.07 (td, $J = 13.1, 3.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.6, 169.5, 160.0, 159.7, 155.0, 145.1, 132.5, 127.9, 96.1, 95.4, 55.5, 55.1, 52.5, 52.2, 52.0, 51.8, 43.9, 36.9, 34.2, 33.0, 26.3, 26.1, 22.3, 18.9; **IR** (Neat):

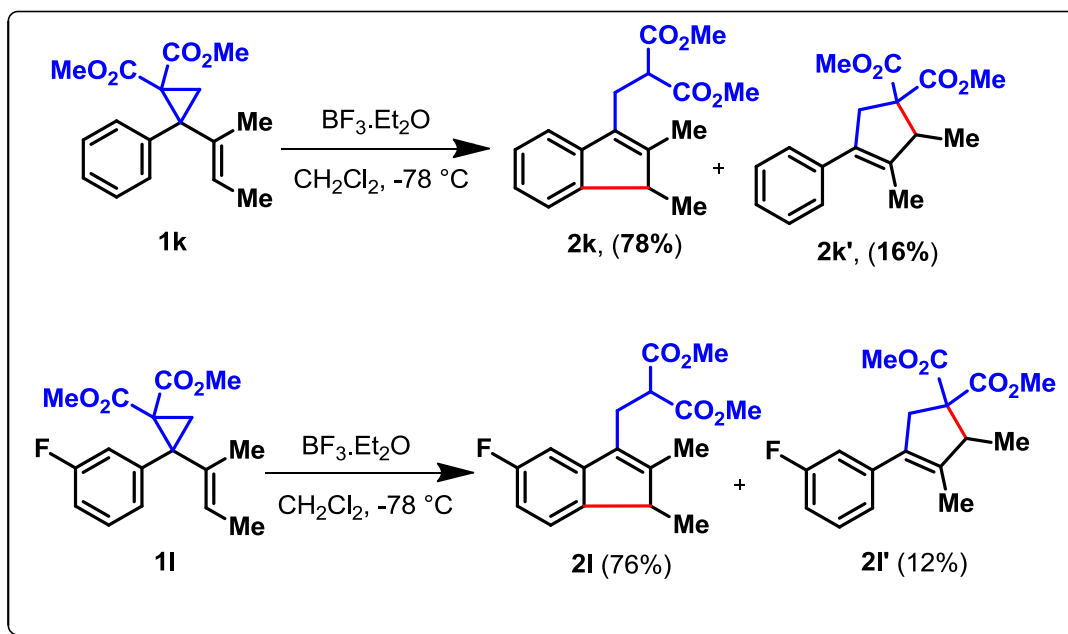
ν_{\max} 2923, 2851, 1753, 1737, 1601, 1484, 1463, 1436, 1346, 1251, 1201, 1150, 826; **HRMS** (ESI): calcd for $C_{24}H_{32}O_6Na$ ($M+Na$)⁺ 439.2078, found 439.2091.

Compound 2j: Compound **2j** was synthesized from **1j** by following the standard procedure.

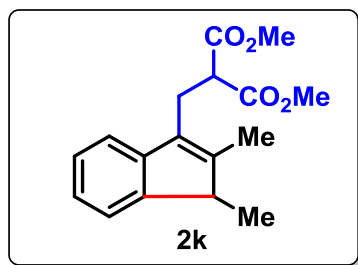


Yield: 165 mg, (95%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); $[\alpha]_D^{32} = +30.17$ ($c = 0.0175$, $CHCl_3$); (The data of 1H NMR and ^{13}C NMR is also given in Table S1) **1H NMR** (300 MHz, $CDCl_3$): δ 6.47 (d, $J = 1.9$ Hz, 1H), 6.29 (d, $J = 1.9$ Hz, 1H), 4.00 (t, $J = 8.8$ Hz, 1H), 3.84 (s, 3H),

3.83 (s, 3H), 3.81 (m, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.19 (t, $J = 5.5$ Hz, 1H), 3.07 (d, $J = 7.4$ Hz, 1H), 2.79-2.66 (m, 2H), 2.11 (m, 1H), 1.85 (m, 1H), 1.41 (s, 3H), 1.19 (s, 3H), 0.64 (d, $J = 9.3$ Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.5, 160.4, 158.0, 155.5, 147.9, 126.0, 125.6, 96.0, 94.4, 55.6, 55.2, 52.4, 52.3, 50.9, 46.2, 44.3, 42.4, 39.9, 39.6, 29.9, 28.3, 24.7, 23.7; **IR** (Neat): ν_{\max} 2934, 2839, 1736, 1603, 1587, 1459, 1435, 1323, 1277, 1203, 1147, 1044, 932, 827; **HRMS** (ESI): calcd for $C_{24}H_{30}O_6Na$ ($M+Na$)⁺ 437.1933, found 437.1934.



Dimethyl 2-((1,2-dimethyl-1*H*-inden-3-yl)methyl)malonate (2k): Compounds **2k** & **2k'** were



synthesized from the **1k** under the standard procedure. Yield: 78

mg, (78%); colorless oil; $R_f = 0.5$ (10% EtOAc/hexanes); ^1H

NMR (400 MHz, CDCl_3): δ 7.33 (d, $J = 7.3$ Hz, 1H), 7.27-7.18

(m, 2H), 7.14 (td, $J = 7.2, 1.4$ Hz, 1H), 3.72 (t, $J = 7.7$ Hz, 1H),

3.69 (s, 3H), 3.67 (s, 3H), 3.18 (q, $J = 7.5$ Hz, 1H), 3.14 (d, $J = 7.7$ Hz, 2H), 1.98 (s, 3H), 1.24

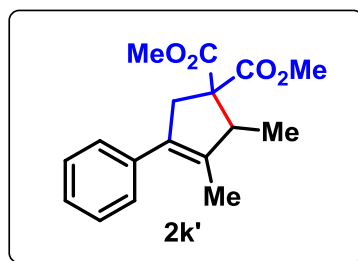
(d, $J = 7.5$ Hz, 3H); ^{13}C **NMR** (125 MHz, CDCl_3): δ 169.5, 169.4, 148.2, 146.7, 144.0, 131.0,

126.3, 124.0, 122.3, 117.8, 52.5, 52.4, 50.3, 47.1, 24.8, 15.8, 12.0; **IR** (Neat): ν_{max} 2954, 2923,

2852, 1736, 1604, 1590, 1481, 1456, 1435, 1339, 1273, 1236, 1143, 1121, 1063; **HRMS** (ESI):

calcd for $\text{C}_{17}\text{H}_{21}\text{O}_4$ ($\text{M}+\text{H}$) $^+$ 289.1432, found 289.1434.

Dimethyl 2,3-dimethyl-4-phenylcyclopent-3-ene-1,1-dicarboxylate (2k'):



Yield: 16 mg, (16%); colorless oil; $R_f = 0.6$ (10%

EtOAc/hexanes); ^1H **NMR** (400 MHz, CDCl_3): δ 7.29-7.12 (m,

5H), 3.67 (s, 3H), 3.66 (s, 3H), 3.59 (m, 1H), 3.46 (q, $J = 7.3$ Hz,

1H), 2.97 (dq, $J = 16.1, 1.1, 0.7$ Hz, 1H), 1.75 (s, 3H), 0.98 (d, J

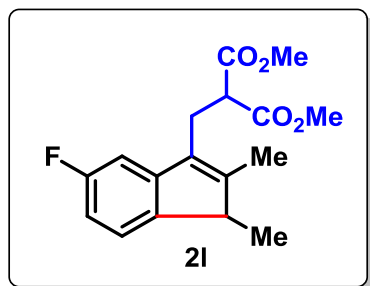
$= 7.3$ Hz, 3H); ^{13}C **NMR** (100 MHz, CDCl_3): δ 172.6, 170.9, 137.1, 136.8, 130.7, 128.0, 127.6,

126.5, 62.4, 52.7, 52.2, 49.9, 42.2, 13.8, 13.5; **IR** (Neat): ν_{max} 2952, 2922, 2852, 1733, 1599,

1494, 1459, 1434, 1377, 1250, 1198, 1161, 1059, 763, 700; **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{21}\text{O}_4$

($\text{M}+\text{H}$) $^+$ 289.1449, found 289.1445.

Dimethyl 2-((5-fluoro-1,2-dimethyl-1*H*-inden-3-yl)methyl)malonate (2l): Compounds **2l** &



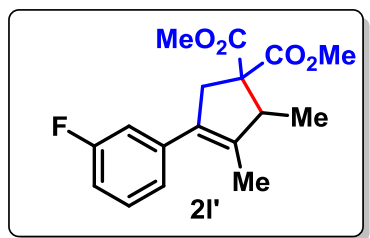
2l' were synthesized from **1l** by following the standard procedure.

Yield: 152 mg, (76%); colorless oil; R_f = 0.5 (10% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.23 (dd, J = 8.0, 5.1 Hz, 1H), 6.89 (dd, J = 9.4, 2.3 Hz, 1H), 6.81 (ddd, J = 9.4, 8.0, 2.3 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.67 (t, J = 7.8

Hz, 1H), 3.15 (q, J = 7.5 Hz, 1H), 3.10 (d, J = 7.8 Hz, 2H), 1.98 (s, 3H), 1.22 (d, J = 7.5 Hz, 3H);

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 169.4, 169.3, 162.4 (d, J = 241.5 Hz), 149.3, 146.0 (d, J = 8.1 Hz), 143.4, 130.7 (d, J = 2.7 Hz), 123.0 (d, J = 9.0 Hz), 110.3 (d, J = 22.7 Hz), 110.2 (d, J = 23.6 Hz), 52.6, 52.5, 50.3, 46.6, 24.7, 15.8, 12.3; **IR** (Neat): ν_{max} 2956, 2922, 2850, 1736, 1612, 1475, 1450, 1277, 1041, 888, 858, 618; **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{19}\text{O}_4\text{FNa}$ ($\text{M}+\text{Na}$) $^+$ 329.11748, found 329.11596.

Dimethyl 4-(3-fluorophenyl)-2,3-dimethylcyclopent-3-ene-1,1-dicarboxylate (2l'):

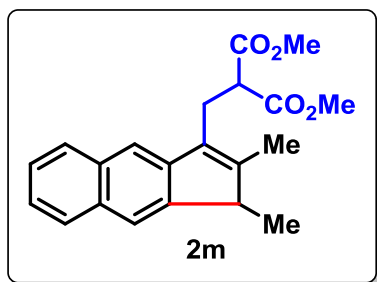


Yield: 24 mg, (12%); colorless oil; R_f = 0.6 (10% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.29 (dd, J = 6.2, 1.9 Hz, 1H), 7.05 (td, J = 7.8, 1.1 Hz, 1H), 6.97 (dt, J = 10.3, 1.5 Hz, 1H), 6.92 (dd, J = 8.5, 2.5 Hz, 1H), 3.75 (s, 3H), 3.74 (s,

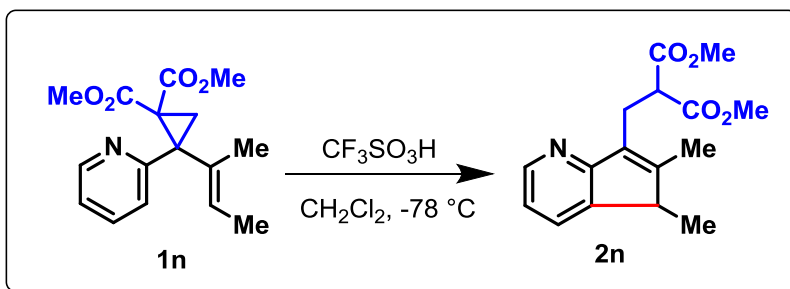
3H), 3.62 (m, 1H), 3.54 (q, J = 7.2 Hz, 1H), 3.02 (dq, J = 16.1, 1.8, 0.7 Hz, 1H), 1.83 (s, 3H),

1.05 (d, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.5, 170.7, 162.6 (d, J = 245.0 Hz), 139.3 (d, J = 7.3 Hz), 138.1, 129.8, 129.5 (d, J = 8.8 Hz), 123.3 (d, J = 2.2 Hz), 114.5 (d, J = 21.2 Hz), 113.4 (d, J = 21.2 Hz), 62.3, 52.7, 52.3, 49.9, 42.2, 13.8, 13.6; **IR** (Neat): ν_{max} 2953, 2919, 2850, 1732, 1611, 1580, 1486, 1434, 1247, 1201, 1160, 1099, 1057, 869, 828, 784, 696; **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{19}\text{O}_4\text{FNa}$ ($\text{M}+\text{Na}$) $^+$ 329.11745, found 329.11596.

Dimethyl 2-((1,2-dimethyl-1H-cyclopenta[b]naphthalen-3-yl)methyl)malonate (2m):



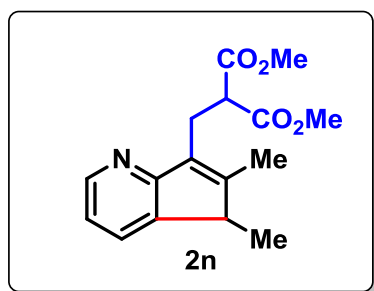
Compound **2m** was synthesized from **1m** by following the standard procedure. Yield: 144 mg, (96%); colorless oil; $R_f = 0.5$ (10% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.95 (d, $J = 8.2$ Hz, 1H), 7.88 (d, $J = 8.2$ Hz, 1H), 7.79 (d, $J = 8.3$ Hz, 1H), 7.49 (t, $J = 8.2$ Hz, 1H), 7.46 (d, $J = 8.2$ Hz, 1H), 7.38 (t, $J = 8.2$ Hz, 1H), 3.78 (t, $J = 7.9$ Hz, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.60 (q, $J = 7.4$ Hz, 1H), 3.26 (dd, $J = 14.1, 7.9$ Hz, 1H), 3.23 (dd, $J = 14.1, 7.9$ Hz, 1H), 2.09 (s, 3H), 1.42 (d, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.5, 169.4, 147.5, 143.6, 141.2, 131.5, 131.2, 129.2, 129.1, 127.3, 125.9, 123.9, 123.2, 117.9, 52.5, 52.4, 50.6, 46.8, 24.9, 17.4, 12.2; **IR** (Neat): ν_{max} 3052, 2929, 2852, 1745, 1586, 1516, 1492, 1331, 1275, 1231, 1201, 1037, 1022, 969, 921, 862, 852, 749; **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 361.1407, found 361.1410.



Modified procedure for the synthesis of 2n from 1n: Dienyl donor-acceptor cyclopropane 1,1-dicarboxylates (**1n**) (20 mg, 0.069 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (1 mL) under argon and cooled to -78 °C. To this, triflic acid (0.03 mL, 0.346 mmol, 5.0 equiv.) was added drop wise. The dark color reaction was stirred at -78 °C further 2-3h and brought to 0 °C over 1-2 hours. The reaction mixture was quenched with the saturated aqueous NaHCO_3 (1 mL) at 0 °C. The aqueous phase was extracted with EtOAc (10 mL) and the combined organic layers were washed with brine solution (2 mL), dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The

residue was purified by using flash column chromatography to afford the desired product as yellow oil.

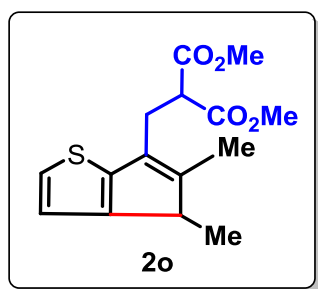
Dimethyl 2-((5,6-dimethyl-5*H*-cyclopenta[*b*]pyridin-7-yl)methyl)malonate (2n): Yield: (crude-15 mg, 78%); yellow oil; $R_f = 0.4$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ



8.38 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.54 (dd, $J = 7.4, 1.3$ Hz, 1H), 7.00 (dd, $J = 7.4, 5.0$ Hz, 1H), 4.22 (t, $J = 8.0$ Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.20 (d, $J = 8.0$ Hz, 2H), 3.17 (q, $J = 7.7$ Hz, 1H), 2.04 (s, 3H), 1.25 (d, $J = 7.7$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.5, 169.4, 149.1, 135.2, 128.3, 128.3, 119.8, 118.8,

114.0, 52.5, 52.4, 49.3, 44.7, 24.3, 18.8, 14.1; **IR** (Neat): ν_{max} 2953, 2923, 2852, 1736, 1584, 1434, 1340, 1277, 1236, 1201, 1153, 1042, 910, 792, 753; **HRMS** (ESI): calcd for $\text{C}_{16}\text{H}_{20}\text{O}_4\text{N}$ ($\text{M}+\text{H}$) $^+$ 290.1400, found 290.1386.

Dimethyl 2-((4,5-dimethyl-4*H*-cyclopenta[*b*]thiophen-6-yl)methyl)malonate (2o): Compound



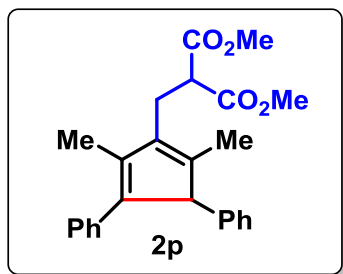
2o was synthesized from **1o** by following the standard procedure.

Yield: 116 mg, (89%); colorless oil; $R_f = 0.5$ (15% EtOAc/hexanes);

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.09 (d, $J = 4.7$ Hz, 1H), 6.97 (d, $J = 4.7$ Hz, 1H), 3.77 (t, $J = 7.7$ Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.08 (q, $J = 7.7$ Hz, 1H), 3.07 (d, $J = 7.7$ Hz, 2H), 1.96 (s, 3H), 1.21 (d, $J =$

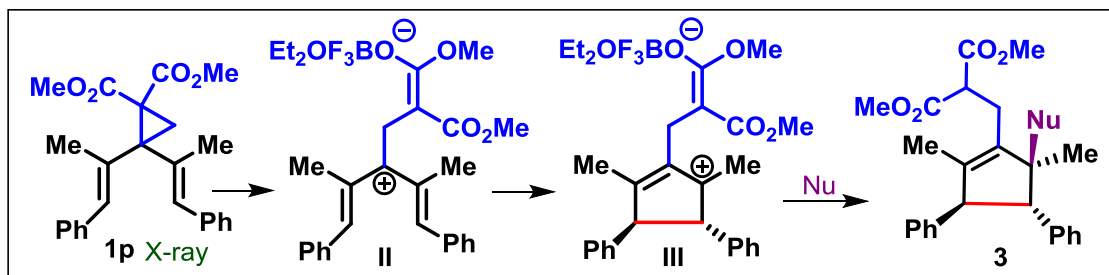
7.7 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.3, 169.2, 150.8, 147.0, 144.5, 128.5, 123.4, 121.3, 52.6, 52.5, 50.5, 44.8, 26.2, 15.3, 12.2; **IR** (Neat): ν_{max} 2955, 2923, 2852, 1736, 1606, 1500, 1435, 1265, 1231, 1199, 1152, 1030, 960, 836, 812; **HRMS** (ESI): calcd for $\text{C}_{15}\text{H}_{19}\text{O}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 295.1016, found 295.0998.

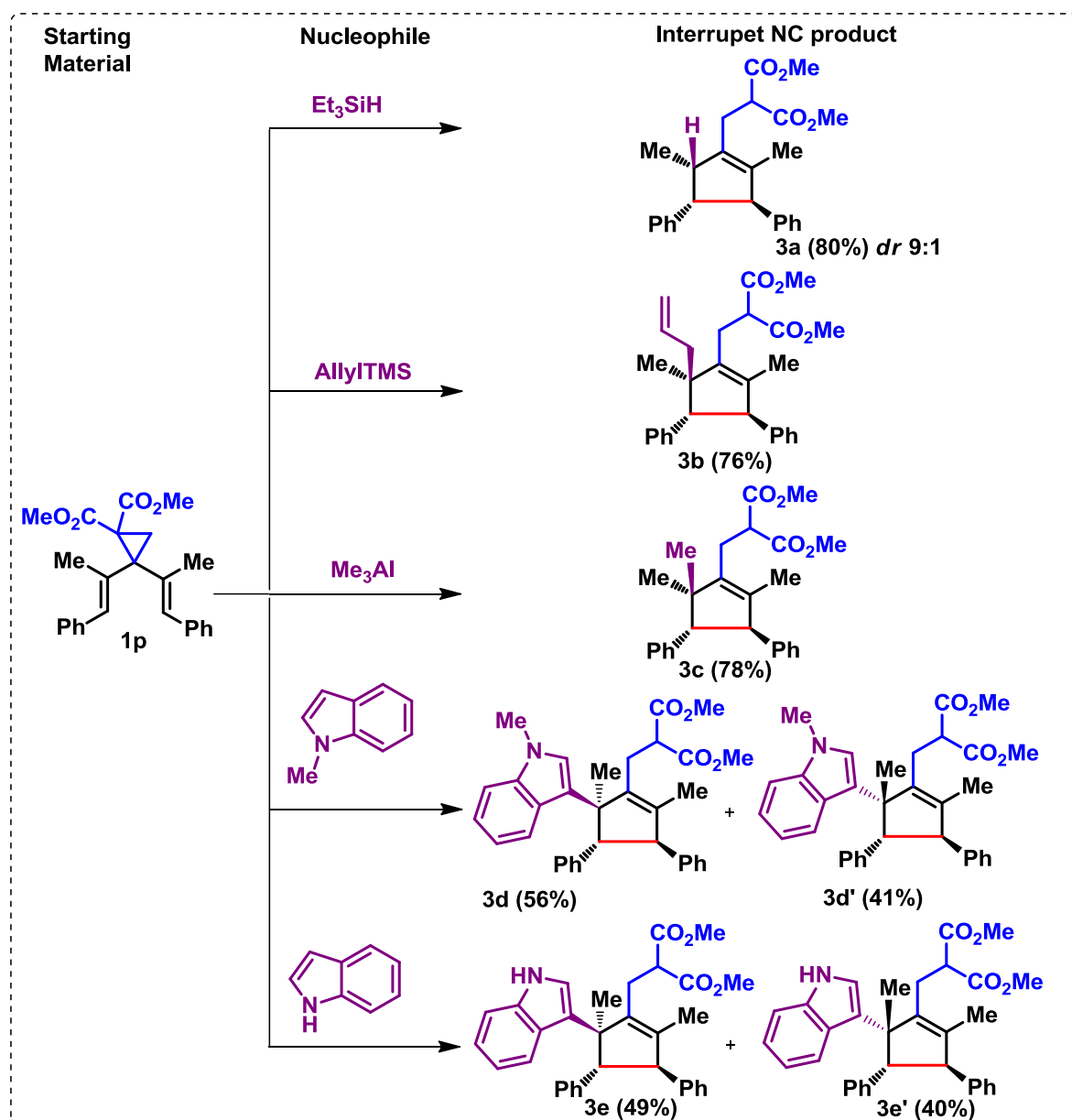
Dimethyl 2-((2,5-dimethyl-3,4-diphenylcyclopenta-1,4-dienyl)methyl)malonate (2p):



Compound **2p** was synthesized from **1p** by following the standard procedure. Yield: 112 mg, (94%); greenish oil; $R_f = 0.5$ (10% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.20 (t, $J = 7.9$ Hz, 2H), 7.17-7.12 (m, 4H), 7.09-7.04 (m, 2H), 6.91 (d, $J = 6.8$ Hz, 2H), 4.23 (s, 1H), 3.77 (s, 3H), 3.66 (dd, $J = 9.4, 6.5$ Hz, 1H), 3.64 (s, 3H), 3.07 (dd, $J = 14.1, 9.4$ Hz, 1H), 2.92 (dd, $J = 14.1, 6.5$ Hz, 1H), 2.13 (d, $J = 1.6$ Hz, 3H), 1.72 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.3, 144.9, 143.4, 138.8, 137.6, 136.4, 135.8, 128.3, 128.2, 128.0, 127.8, 126.1, 125.6, 62.8, 52.6, 52.5, 51.2, 25.3, 12.8, 12.3; **IR** (Neat): ν_{max} 2953, 2921, 2851, 1735, 1599, 1493, 1436, 1244, 1221, 1155, 1075, 1028, 771, 700; **HRMS** (ESI): calcd for $\text{C}_{25}\text{H}_{26}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 413.1715, found 413.1723.

5. Interrupted Nazarov cyclization of dienyl Donor -Acceptor Cyclopropanes



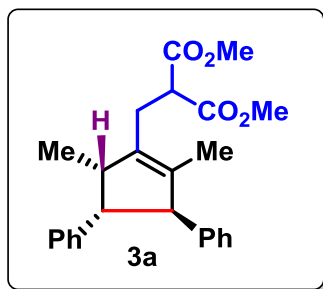


Standard Procedure for interrupted Nazarov cyclization:^[12]

Dimethyl 2,2-bis((*E*)-1-phenylprop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (**1p**) (1.025 mmol, 1 equiv) and nucleophile (Nu) (2.051 mmol, 2 equiv) were dissolved in CH_2Cl_2 (10 mL) under argon. Then, the reaction mixture was cooled to -78°C (acetone/dry ice bath) and added $\text{BF}_3\cdot\text{Et}_2\text{O}$ (1.127 mmol, 1.1 equiv) drop wise. The orange color reaction mixture was stirred at the same temperature for 2-3h and was quenched with saturated aqueous NaHCO_3 (5 mL). The

aqueous layer was extracted with EtOAc (50 mL), the combined organic layers were washed with brine solution (8 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed by rotary evaporation providing a crude residue that was purified by using silica gel column chromatography to provide the desired product.

(±)-Dimethyl 2-(((3*S*,4*S*,5*R*)-2,5-dimethyl-3,4-diphenylcyclopent-1-enyl)methyl)malonate (3a): (*dr* 9:1)



Yield: 80 mg, (80%); colorless oil; R_f = 0.6 (10% EtOAc/hexanes);

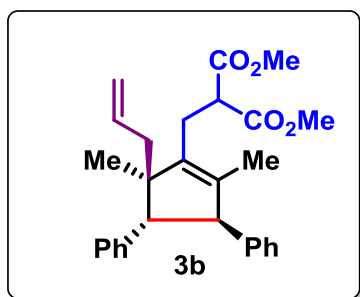
¹H NMR (400 MHz, CDCl₃): δ 7.20-7.13 (m, 4H), 7.12-7.06 (m, 2H), 7.04-6.98 (m, 2H), 6.93-6.88 (m, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 3.58 (d, J = 7.7 Hz, 1H), 3.52 (dd, J = 9.7, 6.3 Hz, 1H), 2.89 (dd, J = 13.9, 9.7 Hz, 1H), 2.75 (m, 1H), 2.65 (dd, J = 13.9, 6.3 Hz,

1H), 2.56 (t, J = 7.7 Hz, 1H), 1.39 (s, 3H), 1.03 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 169.6, 169.4, 144.4, 144.1, 136.0, 135.4, 128.3, 128.2, 128.0, 127.6, 126.2, 126.1, 64.4, 63.0, 52.6, 52.4, 50.0, 48.8, 26.2, 18.8, 12.8; IR (Neat): ν_{max} 3371, 2956, 2927, 2866, 1754, 1737, 1493, 1461, 1441, 1361, 1119, 1073, 1053, 1029, 971, 945, 884, 771, 701; HRMS (ESI): calcd for C₂₅H₂₈O₄Na (M+Na)⁺ 415.1871, found 415.1880.

