

Supplementary Information

Photoredox Chromium and Cobalt Dual Catalysis for Carbonyl Allylation with Butadiene via Allyl Radical Intermediates

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1. General information

Unless otherwise noted, all reactions of substrates preparation were conducted in flame-dried glassware under a nitrogen atmosphere using anhydrous solvent passed through an activated alumina column (Innovative Technology). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Huanghai TLC silica gel plates HSG F254 and visualized using UV light, anisaldehyde or potassium permanganate. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L) with 10 W LED. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker 400M spectrometer. Chemical shifts in ^1H NMR spectra were reported in parts per million (ppm) on the $\delta =$ scale from an internal standard of residual CDCl_3 (7.26 ppm). Data for ^1H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift in ppm from the central peak of CDCl_3 (77.00 ppm). ESI mass spectra were obtained from an HPLC-Q-ToF mass spectrometer using acetonitrile as the mobile phase.

2. Picture of reaction set-up

The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L).



Figure S1 Picture of the photoreactor

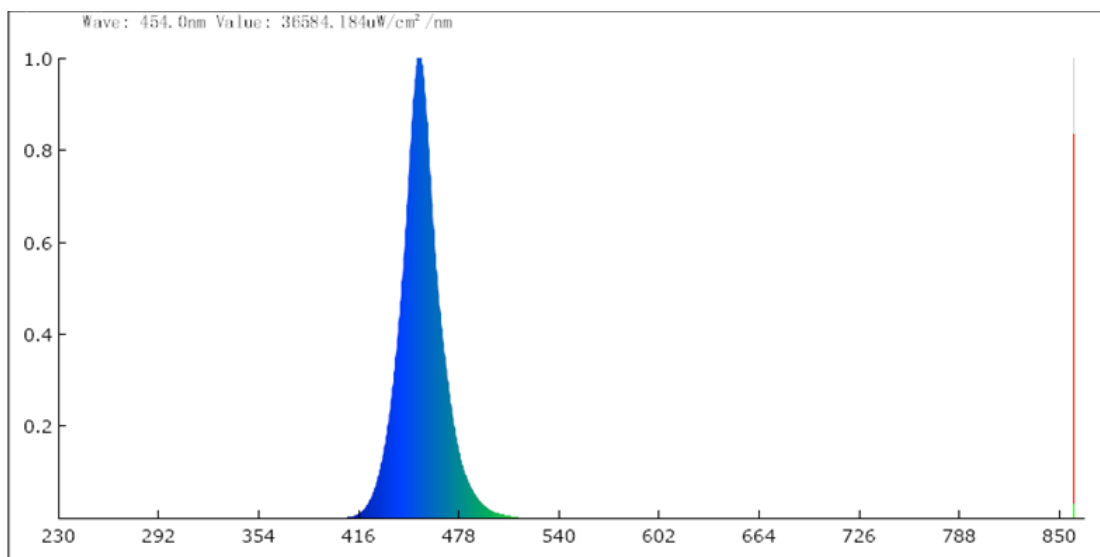
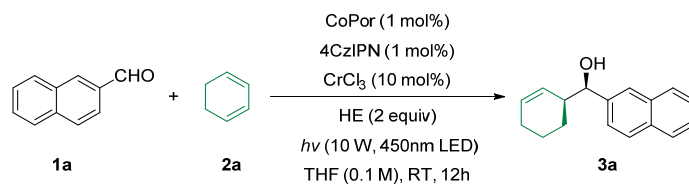


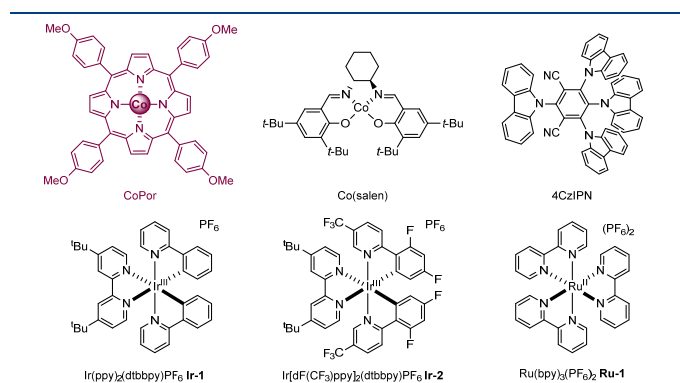
Figure S2 Emission spectra of the 10 W blue LED lamp (maximum emission at $\lambda = 454$ nm). Wave length: 450 nm-455 nm Quartz glass was used as reaction vessel. Distance between light source and quartz tube was approximately 0.5 cm and no filter was used for the reaction

3. Detailed optimizations of conditions

Table S1. Reaction Optimization ^{a, b, c}.



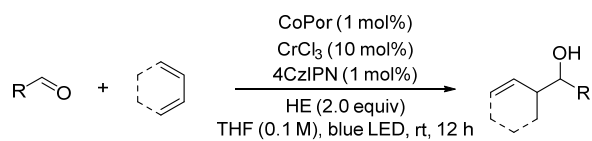
entry	variation from standard conditions	yield (%)
1	none	89
2	Vitamin B12 instead of CoPor	0
3	Co(dmgh) ₂ PyCl(II) instead of CoPor	0
4	Co(salen) instead of CoPor	0
5	CoBr ₂ (10 mol%)+dppb (10 mol%) instead of CoPor	trace
6	CoBr ₂ (10 mol%)+dppb (10 mol%) instead of CoPor+CrCl ₃	trace
7	DCM	trace
8	MeCN	74
9	DMF	33
10	PhMe	7
11	EtOH	75
12	CoPor (0.1 mol%) used	88
13	CoPor (0.01 mol%) used	30
14	Ru-1 instead of 4CzIPN	72
15	Ir-1 instead of 4CzIPN	85
16	Ir-2 instead of 4CzIPN	79
17	No <i>hν</i>	0
18	No CoPor	0
19	No CrCl ₃	0
20	No 4CzIPN	0
21	No HE	0



^aReactions were performed on a 0.2 mmol scale of **1a**, **2a** (2.0 equiv.), 4CzIPN (1 mol%), CoPor (1 mol%), CrCl₃ (10 mol%), HE (2.0 equiv.), THF (c = 0.1M), 10 W blue LEDs, RT, 12 h. ^bYields were determined by ¹H NMR spectroscopy versus dimethyl terephthalate as an internal standard.

^cDiastereomeric ratios were determined by ¹H NMR spectroscopy of crude products.

4. General procedure



General procedure : In a nitrogen-filled glovebox, a 25 mL Schlenk tube was charged with 4CzIPN (4.0 mg, 0.005 mmol, 1 mol%), CoPor (4.0 mg, 0.005 mmol, 1 mol%), CrCl₃ (7.9 mg, 0.05 mmol, 10 mol%), HE (253.3 mg, 1 mmol, 2.0 equiv.). Then the Schlenk tube was sealed with a plug and removed from glovebox. Under nitrogen atmosphere, aldehyde (0.5 mmol), diene (1.0 mmol) and THF (5 mL, 0.1 M) was sequentially added into the tube. The tube was stirred under irradiation with 450 nm LED at room temperature for 12 h. The mixture was then concentrated in vacuo. The crude product was purified by flash column chromatography (silica gel, PE/EA) to afford the desired product.

5. Theoretical calculations

Computational details: DFT calculations were performed with Gaussian 16^[1]. Geometries for intermediates and transition states were optimized in the gas phase using the ω B97XD functional^[2]. Cobalt atom was represented by the LANL2TZ(f) basis set^[3]. All atoms of 1,3-butadiene, N atoms in the porphyrin and the hydride H atom were described by 6-31G** basis set^[4]. Four substituents on the porphyrin were described by STO-3G basis set^[5]. Other atoms in the porphyrin were described by 6-31G basis set.

