## Supporting Information

# Regio- and Stereoselective Electrochemical Alkylation of Morita-Baylis-Hillman Adducts. 

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## General Methods.

${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra were recorded on Varian $400(400 \mathrm{MHz})$ spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.24 ppm ). Data are reported as follows: chemical shift, multiplicity ( $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{dd}=$ doublet doublet, $\mathrm{t}=$ triplet, $\mathrm{td}=$ triple doublet, $\mathrm{dt}=$ double triplet, $\mathrm{q}=$ quartet, sext = sextet, sept = septet, $p=$ pseudo, $b=$ broad, $m=$ multiplet), coupling constants $(\mathrm{Hz}) .{ }^{13} \mathrm{C}-$ NMR spectra were recorded on a Varian $400(100 \mathrm{MHz})$ spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm ).
HRMS spectra were obtained with a G2XS QTof mass spectrometer using either ESI or APCI ionization techniques, as specified case by case.
Chromatographic purification was done with 240-400 mesh silica gel. Other anhydrous solvents were supplied by Sigma Aldrich in Sureseal $®$ bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification. Melting points were determined with Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are not corrected.
Anhydrous DMF was purchased from Merck and used as received. All other commercially available starting materials and (non-anhydrous) solvents were purchased from Merck, TCI chemicals, Fluorochem or Alfa Aesar and were used as such without further purification.
MBH acetates 1 are known compounds and were synthesized according to literature procedures. ${ }^{1}$
RAEs 2 are known compounds and were synthesized according to literature procedures. ${ }^{2}$ For characterization see: $\mathbf{2 a},{ }^{2} \mathbf{2 b},{ }^{3} \mathbf{2 c},{ }^{2} \mathbf{2 d},{ }^{2} \mathbf{2 e},{ }^{4} \mathbf{2 f},{ }^{3} \mathbf{2 g},{ }^{4} \mathbf{2 h},{ }^{5} \mathbf{2 i},{ }^{2} \mathbf{2 j} .{ }^{2}$

## Table S1. Optimization of reaction conditions, additional data.



Reaction conditions: 1a ( 0.15 mmol ), 2a ( 0.30 mmol ), electrolyte ( 0.30 mmol ), dry DMF ( 3 mL ). CCE (10, 4 or 2 mA ; $2 \mathrm{~F} / \mathrm{mol}_{2 \mathrm{a}}$ ), rt.

In entries 6, 7, and 8 the use of $\mathrm{PPh}_{3}$ as an additive was explored. Unfortunately, this did not result in a regioselectivity switch ( $\mathrm{S}_{\mathrm{N}} 2$ instead of $\mathrm{S}_{\mathrm{N}} 2$ ' adduct, see Scheme S 1 ) as it was postulated. The use of $\mathrm{PPh}_{3}$ in stoichiometric amount resulted in a lower yield of isolated product 3aa due to decomposition of 1a (entry 6). Nonetheless, its presence, in catalytic amount, improved the yield slightly when the reaction was carried out at 4 mA , with complete consumption of 1a (compare entry 7 with entry 4 of Table 1, main text). However, when the reaction was repeated at 2 mA , a slightly lower yield was recorded if compared to the reaction run in the absence of $\mathrm{PPh}_{3}$ (compare entry 8 with entry 5 of Table 1, main text).


Scheme S1. Possible product distribution when $\mathrm{PPh}_{3}$ is employed as an additive in the eChem alkylation of MBH adducts.

## Limitation of the methodology: unsuccessful substrates.





$1 r$


2k, $\mathrm{R}=\mathrm{Ph}$
2l, R = Bn
2m, R = allyl
2n, R = cinnamyl
Figure S1. Unsuccessful substrates.
MBH acetates $\mathbf{1 p - 1 r}$ were tested under the optimal reaction conditions (RAE 2a) but failed to give the desired products. A complex reaction mixture was observed by ${ }^{1} \mathrm{H}$ NMR spectroscopy when compound 1p was employed. Successive de-iodination, reduction, radical alkylation sequences were observed when 1q was subjected to the reaction mixture (compounds 1a, 3aa and 1a' were observed). No reaction occurred with cyclohexanone-derived compound 1r.

RAEs $\mathbf{2 k} \mathbf{- 2 n}$ were tested under the optimal reaction conditions (MBH acetate 1a) but failed to give the desired products. In all cases, decomposition of RAE 2 was observed but no productive trapping of the radical by $\mathbf{1 a}$ occurred. Substantial amounts of 1a' and recovered 1a were observed.

## Cyclovoltammetry experiments



Figure S2. Cyclovoltammetry of RAE 2a.


Figure S3. Cyclovoltammetry of RAE 2a and ferrocene.


Figure S4. Cyclovoltammetry of MBH acetate 1a.

Cyclovoltammetry experiments were carried out using the ElectraSyn 2.0 apparatus with a Pt counter electrode, an RVC working electrode and an $\mathrm{Ag} / \mathrm{Ag}^{+}$reference electrode ( Ag wire in a $10 \mathrm{mM} \mathrm{AgNO}_{3}$ and $0.1 \mathrm{M} \mathrm{TBACIO}_{4}$ acetonitrile solution).
For 2a: 4.8 mg of $\mathbf{2 a}$ and 100 mg TBAPF $_{6}$ were dissolved in 3 mL of anhydrous DMF, stirred while purging with $\mathrm{N}_{2}$ (balloon) and then subjected to the CV experiment at $350 \mathrm{mV} \cdot \mathrm{s}^{-1}$ (Figure S2). Then, 3.0 mg of ferrocene were added and the CV experiment was repeated (Figure S3). An irreversible peak between -1.27 and -1.49 V is observed. This is then calculated to be -1.57 V vs ferrocene (reversible peak between 0.072 and 0.325 V ).
For 1a: 3.7 mg of $\mathbf{2 a}$ and 100 mg TBAPF $_{6}$ were dissolved in 3 mL of anhydrous DMF, stirred while purging with $\mathrm{N}_{2}$ (balloon) and then subjected to the CV experiment at $350 \mathrm{mV} \cdot \mathrm{s}^{-1}$ (Figure
S4) No cathodic event is observed apart from reduction of the solvent occurring below -1.50 V .