(±)-Dimethyl

2-(((3*S*,4*S*,5*S*)-5-allyl-2,5-dimethyl-3,4-diphenylcyclopent-1-

enyl)methyl)malonate (3b): Compound **3b** was synthesized from

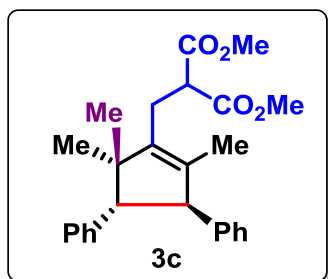


1p by following the standard procedure. Yield: 255 mg, (76%); colorless oil; R_f = 0.6 (10% EtOAc/hexanes); ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.02 (m, 10H), 5.46 (m, 1H), 4.92-4.80 (m, 2H), 4.07 (d, J = 10.5 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.68

(dd, J = 10.0, 6.1 Hz, 1H), 3.05 (d, J = 10.5 Hz, 1H), 2.97 (dd, J = 14.3, 10.0 Hz, 1H), 2.57 (dd, J

= 14.3, 6.1 Hz, 1H), 1.92 (dd, J = 14.0, 8.1 Hz, 1H), 1.75 (dd, J = 14.0, 6.4 Hz, 1H), 1.45 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.6, 169.5, 143.3, 138.3, 138.1, 137.9, 135.6, 129.5, 128.3, 128.1, 127.8, 126.4, 126.1, 116.7, 66.4, 57.1, 53.0, 52.5, 52.4, 51.6, 41.4, 26.1, 24.8, 13.4; **IR** (Neat): ν_{max} 2953, 2923, 2853, 1736, 1495, 1452, 1435, 1288, 1239, 1198, 1152, 1042, 913, 767, 701, 615; **HRMS** (ESI): calcd for $\text{C}_{28}\text{H}_{32}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 455.2184, found 455.2193.

(±)-Dimethyl 2-(((3*S*,4*S*)-2,5,5-trimethyl-3,4-diphenylcyclopent-1-enyl)methyl)malonate

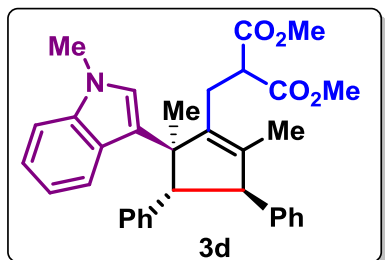


(3c): Compound **3c** was synthesized from **1p** by following the standard procedure. Yield: 81 mg, (78%); colorless oil; R_f = 0.6 (10% EtOAc/hexanes); ^1H NMR (500 MHz, CDCl_3): δ 7.22-6.93 (m, 10H), 3.93 (d, J = 10.1 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.62

(dd, J = 9.9, 6.2 Hz, 1H), 2.89 (d, J = 10.1 Hz, 1H), 2.87 (dd, J = 14.1, 9.9 Hz, 1H), 2.54 (dd, J = 14.1, 6.2 Hz, 1H), 1.36 (s, 3H), 1.07 (s, 3H), 0.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 169.5, 143.3, 139.3, 139.0, 136.4, 129.4, 128.2, 128.1, 127.7, 126.3, 126.1, 66.2, 57.6, 52.5, 52.4, 51.5, 49.5, 26.5, 25.3, 23.1, 13.3; **IR** (Neat): ν_{max} 3026, 2953, 2922, 2852, 1735, 1494, 1435, 1344, 1239, 1226, 1152, 1071, 1051, 768, 701, 601; **HRMS** (ESI): calcd for $\text{C}_{26}\text{H}_{30}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 429.2024, found 429.2036.

Compounds **3d** & **3d'** were synthesized from **1p** by following the standard procedure.

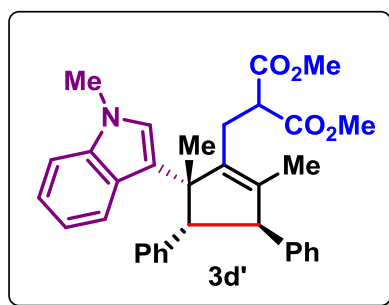
(±)-Dimethyl 2-(((3*S*,4*S*,5*S*)-2,5-dimethyl-5-(1-methyl-1*H*-indol-3-yl)-3,4-diphenylcyclopent-1-enyl)methyl)malonate (3d**): Bottom (Major)-**



Yield: 74 mg, (56%); colorless oil; R_f = 0.5 (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 7.9 Hz, 1H), 7.36-7.09 (m,

8H), 7.07-7.02 (m, 3H), 6.77 (m, 2H), 6.58 (s, 1H), 4.28 (d, $J = 11.0$ Hz, 1H), 4.05 (d, $J = 11.0$ Hz, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 3.37 (dt, $J = 8.1, 7.2$ Hz, 1H), 2.80 (dd, $J = 14.4, 8.1$ Hz, 1H), 2.50 (dd, $J = 14.4, 7.2$ Hz, 1H), 1.63 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 169.7, 169.6, 142.8, 139.0, 138.5, 138.0, 137.4, 128.9, 128.6, 128.3, 127.7, 127.2, 126.5, 126.2, 126.0, 121.3, 120.8, 119.2, 118.7, 109.4, 63.9, 55.6, 53.1, 52.3, 50.6, 32.7, 26.4, 20.8, 13.5; **IR** (Neat): ν_{max} 2956, 2920, 2851, 1736, 1462, 1370, 1221, 1156, 1040, 772, 743, 701; **HRMS** (ESI): calcd for $\text{C}_{34}\text{H}_{35}\text{O}_4\text{NNa}$ ($\text{M}+\text{Na}$) $^+$ 544.2449, found 544.2458.

(±)-Dimethyl 2-(((3*S*,4*S*,5*R*)-2,5-dimethyl-5-(1-methyl-1*H*-indol-3-yl)-3,4-diphenylcyclopent-1-enyl)methyl)malonate (3d'): Top (minor)

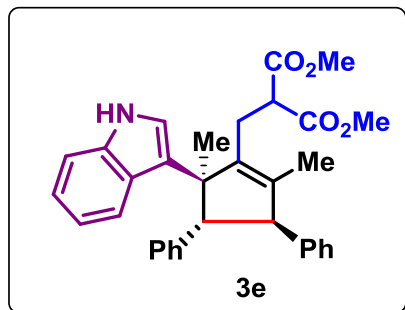


Yield: 55 mg, (41%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.21-7.07 (m, 6H), 7.04-6.99 (m, 2H), 6.93-6.86 (m, 2H), 6.81 (t, $J = 7.7$ Hz, 2H), 6.57 (d, $J = 7.7$ Hz, 2H), 6.28 (brs, 1H), 4.01 (d, $J = 10.3$ Hz, 1H), 3.74 (s, 3H), 3.72 (dd, $J = 9.2, 6.4$ Hz, 1H), 3.62 (s,

3H), 3.59 (s, 3H), 3.21 (d, $J = 10.3$ Hz, 1H), 3.03 (dd, $J = 14.1, 9.2$ Hz, 1H), 2.66 (dd, $J = 14.1, 6.4$ Hz, 1H), 1.70 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 169.8, 169.4, 143.4, 139.1, 138.9, 138.0, 137.3, 129.2, 128.2, 128.1, 127.8, 127.6, 126.9, 126.0, 125.8, 120.7, 120.5, 118.7, 116.7, 108.8, 68.5, 59.5, 55.0, 52.4, 52.3, 51.0, 32.5, 26.5, 13.5; **IR** (Neat): ν_{max} 2954, 2923, 2852, 1735, 1491, 1452, 1435, 1360, 1330, 1273, 1241, 1221, 1155, 740, 663; **HRMS** (ESI): calcd for $\text{C}_{34}\text{H}_{35}\text{O}_4\text{NNa}$ ($\text{M}+\text{Na}$) $^+$ 544.2455, found 544.2458.

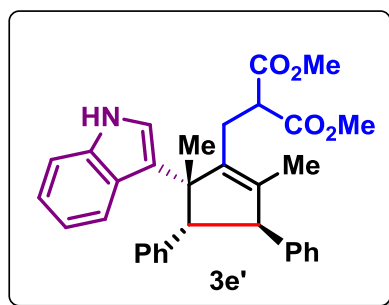
Compounds **3e** & **3e'** were synthesized from **1p** by following the standard procedure.

(±)-Dimethyl 2-(((3*S*,4*S*,5*S*)-5-(1*H*-indol-3-yl)-2,5-dimethyl-3,4-diphenylcyclopent-1-enyl)methyl)malonate (**3e**): Bottom (Major)



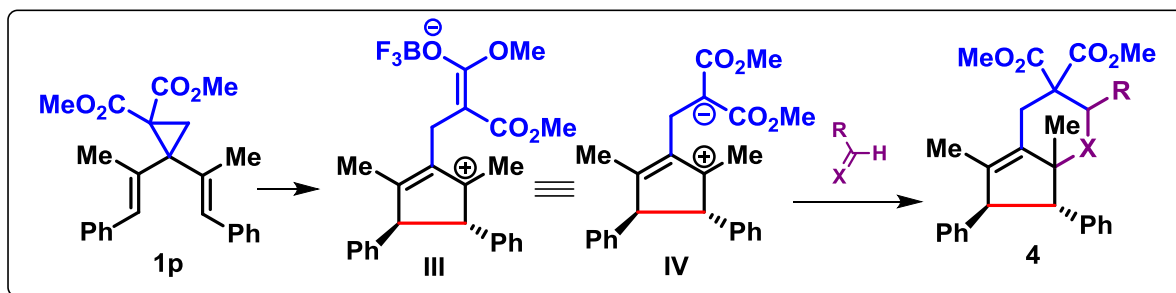
Yield: 63 mg, (49%); brownish oil; $R_f = 0.5$ (20% EtOAc/hexanes); (The data of ^1H NMR and ^{13}C NMR has been given in Table S2); IR (Neat): ν_{\max} 3389, 2953, 2923, 2852, 1735, 1494, 1452, 1435, 1344, 1275, 1218, 1153, 1044, 772, 744, 700; HRMS (ESI): calcd for $\text{C}_{33}\text{H}_{33}\text{O}_4\text{NNa}$ ($\text{M}+\text{Na}$) $^+$ 530.2294, found 530.2302.

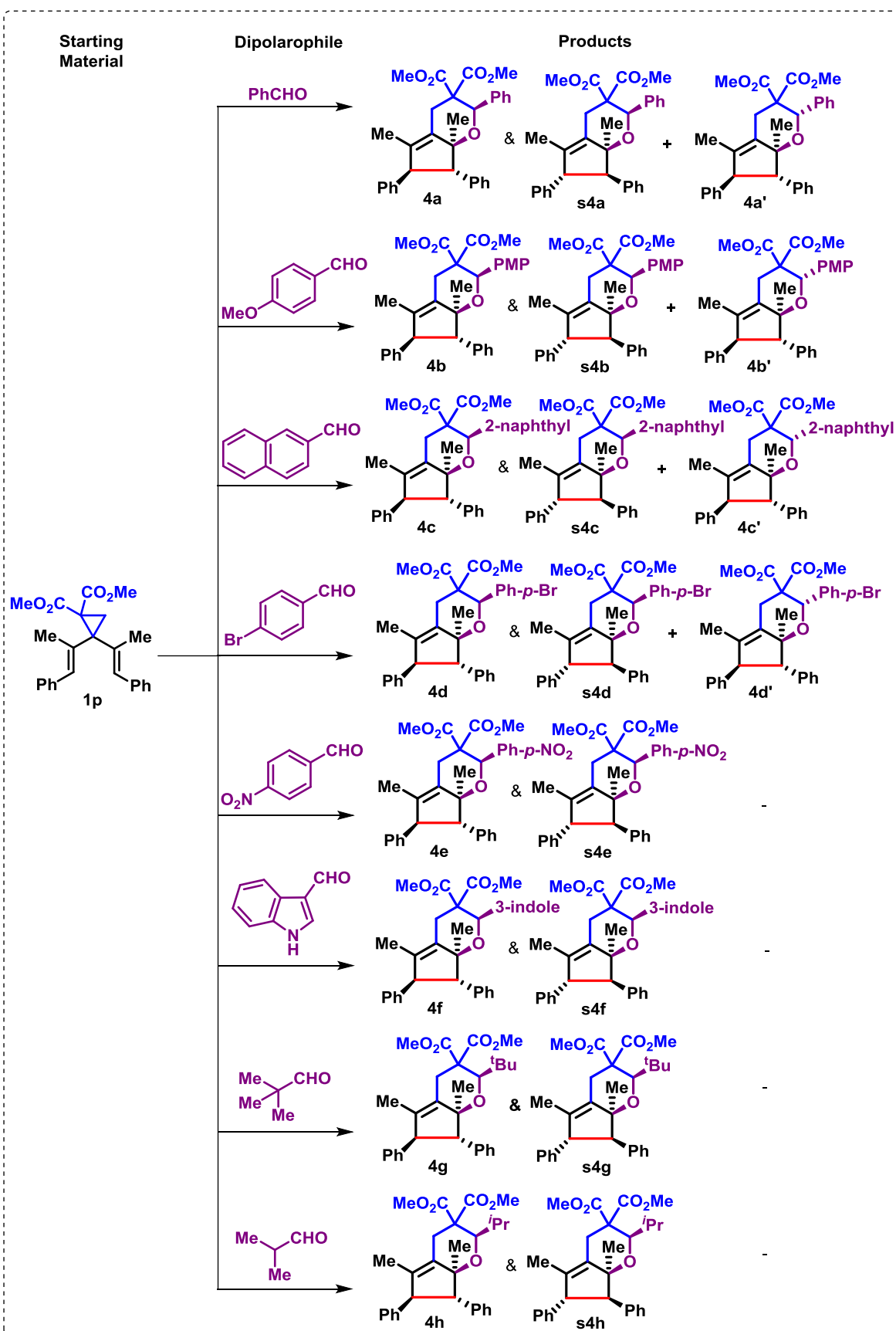
(±)-Dimethyl 2-(((3*S*,4*S*,5*R*)-5-(1*H*-indol-3-yl)-2,5-dimethyl-3,4-diphenylcyclopent-1-enyl)methyl)malonate (**3e'**): Top (Minor)




Yield: 51 mg, (40%); brownish oil; $R_f = 0.5$ (20% EtOAc/hexanes); (The data of ^1H NMR and ^{13}C NMR has been given in Table S3); IR (Neat): ν_{\max} 3410, 3026, 2953, 2923, 2852, 1734, 1452, 1435, 1335, 1275, 1239, 1218, 1153, 1042, 770, 700; HRMS (ESI): calcd for $\text{C}_{33}\text{H}_{33}\text{O}_4\text{NNa}$ ($\text{M}+\text{Na}$) $^+$ 530.2298, found 530.2302.

6. Nazarov Cyclization Followed by [4+2]-Cycloaddition from dienyl Donor-Acceptor Cyclopropanes (DACs)





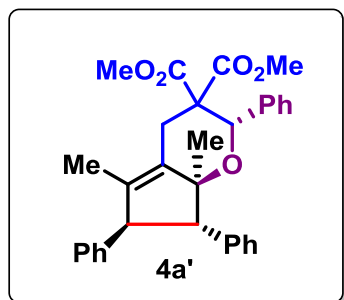
Dimethyl 2,2-bis((*E*)-1-phenylprop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (**1p**) (500 mg, 1.282 mmol, 1 equiv) and benzaldehyde (0.52 mL, 5.128 mmol, 4 equiv) were dissolved in CH₂Cl₂ (13 mL) under argon and cooled to -78 °C (acetone/dry ice bath). BF₃.Et₂O (0.24 mL, 1.923 mmol, 1.5 equiv) was added dropwise. The reaction mixture was stirred at the same temperature for 1-2h, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was quenched with saturated aqueous NaHCO₃ (4 mL). The aqueous layer was extracted with EtOAc (60 mL), the combined organic layers were washed with brine solution (8 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed by rotary evaporation to provide a crude residue that was purified by using silica gel column chromatography to furnish the separable isomers **4a** & **4a'**.



4a

519.2142.

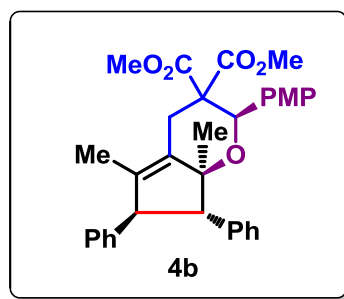
(±)- (2*S*,6*S*,7*S*,7*aS*)-dimethyl 5,7*a*-dimethyl-2,6,7-triphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (**4a'**):



Top (minor): 4a' Yield: 76 mg, (12%); white foam; R_f = 0.6 (10% EtOAc/hexanes); (The data of ^1H NMR and ^{13}C NMR has been given in **Table S6**); **IR** (Neat): ν_{\max} 3027, 2951, 2923, 2852, 1727, 1494, 1453, 1433, 1264, 1199, 1175, 1082, 1042, 772, 752, 699; **HRMS** (ESI): calcd for $\text{C}_{32}\text{H}_{36}\text{NO}_5$ ($\text{M}+\text{NH}_4$)⁺ 514.2603, found 514.2601.

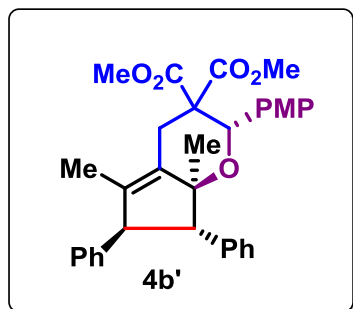
Compounds **4b** & **4b'** were synthesized from **1p** by following standard procedure.

(±)- (2*R*,6*S*,7*S*,7*aR*)-dimethyl 2-(4-methoxyphenyl)-5,7*a*-dimethyl-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (**4b**):



Bottom (major): Yield: 276 mg, (82%); colorless oil; R_f = 0.5 (20% EtOAc/hexanes); ^1H NMR (500 MHz, CDCl_3): δ 7.48 (d, J = 8.8 Hz, 2H), 7.35-7.08 (m, 10H), 6.88 (d, J = 8.8 Hz, 2H), 5.28 (s, 1H), 4.08 (d, J = 10.0 Hz, 1H), 3.82 (s, 3H), 3.77 (d, J = 10.0 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.31 (d, J = 13.8 Hz, 1H), 2.96 (d, J = 13.8 Hz, 1H), 1.44 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 170.8, 168.4, 158.8, 141.9, 138.1, 134.5, 132.6, 131.2, 129.3, 128.9, 128.6, 128.3, 127.8, 126.4, 126.3, 112.5, 86.3, 76.5, 65.1, 61.5, 55.1, 54.8, 52.5, 51.6, 31.4, 17.1, 11.8; **IR** (Neat): ν_{\max} 3026, 2951, 2922, 2852, 1727, 1513, 1456, 1435, 1249, 1175, 1068, 1040, 753, 700, 606; **HRMS** (ESI): calcd for $\text{C}_{33}\text{H}_{34}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$)⁺ 549.2235, found 549.2248.

(±)- (2*S*,6*S*,7*S*,7*aR*)-dimethyl 2-(4-methoxyphenyl)-5,7*a*-dimethyl-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (**4b'**):

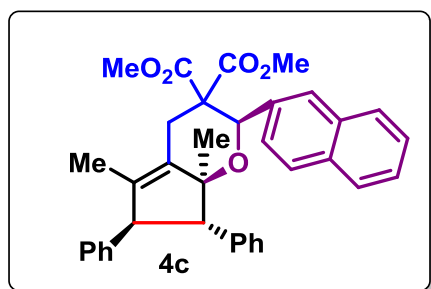


Top (minor): Yield: 49 mg, (14%); colorless oil; $R_f = 0.6$ (20% EtOAc/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.46 (d, $J = 8.7$ Hz, 2H), 7.33-7.27 (m, 4H), 7.23-7.08 (m, 6H), 6.85 (d, $J = 8.7$ Hz, 2H), 5.82 (s, 1H), 4.08 (d, $J = 10.2$ Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.77 (d, $J = 10.2$ Hz, 1H), 3.34 (dq, $J = 14.0, 1.1$ Hz, 1H),

3.21 (s, 3H), 3.01 (d, $J = 14.0$ Hz, 1H), 1.42 (s, 3H), 0.98 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 172.0, 169.9, 158.8, 141.8, 138.2, 134.9, 134.5, 131.2, 128.7, 128.6, 128.5, 128.4, 127.8, 126.5, 126.2, 112.8, 88.2, 73.4, 63.9, 60.2, 55.2, 54.5, 52.6, 52.1, 28.3, 20.4, 12.2; **IR** (Neat): ν_{max} 2952, 2920, 2851, 1736, 1460, 1256, 1220, 1158, 1075, 772, 699, 672; **HRMS** (ESI): calcd for $\text{C}_{33}\text{H}_{38}\text{NO}_6$ ($\text{M}+\text{NH}_4$)⁺ 544.2699, found 544.2695.

Compounds **4c** & **4c'** were synthesized from **1p** by following the standard procedure.

(±)- (2*R*,6*S*,7*S*,7*aR*)-dimethyl 5,7*a*-dimethyl-2-(naphthalen-2-yl)-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (**4c**):



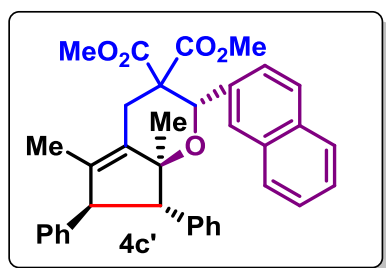
Bottom (major): Yield: 225 mg, (80%); colorless oil; $R_f = 0.5$ (10% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.84 (s, 1H), 7.80-7.68 (m, 3H), 7.40-7.26 (m, 4H), 7.25-7.00 (m, 9H), 5.43 (s, 1H), 4.02 (d, $J = 10.0$ Hz, 1H), 3.76 (d, $J = 10.0$ Hz, 1H), 3.56 (s, 3H), 3.54 (s, 3H), 3.28 (d, $J =$

13.9 Hz, 1H), 2.95 (d, $J = 13.9$ Hz, 1H), 1.38 (s, 3H), 0.99 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.8, 168.3, 141.9, 138.1, 136.7, 134.7, 132.9, 132.6, 132.5, 128.8, 128.6, 128.4,

128.0, 127.9, 127.5, 126.6, 126.5, 126.4, 126.3, 126.1, 125.7, 125.6, 86.4, 65.1, 61.7, 54.8, 52.5, 51.6, 31.4, 17.2, 11.9; **IR** (Neat): ν_{\max} 2951, 2853, 1728, 1601, 1451, 1434, 1372, 1254, 1069, 769, 751, 700; **HRMS** (ESI): calcd for $C_{36}H_{34}O_5Na$ ($M+Na$)⁺ 569.2290, found 569.2298.

(±)- (2*S*,6*S*,7*S*,7*aR*)-dimethyl 5,7*a*-dimethyl-2-(naphthalen-2-yl)-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (**4c'**):

Top (minor): Yield: 45 mg, (16%); colorless oil; R_f = 0.6 (10% EtOAc/hexanes); **¹H NMR** (400

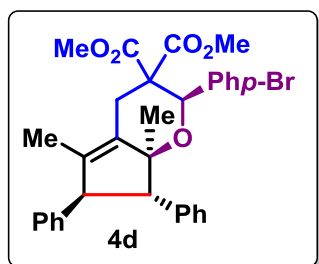


MHz, CDCl₃): δ 8.02 (s, 1H), 7.92-7.74 (m, 3H), 7.66 (dd, J = 8.5, 1.3 Hz, 1H), 7.50-7.42 (m, 2H), 7.32 (d, J = 4.4 Hz, 4H), 7.22-7.06 (m, 6H), 6.03 (s, 1H), 4.11 (d, J = 10.1 Hz, 1H), 3.83 (d, J = 10.1 Hz, 1H), 3.80 (s, 3H), 3.43 (d, J = 14.0 Hz, 1H),

3.04 (d, J = 14.0 Hz, 1H), 3.00 (s, 3H), 1.45 (s, 3H), 1.05 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.9, 141.8, 138.1, 136.6, 134.9, 134.8, 132.9, 128.7, 128.6, 128.5, 128.2, 127.8, 127.5, 126.8, 126.5, 126.3, 126.2, 125.8, 125.7, 125.5, 125.5, 88.3, 73.9, 63.9, 60.3, 54.5, 52.6, 51.9, 28.5, 20.4, 12.2; **IR** (Neat): ν_{\max} 2950, 2924, 2853, 1726, 1615, 1495, 1451, 1433, 1267, 1220, 1195, 1080, 1042, 905, 773, 750, 700; **HRMS** (ESI): calcd for $C_{36}H_{34}O_5Na$ ($M+Na$)⁺ 569.2286, found 569.2298.

Compounds **4d** & **4d'** were synthesized from **1p** by following standard procedure.

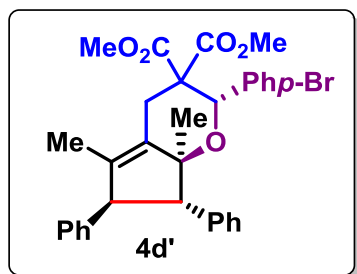
(±)- (2*R*,6*S*,7*S*,7*aR*)-dimethyl 2-(4-bromophenyl)-5,7*a*-dimethyl-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (**4d**):



Bottom (major): Yield: 237 mg, (80%); colorless oil; R_f = 0.5 (15% EtOAc/hexanes); **¹H NMR** (500 MHz, CDCl₃): δ 7.40-7.32 (m, 4H),

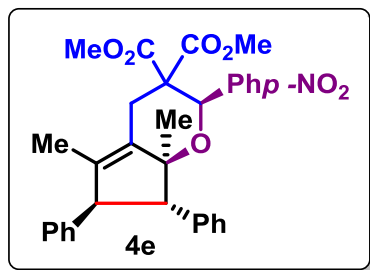
7.28 (d, $J = 7.4$ Hz, 2H), 7.22-7.17 (m, 2H), 7.17-7.12 (m, 4H), 7.12-7.04 (m, 2H), 5.20 (s, 1H), 4.00 (d, $J = 9.9$ Hz, 1H), 3.66 (d, $J = 9.9$ Hz, 1H), 3.59 (s, 3H), 3.59 (s, 3H), 3.24 (d, $J = 13.8$ Hz, 1H), 2.86 (qd, $J = 13.8, 1.8$ Hz, 1H), 1.36 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.6, 168.2, 141.7, 138.2, 137.9, 134.8, 132.2, 130.2, 129.5, 128.8, 128.5, 128.4, 127.9, 126.5, 126.4, 121.5, 86.4, 76.2, 65.1, 61.3, 54.8, 52.5, 51.6, 31.3, 17.1, 11.8; **IR** (Neat): ν_{max} 3027, 2950, 2923, 2853, 1729, 1488, 1452, 1433, 1255, 1222, 1069, 1044, 1010, 795, 758, 700; **HRMS** (ESI): calcd for $\text{C}_{32}\text{H}_{31}\text{O}_5\text{BrNa}$ ($\text{M}+\text{Na}$) $^+$ 597.1240, found 597.1247.