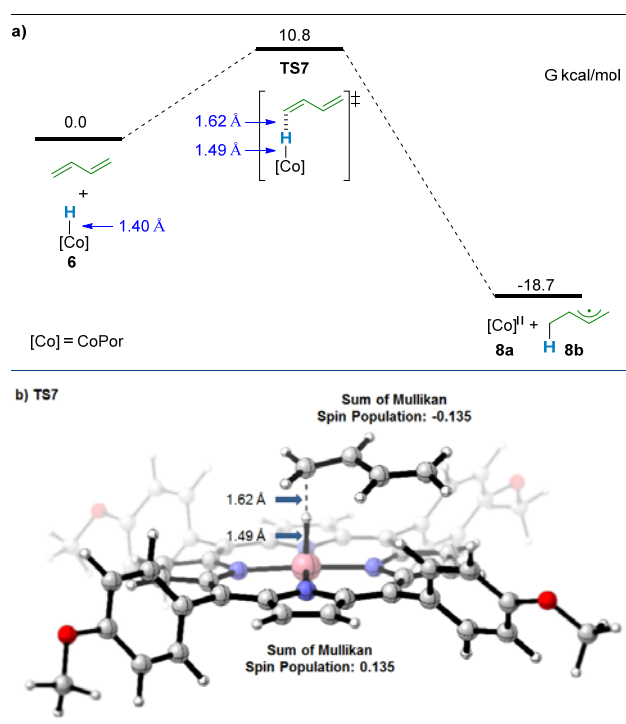


Figure S3. a) Computed energy profile of the MHAT between H- CoPor and 1,3-butadiene. b) Computed structure of the transition state TS7 of the MHAT between CoPor hydride complex and 1,3-butadiene.

Co(Por)(H)_1,3-butadiene_Reactant Adduct

SCRF in THF: -3910.196926 Hartree

Lowest frequency: 7.75 cm-1

Gibbs energy in THF: -3909.418901 Hartree

Charge: 0 Multiplicity: 1

Co	-0.08973600	0.08561100	-0.19048600
N	0.10668200	-1.87706100	-0.31610900
N	-2.04774900	-0.11284000	-0.21967200
N	-0.28584000	2.04665300	-0.21813900
N	1.86913000	0.28268200	-0.30732400
C	1.27774200	-2.60265000	-0.41656000
C	1.00219600	-4.01664900	-0.39925400
C	-0.33851000	-4.15363200	-0.24837200
C	-0.89281600	-2.82414700	-0.21398100
C	-2.25485500	-2.57448700	-0.09345400
C	-2.76969700	-1.28408500	-0.11664900
C	-4.18416500	-1.00837500	-0.08849200
C	-4.32274200	0.33802800	-0.16496100
C	-2.99375000	0.89094900	-0.24068700
C	-2.74889200	2.25862600	-0.27207000
C	-1.45839300	2.77410000	-0.24034300
C	-1.17942100	4.18748300	-0.19249000
C	0.16617500	4.31847400	-0.09029500
C	0.71866300	2.98796700	-0.12186500
C	2.08400500	2.73466400	-0.07316900
C	2.59612600	1.44726800	-0.17921000
C	4.01016500	1.17270700	-0.22509900
C	4.14454600	-0.16905300	-0.37015000
C	2.81245100	-0.71801400	-0.41586100
C	2.56597700	-2.08436100	-0.48443500
H	1.76464800	-4.77510600	-0.45428600
H	-0.93358700	-5.04933300	-0.19325700
H	-4.94017500	-1.77008000	0.00161500
H	-5.21892900	0.93473400	-0.18710300
H	-1.94150400	4.94828500	-0.19557300
H	0.76506000	5.21132600	-0.02957300
H	4.76960200	1.93059300	-0.13223100
H	5.03793800	-0.76389500	-0.45847000
C	3.02877700	3.86726000	0.07186100
C	3.10214000	4.88188700	-0.90873300
C	3.88410000	3.94085400	1.20216200
C	3.98940100	5.95819800	-0.77134200
H	2.46861500	4.80752100	-1.80143400
C	4.78298800	4.99693500	1.34081700

H	3.81497100	3.16371500	1.97396300
C	4.84243100	6.02356200	0.35758200
H	4.02296000	6.72426500	-1.54921800
H	5.44417800	5.06357700	2.21165400
C	-3.90104000	3.19097500	-0.29503000
C	-4.11360900	4.10861300	0.76726400
C	-4.81088500	3.17459900	-1.37561500
C	-5.19212300	4.99083600	0.73416400
H	-3.43056900	4.09991800	1.62575500
C	-5.90908900	4.04459300	-1.41164000
H	-4.63759400	2.47914400	-2.20660600
C	-6.10611600	4.96814400	-0.35606700
H	-5.36480800	5.70022400	1.55081500
H	-6.59096600	4.00795800	-2.26415400
C	-3.19026500	-3.71582400	0.04404100
C	-3.30293600	-4.68765000	-0.97551500
C	-3.99232300	-3.84512200	1.20777200
C	-4.17743100	-5.77514300	-0.84539400
H	-2.71004400	-4.57058500	-1.89122100
C	-4.87830300	-4.91265600	1.34093700
H	-3.89269800	-3.10233800	2.00929900
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H	-4.24212800	-6.50696800	-1.65367800
H	-5.49833700	-5.02206000	2.23734800
C	3.71662400	-3.01514700	-0.56222200
C	3.96499200	-3.94092300	0.48521700
C	4.59115700	-2.98503900	-1.67092200
C	5.04435700	-4.81926600	0.40998800
H	3.30988600	-3.94041900	1.36572800
C	5.69003500	-3.85152900	-1.74939500
H	4.38963500	-2.28208700	-2.48897900
C	5.92278200	-4.78395100	-0.70887500
H	5.24537200	-5.53484500	1.21468100
H	6.34473000	-3.80511400	-2.62248100
O	6.97231700	-5.71915300	-0.65097700
O	5.78563100	7.03175600	0.62890000
O	-7.15047200	5.90562000	-0.25634100
O	-5.90238800	-6.92123000	0.58668500
C	7.86310600	-5.65097500	-1.81176200
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H	8.63283300	-6.42396600	-1.64046500
H	7.33226600	-5.87512600	-2.75806900
C	-5.97541900	-7.92029900	-0.48204900
H	-5.00597400	-8.43270700	-0.64033200

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H	-8.57774600	4.86482800	-1.47014400
H	-8.83964200	6.62345000	-1.18622600
H	-7.57666200	6.08166000	-2.34944900
C	5.81653600	8.07637700	-0.39742200
H	6.58221900	8.79818900	-0.06265600
H	6.10737000	7.67751200	-1.38933400
H	4.84418200	8.59942500	-0.48907800
H	2.91446800	0.18926500	4.22415100
H	3.65186400	-0.18646400	2.56046600
C	2.83498000	-0.31576100	3.26386300
C	1.76514200	-1.04839800	2.94612100
H	1.71742200	-1.52724700	1.97187600
C	0.60391500	-1.24514600	3.81023500
H	0.64777200	-0.79778500	4.80323400
C	-0.48550800	-1.91813200	3.42923700
H	-0.55807800	-2.35513000	2.43628300
H	-1.33932800	-2.03651000	4.08888400
H	-0.07169700	0.06640000	1.20864300

TS-HAT'

SCRF in THF: -3910.180690 Hartree

Lowest frequency: -1743.73 cm⁻¹

Gibbs energy in THF: -3909.402062 Hartree

Charge: 0 Multiplicity: 1

Co	-0.11172600	0.43535700	-0.41186000
N	-0.36630800	-1.35186900	-1.22576200
N	-1.98008000	0.38889800	0.25323200
N	0.09591600	2.26712900	0.30633300
N	1.70725100	0.53269500	-1.18047300
C	0.58651600	-2.10938700	-1.87186300
C	0.05815400	-3.40686000	-2.21349900
C	-1.21424400	-3.44544600	-1.74981800
C	-1.47814800	-2.16275000	-1.14347500
C	-2.67695200	-1.85967700	-0.50517300
C	-2.88632400	-0.64436300	0.13684100
C	-4.11745100	-0.31678200	0.81247300
C	-3.94774200	0.90972500	1.36603900
C	-2.62023400	1.34705200	1.01168800
C	-2.09366600	2.56896600	1.41791400
C	-0.81126700	2.97646100	1.06496400
C	-0.26768600	4.25906400	1.43866900
C	0.98245300	4.32204600	0.91737200
C	1.20273700	3.08468600	0.21019000
C	2.39471100	2.79101400	-0.44322500
C	2.60558500	1.57460200	-1.08418500
C	3.84287900	1.24000200	-1.74541700
C	3.70795800	-0.02577600	-2.21282300
C	2.37621500	-0.45804300	-1.86806800
C	1.88201600	-1.71701900	-2.19100400
H	0.62824700	-4.17298100	-2.71144100
H	-1.93445900	-4.24330900	-1.80171200
H	-4.97188900	-0.97119000	0.85954300
H	-4.63937700	1.50284600	1.94010000
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H	1.70439900	5.11987200	0.96372400
H	4.69335400	1.89902400	-1.79378100
H	4.40786800	-0.62969600	-2.76528800
C	3.47938500	3.80216000	-0.44459700
C	3.27897300	5.06559000	-1.04424300
C	4.73529800	3.51920900	0.15324800
C	4.29198500	6.03424400	-1.05112400
H	2.31738900	5.27793100	-1.52839300
C	5.75676100	4.46752100	0.13689200