## Photoisomerization of E-3aa

In a flame-dried Schlenk tube equipped with a magnetic stirring bar, E-3aa ( $0.10 \mathrm{mmol}, 25.8$ mg ) and $\operatorname{Ir}\left[\mathrm{dF}\left(\mathrm{CF}_{3}\right) \mathrm{ppy}\right]_{2}(\mathrm{dtbppy}) \mathrm{PF}_{6}(1 \mathrm{mg})$ were dissolved in dry NMP (1 mL) under $\mathrm{N}_{2}$ atmosphere. The Schlenk flask was then sealed, and the content was stirred vigorously for 18 h under blue-light irradiation ( 20 W Kessil lamp, 427 nm , at a distance of approximately 6 cm ). Then, EtOAc $(5 \mathrm{~mL})$ and $\mathrm{HCl}_{(\mathrm{aq})}(1 \mathrm{M}, 5 \mathrm{~mL})$ were added and the biphasic crude mixture was placed in a separatory funnel. The organic layer was separated, the aqueous layer was extracted with EtOAc ( $2 \times 10 \mathrm{~mL}$ ) and the combined organic layers were washed with $\mathrm{HCl}_{(\mathrm{aq})}$ ( $0.1 \mathrm{M}, 3 \times 10 \mathrm{~mL}$ ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated in vacuo. ${ }^{1} \mathrm{H}$ NMR of the crude mixture revealed that isomerization of the double bond occurred showing a Z-3aa:E-3aa ratio $=1.7: 1$.


Figure S5. ${ }^{1} \mathrm{H}$ NMR of $E$-3aa and $\mathbf{Z}$-3aa (1:1.7 mixture)

Optimized general procedure for the eChem alkylation of MBH adducts.


The ElectraSyn vial ( 5 mL ), equipped with a stir bar, was charged with MBH acetate 1 or 5 ( 0.15 $\mathrm{mmol})$, RAE 2 ( 0.30 mmol ) and $\mathrm{TEABF}_{4}(65.1 \mathrm{mg}, 0.30 \mathrm{mmol})$. The ElectraSyn vial cap, equipped with anode ( Zn ) and cathode (graphite) was inserted into the mixture and closed with a rubber septum. The vessel was evacuated and backfilled with $\mathrm{N}_{2}$ three times, then dry DMF ( 3 mL ) was added, and the solution bubbled with $\mathrm{N}_{2}$ (balloon) under stirring for 1 min . The reaction mixture was electrolyzed (under $\mathrm{N}_{2}$, balloon) at a constant current of 2 mA , until a total charge of $0.60 \mathrm{~F}\left(4 \mathrm{~F} / \mathrm{mol}_{1}\right)$ was reached (ca. 8 h$)$. The ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc ( 10 mL ) and $\mathrm{HCl}_{(\mathrm{aq})}(1 \mathrm{M}, 10 \mathrm{~mL})$, which were combined with the crude mixture in a separatory funnel. Then, the organic layer was separated, the aqueous layer was extracted with EtOAc $(2 \times 10 \mathrm{~mL})$ and the combined organic layers were washed with $\mathrm{HCl}_{(\mathrm{aq})}(0.1 \mathrm{M}, 3 \times 10 \mathrm{~mL})$, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated in vacuo. The crude product was finally purified by flash chromatography ( $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}$ mixtures) to afford pure products $\mathbf{3}$ or 6.


3aa. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}$ : 25:1. Yield $=79 \%$, ( $0.119 \mathrm{mmol}, 30.6 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $=7.66(\mathrm{~s}, 1 \mathrm{H}), 7.41-7.33(\mathrm{~m}, 4 \mathrm{H}), 7.32-7.26(\mathrm{~m}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H})$, 2.47 (d, J = 7.1 Hz, 2H), $1.71-1.42(\mathrm{~m}, 6 \mathrm{H}), 1.28-1.00(\mathrm{~m}, 3 \mathrm{H}), 0.93$ -0.78 (m, 2H); ${ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta=169.4,139.4,136.0$, 132.7, 129.3 (2C), 128.4 (2C), 128.1, 52.0, 37.8, 34.4, 33.2 (2C), 26.4, 26.3 (2C); HRMSI (APCI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{17} \mathrm{H}_{23} \mathrm{O}_{2}$ 259.1693; found 259.1698.

Example of mmol scale synthesis of 3aa. The ElectraSyn vial ( 10 mL ), equipped with a stir bar, was charged with MBH acetate 1a ( $234 \mathrm{mg}, 1.0 \mathrm{mmol}$ ), RAE 2a ( $546 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) and $\mathrm{TEABF}_{4}(434 \mathrm{mg}, 2.0 \mathrm{mmol})$. The ElectraSyn vial cap, equipped with anode ( Zn ) and cathode (graphite) was inserted into the mixture and closed with a rubber septum. The vessel was evacuated and backfilled with $\mathrm{N}_{2}$ three times, then dry DMF ( 9 mL ) was added, and the solution bubbled with $\mathrm{N}_{2}$ (balloon) under stirring for 1 min . The reaction mixture was electrolyzed (under $\mathrm{N}_{2}$, balloon) at a constant current of 3 mA , until a total charge of 4.0 F ( $4 \mathrm{~F} / \mathrm{mol}_{1 \mathrm{a}}$ ) was reached (ca. 36 h ). The ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc ( 25 mL ) and $\mathrm{HCl}_{(\mathrm{aq})}(1 \mathrm{M}, 25 \mathrm{~mL})$, which were combined with the crude mixture in a separatory funnel. Then, the organic layer was separated, the aqueous layer was extracted with EtOAc $(2 \times 25 \mathrm{~mL})$ and the combined organic layers were washed with $\mathrm{HCl}_{(\mathrm{aq})}(0.1 \mathrm{M}, 3 \mathrm{x}$ 25 mL ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated in vacuo. The crude product was finally purified by flash chromatography ( $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}$ mixtures) to afford pure products 3aa in $83 \%$ yield ( 0.83 mmol, 244 mg ).