(±)- (2*S*,6*S*,7*S*,7*aR*)-Dimethyl 2-(4-bromophenyl)-5,7*a*-dimethyl-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (4*d'*):



Top (minor): Yield: 44 mg, (14%); colorless oil; $R_f = 0.6$ (15% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.48-7.40 (m, 4H), 7.36-7.24 (m, 5H), 7.22-7.06 (m, 5H), 5.81 (s, 1H), 4.08 (d, $J = 10.0$ Hz, 1H), 3.79 (s, 3H), 3.74 (d, $J = 10.0$ Hz, 1H), 3.34 (d, $J = 14.1$ Hz, 1H), 3.21 (s, 3H), 3.01 (d, $J = 14.1$ Hz, 1H), 1.43 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 169.6, 141.7, 138.1, 138.0, 135.0, 134.5, 130.6, 129.1, 128.5, 127.8, 126.6, 126.3, 121.5, 88.3, 73.1, 63.7, 60.3, 54.2, 52.7, 52.1, 28.4, 20.3, 12.2; **IR** (Neat): ν_{max} 2950, 2924, 2853, 1727, 1488, 1451, 1433, 1270, 1237, 1221, 1198, 1072, 1011, 925, 840, 754, 699; **HRMS** (ESI): calcd for $\text{C}_{32}\text{H}_{31}\text{O}_5\text{BrNa}$ ($\text{M}+\text{Na}$) $^+$ 597.1240, found 597.1243.

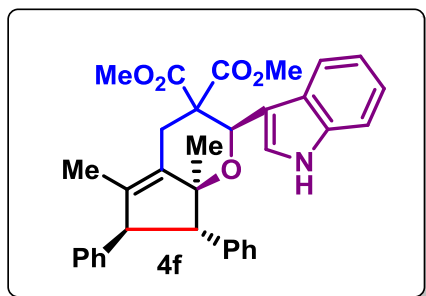
(±)- (2*R*,6*S*,7*S*,7*aR*)-Dimethyl 5,7*a*-dimethyl-2-(4-nitrophenyl)-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (4*e*):



Compound **4e** was synthesized from **1p** by following standard procedure. Yield: 255 mg, (92%); Recrystallization from EtOH

yielded in a crystalline form; m.p. 180-182 °C; R_f = 0.5 (15% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.20 (d, J = 8.9 Hz, 2H), 7.72 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 7.4 Hz, 2H), 7.32-7.08 (m, 8H), 5.42 (s, 1H), 4.10 (d, J = 9.9 Hz, 1H), 3.76 (d, J = 9.9 Hz, 1H), 3.70 (s, 3H), 3.67 (s, 3H), 3.37 (d, J = 13.9 Hz, 1H), 2.97 (qd, J = 13.9, 1.8 Hz, 1H), 1.47 (s, 3H), 1.05 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.5, 168.0, 147.2, 146.7, 141.6, 137.7, 135.4, 131.7, 128.8, 128.7, 128.5, 128.4, 128.0, 126.6, 126.5, 122.3, 86.7, 75.9, 65.2, 61.4, 54.9, 52.8, 51.8, 31.3, 17.1, 11.9; **IR** (Neat): ν_{max} 2952, 2923, 2853, 1729, 1602, 1519, 1494, 1452, 1433, 1346, 1255, 1222, 1068, 1045, 855, 757, 697, 606; calcd for $\text{C}_{32}\text{H}_{32}\text{NO}_7$ ($\text{M}+\text{H}$) $^+$ 542.2181, found 542.2176.

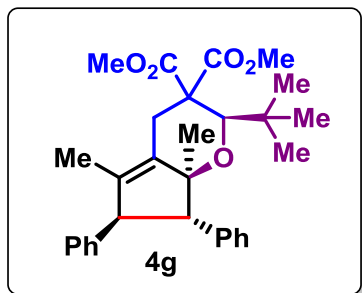
(±)- (2*R*,6*S*,7*S*,7*aS*)-dimethyl 2-(1*H*-indol-3-yl)-5,7*a*-dimethyl-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate



(**4f**): Compound **4f** was synthesized from **1p** by following standard procedure. Yield: 240 mg, (88%); R_f = 0.4 (20% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.07 (s, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.32-

7.16 (m, 7H), 7.13-6.98 (m, 6H), 5.60 (s, 1H), 4.01 (qd, J = 9.9, 1.3 Hz, 1H), 3.72 (d, J = 9.9 Hz, 1H), 3.54 (s, 3H), 3.38 (s, 3H), 3.28 (d, J = 14.0 Hz, 1H), 2.92 (qd, J = 14.0, 1.7 Hz, 1H), 1.38 (s, 3H), 1.03 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 170.8, 168.8, 142.1, 138.2, 135.4, 134.4, 132.8, 128.9, 128.6, 128.4, 127.8, 126.8, 126.4, 126.2, 124.6, 121.5, 120.0, 119.4, 113.8, 110.9, 86.3, 72.2, 65.1, 60.8, 54.9, 52.5, 51.7, 31.5, 17.2, 11.8; **IR** (Neat): ν_{max} 3391, 3026, 2951, 2924, 2853, 1727, 1601, 1495, 1454, 1433, 1258, 1222, 1067, 1037, 757, 701; **HRMS** (ESI): calcd for $\text{C}_{34}\text{H}_{33}\text{NNaO}_5$ ($\text{M}+\text{Na}$) $^+$ 558.2256, found 558.2262.

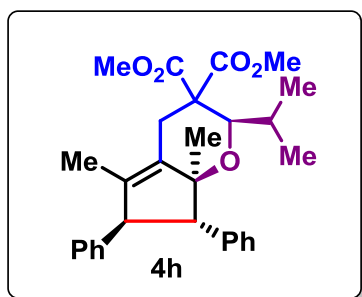
(±)- (2*R*,6*S*,7*S*,7*aS*)-dimethyl 2-*tert*-butyl-5,7*a*-dimethyl-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (4*g*):



Compound **4g** was synthesized from **1p** by following standard procedure. Yield: 115 mg, (94%); colorless oil; $R_f = 0.5$ (10% EtOAc/hexanes); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.36 (d, $J = 7.5$ Hz, 2H), 7.31-7.20 (m, 6H), 7.19-7.12 (m, 2H), 4.47 (s, 1H), 4.04

(d, $J = 9.4$ Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.64 (d, $J = 9.4$ Hz, 1H), 3.39 (d, $J = 14.1$ Hz, 1H), 2.70 (d, $J = 14.1$ Hz, 1H), 1.37 (s, 3H), 1.05 (s, 9H), 0.99 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.2, 171.3, 142.4, 138.6, 134.5, 134.2, 128.8, 128.5, 128.4, 127.8, 126.4, 126.2, 88.8, 80.0, 61.1, 59.2, 55.8, 52.3, 52.2, 35.1, 31.4, 27.1, 20.9, 12.0; **IR** (Neat): ν_{max} 3027, 2951, 2921, 2852, 1733, 1494, 1434, 1370, 1257, 1194, 1164, 1076, 1015, 903, 759, 700; **HRMS** (ESI): calcd for $\text{C}_{30}\text{H}_{36}\text{O}_5\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 499.2454, found 499.2455.

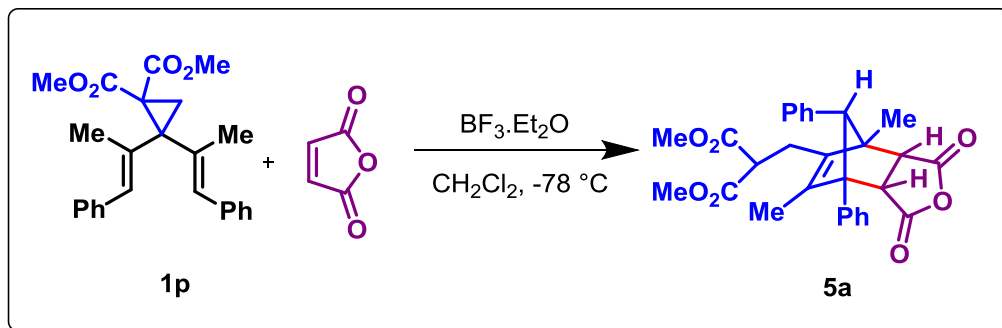
(±)- (2*R*,6*S*,7*S*,7*aR*)-Dimethyl 2-isopropyl-5,7*a*-dimethyl-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (4*h*):



Compound **4h** was synthesized from **1p** by following standard procedure. Yield: 113 mg, (95%); $R_f = 0.5$ (10% EtOAc/hexanes); (The data of $^1\text{H NMR}$ and $^{13}\text{C NMR}$ has been given in **Table S7**); **IR** (Neat): ν_{max} 2965, 2928, 2871, 1730, 1434, 1370, 1246,

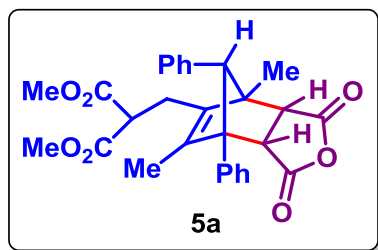
1200, 1069, 1040, 1016, 771, 730, 700; **HRMS** (ESI): calcd for $\text{C}_{29}\text{H}_{34}\text{O}_5\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 485.2293, found 485.2298.

7. Nazarov Cyclization Followed by [4+2]-Cycloaddition (Diels-Alder reaction) from dienyl Donor-Acceptor Cyclopropanes (DACs)



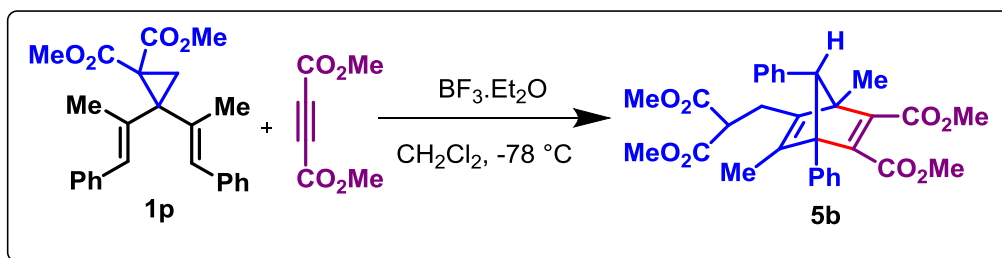
General procedure for Nazarov Cyclization followed by Diels-Alder Reaction: Dimethyl 2,2-bis((*E*)-1-phenylprop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (1p**)** (500 mg, 1.282 mmol, 1 equiv) was dissolved in CH₂Cl₂ (8 mL) under argon. Then, the reaction mixture was cooled to -78 °C (acetone/dry ice bath), and BF₃·Et₂O (0.24 mL, 1.923 mmol, 1.5 equiv) was added dropwise, and stirred at the same temperature for 1-2 h. The reaction mixture was brought into 0 °C over additional 1-2h. At 0 °C, maleic anhydride (503 mg, 5.128 mmol, 4.0 equiv) in CH₂Cl₂ (5 mL) was added dropwise. The reaction mixture was monitored by TLC and quenched with saturated aqueous NaHCO₃ (4 mL) solution at 0 °C. The aqueous layer was extracted with EtOAc (80 mL), the combined organic layers were washed with brine solution (6 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed by rotary evaporation to provide a crude residue that was purified by using silica gel column chromatography to furnish the desired compound (**5a**).

Compound 5a: Yield: 600 mg, (96%); white foam; $R_f = 0.5$ (20% EtOAc/hexanes); (The data of



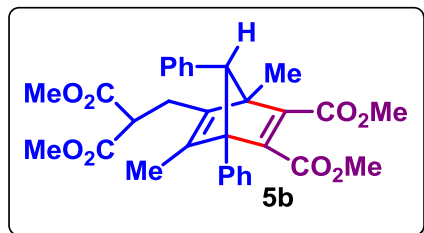
^1H NMR and ^{13}C NMR has been given in **Table S8**); **IR** (Neat):

ν_{\max} 2955, 2923, 2852, 1856, 1775, 1734, 1496, 1435, 1282, 1229, 1153, 1078, 920, 752, 699, 665; **HRMS** (ESI): calcd for $\text{C}_{29}\text{H}_{32}\text{NO}_7$ ($\text{M}+\text{NH}_4$) $^+$ 506.2179, found 506.2178.



Compound **5b** was synthesized from **1p** by following standard procedure.

(±)- dimethyl 5-(3-methoxy-2-(methoxycarbonyl)-3-oxopropyl)-4,6-dimethyl-1,7-diphenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**5b**):

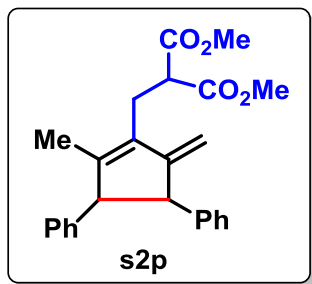


Yield: 112 mg, (82%); colorless oil; $R_f = 0.5$ (20% EtOAc/hexanes); ^1H NMR (500 MHz, CDCl_3): δ 7.21-7.11 (m, 6H), 7.08-7.03 (m, 2H), 6.82 (d, $J = 6.7$ Hz, 2H), 4.02 (s, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 3.59 (dd, $J = 11.3, 4.1$ Hz,

1H), 2.97 (dd, $J = 14.0, 11.3$ Hz, 1H), 2.54 (d, $J = 14.0, 4.1$ Hz, 1H), 1.99 (s, 3H), 1.50 (s, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 169.6, 169.2, 167.4, 163.8, 163.1, 147.8, 145.4, 142.6, 136.5, 135.0, 130.3, 128.9, 127.8, 127.7, 127.0, 126.9, 89.8, 72.0, 61.8, 52.7, 52.6, 51.8, 51.7, 48.7, 26.2, 13.7, 12.8; **IR** (Neat): ν_{\max} 2951, 2923, 2852, 1735, 1732, 1618, 1435, 1284, 1236, 1195, 1145, 1080, 1047, 1034, 960, 772, 756, 704; **HRMS** (ESI): calcd for $\text{C}_{31}\text{H}_{32}\text{O}_8\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 555.1977, found 555.1989.

Dimethyl 2-((2-methyl-5-methylene-3,4-diphenylcyclopent-1-enyl)methyl)malonate (s2p):



Yield: 92 mg, (92%); greenish oil; $R_f = 0.6$ (10% EtOAc/hexanes); ^1H

NMR (400 MHz, CDCl_3): δ 7.36-7.16 (m, 6H), 7.10-6.99 (m, 4H), 4.90 (d, $J = 2.0$ Hz, 1H), 4.55 (d, $J = 2.0$ Hz, 1H), 3.79 (t, $J = 8.0$ Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.71 (dd, $J = 3.4, 2.0$ Hz, 1H), 3.62 (d, $J = 3.4$ Hz, 1H), 3.01 (qd, $J = 8.0, 5.8$ Hz, 2H), 1.63 (s, 3H); ^{13}C

NMR (100 MHz, CDCl_3): δ 169.5, 156.9, 147.5, 145.2, 143.7, 134.4, 128.5, 128.4, 127.6, 127.4, 126.5, 126.1, 101.8, 64.4, 58.3, 52.5, 52.5, 50.0, 24.7, 13.7; **IR** (Neat): ν_{max} 2952, 2923, 2852, 1735, 1599, 1493, 1450, 1435, 1332, 1272, 1235, 1153, 1073, 1047, 1028, 963, 912, 755, 699; **HRMS** (ESI): calcd for $\text{C}_{25}\text{H}_{27}\text{O}_4$ ($\text{M}+\text{H}$) $^+$ 391.1919, found 391.1915.

8. 2D NMR of 2j, 3e, 3e', 4a, s4a, 4a', 4h and 5a

The compounds **3e** and **3e'** are the separable diastereomers with change in configuration only at C-9 chiral carbon. The notable change in the upfield or downfield shift of chemical shifts of protons in two compounds is attributed to the anisotropic magnetic shielding effect of aryl substituents.

(+)-Dimethyl 2-(((1*R*,3*S*,4*aS*)-5,7-dimethoxy-2,2-dimethyl-2,3,4,4*a*-tetrahydro-1*H*-1,3-methanofluoren-9-yl)methyl)malonate (2j**):**

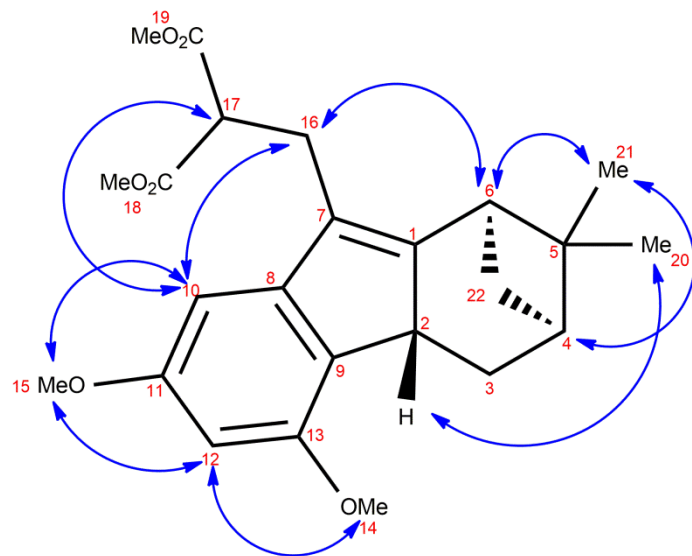
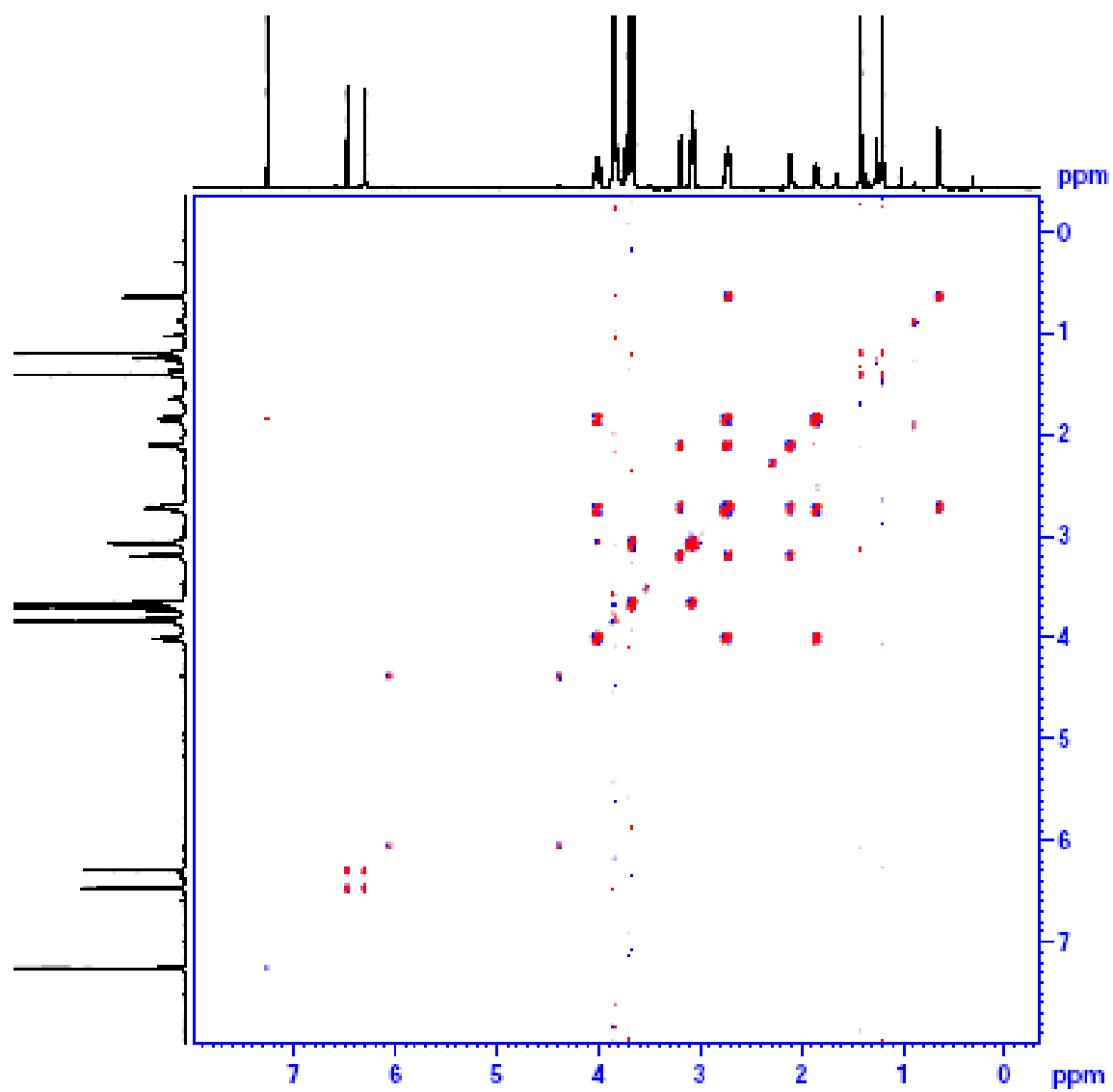


Figure S1: Schematic representation of the chemical structure and observed characteristic NOE correlations (blue arrows) of compound-**2j**.

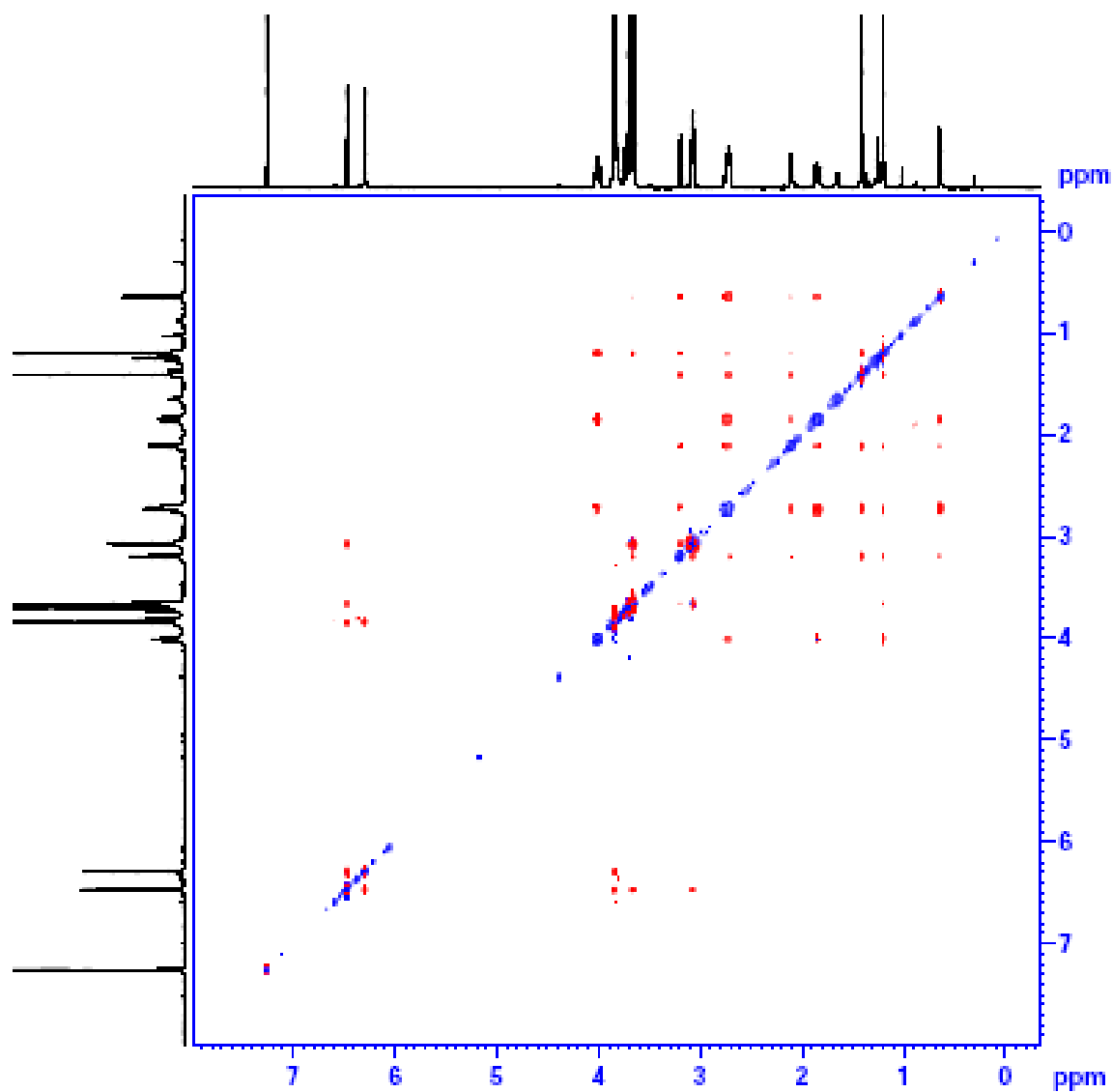
The chemical shift assignment of compound-**2j** was carried out using 2D-DQFCOSY, HSQC, and HMBC analysis. The relative stereochemistry at C-2, C-4, and C-6 chiral centres of compound-**2j** was unequivocally established using 2D NOESY and *J*-coupling (Table S1) analysis. The observed strong NOE correlation between H-2 and Me-20 clearly suggest that the protons are in spatial proximity. Further, the characteristic NOE cross-peaks between H-16/H-6, H-6/Me-21, and H-4/Me-21 protons strongly support the relative stereochemistry at C-4 and C-6 chiral carbons as depicted in Figure S1.

Table S1: ^1H and ^{13}C NMR spectral data of compound-**2j** (CDCl_3 , 298 K).