H	4.88622400	2.55075500	0.64597600
C	5.54633500	5.74017100	-0.46312700
H	4.10350500	6.99941300	-1.52645200
H	6.72785700	4.25756100	0.59820900
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C	-2.51409500	3.85147000	3.54724500
C	-4.14923600	3.98148800	1.74284600
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H	-3.70282500	-2.95148500	1.77185700
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H	-5.53406600	-5.04264400	-2.39782000
H	-5.27233800	-4.89725400	1.94310600
C	2.76258200	-2.67377700	-2.90463300
C	3.12261500	-3.90763300	-2.30293800
C	3.25215400	-2.37590800	-4.19588000
C	3.93842300	-4.81360700	-2.97879800
H	2.76356600	-4.13228700	-1.29087800
C	4.08901600	-3.27007900	-4.87783700
H	2.95091900	-1.43622800	-4.67552900
C	4.43668200	-4.50332000	-4.27461700
H	4.22236200	-5.76710800	-2.52039500
H	4.44763500	-3.00901000	-5.87598500
O	5.25495300	-5.50170000	-4.83544100
O	6.65754500	6.60146600	-0.40036900
O	-5.21360000	6.06409700	4.69552500
O	-6.35248600	-6.20556800	0.03556400
C	5.75511400	-5.14882000	-6.16605500
H	6.38093600	-4.23476200	-6.14732200
H	6.37757500	-6.00330000	-6.48505500
H	4.93388700	-5.00939400	-6.89662000
C	-6.86046700	-6.82057300	-1.19323500
H	-6.04423800	-7.22031900	-1.82676000

H	-7.50153500	-7.65676500	-0.86291400
H	-7.46979900	-6.11422400	-1.79103200
C	-6.47941400	6.55573600	4.14658600
H	-7.18601600	5.73152200	3.92550900
H	-6.91322000	7.19920500	4.93215600
H	-6.32964800	7.15902300	3.22943000
C	6.40588500	7.90415900	-1.02083900
H	7.34306100	8.47571300	-0.90085300
H	6.17526500	7.81389600	-2.10076200
H	5.58336000	8.45232100	-0.52037000
H	-0.18177900	-0.30468700	2.66506300
H	1.63892600	-0.41504500	2.37861400
C	0.66115300	-0.87699200	2.28451800
C	0.53771000	-2.22028700	2.06982600
H	1.41769800	-2.80295200	1.80383300
C	-0.74427200	-2.87887400	2.00520200
H	-1.60580900	-2.25054200	2.22911300
C	-0.94748700	-4.14673500	1.61714400
H	-0.12029200	-4.79765800	1.34743200
H	-1.95667000	-4.52320700	1.48428800
H	0.39935700	-0.20837900	0.82898400

Co(Por)(allyl)'

SCRF in THF: -3910.232132 Hartree

Lowest frequency: 8.19 cm-1

Gibbs energy in THF: -3909.445948 Hartree

Charge: 0 Multiplicity: 1

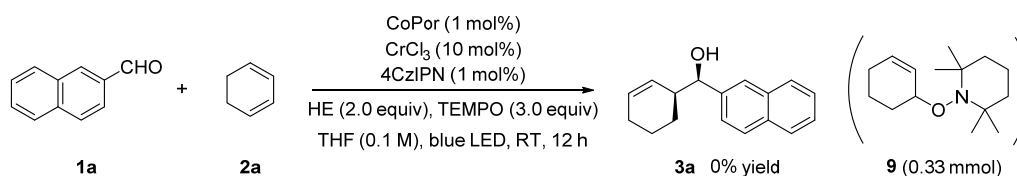
Co	-0.12997300	0.00404000	-0.12984000
N	1.76114600	0.58429900	-0.37454400
N	0.43332400	-1.88693900	-0.30585600
N	-2.03471700	-0.56494200	-0.13600500
N	-0.70592800	1.90631200	-0.16131400
H	1.58195600	1.13665000	2.44619900
C	2.24110100	1.87662300	-0.38140800
C	3.68377000	1.88030100	-0.38966400
C	4.07773600	0.58414800	-0.34089100
C	2.87749600	-0.21868900	-0.35109000
C	2.88996000	-1.61084800	-0.29516200
C	1.72168600	-2.36861800	-0.31320500
C	1.72144400	-3.81119400	-0.35514300
C	0.42326200	-4.20392600	-0.35696700
C	-0.37570700	-3.00355200	-0.32205200
C	-1.76541400	-3.02045400	-0.26051600
C	-2.52029900	-1.85404400	-0.16232100
C	-3.95908600	-1.85444900	-0.06593700
C	-4.34451000	-0.55918300	0.05341600
C	-3.14554200	0.24017900	-0.00413600
C	-3.15496700	1.63109700	0.06407300
C	-1.99092100	2.38869000	-0.02605500
C	-1.99195400	3.83115000	-0.02565800
C	-0.69940900	4.22421300	-0.14642600
C	0.09536300	3.02375600	-0.23463200
C	1.48410400	3.04194100	-0.33659100
H	4.28088900	2.77660800	-0.38501500
H	5.07343600	0.17633500	-0.31601500
H	2.61325000	-4.41516600	-0.36549100
H	0.00984500	-5.19745600	-0.39820900
H	-4.55844900	-2.74930700	-0.05863700
H	-5.33561200	-0.14748000	0.14193400
H	-2.88153900	4.42923600	0.07960900
H	-0.28855800	5.21832500	-0.19921100
C	-4.45172400	2.33440100	0.21254400
C	-5.45592100	2.20740700	-0.77354200
C	-4.70202700	3.15404000	1.34385400
C	-6.68788400	2.86249700	-0.64230400
H	-5.25244000	1.60151100	-1.66542100

C	-5.91656300	3.82494400	1.47696200
H	-3.93364200	3.23890300	2.12240200
C	-6.92839800	3.68273500	0.48708000
H	-7.44062500	2.74439000	-1.42491800
H	-6.11867900	4.45644700	2.34891500
C	-2.46474600	-4.32776500	-0.27891500
C	-3.26435900	-4.73849700	0.81963500
C	-2.34282600	-5.18783300	-1.39315300
C	-3.92805300	-5.96396700	0.79260600
H	-3.33781100	-4.08803800	1.70005000
C	-2.99031400	-6.43047100	-1.42440600
H	-1.74517900	-4.86178300	-2.25364500
C	-3.79600000	-6.82833100	-0.32969200
H	-4.54473100	-6.28926700	1.63748900
H	-2.87659200	-7.06883200	-2.30335000
C	4.19213700	-2.30494100	-0.16516500
C	5.22099900	-2.12213700	-1.11714100
C	4.44307900	-3.14178300	0.95803600
C	6.48200300	-2.70974100	-0.94573000
H	5.01656100	-1.52487800	-2.01414800
C	5.69385600	-3.73742800	1.13564000
H	3.64023700	-3.31701000	1.68442500
C	6.73390500	-3.51823100	0.19092300
H	7.25236300	-2.54699800	-1.70311900
H	5.89382400	-4.37606000	2.00310300
C	2.17816900	4.35283600	-0.36556000
C	3.06992000	4.72411900	0.67429000
C	1.95651200	5.25550200	-1.42913700
C	3.72756500	5.95270900	0.63749900
H	3.22086000	4.03973600	1.51843000
C	2.59682800	6.50180100	-1.46764900
H	1.28417400	4.96140200	-2.24486100
C	3.49583000	6.85981800	-0.43363000
H	4.41579900	6.24748300	1.43710200
H	2.40419900	7.17446100	-2.30636300
O	4.21672500	8.06484800	-0.33902500
O	-8.10565000	4.40611700	0.75331900
O	-4.51138400	-8.03508300	-0.21935300
O	7.94408200	-4.16563500	0.49851300
C	3.94827700	8.97929900	-1.45124400
H	2.88244400	9.27830800	-1.49706700
H	4.56392700	9.87457400	-1.25423100
H	4.24436300	8.54669900	-2.42734500
C	8.99559500	-3.91080000	-0.48922200