3aa is a known compound and the reported spectroscopic data match with the ones reported in the literature ( $E / Z$ ratio: 1:1.7). ${ }^{6}$


3ba. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}: 25: 1$. Yield $=$ $76 \%$, ( $0.114 \mathrm{mmol}, 33.3 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta=7.59(\mathrm{~s}, 1 \mathrm{H}), 7.35-7.30(\mathrm{~m}, 2 \mathrm{H}), 7.29-7.25(\mathrm{~m}, 2 \mathrm{H})$, 3.79 (s, 3H), 2.43 (d, J = $7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.71$ - 1.41 (m, 6H), 1.25 0.99 (m, 3H), $0.92-0.74(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $=169.1,138.0,134.4,134.0,133.3,130.5$ (2C), 128.6 (2C), 52.0, 37.8, 34.4, 33.2 (2C), 26.3, 26.2 (2C); HRMS (ESI) m/z: [M+H] ${ }^{+}$calcd. for $\mathrm{C}_{17} \mathrm{H}_{22}{ }^{35} \mathrm{CIO}_{2}$ 293.1303; found 293.1303; calcd. for $\mathrm{C}_{17} \mathrm{H}_{22}{ }^{37} \mathrm{ClO}_{2}$, 295.1274; found 295.1275 .



3ca. Viscous colorless oil. FC eluent: $n \mathrm{Hex}^{\left(E t_{2} \mathrm{O}: 25: 1\right.}$. Yield $=$ $70 \%$, ( $0.105 \mathrm{mmol}, 35.4 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta=7.57(\mathrm{~s}, 1 \mathrm{H}), 7.52-7.40(\mathrm{~m}, 2 \mathrm{H}), 7.21-7.15(\mathrm{~m}, 2 \mathrm{H})$, $3.79(\mathrm{~s}, 3 \mathrm{H}), 2.42(\mathrm{~d}, \mathrm{~J}=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.66-1.41(\mathrm{~m}, 6 \mathrm{H}), 1.19-$ $1.02(\mathrm{~m}, 3 \mathrm{H}), 0.90-0.74(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $=169.1,138.1,137.5,134.9,133.4,131.6(2 \mathrm{C}), 130.8(2 \mathrm{C}), 52.0,37.8,34.4,33.2(2 \mathrm{C}), 26.3$, 26.2 (2C); HRMS (APCI) m/z: [M+H] ${ }^{+}$calcd. for $\mathrm{C}_{17} \mathrm{H}_{22}{ }^{79} \mathrm{BrO}_{2}$ 337.0798; found 337.0792; calcd. for $\mathrm{C}_{17} \mathrm{H}_{22}{ }^{81} \mathrm{BrO}_{2}$ 339.0778; found 339.0783.

$\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=168.6,140.8,137.1,135.6,132.2(2 \mathrm{C}), 129.6$ (2C), 118.6, 111.5, 52.2, 37.7, 34.6, 33.2 (2C), 26.2, 26.2 (2C); HRMS (APCI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{NO}_{2}$ 284.1645; found 284.1653.


3ea. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}: 15: 1$. Yield $=$ 67\%, ( $0.101 \mathrm{mmol}, 28.9 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.60(\mathrm{~s}, 1 \mathrm{H}), 7.39-7.30(\mathrm{~m}, 2 \mathrm{H}), 6.94-6.85$ (m, 2H), $3.82(\mathrm{~s}, 3 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 2.49(\mathrm{~d}, \mathrm{~J}=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.72$ $-1.45(\mathrm{~m}, 6 \mathrm{H}), 1.26-1.05(\mathrm{~m}, 3 \mathrm{H}), 0.98-0.85(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$
NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta=169.7,159.6,139.0,131.1$ (2C), 130.6, 128.4, 113.9 (2C), 55.2, 51.8, 37.9, 34.4, 33.3 (2C), 26.4, 26.3 (2C); HRMS (APCI) m/z: [M+H] calcd. for $\mathrm{C}_{18} \mathrm{H}_{25} \mathrm{O}_{3}$ 289.1798; found 289.1805 .


3fa. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}: 30: 1$. Yield $=$ 61\%, ( $0.092 \mathrm{mmol}, 28.7 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.63(\mathrm{~s}, 1 \mathrm{H}), 7.42-7.37(\mathrm{~m}, 2 \mathrm{H}), 7.36-7.30$ (m, 2H), 3.79 (s, 3H), 2.51 (d, J = $7.1 \mathrm{~Hz}, 2 \mathrm{H}$ ), 1.72 - 1.47 (m, $6 \mathrm{H}), 1.32(\mathrm{~s}, 9 \mathrm{H}), 1.23-1.07(\mathrm{~m}, 3 \mathrm{H}), 1.01-0.86(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=169.6,151.5,139.2,133.0,131.8,129.4$ (2C), 125.4 (2C), 51.9 , 37.9, 34.7, 34.5, 33.3 (2C), 31.2 (3C), 26.4, 26.3 (2C); HRMS (APCI) m/z: [M+H] calcd. for $\mathrm{C}_{21} \mathrm{H}_{31} \mathrm{O}_{2} 315.2319$; found 315.2326 .