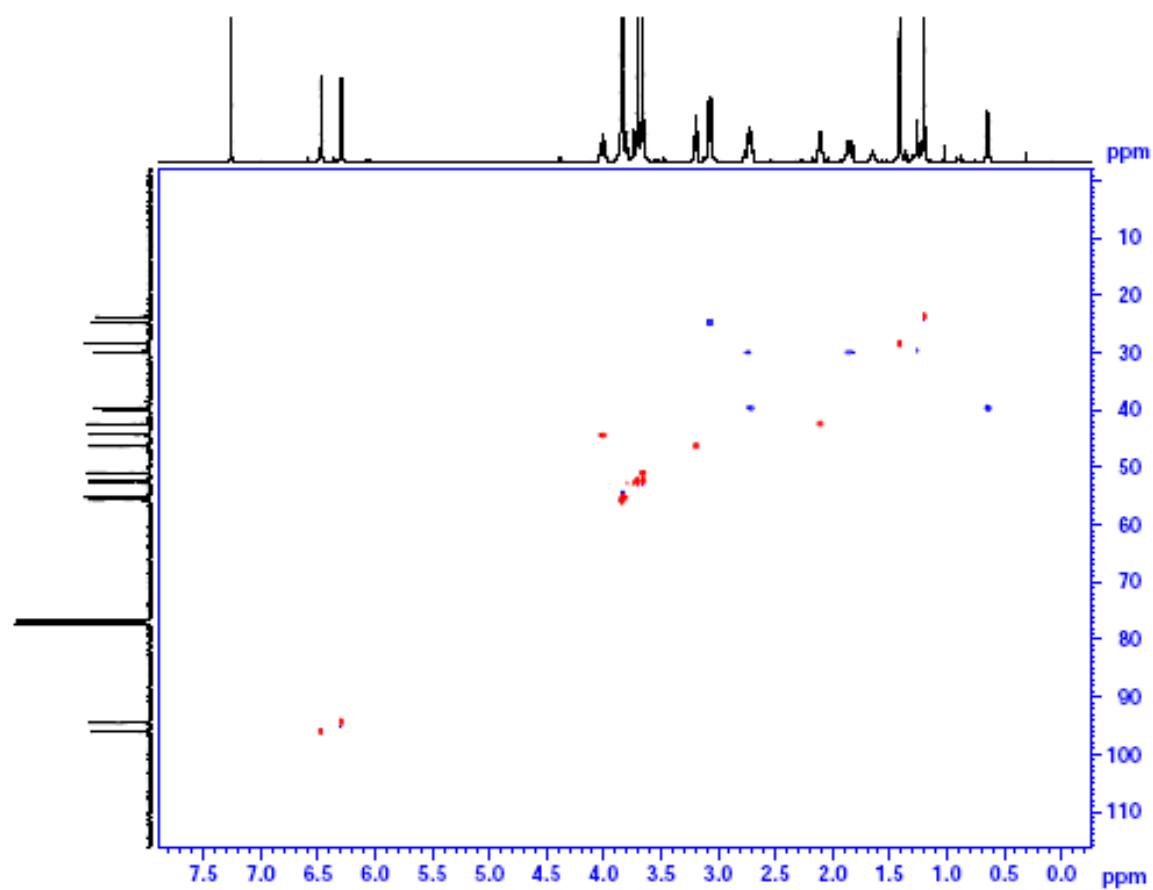
Position	^1H		^{13}C chemical shift δ (ppm)
	Chemical shift δ (ppm)	Scalar coupling J (Hz)	
10	6.47 (1H, d)	2.0	96.0
12	6.30 (1H, d)	2.0	94.4
2	4.01 (1H, dd)	10.6, 8.5	44.3
15	3.85 (3H, s)	-	55.6
14	3.83 (3H, s)	-	55.2
18	3.71 (3H, s)	-	52.5
19	3.66 (3H, s)	-	52.3
17	3.66 (1H, t)	7.4	50.9
6	3.19 (1H, t)	5.6	46.2
16	3.07 (1H, m)	-	24.7
3,22	2.81-2.66 (2H, m)	-	-
4	2.11 (1H, m)	-	42.4
3'	1.85 (1H, ddd)	13.4, 8.5, 1.5	30.0
21	1.41 (3H, s)	-	28.3
20	1.20 (3H, s)	-	23.7
22'	0.64 (1H, d)	9.4	39.6



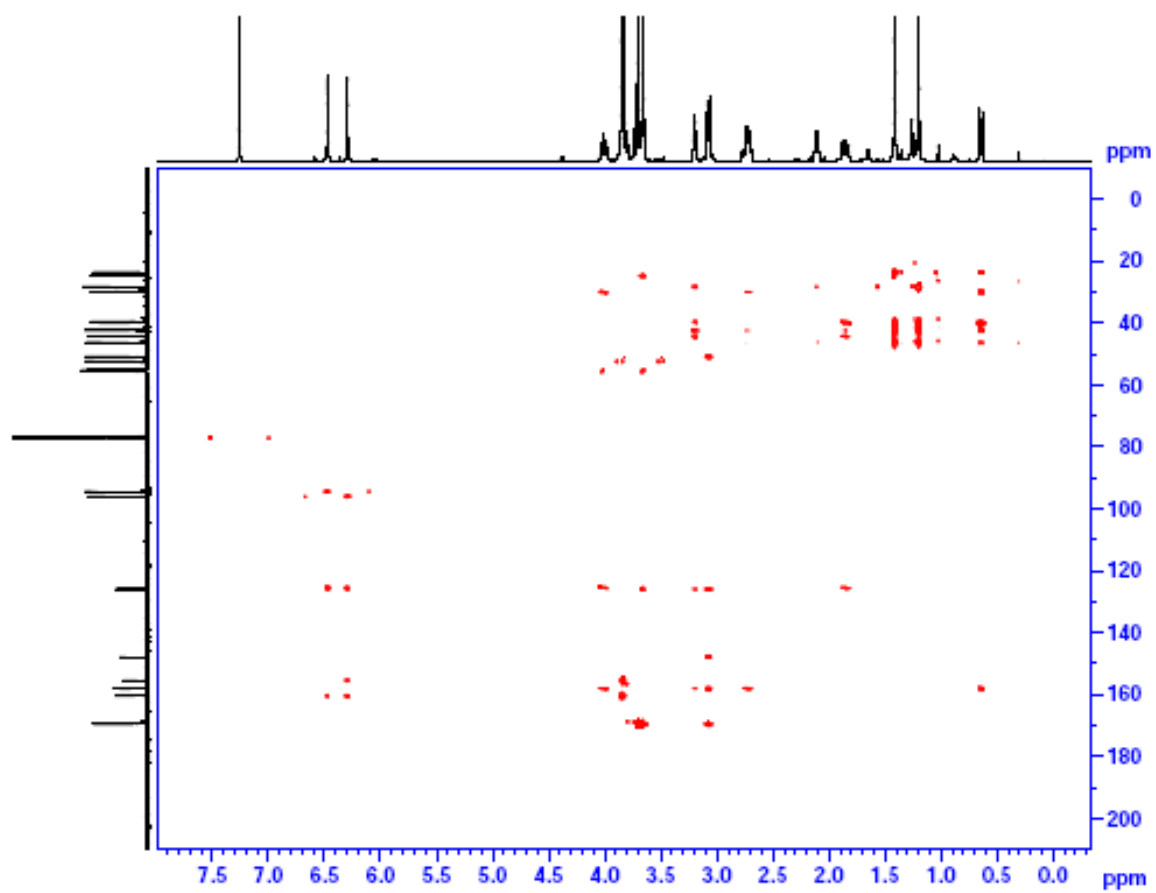
^1H - ^1H DQFCOSY (Double-quantum Filtered Correlation Spectroscopy) spectrum of compound-**2j** (CDCl_3 , 298 K)



^1H - ^1H NOESY (Nuclear Overhauser Effect Spectroscopy) spectrum of compound-**2j** (CDCl_3 , 298 K)



^{13}C - ^1H HSQC (Heteronuclear Single Quantum Correlation) spectrum of compound-**2j** (CDCl_3 , 298 K)



^{13}C - ^1H HMBC (Heteronuclear Multiple Bond Correlation) spectrum of compound-**2j** (CDCl_3 , 298 K)

(±)-Dimethyl 2-(((3*S*,4*S*,5*S*)-5-(1*H*-indol-3-yl)-2,5-dimethyl-3,4-diphenylcyclopent-1-enyl)methyl)malonate (**3e**): Bottom (Major)

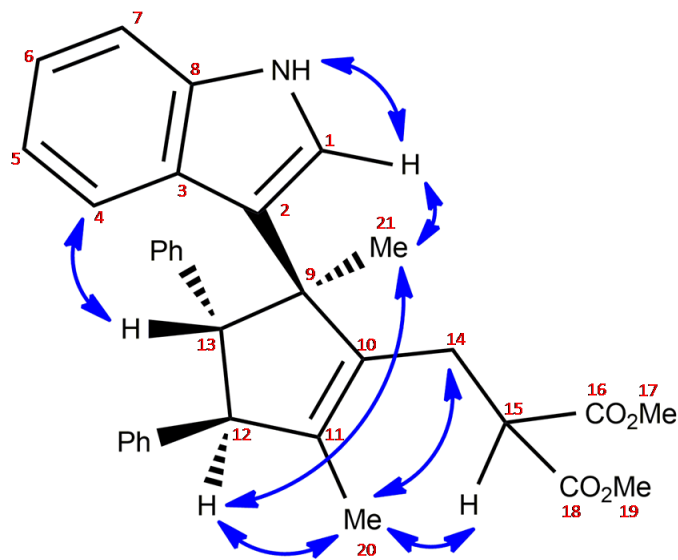
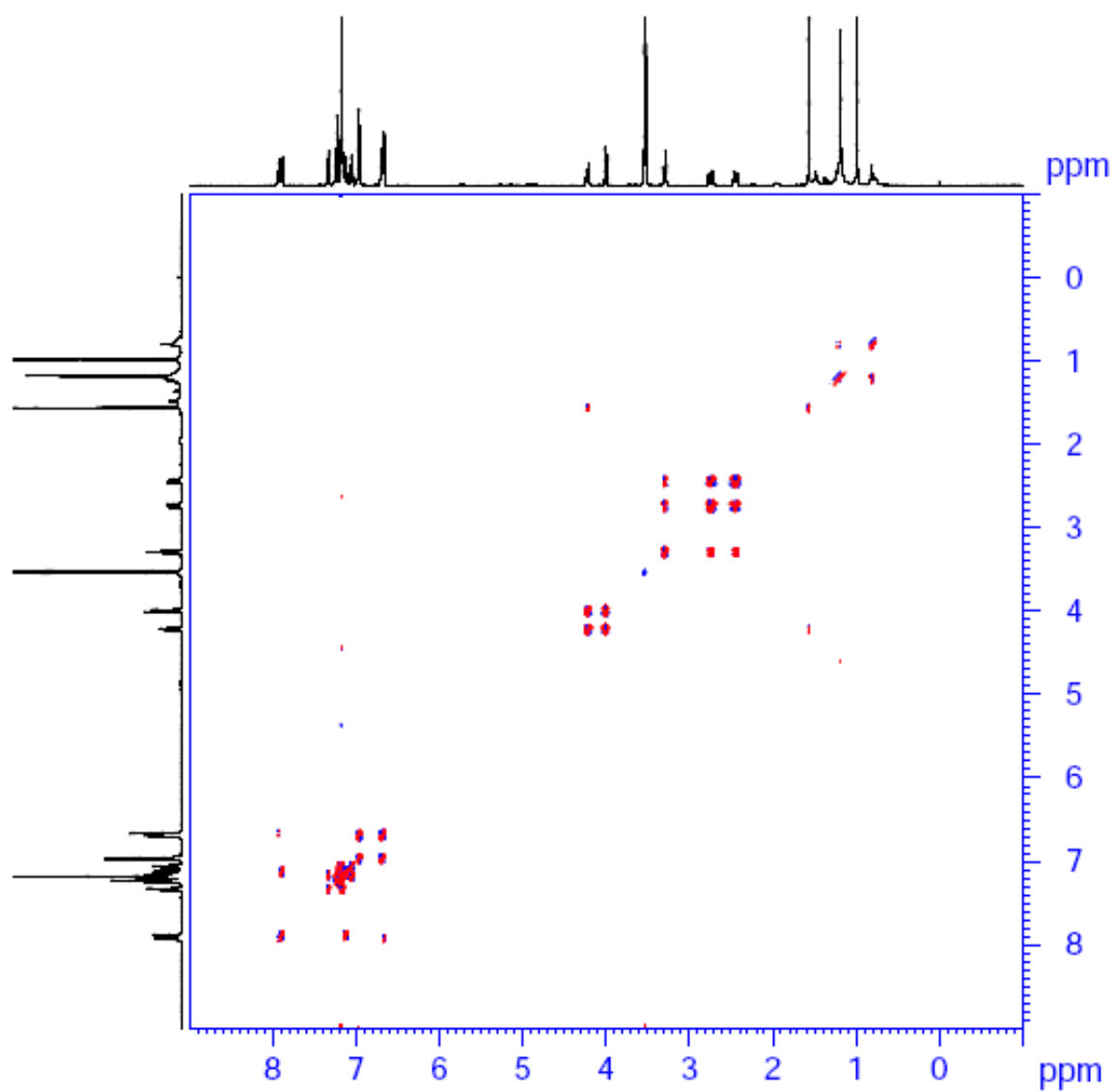


Figure S2: Schematic representation of the chemical structure and observed characteristic NOE correlations of compound-**3e**.

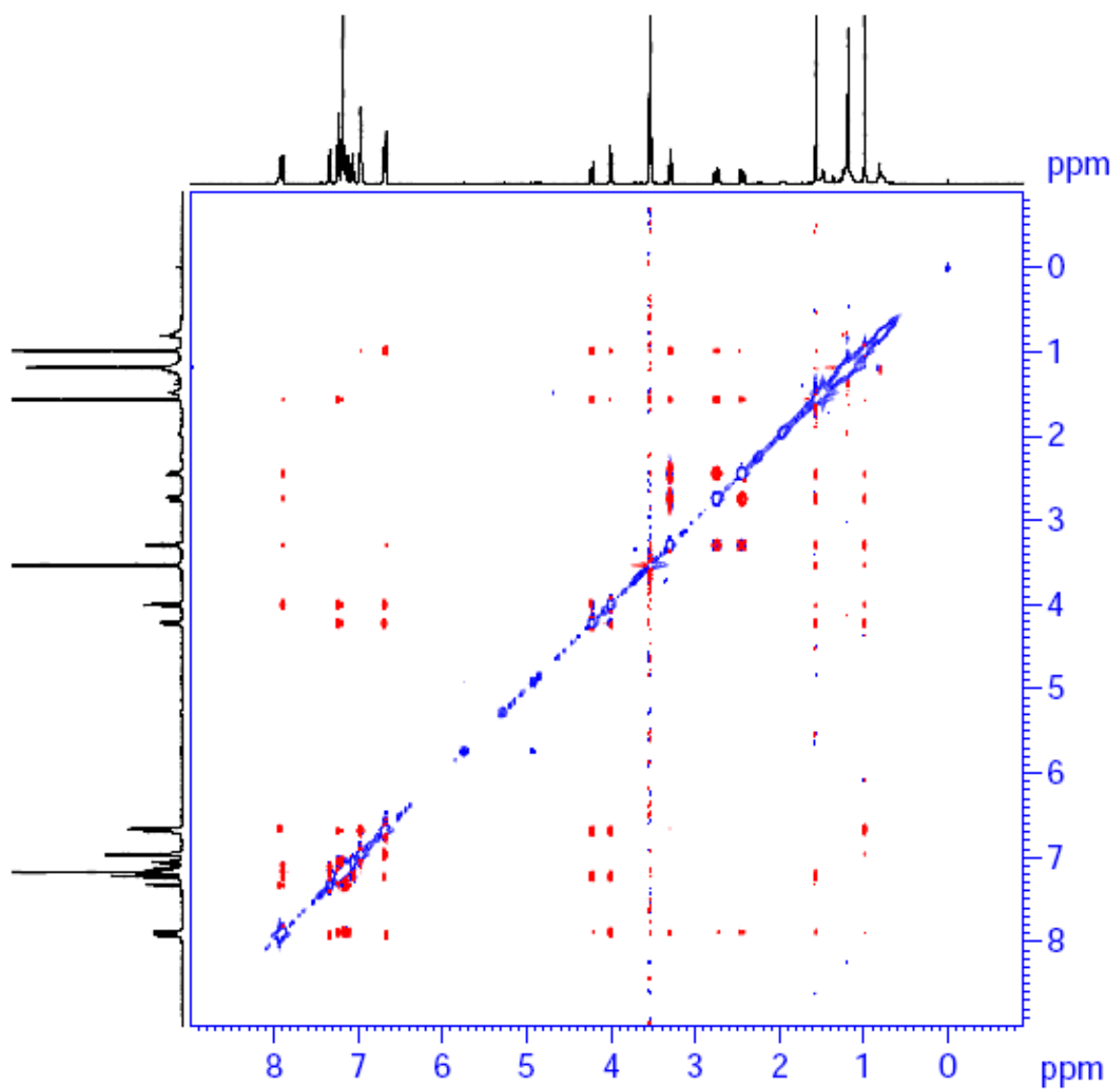
The complete assignment of ¹H and ¹³C chemical shifts of compound-**3e** is given in Table S1. In ¹H NMR spectrum of compound-**3e**, N-H and H-1 protons appeared as doublets at 7.93 and 6.66 ppm, respectively. The observed COSY and NOE cross peaks between N-H and H-1 protons support the position of H-1 as shown in Fig.S2. The observed strong NOE cross peak between Me-21/H-12 protons indicate that Me-21 and H-12 are in *syn* relationship as shown in Fig.S2. The β-orientation of the H-13 proton is assigned from the observed NOE correlation between H-13 and H-4 (Ar-ortho) proton and the strong scalar coupling ³J_{H-13/H-12} = 10.9 Hz. Further, the NOE correlation between Me-21/H-1 protons clearly support that they are in spatial proximity.

Table S2: ^1H and ^{13}C NMR spectral data of compound-**3e** (CDCl_3 , 298 K).

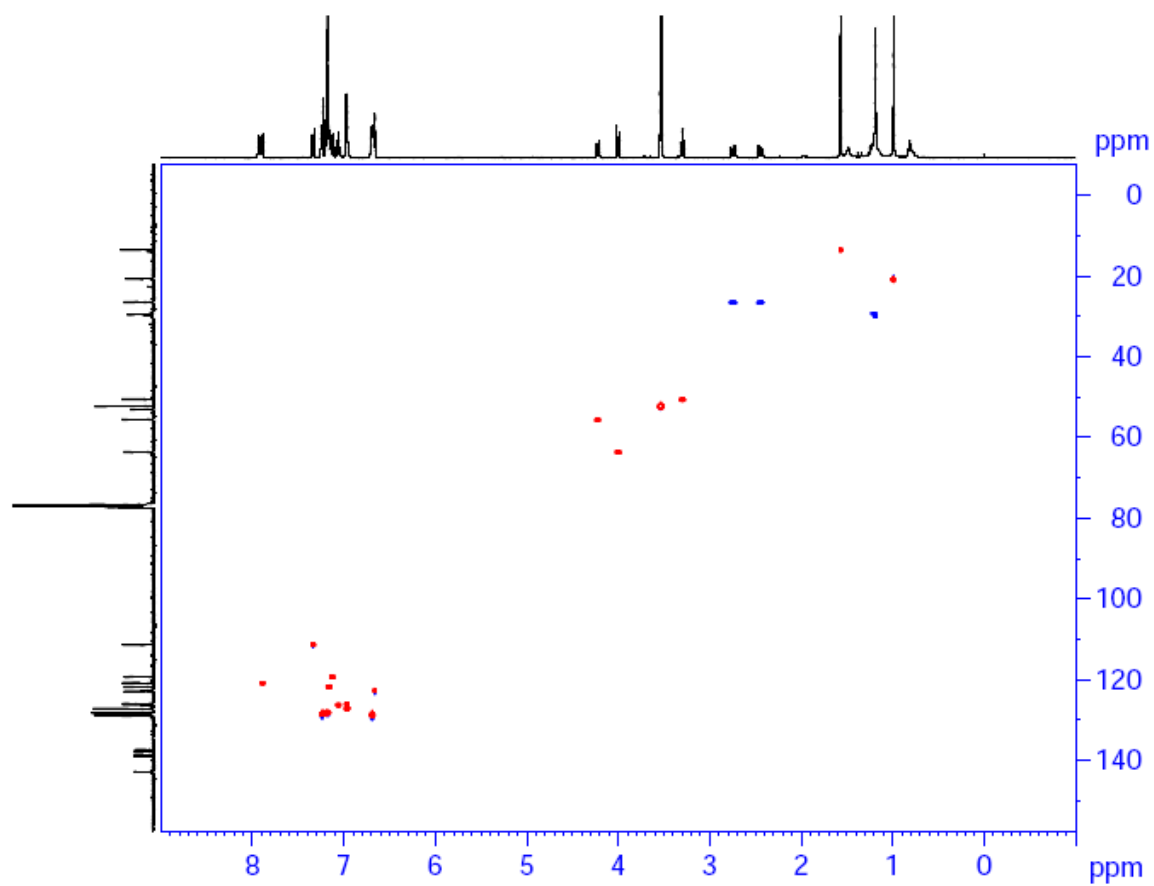
Position	^1H		^{13}C chemical shift δ (ppm)
	Chemical shift δ (ppm)	Scalar coupling J (Hz)	
-NH-	7.93 (1H, d)	2.3	-
4	7.89 (1H, dd)	7.5, 1.2	120.8
Aromatic	7.36-6.92 (11H, m)	-	-
Aromatic	6.72-6.67 (2H, m)	-	-
1	6.66 (1H, d)	2.3	122.9
12	4.22 (1H, m)	-	55.6
13	4.00 (1H, d)	11.0	63.7
19	3.54 (3H, s)	-	52.4
17	3.52 (3H, s)	-	52.4
15	3.29 (1H, dd)	7.96, 7.26	50.6
14	2.74 (1H, m)	-	26.5
14'	2.44 (1H, m)	-	26.5
20	1.57 (3H, m)	-	13.6
21	0.99 (3H, s)	-	20.8
2	-	-	120.8
9	-	-	53.1
10	-	-	139.0
11	-	-	137.6
16	-	-	169.6
18	-	-	169.6



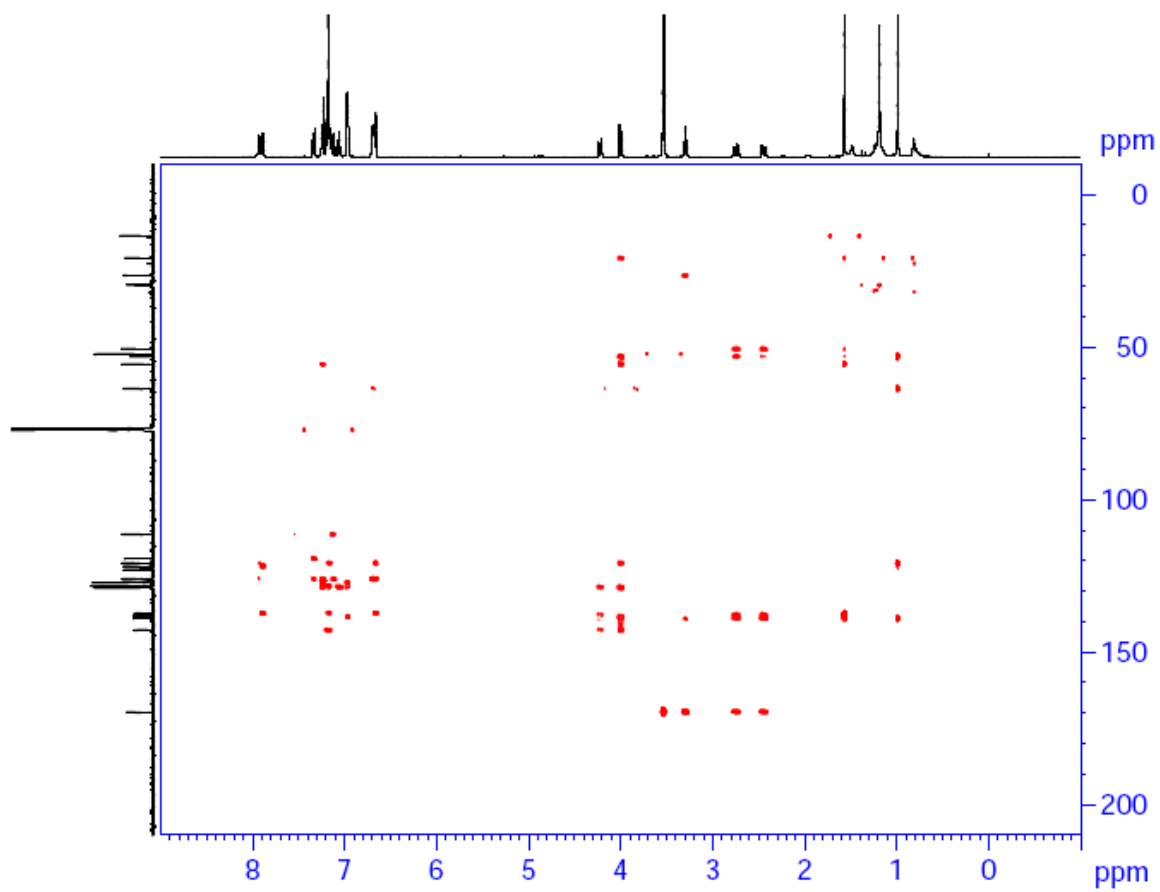
^1H - ^1H DQFCOSY (Double-quantum Filtered Correlation Spectroscopy) spectrum of compound-**3e** (CDCl_3 , 298 K)



¹H-¹H NOESY (Nuclear Overhauser Effect Spectroscopy) spectrum of compound-**3e** (CDCl₃, 298 K)



^{13}C - ^1H HSQC (Heteronuclear Single Quantum Correlation) spectrum of compound-**3e** (CDCl_3 , 298 K)



^{13}C - ^1H HMBC (Heteronuclear Multiple Bond Correlation) spectrum of compound-**3e** (CDCl_3 , 298 K)

(±)-Dimethyl 2-(((3*S*,4*S*,5*R*)-5-(1*H*-indol-3-yl)-2,5-dimethyl-3,4-diphenylcyclopent-1-enyl)methyl)malonate (3e'): Top (Minor)

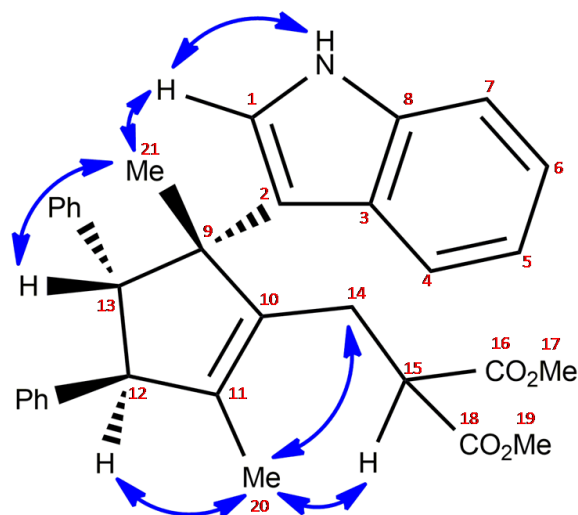
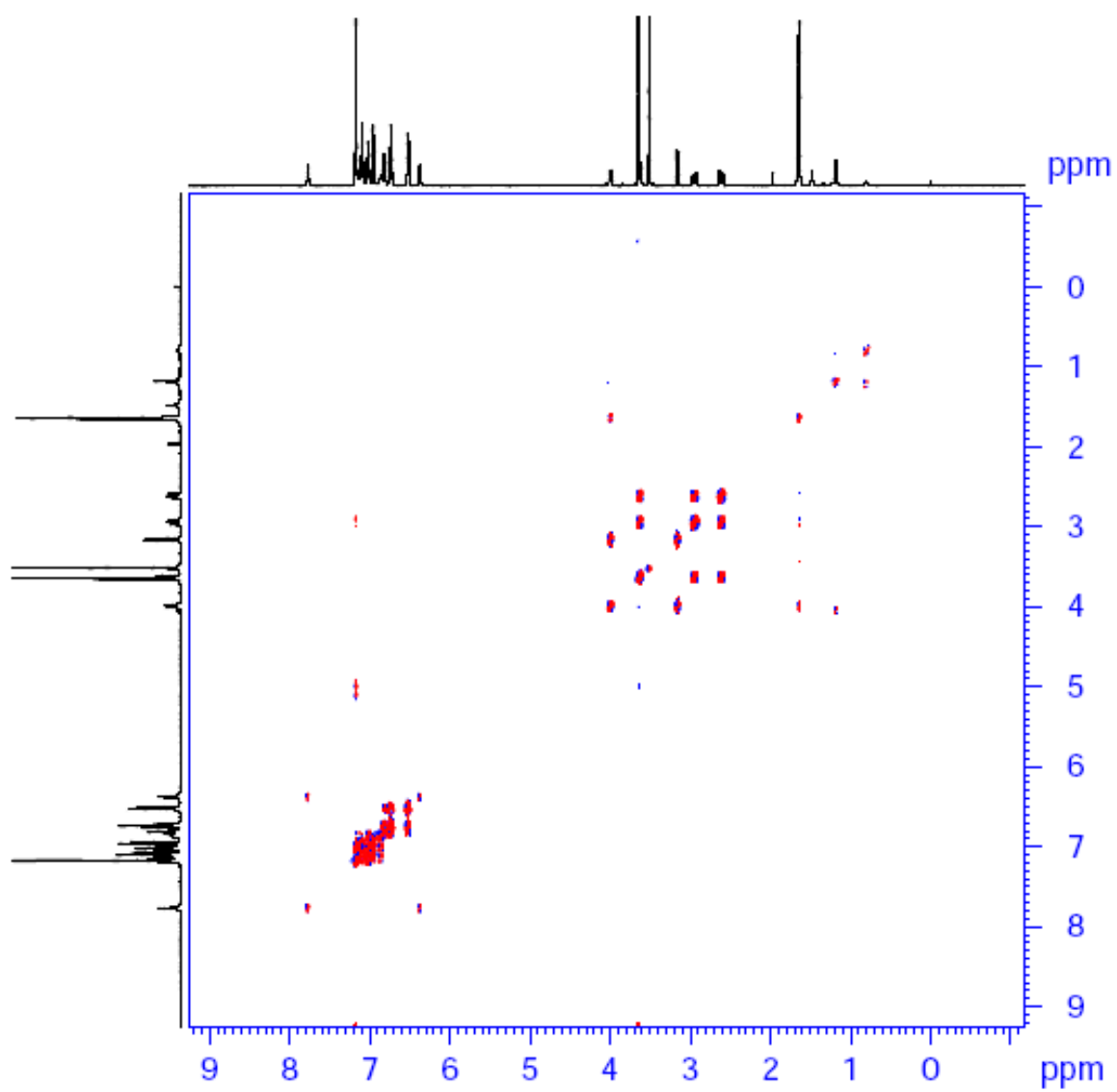


Figure S3: Schematic representation of the chemical structure and observed characteristic NOE correlations of compound-**3e'**.