H	9.24241000	-2.83350600	-0.56598100
H	9.88297900	-4.45769500	-0.12486800
H	8.72488200	-4.29263700	-1.49345800
C	-4.34729700	-8.90488200	-1.38640300
H	-3.29125000	-9.20343600	-1.53845500
H	-4.94762400	-9.80631700	-1.17107200
H	-4.72658900	-8.43312200	-2.31437900
C	-9.12902300	4.23179100	-0.28002700
H	-9.99047400	4.83838000	0.05058200
H	-8.78938900	4.59818600	-1.26895200
H	-9.44836200	3.17526900	-0.37626700
H	-0.53063300	-1.11658600	2.15593900
H	-0.84205200	0.68617500	2.17946600
C	-0.12627000	-0.11563100	2.01391100
C	1.22777100	0.10541100	2.44863300
C	2.10458100	-0.87214300	2.76769400
H	1.75484200	-1.90478900	2.74320100
C	3.54601900	-0.65010200	3.10614600
H	3.77138500	-0.94993100	4.13794700
H	4.18599000	-1.25219000	2.45059500
H	3.82338400	0.40062600	2.98213300

6. Mechanistic studies

Radical capture experiments



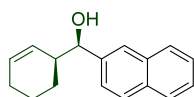
An oven-dried Schlenk tube containing a stir bar was charged with TEMPO (234 mg, 1.5 mmol, 3.0 equiv.), CoPor (4.0 mg, 0.005 mmol, 1 mol%), 4CzIPN (4.0 mg, 0.005 mmol, 1.0 mol%) and HE (253.3 mg, 1.0 mmol, 2.0 equiv.), CrCl₃ (7.9 mg, 0.05 mmol, 10 mol%) in THF (5 mL, 0.1 M) under argon. Then, **1a** (78.1 mg, 0.5 mmol, 1.0 equiv.), **2a** (1.0 mmol, 2.0 equiv.) was added. The reaction was stirred at room temperature under 450 nm LED irradiation for 12 h. Then the reaction mixture was concentrated in vacuo, the product **3a** could not be detected by ¹H NMR analysis, 0.33 mmol allyl radical adduct **9** was detected and confirmed by HRMS and NMR spectra, indicating that radical intermediate may be involved in the reaction.

¹H NMR (400 MHz, CDCl₃): δ 5.97 – 5.88 (m, 1H), 5.79 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.23 (s, 1H), 2.03 (d, *J* = 18.2 Hz, 1H), 1.90 (ddd, *J* = 16.3, 7.3, 3.6 Hz, 2H), 1.81 – 1.70 (m, 2H), 1.62 – 1.42 (m, 6H), 1.32 (m, 1H), 1.14 (m, 12H).

¹³C NMR (101 MHz, CDCl₃): δ 129.97, 128.98, 77.49, 60.05, 59.28, 40.23, 34.62, 34.26, 29.48, 25.33, 20.32, 20.21, 19.70, 17.24.

HRMS (ESI) [M+H]⁺ calculated for C₁₈H₂₉N₂O₃⁺: 238.2165, found: 238.2158.

7. Characterization of products

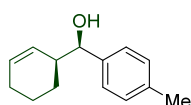


3a, $R_f = 0.7$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 94% (111.9 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.86 – 7.82 (m, 3H), 7.80 (s, 1H), 7.53 – 7.43 (m, 3H), 5.89 – 5.75 (m, 1H), 5.46 – 5.38 (m, 1H), 4.76 (d, $J = 6.5$ Hz, 1H), 2.66 – 2.53 (m, 1H), 2.07 – 1.96 (m, 2H), 1.88 (s, 1H), 1.83 – 1.66 (m, 2H), 1.64 – 1.45 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 140.26, 133.14, 132.88, 130.53, 127.96, 127.94, 127.93, 127.63, 126.03, 125.71, 125.32, 124.52, 77.43, 42.87, 25.20, 23.82, 21.09.

HRMS (ESI) $[\text{M-OH}]^+$ calculated for $\text{C}_{17}\text{H}_{17}^+$: 221.1325, found: 221.1320.

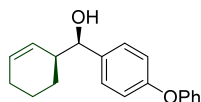


3b, $R_f = 0.7$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 78% (78.8 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.23 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 5.87 – 5.70 (m, 1H), 5.41 – 5.30 (m, 1H), 4.53 (d, $J = 6.7$ Hz, 1H), 2.53 – 2.43 (m, 1H), 2.35 (s, 3H), 2.02 – 1.95 (m, 2H), 1.88 (s, 1H), 1.75 (dd, $J = 14.3, 4.1$ Hz, 2H), 1.55 – 1.47 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 139.89, 136.99, 130.13, 128.87, 128.06, 126.43, 77.30, 42.90, 25.20, 24.00, 21.09, 21.08.

HRMS (ESI) $[\text{M-OH}]^+$ calculated for $\text{C}_{14}\text{H}_{17}^+$: 185.1325, found: 185.1321.

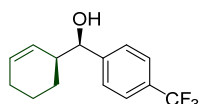


3c, $R_f = 0.5$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 83% (116.2 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.38 – 7.28 (m, 2H), 7.11 (t, $J = 7.4$ Hz, 1H), 7.01 (t, $J = 8.6$ Hz, 2H), 5.83 (dq, $J = 9.8, 3.4$ Hz, 1H), 5.45 – 5.36 (m, 1H), 4.56 (d, $J = 6.7$ Hz, 1H), 2.53 – 2.45 (m, 1H), 2.05 – 1.93 (m, 4H), 1.76 (dt, $J = 8.1, 3.7$ Hz, 2H), 1.53 (dd, $J = 11.8, 5.3$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 157.21, 156.43, 137.73, 130.38, 129.68, 127.89, 127.84, 123.16, 118.78, 118.55, 76.95, 42.99, 25.20, 23.97, 21.04.

HRMS (ESI) $[\text{M-OH}]^+$ calculated for $\text{C}_{19}\text{H}_{19}\text{O}^+$: 263.1430, found: 263.1432.

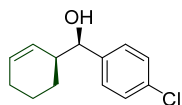


3d, $R_f = 0.6$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 62% (73.4 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.60 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 8.1$ Hz, 2H), 5.92 – 5.84 (m, 1H), 5.41 (dd, $J = 10.2, 2.5$ Hz, 1H), 4.69 (d, $J = 5.8$ Hz, 1H), 2.51 (dq, $J = 5.4, 2.7$ Hz, 1H), 2.04 – 1.96 (m, 3H), 1.78 – 1.71 (m, 1H), 1.64 – 1.46 (m, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 146.71, 131.33, 129.48 (d, J = 32.3 Hz), 127.41, 126.70, 125.08 (q, J = 3.8 Hz), 124.19 (d, J = 272.7 Hz), 76.50, 43.01, 25.12, 23.20, 21.01.

HRMS (ESI) [M-OH]⁺ calculated for C₁₄H₁₄F₃⁺: 239.1042, found: 239.1037

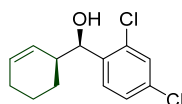


3e, R_f = 0.7 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 79% (87.7 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.31 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H), 5.87 – 5.79 (m, 1H), 5.41 – 5.35 (m, 1H), 4.59 (d, J = 6.2 Hz, 1H), 2.46 (dq, J = 6.0, 2.9 Hz, 1H), 2.03 – 1.94 (m, 2H), 1.78 – 1.70 (m, 2H), 1.68 – 1.60 (m, 1H), 1.53 – 1.45 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 141.24, 132.96, 130.90, 128.30, 127.83, 127.56, 76.58, 42.99, 25.16, 23.55, 21.03.