3ga. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et} 2 \mathrm{O}: 25: 1$. Yield $=77 \%$, ( $0.115 \mathrm{mmol}, 33.9 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) ठ $=7.68(\mathrm{~s}, 1 \mathrm{H}), 7.43-7.35(\mathrm{~m}, 1 \mathrm{H}), 7.28-7.23(\mathrm{~m}, 3 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H})$, 2.30 (d, J = $7.1 \mathrm{~Hz}, 2 \mathrm{H}$ ), $1.65-1.51$ (m, 5H), $1.50-1.37$ (m, 1H), 1.19 $-0.93(\mathrm{~m}, 3 \mathrm{H}), 0.76-0.62(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=$ 168.6, 136.9, 134.9, 134.3, 133.8, 130.1, 129.5, 129.1, 126.4, 52.0, 37.3, 34.6, 33.0 (2C), 26.3, 26.2 (2C); HRMS (APCI) m/z: [M+H] calcd. for $\mathrm{C}_{17} \mathrm{H}_{22}{ }^{35} \mathrm{ClO}_{2} 293.1303$; found, 293.1309; calcd. for $\mathrm{C}_{17} \mathrm{H}_{22}{ }^{37} \mathrm{ClO}_{2} 295.1274$; found 295.1286.


3ha. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}$ : 25:1. Yield $=70 \%$, ( $0.105 \mathrm{mmol}, 32.4 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=7.87-7.80(\mathrm{~m}, 5 \mathrm{H}), 7.53-7.46(\mathrm{~m}, 3 \mathrm{H}), 3.83(\mathrm{~s}, 3 \mathrm{H}), 2.57(\mathrm{~d}$, $J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.74-1.50(\mathrm{~m}, 6 \mathrm{H}), 1.27-1.02(\mathrm{~m}, 3 \mathrm{H}), 0.94-$ $0.80(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=169.4,139.4,133.5$, 133.1, 132.9, 132.8, 129.0, 128.3, 128.0, 127.6, 126.8, 126.6, 126.4, 52.0, 37.9, 34.6, 33.3 (2C), 26.4, 26.3 (2C); HRMS (APCI) m/z: [M+H] ${ }^{+}$calcd. for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{O}_{2}$ 309.1849; found 309.1849.


3ia. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}$ : 25:1. Yield $=71 \%$, $(0.107 \mathrm{mmol}, 28.1 \mathrm{mg}), \mathrm{E} / \mathrm{Z}$ ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $=7.83(\mathrm{~s}, 1 \mathrm{H}), 7.43(\mathrm{dt}, J=5.1,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.27-7.21(\mathrm{~m}, 1 \mathrm{H}), 7.06$ (dd, $J=5.2,3.7 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.78 (s, 3H), 2.61 (d, $J=7.2 \mathrm{~Hz}, 2 \mathrm{H}$ ), $1.77-$ $1.52(\mathrm{~m}, 7 \mathrm{H}), 1.27-0.96(\mathrm{~m}, 4 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=$ 169.3, 138.7, 132.5, 132.0, 128.8, 128.8, 127.1, 51.9, 37.8, 35.2, 33.3 (2C), 26.4, 26.4 (2C); HRMS (APCI) m/z: [M+H]+ calcd. for $\mathrm{C}_{15} \mathrm{H}_{21} \mathrm{O}_{2} \mathrm{~S}$ 265.1257; found 265.1260.


3ja'. Viscous colorless oil. FC eluent: $n H e x / E t O A c: ~ 10: 1$. Yield $=$ $64 \%,(0.096 \mathrm{mmol}, 29.9 \mathrm{mg})$, clean reduction of the double bond occurred, 3ia not detected. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=8.05-$ $7.95(\mathrm{~m}, 2 \mathrm{H}), 7.75$ (dd, $J=8.0,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.65$ (ddd, $J=8.5,6.9$, $1.5 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.46 (ddd, $J=8.1,6.9,1.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.23 (d, $J=8.7 \mathrm{~Hz}$, 1 H ), 3.59 (s, 3H), 3.27 (dd, $J=13.5,8.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.19 (tt, $J=8.9,5.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.06 (dd, $J=$ $13.5,5.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), $1.85-1.76(\mathrm{~m}, 1 \mathrm{H}), 1.74-1.56(\mathrm{~m}, 5 \mathrm{H}), 1.39$ (ddd, $J=13.5,8.3,5.2 \mathrm{~Hz}$, 1H), $1.32-1.03(\mathrm{~m}, 3 \mathrm{H}), 0.94-0.74(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=176.6,159.9$, 147.9, 136.1, 129.3, 129.0, 127.4, 126.8, 125.8, 121.6, 51.4, 42.8, 41.6, 40.2, 35.6, 33.6, 32.8, 26.5, 26.2, 26.2; HRMS (APCI) m/z: [M+H] calcd. for $\mathrm{C}_{20} \mathrm{H}_{26} \mathrm{NO}_{2} 312.1958$; found 312.1963.


3ka. Viscous colorless oil. FC eluent: $n H e x / E t_{2} \mathrm{O}: 25: 1$. Yield $=$ $62 \%$, ( $0.093 \mathrm{mmol}, 28.8 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.32-7.26(\mathrm{~m}, 2 \mathrm{H}), 7.22-7.14(\mathrm{~m}, 3 \mathrm{H}), 6.82$ (t, J=7.4 Hz, 1H), 3.71 (s, 3H), 2.73 (dd, $J=9.0,6.7 \mathrm{~Hz}, 2 \mathrm{H}$ ), 2.48 (q, J = $7.6 \mathrm{~Hz}, 2 \mathrm{H}$ ), 2.16 (d, J=7.1 Hz, 2H), $1.70-1.57$ (m, 5 H ), $1.43-1.27(\mathrm{~m}, 1 \mathrm{H}), 1.27-1.02(\mathrm{~m}, 3 \mathrm{H}), 0.93-0.79(\mathrm{~m}, 2 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=168.6,142.0,141.2,131.5,128.4$ (2C), 128.3 (2C), 126.1, 51.6, 37.7, 35.0, 34.3, 33.2 (2C), 30.9, 26.4, 26.3 (2C); HRMS (APCI) m/z: [M+H] calcd. for $\mathrm{C}_{19} \mathrm{H}_{27} \mathrm{O}_{2} 287.2006$; found: 287.2014.