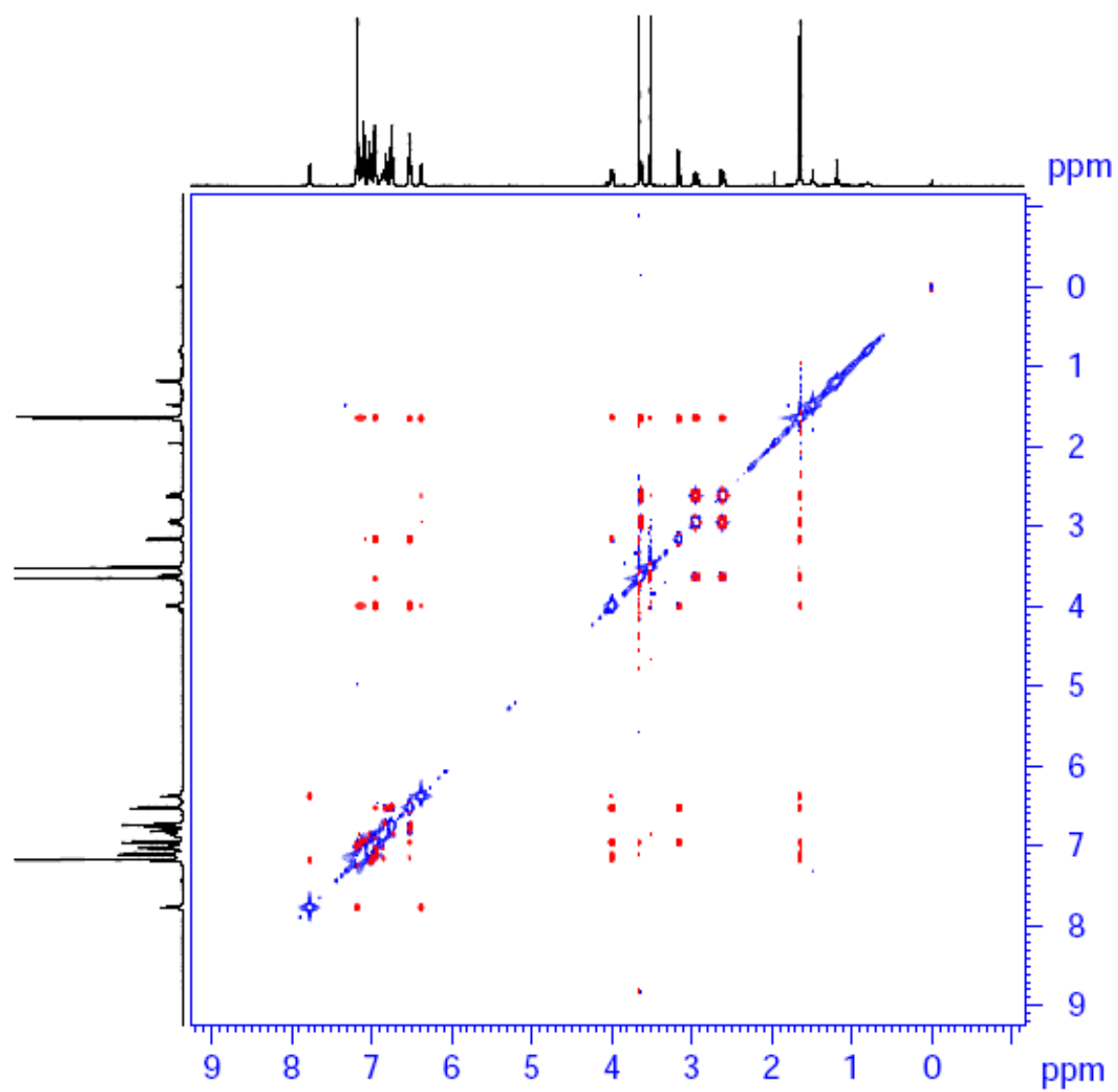
The complete assignment of ^1H and ^{13}C chemical shifts of compound-**3e'** is given in Table S2. In ^1H NMR spectrum of compound-**3e'**, N-H and H-1 protons appeared as doublets at 7.77 and 6.38 ppm, respectively. The observed COSY and NOE cross peaks between N-H and H-1 protons suggest that these are directly coupled protons. The observed strong NOE cross peak between Me-21/H-13 protons indicate that Me-21 and H-13 are in β -orientation and are in *syn* relationship as shown in Fig.S3. Further, the NOE correlation between Me-21/H-1 protons clearly support that they are in spatial proximity.

Table S3: ^1H and ^{13}C NMR spectral data of compound-**3e'** (CDCl_3 , 298 K).

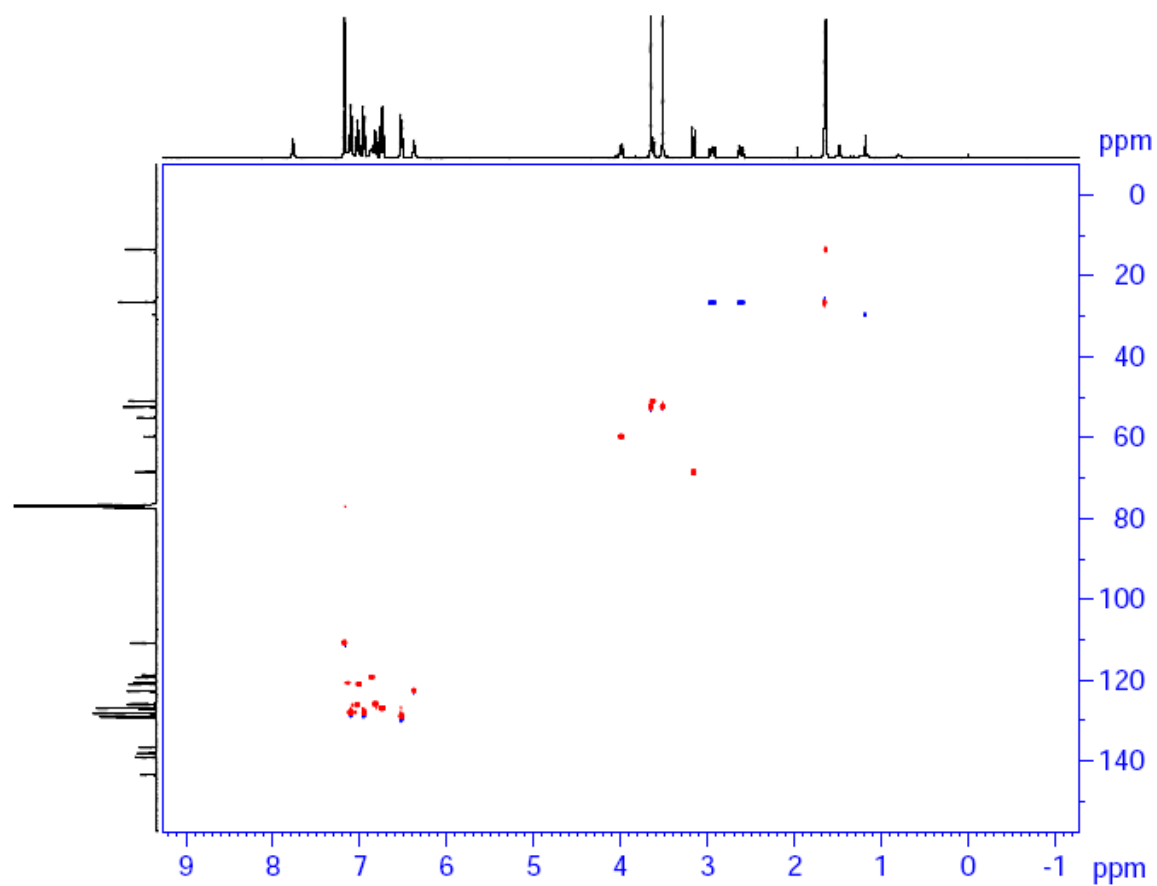
Position	^1H		^{13}C chemical shift δ (ppm)
	Chemical shift δ (ppm)	Scalar coupling J (Hz)	
-NH-	7.77 (1H, d)	1.7	-
Aromatic	7.20-6.70 (12H, m)	-	-
Aromatic	6.55-6.49 (2H, m)	-	129.2
1	6.38 (1H, d)	1.7	122.8
12	4.00 (1H, m)	-	59.8
19	3.65 (3H, s)	-	52.5
15	3.63 (1H, dd)	8.9, 6.7	50.9
17	3.52 (3H, s)	-	52.4
13	3.16 (1H, d)	10.4	68.5
14	2.95 (1H, m)	-	26.5
14'	2.61 (1H, m)	-	26.5
21	1.65 (3H, s)	-	26.5
20	1.64 (3H, m)	-	13.5
2	-	-	118.7
9	-	-	55.0
10	-	-	138.0
11	-	-	139.0
16	-	-	169.5
18	-	-	170.0



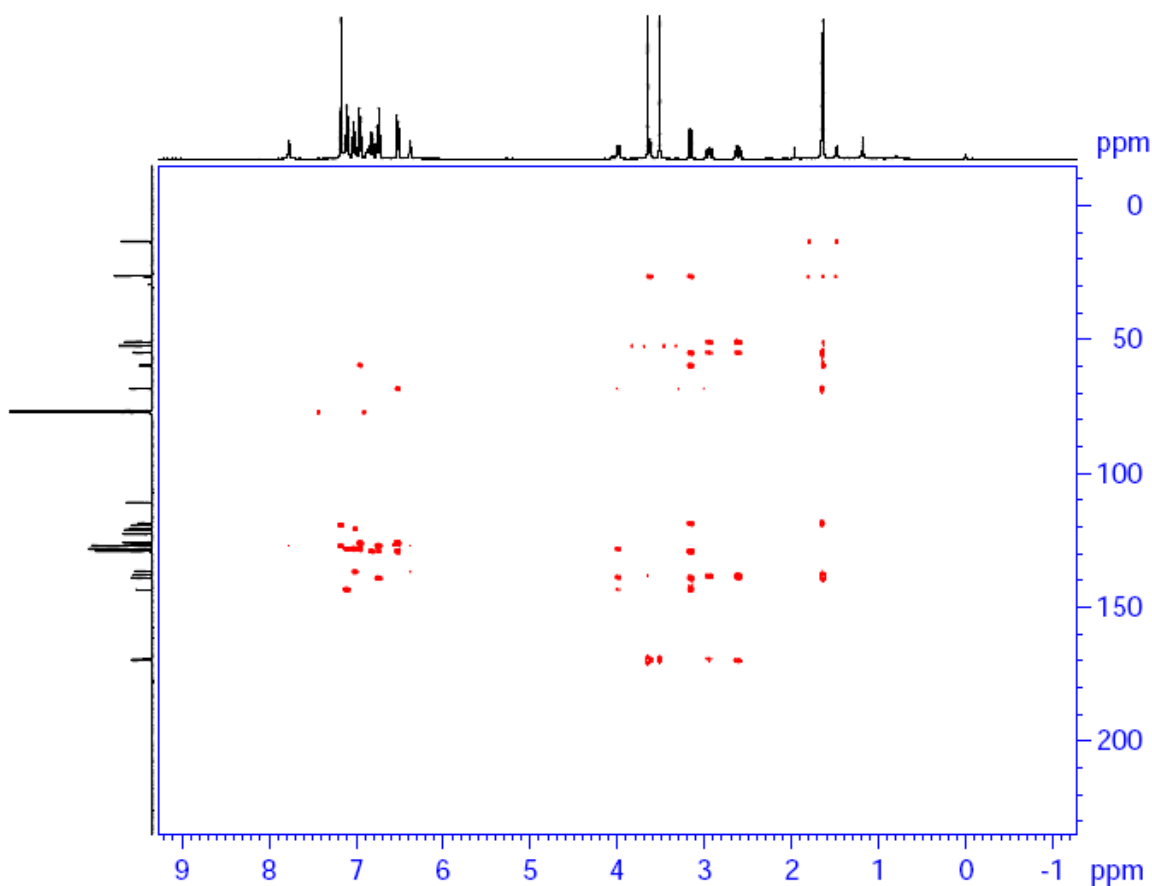
^1H - ^1H DQFCOSY (Double-quantum Filtered Correlation Spectroscopy) spectrum of compound-**3e'** (CDCl_3 , 298 K)



^1H - ^1H NOESY (Nuclear Overhauser Effect Spectroscopy) spectrum of compound-**3e'** (CDCl_3 , 298 K)



^{13}C - ^1H HSQC (Heteronuclear Single Quantum Correlation) spectrum of compound-**3e'** (CDCl_3 , 298 K)



^{13}C - ^1H HMBC (Heteronuclear Multiple Bond Correlation) spectrum of compound-**3e'** (CDCl_3 , 298 K)

The complete assignment of ^1H and ^{13}C chemical shifts of compound-**4a** major and **4a'** minor isomers is given in Table S4 & S6. ^1H NMR spectrum of compound-**4a** shows the presence of two isomers **4a** & **s4a** with 90:10 ratio. Structure and relative stereochemistry of the major and minor isomers were unambiguously assigned as shown in Fig.S4 and Fig. S5, respectively.

(±)- (2*R*,6*S*,7*S*,7*aS*)-dimethyl5,7*a*-dimethyl-2,6,7-triphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (**4a**):

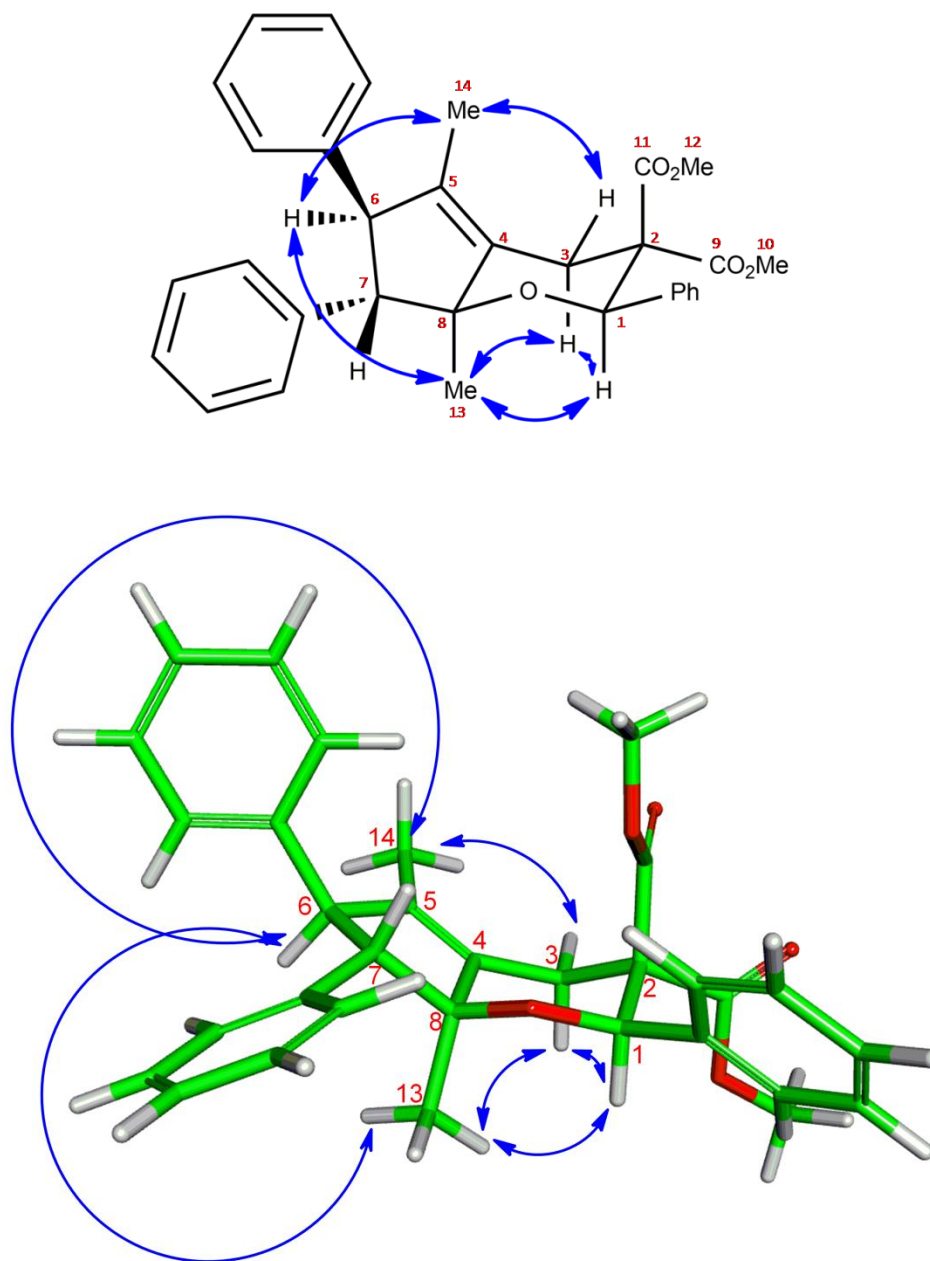


Figure S4: Schematic representation of the chemical structure and observed characteristic NOE correlations and energy minimized 3D molecular structure and observed characteristic NOE correlations (blue arrows) of compound-**4a** (major isomer, bottom).

In major isomer, H-1 proton is appeared as a singlet at 5.36 ppm. The observed strong NOE cross peaks between Me-13/H-1, Me-13/H-3_{ax}, and H-3_{ax}/H-1 clearly suggest that these protons are in 1,3-diaxial relationship in a chair conformation of 6-membered ring as shown in Fig.S4. The characteristic NOE correlation between Me-13 and H-6 protons and strong scalar coupling $^3J_{\text{H-6/H-7}} = 9.9$ Hz indicate that H-6 and H-7 protons are in *anti* orientation.

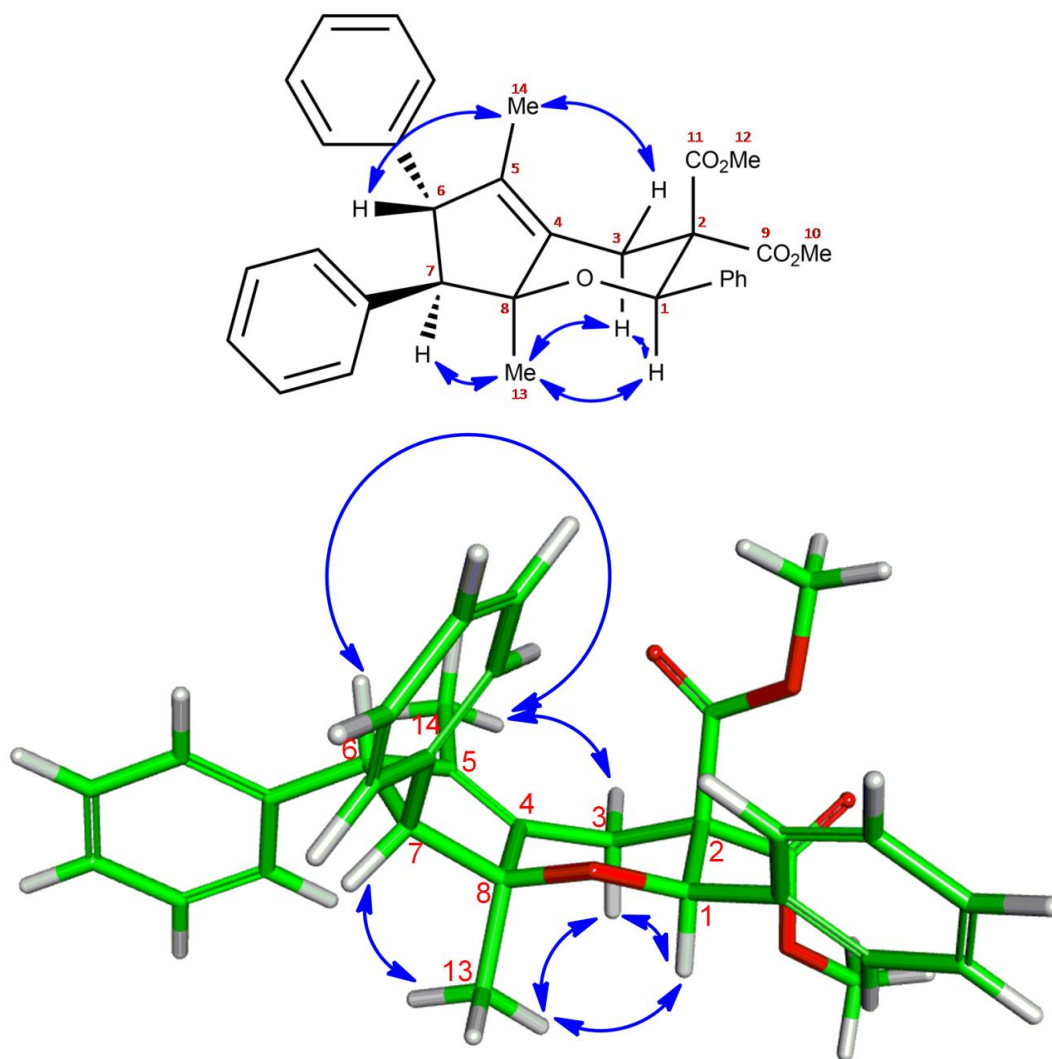


Figure S5: Schematic representation of the chemical structure and observed characteristic NOE correlations and energy minimized 3D molecular structure and observed characteristic NOE correlations (blue arrows) of compound-**s4a** (minor isomer).

In minor isomer, the observed strong NOE cross peaks between Me-13/H-1, Me-13/H-3_{ax}, and H-3_{ax}/H-1 protons clearly suggest that these are in 1,3-diaxial relationship in a chair conformation of 6-membered ring as shown in Fig.S5. The characteristic NOE correlation between Me-13/H-7 and Me-14/H-6 protons support the relative stereochemistry of the minor isomer at C-6 and C-7 is as shown in Fig.S5.