HRMS (ESI) [M-OH]⁺ calculated for C₁₃H₁₄Cl⁺: 205.0779, found: 205.0777

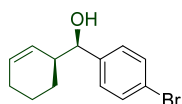


3f, R_f = 0.6 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 76% (97.7 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 2.1 Hz, 1H), 7.27 (dd, J = 8.4, 2.1 Hz, 1H), 5.97 – 5.88 (m, 1H), 5.54 – 5.47 (m, 1H), 5.07 (d, J = 4.9 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.09 – 1.99 (m, 3H), 1.82 – 1.73 (m, 1H), 1.56 – 1.46 (m, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 138.52, 133.25, 132.51, 131.45, 129.16, 128.97, 127.62, 126.93, 72.70, 40.70, 25.06, 22.67, 21.21.

HRMS (ESI) [M-OH]⁺ calculated for C₁₃H₁₃Cl₂⁺: 239.0382, found: 239.0384

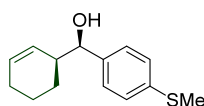


3g, R_f = 0.7 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 95% (126.4 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.48 – 7.44 (m, 2H), 7.23 – 7.19 (m, 2H), 5.84 (dq, J = 9.9, 3.5 Hz, 1H), 5.38 (dd, J = 10.2, 1.9 Hz, 1H), 4.57 (d, J = 6.2 Hz, 1H), 2.46 (dq, J = 5.7, 3.0 Hz, 1H), 2.01 – 1.94 (m, 2H), 1.82 (s, 1H), 1.78 – 1.70 (m, 1H), 1.68 – 1.60 (m, 1H), 1.52 – 1.45 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 141.77, 131.25, 130.93, 128.19, 127.54, 121.08, 76.60, 42.95, 25.16, 23.52, 21.02.

HRMS (ESI) [M-OH]⁺ calculated for C₁₃H₁₄Br⁺: 249.0273, found: 249.0270

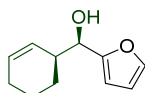


3h, $R_f = 0.5$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 90% (105.3 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.32 – 7.18 (m, 4H), 5.81 (m, 1H), 5.37 (m, 1H), 4.53 (d, $J = 6.6$ Hz, 1H), 2.48 (m, 4H), 1.98 (m, 2H), 1.93 (s, 1H), 1.78 – 1.68 (m, 2H), 1.50 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 139.81, 137.24, 130.42, 127.81, 127.03, 126.45, 76.96, 42.91, 25.17, 23.85, 21.04, 15.90.

HRMS (ESI) [M-OH] $^+$ calculated for $\text{C}_{14}\text{H}_{17}\text{S}^+$: 217.1045, found: 217.1049.

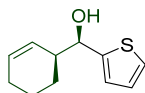


3i, $R_f = 0.6$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 60% (53.5 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.38 – 7.37 (m, 1H), 6.34 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.26 (d, $J = 3.2$ Hz, 1H), 5.84 – 5.74 (m, 1H), 5.42 – 5.33 (m, 1H), 4.53 (d, $J = 7.4$ Hz, 1H), 2.74 – 2.52 (m, 1H), 2.02 – 1.95 (m, 3H), 1.87 – 1.73 (m, 2H), 1.59 – 1.50 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 155.57, 141.77, 130.10, 127.17, 110.08, 106.76, 71.25, 40.69, 25.15, 24.42, 20.91.

HRMS (ESI) [M-OH] $^+$ calculated for $\text{C}_{11}\text{H}_{13}\text{O}^+$: 161.0960, found: 161.0961.

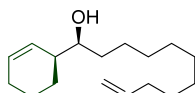


3j, $R_f = 0.6$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 55% (53.4 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.27 – 7.24 (m, 1H), 6.99 – 6.96 (m, 2H), 5.83 (dq, $J = 10.0, 3.5$ Hz, 1H), 5.51 – 5.40 (m, 1H), 4.81 (d, $J = 7.0$ Hz, 1H), 2.57 (dd, $J = 9.5, 5.1$ Hz, 1H), 2.03 – 1.97 (m, 3H), 1.90 – 1.81 (m, 1H), 1.81 – 1.71 (m, 1H), 1.60 – 1.46 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 146.77, 130.51, 127.34, 126.45, 124.61, 124.44, 73.69, 43.44, 25.20, 24.45, 21.02.

HRMS (ESI) [M-OH] $^+$ calculated for $\text{C}_{11}\text{H}_{13}\text{S}^+$: 177.0732, found: 177.0729.

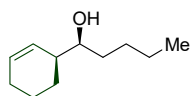


3k, $R_f = 0.6$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 85% (106.3 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 5.92 – 5.74 (m, 2H), 5.59 – 5.51 (m, 1H), 5.04 – 4.95 (m, 1H), 4.92 (d, $J = 10.1$ Hz, 1H), 3.56 (q, $J = 5.8, 4.8$ Hz, 1H), 2.20 (s, 1H), 2.10 – 1.94 (m, 4H), 1.74 (m, 2H), 1.49 (m, 5H), 1.40 – 1.23 (m, 12H).

¹³C NMR (101 MHz, CDCl₃): δ 139.19, 130.34, 128.81, 114.07, 74.54, 41.20, 33.77, 29.69, 29.54, 29.42, 29.09, 28.89, 26.08, 25.21, 22.62, 21.42.

HRMS (ESI) [M-OH]⁺ calculated for C₁₇H₂₉⁺: 233.2264, found: 233.2261.

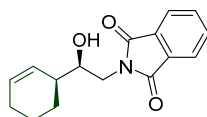


3l, R_f = 0.6 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 87% (73.1 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.95 – 5.80 (m, 1H), 5.64 – 5.49 (m, 1H), 3.57 (q, J = 5.7, 5.2 Hz, 1H), 2.21 (s, 1H), 2.03 – 1.95 (m, 2H), 1.75 (m, 2H), 1.50 (m, 5H), 1.40 – 1.26 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 130.35, 128.83, 74.53, 41.20, 33.47, 28.28, 25.22, 22.77, 22.62, 21.43, 14.05.

HRMS (ESI) [M-OH]⁺ calculated for C₁₁H₁₉⁺: 151.1481, found: 151.1481.

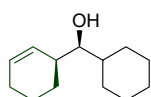


3m, R_f = 0.3 (EA:PE=1:2), column solvent: hexane/EtOAc = 4:1, 88% (119.2 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.83 (dd, J = 5.3, 3.0 Hz, 2H), 7.70 (dd, J = 5.3, 3.0 Hz, 2H), 5.90 – 5.82 (m, 1H), 5.63 (d, J = 10.1 Hz, 1H), 3.88 – 3.76 (m, 2H), 2.54 (s, 1H), 2.30 (s, 1H), 1.99 (s, 2H), 1.81 (t, J = 11.9 Hz, 4H), 1.65 – 1.49 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 168.92, 134.03, 131.91, 130.54, 127.00, 123.34, 73.13, 42.16, 39.88, 25.08, 23.32, 21.06.

HRMS (ESI) [M+Na]⁺ calculated for C₁₆H₁₇NNaO₃⁺: 294.1101, found: 294.1099.

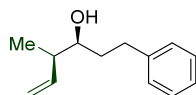


3n, R_f = 0.6 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 86% (83.4 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.87 (m, 1H), 5.52 – 5.43 (m, 1H), 3.22 (dd, J = 7.4, 4.5 Hz, 1H), 2.40 – 2.28 (m, 1H), 2.02 – 1.92 (m, 3H), 1.72 (m, 3H), 1.68 – 1.61 (m, 2H), 1.61 – 1.38 (m, 5H), 1.29 – 1.09 (m, 3H), 1.06 – 0.91 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 130.69, 129.23, 78.47, 39.69, 37.87, 29.34, 28.66, 26.41, 26.21, 25.94, 25.13, 21.91, 21.28.

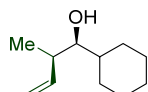
HRMS (ESI) [M-OH]⁺ calculated for C₁₃H₂₁⁺: 177.1638, found: 177.1634.