3la. Pale yellow solid. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}: 25: 1$. Yield $=57 \%$, ( $0.086 \mathrm{mmol}, 24.3 \mathrm{mg}$ ), E/Z ratio: >20:1. MP: $106-108{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.47-7.43(\mathrm{~m}, 2 \mathrm{H}), 7.40(\mathrm{~d}, \mathrm{~J}=11.3$ $\mathrm{Hz}, 1 \mathrm{H}$ ), $7.37-7.32$ (m, 2H), $7.31-7.25$ (m, 1H), 7.03 (dd, $J=$ $15.4,11.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.85(\mathrm{~d}, \mathrm{~J}=15.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}), 2.39$ (d, $J=7.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 1.67 (ddd, $J=21.5,16.4,9.7 \mathrm{~Hz}, 5 \mathrm{H}), 1.55-1.38(\mathrm{~m}, 1 \mathrm{H}), 1.27-1.09$ (m, 3H), $1.02-0.88$ (m, 2H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=168.8,139.3,139.1,136.6,130.9$, 128.8 (2C), 128.6, 127.0 (2C), 124.2, 51.7, 38.3, 34.7, 33.4 (2C), 26.5, 26.3 (2C); HRMS (ESI) $\mathrm{m} / \mathrm{z}:[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{19} \mathrm{H}_{25} \mathrm{O}_{2} 285.1849$; found 285.1852.


3ma. Viscous colorless oil. FC eluent: $n \mathrm{Hex}^{2} \mathrm{Et}_{2} \mathrm{O}$ : 25:1. Yield $=76 \%,(0.114 \mathrm{mmol}, 42.0 \mathrm{mg}), E / Z$ ratio: $>20: 1 .{ }^{1} \mathrm{H}$ NMR (400 MHz, CDCl3) $\delta=7.63(\mathrm{~s}, 1 \mathrm{H}), 7.43-7.36(\mathrm{~m}$, $4 \mathrm{H}), 7.36-7.30(\mathrm{~m}, 3 \mathrm{H}), 7.29-7.25(\mathrm{~m}, 2 \mathrm{H}), 5.24(\mathrm{~s}, 2 \mathrm{H})$, 2.45 (d, J = $7.1 \mathrm{~Hz}, 2 \mathrm{H}$ ), $1.70-1.54(\mathrm{~m}, 5 \mathrm{H}), 1.54-1.44$ $(\mathrm{m}, 1 \mathrm{H}), 1.19-1.01(\mathrm{~m}, 3 \mathrm{H}), 0.90-0.76(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=168.4,138.2$, 136.1, 134.4, 134.0, 133.4, 130.5 (2C), 128.6 (2C), 128.5 (2C), 128.2, 128.1 (2C), 66.6, 37.8, 34.5, 33.2 (2C), 26.3, 26.2 (2C); HRMS (APCI) m/z: [M+H] calcd. for $\mathrm{C}_{23} \mathrm{H}_{26}{ }^{35} \mathrm{ClO}_{2}$ 369.1616; found 369.1617; calcd. for $\mathrm{C}_{23} \mathrm{H}_{26}{ }^{37} \mathrm{ClO}_{2} 371.1587$; found 371.1596 .


3na. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}: 25: 1$. Yield $=74 \%,(0.111 \mathrm{mmol}, 35.1 \mathrm{mg}), E / Z$ ratio: $>20: 1 .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.64(\mathrm{~s}, 1 \mathrm{H}), 7.37-7.32(\mathrm{~m}, 2 \mathrm{H}), 7.30$ $-7.26(\mathrm{~m}, 2 \mathrm{H}), 4.80(\mathrm{~d}, \mathrm{~J}=2.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.48(\mathrm{t}, \mathrm{J}=2.4 \mathrm{~Hz}$, $1 \mathrm{H}), 2.45(\mathrm{~d}, \mathrm{~J}=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.68-1.54(\mathrm{~m}, 5 \mathrm{H}), 1.54-$ $1.44(\mathrm{~m}, 1 \mathrm{H}), 1.22-1.02(\mathrm{~m}, 3 \mathrm{H}), 0.91-0.77(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{33} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=167.7$, 139.0, 134.2, 134.2, 132.7, 130.6 (2C), 128.7 (2C), 77.8, 74.8, 52.3, 37.8, 34.4, 33.2 (2C), 26.3, 26.2 (2C); HRMS (APCI) m/z: [M+H] calcd. for $\mathrm{C}_{19} \mathrm{H}_{22}{ }^{35} \mathrm{ClO}_{2} 317.1303$; found 317.1309; calcd. for $\mathrm{C}_{19} \mathrm{H}_{22}{ }^{37} \mathrm{ClO}_{2}$ 319.1274; found 319.1285.


3oa. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}$ : 15:1. Yield $=73 \%$, ( $0.110 \mathrm{mmol}, 26.5 \mathrm{mg}$ ), E/Z ratio: $>20: 1$. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $=7.47(\mathrm{~s}, 1 \mathrm{H}), 7.42-7.35(\mathrm{~m}, 4 \mathrm{H}), 7.34-7.28(\mathrm{~m}, 1 \mathrm{H}), 2.46(\mathrm{~d}, \mathrm{~J}=7.1$ $\mathrm{Hz}, 2 \mathrm{H}), 2.43(\mathrm{~s}, 3 \mathrm{H}), 1.66-1.52(\mathrm{~m}, 5 \mathrm{H}), 1.50-1.35(\mathrm{~m}, 1 \mathrm{H}), 1.20-$ $0.99(\mathrm{~m}, 3 \mathrm{H}), 0.91-0.76(\mathrm{~m}, 2 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=$ $200.8,142.3,139.7,136.0,129.2$ (2C), 128.5 (2C), 128.3, 37.6, 33.3 (2C), 33.2, 26.3, 26.3, 26.3 (2C); HRMS (APCI) m/z: $[M+H]^{+}$calcd. for $\mathrm{C}_{17} \mathrm{H}_{23} \mathrm{O}$ 243.1743; found 243.1743.