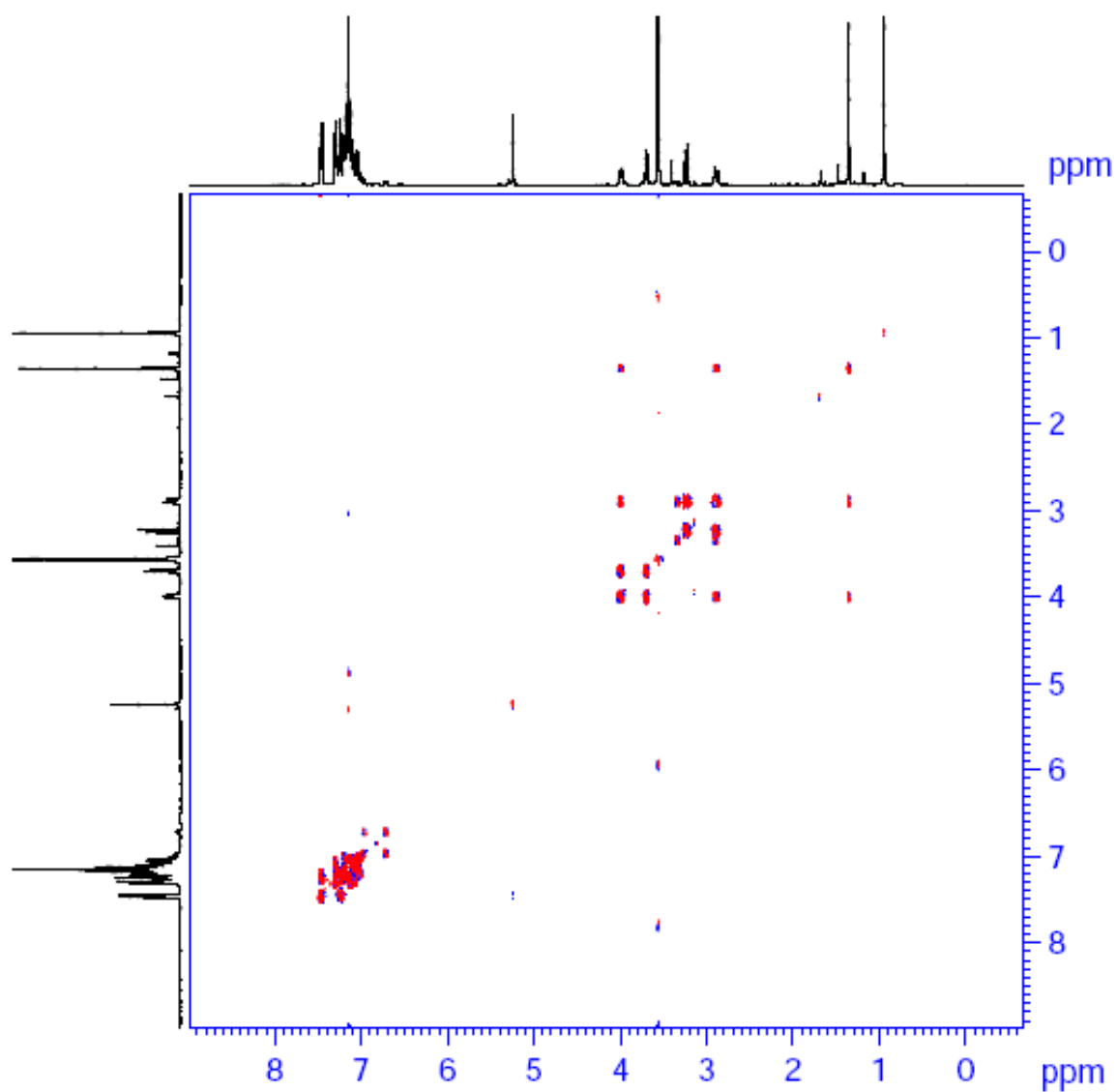
Table S4: ¹H and ¹³C NMR spectral data of compound-**4a** -major (CDCl₃, 298 K).

Position	¹ H		¹³ C chemical shift δ (ppm)
	Chemical shift δ (ppm)	Scalar coupling J (Hz)	
Aromatic	7.70-6.68 (15H, m)	-	-
1	5.36 (1H, s)	-	76.7
6	4.12 (1H, m)	-	54.8
7	3.82 (1H, d)	9.9	65.1
12	3.69 (1H, s)	-	51.5
14	3.68 (1H, s)	-	52.4
3 _{eq}	3.35 (1H, d)	13.9	31.5
3 _{ax}	3.00 (1H, m)	-	31.5
10	1.47 (1H, t)	1.4	11.8
9	1.06 (1H, s)	-	17.1
2	-	-	61.5
4	-	-	132.6
5	-	-	134.6
8	-	--	86.3
11	-	-	170.8
13	-	-	168.3

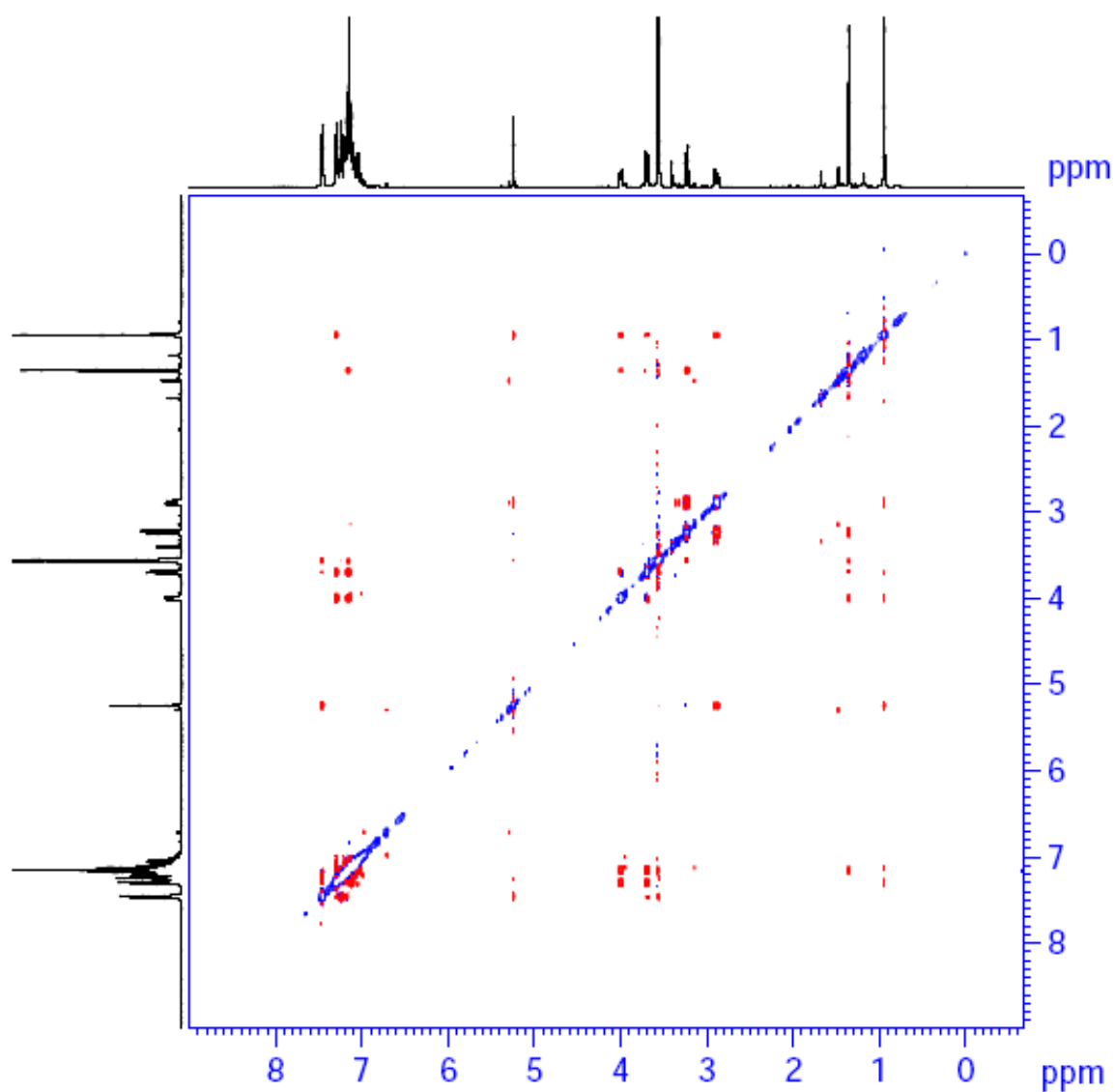
Table S5: ¹H and ¹³C NMR spectral data of compound-**s4a**-minor (CDCl₃, 298 K).

Position	¹ H		¹³ C chemical shift δ (ppm)
	Chemical shift δ (ppm)	Scalar coupling J (Hz)	
Aromatic	-	-	-
1	5.41 (1H, s)	-	75.9
6	4.08 (1H, m)	-	63.5
7	3.26 (1H, d)	3.1	65.1
12	-	-	-
14	3.52 (1H, s)	-	51.4
3 _{eq}	3.46 (1H, d)	13.5	30.8
3 _{ax}	3.00 (1H, m)	-	30.8

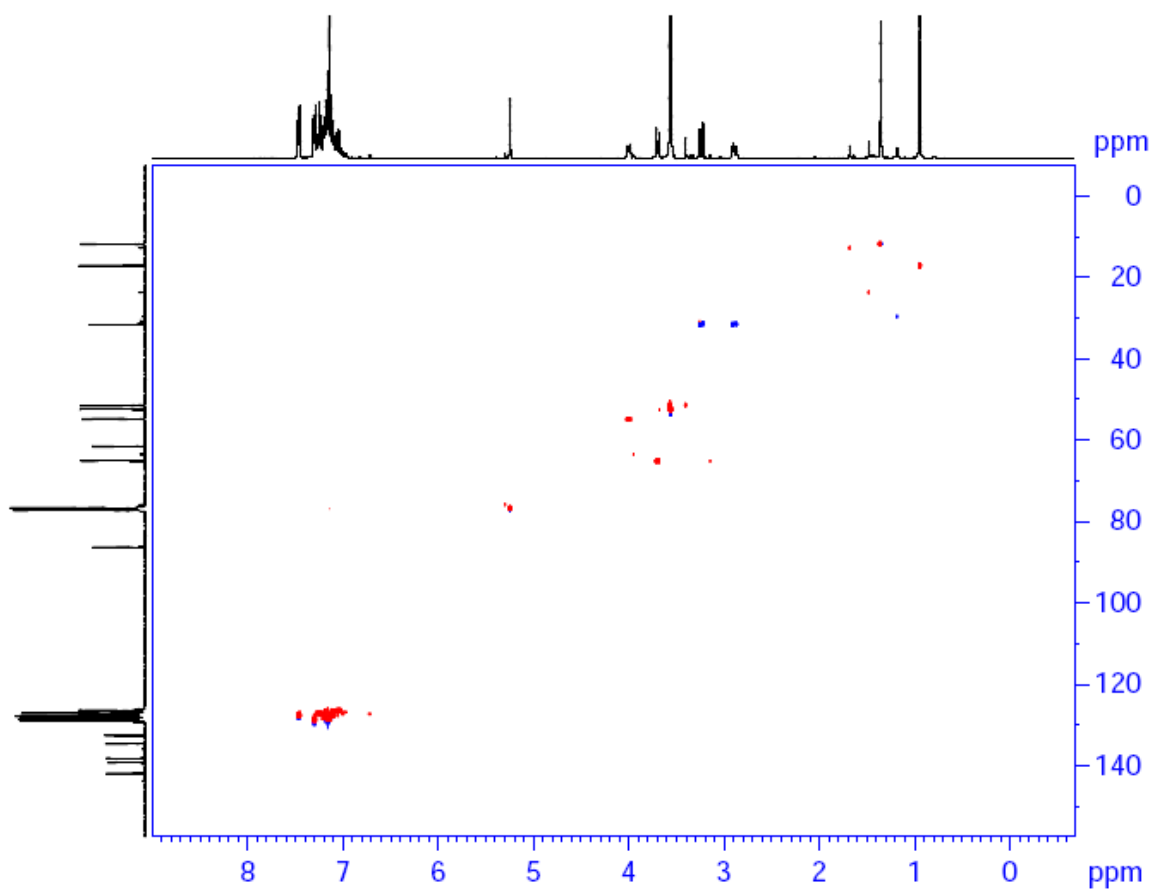
10	1.80 (1H, bs)	-	12.7
9	1.60 (1H, s)	-	23.7
2	-	-	-
4	-	-	132.8
5	-	-	136.0
8	-	--	-
11	-	-	171.0
13	-	-	168.5



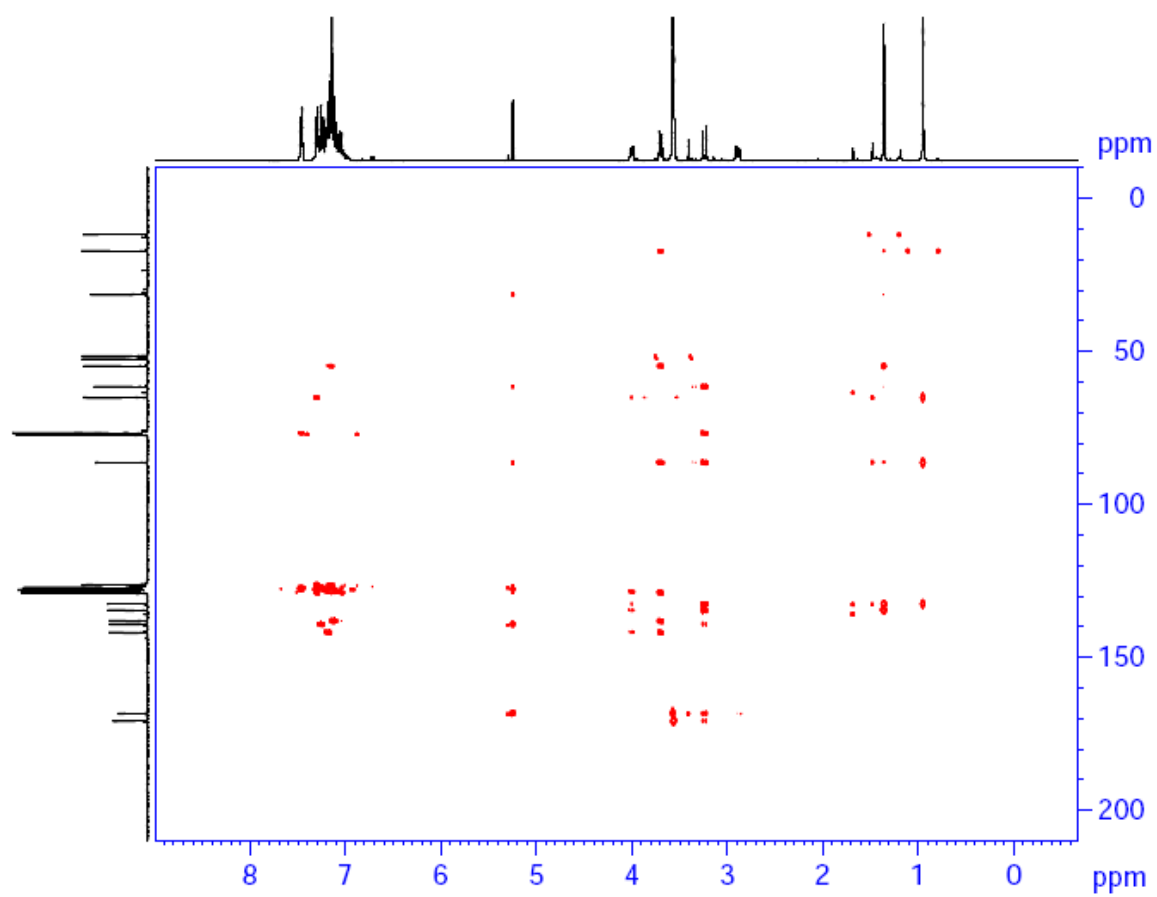
^1H - ^1H DQFCOSY (Double-quantum Filtered Correlation Spectroscopy) spectrum of compound-**4a** (CDCl_3 , 298 K)



^1H - ^1H NOESY (Nuclear Overhauser Effect Spectroscopy) spectrum of compound-**4a** (CDCl_3 , 298 K)



^{13}C - ^1H HSQC (Heteronuclear Single Quantum Correlation) spectrum of compound-**4a** (CDCl_3 , 298 K)



^{13}C - ^1H HMBC (Heteronuclear Multiple Bond Correlation) spectrum of compound-**4a** (CDCl_3 , 298 K)

(±)- (2*S*,6*S*,7*S*,7*aS*)-Dimethyl 5,7*a*-dimethyl-2,6,7-triphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (**4a'**): (Top, minor):

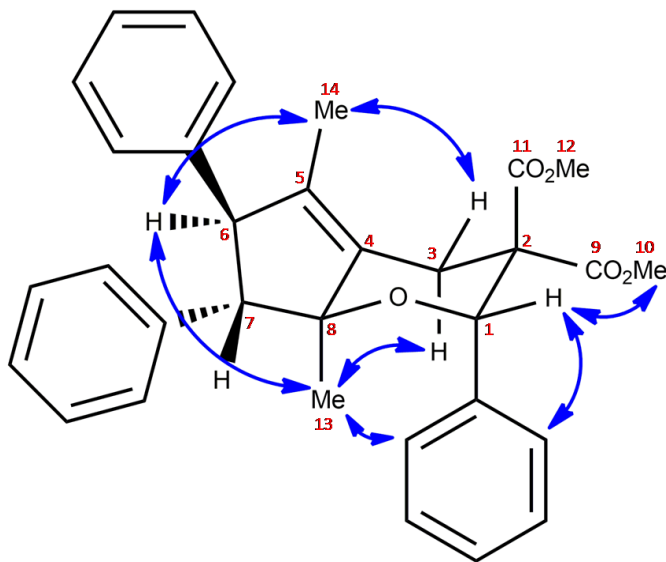
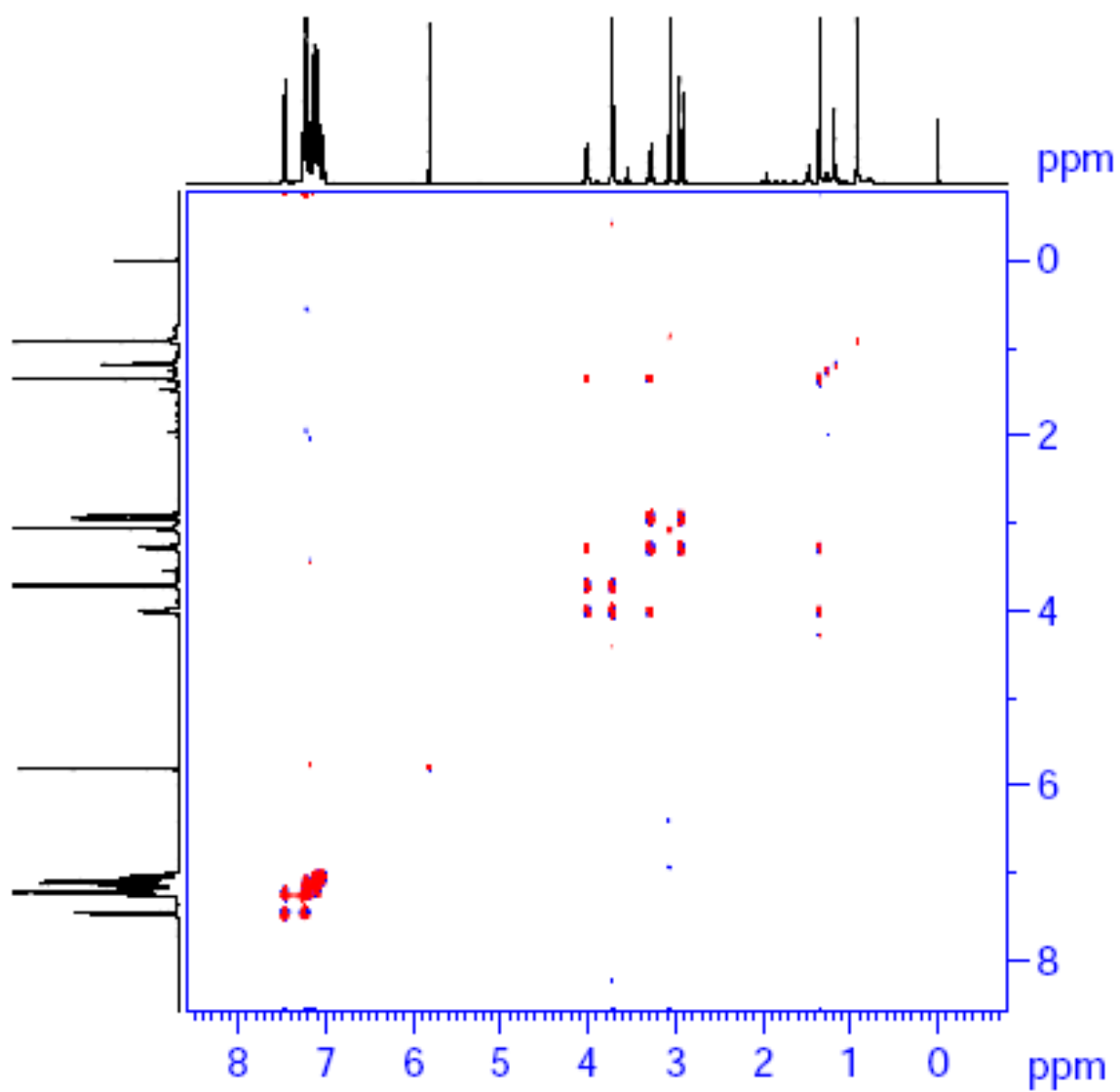


Figure S6: Schematic representation of the chemical structure and observed characteristic NOE correlations of compound-**4a'**.

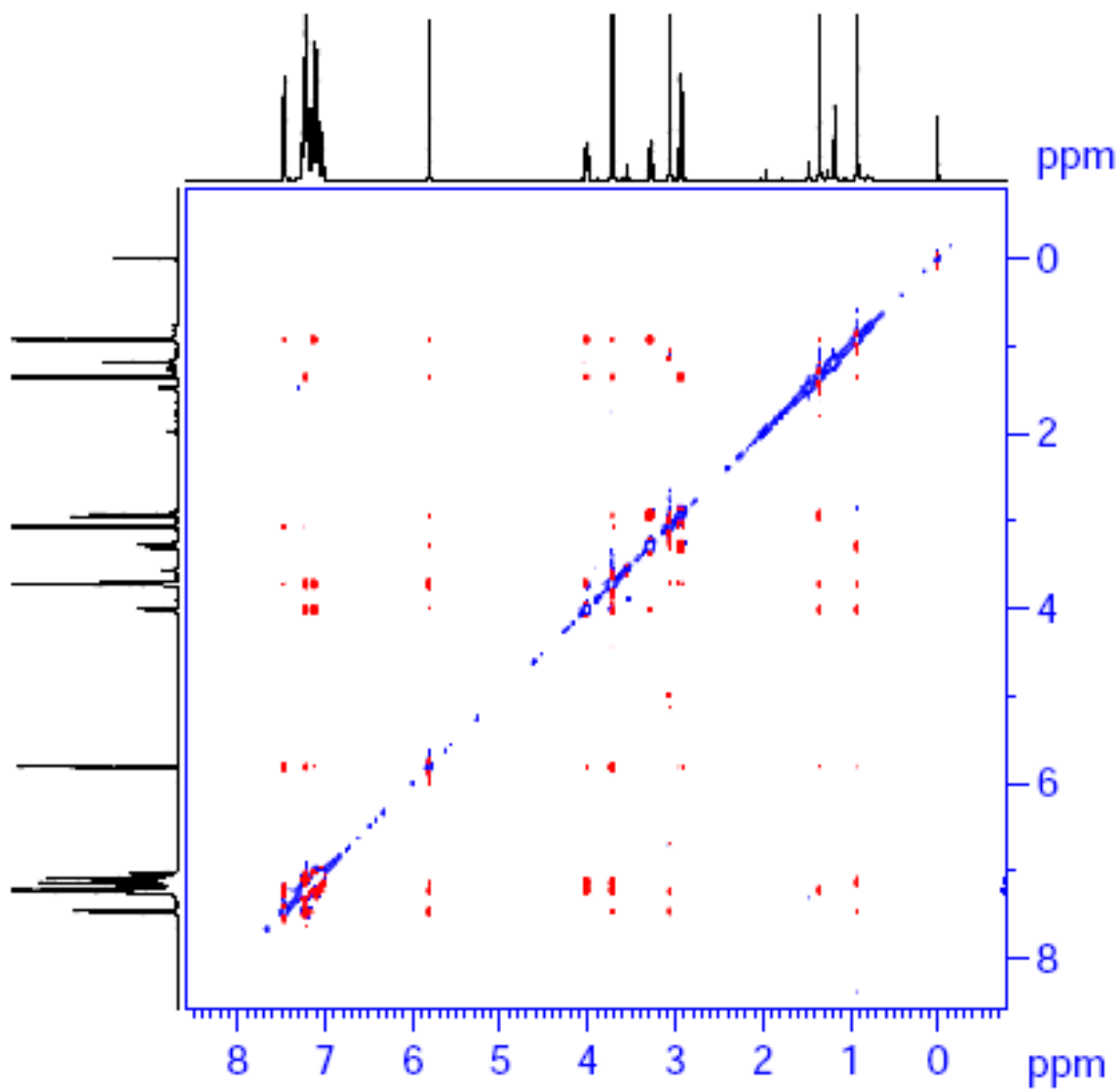
The observed strong NOE cross peaks between Me-13/H-3_{ax} and Me-13/Ar-H (ortho) protons indicate that these groups are in 1,3-diaxial relationship in a chair conformation of 6-membered ring as shown in Fig S6. The characteristic NOE correlation between Me-13 and H-6 protons and strong scalar coupling $^3J_{\text{H-6/H-7}} = 9.6$ Hz indicate that H-6 and H-7 protons are in *anti* orientation.

Table S6: ^1H and ^{13}C NMR spectral data of compound-**4a'** (CDCl_3 , 298 K).