4a, $R_f = 0.6$ (EA/PE = 1:4), column solvent: hexane/EtOAc = 10:1, 77% yield (73.2 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.30 (t, $J = 7.4$ Hz, 2H), 7.21 (m, 3H), 5.76 (ddd, $J = 16.4, 11.1, 8.3$ Hz, 1H), 5.19 – 5.07 (m, 2H), 3.43 (td, $J = 9.2, 3.8$ Hz, 1H), 2.86 (ddd, $J = 15.2, 10.2, 5.2$ Hz, 1H), 2.69 (ddd, $J = 13.7, 9.9, 6.6$ Hz, 1H), 2.24 (h, $J = 6.8$ Hz, 1H), 1.85 (dddd, $J = 13.6, 10.1, 6.6, 3.2$ Hz, 1H), 1.72 (ddd, $J = 14.5, 9.8, 5.0$ Hz, 1H), 1.66 (s, 1H), 1.04 (d, $J = 6.8$ Hz, 3H).

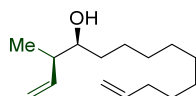
$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 142.27, 140.15, 128.44, 128.34, 125.74, 116.50, 73.94, 44.32, 36.08, 32.13, 16.20.



4b, $R_f = 0.7$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 78% yield (65.5 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 5.77 (ddd, $J = 16.7, 10.9, 8.2$ Hz, 1H), 5.11 (s, 1H), 5.09 – 5.05 (m, 1H), 3.08 (q, $J = 5.5$ Hz, 1H), 2.36 (m, $J = 6.8$ Hz, 1H), 1.84 – 1.71 (m, 3H), 1.63 (td, $J = 12.5, 10.5, 3.1$ Hz, 2H), 1.50 (d, $J = 4.4$ Hz, 1H), 1.43 – 1.34 (m, 1H), 1.26 – 1.06 (m, 5H), 1.01 (d, $J = 6.9$ Hz, 3H).

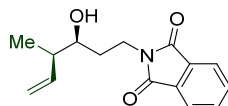
$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 140.35, 116.01, 78.79, 40.50, 40.31, 29.96, 27.03, 26.47, 26.41, 26.10, 16.94.



4c, $R_f = 0.7$ (EA:PE = 1:4), column solvent: hexane/EtOAc = 10:1, 71% yield (79.5 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 5.89 – 5.68 (m, 2H), 5.12 (s, 1H), 5.11 – 5.06 (m, 1H), 4.98 (dd, $J = 17.1, 1.7$ Hz, 1H), 4.92 (dd, $J = 10.7, 1.4$ Hz, 1H), 3.42 – 3.33 (m, 1H), 2.20 (h, $J = 6.8$ Hz, 1H), 2.03 (q, $J = 6.9$ Hz, 2H), 1.58 (s, 1H), 1.48 (m, 2H), 1.41 – 1.22 (m, 12H), 1.02 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 140.35, 139.20, 116.20, 114.07, 74.66, 44.09, 34.21, 33.78, 29.68, 29.54, 29.42, 29.10, 28.89, 25.70, 16.27.

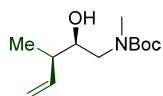


4d, $R_f = 0.3$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 56% yield (72.5 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.83 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.70 (dd, $J = 5.4, 3.0$ Hz, 2H), 5.75 (ddd, $J = 16.7, 10.8, 8.1$ Hz, 1H), 5.08 (s, 1H), 5.04 (d, $J = 8.3$ Hz, 1H), 3.85 (m, $J = 6.7, 6.0, 2.8$ Hz, 2H), 3.40 (ddd, $J = 9.9, 5.3, 2.6$ Hz, 1H), 2.49 (s, 1H), 2.21 (m, $J = 6.8$ Hz, 1H), 1.83 (m, $J = 15.6, 7.8, 2.7$ Hz, 1H), 1.70 (ddt, $J = 14.3, 10.5, 5.6$ Hz, 1H), 1.02 (d, $J = 6.9$ Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 168.74, 139.94, 133.95, 132.05, 123.25, 116.03, 71.81, 43.93, 34.99, 33.20, 16.20.

HRMS (ESI) [M+H]⁺ calculated for C₁₅H₁₈NO₃⁺: 260.1281, found: 260.1282.

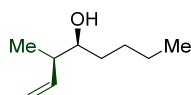


4e, R_f = 0.3 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 76% yield (87.0 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.80 (dt, J = 18.5, 9.2 Hz, 1H), 5.05 (m, 2H), 3.65 (s, 1H), 3.49 – 2.96 (m, 3H), 2.88 (s, 3H), 2.22 (h, J = 6.9 Hz, 1H), 1.42 (s, 9H), 1.05 (d, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 157.59, 139.51, 115.65, 79.91, 73.95, 53.30, 42.26, 35.89, 28.33, 15.81.

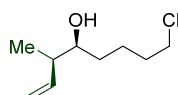
HRMS (ESI) [M+Na]⁺ calculated for C₁₂H₂₃NNaO₃⁺: 252.1570, found: 252.1571.



4f, R_f = 0.7 (EA:PE = 1:4), column solvent: hexane/EtOAc = 10:1, 74% yield (52.5 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.76 (ddd, J = 16.6, 10.9, 8.2 Hz, 1H), 5.13 (s, 1H), 5.11 – 5.08 (m, 1H), 3.39 (m, 1H), 2.21 (m, 1H), 1.54 – 1.47 (m, 2H), 1.42 – 1.26 (m, 5H), 1.03 (d, J = 6.9 Hz, 3H), 0.91 (t, J = 7.1 Hz, 3H).

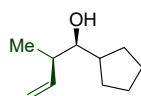
¹³C NMR (101 MHz, CDCl₃): δ 140.37, 116.24, 74.67, 44.10, 33.91, 27.90, 22.76, 16.29, 14.07.



4g, R_f = 0.7 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 82% yield (72.2 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.74 (ddd, J = 16.9, 10.7, 8.3 Hz, 1H), 5.14 (s, 1H), 5.11 (d, J = 8.3 Hz, 1H), 3.55 (t, J = 6.7 Hz, 2H), 3.39 (ddd, J = 8.9, 6.1, 3.2 Hz, 1H), 2.20 (dq, J = 14.2, 7.0 Hz, 1H), 1.81 (qd, J = 12.0, 11.4, 6.0 Hz, 2H), 1.68 – 1.60 (m, 1H), 1.56 – 1.49 (m, 2H), 1.40 (dd, J = 13.2, 8.7 Hz, 1H), 1.04 (d, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 140.13, 116.55, 74.35, 44.98, 44.21, 33.33, 32.61, 23.10, 16.25.

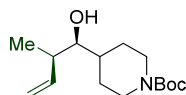


4h, R_f = 0.7 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 45% yield (34.7 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.82 (ddd, *J* = 17.0, 10.6, 8.2 Hz, 1H), 5.11 (dd, *J* = 2.5, 1.6 Hz, 1H), 5.10 – 5.06 (m, 1H), 3.25 (dt, *J* = 7.4, 4.8 Hz, 1H), 2.30 (m, *J* = 14.0, 7.0 Hz, 1H), 1.95 (m, *J* = 7.7 Hz, 1H), 1.79 – 1.65 (m, 2H), 1.65 – 1.58 (m, 2H), 1.58 – 1.47 (m, 2H), 1.43 (d, *J* = 5.1 Hz, 1H), 1.38 (m, *J* = 12.0, 8.0 Hz, 1H), 1.30 – 1.19 (m, 1H), 1.07 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 139.81, 115.96, 78.94, 43.68, 42.36, 29.11, 28.32, 25.63, 25.56, 17.23.

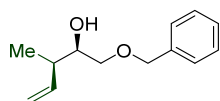
HRMS (ESI) [M+H]⁺ calculated for C₁₀H₁₉O⁺: 155.1430, found: 155.1428.



4i, R_f = 0.2 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 85% yield (114.3 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.77 (ddd, *J* = 17.1, 10.4, 8.3 Hz, 1H), 5.15 – 5.07 (m, 2H), 4.13 (s, 2H), 3.14 (q, *J* = 5.5 Hz, 1H), 2.64 (s, 2H), 2.36 (m, *J* = 6.9 Hz, 1H), 1.80 – 1.70 (m, 1H), 1.61 – 1.48 (m, 2H), 1.44 (s, 9H), 1.30 (dd, *J* = 33.1, 15.3 Hz, 2H), 1.04 (d, *J* = 6.9 Hz, 3H).