3ab. Viscous colorless oil. FC eluent: $n \mathrm{Hex}^{2} / \mathrm{Et}_{2} \mathrm{O}: 25: 1$. Yield $=49 \%$, ( $0.074 \mathrm{mmol}, 14.0 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $=7.64(\mathrm{~s}, 1 \mathrm{H}), 7.41-7.27(\mathrm{~m}, 5 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 2.53(\mathrm{q}, \mathrm{J}=7.4 \mathrm{~Hz}$, $2 \mathrm{H}), 1.16(\mathrm{t}, \mathrm{J}=7.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=168.8$, 138.6, 135.7, 134.7, 129.2 (2C), 128.4 (2C), 128.3, 51.9, 20.8, 13.9; HRMS (APCI) m/z: [M+H] ${ }^{+}$ calcd. for $\mathrm{C}_{12} \mathrm{H}_{15} \mathrm{O}_{2}$ 191.1067; found 191.1073 .


3ac. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}: 25: 1$. Yield $=55 \%$, ( $0.083 \mathrm{mmol}, 18.0 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=7.64(\mathrm{~s}, 1 \mathrm{H}), 7.41-7.28(\mathrm{~m}, 5 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 2.55-2.46(\mathrm{~m}$, $2 \mathrm{H}), 1.55-1.46(\mathrm{~m}, 2 \mathrm{H}), 1.42-1.31(\mathrm{~m}, 2 \mathrm{H}), 0.90(\mathrm{t}, \mathrm{J}=7.3 \mathrm{~Hz}, 3 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta=169.0,138.7,135.8,133.6,129.2$ (2C), 128.4 (2C), 128.3, 51.9, 31.4, 27.3, 22.8, 13.8; HRMS (APCI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{14} \mathrm{H}_{19} \mathrm{O}_{2} 219.1380$; found: 219.1379.

3ac is a known compound and the reported spectroscopic data match with the ones reported in the literature ( $E / Z$ ratio: 1:1.7). ${ }^{6}$


3ad. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{Et}_{2} \mathrm{O}$ : 25:1. Yield $=69 \%$, ( $0.104 \mathrm{mmol}, 18.0 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $=7.67(\mathrm{~s}, 1 \mathrm{H}), 7.36(\mathrm{~d}, J=5.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.31-7.25(\mathrm{~m}, 1 \mathrm{H}), 3.79(\mathrm{~s}$, 3 H ), 2.47 (d, $J=7.2 \mathrm{~Hz}, 2 \mathrm{H}$ ), 1.85 (sept, $J=6.9 \mathrm{~Hz}, 1 \mathrm{H}$ ), 0.84 (d, $J=$ $6.7 \mathrm{~Hz}, 6 \mathrm{H}$ ); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=169.3,139.4,136.0$, 133.1, 129.2 (2C), 128.4 (2C), 128.1, 51.9, 35.6, 28.2, 22.4 (2C); HRMS (APCI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$ calcd. for $\mathrm{C}_{14} \mathrm{H}_{19} \mathrm{O}_{2}$ 219.1380; found 219.1389.
3ad is a known compound and the reported spectroscopic data match with the ones reported in the literature ( $E / Z$ ratio: 1:1.7). ${ }^{6}$


3ae. Viscous colorless oil. FC eluent: $n \mathrm{Hex}^{\left(E t_{2} \mathrm{O}: 25: 1 .\right.}$ Yield $=80 \%$, ( $0.120 \mathrm{mmol}, 27.9 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $=7.66(\mathrm{~s}, 1 \mathrm{H}), 7.39-7.31(\mathrm{~m}, 4 \mathrm{H}), 7.29-7.25(\mathrm{~m}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H})$, $2.63(\mathrm{~s}, 2 \mathrm{H}), 0.73(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=170.3,139.9$, 136.6, 132.6, 128.9 (2C), 128.3 (2C), 127.7, 51.9, 38.2, 33.4, 29.5 (3C); HRMSI (APCI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{15} \mathrm{H}_{21} \mathrm{O}_{2}$ 233.1536; found 233.1545.


3af. Viscous colorless oil. FC eluent: $n \mathrm{Hex}^{2} / \mathrm{Et}_{2} \mathrm{O}$ : 25:1. Yield $=69 \%$, ( $0.104 \mathrm{mmol}, 29.2 \mathrm{mg}$ ), $\mathrm{E} / \mathrm{Z}$ ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=7.65(\mathrm{~s}, 1 \mathrm{H}), 7.29(\mathrm{dt}, J=4.4,1.9 \mathrm{~Hz}, 4 \mathrm{H}), 7.27-7.22(\mathrm{~m}, 2 \mathrm{H})$, $7.22-7.15(\mathrm{~m}, 4 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 2.68(\mathrm{t}, \mathrm{J}=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.61-2.52$ (m, 2H), $1.95-1.83(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=168.9,141.9,139.1,135.6,133.0$, 129.2 (2C), 128.5 (2C), 128.4 (2C), 128.3, 128.3 (2C), 125.8, 52.0, 35.8, 30.6, 27.1; HRMS (APCI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{19} \mathrm{H}_{21} \mathrm{O}_{2}$ 281.1536; found 281.1544.


3ag. White solid. FC eluent: $n H e x / E t O A c: 5: 1$. Yield $=61 \%,(0.092$ mmol, 29.2 mg ), $\mathrm{E} / \mathrm{Z}$ ratio: >20:1. MP: $95-98{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta=7.89(\mathrm{bs}, 1 \mathrm{H}), 7.62(\mathrm{~s}, 1 \mathrm{H}), 7.60(\mathrm{dd}, \mathrm{J}=7.8,1.2 \mathrm{~Hz}, 1 \mathrm{H})$, $7.36(\mathrm{dt}, J=8.1,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.23-7.08(\mathrm{~m}, 7 \mathrm{H}), 6.93(\mathrm{~d}, J=2.3 \mathrm{~Hz}$, $1 \mathrm{H}), 3.79(\mathrm{~d}, J=1.3 \mathrm{~Hz}, 3 \mathrm{H}), 2.84(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 2.64-2.55(\mathrm{~m}$, 2H), $2.06-1.92(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta={ }^{13} \mathrm{C}$ NMR ( 101 MHz, cdcl $_{3}$ ) $\delta 169.0,138.9,136.4,135.6,133.2,129.2$ (2C), 128.3 (2C), 128.2, 127.5, 121.9, 121.5, 119.2, 119.0, 116.0, 111.0, 51.9, 29.1, 27.3, 25.1; HRMS (APCI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{21} \mathrm{H}_{22} \mathrm{NO}_{2}$ 320.1645; found 320.1651.