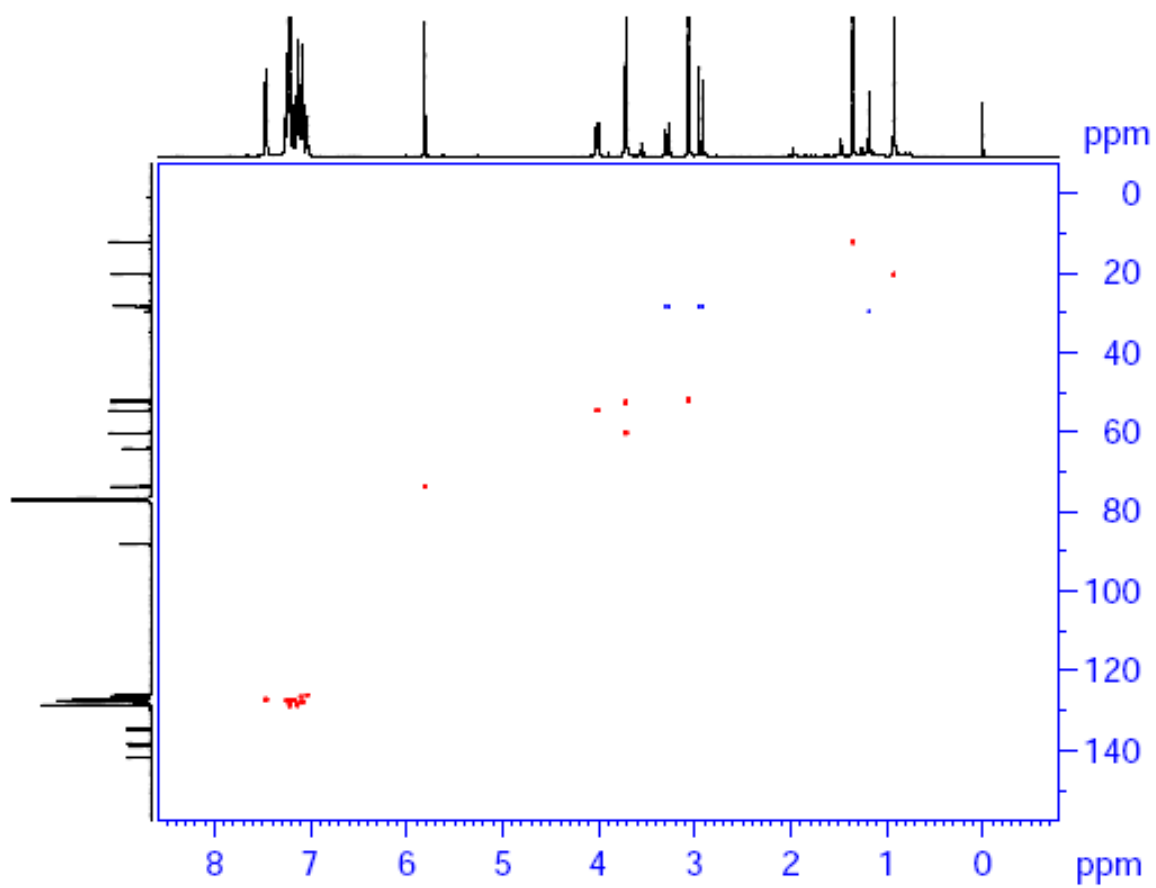
Position	^1H		^{13}C chemical shift δ (ppm)
	Chemical shift δ (ppm)	Scalar coupling J (Hz)	
Aromatic	7.40-7.00 (15H, m)	-	-
1	5.8 (1H, s)	-	73.7
6	4.01 (1H, m)	-	54.6
10	3.72 (3H, s)	-	52.6
7	3.72 (1H, d)	9.6	60.2
3 _{ax}	3.29 (1H, m)	-	28.5
12	3.06 (3H, s)	-	52.0
3 _{eq}	2.93 (1H, d)	13.9	28.5
14	1.35 (3H, m)	-	12.2
13	0.92 (3H, s)	-	20.4
2	-	-	64.1
4	-	-	134.9
5	-	-	134.7
9	-	-	172.0
11	-	-	169.8



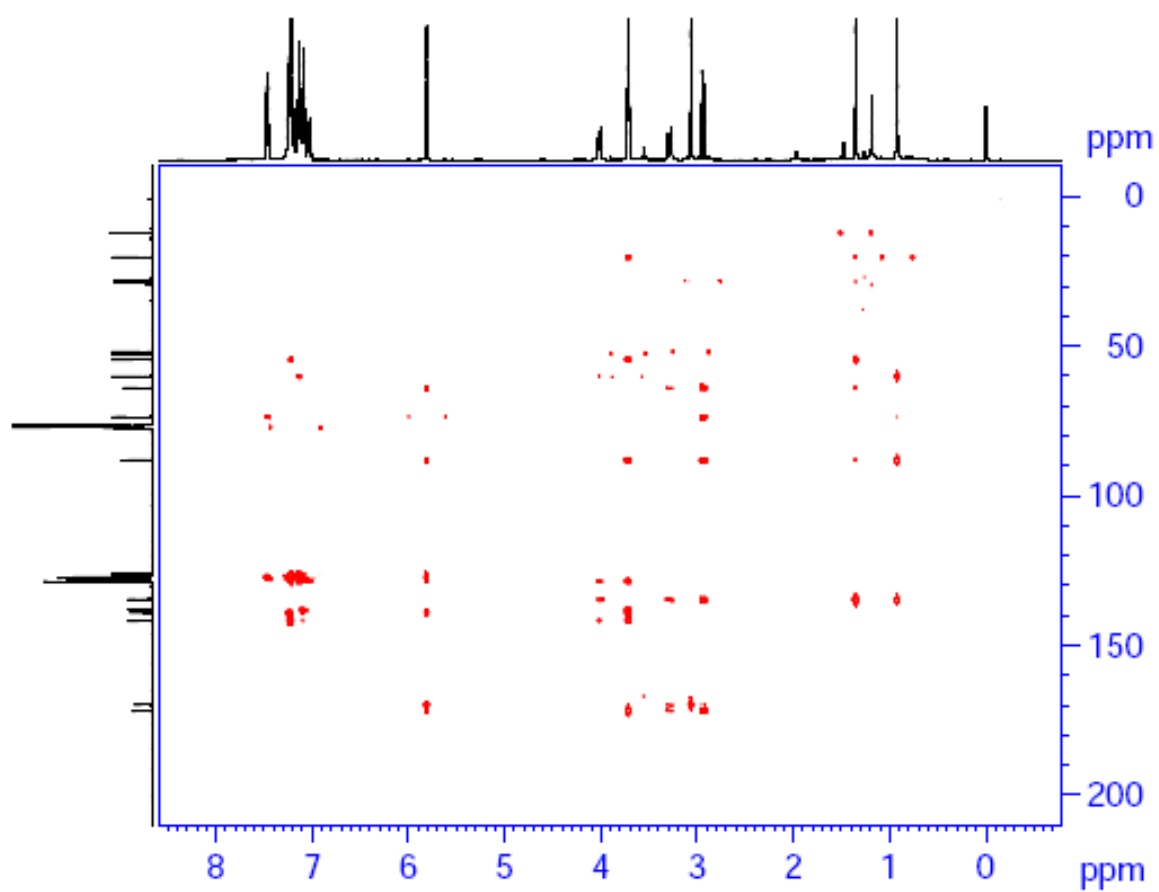
^1H - ^1H DQFCOSY (Double-quantum Filtered Correlation Spectroscopy) spectrum of compound-**4a'** (CDCl_3 , 298 K)



^1H - ^1H NOESY (Nuclear Overhauser Effect Spectroscopy) spectrum of compound-**4a'** (CDCl_3 , 298 K)



^{13}C - ^1H HSQC (Heteronuclear Single Quantum Correlation) spectrum of compound-**4a'** (CDCl_3 , 298 K)



^{13}C - ^1H HMBC (Heteronuclear Multiple Bond Correlation) spectrum of compound-**4a'** (CDCl_3 , 298 K)

(±)- (2*R*,6*S*,7*S*,7*aR*)-Dimethyl 2-isopropyl-5,7*a*-dimethyl-6,7-diphenyl-4,6,7,7*a*-tetrahydrocyclopenta[*b*]pyran-3,3(2*H*)-dicarboxylate (**4h**):

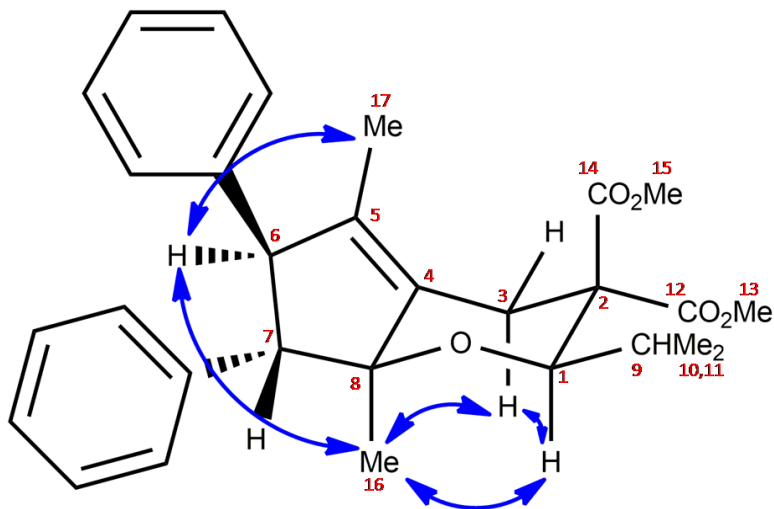


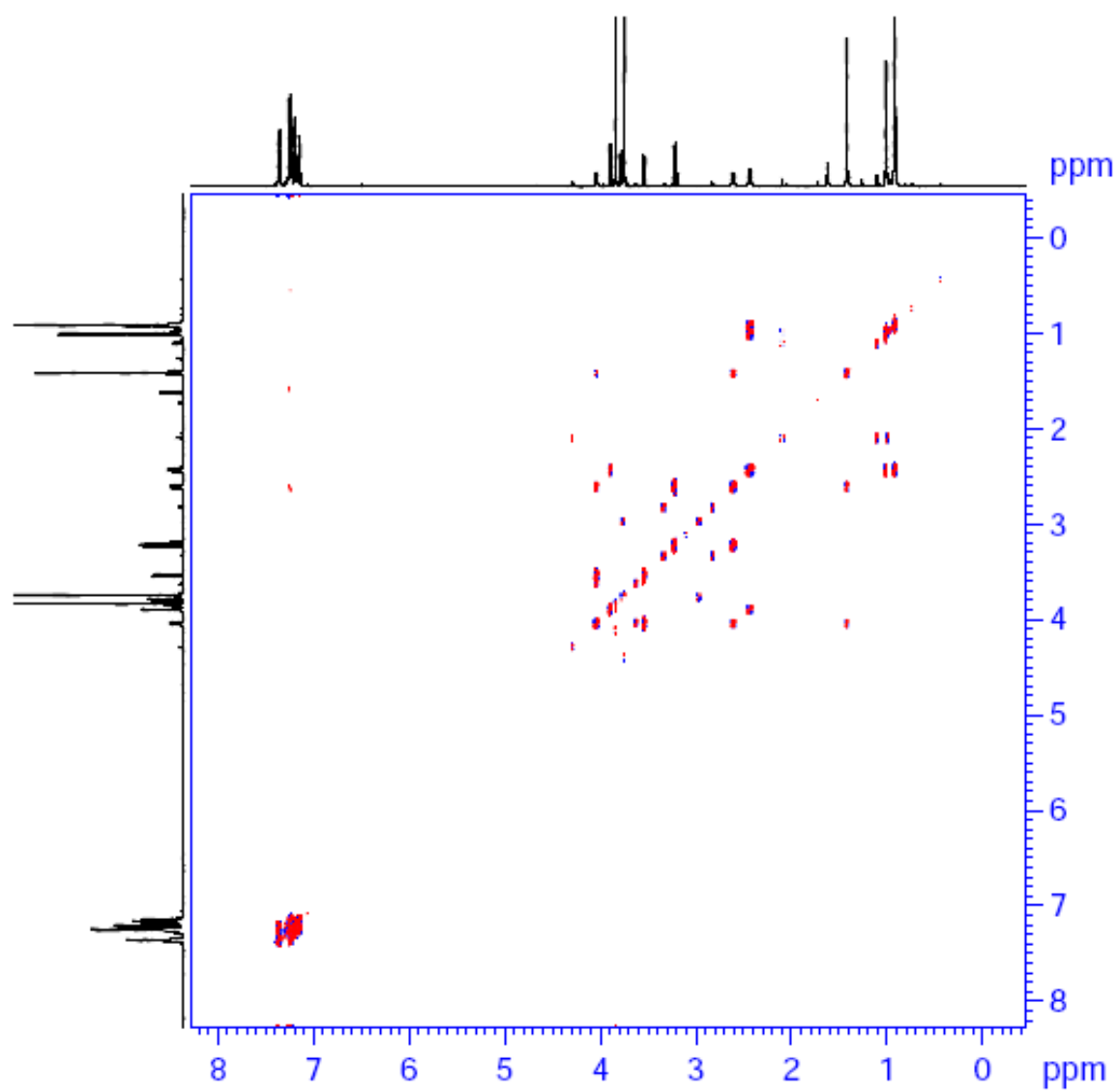
Figure S7: Schematic representation of the chemical structure and observed characteristic NOE correlations of compound-**4h**.

The complete assignment of ^1H and ^{13}C chemical shifts of compound-**4h** is given in Table S6. ^1H NMR spectrum of compound-**4h** shows the presence of two isomers with 90:10 ratio. Structure and relative stereochemistry of the major isomer was unambiguously assigned as shown in Fig.S7.

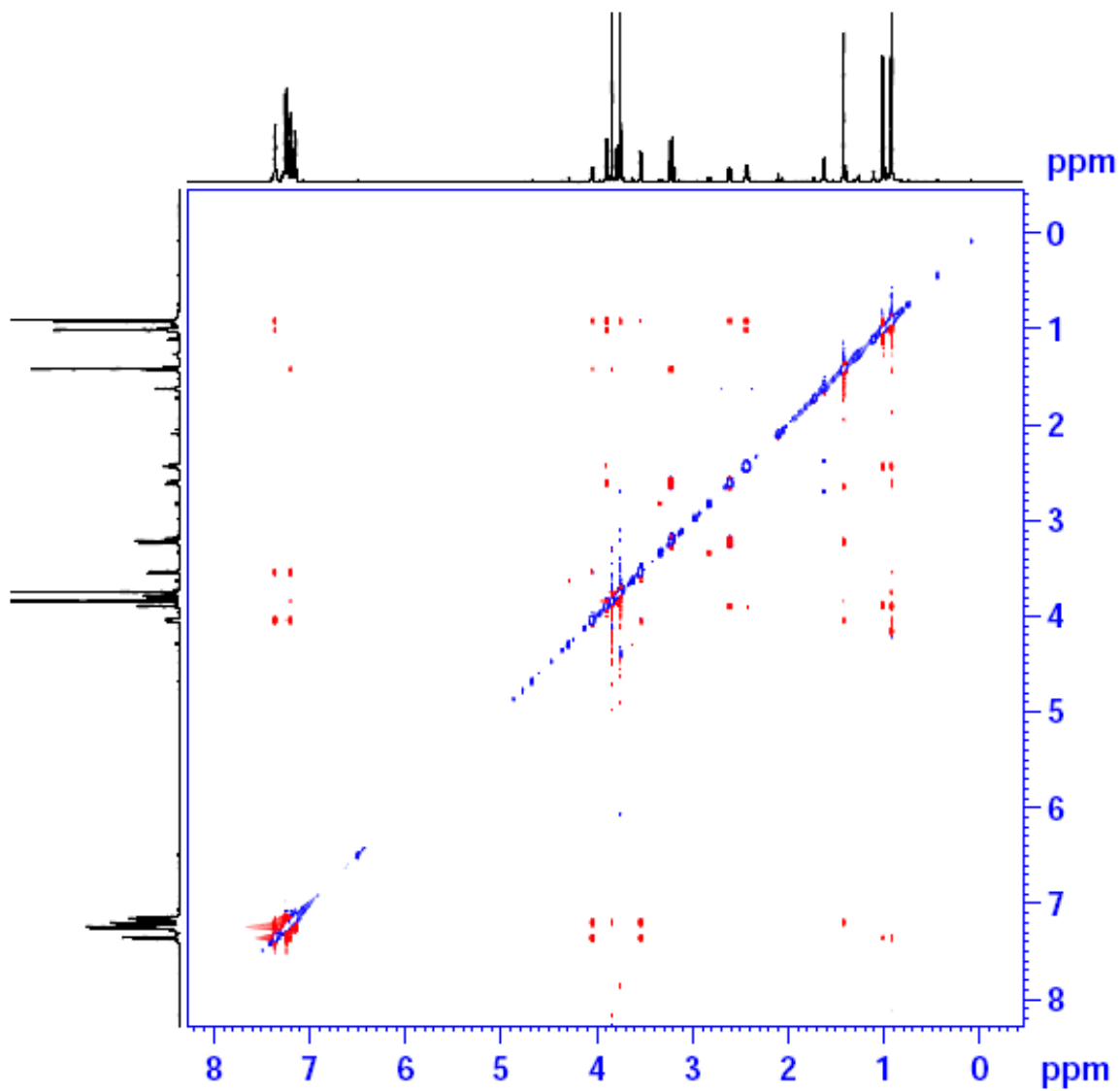
In major isomer, the multiplet at 2.35 ppm is assigned as H-9 from the observed COSY cross peaks between Me-10/H-9 and Me-11/H-9 protons. H-1 proton is appeared as a doublet at 3.81 ppm. The observed strong NOE cross peaks between Me-16/H-1, Me-16/H-3_{ax}, and H-3_{ax}/H-1 clearly suggest that these protons are in 1,3-diaxial relationship in a chair conformation of 6-membered ring as shown in Fig.S7. The characteristic NOE correlation between Me-16 and H-6 protons and strong scalar coupling $^3J_{\text{H-6/H-7}} = 10.0$ Hz indicate that H-6 and H-7 protons are in *anti* relationship.

Table S7: ^1H and ^{13}C NMR spectral data of compound-**4h** (CDCl_3 , 298 K).

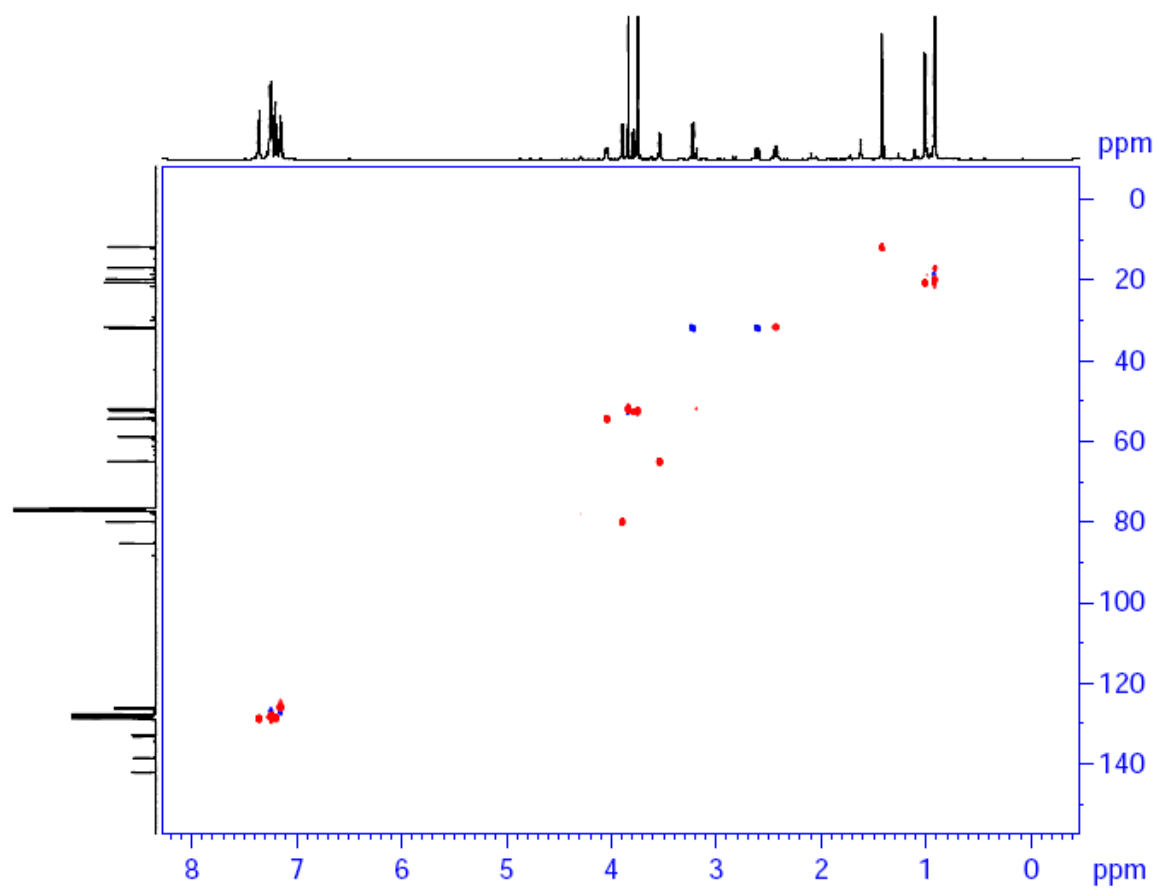
Position	^1H		^{13}C chemical shift δ (ppm)
	Chemical shift δ (ppm)	Scalar coupling J (Hz)	
Aromatic	7.33-7.00 (10H, m)	-	-
6	3.96 (1H, m)	-	54.3
1	3.81 (1H, d)	7.7	80.0
13	3.76 (3H, s)	-	52.0
15	3.67 (3H, s)	-	52.5
7	3.46 (1H, d)	10.0	65.0
3 _{eq}	3.14 (1H, d)	13.8	32.0
3 _{ax}	2.53 (1H, m)	-	32.0
9	2.35 (1H, m)	-	31.7
17	1.34 (3H, m)	-	11.8
11	0.93 (3H, d)	6.6	20.6
10	0.84 (3H, d)	5.9	19.7
16	0.83 (3H, s)	-	17.0
2	-	-	59.0
4	-	-	133.0
5	-	-	133.3
8	-	-	85.3
12	-	-	169.3
14	-	-	172.0



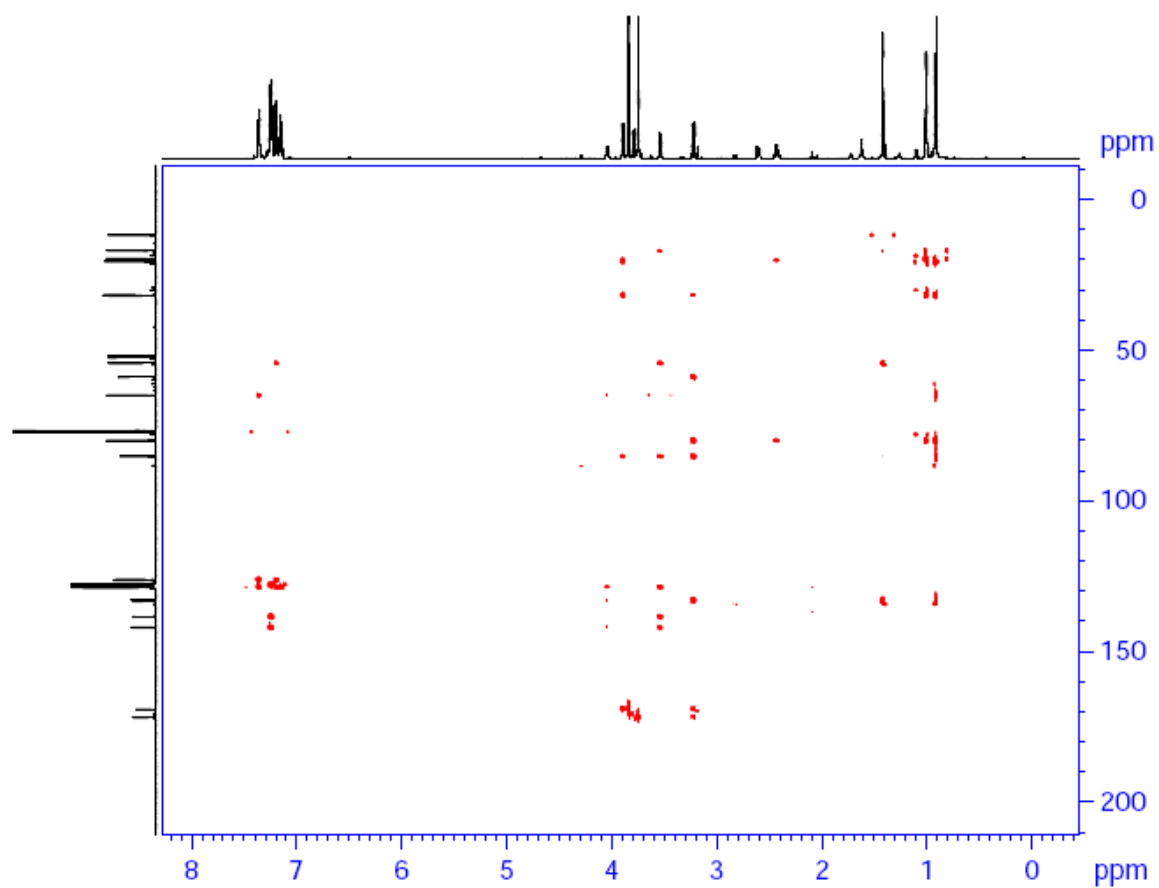
^1H - ^1H DQFCOSY (Double-quantum Filtered Correlation Spectroscopy) spectrum of compound-**4h** (CDCl_3 , 298 K)



^1H - ^1H NOESY (Nuclear Overhauser Effect Spectroscopy) spectrum of compound-**4h** (CDCl_3 , 298 K)



^{13}C - ^1H HSQC (Heteronuclear Single Quantum Correlation) spectrum of compound-**4h** (CDCl_3 , 298 K)



^{13}C - ^1H HMBC (Heteronuclear Multiple Bond Correlation) spectrum of compound-**4h** (CDCl_3 , 298 K)

Compound 5a:

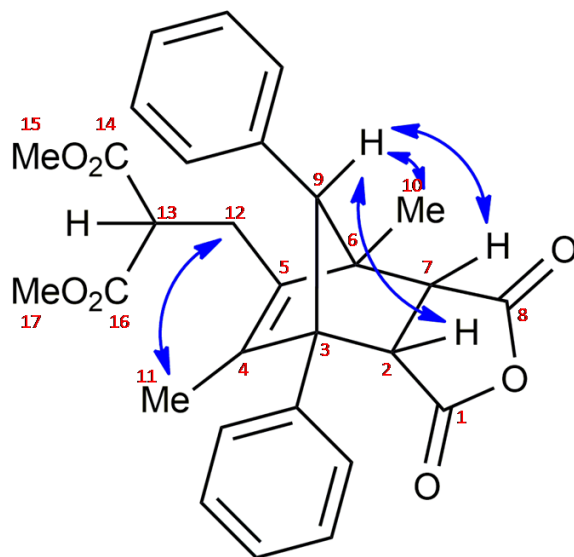
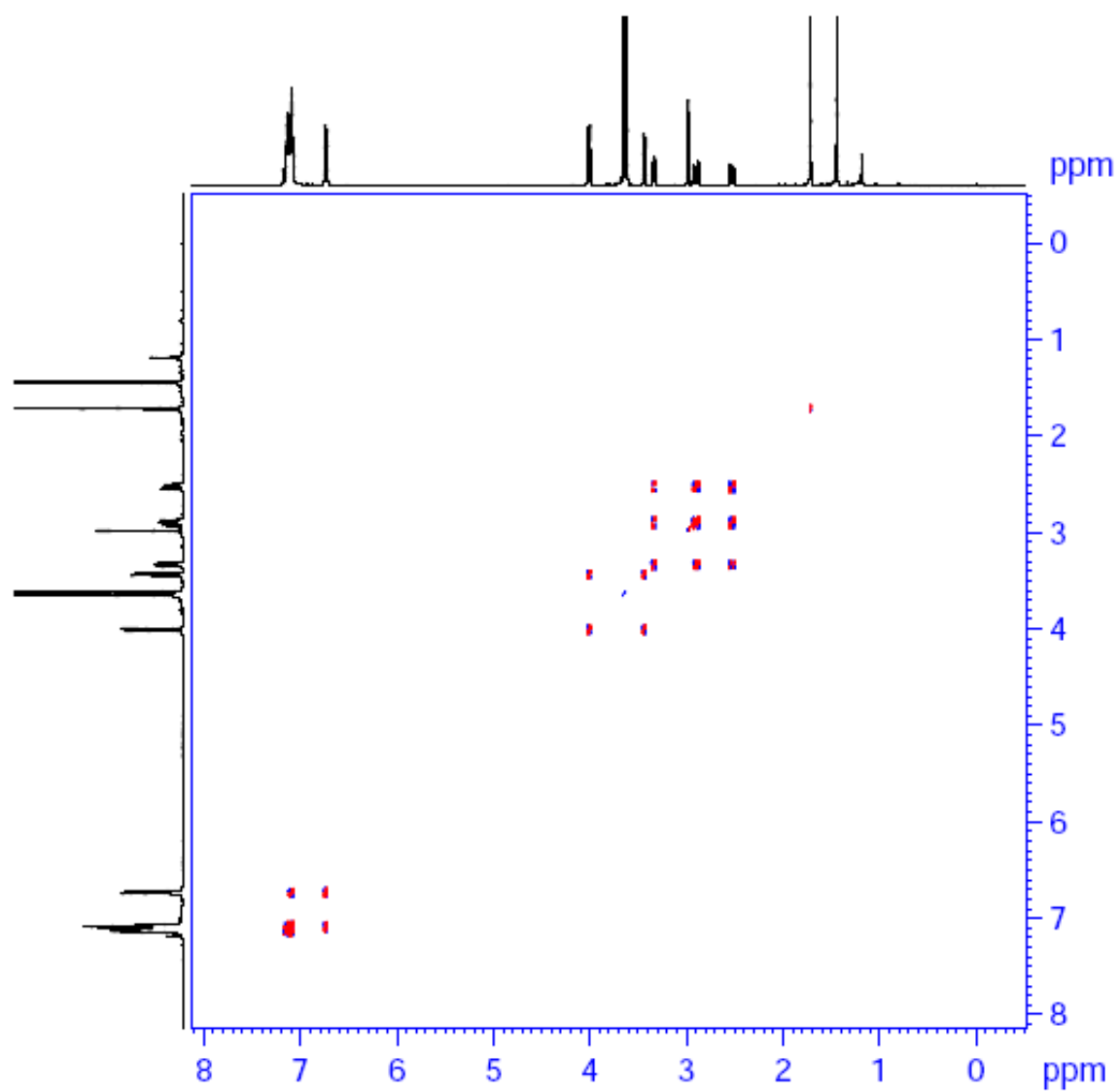


Figure S8: Schematic representation of the chemical structure and observed characteristic NOE correlations of compound-**5a**.