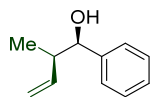
¹³C NMR (101 MHz, CDCl₃): δ 154.77, 139.58, 116.58, 79.22, 77.89, 43.73, 40.48, 38.93, 28.43, 26.74, 17.01.



4j, R_f = 0.6 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 80% yield (82.4 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.41 – 7.27 (m, 5H), 5.90 – 5.76 (m, 1H), 5.10 (d, *J* = 3.8 Hz, 1H), 5.07 (s, 1H), 4.56 (s, 2H), 3.68 (ddd, *J* = 7.6, 6.0, 3.2 Hz, 1H), 3.55 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.43 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.36 (m, 2H), 1.05 (d, *J* = 6.9 Hz, 3H).

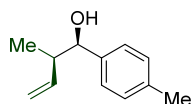
¹³C NMR (101 MHz, CDCl₃): δ 140.02, 137.96, 128.39, 127.71, 127.68, 115.52, 73.47, 73.34, 72.47, 40.76, 16.14.



4k, R_f = 0.5 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 45% yield (36.5 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.46 – 7.21 (m, 5H), 5.82 (ddd, *J* = 17.3, 10.3, 8.2 Hz, 1H), 5.25 – 5.19 (m, 1H), 5.18 (d, *J* = 3.0 Hz, 1H), 4.36 (dd, *J* = 7.9, 2.5 Hz, 1H), 2.49 (h, *J* = 7.0 Hz, 1H), 2.25 (s, 1H), 0.88 (d, *J* = 6.8 Hz, 3H).

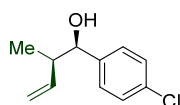
¹³C NMR (101 MHz, CDCl₃): δ 142.36, 140.58, 128.15, 127.56, 126.77, 116.72, 77.76, 46.19, 16.45.



4l, $R_f = 0.5$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 78% yield (68.7 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.23 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 5.83 (ddd, $J = 17.3, 10.3, 8.2$ Hz, 1H), 5.25 – 5.15 (m, 2H), 4.32 (d, $J = 7.9$ Hz, 1H), 2.48 (h, $J = 7.0$ Hz, 1H), 2.36 (s, 3H), 2.25 – 2.12 (s, 1H), 0.88 (d, $J = 6.8$ Hz, 3H).

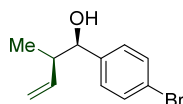
$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 140.77, 139.40, 137.13, 128.82, 126.68, 116.50, 77.62, 46.10, 21.06, 16.45.



4m, $R_f = 0.5$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 74% yield (72.5 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.30 (d, $J = 8.6$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 5.75 (ddd, $J = 17.8, 9.8, 8.2$ Hz, 1H), 5.17 (dd, $J = 14.7, 2.1$ Hz, 2H), 4.31 (d, $J = 7.7$ Hz, 1H), 2.41 (dq, $J = 14.6, 7.0$ Hz, 1H), 2.33 (s, 1H), 0.86 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 140.80, 140.08, 133.15, 128.26, 128.11, 117.10, 77.00, 46.23, 16.29.

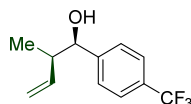


4n, $R_f = 0.5$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 62% yield (74.4 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.48 – 7.42 (m, 2H), 7.21 – 7.15 (m, 2H), 5.81 – 5.69 (m, 1H), 5.22 – 5.12 (m, 2H), 4.30 (dd, $J = 7.7, 2.3$ Hz, 1H), 2.40 (h, $J = 7.1$ Hz, 1H), 2.34 (d, $J = 2.6$ Hz, 1H), 0.86 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 141.30, 140.03, 131.20, 128.47, 121.29, 117.14, 77.02, 46.17, 16.28.

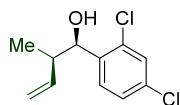
HRMS (ESI) $[\text{M}-\text{OH}]^+$ calculated for $\text{C}_{11}\text{H}_{12}\text{Br}^+$: 223.0117, Found: 223.0113.



4o, $R_f = 0.5$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 83% yield (95.5 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.60 (d, $J = 8.1$ Hz, 2H), 7.44 (d, $J = 8.5$ Hz, 2H), 5.84 – 5.70 (m, 1H), 5.22 (s, 1H), 5.20 – 5.16 (m, 1H), 4.42 (d, $J = 7.5$ Hz, 1H), 2.46 (h, $J = 6.9$ Hz, 1H), 2.32 (s, 1H), 0.90 (d, $J = 6.8$ Hz, 3H).

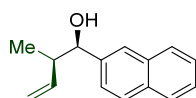
¹³C NMR (101 MHz, CDCl₃): δ 146.34, 139.74, 129.76 (q, *J* = 32.3 Hz), 127.12, 125.11 (q, *J* = 3.8 Hz), 124.14 (q, *J* = 272.7 Hz), 117.54, 77.10, 46.33, 16.30.



4p, *R_f* = 0.5 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 70% (80.9 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.25 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.77 (ddd, *J* = 18.2, 10.3, 7.9 Hz, 1H), 5.19 – 5.06 (m, 2H), 4.89 (d, *J* = 6.6 Hz, 1H), 2.51 (m, *J* = 7.0 Hz, 1H), 2.21 (s, 1H), 1.01 (d, *J* = 6.9 Hz, 3H).

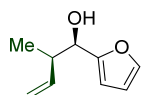
¹³C NMR (101 MHz, CDCl₃): δ 139.07, 138.95, 133.43, 133.12, 129.02, 128.93, 127.19, 117.41, 72.87, 45.12, 16.38.



4q, *R_f* = 0.5 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 90% (95.4 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.89 – 7.83 (m, 3H), 7.78 (s, 1H), 7.50 (m, 3H), 5.87 (ddd, *J* = 17.4, 10.3, 8.1 Hz, 1H), 5.28 – 5.19 (m, 2H), 4.53 (d, *J* = 7.8 Hz, 1H), 2.61 (h, *J* = 7.1 Hz, 1H), 2.37 (s, 1H), 0.92 (d, *J* = 6.8 Hz, 3H).

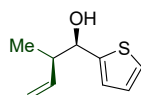
¹³C NMR (101 MHz, CDCl₃): δ 140.51, 139.81, 133.08, 133.01, 127.99, 127.88, 127.61, 125.99, 125.86, 125.74, 124.60, 116.84, 77.90, 46.07, 16.54.



4r, *R_f* = 0.5 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 55% (41.8 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.40 – 7.37 (m, 1H), 6.36 – 6.30 (m, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 5.80 (ddd, *J* = 17.6, 10.3, 8.1 Hz, 1H), 5.25 – 5.14 (m, 2H), 4.42 (d, *J* = 7.7 Hz, 1H), 2.70 (h, *J* = 7.2 Hz, 1H), 2.17 (s, 1H), 0.94 (d, *J* = 6.8 Hz, 3H).

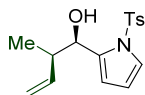
¹³C NMR (101 MHz, CDCl₃): δ 154.94, 141.93, 139.94, 116.94, 110.03, 107.20, 71.30, 43.55, 16.18.



4s, *R_f* = 0.5 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 50% (42.0 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.26 (m, 1H), 6.97 (m, 2H), 5.83 (ddd, *J* = 18.1, 10.3, 8.1 Hz, 1H), 5.28 – 5.16 (m, 2H), 4.65 (d, *J* = 7.7 Hz, 1H), 2.54 (h, *J* = 7.2 Hz, 1H), 2.36 (s, 1H), 0.96 (d, *J* = 6.8 Hz, 3H).

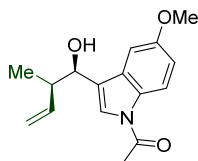
¹³C NMR (101 MHz, CDCl₃): δ 146.27, 140.04, 126.33, 124.74, 124.70, 117.24, 73.77, 46.67, 16.45.