3ah. Viscous colorless oil. FC eluent: $n \mathrm{Hex} / \mathrm{EtOAc}$ : 10:1. Yield $=$ $67 \%$, ( $0.101 \mathrm{mmol}, 32.1 \mathrm{mg}$ ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta=7.75(\mathrm{~s}, 1 \mathrm{H}), 7.41-7.26(\mathrm{~m}, 5 \mathrm{H}), 4.50(\mathrm{bs}, 1 \mathrm{H}), 3.92(\mathrm{bs}$, 1 H ), $3.82(\mathrm{~s}, 3 \mathrm{H}), 2.73-2.56(\mathrm{~m}, 2 \mathrm{H}), 1.38(\mathrm{~s}, 9 \mathrm{H}), 1.09(\mathrm{~d}, \mathrm{~J}=6.6$
$\mathrm{Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=169.1,155.2,141.2,135.6$, 130.4, 129.1 (2C), 128.5 (2C), 128.4, 78.8, 52.1, 46.8, 34.4, 28.3 (3C), 21.6; HRMS (ESI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{18} \mathrm{H}_{26} \mathrm{NO}_{4}$ 320.1856; found: 320.1852.


3ai. Pale yellow oil. FC eluent: $n \mathrm{Hex} / \mathrm{EtOAc}$ : 10:1. Yield $=75 \%$, ( 0.113 mmol, 38.9 mg ), E/Z ratio: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $\left.400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right) \delta=7.77$ (s, 1H), $7.44-7.35(\mathrm{~m}, 3 \mathrm{H}), 7.35-7.26(\mathrm{~m}, 2 \mathrm{H}), 4.20$ (dddd, $J=8.8$, $7.1,5.6,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.19(\mathrm{q}, \mathrm{J}=9.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.93-2.80$ (m, 2H), $2.53(\mathrm{td}, J=16.8,13.4,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.88-1.51(\mathrm{~m}, 4 \mathrm{H}), 1.39$ ( $\mathrm{s}, 9 \mathrm{H}$ ) some signals appear doubled due to the slow rotation of the $\mathrm{C}-\mathrm{N}$ bond of the Boc moiety; ${ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CD}_{3} \mathrm{OD}\right) \delta=172.5,159.0,145.1,139.6,134.4,132.4,132.2$ (2C), 132.0 (2C), 83.6, 60.3, 55.0, 49.2, 35.4, 34.4, 31.2 (3C), 25.8 some signals appear doubled due to the slow rotation of the $\mathrm{C}-\mathrm{N}$ bond of the Boc moiety; HRMS (ESI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{20} \mathrm{H}_{28} \mathrm{NO}_{4} 346.2013$; found 346.2009.

3ai is a known compound and the reported spectroscopic data match with the ones reported in the literature ( $E / Z$ ratio: 1:1). ${ }^{6}$


3aj. White solid. FC eluent: $n H e x / E t O A c: 1: 1$. Yield $=66 \%$, $(0.099$ mmol, 52.7 mg ), E/Z ratio: >20:1. MP: $186-188{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.62(\mathrm{~s}, 1 \mathrm{H}), 7.40-7.26(\mathrm{~m}, 5 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 2.93$ $-2.76(\mathrm{~m}, 3 \mathrm{H}), 2.57-2.36(\mathrm{~m}, 2 \mathrm{H}), 2.37-2.04(\mathrm{~m}, 7 \mathrm{H}), 2.04-1.87$ (m, 4H), 1.81 (td, $J=11.1,7.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.73-1.53(\mathrm{~m}, 3 \mathrm{H}), 1.51-$ $1.38(\mathrm{~m}, 1 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}), 1.35-1.08(\mathrm{~m}, 5 \mathrm{H}), 1.02(\mathrm{~s}, 3 \mathrm{H}), 0.81(\mathrm{~d}$, $J=6.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=212.0,209.0,208.7$, 168.9, 138.7, 135.8, 133.6, 129.1 (2C), 128.4 (2C), 128.3, 56.9, 51.9, $51.8,49.0,46.8,45.8,45.5,45.0,42.8,38.6,36.5,36.0,35.7,35.3$, 35.2, 27.8, 27.7, 26.2, 25.2, 21.9, 18.9, 11.8; HRMS (ESI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$ calcd. for $\mathrm{C}_{34} \mathrm{H}_{45} \mathrm{O}_{5} 533.3262$; found 533.3257 .


6aa. Colourless sticky foam. FC eluent: $n \mathrm{Hex} / E t O A c: ~ 3: 1$. Yield $=57 \%$, $(0.086 \mathrm{mmol}, 26.9 \mathrm{mg}), d r .>20: 1 .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta={ }^{1} \mathrm{H}$ NMR (401 MHz, cdcl ${ }_{3}$ ) $\delta 7.31-7.20(\mathrm{~m}, 2 \mathrm{H}), 7.01$ (td, $J=7.5,1.0 \mathrm{~Hz}$, $1 \mathrm{H}), 6.80$ (d, $J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.74(\mathrm{~d}, J=3.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.71(\mathrm{~s}, 3 \mathrm{H}), 3.29$ (ddd, $J=9.6,5.0,3.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.19$ (s, 3H), $1.82-1.48$ (m, 7H), $1.30-$ $0.97(\mathrm{~m}, 4 \mathrm{H}), 0.86-0.66(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=171.7$, 170.5, 140.2, 123.9, 121.7, 120.4, 118.0, 103.6, 47.6, 42.7, 38.5, 31.2, 30.8, 29.1, 28.3, 26.7, 25.6, 22.1, 21.9; HRMS (APCI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$ calcd. for $\mathrm{C}_{19} \mathrm{H}_{26} \mathrm{NO}_{3} 316.1907$; found 316.1915.