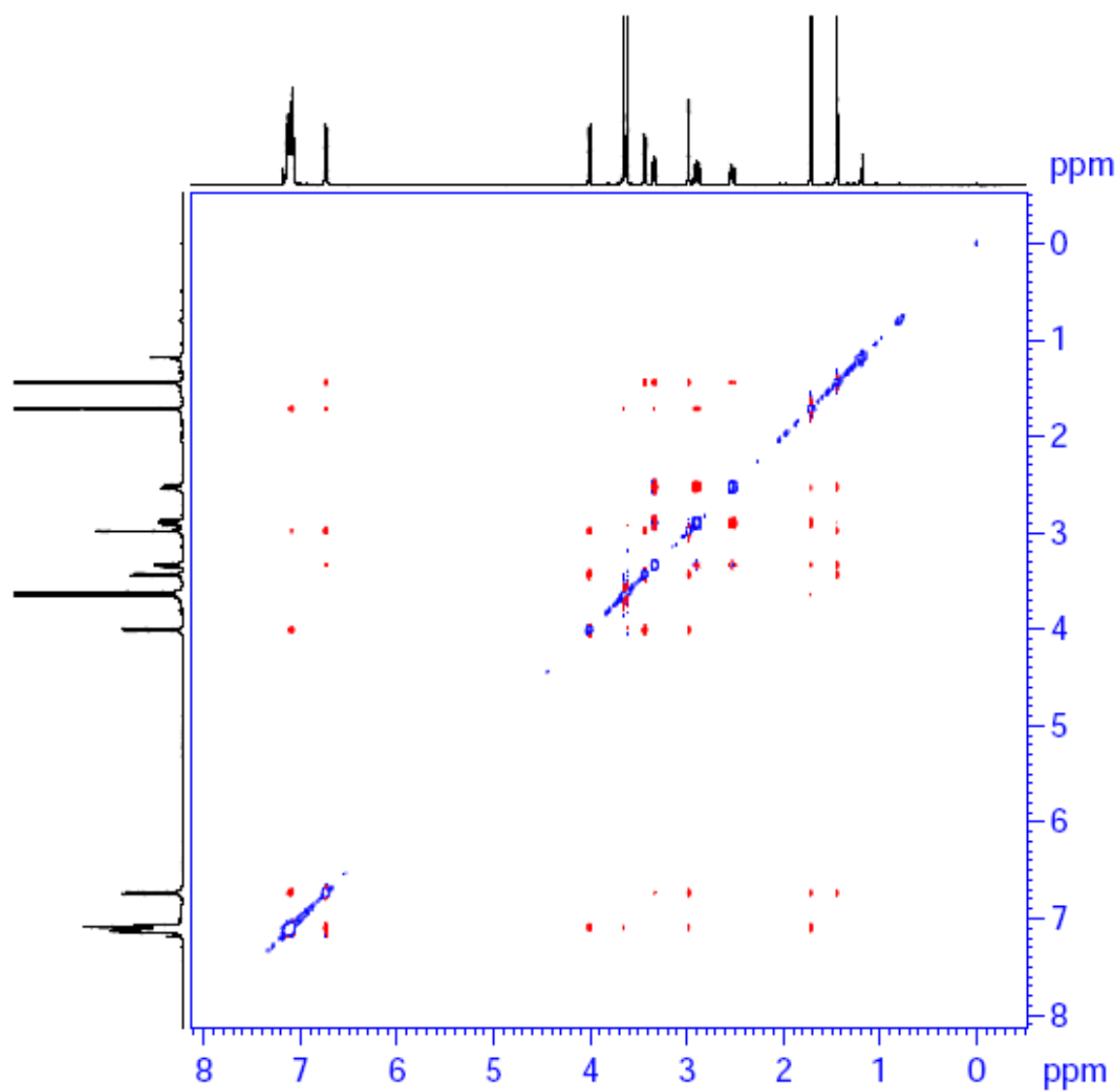
The complete assignment of ¹H and ¹³C chemical shifts of compound-**5a** is given in Table S7. In compound-1453, H-9 proton appeared as a singlet at 2.98 ppm. The protons H-2 and H-7 appeared as doublets at 4.00 and 3.43 ppm, respectively. The observed characteristic NOE correlations between H-2/H-9, H-7/H-9, H-9/Me-10, and H-7/Me-10 strongly support that the compound-1453 exist as an *endo* isomer as shown in Fig.S8.

Table S8: ^1H and ^{13}C NMR spectral data of compound-1453 (CDCl_3 , 298 K).

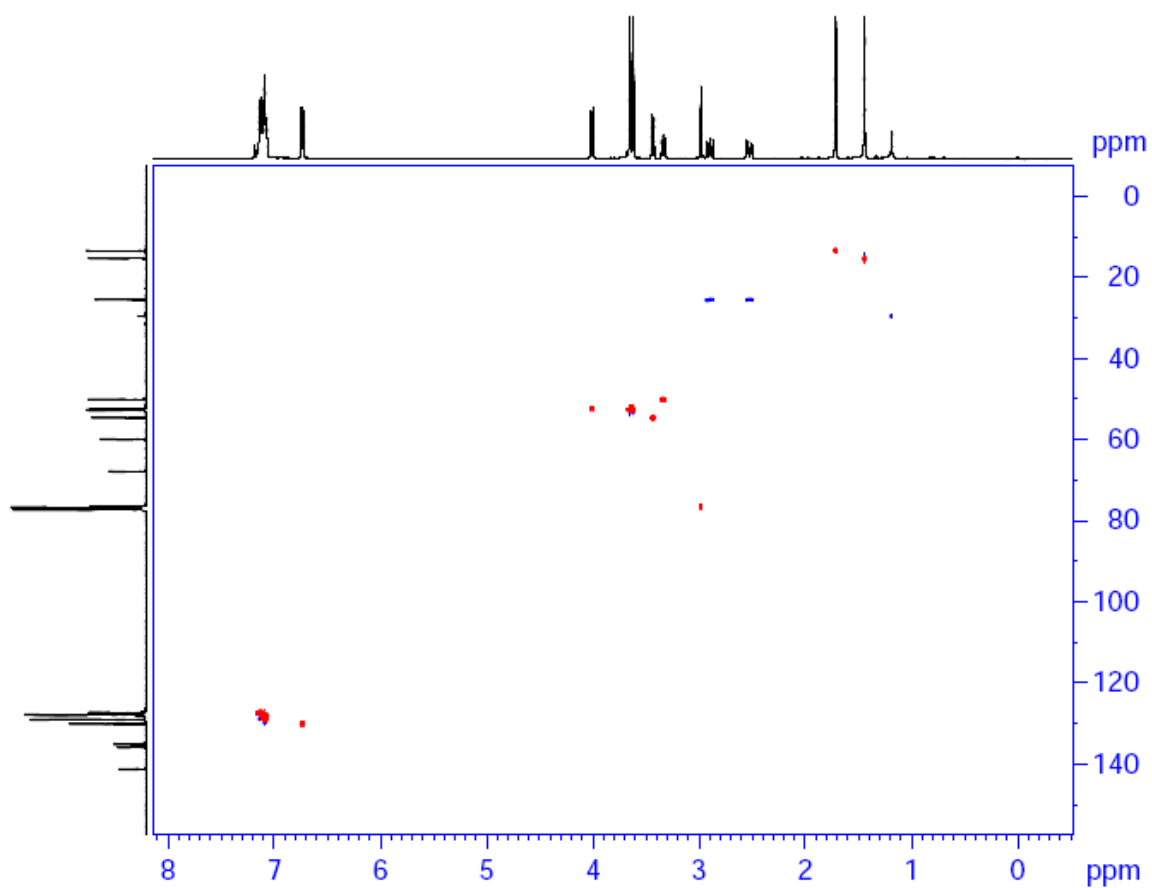
Position	^1H		^{13}C chemical shift δ (ppm)
	Chemical shift δ (ppm)	Scalar coupling J (Hz)	
Aromatic	7.20-7.05 (8H, m)	-	-
Aromatic	6.76-6.70 (2H, m)	-	-
2	4.00 (1H, d)	8.0	52.5
15	3.65 (3H, s)	-	52.7
17	3.62 (3H, s)	-	52.8
7	3.43 (1H, d)	8.0	54.6
13	3.33 (1H, dd)	8.5, 5.6	50.1
9	2.98 (1H, s)	-	76.5
12	2.90 (1H, dd)	14.7, 8.5	25.5
12'	2.52 (1H, dd)	14.7, 5.6	25.5
11	1.71 (3H, s)	-	13.5
10	1.44 (3H, s)	-	15.4
1	-	-	170.0
3	-	-	67.9
4	-	-	141.2
5	-	-	135.1
6	-	-	60.0
8	-	-	170.6
14	-	-	169.0
16	-	-	168.9



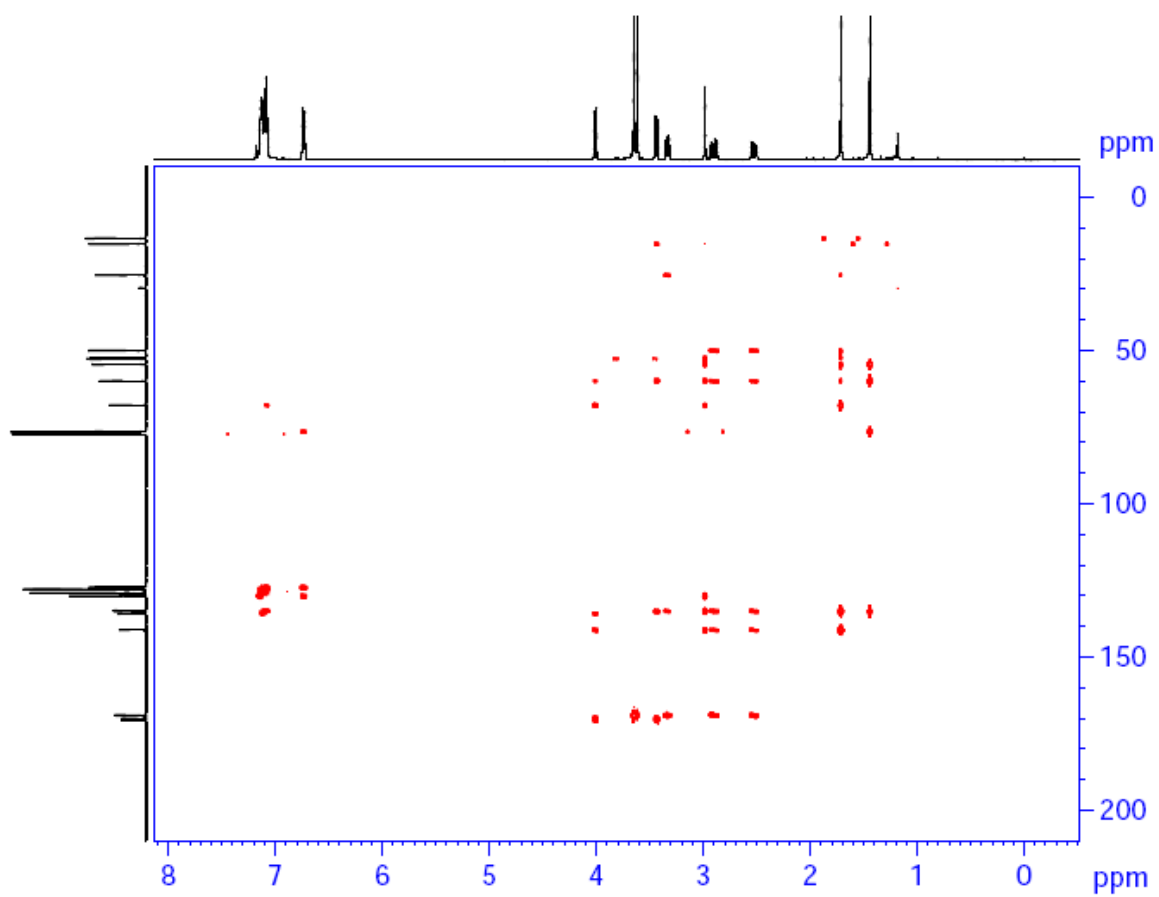
^1H - ^1H DQFCOSY (Double-quantum Filtered Correlation Spectroscopy) spectrum of compound-**5a** (CDCl_3 , 298 K)



^1H - ^1H NOESY (Nuclear Overhauser Effect Spectroscopy) spectrum of compound-**5a** (CDCl_3 , 298 K)



^{13}C - ^1H HSQC (Heteronuclear Single Quantum Correlation) spectrum of compound-**5a** (CDCl_3 , 298 K)



^{13}C - ^1H HMBC (Heteronuclear Multiple Bond Correlation) spectrum of compound-**5a** (CDCl_3 , 298 K)

9. X-ray Crystallography Information

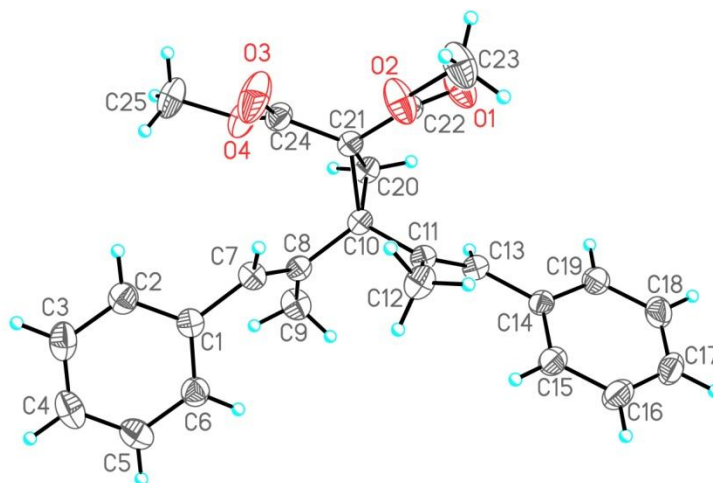


Figure caption: The molecular structure of **1p** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for 1p: $C_{25}H_{26}O_4$, $M = 390.46$, crystal size $0.42 \times 0.40 \times 0.35 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.9916(1)$, $b = 16.6891(15)$, $c = 12.3742(11) \text{ \AA}$, $\alpha = 90$, $\beta = 108.465(2)$, $\gamma = 90^\circ$, $V = 2153.1(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.204 \text{ g/cm}^3$, $F_{000} = 832$, CCD area detector, MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 293(2) \text{ K}$, $2\theta_{\text{max}} = 55^\circ$, 24372 reflections collected, 4931 unique ($R_{\text{int}} = 0.031$), Final $Goof = 1.05$, $R1 = 0.0606$, $wR2 = 0.1584$, R indices based on 3666 reflections with $I > 2\sigma(I)$ (refinement on F^2), 266 parameters, $\mu = 0.081 \text{ mm}^{-1}$, Min. and Max. Resd. Dens. = $-0.28, 0.49 \text{ e/\AA}^3$. CCDC **1550328** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>

Data collection and structure solution of 1p: X-ray data for the compound was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK α radiation ($\lambda=0.71073\text{\AA}$) with ω -scan method.¹³ Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 5560 reflections for BE39 data. Integration and scaling of intensity data were accomplished using SAINT program.¹³ The structures were solved by Direct Methods using SHELXS97¹⁴ and refinement was carried out by full-matrix least-squares technique using SHELXL 2014/7.¹⁴⁻¹⁵ Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}$ for methyl atoms.

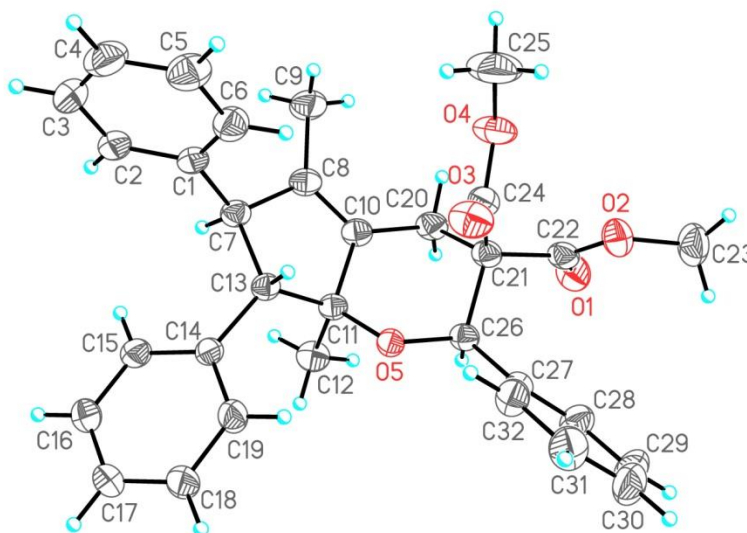


Figure caption: The molecular structure of **4a** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for 4a: $C_{32}H_{32}O_5$, $M = 496.51$, crystal size $0.34 \times 0.28 \times 0.22 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.262(4)$, $b = 16.508(6)$, $c = 15.548(5) \text{ \AA}$, $\alpha = 90$, $\beta = 107.246(7)$, $\gamma = 90^\circ$, $V = 2760.6(17) \text{ \AA}^3$, $Z = 4$, $D_c = 1.195 \text{ g/cm}^3$, $F_{000} = 1056$, PHOTON 100 area detector, MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 293(2) \text{ K}$, $2\theta_{\text{max}} = 52^\circ$, 22077 reflections collected, 5404 unique ($R_{\text{int}} = 0.034$), Final $GooF = 1.03$, $R1 = 0.0491$, $wR2 = 0.1384$, R indices based on 5404 reflections with $I > 2\sigma(I)$ (refinement on F^2), 338 parameters, $\mu = 0.080 \text{ mm}^{-1}$, Min. and Max. Resd. Dens. = $-0.18, 0.16 \text{ e/\AA}^3$. CCDC **1567507** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>

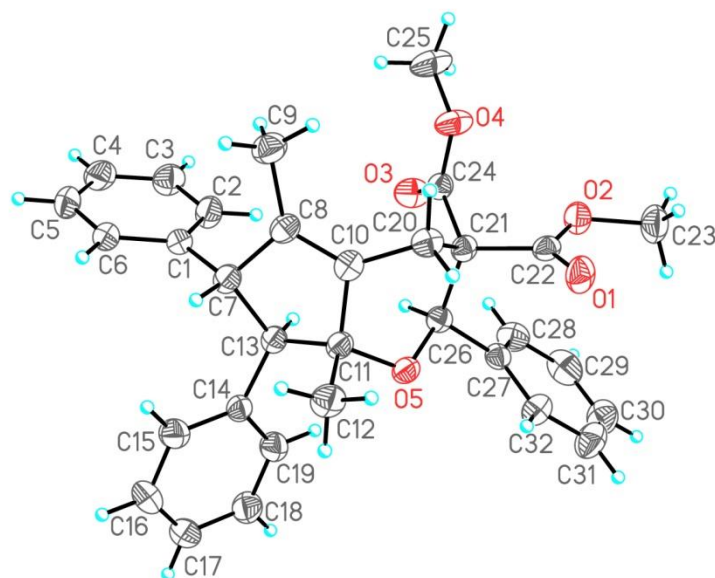


Figure caption: The molecular structure of **4a'** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for 4a': C₃₂H₃₁NO₇, $M = 496.5$, crystal size 0.43 x 0.40 x 0.29 mm³, orthorhombic, space group $Pca2_1$ (No. 29), $a = 16.045(3)$, $b = 16.266(4)$, $c = 20.695(5)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 5401(2)$ Å³, $Z = 4$, $D_c = 1.221$ g/cm³, $F_{000} = 2112$, PHOTON 100 detector, MoK α radiation, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $2\theta_{\max} = 52^\circ$, 27490 reflections collected, 10271 unique ($R_{\text{int}} = 0.040$), Final $GooF = 1.04$, $RI = 0.0505$, $wR2 = 0.1275$, R indices based on 7394 reflections with $I > 2\sigma(I)$ (refinement on F^2), 675 parameters, $\mu = 0.082$ mm⁻¹, Min. and Max. Resd. Dens. = -0.19, 0.34 e/Å³. CCDC **1567508** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>

Data collection and structure solution of 4a and 4a': Single crystal X-ray data for two compounds were collected at room temperature on a Bruker D8 QUEST equipped with a four circle kappa diffractometer and Photon 100 detector. An I μ s microfocus Mo source ($\lambda = 0.71073$ Å) supplied the multi-mirror monochromated incident beam. A combination of Phi and Omega scans were used to collect the necessary data. Unit cell dimensions were determined using 8269 reflections for **4a** and 9981 reflection for **4a'** data sets. Integration and scaling of intensity data were accomplished using SAINT program.¹³ The structures were solved by Direct Methods using SHELXS97² and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7.¹⁴⁻¹⁵ Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms with C-H distances of 0.93--0.97 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}$ for methyl atoms.

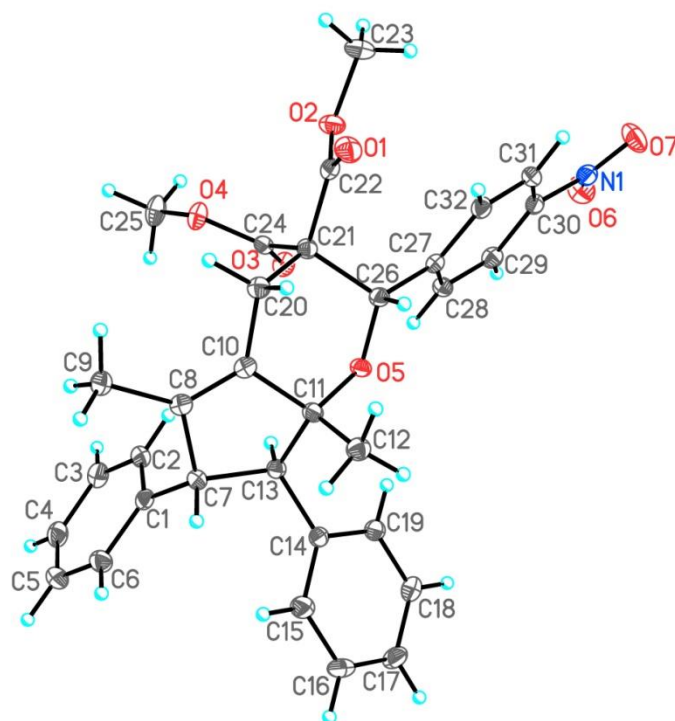


Figure caption: The molecular structure of **4e** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for 4e: $C_{32}H_{31}NO_7$, $M = 541.58$, crystal size $0.40 \times 0.30 \times 0.12 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.548(3)$, $b = 19.304(5)$, $c = 13.589(3) \text{ \AA}$, $\alpha = 90$, $\beta = 115.034(6)$, $\gamma = 90^\circ$, $V = 2744.7(12) \text{ \AA}^3$, $Z = 4$, $D_c = 1.311 \text{ g/cm}^3$, $F_{000} = 1144$, PHOTON 100 detector, MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 100(2) \text{ K}$, $2\theta_{\text{max}} = 55^\circ$, 44764 reflections collected, 6298 unique ($R_{\text{int}} = 0.034$), Final $GooF = 1.07$, $R1 = 0.0397$, $wR2 = 0.0985$, R indices based on 6298 reflections with $I > 2\sigma(I)$ (refinement on F^2), 365 parameters, $\mu = 0.092 \text{ mm}^{-1}$, Min. and Max. Resd. Dens. = $-0.26, 0.31 \text{ e/\AA}^3$. CCDC **1550329** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>

Data collection and structure solution of 4e: Single crystal X-ray data for the compound was collected at low temperature (100K) on a Bruker D8 QUEST equipped with a four circle kappa diffractometer and Photon 100 detector. An I μ s microfocus Mo source ($\lambda=0.71073\text{\AA}$) supplied the multi-mirror monochromated incident beam. A combination of Phi and Omega scans were used to collect the necessary data. Unit cell dimensions were determined using 9867 reflections. Integration and scaling of intensity data were accomplished using SAINT program.¹³ The structures were solved by Direct Methods using SHELXS97¹⁴ and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7.¹⁴⁻¹⁵ Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms with C-H distances of 0.93--0.97 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}$ for methyl atoms.

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11. Spectral Data of All New Compounds