4t, $R_f = 0.3$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 70% (106.8 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.68 (d, $J = 8.4$ Hz, 2H), 7.30 – 7.27 (m, 2H), 7.26 (s, 1H), 6.31 – 6.28 (m, 1H), 6.27 – 6.22 (m, 1H), 5.91 – 5.78 (m, 1H), 5.14 (s, 1H), 5.11 (dd, $J = 5.8, 1.5$ Hz, 1H), 4.78 (d, $J = 7.6$ Hz, 1H), 2.69 – 2.61 (m, 1H), 2.38 (s, 3H), 2.31 (s, 1H), 0.88 (d, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 145.00, 140.05, 136.77, 136.39, 129.97, 126.66, 123.35, 116.43, 113.11, 111.69, 69.29, 43.83, 21.57, 17.30.

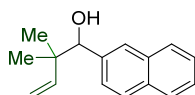


4u, $R_f = 0.2$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 70% (80.6 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.28 (d, $J = 7.7$ Hz, 1H), 7.26 (s, 1H), 7.08 (d, $J = 2.5$ Hz, 1H), 6.92 (dd, $J = 9.0, 2.5$ Hz, 1H), 5.84 (ddd, $J = 18.2, 10.3, 7.9$ Hz, 1H), 5.25 – 5.15 (m, 2H), 4.62 (d, $J = 7.4$ Hz, 1H), 3.84 (s, 3H), 2.74 (dp, $J = 14.3, 7.0, 6.2$ Hz, 1H), 2.49 (m, 4H), 0.99 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.24, 156.12, 140.12, 130.77, 129.69, 123.73, 123.34, 117.33, 116.87, 113.19, 103.14, 71.39, 55.61, 44.41, 23.53, 16.73.

HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{19}\text{NNaO}_3^+$: 296.1257, found: 296.1253.

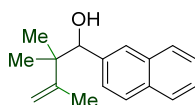


4v, $R_f = 0.6$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 88% (99.4 mg), colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.89 – 7.83 (m, 2H), 7.80 (d, $J = 8.5$ Hz, 1H), 7.76 (s, 1H), 7.53 – 7.43 (m, 3H), 5.98 (dd, $J = 17.5, 10.8$ Hz, 1H), 5.18 (dd, $J = 10.8, 1.3$ Hz, 1H), 5.12 (dd, $J = 17.5, 1.2$ Hz, 1H), 4.60 (s, 1H), 2.20 (s, 1H), 1.08 (s, 3H), 1.03 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 145.03, 138.36, 132.86, 132.71, 127.96, 127.53, 126.86, 126.57, 126.04, 125.86, 125.68, 113.93, 80.65, 42.48, 24.50, 21.12.

HRMS (ESI) $[\text{M}-\text{OH}]^+$ calculated for $\text{C}_{16}\text{H}_{17}^+$: 209.1325, found: 209.1321.

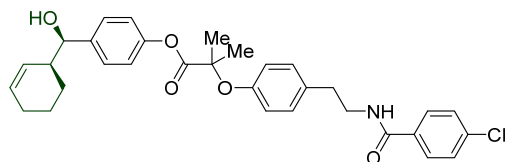


4w, $R_f = 0.6$ (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 85% (102.1 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.91 – 7.85 (m, 2H), 7.82 (m, 2H), 7.51 (m, 3H), 5.09 (s, 1H), 5.03 (s, 1H), 4.82 (s, 1H), 2.35 (s, 1H), 1.93 (s, 3H), 1.08 (s, 3H), 1.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 150.52, 137.93, 132.82, 132.70, 127.91, 127.48, 126.73, 126.69, 126.20, 125.75, 125.56, 113.19, 77.49, 44.71, 24.24, 20.19, 19.79.

HRMS (ESI) [M-OH]⁺ calculated for C₁₇H₁₉⁺: 223.1481, found: 223.1478.

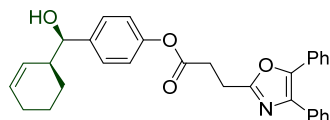


5a, R_f = 0.2 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 68% (186.0mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.60 – 7.58 (m, 1H), 7.58 – 7.56 (m, 1H), 7.34 – 7.27 (m, 4H), 7.11 (s, 1H), 7.09 (s, 1H), 6.98 – 6.96 (m, 1H), 6.96 – 6.94 (m, 1H), 6.92 – 6.91 (m, 1H), 6.90 – 6.88 (m, 1H), 6.38 (t, J = 5.8 Hz, 1H), 5.84 – 5.74 (m, 1H), 5.35 (dd, J = 10.1, 2.5 Hz, 1H), 4.55 (d, J = 6.4 Hz, 1H), 3.59 (q, J = 6.7 Hz, 2H), 2.83 (t, J = 7.0 Hz, 2H), 2.49 – 2.37 (m, 1H), 2.27 (s, 1H), 1.99 – 1.92 (m, 2H), 1.76 – 1.64 (m, 8H), 1.52 – 1.43 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 172.92, 166.39, 153.97, 149.54, 140.90, 137.46, 132.82, 132.65, 130.40, 129.52, 128.65, 128.22, 127.67, 127.54, 120.74, 119.33, 79.16, 76.56, 42.90, 41.21, 34.59, 25.34, 25.10, 23.70, 20.95.

HRMS (ESI) [M+Na]⁺ calculated for C₃₂H₃₄ClNNaO₅⁺: 570.2018, found: 570.2013.

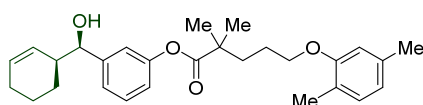


5b, R_f = 0.3 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 63% (150.9 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.68 – 7.66 (m, 1H), 7.66 – 7.64 (m, 1H), 7.61 – 7.59 (m, 1H), 7.59 – 7.57 (m, 1H), 7.41 – 7.31 (m, 8H), 7.11 – 7.09 (m, 2H), 7.08 – 7.06 (m, 1H), 5.85 – 5.77 (m, 1H), 5.38 (dd, J = 10.2, 2.4 Hz, 1H), 4.57 (d, J = 6.4 Hz, 1H), 3.29 (t, J = 7.0 Hz, 2H), 3.16 (t, J = 7.1 Hz, 2H), 2.53 – 2.39 (m, 1H), 2.07 (s, 1H), 2.01 – 1.91 (m, 2H), 1.77 – 1.66 (m, 2H), 1.56 – 1.44 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 170.61, 161.42, 149.72, 145.52, 140.57, 135.10, 132.32, 130.47, 128.87, 128.60, 128.51, 128.46, 128.04, 127.84, 127.78, 127.47, 126.48, 121.14, 76.68, 42.93, 31.21, 25.15, 23.70, 23.46, 21.00.

HRMS (ESI) [M+Na]⁺ calculated for C₃₁H₂₉NNaO₄⁺: 302.1989, found: 302.1986.



5c, R_f = 0.6 (EA:PE=1:4), column solvent: hexane/EtOAc = 10:1, 65% (141.7 mg), colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.32 (m, 2H), 7.06 – 7.00 (m, 3H), 6.68 (d, J = 7.0 Hz, 1H), 6.64 (s, 1H), 5.88 – 5.79 (m, 1H), 5.45 – 5.35 (m, 1H), 4.60 (d, J = 6.4 Hz, 1H), 4.03 – 3.96 (m, 2H), 2.53 – 2.44 (m, 1H), 2.32 (s, 3H), 2.19 (s, 3H), 2.02 – 1.98 (m, 2H), 1.94 (s, 1H), 1.90 (d, J = 3.0 Hz, 4H), 1.79 – 1.69 (m, 2H), 1.56 – 1.49 (m, 2H), 1.39 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 176.34, 156.83, 150.13, 140.25, 136.43, 130.51, 130.30, 127.78, 127.43, 123.57, 121.17, 120.71, 111.91, 76.77, 67.74, 42.98, 42.38, 37.11, 25.23, 25.17, 25.12, 23.72, 21.36, 21.02, 15.76.

HRMS (ESI) [M+Na]⁺ calculated for C₂₈H₃₆NaO₄⁺: 459.2506, found: 459.2501.

8. Supplementary Reference

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9. ¹H and ¹³C-NMR spectra of compounds