6ac. Pale yellow sticky foam. FC eluent: $n \mathrm{Hex} / E t \mathrm{OAc}$ : 3:1. Yield $=$ $51 \%$, ( $0.077 \mathrm{mmol}, 21.0 \mathrm{mg}$ ), dr: >20:1. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=7.31-7.21(\mathrm{~m}, 2 \mathrm{H}), 7.01(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.81(\mathrm{~d}, J=7.7 \mathrm{~Hz}$, $1 \mathrm{H}), 3.77(\mathrm{~d}, \mathrm{~J}=3.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.72(\mathrm{~s}, 3 \mathrm{H}), 3.20(\mathrm{~s}, 3 \mathrm{H}), 3.18-3.12$ (m, 1H), $1.32-1.13(\mathrm{~m}, 6 \mathrm{H}), 0.78(\mathrm{t}, \mathrm{J}=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=176.1,174.6,144.5,128.2,126.1,124.8,122.3,108.0,51.9,46.9,45.6,29.8$, 27.6, 26.2, 22.4, 13.8; HRMS (APCI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{NO}_{3} 276.1594$; found 276.1595.


6ba. Pale yellow sticky foam. FC eluent: $n \mathrm{Hex} / \mathrm{EtOAc}: 2: 1$. Yield $=62 \%$, ( $0.093 \mathrm{mmol}, 32.1 \mathrm{mg}$ ), dr: >20:1. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDC}_{3}\right) \delta=6.89(\mathrm{dd}, J=2.5,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.79$ (ddd, $J=8.4,2.6$, $0.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.70(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.77$ (s, 3H), 3.71 (s, 3H) overlapped with $3.73-3.65(\mathrm{~m}, 1 \mathrm{H}), 3.29$ (ddd, $J=9.3,5.0,3.6$ $\mathrm{Hz}, 1 \mathrm{H}$ ), 3.17 (s, 3H), 1.73 - 1.51 (m, 7H), $1.21-0.95(\mathrm{~m}, 4 \mathrm{H})$, 0.88 - $0.66(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=171.7$, $170.5,140.2,123.9,121.7,120.4,118.0,103.6,47.6,42.7,38.5$, 31.2, 30.8, 29.1, 28.3, 26.7, 25.6, 22.1, 21.9; HRMS (APCI) m/z: [M+H] ${ }^{+}$calcd. for $\mathrm{C}_{20} \mathrm{H}_{28} \mathrm{NO}_{4}$ 346.2013 ; found 346.2018 .


6bc. Pale yellow sticky foam. FC eluent: $n \mathrm{Hex} / \mathrm{EtOAc}: 3: 1$. Yield $=66 \%$, ( $0.099 \mathrm{mmol}, 30.2 \mathrm{mg}$ ), dr: >20:1. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta=6.91(\mathrm{dd}, J=2.7,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.79(\mathrm{dd}, \mathrm{J}=8.5,2.6$ $\mathrm{Hz}, 1 \mathrm{H}), 6.70(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.81-3.74(\mathrm{~m}, 4 \mathrm{H}), 3.72(\mathrm{~s}$, $3 \mathrm{H}), 3.20-3.10(\mathrm{~m}, 4 \mathrm{H}), 1.27-1.11(\mathrm{~m}, 5 \mathrm{H}), 0.95-0.82(\mathrm{~m}$, $1 \mathrm{H}), 0.78(\mathrm{t}, \mathrm{J}=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta={ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{cdcl}_{3}$ ) $\delta 175.8$, 174.6, 155.7, 138.1, 127.4, 112.6, 112.4, 108.1, 55.8, 51.9, 47.3, 45.5, 29.8, 27.6, 26.3, 22.4, 13.8; HRMS (APCI) m/z: [M+H] calcd. for $\mathrm{C}_{17} \mathrm{H}_{24} \mathrm{NO}_{4} 306.1700$; found 306.1699.
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra

## 3aa ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3aa ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
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## 3ba ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ba ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
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## 3ca ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ca ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


## 3da ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3da ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


## 3ea ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ea ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


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## 3fa ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3fa ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
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3ga ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3ga ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )




## 3ha ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ha ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


## 3ia ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ia ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ja' ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )





## 3ka ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ka ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
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3la ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3la ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
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## $3 m a{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ma ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



## 3na ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3na ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3oa ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3oa ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
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## 3ab ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ab ${ }^{1} \mathrm{H}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )




3ac ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3ac ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ad ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
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## 3ae ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3ae ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )




3af ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3af ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3ag ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3ag ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3ah ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3ah ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3ai ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3ai ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



3aj ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


3aj ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


## 6aa ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



6aa ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )

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## 6ac ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



6ac ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


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6ba ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


6ba ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )




6bc ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


6bc ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


Copies of selected HRMS spectra
HRMS (APCI) of 3aa


HRMS (APCI) of 3ca
Item name: Sample APCI
Item description:


HRMS (APCI) of 3da


HRMS (APCI) of 3ea


HRMS (APCI) of 3fa


## HRMS (APCI) of 3ga



HRMS (APCI) of 3ha


HRMS (APCI) of 3ia


HRMS (APCI) of 3ja'


## HRMS (APCI) of 3ka



HRMS (APCI) of 3ma


HRMS (APCI) of 3na


HRMS (APCI) of 3oa


## HRMS (APCI) of 3ab



HRMS (APCI) of 3ac


HRMS (APCI) of 3ad


HRMS (APCI) of 3ae


HRMS (APCI) of 3af


## HRMS (APCI) of 3ag



HRMS (APCI) of 6aa


HRMS (APCI) of 6ac


## HRMS (APCI) of 6ba



HRMS (APCI) of 6bc


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